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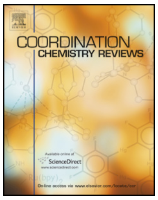

Review

A journey into the electrochemistry of vanadium compounds

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Abbreviations: Ac, acetyl CH_3CO; DCM, dichloromethane; DMSO, dimethylsulfoxide; EGH_2, 1,2-ethanediol (ethylene glycol); FcH, ferrocene; imz, imidazole; MeCN, acetonitrile; $MeNO_2$, nitromethane; PC, 1,2-propanediol carbonate or propylene carbonate; pic, methylpyridine (picoline); Tf, trifluoromethanesulfonate (triflate); THF, tetrahydrofuran; CPE, carbon paste electrode; FTO, fluorine doped tin oxide; NHE, normal hydrogen electrode; SCE, saturated calomel electrode; DPV, differential pulse voltammetry; FESEM, field-emission scanning electron microscope; NPV, normal pulse voltammetry; SEM, scanning electron microscope; TEM, transmission electron microscope; XAS, X-ray absorption spectroscopy.

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ABSTRACT

Vanadium is an element with a fascinating history, a widespread diffusion in bacteria and eukaryan organisms, and rich coordination chemistry. The properties of vanadium compounds attracted the interest of researchers in different fields, such as biochemistry, medicinal chemistry, and catalysis, leading to several reviews. However, although the rich and varied chemistry of vanadium was acknowledged to be due to the variety of easily accessible oxidation states, no review was devoted – to the best of our knowledge – to electrochemical properties of vanadium compounds. The present review aims at filling this lacuna, presenting a survey of electrochemical data related to vanadium compounds, starting from the eighties of the last century until mid 2014. The data are organized in tables, with experimental information necessary for comparisons, according to oxidation states of vanadium, beginning with the largest set, that is that of vanadium(IV) compounds and, within this set, on the basis of ligand coordinating atoms. The original ligands abbreviations were kept, when possible, or adapted, according to recent IUPAC recommendations. We hope to offer the reader a comprehensive – if not complete – overview of electrochemistry of vanadium compounds and to make relatively easy to retrieve the desired information. What is evident is the variety and versatility of vanadium compounds also in redox processes.

1. Introduction

Vanadium is an element with a fascinating history [1], a widespread diffusion in bacteria and eukaryan organisms [1], and a rich coordination chemistry, as it can be inferred even from old reviews [2]. The properties of vanadium compounds attracted the interest of researchers in different fields, such as biochemistry, medicinal chemistry, and catalysis, leading to several reviews. To cite a few of them, even limiting the period to the years from 2010 to 2014, reviews appeared on the natural occurring vanadium complex amavadin [3], on enzymatic and biochemical properties [4–7], on medicinal chemistry [8–11], and of course, on chemical aspects, i.e., synthesis and reactivity [12,13], catalysis and mechanisms [14–20].

Strangely enough, although the rich and varied chemistry of vanadium was acknowledged to be due to the variety of easily accessible oxidation states, no review was devoted – to the best of our knowledge – to electrochemical properties of vanadium compounds. For example, in 1992 a review dealing with soluble metal oxides of molybdenum and vanadium had a section discussing electrochemistry [21], but only molybdenum species were considered. The present review aims at filling this lacuna, presenting a survey of electrochemical data related to vanadium compounds, starting from the eighties of the last century. Although we cannot be sure that all the published data (and we apologize if some is missing) are reported, also because very often the electrochemical information is embedded in papers discussing other aspects, we believe we are presenting a panorama as complete as possible of electrochemical properties of vanadium compounds. The data are organized according to oxidation states of vanadium, beginning with the largest set, that is that of vanadium(IV) compounds.[1]

The original ligands abbreviations were kept, when possible, or adapted, according to recent IUPAC recommendations. However, they are too many to be listed as a footnote. Therefore, a list of abbreviations is presented at the end of the review. The same abbreviations appear under the ligands formulae. Literature is covered from 1980 until mid 2014.

2. Electrochemistry of vanadium(IV) compounds

Electrochemical studies on vanadium compounds date back to early seventies of the last century, when data were collected to understand the structure in solution of new compounds. For more than a decade, Riechel and Sawyer – separately or together – published a number of papers, where electrochemistry was performed on vanadium derivatives with ligands that could provide model complexes, in order to mimic the chemistry of biologically relevant transition metals containing species [22–24].

In some cases the complexes were not isolated, but investigated in solution, such as in the case of oxido-vanadium(IV) gluconate [24], that showed an one-electron oxidation at 0.118 V (vs SCE) at pH 6 and at −0.280 V in 0.5 M NaOH, respectively. In earlier papers, Riechel investigated complexes of V(III), oxido-V(IV), and oxido-V(V), comparing the results obtained with different ligands for each oxidation state. Later, the attention was focused on oxido-V(V) species with tetradentate ligands (vide infra, Section 3.1).

2.1. Oxido-vanadium (IV) species

2.1.1. Complexes with bidentate ligands

The electrochemistry of VOL_2 complexes, with L = bidentate monoanionic ligand, appeared to be strongly influenced by the nature of bonding atoms and the ring size (metal to bidentate ligand), as inferred by comparing potentials of $VO(quinol)_2$, $VO(etdtc)_2$, $VO(acac)_2$, and $VO(sesa)_2$ in Table 1 ([22,23,25,26], entries 1–4, structures and abbreviations in Chart 1, in alphabetical order of abbreviations).

After Riechel's pioneering work, numerous bidentate ligands were used to prepare oxido-vanadium(IV) compounds. *O-O* bidentate ligands as catecholate and the corresponding 3,5-di-*tert*-butyl derivative were used. Complexes of the type VOL_2^{2-} were prepared with 3,5-di-*tert*-butylcatecholate [27] and used in a detailed electrochemical investigation in solution. Results are collected in Table 1 (entry 5). The cyclic voltammograms for $[VO(^tBucat)_2]^{2-}$ were performed in DCM and MeCN, with the same general appearance, even though substantially different potentials for the various electrochemical processes were found. Controlled-potential electrolysis at the peak potential removed one electron per complex to yield a product with the same UV-visible spectrum in both solvents, that was identified as the oxido-V(V) species, $[VO(^tBucat)_2]^{-}$. Oxido-V(V), non-oxido V(IV), and V(III) species were also prepared with the same ligand (see Tables 3 and 5).

Following the studies of catecholato complexes and in view of testing possible anti-proliferative effect against cancer cells,

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[1] The reader, not to get lost among the different reference electrodes, may keep in mind that potentials vs NHE are, roughly, 0.2 for AgCl/Ag, 0.24 for SCE, and 0.4-0.7 V for FcH^+/FcH. However, different solvents, supporting electrolytes and even their concentration can affect potential values significantly, especially as far as ferrocene is concerned (N.G. Connelly, W.E. Geiger, Chem. Rev. 96 (1996) 877).

Table 1
Electrochemical data for oxido-vanadium(IV) compounds with bi- and tridentate ligands.[a]

Entry	Compound	Type of ligand	Process[b]	$E_{1/2}$, V	Supporting electrolyte	Electrochem. reference	Solvent	References
Bidentate ligands								
Mononuclear complexes								
1	VO(quinol)$_2$	*O-N*	V(IV) → V(V)	+0.775 (E_{pa}, irr)	Bu_4NClO_4	SCE	MeCN	[22]
2	VO(etdtc)$_2$	*S-S*	V(IV) → V(III)	–1.35	Et_4NClO_4	SCE	MeCN	[23]
3	VO(acac)$_2$	*O-O*	V(IV) → V(III)	–1.9 (E_{pc}, irr)	Et_4NClO_4	SCE	DMSO	[25]
			V(IV) → V(V)	+0.81				
4	VO(sesa)$_2$	*O-N*	V(IV) → V(V)	+0.65	Et_4NClO_4	SCE	DMSO	[26]
5	VO(^{t}Bucat)$_2$$^{2-}$	*O-O*	V(IV) → V(V)	+0.18	Et_4NClO_4	SCE	DCM	[27]
				–0.13	Et_4NClO_4	SCE	MeCN	
6	VO(ra)	*O-O*	V(IV) → V(III)	+0.041	Et_4NClO_4	$AgNO_3$/Ag	DMSO	[29]
7	VO(acac)(paha)	*O-O*	V(IV) → V(III)	–0.358	KNO_3	AgCl/Ag	MeOH	[30]
8	VO(paha)$_2$	*O-O*	V(IV) → V(III)	–0.303	KNO_3	AgCl/Ag	MeOH	[30]
9	VO(mpo)$_2$	*O-S*	V(IV) → V(V)	+0.825	Bu_4PF_6	NHE	MeCN	[31]
10	$VOCl_3$(pycanH)$^-$	*O-N*	V(IV) → V(III)	–0.21	Not indicated	AgCl/Ag	$MeNO_2$	[32]
11	VO(salampH)$_2$	*O-N*	V(IV) → V(V)	+0.57	Et_4NBF_4	Ag^+/Ag	DCM	[33]
12	VO(pimin)$_2$	*O-N*	V(IV) → V(V)	+0.490 (E_{pa}, irr)	Bu_4NClO_4	AgCl/Ag	DMSO	[35]
13	VO(etpimin)$_2$	*O-N*	V(IV) → V(V)	+0.440 (E_{pa}, irr)	Bu_4NClO_4	AgCl/Ag	DMSO	[35]
14	VO(HOetpimin)$_2$	*O-N*	V(IV) → V(V)	+0.400 (E_{pa}, irr)	Bu_4NClO_4	AgCl/Ag	DMSO	[35]
15	VO(acac)(cpsal)	*O-O*, *O-N*	V(IV) → V(V)	+0.7 (E_{pa}, quasi-rev)	Bu_4NClO_4	AgCl/Ag	DCM	[36]
			V(IV) → V(III)	–1.74				
Dinuclear complexes								
16	$(VO)_2(\mu_2\text{-}SO_4)_2$(^{t}Bu$_2$bipy)$_2$	*N-N*	V(IV,IV) → V(IV,V)	+1.12 irr	Bu_4NBF_4	AgCl/Ag	MeCN	[39]
				+1.19 irr	Bu_4NBF_4	AgCl/Ag	DCM	
Tridentate ligands								
Mononuclear complexes								
17	VO(bpOH)Cl_2	*N-N-N*	V(IV) → V(V)	+0.140	Bu_4NClO_4	FcH^+/FcH	DCM	[40]
			V(IV) → V(III)	–0.65 (irr)				
18	VO(acac)(HBpz$_3$)	*N-N-N*	V(IV) → V(V)	+1.23	Bu_4NPF_6	SCE	MeCN	[42]
				+1.21			DCM	
				+1.32 (irr)			DMF	
19	VO(acac)(HBdmpz$_3$)	*N-N-N*	V(IV) → V(V)	+1.18	Not indicated	SCE	DMF	[41]
				+1.11	Bu_4NPF_6	SCE	MeCN	[42]
				+1.07			DCM	
				+1.19			DMF	
20	VO(Cl)(HBpz$_3$)	*N-N-N*	V(IV) → V(V)	+1.33	Bu_4NPF_6	SCE	MeCN	[42]
				+1.33			DCM	
21	VO(Cl)(HBdmpz$_3$)	*N-N-N*	V(IV) → V(V)	+1.43	Not indicated	SCE	DMF	[41]
				+1.03	Bu_4NPF_6	SCE	MeCN	[42]
				+1.21			DCM	
				+1.36	Bu_4NPF_6	SCE	DCM	[43]
22	VO(benzoate)(HBpz$_3$)	*N-N-N*, *O-O*	V(IV) → V(V)	+1.15	Bu_4NPF_6	SCE	DCM	[43]
23	VO(HBdmpz$_3$)($FcCO_2$)	*N-N-N*	Fe(II) → Fe(III)	+0.70	Bu_4NBF_4	AgCl/Ag	DCM	[44]
			V(IV) → V(V)	+1.41				
24	[VO(pyphen)(phen)]$^{2+}$	*N-N-N*, *N-N*	V(IV) → V(III)	–0.88	Bu_4NClO_4	SCE	DMF/Tris	[45]
25	[VO(pyphen)(dppz)]$^{2+}$	*N-N-N*, *N-N*	V(IV) → V(III)	–0.89	Bu_4NClO_4	SCE	DMF/Tris	[45]
26	[VO(pydppz)(phen)]$^{2+}$	*N-N-N*, *N-N*	V(IV) → V(III)	0.90	Bu_4NClO_4	SCE	DMF/Tris	[45]
27	[VO(pydppz)(dppz)]$^{2+}$	*N-N-N*, *N-N*	V(IV) → V(III)	–0.86	Bu_4NClO_4	SCE	DMF/Tris	[45]
28	VO(hida)	*O-O-O*	V(IV) → V(V)	+0.78 (E_{pa}, irr)	Bu_4NClO_4	NHE	DMF	[49]
			V(IV) → V(III)	–1.33				
29	(CpP^{OMe}Co)VOCl(OH_2)	*O-O-O*	V(IV) → V(V)	+0.845	Bu_4NBF_4	AgCl/Ag	MeCN	[50]
30	VO(dipic)(H_2O)$_2$	*O-N-O*	V(IV) → V(III)	–1.04 (E_{pc}, irr)	Et_4NClO_4	SCE	DMF	[51]
			V(IV) → V(V)	+0.98				
31	VO(dipic)(phen)	*O-N-O*, *N-N*	V(IV) → V(III)	–1.08	Et_4NClO_4	SCE	DMF	[51]
			V(IV) → V(V)	+0.85				
32	VO(dipic)(bipy)	*O-N-O*, *N-N*	V(IV) → V(III)	–1.08	Et_4NClO_4	SCE	DMF	[51]
			V(IV) → V(V)	+0.84				
33	VO(iminac)	*O-N-O*	V(IV) → V(V)	–0.384	Bu_4NClO_4	SCE	DCM	[52]
34	VO(salgly)(bipy)	*O-N-O*, *N-N*	V(IV) → V(V)	+0.58	Bu_4NClO_4	AgCl/Ag	DMF	[53]
35	VO(salgly)(phe)	*O-N-O*, *N-N*	V(IV) → V(V)	+1.242	Bu_4NClO_4	AgCl/Ag	DMF	[53]
36	VO(apf)(acac)	*N-N-O*, *O-O*	V(IV) → V(V)	+0.921 irr	Bu_4NBF_4	AgCl/Ag	DCM	[54]
37	VO(salphol)	*O-N-O*	V(IV) → V(V)	+0.237	Bu_4NClO_4	AgCl/Ag	MeCN	[54]
38	VO(sal^{Br}phol)	*O-N-O*	V(IV) → V(V)	+0.318	Bu_4NClO_4	AgCl/Ag	MeCN	[54]
39	VO(sal^{3OMe}phol)	*O-N-O*	V(IV) → V(V)	+0.225	Bu_4NClO_4	AgCl/Ag	MeCN	[54]
40	VO(sal^{4OMe}phol)	*O-N-O*	V(IV) → V(V)	+0.228	Bu_4NClO_4	AgCl/Ag	MeCN	[54]
41	VO(sal^{5OMe}phol)	*O-N-O*	V(IV) → V(V)	+0.210	Bu_4NClO_4	AgCl/Ag	MeCN	[54]
42	VO(sal^{NO2}phol)	*O-N-O*	V(IV) → V(V)	+0.441	Bu_4NClO_4	AgCl/Ag	MeCN	[54]
43	VO(salph^{Cl}ol)	*O-N-O*	V(IV) → V(V)	+0.301	Bu_4NClO_4	AgCl/Ag	MeCN	[54]
44	VO(acacbhy)(bipy)	*O-N-O*, *N-N*	V(IV) → V(V)	+0.67 E_{pa}	Bu_4NClO_4	SCE	MeCN	[56]
45	VO(acacbhy)(phen)	*O-N-O*, *N-N*	V(IV) → V(V)	+0.67	Bu_4NClO_4	SCE	MeCN	[56]
46	VO(achyac)(bipy)	*O-N-O*, *N-N*	V(IV) → V(V)	+0.68 E_{pa}	Bu_4NClO_4	SCE	DMSO	[57]
47	VO(achyac)(phen)	*O-N-O*, *N-N*	V(IV) → V(V)	+0.50 E_{pa}	Bu_4NClO_4	SCE	DMSO	[57]
48	VO(salhyac)(bipy)	*O-N-O*, *N-N*	V(IV) → V(V)	+0.70 E_{pa}	Bu_4NClO_4	SCE	DMSO	[57]
49	VO(salhyac)(phen)	*O-N-O*, *N-N*	V(IV) → V(V)	+0.56 E_{pa}	Bu_4NClO_4	SCE	DMSO	[57]

Table 1 (*Continued*)

Entry	Compound	Type of ligand	Process[b]	$E_{1/2}$, V	Supporting electrolyte	Electrochem. reference	Solvent	References
50	VO(bzacbhy)(bipy)	*O-N-O, N-N*	V(IV) → V(V)	+0.54	$\mathrm{Et_4NClO_4}$	SCE	DCM	[58]
51	VO(bzacbhy)(phen)	*O-N-O, N-N*	V(IV) → V(V)	+0.64	$\mathrm{Et_4NClO_4}$	SCE	DCM	[58]
52	VO(bupbhy)(bipy)	*O-N-O, N-N*	V(IV) → V(V)	+0.62	$\mathrm{Et_4NClO_4}$	SCE	DCM	[58]
53	VO(bupbhy)(phen)	*O-N-O, N-N*	V(IV) → V(V)	+0.65	$\mathrm{Et_4NClO_4}$	SCE	DCM	[58]
54	VO(salbhy)(bipy)	*O-N-O, N-N*	V(IV) → V(V)	+0.70	$\mathrm{Et_4NClO_4}$	SCE	DCM	[58]
55	VO(salbhy)(phen)	*O-N-O, N-N*	V(IV) → V(V)	+0.76	$\mathrm{Et_4NClO_4}$	SCE	DCM	[58]
56	VO(naphhy)(bipy)	*O-N-O, N-N*	V(IV) → V(V)	+0.74	$\mathrm{Et_4NClO_4}$	SCE	DCM	[58]
57	VO(naphhy)(phen)	*O-N-O, N-N*	V(IV) → V(V)	+0.82	$\mathrm{Et_4NClO_4}$	SCE	DCM	[58]
58	VO(acacbh)(bipy)	*O-N-O, N-N*	V(IV) → V(V)	+0.87	$\mathrm{Et_4NClO_4}$	SCE	DCM	[59]
59	VO(bzacbh)(bipy)	*O-N-O, N-N*	V(IV) → V(V)	+0.89	$\mathrm{Et_4NClO_4}$	SCE	DCM	[59]
60	$\mathrm{VO(pymaph)(ibs^{\bullet -})}$	*N-N-O, N-O*	V(IV) → V(V)	+0.32 (E_{pa}, irr)	$\mathrm{Bu_4NPF_6}$	$\mathrm{FcH^+/FcH}$	DCM	[61,62]
61	$\mathrm{VO(pynaph)(ibs^{\bullet -})}$	*N-N-O, N-O*	V(IV) → V(V)	+0.41 (E_{pa}, irr)	$\mathrm{Bu_4NPF_6}$	$\mathrm{FcH^+/FcH}$	DCM	[61,62]
62	$\mathrm{VO(pynaph)(mibs^{\bullet -})}$	*N-N-O, N-O*	V(IV) → V(V)	+0.28	$\mathrm{Bu_4NPF_6}$	$\mathrm{FcH^+/FcH}$	DCM	[61,62]
Dinuclear complexes								
63	$\mathrm{V_2O_2(\mu\text{-}malonate)(HBpz_3)_2}$	*N-N-N, O-O*	V(IV) → V(V)	+0.92	$\mathrm{Bu_4NPF_6}$	SCE	DCM	[43]
64	$\mathrm{V_2O_2(iminol)_2}$	*O-N-O*	V(IV) → V(V)	−0.496	$\mathrm{Bu_4NClO_4}$	SCE	DCM	[52]
65	$\mathrm{[CpP^{OMe}Co]_2V_2O_2(\mu\text{-}oxa)}$	*O-O-O*	V(IV,IV) → V(IV,V) V(IV,V) → V(V,V)	+0.74 +1.095	$\mathrm{Bu_4NBF_4}$	AgCl/Ag	MeCN	[50]
66	$\mathrm{(CpP^{OMe}Co)_2V_2O_2(\mu\text{-}OP^{Ph,Ph}O)_2}$	*O-O-O*	V(IV,IV) → V(IV,V) V(IV,V) → V(V,V)	+0.78 (E_{pa}, quasi-rev) +1.360 (E_{pa}, quasi-rev)	$\mathrm{Bu_4NBF_4}$	AgCl/Ag	MeCN	[50]
67	$\mathrm{(CpP^{OMe}Co)_2V_2O_2(\mu\text{-}OP^{H,Ph}O)_2}$	*O-O-O*	V(IV,IV) → V(IV,V) V(IV,V) → V(V,V)	+0.800 (E_{pa}, quasi-rev) +1.280 (E_{pa}, quasi-rev)	$\mathrm{Bu_4NBF_4}$	AgCl/Ag	MeCN	[50]
68	$\mathrm{(CpP^{OMe}Co)_2V_2O_2(\mu\text{-}OP^{OH,Ph}O)_2}$	*O-O-O*	V(IV,IV) → V(IV,V) V(IV,V) → V(V,V)	+0.500 (E_{pa}, quasi-rev) −0.900 (E_{pa}, quasi-rev)	$\mathrm{Bu_4NBF_4}$	AgCl/Ag	MeCN	[50]
69	$\mathrm{(CpP^{OMe}Co]_2V_2O_2(\mu\text{-}OP^{OH,OPh}O)_2}$	*O-O-O*	V(IV,IV) → V(IV,V) V(IV,V) → V(V,V)	+0.920 (E_{pa}, quasi-rev) –	$\mathrm{Bu_4NBF_4}$	AgCl/Ag	MeCN	[50]
70	$\mathrm{[CpP^{OMe}Co)_2V_2O_2(\mu\text{-}OP^{OH,OPhNO}O)_2}$	*O-O-O*	V(IV,IV) → V(IV,V) V(IV,V) → V(V,V)	+0.880 +1.500	$\mathrm{Bu_4NBF_4}$	AgCl/Ag	MeCN	[50]
71	$\mathrm{(CpP^{OMe}Co)_2V_2O_2(\mu\text{-}OP^{OH,Me}O)_2}$	*O-O-O*	V(IV,IV) → V(IV,V) V(IV,V) → V(V,V)	+0.790 −1.090	$\mathrm{Bu_4NBF_4}$	AgCl/Ag	MeCN	[50]

[a] Structures and abbreviations of ligands are in Charts 1 and 2, in alphabetical order.

[b] The process indicates which is the initial and the final oxidation state, without hints about reversibility, that can be inferred by the $E_{1/2}$ column.

analogous ligands, such as 2,3-naphthalenediol, were investigated [28]. However, electrochemical data of VO complexes were assigned to the oxidation of the naphthol ligand.

Due to the interest in the highly colored complexes of hydroxamic acids with vanadium (hydroxamic acids as analytical reagents to detect this metal), the structures of the VO complex with the naturally occurring dihydroxamic acid, rhodotorulic acid ($\mathrm{raH_2}$), was investigated and the electrochemical and spectroelectrochemical data were collected [29]. VO(ra) formed in DMSO solution, mixing vanadyl sulfate and rhodotorulic acid. The reduction potentials (Table 1, entry 6) were different when determined with the isolated VO(ra) or with the formed compound in situ. In aqueous solutions, potentials changed with pH, probably as a consequence of hydrolytic reactions. The authors discuss the effect of stoichiometric reagents ratio and nature of axially bound ligand (OH or OR) on redox values. Hydroxamate as well as catecholate complexes underwent reduction to V(III) species, with loss of vanadyl oxygen.

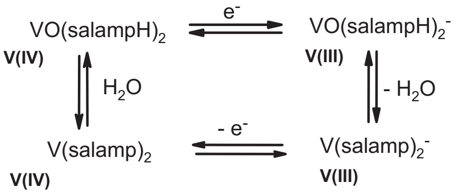
Later, complexes with simpler hydroxamic acids were investigated, because of their antibacterial activity [30]. Cyclic voltammetric measurements in methanol with VO complexes, containing either two phenoxyacetohydroxamate (paha) ligand or one phenoxyacetohydroxamate and one acetylacetonate group, showed a single reversible process (Table 1, entries 7,8). V(IV) species resulted relatively stable to oxidation, but were easily reduced to V(III).

An example of oxido-vanadium(IV) complex with *S-O* bidentate ligand was reported [31]. The anion from-2-sulfanylpyridine-*N*-oxide (mpo) gave the complex $\mathrm{VO(mpo)_2}$, that was investigated in different solvents. The reversible V(IV) → V(V) (Table 1, entry 9) and an irreversible V(IV) → V(III) couples were identified, no value reported for the latter. In DMF a coupled chemical reaction was identified after the charge-transfer process. In both MeCN and DMF one irreversible V(IV) → V(III) reduction was observed. On the other hand, in dichloromethane there was evidence that the initial V(IV) compound transforms into a different oxido-V(IV) species.

N-O bidentate ligands were initially chosen to prepare model compounds for vanadium-protein interactions, where the —NHCO— group plays a significant role [32]. With *N*-(2-nitrophenyl)pyridine-2-carboxamidato anion (pycan), oxidovanadium IV and V complexes were both prepared, but only the latter had an easily understandable electrochemical behavior, with the VO(IV) species formed in solution undergoing an irreversible reduction to the V(III) form (Table 1, entry 10).

2-(*N*-salicylideneaminoethyl)phenol ($\mathrm{salampH_2}$) acted as a tridentate ligand forming dinuclear μ-O vanadium species, but behaved as a bidentate ligand in complexation of mononuclear $\mathrm{VO^{2+}}$ species [2]. A completely reversible oxidation response was found for $\mathrm{VO(salampH)_2}$ in DCM and in MeCN. Instead, in the negative potential range a complex cyclic response was observed and attributed to the transformation V(IV) → V(III), followed by loss of vanadyl oxygen, according to Scheme 1 (Table 1, entry 11).

The potentially tetradentate *S-N-N-O* ligand, the Schiff base methyl 2-[2-(salicylideneamino)ethylamino]cyclopent-1-ene-1-dithiocarboxylate, actually behaved as a bidentate *N-O* ligand [34], as shown in Scheme 2. However, both oxido-V(IV) complexes obtained showed no redox activity attributable to vanadium.



Scheme 1. Redox behavior of $\mathrm{VO(salampH)_2}$ in the negative range of potentials [33].

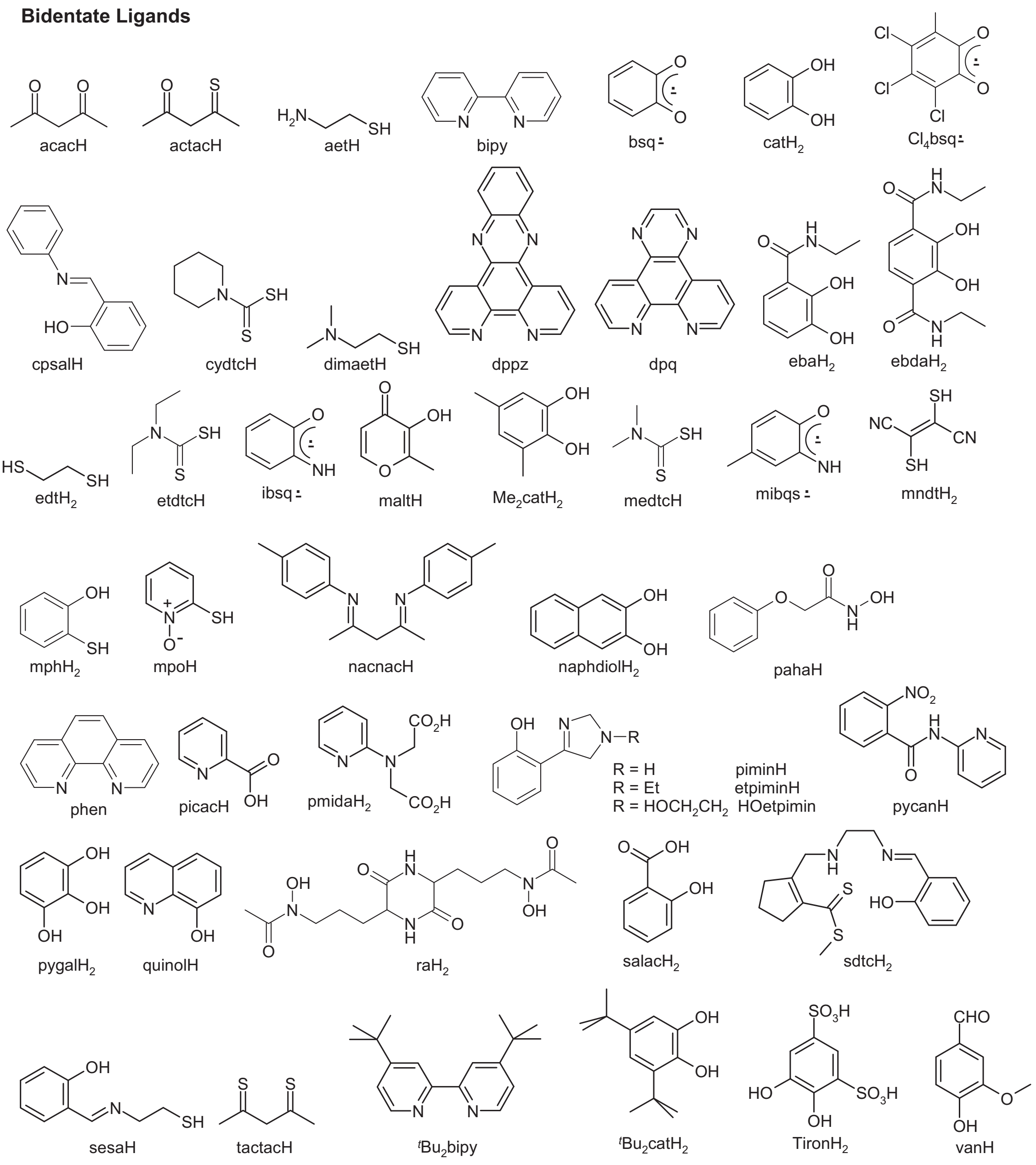
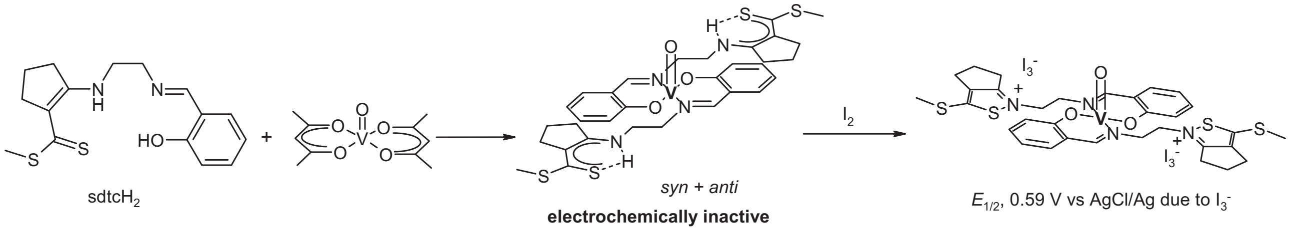


Chart 1. Bidentate ligands used in electrochemical investigation of vanadium complexes. Structures are reported according to alphabetical order of abbreviations. H atoms corresponding to those substituted by vanadium upon complexation are indicated in abbreviations.

More recently, considering the anti-diabetic efficiency of vanadium and of some imidazoline compounds, this heterocycle was chosen as binding moiety to oxidovanadium [35]. All oxido-V(IV) complexes obtained with these ligands displayed irreversible V(IV) → V(V) oxidation at relatively low potentials (Table 1, entries 12–14), that are in agreement with the facile aerobic oxidation observed in solution.

Prompted by the anti-cancer and insulin mimetic properties of some VO^{2+} complexes, a number of oxido-V(IV) compounds were prepared, with mixed bidentate ligands (*O-O* β-diketonato and



Scheme 2. Oxido-vanadium(IV) complexes with scdtcH_2 ligand [34].

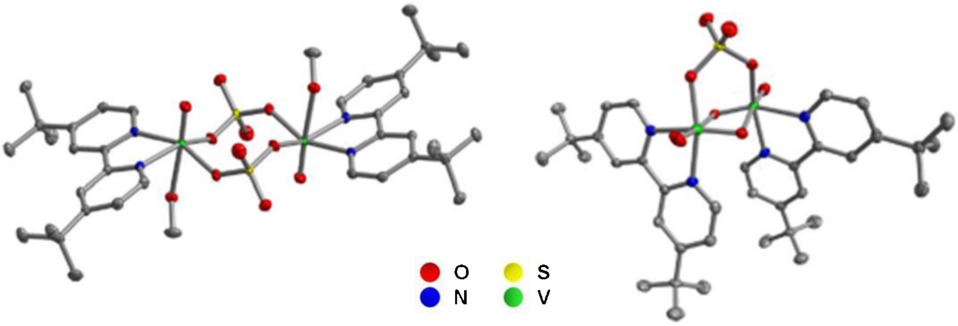


Fig. 1. Molecular structures of binuclear oxido-V(IV) compound, $(VO)_2(\mu_2\text{-}SO_4)_2({}^t\text{Bu}_2\text{bipy})_2$ (left) and oxido-V(V) derivative, $(VO)_2(\mu_2\text{-}O)_2(\mu_2\text{-}SO_4)({}^t\text{Bu}_2\text{bipy})_2$ (right). Adapted from [39], reprinted with permission of Elsevier.

N-O Schiff bases) [3]. The authors claim they examined the redox behavior of all the complexes, but results were reported only for VO(acac)(cpsal) (Table 1, entry 15).

Dinuclear oxido-V(IV) complexes were also reported. Dialkyldithiocarbamate provided the bidentate *S-S* ligands and sulfur bridges linked the two VO^{2+} moieties [37,38]. Diethyl, dimethyl and *N*,*N*-pentamethylene alkyl groups were used, giving compounds of general formula $V_2O_2S_2(R_2dtc)$, that presented common features in electrochemistry: a quasi-reversible V(IV) → V(III) reduction (at −0.60 to −0.73 V vs SCE), an irreversible one-electron oxidation (at +0.5 to +0.73 V vs SCE), and an irreversible oxidation of the dithiocarbamate ligand (at 0.02 to 0.1 V vs SCE). Values for individual compounds were not given, therefore it was not possible to insert them in Table 1.

Another binuclear oxido-V(IV) complex was obtained with 4,4′-di-*tert*-butyl-2,2′-bipyridine (${}^t\text{Bu}_2\text{bipy}$) with a sulfate bridge between the two VO^{2+} moieties [39]. The structure is shown in Fig. 1, together with that of the VO^{3+} compound derived from it, containing oxygen-bridges and oxido-V(V) species.

The electrochemical properties of $(VO)_2(\mu_2\text{-}SO_4)_2({}^t\text{Bu}_2\text{bipy})_2$ (Table 1, entry 16) were investigated in MeCN, ethanol and in DCM. Two successive redox transitions were observed in MeCN at anodic potentials. The peak potentials at platinum (Pt) and glassy carbon (GC) electrodes have similar values (1.12 and 1.37 V at Pt and 1.15 and 1.43 V at GC). The first peak involves the oxidation of one of the vanadium centers and is followed by the irreversible chemical transformation of the complex, that is further oxidized. The cyclic voltammogram obtained in DCM was similar (two successive peaks 1.19 and 1.48 V at Pt). Instead, no distinguishable oxidation peaks were observed in ethanol in anodic region up to 1.2 V, probably due to the decomposition of the complex in this solvent. All potentials are vs AgCl/Ag.

2.1.2. Complexes with tridentate ligands

The interest for insulin-enhancing activity of vanadium derivatives was behind the preparation of oxido-V(IV) complexes with tridentate ligands, such as the tertiary amine (bis[(pyrid-2-yl)methyl][(2-hydroxyphenyl)methyl]amine (bpOH, Chart 2) [40]. The oxidation at 0.140 V (vs FcH^+/FcH) was quasi-reversible and the plot of peak current as a function of the square root of the scan rate was linear for both the forward and reverse scans. An irreversible reduction at −0.65 V was also observed (Table 1, entry 17).

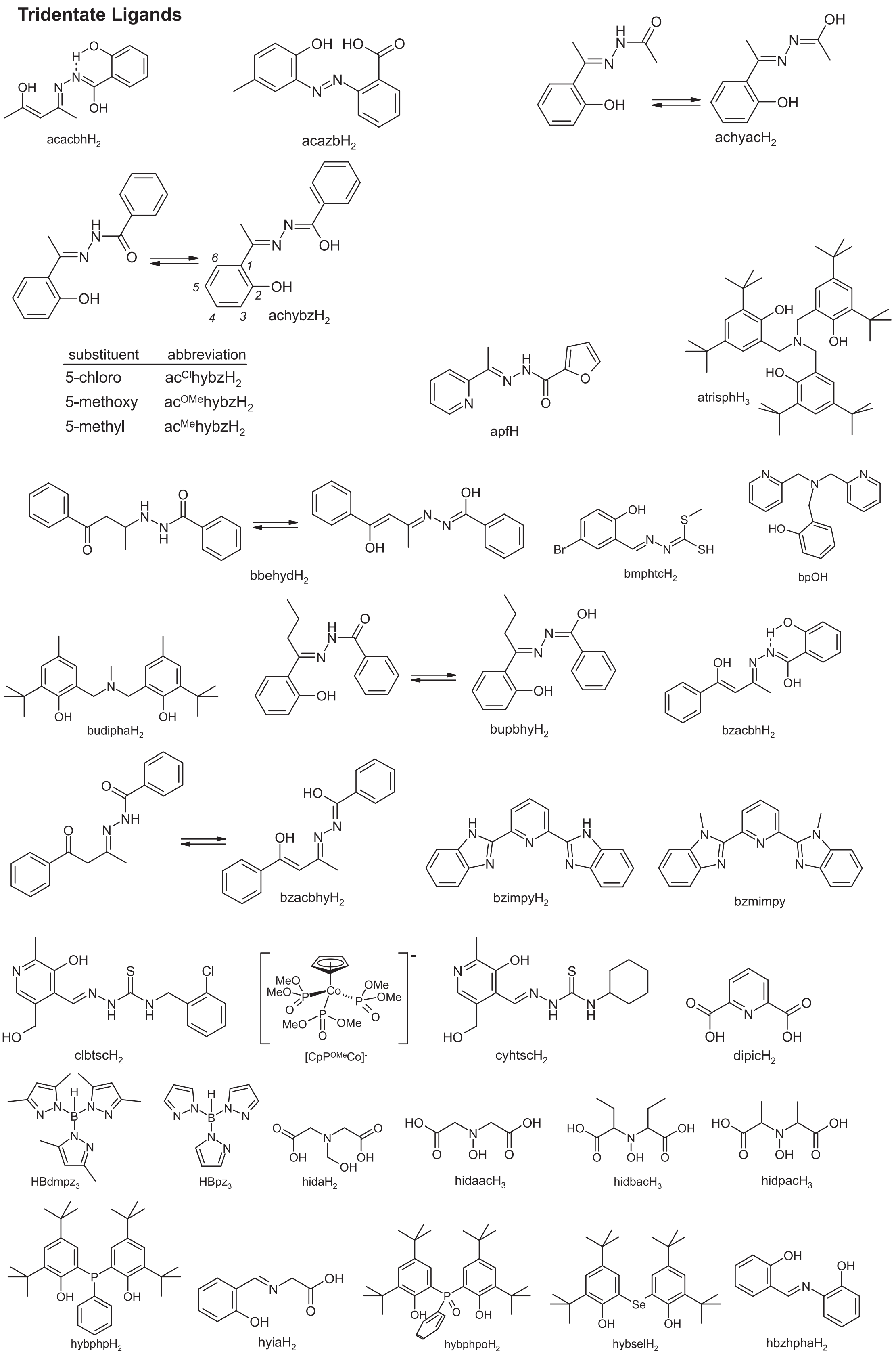
A different tridentate *N-N-N* ligand, hydridotris(pyrazolyl)-borate, $HBpz_3$, was chosen as a model for vanadium–histidine interaction of haloperoxidases from marine algae [41,42]. A series of V(III) (vide infra, Section 4) and oxido-V(IV) complexes were prepared with this ligand and its 3,5-dimethyl derivative, that were characterized, inter alia, by cyclic voltammetry in different solvents (Table 1, entries 18–21). All the complexes display a quasi-reversible redox process, corresponding to oxidation of the metal center at positive potentials. As expected, the 3,5-dimethyl analogs were oxidized at lower potentials, due to electron-donating properties of methyl groups. It is to be noted that, although the redox process was reversible on the CV time scale, it was not so upon bulk electrolysis [42]. Changing the monoanionic ligand from Cl to benzoate, a decrease in oxidation potential was observed, which is consistent with the greater π-donor ability of the carboxylate ligand compared to that of chloride [43] (Table 1, entry 22). Replacement of benzoate with malonate resulted in a dinuclear species (Table 1, entry 63) that, after an initial oxidation process at fast scan rates, exhibited a secondary process, probably due to a decomposition compound formed from the initially oxidized species.

$HBdmpz_3$ ligand was used to prepare an oxido-V(IV) complex with ferrocenecarboxylate as a monodentate additional ligand [44]. The cyclic voltammetry of $VO(HBdmpz_3)(FcCO_2)$ at room temperature presented a chemically and electrochemically reversible one-electron oxidation relative to Fe(II) → Fe(III) and a second quasi-reversible one-electron oxidation assigned to the vanadium center (Table 1, entry 23). Different tridentate *N-N-N* ligands based on polypyridines [45,46], were used to investigate the photocytotoxicity of their oxido-V(IV) complexes. The complexes with pyrenylterpyridine did not show any oxidative cyclic voltammetric response. The V(IV) → V(III) couple was observed as an irreversible voltammetric response in the potential range of −0.7 to −1.0 V vs SCE [46]. More detailed information was reported for phenanthroline and phenazine derivatives [45] (Table 1, entries 24–27).

Tridentate *O-O-O* ligands are quite rare. The complex of VO^{2+} with the tri-anion of *cis*-inositol (ino) was reported to form slowly from the corresponding non-oxido V(IV) species (see Section 2.2) in alkaline solution [47]. In 2013 the reactivity of VO^{2+} complex with oxydiacetate (oda) as scavenger of superoxide radical was electrochemically investigated [48] (see Section 7).

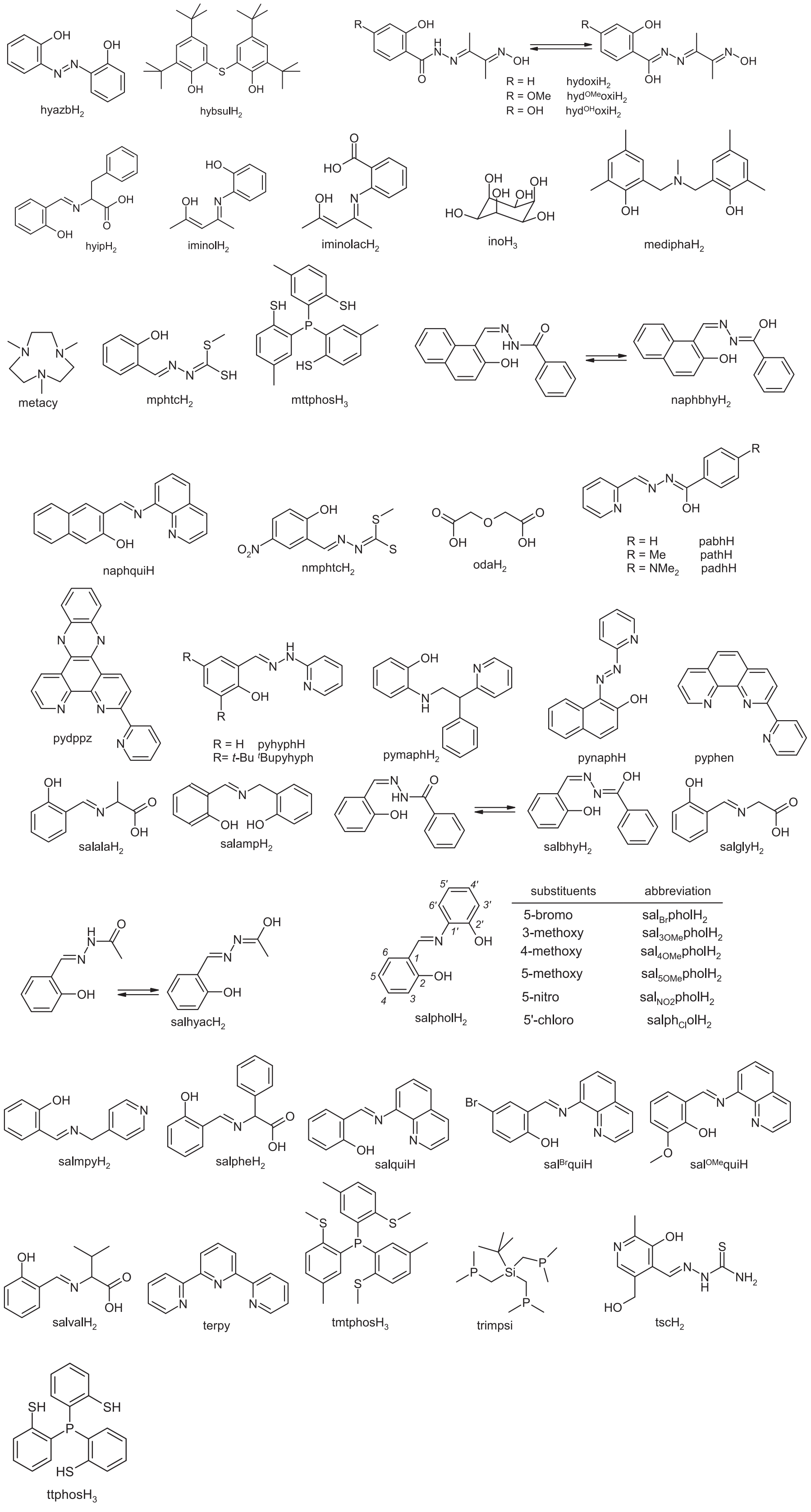
With the dianionic tridentate *O-O-O* ligand *N*-(2-hydroxyethyl)iminodiacetate (hida) an oxido-V(IV) complex was prepared, together with the corresponding dioxide-V(V) and the mixed-valence V(IV,V) complexes [49]. The cyclic voltammogram of VO(hida) shows the presence of two one-electron irreversible waves, the oxidation anodic peak and the reduction cathodic peak (Table 1, entry 28).

A series of dinuclear organophosphorus-bridged oxido-V(IV) complexes with the Kläui ligand, $[Cp^{POMe}Co]^-$, have been synthesized to model the catalytic activity of industrially used vanadium phosphate oxidation catalysts [50]. The dinuclear complexes had either an oxalate or a phosphonate/phosphinate bridge, with different substituents. The electrochemical behavior (CV) of these dinuclear complexes as well as that of mononuclear analog (structures in Scheme 3), has been investigated (Table 1, entries 29 and 65–71). Most dimeric complexes exhibited two unique oxidation events, attributed to the one-electron oxidation of one metal center in the dinuclear species, namely V(IV,IV) → V(IV,V), followed



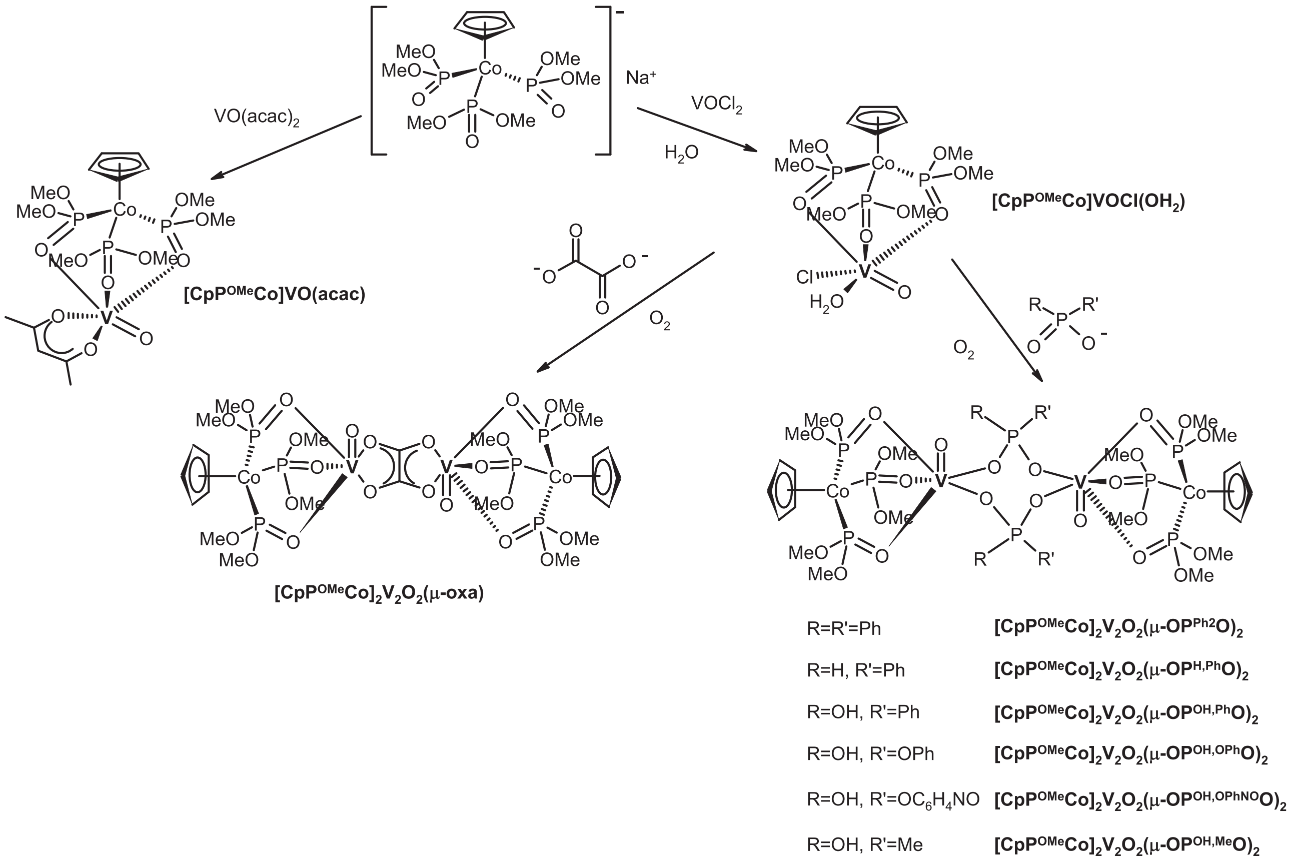
substituent	abbreviation
5-chloro	$ac^{Cl}hybzH_2$
5-methoxy	$ac^{OMe}hybzH_2$
5-methyl	$ac^{Me}hybzH_2$

Chart 2. Tridentate ligands used in electrochemical investigation of vanadium complexes. Structures are reported according to alphabetical order of abbreviations. H atoms corresponding to those substituted by vanadium upon complexation are indicated in abbreviations.



substituents	abbreviation
5-bromo	sal$_{Br}$pholH$_2$
3-methoxy	sal$_{3OMe}$pholH$_2$
4-methoxy	sal$_{4OMe}$pholH$_2$
5-methoxy	sal$_{5OMe}$pholH$_2$
5-nitro	sal$_{NO2}$pholH$_2$
5'-chloro	salph$_{Cl}$olH$_2$

Chart 2. (*Continued*)



Scheme 3. Mono-and dinuclear oxido-V(IV) complexes with Kläui ligand, [Cp^{POMe}Co]$^-$ [50].

by the subsequent oxidation of the second vanadium center, i.e. V(IV, V) → V(V,V). No correlation was found between oxidation potentials and the donor ability of the phosphonate/phosphinate bridge substituents.

Not surprisingly, tridentate ligand with both O and N coordinating atoms are more numerous. A very simple tridentate *O-N-O* ligand was pyridine-2,6-dicarboxylate (dipic), that, together with phenanthroline and bipyridine, was used to prepare oxido-V(IV) homo- and heterochelates complexes [51]. Electrochemical data are reported in Table 1 (entries 30–32) and indicate that the differences between the V(IV) → V(III) and V(IV) → V(V) potentials of the three compounds are quite small. Such small differences, in line with the spectral and magnetic moment data, were attributed to the presence of the same principal ligand, dipic, in the same disposition of its donor points in all the three complexes, with a consequent structural similarity.

With the tridentate Schiff bases derived from condensation of acetylacetone and 2-aminophenol (iminolH$_2$) or 2-aminobenzoic acid (iminacH$_2$) both mono- and dinuclear oxido-V(IV) complexes were prepared, a dinuclear one with the former ligand, a mononuclear one with the latter [52]. Both exhibit one-electron reversible oxidation behavior (Table 1, entries 64 and 33, respectively). The negative and small values of half-wave potentials have been ascribed to a ready redox susceptibility of the compounds [52].

A tridentate monoanionic ligand was reported, obtained from salicylaldehyde and glycine (salgly) [53]. With this ligand and 2,2′-bipyridine or 1,10-phenantroline, VO^{2+} complexes were prepared and investigated by different techniques, cyclic voltammetry included. Redox data relative to vanadium are in Table 1, entries 34 and 35. According to the authors, redox processes were irreversible, as suggested by further cathodic peak potentials. When 4,4′-bipyridine was used as the ancillary ligand, a dioxido-V(V) complex was obtained. The value for the dioxido-V(V) analog is in Table 5 (entry 84).

The VO(IV) complexes of tridentate *O-N-O* Schiff ligands obtained from substituted salicyl aldehydes and 2-aminobenzenediol (salpholH$_2$) were investigated by cyclic voltammetry [54]. A good correlation was observed between the oxidation potentials and the electron withdrawing character of the substituents on the Schiff base ligands, with trend: MeO < H < Br < NO$_2$ for substituents in salicylaldehyde and H < Cl for substituent in the amine ring (Table 1, entries 37–43).

A great deal of work involved tridentate *O-N-O* hydrazone-type ligands, obtained from substituted hydrazines (generally *N*-acyl substituted ones), and a variety of carbonyl compounds (i.e. from hydroxyl-substituted aromatic aldehydes and ketones to β-diketones), so that an additional binding OH was present. In all cases, it was the enol form of hydrazone to coordinate vanadium ions and, when monohydrazones of β-diketones were involved, also the remaining CO coordinated in the enol form.

The oxido-V(IV) complex obtained with the anion of 2-acetylpyridine-2-furanoylhydrazone (apf) [55] presented an irreversible oxidation peak in cyclic voltammetry (Table 1, entry 36), with the formation of dioxido-V(V) species, in agreement with the same reaction observed in solution.

Mixed-ligand oxido-V(IV) complexes were prepared with a tridentate di-negative *O-N-O* donor Schiff base ligand, viz. the enol form of 2,4-pentanedione *N*-benzoylhydrazone, and bidentate *N-N* ligands, bipy and phen [56]. They exhibited an one-electron irreversible oxidation peak in MeCN solution (Table 1, entries 44,45).

The same approach was exploited with the enol forms of 2-hydroxybenzenecarbaldeyde *N*-acetylhydrazone (salhyacH$_2$) and

2-hydroxyphenylethanone *N*-acetylhydrazone (achyacH_2), respectively, as *O-N-O* tridentate dianionic ligands together with bipy or phen [57]. All oxido-V(IV) complexes showed a one-electron irreversible oxidation peak in DMSO solution near +0.60 V vs SCE (Table 1, entries 46–49).

N-benzoylhydrazones were formed starting from different carbonyl compounds (2-hydroxybenezenecarbaldehyde, 1-(2-hydroxyphenyl)-1,3-butanedione, and 1-(2-hydroxyphenyl-1-butanone) and used to prepare oxido-V(IV) complexes with bipy or phen as heteroligands [58]. The complexes uniformly exhibited a quasi-reversible cyclic voltammetric response in DCM solution (Table 1, entries 50–57).

Other hydrazones that act as tridentate ligands, even if more than three coordinating atoms are present, were prepared from 2-hydroxybenzoylhydrazide and acetylacetone or benzoylacetone. Heterochelated VO^{2+} complexes were prepared using, as the second ligand, bipyridine, 8-quinolinol, or vanilline, in order to compare the properties of complexes having a neutral *N*,*N* and monoanionic *O-N* and *O-O* ligands, respectively [59]. Only with bipyridine vanadium is the oxidation state IV, whereas the other complexes have V(V) (see Section 3). The oxido-V(IV) complexes exhibit a quasi-reversible one-electron oxidation peak in DCM solution (Table 1, entries 58 and 59).

Analogous hydrazones containing sulfur atoms in the substituents, as *S*-methyl-3-(2-hydroxyphenyl)dithiocarbazate (mphtcH_2), behaved as *O-N-S* tridentate ligands [60]. Both oxido-V(IV) and dioxide-V(V) complexes were prepared, with different imidazoles as ancillary ligands. No electrochemical information is given for VO^{2+} compounds, while V(V) complexes are reported to be electrochemically inactive in the potential range −1.0 to +1.0 V vs SCE. However, they are photoreduced to mixed-valence species, that present electrochemical activity (see Section 2.3).

In a complex and complete study, P. Ghosh and coworkers explored the nature of oxido-V(IV) complexes of iminobenzosemiquinonate anion radical ligands [61,62], according to Scheme 4.

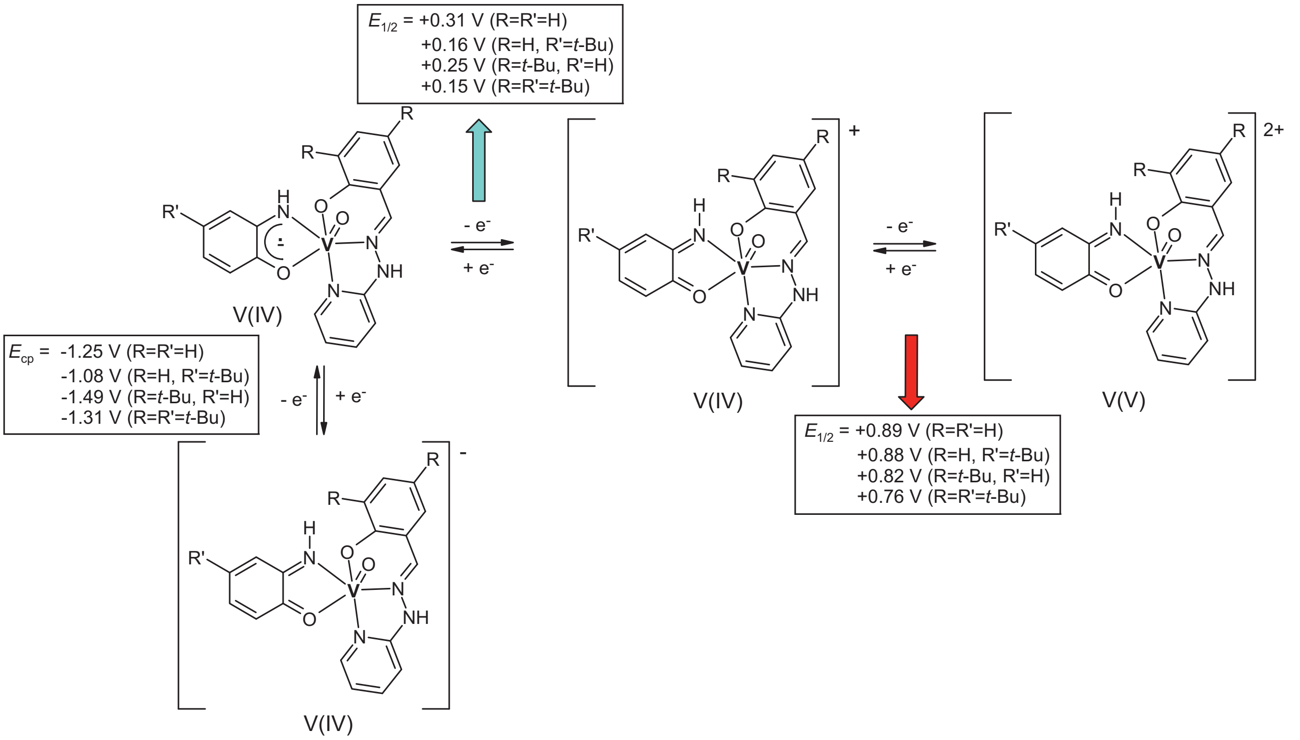
Two different benzosemiquinonates were used in conjunction with tridentate monoanionic *N-N-O* donor ligands. The coordination chemistry of redox non-innocent *o*-aminophenols with a redox non-innocent VO^{2+} core has been investigated and electrochemical data were corroborated by spin density calculations. Electrochemistry and spectroelectrochemistry allowed to detect an oxidation wave due to V(IV) → V(V) (Table 1, entries 60–62) process and reduction peaks due to electron transfer to the ligands.

2.1.3. Complexes with tetradentate ligands

Tetradentate ligands (Charts 3 and 4), occupying four coordination sites on the same plane, have the advantage to give complexes with well definite geometry and stable configuration.

The oxido-V(IV) complex containing the Schiff base derived from condensation of 2,4-pentanedione (acetylacetone, acacH) and 1,2-diaminoethane (ethylenediamine) was investigated by Riechel, in comparison with the corresponding thioxido-V(IV) complex [63]. Both VO(acen) and VS(acen) are reversibly oxidized by one electron per vanadium (Table 2, entries 1 and 2). The oxidation of VS(acen) is somewhat easier than that of VO(acen), sulfur being less electronegative than oxygen.

Macrocyclic tetra-aza ligands are an important class of tetradentate ligands, the coordination chemistry of which is exceedingly rich and investigated. VO^{2+} complexes of a number of differently substituted porphyrins were prepared and their electrochemistry investigated by cyclic voltammetry, rotating-disk voltammetry, and spectroelectrochemistry [64]. The dianions of 5,10,15,20-tetrapyridylporphyrin (TPyP), 5,10,15,20-tetrakis(*p*-diethylaminophenyl)porphyrin (TetaPP), and 5,10,15,20-tetrakis(*p*-sulfonatophenyl) porphyrin (TsulfPP) were used. The reduction of VO(TpyP) gave reversible processes at $E_{1/2}$ = −0.82 and −1.27 V in DMF (vs SCE, supporting electrolyte Bu_4NClO_4). At room temperature VO(Tsulfo)PP was reduced at $E_{1/2}$ = −0.96 and −1.48 V; VO(TetaPP) underwent reductions at $E_{1/2}$ = −1.08 and −1.57 V and oxidations at $E_{1/2}$ = +0.68 V and



Scheme 4. Electrochemical behavior of VO(iminobenzosemiquinonates)(catecholates) complexes [61,62]. CV measurements were in DCM, with Bu_4NPF_6 as the supporting electrolyte and potentials are referred to the couple FcH^+/FcH.

Tetradentate Ligands

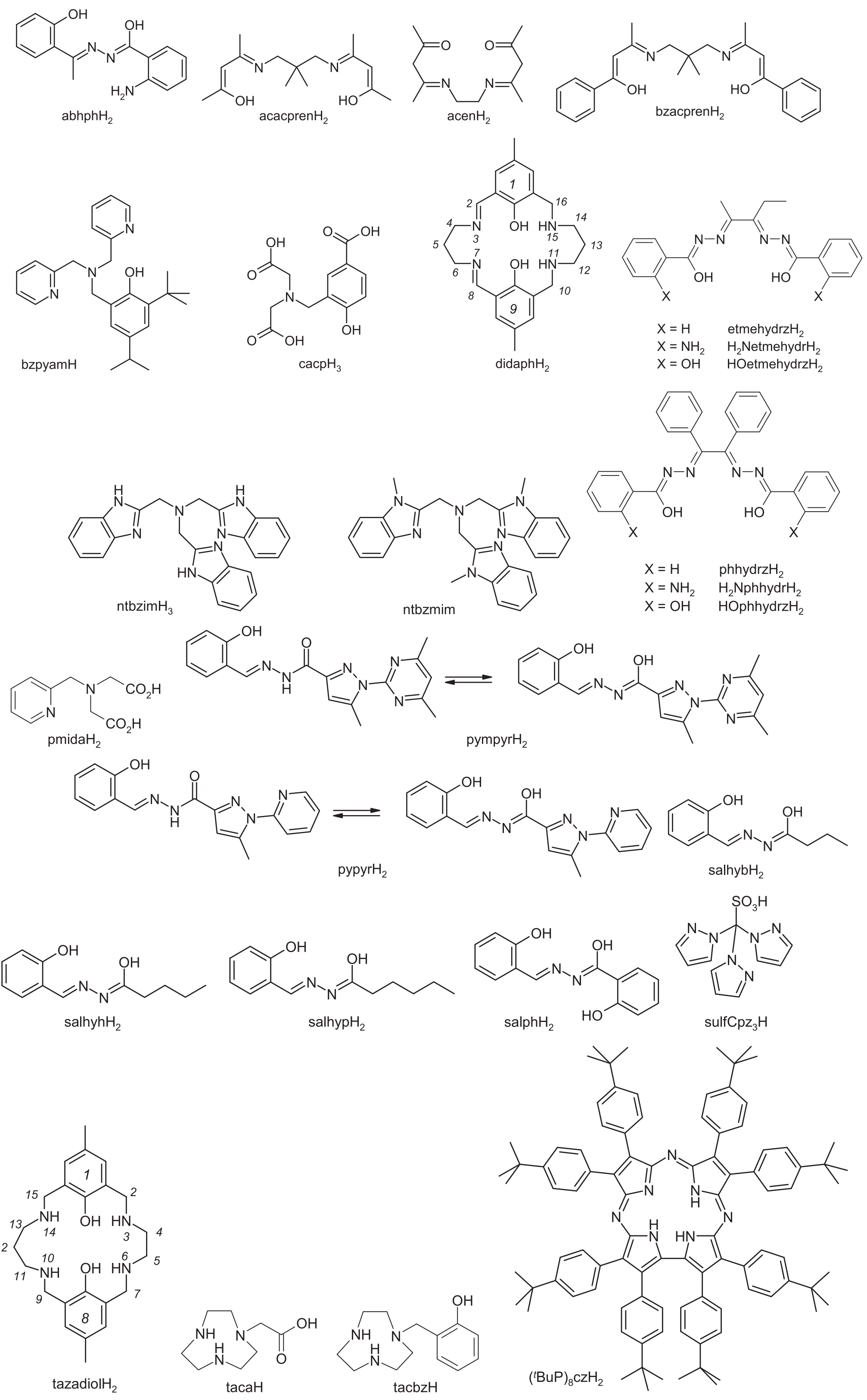


Chart 3. Tetradentate ligands used in electrochemical investigation of vanadium complexes. Structures are reported according to alphabetical order of abbreviations. H atoms corresponding to those substituted by vanadium upon complexation are indicated in abbreviations.

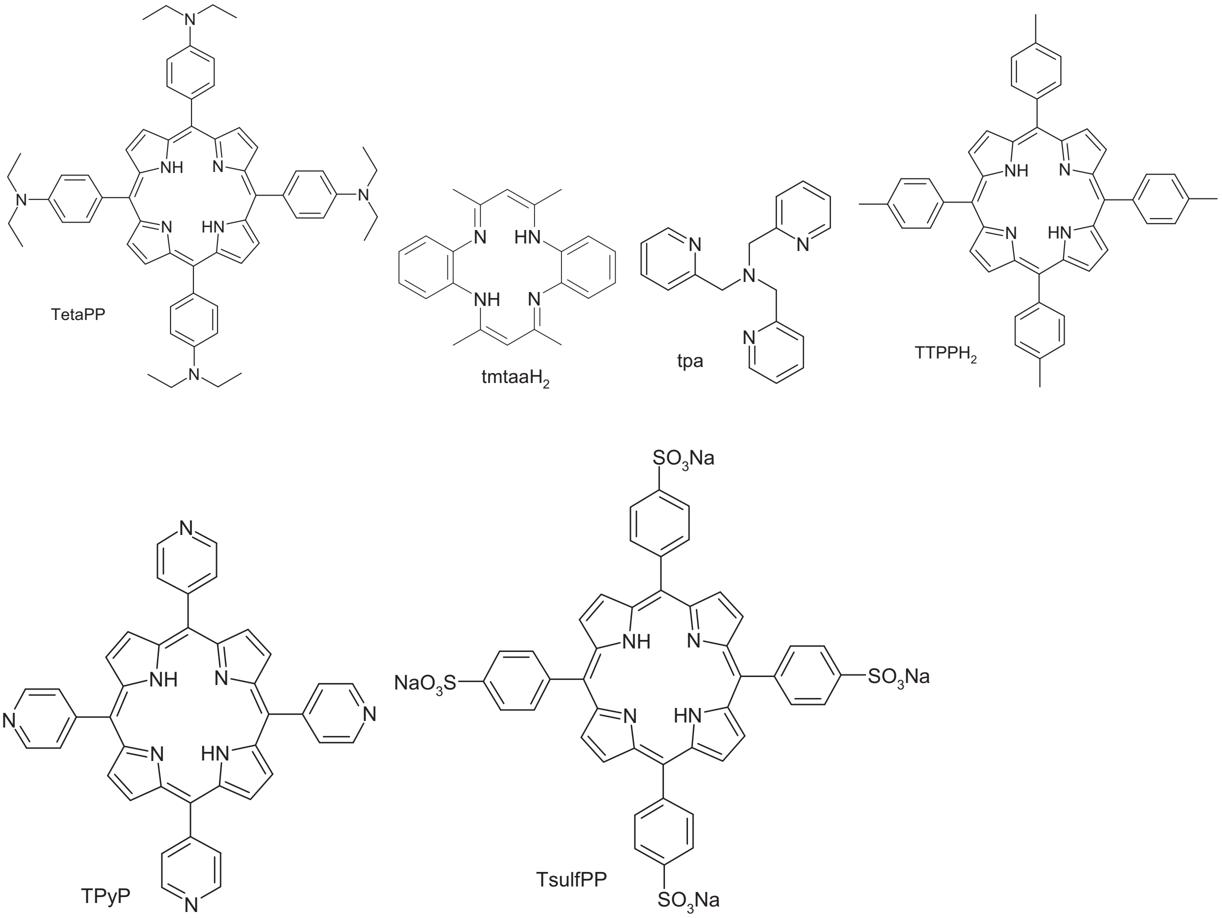


Chart 3. (*Continued*)

+1.04 V. Spectroelectrochemistry and ESR, as well as the linear correlation of $E_{1/2}$ potentials of complexes vs $E_{1/2}$ potentials of free bases porphyrins all suggest that redox events are ligand-centered. Different was the result with a corrazolinato ligand [65]. The VO^{2+} complex with the dianion of octakis(*p-tert*-butylphenyl)corrazoline, $(^t\mathrm{BuP})_8$cz, gave an irreversible reduction (Table 2, entry 3), that was attributed to the metal. At positive potentials two overlapping processes, appeared, which could be either ring- or metal-centered. To note, it is easier to reduce $VO(^t\mathrm{BuP})_8$cz than porphyrins vanadyl complexes, contrary to the usual pattern of a corrole being more difficult to reduce than an analogous porphyrin. Nevertheless, the authors are convinced that the process is metal-centered and this discrepancy was attributed to the "extra" labile proton, that makes $(^t\mathrm{BuP})_8$cz to behave more like a porphyrazine than a corrolazine and therefore being more easily reduced [65].

Vanadium phthalocyanine (Pc) complexes exhibit variable oxidation states, which make them useful as potential electrocatalysts. However, the first oxido-V(IV)Pc derivatives reported in literature [66,67] showed only ring based redox processes. Taking into consideration that the nature of the redox processes in some metallophthalocyanines depends on the substituents on the ring, the VOPc complex with eight pentylsulfanyl substituents was prepared [68]. The cyclic and square wave voltammetries of the purple complex (that became green on reduction) showed five redox couples, but also in this case the spectroelectrochemical data indicated only ring based processes. VO-phthalocyanine, bearing peripheral 2-naphthoxy groups, was synthesized by cyclotetramerization of the corresponding phthalonitrile derivative [69]. CV in DMSO and in DCM, with Bu_4NClO_4 as supporting electrolyte, presented several redox waves, all related to ligand oxidations and reductions, differently from what found with Co and Mn complexes with the same ligand. The same result, i.e. ligand-based redox processes, was obtained with other vanadium phthalocyanynes, peripherically substituted with sulfur containing groups [70].

A different kind of macrocycle investigated is the cyclophane tazadiolH$_2$ (Chart 3), with which VO^{2+} complexes were prepared [71]. It has different coordinating atoms (N and O) and, although potentially hexadentate, it behaved as a tetradentate complex, forming oxido-V(IV) derivatives [VO(tazadiol)(SO$_4$)] and [VO(tazadiolH$_2$)]$^{2+}$ (Table 2, entries 4,5). Moreover, the remaining cavity could accommodate the Ni^{2+} ion, thus forming the heterodinuclear complexes [VO(tazadiol)Ni]$^{2+}$ and [VO(tazadiol)Ni(SO$_4$)] (Table 2, entries 6,7). All the complexes underwent one electron oxidation, V(IV) → V(V), whose redox potentials and heterogeneous electron transfer rates did not show dependence on the presence of the neighboring nickel(II) ion (see, for examples, entries 4 and 7 in Table 2. The low-spin nickel(II) plays a spectator role in the redox process, when oxido-vanadium(IV) occupies the larger ligand compartment.

A similar ligand was reported later, with diamine and diimine moieties (didadph), that acted as a tetradentate ligand, forming the [VO(didaph)]$^{2+}$ complex [72]. Cyclic voltammograms showed typical reversible behavior between −0.75 and 1.25 V vs Ag^+/Ag, assigned to the V(IV) → V(V) process (Table 2, entry 8), and two irreversible waves below −1 V, ascribed to the successive reduction of the macrocyclic ligand.

A much simpler tetradentate *N-N-N-N* ligand was provided by tris(2-pyridylmethyl)amine (tpa), with which some VO^{2+} complexes were prepared and investigated [73], namely VO(tpa)(SO$_4$),

Table 2
Electrochemical data for oxido-vanadium(IV) compounds with tetradentate ligands.[a]

Entry	Compound	Type of ligand	Process[b]	$E_{1/2}$, V	Supporting electrolyte	Electrochem. reference	Solvent	References
Tetradentate ligands								
Mononuclear complexes								
1	VO(acen)	*O-N-N-O*	V(IV) → V(V)	+0.66	Et_4NClO_4	SCE	DCM	[63]
2	VS(acen)	*O-N-N-O*	V(IV) → V(V)	+0.45	Et_4NClO_4	SCE	DCM	[63]
3	$(^tBuP)_8cz$	*N-N-N-N*	V(IV) → V(III)	−0.65	Bu_4NPF_6	AgCl/Ag	DCM	[65]
4	VO(tazadiol)(SO_4)	*O-N-N-O*	V(IV) → V(V)	+0.57	Bu_4NClO_4	AgCl/Ag	MeCN–MeOH 2:1	[71]
5	$[VO(tazadiolH_2)]^{2+}$	*O-N-N-O*	V(IV) → V(V)	+0.79	Bu_4NClO_4	AgCl/Ag	MeCN–MeOH 2:1	[71]
6	$[VO(tazadiol)Ni]^{2+}$	*O-N-N-O*	V(IV) → V(V)	+0.80	Bu_4NClO_4	AgCl/Ag	MeCN–MeOH 2:1	[71]
7	VO(tazadiol)Ni(SO_4)	*O-N-N-O*	V(IV) → V(V)	+0.57	Bu_4NClO_4	AgCl/Ag	MeCN–MeOH 2:1	[71]
8	$[VO(didaph)]^{2+}$	*O-N-N-O*	V(IV) → V(V)	+1.30	Et_4NClO_4	NHE	MeCN	[72]
9	$[VO(tpa)Cl]^+$	*N-N-N-N*	V(IV) → V(III)	−1.59 quasi-rev	Bu_4NPF_6	FcH^+/FcH	MeCN	[73]
			V(IV) → V(V)	+1.28				
10	VO(salen)	*O-N-N-O*	V(IV) → V(III)	−1.55 (E_{pc})	Et_4NClO_4	SCE	DMF	[74]
				−1.555 (polarography)	Et_4NClO_4	SCE	DMF	[74]
				−1.555 (polarography)	$KClO_4$	SCE	DMF	[74]
				−1.555 (polarography)	$NaClO_4$	SCE	DMF	[74]
				−1.555 (polarography)	$LiClO_4$	SCE	DMF	[74]
				−1.6 (E_{pc},irrev)	Et_4NClO_4	SCE	DMSO	[75]
				−1.6 (E_{pc},irrev)	Et_4NClO_4	SCE	DCM	[75]
				−1.58 irrev	Bu_4NClO_4	SCE	DMF	[79]
				−1.6 ca. irrev	Bu_4NBF_4	AgCl/Ag	MeCN	[77]
				+0.88	None	AgCl/Ag	MeCN	[80]
			V(IV) → V(V)	+0.38	Et_4NClO_4	SCE	DMF	[74]
				+0.29	Et_4NClO_4	SCE	DMSO	[75]
				+0.64	Et_4NClO_4	SCE	DCM	[75]
				+0.47	Bu_4NPF_6	SCE	MeCN	[76]
				+0.300	Bu_4NPF_6	SCE	MeOH	[82]
				+0.460	Bu_4NPF_6	SCE	MeCN	
				+0.375	Bu_4NPF_6	SCE	DMF	
				+0.40	Bu_4NClO_4	SCE	DMF	[84]
				+0.55	Bu_4NBF_4	AgCl/Ag	MeCN	[77]
				+0.698	Bu_4NBF_4	AgCl/Ag	DCM	[80]
				+0.51	None	AgCl/Ag	MeCN	[81]
				+0.58	Bu_4NBF_4	SCE	DCM	[79]
				+0.419	Bu_4NClO_4	AgCl/Ag	DMF	[87]
				+0.386	Bu_4NClO_4	AgCl/Ag	MeOH	
				+0.396	Bu_4NClO_4	AgCl/Ag	MeCN	
				+0.346	Bu_4NClO_4	AgCl/Ag	THF	
				+0.38	Bu_4NPF_6	SCE	DMF	[89]
				+0.47	Bu_4NPF_6	SCE	MeCN	[89]
				+0.43	Bu_4NPF_6	SCE	THF	[89]
				+0.38	Bu_4NPF_6	AgCl/Ag	DMF	[90]
11	VO(salpren)	*O-N-N-O*	V(IV) → V(V)	+0.737	Bu_4NBF_4	AgCl/Ag	DCM	[80]
				+0.534	Bu_4NClO_4	AgCl/Ag	DMF	[87]
				−0.528	Bu_4NClO_4	AgCl/Ag	MeOH	
				+0.433	Bu_4NClO_4	AgCl/Ag	MeCN	
				0.348	Bu_4NClO_4	AgCl/Ag	THF	
12	VO(ehpg)	*O-N-N-O*	V(IV) → V(V)	+0.46	Bu_4NPF_6	SCE	H_2O	[82]
				+0.310	Bu_4NPF_6	SCE	MeOH	
				+0.208	Bu_4NPF_6	SCE	MeCN	
				+0.176	Bu_4NPF_6	SCE	DMF	
13	VO(eghs)	*O-N-N-O*	V(IV) → V(V)	+0.285	Bu_4NPF_6	SCE	H_2O	[82]
				+0.134	Bu_4NPF_6	SCE	MeOH	
				+0.065	Bu_4NPF_6	SCE	MeCN	
				+0.020	Bu_4NPF_6	SCE	DMF	
14	VO(tsalen)	*S-N-N-S*	V(IV) → V(III)	−1.29	Bu_4NClO_4	SCE	DMF	[84]
			V(IV) → V(V)	+0.56				
15	VO(phepca)	*N-N-N-O*	V(IV) → V(III)	−1.536 E_{pc}	Bu_4NBF_4	NHE	DCM	[85]
				−1.387 E_{pc}	Et_4NClO_4	NHE	MeCN	
16	VO(thipca)	*N-N-N-S*	V(IV) → V(III)	−1.45 E_{pc}	Bu_4NBF_4	NHE	DCM	[85]
				−1.21 E_{pc}	Et_4NClO_4	NHE	MeCN	
17	$[VO(Hypyb)]^-$	*N-N-N-O*	V(IV) → V(III)	+0.500	Bu_4NBF_4	NHE	DCM	[85]
				+0.581	Et_4NClO_4	NHE	MeCN	
18	$[VO(hybeb)]^{2-}$	*O-N-N-O*	V(IV) → V(III)	−0.167	Bu_4NBF_4	NHE	DCM	[85]
				−0.047	Et_4NClO_4	NHE	MeCN	
19	VO($sal^{diMe}en$)	*O-N-N-O*	V(IV) → V(V)	+0.59	Bu_4NBF_4	SCE	DCM	[79]
20	VO($sal^{diMe}pren$)	*O-N-N-O*	V(IV) → V(V)	+0.64	Bu_4NBF_4	SCE	DCM	[79]
21	VO($salen_{5,5'diMe}$)	*O-N-N-O*	V(IV) → V(V)	+0.50	Bu_4NBF_4	SCE	DCM	[79]
				+0.380	Bu_4NClO_4	AgCl/Ag	DMF	[87]
22	VO($salen_{5,5'diOMe}$)	*O-N-N-O*	V(IV) → V(V)	+0.48	Bu_4NBF_4	SCE	DCM	[79]
				+0.45	Bu_4NClO_4	AgCl/Ag	MeCN	[86]
				+0.358	Bu_4NClO_4	AgCl/Ag	DMF	[87]
				+0.30	Bu_4NPF_6	SCE	DMF	[89]

Table 2 (*Continued*)

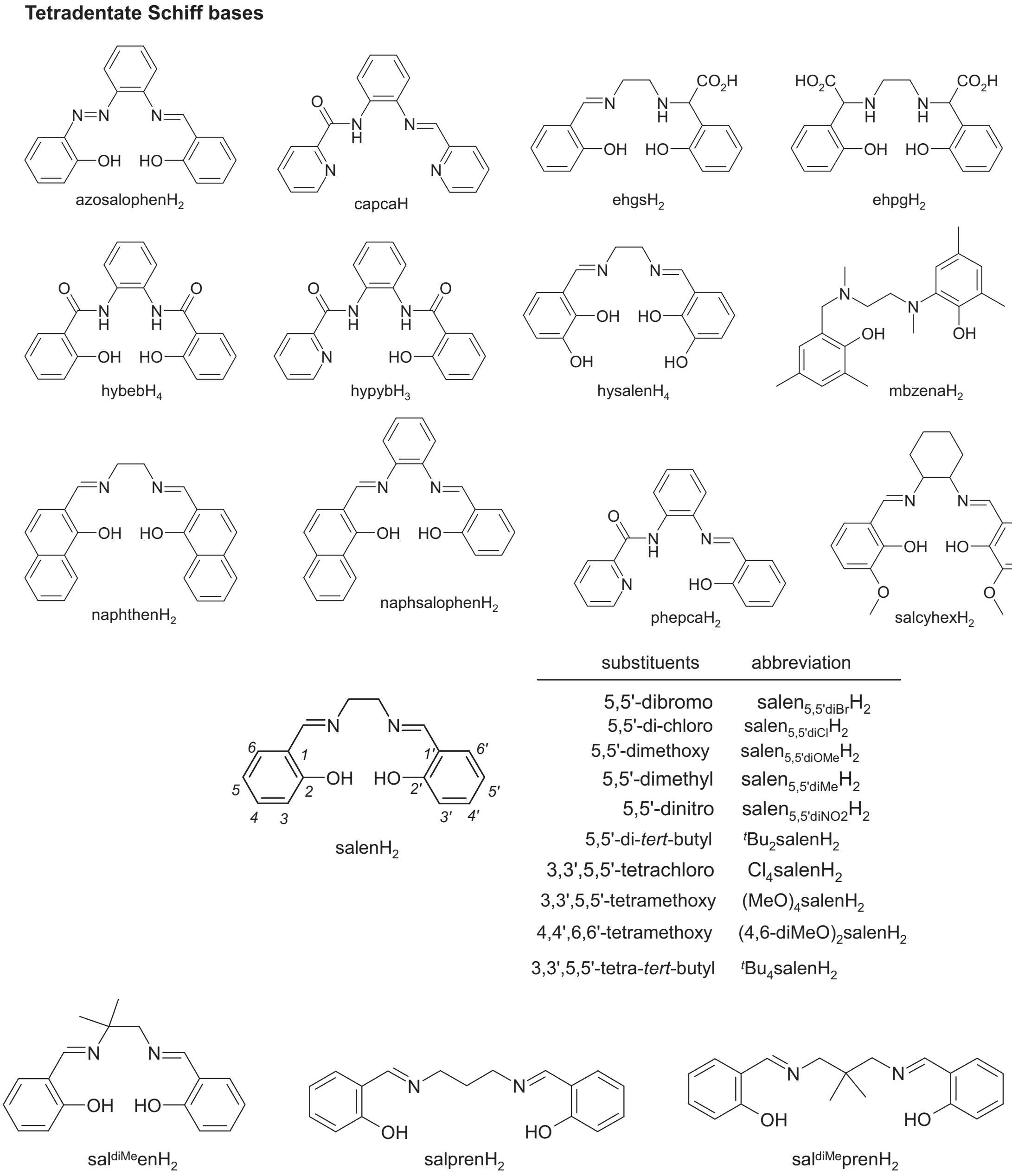
Entry	Compound	Type of ligand	Process[b]	$E_{1/2}$, V	Supporting electrolyte	Electrochem. reference	Solvent	References
				+0.51	Bu_4NPF_6	SCE	MeCN	[89]
				+0.39	Bu_4NPF_6	SCE	THF	[89]
				+0.30	Bu_4NPF_6	AgCl/Ag	DMF	[90]
23	VO(salen$_{5,5'\mathrm{diBr}}$)	*O-N-N-O*	V(IV) → V(V)	+0.508	Bu_4NClO_4	AgCl/Ag	DMF	[87]
24	VO(salen$_{5,5'\mathrm{diCl}}$)	*O-N-N-O*	V(IV) → V(V)	+0.45	Bu_4NPF_6	SCE	DMF	[89]
				+0.49	Bu_4NPF_6	SCE	MeCN	[89]
				+0.54	Bu_4NPF_6	SCE	THF	[89]
				+0.45	Bu_4NPF_6	AgCl/Ag	DMF	[90]
25	VO(salen$_{5,5'\mathrm{diNO2}}$)	*O-N-N-O*	V(IV) → V(V)	+0.685	Bu_4NClO_4	AgCl/Ag	DMF	[87]
26	VO(Cl_4salen)	*O-N-N-O*	V(IV) → V(V)	+0.56	Bu_4NPF_6	SCE	DMF	[89]
				+0.64	Bu_4NPF_6	SCE	MeCN	[89]
				+0.80	Bu_4NPF_6	SCE	THF	[89]
				+0.56	Bu_4NPF_6	AgCl/Ag	DMF	[89]
27	VO(^{t}Bu$_2$salen)	*O-N-N-O*	V(IV) → V(V)	+0.35	Bu_4NPF_6	SCE	DMF	[89]
				+0.44	Bu_4NPF_6	SCE	MeCN	[89]
				+.42	Bu_4NPF_6	SCE	THF	[89]
				+0.35	Bu_4NPF_6	AgCl/Ag	DMF	[90]
28	VO[(MeO)$_4$salen]	*O-N-N-O*	V(IV) → V(V)	+0.43	Bu_4NClO_4	AgCl/Ag	MeCN	[86]
29	VO(^{t}Bu$_4$salen)	*O-N-N-O*	V(IV) → V(V)	+0.40	Bu_4NClO_4	AgCl/Ag	MeCN	[86]
				+0.34	Bu_4NPF_6	SCE	DMF	[89]
				+0.32	Bu_4NPF_6	SCE	MeCN	[89]
				+0.36	Bu_4NPF_6	SCE	THF	[89]
				+0.34	Bu_4NPF_6	AgCl/Ag	DMF	[90]
				+0.255	Bu_4NClO_4	AgCl/Ag	DMSO	[92]
30	VO(^{t}Bu$_4$sal$^{\mathrm{Me}}$en)	*O-N-N-O*	V(IV) → V(V)	+0.266	Bu_4NClO_4	AgCl/Ag	DMSO	[92]
31	VO(^{t}Bu$_4$salpren)	*O-N-N-O*	V(IV) → V(V)	+0.312	Bu_4NClO_4	AgCl/Ag	DMSO	[92]
32	VO(^{t}Bu$_4$sal$^{\mathrm{diMe}}$pren)	*O-N-N-O*	V(IV) → V(V)	+0.285	Bu_4NClO_4	AgCl/Ag	DMSO	[92]
33	VO(^{t}Bu$_4$salbuten)	*O-N-N-O*	V(IV) → V(V)	+0.313	Bu_4NClO_4	AgCl/Ag	DMSO	[92]
34	VO(^{t}Bu$_4$salpenen)	*O-N-N-O*	V(IV) → V(V)	+0.280	Bu_4NClO_4	AgCl/Ag	DMSO	[92]
35	VO(^{t}Bu$_4$salhexen)	*O-N-N-O*	V(IV) → V(V)	+0.317	Bu_4NClO_4	AgCl/Ag	DMSO	[92]
36	VO(naphthen)	*O-N-N-O*	V(IV) → V(V)	+0.65	Bu_4NClO_4	AgCl/Ag	MeCN	[86]
37	VO(salophen)	*O-N-N-O*	V(IV) → V(V)	+0.64	Bu_4NClO_4	AgCl/Ag	MeCN	[86]
				+0.522	Bu_4NClO_4	AgCl/Ag	DMF	[87]
				+0.464	Bu_4NClO_4	AgCl/Ag	MeOH	
				+0.504	Bu_4NClO_4	AgCl/Ag	MeCN	
				+0.516	Bu_4NClO_4	AgCl/Ag	THF	
				+0.580	Bu_4NPF_6	SCE	DMF	[88]
				+0.49	Bu_4NPF_6	AgCl/Ag	DMF	[90]
38	VO(salophen$_{5,5'\mathrm{diOMe}}$)	*O-N-N-O*	V(IV) → V(V)	+0.470	Bu_4NClO_4	AgCl/Ag	DMF	[87]
				+0.46	Bu_4NPF_6	AgCl/Ag	DMF	[90]
39	VO(salophen$_{5,5'\mathrm{diBr}}$)	*O-N-N-O*	V(IV) → V(V)	+0.593	Bu_4NClO_4	AgCl/Ag	DMF	[87]
				+0.660	Bu_4NPF_6	SCE	DMF	[88]
40	VO(Cl_2salophen)	*O-N-N-O*	V(IV) → V(V)	+0.59	Bu_4NPF_6	AgCl/Ag	DMF	[90]
41	VO(salophen$_{5\mathrm{Br}}$)	*O-N-N-O*	V(IV) → V(V)	+0.590	Bu_4NPF_6	SCE	DMF	[88]
42	VO(salophen$_{\mathrm{Br,OMe}}$)	*O-N-N-O*	V(IV) → V(V)	+0.682	Bu_4NPF_6	SCE	DMF	[88]
43	VO(salophen$_{5\mathrm{NO2}}$)	*O-N-N-O*	V(IV) → V(V)	+0.670	Bu_4NPF_6	SCE	DMF	[88]
44	VO(salophen$_{\mathrm{diBr,OMe}}$)	*O-N-N-O*	V(IV) → V(V)	+0.655	Bu_4NPF_6	SCE	DMF	[88]
45	VO(salophen$_{\mathrm{diBr,diOMe}}$)	*O-N-N-O*	V(IV) → V(V)	+0.660	Bu_4NPF_6	SCE	DMF	[88]
46	VO(salophen$_{\mathrm{Br,OMe,NO2}}$)	*O-N-N-O*	V(IV) → V(V)	+0.702	Bu_4NPF_6	SCE	DMF	[88]
47	VO(salophen$_{5,5'\mathrm{diNO2}}$)	*O-N-N-O*	V(IV) → V(V)	+0.750	Bu_4NPF_6	SCE	DMF	[88]
48	VO(^{t}Bu$_2$salophen)	*O-N-N-O*	V(IV) → V(V)	+0.47	Bu_4NPF_6	AgCl/Ag	DMF	[90]
49	VO(salophen$_{\mathrm{Br,NO2}}$)	*O-N-N-O*	V(IV) → V(V)	+0.710	Bu_4NPF_6	SCE	DMF	[88]
50	VO(Cl_4salophen)	*O-N-N-O*	V(IV) → V(V)	+0.81	Bu_4NPF_6	AgCl/Ag	DMF	[90]
51	VO(^{t}Bu$_4$salophen)	*O-N-N-O*	V(IV) → V(V)	+0.60	Bu_4NClO_4	AgCl/Ag	MeCN	[86]
				+0.56	Bu_4NPF_6	AgCl/Ag	DMF	[90]
52	VO(salodinphen)	*O-N-N-O*	V(IV) → V(V)	+0.665	Bu_4NPF_6	AgCl/Ag	DMSO	[91]
53	VO(salodinphen$_{3,3'\mathrm{diOMe}}$)	*O-N-N-O*	V(IV) → V(V)	+0.635	Bu_4NPF_6	AgCl/Ag	DMSO	[91]
54	VO(salodinphen$_{4,4'\mathrm{diOMe}}$)	*O-N-N-O*	V(IV) → V(V)	+0.640	Bu_4NPF_6	AgCl/Ag	DMSO	[91]
55	VO(salodinphen$_{5,5'\mathrm{diBr}}$)	*O-N-N-O*	V(IV) → V(V)	+0.755	Bu_4NPF_6	AgCl/Ag	DMSO	[91]
56	VO(salpren$_{5,5'\mathrm{diOMe}}$)	*O-N-N-O*	V(IV) → V(V)	+0.410	Bu_4NClO_4	AgCl/Ag	DMF	[87]
57	VO(salpren$_{5,5'\mathrm{diBr}}$)	*O-N-N-O*	V(IV) → V(V)	+0.570	Bu_4NClO_4	AgCl/Ag	DMF	[87]
58	VO(salpren$_{5,5'\mathrm{diNO2}}$)	*O-N-N-O*	V(IV) → V(V)	+0.786	Bu_4NClO_4	AgCl/Ag	DMF	[87]
59	VO(sal$^{\mathrm{Me}}$en)	*O-N-N-O*	V(IV) → V(V)	+0.55	Bu_4NBF_4	SCE	DCM	[79]
				+0.442	Bu_4NPF_6	SCE	DMF	[88]
60	VO(sal$^{\mathrm{Me}}$en$_{5\mathrm{Br}}$)	*O-N-N-O*	V(IV) → V(V)	+0.485	Bu_4NPF_6	SCE	DMF	[88]
61	VO(sal$^{\mathrm{Me}}$en$_{\mathrm{Br,OMe}}$)	*O-N-N-O*	V(IV) → V(V)	+0.327	Bu_4NPF_6	SCE	DMF	[88]
62	VO(sal$^{\mathrm{Me}}$en$_{5\mathrm{NO2}}$)	*O-N-N-O*	V(IV) → V(V)	+0.587	Bu_4NPF_6	SCE	DMF	[88]
63	VO(sal$^{\mathrm{Me}}$en$_{\mathrm{Br,NO2)}}$	*O-N-N-O*	V(IV) → V(V)	+0.657	Bu_4NPF_6	SCE	DMF	[88]
64	VO(sal$^{\mathrm{Me}}$en$_{5,5'\mathrm{diBr}}$)	*O-N-N-O*	V(IV) → V(V)	+0.517	Bu_4NPF_6	SCE	DMF	[88]
65	VO(sal$^{\mathrm{Me}}$en$_{\mathrm{diBr,OMe}}$)	*O-N-N-O*	V(IV) → V(V)	+0.680	Bu_4NPF_6	SCE	DMF	[88]
66	VO(sal$^{\mathrm{Me}}$en$_{\mathrm{diBr,OMe}}$)	*O-N-N-O*	V(IV) → V(V)	+0.507	Bu_4NPF_6	SCE	DMF	[88]
67	VO(sal$^{\mathrm{Me}}$en $_{\mathrm{Br,OMe,NO2}}$)	*O-N-N-O*	V(IV) → V(V)	+0.381	Bu_4NPF_6	SCE	DMF	[88]
68	VO(sal$^{\mathrm{Me}}$en$_{5,5'\mathrm{diNO2}}$)	*O-N-N-O*	V(IV) → V(V)	+0.239	Bu_4NPF_6	SCE	DMF	[88]
69	VO(acacpren)	*O-N-N-O*	V(IV) → V(V)	−0.827	Bu_4NBF_4	AgCl/Ag	DMF	[93]
70	VO(bzacpren)	*O-N-N-O*	V(IV) → V(V)	−0.749	Bu_4NBF_4	AgCl/Ag	DMF	[93]
71	VO(azosalophen)	*O-N-N-O*	V(IV) → V(V)	+0.7	Et_4NClO_4	SCE	DCM–MeCN	[94]

Table 2 (*Continued*)

Entry	Compound	Type of ligand	Process[b]	$E_{1/2}$, V	Supporting electrolyte	Electrochem. reference	Solvent	References
72	VO(naphsalophen)	*O-N-N-O*	V(IV) → V(V)	+0.529	Et_4NClO_4	Ag^+/Ag	DMSO	[95]
73	VO(naphsalophen$_{5Cl}$)	*O-N-N-O*	V(IV) → V(V)	+0.571(5)	Et_4NClO_4	Ag^+/Ag	DMSO	[95]
74	VO(naphsalophen$_{3OEt}$)	*O-N-N-O*	V(IV) → V(V)	+0.510(5)	Et_4NClO_4	Ag^+/Ag	DMSO	[95]
75	VO(salcyhex)	*O-N-N-O*	V(IV) → V(V)	+0.392	Bu_4NPF_6	SCE	MeCN	[110]
76	(acac)NiVO(mbzena)(acac)	*O-N-N-O*, *O-O*	V(IV) → V(V)	+0.6	Bu_4NClO_4	AgCl/Ag	MeCN	[96]
77	(bzac)NiVO(mbzena)(bzac)	*O-N-N-O*, *O-O*	V(IV) → V(V)	+0.66	Bu_4NClO_4	AgCl/Ag	MeCN	[96]
Pentadentate ligands								
78	(tcdaH$_2$)	*O-N-N-N-O*	V(IV) → V(V)	+0.427	Bu_4NPF_6	FcH^+/FcH	MeCN	[97]
79	(docdaH$_2$)	*O-N-O-N-O*	V(IV) → V(V)	+0.622	Bu_4NPF_6	FcH^+/FcH	MeCN	[97]

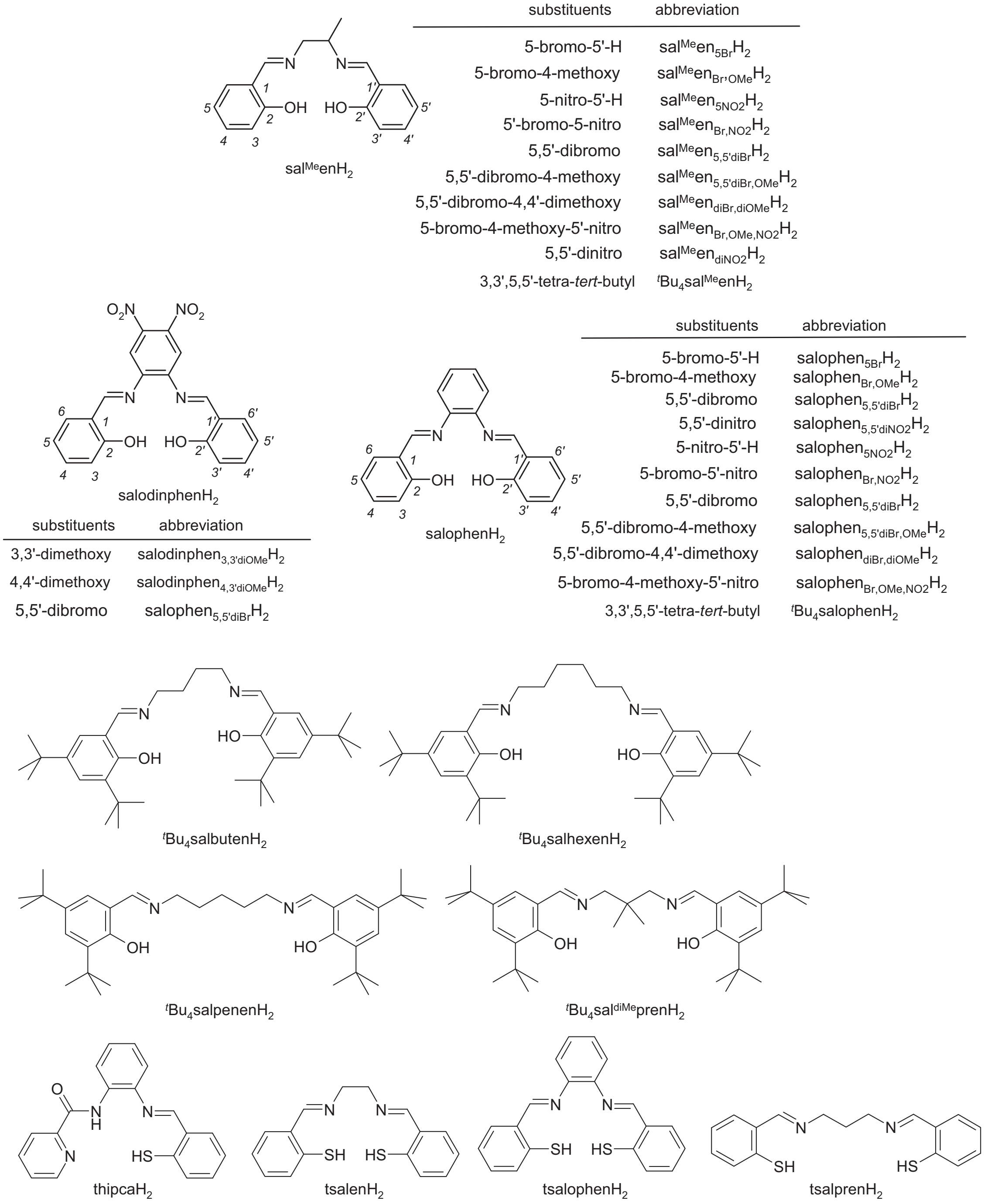
[a] Structures and abbreviations of ligands are in Charts 3 and 4, in alphabetical order.

[b] The process indicates which is the initial and the final oxidation state, without hints about reversibility that can be inferred by the $E_{1/2}$ column.



substituents	abbreviation
5,5'-dibromo	salen$_{5,5'diBr}$H$_2$
5,5'-di-chloro	salen$_{5,5'diCl}$H$_2$
5,5'-dimethoxy	salen$_{5,5'diOMe}$H$_2$
5,5'-dimethyl	salen$_{5,5'diMe}$H$_2$
5,5'-dinitro	salen$_{5,5'diNO2}$H$_2$
5,5'-di-*tert*-butyl	^{t}Bu$_2$salenH$_2$
3,3',5,5'-tetrachloro	Cl$_4$salenH$_2$
3,3',5,5'-tetramethoxy	(MeO)$_4$salenH$_2$
4,4',6,6'-tetramethoxy	(4,6-diMeO)$_2$salenH$_2$
3,3',5,5'-tetra-*tert*-butyl	^{t}Bu$_4$salenH$_2$

Chart 4. Schiff bases and related tetradentate ligands. Structures are reported according to alphabetical order of abbreviations. H atoms corresponding to those substituted by vanadium upon complexation are indicated in abbreviations.



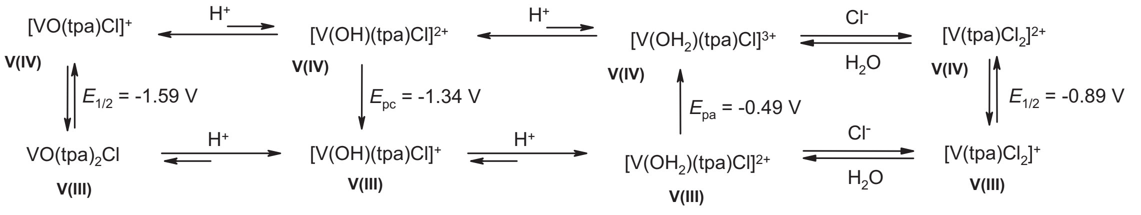
substituents	abbreviation
5-bromo-5'-H	$sal^{Me}en_{5Br}H_2$
5-bromo-4-methoxy	$sal^{Me}en_{Br,OMe}H_2$
5-nitro-5'-H	$sal^{Me}en_{5NO2}H_2$
5'-bromo-5-nitro	$sal^{Me}en_{Br,NO2}H_2$
5,5'-dibromo	$sal^{Me}en_{5,5'diBr}H_2$
5,5'-dibromo-4-methoxy	$sal^{Me}en_{5,5'diBr,OMe}H_2$
5,5'-dibromo-4,4'-dimethoxy	$sal^{Me}en_{diBr,diOMe}H_2$
5-bromo-4-methoxy-5'-nitro	$sal^{Me}en_{Br,OMe,NO2}H_2$
5,5'-dinitro	$sal^{Me}en_{diNO2}H_2$
3,3',5,5'-tetra-*tert*-butyl	$^tBu_4sal^{Me}enH_2$

substituents	abbreviation
3,3'-dimethoxy	$salodinphen_{3,3'diOMe}H_2$
4,4'-dimethoxy	$salodinphen_{4,3'diOMe}H_2$
5,5'-dibromo	$salophen_{5,5'diBr}H_2$

substituents	abbreviation
5-bromo-5'-H	$salophen_{5Br}H_2$
5-bromo-4-methoxy	$salophen_{Br,OMe}H_2$
5,5'-dibromo	$salophen_{5,5'diBr}H_2$
5,5'-dinitro	$salophen_{5,5'diNO2}H_2$
5-nitro-5'-H	$salophen_{5NO2}H_2$
5-bromo-5'-nitro	$salophen_{Br,NO2}H_2$
5,5'-dibromo	$salophen_{5,5'diBr}H_2$
5,5'-dibromo-4-methoxy	$salophen_{5,5'diBr,OMe}H_2$
5,5'-dibromo-4,4'-dimethoxy	$salophen_{diBr,diOMe}H_2$
5-bromo-4-methoxy-5'-nitro	$salophen_{Br,OMe,NO2}H_2$
3,3',5,5'-tetra-*tert*-butyl	$^tBu_4salophenH_2$

Chart 4. (*Continued*)

$[VO(tpa)Cl]^+$, and $[VO(tpa)Br]^+$. A detailed discussion accompanied the electrochemical experiments. The voltammograms in methanol were complicated by dissociation of the ligands and dimerization to form μ-oxo-bridged, due to water eventually present in the solvent. The chloro- and bromo-complexes could be investigated in MeCN, whereas the other one was not soluble. The Cl^- complex, [VO(tpa)Cl]Cl, showed a quasi-reversible redox wave (Table 2, entry 9), but the Br^- complex only gave irreversible waves. On addition of



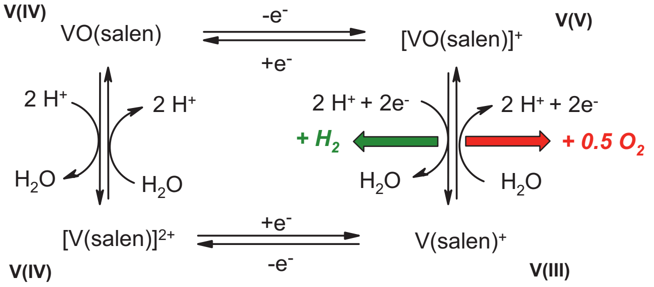
Scheme 5. Overall reaction scheme for the proton-coupled redox reaction in MeCN of $[VO(tpa)Cl]^+$ reported in [73]. Potentials are referred to AgCl/Ag.

p-toluenesulfonic acid, new waves appeared and the final reaction product contained V(III), with loss of vanadyl oxygen upon protonation. The reactions could be reversed neutralizing the acid with equivalent amounts of triethylamine. The processes involved are in Scheme 5.

The most frequently investigated tetradentate ligands are Schiff bases formed between a —OH substituted aromatic aldehyde (generally, 2-hydroxybenzenecarbaldehyde, i.e., salicylaldehyde) and diamines such as, mainly, 1,2-ethanediamine (previously named *N*,*N*′-ethylenediamine) or 1,2-benzenediamine (previously *o*-phenylenediamine). The two families of ligands are known as salen and salophen (or salphen), respectively.

Several papers dealt with vanadium salen complexes, with the metal in different oxidation states. In early studies, both oxido- and non-oxido V(IV) complexes were prepared [74,75]. VO(salen) species gave a reversible oxidation and an irreversible reduction in different solvents. The results in DMSO were virtually identical with those reported DMF, while the oxidation couple is shifted positively about 0.3 V in DCM (Table 2, entry 10). Acidification of VO(salen) was investigated by CV [76]. Under aerobic conditions, the addition of anhydrous HCl to VO(salen) in MeCN resulted in the protonation and dissociation of the vanadyl oxygen atom, giving the dark blue non oxido species, V(salen)Cl_2. This complex exhibited a reversible one-electron reduction to $[V(salen)Cl_2]^-$. In contrast, when perchloric acid was added, a different dark blue complex, $[VO(salen)]^+ClO_4^-$, was isolated. Pecoraro and Carrano attributed the formation of this species to a disproportionation reaction giving both $VO(salen)^+$ and an incompletely characterized V(III) species, subsequently oxidized to $VO(salen)^+$ dioxygen. Transient species were monitored by CV.

The acid-promoted deoxygenation of oxido-V(IV) complexes was the object of electrochemical investigation by Tsuchida and coworkers, in the course of a decade. VO(salen) was deoxygenated in strongly acidic non-aqueous media (trifluoromethanesulfonic acid, CF_3SO_3H, or triphenylmethyl tetrafluoborate, $Ph_3C^+BF_4^-$) and the deoxygenated complex reacted with VO(salen) itself to form a μ-oxo dinuclear vanadium complex, $[(salen)VOV(salen)]X_2$, ($X = CF_3SO_3^-$ or BF_4^-) [77], thus confirming previous data [76]. Electrochemical measurements were used to define the redox properties of the complexes involved and to monitor the slow dimerization reaction. Cyclic voltammograms of VO(salen) in the presence of CF_3SO_3H or Ph_3CBF_4 exhibited reversible waves with potentials near 0.5 and 0.8 V (vs AgCl/Ag, in MeCN). The cathodic wave at 0.5 V was attributed to the combined reduction of $V(salen)^{2+}$ and the dimeric complex and the wave at 0.8 V from the oxidation of the $V(salen)^{2+}$ complex. Selected data are in Table 3, entry 40. $[(salen)VOV(salen)](BF_4)_2$ was used in synthetic (electroreduction to prepare other dinuclear species) or catalytic (homogeneous electroreduction of dioxygen) electrochemical applications [78] (see Section 8). Comparing the potential values for VO(salen) in different solvents, apart from dependence on solvent polarity, it emerged a puzzling dependence on supporting electrolyte, when DCM was the solvent. In fact, with Bu_4NClO_4 or Bu_4NBF_4 as the supporting electrolyte, a single oxidation-reduction couple was observed at higher potentials (near 0.64 V vs SCE) than in polar solvents, while it splitted into two reversible couples separated by ca. 0.1 V with Bu_4NPF_6 and at concentrations of VO(salen) > 1 mM [79]. In order to verify if the tentative explanation for this redox response held – that is the association of mononuclear species to form dinuclear VOVO, in absence of other coordinating species for the VO^{3+} formed – the oxidation of VO(salen) to $[VO(salen)]^+$, believed to be responsible for the voltammetric wave in DCM in the presence of Bu_4NBF_4, was investigated [80]. As a matter of fact, by an extended set of electrochemical experiments and a careful inspection of cyclic voltammograms it was concluded that BF_4^- actually coordinates to oxidized $VO(salen)^+$, to form a neutral complex formulated as $[VO(salen)BF_4]$, although the interaction is weak. That the phenomenon appeared only in DCM was easily explained, because solvents like MeCN can strongly coordinate to VO^{3+}. Moreover, it was possible to understand which one of the two couples observed with Bu_4NPF_6 is that relative to the electron transfer $VO^{2+} \rightarrow VO^{3+}$. A weak coordination could be detected even with perchlorate, but the affinity of VO^{2+} for tetrafluoborate resulted lower with a very similar Schiff base as salpren. All electrochemical data relative to VO(salen) are in entry 10 of Table 2.



Scheme 6. Redox and related reactions occurring in acidic (CF_3SO_3H) anhydrous acetonitrile [81].

The electrochemistry of VO(salen) was reexamined in 2000 by Anson, using microelectrodes, in order to allow measurements in the absence of supporting electrolyte [81]. Investigation in acetonitrile in the presence of triflic acid (trifluoromethanesulfonic acid, CF_3SO_3H), but no other supporting electrolyte, established that disproportionation induced by the added acid controls the electrochemical behavior. It was confirmed that reduction of VO^{2+} accompanied protonation and consequent loss of VO oxygen, with formation of water. The interconversion among vanadium salen complexes is summarized in Scheme 6.

Structural variations were introduced in the salen ligand using phenylglycine, in order to approach the biological role of vanadium, studying models for vanadium binding sites in biomolecules [82,83]. VO(ehpg) and VO(ehgs) (see list of ligands abbreviations and Chart 4) electrochemistry was investigated in different solvents (Table 2, entries 12 and 13). Both compounds underwent reversible one-electron oxidation, but careful controlled conditions were necessary with the former, to avoid subsequent reactions. Instead, VO(ehgs), upon reduction of the oxidized form, returned unchanged and the process could be repeated many times without any evident chemical degradation. The corresponding oxido-V(V) compounds were also investigated (Table 5, entries 91,92). Redox potentials showed a similar solvent dependence, $H_2O < MeOH < MeCN < DMF$ that was related to the polarity of the solvent. Moreover, electrochemical study of the two complexes of ehpg with VO^{2+} and VO^{3+} showed that they are interrelated [83], as opposite corners of an ECEC square mechanism (E = electron-transfer step, C = chemical step). The mechanism was investigated in several solvents and rates were determined for the chemical steps. An oxidation-state-dependent change in the coordination environments of the complexes was identified as the process occurring in the chemical steps of the mechanism.

Structurally related Schiff bases and the corresponding oxido-V(IV) complex were prepared replacing the phenolic oxygen atoms with a sulfur atoms, as in tsalen (Chart 4) [84], with the aim to verify how the redox properties were affected by changing the in-plane ligand donors from *O-N-N-O* to *S-N-N-S*. VO(tsalen) was more difficult to oxidize and more easy to reduce than the corresponding VO(salen) (Table 2, entry 14), result compatible with the *S-N-N-S* donor set ability at stabilizing the lower oxidation states. A non-oxido V(IV) species, $V(sal_{SNO})_2$, was also prepared, in which the

Table 3
Electrochemical data for non-oxido vanadium(IV) compounds.[a]

Entry	Compound	Type of ligand	Process[b]	$E_{1/2}$, V	Supporting electrolyte	Electrochem. reference	Solvent	References
Bidentate ligands								
1	$V(cat)_3^{2-}$	*O-O*	V(IV) → V(III)	−0.72	KCl	SCE	H_2O	[100]
				−0.86	Et_4NClO_4	SCE	MeCN	
			V(IV) → V(V)	−0.035	Et_4NClO_4	SCE	MeCN	
2	$V(Tiron)_3^{2-}$	*O-O*	V(IV) → V(III)	−0.43	KCl	SCE	H_2O	[100]
3	$V(^tBu_2cat)_3^{2-}$	*O-O*	V(IV) → V(III)	−1.21	Et_4NClO_4	SCE	MeCN	[100]
4	$VCl_2(^tBu_2cat)_2^{2-}$	*O-O*	V(IV) → V(III)	+0.11	Et_4NClO_4	SCE	DCM	[27]
			V(III) → V(II)	−0.41				
			V(II) → V(I)	−1.23				
			V(IV) → V(V)	+1.13 (E_{pa})				
5	$V(Cl_4cat)]^{2-}$	*O-O*	V(IV) → V(III)	−0.581	Bu_4NBF_4	AgCl/Ag	DMF	[190]
				−1.088	Bu_4NBF_4	FcH^+/FcH	DMF	
6	$[V(mph)_3]^{2-}$	*O-S*	V(IV) → V(V)	−0.12 quasi-rev	Bu_4NClO_4	AgCl/Ag	MeCN	[102]
7	$[V(mmph)_3]^{2-}$	*O-S*	V(IV) → V(V)	−0.27	Bu_4NClO_4	AgCl/Ag	MeCN	[102]
			V(IV) → V(III)	−1.08				
8	$V(acac)_3^+$	*O-O*	V(IV) → V(V)	+0.94	Et_4NClO_4	AgCl/Ag	Acetone	[104]
			V(IV) → V(III)	−1.33				
9	$V(bzac)_3^+$	*O-O*	V(IV) → V(V)	+0.90	Et_4NClO_4	NHE	DCM	[105]
			V(IV) → V(III)	+0.58				
10	$V(tactac)_3^+$	*S-S*	V(IV) → V(V)	+0.77 irr	Et_4NClO_4	AgCl/Ag	Acetone	[104]
			V(IV) → V(III)	−0.45				
11	$V(actac)_3^+$	*O-S*	V(IV) → V(V)	+0.82	Et_4NClO_4	AgCl/Ag	Acetone	[104]
			V(IV) → V(III)	−0.84				
12	$V(cat)(acac)_2$	*O-O*	V(IV) → V(III)	−0.22	Et_4NClO_4	NHE	MeCN	[106]
				−0.39			DCM	
13	$V(cat)(bzac)_2$	*O-O*	V(IV) → V(III)	−0.26	Et_4NClO_4	NHE	MeCN	[106]
				−0.38				
14	$V(^tBu_2cat)(bzac)_2$	*O-O*	V(IV) → V(III)	−0.37	Et_4NClO_4	NHE	MeCN	[106]
				−0.56				
15	$VCl(bzac)_2(phph^2ol)$	*O-O*	V(IV) → V(III)	−0.5757 E_{pc}	KNO_3	AgCl/Ag	5% DMSO in H_2O	[125]
16	$V(bzac)_2(phph^2ol)_2$	*O-O*	V(IV) → V(III)	−0.7242 E_{pc}	KNO_3	AgCl/Ag	5% DMSO in H_2O	[125]
17	$VCl(bzac)_2(phph^4ol)$	*O-O*	V(IV) → V(III)	−0.8234 E_{pc}	KNO_3	AgCl/Ag	5% DMSO in H_2O	[125]
18	$V(bzac)_2(phph^4ol)_2$	*O-O*	V(IV) → V(III)	−0.8782 E_{pc}	KNO_3	AgCl/Ag	5% DMSO in H_2O	[125]
19	$[V(mndt)_3]^{2-}$	*S-S*	V(IV) → V(III)	−0.32	Bu_4NPF_6	AgCl/Ag	DCM	[103]
			V(III) → V(II)	−1.57 partially rev				
			V(IV) → V(V)	+0.72				
20	$V(^tBu_2cat)_2(phe)$	*O-O, N-N*	V(IV) → V(III)	−0.79	Bu_4NBF_4	NHE	MeCN	[107,108]
				−0.89			DCM	
			V(IV) → V(V)	+0.42				
21	$V(^tBu_2cat)_2(bipy)$	*O-O, N-N*	V(IV) → V(III)	−0.71	Bu_4NBF_4	NHE	MeCN	[107,108]
				−0.88			DCM	
			V(IV) → V(V)	+0.48				
22	$V(Cl_4cat)_2(bipy)$	*O-O, N-N*	V(IV) → V(III)	−0.35	Bu_4NBF_4	$FcH^{+/}FcH$	MeCN	[109]
				−0.50			DCM	
23	$V(eba)_3^{2-}$	*O-O*	V(IV) → V(V)	+0.28	Bu_4NPF_6	SCE	DMF	[112]
24	$V(ebda)_3^{2-}$	*O-O*	V(IV) → V(V)	+0.72 irrev	Bu_4NPF_6	SCE	DMF	[118]
25	V(PhC(O)═C(O)Ph)(tmeda)	*O-O, N-N*	V(IV) → V(V)	+0.27	Bu_4NClO_4	SCE	DMF	[128]
			V(IV) → V(III)	−1.080				
Tridentate ligands								
26	$[V(ino)_2]^{2-}$	*O-O-O*	V(IV) → V(III)	−0.64		NHE	H_2O/KOH	[47]
			V(IV) → V(V)	+0.64				
27	$V(medipha)_2$	*O-N-O*	V(IV) → V(III)	−0.882	Bu_4NPF_6	FcH^+/FcH	DCM	[113]
			V(IV) → V(V)	+0.177				
28	$V(budipha)_2$	*O-N-O*	V(IV) → V(III)	−0.85 quasi rev.	Bu_4NPF_6	FcH^+/FcH	DCM	[113]
			V(IV) → V(V)	+0.226				
29	$V(hybsul)_2$	*O-S-O*	V(IV) → V(III)	−0.929	Bu_4NPF_6	FcH^+/FcH	DCM	[115]
			V(IV) → V(V)	+0.595				
30	$V(hybsel)_2$	*O-Se-O*	V(IV) → V(III)	−0.951	Bu_4NPF_6	FcH^+/FcH	DCM	[115]
			V(IV) → V(V)	+0.464				
31	$V(hybphp)_2$	*O-P-O*	V(IV) → V(III)	−1.060	Bu_4NPF_6	FcH^+/FcH	DCM	[115]
			V(IV) → V(V)	−0.175				
32	$V(hybphpo)_2$	*O-P-O*	V(IV) → V(III)	−0.987	Bu_4NPF_6	FcH^+/FcH	DCM	[115]
			V(IV) → V(V)	+0.193				
33	$V(ttphos)_2$		V(IV) → V(III)	−0.818 E_{pa} irrev	Bu_4NBF_4	FcH^+/FcH	DCM	[116]
			V(IV) → V(V)	+0.149 E_{pa} irrev.				
34	$V(mttphos)_2$	*S-P-S*	V(IV) → V(III)	−0.872	Bu_4NBF_4	FcH^+/FcH	DCM	[116]
			V(IV) → V(V)	−0.107				
35	$V(sal_{SNO})_2$	*O-N-S*	V(IV) → V(III)	−0.24	Bu_4NClO_4	SCE	DMF	[84]
			V(III) → V(II)	−1.57				
36	$[V(hidipicc)_2]^{2-}$	*O-N-O*	V(IV) → V(V)	+0.53	KNO_3, KCl	SCE	H_2O	[119]
				+0.03	Et_4NClO_4	SCE	DMSO	
				+0.18	Et_4NClO_4	SCE	DMF	
				+0.49	KCl	SCE	H_2O	[120]

Table 3 (*Continued*)

Entry	Compound	Type of ligand	Process[b]	$E_{1/2}$, V	Supporting electrolyte	Electrochem. reference	Solvent	References
37	$[V(hidaac)_2]^{2-}$	*O-N-O*	V(IV) → V(V)	+0.52	KCl	SCE	H_2O	[120]
				+0.41	Bu_4NBF_4	SCE	MeOH	[122]
38	$[V(hidbac)_2]^{2-}$	*O-N-O*	V(IV) → V(V)	+0.43	KCl	SCE	H_2O	[121]
				−0.07	Bu_4NClO_4	SCE	DMSO	
Tetradentate ligands								
39	$VCl_2(acen)$	*O-N-N-O*	V(IV) → V(V)	+0.07	Bu_4NClO_4	SCE	DCM	[99]
				+0.0			DMSO	
			V(IV) → V(III)	−1.7			DCM	
				−1.8			DMSO	
40	$[V(salen)]^{2+}$	*O-N-N-O*	V(IV) → V(III)	−0.48		SCE	DMF	[74]
				+0.5	Bu_4NBF_4	AgCl/Ag	MeCN	[77]
			V(IV) → V(V)	+0.8				
41	$V(salen)Cl_2$	*O-N-N-O*	V(IV) → V(III)	+0.05	Et_4NCl	SCE	MeCN	[76]
42	$V(salcyhex)Cl_2$	*O-N-N-O*	V(IV) → V(V)	+1.208	Bu_4NPF_6	SCE	DCM	[110]
			V(IV) → V(III)	+0.075				
43	V(salen)(diphaa)	*O-N-N-O, O-O*	V(IV) → V(III)	−0.338	Not indicated	SCE	MeCN	[123]
			V(IV) → V(V)	+0.92				
44	V(atrisph)(OMe)	*O-N-O-O*	V(IV) → V(III)	−1.206 quasi-rev.	Bu_4NBF_4	FcH^+/FcH	DCM	[117]
			V(IV) → V(V)	+0.929 quasi-rev.				
45	V(atrisph)(acac)	*O-N-O-O, O-O*	V(IV) → V(III)	−1.224	Bu_4NBF_4	FcH^+/FcH	DCM	[117]
			V(IV) → V(V)	+0.374				
46	$V(phhydrz)_2$	*O-N-N-O*	V(IV) → V(V)	+1.14	Et_4NClO_4	SCE	DCM	[124]
47	$V(H_2Nphhydrz)_2$	*O-N-N-O*	V(IV) → V(V)	+1.18	Et_4NClO_4	SCE	DCM	[124]
48	$V(HOphhydrz)_2$	*O-N-N-O*	V(IV) → V(V)	+1.17	Et_4NClO_4	SCE	DCM	[124]
49	$V(etmehydrz)_2$	*O-N-N-O*	V(IV) → V(V)	+1.18	Et_4NClO_4	SCE	DCM	[124]
50	$V(H_2Netmehydrz)_2$	*O-N-N-O*	V(IV) → V(V)	+1.17	Et_4NClO_4	SCE	DCM	[124]
51	$V(HOphhydrz)_2$	*O-N-N-O*	V(IV) → V(V)	+1.15	Et_4NClO_4	SCE	DCM	[124]
52	V(tmtaa)(=NMe)	*N-N-N-N*	V(IV) → V(V)	+0.30	Bu_4NClO_4	SCE	DCM	[131]
53	V(tmtaa)(=N^tBu)	*N-N-N-N*	V(IV) → V(V)	+0.30	Bu_4NClO_4	SCE	DCM	[131]
54	V(tmtaa)(=NPh)	*N-N-N-N*	V(IV) → V(V)	+0.34	Bu_4NClO_4	SCE	DCM	[131]
55	V(tmtaa)(=NC_6F_5)	*N-N-N-N*	V(IV) → V(V)	+0.31	Bu_4NClO_4	SCE	DCM	[131]
56	V(tmtaa)(=$NNMe_2$)	*N-N-N-N*	V(IV) → V(V)	+0.31	Bu_4NClO_4	SCE	DCM	[131]
57	$VCl_3(sulfCpz_3)$	*N-N-N-O*	V(IV) → V(V)		Bu_4NBF_4	SCE	DCM	[130]
Hexadentate ligands								
58	$V(trencam)^{2-}$	*O-O∩O-O∩O-O*	V(IV) → V(III)	−0.37	$NaClO_4$	NHE	H_2O, pH11.7	[111]
			V(IV) → V(III)	−0.544	Bu_4NClO_4	NHE	DMF	[112]
			V(IV) → V(V)	+0.531				
				+0.24	Bu_4NPF_6	SCE	DMF	[112]
59	$V(trenpam)^{2-}$	*O-O∩O-O∩O-O*	V(IV) → V(III)	−0.67	$NaClO_4$	NHE	H_2O, pH11.7	[111]
60	$V(tprcam)^{2-}$	*O-O∩O-O∩O-O*	V(IV) → V(V)	+0.28	Bu_4NPF_6	SCE	DMF	[112]
61	$V(ent)^{2-}$	*O-O∩O-O∩O-O*	V(IV) → V(V)	+0.39	Bu_4NPF_6	SCE	DMF	[112]
62	$V(tben)_4$	*O-N-O∩O-N-O*	V(IV) → V(V)	+0.16	Bu_4NPF_6	FcH^+/FcH	DMF	[114]
63	$V(^{bicapped}trencam)^{2-}$	*O-O∩O-O∩O-O*	V(IV) → V(V)	+0.67	Bu_4NPF_6	SCE	DMF	[118]
64	$V(^{bicapped}trentprcam)^{2-}$	*O-O∩O-O∩O-O*	V(IV) → V(V)	+0.64	Bu_4NPF_6	SCE	DMF	[118]
65	$V(^{bicapped}tprcam)^{2-}$	*O-O∩O-O∩O-O*	V(IV) → V(V)	+0.66	Bu_4NPF_6	SCE	DMF	[118]
Dinuclear complexes								
65	$[(salen)VOV(salen)]^{2+}$	*O-N-N-O*	V(IV,IV) → V(IV,V)	+0.54	Bu_4NBF_4	AgCl/Ag	MeCN	[77]

[a] Structures and abbreviations of ligands are in Charts 1–5, in alphabetical order.

[b] The process indicates which is the initial and the final oxidation state, without hints about reversibility that can be inferred by the $E_{1/2}$ column.

ligand behaved as a tridentate one. Redox values are in Table 3, entry 35.

1,2-Benzenediamine was used to obtain tetradentate coordinating ligands, via amide functionality. A number of ligands with different coordinating atoms and abilities was easily prepared, simply changing the combination of diamide or iminoamide with the acid (benzene- or pyridine-carboxylic) [85]. Electrochemical properties of the corresponding oxido-V(IV) complexes were investigated by cyclic voltammetry and polarography. Results are in Table 2, entries 15–18. One-electron reversible processes were observed for all the complexes, both in MeCN and DCM.

The simplest structural variation relative to VO(salen) was to introduce substituents into aromatic rings or, less frequently, varying the diimine moiety. A number of papers appeared reporting families of oxido-V(IV) complexes and looking for trends in redox potentials with electronic substituent effects.

A family of salen-related Schiff bases was reported in 1999, with a large number of ligands (and VO^{2+} complexes) prepared, either with diamines different from 1,2-ethanediamine or with substituted salicylaldehydes [79]. Electrochemical studies involved only a part of the seventeen oxido-V(IV) complexes prepared, i.e. those with 1,3-propanediamine, 1-methyl-1,2-ethanediamine,

Table 4
Electrochemical data for mixed-valence vanadium(IV,V) compounds.[a]

Entry	Compound	Type of ligand	Process[b]	$E_{1/2}$, V	Supporting electrolyte	Electrochem. reference	Solvent	References
1	$[(\mathrm{quinol})_2\mathrm{VO\text{-}O\text{-}VO}(\mathrm{quinol})_2]^-$	*O-N*	V(IV,V) → V(V,V)	+0.25	Bu_4NClO_4	SCE	MeCN	[22]
2	$[(\mathrm{Hdmpz})\mathrm{OV}(\mu\text{-acac})(\mu\text{-O})(\mu\text{-OAc})\mathrm{VO(acac)}]$	*O-O, N*	V(IV,V) → V(V,V)	+0,43	Bu_4NClO_4	AgCl/Ag	MeOH	[147]
			V(IV,V) → V(IV,IV)	−0.21				
3	$[(\mathrm{salala})\mathrm{VO\text{-}O\text{-}VO}(\mathrm{salala})]^-$	*O-N-O*	V(IV,V) → V(V,V)	+0.44	Et_4NClO_4	SCE	DCM	[136]
4	$[(\mathrm{salphe})\mathrm{VO\text{-}O\text{-}VO}(\mathrm{salphe})]^-$	*O-N-O*	V(IV,V) → V(V,V)	+0.44	Et_4NClO_4	SCE	DCM	[136]
5	$[(\mathrm{salval})\mathrm{VO\text{-}O\text{-}VO}(\mathrm{salval})]^-$	*O-N-O*	V(IV,V) → V(V,V)	+0.46	Et_4NClO_4	SCE	DCM	[136]
6	$[\mathrm{V_2O_2}(\mu\text{-O})(\mathrm{hida})_2]^-$	*O-O-O*	V(IV,V) → V(V,V)	+0.50 (E_{pa}, irr)	Bu_4NClO_4	NHE	DMF	[49]
			V(IV,V) → V(IV,IV)	−0.92 (E_{pc}, irr)				
7	$\mathrm{V_2O_2}(\mu\text{-O})(\mathrm{mphtc})_2$	*O-N-S*	V(IV,V) → V(V,V)	+0.42	Et_4NClO_4	SCE	MeCN	[137]
				+0.42	Et_4NClO_4	SCE	MeCN	[140]
				+0.44	Et_4NClO_4	SCE	MeCN	[138]
				+0.50	Et_4NClO_4	SCE	MeCN	[140]
8	$[\mathrm{V_2O_2}(\mu\text{-O})(\mathrm{mphtc})(\mathrm{OMe})_2]^-$	*O-N-S*	V(IV,V) → V(V,V)	+0.42	Et_4NClO_4	SCE	DCM	[137]
9	$\mathrm{V_2O_2}(\mu\text{-O})(\mathrm{mphtc})(\mathrm{bmphtc})$	*O-N-S, O-N-S*	V(IV,V) → V(V,V)	+0.44	Et_4NClO_4	SCE	MeCN	[139]
10	$\mathrm{V_2O_2}(\mu\text{-O})(\mathrm{bmphtc})_2$	*O-N-S*	V(IV,V) → V(V,V)	+0.50	Et_4NClO_4	SCE	MeCN	[60]
		O-N-S	V(IV,V) → V(V,V)	+0.44	Et_4NClO_4	SCE	MeCN	[140]
11	$\mathrm{V_2O_2}(\mu\text{-O})(\mathrm{nmphtc})_2$	*O-N-S*	V(IV,V) → V(V,V)	+0.63	Et_4NClO_4	SCE	MeCN	[60]
12	$[(\mathrm{tacbz})\mathrm{V(O)\text{-}O\text{-}VO}(\mathrm{tacbz})]^+$	*N-N-N-O*	V(IV,V) → V(V,V)	+0.59	Bu_4NPF_6	AgCl/Ag	MeCN	[135]
			V(IV,V) → V(IV,IV)	−0.75				
13	$\mathrm{VO}(\mathrm{salen}_{5,5'\mathrm{diMe}})$	*O-N-N-O*	V(IV,V) → V(IV,IV)	+0.52	Bu_4NBF_4	SCE	DCM	[79]
14	$[\mathrm{V_2O_3}(\mathrm{pmida})_2]^-$	*O-N-N-O*	V(IV,V) → V(V,V)	+0.76	Bu_4NPF_6	SCE	MeCN	[134]
			V(IV,V) → V(IV,IV)	−0.68				
15	$[\mathrm{V_2O_3}(\mathrm{tpa})_2]^{3+}$	*N-N-N-N*	V(IV,V) → V(V,V)	+1.62	Bu_4NClO_4	NHE	MeCN	[141]
			V(IV,V) → V(IV,IV)	+0.25				
16	$[\mathrm{V_2O_2}(\mu\text{-O})(\mathrm{ntbzimH_3})_2]^{3+}$	*N-N-N-N*	V(IV,V) → V(V,V)	+1.13	Et_4NClO_4	AgCl/AgO_4	MeCN	[144]
			V(IV,V) → V(IV,IV)	−0.41				
17	$[\mathrm{V_2O_2}(\mu\text{-O})(\mathrm{ntbzim})_2]^{3+}$	*N-N-N-N*	V(IV,V) → V(V,V)	+1.12	Et_4NClO_4	AgCl/AgO_4	MeCN	[144]
			V(IV,V) → V(IV,IV)	−0.41				
18	$[(\mathrm{VO})_4(\mu\text{-O})_3(\mu\text{-cahq})_3]^{6-}$	*O-N-O-O∩O-N-O-O*	V(IV,V_3) → V(IV_2,V_2)	+0.48	-	NHE	H_2O	[142]
			V(IV_2,V_2) → V(IV_3,V)	+0.10				
19	$[(\mathrm{VO})_2(\mu\text{-O})(\mu\text{-capc})_2]^{3-}$	*O-N-O-O*	V(IV,V) → V(IV,IV)	+0.60	-	NHE	H_2O	[142]
20	$[\mathrm{V_2OS_4}(\mathrm{edt})]^{3-}$	*N-S*	V(IV,V) → V(IV,IV)	−1.23	Bu_4NClO_4	NHE	MeCN	[145]
21	$(\mathrm{VO})_3(\mathrm{hysalen})(\mu\text{-OMe})(\mathrm{OMe})_2$	*O-O-N-N-O-O*	V(IV,V,V) → V(IV,IV,IV)	+0.52	Bu_4NClO_4	AgCl/Ag	DMF	[148]

[a] Structures and abbreviations of ligands are in Charts 1–5, in alphabetical order.

[b] The process indicates which is the initial and the final oxidation state, without hints about reversibility that can be inferred by the $E_{1/2}$ column.

1,1-dimethylethanediamine, 2-methyl-1,3-propanediamine as the parent diamine and 2-hydroxy-5-methylbenzenecarbaldehyde and 2-hydroxy-5-methoxybenzenecarbaldehyde as the parent aldehyde. Results are in Table 2, entries 10, 19–21. Moreover, an oxido-V(V) and a dinuclear V_2(IV, V) complex were studied (Tables 4 and 5, respectively). The voltammetric behavior observed led to the hypothesis that association occurs following oxidation of mononuclear VO^{2+} complex, to yield a V(IV)/V(V) adduct as soon as the vanadium(V) species is produced and in which subsequent oxidation of the vanadium(IV) partner yields mononuclear VO^{3+} complex, with the association/dissociation process being fast on the voltammetric timescale.

Another set of VO(salen)-type complexes was obtained introducing, not only other substituents in the aldehyde ring, but also 1,2-benzenediamine as the parent diamine for Schiff base and also using 2-hydroxy-1-naphthalencarbaldehyde [86]. Also in this case, electrochemistry was investigated only for some compounds, selecting those with satisfactory elemental analyses. The oxido-vanadium(IV) complexes showed reversible oxidation to oxido-vanadium(V) at potentials between 0.4 and 0.6 V (Table 2, entries 22, 28, 29, 36, 37, 51) and reversible disproportionation to deoxygenated V(III) and oxido-V(V) species in the presence of acid in a reaction (Scheme 7) that is governed by equilibrium constants of ca.10^5–10^8 M^{-1}.

A large number of ring-substituted VO(salen), VO(sal^{Me}en), and VO(salophen) complexes were reported in two 2007 and 2008 papers [87,88]. Results are collected in Table 2, entries 10, 11, 21–23, 25, 37–39, 41–47, 49, 56–68. Some doubts remain about the purity of VO(sal^{Me}en)H_2 ligands obtained with differently substituted salicylaldehydes and 1,2-propanediamine. In fact, although the reaction was stepwise, there is no indication about the regiochemistry of the first step [88]. Attempts were made to correlate oxidation potentials with substituent electronic effects, plotting E_{pa} vs Hammett σ_p. Plots are linear [87], but the number of points is too scarce to allow a reliable interpretation. Moreover, it is questionable that with these compounds σ_p is the appropriate set of substituent constants. The authors concluded that electron-withdrawing groups affected vanadium through π-acceptor properties of imine and electron-donating groups through π- and σ-donation via phenolic oxygen.

Electrochemistry of VO(salen) complexes was investigated with different substituents in the aromatic ring [89]. The results revealed (Table 2, entries 10, 22, 24, 26, 27, 29) that the salen structure stabilizes the oxidized forms and that the effects of substituents on oxidation potential correlate with the electronic density of the metal. Also the role of the donicity of the solvent in influencing the redox potentials of the studied complexes has been demonstrated. Moreover, the variations of the observed potentials could be qualitatively correlated to the catalytic activity of VO(salen) derivatives in the oxidation of thioethers.

Substituted VO(salophen) complexes were also investigated [90] (Table 2, entries 37, 38, 40, 48, 50), even with nitro groups in positions 4 and 5 of 1,2-benzenediamine [91] (Table 2, entries 52–55). With the latter set of compounds, quasi-reversible V(IV → V(V) processes were observed.

Table 5
Electrochemical data for mononuclear oxido-vanadium(V) compounds.[a]

Entry	Compound	Type of ligand	Process[b]	$E_{1/2}$, V	Supporting electrolyte	Electrochem. reference	Solvent	References
1	VO(OMe)(quinol)$_3$	*O-N*	V(V) → V(IV)	−0.40	Bu_4NClO_4	SCE	MeCN	[22]
2	VO(etdtc)$_3$	*S-S*	V(V) → V(IV)	−0.90	Et_4NClO_4	SCE	MeCN	[23]
3	VO$_2$(acac)(phen)	*O-O*, *N-N*	V(V) → V(IV)	−1.45	Et_4NClO_4	SCE	DMSO	[149]
4	VOCl$_3$(pycan)	*O-N*	V(V) → V(IV)	+0.85	Not indicated	AgCl/Ag	$MeNO_2$	[32]
5	VO(salgy)(catH)	*O-N*, *O-O*	V(V) → V(IV)	−0.60	Et_4NClO_4	SCE	MeCN	[165]
6	VO(salala)(catH)	*O-N*, *O-O*	V(V) → V(IV)	−0.77	Et_4NClO_4	SCE	MeCN	[165]
7	VO(salval)(catH)	*O-N*, *O-O*	V(V) → V(IV)	−0.78	Et_4NClO_4	SCE	MeCN	[165]
8	VO(salgy)(^{t}Bu$_2$catH)	*O-N*, *O-O*	V(V) → V(IV)	−0.73	Et_4NClO_4	SCE	MeCN	[165]
9	VO(salala)(^{t}Bu$_2$catH)	*O-N*, *O-O*	V(V) → V(IV)	−0.84	Et_4NClO_4	SCE	MeCN	[165]
10	VO(salval)(^{t}Bu$_2$catH)	*O-N*, *O-O*	V(V) → V(IV)	−0.81	Et_4NClO_4	SCE	MeCN	[165]
11	VO(salmpy)(cat)	*O-N*, *O-O*	V(V) → V(IV)	−0.29	Et_4NClO_4	SCE	MeCN	[165]
12	VO(salmpy)(^{t}Bu$_2$cat)	*O-N*, *O-O*	V(V) → V(IV)	−0.40	Et_4NClO_4	SCE	MeCN	[165]
13	VO(HBdmpz$_3$)(OMe)$_2$	*N-N-N*	V(V) → V(IV)	−0.96 E_{pc}	Bu_4NPF_6	SCE	DCM	[151]
				−0.26	Bu_4NPF_6	SCE	MeOH	
14	VO(bmphtc)(OMe)	*O-N-S*	V(V) → V(IV)	+0.41	Et_4NClO_4	SCE	DCM	[137]
15	VO(bmphtc)(OEt)	*O-N-S*	V(V) → V(IV)	+0.40	Et_4NClO_4	SCE	DCM	[137]
16	VO(bmphtc)(O^{i}Pr)	*O-N-S*	V(V) → V(IV)	+0.39	Et_4NClO_4	SCE	DCM	[137]
17	VO$_2$(tscH)	*O-N-S*	V(V) → V(IV)	−1.15 E_{pc}	Bu_4NBF_4	Not indicated	MeCN	[158]
18	VO$_2$(cyhtscH)	*O-N-S*	V(V) → V(IV)	−1.25 E_{pc}	Bu_4NBF_4	Not indicated	MeCN	[158]
19	VO$_2$(clbtscH)	*O-N-S*	V(V) → V(IV)	−1.27 E_{pc}	Bu_4NBF_4	Not indicated	MeCN	[158]
20	[VO$_2$(bzimpyH)]	*N-N-N*	V(V) → V(IV)	−1.53 irr.E_{pc}	Et_4NClO_4	AgCl/AgO$_4$	DMF	[144]
21	[VO(bzimpyH$_2$)]$^{2+}$ [c]	*N-N-N*	V(IV) → V(III)	−1.47 irr.E_{pc}	Et_4NClO_4	AgCl/AgO$_4$	DMF	[144]
22	[VO$_2$(bzmimpy)]$^+$	*N-N-N*	V(V) → V(IV)	−1.59 irr.E_{pc}	Et_4NClO_4	AgCl/AgO$_4$	MeCN	[144]
23	[VO(bzmimpy)]$^{2+}$ [c]	*N-N-N*	V(IV) → V(III)	−1.33 irr.E_{pc}	Et_4NClO_4	AgCl/AgO$_4$	MeCN	[144]
24	[VO(ntbzimH$_3$)]$^{2+}$ [c]	*N-N-N-N*	V(IV) → V(III)	−1.43 irr.E_{pc}	Et_4NClO_4	AgCl/AgO$_4$	MeCN	[144]
25	VO(hyia)(quinol)	*O-N-O*, *O-N*	V(V) → V(IV)	+0.07	Et_4NClO_4	SCE	DCM	[152]
26	VO(hyip)(quinol)	*O-N-O*, *O-N*	V(V) → V(IV)	−0.06	Et_4NClO_4	SCE	DCM	[152]
27	VO(cat)(salqui)	*N-N-O*, *O-O*	V(V) → V(IV)	−0.257	Et_4NBr	AgCl/Ag	DCM	[155]
			V(IV) → V(III)	−1.620 E_{pc}				
			V(V) → V(IV)	−0.257	Et_4NBr	AgCl/Ag	DMSO	
			V(IV) → V(III)	−1.491 E_{pc}				
28	VO(cat)(naphqui)	*N-N-O*, *O-O*	V(V) → V(IV)	−0.277	Et_4NBr	AgCl/Ag	DCM	[156]
			V(IV) → V(III)	−1.574 E_{pc}				
			V(V) → V(IV)	−0.259	Et_4NBr	AgCl/Ag	DMSO	
			V(IV) → V(III)	−1.486 E_{pc}				
29	VO(cat)(sal^{OMe}qui)	*N-N-O*, *O-O*	V(V) → V(IV)	−0.266	Et_4NBr	AgCl/Ag	DCM	[156]
			V(IV) → V(III)	−1.550 E_{pc}				
			V(V) → V(IV)	−0.250	Et_4NBr	AgCl/Ag	DMSO	
			V(IV) → V(III)	−1.518 E_{pc}				
30	VO(cat)(sal^{Br}qui)	*N-N-O*, *O-O*	V(V) → V(IV)	−0.241	Et_4NBr	AgCl/Ag	DCM	[156]
			V(IV) → V(III)	−1.441 E_{pc}				
			V(V) → V(IV)	−0.207	Et_4NBr	AgCl/Ag	DMSO	
			V(IV) → V(III)	−1.394 E_{pc}				
31	VO(^{t}Bucat)(salqui)	*N-N-O*, *O-O*	V(V) → V(IV)	−0.332	Et_4NBr	AgCl/Ag	DCM	[156]
			V(IV) → V(III)	−1.653 E_{pc}				
			V(V) → V(IV)	−0.304	Et_4NBr	AgCl/Ag	DMSO	
			V(IV) → V(III)	−1.519				
32	VO(^{t}Bucat)(naphqui)	*N-N-O*, *O-O*	V(V) → V(IV)	−0.341	Et_4NBr	AgCl/Ag	DCM	[156]
			V(IV) → V(III)	−1.613 E_{pc}				
			V(V) → V(IV)	−0.317	Et_4NBr	AgCl/Ag	DMSO	
			V(IV) → V(III)	−1.570				
33	VO(^{t}Bucat)(sal^{OMe}qui)	*N-N-O*, *O-O*	V(V) → V(IV)	−0.330	Et_4NBr	AgCl/Ag	DCM	[156]
			V(IV) → V(III)	−1.580 E_{pc}				
			V(V) → V(IV)	−0.302	Et_4NBr	AgCl/Ag	DMSO	
			V(IV) → V(III)	−1.507				
34	VO(^{t}Bucat)(sal^{Br}qui)	*N-N-O*, *O-O*	V(V) → V(IV)	−0.289	Et_4NBr	AgCl/Ag	DCM	[156]
			V(IV) → V(III)	−1.427 E_{pc}				
			V(V) → V(IV)	−0.268	Et_4NBr	AgCl/Ag	DMSO	
			V(IV) → V(III)	−1.418				
35	VO(pygal)(salqui)	*N-N-O*, *O-O*	V(V) → V(IV)	−0.365	Et_4NBr	AgCl/Ag	DCM	[156]
			V(IV) → V(III)	−1.329 E_{pc}				
			V(V) → V(IV)	−0.345	Et_4NBr	AgCl/Ag	DMSO	
			V(IV) → V(III)	−1.349				
36	VO(pygal)(naphqui)	*N-N-O*, *O-O*	V(V) → V(IV)	−0.238	Et_4NBr	AgCl/Ag	DCM	[156]
			V(IV) → V(III)	−1.440 E_{pc}				
			V(V) → V(IV)	−0.303	Et_4NBr	AgCl/Ag	DMSO	
			V(IV) → V(III)	−1.438				
37	VO(pygal)(sal^{OMe}qui)	*N-N-O*, *O-O*	V(V) → V(IV)	−0.248	Et_4NBr	AgCl/Ag	DCM	[156]
			V(IV) → V(III)	−1.480 E_{pc}				
			V(V) → V(IV)	−0.310	Et_4NBr	AgCl/Ag	DMSO	
			V(IV) → V(III)	−1.462				
38	VO(pygal)(sal^{Br}qui)	*N-N-O*, *O-O*	V(V) → V(IV)	−0.350	Et_4NBr	AgCl/Ag	DCM	[156]
			V(IV) → V(III)	−1.255 E_{pc}				
			V(V) → V(IV)	−0.281	Et_4NBr	AgCl/Ag	DMSO	
			V(IV) → V(III)	−1.339				

Table 5 (*Continued*)

Entry	Compound	Type of ligand	Process[b]	$E_{1/2}$, V	Supporting electrolyte	Electrochem. reference	Solvent	References
39	VO(acacbhy)(quinol)	*O-N-O, O-N*	V(V) → V(IV)	−0.287	Et_4NClO_4	AgCl/Ag	DCM	[159]
40	VO(acacbhy)(EGH)	*O-N-O, O-O*	V(V) → V(IV)	−0.20 E_{pc}	Bu_4NClO_4	SCE	DCM	[56]
41	VO(acacbhy)(sal)	*O-N-O, O-O*	V(V) → V(IV)	+0.25	Bu_4NClO_4	SCE	DCM	[56]
42	VO(acacbhy)(van)	*O-N-O, O-O*	V(V) → V(IV)	+0.27	Bu_4NClO_4	SCE	DCM	[56]
43	VO(achyac)(quinol)	*O-N-O, O-N*	V(V) → V(IV)	−0.16 E_{pc}	Bu_4NClO_4	SCE	DCM	[57]
44	VO(salhyac)(quinol)	*O-N-O, O-N*	V(V) → V(IV)	−0.08 E_{pc}	Bu_4NClO_4	SCE	DCM	[57]
45	VO(bzacbhy)(quinol)	*O-N-O, O-N*	V(V) → V(IV)	−0.17	Et_4NClO_4	SCE	DCM	[58]
46	VO(bupbhy)(quinol)	*O-N-O, O-N*	V(V) → V(IV)	−0.11	Et_4NClO_4	SCE	DCM	[58]
47	VO(salbhy)(quinol)	*O-N-O, O-N*	V(V) → V(IV)	−0.05	Et_4NClO_4	SCE	DCM	[58]
48	VO(naphhy)(quinol)	*O-N-O, O-N*	V(V) → V(IV)	+0.07	Et_4NClO_4	SCE	DCM	[58]
49	VO_2(salhyac)	*O-N-O*	V(V) → V(IV)	−0.36 E_{pc}	Bu_4NClO_4	SCE	MeOH	[161]
50	VO_2(achyac)	*O-N-O*	V(V) → V(IV)	−0.31	Bu_4NClO_4	SCE	MeOH	[161]
51	VO(achybz)(van)	*O-N-O, O-O*	V(V) → V(IV)	+0.17	Et_4NClO_4	SCE	DCM	[163]
			V(IV) → V(III)	+0.37				
52	VO(ac^{Cl}hybz)(van)	*O-N-O, O-O*	V(V) → V(IV)	+0.22	Et_4NClO_4	SCE	DCM	[163]
			V(IV) → V(III)	+0.41				
53	VO(ac^{OMe}hybz)(van)	*O-N-O, O-O*	V(V) → V(IV)	+0.11	Et_4NClO_4	SCE	DCM	[163]
			V(IV) → V(III)	+0.30				
54	VO(ac^{Me}hybz)(van)	*O-N-O, O-O*	V(V) → V(IV)	+0.15	Et_4NClO_4	SCE	DCM	[163]
			V(IV) → V(III)	+0.34				
55	VO(achybz)(OMe)(py)	*O-N-O*	V(V) → V(IV)	+0.16	Et_4NClO_4	SCE	DCM	[164]
56	VO(ac^{Cl}hybz)(OMe)(py)	*O-N-O*	V(V) → V(IV)	+0.22	Et_4NClO_4	SCE	DCM	[164]
57	VO(OEt)(salph)	*O-N-O*	V(V) → V(IV)	+0.42	Et_4NClO_4	SCE	MeCN	[166]
58	VO(OMe)(salph)	*O-N-O*	V(V) → V(IV)	+0.416	Et_4NClO_4	SCE	MeCN	[166]
59	VO(OBu)(salph)	*O-N-O*	V(V) → V(IV)	+0.408	Et_4NClO_4	SCE	MeCN	[166]
60	VO(OEt)(salph)(py)	*O-N-O*	V(V) → V(IV)	+0.415	Et_4NClO_4	SCE	MeCN	[166]
61	[imz][VO_2(salph)]	*O-N-O*	V(V) → V(IV)	+0.439	Et_4NClO_4	SCE	MeCN	[166]
62	[2-pic][VO_2(salph)]	*O-N-O*	V(V) → V(IV)	+0.442	Et_4NClO_4	SCE	MeCN	[166]
63	[3-pic][VO_2(salph)]	*O-N-O*	V(V) → V(IV)	+0.453	Et_4NClO_4	SCE	MeCN	[166]
64	[4-pic][VO_2(salph)]	*O-N-O*	V(V) → V(IV)	+0.445	Et_4NClO_4	SCE	MeCN	[166]
65	VO(acazb)(quinol)	*O-N-O, O-N*	V(V) → V(IV)	+0.17	Et_4NClO_4	SCE	MeCN	[153]
66	VO(salhyp)(quinol)	*O-N-O, O-N*	V(V) → V(IV)	+0.355	Bu_4NPF_6	AgCl/Ag	MeCN	[176]
67	VO(achybz)(quinol)	*O-N-O, O-N*	V(V) → V(IV)	−0.12	Et_4NClO_4	SCE	DCM	[168]
68	VO(ac^{Me}hybz)(quinol)	*O-N-O, O-N*	V(V) → V(IV)	−0.15	Et_4NClO_4	SCE	DCM	[168]
69	VO(ac^{OMe}hybz)(quinol)	*O-N-O, O-N*	V(V) → V(IV)	−0.13	Et_4NClO_4	SCE	DCM	[168]
70	VO(ac^{Cl}hybz)(quinol)	*O-N-O, O-N*	V(V) → V(IV)	−0.07	Et_4NClO_4	SCE	DCM	[168]
71	VO(achybz)(OMe)	*O-N-O*	V(V) → V(IV)	+0.26 quasi-rev.	Et_4NClO_4	SCE	DCM	[170]
72	VO(ac^{Me}hybz)(OMe)	*O-N-O*	V(V) → V(IV)	+0.22 quasi-rev.	Et_4NClO_4	SCE	DCM	[170]
73	VO(ac^{OMe}hybz)(OMe)	*O-N-O*	V(V) → V(IV)	+0.20 quasi-rev.	Et_4NClO_4	SCE	DCM	[170]
74	VO(ac^{Cl}hybz)(OMe)	*O-N-O*	V(V) → V(IV)	+0.31 quasi-rev.	Et_4NClO_4	SCE	DCM	[170]
75	VO(achybz)(OMe)py	*O-N-O*	V(V) → V(IV)	+0.22 quasi-rev.	Et_4NClO_4	SCE	DCM	[164]
76	VO(ac^{Cl}hybz)(OMe)py	*O-N-O*	V(V) → V(IV)	+0.38 quasi-rev.	Et_4NClO_4	SCE	DCM	[164]
77	VO(hydoxi)(OEt)	*O-N-O*	V(V) → V(IV)	+0.36	Et_4NClO_4	AgCl/Ag	MeCN	[171]
78	VO(hyd^{OMe}oxi)(OEt)	*O-N-O*	V(V) → V(IV)	+0.31	Et_4NClO_4	AgCl/Ag	MeCN	[171]
79	VO(hyd^{OH}oxi)(OEt)	*O-N-O*	V(V) → V(IV)	+0.29	Et_4NClO_4	AgCl/Ag	MeCN	[171]
80	VO(acacbh)(quinol)	*O-N-O, O-N*	V(V) → V(IV)	−0.08	Et_4NClO_4	SCE	DCM	[59]
81	VO(bzacbh)(quinol)	*O-N-O, O-N*	V(V) → V(IV)	−0.07	Et_4NClO_4	SCE	DCM	[59]
82	VO(acacbh)(van)	*O-N-O, O-O*	V(V) → V(IV)	+0.06	Et_4NClO_4	SCE	DCM	[59]
			V(IV) → V(III)	+0.38				
83	VO(bzacbh)(van)	*O-N-O, O-O*	V(V) → V(IV)	+0.07	Et_4NClO_4	SCE	DCM	[59]
			V(IV) → V(III)	+0.40				
84	VO_2(salgly)(bipy)	*O-N-O, N-N*	V(V) → V(IV)	+0.539 E_{pc}	Bu_4NClO_4	AgCl/Ag	DMF	[53]
85	VO(pyhyph)(cat)	*O-N-N, O-O*	V(V) → V(IV)	−0.58	Bu_4NPF_6	FcH^+/FcH	DCM	[62]
86	VO(pyhyph)(^{t}Bu$_2$cat)	*O-N-N, O-O*	V(V) → V(IV)	−0.72	Bu_4NPF_6	FcH^+/FcH	DCM	[62]
87	VO(pyhyph)(Me$_2$cat)	*O-N-N, O-O*	V(V) → V(IV)	−0.62	Bu_4NPF_6	FcH^+/FcH	DCM	[62]
88	VO(^{t}Bu$_2$pyhyph)(cat)	*O-N-N, O-O*	V(V) → V(IV)	−0.70	Bu_4NPF_6	FcH^+/FcH	DCM	[62]
89	VO(^{t}Bu$_2$pyhyph)(^{t}Bu$_2$cat)	*O-N-N, O-O*	V(V) → V(IV)	−0.87	Bu_4NPF_6	FcH^+/FcH	DCM	[62]
90	[VO(salen)]$^+$	*O-N-N-O*	V(V) → V(IV)	+0.47	Bu_4NPF_6	SCE	MeCN	[76]
91	[VO(ehpg)]$^+$	*O-N-N-O*	V(V) → V(IV)	−0.003	Bu_4NPF_6	SCE	MeOH	[82]
				−0.050	Bu_4NPF_6	SCE	MeCN	[82]
				−0.104	Bu_4NPF_6	SCE	DMF	[82]
92	[VO(eghs)]$^+$	*O-N-N-O*	V(IV) → V(V)	+0.285	Bu_4NPF_6	SCE	H_2O	[82]
				+0.137	Bu_4NPF_6	SCE	MeOH	[82]
				+0.065	Bu_4NPF_6	SCE	MeCN	[82]
				+0.020	Bu_4NPF_6	SCE	DMF	[82]
93	VO(salen)(μ-O)ReO$_3$	*O-N-N-O*	V(V) → V(IV)	+0.59	Bu_4NClO_4	AgCl/Ag	DCM	[173]
				+0.45	Bu_4NClO_4	AgCl/Ag	DMSO	
94	VO(salen$_{3,3'diOMe}$)(μ-O)ReO$_3$	*O-N-N-O*	V(V) → V(IV)	+0.59	Bu_4NClO_4	AgCl/Ag	DCM	[173]
95	VO_2(pabh)	*O-N-N-N*	V(V) → V(IV)	−0.64 E_{pc}	Bu_4NClO_4	AgCl/Ag	DCM	[160]
96	VO_2(path)	*O-N-N-N*	V(V) → V(IV)	−0.67 E_{pc}	Bu_4NClO_4	AgCl/Ag	DCM	[160]
97	VO_2(padh)	*O-N-N-N*	V(V) → V(IV)	−0.72 E_{pc}	Bu_4NClO_4	AgCl/Ag	DCM	[160]
98	VO(pympyr)$_2$(OMe)	*O-N-N-N*	V(V) → V(IV)	−0.197	Et_4NClO_4	SCE	MeOH	[174]
99	VO(hebab)$_3$	*O-N-N-O-O*	V(V) → V(IV)	−0.670 E_{pc}	Bu_4NClO_4	NHE	DMF	[175]
100	VO(hebab^{Br})$_3$	*O-N-N-O-O*	V(V) → V(IV)	−0.620 E_{pc}	Bu_4NClO_4	NHE	DMF	[175]
101	VO(hebab^{OMe})$_3$	*O-N-N-O-O*	V(V) → V(IV)	−0.680 E_{pc}	Bu_4NClO_4	NHE	DMF	[175]
102	VO(hebab^{NO2})$_3$	*O-N-N-O-O*	V(V) → V(IV)	−0.490 E_{pc}	Bu_4NClO_4	NHE	DMF	[175]

Table 5 (*Continued*)

Entry	Compound	Type of ligand	Process[b]	$E_{1/2}$, V	Supporting electrolyte	Electrochem. reference	Solvent	References
103	$VO(sabhea)_3$	*O-N-N-O-O*	V(V) → V(IV)	−0.660 E_{pc}	Bu_4NClO_4	NHE	DMF	[175]
104	$VO(sa^{Br}bhea)_3$	*O-N-N-O-O*	V(V) → V(IV)	−0.600 E_{pc}	Bu_4NClO_4	NHE	DMF	[175]
105	$VO(sa^{OMe}bhea)_3$	*O-N-N-O-O*	V(V) → V(IV)	−0.730 E_{pc}	Bu_4NClO_4	NHE	DMF	[175]
106	$VO(sa^{NO2}bhea)_3$	*O-N-N-O-O*	V(V) → V(IV)	−0.320 E_{pc}	Bu_4NClO_4	NHE	DMF	[175]
107	$VO(Cl)_3(mesim)$	Carbene	V(V) → V(IV)	+0.50	Bu_4NBF_4	Not indicated	DCM	[181]
108	$(bmphtc)VO\text{-}O\text{-}Fe(salen_{3,3'diOMe})$	*O-N-S*	V(V) → V(IV)	−1.78	Bu_4NClO_4	AgCl/Ag	DMF	[184]
109	$(mmphtc)VO\text{-}O\text{-}Fe(salen_{3,3'diOMe})$	*O-N-S*	V(V) → V(IV)	−1.81	Bu_4NClO_4	AgCl/Ag	DMF	[184]

[a] Structures and abbreviations of ligands are in Charts 1–5, in alphabetical order.

[b] The process indicates which is the initial and the final oxidation state, without hints about reversibility that can be inferred by the $E_{1/2}$ column.

[c] V(IV) complex, reported here for immediate comparison.

Oxido V(IV) complexes with sterically hindered *N*,*N*′-polymethylenebis(3,5-di-*tert*-butylsalicylaldimine) ligands [92] gave in DMSO a quasi-reversible or reversible vanadium centered oxidation wave, accompanied in some cases by an irreversible ligand-centered process. Relevant data are in Table 2, entries 29–35).

VO^{2+} complexes were prepared with tetradentate Schiff bases of 2,2-dimethyl-1,3-diaminopropane and β-diketones [93]. Cyclic voltammetries of VO(acacpren) and VO(bzacpren) gave one quasi-reversible oxidation waves (Table 2, entries 69, 70).

A more profound structural variation was introduced preparing an azosalophen ligand, that has the same coordination mode (*O-N-N-O*) and charge (−2) as salen, but was expected to have different properties, due, for example, to the considerable π acid character of the coordinated diazo (—N═N—) nitrogen [94]. The redox properties of VO(azosalophen), investigated by CV, displayed two reversible responses at 0.7 V and −0.65 V vs SCE) (Table 2, entry 71). From DFT investigation, the oxidation resulted metal-centered, V(IV) → V(V), while reduction was ligand-centered.

$$\underset{\textbf{V(IV)}}{2\ \mathrm{VO(Schiff\ Base)}} + 2\ \mathrm{H^+} \rightleftharpoons \underset{\textbf{V(III)}}{\mathrm{V(Schiff\ Base)^+}} + \underset{\textbf{V(V)}}{\mathrm{VO(Schiff\ Base)^+}} + \mathrm{H_2O}$$

complex	10^5 x K, M^{-1}
$VO(salen_{5,5'diOMe})$	300
$VO[(MeO)_4salen]$	500
$VO(^tBu_4salen)$	600
VO(salophen)	3.3
$VO(^tBu_4salophen)$	10
VO(naphthen)	3.2

1st half reaction (two electron reduction)

$$\underset{\textbf{V(V)}}{\mathrm{VO(Schiff\ Base)^+}} + 2\ \mathrm{H^+} + 2\ e^- \rightleftharpoons \underset{\textbf{V(III)}}{\mathrm{V(Schiff\ Base)^+}} + \mathrm{H_2O}$$

complex	$E_{1/2}$, V (vs AgCl/Ag)
$VO(salen_{5,5'diOMe})$	+0.67
$VO[(MeO)_4salen]$	+0.66
$VO(^tBu_4salen)$	+0.63
VO(salophen)	+0.81
$VO(^tBu_4salophen)$	+0.78
VO(naphthen)	+0.81

2nd half reaction (one electron reduction)

$$\underset{\textbf{V(IV)}}{\mathrm{VO(Schiff\ Base)}} + 2\ \mathrm{H^+} + e^- \rightleftharpoons \underset{\textbf{V(III)}}{\mathrm{V(Schiff\ Base)^+}} + \mathrm{H_2O}$$

complex	$E_{1/2}$, V (vs AgCl/Ag)
$VO(salen_{5,5'diOMe})$	+0.88
$VO[(MeO)_4salen]$	+0.88
$VO(^tBu_4salen)$	+0.85
VO(salophen)	+0.97
$VO(^tBu_4salophen)$	+0.95
VO(naphthen)	+0.97

Scheme 7. Acid-induced disproportionation of VO(Schiff Base) complexes and related electrochemical data [86].

Non-symmetrically substituted diimines were prepared stating from 1,2-ethanediamine, 2-hydroxy-1-naphthalencarbaldehyde and salicylaldehyde (unsubstituted and substituted with Cl or ethoxy groups) [95]. Not completely reversible oxidation waves were observed and are in Table 2, entries 72–74.

At variance to diimines, tetradentate ligands based on diamines were also explored. With the dianion of *N*,*N*′-bis(2-hydroxy-3,5-dimethylbenzyl)-*N*,*N*′-dimethyl-1,2-ethanediamine (mbzenaH$_2$) the hetero-bimetallic oxido-V(IV) complexes containing Ni(II), of [(acac)NiVO(mbzena)(acac)] and [(bzac)NiVO(mbzena)(bzac)] formulae, were prepared [96]. The interactions between paramagnetic Ni(II) and V(IV) centers resulted antiferromagnetic and cyclic voltammetry of both complexes showed a reversible oxidation wave, while a reduction wave appeared only with the latter and was attributed to the Ni(II) → Ni(I) couple (Table 2, entries 76,77).

2.1.4. Complexes with pentadentate ligands

1,4-bis(carboxymethyl)-1,4,7-triazacyclononane (tcdaH$_2$) and 4,7-bis(carboxymethyl)-4,7-diaza-1-oxacyclononane (docdaH$_2$) were the starting compounds for pentadenate ligands that allowed formation of VO^{2+} complexes [97]. The cyclic voltammograms of both complexes in dry acetonitrile exhibited one reversible electron-transfer process (Table 2, entries 78,79). In aqueous solution only an irreversible oxidation peak has been observed for both complexes, indicating the instability of the VO^{3+} species in this medium.

2.1.5. Complexes with octadentate ligands

Actually, we found only one example of this type of ligands (Chart 5), that gave a tetranuclear VO^{2+} complex, a macrocycle-semiquinonate compound, with two oxygen atoms bridging VO moieties two by two [98]. Cyclic voltammetry, rotating disk voltammetry and coulometry gave a reversible and a quasi-reversible one-electron metal centered redox processes, at 0.48 V vs. NHE for the $V(IV)_4 \rightarrow V(IV)_3,V(V)$ oxidation and 0.10 V for the $V(IV)_4 \rightarrow V(IV)_3,V(III)$ reduction, respectively.

2.2. Non-oxido vanadium(IV) species

Vanadium in its high oxidation states, +4 and +5, is very oxophilic and, as a consequence, oxido- (VO^{2+}, VO^{3+}) and dioxido- (VO_2, $VO_2{}^+$) compounds were by and large the most investigated species. However, the so-called “bare” or non-oxido compounds, although difficult to obtain, are of great interest, since they are present in nature (for example in amavadin from *Amanita muscaria* [3]). In 1986 Riechel prepared a dichlorovanadium (IV) compound with the dianion of the Schiff base form 2,4-pentanedione and 1,2-ethanediamine (acenH$_2$), to find that the residual water in DCM, instead of hydrolyzing the complex, added to it, forming $[VO(acenH_2)Cl]^+$ [99]. The conversion of $VCl_2(acen)$ to $[VO(H_2acen)Cl]^+$ in DCM has been monitored by cyclic voltammetry. The voltammograms were quite complex, with peaks present immediately after $VCl_2(acen)$ dissolution and disappearing with time, accompanied by the appearance of new waves, some of them transient. By comparison with other complexes, the authors attributed some of these peaks to metal-centered redox reactions (Table 3, entry 39).

Dianion ligands from 1,2-dibenzenols, when used in excess with $VOSO_4$, were able to give non-oxido V(IV) species, with loss of vanadyl oxygen, as it was demonstrated in a meticulous paper in 1982 [100]. $V(cat)_3{}^{2-}$, $V(Tiron)_3{}^{2-}$, and $V({}^tBu_2cat)_3{}^{2-}$ all gave reversible reduction (Table 3, entries 1–3) to V(III), that is consistent with the non-oxido nature, since the reduction $VO^{2+} \rightarrow V^{3+}$, with loss of O, is irreversible (see, for example, Table 1, entry 8). The relatively small difference between reduction potentials in water and acetonitrile was attributed to a strong hydrogen bond interaction with the counterion, Et_3NH^+, that is evident in the solid state and, apparently, persistent in solution. The anodic shift in reduction potential for the Tiron complex relative to that of catechol is consistent with the electron-withdrawing effect of the two sulfonate groups. For the 3,5-di-*tert*-butylcatechol complex the reduction potential is shifted cathodically, as expected for electron-releasing alkyl groups. No evidence was obtained for further reduction to divalent vanadium complexes. When catecholate was substituted with four electron-withdrawing chlorine atoms, either the non-oxido V(V) $[V(Cl_4cat)_3]^-$ or the V(III) $V(Cl_4bsq^{\bullet -})_3$ were obtained [101], for both of which a complex electrochemical behavior is reported.

A non-oxido V(IV) complex was isolated reacting $[VO({}^tBucat)_2]^{2-}$ with $SOCl_2$ [27]. In the cyclic voltammetry of $VCl_2({}^tBu_2cat)_2{}^{2-}$, an initial negative scan yielded three reduction peaks, each coupled to oxidation peaks that appear with a reverse scan. The first peak occurred at +0.08 V vs. SCE and was coupled to an oxidation at +0.13 V. Likewise, the reduction peaks at −0.44 and −1.25 V were coupled to oxidation peaks at −0.38 and −1.20 V, respectively. Controlled-potential electrolysis established that each peak represents a one-electron reduction, presumably at the metal center, because they do not correspond to ligand reductions. In contrast to the cathodic peaks, the anodic electrochemistry was completely irreversible. $E_{1/2}$ values are in Table 3, entry 4.

An obvious extension was to investigate sulfanyl phenols. Complexes of vanadium with ligands that provide a mix of O and S donors are rare but interesting, in light of the related and sometimes different features of otherwise identical ligands with *O-O* and *O-S* donor atoms. 2-Sulfanylbenzenol (mphH$_2$) and 4-methyl-2-sulfanylbenzenol (mmphH$_2$) gave V(IV) complexes without vanadyl oxygen [102]. The cyclic voltammogram of $[V(mmph)_3]^{2-}$ in MeCN solution vs Ag^+/Ag showed a reversible one-electron process and irreversible reduction at −1.08 V (Table 3, entries 6,7), together with oxidations (at +0.59, +0.81, and +1.49 V), that resulted ligand-centered. As to $[V(mph)_3]^{2-}$, its electrochemical behavior is described as entirely analogous. A $[VO(mph)_2]^{2-}$ complex was also isolated, but all the observed redox processes are ligand-centered.

Dithiolate anions also allowed the preparation of non-oxido V(IV) complex: with the dianion of *cis*-2,3-disulfanylbutenedinitrile, mndtH$_2$, $[V(mndt)_3]^{2-}$ was prepared [103], together with Mo and Re complexes of the same ligand, and electrochemically investigated in carefully dried dichloromethane-electrolyte solutions, both at room temperature and −60 °C (Table 3, entry 19).

Later, it was realized that it was possible to obtain non-oxido V(IV) species occupying all vanadium coordination sites also with three β-diketonate or β-dithioketonate ligands [104,105], or with two β-diketonates and one catecholate ligand [106]. $V(acac)_3{}^+$ and $V(bzac)_3{}^+$ gave reversible oxidation and reduction couples; going from diketonate to dithioketonate the ease of reduction increases monotonically with the increasing number of sulfur atoms (Table 3, entries 8–11). The bis(β-diketonato)(catecholate)V(IV) complexes prepared with the dianions of 1,2-benzenediol (cat) and 3,5-di-*tert*-butyl-1,2-benzendiol (^{t}Bu$_2$cat) were more stable to disproportionation than the corresponding tris(β-diketonate) complexes. They showed reversible one-electron reduction to the vanadium(III) state (Table 3, entries 12–14), while oxidation to the vanadium(V) state does not occur at potentials less positive than 1.0 V, at which the catecholate ligand oxidation takes place.

Two catecholate ligands gave non-oxido V(IV) complexes also in combination with neutral *N-N* bidentate ligands [107,108]. In acetonitrile (CV and polarographic studies) $V({}^tBu_2cat)(phe)$ and $V({}^tBu_2cat)(bipy)$ revealed a reversible one-electron reduction process. In DCM, two reversible one-electron processes were observed (Table 3, entries 20,21).

Also catechol with electron-withdrawing substituents, as tetrachlorocatechol (Cl_4catH_2), gave $V(Cl_2cat)_2(bipy)$, that underwent a reversible reduction and an irreversible oxidation [109]. Despite some uncertainties in attributing the processes to metal or to the ligand, comparison with similar species pointed at metal-centered redox processes reasonably (Table 3, entry 22). In the same paper V(III) complexes with tetrachlorocathhecol were prepared and their electrochemical behavior described (Table 8, entries 14,15).

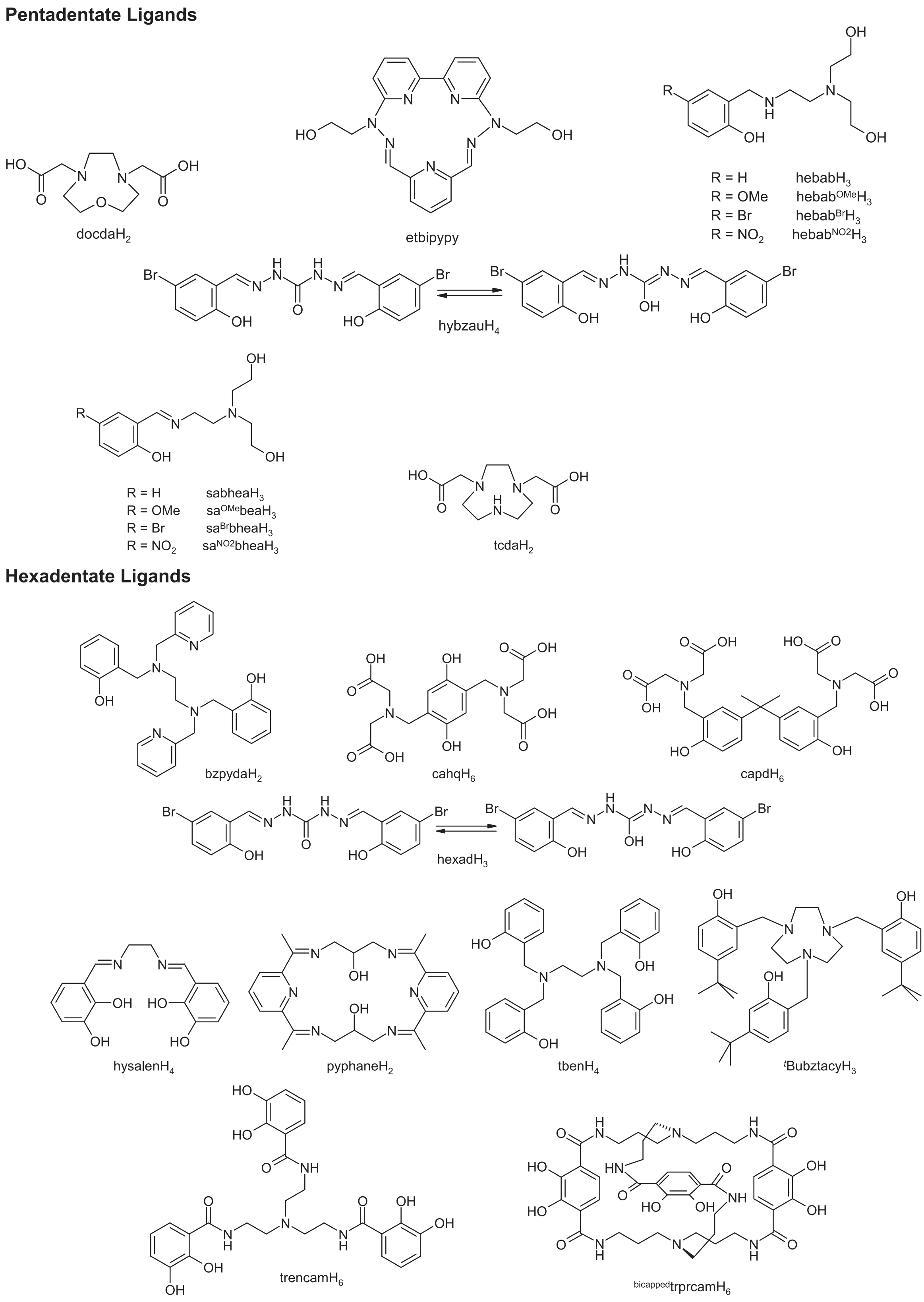
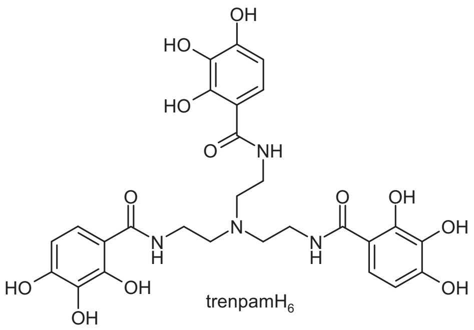
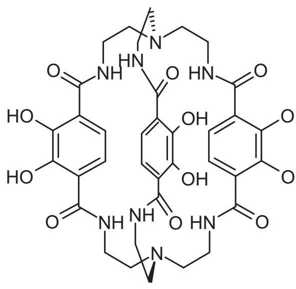


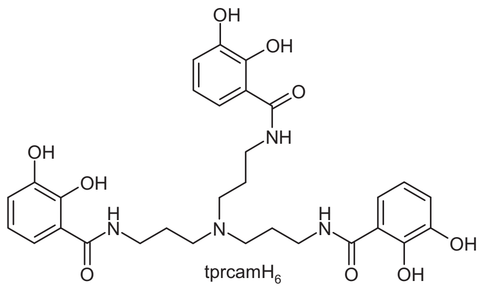
Chart 5. Penta-, hexa-, octa- and nonadentate ligands used in electrochemical investigation of vanadium complexes. Structures are reported according to alphabetical order of abbreviations. H atoms corresponding to those substituted by vanadium upon complexation are indicated in abbreviations.



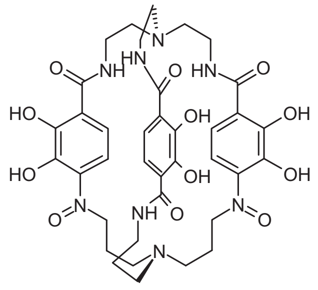
trenpamH_6



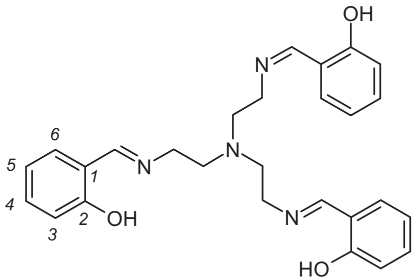
$^{\text{bicapped}}$trenpamH_6



tprcamH_6



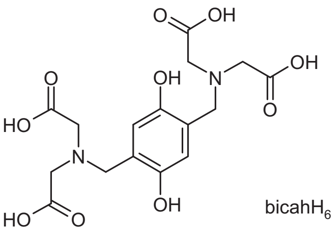
$^{\text{bicapped}}$trentprcamH_6



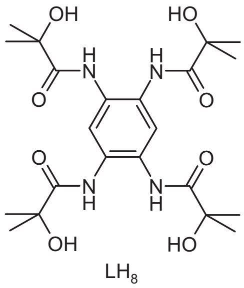
trisalenH_3

substituents	abbreviation
4-Me	trisalen$_{4\text{Me}}\text{H}_3$
5-Me	trisalen$_{5\text{Me}}\text{H}_3$
3,5-Cl_2	trisalen$_{3,5\text{diCl}}\text{H}_3$

Octadentate Ligands

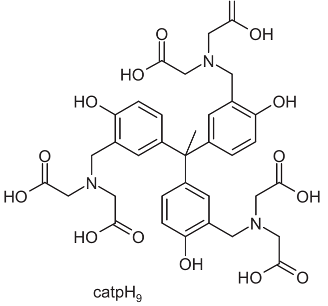


bicahH_6



LH_8

Nonadentate ligand



catpH_9

Chart 5. (*Continued*)

Salen-type ligands allowed to obtain non-oxido V(IV) complexes, with the remaining coordination sites occupied by Cl ligands [110]. *N*,*N*′-bis(2-hydroxy-3-methoxybenzylidene)-1,2-cyclohexanediamine (salcyhexH_2) gave V(salcyhex)Cl_2, that presented reversible, metal-centered electrochemical oxidation and reduction (Table 3, entry 42). A direct comparison with VO(salcyhex) electrochemical properties (Table 2, entry 75) is affected by the different solvents used.

An interesting development was to incorporate the 1,2-benezenediol moiety in a complex structure of a tertiary amine, in order to have hexadentate ligands [111]. With the hexa-anionic ligands (trencam and trenpam), non-oxido V(IV) complexes were prepared and analyzed. In aqueous basic solution (pH 11.7) a quasi reversible reduction wave was observed with $V(trencam)^{2-}$, that in DMF gave quasi-reversible waves for oxidation and reduction (Table 3, entry 58). Above pH 7.0 the cyclic voltammograms of $V(trenpam)^{2-}$ exhibited a formal potential that became more negative with an increasing basicity of the solution. This was attributed to the higher negative charge developed on the complex, as the hydroxyl groups in the 4-position, not involved in coordination of vanadium, becomes fully deprotonated, thus making reduction more difficult. The value reported in Table 3 (entry 59) was taken at pH 11.7.

The complex of V(IV) with the structurally related siderophore enterobactin (entH_6) was also investigated [112] (Table 3, entry 61) and compared with V(IV) complex of the model *N*-ethyl-2,3-dihydroxybenzenecarbamide (Table 3, entry 23).

More simple ligands, such as tertiary amines with phenolic moieties were also able to give non-oxido V(IV) complexes. Mononuclear non-oxido V(IV) complexes were obtained with the dianion of bis-phenol substituted methanamine, $V(medipha)_2$ and $V(budipha)_2$ [113]. The cyclic voltammogram of the former compound displayed two reversible and one irreversible waves, whereas the latter exhibited three reversible ones. Coulometric experiments showed that the waves are due to one-electron transfer processes. Spectroelectrochemistry allowed to attribute the reduction and first oxidation waves to vanadium (Table 3, entries 27,28), while the second oxidation represents the formation of a V(V) phenoxyl radical species.

V(tben) was another example of vanadium(IV) complex with ligands made of tertiary amines with phenolic groups [114]. According to X-ray structure, $tben^{4-}$ gave a mononuclear V(tben) complex, whose electrochemical properties have been investigated by cyclic voltammetric (CV) and coulometric techniques. Well defined reversible one-electron-transfer waves were detected and attributed to oxidation and reduction, respectively (Table 3, entry 62). The starting material was regenerated with re-electrolysis at 0.0 V vs. FcH^+/FcH.

Following the same guide-line, that is to occupy all vanadium coordination sites with ligands difficult to displace, the trianion from *cis*-inositol allowed to obtain a non-oxido V(IV) complex [47], $[V(ino)_2]^{2-}$, Fig. 2.

In freshly prepared, strongly alkaline solutions, cyclic voltammetric measurements established two major one-electron transitions, which correspond to a reduction and an oxidation of the $[V(ino)_2]^{2-}$ complex (Table 3, entry 26). Below pH 9, the CVs were exceedingly complex (probably due to equilibria in solution) and a straightforward interpretation was not possible.

Tridentate bisphenol ligands containing S, Se or P yielded non-oxido V(IV) complexes [115], with electrochemical results that suggest metal-centered oxidations to V(V) (Table 3, entries 29–32). Other tridentate ligand were sulfur based phosphanes [116]. The presence of three —SH notwithstanding, tris(2-sulfanylphenyl)phosphane and tris(5-methyl-2-sulfanylphenyl)phosphane behave as *S-P-S* tridentate ligands, according to X-rays structures, with the uncoordinated sulfur atoms being involved in disulfide bridges. CVs of V(IV) complexes, $V(ttphos)_2$ displayed two well-separated reversible waves of equal size as one-electron-reduction and one-electron-oxidation processes. The reduction processes were considered metal-centered reductions to V(III) species, since the thiolate ligands are not reduced in the examined potential range. The oxidation processes were also attributed to vanadium, because the oxidation of thiolate to thiyl radical is usually irreversible. Results are in Table 3, entries 33,34.

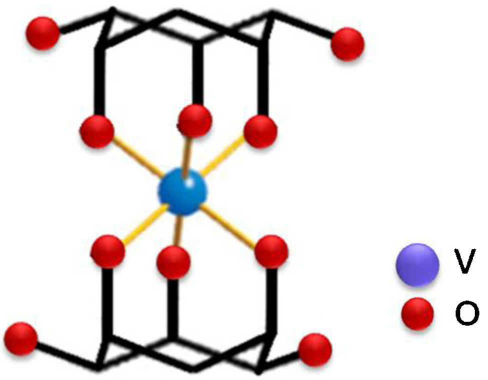


Fig. 2. Structure of $[V(ino)_2]^{2-}$.
Adapted from [47]. Copyright 2007 American Chemical Society.

A tripodal similar aminetris(phenol) ligand, tris(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine actually acted as a tetradentate ligand, allowing to prepare V(IV) complexes [117]. [V(atrisph)(OMe)] and [V(atrisph)(acac)] showed vanadium metal-centered redox processes (Table 3, entries 44,45). No stabilization of the V(IV)-phenoxyl radical species has been observed.

More complicated systems derived from hexadentate trecam and related species. In fact, the complexes formed possessed macrobicyclic ligands and were investigated with the aim to envisage influence of ligand size on the electronic spectra and electrochemistry [118]. Structures of ligands are in Chart 5, electrochemical data in Table 3, entries 63–65, together those of the reference complex $V(ebda)_3{}^{2-}$ (Table 3, entry 24). Quasi-reversible or “essentially reversible” waves were observed for all the complexes, but no particular effect of the bicyclic ring size emerged.

The interest in amavadin, the vanadium containing protein found in *Amanita* mushrooms, prompted the interest in tridentate ligands containing two $—CO_2H$ and one —NOH groups, as those present in the naturally occurring complex [119]. To investigate the mechanism of amavadin mediated oxidation of biological thiols in aqueous medium, the model complexes $V(hidaac)_2{}^{2-}$, $V(hidipicc)_2{}^{2-}$, and $V(hidbac)_2{}^{2-}$ were electrochemically investigated [120,121] as such and in the presence of HS-containing compounds [120]. The complexes underwent a fully reversible oxidation (Table 3, entries 36–38), also in the presence of selected thiols.

The amavadin model $[V(hidaac)_2]^{2-}$ was studied also by another research group [122]. The compound underwent a single-electron reversible oxidation corresponding to the V(IV)/V(V) couple (Table 3, entry 37).

One-electron oxidation and one-electron reduction, both reversible (Table 3, entry 43), were obtained with the V(IV) complex where a bidentate *O-O* ligand from the dianion of 2,2-diphenyl-2-hydroxyacetic acid, $(diphaa)^{2-}$, was used together with salen [123].

More recently, tetradentate salen-type hydrazones were prepared, these too for investigating amavadin models [124]. Cyclic voltammetric data for all the complexes (Table 3, entries 46–51) displayed an electrochemical irreversible (but chemical reversible) one-step one-electron response corresponding to V(IV)→V(V) oxidation.

Within the frame of search of antimicrobial-active compounds, non-oxido V(IV) complexes were prepared, with the *O-O* bidentate benzoylacetonate ligand accompanied by 2- or 4-hydroxybiphenyl (phph^{2}ol and phph^{4}ol, respectively) and Cl ligands [125]. Comparison of cyclic voltammetric studies (Table 3, entries 15–18) indicated that, replacing the electron-withdrawing Cl ligand with the electron-donating phenoxide one, the increased electron density on vanadium renders the compound more difficult to reduce.

An important aspect of electrochemistry is the involvement of ligands in redox properties of complexes. Interest in redox noninnocent ligands revived in recent years, because of their identification in many highly reactive catalytic species and a forum article appeared on the topic [126]. Ligand noninnocence occurs for complexes composed of redox-active ligands and metals, with frontier orbitals of similar energy. Nevertheless, according to Pierpont, cases where the metal oxidation state and ligand charge are unclear are unusual [126]. A striking example can be found in ligands derived from *o*-benzoquinones, that can bind metals as radical semiquinonates ($SQ^{\bullet -}$) or as catecholates (Cat^{2-}), depending also on the metal. Thus, the dianion from bis(2-hydroxy-3,5-di-*tert*-butylphenyl)amine with V(IV) is a catecholate and a semiquinonate contemporarily [127]. V(Cat-N-SQ) showed a quite complicated redox pattern. Only the reduction at −0.35 V vs. FcH^+/FcH was attributed to a V(IV)V(III) reaction, but only tentatively. More clear-cut was the situation when 1,2-diketones were used as ligands. Instead, using 1,2-bis(diaminomethyl)ethane (once called *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, tmeda) as a ligand together with 1,2-diphenylethanedione, V(tmeda)(enediolate) complex was obtained [128]. The CV exhibited a reversible one-electron reduction step and an irreversible oxidation (Table 3, entry 25). Analogously, also the more crowded 1,2-bis(2,6-di-*tert*-butylphenyl)ethanedione coordinated to V(IV) in its reduced enediolate form, $(L^{Red})^-$ [129]. $V(L^{Red})_3$ had two quasi-reversible oxidation processes at −1.00 and +0.25 V vs FcH^+/FcH. The complex was electrochemically oxidized by one and two electrons, generating a monoanion, $[V(L)_3]^{1-}$, and a neutral species, $[V(L)_3]^0$, respectively. DFT calculations, using the hybrid B3LYP functional, showed that the one-electron oxidized product contains an octahedral V(IV) ion coupled antiferromagnetically to one monoanionic ligand π-radical $[V(IV)(L^{\bullet})(L^{Red})_2]^{1-}$ while the two-electron oxidized product contains a V(III) ion coupled antiferromagnetically to three ligand π-radicals $[V(III)(L^{\bullet})_3]^0$.

With tris(pyrazolyl)methanesulfonate a non-oxido V(IV) complex was obtained that exhibited only one-electron fully reversibile oxidation, corresponding to the V(IV) → V(V) process [130] (Table 3, entry 57).

An unusual series of V(IV) complexes that are formally non-oxido species, but actually very close to them, was represented by compounds prepared with a tetraazamacrocycle and some primary amines [131]. CV measurements for this family of complexes presented a reversible oxidation in the range 0.30–0.34 V (Table 3, entries 52–56) and an irreversible reduction at ca. −1.95 V vs SCE, that was not assigned These values are very similar to oxidation potential of the corresponding oxido-V(IV) compound (+0.35 V [132]) and of related substituted macrocyclic systems, that, however, were considered to be ligand based [133].

2.3. Mixed-valence V(IV,V) species

Isolated dinuclear complexes containing (VO^{2+}, VO^{3+}) cation are rare, their electrochemical investigation even less so. Most of them formed only in solution, after electrochemical controlled oxidation of $(V_2O_3)^{2+}$ species (Table 4, entry 1 [22]), but increasing interest in mixed-valence species led to isolation of a number of complexes containing vanadium in both IV and V oxidation states.

One of the first isolated and characterized was $[V_2O_3(pmida)_2]^-$, where pmida is the dianion of (2-pyridylmethyl)bis(carboxymethylamine) [134]. It exhibited two reversible waves in acetonitrile, that correspond to the anodic V(IV,V) → V(V,V) and cathodic V(IV,V) → V(IV,IV) processes (Table 4, entry 14). The authors computed a very large comproportionation constant K_c (about 10^{24}), that was taken as an indication of a strong delocalization in the mixed-valence complex.

In other cases, the formation in solution was unforeseen, but shown by cyclic voltammetry. Thus, the cyclic voltammogram of VO(tacbz)(NCS) in MeCN displayed, besides a reversible one-electron transfer wave at +0.26 V vs AgCl/Ag, which corresponds to the V(IV) → V(V) couple, a second reversible one-electron transfer wave, attributed to the formation of a dinuclear V(IV,V) complex [135]. As a matter of fact, the species $[(tacbz)V(O)\text{-}O\text{-}VO(tacbz)]^+$ was then isolated and characterized. Electrochemical data are in Table 4 (entry 12).

The tridentate *O-N-O* ligands prepared from salicyl aldehyde and natural aminoacids (alanine, phenylalanine and valine) gave binuclear $(V_2O_3)^{3+}$ complexes, under preparative electroreduction of $(V_2O_3)^{4+}$ [136]. These mixed-valence compounds, substantially with valence localization in the solid state, presented delocalization in solution (EPR measurements) and cyclic voltammetries with reversible one-electron oxidation (Table 4, entries 3–5).

A mixed-valence divanadium(IV,V) complex, $[V_2O_3(mphtc)_2]^-$ was prepared from mononuclear V(IV) and V(V) precursors [137] (electrochemical data in Table 4, entry 7) and exhibited a trapped-valence structure in the solid state, while undergoing valence delocalization in solution.

The same compound was obtained [138] by photoreduction of the electrochemically inactive dioxido-V(V) complex, $VO_2(mphtc)$ and identified on the basis of electrochemical properties (Table 4, entry 7). Similar results were obtained with two different dithiocarbazate complexes [137,139], i.e., with $[V_2O_3(mphtc)(OMe)^2]^-$ and $[V_2O_3(mphtc)(bmphtc)]^-$ (Table 4, entries 8,9). The photoreduced products obtained irradiating with a visible light $VO_2(mphtc)(imidazole)$ and the corresponding complexes with bmphtc or nmphtc ligands, differently from their precursors, gave a definite electrochemical response, with a nearly reversible one-electron oxidation wave [60] (Table 4, entries 10,11). The potential depends on the substituent, the oxidation being more difficult with the strong electron-withdrawing nitro group. With tridentate dithiocarbazate-based Schiff base ligands dioxido-V(V) species were obtained by the same research group; they were the precursors for photoreduced divanadium(IV,V) species [140]. These mixed-valence compounds could not be isolated in the solid state but, unlike their precursors, were electrochemically active in the potential range −1.0 to +1.0 V vs SCE. They displayed a reversible oxidation process involving single-electron transfer (Table 4, entries 7,10).

The blue $[(tpa)V(O)\text{-}O\text{-}V(O)(tpa)]^{3+}$, obtained by chemical oxidation of the diamagnetic V(IV,IV) complex with $NOBF_4$, was the first cation in its class for which both solid state and solution-phase characteristics are fully consistent with expectations for a Robin-Day type III mixed-valence complex (the two vanadium atoms resulted equivalent) [141]. Two one-electron reversible waves were observed (Table 4, entry 15).

The cyclic voltammogram of $[V_2O_2(\mu\text{-}O)(hida)_2]^-$ [49] shows the presence of two one-electron irreversible waves, the first of which was attributed to the oxidation to a dinuclear vanadium(V) species, hydrolytically instable (Table 4, entry 6). The second irreversible peak was the reduction; however, the broadness of the peak suggested that the process may be not a simple reduction to the vanadium(IV) compound. According to the authors, the detailed understanding of these reactions should require exhaustive electrolysis and characterization of stable species formed during the reaction.

Substituted VO(salen) complexes gave $[V_2O_2L_2]^+$ species either by (slow) acid oxidation or by cocrystallization of vanadium(IV) and vanadium(V) complexes [79]. One oxidation wave was obtained with $[\{VO(salen_{5,5'diMe})\}_2]^+$ (Table 4, entry 13) virtually identical to that of $VO(salen_{5,5'diMe})$ (Table 2, entry 21).

By complexation of vanadium ion with multifunctional phenolic ligands ($cacpH_3$, $cahqH_6$, $capdH_6$, $catpH_9$, see Charts 3 and 5) multinuclear O-bridged mixed-valence compounds were obtained [142]. The results of the cyclic voltammetric and coulometric studies may be summarized as follows (Table 4, entries 18,19). $[(VO)_4(\mu\text{-}O)_3(\mu\text{-}cahq)_3]^{6-}$, containing V(IV,V,V,V), displayed two metal-centered one-electron reductions; reduction of an aqueous solution of $[(VO)_2(\mu\text{-}O)(\mu\text{-}capc)_2]^{3-}$ by exhaustive electrolysis at 0.30 V gave an almost colorless solution indicating the formation of a monomeric V(IV) species; the multinuclear complexes $[(VO)_4(\mu\text{-}O)_2(\mu\text{-}capd)_2]^{3-}$ and $[(VO)_6(\mu\text{-}O)_3(\mu_3\text{-}catp)_2]^{6-}$ displayed one broad cathodic wave of two and three electrons per molecule at 0.20 V vs NHE. The broadness of the anodic peak was probably due to the multi-electron processes that occur in steps of one electron that have similar reduction potential. Later, the same authors isolated various tetranuclear compounds using 2,5-bis(carboxymethyl)aminomethyl-1,4-benzenediol under different pH conditions [143]; among them the $V_2(IV)V_2(V)$ species with two bicah ligands, one coordinated as a catecholate and the other one as a semiquinonate, is worth noting. A complex electrochemical investigation was performed and discussed in detail. However, the non-innocent ligand was always involved in electron transfer reactions.

With polycyclic benzymidazole substituted pyridine and trimethylamine, different type of vanadium complexes were prepared [144]. The mixed-valence complexes $[(ntbzimH_3)VO\text{-}\mu O\text{-}VO(ntbzimH_3)]^{3+}$ and $[(ntbzmim)VO\text{-}\mu O\text{-}VO(ntbzim)]^{3+}$ showed reversible cyclic voltammograms in MeCN (Table 4, entries 16 and 17), which are consistent with electron delocalization over both vanadium centers. These data, along with the ESR and electronic spectra, imply that the mixed-valence compounds persist in solution, with the single unpaired electron delocalized over the two vanadium centers at ambient temperature.

A mixed valence V(IV,V) species was obtained by oxidation of VCl_3 with elemental sulfur in the presence of sodium 1,2-ethanedithiolate (edt) [145]. $[V_2OS_4(edt)]^{3-}$ displayed a reversible one-electron reduction (Table 4, entry 20).

Highly oxidized, sulfur-rich V(IV,V) complexes of the type $[V_2(\mu\text{-}S_2)_2(S_2CNR_2)_4]BF_4$ (R = Et, ^{i}Pr, ^{t}Bu) were isolated [146]. Electrochemical studies in DCM showed a quasi-reversible, one-electron, oxidation at ca. 0.08 V vs ferrocene, followed by an irreversible oxidation at higher potentials (ca. 1.0 V vs ferrocene), but no further detail was offered.

A novel, unsymmetrical, chiral, mixed-valent, triply bridged, dinuclear vanadium(IV/V) complex having the formula $[(Hdmpz)OV(\mu\text{-}acac)(\mu\text{-}O)(\mu\text{-}OAc)VO(acac)]$ (Hdmpz = 3,5-dimethylpyrazole) was obtained in acetonitrile, by reaction of $[VO(acac)_2]$ and acetylhydrazine ($CH_3CONHNH_2$) in a 2:1 molar ratio [147]. The electron transfer behavior of the complex in methanol displayed two one-electron quasi-reversible responses at the cathodic and anodic sides of the AgCl/Ag reference electrode (Table 4, entry 2).

A complex with a triangular V(V)–V(IV)–V(V) all-oxido core (Fig. 3) has been synthesized using an hexadentate Schiff base, 1,2-bis(2,3-dihydroxybenzylidene)-1,2-ethanediamine ($hysalenH_4$) [148]. The voltammogram presented a reversible electron transfer arising from a metal-based oxidation and a second oxidation at higher anodic potential, likely ligand-based (Table 4, entry 21).

3. Electrochemistry of vanadium(V) compounds

Investigations on redox properties of vanadium(V) compounds were, at the beginning, performed on species electrochemically generated in solution, without isolation, because the supporting electrolyte was present in concentrations much higher than the electrogenerated V(V) compounds and therefore purification workup was not practicable [22,23, Table 5, entries 1,2]. Subsequently, independent synthetic procedures were established and electrochemistry of vanadium(V) compounds could be performed on isolated and well characterized species. Tridentate or tetradentate ligands, based on substituted azobenzenes, hydrazones, Schiff bases of mono- and diamines, carbazones and thiocarbazones were used in the synthesis of families of oxido- or dioxido-V(V) complexes. Modulation of ligand structure was pursued with the aim to elucidate – and eventually to fine-tune – the features that make these compounds appealing in catalysis and in medicinal chemistry. Redox properties are an immediate and easy to collect probe of influence of ligands on metal electron density.

3.1. Oxido- and dioxido-vanadium(V) species

In the pioneering Riechel work on redox chemistry of vanadium–catechol complexes [27], an examination of the electrochemistry of the species tentatively identified as $[VO(^tBucat)_2]^-$, in DMSO, MeCN, and DCM solution, indicated that material probably was polymeric, with two oxidation peaks corresponding to ligand oxidations. The cyclic voltammogram of $[VO(OMe)(^tBucat)_2]^{2-}$ showed no reduction to V(IV) and two irreversible ligand oxidation waves. The same research group studied the electrochemistry of $VO_2(acac)(phen)$ and $V_2O_4(acac)_2$ by cyclic voltammetry and controlled-potential coulometry in DMSO at a platinum electrode [149]. The former compound was reduced at −1.45 V vs SCE, and the latter was reduced at −1.30 V. The major product in both cases resulted $VO(acac)_2$. If excess ligand was present, the reduction processes required three electrons and gave $V(acac)_3{}^-$ as the final product (Table 5, entry 3, Table 6, entry 1).

In a series of V(V), Cr(VI), Mo(VI), and W(VI) oxido-peroxido metal complexes, containing as ligand the anion of pyridine-2-carboxylic acid or of pyridine-*N*-oxide-2-carboxylic acid, a correlation as found between their oxygen-oxygen bond strengths and their ability to act as one-electron acceptors, provided by the reduction potentials [150]. For the V(V) complexes, the same value $E_{pc} = -1{,}26$ V (vs SCE, in DMF, with Bu_4NClO_4 as the supporting electrolyte) was registered with both ligands.

In some cases VO^{3+} complexes were prepared together the VO^{2+} analogs. For example, investigation of $VOCl_2(pycan)$ was accompanied by that of $VOCl_3(pycan)$ [32], where pycanH is *N*-(2-nitrophenyl)pyridine-2-carboxamide. Cyclic voltammetry of the latter complex (Table 5, entry 4) displayed both reversible and irreversible redox processes, to V(IV) and V(III), respectively. The irreversibility of the second process suggests some further reaction, such as the loss of vanadyl oxygen.

Vanadium(V) dialkoxo complexes of the ligands hydridotris(pyrazolyl)borate ($HBpz_3$) and hydridotris(3,5-dimethylpyrazolyl)borate ($HBdmpz_3$) were prepared [151]. In acetonitrile, dichloromethane, and *N*,*N*-dimethylformamide, DMF, they displayed more or less irreversible, reductive electrochemistry. The nature of the R group in the alkoxide appeared to be unimportant. The electrochemistry of the dimethoxy complex $VO(HBdmpz_3)(OMe)_2$ was examined in some detail (Table 5, entry 13). In DCM, vs SCE, a reduction wave was observed at −0.96 V

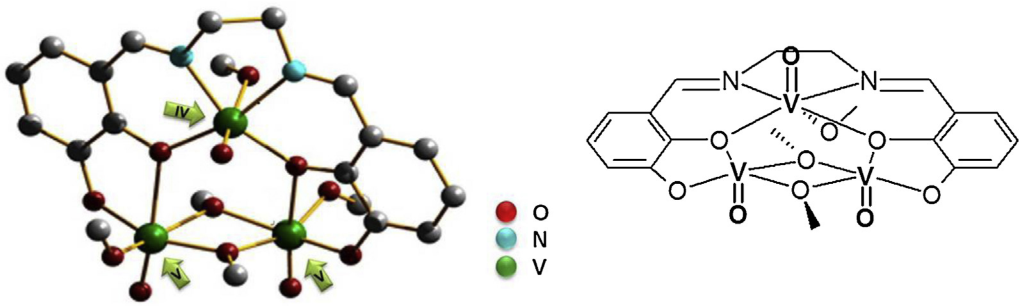


Fig. 3. Triangular V(V)–V(IV)–V(V) all-oxido (hysaled) complex.
Adapted from [148]. Copyright 2013 American Chemical Society.

with only a very small return re-oxidation at −0.40 V, explained with an alkoxide loss in the reduced V(IV) state. In methanol as a solvent, a quasi-reversible wave appeared, that became reversible in presence of trace Bu_4NOH, that generates methoxide, therefore disfavoring ligand dissociation.

Together with the oxido-V(IV) compound, the dimuclear $V_2O_2(salamp)_2(\mu\text{-}O)$ complex was obtained [33], with which an irreversible one-electron oxidation was observed to a stable mixed-valence (IV,V) species (Table 6, entry 2).

That with the same ligand VO^{2+} and VO^{3+} complexes can be prepared is not unusual. Thus, with bis(2-hydroxy-3,5-di-*tert*-butylphenyl)phenylphosphinoxide, beside a mononuclear oxido-V(IV) complex, the dimeric $(VO)_2(hybphpo)_2(\mu\text{-}OH)_2$ was obtained [114], that presented an irreversible oxidation at +0.867 V in DCM, vs FcH^+/FcH.

The mono-oxido-V(IV) complex of tpa was accompanied by the dioxido-V(V) complex, $[V(O)_2(tpa)]^+$, that in acetonitrile showed a major irreversible reduction wave at −1.48 V vs FcH^+/FcH [73]; this was assigned to the reduction of the central metal ion from V(V) to V(IV), as the reduction of the ligand is not expected in such range. Additional irreversible reduction waves were observed at more negative potentials, which have not been precisely assigned. The metal reduction potentials of the oxidovanadium(IV) and dioxidovanadium(V) species were surprisingly very close, but the authors attributed this peculiar finding to stabilization of vanadium(V) oxidation state by the presence of the additional oxido ligand.

Particular interest was devoted to complexes with heteroligands. The oxido-V(V) complexes with Schiff bases of glycine and phenylalanine and 8-quinolol were prepared from VO^{2+} species, upon oxidation at the air [152]. [VO(hyia)(quinol)] and [VO(hyip)(quinol)] displayed a quasi-reversible one-electron cyclic voltammetric response in dichloromethane near 0.0 V vs the saturated calomel electrode (Table 5, entries 25, 26).

Table 6
Electrochemical data for dinuclear oxido-vanadium(V) compounds. [a]

Entry	Compound	Type of ligand	Process[b]	$E_{1/2}$, V	Supporting electrolyte	Electrochem. reference	Solvent	References
1	$V_2O_4(acac)_2$	*O-O*	V(V) → V(IV)	−1.45	Et_4NClO_4	SCE	DMSO	[149]
2	$V_2O_2(salamp)_2(\mu\text{-}O)$	*O-N-O*	V(V,V) → V(IV,V)	−0.56 E_{pc}, irr	Et_4NBF_4	Ag+/Ag	DCM	[33]
3	$V_2O_3(hyazb)_2$	*O-N-O*	V(V,V) → V(IV,V)	+0.21	Et_4NClO_4	SCE	DCM	[154,155]
4	$V_2O_3(hbzhpha)_2$	*O-N-O*	V(V,V) → V(IV,V)	+0.23	Et_4NClO_4	SCE	DCM	[154]
5	$V_2O_3(bbehyd)_2$	*O-N-O*	V(V,V) → V(IV,V)	+0.30	Et_4NClO_4	SCE	DCM	[154]
6	$[V_2O_3(abhph)_2]$	*O-N-O*	V(V,V) → V(IV,V)	−0.96	Bu_4NClO_4	SCE	DCM	[162]
			V(IV,V) → V(IV,IV)	−1.68				
7	$V_2O_2(\mu\text{-}O)(bmphtc)(salen)$	*O-N-N-O, O-N-S*	V(V,V) → V(IV,V)	+0.45	Bu_4NClO_4	AgCl/Ag	DMSO	[157]
8	$VO(OMe)(hexad)VO_2$	*O-N-O*∩*O-N-O*	$VO^{3+} \rightarrow VO^{2+}$	−0.58	$LiClO_4$	AgCl/Ag	DMSO	[177]
			${VO_2}^+ \rightarrow VO_2$	−0.72				
9	$[V_2O_2(O_2)_2(citrate)_2]^{5-}$	*O-O-O-O*	V(V) → V(IV)	−0.83 E_{pc}, irr	KNO_3	AgCl/Ag	H_2O	[178]
10	$V_2O_2(pympyr)_2(MeOH)(OMe)_2$	*O-N-N-N*	V(V) → V(IV)	−0.098	Et_4NClO_4	SCE	MeOH	[174]
11	$[V_2O_2(\mu\text{-}OH)(salen)_2]^+$	*O-N-N-O*	V(V,V) → V(IV,V)	+0.57	Bu_4NClO_4	AgCl/Ag	MeCN	[172]
			V(IV,V) → V(III,IV)	+0.39				
			V(III,IV) → V(III,III)	+0.04				
12	$[V_2O_2(\mu\text{-}OH)(sal^{Me}en)_2]^+$	*O-N-N-O*	V(V,V) → V(IV,V)	+0.55	Bu_4NClO_4	AgCl/Ag	MeCN	[172]
			V(IV,V) → V(III,IV)	+0.36				
			V(III,IV) → V(III,III)	+0.04				
13	$[V_2O_2(\mu\text{-}OH)(salen_{3,3'diOMe})_2]^+$	*O-N-N-O*	V(V,V) → V(IV,V)	+0.53	Bu_4NClO_4	AgCl/Ag	MeCN	[172]
			V(IV,V) → V(III,IV)	+0.34				
14	$V_2O_2(salph)_2(\mu\text{-}O)$	*O-N-O*	V(V,V) → V(IV,V)	+0.45	Bu_4NClO_4	SCE	MeCN	[167]
15	$V_2O_2(achybz)_2(\mu\text{-}O)$	*O-N-O*	V(V,V) → V(IV,V)	+0.29 quasi-rev.	Et_4NClO_4	SCE	DCM	[169]
16	$V_2O_2(ac^{Me}hybz)_2(\mu\text{-}O)$	*O-N-O*	V(V,V) → V(IV,V)	+0.25 quasi-rev.	Et_4NClO_4	SCE	DCM	[169]
17	$V_2O_2(ac^{OMe}hybz)_2(\mu\text{-}O)$	*O-N-O*	V(V,V) → V(IV,V)	+0.21 quasi-rev.	Et_4NClO_4	SCE	DCM	[169]
18	$V_2O_2(ac^{Cl}hybz)_2(\mu\text{-}O)$	*O-N-O*	V(V,V) → V(IV,V)	+0.30 quasi-rev.	Et_4NClO_4	SCE	DCM	[169]
19	$V_2O_2(achybz)_2(\mu\text{-}OMe)_2$	*O-N-O*	V(V,V) → V(IV,V)	+0.25 quasi-rev.	Et_4NClO_4	SCE	DCM	[170]
20	$V_2O_2(ac^{Me}hybz)_2(\mu\text{-}OMe)_2$	*O-N-O*	V(V,V) → V(IV,V)	+0.21 quasi-rev.	Et_4NClO_4	SCE	DCM	[170]
21	$V_2O_2(ac^{OMe}hybz)_2(\mu\text{-}OMe)_2$	*O-N-O*	V(V,V) → V(IV,V)	+0.19 quasi-rev.	Et_4NClO_4	SCE	DCM	[170]
22	$VO(Cl)_2(OCH_2CHEtO)$	*O-O*	V(V) → V(IV)	−0.6	Bu_4NPF_6	AgCl/Ag	DCM	[182]
			V(IV) → V(III)	−1.1				
23	$[VO(\mu\text{-}cat)]_2{}^{2-}$	*O-O*	V(V) → V(IV)	+0.146 E_{pa}	KCl	SCE	H_2O	[185]

[a] Structures and abbreviations of ligands are in Charts 1–5, in alphabetical order.
[b] The process indicates which is the initial and the final oxidation state, without hints about reversibility that can be inferred by the $E_{1/2}$ column.

VO(acazb)(quinol) [153], where acazb is the dianion of 2-carboxy-2′-hydroxy-5′-methylazobenzene, was isolated and used to electrogenerate in DCM solution the mixed-valence couple $[V_2O_2(acazb)_2(quinol)_2]^-$ (Table 5, entry 65).

The same authors, with other tridentate *O-N-O* ligands of the azobenzene family and analogous structures (2,2′-dihydroxyazobenzene, hyazbH_2; (2-hydroxybenzylidene)(2-hydroxyphenyl)amine, hbzhphaH_2; and the enol form of *N*-benzoyl-*N*-(2-benzoyl-1-methylethyl)hydrazine, bbehydH_2), prepared three binuclear oxido complexes, where the $[OV–O–VO]^{4+}$ core is present [154,155]. These compounds were electrochemically investigated in DCM, where a one-electron cyclic voltammetric response due to the $[V_2O_3L_2] \rightarrow [V_2O_3L_2]^-$ couple was observed (Table 6, entries 3–5). Constant-potential coulometry at −0.1 V afforded $[V_2O_3L_2]^-$ quantitatively and, upon reoxidation at 0.6 V, $[V_2O_3L_2]$ was fully regenerated.

Mixed ligand, monooxidovanadium(V) complexes of Schiff bases with 1,2-benzenediol (catH_2), 4-*tert*-butyl-1,2-benzenediol (^{t}BucatH_2) or 1,2,3-benzenetriol (pygalH_2) have been synthesized [156]. Electrochemistry of these complexes showed one reversible V(V) → V(IV) couple and another irreversible V(IV) → V(III) response (Table 5, entries 27–38). The mixed ligand, VO^{3+} complexes are more resistant to reduction as compared to the corresponding tris(catecholate) complexes.

The mononuclear oxido-V(V) alkoxy complexes of *S*-methyl-3-(5-bromo-2-hydroxyphenyl)dithiocarbazate, VO(bmphtc)OR with R = methyl, ethyl, isopropyl [137], gave cyclic voltammograms with identical features, due to a reduction process corresponding to a V(V) → V(IV) electron transfer (Table 5, entries 14–16). The single-electron stoichiometry of this process was further confirmed by controlled-potential coulometric experiments. In this work also the mixed-valence complex, $[V_2O_2(\mu\text{-}O)(OMe)_2]$ was prepared and characterized, with one-electron oxidation observed in DCM solution with $E_{1/2} = 0.42$ V vs SCE. With the same ligand, the dinuclear V(V,V) complex $[V_2O_2(\mu\text{-}O)(bmphtc)(salen)]$ was investigated [157]. The cyclic voltammogram in DMSO showed a cathodic reversible process (Table 6, entry 7). Results of constant potential coulometry indicated single-electron stoichiometry, thus confirming the generation of a mixed-oxidation divanadium(IV,V) product.

Neutral dioxido-vanadium(V) complexes of general formulae $VO_2(HL)$, where HL is the monoanion of the enol form of thiosemicarbazones, were isolated and characterized, in view of their possible antiamoebic activity [158]. The cyclic voltammograms of these complexes indicated a kinetically facile reduction of vanadium(V) to vanadium(IV) (Table 5, entries 17–19), but no oxidation of vanadium(IV) to vanadium(V). Only in successive cycles a very weak oxidation peak appeared.

The enol form of 2,4-pentanedione *N*-benzoylhydrazone with quinol formed an oxido-V(V)complex [159] with a quasi-reversible redox behavior in DCM, corresponding to V(V) → V(IV) (Table 5, entry 39).

Dioxido-V(V) complexes were prepared with the enol form of aroyl hydrazones derived from pyridine-2-carbaldehyde [160]. Cyclic voltammetries of all complexes displayed irreversible metal-centered reduction (Table 5, entries 95–97). A cathodic shift of the potential was observed with the increasing electron donating ability of the substituents. With salhyac and achyac ligands a dioxido-V(V) complex was also prepared [161] both complexes are electroactive in MeOH, with irreversible reduction peak (Table 5, entries 49–51).

With another aroylhydrazone, the enolic form of the dianion of 2-hydroxyacetophenone (2-aminobenzoyl)hydrazone, $[V_2O_3(abhph)_2]$ was electrogenerated [162]. In dichloromethane solution it underwent two successive one electron reductions, which were assigned to V(V,V) → V(IV,V) and V(IV,V) → V(IV,IV) couples (Table 6, entry 6).

Mixed-ligand oxidoV(V) complexes were prepared with the already discussed enol form of 2,4-pentanedione *N*-benzoylhydrazone [56], and bidentate *O-O* monoanionic ligands from 1,2-ethanediol (EGH_2), salicylaldehyde (salH) and vanillin (vanH). They exhibited either irreversible reduction (with EGH ligand in DMSO) or a quasi-reversible cyclic voltametric response (Table 5, entries 40–42).

Oxido-V(V) complexes were obtained with achyac and salhyac ligands and the anion of 8-hydroxyquinoline [57]. They exhibited quasi-reversible cyclic voltammetric response in DCM near −0.10 V vs SCE, due to VO^{3+}/VO^{2+} couple (Table 5, entries 43,44). VO^{3+} derivatives were prepared with the *N*-benzoylhydrazones already discussed for VO^{2+} complexes, in the presence of the anion of 8-hydroxyquinoline [58]. This set of complexes showed a quasi-reversible CV response in DCM solution (Table 5, entries 45–48).

N-benzoylhydrazones of substituted acetophenones opened the possibility to detect electronic substituent effects. VO^{3+} species contained the vanillin anion as *O-O* heteroligand [163]. All the complexes exhibited two one-electron quasi-reversible reduction peaks in DCM, that were attributed to successive reductions of the VO^{3+} motif, first to VO^{2+} and then to VO^+ (Table 5, entries 51–54). Potentials of both reduction processes were reported as a function of Hammett σ constants, giving linear plots, with the following relations: 1st reduction: $E_{1/2} = 0.17 + 0.21\sigma$ ($r = 0.98$); 2nd reduction: $E_{1/2} = 0.37 + 0.21\sigma$ ($r = 0.97$). From these relationships, it appears that the sensitivity to substituent effect of the two reductions is the same, which is not so obvious if one consider that the vanadium electronic density is quite different in the two processes. Moreover, correlation factor is not satisfactory, probably because of the choice of substituent constants set. Also, there is some incongruence in electrochemical data: probably, the reported sign for the second reduction is not correct, otherwise it would mean a reduction occurring upon potential increase.

Complexes with the same *N*-benzoylhydrazones and different heteroligands [164] displayed one quasi-reversible reduction peak attributed to the VO^{3+}/VO^{2+} couple (Table 5, entries 55,56). Apparently, changing the heteroligand from vanillin to pyridine and methoxy does not affect reduction potentials, but the authors offered no discussion about it.

Tridentate *N-N-N* heterocycles made of pyridine and benzoimidazoles led to oxido-V(IV) and V(V) complexes [144]. Cyclic voltammograms of mononuclear (VO^{2+} and VO^+) bzimpy chelates showed irreversible redox processes (for immediate comparison all of them are reported in Table 5, entries 20–24). It is noteworthy that all the experimentally observed reductions occurred at ca. −1.2 V vs SCE, regardless of whether the electroactive species was V(IV) or V(V). It was suggested that the difference in oxidation state is compensated by the presence of the additional oxo ligand in the V(V) systems; that is, the dioxidovanadium(V) and monooxidovanadium(IV) complexes are redox-potential equivalent.

A family of oxido-V(V) hetero-ligand complexes were prepared coordinating either the dianion or the monoanion of catechols and the monoanion of Schiff bases from aminoacids and the monoanion of (2-hydroxybenzylidene)(4-pyridyl)methylamine [165]. All the compounds presented a quasi-reversible reductive one-electron response V(V) → V(IV) at negative potentials and a virtually irreversible oxidative response catecholate/semiquinonate at positive potentials. The two responses occur respectively at more negative and more positive potentials for the series with monoanionc catecholate than with compounds with the dianionic ligand (Table 5, entries 5–12).

Mono- and di-oxido V(V) complexes were obtained with the enolic form of dianion of 2-hydroxybenzenecarbaldehyde (2-hydroxybenzoyl)hydrazone, $(salph)^{2-}$ [166]. Selected cyclic voltammetric data are in Table 5, entries 57–64. In all the dioxido complexes, the V(V) → V(IV) reductions occurred in the +0.40 to 0.45 V region vs SCE. The $E_{1/2}$ values are close to each other and also close to the $E_{1/2}$ values of the monooxido alkoxy complexes, according to the authors, because of the similarity in the coordination environments of the V(V) center in both classes.

Later, one of the above salph compounds, VO(OEt)(salph), was the precursor of the dinuclear V(V,V) complex, $V_2O_2(salph)_2(\mu\text{-}O)$ [167], that displayed a quasi-reversible cyclic voltammetric response near 0.45 V vs SCE (Table 6, entry 14), generating by electroreduction a mixed-valence vanadium(IV,V) species, which, unfortunately, could not be isolated.

Analogous complexes were prepared with *N*-benzoylhydrazones of substituted 2-hydroxyacetophenones and 8-hydroxyquinoline [168]. These oxidovanadium(V) complexes exhibited quasi-reversible one electron reduction peak near −0.10 V vs SCE due to $VO^{3+} \rightarrow VO^{2+}$ couple (Table 5, entries 67–70). Potentials correlated well with Hammett σ values, E_{pc} (V) = −0.16 + 0.19σ (r = 0.99).

With the same ligands, dinuclear μ-O VO^{3+} complexes were prepared [169], that exhibited a quasi-reversible reduction peak (Table 6, entries 15–18), suggesting an identical electronic environment at both the vanadium centers. A Hammett correlation between potentials and σ was found, very similar to that reported for mononuclear species E_{pc} (V) = 0.20 + 0.19σ (r = 0.98).

Another series of VO^{3+} complexes prepared with the same set of ligands [170] had the formula VOL(OMe), with L = achybz, ac^{Me}hybz and ac^{Cl}hybz; instead, $ac^{OMe}hybzH_2$ gave only the dimeric $V_2O_2(ac^{OMe}hybz)_2(\mu\text{-}OMe)_2$ (from which the authors were, nevertheless, able to obtain the mononuclear complex). Similar dinuclear compounds were prepared independently also with achybz and ac^{Me}hybz ligands (Table 6, entries 19–21). All the complexes, mono- and dinuclear, exhibited one quasi-reversible reduction peak in the +0.19 V to +0.31 V vs SCE region (Table 5, entries 71–74) with potentials linearly correlated with Hammett σ. For monomeric complexes: $E_{1/2}$ (V) = 0.26 + 0.22σ and for the dimeric ones: $E_{1/2}$ (V) = 0.25 + 0.22σ (correlation coefficient is given as ca.1 in both cases).

The corresponding complexes with an extra pyridine ligand [164] resulted electro-active and displayed one quasi-reversible reduction peak, although data are reported for only two of them (Table 5, entries 75, 76).

The hydrazones from 2-hydroxybenzoylhydrazide and acetylacetone or benzoylacetone, already discussed in Section 2.1 [59], with 8-hydroxyquinoline or vanilline as the second ligand, gave VO^{3+} complexes that exhibited a quasi-reversible one-electron reduction peak in DCM solution near 0.08–0.06 V vs SCE, due to the VO^{3+}/VO^{2+} couple. Complexes with vanilline ligand presented also a second quasi-reversible one-electron reduction peak near +0.38 V vs SCE, probably due to $VO^{2+} \rightarrow VO^{+}$ reduction (Table 5, entries 80–83). We are forced to repeat the observation that the second reduction cannot occur at a potential higher than that of the first one.

Ligands containing contemporarily an hydrazone and an oxime functionalities were prepared from 2,3-butanedione and used to prepare V(V) complexes, in view of their potential antibacterial activity [171]. The electrochemical properties of all the oxidovanadium(V) complexes, examined in MeCN by cyclic voltammetry, consisted in a quasi-reversible response in the potential range 0.29–0.36 V vs Ag^{+}/Ag, involving single electron V(V) → V(IV) reduction (Table 5, entries 77–79).

Dinuclear oxidovanadium(V) compounds, coordinated to salen (or structurally related sal^{Me}en and $salen_{3,3'diOMe}$) ligands and connected by an unsupported hydroxy bridge have been obtained upon air oxidation of the corresponding mononuclear oxido-V(IV) precursors [172]. CV, normal pulse voltammogram (NPV), and steady state voltammetry exhibited three cathodic processes, the first and the third process were one-electron reductions, the second one was a two-electron reduction (Table 6, entries 11–13). The reduction processes were identified as V(V,V) → V(V,IV), V(V,IV) → V(IV,III), and V(IV,III) → V(III,III), respectively. The third reduction is absent with the $salen_{3,3'diOMe}$ and the peculiar behavior was attributed to the electron donating OMe groups in the ligand aromatic rings, that increase the coordinated vanadium center electron density, making it less prone to accept the incoming electron. Curiously, this effect was not present in first and second reductions.

With the same salen and $salen_{3,3'diOMe}$ ligands, heterobimetallic complexes of a vanadium(V) and rhenium(VII) combination connected by a μ-oxido bridge were synthesized [173]. For both the complexes the electrochemical results, based on CV, DPV, NPV, and constant potential coulometric experiments, were consistent with two successive one-electron steps, the first step involving V(V) → V(IV) reduction (Table 5, entries 93, 94), while the second one is rhenium reduction, Re(VII) → Re(VI). Apparently, the presence of OMe does not affect the reduction potential, but no comment was offered by the authors.

Finally, it is worth noting *N-N-N-O* tetradentate Schiff bases containing pyrazole and pyridine ($pypyrH_2$) or pyrimidine ($pympyrH_2$) [174]. The mononuclear oxido alkoxy complex, $VO(pympyr)_2(OMe)$ showed an irreversible one electron reductive response (Table 6, entry 98), as well as, surprisingly, did the dinuclear complex $V_2O_2(pympyr)_2(MeOH)(OMe)_2$ (Table 6, entry 10), for which two different peaks were expected, due to the different coordination environment around the two V(V) centers.

The hydrolytically stable trivalent, pentadentate amine alcohol ligands of the type *N*,*N*-bis(2-hydroxyethyl)-*N*′-(2-hydroxybenzyl)-1,2-ethanediamine (with different substituents in the phenyl ring) formed oxido-V(V) complexes, that were compared with those obtained from the corresponding Schiff bases 2-(2-hydroxybenzylideneamino)ethyl-bis(2-hydroxyethyl)amine, with the same substituents [175]. All of them underwent irreversible electrochemical reduction in DMF (Table 5, entries 99–106). The author attributed the irreversibility to the insolubility of the corresponding V(IV) complexes in organic solvents, DMF included. The reduction potentials do not show a linear correlation with the Hammett constants σ_p, which was attributed to the fact that the reduction properties of the complexes should be determined by the LUMO.

Ten years later, Plass obtained VO^{3+} complexes, prepared coordinating *N*-acyloylhydrazones (butanoyl, pentanoyl, and hexanoyl) from salicyl aldehyde and 8-hydroxyquinoline [176]. Electrochemical investigations showed quasi-reversible square wave voltammograms with two one-electron reduction steps for all complexes, the first one relative to V(V) → V(IV), while the second involved the ligand 8-hydroxyquinoline; electrochemistry was discussed in detail only for VO(salhyp)(quinol) (Table 5, entry 66), but all have the same potentials, within ±2 mV.

A neutral dinuclear vanadium complex containing both oxido and dioxidovanadium cores was synthesized with the hydrazone based ligand *N*,*N*′-bis(5-bromo-2-hydroxybenzylideneamino)urea, in its enolic form [177]. The ligand, bis[(*E*)-*N*′-(5-bromo-2-hydroxybenzylidene)]-carbohydrazide, here called $hexadH_3$ for simplicity, in its trianionic enol form, coordinated two vanadium ions, forming polyhedra with a VO_5N distorted octahedron for the mono-oxido-V(V) core and a VO_3N_2 trigonal bipyramid for the dioxide-V(V) core. Cyclic voltammetric experiments in DMSO revealed two quasi-reversible peaks, due to the V(V) → V(IV) reductions of oxido- and dioxido-V(V) centers (Table 6, entry 8).

After the report on *o*-iminobenzosemiquinone radical complexes of the oxido-V(IV) [61,62a], the same group used catechols as redox active organic fragments which can sustain in “malleable” electronic states the oxidovanadium ion.

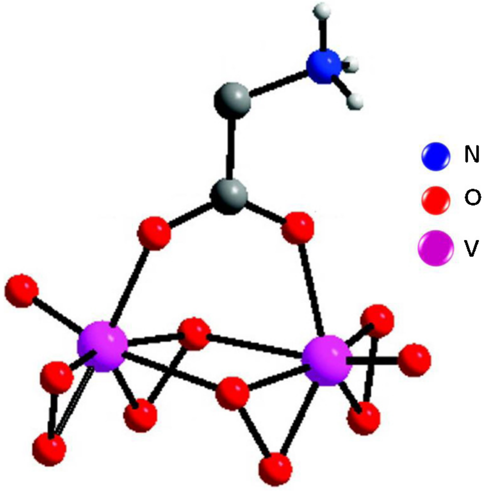


Fig. 4. Structure of $[V_2(O)_2(\mu^2{:}\eta^2{:}\eta^1\text{-}O_2)^2(\eta^2\text{-}O_2)_2(Gly)]$. Adapted from [180]. Copyright 2009 American Chemical Society.

6-[(2-(Pyridin-2-yl)hydrazono)methyl]phenols, with different alkyl groups in 2,4 positions were used as tridentate monoanionic *O-N-N* ligands, together with dianionic bidentate *O-O* catechol ligands, with different alkyl substituents [62b]. Differently from iminobenzosemiquinonate, that preferred the state of anion radical, catecholates behaved as dianions and, as a consequences, oxidation state of the vanadium core resulted +5. The complexes were redox-active (Table 5, entries 85–89). The first cathodic wave (at potentials between −0.58 and −0.87 V vs FcH^+/FcH) were reversible and due to V(V) → V(IV) reduction, as confirmed by EPR spectra and DFT calculations. A second cathodic not-reversible wave was due to the formation of hydrazone anion radical. Only irreversible anodic waves were observed in the range from +0.32 to +0.45 V vs FcH^+/FcH, due to the ligand oxidation, with formation of oxido-V(V) species, which are unstable in solution.

Several studies were performed in aqueous solution, trying to understand which structural features are determinant in affecting the chemical reactivity of V(V) metal ion in a biologically relevant setting.

In 2006 Salifoglou and coll. reported that V_2O_5, citric acid and H_2O_2 reacted at pH 5.5–6.0 to yield a red crystalline product, that was given the $K_{10}[V_2O_2(O_2)_2(citrate)_2][V_2O_2(O_2)_2(citrate)_2]\cdot 20H_2O$ molecular formulation, all vanadium atoms being V(V) [178]. The cyclic voltammetry, studied in endogenous aqueous solutions, in the presence of KNO_3 as a supporting electrolyte, exhibited ill-defined electrochemical waves (Table 6, entry 9). The meaning of the observed irreversibility was not understood.

Later the same research group [179] obtained in solution $(guanidinium)_6[V_2O_4(citrate)_2]$ and the peroxido $(guanidinium)_4[V_2O_2(O_2)_2(citrate)_2]$ species. The cyclic voltammogram of both complexes in aqueous solution presented ill-defined electrochemical behavior, related to irreversible sequential V(V) → V(IV) and V(IV) → V(III) redox processes.

Given that these species bear a physiologically important moiety present in human fluids, it seemed important to investigate whether glycinate V(V)-peroxo species exhibits biological activity, $[V_2(O)_2(\mu^2{:}\eta^2{:}\eta^1\text{-}O_2)^2(\eta^2\text{-}O_2)_2(Gly)]$ (GlyH = glycine [180], Fig. 4). The cyclic voltammetry of the complex in aqueous solutions, in the presence of KNO_3 as a supporting electrolyte, vs AgCl/Ag, exhibited ill-defined electrochemical waves, a reduction wave at $E_{pc} = -1.0$ V, and an oxidation wave at $E_{pa} = -0.7$ V, due to irreversible V(V) → V(IV) redox process.

An *N*-heterocyclic carbene complex of trichloro-oxido-vanadium(V), $VO(Cl)_3(mesim)$, was obtained by reaction of equimolar quantities of 1,3-dimesitylimidazol-2-ylidene and trichloro-oxido-vanadium(V) [181]; the deep red 1:1 adduct (Fig. 5), $VO(Cl)_3(mesim)$, remarkably stable, underwent a one-electron reversible reduction at a potential, +0.5 V, (Table 5, entry 107, reference electrode not indicated) significantly lower than the standard potential of V(V) → V(IV).

Mixed alkoxyalkoxo chloro complexes of formula $[VO(Cl)_2(OCH_2CHRO)]$ were synthesized and characterized [182]. Actually, they are dimeric complexes with Cl bridges – that are broken in THF – and display multi-step reductive chemistry, only partly reversible. However, electrochemical data were given for $[VO(Cl)_2(OCH_2CHEtO)]_2$ only (Table 6, entry 22) and are relative to metal-centered reduction.

Quite rare are the heterodinuclear complexes. An interesting bimetallic complex was prepared using the octadentate ligand 1,2,4,5-tetrakis(2-hydroxy-2-methylpropanamido)benzene, LH_8, that acted as a bis-tetradentate ligand, coordinating two oxido-V(V) groups [183]. However, the electrochemical reduction of $[V_2O_2(L)]^{2-}$ resulted ligand centered.

Unusual heterobimetallic compounds containing a discrete V(V)-μ-O-Fe(III) angular core have been synthesized [184]: Fe was coordinated with the dianion of 3,3′-dimethoxy-1,2-bis(2-hydroxybenzylidene)-1,2-ethanediamine ($salen_{3,3'diOMe}$) and V had the dianion of *S*-methyl-3-(5-bromo-2-hydroxyphenyl)dithiocarbazate (bmphtc) or of the analogous 5-methoxy derivative (mmphtc) as tridentate ligand (Fig. 6). The redox behavior (CV, DMF as the solvent, AgCl/Ag as the reference electrode) presented three cathodic redox processes: a reversible one-electron process at $E_{1/2} = -0.15$ V (process I), an irreversible one-electron process at $E_{pc} = -1.67$ V (process II), and a quasi-reversible two-electrons process at $E_{1/2} = -1.81$ V (process III). Process I was due to Fe(III) → Fe(II) reduction, process II was attributed to ligand-based reduction and process III involved a combination of both vanadium-based $VO^{3+} \rightarrow VO^{2+}$ and ligand-based reduction, thus accounting for the two electron involvement. In Table 5 (entries 108, 109) only values concerning vanadium are reported.

Two binuclear vanadium–catecholate complexes $[VO(\mu\text{-}cat)]_2^{2-}$ and $[VO(\mu\text{-}naphdiol)]_2^{2-}$, to be used in cancer cells, have been synthesized and characterized [185]. The electrochemical properties were studied in water, where the complexes are soluble. $[VO(\mu\text{-}cat)]_2^{2-}$ presented two quasi-reversible waves only the first one being vanadium-related (Table 6, entry 23), while the second one is relative to the ligand. With $[VO(\mu\text{-}naphdiol)]_2^{2-}$, instead, only an irreversible wave due to the ligand was observed, meaning that – according to the authors – V(V) is hard to be reduced in the presence of 2,3-naphthalenediol.

3.2. *Non-oxido vanadium(V) species*

Complexes of V(V) without oxygen bound to vanadium are scarce. The anionic $[V(Cl_4cat)_3]^-$ complex underwent one-electron oxidation and reduction reactions reversibly [101]. However, the latter occurred at a potential considerably more negative than that of the corresponding catechol complex and therefore both electrochemical processes were attributed to the ligand. A discussion of these data, evidencing the role and the noninnocence of the ligand was presented several years later, in a forum article, also in comparison with other first-row transition-metal complexes [186].

The air stable neutral mixed ligand tris bidentate non-oxidoV(V) complex, $V(N_3S_2)(^tBu_2cat)(phen)$ revealed two reversible couples (Table 7, entry 4) corresponding to V(V)V(IV) and V(IV)V(III) redox processes, respectively, indicating that the $S_2N_3^{3-}$ anion is a good ligand for the stabilization of V(V) [187]. On the basis of

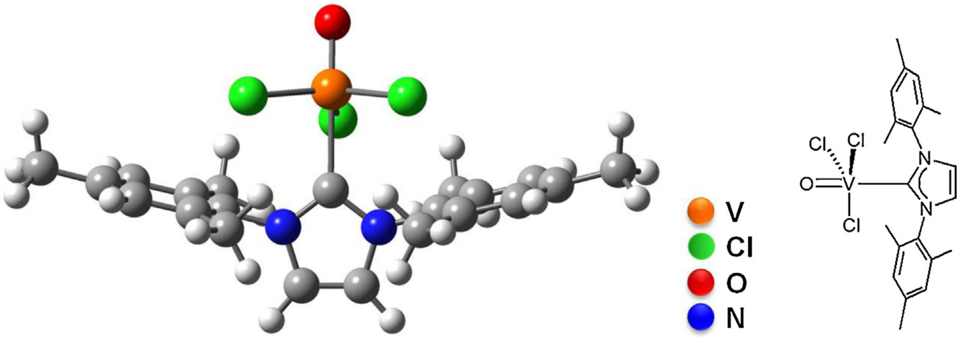


Fig. 5. Structure of $VO(Cl)_3$(mesim) [181].

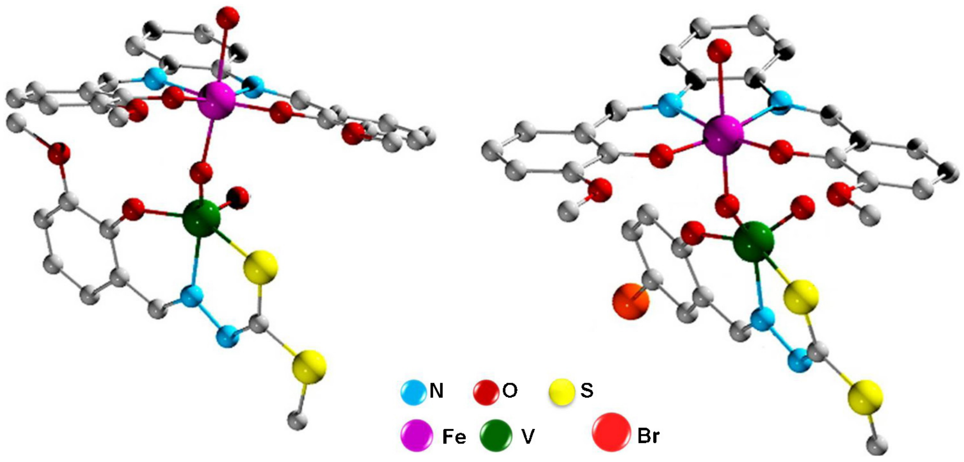


Fig. 6. Structures of (mmphtc)VO-O-Fe(salen$_{3,3'\mathrm{diOMe}}$) (left) and (bmphtc)VO-O-Fe(salen$_{3,3'\mathrm{diOMe}}$) (right).
Adapted from [184]. Copyright 2012 American Chemical Society.

the findings of previous work, other complexes were prepared and electrochemically characterized (Table 7, entries 5–7) [188]. Cyclic voltammetry in dichloromethane, together with polarography revealed the presence of two one-electron reversible redox couples.

Within a research mainly devoted to chromium catecholates, also V(V) complexes were investigated [189]. Cyclic voltammetry studies were used to design the conditions for bulk electrolysis experiments and for subsequent electrochemical X-ray absorption spectroscopy (XAS) studies. Data are in Table 7 (entries 1,2) for V(V) catecholates and in Table 3 (entry 5) for V(IV) complex with tetrachlorocatecholate.

With the aim to investigate the scope of the de-carbonylation reaction observed with a Nb(OCN) complex, the corresponding

Table 7
Electrochemical data for non-oxido vanadium(V) compounds. [a]

Entry	Compound	Type of ligand	Process[b]	$E_{1/2}$, V	Supporting electrolyte	Electrochem. reference	Solvent	References
1	$[V(cat)_3]^-$	*O-O*	V(V) → V(IV)	+0.076	Bu_4NBF_4	AgCl/Ag	DMF	[189]
				−0.431	Bu_4NBF_4	FcH^+/FcH	DMF	
2	$[V(^tBu_2cat)_3]^-$	*O-O*	V(V) → V(IV)	−0.270	Bu_4NBF_4	AgCl/Ag	DMF	[189]
				0.777	Bu_4NBF_4	FcH^+/FcH	DMF	
3	$[V(Cl_4cat)_3]^-$	*O-O*	V(V) → V(IV)	−0.85	Not indicated	FcH^+/FcH	MeCN	[101]
4	$V(N_3S_2)(^tBu_2cat)$(phen)	*O-O, N-N, S-S*	V(V) → V(IV)	+0.37	Bu_4NBF_4	NHE	DCM	[187]
				+0.44		NHE	DCM	[188]
			V(IV) → V(III)	−0.77	Bu_4NBF_4	NHE	DCM	[187]
				−0.70		NHE	DCM	[188]
5	$V(N_3S_2)(^tBu_2cat)$(bipy)	*O-O, N-N, S-S*	V(V) → V(IV)	+0.50	Bu_4NBF_4	NHE	DCM	[187]
				+0.48		NHE	MeCN	[188]
			V(IV) → V(III)	−0.69		NHE	DCM	[187]
				−0.56		NHE	MeCN	[188]
6	$V(N_3S_2)$(cat)(bipy)	*O-O, N-N, S-S*	V(V) → V(IV)	+0.66 E_{pa}	Bu_4NBF_4	NHE	DCM	[188]
			V(IV) → V(III)	−0.54				
7	$V(N_3S_2)$(cat)(phen)	*O-O, N-N, S-S*	V(V) → V(IV)	+0.64 E_{pa}	Bu_4NBF_4	NHE	DCM	[188]
			V(IV) → V(III)	−0.53				
8	$(^t\mathrm{Budman})_3V(OCN)$	*N*	V(V) → V(IV)	−0.11	$Bu_4NB(C_6F_5)_4$	FcH^+/FcH	THF	[190]
			V(IV) → V(III)	−1.56				

[a] Structures and abbreviations of ligands are in Chart 1, in alphabetical order.
[b] The process indicates which is the initial and the final oxidation state, without hints about reversibility that can be inferred by the $E_{1/2}$ column.

V(V) compound was prepared, with one OCN and three anions of (3,5-dimethylphenyl)-*tert*-butylamine (^{t}Budman) [190]. The CV of (^{t}Budman)$_3$V(OCN) is marked by two electrochemical events. The first one was a quasi-reversible reduction V(V) → V(IV). The second event appeared reversible at sweep rates between 10 and 300 mV/s and was assigned to the V^{4+}/V^{3+} couple (Table 7, entry 8). By the way, reduction of (^{t}Budman)$_3$V(OCN) did not led to CO evolution, but to cyanate dissociation and the consequent formation of the corresponding V(III) species, V(^{t}Budman)$_3$.

An unusual compound containing Rh or Ir together V was prepared within a research devoted to sulfur-bridged early late heterobimetallic complexes [191]. $[\{(Me_5Cp)(PMe_3)(\mu\text{-}S)_2Rh\}_2V]^+$ and $[\{(Me_5Cp)(PMe_3)(\mu\text{-}S)_2Ir\}2\,V]^+$ were prepared from VCl_3, that oxidized to V(V) under reaction conditions. Both complexes gave cyclic voltammograms with a reversible one-electron reduction wave at −1.15 V and −1.24 V vs SCE, respectively. Measurements were carried out in DCM, using Bu_4NBF_4 as the supporting electrolyte.

4. Electrochemistry of vanadium(III) compounds

Compounds of V(III) are not particularly difficult to prepare, but more difficult to investigate, because they tend to the stable oxidation states IV and V. This aspect must be kept in mind especially in electrochemical studies, where it is not rare to find reports of additional waves in redox cycles after the first ones, reasonably attributed to oxidation with oxygen uptake and formation of VO^{2+} or similar species. Nevertheless, papers discussing redox properties of V(III) complexes are in substantial number and electrochemical results will be reported here in Table 8 for mononuclear compounds and in Table 9 for di- and trinuclear species.

In earlier publications, quite often V(III) compounds are reported together the corresponding V(IV) or V(V) ones, both oxido and non-oxido. In the course of the development of the synthesis and stereochemistry of complexes of thiolates with divalent and trivalent transition-metal ions, the dinuclear $[V_2(edt)_4]^{2-}$ (where edt is the dianion of 1,2-ethanedithiol) was obtained, indicated as the first vanadium–thiolate complex ever [192]. In acetonitrile solution $[V_2(edt)_4]^{2-}$ exhibited a well-defined one-electron oxidation (Table 9, entry 1). The same compound was re-investigated few years later (Table 9, entry 1b [193]) with results in excellent agreement, at least, according to the authors.

With 3,4,5,6-tetrachloro-1,2-benzenediol (Cl_4catH_2) both the anionic $[V(Cl_4cat)_3]^-$, with V(V) and the neutral V(III) species were prepared, where reduction of vanadium was accompanied by oxidation of catecholate ligand, that therefore was formulated as $V(Cl_4bsq^{\bullet-})_3$, with the semiquinone ligand. Solutions prepared with $[V(Cl_4cat)_3]^-$ and $V(Cl_4bsq^{\bullet-})_3$ in acetonitrile were studied by voltammetry and constant-potential coulometry [101]. The anionic complex underwent one-electron oxidation and reduction reactions reversibly (Table 7, entry 3). The oxidation product was generated coulometrically at a potential of +0.6 V vs FcH^+/FcH. The neutral product, $V(Cl_4bsq^{\bullet-})_3$, showed a very complicated electrochemical behavior, undergoing at +0.86 V an irreversible two-electron oxidation (Table 8, entry 7) to a species that was reduced irreversibly by two electrons at −0.13 V. Further coulometry at +1.1 V gave a dark green product, upon oxidation by two units of charge, and a yellow-orange solution upon further oxidation. Characterization of these products has not been carried out, but was ascribed to intramolecular electron transfer, occurring rapidly on the electrochemical time scale. From these and a series of other experimental data, the authors concluded that the form of the neutral complex investigated electrochemically in solution is different in charge distribution from the form characterized in the solid state.

$V(Cl_4cat)(acac)(bipy)$ underwent reversible oxidations at −0.504 and +0.063 V to V(IV) and V(V) forms, respectively, vs FcH^+/FcH ([109] Table 8, entry 14) and a quasi-reversible reduction at −1.753 V, that, according to the authors, may occur either at the metal to give a V(II) species or at the bipyridine ligand. $[V(Cl_4cat)_2(bipy)]^-$ showed in DCM vs FcH^+/FcH oxidation couples at −0.50 and 0.84 V (Table 8, entry 15), and a reversible reduction at −1.34 V, due to the cobalticenium counterion.

For a while, complexes with low-valent V and ligands with sulfur donating atoms were investigated in connection with the important problem of crude oil hydrodesulfurization.

The vanadium(III) tris-chelate of dithioacetylacetone ($tactacH_2$), monothioacetylacetone ($actacH_2$), and acetylacetone ($acacH_2$) [104] gave voltammetries where the ease of reduction increases monotonically with the increasing number of sulphur donor ligands (Table 8, entries 4–6). The redox potential values of $V(acac)_3$ are in agreement with those reported in [25].

Binuclear V(III) complexes were obtained with 2-aminoethanethiol, aetH, and the corresponding *N*,*N*′-dimethyl derivative, dimaetH [194]. $V_2O(dimaet)_4$ exhibited an irreversible oxidation at −0.37 V vs NHE in MeCN. No cathodic peak was seen in the cyclic voltammogram at 100 mV/s, as well as in DCM and THF and at higher scan speeds. On the other hand, $V_2O(aet)_4$ showed a near reversible oxidation (Table 9, entry 2).

A systematic investigation was performed on the influence of the edt^{2-}/V ratio on reaction product(s) in the presence of elemental S, with the result to isolate a variety of discrete V/S complexes [193]. Redox properties, via CV, indicated that $[V_2(edt)_4]^{2-}$ undergoes two oxidation processes to V(IV) and V(V) (Table 9, entry 1b), while the V(IV) species, formed with one S atom, $[VS(edt)_2]^{2-}$, displays no reversible redox processes, a result already reported by the same authors [195], with only an irreversible oxidation process at $E_{pa} = -0.46$ V vs NHE was observed. The same compound, $[V_2(edt)_4]^{2-}$, was studied again few years later (Table 9, entry 1c [196]).

The dinuclear V(III,III) complex $[V_2(metacy)_2(\mu\text{-}O)(\mu\text{-}OAc)_2]^{2+}$ (where metacy stays for 1,4,7-trimethyl-1,4,7-triazacyclononane) was stable enough to be isolated and crystallyzed as diiodide [197]. The cyclic voltammetric results (Table 9, entry 3) revealed two reversible one-electron waves at −0.02 and −1.87 V vs FcH^+/FcH, leading to mixed valence V(III,IV) or V(III,II), as confirmed by controlled-potential coulometry experiments at potentials +0.5 and −2.1 V. Later, other carboxylates were used by the same research group. Hydrolysis of $V(metacy)Cl_3$, in methanol/water with the sodium salts of a variety of carboxylic acids afforded green dinuclear complexes $[V_2(metacy)_2(\mu\text{-}O)(\mu\text{-}carboxylate)_2]^{2+}$ which have been isolated as solid hexafluorophosphate or iodide salts [198]. Two reversible oxidation waves were observed (Table 9, entries 4–7), that varies with Taft's inductive parameter, σ_I, of the R group of the carboxylato bridges: with increasing electron-withdrawing capacity of R, the V(III) species it becomes more difficult to oxidize and $E_{1/2}$ becomes more positive. In contrast, with increasing electron-withdrawing capacity of R, it is easier to reduce the V(III) complexes and $E_{1/2}$ becomes less negative.

While pursuing the synthesis of $[(metacy)V(CN)_3]$, a reaction was discovered wherein the oligomerization of cyanide lead to formation of a tetracyanide-bridged dinuclear complex, $[(metacy)_2V_2(CN)_4(\mu\text{-}C_4N_4)]$ [199], its CV presented a reversible wave corresponding to reduction to V(II) (Table 9, entry 8).

An interesting complex analogous to $[V_2(metacy)_2(\mu\text{-}O)(\mu\text{-}OAc)_2]^{2+}$ replaced one V(III) with one Cr(III) atom [200]. Reversible one-electron oxidation and reductions observed waves are relative to vanadium (Table 8, entry 22).

Vanadate in basic aqueous solutions afforded $[V(NO)_2(phen)]^+$ and $[V(NO)_2(bipy)]^+$ complexes [201] that exhibited two successive ligand-centered single-electron reductive cyclic responses at

Table 8
Electrochemical data for mononuclear V(III) compounds.[a]

Entry	Compound	Type of ligand	Process[b]	$E_{1/2}$, V	Supporting electrolyte	Electrochem. reference	Solvent	References
1	V(quinol)$_3$	*O-N*	V(III) → V(II)	−1.475	Bu$_4$NClO$_4$	SCE	MeCN	[22]
1b				−1.90	Bu$_4$NBF$_4$	FcH$^+$/FcH	MeCN	[217]
			V(III) → V(IV)	+0.03				
2	V(etdtc)$_3$	*S-S*	V(III) → V(II)	−1.075	Et$_4$NClO$_4$	SCE	MeCN	[23]
			V(III) → V(IV)	+0.35				
3	V(picac)$_3$	*O-N*	V(III) → V(IV)	+0.635	Et$_4$NClO$_4$	AgCl/Ag	DMF	[215]
			V(III) → V(II)	−1.01				
4	V(acac)$_3$	*O-O*	V(III) → V(II)	−1.42	Et$_4$NClO$_4$	SCE	DMSO	[25]
				−1.33	Bu$_4$NClO$_4$	AgCl/Ag	MeCOMe	[104]
			V(III) → V(IV)	+0.76	Et$_4$NClO$_4$	SCE	DMSO	[25]
				+0.94	Bu$_4$NClO$_4$	AgCl/Ag	MeCOMe	[104]
5	V(actac)$_3$	*O-S*	V(III) → V(II)	−0.84	Bu$_4$NClO$_4$	AgCl/Ag	MeCOMe	[104]
			V(III) → V(IV)	+0.82				
6	V(tactac)$_3$	*S-S*	V(III) → V(II)	−0.45	Bu$_4$NClO$_4$	AgCl/Ag	MeCOMe	[104]
			V(III) → V(IV)	−1.19 irr.				
7	V(Cl$_4$bsq$^{\cdot-}$)$_3$	*O-O*	V(III) → V(V)	+0.86 irr.	Not indicated	FcH$^{+/}$FcH	MeCN	[101]
8	[V(NO)$_2$(phen)]$^+$	*N-N*	V(III) → V(IV)	+0.22	Et$_4$NClO$_4$	FcH$^+$/FcH	MeCN	[201]
9	(nacnac)VCl(tol$_2$N)	*N-N*	V(III) → V(V)	+0.47	Bu$_4$NBF$_4$	FcH$^+$/FcH	THF	[202]
			V(III) → V(II)	−1.30				
10	[V(^{t}Bubipy)$_3$]$^{3+}$	*N-N*	V(III) → V(V)	+0.80 irr.	Bu$_4$NPF$_6$	FcH$^+$/FcH	THF	[204]
11	VCl$_2$(acac)(bipy)	*O-O*, *N-N*	V(III) → V(IV)	+1.16	Not indicated	FcH$^+$/FcH	MeCN	[217]
12	[V(acac)(phen)]BF$_4$	*O-O*, *N-N*	V(III) → V(II)	−0.885	Bu$_4$NClO$_4$	AgCl/Ag	Not indicated	[203]
			V(III) → V(IV)	+1.007				
13	[V(acac)(phen)]ClO$_4$	*O-O*, *N-N*	V(III) → V(II)	−0.900	Bu$_4$NClO$_4$	AgCl/Ag	Not indicated	[203]
			V(III) → V(IV)	+1.025				
14	V(Cl$_4$cat)(acac)(bipy)	*O-O*, *N-N*	V(III) → V(IV)	−0.504	Bu$_4$NBF$_4$	FcH$^+$/FcH	DCM	[109]
			V(IV) → V(V)	+0.063				
15	[V(Cl$_4$cat)$_2$(bipy)]$^-$	*O-O*, *N-N*	V(III) → V(IV)	−0.50	Bu$_4$NBF$_4$	FcH$^+$/FcH	DCM	[109]
			V(IV) → V(V)	+0.84				
16	V(^{t}Bubztacy)	*O-O-O*	V(III) → V(IV)	−0.50	Bu$_4$NBF$_4$	FcH$^+$/FcH	MeCN	[205]
			V(IV) → V(V)	+0.38				
			V(III) → V(II)	−2.41				
17	V(HBpz$_3$)(Cl)$_2$DMF	*N-N-N*	V(III) → V(IV)	+1.47	Bu$_4$NPF$_6$	SCE	MeCN	[42]
				+1.28			DCM	
18	V(HBdmpz$_3$)Cl$_2$	*N-N-N*	V(III) → V(IV)	+1.28	Bu$_4$NPF$_6$	SCE	MeCN	[42]
				+1.22			DCM	
19	[V(HBpz$_3$)$_2$]$^+$	*N-N-N*	V(III) → V(II)	−0.42	Bu$_4$NPF$_6$	SCE	MeCN	[42]
				−0.30			DCM	
				−0.29			DMF	
20	[V(HBdmpz$_3$)$_2$]$^+$	*N-N-N*	V(III) → V(II)	−0.69	Bu$_4$NPF$_6$	SCE	MeCN	[42]
				−0.68			DCM	
				−0.51			DMF	
21	V(HBdmpz$_3$)Cl(OMe)	*N-N-N*	V(III) → V(IV)	+0.57	Bu$_4$NPF$_6$	SCE	DCM	[151]
22	[V(metacy)$_2$Cr(μ-O)(μ-OAc)$_2$]$^{2+}$	*N-N-N*	V(III) → V(IV)	+0.01	Bu$_4$NPF$_6$	NHE	MeCN	[200]
			V(III) → V(II)	−0.65				
23	V(dipic)F	*N-N-N*	V(III) → V(II)	−1.26	Et$_4$NClO$_4$	AgCl/Ag	DMF	[216]
			V(III) → V(IV)	+0.56 E_{pa}				
			V(IV) → V(V)	+1.00 E_{pa}				
24	V(dipic)(dipicH)	*N-N-N*	V(III) → V(II)	−0.88	Et$_4$NClO$_4$	AgCl/Ag	DMF	[216]
			V(III) → V(IV)	+0.89 E_{pa}				
			V(IV) → V(V)	+1.05 E_{pa}				
25	V(dipic)(quinol)	*N-N-N*	V(III) → V(II)	−1.31	Et$_4$NClO$_4$	AgCl/Ag	DMF	[216]
			V(III) → V(IV)	+0.70 E_{pa}				
			V(IV) → V(V)	+1.08 E_{pa}				
26	V(dipic)(picac)	*N-N-N*	V(III) → V(II)	−1.09	Et$_4$NClO$_4$	AgCl/Ag	DMF	[216]
			V(III) → V(IV)	+0.68 E_{pa}				
			V(IV) → V(V)	+1.05 E_{pa}				
27	V(dipic)(salac)	*N-N-N*	V(III) → V(II)	−1.48	Et$_4$NClO$_4$	AgCl/Ag	DMF	[216]
			V(III) → V(IV)	+0.66 E_{pa}				
			V(IV) → V(V)	+1.05 E_{pa}				
28	V(bzpyam)(Br)$_2$	*O-N-N-N*	V(III) → V(IV)	+0.100	Bu$_4$NPF$_6$	FcH$^{+/}$FcH	DCM	[218]
			V(III) → V(II)	−1.35				
29	[V(etbipypy)$_{3(}$Cl)$_2$]$^+$	*N-N-N-N-N*	V(III) → V(II)	−0.97	Not indicated	AgCl/Ag	DMSO	[208]
30	V(bzpyda)]$^+$	*O-N-N-N-N-O*	V(III) → V(IV)	+0.27	Bu$_4$NPF$_6$	FcH$^+$/FcH	MeCN	[208]
			V(IV) → V(V)	+1.11				
			V(III) → V(II)	−1.79				
31	V(trisalen)	*O-N*$^\cap$*O-N*$^\cap$*O-N*	V(III) → V(IV)	−1.46	Bu$_4$NClO$_4$	SCE	DMF	[209]
			V(III) → V(II)	+0.27				
32	V(trisalen$_{4Me}$)	*O-N*$^\cap$*O-N*$^\cap$*O-N*	V(III) → V(IV)	−1.50	Bu$_4$NClO$_4$	SCE	DMF	[209]
			V(III) → V(II)	+0.26				
33	V(trisalen$_{5Me}$)	*O-N*$^\cap$*O-N*$^\cap$*O-N*	V(III) → V(IV)	−1.52	Bu$_4$NClO$_4$	SCE	DMF	[209]
			V(III) → V(II)	+0.21				
34	V(trisalen$_{3,5dCl}$)	*O-N*$^\cap$*O-N*$^\cap$*O-N*	V(III) → V(IV)	−1.34	Bu$_4$NClO$_4$	SCE	DMF	[209]
			V(III) → V(II)	+0.54				
35	V(mes)$_3$	*C*	V(III) → V(IV)	+0.16	NaBPh$_4$	SCE	THF	[221]

Table 8 (*Continued*)

Entry	Compound	Type of ligand	Process[b]	$E_{1/2}$, V	Supporting electrolyte	Electrochem. reference	Solvent	References
			V(III) → V(II)	−2.09				
36	$[V(Cl_5ph)_4]^-$	*C*	V(III) → V(IV)	+0.88	Bu_4NPF_6	SCE	DCM	[222]
37	$[V(Cl_3ph)_4]^-$	*C*	V(III) → V(IV)	+0.47	Bu_4NPF_6	SCE	DCM	[222]
38	$[V(Cl_2ph)_4]^-$	*C*	V(III) → V(IV)	+0.30	Bu_4NPF_6	SCE	DCM	[222]
39	$V(silethyneH)_3$	*C*	V(III) → V(IV)	+1.11 irr.	Bu_4NPF_6	SCE	THF	[223]
40	$[(CpP^{OMe}Co)_2V]^+$	*Co*	V(III) → V(IV)	+0.94	Bu_4NPF_6	SCE	PC	[224]
				+0.560	Bu_4NPF_6	FcH^+/FcH		
			V(III) → V(II)	−1.54	Bu_4NPF_6	SCE	PC	
41	$(CpP^{OMe}Co)VCl_2$	*Co*	V(III) → V(IV)	+0.729 irr.	Bu_4NPF_6	$FcH^{+/}FcH$	MeCN	[224]
42	$[V\{Rh(aet)_3\}_2]^{3+}$	*N-S*	V(III) → V(II)	−0.85	Na_2SO_4	AgCl/Ag	H_2O	[225]
			V(III) → V(IV)	+1.04				
43	$[V\{Ir(aet)_3\}_2]^{3+}$	*N-S*	V(III) → V(II)	−0.88	Na_2SO_4	AgCl/Ag	H_2O	[225]
			V(III) → V(IV)	+0.94				

[a] Structures and abbreviations of ligands are in Charts 1–5, in alphabetical order.
[b] The process indicates which is the initial and the final oxidation state, without hints about reversibility that can be inferred by the $E_{1/2}$ column.

negative potentials. Also oxidations are ligand-based, apart from the phen complex, that showed one metal-centered oxidative cyclic response (Table 8, entry 8).

Electrochemistry of V(III) complex of the 2,4-pentanedione *N*,*N*′-di(4-methylphenyl)dihydrazone (nacnacH) was investigated to find the best conditions that may give the corresponding V(II) complex upon reduction. The other ligands were Cl^- and the anion from bis(4-methylphenyl)amine (Tol_2NH) [202]. Electrochemical studies of $[(nacnac)VCl(tol_2N)]$ showed irreversible anodic and reversible cathodic waves (Table 8, entry 9).

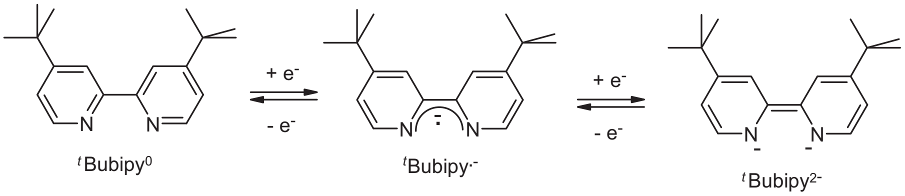
The β-diketonato (acac)V(III) complexes with a neutral heteroligand (phen) and different counterions (tetrafluoborate and perchlorate [203]) gave very similar cyclic voltammograms (with a reversible one-electron reduction and a quasi-reversible one-electron oxidation, Table 8, entries 12,13) and resulted stable to oxidation.

A series of vanadium complexes containing the substituted ligand 4,4′-di-*tert*-butyl-2,2′-bipyridine (^{t}Bubipy) have been synthesized: $[V(^tBubipy)_3]^-$, $[V(^tBubipy)_3]$, $[V(^tBubipy)_3]^{2+}$, and $[V(^tBubipy)_3]^{3+}$ [204]. The last one is a V(III) complex, while the

Table 9
Electrochemical data for di- and trinuclear V(III) compounds.[a]

Entry	Compound	Type of ligand	Process [b]	$E_{1/2}$, V	Supporting electrolyte	Electrochem. reference	Solvent	Ref.
Dinuclear compounds								
1	$[V_2(edt)_4]^{2-}$	*S-S*	V(III) → V(IV)	−0.62	Not indicated	SCE	MeCN	[192]
1b			V(III) → V(IV)	−0.63	Bu_4NClO_4	NHE	MeCN	[193]
			V(IV) → V(V)	−0.16				
1c			V(III) → V(IV)	−0.48	Bu_4NPF_6	AgCl/Ag	MeCN	[197]
			V(IV) → V(V)	−0.01				
2	$V_2O(dimaet)_4$	*S-S*	V(III,III) → V(III,IV)	−0.37	Bu_4NClO_4	NHE	MeCN	[194]
3	$[V_2(metacy)_2(\mu\text{-}O)(\mu\text{-}OAc)_2]^{2+}$	*N-N-N*	V(III,III) → V(III,II)	−1.87	Bu_4NPF_6	FcH^+/FcH	MeCN	[197]
			V(III,III) → V(III,IV)	−0.02				
4	$[V_2(metacy)_2(\mu\text{-}O)(\mu\text{-}OCOCF_3)_2]^{2+}$	*N-N-N*	V(III,III) → V(III,II)	−1.43	Bu_4NPF_6	FcH^+/FcH	MeCN	[198]
			V(III,III) → V(III,IV)	+0.58				
5	$[V(metacy)_2(\mu\text{-}O)(\mu\text{-}OCOCH_2F)_2]^{2+}$	*N-N-N*	V(III,III) → V(III,II)	−1.71	Bu_4NPF_6	FcH^+/FcH	MeCN	[198]
			V(III,III) → V(III,IV)	+0.16				
6	$[V_2(metacy)_2(\mu\text{-}O)(\mu\text{-}OCOCH_2Cl)_2]^{2+}$	*N-N-N*	V(III,III) → V(III,II)	−1.85	Bu_4NPF_6	FcH^+/FcH	MeCN	[198]
			V(III,III) → V(III,IV)	+0.18				
7	$[V_2(metacy)_2(\mu\text{-}O)(\mu\text{-}OCOCH_2Br)_2]^{2+}$	*N-N-N*	V(III,III) → V(III,II)	−1.81	Bu_4NPF_6	$FcH^{+/}FcH$	MeCN	[198]
			V(III,III) → V(III,IV)	+0.21				
8	$[(metacy)_2V_2(CN)_4(\mu\text{-}C_4N_4)]$	*N-N-N*	V(III) → V(II)	−1.098	Not indicated	FcH^+/FcH	MeCN	[199]
9	$[V_2(metacy)_2(\mu\text{-}O)(\mu\text{-}OCOPh)_2]^{2+}$	*N-N-N*	V(III,III) → V(III,II)	−1.84	Bu_4NPF_6	FcH^+/FcH	MeCN	[206]
			V(III,III) → V(III,IV)	+0.20				
			V(III,II) → V(II,II)	−2.10				
10	$[V_2(metacy)_2(\mu\text{-}O)(acac)_2]^{2+}$	*N-N-N*	V(III,III) → V(III,II)	−1.805	Bu_4NPF_6	FcH^+/FcH	MeCN	[206]
			V(III,III) → V(III,IV)	−0.095				
11	$[V_2(metacy)_2(\mu\text{-}O)(NCO)_2]^{2+}$	*N-N-N*	V(III,III) → V(III,IV)	−0.43	Bu_4NPF_6	FcH^+/FcH	MeCN	[206]
12	$[V_2(pyphane)]^{4+}$	*N-N-N-O*	V(III,III) → V(III,II)	−0.53	Bu_4NClO_4	SCE	MeCN	[211]
			V(III,II) → V(II,II)	−0.65				
13	$V_2(bicah)$	*N-O-O-O*	V(III,III) → V(III,IV)	+0.48	KNO_3	NHE	H_2O, pH 3.2	[220]
Trinuclear compounds								
14	$[V_3O(pic)_3(\mu\text{-}OCOMe)_6]^+$	*O-O*	V(III,III,III) → V(II,III,III)	−1.48	Bu_4NClO_4	FcH^+/FcH	DCM	[212]
15	$[V_3O(pic)_3(\mu\text{-}OCOEt)_6]^+$	*O-O*	V(III,III,III) → V(II,III,III)	−1.61	Bu_4NClO_4	FcH^+/FcH	DCM	[212]
16	$[V_3O(pic)_3(\mu\text{-}OCOC_6H_4\text{-}p\text{OMe})_6]^+$	*O-O*	V(III,III,III) → V(II,III,III)	−1,53	Bu_4NClO_4	FcH^+/FcH	DCM	[212]
17	$[V_3O(pic)_3(\mu\text{-}OCOPh)_6]^+$	*O-O*	V(III,III,III) → V(II,III,III)	−1.40	Bu_4NClO_4	FcH^+/FcH	DCM	[212]
18	$[V_3O(pic)_3(\mu\text{-}OCOC_6H_4\text{-}p\text{Cl})_6]^+$	*O-O*	V(III,III,III) → V(II,III,III)	−1.32 irr.	Bu_4NClO_4	FcH^+/FcH	DCM	[212]
19	$[V_3(HBpz_3)_2(\mu\text{-}phosphate)_6]$	*N-N-N*	V(III,III,III) → V(II,III,III)	−0.89	Bu_4NPF_6	$AgNO_3/Ag$	MeCN	[210]
			V(II,III,III) → V(II,III,II)	−1.02				
20	$[V_3(HBpz_3)_2(\mu\text{-}phosphate)_4(\mu\text{-}OH)]$	*N-N-N*	V(III,III,III) → V(II,III,III)	−1.00	Bu_4NPF_6	$AgNO_3/Ag$	MeCN	[210]
			V(II,III,III) → V(II,III,II)	−1.20				

[a] Structures and abbreviations of ligands are in Charts 1–4, in alphabetical order.
[b] The process indicates which is the initial and the final oxidation state, without hints about reversibility that can be inferred by the $E_{1/2}$ column.



Scheme 8. Redox reactions of the redox-active ^{t}Bubipy ligand [204].

other are best described as V(II) compounds, on the basis of computational results with density functional theory (DFT) using B3LYP functional. In fact, 2,2′-bipyridine (bipy) is redox-active and can exist in coordination compounds as either a neutral bidentate ligand (bipy^0), a π radical anion, (bipy$^\bullet$)$^{1-}$, or a diamagnetic dianion (bipy)$^{2-}$ (Scheme 8). The tricationic complex, $[\mathrm{V}({}^t\mathrm{Bubipy})_3]^{3+}$, by one-electron reduction (gave the dicationic complex $[\mathrm{V}({}^t\mathrm{Bubipy})_3]^{2+}$, with V(II) and (bipy^0); the next three one-electron reductions are ligand-based, giving monocationic $[\mathrm{V}({}^t\mathrm{Bubipy})_3]^{+}$, with V(II) and (bipy$^\bullet$)$^{1-}$, the neutral $[\mathrm{V}({}^t\mathrm{Bubipy})_3]$ and the anionic $[\mathrm{V}({}^t\mathrm{Bubipy})_3]^{-}$, both containing V(II).

A different approach was based on the triazacyclononane moiety: an hexadentate ligand, 1,4,7-tri(5-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane (^{t}BuztacyH$_3$), was used to prepare the V(III) complex V(^{t}Bubztacy) [205]. By cyclic voltammetry and coulometric measurements three reversible one-electron waves were detected for V(^{t}Bubztacy) (Table 8, entry 16), relative to oxidations to V(IV) and V(V) states. The corresponding compounds were isolated and gave the same redox waves. On the contrary, the species formed in the third process, V(^{t}Bubztacy)$^-$, could not be isolated. Moreover, three binuclear complexes were examined, containing the $[\mathrm{V^{III}{-}O{-}V^{III}}]^{4+}$ unit and the tridentate triaza-macrocyclic ligand metacy [206]. Reversible waves were observed, as reported in Table 9 (entries 9–11). Substitution of the acetato bridge by benzoato one brought about an anodic shift of $E_{1/2}$ of 220 and 30 mV for the two waves.

Other nitrogen heterocycles have been also used; with the hexadentate ligand derived from 1,2-ethanediamine containing phenolate-type and 2-pyridyl pendant arms, bzpydaH$_2$, V(bzpyda)]$^+$ was isolated [207] and three quasi-reversible one-electron transfer processes were detected (Table 8, entry 30), indicating the accessibility of V(II), V(III), V(IV) and V(V) formal oxidation states.

VCl$_3$ coordinated the 3,3′-bis([*N*-(2-hydroxyethyl)]hydrazine-2,2′-bipyridine and the complex acted as a template in the reaction with 2,6-pyridinbedicarbaldehyde, forming a V(III) complex with the pentadentate macrocycle synthesized (etbipypy) [208]. The cyclic voltammogram of a purple solution of $[\mathrm{V(etbipypy)_3Cl_2}]^+$ in DMSO exhibited a single reversible reduction (Table 8, entry 29).

Vanadium(III) complexes were obtained with hexadentate Schiff base ligands prepared from substituted salicyl aldehydes and tris(2-aminoethyl)amine (trisalenH$_3$) [209]. Electrochemical experiments were carried out to investigate the suitability of these ligands to stabilize the vanadium(III) oxidation state toward reduction and to explore the possibility of isolating a non-oxido vanadium(IV) species (Table 8, entries 31–34). Quasi-reversible reductions were observed, with potentials sensitive to the substituent, with values increasing with decreasing substituent electron-donating ability. Also oxidation waves were nearly reversible and depended on the substituent.

The vanadium(III) complexes HBpz$_3$VCl$_2$DMF and HBdmpz$_3$VCl$_2$DMF underwent reversible oxidations [42]. When the two chlorides and the DMF were replaced with another tris(pyrazoly1)borate unit to form the “sandwich” complexes [L$_2$V]$^+$, the V(III) oxidation state was greatly stabilized. This stabilization was evident from the electrochemistry, since no oxidative process was visible up to +2.0 V. Instead, a facile ***reduction*** V(III) → V(II) was observed (Table 8, entries 17–20). As expected, the 3,5-dimethyl derivatives, while easier to oxidize, were harder to reduce than their unsubstituted counterparts. The reductions of $[\mathrm{V(HBpz_3)_2}]^+$ and $[\mathrm{V(HBdmpz_3)_2}]^+$ were completely reversible, not only on the CV time scale, but on bulk electrolysis as well. Thus, controlled potential electrolysis in either MeCN or DCM consumed one electron and re-oxidation at 0.0 V restored the original species. This process could be repeated many times without evident degradation and the stability to oxidative or hydrolytic reactions was attributed to the nature of the ligands, that tightly encapsulated the vanadium centers.

Vanadium(III) alkoxo complexes of the ligands hydridotris(pyrazolyl)borate (HBpz$_3$) and hydridotris(3,5-dimethylpyrazolyl)borate (HBdmpz$_3$) were prepared [151]. Electrochemistry of the latter in DMF (Table 8, entry 21) demonstrated that the vanadium-(III) monoalkoxide could be reversibly oxidized at modest potentials (+0.57 V vs SCE).

Two linear trinuclear V(III) complexes, containing two terminal V(III) ions capped by a hydridotris(pyrazolyl)-borate group (HBpz$_3$) and each linked to a central V(III) by three diphenyl phosphate bridges or by two diphenyl phosphate and one OH bridges, were prepared within the frame of a research on new materials [210]. Both complexes, [V(HBpz$_3$)(μ-phosphate)$_3$-V-(μ-phosphate)$_3$V(HBpz$_3$)] and [V(HBpz$_3$)(μ-phosphate)$_2$(μ-OH)-V-(μ-phosphate)$_2$V(HBpz$_3$)], where phosphate is (PhO)$_2$PO$_2{}^-$, showed two equal current reductive cyclic voltammetric waves (Table 9, entries 19,20), indicating communication between the terminal V(III) atoms. The central V(III) reduction was not detected because, being in an all oxygen environment, is expected at a much more negative potential, outside the potential window observable on Pt in acetonitrile.

A macrocyclic tetraimine Schiff base (pyphaneH$_2$) incorporated two V(III) ions, giving a dinuclear complex [211], $[\mathrm{V_2(pyphane)}]^{4+}$, that underwent two successive quasi-reversible reduction (Table 9, entry 12).

Trinuclear V(III) compounds with different μ-carboxylate ligands, of general formulation $[\mathrm{V_3O(pic)_3(\mu\text{-}OCOR)_6}]^+$, were electrochemically investigated [212] and all exhibited a reversible one-electron reduction, a second, irreversible reduction, and an oxidation that appeared reversible only at higher scan rates, suggesting a slow subsequent transformation. Results are in Table 9, entries 14–18. The first reduction occurred at potential consistent with the formation of V(II) species. The irreversible reductions (in the range $-1.7 \div -1.9$ V vs FcH$^+$/FcH) and the oxidation (in the range $+0.47 \div +0.88$ V vs FcH$^+$/FcH) were not discussed.

An interesting and completely different study was performed with [V(edta)]$^-$ [213]. The effect of the solvent composition for water-ethylene glycol (EG) mixtures, in the mole fraction range $X_{\mathrm{EG}} = 0$–1, on the diffusion coefficients and reduction potentials of [V(edta)]$^-$ redox reaction has been examined at a mercury electrode using convolution potential sweep voltammetry, demonstrating the dependence of the redox potential from the solvent composition. Such a behavior has been illustrated with a two-step solvent exchange mechanism, which describes the solvation of the reactant and product. Preferential solvation of the more negatively charged V(II) complex relative to the V(III) counterpart by water has been found. Acceptor numbers for the mixtures have been proposed. Then the same authors presented an investigation concerning the kinetics of the electrode reaction [214]. As expected, the composition of the solvation shell of the activated complex resulted intermediate between that of the reactant and the product. The authors concluded that it is possible to experimentally obtain information about the composition of the solvation shell of the transition state for an electron transfer reaction.

The V(III) complex of 2-pyridine carboxylic acid (picolinic acid), V(picac)$_3$, resulted remarkably stable and could be kept in open air for days and heated up to 180 °C without oxidation [215]. Cyclic voltammetric data are in Table 8 (entry 3). The stability was attributed to (i) hard-hard interaction of V(III) with *O-N* bidentate ligand, (ii) to the uncharged nature of the complex, and (iii) to the extensive delocalization of the *d*-electrons. As an extension, 2,6-pyridinedicarboxylic acid (dipicolinic acid, dipicH$_2$) was used as a ligand for homo- and heterochelated V(III) complexes [216], all of which presented a reversible V(III)/V(II) couple, followed by a second, from quasi-reversible to irreversible, ligand reduction. On the anodic side, two irreversible oxidation peaks were found, attributable to successive oxidations to V(IV) and V(V). Results are in Table 8 (entries 23–27).

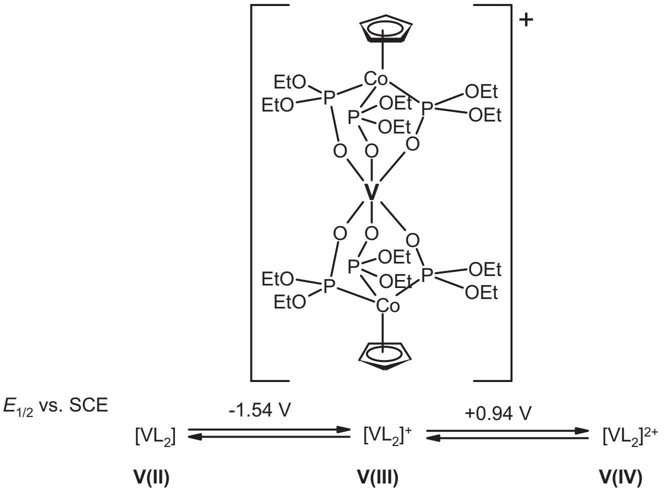
V(III) compounds were easily obtained from V(IV) species in the presence of bipy or quinolH [217]. The redox-properties of [V(quin)$_3$] in MeCN and in the non-coordinating solvents DCM and MeNO$_2$ have been studied by cyclic voltammetry and polarographic techniques. In acetonitrile, the compound displayed two reversible one-electron redox processes (Table 8, entry 1b), while in DCM the reduction was shadowed by solvent reduction. [VCl$_2$(acac)(bipy)] revealed one-electron redox process assigned to the oxidation of V(III) to V(IV) (Table 8, entry 11).

The tetradentate monoanionic ligand from (2-hydroxy-3,5-di-*tert*-butylbenzyl)bis(2-pyridylmethyl)amine (bzpyam) gave complexes with several metals, among which vanadium(III) [218]. V(bzpyam)(Br)$_2$ gave a cyclic voltammogram with a reversible oxidation and an irreversible reduction (Table 8, entry 28).

As a part of research program on the interaction of metal polypyridyl complexes with DNA, a series of mixed ligand V(III) complexes was prepared [219], that contained the monoanion of 3-hydroxy-2-methyl-4*H*-pyran-4-one (maltH) and a *N-N* heterocyclic ligand, i.e., 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), dipyrido[3,2-*d*:2′,3′-*f*]quinoxaline (dpq), and dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz). Cyclic voltammetry in MeCN (Et$_4$NClO$_4$ as the supporting electrolyte) of [V(malt)$_2$(*N-N*)]$^+$ showed an irreversible peak around +0.80 V vs AgCl/Ag, corresponding to a one electron oxidation of V(III) to V(IV). No value was reported for E_{pa} of individual compounds.

The hexaanion from 2,5-bis(dicarboxymethyl)aminomethyl-1,4-benzenediol (bicahH$_6$) coordinated two V(III) ions [220], giving a species that at pH 3.2 underwent reversible oxidation to V(IV) (Table 9, entry 13), whereas reductions resulted ligand-centered.

A few examples can be found with C as the donor atom. V(mes)$_3$ (where mes is the anion of 2,4,6-trimethylphenyl or mesityl) was prepared and used to investigate the possibility of dinitrogen fixation [221]. Mesityl was chosen because aryl groups are particularly appropriate as ancillary ligands, since they are almost exclusively σ-donor in character, being unable to accommodate electron density from the metal. An accurate electrochemical investigation was performed in argon and under dinitrogen atmosphere. Under argon a single oxidation process was displayed in the anodic window, relative to an almost reversible one-electron oxidation to V(IV). The cathodic sweep showed a well-behaved peak couple consistent with a one-electron semireversible reduction process to [V(mes)$_3$]$^-$ (Table 8, entry 35). When CV was performed bubbling dinitrogen, the scenario became more complicated and the authors were able to individuate the formation of dinuclear species containing μ-N$_2$ ligand.



Scheme 9. Redox processes of V{CpCo[P(O)(OEt)$_2$]$_3$}$_2$PF$_6$, in PC (propylene carbonate), with Bu$_4$NPF$_6$ as the supporting electrolyte and SCE as the reference electrode [226].

The arylation of [VCl$_3$(thf)$_3$] with LiAr$_{Cl}$, where Ar$_{Cl}$ is a polychlorinated phenyl group, i.e. pentachlorophenyl (Cl$_5$ph), 2,4,6-trichlorophenyl (Cl$_3$ph), or 2,6-dichlorophenyl (Cl$_2$ph), gave four-coordinated homoleptic organovanadium(III) derivatives, [Li(thf)$_4$]$^+$[V(Ar$_{Cl}$)$_4$]$^-$, [222] electrochemically related to the neutral organovanadium(IV) species, [V(Ar$_{Cl}$)$_4$], independently prepared. The redox potentials of the V(III)V(IV) oxidation in DCM decreased with decreasing chlorination of the phenyl ring (Table 8, entries 36–38).

With the bulky silyl substituted acetylide anion obtained from 2,6-bis(trimethylsilyl)phenylethyne (silethyneH), it was possible to prepare V(III) complexes, besides those of Fe(II) and Mn(II) [223]. CV measurements presented an irreversible oxidation wave (Table 8, entry 39); while, reduction wave (present at the same potential in complexes with the other metals) likely due to the ligand, resulted reversible.

Some V(III) derivatives were prepared with ligands containing other transition metals.

Ligand (CpP^{OMe}Co)$^-$, already discussed in oxido-V(IV) paragraph (Section 2.1, Table 1) was used also to prepare a V(III) complex, (CpP^{OMe}Co)VCl$_2$, that came twenty year after [(CpP^{OMe}Co)$_2$V]$^+$ [224] (CpP^{OMe}Co)VCl$_2$ showed an irreversible oxidation (Table 8, entry 41), at a potential higher than that of [(CpP^{OMe}Co)$_2$V]$^+$, (Table 8, entries 40,41), thus implying that Ligand (CpP^{OMe}Co)$^-$ ligand is a poorer σ-donor than Cl$^-$.

Reaction of [M(aet)$_3$], where M is Rh(III) or Ir(III) and aetH is 2-aminoethanethiole, with an excess of VCl$_3$ gave linear-type S-bridged trinuclear complexes [225], where V maintains its oxidation state, at variance from what happened with sulfur bridged Rh and Ir complexes (see Section 3.2). [V{Rh(aet)$_3$}$_2$]$^{3+}$ and [V{Ir(aet)$_3$}$_2$]$^{3+}$ both displayed an irreversible reduction wave relative to the V(III) → V(II) process and irreversible oxidation waves, some of which appeared only after the reduction scan and therefore may be due to species forming after decomposition. The oxidation waves reported in Table 8 (entries 42, 43) were thought to be dominated by V(III) → V(IV) oxidation process.

Quite unusual [ML$_2$]$^+$ complexes were prepared using as L the anion cyclopentadienyl cobalt tris(diethyl)phosphito, CpCo[P(O)(OEt)$_2$]$_3$ and salts of transition metals [226]. Among them, V(III) complex showed the reversible processes illustrated in Scheme 9.

Table 10
Electrochemical data for Vanadium(II) compounds.[a]

Entry	Compound	Type of ligand	Process[b]	$E_{1/2}$, V	Supporting electrolyte	Electrochem. reference	Solvent	References
1	$[V(phe)_3]^{2+}$	*N-N*	V(II) → V(III)	+0.60	Bu_4NTf	AgCl/Ag	MeCN	[227]
				+0.63	Bu_4NTf	AgCl/Ag	DCM	[228]
			V(II) → V(I)	−0.34	Bu_4NTf	AgCl/Ag	MeCN	[227]
				−0.97	Bu_4NTf	AgCl/Ag	DCM	[228]
			V(I) → V(0)	−1.16				
2	$[V(dphphe)_3]^{2+}$	*N-N*	V(II) → V(III)	+0.58	Bu_4NTf	AgCl/Ag	DCM	[229]
			V(II) → V(I)	−0.89				
			V(I) → V(0)	−1.05				
			V(0) → V(−1)	−1.53				
3	$[V(tmphe)_3]^{2+}$	*N-N*	V(II) → V(III)	+0.50	Bu_4NTf	AgCl/Ag	DCM	[229]
			V(II) → V(I)	−1.22				
			V(I) → V(0)	−1.45				
4	$[V(bipy)_3]^{2+}$	*N-N*	V(II) → V(III)	+0.57	Bu_4NTf	AgCl/Ag	MeCN	[227]
				+0.52 quasi rev.	Bu_4NTf	AgCl/Ag	DCM	[229]
			V(II) → V(I)	−0.52 E_{pc}	Bu_4NTf	AgCl/Ag	MeCN	[227]
				−0.97	Bu_4NTf	AgCl/Ag	DCM	[229]
			V(I) → V(0)	−1.19				
5	$[V(dmbipy)_3]^{2+}$	*N-N*	V(II) → V(III)	+0.52 E_{pa}	Bu_4NTf	AgCl/Ag	DCM	[229]
			V(II) → V(I)	−1.12				
			V(I) → V(0)	−1.28				
6	$V(bipy)_2Cl_2$	*N-N*	V(II) → V(III)	−0.28	Bu_4NPF_6	NHE	DCM	[230]
7	$[V(terpy)_2]^{2+}$	*N-N-N*	V(II) → V(III)	+0.46	Bu_4NPF_6	NHE	DCM	[230]
			V(II) → V(I)	−0.70				
			V(I) → V(0)	−0.85				
			V(0) → V(−1)	−1.38				
8	$[V(terpy)(bipy)]^{2+}$	*N-N-N, N-N*	V(II) → V(III)	+0.52	Bu_4NPF_6	NHE	DCM	[230]
			V(II) → V(I)	−0.85				
			V(I) → V(0)	−1.09				
9	$[V(terpy)(bipy)Cl]^{+}$	*N-N-N, N-N*	V(II) → V(III)	+0.17	Bu_4NPF_6	NHE	DCM	[230]
			V(I) → V(0)	−0.97				
			V(0) → V(−1)	−1.20				
10	$[V(^tBuNC)_6]^{2+}$	*C*	V(II) → V(I)	−0.95	Bu_4NTf	AgCl/Ag	DCM	[229]
			V(I) → V(0)	−1.5				
			V(II) → V(III)	−0.2				
			V(III) → V(IV)	+0.4				
11	$[V(dppe)_3][V(CO)_6]_2$	*P-P*	V(II) → V(I)	−0.43	Bu_4NTf	AgCl/Ag	DCM	[229]
			V(II) → V(III)	+0.25				
			V(−1) → V(0)	−0.02				

[a] Structures and abbreviations of ligands are in Charts 1 and 2, in alphabetical order.
[b] The process indicates which is the initial and the final oxidation state, without hints about reversibility that can be inferred by the $E_{1/2}$ column.

5. Electrochemistry of vanadium compounds at oxidation states of II or lower

The ability of vanadium to exist in various oxidation states renders this ion ideal for multi-electron reactions and, therefore, also oxidation states difficult to reach, such as V(II), are appealing, in view of combine in a single molecule the function of multi-electron redox and sensitizer agent. In fact, vanadium(II) (d^3) should be able to participate in photochemical redox reactions. If photooxidation of V(II) is followed by a second thermal electron transfer to V(IV), the overall transformation would result in a photochemically initiated two-electron-transfer reaction. The purpose of research was to identify ligands able to somewhat stabilize low-valent vanadium ion.

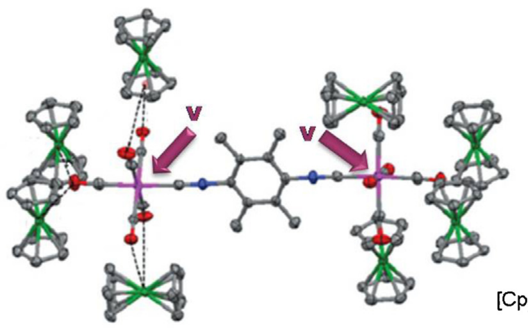
5.1. Vanadium (II) species

Polypyridines were explored as ligands for V(II) species [227]. With 1,10-phenanthroline and 2,2′-bipyridine, $[V(phe)_3]^{2+}$ and $[V(bipy)_3]^{2+}$ were obtained and both showed one-electron oxidation, with a greater degree of electrochemical reversibility for the phenanthroline species (Table 10, entries 1,4). In DCM the cyclic voltammograms were considerably better resolved [228]. The reversible wave at positive potentials was attributed to vanadium oxidation. The two other closely spaced one-electron reversible waves were assigned to reductions to V(I) and V(0), respectively, in analogy with values presented by similar compounds. For comparison, a V(III) complex, the dinuclear $[V_2(phen)_4(\mu\text{-}OH]^{4+}$, was electrochemically investigated under the same conditions and revealed a number of anodic and cathodic waves, probably with formation of oxido species. The investigation was extended to complexes of V(II) with other polypyridines, such as 4,4′-dimethyl-2,2′ bipyridine (dmbipy), 4,7-diphenyl-1,10-phenanthroline (dphphe), and 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphe) [229]. The half-wave potentials within the polypyridine series changed significantly with substitution on the ligand framework, the largest variation occurring in the reductions (Table 10, entries 2–5).

In the same paper, a V(II) complex with *tert*-butylisocyanide, $[V(^tBuNC)_6]^{2+}$, was investigated, together a cation containing V(II) with 1,2-bis(diphenylphosphano)ethane (dppe) and an anion containing V(-1), of formula $[V(dppe)_3]^{2+}[V(CO)_6]^{-}{}_2{\cdot}[V(^tBuNC)_6]^{2+}$ showed one reversible and one quasi-reversible reduction waves and two irreversible oxidation waves, all attributed to the metal (Table 10, entries 10,11). In DCM solutions of $[V(dppe)_3][V(CO)_6]_2$ one quasi-reversible reduction and one reversible one-electron oxidation waves were found and attributed to V(II)-dppe species, while the reversible wave near the center of the voltammogram was considered as due to oxidation of V(-1) counterion.

Another different polypyridine, used for the same reason, was 2,2′:6′,2″-terpyridine, terpy, [230]. $[V(terpy)_2]^{2+}$ and $[V(terpy)(bipy)Cl]^{+}$ presented generally reversible redox waves (Table 10, entries 6–9). The authors considered all the processes as metal-centered, excluding the excess electron localization in ligand π^* orbital.

It is worth signaling that, to understand solvent effects on the reactivity of V(II) salts, an investigation of speciation in



	$E_{1/2}$, V vs FcH^+/FcH	
	V(-1)→V(0)	V(0)→V(I)
$[Cp_2Co][V(CO)_4]$	-0.35	
$[Cp_2CO][(CO)_5V\text{-}CN\text{-}C_6Me_4NC]$	-0.75	-0.75
$[(CO)_5V\text{-}CN\text{-}C_6Me_4NC\text{-}V(VO_5)]^-$	-0.69	-0.38
$[Cp_2CO]_2[(CO)_5V\text{-}CN\text{-}C_6Me_4NC\text{-}V(VO_5)]$	-0.69	-0.39

Fig. 7. Supramolecular complex between Cp_2Co and $V(CO)_5$-1,4-diisocyano-2,3,5,6-tetramethylbenzene and electrochemistry of related compounds (Solvent: MeCN, supporting electrolyte not indicated).

Adapted from [234], reprinted with permission of RSC.

different solvents was carried out, also by electrochemical technique [231,232]. The measurements, when interpretation of electrochemical results was practicable, added little to the evidence spectroscopically obtained, being in agreement with it.

5.2. Other vanadium species

Exploration of nitrosyl cation as ligand for group 15 metals lead to the isolation, among alia, of the neutral 18 electrons species $V(trimpsi)(CO)_2(NO)$, where trimpsi is tris(dimethylphosphanomethyl)-*tert*-butylsilane [233]. Its cyclic voltammogram in DCM (Bu_4NPF_6 as the supporting electrolyte) showed a reversible oxidation feature to the 17e cation $[V(trimpsi)(CO)_2(NO)]^+$, at −0.74 V (vs FcH^+/FcH) followed by an irreversible feature (0.61 V vs FcH^+/FcH) to an unstable 16e dication.

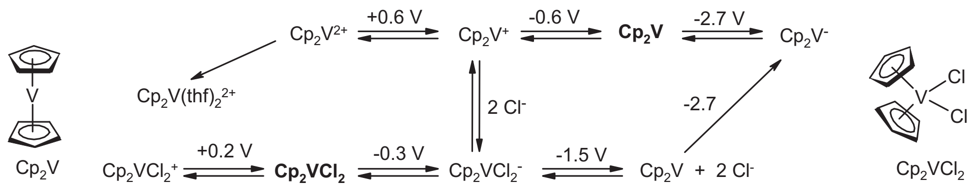
Pentacarbonylvanadate(−1) linked to 1,4-diisocyano-2,3,5,6-tetramethylbenzene was used in the field of organometallic crystal engineering, since it gave supramolecular complex with cobaltocene [234] (Fig. 7).

In addition to a reversible Co(II) → (III) wave, the cyclic voltammograms of $[CpCo][(CO)_5V\text{-}CN\text{-}C_6Me_4\text{-}NC]$ and $[CpCo]_2[(CO)_5V\text{-}CN\text{-}C_6Me_4\text{-}NC\text{-}V(CO)_5]$ in CH_3CN feature two vanadium-centered processes, both of which are only partially reversible presumably because the instability of the oxidized vanadium species in MeCN.

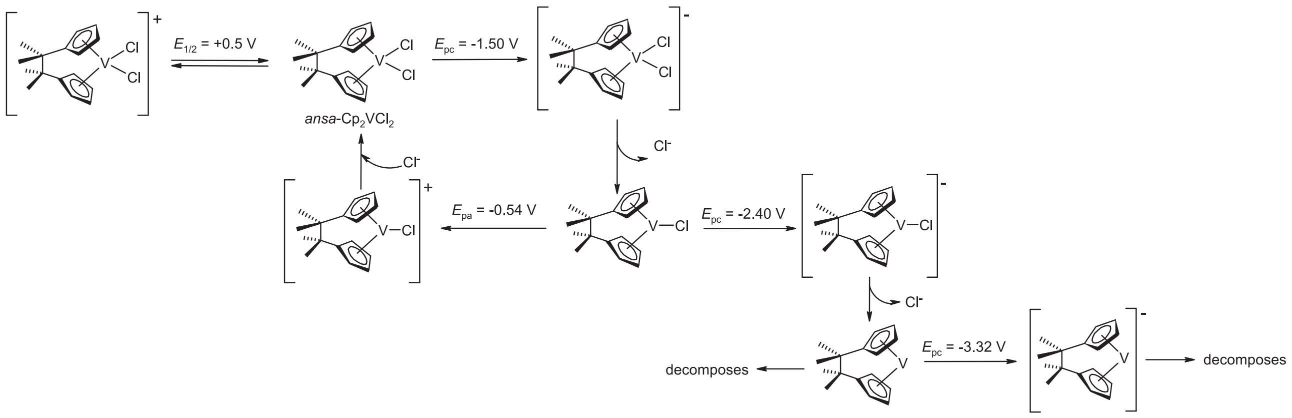
6. π-Coordinated vanadium species

After initial reports on electron-transfer reactions of metallocenes, including vanadocene and dicyclopentadienyl vanadium dichloride [235] (Scheme 10), some papers appeared in the nineties of the last century and at the beginning of the present one.

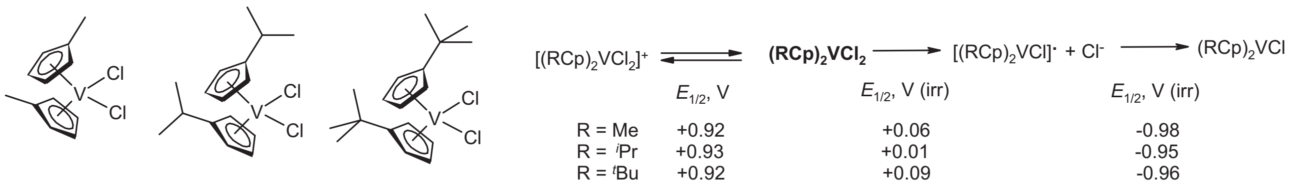
The tetramethylethano-bridged vanadocene dichloride was investigated a few years later [236], to get information about the nature of alkene polymerization catalysts. Instead, the ring-bridged vanadocene could not be isolated and cyclovoltammetry indicated that this V(II) complex (in contrast to its unbridged counterpart decays within seconds after its formation by electrochemical reduction of its chloro derivative. The result is summarized in Scheme 11.



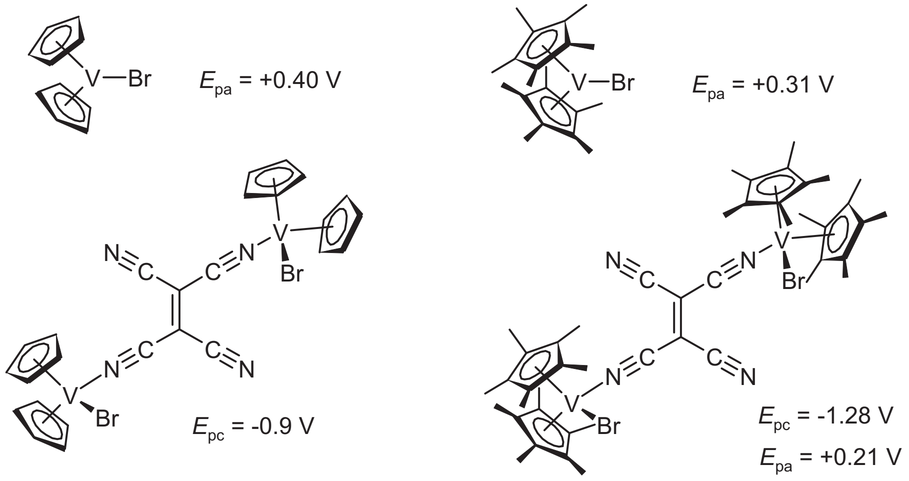
Scheme 10. Structure of vanadocene and vanadocene dichloride, and relative redox pathways. CVs were performed in THF, with Bu_4NPF_6 as the supporting electrolyte. Potentials are vs SCE [235].



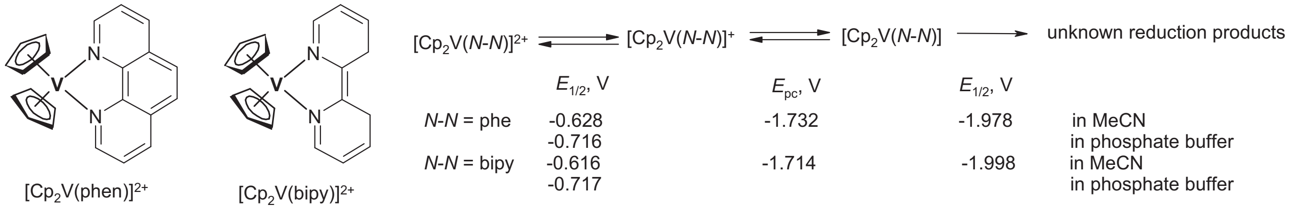
Scheme 11. Electrochemistry of *ansa*-dicyclopentadienyl vanadium dichloride in THF at 10 °C, with Bu_4NPF_6 as the supporting electrolyte and Ag/Ag^+ as the reference electrode [236].



Scheme 12. Electrochemical data for 1,1′-dialkylsubstituted dicyclopentadienyl vanadium dichloride. CVs performed in MeCN, with Bu_4NPF_6 as supporting electrolyte. Potentials are referred to FcH^+/FcH couple [237].



Scheme 13. Electrochemistry of $(R_5C_5)_2VBr$ and $[(R_5C_5)_2V]_2(TCNE)$. Bu_4NClO_4 or Bu_4NPF_6 as supporting electrolyte. Potentials are referred to FcH^+/FcH [238].



Scheme 14. Structure and electrochemistry of $[Cp_2V(phen)](OTf)_2$ and $[Cp_2V(bipy)](OTf)_2$. Bu_4NPF_6 as supporting electrolyte. Potentials are referred to FcH^+/FcH [239].

Introduction of alkyl substituents into cyclopentadienyl rings affected redox potentials with small differences among different alkyl groups [237] (Scheme 12).

The reactions between tetracyanoethene (TCNE) and organometallic 16 valence electron fragments from the early, middle and late transition series yielded complexes which exhibited rather different electronic structures as evident from spectroscopy and electrochemistry [238]. Among them there are vanadium compounds, such as vanadocene (bromodicyclopentadienylvanadium, Cp_2V_2) and the analogous pentamethylcyclopentadienyl complex. Dimeric species with TCNE and $(Me_5C_5)_2VBr$ were observed (Scheme 13). Cyclic voltammetry was performed in 1,2-dichloroethane, DCE, for dimeric species, giving irreversible peaks in all cases. Electrochemical information, in agreement with other experimental data, confirmed the non-conjugated structures of the vanadium dimers.

Replacing the two Cl ligands with N atoms from 1,10-phenanthroline and 2,2′-bipyridine led to complexes that underwent identical electron-transfer processes over the potential range +2.1 to −2.5 V [239] (Scheme 14).

The two Cl ligands were also replaced with S atoms present in one pyrrole ring of porphyrazines, ligands used also to coordinate Mo from molybdenocene [240]. However, cyclic voltammetry data are reported for the molybdenum analogs only.

A dinuclear vanadium derivative of pentalene (C_8H_6, bicyclo[3.3.0]octatetraene, Pn) was obtained, where the ligand supported a direct M–M interaction, specifically a rare example of a V≡V bond [241]. Cyclic voltammetry was performed in THF, with Bu_4NPF_6 as the supporting electrolyte, presented one reversible and one irreversible process (Fig. 8).

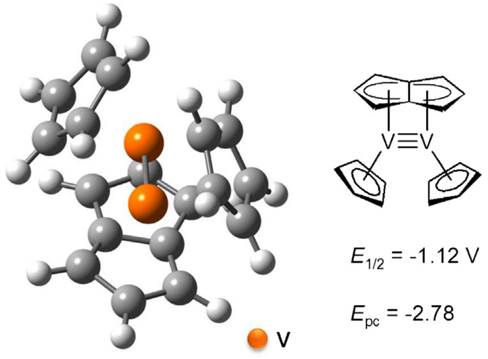
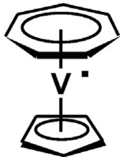
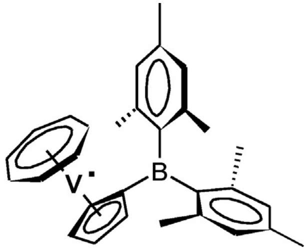
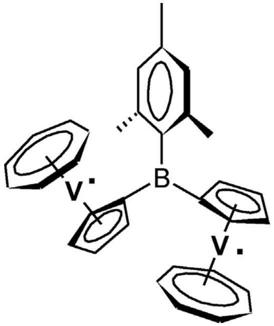
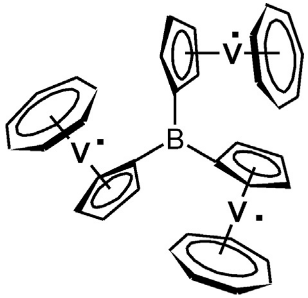
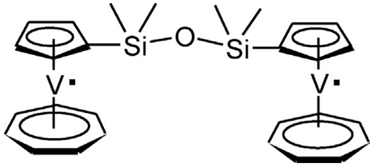
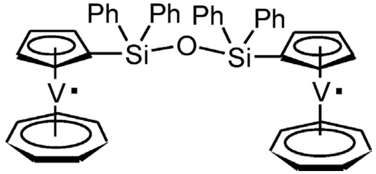
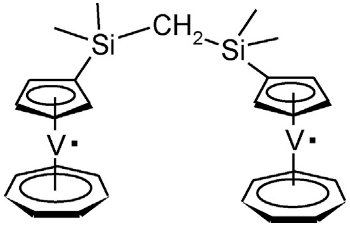
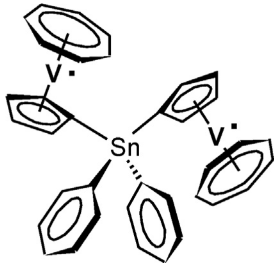


Fig. 8. Structure and electrochemistry of PnV_2Cp_2 in THF, with Bu_4NPF_6 as supporting electrolyte. Potentials vs. FcH^+/FcH [241].

Table 11
Electrochemical data of [5]trovacene and derivatives. CVs were performed in DME with Bu_4NClO_4 as supporting electrolyte. Potentials are referred to SCE.

Compound	Process[a]	$E_{1/2}$, V	Temperature, °C	References	Compound	Process[a]	$E_{1/2}$, V	Temperature, °C	References
	0 → −1 0 → +1	−2.55 +0.26	−33	[242]		0 → −1 0 → +1	−2.067 +0.431	Not indicated	[244]
	0 → −1 0 → +1 +1 → +2	−2.095 +0.362 +0.500	Not indicated	[244]		0 → −1	−2.067	Not indicated	[244]
	0 → −1−1 → −20 → +1	−2.41 −2.54 +0.28	−40	[245]		0 → −1 −1 → −2 0 → +1	−2.49 −2.53 +0.24	−40	[245]
	0 → −1 −1 → −2 0 → +1	−2.48 −2.56 +0.25	−40	[245]		0 → −n 0 → +1 +1 → +2	−2.275[b] −0.202[b] −0.110[b]	−25	[246]

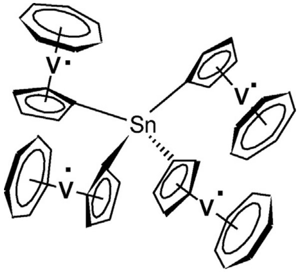
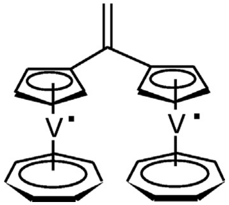
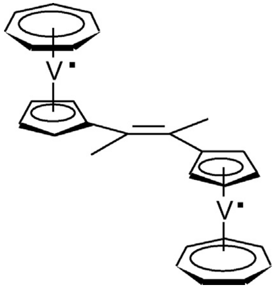
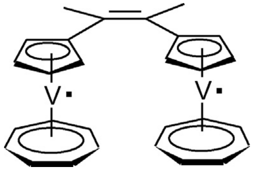
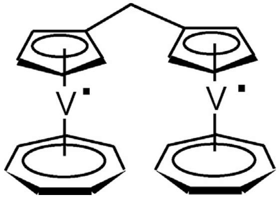
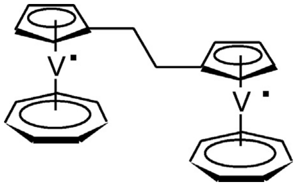
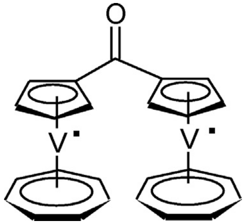
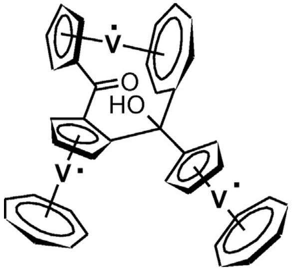
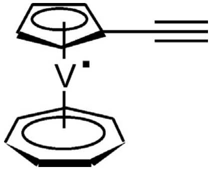
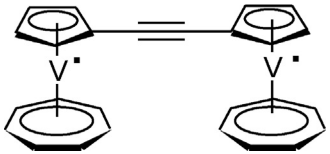
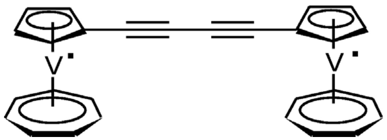
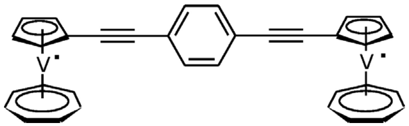
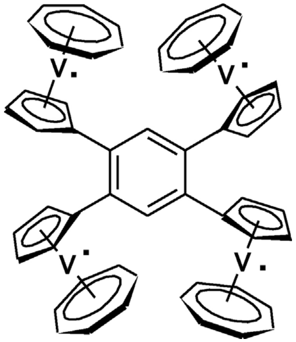
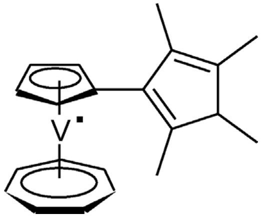
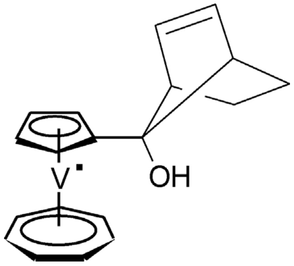
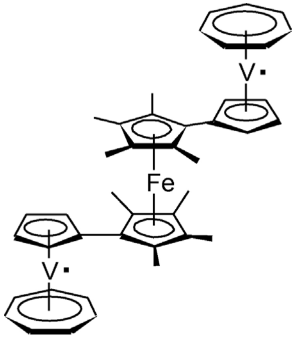
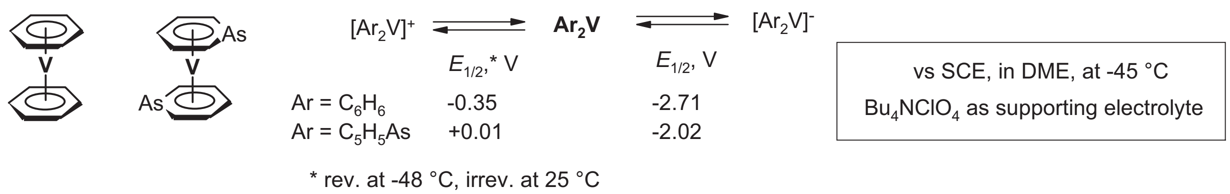
	0 → −*n* 0 → +1 +1 → +2	−2.278[b] −0.241[b] −0.140[b]	−25	[246]		0 → −1 −1 → −2 −2 → −3 0 → +2	−2.43 −2.50 −2.59 +0.31	−40	[248]
	0 → −1 −1 → −2 0 → +1 +1 → +2	−2.43 −2.60 +0.27 +0.27	−40	[248]		0 → −1 −1 → −2 0 → +1 +1 → +2	−2.48 −2.61 +0.25 +0.31	−40	[248]
	0 → −1 −1 → −2 0 → +2	−2.46 −2.56 +0.19	−40	[248]		0 → −1 −1 → −2 0 → +2	−2.51 −2.59 +0.19	−40	[248]
	0 → −1 −1 → −2 −2 → −3 0 → +1 +1 → +2	−2.06 −2.43 −2.62 +0.41 +0.51	−35	[247]		0 → −1 −1 → −4 0 → +1 +1 → +2 +2 → +3	−1.78 −2.64 +0.29 +0.45 +0.64	−35	[247]

Table 11 (*Continued*)

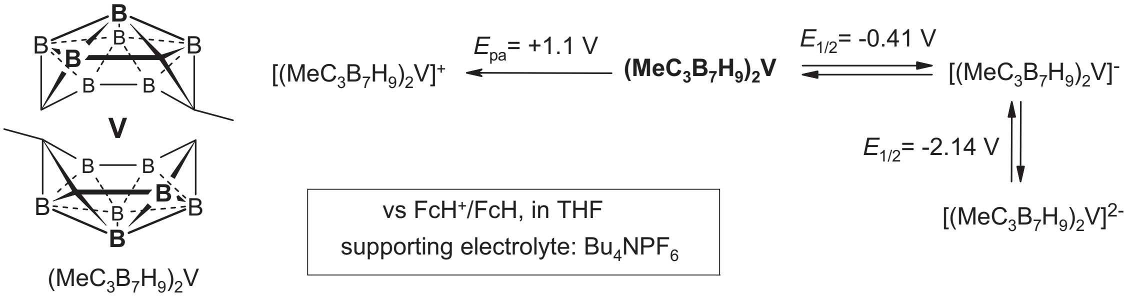
Compound	Process[a]	$E_{1/2}$, V	Temperature, °C	References	Compound	Process[a]	$E_{1/2}$, V	Temperature, °C	References
	0 → −1 0 → +1	−2.40 +0.39	−35	[249]		0 → −1 −1 → −2 0 → +2	−2.37 −2.52 +0.37	−35	[249]
	$E_{pc,1}$ $E_{pc,2}$ $E_{pc,3}$ 0 → +2	−2.31 −2.48 −2.58 +0.41	−35	[249]		– 0 → +2	– +0.40	−35	[249]
	0 → +1 0 → −1 −1 → −2 −2 → −3 −3 → −4	+0.31 −2.34 −2.45 −2.59 −2.72	−40	[251]		0 → −1 0 → +1	2.440 +0.271	−40	[250]
	0 → −1 0 → +1	−2.336 +0.221	−50	[250]		0 → −1 −1 → −2 0 → +1 +1 → +2 +2 → +3	−2.453 −2.56 +0.169 +0.364 +0.451	−40	[250]

[a] The process indicates which is the initial and the final oxidation state, without hints about reversibility, that can be inferred by the $E_{1/2}$ column.

[b] vs FcH⁺/FcH in PhCN.



Scheme 15. Structure and electrochemistry of PnV_2Cp_2 in THF, with Bu_4NPF_6 as supporting electrolyte. Potentials vs. FcH^+/FcH [241].



Scheme 16. Electrochemical data for $(\eta^6\text{-}C_6H_6)_2V$ and $(\eta^6\text{-}C_5H_5As)_2V$ [243].

A π system extensively investigated by Elschenbroich is that of (η^5-cyclpentadienyl)(η^7-cycloheptatrienyl)vanadium, called [5]trovacene. The rationale for investigating this compound and its derivatives was the possibility of developing molecular components to construct nanoscale electronic devices. One method for testing electronic communication through a possible molecular wire is to examine the interaction between two redox centers, which are located at the termini of the chain. It is well known that multiple unsaturated bonds as components of molecular wires (double and triple C—C bonds, triple C—N bond) can efficiently transmit along the molecular line from one center (donor) to another one (acceptor). At first, [5]trovacene itself was investigated by cyclic voltammetry and compared with bis(η^6-benzene)vanadium [242] in order to gain insight into the factors that govern the redox processes (Table 11). Then, the substitution of benzene with arsenabenzene was accomplished, trying to solve the question of whether interannular "secondary bonding" between the heavier group 15 elements could stabilize the synperiplanar conformation of bis-arene complexes [243] Results are in Scheme 15).

Successively, [5]trovacenyl units were connected with different spacers: boron [244], silicon [245] and tin [246], a carbonyl group [247], methylene, ethylene and various groups with double bonds [248], triple bonds and extensively conjugated triple bonds [249] to the most recent, octamethylferrocene-1,1′-diyl [250]. Up to four [5]-trovacenyl groups were assembled into a benzene ring [251]. Structures and electrochemical data for trovacenes are in Table 11.

The interested reader can find detailed discussion on electrochemical data and electronic communication between metal centers in the original papers.

Because of their equivalent charges and electron-donating abilities, the coordination properties of the tricarbadecaboranyl and cyclopentadienide monoanions are similar. Therefore the bis(methyltridecacarboranyl)vanadium complex was inserted in this section. Since the original tricarbadecaboranyl ligand has a −1 charge, the vanadium has a formal +2 charge. $(MeC_3B_7H_9)_2V$ [252] underwent a well-behaved, reversible, one-electron reduction and an oxidation that resulted much more difficult than that of vanadocene (Scheme 16). This result is in agreement with the high stability of $(MeC_3B_7H_9)_2V$ to air and was attributed to the strong electron-withdrawing ability of the tricarbadecaboranyl ligand which allows to stabilize metals in low oxidation states.

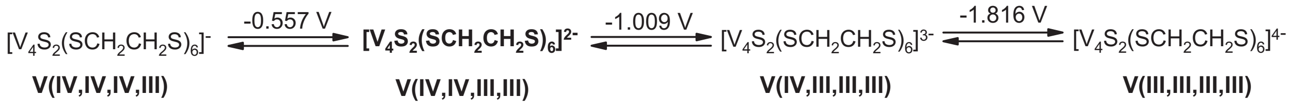
7. Vanadium clusters and polyoxometalates

Electrochemical aspects are important also for inorganic vanadium chemistry: just to give one example, electrochemical analysis was used to follow surface to follow surface evolution of Ni-V mixed oxide electrode upon Li insertion [253]. However, neither surfaces nor inorganic compounds will be treated in this review, apart few selected cases, for which important electrochemical applications have been developed. The families of compounds discussed in the following can be divided in three groups: (i) clusters compounds (that is with more than two V atoms) that are the direct evolution of some previously discussed V_2 species; (ii) vanadium containing polyoxometalates (POMs), and (iii) V_2O_5 (and related species).

7.1. Vanadium clusters

Most of vanadium clusters contained sulfur atoms, which is not surprising, considering that vanadium sulfide complexes were considered to be likely intermediates during hydrodemetalation and hydrodesulfurization in the processing of crude oil.

$V_4S_2(SCH_2CH_2S)_6{}^{2-}$, with a V_4S_2 central core with two μ^3-sulfur atoms, one above and on below an exactly planar V_4 parallelogram was obtained [254] reacting VCl_3 with Li_2S and $edtNa_2$ in the presence of Et_4NBr in MeCN. In the CV experiments a reversible one-electron oxidation and two one-electron reductions were observed (Scheme 17).



Scheme 17. Electrochemical behavior of $V_4S_2(SCH_2CH_2S)_6{}^{2-}$, in MeCN, with Bu_4NClO_4 as supporting electrolyte, referred to NHE [254].

$$[V_3S_7(R_2dtc)]^0 \rightleftharpoons \mathbf{[V_3S_7(R_2dtc)]^-} \rightleftharpoons [V_3S_7(R_2dtc)]^{2-}$$

	$E_{1/2}$, V	$E_{1/2}$, V
R = Me	-0.01	-1.03
R = Et	-0.015	-1.14
R = $HOCH_2CH_2$	0.00	-1.15

Scheme 18. Electrochemical data relative to CVs of formula $[V_3(\mu_3\text{-}S)(\eta^2\text{-}\mu\text{-}S_2)_3(R_2dtc)_3]$ clusters, in DMF, vs SCE, with Bu_4NClO_4 as supporting electrolyte [256].

Cyclic voltammetry of the trinuclear $[V_3O(\mu\text{-}O)_2(\mu\text{-}S)_2(etdtc)_3]^-$ in DMF [255] showed a series of redox processes: reductions at −0.77 and −1.15 V on the cathodic scan and oxidations at −0.65, +0.15, and +0.77 V on the return scan (vs SCE, with Bu_4NClO_4 as supporting electrolyte), some of which might come from mononuclear or dinuclear fragments. The same research group prepared and characterized electrochemically trinuclear vanadium dialkylcarbamate complexes of general formula $[V_3(\mu_3\text{-}S)(\eta^2\text{-}\mu\text{-}S_2)_3(R_2dtc)_3]$ (with R = Me, Et, or $HOCH_2CH_2$) [256], as illustrated in Scheme 18.

In other clusters, different metals were present. For example, the electrochemistry and spectroelectrochemistry of $[Cl_2FeS_2VS_2FeCl_2]^{3-}$ were examined [257]. Spectral changes were observed in the reduction of the cluster, but they were not reversible. Two irreversible waves (at +0.23 and +0.58 V) were observed for the oxidation in DMF; an $E_{pc} = -1.14$ V vs SCE was recorded in reduction. In acetonitrile, the first oxidation wave for the cluster was quasi-reversible, with an $E_{1/2}$ of +0.12 V (All the data were taken with Bu_4NClO_4 as electrolyte and are referred to SCE).

The tetranuclear V(III) complex, $[HB(pz)_3]_4V_4(\mu\text{-}C_6H_5OPO_3)_4$ [258], was electrochemically investigated in MeCN and in DCM. In acetonitrile two reversible oxidations of the cluster were observed at +0.68 and +1.13 V (vs AgCl/Ag, Bu_4NPF_6 as supporting electrolyte). Extending the sweep range led to additional poorly resolved oxidation processes, that resulted in the degradation of the core structure. In DCM the electrochemical behavior was similar, with a decrease in the reversibility of the oxidations.

Vanadium and molybdenum cofactor clusters are found in nitrogenase, prompting biomimetic research and suggesting the preparation of a series of single cubane (SC) and edge-bridged double cubane clusters containing the cores $[VFe_3(\mu_3\text{-}S)_4]^{2+}$ and $[V_2Fe_6(\mu_3\text{-}S)_6(\mu_4\text{-}S)_2]^{2+}$ [259]. Vanadium SCs, characterized by the presence of one $HBpz_3$ and three L anionic ligands, exhibited three-member electron transfer series, as shown in Scheme 19.

A number of divanadium compounds with the paddlewheel geometry bridged by nitrogen-donating ligands, although containing only two vanadium atoms, find a more opportune collocation in this section. Five of them contain the diamagnetic V_2^{4+} core with short V–V distances of less than 2.0 Å, consistent with a formal triple bond [260]. Nitrogen ligands are reported in Fig. 9, together with electrochemical data of divanadium compounds.

7.2. Polyoxovanadates and other vanadium-containing polyoxometalates (POMs)

Polyoxovanadates constitutes an important group of vanadium cluster compounds. The extensive series of polyoxovanadates of the general type $[V_6O_{13-n}\text{-}(OH)_n(tris)_2]^{2-}$ (with n = 0, 2, 3, 4 and

$$(HBpz_3)VFe_3S_4L_3]^- \rightleftharpoons (HBpz_3)VFe_3S_4L_3]^{2-} \rightleftharpoons (HBpz_3)VFe_3S_4L_3]^{3-}$$

L	$E_{1/2}$, V	$E_{1/2}$, V
F^-	-0.25	-1.57
Cl^-	-0.10	-1.36
N_3^-	-011	-1.29
PhS^-	-0.42	-1.50
CN^-	-0.04 (irr)	-1.18

Scheme 19. Redox potentials of V single cubane (SC) clusters. Data taken in MeCN, with Bu_4PF_6 as supporting electrolyte, and referred vs. SCE [259].

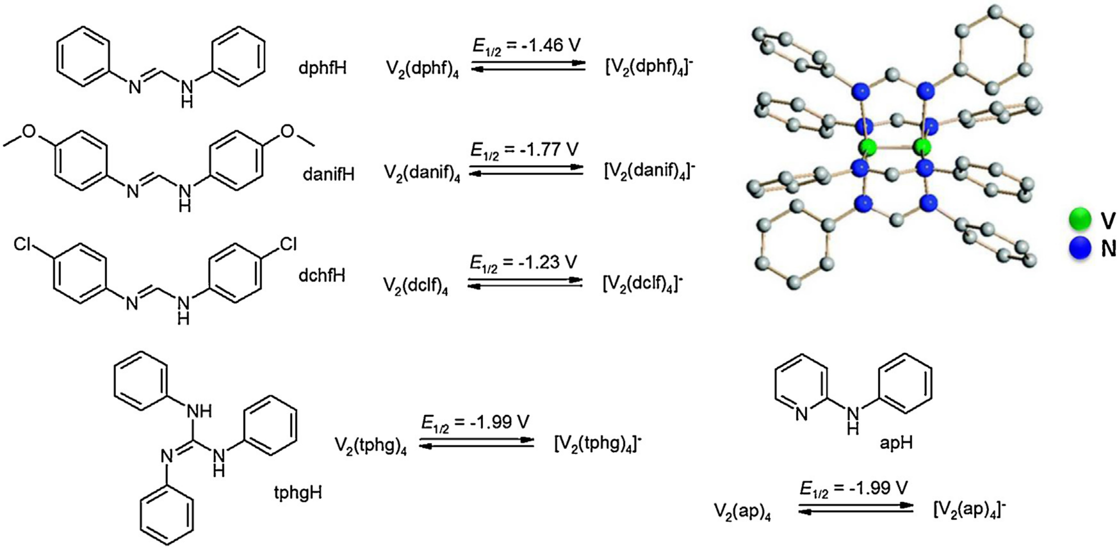
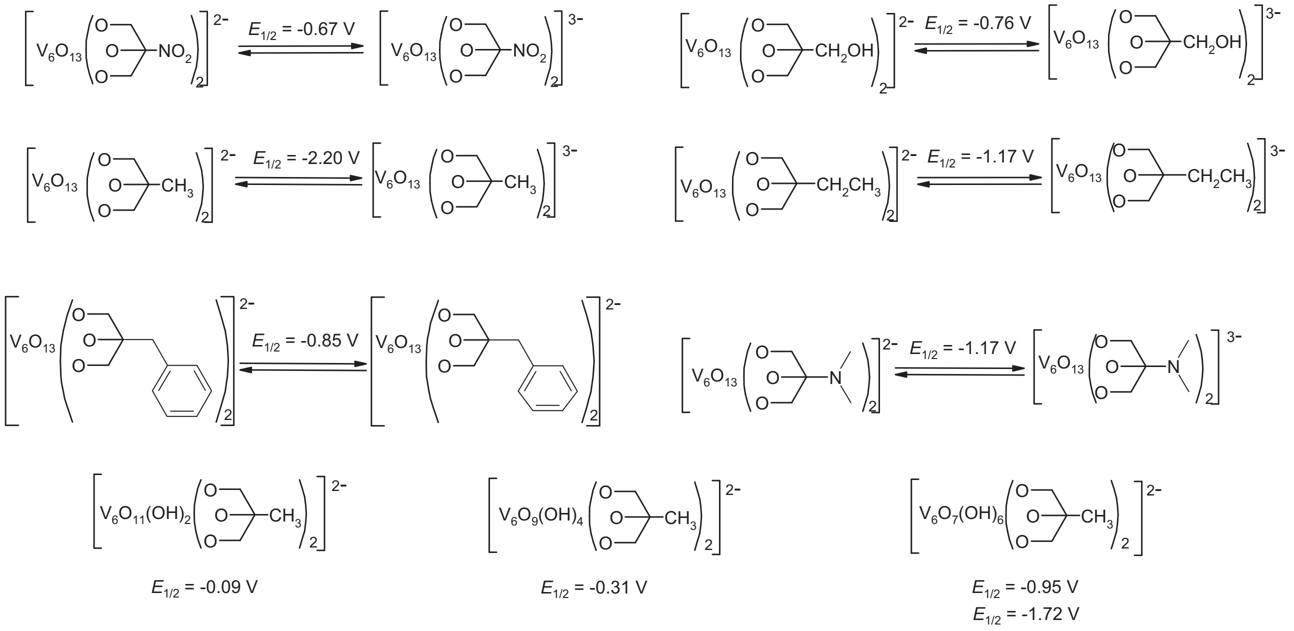


Fig. 9. Nitrogen ligands and their divanadium complexes. CVs were performed in THF, with Bu_4NPF_6 as supporting electrolyte. Values are vs AgCl/Ag. On the right, the paddle-wheel structure of $V_2(dphf)_4$ is shown.

Adapted from [260]. Copyright 2003 American Chemical Society.

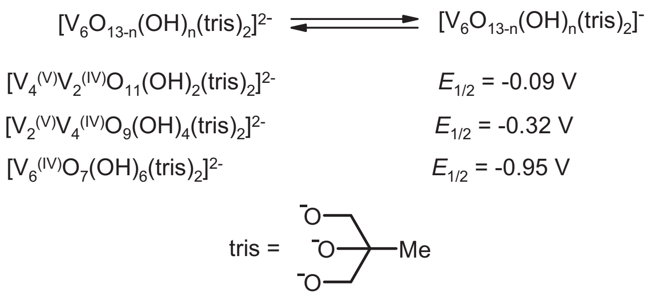


Scheme 20. Redox potentials for $[V_6O_{13-n}\text{-}(OH)_n(tris)_2]^{2-}$ polyoxovanadates in MeCN or DMF, with Bu_4NPF_6 as supporting electrolyte. Values are vs FcH^+/FcH [261].

6 and tris = polyalkoxide ligand from tris(hydroxymethyl)alkane) has been investigated [261]. Relevant data are summarized in Scheme 20. The cyclic voltammograms of the oxidized clusters (all vanadium are V(V) species) show a single one-electron reversible reduction at moderately negative potentials with respect to FcH^+/FcH couple. The substituent R of the triol ligand produced a significant effect on the potential of the reduction and a correlation was found between $E_{1/2}$ and the Hammett σ_m constants (the chosen substituent contants, however, should not be used in a non-conjugated system).

Protonation of oxygen atoms, with consequent increase of OH number, affects the relative ease of oxidation, that correlates with the number of reduced V(IV) centers associated with the cluster (Scheme 21)

Exploiting the techniques of hydrothermal synthesis allowed to extend the chemistry of polyoxoalkoxometalate clusters. The hydrothermal reactions of vanadium oxide precursors with trialkoxy ligands of the class $(HOCH_2)_3CR$ (with R = Me, Et) yielded polyalkoxyoxovanadium clusters with a hexametalate core [262]. Only some of them were soluble enough to be electrochemically investigated and data are collected in Scheme 22. Comparing potentials with those of the related series with reduced centers, $[V_6O_7(OH)_6(tris)_2]^{2-}$, in the previous Scheme 21, it is apparent that the introduction of additional trialkoxy ligands around the hexavanadium core makes the cluster more difficult to oxidize.



$$[V_6O_{13-n}(OH)_n(tris)_2]^{2-} \rightleftharpoons [V_6O_{13-n}(OH)_n(tris)_2]^{-}$$

$[V_4^{(V)}V_2^{(IV)}O_{11}(OH)_2(tris)_2]^{2-}$ $E_{1/2}$ = -0.09 V

$[V_2^{(V)}V_4^{(IV)}O_9(OH)_4(tris)_2]^{2-}$ $E_{1/2}$ = -0.32 V

$[V_6^{(IV)}O_7(OH)_6(tris)_2]^{2-}$ $E_{1/2}$ = -0.95 V

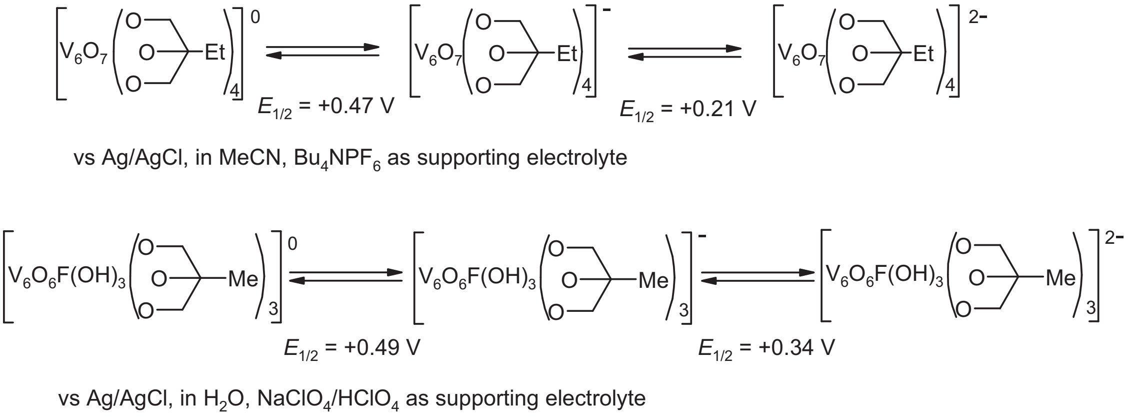
Scheme 21. Variation of oxidation potentials with protonation of $[V_6O_{13-n}\text{-}(OH)_n(tris)_2]^{2-}$ clusters. Values are vs FcH^+/FcH [261].

The alkoxo-polyoxovanadium clusters $[V_6O_7(OR)_{12}]$, with R = Me, Et, that is, fully alkylated derivatives comprising a hexavanadate core with the vanadium ions organized in an octahedral fashion, showed complex cyclic voltammetries [263], displaying four reversible single-electron transfers, as illustrated in Scheme 23.

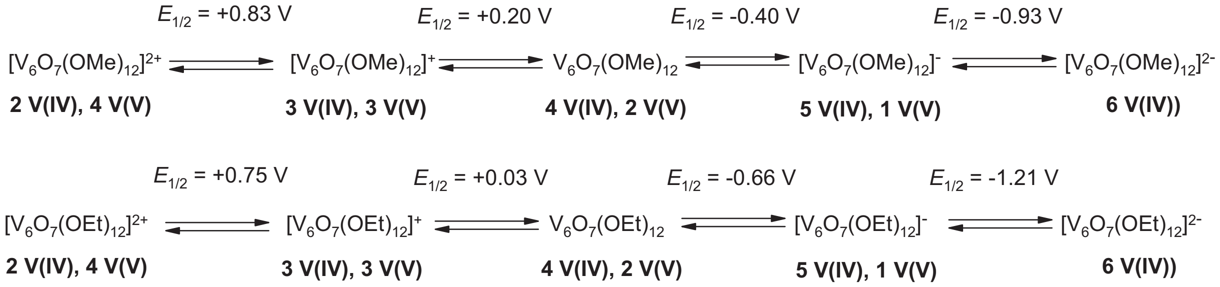
The neutral mixed-valence methoxo-polyoxovanadium cluster $[V_6O_8(OMe)_{11}]$ comprises a hexanuclear polyoxovanadate core, of which all but one of the μ-bridging oxo ligands are substituted by methoxo groups [264]. The cluster is highly redox active, displaying several successive thermodynamically stable V(IV,V) mixed-valence redox derivatives. The comparison of the cyclic voltammograms of this and $[V_6O_7(OMe)_{12}]$ showed an unexpectedly pronounced discrepancy in all but one of their corresponding redox potentials. For a detailed analysis of the electrochemical conversions the reader can consult the original paper.

Inorganic–organic polyoxovanadate-based coordination polymers were obtained using the ligand 1,4-bis(1-imidazolyl)butane (bib) under hydrothermal conditions [265]. Besides the interesting three-dimensional structure, these compounds allowed to prepare modified carbon paste electrodes (CPE) with excellent electrochemical property of V(V)/V(IV) couples, that is one of the most important properties of polyoxovanadates. In 1 M H_2SO_4 aqueous solution bare CPE presented no peak, whereas $[Co_2(bib)(V_2O_6)_2(H_2O)_2]$-CPE displayed one quasi reversible oxidation peak with $E_{1/2}$ = 0.752 V vs SCE, $[Mn_2(bib)(V_2O_6)_2(H_2O)_2]$-CPE showed $E_{1/2}$ = 0.754 V vs SCE, and with $[Ni_2(bib)_3V_4O_{12}]\cdot 4H_2O$-CPE $E_{1/2}$ = 0.718 V vs SCE was observed.

In order to investigate the association of vanadium with physiological substrates in materials capable of exerting anticancer biological activity, reaction between V_2O_5 and triethyl ammonium acetate/trigonelline (= *N*-methylpyridinium-3-carboxylate) in aqueous and mixed organic-aqueous media led to the isolation of three binary composite materials, two of which were electrochemically investigated [266]. In aqueous solution, with KNO_3 as supporting electrolyte, $[(Me\text{-}N^+C_5H_4CO_2H)_2][V_{10}O_{28}H_2]^{2-}$ presented a quasi-reversible redox wave at $E_{1/2}$ = −0.180 V vs AgCl/Ag; under the same conditions, the quasi-reversible wave of $[(Me\text{-}N^+C_5H_4CO_2H)_4][V_{10}O_{28}H_2][(Me\text{-}N^+C_5H_4CO_2{}^-)_2]$ occurred at $E_{1/2}$ = −0.300 V. The different $E_{1/2}$ values suggested that the core



Scheme 22. Electrochemical data of $V_6O_7[(OCH_2)_3CEt]_4$ and $V_6O_6F(OH)_3[(OCH_2)_3CMe]_3$ [262].



Scheme 23. Redox potentials of $[V_6O_7(OMe)_{12}]$ and $[V_6O_7(OEt)_{12}]$, obtained by CVs in DCM, with Bu_4NPF_6 as the supporting electrolyte and referred to FcH^+/FcH couple [263].

$[V_{10}O_{28}H_2]^{4-}$ is the active redox center and it is influenced by the presence of the betaine.

Considering that the vanadium phosphate system is an important family of vanadium oxides, noticeable for their structural diversity and potential applications in catalysis and material science, the synthesis of phosphate with large cavity and polynuclear vanadium was undertaken [267]. $V(H_2O)_2[(V_2O_2)_2(OH)_2(HPO_4)_2(PO_4)_2]_2$ presented $E_{1/2} = 0.743$ V vs AgCl/Ag (in aqueous Na_2SO_4/H_2SO_4), as a reversible peak, attributed to one-electron reduction of V^{5+}/V^{4+}.

A new hybrid compound, $[Cu(en)_2]_4[Na_2V(V)_{14}V(IV)_2O_{42}(V(IV)O_4)]\cdot 2H_2O$ (where en = 1,2-ethanediamine), has been hydrothermally synthesized [268]. It contains a bisodium-substituted $[Na_2V_{16}O_{42}(VO_4)]^{8-}$ cluster with an encapsulated $[VO_4]^{4-}$ core (Fig. 10).

The electrochemical behavior of carbon paste electrode modified with $[Na_2V_{16}O_{42}(VO_4)]^{8-}$ cluster has been investigated in 1 M H_2SO_4. Three reversible redox peaks (vs AgCl/Ag) appeared: $E_{1/2} = +1.527$ V, attributed to V(IV) → V(V), $E_{1/2} = +0.488$ V, due to V(III) → V(IV), and $E_{1/2} = -0.276$ V, related to the Cu(I)/Cu(II) couple.

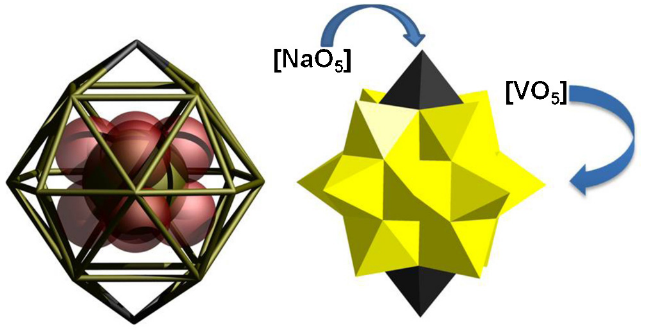


Fig. 10. Na_2V_{16} cluster with an encapsulated $[VO_4]^{4-}$ core (left) and polyhedral view of Na_2V_{16} cluster (right).

Adapted from [268], reprinted with permission of Elsevier.

A mixed-valence V(IV)/V(V) tetrametallate cluster, neutral and stable in solution, could be characterized by cyclic voltammetry in DMSO [269]. $V_4O_8(acac)_2(tham)_2$ (where tham is tris(hydroxymethylaminomethane) showed two independent cathodic waves at ca. −2.54 and −1.50 V vs FcH^+/FcH (Bu_4NPF_6 as supporting electrolyte), ascribed to vanadium-centered subsequent reductions. After second reduction, the complex is unstable.

POMs generally contain more than one type of metal and have been increasingly recognized as the core where it is possible to find photocatalytic and photoelectrochemical activities. Just to cite one example, a survey of advances in environmental remediation by photocatalysis and biomimetic approaches to solar energy conversion [270] and a review on polyoxometalate as water oxidation catalysts and the production of green fuel [271] have been published. Fundamental polyoxometalate structures are: (i) the iso-polyoxometalate type ($M_6O_{19}{}^{n-}$, Lindqvist type POMs), (ii) heteropolyoxometalates with tetrahedrically coordinated heteroatoms, such as P or Si ($XM_{12}O_{40}{}^{n-}$, Keggin type POMs; $X_2M_{18}O_{62}{}^{n-}$ Dawson type POMs), (iii) structure with an octahedral central atom, such as Al ($XM_6O_{24}{}^{n-}$, Anderson type POMs).

Investigation of electrochemical behavior of Dawson-type complexes derived from $[(1),2,2,\text{-}PMo_2W_{15}O_{61}]^{10-}$ and first transition metal ions, among which V(IV) [272], led to a detailed discussion of effect of Mo proximity and of pH. The V(IV) centers were oxidizable, far in potential from the reduction of the Mo moieties.

Exploitation of As—V—O cluster and transition metal complexes to construct extended framework has resulted in four novel compounds, $[Zn(en)_2][(H_2O)Zn(en)_2As_8V_{14}O_{42}(H_2O)]$, where en = 1,2-ethanediamine, $[(H_2O)Zn(phen)_2]_2[As_8V_{14}O_{42}(H_2O)]$, $[\{(H_2O)Zn(bipy)_2\}\{Zn(bipy)_2\}As_8V_{14}O_{42}(H_2O)_{0.5}]_2[\{(H_2O)Zn(bipy)_2As_8V_{14}$

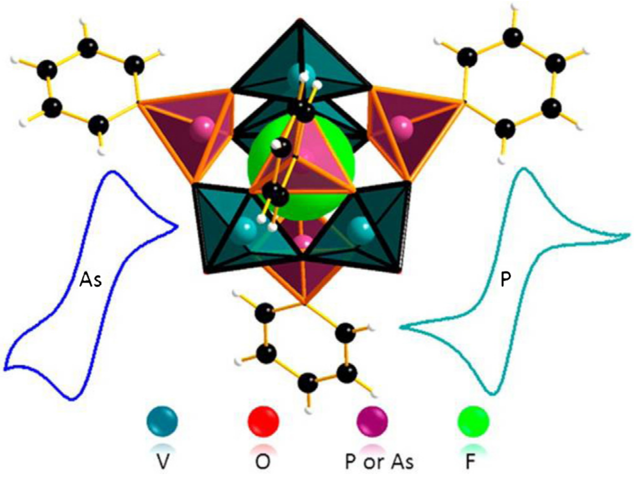


Fig. 11. $Ph_4P[(V_2O_3)_2(PhAsO_3)_4 \subset F]$ and $Ph_4P[(V_2O_3)_2(PhPO_3)_4 \subset F]$. Reprinted with permission from [276]. Copyright 2014 American Chemical Society.

$O_{42}(H_2O)_{0.5}\}\{Zn(bipy)_2\}_2]$, and $[(H_2O)Zn(bipy)_2][As_8V_{14}O_{42}(H_2O)]$, all with V(IV) [273]. The redox behavior of these compounds was investigated by cyclic voltammetry in 1 M H_2SO_4 with carbon paste modified electrodes; similar redox peaks were observed vs SCE: three quasi-reversible peaks were detected, the first of which ($E_{1/2}$ = +0.836, +0.806, +0.824, +0.806 V, for the four clusters, respectively) was attributed to the V(V)/V(IV) couple, the second one ($E_{1/2}$ = +0.471, +0.452, +0.493, +0.464 V) was attributed to the V(IV)/V(III) couple, while the third peak, between −0.540 and −0.600 V was due to the As(III)/As(IV) couple.

Hydrothermal synthesis allowed preparation of a Keggin-type polyoxoanion $[PMo_{12}O_{40}]^{3-}$ together with organic-inorganic hybrid cations $[Mo_9VO_{28}(bipy)_9]^{3+}$ [274], with all vanadium centers in the oxidation state +5. The cyclic voltammetry behavior of CPE modified with $[PMo_{12}O_{40}][Mo_9VO_{28}(bipy)_9]$ was recorded in 1 M H_2SO_4, showing three reversible redox peaks in the potential range of +0.600 to −0.200 V, all ascribed to three consecutive two-electron redox processes of Mo.

A hexanuclear cobalt(II) cluster incorporated in a banana-shaped tungstovanadate was prepared [275]. The cyclic voltammogram of $[(Co(OH_2)Co_2VW_9O_{34})^{2-}(VW_6O_{26})]^{17-}$ in sodium acetate buffer solution (pH 4.8) presented three quasi-reversible redox couples in the potential range from +0.6 to −0.6 V vs AgCl/Ag, the first couple being due to tungsten-centered redox processes. The other couples ($E_{1/2}$ = +0.017 and 0.203 V) were assigned as the redox processes associated with the V centers, V(IV)/V(III) and V(V)/V(IV), respectively.

The organic–inorganic hybrid compound $Ph_4P[(V_2O_3)_2(PhAsO_3)_4 \subset F]$ (VAsF) has been prepared [276] and its redox properties have been investigated by cyclic voltammetry, in comparison to $Ph_4P[(V_2O_3)_2(PhPO_3)_4 \subset F]$ (VPF) analog (Fig. 11). The VAsF cluster has a lower redox potential and higher electrochemical stability in solution, while it is thermally less stable in the solid state. CVs were performed in MeCN with Bu_4NPF_6 as supporting electrolyte and potentials are vs FcH^+/FcH. VAsF: $E_{1/2}$ = −0.141, −0.436 V; VPF: $E_{1/2}$ = +0.164, −0.340 V.

Density functional theory (DFT) calculations, at the hybrid functional B3LYP/6-31G* level, showed that the difference in the redox potential is due to the different electron affinities of VPF and VAsF.

7.3. V_2O_5 and related species

The main electrochemical interest in V_2O_5 is to coat electrodes with it. We report here only few examples, in view of applications to be discussed in Section 8.

Vanadium oxide gels can be synthesized either from vanadic acid or vanadium alkoxides. A discussion of different methods and different consequent morphologies was reported [277], together with a comparison of electrochemical properties. Thus, the discharge curve of crystalline V_2O_5 in $Li/LiClO_4$-propylene carbonate exhibited several steps, corresponding to the formation of different $Li_xV_2O_5$ phases. The discharge curve of vanadium pentoxide gels is different, with a single plateau observed around 3.1 V. The electrochemical behavior of amorphous thin films deposited from vanadium alkoxides is even more different, with a continuous decrease of the discharge curve rather than a large plateau. Cyclic voltammograms also show different electrochemical behaviors depending on the sol–gel synthetic route.

Vanadium pentoxide xerogels ($V_2O_5 \cdot nH_2O$) consist of ribbon-like V_2O_5 layers separated by intercalated water and are mixed valence semiconductors [278], that, upon electrochemical intercalation, become interesting materials for electrode surface modification. The cyclic voltammograms of spin-coated $V_2O_5 \cdot nH_2O$ in water depended on the potential range used: cycling over positive potentials gave reversible oxidation-reduction of 4–5% of the vanadium centers in the gel, while cycling to negative potentials resulted in irreversible reduction of a large proportion of the film vanadium atoms, accompanied by the loss of much of the layered structure of the gel. Electron transfer between V^{4+} in the V_2O_5 layers and the electrochemically oxidized intercalated cations were observed upon treatment of xerogel with $[M(bipy)_2]^{2+}$ (M = Fe, Ru, Os).

A different approach was immobilization of anionic complexes on a V_2O_5-surfactant nanocomposite [279]. The electrode was modified combining the intrinsic conductivity property of vanadium pentoxide xerogel with its water insolubility in the presence of the cationic surfactant hexadecyltrimethylammoniumbromide (CTABr). The obtained hybrid compound enabled the immobilization of electroactive anions such as hexacyanoferrate (III) ($[Fe(CN)_6]^{3-}$) and its analog pentacyanonitrosylferrate (II) ($[Fe(CN)_5NO]^{2-}$). After incorporation, the modified electrode exhibited the same electrochemical peaks of its complex in solution.

Analysis of Mg^{2+} intercalation into thin film electrodes of layered oxides, V_2O_5 and MoO_3, was performed, in view of possible application in rechargeable Mg batteries [280]. The study showed that highly reversible Mg insertion/deinsertion was possible. V_2O_5 thin-film electrodes could be cycled over a potential range of 2.2–3.0 V vs Mg^{2+}/Mg with a specific capacity of 150 mA h g^{-1} corresponding to one e^- transfer per unit.

Cucumber-like MnO_2 nanoparticles-enriched V_2O_5/PEDOT (= poly-3,4(O—CH_2CH_2O—)thiophene) coaxial nanowires were synthesized by layer-by-layer assembly [281]. This heterostructured nanomaterial exhibited enhanced electrochemical cycling performance. For example, the authors showed that decreases of capacity faded during 200 cycles from 0.557 to 0.173% over V_2O_5 nanowires at the current density of 100 mA g^{-1}. The improvement of the electrochemical cycling performance and stability of nanowire electrodes, especially at low rate, is promising for application in rechargeable lithium batteries.

Hierarchical V_2O_5 microspheres, composed of stacked platelets, prepared from ammonium vanadate, manifested a high capacity (266 mA h g^{-1}), excellent rate capability (223 mA h g^{-1} at a current density 2400 mA g^{-1}), and good cycling stability (200 mA h g^{-1} after 100 cycles) [282], all properties useful for lithium-ion batteries cathodic material.

The controllable synthesis of uniform VO_2 microspheres with various hollow structures, including yolk-shelled, multi-shelled, and single-shelled structures, through a one-step template-free solvothermal method was described [283]. The resulting VO_2 hollow complex structures were robust and could be readily

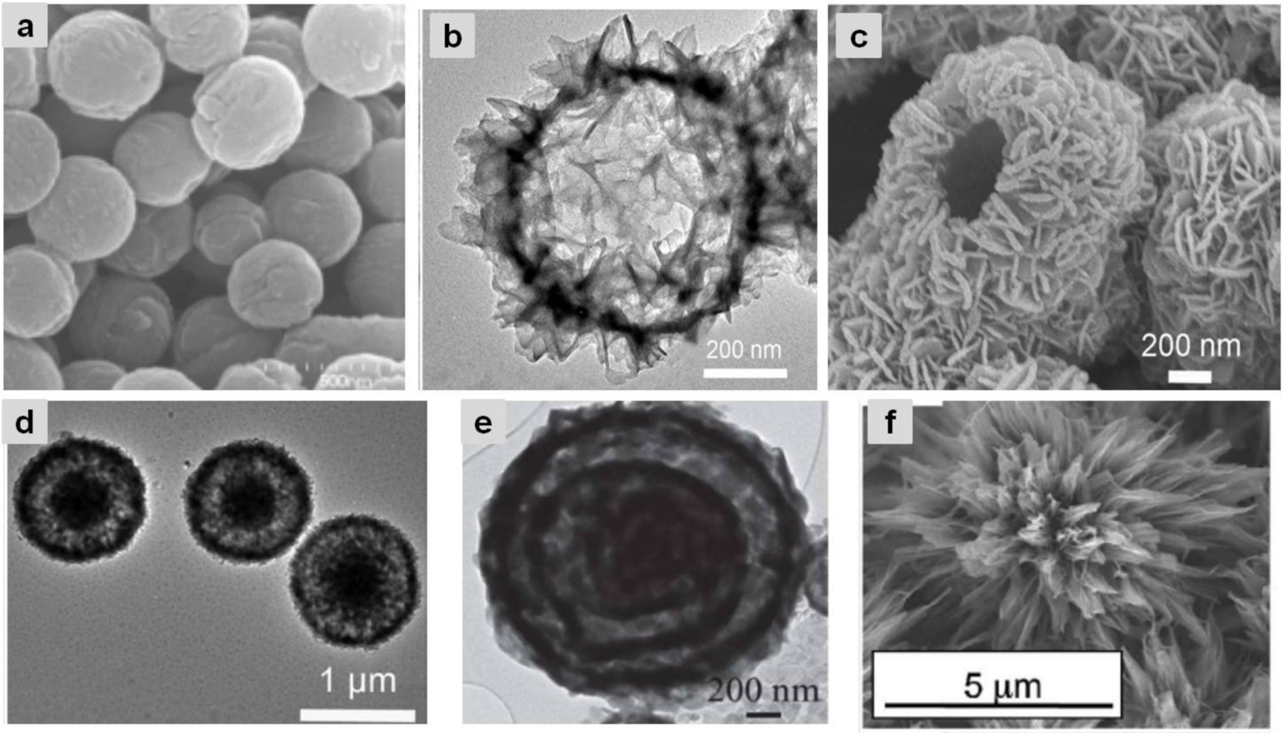


Fig. 12. Examples of different V_2O_5 morphologies: (a) SEM image of microsphere, adapted from [282]. Copyright 2013 American Chemical Society; (b) FESEM and (c) TEM images of hollow microspheres, adapted from [284], reprinted with permission of Wiley; (d) TEM images of yolk-shelled microsphere, adapted from [283], reprinted with permission of Wiley; (e) TEM images of low melting yolk-shelled microsphere, adapted from [285] reprinted with permission of RSC; (f) FESEM of flowers, adapted from [286] reprinted with permission of Wiley-RSC.

transformed into V_2O_5 hollow microspheres, the electrochemical properties of which were evaluated by cyclic voltammetry: three cathodic peaks at the potentials of 3.35, 3.13, and 2.21 V (vs Li/Li^+) indicated the multi-step lithium ion insertion process in the active materials, and corresponded to the phase changes of from α-V_2O_5 to ε-$Li_{0.5}V_2O_5$, then δ-LiV_2O_5, and, finally, γ-$Li_2V_2O_5$. The observed anodic peaks at the potentials of 2.60, 3.27, and 3.46 V corresponded to the lithium de-intercalation, via the same phase changes, in reverse order.

Nanosheet-assembled hierarchical V_2O_5 hollow microspheres were obtained by the same authors from V-glycolate precursor hollow microspheres, which in turn were synthesized by a template-free solvothermal method [284]. When evaluated as cathode materials for lithium ion batteries, the as-prepared hierarchical V_2O_5 hollow spheres delivered a specific discharge capacity very close to the theoretical capacity for one Li^+ insertion per V_2O_5. Moreover, they presented excellent cycling stability.

A convenient process for yolk–shell powders with a low melting temperature by spray pyrolysis was presented [285]. The electrochemical properties of such material and dense structured V_2O_5 powders, prepared by the same spray pyrolysis process, were compared; the former one had higher charge and discharge capacities and better rate performances at high current densities, because of the very yolk–shell structure.

Hierarchical Cu doped vanadium pentoxide flowers were prepared via hydrothermal approach followed by an annealing process [286]. The Cu doped V_2O_5 samples exhibited improved electrochemical performance compared to the un-doped ones, although the same peaks (cathodic ones, appearing at around 3.38, 3.16 and 2.27 V) were present.

Selected images of different V_2O_5 morphologies are collected in Fig. 12.

8. Electrochemical applications of vanadium compounds

Applications of vanadium compound are numerous and profoundly different. Many reviews were published during the years and even quite recently, discussing the use of vanadium species in catalysis (see Introduction), especially for oxidation reactions. Also, water oxidation by polyoxometalates (including the V containing ones) with the perspective of producing green fuel has been reviewed [271].

Here we limit to examples of applications where electrochemistry is directly involved.

8.1. Electrochemical synthesis

The synthesis of some vanadium compounds was accomplished electrochemically. For example, hexacarbonylvanadate anion $V(CO)_6^-$, previously prepared with strong reducing agents (Mg or Na) under pressure of CO, was easily obtained by electrochemical reduction, in anhydrous solvents saturated with CO at low and medium pressures, from V(II) compounds [287].

V(TTP)Cl was prepared by electrosynthesis after an exhaustive controlled-potential electrolysis of $V(TTP)Cl_2$, evaporation of the solvent, and extraction with toluene [288]. Controlled-potential reduction of V(TTP)Cl at −1.1 V gave the V(II) complex, V(TTP).

Preparative scale electrolysis of RS-SR ($R = -CH_2CO_2H$ or $-CH_2CH_2CO_2H$) in the presence of $V(hidaac)_2$ was performed, with complete conversion of the V(IV) complex into the V(V) analog [120].

The mixed valence divanadium V(III,IV) complex, $[(salen)VOV(salen)]^+$ was prepared by electroreduction of the corresponding V(IV,IV) complex [78].

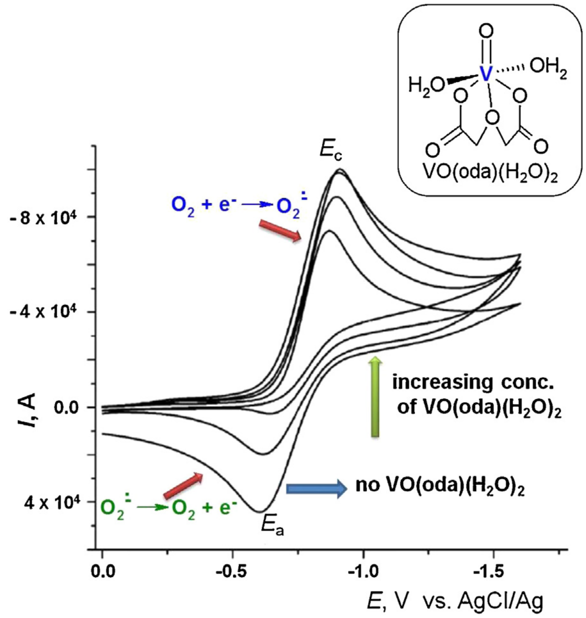


Fig. 13. Cyclic voltammograms of dioxygen in DMSO with 0.1 M Bu_4NClO_4 on platinum electrode, in absence and in presence of VO(oda) at different concentrations. Potentials are referred to AgCl/Ag.

Adapted from [48], reprinted with permission of Wiley.

Metal mediated electrochemical decarboxylation of 1,1′-bis[(2-hydroxyphenyl)carboxymethyl]-1,2-diaminoethane ligand to produce VO(ehpg) was observed, which eventually led also to VO(salen) derivative [82].

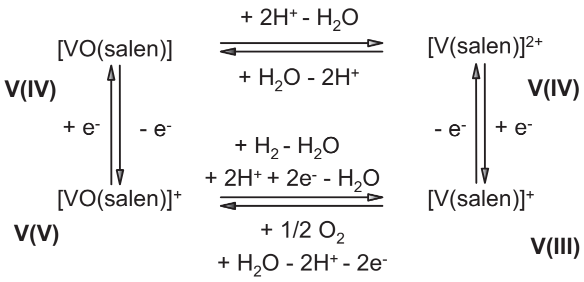
The reactivity of electrochemically generated superoxide free radicals ($O_2^{\bullet-}$) toward VO(oda)(H_2O)$_2$ was examined by cyclic voltammetry and compared with that of Co and Ni complexes with the same tridentate ligand [48]. The measurements were carried out in DMSO solution using a platinum electrode. Based on the height of the anodic peak E_a, that corresponds to electrochemical oxidation $O_2^{\bullet-} \rightarrow O_2 + e^-$, in the absence and in the presence of such compounds in the mixture, their $O_2^{\bullet-}$ scavenge ability was assessed (Fig. 13).

8.2. Electrochemical catalysis

Needless to say, electrochemical catalysis was more appealing for researchers.

The amavadin model [V(hidaac)$_3$]$^{2-}$ acted as an electron-transfer mediator in the electrocatalytic oxidation of 1,2,3-trihydroxybenzene (pyrogallol) [122].

[(salen)VOV(salen)][BF$_4$]$_2$ was used as homogeneous catalyst in electroreduction of O_2 (in CF_3CO_2H containing DCM) at graphite electrode [78]. A large catalytic current was observed at $E_p = +0.17$ V vs AgCl/Ag, with the reduction of O_2 beginning near the redox potential of the vanadium complex (+0.44 V vs AgCl/Ag). Using a rotating ring-disk electrode, it was assessed that the vanadium complex resulted in catalysis to allow four-electron reduction of O_2 to H_2O, whereas it showed no catalytic activity in the reduction of H_2O_2. The same authors investigated the electrocatalytic reduction of dioxygen to water adding trifluoromethanesulfonic acid to a DCM solution of VO(salen) [289]. The reduced, deoxygenated V(III) species [V(salen)]$^+$ was identified as the essential species in the catalysis of the electroreduction of O_2 by four electrons, modifying previous interpretation [78]. The catalytic oxidation of pyrrole by the mixed valence V(IV,V) [(salen)VOV(salen)]$^{3+}$ cation, which was formed on an electrode surface by oxidation of V(IV,IV) cation [(salen)VOV(salen)]$^{2+}$, was examined by hydrodynamic voltammetry at a rotating glassy carbon disk electrode [290]. The polymerization was rate-determined by the reoxidation step of the catalyst by O_2.



Scheme 24. Interconversion among the V(salen) complexes involved in reaction with dioxygen [81].

The stoichiometry and kinetics of the reaction between O_2 and the V(III)-salen complex were examined, and a possible mechanism for this four-electron reduction of O_2 was suggested [81]. The interconversions among the several V(salen) complexes can be summarized as in Scheme 24.

Steady-state voltammetry with a carbon microelectrode was employed to monitor the course of disproportionation reaction of VO(salen) (or oxido-V(IV) complexes with structurally related Schiff bases) in acidic medium to give the V(III) and V(V) species, [V(salen)]$^+$ and [VO(salen)]$^+$, respectively [86]. When electrolysis was carried out with O_2-saturated MeCN, the flow of charge decreased to background levels only after all of the acid present was consumed in the reduction of O_2 to H_2O, with the catalytic electroreduction resumed when additional acid was provided.

Successively, the same research group evidenced that the otherwise slow reaction between O_2 and decamethylferrocene or between O_2 and [V(salen)]$^+$ was significantly accelerated if all the three reactants are present, becoming catalytic in the presence of acid [291]. Steady state voltammetry was of help in investigating the system.

V_8C_7 particles (1–3 nm) on graphitized ion-exchange resin were synthesized [292] and promoted the activity of Pd for ethanol oxidation in alkaline media. V_8C_7 gave a Pd electrocatalyst with improved performance in terms of activity, stability and overpotential.

Electrocatalytic oxidations of biologically relevant molecules were investigated. Self-assembled monolayers (SAMs) based on octapentylthiophthalocyanine complexes of oxido-V(IV) (and of other metal ions) were used for electrocatalytic cysteine oxidation [293]. Ti and V were efficient electrocatalysts for such oxidation. Since cysteine is a well known analyte, it was also used in this work to characterize the new SAMs.

Owing to the very high stability of the V(IV)-substituted [(1),2,2,-PMo$_2$W$_{15}$O$_{61}$]$^{10-}$ complex throughout the whole pH range, the electrocatalytic oxidation of NADH to NAD$^+$ was investigated at pH 8 [272], considering that stability domain for efficient use of NADH is above pH 6.8, where fast hydrolysis is avoided.

A vanadium(III) thiolate complex, [V{P(ArS)$_3$}Cl]$^-$ (where Ar is the monoanion of 3-trimethylsilyl-2-sulfanylphenyl) is the precursor of catalytic reduction of hydrazine to ammonia [294]. On the basis of spectroscopic and electrochemical studies, the authors proposed a rationale for this behavior.

The electrocatalytic reduction of nitrite ion in 1 M H_2SO_4 medium was investigated at the [PMo$_{12}$O$_{40}$][Mo$_9$VO$_{28}$(bipy)$_9$]-CPE [274]. While direct electroreduction of nitrite ion requires a large overpotential at a bare electrode surface and no obvious response was observed at a bare CPE, the polyoxometalate-modified electrode had good electrocatalytic activity toward the reduction of nitrite.

On the other hand, electrocatalytic oxidation and detection of nitrite at a carbon paste electrode chemically modified with VO(salophen^{4Me}) gave anodic oxidation of nitrite (at pH 4) at low overpotential (0.87 V vs AgCl/Ag) [295]. The modified electrode exhibited good catalytic activity for the oxidation of nitrite with good sensitivity over a wide nitrite concentration range (three order of magnitude) and a detection limit of 6.13×10^{-7} M.

8.3. Vanadium flow-batteries (VFB)

Renewable energy sources such as solar and wind have necessarily an intermittent output and therefore it is important to develop large-scale stationary energy storage systems, in order to integrate them into the current electricity grid. To address the problem, redox flow batteries are among the most promising technologies. They utilize the reactions of two redox couples to perform reversible charging and discharging and are able to store large amounts of electrical energy relatively cheaply and efficiently. Important features of redox flow batteries are reviewed [296], with particular emphasis on vanadium-base ones [297,298]. Therefore, only few very recent examples will be discussed here.

The stability and electrochemical behavior of the V(V) electrolyte with and without several additives (chelating agents, surfactant or polymers) were investigated and compared [299]. The electrochemical properties, including the reversibility of electrode reaction, the diffusivity and polarization resistance of V(V) species and the feasibility of charge transfer V(V)/V(IV) was improved with all the additives, when compared with the pristine solution.

Mixed addenda (vanadium and tungsten) phosphorous-based POMs were investigated in order to determine what features on these highly tunable compounds are most important for improved battery performance [300]. Laboratory-scale flow cell testing of $[\text{A-}\alpha\text{-PV}_3\text{W}_9\text{O}_{40}]^{6-}$ (AP), $\text{K}_6[\text{B-}\alpha\text{-PV}_3\text{W}_9\text{O}_{40}]\cdot 4\text{H}_2\text{O}$ (BP), indicated that the coulombic efficiency of corner-sharing AP (Keggin-type POM with the more reversible vanadium electrochemistry) was greater than its edge-sharing analog BP. Testing of the Wells-Dawson POM, $[\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]^{9-}$ suggested higher charge density clusters were not as suitable as the Keggin structures for a redox flow battery due to the poor stability and inaccessibility of the highly reduced materials.

Perfluorosulfonic acid ionomers (PFSI) with different side-chain lengths have been investigated in vanadium flow batteries (VFB) [301]. The variations in the morphology and VFB properties of PFSI depended on the nature of side chain, a membrane with short side chains resulting the ideal option in the fabrication of high-performance VFBs with low capacity loss.

A simulated multi-physics model for a vanadium redox flow battery, accounting for the electrochemical reactions, pump losses, temperature changes within the VFB and aging prediction, was devised [302]. The model is applicable for a wide range of different vanadium redox batteries, with different nominal power ratings, nominal capacities and different vanadium and sulfuric acid concentrations and is with experimental data.

Finally, we present here a paper on applications of vanadium redox reactions in microfluidic fuel cells [303]. As the authors say, microfluidic vanadium redox fuel cells are membraneless and catalyst-free fuel cells comprising a microfluidic channel network with two porous carbon electrodes. The anolyte and catholyte for fuel cell operation are V(II) and V(V) in sulfuric acid based aqueous solution. The investigated electrochemical characteristics of the vanadium redox reactions on porous carbon paper electrodes were compared to a standard solid graphite electrode as baseline. From the cyclic voltammograms, both half-cell redox reactions resulted irreversible, whereas the kinetic parameters of the carbon paper electrode were in agreement with experimentally measured fuel cell polarization curves. On the basis of the obtained results, recommendations for microfluidic vanadium redox fuel cell design and operation were provided.

8.4. Lithium batteries

The other important electrochemical application of vanadium compounds is in the field of lithium batteries. Rechargeable batteries, in particular lithium ion ones, are energy storage devices that convert off-peak electricity into chemical energy and release the stored energy reversely during the on-peak period and are ubiquitous in modern society with different shapes and uses. A typical lithium ion battery (LIB) may be sketched as made of a negative electrode (anode) and a positive electrode (cathode) separated and connected by a Li^+ conducting electrolyte. The battery performance obviously depends on the intrinsic chemistry electrodes. Requirements for choosing good electrodes are numerous and include a high charge density and high specific charge, a high (cathode) and low (anode) standard redox potential, electrochemical compatibility with the electrolyte solution, and reversibility. It is advisable if also environmental benignity, safety and moderate cost are satisfied. Much research is devoted to find better and better electrode materials and much improvement was achieved from initially used graphite (as the anode) and the layered LiCoO_2 (as the cathode) [304]. A promising material for cathode is $\text{Li}_3\text{V}^2(\text{PO}_4)_3$ (LVP) and the state of the art in achievements with this cathode material was recently reviewed [305].

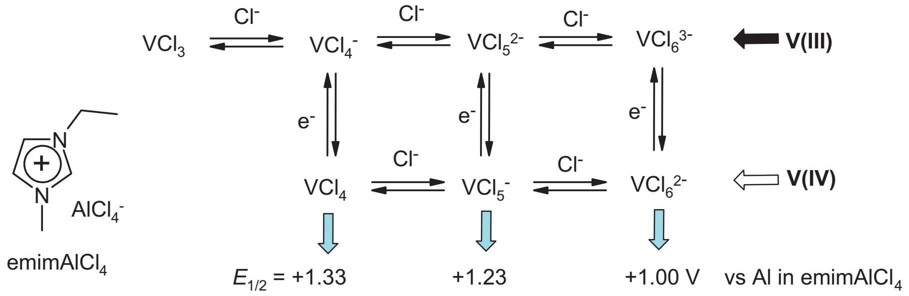
Vanadium is increasingly entering in materials for the cathode and the research in the field is very active. Examples of recent achievements will be reported in the following, but we wish to start with a work on electrolyte. One of the first investigation concerning battery electrolytes was published by Riechel [306], who studied an electrolyte made of an ionic liquid (IL, at that time called "room-temperature molten salt), 1-ethyl-3-methylimidazolium tetrachloroaluminate, and VCl_3, with formation of high order chloride complexes, $\text{VCl}_4{}^-$, $\text{VCl}_5{}^{2-}$, and $\text{VCl}_6{}^{4-}$. A detailed electrochemical investigation was carried out and results are shown in Scheme 25.

The authors suggested that vanadium compounds might be useful as cathodes in rechargeable cells using room-temperature chloroaluminate molten salt electrolytes. However, probably because of difficulties in working with first-generation ILs and corrosion problems presented by AlCl_3, the suggestion was not followed.

As to development of cathodic materials, studies aimed at understanding factors regulating lithium ion intercalation have been important to build efficient cathodes. Thus, a π-stacked coordination solid, $[(\text{VO})_2(\text{OH})_2(\text{C}_4\text{O}_4)(\text{phen})_2]$, was thermally stable up to 250 °C [307]. ^{7}Li NMR and cyclic voltammetry confirmed lithium ion intercalation. The voltammogram recorded for Li^+-$[(\text{VO})_2(\text{OH})_2(\text{C}_4\text{O}_4)(\text{phen})_2]$ in AcOH exhibited three peaks at 0.8, 0.33, and −0.19 V vs Ag^+/AgCl in the course of oxidation scans.

Since it is known that intercalation–deintercalation of Li^+ in V_2O_5 occurs during the reversible redox process $\text{V}_2\text{O}_5 + x\text{Li}^+ \leftrightarrows \text{Li}_x\text{V}_2\text{O}_5$, cyclic voltammograms were recorded to study the electrochemical behavior of Li^+ with V_2O_5 nanostrip [308], accompanied by galvanostatic charge–discharge cycling, galvanostatic intermittent titration technique, and electrochemical impedance spectroscopy.

Research in cathode materials with superior performance is continuing. Ultrathin $\text{Na}_{1.1}\text{V}_3\text{O}_{7.9}$ nanobelts, with a thickness around 20 nm, were evaluated as cathodic materials [309]. The authors state that these nanobelts exhibit superior electrochemical performance including high specific capacity, high rate capability, and superior long-term cyclic stability when compared to the previous results of vanadium-based oxides and vanadates. This is likely



Scheme 25. Redox processes of chloride complexes in 1-ethyl-3-methylimidazolium tetrachloroaluminate [306].

due to the structure that shorten the Li^+ ion diffusion and electron transportation distance, and to the structure stability upon cycling.

The same principle was followed by researchers that investigated mesoporous lithium vanadium oxide as a thin film electrode [310]. Cyclic voltammetry and galvanostatic charge/discharge cycling were used to characterize the electrochemical performance of the Li—V—O and V—O films, deposited on FTO-coated glass. Performance was slightly better with V_2O_5, but LiV_2O_5 has the advantage of not requiring a metallic lithium negative electrode as lithium source.

The reversible electrochemical lithium insertion in the potassium vanadium bronze $K_{0.5}V_2O_5$ leading to $Li_xK_{0.5}V_2O_5$ with $0 < x \leq 1.5$ was reported [311]. The electrochemical performance of this cathode material (specific capacity of 210 mA h g^{-1} is at an average voltage of 2.6 V, without any significant structural changes even after extended cycling experiments; excellent capacity retention with still 200 mA h g^{-1} at C/10 after 70 cycles; good rate capability with 140 and 120 mA h g^{-1} at 1 C and 1.4 C, respectively) is, according to the authors, one of the best among vanadium bronzes.

Potassium vanadates with ratio K/V = 1:3, 1:4, and 1:8, were investigated as positive electrode materials in lithium batteries [312]. The potassium-richer compound, KV_3O_8, showed a good rechargeability but a low discharge capacity of 70 mA h g^{-1}; the potassium-poorer bronze $K_{0.25}V_2O_5$ exhibited the highest specific capacity of 230 mA h g^{-1}, but a slow and continuous capacity fade with cycling was observed. Finally, $K_{0.5}V_2O_5$, with double-sheet V_2O_5 layered framework characterized by a large interlayer spacing of 7.7 Å, is the best candidate as positive electrode for lithium battery among the potassium–vanadium bronzes and oxides, presenting a remarkable specific capacity of 210 mA h g^{-1}, combined with excellent capacity retention.

The theoretical capacity of $LiVOPO_4$ could be increased from 159 to 318 mA h g^{-1} with the insertion of a second Li^+ ion into the lattice to form Li_2VOPO_4, significantly enhancing the energy density of lithium-ion batteries [313].

A new method for enhancing Li ion transport at the surface of $Li_3V_2(PO_4)_3$ particles through superionic pathways built along an ionic conductor has been very recently reported [314]. The $Li_3V_{1.95}Zr_{0.05}(PO_4)_3/C$ composite had higher initial discharge capacity, superior rate-capability, and excellent cycling performance when compared with pristine $Li_3V_2(PO_4)_3/C$, attributed to the occupation of vanadium sites by Zr^{4+} ions, that allow facile Li ion migration.

A vanadium pentoxide electrode was prepared in the amorphous form (a-V_2O_5). The electrode performance was compared with those for its crystalline counterpart (c-V_2O_5) [315]. The a-V_2O_5 electrode outperformed c-V_2O_5, since it was free from irreversible phase transitions and Li trapping. Consequently, it presented a larger reversible capacity (>600 mA h g^{-1}, Fig. 14) than that given by c-V_2O_5. Finally, it showed an excellent rate property.

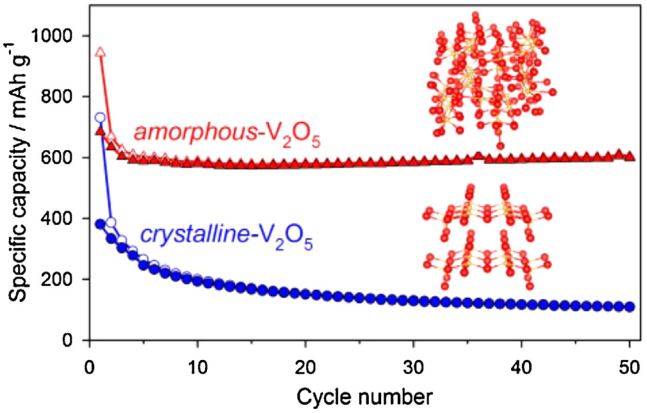


Fig. 14. Comparison of electrochemical performance of amorphous vs crystalline vanadium pentoxide as cathodic material in lithium batteries.

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Vanadium compounds have been investigated also as anodic materials, although to a less extent. There is a mention of $LaVO_4$, examined together with other lanthanum transition-metal oxides as new negative anodic materials for alkaline batteries [316], but performance of V was inferior to that of other metals. Also from a comparison of $LiVPO_4F$ to $Li_4Ti_5O_{12}$ as anode materials [317], it resulted that electrochemical performances were better for the latter. Therefore, it seems that vanadium-based materials have promising characteristic for cathodic materials, but not for anodic ones.

Finally, a paper dealing with electrochemical performance of a novel all solid-state sodium-ion symmetrical battery with $Na_3Zr_2Si_2PO_{12}$ (NASICON) as a solid electrolyte and $Na_3V_2(PO_4)_3$ as the active electrode material was reported [318]. The electrochemical characterization of the $Na_3V_2(PO_4)_3$ active material in the metallic sodium half-cells at 80 °C indicated that the NASICON-related phosphate underwent reversible sodium extraction/insertion reactions at electrode potentials of 1.6 and 3.4 V vs Na. The cell can work as a secondary battery and showed first discharge capacities of 68 and 32 mA h g^{-1} at the current densities of 1.2 and 10 μA cm^{-2}, respectively.

9. Conclusions

In the span of years examined in this review (1980–2014), a huge amount of data is available, but scattered or even "hidden" in papers mainly devoted to aspects of vanadium chemistry other than electrochemistry. Screening the literature, we found that quite often the same ligands were indicated with different abbreviations or, vice versa, the same abbreviation was used to indicate different ligands. In an effort to give a panorama as clear as possible, an attempt was made to exit this labyrinth, keeping original abbreviations when possible, but modifying them when necessary, maintaining hints to the real structure. Electrochemical data were collected in Tables, with experimental information necessary for comparisons, organizing the material on the basis of oxidation state of complexes and, within this set, on the basis of ligand coordinating atoms. We hope to offer the reader a comprehensive – if not complete – overview of electrochemistry of vanadium compounds and to make relatively easy to retrieve the desired information. Electrochemical applications, although marginally considered, are an important topic that justifies the need for better understanding electrochemistry of vanadium compounds.

Looking at all the results collected and considering the difficulties in comparing the electrochemical information from diverse sources, we recommend that electrochemistry studies should be performed with a more standardized protocol; to this aim, we suggest that a possible improvement might be to measure the open cell-static potential of solutions *before* starting CV runs, ensuring the correct analysis of the redox processes.

To conclude, we believe it is evident, from the journey we have done into the electrochemistry of vanadium in its different oxidation states, that the variety and versatility of V-compounds are not limited to catalysis and reactivity but are extended also in redox processes.

List of ligand abbreviations

A

abhphH$_2$	2-hydroxyacetophenone (2-amino)hydrazone
acacH	2,4-pentanedione (acetylacetone)
acacbhH$_2$	2,4-pentanedione *N*-(2-hydroxybenzoyl)hydrazone
acacbhyH$_2$	2,4-pentanedione *N*-benzoylhydrazone
acacprenH$_2$	*N*,*N*′-(3-oxo-1-methylbutyl)-2,2-dimethyl-1,3-propanediamine
acazbH$_2$	2-carboxy-2′-hydroxy-5′-methylazobenzene
acenH$_2$	diimine of 2,4-pentanedione and 1,2-diaminoethane (ethylenediamine)
achyacH$_2$	(2-hydroxyphenyl)ethanone *N*-acetylhydrazone (acetophenone *N*-acetylhydrazone)
achybzH$_2$	2-hydroxyacetophenone *N*-benzoylhydrazone
ac^{Cl}hybzH$_2$	5-chloro-2-hydroxyacetophenone *N*-benzoylhydrazone
ac^{Me}hybzH$_2$	2-hydroxy-5-methylacetophenone *N*-benzoylhydrazone
ac^{OMe}hybzH$_2$	2-hydroxy-5-methoxyacetophenone *N*-benzoylhydrazone
actacH	4-thioacetyl-2-pentanone (thioacetylacetone)
aetH	2-aminoethanethiol
apfH	2-acetylpyridine-2-furanoylhydrazone
atrisphH$_3$	tris(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine

B

bbehydH$_2$	*N*-benzoyl-*N*-(2-benzoyl-1-methylethyl)hydrazine (or 1-phenyl-1,3-butandione *N*-benzoylhydrazone)
bicahH$_6$	2,5-bis(dicarboxymethyl)aminomethyl-1,4-benzenediol
bipy	2,2′-bipyridine (4,4′-bipy = 4,4′-bipyridine)
bmphtcH$_2$	*S*-methyl-3-(5-bromo-2-hydroxyphenyl)dithiocarbazate
bpOH	bis[(pyrid-2-yl)methyl][(2-hydroxyphenyl)methyl] amine
bsq$^{\bullet-}$	1,2-benzosemiquinonate anion radical
budiphaH$_2$	bis(2-hydroxy-3,5-*tert*-buthylphenyl)metilmethanamine
bupbhyH$_2$	1-(2-hydroxyphenyl)-1-butanone *N*-benzoylhydrazone
bzacH	1-phenyl-1,3-butandione (benzoylacetone)
bzacbhH$_2$	1-phenyl-1,3-butandione *N*-(2-hydroxybenzoyl)hydrazone
bzacbhyH$_2$	1-phenyl-1,3-butandione *N*-benzoylhydrazone
bzacprenH$_2$	*N*,*N*′-(3-phenyl-3-oxo-1-methylpropyl)-2,2-dimethyl-1,3-propanediamine
bzimpyH$_2$	2,6-bis(benzoimidazol-2-yl)pyridine
bzmimpy	2,6-bis(3-methylbenzoimidazol-2-yl)pyridine
bzpydaH$_2$	*N*,*N*′-bis(2-hydroxybenzyl)-*N*,*N*′-bis(2-pyridyl)methyl-1,2-ethanediamine

C

cacpH$_3$	3-dicarboxymethylaminomethyl-4-hydroxybenzoic acid
cahqH$_6$	2,5-bis(dicarboxymethylaminomethyl)-1,4-benzenediol
capdH$_6$	2,2-bis(3-dicarboxymethylaminomethyl-4-hydroxy)phenylpropane
catH$_2$	1,2-benzenediol (catechol)
catpH$_9$	1,1,1-tris(3-dicarboxymethylaminomethyl-4-hydroxy)phenylethane
Cl$_4$bsq$^{\bullet-}$	tetrachloro-1,2-benzosemiquinonate anion radical
clbtscH$_2$	*N*-(2-chlorophenyl)methyl-*N*′-(2-hydroxy-6-hydroxymethyl-3-methylpyridine-4-yl)methylideneaminothiourea
Cl$_2$phH	1,3-dichlorobenzene
Cl$_3$phH	1,3,5-trichlorobenzene
Cl$_4$catH$_2$	tetrachloro-1.2-benzenediol (tetrachlorocatechol)
Cl$_5$phH	pentachlorobenzene
CpH	cyclopentadiene
cpsalH	*p*-chlorophenylsalicylimine
cydtcH	*N*,*N*-pentamethylenedithiocarbamic acid
cyhtscH$_2$	*N*-(cyclohexyl)-*N*′-(2-hydroxy-6-hydroxymethyl-3-methylpyridine-4-yl)methylideneamino thiourea

D

didaphH$_2$	2^1,2^9-dihydroxy-4^1,4^9-dimethyl-1,9-bis[1,3-benza]-3,7,11,15-tetraazahexadecaph-2,6-diene (named according the cyclophane nomenclature proposed by Hirakayama, Tetrahedron Lett. (1972) 2109)
dimaetH	2-(dimethylamino)ethanethiol
dipicH$_2$	2,6-pyridinedicarboxylic acid (dipicolinic acid)
dmbipy	4,4′-dimethyl-2,2′-bipyridine
dmpzH	3,5-dimethylpyrazole
docdaH$_2$	4,7-bis(carboxymethyl)-4,7-diaza-1-oxacyclononane
dpaH$_2$	pyridine-2,6-dicarboxylic acid (dipicolinic acid)
dphphe	4,7-diphenyl-1,10-phenanthroline
dppe	1,2-bis(diphenylphosphano)ethane
dppz	dipyrido[3,2-*a*:2′,3′-*c*]phenazine
dpq	dipyrido[3,2-*d*:2′,3′-*f*]quinoxaline

E

ebaH$_2$	*N*-ethyl-2,3-dihydroxybenzenecarbamide
ebdaH$_2$	*N*-*N*′-diethyl-2,3-dihydroxy-1,4-benzenedicarbamide
edtH$_2$	1,2-ethanedithiol
edtaH$_4$	*N*,*N*,*N*′,*N*′-tetracarboxymethyl-1,2-ethanediamine (previously ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid)
ehgsH$_2$	1-[(2-hydroxyphenyl)carboxymethyl]-2-(2-hydroxybenzyliden)-1,2-ethanediamine previously, *N*-[2-(*o*-salicylideneamino)ethyl](*o*-hydroxyphenyl)glycine
ehpgH$_2$	1,1′-bis[(2-hydroxyphenyl)carboxymethyl]-1,2-diaminoethane previously, *N*,*N*′-ethylenebis[(*o*-hydroxyphenyl)glycine]
entH$_6$	enterobactin
etbipypy	2,6-pyridinbedicarbaldehyde 3,3′bis[*N*-(2-hydroxyethyl]-2,2′-bipyridine dihydrazone
etdtcH	*N*,*N*-diethyldithiocarbamic acid

etmehydrzH$_2$ *N*,*N*′-bis(benzoyl)dihydrazone of 2,4-pentanedione (enol form)
etpiminH 2-(2-hydroxyphenyl)-1-ethylimidazoline

H

HBpz$_3$ hydridotris(pyrazolyl)borate
HBdmpz$_3$ hydridotris(3,5-dimethylpyrazolyl)borate
hbzhphaH$_2$ (2-hydroxybenzylidene)(2-hydroxyphenyl)amine
hebabH$_3$ *N*,*N*-bis(2-hydroxyethyl)-*N*′-(2-hydroxybenzyl)-1,2-ethanediamine
hebab^{Br}H$_3$ *N*,*N*-bis(2-hydroxyethyl)-*N*′-(5-bromo2-hydroxybenzyl)-1,2-ethanediamine
hebab^{OMe}H$_3$ *N*,*N*-bis(2-hydroxyethyl)-*N*′-(2-hydroxy-5-methoxybenzyl)-1,2-ethanediamine
hebab^{NO2}H$_3$ *N*,*N*-bis(2-hydroxyethyl)-*N*′-(2-hydroxy-5-nitrobenzyl)-1,2-ethanediamine
hidaH$_2$ bis(carboxymethyl)(2-hydroxyethyl)amine (*N*-(2-hydroxyethyl)iminodiacetic acid)
hidaacH$_3$ 2-hydroxyiminodiacetic acid
hidbacH$_3$ 2-hydroxyiminodibutanoic acid
hidpacH$_3$ 2-hydroxyiminodipropanoic acid
H$_2$NetmehydrzH$_2$ *N*,*N*′-bis(2-aminobenzoyl)dihydrazone of 2,4-pentanedione (enol form)
H$_2$NphhydrzH$_2$ *N*,*N*′-bis(2-aminobenzoyl)dihydrazone of diphenylethanone (enol form)
HOetmehydrzH$_2$ *N*,*N*′-bis(2-hydroxybenzoyl)dihydrazone of 2,4-pentanedione (enol form)
HOetpiminH 2-(2-hydroxyphenyl)-1-(2-hydroxyethyl)imidazoline
HOphhydrzH$_2$ *N*,*N*′-bis(2-hydroxybenzoyl)dihydrazone of diphenylethanone (enol form)
hyazbH$_2$ 2,2′-dihydroxyazobenzene
hybebH$_4$ 1,2-bis(2-hydroxyphenylcarbonyl)-1,2-benzenediamine
hybphpoH$_2$ bis(2-hydroxy-3,5-di-*tert*-butylphenyl)phenylphosphaneoxide
hybphpH$_2$ bis(2-hydroxy-3,5-di-*tert*-butylphenyl)phenylphosphane
hybselH$_2$ bis(2-hydroxy-3,5-di-*tert*-butylphenyl)selenide
hybsulH$_2$ bis(2-hydroxy-3,5-di-*tert*-butylphenyl)sulfide
hybzauH$_4$ *N*,*N*′-bis(5-bromo-2-hydroxybenzylideneamino)urea
hydoxiH$_2$ 2,3-butanedione *N*-(2-hydroxybenzoyl)monohydrazone monoxime
hyd^{OMe}oxiH$_2$ 2,3-butanedione *N*-(2-hydroxy-4-methoxybenzoyl)monohydrazone monoxime
hyd^{OH}oxiH$_2$ 2,3-butanedione *N*-(2,4-dihydroxybenzoyl)monohydrazone monoxime
hyiaH$_2$ 2-(2-hydroxybenzylidene)iminoacetic acid
hyipH$_2$ 2-(2-hydroxybenzylidene)imino-3-phenylpropanoic acid
hypybH$_3$ 1-(2-hydroxyphenylcarbonyl)-2-(2-pyridylcarbonyl)-1,2-benzenediamine
hysalenH$_4$ 1,2-bis(2,3-dihydroxybenzylidene)-1,2-ethanediamine

I

inoH$_3$ *cis*-inositol
ibsq$^{\bullet-}$ iminobenzosemiquinonate anion radical

M

maltH 3-hydroxy-2-methyl-4*H*-pyran-4-one
Me$_2$catH$_2$ 3,5-dimethyl-1,2-benzendiol (3,5-dimethylcatechol)
mediphaH$_2$ bis(2-hydroxy-3,5-dimethylphenyl)metilmethanamine
medtcH *N*,*N*-dimethyldithiocarbamic acid
mesH 1,3,5-trimethylbenzene
metacy 1,4,7-trimethyl-1,4,7-triazacyclononane
mbzenaH$_2$ *N*,*N*′-bis(2-hydroxy-3,5-dimethylbenzyl)-*N*,*N*′-dimethyl-1,2-ethanediamine
mibsq$^{\bullet-}$ *o*-imino-*p*-methylbenzosemiquinonate anion radical
mmphH$_2$ 4-methyl-2-sulfanylbenzenol (previously 4-methyl-2-mercaptophenol)
mmphtcH$_2$ *S*-methyl-3-(2-hydroxy-5-methoxyphenyl)dithiocarbazate
mndtH$_2$ *cis*-2,3-disulfabutenedinitrile (maleonitriledithiolate)
mphH$_2$ 2-sulfanylbenzenol (previously 2-mercaptophenol)
mphtcH$_2$ methyl *N*-[(2-hydroxyphenyl)methylamino]carbamodithioate or *S*-methyl-3-(2-hydroxyphenyl)dithiocarbazate
mpoH 2-sulfanylpyridine-*N*-oxide (previously, 2-mercapto)
mttphosH$_3$ tris(5-methyl-2-sulfanylphenyl)phosphane

N

nacnacH 2,4-pentanedione *N*,*N*′-di(4-methylphenyl)dihydrazone
naphbhyH$_2$ 2-hydroxynaphthalenecarbaldehyde *N*-benzoylhydrazone
naphdiolH$_2$ 2,3-naphthalenediol
naphquiH 8-(3-hydroxynapth-2-yl)methylidenequinoline
nmphtcH$_2$ *S*-methyl-3-(2-hydroxy-5-nitrophenyl)dithiocarbazate
ntbzimH$_3$ tris(benzoimidazol-2-yl)methylamine
ntbzmim tris(3-methylbenzoimidazol-2-yl)methylamine

O

odaH$_2$ dicarboxyethyl ether (oxydiacetic acid)

P

pabhH *N*-(pyridine-2-yl)methylideneaminobenzenammide
padhH 4-nitro-*N*-(pyridine-2-yl)methylideneaminobenzenammide
pahaH phenoxyacetohydroxamic acid
pathH 4-methyl-*N*-(pyridine-2-yl)methylideneaminobenzenammide
PcH$_2$ phthalocyanine
phen 1,10-phenanthroline
phepcaH$_2$ 1-(2-hydroxybenzyliden)-2-(2-pyridylcarbonyl)-1,2-benzenediamine
phhydrzH$_2$ *N*,*N*′-bis(benzoyl)dihydrazone of diphenylethanone (enol form)
pic 4-methylpyridine (4-picoline)
picacH 2-pyridinecarboxylic acid (once picolinic acid)
piminH 2-(2-hydroxyphenyl)-1*H*-imidazoline
pmidaH$_2$ (2-pyridylmethyl)bis(carboxymethylamine)
pycanH *N*-(2-nitrophenyl)pyridine-2-carboxamide
pydppz 6-(2-pyridyl)dipyrido[3,2-*a*:2′,3′-*c*]phenazine
pygalH$_2$ 1,2,3-benzenetriol (once pyrogallol)
pyhyphH 6-[(2-(pyridin-2-yl)hydrazono)methyl]phenol
pymaphH$_2$ 2-(phenylpyridin-2-yl-methyl)aminophenol
pympyrH$_2$ 1-(4,6-dimethylpyrimidin-2-yl)-*N*′-(2-hydroxybenzylidene)-5-methyl-1*H*-pyrazole-3-carbohydrazide
pynaphH 1-(2-pyridylazo)-2-naphthalenol
pyphen 2-(2-pyridyl)-1,10-phenanthroline
pypyrH$_2$ *N*′-(2-hydroxybenzylidene)-5-methyl-1-(pyridin-2-yl)-1*H*-pyrazole-3-carbohydrazide

Q

quinolH 8-hydroxyquinoline (8-quinolynol)

R

raH$_2$ rhodotorulic acid

S

sabheaH$_3$	2-(2-hydroxybenzylideneamino)ethyl-bis(2-hydroxyethyl)amine
sa^{Br}bheaH$_3$	2-(5-bromo-2-hydroxybenzylideneamino)ethyl-bis(2-hydroxyethyl)amine
sa^{OMe}bheaH$_3$	2-(2-hydroxy-5-methoxybenzylideneamino)ethyl-bis(2-hydroxyethyl)amine
sa^{NO2}bheaH$_3$	2-(2-hydroxy-5-nitrobenzylideneamino)ethyl-bis(2-hydroxyethyl)amine
salH	2-hydroxybenzenecarbaldehyde (salicyl aldehyde)
salacH$_2$	2-hydroxybenzenecarboxylic acid (salcylic acid)
salalaH$_2$	2(-2-hydroxybenzylideneimino)propanoic acid (*N*-saicylidenealanine)
salampH$_2$	2-(2-hydroxybenzilideneamino)ethylbenzenol 2-(*N*-salicylideneaminoethyl)phenol
salbhyH$_2$	2-hydroxybenzenecarbaldehyde *N*-bennoylhydrazone
salenH$_2$	1,2-bis(2-hydroxybenzylidene)-1,2-ethanediamine (previously, *N*,*N*′-ethylenebis(salicylidene))
sal^{Me}enH$_2$	1,2-bis(2-hydroxybenzylidene)-1,2-propanediamine
salglyH$_2$	2(-2-hydroxybenzylideneimino)ethanoic acid *N*-salicylideneglycine
salhyacH$_2$	2-hydroxybenzenecarbaldeyde *N*-acetylhydrazone
salmpyH$_2$	(2-hydroxybenzylidene)(4-pyridyl)methylamine
salophenH$_2$	1,2-bis(2-hydroxybenzylidene)-1,2-benzenediamine
salophen^{4Me}H$_2$	1,2-bis(2-hydroxybenzylidene)-4-methyl-1,2-benzenediamine
salphH$_2$	2-hydroxybenzenecarbaldehyde (2-hydroxybenzoyl)hydrazone
salpheH$_2$	2(-2-hydroxybenzylideneimino)-2-phenylethanoic acid (*N*-salycilidenphenylalanine)
salpholH$_2$	(2-hydroxybenzylidene)(2-hydroxyphenyl)amine
sal^{Br}pholH$_2$	(5-bromo-2-hydroxybenzylidene)(2-hydroxyphenyl)amine
sal^{3OMe}pholH$_2$	(2-hydroxy-3-methoxybenzylidene)(2-hydroxyphenyl)amine
sal^{4OMe}pholH$_2$	(2-hydroxy-4-methoxybenzylidene)(2-hydroxyphenyl)amine
sal^{5OMe}pholH$_2$	(2-hydroxy-5-methoxybenzylidene)(2-hydroxyphenyl)amine
sal^{NO2}pholH$_2$	(2-hydroxy-5-nitrobenzylidene)(2-hydroxyphenyl)amine
salph^{Cl}olH$_2$	(2-hydroxybenzylidene)(5-chloro-2-hydroxyphenyl)amine
salprenH$_2$	1,3-bis(2-hydroxybenzylidene)-1,3-propanediamine
salquiH	8-(2-hydroxybenzylideneamino)quinoline (8-salicylideneaminoquinoline)
sal^{Br}quiH	8-(4-bromo-2-hydroxybenzylideneamino)quinoline
sal^{OMe}quiH	8-(2-hydroxy-3-methoxybenzylideneamino)quinoline
salvalH$_2$	2(-2-hydroxybenzylideneimino)-2-methylbutanoic acid (*N*-salicylidenevaline)
sesaH	*N*-(2-sulfanylethyl)salicylideneamine
silethyneH	2,6-bis(trimethylsilyl)phenylethyne
sulfCpz$_3$H	tris(pyrazolyl)methanesulfonic acid

T

tacaH	(1,4,7-triazacyclonon-1-yl)ethanoic acid (1,4,7-triazacyclononane-*N*-acetic acid)
tacbzH	2-(1,4,7-triazacyclonon-1-yl)methylbenzenol (*N*-(2-hydroxybenzyl)-1,4,7-triazacyclononane)
tactacH	2,4-pentanedithione (dithioacetylacetone)
tazadiolH$_2$	2^1,2^8-dihydroxy-4^1,4^8-dimethyl-1,8-bis[1,3-benza]-3,6,10,14-tetraazapentadecaphane (named according the cyclophane nomenclature proposed by Hirakayama, Tetrahedron Lett. (1972) 2109)
tbenH$_4$	*N*,*N*,*N*′,*N*′-tetrakis(2-hydroxyphenylmethyl)-1,2-ethanediamine
^{t}BucatH$_2$	4-*tert*-butyl-1,2-benzendiol (3,5-di-*tert*-butylcatechol)
^{t}Bu$_2$catH$_2$	3,5-di-*tert*-butyl-1,2-benzendiol (3,5-di-*tert*-butylcathecol)
^{t}Bu$_2$bipy	5,5′-di-*tert*-butyl-2,2′-bipyridine
^{t}BubztacyH$_3$	1,4,7-tri(5-tert-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane
^{t}BudmanH	(3,5-dimethylphenyl)-*tert*-butylamine or *N*-*tert*-butyl-3,5-dimethylaniline
(^{t}BuP)$_8$czH$_2$	octakis(*p*-*tert*-butylphenyl)corrazoline
^{t}Bu$_2$pyhyphH	6-[(2-(pyridin-2-yl)hydrazono)methyl]-2,4-di-*tert*-butyl-phenol
^{t}Bu$_4$salbutenH$_2$	1,4-bis(2-hydroxy-3,5-di-*tert*-butylbenzylidene)-1,4-butanediamine
^{t}Bu$_4$salenH$_2$	1,2-bis(2-hydroxy-3,5-di-*tert*-butylbenzylidene)-1,2-ethanediamine
^{t}Bu$_4$sal^{Me}enH$_2$	1,2-bis(2-hydroxy-3,5-di-*tert*-butylbenzylidene)-1,2-propanediamine
^{t}Bu$_4$sal^{diMe}enH$_2$	1,2-bis(2-hydroxy-3,5-di-*tert*-butylbenzylidene)-2,2-dimethyl-1,3-propanediamine
^{t}Bu$_4$salhexenH$_2$	1,6-bis(2-hydroxy-3,5-di-*tert*-butylbenzylidene)-1,6-hexanediamine
^{t}Bu$_4$salpenenH$_2$	1,5-bis(2-hydroxy-3,5-di-*tert*-butylbenzylidene)-1,5-pentanediamine
^{t}Bu$_4$salprenH$_2$	1,3-bis(2-hydroxy-3,5-di-*tert*-butylbenzylidene)-1,3-propanediamine
tcdaH$_2$	1,4-bis(carboxymethyl)-1,4,7-triazacyclononane
terpy	2,6-bis(2-pyridyl)pyridine (or 2,2′:6′,2″-terpyridine)
TetaPPH$_2$	5,10,15,20-tetrakis(*p*-diethylaminophenyl)porphyrins
thipcaH$_2$	1-(2-sulfanylbenzyliden)-2-(2-pyridylcarbonyl)-1,2-benzenediamine
TironH$_2$	4,5-dihydroxy-1,3-benzenedisulfonic acid
tmeda	1,2-bis(diaminomethyl)ethane (previously *N*,*N*,*N*′,*N*′-tetramethylethylenediamine)
tmphe	3,4,7,8-tetramethyl-1,10-phenanthroline
tmtaaH$_2$	2,5,9,11-tetramethyl-1,7-bis[1,2-benza]-2,6,8,12-tetraazadodecaph-2,4,8,10-tetraene (named according the cyclophane nomenclature proposed by Hirakayama, Tetrahedron Lett. (1972) 2109)
tpa	tris(2-pyridylmethyl)amine
tprcamH$_6$	triamide of 2,3-dihydroxybenzoic acid and tris(3-aminopropyl)amine
TPyPH$_2$	5,10,15,20-tetrapyridylporphyrin
trencamH$_6$	triamide of 2,3-dihydroxybenzoic acid and tris(2-aminoethyl)amine
trenpamH$_6$	triamide of 2,3,4-trihydroxybenzoic acid and tris(2-aminoethyl)amine
trimpsi	tris(dimethylphosphanomethyl)-*tert*-butylsilane
trisalenH$_3$	tris[2-(2-hydroxybenzylideneamino)ethyl]amine
tscH$_2$	*N*-(2-chlorphenyl)methylthiourea
TsulfPPH$_2$	5,10,15,20-tetrakis(*p*-sulfonatophenyl) porphyrin
ttphosH$_3$	tris(2-sulfanylphenyl)phosphane
TTPH$_2$	5,10,15,20-tetrakis(4-methylphenyl)porphyrin

V

vanH	4-hydroxy-3-methoxybenzenecarbaldehyde (vanillin)

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