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MONOPEROXIDOVANADIUM (V) COMPLEXES: SYNTHESIS, STRUCTURE AND SOLUTION PROPERTIES

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To our colleague Dr. Enrique J. Baran for his remarkable contributions to the field of Vanadium Bioinorganic Chemistry

Review Article

Abstract

The review is dealing with monoperoxidovanadium (V) complexes, intensively studied in many laboratories during the last decades, due to their importance in biocoordination chemistry which is based mainly on the fact that they represent synthetic structural and functional models for the peroxo form of the vanadium haloperoxidase enzyme (VHPO), or can exhibit insulin mimetic properties or antitumor activity. We discuss here the methods of synthesis from the viewpoint of composition of reaction solutions and reaction conditions. A complete summarization of seventy two structurally characterized mono- and dinuclear monoperoxidovanadium (V) complexes, with their chemical composition, set of donor atoms and space groups, is given. The general features in

their molecular structure and intermolecular interactions are discussed. Besides UV-vis, their IR, Raman and ^{51}V NMR spectral data are presented.

Keywords: peroxo, vanadium complex, crystal structure, ^{51}V NMR spectra.

Resumen

Este trabajo de revisión trata acerca de los complejos del monoperoxidovanadium (V), los cuales fueron estudiados intensivamente en muchos laboratorios durante las décadas pasadas, debido a su importancia en la química de la biocoordinación lo cual se basa principalmente en el hecho de que estos complejos representan los modelos estructurales y funcionales sintéticos para la forma peroxo de la enzima vanadio haloperoxidasa (VHPO), o pueden exhibir características mimeticas de la insulina o actividad antitumoral. Discutimos aquí los métodos de síntesis desde el punto de vista de la composición de las soluciones y de las condiciones de la reacción. Se muestra un resumen completo de setenta y dos complejos mono y dinucleares estructuralmente caracterizados del monoperoxidovanadium (V), con su composición química, su serie de de átomos donores y grupos espaciales. Se presentan además, los espectros de UV-vis, IR, Raman and ^{51}V NMR.

Palabras clave: peroxo, complejos de vanadio, estructura cristalina, espectros de ^{51}V NMR.

Introduction

In the last decades, an immense attention has been paid to the vanadium chemistry due to the discovery of the role of vanadium in biological systems, found presence of vanadium in the active site of some enzymes (VHPO [1] or nitrogenases [2]), and insulin mimetic properties of many vanadium (IV) complexes, polyoxidovanadates or coordination compounds of vanadium (V). [3] The examination of the antitumor activity of these compounds, such as dioxidovanadium (V) complex of oxodiacetic acid [4] salicylaldehyde semicarbazone derivatives [5] must also be mentioned. All these studies related to vanadium biochemistry or bio-coordination chemistry, are focused on interaction of different ionic forms of vanadium (IV or V) with biomolecules or biologically active organic molecules, e.g. carbohydrates, [6] with the aim to elucidate the structure of the species formed in solution and in the solid state, which allow then a competent study of their function in individual biochemical processes.

As recent examples of insulin mimetic compounds, the bis(ethylmaltolato) oxidovanadium(IV) complex, [7] salicylaldehyde semicarbazone dioxidovanadium (V) complex [8] $NH_4[VO_2(dipic)]$ [9] which was found to be the most effective insulin-enhancing agent or complexes with derivatives of dipicolinic acid, $[VO(H_2O)(5R^1NHdipic)_2]$ (R^1 is the ethyl-protected L-amino acid residues Gly, Ala, Val or Phe) and $[VO(H_2O)(5R^2Odipic)_2]$ (R^2 is diisopropyl-D-galactose or myo-inositol-orthoformate), [10] can be mentioned.

The oxidovanadium compounds as functional and structural models for the native form of VHPO were recently discussed in a review by Rehder [11], the function and perspectives of these compounds as insulin mimics in treatment of *diabetes* were reviewed in ref. [7] Other useful reviews on peroxidovanadium compounds were published by Butler et. al., [12] and Bortolini and Conte. [13]

The peroxidovanadium (V) complexes, mainly the monoperoxido ones, represent an important type of vanadium compounds related to the three biological functions mentioned above. The discovery that in the active site of the peroxido form of VHPO the pentacoordinated vanadium atom is present in form of the V^V–(η^2-O_2^{2-}) monoperoxido group [14], with two oxido oxygen atoms and one nitrogen atom from histidine completing the coordination sphere of vanadium, was for many research groups an impulse for intensive investigations focused on preparation and structural characterization of oxido-monoperoxidovanadium (V) complexes with different

polydentate ligands providing a N_xO_y donor set. Despite the fact that the vanadium atoms in the synthetized monoperoxidovanadium (V) complexes have higher coordination number (six or seven) than found in the peroxido form of VHPO (five), they are good structural and even functional models for this enzyme, indeed.

Some peroxidovanadium (V) complexes were found to have insulin mimetic properties, too. For example, the diperoxido complexes, $[VO(O_2)_2(pic)]^{2-}$ and $[VO(O_2)_2(phen)]^-$, both inhibit the G-6-Pase *in vivo* (swine), the latter complex being a potent protein phosphotyrosine phosphatase inhibitor, lowering the blood glucose level even when transdermally delivered to mouse. [15]

Cytostatic effects were observed, for example, for $K_2[VO(O_2)(nta)]$, $K[VO(O_2)_2(phen)]$ and $[VO(O_2)_2(Me_2phen)]^-$. The latter complex was found to inhibit certain tumor cell growth in mice by 80 %. [16]

In this review, we deal with X-ray structurally characterized monoperoxidovanadium (V) complexes: their synthesis, molecular structure, supramolecular architecture and spectral properties (UV-vis, IR, Raman and ^{51}V NMR). The abbreviations used for the heteroligands, organic counterions and solvate molecule and their structural formulae are presented in Charts 1 and 2.

Methods of preparations

The reaction systems, generally used for preparation of vanadium (V) monoperoxido complexes, have following composition:

vanadium compound—H_2O_2—ligand/s—solvent

In the vast majority of the published synthesis, as starting compounds V_2O_5, NH_4VO_3 or KVO_3 were used, in some cases also $VOSO_4$ or VCl_3. Just four complexes were synthesized so far using a vanadium complex as precursor [17,18,19]. The vanadium pentoxide is usually dissolved under cooling (in ice bath) in diluted hydrogen peroxide solution or in an aqueous solution of a base (hydroxide, ammine, ammonia, carbonate), in this case sometimes under gentle heating. NH_4VO_3 is mostly used in synthesis of anionic peroxido complexes with ammonium cation as counterion, but also when other counterions are preferred, e. g. tetraalkylammonium hydroxide was added to the reaction solution with subsequent brief boiling of the reaction solution to remove ammonia. [20]

The ligands can be added to the reaction system as solids or in form of their solutions in water or in appropriate organic solvent (mostly acetonitrile, ethanol or methanol). When necessary, the pH value is adjusted by either acids (perchloric, hydrochloric) or bases (alkali hydroxides, ammonia). The cationic monoperoxido complexes, $[VO(O_2)(L)]^{n+}$, can be usually obtained from very acidic solutions (pH 0.3 to 1.7), neutral complexes, $[VO(O_2)(L)]$, from less acidic solutions (pH 1.2 to 2.2, average value 1.7), and anionic ones $[VO(O_2)(L)]^{n-}$ from medium acidic to neutral solutions (pH 1.8 to 6.8, average value 4.0).

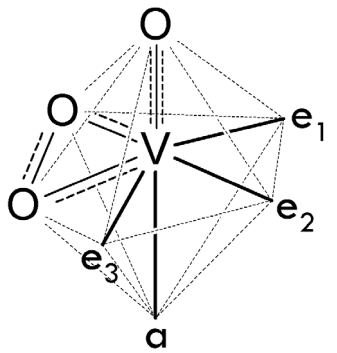
The crystallization is often initiated by addition of organic co-solvent (ethanol, methanol), in a small amount to avoid formation of a stable precipitate. The crystalline products in form of monocrystals suitable for X-ray analysis are usually formed within hours to weeks (or even months) from a reaction solutions being kept at temperatures ranging from –70 °C to room temperature (20 – 25 °C). In some cases, recrystallization is necessary to obtain suitable monocrystals.

A relation between the method of preparations and the solubility of a complex formed exist: generally, the anionic complexes with simple inorganic cations are soluble in water and insoluble in many organic solvents. However, anionic complexes with hydrophobic organic cations (e. g. tetraalkylammonium) are soluble both in water and organic solvents as well. The neutral complexes usually have a low solubility. On dissolution, the vanadium (V) monoperoxido complexes often undergo solvolysis which can be confirmed by ^{51}V NMR spectra (see corresponding part), some complexes preserve their parent structure also in solution for a long time.

In the literature, only one description of synthesis of a peroxido complex carried out without using hydrogen peroxide can be found, namely that of $[VO(O_2)(pan)(py)]$. [21]

Molecular structures and supramolecular interactions in monoperoxidovanadium(V) complexes.

Tables 1 and 2 involve all 72 monoperoxidovanadium (V) complexes so far structurally characterized. Except the complexes 35 which is hexa-coordinated and 47 which is the only penta-coordinated peroxido complex of vanadium (V) having the same coordination number of the vanadium atom and the same coordination geometry (tetragonal pyramid) as found in the native form of VHPO, all other complexes given in Table 1 have mononuclear molecular structure, with hepta-coordinated vanadium atom and donor atoms occupying the positions of a distorted pentagonal bipyramid (Scheme 1). Three positions in the coordination polyhedron are occupied by *cis* arranged oxido and η^2-peroxido ligands forming the „central" $VO(O_2)^+$ moiety. The vanadium to oxido oxygen atom bond in one apical position (≈1.6 Å) was found to have a partially triple character, and even the bonds between the vanadium and peroxido oxygen atoms have a partially multiple character. [22] As a consequence, the vanadium atom is always displaced from the least square pentagonal plane (defined by the peroxido oxygen atoms and donor atoms in e_1, e_2 and e_3 position, Scheme 1) towards the triply bonded oxido ligand by approx. 0.20–0.25 Å. The interatomic distance between the vanadium atom and the donor atom (oxygen or nitrogen) in the apical position (a) *trans* to the oxido ligand indicates that these bond is always the weakest one. The $V(\eta^2\text{-}O_2)$ group is more or less asymmetric. The four remaining „free" positions of the pentagonal bipyramid (e_1 – e_3 and a in Scheme1) are occupied by: tetradentate, tridentate + monodentate, two bidentate or bidentate + two monodentate heteroligands providing a total N_xO_y donor set.



Scheme 1. Four "free" positions (e_1, e_2, e_3 and a) for coordination of the donor atoms to the $VO(O_2)^+$ moiety.

Based on analysis of the occupation of these four positions by nitrogen or oxygen donor atoms of two bidentate ligands (anionic or neutral) in structures of all such complexes, we have formulated the following empirical rules: [23,24] i), the more negatively charged bidentate ligand is coordinated in two equatorial positions (e_1, e_2) while the remaining ligand in one equatorial (e_3) and one apical position (a), and ii) the two nitrogen atoms of two NO donor set ligands coordinate in equatorial positions (e_1, e_3) *cis* to the peroxido oxygen atoms, while the two oxygen atoms in the equatorial position (e_2) *trans* to the peroxido ligand, and in the apical position (a) *trans* to the oxido ligand. It seems that these rules will be valid also for the complexes with bidentate NO donor ligand and monodentate N- and monodentate O-ligands, however, only one structure of such a complex is known so far: $[VO(O_2)(pic)(pcaa)(H_2O)] \cdot H_2O$. [22] Examples of molecular structures of monoperoxidovanadium(V) complexes are shown in Fig. 1 – 3.

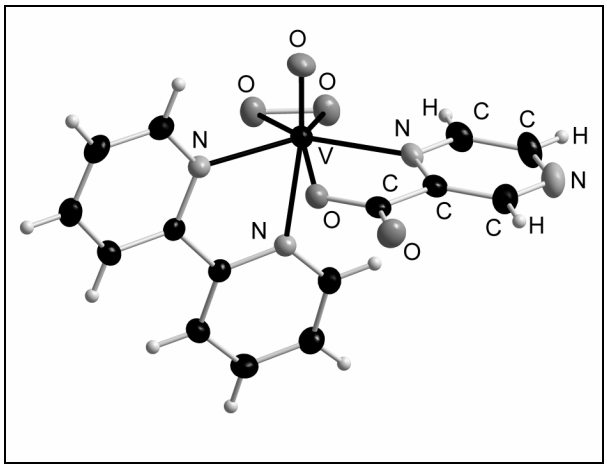


Figure 1. Mononuclear molecular structure of $[VO(O_2)(pic)(bpy)]$ (Table 1, compound No. 3).

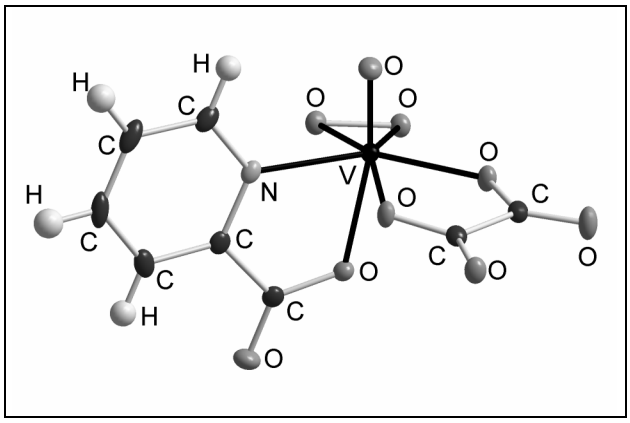


Figure 2. Mononuclear molecular structure of $[VO(O_2)(ox)(pic)]^{2-}$ (Table 1, compound No. 25).

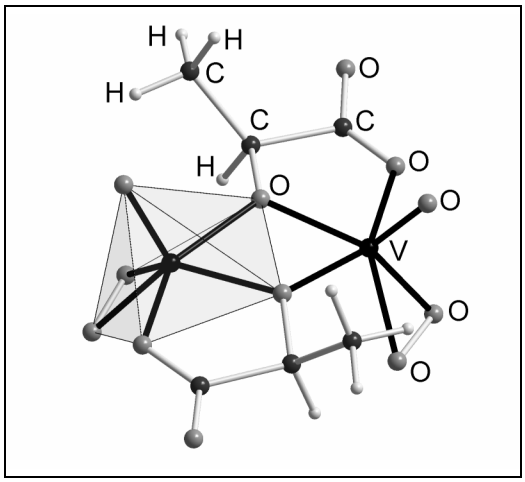


Figure 3. Dinuclear molecular structure of $[V_2O_2(O_2)_2(S\text{-lact})_2]^{2-}$ (Table 2, compound No. 9).

The vanadium atoms in the monoperoxido complexes are chirotopic. [25] Generally, these complexes with achiral or racemic heteroligands crystallize as: i) racemic compounds, which all have unit cells with center or plane of symmetry, ii) racemic conglomerates (e.g. $NH_4[VO(O_2)(ida)]$ with polymeric chain structure), [26] iii) *meso*-compounds (dinuclear complexes formed mainly with α-hydroxycarboxylates, e.g. $(Bu_4N)_2[V_2O_2(O_2)_2(glyc)_2] \cdot H_2O$ [70]) or iv) achiral compounds (e.g. nta-, ada- or dipic- complexes).

Table 1. Mononuclear oxido-monoperoxidovanadium(V) complexes with the $VO(O_2)^+$ moiety and organic heteroligand/s.[a]

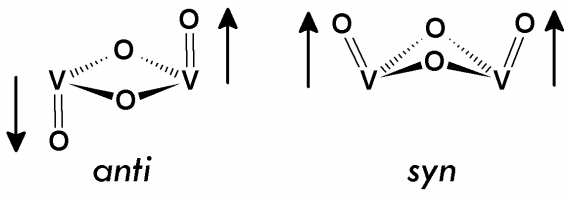
No.	Compound	Donor set/s[b]	Space group	Ref.
	Neutral complexes			
1	$[VO(O_2)(pic)(phen)] \cdot 0{,}5CH_2Cl_2$	NO, NN	$P2_1/a$	[17]
2	$[VO(O_2)(pic)(bpy)] \cdot H_2O$	NO, NN	$P2_1/a$	[27]
3	$[VO(O_2)(pca)(bpy)]$	NO, NN	$P2_1/c$	[22]
4	$[VO(O_2)(pca)(phen)]$	NO, NN	$Pca2_1$	[22]
5	$[VO(O_2)(pca)(pa)] \cdot H_2O$	NO, NO	$P\bar{1}$	[28]
6	$[VO(O_2)(pic)(H_2O)_2]$	NO, O, O	$P2_1/n$	[29]
7	$[VO(O_2)(pan)(py)]$	NNO, N	$P2_1/c$	[21]
8	$[VO(O_2)(pic)(pcaa)(H_2O)] \cdot H_2O$	NO, N, O	$P\bar{1}$	[22]
9	$[VO(O_2\text{-t-Bu})(dipic)(H_2O)]$	ONO, O	$P2_1/n$	[30]
10	$[VO(O_2)(Hsalhyhb)(H_2O)] \cdot H_2O$	ONO, O	$P2_1/n$	[31]
11	$[VO(O_2)\{HB(pz)_3\}(Hpz)]$	NNN, N	$P2_12_12_1$	[32]
12	$[VO(O_2)(tp^{pri2})(Hpz^{pri2})] \cdot Thf$	NNN, N	$P2_1/n$	[18]
13	$[VO(O_2)(bpg)] \cdot H_2O$	NNNO	Cc	[19]
14	$[VO(O_2)(Hbpa)]_2(ClO_4)_2 \cdot [VO(O_2)(bpa)] \cdot 2{,}25H_2O$	NNNO	$C2$	[33]
	Cationic complexes			
15	$[VO(O_2)(pa)_2]ClO_4 \cdot 3H_2O$	NO, NO	$Pna2_1$	[28]
16	$[VO(O_2)(bpy)_2]ClO_4$	NN, NN	$P\bar{1}$	[34]
17	$[VO(O_2)(phen)_2]ClO_4$	NN, NN	$P2_1/a$	[34]
18	$[VO(O_2)(phen)(H_2O)_2]Cl \cdot 0{,}38H_2O$	NN, O, O	$P\bar{1}$	[17]
19	$[\{VO(O_2)\}_2\{H(bpg)\}_2]ClO_4 \cdot CH_3CH_2CN$	NNNO	$C2/c$	[19]
20	$[VO(O_2)(L\text{-}N_4Me_2)][Ph_4B]$	NNNN	$Pna2_1$	[35]
21	$[VO(O_2)(Hbpa)]ClO_4 \cdot 2H_2O$	NNNO	$C2/c$	[36]
	Anionic complexes			
22	$Ph_4P[VO(O_2)(pic)_2] \cdot 2{,}5H_2O$	NO, NO	$P2_1/c$	[17]
23	$K[VO(O_2)(ox)(bpy)] \cdot 3H_2O$	OO, NN	$P2_1/c$	[23]
24	$Pr_4N[VO(O_2)(ox)(phen)]$	OO, NN	$C2/c$	[23]
25	$H_2en[VO(O_2)(ox)(pic)] \cdot 2H_2O$	OO, NO	$P2_1/c$	[24]
26	$H_2en[VO(O_2)(ox)(pca)]$	OO, NO	$P2_1/n$	[24]
27	$NH_4[VO(O_2)(3OH\text{-}pic)_2] \cdot H_2O$	NO, NO	$P\bar{1}$	[33]
28	$NH_4[VO(O_2)(pca)_2] \cdot 2H_2O$	NO, NO	$P2_1/c$	[37]
29	$K_3[VO(O_2)(2,5\text{-}pdc)] \cdot 4{,}5H_2O$	NO, NO	$P\bar{1}$	[38]
30	$K_3[VO(O_2)(ox)_2] \cdot 0{,}5\ H_2O$	OO, OO	$P2/c$	[39]
31	$H_3tren[VO(O_2)(ox)_2] \cdot 3H_2O$	OO, OO	$P\bar{1}$	[40]

No.	Compound	Donor set/s[b]	Space group	Ref.
32	$NH_4[VO(O_2)(bpy)F_2] \cdot 2H_2O$	NN, F, F	$P2_1/n$	[41]
33	$NH_4[VO(O_2)(dipic)(H_2O)]$	ONO, O	*Pcca*	[42]
34	$NH_4[VO(O_2)(dipic)(H_2O)] \cdot xH_2O$	ONO, O	C_2/c	[43]
35	$K[VO(O_2)(ada)] \cdot 4H_2O$	ONOO	$P2_1/c$	[44]
36	$K[VO(O_2)(rac\text{-cmhist})] \cdot H_2O$	ONON	*Pbca*	[45,46]
37	$Cs[VO(O_2)(ceida)] \cdot H_2O$	ONOO	$P2_1/n$	[47]
38	$K[VO(O_2)(ceida)] \cdot 2H_2O$	ONOO	$P2_1/n$	[48]
39	$K_2[VO(O_2)(heida)] \cdot 2H_2O$	NOOO	*Pbcn*	[33]
40	$K[VO(O_2)(Hheida)] \cdot H_2O$	ONOO	$P2_1/n$	[49]
41	$(NH_4)_2[VO(O_2)(Hedta)] \cdot 4H_2O$	ONON	*Fdd*2	[50,51]
42	$K_2[VO(O_2)(Hedta)] \cdot 4H_2O$	ONON	*Fdd*2	[50,51]
43	$Na_2[VO(O_2)(nta)] \cdot 5H_2O$	ONOO	$P2_1/c$	[52]
44	$K_2[VO(O_2)(nta)] \cdot 2H_2O$	ONOO	*Pnam*	[53,54]
46	$K_2[VO(O_2)(nta)]$	ONOO	$P2_1/n$	[55]
45	$Ba[VO(O_2)(nta)] \cdot 3H_2O$	ONOO	$Pna2_1$	[56]
47	$K[VO(O_2)(^{NH}{}_2pyg_2)] \cdot 2H_2O$	NONO	$C2/c$	[57]
48	$K[VO(O_2)(^{BrNH}{}_2pyg_2)] \cdot H_2O$	NONO	$P\text{–}1$	[57]
49	$K[VO(O_2)(omeida)] \cdot H_2O$	NNOO	$P2_1/c$	[58]
50	$Et_4N[VO(O_2)(glygly)] \cdot 1{,}58H_2O$	NNO	$P2_1$	[59]
51	$Ph_4P[(Ph_3SiO)_2VO_2]_x[(Ph_3SiO)_2VO(O_2)]_{1-x}$ (x = 0,57)	O, O	$P2_1/n$	[60]

[a] Abbreviations: see Charts 1 and 2.
[b] Donor set/s are composed of donor atoms coordinated to the vanadium atom in four „free“ positions of the pentagonal bipyramid as defined in Scheme 1, besides three positions occupied by the oxygen atoms of the $VO(O_2)^+$ moiety (in all complexes with exception of compound No. 51 in which the vanadium atom is penta-coordinated).

In the last period, we have focused our detailed studies also on synthesis and crystal structure of monoperoxidovanadium(V) complexes with a relatively great number of anions of biologically important α-hydroxycarboxylic acids as heteroligands. The complexes of this type are summarized in Table 2. The α-hydroxycarboxylato ligands all form dinuclear complexes, with oxido and η^2-peroxido ligands coordinated to each of the two vanadium atoms which are bridged by two oxygen atoms, $(\mu\text{-}O)_2$, originating from the two deprotonated α-hydroxy groups (Scheme 2).

The coordination number (c. n.) of the vanadium atoms can be seven (pentagonal bipyramid) or six (pentagonal pyramid). Dinuclear monoperoxidovanadium(V) complexes with coordinatively non-equivalent vanadium atoms (c. n. 7 and 6) have also been observed. In the $V_2O_4^{2+}$ core, the end-bonded oxido oxygen atoms and the two bridging hydroxy oxygen atoms can adopt two different geometries: i) the $V(\mu\text{-}O)_2V$ group is planar and the V=O groups are *anti*- oriented or ii) the four-atom $V(\mu\text{-}O)_2V$ group is non-planar and the V=O groups are *syn*- oriented (Scheme 2). The formation of some dinuclear α-hydroxycarboxylato monoperoxidovanadium(V) complexes was found to be stereospecific. [61]



Scheme 2. Two types of arrangement of the $V_2O_4^{2+}$ core in α-hydroxycarboxylato monoperoxidovanadium(V) complexes: with planar V_2O_2 group and *anti* oriented VO groups (left) and non-planar V_2O_2 group and *syn* oriented VO groups (right).

The arrangement of the $V_2O_4^{2+}$ core depends on whether the heteroligand is chiral or achiral: while the achiral acids form always complex ions having the i) arrangement, the chiral ones can form structures with both arrangements. When pure enantiomer was used in synthesis, only the arrangement ii) was observed in structures, but using a racemic acid, both arrangements: i) with coordinated *R* + *S* enantiomers and ii) with *R* + *R* and *S* + *S* enantiomers, were observed. The only exception is the complex $K_2[\{VO(O_2)(rac\text{-lact})\}_2]$. [62]

Table 2. Dinuclear oxido-monoperoxidovanadium(V) complexes with $V_2O_4^{2+}$ core and organic heteroligand/s.[a]

No.	Compound	Donor set/s[b]	Space group	Ref.
1	$K_2[\{VO(O_2)(H_2cit)\}_2] \cdot 2H_2O$	OO, OO	$P2_1/n$	[63,64]
2	$(NH_4)_2[V_2O_2(O_2)_2(H_2cit)_2] \cdot 2H_2O$	OO, OO	$P2_1/n$	[64]
3	$K_{10}[V_2O_2(O_2)_2(cit)_2][V_2O_2(O_2)_2(cit)_2] \cdot 20H_2O$	OO, OO	$P\text{–}1$	[65]
4	$(NH_4)_6[V_2O_2(O_2)_2(cit)_2] \cdot 4{,}5H_2O$	OO, OO	$C2/c$	[66]
5	$(Et_4N)_2[V_2O_2(O_2)_2(R\text{-mand})_2]$	OO, OO	$P2_12_12_1$	[20]
6	$(Me_4N)_4[V_2O_2(O_2)_2(R\text{-mand})_2][V_2O_2(O_2)_2(S\text{-mand})_2] \cdot 13H_2O$	OO, OO	$C2/c$	[20]
7	$(Me_4N)_2(NH_4)_2[V_2O_2(O_2)_2(R\text{-mand})_2(H_2O)][V_2O_2(O_2)_2(S\text{-mand})_2(H_2O)] \cdot 4H_2O$	OO, O	$P2_1/c$	[20]
8	$(Bu_4N)_4[V_2O_2(O_2)_2(S\text{-mand})_2][V_2O_2(O_2)_2(R\text{-mand})_2] \cdot (rac\text{-}H_2mand)$	OO, OO	$Pbcn$	[67]
9	$(Bu_4N)_2[V_2O_2(O_2)_2(S\text{-lact})_2] \cdot 2H_2O$	OO, OO	$P2_1$	[61]
10	$(Bu_4N)_2[V_2O_2(O_2)_2(R\text{-lact})(S\text{-lact})] \cdot 2H_2O$	OO, OO	$P2_1/n$	[61]
11	$K_2[\{VO(O_2)(rac\text{-lact})\}_2]$	OO, OO	$C2/c$	[62]
12	$(NH_4)_2[\{VO(O_2)(rac\text{-Hmal})\}_2] \cdot 2H_2O$	OO, OO	$P\text{–}1$	[68]
13	$K_2[V_2O_2(O_2)_2(R\text{-Hmal})(S\text{-Hmal})] \cdot 2H_2O$	OO, OO	$P2_1/c$	[69]
14	$K_4[V_2O_2(O_2)_2(R\text{-mal})(S\text{-mal})] \cdot 4H_2O$	OO, OO	$P2_1/c$	[69]
15	$(NH_4)_4[V_2O_2(O_2)_2(R\text{-mal})(S\text{-mal})] \cdot 3H_2O$	OO, OO	$P\text{–}1$	[69]
16	$(Bu_4N)_2[V_2O_2(O_2)_2(glyc)_2] \cdot H_2O$	OO, OO	$P2_1/n$	[70]
17	$Cs_3[V_2O_2(O_2)_2(dpot)] \cdot 3H_2O$	ONOO	$P2_1/n$	[71]
18	$K_2[\{VO(O_2)(R,R\text{-}H_2tart)\}_2(\mu\text{-}H_2O)] \cdot 5H_2O$	OO, O	$C222_1$	[72]
19	$(Pr_4N)_2[V_2O_2(O_2)_2(R\text{-}\alpha\text{-hhip})(S\text{-}\alpha\text{-hhip})] \cdot 5H_2O$	OO, OO	$P\text{–}1$	[73]
20	$(Bu_4N)_2[V_2O_2(O_2)_2(R\text{-}\alpha\text{-hhip})(S\text{-}\alpha\text{-hhip})] \cdot 5H_2O$	OO, OO	$P2_1/c$	[74]
21	$(Et_4N)(NH_4)_3[V_2O_2(O_2)_2(R\text{-3-phlact})_2][V_2O_2(O_2)_2(S\text{-3-phlact})_2] \cdot 6H_2O$	OO, OO	$Pbcn$	[75]

[a,b] the same as for Table 1.

In the last period, we have paid detailed attention also to the supramolecular structures of structurally characterized complexes. For the complexes summarized in Table 1 and 2, the authors mostly describe only the molecular structures, but they exceptionally too turned attention to the intermolecular interactions, for example to the hydrogen bond formation to the coordinated peroxido ligand which can be regarded as a step to the formation of hydrogenperoxido intermediate playing role in reactions of oxygen transfer to the substrate. [36,76]

Besides the networks of „classical" hydrogen bonds, we have shown that also the C–H···O interactions (the C–H donor groups being mostly from the aromatic rings) may essentially contribute to structure stabilization. [22,28,77] Another non-covalent interactions contributing to the construction of supramolecular architecture of monoperoxidovanadium(V) complexes are the planar or non-planar displaced π-π interactions. In some cases, when ionic attractive electrostatic interactions are missing, as well as the donor groups (N–H and/or O–H) for „classical" hydrogen bond formation, the C–H···O hydrogen bonds and the π-π interactions can be the only intermolecular contacts in crystal structure of complexes. So far, we have found exclusively these interactions in structures of two neutral complexes: $[VO(O_2)(pca)(bpy)]$ and $[VO(O_2)(pca)(phen)]$. [22] Also anion-π interactions take part in supramolecular structures of monoperoxido vanadium(V) complexes, e. g. in $H_2en[VO(O_2)(ox)(pca)]$. [24] (Fig. 4)

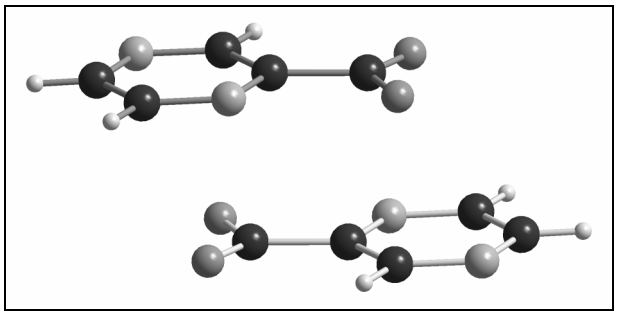


Figure 4. Anion-π interaction between pca-pca ligands in $H_2en[VO(O_2)(ox)(pca)]$ (Table 1, compound No. 26).

Vibrational Spectra

Vibrations of the $VO(O_2)^+$ moiety imprint characteristic features in IR and Raman spectra of monoperoxidovanadium complexes, which are distinctly different from vibrational spectra of diperoxidovanadates. The moiety of four atoms, $VO(O_2)^+$, exhibits four stretching vibrations, which can be coupled to some extend. In principle, these vibrations give rise to four bands, sometimes to three bands due to the accidentally overlapped bands corresponding to stretching vibrations of the $V–O_p$ bonds (O_p is the peroxido oxygen atom), and sometimes to more then four bands as a result of correlation splitting in the unit cell. The vibrational spectra of monoperoxidovanadium complexes with dinuclear structure, which is typical for complexes with α-hydroxycarboxylates, can also exhibit more than four stretching mode absorptions, especially in the case of asymmetric structure of the complexes. The bands corresponding to V=O, $O_p–O_p$ and $V–O_p$ stretches are usually strong (or at least medium) both in infrared and Raman spectra. DFT calculated vibrational wavenumbers (B3LYP, 6-311+G** basis set) confirmed the empirical assignment of the bands. [22] Typical infrared and Raman spectra of monoperoxidovanadium complexes are shown in Fig. 5.

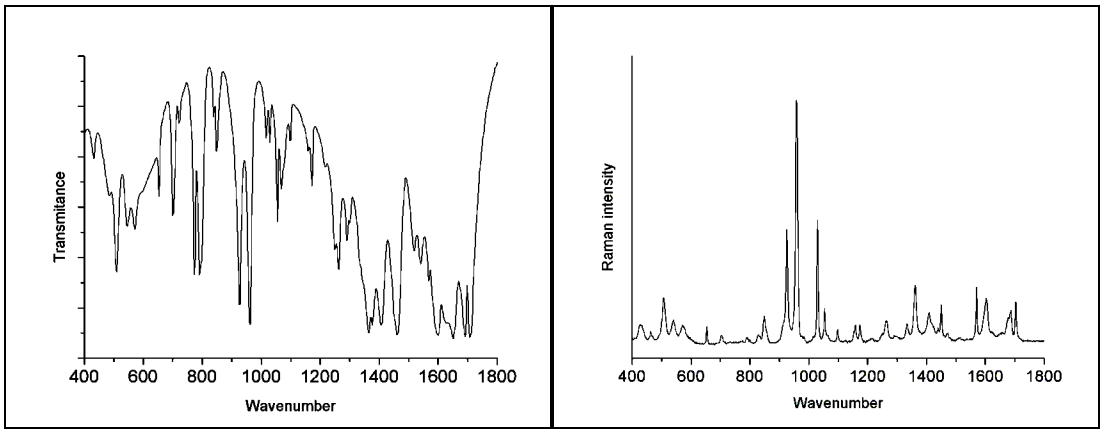


Figure 5. IR (left) and Raman spectrum (right) of H_2en[$VO(O_2)$(ox)(pic)] · $2H_2O$. Strong bands assigned to ν(V=O) and ν(O_p–O_p) can be seen between 900 and 1000 cm^{-1} (Table 1, compound No. 25).

The positions of bands assigned to stretching vibrations of the $VO(O_2)^+$ moiety are confined to quite narrow ranges: 986–943 cm^{-1} for ν(V=O); 947–920 cm^{-1} for ν(O_p–O_p) and 590–535 cm^{-1} for ν(V–O_p) vibrations (Table 3).

Although Raman spectroscopy is an efficient tool for study of aqueous solutions, Raman spectral studies of dissolved monoperoxidovanadium (V) complexes are very scarce. As an example we can mention the Raman spectra of $(NH_4)_2$[$VO(O_2)$(Hedta)] · $4H_2O$, which are analogous for solid complex and for its aqueous solution, thus indicating the similarity of the complex structure in the solid state and in solution (Table 3). [50]

Table 3. Selected bands in infrared (IR) and Raman (R) spectra (in cm^{-1}) of heteroligand[a] monoperoxido vanadium (V) complexes.

Compound	ν(V=O)		ν(O_p–O_p)		ν(V–O_p)		Ref.
	IR	R	IR	R	IR	R	
[$VO(O_2)$(pca)(bpy)]	952 vs		937 s		579 w 546 m		[22]
[$VO(O_2)$(pca)(phen)]	962 vs		933 s		582 w 549 m		[22]
[$VO(O_2)$(pca)(pa)] · H_2O	964[b]		942[b]		586[b]		[28]
[$VO(O_2)$(pic)$(H_2O)_2$]	975[b]		935b		580[b] 555[b]		[29]
[$VO(O_2)$(Hbpa)]$_2(ClO_4)_2$ · [$VO(O_2)$(bpa)] · $2{,}25H_2O$	952[b]		939[b]		561[b]		[33]
[$VO(O_2)(pa)_2$]ClO_4 · $3H_2O$	965[b]		947[b]		573[b]		[28]
Ph_4P[$VO(O_2)(pic)_2$] · $2{,}5H_2O$	965 vs		945 s		578 m 549 m		[17]
K[$VO(O_2)$(ox)(bpy)] · $3H_2O$	957 vs	957 vs	928 vs	927 s	573 m 544 m	573 m, 545 w	[23]
Pr_4N[$VO(O_2)$(ox)(phen)]	948 vs	952 vs	935 vs	935 m	567 m 543 m	556 m	[23]
H_2en[$VO(O_2)$(ox)(pic)] · $2H_2O$	962 vs	960 vs	927 s	926 s	571 m 545 m	572 m 544 m	[24]
H_2en[$VO(O_2)$(ox)(pca)]	956 vs	953 vs	927 vs	929 s	580 m 547 m	578 m 546 m	[24]
H_3tren[$VO(O_2)(ox)_2$] · $3H_2O$	943 vs		932 s		555 m 535 s		[40]
K[$VO(O_2)$(ada)] · $4H_2O$	955 vs		920 vs		568 s		[44]
Cs[$VO(O_2)$(ceida)] · H_2O	958 vs		916 vs		564 s		[47]

$K[VO(O_2)(ceida)] \cdot 2H_2O$	954 vs		927 vs		569 s		[48]
$K[VO(O_2)(Hheida)] \cdot H_2O$	961 s		920 s		570[b]		[49]
$(NH_4)_2[VO(O_2)(Hedta)] \cdot 4H_2O$	956 s	947 vs	935 vs	939 m	560 m	553 s	[50]
aqueous solution of $(NH_4)_2[VO(O_2)(Hedta)] \cdot 4H_2O$	–	957 vs		936 s		552 s	[50]
$Ba[VO(O_2)(nta)] \cdot 3H_2O$	950 vs		917 vs		560 s 535 s		[56]
$K[VO(O_2)(omeida)] \cdot H_2O$	947[b]		928[b]		562[b]		[58]
$(Et_4N)_2[V_2O_2(O_2)_2(R\text{-mand})_2]$	982 s		936 s 927 w		573 s		[20]
$(Me_4N)_4[V_2O_2(O_2)_2(R\text{-mand})_2][V_2O_2(O_2)_2(S\text{-mand})_2] \cdot 13H_2O$	982 vs		922 vs		539 m		[20]
$(Me_4N)_2(NH_4)_2[V_2O_2(O_2)_2(R\text{-mand})_2(H_2O)][V_2O_2(O_2)_2(S\text{-mand})_2(H_2O)] \cdot 4H_2O$	979 sh 969 s		938 s		561 m 540 m		[20]
$(Bu_4N)_2[V_2O_2(O_2)_2(glyc)_2] \cdot H_2O$	978 s		929 vs 922 s		584 m		[70]
$K_2[\{VO(O_2)(R,R\text{-}H_2tart)\}_2(\mu\text{-}H_2O)] \cdot 5H_2O$	986 vs	982 vs	935 vs	934 s	577 m, 552 m	561 s	[72]
$(Pr_4N)_2[V_2O_2(O_2)_2(R\text{-}\alpha\text{-hhip})(S\text{-}\alpha\text{-hhip})] \cdot 5H_2O$	969 vs	967 sh 961 vs	920 s	929 m 921 m	590 m 569 s	574 m 563 sh	[73]
$(Bu_4N)_2[V_2O_2(O_2)_2(R\text{-}\alpha\text{-hhip})(S\text{-}\alpha\text{-hhip})] \cdot 5H_2O$	972 vs		928 vs		590 m 562 m		[74]
$(Et_4N)(NH_4)_3[V_2O_2(O_2)_2(R\text{-3-phlact})_2][V_2O_2(O_2)_2(S\text{-3-phlact})_2] \cdot 6H_2O$	982 s		929 s		575 m		[75]

[a] – abbreviations: see Charts 1 and 2, [b] – intensity data are in literature missing.

^{51}V NMR spectra

^{51}V NMR spectroscopy represents a very effective and useful tool for studying the formation of peroxido complexes in solution and determining their composition and stability in solution. A number of detailed speciation studies was carried out for H^+–$H_2VO_4^-$–H_2O_2–heteroligand systems, [78,79,80,81,82,83] showing how complicated these solution usually are and identifying a great number of species in each system studied. ^{51}V NMR spectra provide also useful, even necessary, information whether the molecular structure of a solid peroxido complex is maintained in solution on dissolution: this is a basic condition for performing a correct kinetic or catalytic study in presence of a well defined peroxidovanadium complex. This method showed that some complexes don't decompose on dissolution in water even within many years when kept at room temperature (e.g. $[VO(O_2)(nta)]^{2-}$ complex [84]), but other complexes undergo an immediate decomposition (e.g. dinuclear monoperoxido α-hydroxycarboxylato complexes [70]). Compared with the numerous ^{51}V NMR data for the *in situ* formed heteroligand peroxidovanadate (V) species reviewed for example by Tracey et al., [85] the ^{51}V NMR data for the solutions of X-ray structurally characterized complexes are less extensive as can be seen also from their summarization in Table 4.

The vanadium (V) chemical shifts (δ_V) in the monoperoxido complexes can be observed in the interval –520 to –650 ppm (Table 4). The δ_V values change with the nature of the heteroligand/s coordinated to the monoperoxido group in either mono- or dinuclear monoperoxido complexes and, for the individual species, it is influenced by the solvent/co-solvent used, temperature, pH (for aqueous solutions), and slightly by the ionic strength.

Recently, a detailed report on ^{51}V NMR spectroscopy was published by Rehder et al., [86] in which the non-heteroligand peroxido species and some heteroligand peroxido complexes are too discussed.

UV-vis spectra

The solid monoperoxidocomplexes of vanadium (V) containing the $VO(O_2)^+$ moiety are red or orange-red compounds. Thus, the UV-vis spectra of their solutions exhibit in the visible region the characteristic band with maximum between 400 and 495 nm, and with molar absorption coefficient (ε) ranging from 212 to 420 mol^{-1} dm^3 cm^{-1} (Table 4). The position of this band within this range and the ε value depend mainly on heteroligand coordinated to the $VO(O_2)^+$ moiety. It is influenced also by the used solvent. An example of typical UV-vis spectrum of a monoperoxido vanadium(V) complex is shown in Fig. 6.

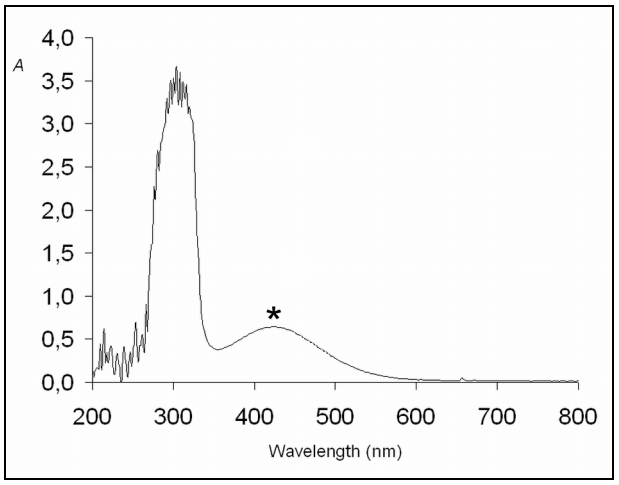


Figure 6. The UV-vis spectrum of aqueous solution of $K[VO(O_2)(ox)(bpy)] \cdot 3H_2O$ (Table 1, compound No. 23); conditions: 0.02 mol/dm^3, 25 °C, 1 mm cuvette.
* – characteristic band for monoperoxidovanadium(V) complexes.

This characteristic absorption band is traditionally assigned to be a LMCT band, corresponding to electron transfer from orbitals of the peroxido ligand to the orbitals of the vanadium atom. [29,68,71] Recently, the quantum chemical calculations (time-dependent DFT) for the $VO(O_2)^+$ moiety showed that this band does not correspond purely to LMCT transition but is combined with a ligand-to-ligand transition. [22] The excitation, which was found to occur from the HOMO orbital, is not effected by other ligands coordinated to the $VO(O_2)^+$ moiety. The excitation of one HOMO electron to the LUMO (in $VO(O_2)^+$) was found to be strictly forbidden, while transitions to the following two orbitals were allowed: the virtual, taking part in a four-centered bond, and the V^V–O^{-II} π^* orbital (orbitals No. 25 and 26 in ref. [22]).

It was shown for calculated UV-vis spectra of $[VO(O_2)(pca)(bpy)]$ and $[VO(O_2)(pca)(phen)]$ that the typical bands originate from the promotion of one HOMO electron to the first two π^* orbitals on both aromatic ligands. [22]

The only UV-vis spectrum, considerably differing from the spectra of other monoperoxido vanadium (V) complexes is that of grayish-violet complex:

$$Ph_4P[(Ph_3SiO)_2VO_2]_x[(Ph_3SiO)_2VO(O_2)]_{1-x}\ (x = 0{,}57)$$

which exhibits in the solid state a band at 558.9 nm (Table 4). [60]

A correct interpretation and utilization of the results of UV-vis spectroscopy in solution studies (mainly kinetic) is possible only in the case that we know the composition of solution and the species present in solution, i.e. such studies require necessarily a preceding ^{51}V NMR investigation.

Table 4. UV-vis (visible region) and ^{51}V NMR data for structurally characterized heteroligand* monoperoxidovanadium (V) complexes.

Compound	λ_{max} (nm) [ε (mol^{-1} dm^3 cm^{-1})]	δ_V (ppm)	Ref.
$[VO(O_2)(pca)(bpy)]$	474 [505][d,t]	–560[d,u]	[22]
$[VO(O_2)(pca)(phen)]$	477 [585][d,t]	–562[d,u]	[22]
$[VO(O_2)(pca)(pa)] \cdot H_2O$	452 [288][h]	–587 and –600[k,u]	[28]
$[VO(O_2)(pic)(H_2O)_2]$	450 – 465[c]		[29]
$[VO(O_2)(Hsalhyhb)(H_2O)] \cdot H_2O$		–551[f]	[31]
$[VO(O_2)\{HB(pz)_3\}(Hpz)]$	490[d]	–623[g]	[32]
$[VO(O_2)(tp^{pri2})(Hpz^{pri2})] \cdot Thf$	495 [280][e]	–552[m]	[18]
$[VO(O_2)(bpg)] \cdot H_2O$	422 [270] and 444 [360][k,l], 448 [350][c]	–543 to –545[c]	[46]
$[VO(O_2)(Hbpa)]_2(ClO_4)_2 \cdot [VO(O_2)(bpa)] \cdot 2{,}25H_2O$		–624[p], –610[r]	[33]
$[VO(O_2)(pa)_2]ClO_4 \cdot 3H_2O$	449 [212][l,t], pH ≈ 1	–603[u], pH 0 to 3.6	[28]
$K[VO(O_2)(ox)(bpy)] \cdot 3H_2O$	422 [320][a]	–615.5[a,u]	[23]
$Pr_4N[VO(O_2)(ox)(phen)]$	428 [294][a]	–612.9[a,u], –555.7[c,u]	[23]
$H_2en[VO(O_2)(ox)(pic)] \cdot 2H_2O$		–620.4[k,u]	[24]
$H_2en[VO(O_2)(ox)(pca)]$		–604.5[k,u]	[24]
$NH_4[VO(O_2)(pca)_2] \cdot 2H_2O$		–600[b]	[37]
$K[VO(O_2)(ada)] \cdot 4H_2O$	428 [430][a,o]		[44]
$K[VO(O_2)(rac\text{-cmhist})] \cdot H_2O$	420, pH 3 or [i]		[45,87]
$Cs[VO(O_2)(ceida)] \cdot H_2O$	438 [390][a]	–583.3[a]	[47]
$K[VO(O_2)(ceida)] \cdot 2H_2O$	438, pH 1.1 to 4.9	–580.5, pH 4.9	[28]
$K_2[VO(O_2)(heida)] \cdot 2H_2O$		–569	[33]
$K[VO(O_2)(Hheida)] \cdot H_2O$	430 [300][a] or org. solvents	–565[b]	[49]
$(NH_4)_2[VO(O_2)(Hedta)] \cdot 4H_2O$	425[a]		[50]
$K_2[VO(O_2)(nta)] \cdot 2H_2O$	425[a or i]		[87,54]
$Ba[VO(O_2)(nta)] \cdot 3H_2O$	434 [435][a]		[56]
$K[VO(O_2)(omeida)] \cdot H_2O$	439 [357][a]	–515[a,u]	[58]
$Et_4N[VO(O_2)(glygly)] \cdot 1{,}58H_2O$		–649 [a,v]	[59]
$Ph_4P[(Ph_3SiO)_2VO_2]_x[(Ph_3SiO)_2VO(O_2)]_{1-x}$ (x = 0,57)	558.9[s]	–595.3 and –596.8[c]	[60]
$K_2[\{VO(O_2)(H_2cit)\}_2] \cdot 2H_2O$	415[j], (450[k] below pH 2), 425[s]		[63]
$K_{10}[V_2O_2(O_2)_2(Hcit)_2][V_2O_2(O_2)_2(cit)_2] \cdot 20H_2O$	415 [798][a]		[65]
$(NH_4)_6[\{VO(O_2)(cit)\}_2] \cdot 4{,}5H_2O$	410 [327][a]		[66]
$(Et_4N)_2[V_2O_2(O_2)_2(R\text{-mand})_2]$	420[c], 400[a]		[20]
$(Me_4N)_4[V_2O_2(O_2)_2(R\text{-mand})_2][V_2O_2(O_2)_2(S\text{-mand})_2] \cdot 13H_2O$	420[c], 400[a]		[20]
$(Me_4N)_2(NH_4)_2[V_2O_2(O_2)_2(R\text{-mand})_2(H_2O)][V_2O_2(O_2)_2(S\text{-mand})_2(H_2O)] \cdot 4H_2O$	420[c], 400[a]		[20]
$(NH_4)_2[\{VO(O_2)(rac\text{-Hmal})\}_2] \cdot 2H_2O$	425 [300][a]		[68]
$K_2[V_2O_2(O_2)_2(R\text{-Hmal})(S\text{-Hmal})] \cdot 2H_2O$	422 [317], pH 4.5		[69]
$(Bu_4N)_2[V_2O_2(O_2)_2(glyc)_2] \cdot H_2O$	420[c], 412[d]	–512.2 and –515.5[c,t], –518.3[d,t]	[70]
$Cs_3[V_2O_2(O_2)_2(dpot)] \cdot 3H_2O$	430[n]	–539, –517, –495,[k]	[71]
$NH_4[VO(O_2)(ida)]$	420[a] (pH 2 to 8), 450 – 460 (below pH 1)		[26]

* – abbreviations: see Charts 1 and 2.
[a] – in H_2O; [b] – in D_2O; [c] – in CH_3CN or CD_3CN; [d] – in CH_2Cl_2 or CD_2Cl_2; [e] – in toluene; [f] – in CD_3OD; [g] – in $CDCl_3$; [h] – in water-dimethylformamide (9 : 1 by vol.), pH 1.5 (by 1.0 mol/dm^3 HCl), 20 °C; [i] – in aqueous solution: CH_3COONa-HCl, I = 1.0 mol/dm^3 (KCl), pH 3.08, 30 °C; [j] – in 0.1 mol/dm^3 KCl(aq); [k] – undergoes decomposition on dissolution; [l] – in an aqueous solution of $HClO_4$; [m] – in C_6D_6; [n] – in aqueous solution of $HClO_4$, I = 1.0 mol/dm^3 ($NaClO_4$), pH 4.51, 30 °C; [o] – data based on *in situ* measurement; [p] – in H_2O-D_2O; [r] – in D_2O-C_2H_5OH; [s] – in solid state; [t] – at room temperature; [u] – at 5 °C; [v] – at 3 °C.

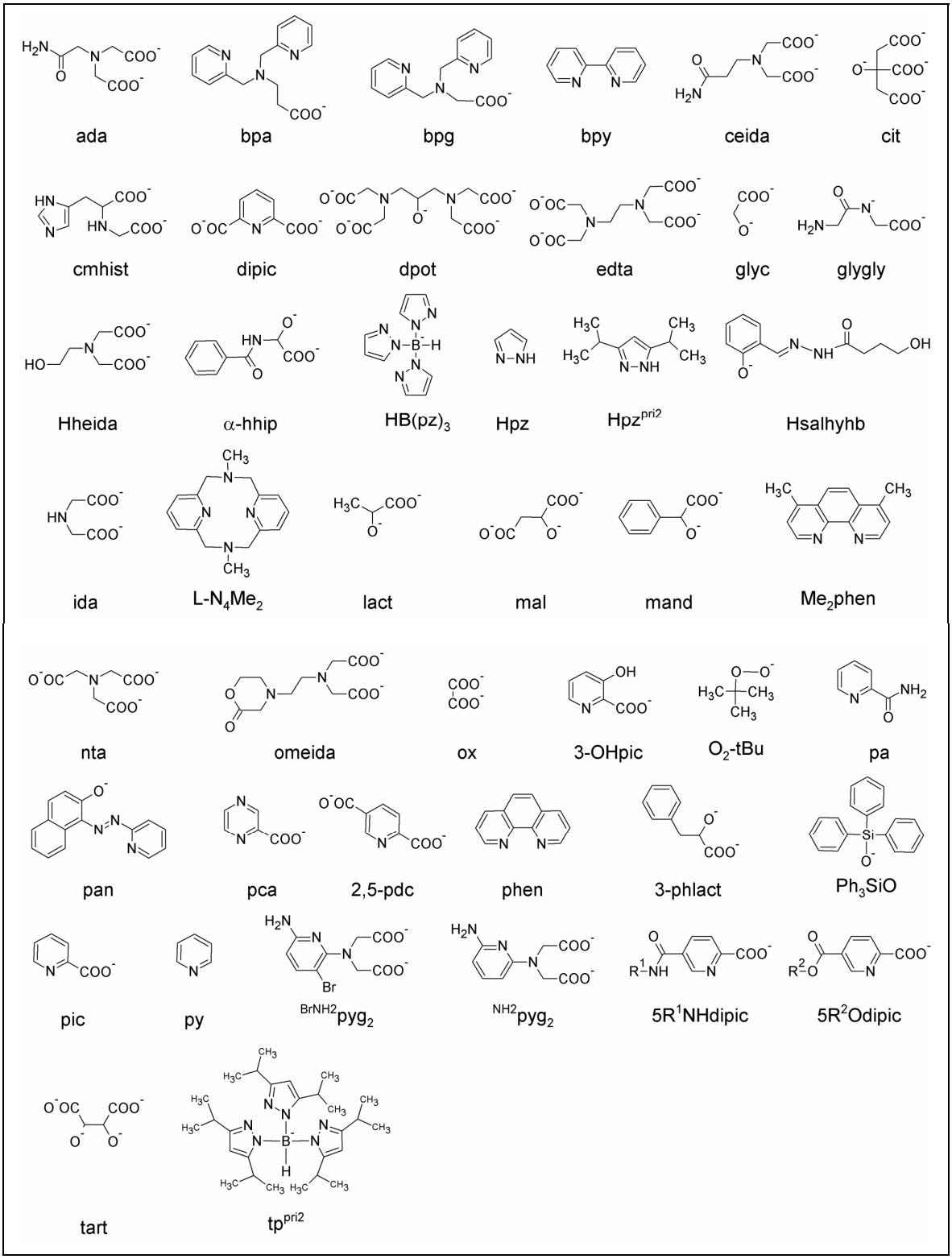

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Chart 1

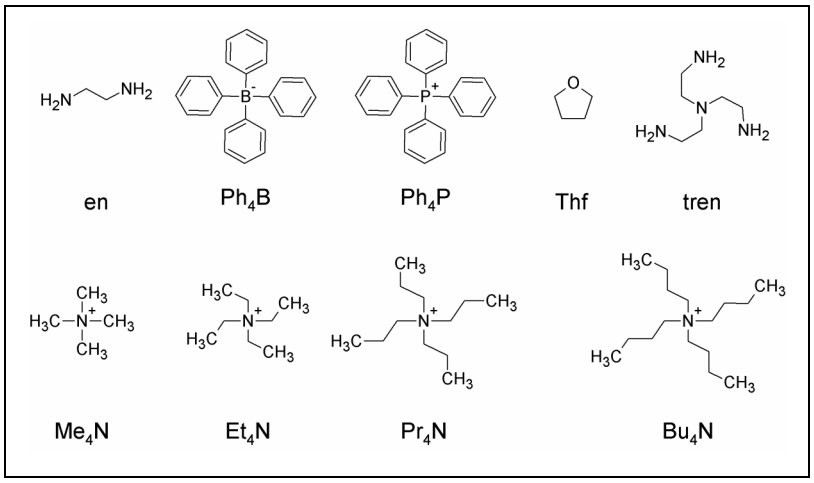

Chart 2

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