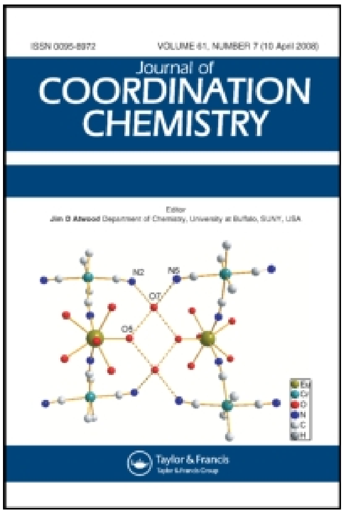

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REVIEW: SPECTROSCOPIC STUDIES OF OXOVANADIUM COORDINATION COMPOUNDS

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REVIEW: SPECTROSCOPIC STUDIES OF OXOVANADIUM COORDINATION COMPOUNDS

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In this review we present selected examples of our studies of oxovanadium(IV) and oxovanadium(V) complexes relevant for the bioinorganic chemistry of vanadium. Some of the investigated complexes are good models for different steps of vanadium metabolism or for a better understanding of the structural and electronic peculiarities of the coordination spheres of these oxocations in biomolecules. The investigated systems include ligands such as nucleotides, carbohydrates, phosphates, amino acids, *oxine* derivatives, porphine-like cores and other simple organic and inorganic ligands. All these complexes have been systematically investigated by means of vibrational (infrared and Raman) and electronic spectroscopy and, in some cases, also by thermal and electrochemical behavior. The potentialities and possibilities of the spectroscopic methodologies are illustrated and discussed and some general trends, useful for the structural characterization of these and similar systems, are emphasized.

Keywords: Review; VO^{2+}; VO_2^+; Coordination compounds; Model complexes; Vibrational spectra; Electronic spectra; Spectra-structure correlations

1. INTRODUCTION

Vanadium presents a wealthy and fascinating chemistry. Relevant as well as singular aspects of its behavior are the very rich structural chemistry of its oxoanions (vanadates), the high stability of the VO^{2+} cation, considered as the most stable diatomic ion known, and the well-developed coordination chemistry of its most usual oxidation states, which range from +2 to +5

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[1–4]. On the other hand, increasing interest has recently arisen around the biochemistry and the biological and pharmacological effects of this element [5–12].

During the last fifteen years we have undertaken systematic research on model systems related to different aspects of the bioinorganic chemistry of vanadium. We have, specifically, tried to attain a wider insight into some relevant aspects of its metabolism [13, 14] and detoxification [14, 15] in the higher forms of life.

The spectroscopic analysis of such models allow establishment of relationships between the structure and the spectral features of well-defined chemical systems and to transfer the results to the characterization of rather complicated natural systems.

On the other hand, it is often very difficult to attain single crystals adequate for diffractometric studies, even of very simple model compounds. Therefore, many of the model complexes investigated by us, as well as by many other specialists in this field of bioinorganic chemistry, could only be characterized by the combination of different spectroscopic techniques. An adequate selection of methodologies sometimes allowed clear insight into aspects such as the oxidation state of the metal center, the geometry of its coordination sphere and the type of ligand atoms involved in metal bonding. Usually, a single technique alone is not enough to obtain all this information and it is necessary to combine and analyze results from several techniques.

In our studies we generally employed vibrational (IR and Raman) spectroscopy as well as electronic spectroscopy (absorption and reflectance techniques). In this review, we present some selected examples of our studies regarding oxovanadium(IV) and oxovanadium(V) complexes to show the potential and possibilities of these methodologies and to illustrate the type of investigated model systems.

2. OXOVANADIUM(IV) COMPOUNDS

2.1. General Aspects

The coordination chemistry of vanadium(IV) is dominated by oxovanadium(IV) complexes containing the very stable VO^{2+} unit. These complexes usually approach one of the three idealized geometries depicted in Figure 1, with retention of the short V—O bond: square pyramidal (1a), square bipyramidal (1b) or trigonal bipyramidal (1c). This last configuration is usually found only in protein complexes.

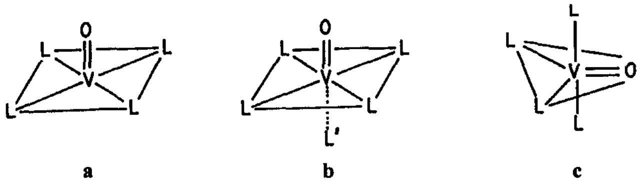

FIGURE 1 Most common coordination geometries of the oxovanadium(IV) cation.

Oxovanadium(IV) species exhibit characteristic electronic absorption spectra that are quite distinct from other vanadium(IV) complexes. The bonding with the oxo ligand has an important influence on the electronic properties of the ion and determines a peculiar sequence of energy levels [16, 17]. Although it has been suggested that one assignment scheme does not work for all the VO^{2+} compounds [17–19], it is generally admitted that under the highest possible symmetry around the metal center (C_{4v}) the ground state is b_2 that is, to a first approximation, nonbonding. And, as shown in Figure 2, three Laporte forbidden d–d transitions are expected: $b_2 \rightarrow e$, $b_2 + b_1$ and $b_2 \rightarrow a_1$. In the aquo complex, $[VO(H_2O)_5]^{2+}$, the first two transitions are found at 760 and 625 nm, respectively [16, 17]. The third

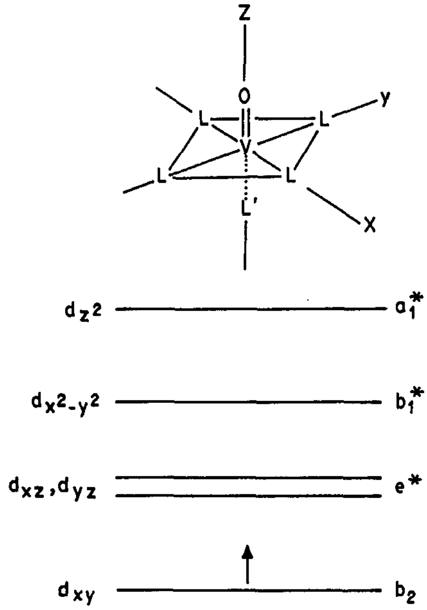

FIGURE 2 Energy level diagram for VO^{2+} complexes under C_{4V}-symmetry, showing the involved metal orbitals.

band is usually seen at higher energies (350–400 nm) and is often masked by charge transfer absorptions. The 10 Dq parameter can be directly determined from the position of the $b_2 \rightarrow b_1$ transition [16, 17].

The relative energies of the b_1 and e levels are mainly determined by a balance between the σ donor strengths of the equatorial ligands and the V—O π-bonding. If the ligand *trans* to the oxo group is removed, the symmetry remains C_{4v} and the effect is a decrease in the energy of the d_z^2 orbital such that the $b_2 \rightarrow a_1$ transition moves from the UV to the visible region. Thus, this behavior offers a valuable criterion to distinguish between five- and six-coordinated oxovanadium(IV) complexes. Besides, a symmetry diminution from C_{4v} to C_{2v} (which often occurs, *e.g.*, in chelate complexes) introduces new bands in the spectra as a consequence of the splitting of the e-level.

In the case of the vibrational spectra, the most characteristic mode is the V=O stretching vibration, which usually appears as a very strong and well defined IR band or Raman line, in the frequency range between 900 and 1030 cm^{-1} (*cf.* [20, 21]). Nevertheless, its position is affected by a number of factors, including electron donation from the ligands in the basal plane, solid state effects, or involvement of the O-atom in hydrogen bonding or in additional interactions with vicinal metal centers. The V-ligand vibrations are often difficult to identify due to their low intensity or to the presence of ligand bands in the same spectral region.

2.2. VO^{2+}/Nucleotide Systems

The interaction of VO^{2+} with phosphates and carbohydrates is of special interest in the context of vanadium biochemistry. Nucleotides offer the interesting possibility to investigate both types of interactions. Remember that nucleotides consist of three structural units: a purine or pyrimidine base, a ribose unit and a phosphate group. The bases are bound to the sugar moiety at C(1') generating the nucleosides; the mono-, di- and triphosphate groups are usually attached to the 5' position of the sugar and generate the monophosphate, diphosphate and triphosphate nucleosides, respectively.

The typical absorption spectrum of a $[VO(H_2O)_5]^{2+}$ solution in acid media is shown in Figure 3A. The interaction of the VO^{2+} cation with tri- and di-phosphate nucleosides generates similar patterns (Fig. 3B and 3C). The main absorption is displaced to lower energies (815–820 nm) and coordination involves only the phosphate groups. As discussed below, the monophosphate nucleosides behave in a different manner, although their bands remain in the same spectral region at low pH-values [22, 23].

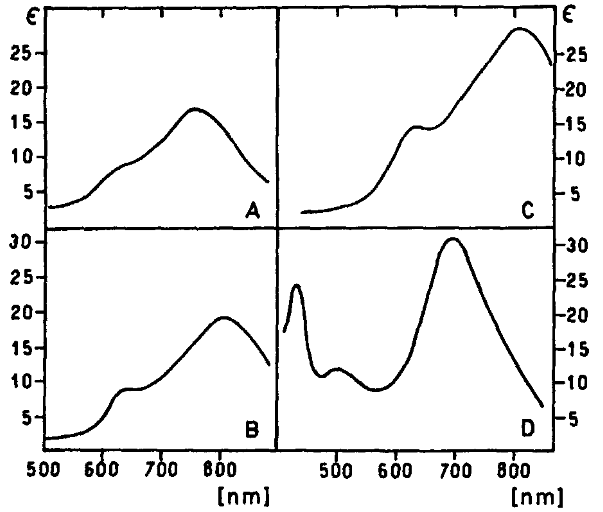

FIGURE 3 Electronic absorption spectra of aqueous solutions at pH = 4.9 of $[VO(H_2O)_5]^{2+}$ (A); VO^{2+}/ATP (B); VO^{2+}/UDP (C) and VO^{2+}/CMP (at pH = 11.5) (D) (Adapted from Ref. [22]).

In basic media, all species show the same spectral pattern (Fig. 3D). In these cases, interaction takes place through the deprotonated 2' and 3' OH groups of the ribose moieties, as shall be discussed later.

More detailed solution studies for the VO^{2+}/ATP system show the existence of different species in equilibriun [24–28]. For di- and triphosphate nucleosides with purine bases, $VO(nucl)_2$ complexes seem to be the predominant species in neutral solutions and at high ligand to metal ratios [26, 28]. At lower ratios, participation of base N atoms probably occurs. In the case of nucleotides containing pyrimidine bases, it has been shown that, at pH values between 3 and 5 and for metal to ligand ratios up to 0.5, the bases are involved in coordination [29].

The behavior of monophosphate nucleosides is more complex. An important ligand rearrangement around the metal center takes place as pH-is increased (Fig. 4). At pH > 5, phosphate groups, together with OH-groups of ribose, participate in coordination [23, 30, 31]. This suggestion is supported by the behavior of D-ribose-5-phosphate which shows a comparable electronic spectrum at this same pH-value [30].

2.3. VO^{2+}/Phosphate Systems

A great number of VO^{2+}/phosphate complexes of different stoichiometries and structures are well known. Some of them are very stable and have

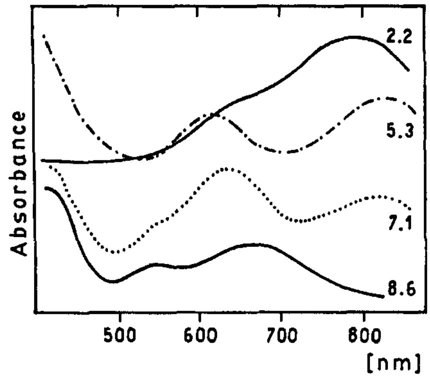

FIGURE 4 Electronic absorption spectra of the VO^{2+}/AMP system (1 : 10 ratio) at different pH-values (Adapted from Ref. [30]).

been well-characterized [23, 26, 32]. On the other hand, interaction of the VO^{2+} cation with biologically relevant phosphates has been often investigated in recent years. As typical examples the VO^{2+}/phytate [23, 33], VO^{2+}/thiamine-diphosphate [23, 34–36] VO^{2+}/glucose-1-phosphate [37] and VO^{2+}/NAD^+ or $NADP^+$ systems [36] can be mentioned. In all these cases, spectroscopic techniques were used to characterize the stoichiometries and/or the metal-to-ligand interactions.

It is also known that, at pH = 5, the VO^{2+}/diphosphate system generates a trinuclear complex with $P_2O_7^{4-}$ acting as a chelating and bridging ligand [32, 38]. A sodium salt of this species, of composition $Na_6[(VO)_3(P_2O_7)]_3 \cdot 7H_2O$ has been recently investigated [38]. The aqueous solution of this salt shows an electronic absorption spectrum with bands at 810 and 595 nm and a shoulder at about 370 nm. The electronic reflectance spectrum of the solid presents a similar spectral pattern (bands at 815, 605 and 375 nm) supporting the presence of the same species in both phases [38]. The typical ν(V=O) stretching vibration, seen as the most intense Raman line, was found at 968 cm^{-1}. On the other hand, the thermal behavior of this compound is especially interesting. After a two-step dehydration, it melts at 464°C and, apparently, depolymerization takes place during this last process, *i.e.*:

$$2Na_6[(VO)_3(P_2O_7)_3] \rightarrow 3Na_4P_2O_7 + 3(VO)_2P_2O_7$$

as supported by UV/vis, IR and ESR measurements [38].

The vibrational (IR and Raman) spectra of a series of highly condensed oxovanadium(IV) phosphates were also recently reported. The characteristic V=O stretching vibrations, together with those of the symmetric stretching vibration of the phosphate groups, are shown in Table I. In all these compounds, except $RbVOPO_4$, the vanadium forms $V^{IV}O_6$-chains presenting alternate short and long V—O bonds. Square pyramidal VO_5 units are present in the rubidium compound. The $\nu(V{=}O)$ values show good correlation with the respective bond lengths. Besides, strong Raman enhancement of the $\nu(V{=}O)$ vibration in comparison with that of the $\nu_s(PO_4)$ mode, was observed in all cases. This behavior is probably related to the highly condensed nature of the phosphate vibrators [39–42].

α-$(NH_4)_2(VO)_3(P_2O_7)_2$, another material with a highly condensed three-dimensional framework, contains three different $V^{IV}O_x$-polyhedra: VO_5 square-pyramids, isolated VO_6 units and VO_6 chains. These different building units present well-differentiated V—O stretching vibrations: 1004 cm^{-1} for the shortest V—O bond of the VO_5 groups, 978 cm^{-1} for the shortest V—O bond in the chains and 915 cm^{-1} for the bonds in the isolated VO_6 octahedra [43].

More complex systems are generated by interaction of oxovanadium(IV) with phosphate sugars, for example D-ribose-5-phosphate (Fig. 5). Two different complex types can be obtained, depending on the pH-value at which the synthesis is performed [44]. Compositions and spectroscopic characteristics are summarized in Table II. The blue species I and II show the typical band shift of the main VO^{2+} absorption, which is characteristic for phosphate coordination. The green complex III presents the three band

TABLE I Positions of the $\nu(V{=}O)$ and $\nu_s(PO_4)$ stretching vibrations in some condensed oxovanadium (IV) phosphates (from Raman data, values in cm^{-1})

Compound	*$\nu(V{=}O)$*	*$\nu_s(PO_4)$*	*Reference*
β-$LiVOPO_4$	884	936	[39]
$NaVOPO_4$	878	930	[39]
$KVOPO_4$	845	891	[40]
$RbVOPO_4$	1005	964	[41]
$Zn_2VO(PO_4)_2$	976	915	[42]

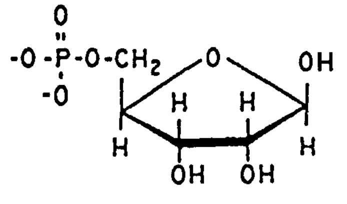

FIGURE 5 Structure of D-ribose-5-phosphate.

TABLE II Electronic (reflectance) spectra and ν(V=O) values of the different complexes of D-ribose-5-phosphate

Complex		*Reflct.bands (nm)*	$\nu(V{=}O)(cm^{-1})$
Na[VO(Rib-5P)(OH)(H_2O)$_2$]·2H_2O	(I)	840, 640	988
[VO(Rib-5P)(H_2O)$_3$]Cl	(II)	830, 630	992
Na_6[VO(Rib-5P)$_2$·6H_2O	(III)	750, 500, 425	933

pattern, which is characteristic of coordination through a pair of deprotonated OH groups of the ribose moiety (*cf.* also Fig. 3D). The lack of reflectance bands at wavelengths above 800 nm excludes phosphate coordination. It was also possible to prepare a solid complex of D-ribose, of composition $Na_3[VO(Rib)_2(OH)] \cdot 4H_2O$, which shows similar spectroscopic behavior to complex **III** [44]. Analysis of the phosphate IR bands is useful to attain an insight into the coordination behavior of this group. It acts as a monodentate ligand in complex **I**, bidentate in complex **II**, and its behavior in complex **III**, conclusively shows that it is not involved in bonding [44]. It is also interesting that, from these results as well as from those obtained with other phosphate complexes, it has been established that if the VO^{2+} group is coordinated by phosphates, the value of the typical ν(V=O) stretching motion is found at about 990 cm^{-1}. But, in the case of sugar moieties in the coordination sphere, this band is usually displaced to lower wavenumbers (920–940 cm^{-1} *cf.* also the next section).

2.4. VO^{2+}/Carbohydrate Complexes

It is well known that sugars interact with metal ions as reductants and/or chelators [13, 14, 45]. Most of them reduce vanadates(V) to oxovanadium(IV) and strongly complex this cation. Oxovanadium(IV) coordination is favored in basic media and only occurs with sugars with adjacent OH-groups [13, 14, 46].

Recently, we prepared and characterized a series of complexes with different carbohydrates. Their compositions and spectroscopic characteristics are shown in Table III. The electronic spectra show the typical three-band pattern of deprotonated OH-groups bonded to the VO^{2+} cation and ν(V=O) is always found in the range 921–941 cm^{-1}.

2.5. VO^{2+}/Carboxylate Complexes

The interaction of VO^{2+} with carboxylic and polycarboxylic acids is of special interest, due to the strong preference of this cation for oxygenated

TABLE III Spectroscopic characteristics of VO^{2+} complexes of carbohydrates

Complex	*Vis.spectr(nm)*	*$\nu(V{=}O)$ (cm^{-1})*	*References*
$Na_3[VO(Rib)_2(OH)\cdot 4H_2O$	740, 500, 425	932	[44]
$Na_4[VO(Glucur)_2]\cdot 8H_2O$	740, 500, 425	941	[47]
$Na_3[VO(Glc)_2(OH)\cdot 5H_2O$	687, 518, 420	925	[48]
$Na_3[VO(Suc)_2(OH)]\cdot H_2O$	785, 525, 420	931	[48]
$Na_3[VO(Tur)_2(OH)]\cdot 3H_2O$	678, 515, 420	924	[48]
$Na_6[(VO)_2(Fru)_5]\cdot 4H_2O$	672, 520, 420	925	[48]
$Na_4[VO(Man)_2]\cdot 8H_2O$	708, 504, 414	930	[49]
$Na_4[VO(Gal)_2]\cdot 5H_2O$	708, 504, 422	925	[49]
$Na_4[VO(Mal)_2]\cdot 10H_2O$	722, 506, 432	925	[49]
$Na_4[VO(D\text{-}Arab)_2]\cdot 5H_2O$	698, 504, 414	929	[49]
$Na_4[VO(L\text{-}Arab)_2]\cdot 5H_2O$	698, 504, 414	929	[49]
$Na_4[VO(Xyl)_2]\cdot 5H_2O$	692, 504, 422	929	[49]
$Na_5[VO(Lyx)_2(OH)]\cdot 6H_2O$	708, 504, 416	921	[49]

environments. Both, malonate and benzylmalonate, generate complexes with a fully oxygenated environment around the metal center.

We have investigated the spectroscopic and thermal behavior of a large series of salts of the complex anion bis(malonato)oxovanadium(IV), $[VO(C_3H_2O_4)_2]^{2-}$ [2–50]. The thermal behavior was investigated by means of TG and DTA techniques. Pyrolysis intermediates and residues were characterized by IR spectroscopy and overall stoichiometries for the degradation processes could be proposed. In most cases orthovanadate/VO_2 mixtures were obtained as final residues in N_2, whereas the corresponding divanadates were produced in air. The $\nu(V{=}O)$ vibration is found between 970 and 998 cm^{-1} in salts of this complex anion [50].

Despite the fact that many of these salts can be obtained only as microcrystalline powders, it was possible to achieve insight into the structural characteristics of this complex anion through a single crystal structural analysis of one of its salts, $(NH_4)_2[VO(C_3H_2O_4)_2]\cdot 2H_2O$. In this compound the VO^{2+} cation is five coordinate with two malonate anions acting as bidentate ligands in the equatorial plane and the oxygen-atom of one of the water molecules, *trans* to the oxo group [51].

The electronic absorption spectrum of this anion shows bands at 798 and 588 nm. A charge transfer masks the third band. In this case, by a combination of these measurements with a series of pre-resonance Raman experiments we could confidently assign the $V{-}O_{Ligand}$ stretching vibration. Using different lines from Ar and Kr lasers (between 457 and 647 nm), we have found that only the 464 cm^{-1} vibrational band shows pre-resonance for the excitation lines within the electronic band at 588 nm. As the involved electronic transition is associated with a M.O. which is mainly related to the

V—O(malonato) bonds (*cf.* Fig. 2), this vibrational mode can be unambiguously assigned to the V—O stretching. All the other vibrations show pre-resonance for the excitation lines towards the absorption band at 798 nm [52].

The synthesis and characterization of some salts of a similar anion, containing benzylmalonate instead of malonate, was recently performed and its electronic, IR, Raman and ESR spectra discussed in detail [53]. The structural characteristics of both anions seem to be similar and their thermal behavior is comparable, too.

Other interesting ligands containing carboxylate groups are the drugs *Suprofen* (α-methyl-4-(2-thienyl-carbonyl) phenylacetic acid) and *Ibuprofen* (2-(4-isobutylphenyl) propionic acid), shown in Figure 6, which present interesting antiinflammatory and analgesic activities. *Suprofen* generates stable complexes with different transition metal cations. The structural, spectroscopic, thermal, magnetic and electrochemical behavior of its Cu(II) complex have recently been reported [54]. Complexes of Fe(III), Co(II) and Ni(II) could also be prepared and characterized [55]. In the case of VO^{2+}, solution studies have shown the formation of a complex of the type [$VO(Sup)_2$] in which the ligand to metal interaction involves the carboxylate groups of two suprofenate moieties, acting as bidentate ligands [56]. The 2 : 1 ligand-to-metal ratio could be unambiguously established by a spectrophotometric titration. This example illustrates another valuable application derived from electronic spectroscopy, in which one monitors absorbance changes as a function of the metal-to-ligand ratio, at constant wavelength [57].

Ibuprofen interacts in the same way with the oxocation, generating a similar 2 : 1 carboxylate-bound complex [56].

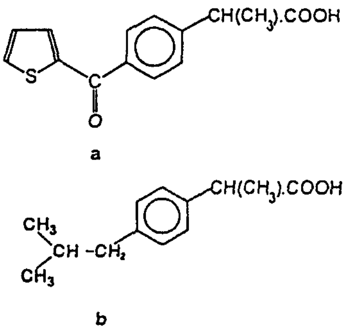

FIGURE 6 Schematic structures of Suprofen (a) and Ibuprofen (b).

2.6. VO^{2+}/Amino Acid and Peptide Complexes

In spite of the fact that the interaction of VO^{2+} with amino acids has been investigated in solution several times [4, 7, 14], the isolation of pure crystalline solid oxovanadium(IV) complexes with amino acids seems to be a difficult task. A L-histidine complex of composition $[VO(his)_4]SO_4 \cdot 2H_2O$, could only recently be obtained from aqueous solution at pH = 7.0. The violet microcrystalline powder was characterized by elemental analysis, diffuse reflectance and IR spectra, thermoanalytical data and magnetic measurements [58]. IR-data show conclusively that L-histidine interacts with the oxocation through the N-atom of imidazole and is present in its zwitterionic form, whereas the sulfate group acts as a non-coordinated counteranion. The diffuse reflectance spectrum has bands at 720 and 530 nm, whereas the characteristic $\nu(V{=}O)$ stretching band lies at $964\,cm^{-1}$, partially overlapped with the symmetric stretching vibration of the sulfate group [58].

During an investigation of the interaction of VO^{2+} with reduced glutathione we also performed some solution studies with its component amino acids glycine, glutamic acid and cysteine [59]. With glycine (gly), and working at high ligand-to-metal ratios, we confirmed, the generation of $VOgly^+$ (at pH = 3) and $VO(gly)_2$ (at pH = 7). A complex of the same stoichiometry, $VO(cys)_2$, was found for cysteine (cys) at pH = 7 in which the deprotonated SH-group of the amino acid is involved in coordination. At this same pH-value glutamic acid, interacts with the oxocation through carboxylate groups. A similar solution study with cystine [60] suggests that in this case interaction takes place through the carboxylate and amino groups of this ligand. Some solid oxovanadium(IV) complexes of cysteine esters could also be isolated and characterized [61].

The interaction of VO^{2+} with the dipeptide β-alanyl-L-histidine (carnosine, Fig. 7) constitutes another interesting and similar example. This system was investigated by electron absorption spectroscopy at high ligand-to-metal ratios and at different pH values [62]. It was shown that in the pH range between 6.0 and 8.5, the oxocation interacts with the imidazole groups

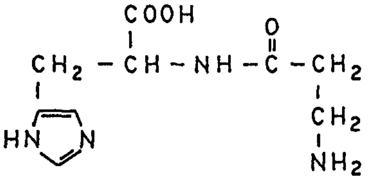

FIGURE 7 Schematic structure of β-alanyl-L-histidine (carnosine).

of four different carnosine molecules. Pure imidazole behaves in a similar manner [62]. Unfortunately, it was impossible to isolate a solid complex, neither with carnosine nor with imidazole, although some crystalline carnosine complexes with other divalent metal cations are known [63].

Relevant aspects of the interaction of VO^{2+} with glycylglycine and with the system glycylglycine/imidazole have also been investigated in solution [62]. With glygly alone, and at $pH = 5.0$, the interaction occurs similar to carnosine at this pH-value, *i.e.*, predominantly through the carboxylate group. The same behavior is also true for glygly/imidazole mixtures at this pH. With both systems at $pH = 7.0$, the involvement of N-donors in bonding becomes apparent from the spectroscopic data. In the case of glygly/imidazole mixtures it is probable, that at this last mentioned pH-value, coordination takes place only through one of the imidazole N-atoms.

2.7. VO^{2+}/Complexes of Porphine-like Ligands

It is well known that particularly large vanadium accumulations are frequently found in coal and petroleum deposits in which it principally appears as oxovanadium(IV) porphyrinic compounds [7]. In order to model these natural systems, we performed some studies with oxovanadium(IV) phthalocyanine (VOPc) and *meso*-tetrpahenylporphyrin (VOTPP).

The X-ray valence bond photoelectronic spectrum of solid VOPc, obtained with Al-Kα radiation [64], was similar in general features to that of other metal phthalocyanines [65]. The results of an extended Hückel-MO-SCCC calculation show that the lowest energy band is not only related to the metal $3d$ electrons, but also to the $2p$ electrons of the oxygen atom of the oxocation and the non-bonding electrons of the N atoms of the ligand. This result points out a strong and very efficient interaction between the cation and the macrocycle [64].

The thermal behavior of VOPc has recently been investigated by means of TG and DTA techniques. In an oxygen atmosphere the degradation occurs in one single step, between 320 and 355°C, generating V_2O_5 as the only pyrolysis residue. Decomposition in a nitrogen atmosphere extends over a wider temperature range and reveals a more complex mechanism and stoichiometry, with generation of VO_2, C and VN as final solid residues [66].

In the case of VOTPPP, the electronic absorption and the, X-ray photoelectronic spectra were recorded and interpreted [67]. The most prominent features of the electron spectrum could be assigned on the basis of the simple four-orbital model, by comparison with known data from previously investigated metalloporphyrins. The three typical transitions were found at

424 (Soret band), 548 (β-band) and 584 nm (α-band). Additional charge transfer bands of the ligand-to-metal type were found at 510 and 634 nm. The effects of different solvents on the electronic transitions were also investigated. The axial bonding of the solvent to the free position on the vanadium atom has an important effect on the spectroscopic behavior [67].

The vibrational behavior of VOTPPP was investigated by infrared and Raman spectroscopy, in the spectral range between 1600 and 200 cm^{-1}. Pre-resonance Raman experiments were performed, using different excitation lines from an argon-ion laser in the energy range between the main electronic transitions (the Soret band and the ($\alpha+\beta$) doublet). The V—N and V=O vibrations could be unambiguously assigned on the basis of these experimental results. On the other hand, analysis of the pre-resonance Raman profiles suggests strong vibronic mixing between the typical $\pi \rightarrow \pi^*$ porphyrinic electronic transitions and the existence of vibrational mixing between phenyl and skeletal porphyrinic modes in the ligand [68].

2.8. VO^{2+}/Complexes of *Oxine* and Derivatives

The ligand 8-hydroxyquinoline ("*oxine*", QH, Fig. 8a) appears particularly useful for model studies related to vanadium biochemistry, because it normally produces bis or tris chelated complexes of the types MQ_2 or MQ_3, generating MN_2O_2 or MN_3O_3 environments. Coordination spheres containing nitrogen and oxygen donors are found, *e.g.*, in the active site of vanadium dependent haloperoxidases [6, 10, 69] and in amavadin [10, 70], a vanadium(IV) complex isolated from the toadstool *Amanita muscaria*.

Although the simplest oxovanadium(IV) complex of *oxine*, VOQ_2 (Fig. 8b), has been widely investigated [71–75], contradictary reports are found in the literature. Most of them are derived from the easy oxidation of this complex generating vanadium(V) species. Our own studies with this complex have shown that it is only stable in the strict absence of air.

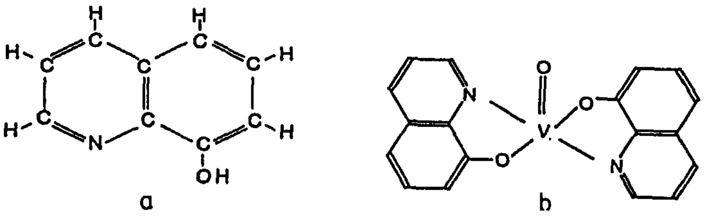

FIGURE 8 8-hydroxyquinoline (*oxine*) (a), coordination scheme of *oxine* to oxovanadium (IV) (b).

To extend these studies we have characterized a series of VO^{2+} complexes with different derivatives of *oxine* as ligands [14], including mono-and di-halogenated oxines [76, 77] N-oxide of *oxine* [78], and the 7-iodo-8-hydroxyquinoline-5-sulphonic acid (the analytic reagent *ferron*) [79]. The electronic spectra of these complexes are dominated by very strong intraligand transitions as well as by ligand-to-metal charge transfers, which obscure the typical "*d–d*" transitions of the oxocation.

Some characteristic infrared spectroscopic data for these complexes are presented in Table IV. The ν(V═O) stretching vibration is appreciably lower in the case of complexes of halogen substituted ligands, compared with those found in the other investigated species, suggesting formation of polymeric species, interacting through ··V═O···V═O·· bridges. This interaction was recently confirmed by of a detailed study of the magnetic behavior of one of these complexes, namely $VO(QCl_2)_2$, which was investigated in the temperature range between 1.9 and 300 K [80]. Below 40 K a ferromagnetic interaction between the VO^{2+} groups was observed, which was also confirmed by an investigation of the magnetization as a function of the magnetic field at 5 K. A similar ··V═O···V═O·· stacking has recently been reported for a series of VO^{2+} complexes with tetradentate Schiff bases derived from aromatic aldehydes and ketones and aliphatic diamines [81]. Also in these cases the ν(VO) stretching vibrations are found in the 860–870 cm^{-1} range.

On the other hand, and in order to obtain a wider insight into the spectroscopic properties of vanadium complexes of *oxine* and its derivatives, we have investigated the simplest species of this type containing V(III), the well known tris(8-hydroxyquinolinato)vanadium(III) [71]. A detailed analysis of its electronic, infrared and Raman spectra, complemented with pre-resonance Raman studies and MO calculations, allowed a straightforward interpretation of its electronic and vibrational behavior [82].

TABLE IV IR-data of some oxovanadium (IV) complexes with *oxine* and *oxine* derivatives as ligands (values in cm^{-1})

Complex	$\nu(V═O)$	$\nu(V—L)$	*Refer.*
$VO(Q)_2$	970	406, 352	[76]
$VO(QCl)_2$	892	406, 354	[76]
$VO(QClI)_2$	887	485, 359	[76]
$VO(QCl_2)_2$	881	496, 348	[76]
$VO(QBr_2)_2$	881	479, 348	[76]
$VO(QI_2)_2$	880	471, 342	[76]
$VO(NOQ)_2$	977	399, 362	[78]
$VO(ferron)_2$	984	480, 373	[79]

2.9. Other VO^{2+} Complexes of Simple Organic and Inorganic Ligands

As the information on cyano compounds of oxovanadium (IV) remains very scarce, we have performed some studies with complexes of this type. For example, the simple hexacyano complex $(VO)_2[Fe(CN)_6] \cdot 10H_2O$ can be prepared in a very pure form by dropwise addition of a solution of $Li_4[Fe(CN)_6]$ to a $VOSO_4$ solution in stoichiometric proportions. The complex precipitates immediately in the form of a voluminous green mass, which after desiccation in vacuum over H_2SO_4, corresponds to the formula given above [83]. This compound was characterized by IR and Mössbauer spectroscopy [83]. Its thermal behavior in a nitrogen atmosphere is particularly interesting as, together with the release of H_2O, HCN and C_2N_2, metallic iron and VO_2 are found as the final solid residues [84].

Another simple complex of this type is $VO[Fe(CN)_5NO] \cdot 2H_2O$ ('oxovanadium(IV) nitroprusside'), which can be obtained by double decomposition of $Ba[Fe(CN)_5NO]$ and $VOSO_4$ solutions. This light green and highly insoluble compound was characterized by electronic, infrared and Mössbauer spectroscopy [83]. Photoelectron spectroscopy suggested interaction of VO^{2+} with both the CN^- and NO^+ ligands of the complex anion [85].

Moreover, this complex presents very peculiar thermal behavior: gaseous H_2O, HCN and C_2N_2, are liberated during the thermolysis, whereas $FeVO_4$ remains as the unique final solid residue [83]. The formation of this material is especially remarkable, because its synthesis by conventional solid state reactions is not easy and requires long reaction times [86, 87].

Another VO^{2+} compound with interesting thermal behavior is the dimethylsulfoxide complex $[VO(DMSO)_3SO_4]$ which generates an intermediate, probably a polymeric species of composition $(VO(DMSO)SO_4]$, with an unexpected high thermal stability surpassing the boiling point of pure DMSO by more than 100°C. On the other hand, and even though the thermolysis was investigated in a N_2 atmosphere, V_2O_5 appears as the final solid residue [88].

A very interesting complex of saccharin (p-sulfobenzimide, Hsac) of composition $[VO(Sac)(Hsac)(H_2O)_2]$ was recently characterized. In this complex the $VO(OH)^+$ moiety appears coordinated to a neutral saccharin molecule through its carbonyl group and to a saccharinate anion through its deprotonated N-atom, constituting so far the only example of a bis(saccharin) complex in which the two ligands are bonded in two different ways to the metal center [89]. IR spectroscopy was very useful to establish these bonding peculiarities.

The IR spectrum of $VO(OH)_2$, which is a very useful starting material for the preparation of simple VO^{2+} salts and complexes, together with that of its deuterated form, $VO(OD)_2$, has also been reported. The structure of this material is based on single octahedral VO_6 chains, joined into sheets parallel to (100) by sharing vertices. The characteristic $\nu(V{=}O)$ stretching vibration as found to lie at $968\,cm^{-1}$, suggesting that the interlayer $\cdots V{=}O\cdots V{=}O\cdots$ interactions are not very strong [90].

3. OXOVANADIUM(V) COMPOUNDS

3.1. General Aspects

Together with VO^{2+}, vanadium(V) is the other important oxidation state involved in biological systems. It is the usual state in an inorganic environment and is easily reduced after incorporation in a living system. It can also be present in the form of vanadate as a part of large biomolecules [7] and can induce important biological responses, including enzymatic inhibition or stimulation. Vanadium(V) also has a versatile coordination geometry, presenting coordination numbers between four and seven. Because of its d^0 electron configuration, the +5 oxidation state is diamagnetic and lacks "*d–d*" transitions.

IR and Raman spectroscopies are useful for the characterization of V^V—O— bonds. Monooxovanadium(V) complexes show a small but definite shift to higher wavenumbers in comparison with their VO^{2+} analogues, as expected from the increase in oxidation state [91]. Differences were also found for six and five coordinate, complexes containing *cis*-dioxo V^V-moieties [92]. For VO_4^{3-} compounds, stretching vibrations usually lie at $850-780\,cm^{-1}$, whereas the corresponding bending vibrations are found around $400-350\,cm^{-1}$, [93–95]. The reinforcement of the vanadium-oxygen bonds in condensed vanadates containing terminal VO_3 or VO_2-units, as in divanadates and metavanadates, is also clearly reflected by an increment in the V—O stretching frequencies [96–98]. The vibrational spectroscopic behavior of V—O—V bridges has also been investigated in detail [96, 98, 99].

Due to the absence of *d*-electrons, vanadium (V) species show no electronic transition in the visible region of the spectrum. The yellow color observed in some vanadium(V) solutions arises from an intense absorption tailing in from the UV region. These absorptions originate in O → V charge transfer transitions which generate high intensity bands with ε-values of the order of $10^3-10^4\ L\cdot Mol^{-1}\cdot cm^{-1}$ [100, 101].

In our studies of vanadium model systems, and in order to complement the information obtained with oxovanadium(IV) species, we have also investigated some vanadium(V) complexes containing the VO_2^+ moiety.

3.2. Oxovanadium(V) Complexes of Oxine and Derivatives

The coordination chemistry of oxovanadium(V) complexes of these ligands is particularly interesting due to the fact that hydroxobis(8-hydroxyquinolinato)oxo-vanadium(V), QVO(OH) (Fig. 9a) can be considered as an "inorganic analogue" of a carboxylic acid [14, 102]. In agreement with this view, it is possible to prepare salts (Fig. 9b), esters (Fig. 9c) and dimer anhydrides (Fig. 9d). Examples of all these species have been prepared and investigated in our laboratory.

The spectroscopic behavior of the sodium salt of composition $Na[VO_2Q_2]$ has been investigated in detail [103]. Its IR and Raman spectra were assigned by comparison with those of related species. The excitation profiles of the Raman modes that show pre-resonance on excitation, using different laser lines within the electronic bands, were reported and different profile types could be found.

The analysis of these profiles gave additional support of some of the assignments. The two terminal, free V—O, bonds have a *cis* configuration and both bonds have similar lengths [102]. The frequencies related to these bonds were at 885 and 915 cm^{-1} in the Raman spectrum (888 and 913 cm^{-1} in the IR). Considering the V-ligand vibrational modes, the V—O modes appear at higher frequencies than the V—N modes. IR bands at 320 and 346 cm^{-1} were assigned to the latter vibrations. Only one Raman band, at 353 cm^{-1}, was identified in this range. The corresponding V—O vibrations were found at 523 and 400 cm^{-1} in the Raman spectrum. On the basis of its pre-resonance behavior the former could be confidently assigned to the

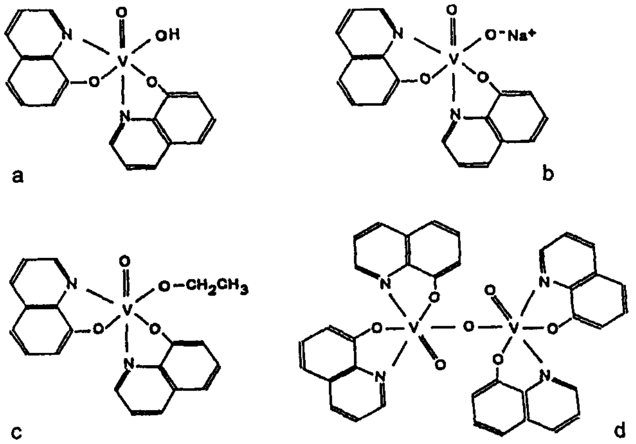

FIGURE 9 Different oxovanadium(V)/*oxine* compounds.

symmetric stretching mode. Finally, the weak intensity Raman line located at 1278 cm^{-1} could be assigned to a VO_2 in-plane bending mode of this V—O—linkage.

On the other hand, the electronic spectrum of the $[VO_2Q_2]^-$ anion could be interpreted with the aid of a semi-empirical MO calculation [103]. An aqueous solution of the sodium salt shows three bands at 364 ($\varepsilon = 5.1 \times 10\,L \cdot M^{-1} \cdot cm^{-1}$), 242 ($\varepsilon = 3.6 \times 10\,L \cdot M^{-1} \cdot cm^{-1}$) and 200 nm ($\varepsilon = 4.8 \times 10\,L \cdot M^{-1} \cdot cm^{-1}$).The highest energy band is assigned to a complex O → V charge transfer process which involves the oxygen atoms of the ligands and the free O-atoms. These transitions can be correlated with the 222 nm band of the VO_4^{3-} anion [101]. The 242 nm band is assigned an intraligand transition, which in the free ligand is found at 248 nm. The two involved MOs are localized on carbon atoms of the ligand. The third band, found at 364 nm, is essentially related to a N → V charge transfer transition involving the N-atom of the coordinated *oxine*.

For the similar potassium salt of the anion derived from *ferron*, $K[VO_2(\text{ferron})_2] \cdot 4H_2O$, the corresponding electronic transitions were found at 206, 262 and 372 nm [79]. The vibrational behavior of this anion also presents some interesting aspects. In this case, and as demonstrated by pre-resonance Raman measurements, the symmetric stretching vibration of the VO_2 moiety is located at lower frequencies than the corresponding antisymmetric mode [79], *i.e.*, they are inverted in comparison with the relative positions in the formerly discussed *oxine* complex [103]. These differences can surely be related to somewhat different VO_2 angles, because the relative energies of these stretching modes are strongly dependent on this magnitude, as shown by the spectroscopic behavior of related systems [98, 99]. On the other hand, the V-ligand vibrations are found at slightly higher energies than in the *oxine* complex (ν(V—O) at 547 and 463 cm^{-1} and ν(V—N) at 369 cm^{-1}) [79].

A number of "acids" (Fig. 9a) have also been investigated. Characteristic vibrations of the metal-to-ligand linkages are presented in Table V. In the case of the N-oxide of *oxine*, the V—O vibrations related to the oxygen atom bonded to the N atom are found at 509 and 345 cm^{-1} [78]. The electronic spectra of these compounds also show a series of characteristic ligand to metal charge transfer bands. Interactions of the complexes with the solvents also become evident [76, 79].

The oxovanadium(IV) complex and the "acid" derived from 5-chloro-8-hydroxyquinoline show a particularly complex solution behavior that includes redox phenomena, ligand loss and different types of interactions with the solvent [76].

TABLE V Characteristic IR bands of some vanadium(V) "acids" with *oxine* derivatives as ligands (values in cm^{-1})

	$VO(QCl)_2OH$	$VO(ferron)_2OH$	$VO(NOQ)_2OH$
ν(V=O)	956	965	986
ν(V—OH)	715	?	708
δ(V—OH)	?	919	968
$\delta(VO_2)$	345/307	?	278 (?)
ν(V—O)	544, 458	544, 471	568, 350
ν(V—N)	373, 351	384, 373	–
Refer.	[76]	[79]	[78]

Typical examples of ester-like derivatives (Fig. 9c), are the isopropyl ester from $VOQ_2(OH)$ [104] and the recently prepared ethyl ester of the acid generated with 5,7-dichloro-8-hydroxyquinoline. The structure of this last compound could be solved by single crystal X-ray diffraction [105]; its structural characteristics are similar to those of the isopropyl ester. In the vibrational spectrum of the ethyl ester the ν(V=O) band is seen at $963\,\mathrm{cm}^{-1}$ whereas that related to the V—O bond involved in the ester linkage lies at $744\,\mathrm{cm}^{-1}$. Bands related to the V-oxine bonds are found at $513/480\,\mathrm{cm}^{-1}$ (V—O bonds) and $375\,\mathrm{cm}^{-1}$ (V—N bonds) [105].

Some of these ester-like compounds present very interesting electrochemical behavior [106]. Different species are generated in organic solvents during cyclic voltamperometric experiments. On the other hand, the presence of water in the solvents modifies the electrochemical behavior as a consequence of the formation of a mixed valence dimer of the type $[Q_2VO—O—OVQ_2]^-$ containing vanadium(IV) and vanadium(V). Such a mixed valence dimer can also be prepared by mixing an acetonitrile solution of the $[VO_2Q_2]^-$ anion with Q_2VO [107]. Interestingly, this complex shows no electronic interaction between the d^0 and d^1 metal centers. On the contrary, in the case of similar complexes stabilized with nitrilotriacetate [108] or pyridyl-methyl-iminodiacetate [109] strong delocalization of the unpaired electron has been observed.

In relation to the dimeric anhydrides of vanadium(V) (Fig. 9d), it is interesting to remember that the simple "acid" derived from *oxine*, VOQ_2OH, is highly unstable in air and generates the corresponding anhydride $[VOQ_2—O—VOQ_2]$. [102, 110, 111]. The two nitrogen atoms are coordinated *trans* to the terminal and bridging oxygen atoms, and these two oxygen atoms are *cis*. Interestingly, this dimer can be clearly differentiated from the mixed-valence dimer by its electronic absorption spectra [112].

It is very difficult to differentiate between the "acid" and the "anhydride" by the usual spectroscopic methods. However, we recently showed that they can be clearly differentiated by their corresponding reduction peaks obtained from cyclic voltammograms scanned in acetonitrile solutions [113].

4. CONCLUSIONS

Our studies of oxovanadium(IV) and oxovanadium(V) coordination compounds with a great number of ligands with a variety of bonding possibilities clearly demonstrate the usefulness of vibrational (IR and Raman) spectroscopy in the characterization of metal-ligand linkages and as a simple tool for the attainment of structural information. In most cases, the position of the characteristic $\nu(V{=}O)$ stretching vibration is strongly dependent on the environment present in VO^{2+}-complexes. In other cases, these techniques allow insight into the type and form of metal-to-ligand interactions.

Resonance Raman measurements are especially useful for the study of this type of compounds and, together with data obtained from electronic spectra, are an important assignment tool for both electronic and vibrational transitions.

Analysis of electronic spectra provides useful information about oxidation state, coordination geometry and metal-to-ligand interactions. Nevertheless, these spectra are often complicated by the presence of strong intraligand transitions. Their analysis can be facilitated using simple theoretical approaches.

Finally, it should be emphasized that electrochemical techniques, such as cyclic voltamperometry, which so far have not been widely used for the investigation of these types of complex compounds, are a very useful and potent tool for characterization, and can be used as a kind of "electrochemical spectroscopy". On the other hand, it also provides useful information about complex equilibria between vanadium(IV) and vanadium(V) species in solution.

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ABBREVIATIONS

AMP	adenosine monophosphate
ATP	adenosine triphosphate
CTP	citidine monophosphate
D-Arab	D-arabinose
DMSO	dimethylsulfoxide
DTA	differential thermal analysis
ESR	electron spin resonance
ferron	7-iodo-8-hydroxyquinoline-5-sulfonic acid
Fru	D-fructose
Gal	D-galactose
Glc	D-glucose
Glucur	glucuronic acid
IR	Infrared
L-Arab	L-arabinose
Lyx	D-lyxose
Mal	maltose
Man	D-mannose
NAD^+	β-nicotinamide adenine dinucleotide
$NADP^+$	β-nicotinamide adenine dinucleotide phosphate
NOQ	8-hydroxyquinoline-N-oxide
nucl	nucleotide
Pc	phthalocyanine
Q	8-hydroxyquinolinate (*oxinate*)
QH	8-hydroxyquinoline (*oxine*)
QBr_2	5,7-dibromo-8-hydroxyquinolinate
QCl	5-chloro-8-hydroxyquinolinate
QCl_2	5,7-dichloro-8-hydroxyquinolinate
QClI	5-chloro-7-iodo-8-hydroxyquinolinate
QI_2	5,7-diiodo-8-hydroxyquinolinate
Rib	D-ribose
Rib-5P	D-ribose-5-phosphate
Suc	sucrose
TG	thermogravimetry
TPP	tetraphenylporphyrin

Tur	D-turanose
UDP	uridine diphosphate
UV/vis	ultraviolet/visible
Xyl	D-xylose

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