Inorg. Chem. **2003**, *42*, 3981–3987

Inorganic Chemistry
Article

Electronic Structure of Oxovanadium(IV) Complexes of α-Hydroxycarboxylic Acids

Eugenio Garribba,* Giovanni Micera,* and Angelo Panzanelli

Dipartimento di Chimica, Università degli Studi di Sassari, Via Vienna 2, 07100 Sassari, Italy

Daniele Sanna

Istituto CNR di Chimica Biomolecolare, Traversa La Crucca 3, 07040 Li Punti, Sassari, Italy

Received September 24, 2002

A series of $V^{IV}O$ bis chelated complexes of α-hydroxycarboxylic acids with a 2(COO^-, O^-) coordination set was analyzed by electronic absorption and EPR spectroscopy in aqueous solution. All the complexes exhibit a square-pyramidal geometry distorted toward trigonal bipyramid. The influence of the distortion of the geometry, as deduced from the steric hindrance produced by the substituents at the α-carbon atom of the ligands, on the spectroscopic parameters has been studied. The observed trends were related to the electronic structure of the metal ion in the distorted geometry.

Introduction

The common geometries of vanadium in $V^{IV}O$ complexes are the square pyramid, the distorted octahedron, and the trigonal bipyramid. In square-pyramidal compounds the V═O bond length is ca. 1.6 Å, the equatorial bonds are in the range 1.9−2.0 Å, and the angle formed by the V═O bond with the equatorial donors is ca. 100−110°. The geometry becomes octahedral if a sixth ligand coordinates in the trans position to the oxo ligand. For instance, in the bis complex of malonic acid, *trans*-[VO(malonato)$_2$(H$_2$O)],[1] a water molecule occupies the apical position at 2.3 Å from the vanadium atom. In solution, there is no unambiguous proof that can establish whether a trans complex is five- or six-coordinated; e.g., the position opposite to the oxo group is empty or filled by a solvent molecule. Since the interaction of this solvent molecule is generally weak, very similar properties are expected for the two different species.

Among five-coordinated $V^{IV}O$ complexes, those with square-pyramidal geometry are the most common. Only a few examples of a geometry close to the trigonal bipyramid were described, which suggests that electronic and/or steric requirements preclude the achievement of this stereochemistry. One of these is the bis chelated complex of benzilic acid.[2] An electronic absorption spectrum consisting of four transitions at 417, 540, 599, and 847 nm was considered distinctive of the distorted geometry.

Also monomeric bis chelated complexes formed by tartrates can exhibit electronic absorption spectra characterized by four absorptions. Particularly, three absorption bands were reported for DL-tartrate (421, 536, and 737 nm) and four absorptions for D-tartrate (399, 533, 590, and 902 nm).[3] According to the authors, these findings substantiate that the bidentate ligands with (COO^-, O^-) donor set are arranged trans in the D (or L) isomer and cis in the DL isomer. Analogously, the trans $V^{IV}O$ complexes with α-hydroxycarboxylic ligands, e.g. lactic acid, exhibit four absorption bands.[4]

In this work we examined a series of $V^{IV}O$ species formed by α-hydroxycarboxylic acids: glycolic acid and its derivatives (DL-lactic, 2-hydroxyisobutyric, 2-methyl-DL-2-hydroxybutyric, 2-ethyl-2-hydroxybutyric, DL-mandelic, and benzilic acids), D-quinic acid, and DL-isoserine (Chart 1). We compared the electronic absorption and the anisotropic EPR spectra of the bis chelated complexes of these ligands. This approach allowed us to correlate the absorption and EPR spectral properties of the complexes and to evaluate the effect

---

* To whom correspondence should be addressed. E-mail: micera@uniss.it (G.M.). Tel: +39-079-229541. Fax: +39-079-229559.

(1) Pajunen, A.; Pajunen, S. *Acta Crystallogr.* **1980**, *B36*, 2425.

(2) Chasteen, N. D.; Belford, R. L.; Paul, I. C. *Inorg. Chem.* **1969**, *8*, 408.

(3) Holland, R. M.; Tapscott, R. E. *J. Coord. Chem.* **1981**, *11*, 17.

(4) Micera, G.; Sanna, D.; Dessì, A.; Kiss, T.; Buglyò, P. *Gazz. Chim. Ital.* **1993**, *123*, 573.

10.1021/ic0260567 CCC: $25.00

Table 1. Electronic Absorption Parameters of $V^{IV}O$ Bis Complexes with α-Hydroxycarboxylates[a]

ligand	c_L/c_M	pH	λ_4 (ϵ_4)	λ_3 (ϵ_3)	λ_2 (ϵ_2)	λ_1 (ϵ_1)	$\Delta\lambda_1$	$\Delta\lambda_2$
glycolate	5	7.8	405 (35)	532 (28)	606 (27)	804 (22)	74	198
DL-lactate	8	7.0	409 (29)	536 (22)	602 (22)	820 (18)	66	218
2-hydroxyisobutyrate	2	6.4	416 (29)	537 (26)	596 (29)	850 (24)	59	254
2-methyl-DL-2-hydroxybutyrate	4	6.6	416 (31)	536 (24)	594 (26)	858 (24)	58	264
2-ethyl-2-hydroxybutyrate	4	6.4	416 (29)	539 (26)	592 (26)	860 (20)	53	268
DL-mandelate	5	6.6	412 (32)	538 (27)	598 (27)	822 (28)	60	224
benzilate	2	5.7	415 (40)	541 (27)	586 (26)	859 (33)	45	273
DL-isoserinate	5	6.5	404 (34)	535 (25)	613 (26)	771 (19)	78	158
D-quinate	10	7.9	416 (31)	536 (33)	603 (31)	815 (24)	67	212

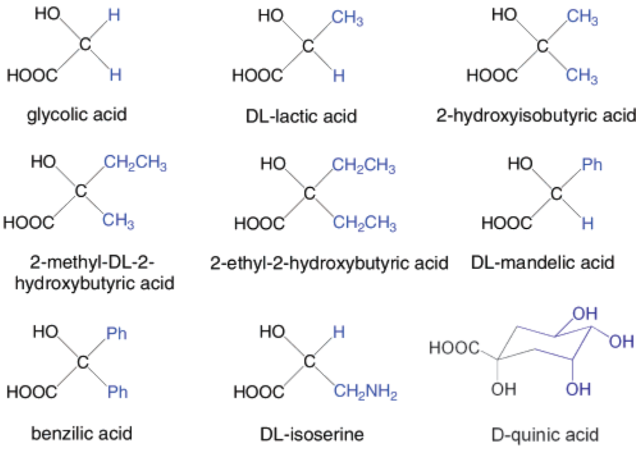
[a] c_L/c_M is the ligand to metal molar ratio; λ is expressed in nm, and ϵ in $dm^3\ mol^{-1}\ cm^{-1}$. $\Delta\lambda_1$ is $\lambda_2 - \lambda_3$; $\Delta\lambda_2$ is $\lambda_1 - \lambda_2$.

Table 2. Anisotropic EPR Parameters of the $V^{IV}O$ Complexes with α-Hydroxycarboxylates[a]

ligand	c_L/c_M	pH	g_x	g_y	g_z	A_x	A_y	A_z	$\|A_x - A_y\|$
glycolate	5	7.8	1.986	1.974	1.952	47.0	53.0	157.2	6.0
DL-lactate	8	7.0	1.986	1.974	1.951	46.4	53.8	156.6	7.4
2-hydroxyisobutyrate	2	6.4	1.985	1.975	1.951	42.8	51.2	153.6	8.4
2-methyl-DL-2-hydroxybutyrate	4	6.6	1.985	1.975	1.951	42.4	51.2	154.2	8.8
2-ethyl-2-hydroxybutyrate	4	6.4	1.985	1.975	1.950	42.4	51.6	154.6	9.2
DL-mandelate	5	6.6	1.985	1.975	1.950	44.0	52.4	154.6	8.4
benzilate	2	5.7	1.984	1.976	1.950	39.4	51.6	152.1	12.2
DL-isoserinate	5	6.5	1.988	1.973	1.951	45.5	52.8	156.2	7.3
D-quinate	10	7.9	1.986	1.973	1.951	43.2	51.4	155.4	8.2

[a] c_L/c_M is the ligand to metal molar ratio; A_x, A_y, A_z, and $|A_x - A_y|$ are in 10^{-4} cm^{-1} units.

Chart 1



of the size of the α-carbon substituents on the distortion of the coordination geometry toward the trigonal bipyramid.

Experimental Section

Chemicals. All the ligands were Aldrich, Fluka, or Sigma products of puriss quality. $VOSO_4{\cdot}5H_2O$ was used as a $V^{IV}O$ source.

Solutions. All the solutions were prepared by dissolving 0.0253 g of $VOSO_4{\cdot}5H_2O$ in 25 mL of degassed water to obtain a 4 mM concentration and then adding the ligand until to obtain the appropriate ligand to metal molar ratio. All the solutions were stirred and handled under an argon flow. The pH and c_L/c_M values listed in Tables 1 and 2 were chosen to obtain the maximum extent of formation of the bis chelated complexes. The formation of the bis chelated species in solution could be evaluated easily since their EPR spectra are very distinctive and different from those of the mono chelated (see below, Figure 2) and hydrolytic complexes. Moreover, EPR spectroscopy allows us to detect even trace amounts of any EPR-active species present in aqueous solution in addition to the bis chelated complex. Once these experimental conditions were established, the UV−vis spectra of the bis chelated species were also recorded.

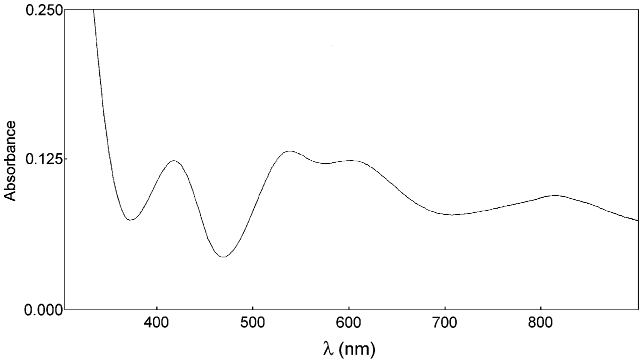


Figure 1. Electronic absorption spectrum recorded on the $V^{IV}O$−D-quinate system at pH 7.9 with a ligand to metal molar ratio of 10:1 ($c_{VO} = 4 \times 10^{-3}$ mol dm^{-3}).

Spectroscopic Measurements. Anisotropic EPR spectra were recorded on aqueous solutions with a X-band (9.15 GHz) Varian E-9 spectrometer at 120−140 K. As usual for low-temperature measurements, a few drops of DMSO were added to the samples to ensure a good glass formation. Electronic absorption spectra of the complexes were recorded on a Jasco Uvidec 610 spectrophotometer.

EPR Spectra Simulation. The EPR spectra of all the bis chelated species were simulated with the Bruker WinEPR SimFonia program at a microwave frequency of 9.15 GHz and with a line width of 1−1.2 mT in the *x*, *y*, and *z* directions.

Results

Electronic Spectra. The d−d absorption spectra of $V^{IV}O$ complexes are generally interpreted according to the scheme proposed by Ballhausen and Gray for the C_{4v} symmetry, corresponding to the square pyramid.[5] The V═O bond defines the *z* axis, and the *x* and *y* axes are in the equatorial

---

(5) Ballhausen, C. J.; Gray, H. B. *Inorg. Chem.* **1962**, *1*, 111.

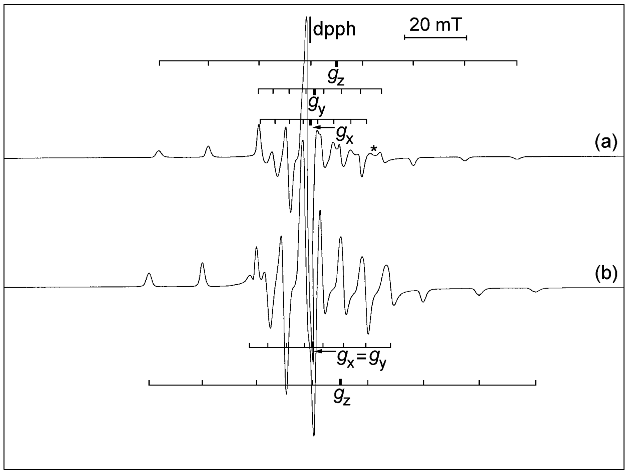


Figure 2. X-band anisotropic EPR spectrum recorded at 140 K on the $V^{IV}O$−glycolate system in aqueous solution ($c_{VO} = 4 \times 10^{-3}$ mol dm^{-3}): (a) bis chelated complex; (b) mono chelated complex. The asterisk indicates the region in which the differences in the symmetry of the complexes are more easily observable. Diphenylpicrylhydrazyl (dpph) is the standard field marker ($g = 2.0036$).

plane. In this scheme the following energy order is predicted for the 3d levels: d_{xy} (b_2) < d_{xz}, d_{yz} (e) < $d_{x^2-y^2}$ (b_1) < d_{z^2} (a_1). Three transitions are expected: in $[VO(H_2O)_5]^{2+}$ the absorption bands occur at 760 nm for $d_{xy} \rightarrow d_{xz}$, d_{yz} (band I), at 625 nm for $d_{xy} \rightarrow d_{x^2-y^2}$ (band II), and below 400 nm for $d_{xy} \rightarrow d_{z^2}$ (band III).[6] The increase of the ligand field strength is responsible for a blue shift of the absorption bands. Therefore, the excitation to the d_{z^2} orbital (band III) occurs at 350−400 nm and can be masked by intraligand or charge-transfer bands.[7]

The nonequivalence of equatorial donors, if a geometry close to a square pyramid is kept, does not affect significantly the above pattern. Indeed, an examination of literature data for $V^{IV}O$ species substantiates that electronically different ligand functions are not able to split the absorption bands, unless a significant distortion in geometry occurs. Therefore, for the sake of simplicity, a *trans*-bis(α-hydroxycarboxylato)-oxovanadium(IV) complex in the limit of a regular square pyramidal geometry can be treated using the $VO(O_4)$ model system under C_{4v} symmetry.

In this model, a distortion toward the trigonal bipyramid lowers the symmetry to C_{2v} and removes the degeneracy of the d_{xz} and d_{yz} orbitals. The $^2E(d_{xz}, d_{yz})$ term splits into two levels, and four bands are resolved in the electronic spectrum. This is the typical behavior of all the bis chelated complexes analyzed in this study. The absorption data are summarized in Table 1, where, beside the maxima, the experimental conditions, e.g. the pH and the ligand to metal molar ratio used to obtain the maximum extent of bis chelated complex formation, are reported. The electronic absorption spectrum of D-quinate is shown in Figure 1.

A feature shared by all the spectra, except that of DL-isoserinate, is the maximum above 800 nm, whereas the high-energy absorption falls above 400 nm. The four bands are weak, with extinction coefficients in the range 18−40 dm^3 mol^{-1} cm^{-1}, consistent with the d−d origin of the transitions.

With increasing size of the α-carbon substituents, e.g. with increasing distortion of the geometry, the following effects take place (Table 1): (i) Both the high- and low-energy absorptions are red-shifted; indeed, the bis complex of glycolate absorbs at 405 and 804 nm, whereas benzilate exhibits bands at 415 and 859 nm. (ii) λ_2 decreases and λ_3 increases, so the $\Delta\lambda_1$ splitting between the central bands ($\lambda_2 - \lambda_3$) becomes smaller on going from glycolate (74 nm) to benzilate (45 nm). Therefore, the coordination geometry of the complexes, which can be described as intermediate between the square pyramid and the trigonal bipyramid, has significant effects on the absorption spectra.

EPR Spectra. The symmetry reduction due to geometry distortion produces significant changes in EPR spectra too. For square pyramidal complexes with C_{4v} symmetry—the V═O bond is along z and the other four donor atoms are along the x, y axes—an anisotropic EPR spectrum is expected, exhibiting two g ($g_z = g_{\parallel} < g_{\perp} = g_x = g_y$) and two A ($A_z = A_{\parallel} > A_{\perp} = A_x = A_y$) values. If the symmetry decreases to C_{2v}, the spectrum becomes rhombic with three g ($g_z < g_x \neq g_y$) and three A ($A_z > A_x \neq A_y$) values. The EPR parameters of the complexes are listed in Table 2.

The conversion from tetragonal to rhombic anisotropy can be followed by comparing the EPR spectra of the mono and bis chelated complexes of glycolate, [VO(glycolato)] and $[VO(glycolato)_2]^{2-}$ (Figure 2). The former spectrum does not exibit x, y magnetic anisotropy: the measured EPR parameters are $g_{\parallel} = 1.941$, $g_{\perp} = 1.980$, $A_{\parallel} = 168.4 \times 10^{-4}$, and $A_{\perp} = 60.0 \times 10^{-4}$ cm^{-1}. The latter spectrum is rhombic, with three g ($g_z < g_y < g_x$) and three A ($A_z > A_y > A_x$) values: $g_x = 1.986$, $g_y = 1.974$, $g_z = 1.952$; $A_x = 47.0 \times 10^{-4}$, $A_y = 53.0 \times 10^{-4}$, and $A_z = 157.2 \times 10^{-4}$ cm^{-1}. This confirms that the lifting of the degeneracy of d_{xz} and d_{yz} orbitals does not derive from electronically distinct ligand functions but is mainly due to the distortion of the complex geometry.

An examination of Table 2 indicates that the g_z value is insensitive, within the experimental error, to the degree of distortion of the complex structure. The g_x and g_y parameters exhibit a greater variation; however, they change in a random manner and are little sensitive to the steric constraints of the ligand. On this basis, it is difficult to correlate the amount of $|g_x - g_y|$ anisotropy with the size of the substituents on the α-carbon atom. For example, $|g_x - g_y|$ is 0.012 with the unhindered glycolate ligand, 0.008 with the bulky benzilate ligand, 0.013 with D-quinate, and 0.010 with 2-methyl-DL-hydroxybutyrate and 2-ethyl-2-hydroxybutyrate. The greatest $|g_x - g_y|$ anisotropy (0.015) is observed for DL-isoserinate. Also the A_y constant is little influenced by the distortion of the structure and ranges between 51.2 and 53.8×10^{-4} cm^{-1}. A_x is more sensitive to the complex distortion and exhibits values of 47.0×10^{-4} and 39.4×10^{-4} cm^{-1} for glycolate and benzilate, respectively.

The highest correlation with the distortion of the geometry is found with the $|A_x - A_y|$ value. The largest difference is

---

[6] Bridgland, B. E.; Fowles, G. W. A.; Walton, R. A. *J. Inorg. Nucl. Chem.* **1965**, *27*, 389.

[7] Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984.

12.2×10^{-4} cm^{-1} for benzilate, certainly the most distorted complex because of the two phenyl substituents on the α carbon atom. A value of 6.0×10^{-4} cm^{-1} is measured for the simple glycolate complex (two hydrogen atoms on the α-carbon atom of the ligand). Significantly, within the series of simple α-hydroxycarboxylates, $|A_x - A_y|$ increases in the order glycolate < DL-lactate < mandelate ≈ 2-hydroxyisobutyrate < 2-methyl-DL-2-hydroxybutyrate < 2-ethyl-2-hydroxybutyrate < benzilate, which reflects the order of steric hindrance expected due to substituents: (H, H) < (H, CH_3) < (H, Ph) ≈ (Me, Me) < (Me, Et) < (Et, Et) < (Ph, Ph).

According to the literature,[8] the $|A_x - A_y|$ anisotropy is given by the following expression:

$$|A_x - A_y| = P[(g_x - g_y) + 3\xi(\Lambda_x - \Lambda_y)]$$

Here $P = g_e g_N \beta_e \beta_N <r^{-3}>$ and r is the unpaired electron−nucleus distance, ξ is the spin−orbit coupling constant, and Λ_x and Λ_y are the tensors that mix the excited-state orbital angular momentum into the ground state.

In our case, by assuming P in the range (120−150) × 10^{-4} cm^{-1},[8,9] the term $P(g_x - g_y)$ is small and ranges between 1.0×10^{-4} and 2.2×10^{-4} cm^{-1}. So, the greatest contribution to $|A_x - A_y|$, around 80%, arises from the terms ξ and $(\Lambda_x - \Lambda_y)$.

It is worth noting that the thermodynamic stability too of the bis chelated species follows closely the degree of distortion. A previous work of ours[4] demonstrated that the degree of distortion of monomeric α-hydroxycarboxylate complexes of $V^{IV}O$, as deduced from the steric hindrance of substituents at the α-carbon atom of the ligands, is inversely proportional to (i) the pK_a of deprotonation of the VOA_2H_{-1} species with the donor set (COO^-, O^-; COO^-, OH) to form the bis chelated species VOA_2H_{-2} with coordination mode (COO^-, O^-; COO^-, O^-), (ii) the value of log K_2 for the formation of VOA_2H_{-2}, and (iii) the value of log(K_1/K_2), where K_1 and K_2 are the formation constants of $VOAH_{-1}$ and VOA_2H_{-2}, respectively. The p$K_{VOA_2H_{-1}}$ values are the following: 3.53 (benzilate); 3.88 (2-ethyl-2-hydroxybutyrate); 4.16 (2-methyl-DL-2-hydroxybutyrate); 4.62 (DL-mandelate); 4.67 (2-hydroxyisobutyrate); 4.97 (glycolate); 5.24 (DL-lactate). The log$K_{VOA_2H_{-2}}$ values are the following: −1.08 (benzilate); −1.76 (2-ethyl-2-hydroxybutyrate); −1.82 (2-methyl-DL-2-hydroxybutyrate); −2.00 (2-hydroxyisobutyrate); −2.06 (DL-mandelate); −2.46 (DL-lactate); −2.63 (glycolate). The log($K_{VOAH_{-1}}/K_{VOA_2H_{-2}}$) values are the following: 0.16 (benzilate); 0.67 (2-ethyl-2-hydroxybutyrate); 0.77 (2-methyl-DL-2-hydroxyisobutyrate); 0.97 (2-hydroxyisobutyrate); 1.02 (DL-mandelate); 1.12 (DL-lactate); 1.28 (glycolate).

Discussion

A search in the literature from the Cambridge Structural Database for $V^{IV}O$ complexes of α-hydroxycarboxylic ligand yields 16 crystal structures.[10] Among them, 14 concern the well-known dimeric complex of tartrates (in the D, L, and DL forms), characterized for the first time with L isomer by Forrest and Prout,[11] and only 2 belong to monomeric species.

The Na,NEt_4[VO(benzilato)$_2$] monomeric complex is five-coordinated with a trans arrangement of the two ligands around the $V^{IV}O$ ion.[2] The distances between the vanadium atom and the hydroxyl oxygen atoms are 1.90 and 1.93 Å; the two oxygen atoms of carboxylate group are located at a distance of 1.97 Å from vanadium. The O−V−O angle between the deprotonated hydroxyl oxygens is 132.9°, while that formed by the carboxylates is 151.6°. Therefore, the geometry is distorted toward the trigonal bipyramid: the oxygen atoms belonging to $V^{IV}O$ and to the deprotonated hydroxyl groups are the equatorial donors, whereas the carboxylate oxygens are in the axial positions.

Cornman and co-workers introduced the τ parameter to measure the distortion of a square pyramidal structure toward the trigonal bipyramid.[8] This parameter is $(\alpha - \beta)/60$, where α is the angle formed by the two pseudoapical atoms at the vanadium atom and β is the angle formed by the two pseudoequatorial atoms: τ is 0 for a square pyramid and 1 for a trigonal bipyramid. The τ value for the bis chelated complex of benzilate is 0.31, indicating a significant distortion toward the trigonal bipyramid form.

Another monomeric structure is exhibited by the bis chelated complex 2-ethyl-2-hydroxybutyrate, NH_4[VO(OC(Et)$_2$COO)(HOC(Et)$_2$COO)].[12] In this compound the distances between vanadium and the hydroxyl oxygens are 1.88 and 1.99 Å, whereas the two oxygen atoms of the carboxylate groups are in the axial positions at distances of 1.95 and 1.98 Å from the metal ion. The O−V−O equatorial angle is 136.3°, while the axial angle is 147.8°. Also in this case the geometry is distorted toward the trigonal bipyramid, but the degree of distortion is lower ($\tau = 0.19$) than in the benzilate complex because of the presence of less bulky substituents on the α-carbon atom of the ligand.

Another search on the Cambridge Structural Database has shown that the only well-characterized series of isostructural complexes of $V^{IV}O$ with bidentate ligands are those formed by the derivatives of the Schiff base salicylaldimine. These ligands bind the metal ion through two imine nitrogens and two phenolate oxygen atoms in a trans cooordination mode. The steric hindrance of the ligand changes progressively with changing R substituent on the nitrogen atom and R′ substituent on the aromatic carbon in *ortho* position to the coordinating hydroxyl group (see Chart 2).

In 6 of 8 compounds so far investigated in this series R′ is H. If R too is a hydrogen atom, a minor distortion is observed and a τ value of 0.22 is calculated.[13] The τ value increases parallelly to the steric hindrance of the R group,

---

[8] Cornman, C. R.; Geisre-Bush, K. M.; Rowley, S. R.; Boyle, P. D. *Inorg. Chem.* **1997**, *36*, 6401.

[9] Mabbs, F. E.; Collison, D. *Electronic Paramagnetic Resonance of d Transition Metal Compounds*; Elsevier: Amsterdam, 1992.

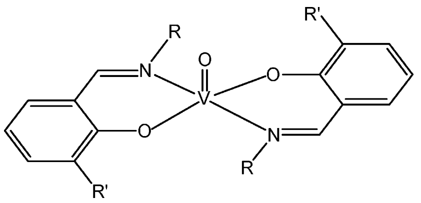
[10] Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31.

[11] Forrest, J. G.; Prout, C. K. *J. Chem. Soc. A* **1967**, 1312.

[12] Barr-David, G.; Hambley, T. W.; Irwin, J. A.; Judd, R. J.; Lay, P. A.; Martin, B. D.; Bramley, R.; Dixon, N. E.; Hendry, P.; Ji, J.-Y.; Baker, R. S. U.; Bonin, A. M. *Inorg. Chem*. **1992**, *31*, 4906.

[13] Choudhary, N.; Hughes, D. L.; Kleinkes, U.; Larkworthy, L. F.; Leigh, G. J.; Maiwald, M.; Marmion, C. J.; Sanders, J. R.; Smith, G. W.; Sudbrake, C. *Polyhedron* **1997**, *16*, 1517.

Chart 2



ranging from 0.23 and 0.34 if the imine nitrogen atom belongs to a 5-ethyl-oxazoline or a 5-isopropyloxazoline cycle[14] to 0.40−0.43 if R is CH_2CH_2OH or a larger substituent like *p*-$C_6H_4OCF_3$ or *p*-C_6H_4Cl.[15−17] The greatest distortion occurs if a substituent is introduced into the *ortho* position to the coordinating hydroxyl group. Particularly, τ is 0.58 for [VO(*N*-isopropyl-*o*-methylsalicylaldiminato)$_2$] (R = isopropyl; R′ = methyl)[8] and 0.70 for [VO(*N*-methyl-*o*-*tert*-butyl-*p*-methylsalicylaldiminato)$_2$] (R = methyl; R′ = *tert*-butyl).[8] This last compound is, to our knowledge, the $V^{IV}O$ complex with the maximum degree of distortion toward the trigonal bipyramid so far reported in the literature: the pseudoequatorial angle O−V−O is 124.0°, very close to the value of 120.0° expected for a trigonal bipyramid.

It is well-known that the trigonal bipyramidal geometry reduces the sterical interactions between the ligands in the metal environment. Therefore, although most $V^{IV}O$ compounds prefer the square pyramidal arrangement because of the strong π-bond formed by the axial oxo ligand with vanadium, the presence of a bulky ligand can stabilize energetically unfavorable coordination geometries such as the trigonal bipyramid.

The above conclusions can be extended to $V^{IV}O$ α-hydroxycarboxylates although these systems are structurally poorly characterized in the solid state. We can assume that the distortion toward the trigonal bipyramid is increasingly favored for $V^{IV}O$ species with increasing steric hindrance of the ligands. This assumption is fully consistent with all the structural (and thermodynamic) data available in the literature and is also in agreement with previous conclusions (see ref 8, for instance). On this basis the electronic structure of $V^{IV}O$ complexes with α-hydroxycarboxylic acids can be discussed as follows.

Many efforts were carried out in the past to find correlation schemes between the coordination geometry and the electronic spectra of $V^{IV}O$ complexes, mainly based on crystal field considerations. An energy level scheme was presented by Chasteen and co-workers[2] to interpret the spectra of bis chelated complex of benzilate and of dimeric cis and trans species of DL- and D-tartrate: $d_{xy} \rightarrow d_{x^2-y^2}$ (∼850 nm), $d_{xy} \rightarrow d_{xz}$, d_{yz} (∼590−530 nm), and $d_{xy} \rightarrow d_{z^2}$ (∼410 nm). The splitting of the central band was assigned to the separation of d_{xz} and d_{yz} orbitals, but the EPR results were hard to reconcile with this hypothesis. Later Chasteen and coworkers[18] proposed two different assignments [$d_{xy} \rightarrow d_{yz}$, $d_{xy} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{xz}$, and $d_{xy} \rightarrow d_{z^2}$ in order of increasing energy or $d_{xy} \rightarrow d_{xz} \sim d_{yz}$ (first band), $d_{xy} \rightarrow d_{x^2-y^2}$ (second band), $d_{xy} \rightarrow d_{z^2}$ (third band), and charge transfer (fourth band)] that produced a better agreement with EPR results.

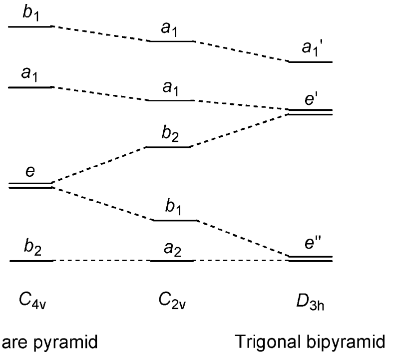
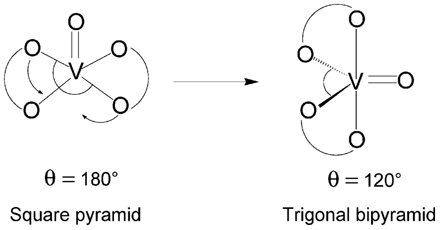


Figure 3. Orbital correlation diagram for the transformation of a square pyramid (C_{4v}) into a trigonal bipyramid (D_{3h}).

Scheme 1



We propose an assignment on the basis of the conversion of the square pyramidal geometry into the trigonal bipyramid, as measured by the θ angle between the two opposite equatorial donors. This angle is 180° in the square pyramid and goes to 120° in the trigonal bipyramid (Scheme 1).

The transformation is well described by the orbital correlation diagram calculated by Rossi and Hoffmann[19] and displayed in Figure 3.

The e term, corresponding to the d_{xz} and d_{yz} atomic orbitals in a square pyramid, splits into the two levels b_1 (d_{xz}) and b_2 (d_{yz}) as θ deviates from 180°, with the d_{yz} orbital increasing and d_{xz} orbital decreasing in energy. Moreover, the energy difference between a_1 and b_2 ($d_{x^2-y^2}$ and d_{yz}, respectively) decreases with decreasing θ. Finally, the highest term, a_1, corresponding to the d_{z^2} orbital, shifts to lower energy.

A comparison of the complexes formed by simple α-hydroxycarboxylates indicates that there is an excellent agreement of the spectral data with the above scheme if it is assumed that the θ angle decreases in the following order: glycolate < DL-lactate < 2-hydroxyisobutyrate ≈ DL-mandelate < 2-methyl-DL-2-hydroxybutyrate < 2-ethyl-2-hydroxybutyrate < benzilate (see Figure 4), which is the order of increasing distortion of the geometry.

The results of the above discussion can be summarized by the correlation diagram displayed in Figure 5.

---

(14) Bolm, C.; Thi Kim Khanh Luong; Harms K. *Chem. Ber.* **1997**, *130*, 887.

(15) Carrano, C. J.; Nunn, C. M.; Quan, R.; Bonadies, J. A.; Pecoraro, V. L. *Inorg. Chem.* **1990**, *29*, 944.

(16) Burgess, J.; Fawcett, J.; Palma, V.; Gilani, S. R. *Acta Crystallogr., Sect. C* **2001**, *57*, 277.

(17) Pasquali, M.; Marchetti, F.; Floriani, C.; Merlino S. *J. Chem. Soc., Dalton Trans.* **1977**, 139.

(18) Belford, R. L.; Chasteen, N. D.; So, H.; Tapscott, R. E. *J. Am. Chem. Soc.* **1969**, *91*, 4675.

(19) Rossi, R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

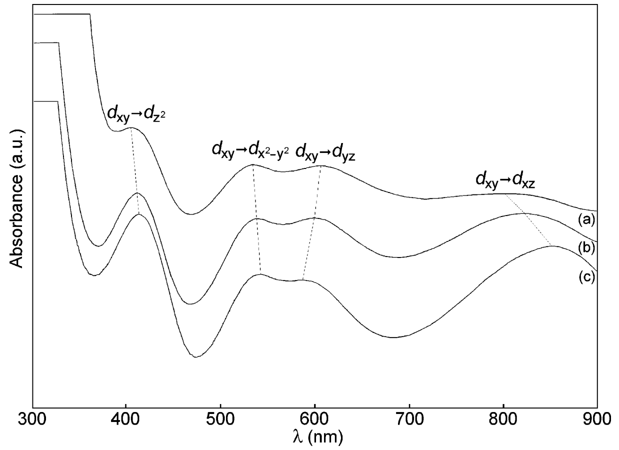


Figure 4. Electronic absorption spectra of the bis chelated oxovanadium(IV) complexes of (a) glycolate, (b) DL-mandelate, and (c) benzilate.

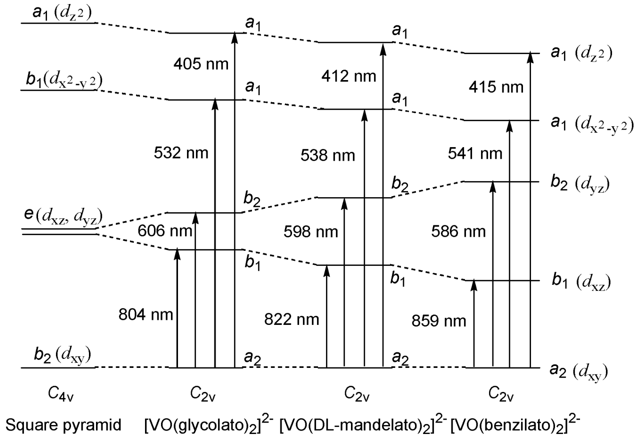


Figure 5. Electronic transitions and energy sequence of the d orbital for bis chelated complexes of $V^{IV}O$ with glycolate, DL-mandelate, and benzilate.

The energy sequence of the d atomic orbitals is the same as proposed by Drake et al. to explain the electronic spectrum of $[VO(NMe_3)_2Cl_2]$ and Stoklosa et al. for $[VOCl_4]^{2-}$ and $[VO(8\text{-hydroxyquinaldinato})_2]$.[20,21] The inversion of the $d_{x^2-y^2}$ and d_{yz} levels, proposed by Chasteen et al.,[2] is not in agreement with the decrease of the $\Delta\lambda_1$ splitting of the central bands with increasing geometric distortion. Indeed, $\Delta\lambda_1$ does exhibit an inverse correlation with the degree of distortion toward the trigonal bipyramid. This parameter decreases in the order glycolate > DL-lactate > DL-mandelate ≈ 2-hydroxyisobutyrate ≈ 2-methyl-DL-2-hydroxybutyrate > 2-ethyl-2-hydroxybutyrate > benzilate, substantiating the same distortion trend deduced by EPR analysis and expressed by the $|A_x - A_y|$ parameter.

An examination of Figure 5 substantiates that the parameter $\Delta\lambda_2 = \lambda_1 - \lambda_2$ too, related to the splitting of the d_{yz} and d_{xz} levels, can be used for establishing the geometrical distortion (Table 1). In particular, $\Delta\lambda_2$ increases with increasing distortion: glycolate (198 nm) < DL-lactate (218 nm) < DL-mandelate (224 nm) < 2-hydroxyisobutyrate (254 nm) < 2-methyl-DL-2-hydroxybutyrate (264 nm) < 2-ethyl-2-hydroxybutyrate (268 nm) < benzilate (273 nm).

Table 3. Experimental and Calculated EPR Parameters of α-Hydroxycarboxylates complexes of $V^{IV}O$

ligand	VOA		VOA_2		diff
	g_z	$A_z{}^a$	A_z(calc)^a	A_z(exp)^a	%
glycolate	1.941	168.4	157.4	157.2	−0.1
DL-lactate	1.942	168.2	157.0	156.6	−0.2
2-hydroxyisobutyrate	1.940	166.8	154.2	153.6	−0.4
2-methyl-DL-2-hydroxybutyrate	1.940	167.1	154.8	154.2	−0.4
2-ethyl-2-hydroxybutyrate	1.940	167.6	155.8	154.6	−0.8
DL-mandelate	1.941	167.4	155.4	154.6	−0.5
benzilate	1.941	167.1	154.8	152.1	−1.8
DL-isoserinate	1.940	169.0	158.6	156.2	−1.5
D-quinate	1.943	168.1	156.8	155.4	−0.9

[a] A_z is measured in 10^{-4} cm^{-1} units.

On the basis of $\Delta\lambda_1$ and $\Delta\lambda_2$ values, the lactate complex is more distorted than the DL-isoserinate species, though the ligand are sterically similar. However, the difference between methyl and aminomethyl groups and, possibly, the repulsion between the positively charged amino groups of DL-isoserinate under the experimental conditions used can explain the different degree of distortion.

Using the EPR data listed in the Table 3, one can check the order of the energy levels. The following expressions are valid for the g values in the case of a d_{xy} ground state and a C_{2v} symmetry:[9]

$$g_z = g_e - \frac{8\alpha^2\beta^2\xi}{\Delta E(x^2 - y^2)}$$

$$g_x = g_e - \frac{2\beta^2{\gamma_2}^2\xi}{\Delta E(xz)}$$

$$g_y = g_e - \frac{2\beta^2{\gamma_1}^2\xi}{\Delta E(yz)}$$

Here α, β, γ_1, and γ_2 are the vanadium $d_{x^2-y^2}$, d_{xy}, d_{xz}, and d_{yz} orbital populations, ξ is the spin−orbit constant, and $\Delta E(x^2 - y^2)$, $\Delta E(xz)$, and $\Delta E(yz)$ are the energy differences between the $d_{x^2-y^2}$, d_{xz}, and d_{yz} excited states, respectively, and the d_{xy} ground state.

If g_z, g_x, and g_y are plotted as a function of the reciprocal value of the energy differences $\Delta E(x^2 - y^2)$, $\Delta E(xz)$, and $\Delta E(yz)$, respectively, we expect a linear relation with g_e intercept and $8\alpha^2\beta^2\xi$, $2\beta^2{\gamma_2}^2\xi$, and $2\beta^2{\gamma_1}^2\xi$ as negative angular coefficients. The results are shown in Figure 6.

The correlation coefficients of 0.87, 0.83, and 0.83 obtained for the three plots in Figure 6a−c, respectively, are quite acceptable, the three intercept values being 2.0023 (g_e) within the experimental error. Instead, no linear fit between the g values and the energy differences can be obtained if the energetic schemes proposed by Chasteen and coworkers[2,18] are assumed.

The final considerations concern the effect of the symmetry reduction of “normal” $V^{IV}O$ complexes on the hyperfine coupling constant of the bis chelated species. As a basis for the discussion, we suppose that the mono chelated complexes formed by α-hydroxycarboxylic acids are almost tetragonal with a geometry close to the square pyramid. This is a quite reasonable assumption because mono chelated species exhibit

---

(20) Drake, V.; Vekris, J.; Wood, J. S. *J. Chem. Soc. A* **1968**, 1000.
(21) Stoklosa, H. J.; Wasson, J. R.; McCormick, B. J. *Inorg. Chem.* **1974**, *13*, 592.

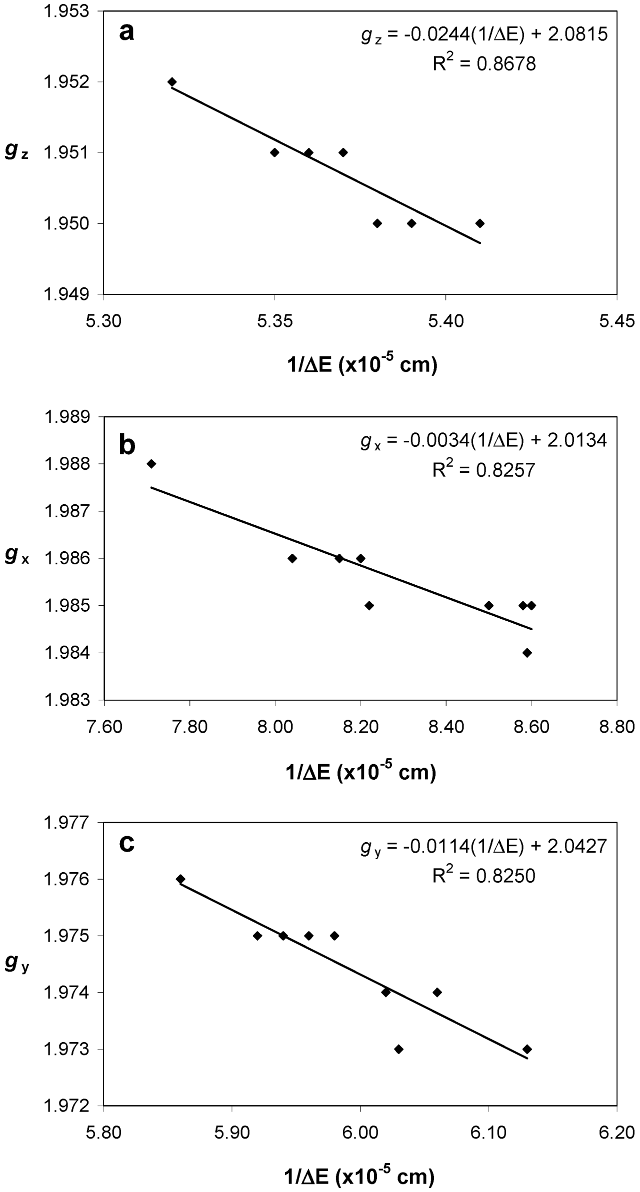


Figure 6. Plots of the *g* values vs the energy differences between the excited and ground states: (a) g_z vs $1/\Delta E(x^2 - y^2)$; (b) g_x vs $1/\Delta E(xz)$; (c) g_y vs $1/\Delta E(yz)$.

axial EPR spectra (Figure 2) and electronic absorption spectra consisting of three bands. The parallel hyperfine coupling constant (A_z or $A_{\|}$) can be calculated from the sum of the contribution of each donor atoms in the equatorial plane, according to the “additivity relationship” proposed by Wütrich and developed by Chasteen and, later, by Cornman and Pecoraro:[22−25]

$$A_{\|}(\text{expected}) = \sum_i n_i A_{\|,i}$$

Here n_i is the number of equatorial ligands of *i* type and $A_{\|,i}$ is the empirical contribution from each *i* equatorial ligand. The contribution of the donor set (COO^-, O^-) is easily found on the basis of the $A_{\|}$ values of the mono chelated species and of the water (measured from the spectrum of the aqua ion):

$$A_{\|,\mathrm{exp}}(\text{mono chelated}) = A_{\|}(\mathrm{COO^-}) + A_{\|}(\mathrm{O^-}) + 2A_{\|}(\text{aqua ion})$$

$$A_{\|}(\mathrm{COO^-}) + A_{\|}(\mathrm{O^-}) = A_{\|,\mathrm{exp}}(\text{mono chelated}) - 2A_{\|}(\text{aquaion})$$

The difference between the calculated and the experimental values (Table 3) can be attributed to the distortion of the structure toward the trigonal bipyramid. It is noticeable that for the bis complexes the measured values of A_z are all lower than expected by an amount reaching 1.8% in the case of benzilate.

Therefore, we can conclude that the distortion of a square pyramid toward the trigonal bipyramid has a minor effect on the A_z value and the “additivity relationship” is still valid. Similarly, Cornman et al. reported a decrease of the hyperfine coupling constant along the *z* axis, A_z, within 2% for distorted $V^{IV}O$ complexes.[8]

Conclusions

We analyzed nine bis chelated $V^{IV}O$ α-hydroxycarboxylate complexes characterized by a different degree of distortion toward the trigonal bipyramid. The d−d absorption and EPR spectroscopic features are peculiar of this kind of arrangement and give reliable information about the distortion of the geometry. Concomitantly with the appearance of a fourth band in the electronic spectrum, g_x, g_y, and A_x, A_y splittings are observed in the EPR spectra. The greater are the steric constraints of the substituents on the α-carbon atom, the higher is the EPR anisotropy. The A_x, A_y anisotropy, namely the $|A_x - A_y|$ parameter, can be used to measure the degree of distortion. Because structural data in $V^{IV}O$ chemistry with these geometries are lacking, this study could be of aid for extracting information otherwise not available.

IC0260567

---

(22) Wütrich, K. *Helv. Chim. Acta* **1965**, *48*, 1012.

(23) Chasteen, N. D. In *Biological Magnetic Resonance*; Berliner, L. J., Reuben, J., Eds.; Plenum Pess: New York, 1981; Vol. 3, pp 53−119.

(24) Cornman, C. R.; Zovinka, E. P.; Boyajian, Y. D.; Geiser-Bush, K.; Boyle, P. D.; Singh, P. *Inorg. Chem.* **1995**, *34*, 4213.

(25) Smith, T. S., II; Root, C. A.; Kampf, J. W.; Rasmussen, P. G.; Pecoraro, V. L. *J. Am. Chem. Soc.* **2000**, *122*, 767.