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Oxovanadium(IV) Complexes with Pyrazinecarboxylic Acids: The Coordinating Properties of Ligands with the ($N_{aromatic}$, COO^-) Donor Set

Eugenio Garribba,*[a] Giovanni Micera,*[a] Elzbieta Lodyga-Chruscinska,[b] and Daniele Sanna[c]

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Complex formation between the $V^{IV}O$ ion and four pyrazine derivatives, 2-pyrazinecarboxylic acid (pzc), 5-methyl-2-pyrazinecarboxylic acid (5-Mepzc), 2,3-pyrazinedicarboxylic acid (3-COOHpzc) and 5-hydroxy-2-pyrazinecarboxylic acid (5-OHpzc), was studied in aqueous solution and in the solid state through the combined application of potentiometric and spectroscopic (EPR and FT-IR) techniques. The results indicate that in acidic and neutral aqueous solution all the ligands form mono(chelated), bis(chelated) and dinuclear species of composition VOL, VOL_2 and $(VO)_2L_2H_{-2}$. Hexacoordinated VOL_2 complexes are characterised by a *cis*/*trans* isomerism, where *cis* and *trans* are the species with a water molecule bound in the *cis* or *trans* position with respect to the V=O group. The *trans* arrangement is favoured over the *cis* arrangement. Three solid derivatives, $[VO(5\text{-}Mepzc)_2]$ (**1**), *cis*-$[VO(pzc)_2(H_2O)]$ (**2**) and *cis*-$[VO(3\text{-}COOHpzc)_2(H_2O)]$ (**3**), were isolated and characterised. Based on the experimental results and on the data in the literature, the stability of *cis* and *trans* isomers in aqueous solution and in the solid state has been discussed, showing that with ligands of comparable basicity and size of the chelate ring the hydrophilicity favours the *cis* species and determines the relative amount of the two isomers. The analysis of the magnetic properties of the hydroxo-bridged $V^{IV}O$ dimers suggests that for the $(VO)_2L_2H_{-2}$ species the *anti*-coplanar arrangement is realised.

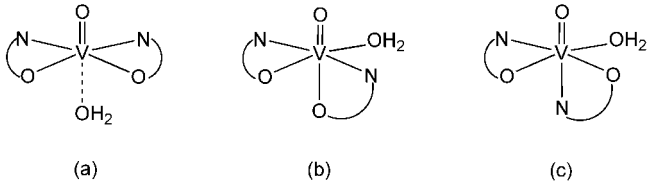
Introduction

Vanadium plays a number of roles in biological systems.[1] Among others, a growing interest is devoted to the insulin-mimetic activity of its compounds.[2] Initially, both V^V and V^{IV} inorganic salts were extensively used as insulin mimics, but the introduction of V^{IV} complexes has considerably improved their pharmacological potential by minimising the dose required for effective diabetic control.[2b]

The insulin-mimetic properties of complexes with coordination modes $VO(O_4)$,[3,4] $VO(N_2S_2)$,[3,5] $VO(S_4)$,[6] $VO(S_2O_2)$,[7] $VO(N_4)$[8] and $VO(N_2O_2)$[9,10] have been examined. Generally, N,O ligation is more efficient than O,O or O/N,S coordination, irrespective of the vanadium oxidation state.[11]

$V^{IV}O$ compounds with N_2O_2 coordination are very promising in the treatment of insulin-dependent diabetes mellitus.[12] In particular, $V^{IV}O(picolinato)_2(H_2O)$ and $V^{IV}O(6\text{-methylpicolinato})_2$ are strong inhibitors of the mobilisation of fatty acids and effective in the treatment of rats affected by diabetes induced with streptozotocin (STZ).[9,10] In addition, the complex formed by 6-methylpicolinate, with long-acting character and low toxicity, is the most effective in the treatment of insulin-dependent diabetes mellitus (IDDM) as well as non-insulin-dependent diabetes mellitus (NIDDM) when administrated orally.[13]

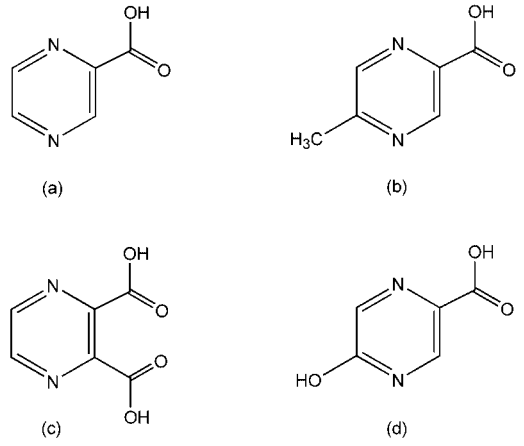
In the last few years several studies have been devoted to the complexation of the $V^{IV}O$ ion by bidentate ligands provided with an aromatic nitrogen atom and a carboxylate oxygen atom as donors.[14] Usually, VOL and VOL_2 species are formed in aqueous solution, with the possibility of *cis*/*trans* isomerism for the hexacoordinate bis(complexes) (Scheme 1).[15] The presence of di-μ-hydroxo EPR-silent species of composition $(VO)_2L_2H_{-2}$ has been proposed in some systems.[14b,14c,14e]



Scheme 1. Possible structures for the isomers of a bis(chelated) $V^{IV}O$ complex: (a) *trans* arrangement; (b) and (c) *cis* arrangements.

[a] Department of Chemistry, University of Sassari, Via Vienna 2, 07100 Sassari, Italy
Fax: +39-079-229559
E-mail: garribba@uniss.it
micera@uniss.it
[b] Institute of General Food Chemistry, Technical University of Lodz, ul. Stefanowskiego 4/10, 90924 Lodz, Poland
[c] Istituto C.N.R. di Chimica Biomolecolare, Trav. La Crucca 3, 07040 Li Punti, Sassari, Italy

In this work we investigated the $V^{IV}O$ complex formation with four pyrazine derivatives: 2-pyrazinecarboxylic (pzc), 5-methyl-2-pyrazinecarboxylic (5-Mepzc), 2,3-pyrazinedicarboxylic (3-COOHpzc) and 5-hydroxy-2-pyrazinecarboxylic (5-OHpzc) acids (Scheme 2). Only one potentiometric study, although not supported by spectroscopic measurements, is available on the interaction of the $V^{IV}O$ ion with 2-pyrazinecarboxylic and 2,3-pyrazinedicarboxylic acids in aqueous solution.[16] To the best of our knowledge, no data on the formation of solid complexes have been reported. Here, the behaviour in aqueous solution and in the solid state of the four ligands is presented together with a discussion of the coordinating properties of ligands provided with the ($N_{aromatic}$, COO^-) donor set.



Scheme 2. Ligands: (a) 2-pyrazinecarboxylic acid (pzc), (b) 5-methyl-2-pyrazinecarboxylic acid (5-Mepzc), (c) 2,3-pyrazinedicarboxylic acid (3-COOHpzc) and (d) 5-hydroxy-2-pyrazinecarboxylic acid (5-OHpzc).

Results

Studies in Aqueous Solution

Fully protonated forms of 2-pyrazinecarboxylic and 5-methyl-2-pyrazinecarboxylic acids in aqueous solution can be denoted as H_3L^{2+} and those of 2,3-pyrazinedicarboxylic and 5-hydroxy-2-pyrazinecarboxylic acids as H_4L^{2+}.

Two deprotonation processes are measurable for pzc, 5-Mepzc and 3-COOHpzc in the titrable pH range with pK_a values of 1.83 and 2.73 for pzc, 2.06 and 3.13 for 5-Mepzc, and 1.50 and 3.25 for 3-COOHpzc (Table 1). The two processes can be assigned to the pyrazine $–NH^+$ and the –COOH groups, respectively. The values measured for pzc and 3-COOHpzc are in very good agreement with those previously reported.[16] Owing to its very high acidity, the deprotonation of the first $–NH^+$ group is not detectable. A comparison with 2-pyridinecarboxylic acid, for which pK_a values of about 1 and 5.19 are reported,[14b] indicates that the presence of a second nitrogen atom in the aromatic ring significantly reduces the basicity of the $–NH^+$ group. On the other hand, the carboxylic group slightly increases the basicity of the second $–NH^+$ group with respect to pyrazine, for which a pK_a of 0.65 is reported.[17] The increase in basicity is due to the formation of a cyclic structure, which stabilises the $–NH^+$ form through an internal hydrogen bond between the protonated pyrazine nitrogen atom and the –COOH group. The value for the deprotonation of the carboxylic group of pzc is comparable with that measured by Toma and Borges (2.82).[18] The electron-releasing effect of the methyl group reduces the acidity of both the $–NH^+$ and –COOH groups in 5-Mepzc (Table 1).

Table 1. Protonation constants of the ligands (log K) and stability constants of the $V^{IV}O$ complexes (log β_{pqr}) at 25.0 ± 0.1 °C and I = 0.1 M (KNO_3).

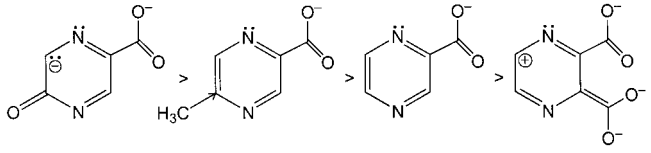
log K/log β_{pqr}	pzc	5-Mepzc	3-COOHpzc	5-OHpzc
$–N1_{pyr}H^+$	<1	<1	<1	<1
$–N2_{pyr}H^+$	1.83	2.06	1.50	<1
–COOH1	2.73	3.13	3.25	3.44
–COOH2	–	–	<1	–
–OH	–	–	–	7.78
VOL	3.42(2)	3.49(2)	3.99(2)	7.01(2)
VOL_2	6.09(2)	6.99(2)	7.02(3)	12.97(2)
$(VO)_2L_2H_{-2}$	0.11(3)	0.58(2)	1.79(3)	5.85(3)

Only two deprotonation steps, of the four possible ones, can be determined for 2,3-pyrazinedicarboxylic acid. Owing to the strong internal hydrogen bond between COOH and COO^-, one of the two carboxylic groups is protonated only at pH < 1. This effect had already been observed for 2,3-pyridinedicarboxylic[19] and 4,5-imidazoledicarboxylic acids.[14a] For the same reason, the deprotonation of the second –COOH group takes place at higher pH values with respect to pzc and 5-Mepzc. Moreover, the electron-withdrawing properties of the carboxylic group increase the acidity of the pyrazine nitrogen atom in comparison with pzc and 5-Mepzc.

The carboxylic group of 5-OHpzc is more basic than in other ligands for the presence of an –OH group in the *para* position according to the Hammett equation;[20] pK_a values of 0.1 and 8.23 are reported for the $–NH^+$ and –OH groups in 2-hydroxypyrazine,[17] and of 6.85 for the –OH group in 2-hydroxy-5-nitropyridine.[21] The presence of –COOH, more efficient in the electron-withdrawing effect than –H and less than $–NO_2$, explains the value of 7.78 measured for 5-OHpzc, intermediate between the other two pK_a values.

According to the potentiometric results, all the ligands form VOL, VOL_2 and $(VO)_2L_2H_{-2}$ species, in which five-membered chelate rings are formed by the (N_{pyr}, COO^-) donor set. The formation constants of the complexes are listed in Table 1 and the order of stability is 5-OHpzc >> 5-Mepzc > pzc ≈ 3-COOHpzc. For example, the higher stability of the bis(chelated) species formed by 5-OHpzc is reflected by the values of the stability constant for the reaction VOL + HL → VOL_2 + H^+ (2.52 for 5-OHpzc, 0.37 for 5-Mepzc, –0.06 for pzc and –0.22 for 3-COOHpzc). The amount of $(VO)_2L_2H_{-2}$ dimers increases in solution with decreasing stability of VOL and VOL_2 species; in equimolar solutions at pH = 6 with a $V^{IV}O$ concentration of 5×10^{-2} M, it is 88.5% with 3-COOHpzc, 65.9% with pzc, 63.4% with 5-Mepzc and 38.2% with 5-OHpzc. The

strength of the ligands can be explained by the effect of the substituents on the aromatic ring of their fully deprotonated forms, displayed in Scheme 3: $-O^-$ is the most effective electron-releasing group, followed by $-CH_3$, whereas –COOH is an electron-withdrawing group. To reduce the hydrolytic processes, the EPR spectra were recorded with a ligand/metal molar ratio of 2 with 5-OHpzc, 5 with 5-Mepzc and 10 with pzc and 3-COOHpzc.



Scheme 3. Resonance forms of the fully deprotonated ligands.

The distribution curves of the species as a function of pH, calculated from the stability constants reported in Table 1, for the weaker (3-COOHpzc) and the stronger ligand (5-OHpzc) are shown in Figures 1 and 2, respectively.

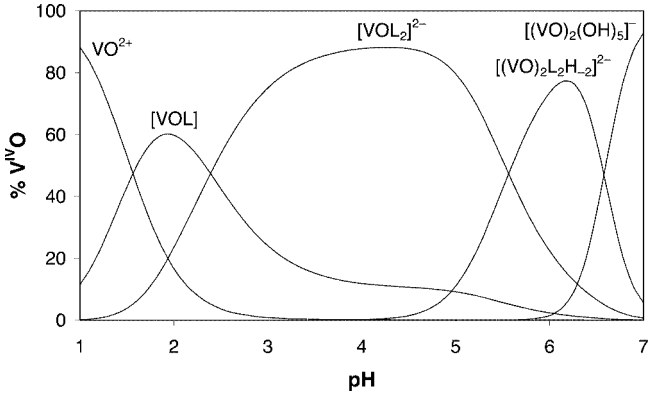


Figure 1. Species distribution for the $V^{IV}O$/3-COOHpzc system with a metal/ligand molar ratio of 1:10 and a $V^{IV}O$ concentration of 1 mM.

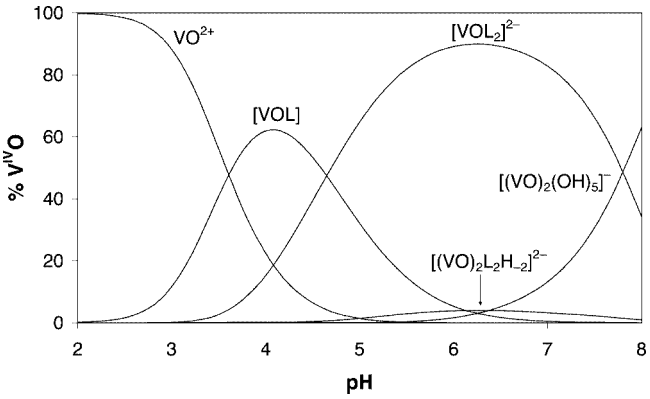


Figure 2. Species distribution for the $V^{IV}O$/5-OHpzc system with a metal/ligand molar ratio of 1:3 and a $V^{IV}O$ concentration of 1 mM.

The $g_\parallel$ and $A_\parallel$ values (Table 2) of the mono(chelated) complexes VOL (**I** in Figure 3) are consistent with the donor set (N_{pyr}, COO^-).[14b] By applying the additivity rule of Chasteen,[22] corrected for carboxylate by Kiss and Costa Pessoa,[23] a value of about 174×10^{-4} cm^{-1} is predicted for $A_\parallel$.

In the range of existence of the bis(chelated) complexes, the EPR spectra show two partly overlapped resonances, indicating the presence of the *cis* and *trans* isomers (**II** and **III** in Figure 3). The $A_\parallel$ value of the *trans* species (Table 2) is similar to that measured with 4-imidazoleacetic acid[14a] and corresponds to an [(N_{pyr}, COO^-); (N_{pyr}, COO^-); H_2O^{ax}] set, with a water molecule weakly coordinated in the axial position (see Scheme 1a).

Two different arrangements of the two ligand molecules are possible for the *cis* species (Scheme 1b and c): one with two aromatic nitrogen atoms and one carboxylate oxygen atom, and another with one aromatic nitrogen atom and two carboxylate oxygen atoms in the equatorial plane of the vanadyl ion. The additivity rule assigns to an aromatic nitrogen atom a lower contribution to the parallel hyperfine coupling constant (40.7×10^{-4} cm^{-1})[22] in comparison with

Table 2. EPR parameters and donor sets for the $V^{IV}O$ complexes in aqueous solution.

Ligand	Complex	$g_\parallel$	$A_\parallel$[a]	D[b]	Donor set
pzc	VOL	1.938	174		[(N_{pyr}, COO^-); H_2O; H_2O; H_2O^{ax}]
	cis-VOL_2	1.943	170		[(N_{pyr}, COO^-); (N_{pyr}, COO^{-ax}); H_2O]
	trans-VOL_2	1.945	164		[(N_{pyr}, COO^-); (N_{pyr}, COO^-); H_2O^{ax}]
	$(VO)_2L_2H_{-2}$	1.968	85	0.0603	[(N_{pyr}, COO^-); H_2O; OH^-; OH^{-ax}]
5-Mepzc	VOL	1.938	173		[(N_{pyr}, COO^-); H_2O; H_2O; H_2O^{ax}]
	cis-VOL_2	1.942	169		[(N_{pyr}, COO^-); (N_{pyr}, COO^{-ax}); H_2O]
	trans-VOL_2	1.945	163		[(N_{pyr}, COO^-); (N_{pyr}, COO^-); H_2O^{ax}]
	$(VO)_2L_2H_{-2}$	1.967	85	0.0607	[(N_{pyr}, COO^-); H_2O; OH^-; OH^{-ax}]
3-COOHpzc	VOL	1.938	174		[(N_{pyr}, COO^-); H_2O; H_2O; H_2O^{ax}]
	cis-VOL_2	1.943	168		[(N_{pyr}, COO^-); (N_{pyr}, COO^{-ax}); H_2O]
	trans-VOL_2	1.945	163		[(N_{pyr}, COO^-); (N_{pyr}, COO^-); H_2O^{ax}]
	$(VO)_2L_2H_{-2}$	1.965	86	0.0608	[(N_{pyr}, COO^-); H_2O; OH^-; OH^{-ax}]
5-OHpzc	VOL	1.937	173		[(N_{pyr}, COO^-); H_2O; H_2O; H_2O^{ax}]
	cis-VOL_2	1.944	168		[(N_{pyr}, COO^-); (N_{pyr}, COO^{-ax}); H_2O]
	trans-VOL_2	1.946	163		[(N_{pyr}, COO^-); (N_{pyr}, COO^-); H_2O^{ax}]
	$(VO)_2L_2H_{-2}$	1.965	86	0.0601	[(N_{pyr}, COO^-); H_2O; OH^-; OH^{-ax}]

[a] $A_\parallel$ measured in 10^{-4} cm^{-1} units. [b] D measured in cm^{-1} units.

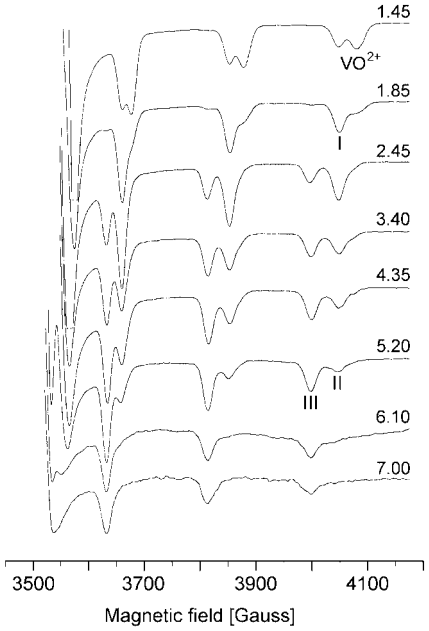


Figure 3. High-field region of the X-band anisotropic EPR spectra recorded at 140 K as a function of pH on an aqueous solution of $V^{IV}O$ and 5-Mepzc with a metal/ligand molar ratio of 1:5 and a $V^{IV}O$ concentration of 4 mM. **I**, **II** and **III** denote VOL, *cis*-VOL_2 and *trans*-VOL_2 complexes.

a carboxylate oxygen atom (42.1×10^{-4} cm^{-1}).[23] Therefore, a lower value of $A_{\parallel}$ is expected for the set [(N_{pyr}, COO^{-}); (N_{pyr}, COO^{-ax}); H_2O] than for [N_{pyr}, COO^{-}); (N_{pyr}^{ax}, COO^{-}); H_2O]. The experimental data are in agreement with the first possibility. This is in agreement with the structures in the solid state formed by 5-methoxycarbonylpicolinic acid (5MeOpicH), *cis*-[$V^{IV}O(5MeOpic)_2(H_2O)$],[14e] and by 4,5-dicarboxy-1-methylimidazole (H_2MDCI), *cis*-[$V^{IV}O(HMDCI)_2(H_2O)$].[24] They have two aromatic nitrogen atoms in the equatorial plane and $A_{\parallel}$ values of 168 and 171×10^{-4} cm^{-1}, comparable with those measured in this study for the *cis* isomers.

As an example, the anisotropic EPR spectra of the system with 5-Mepzc as a function of pH are presented in Figure 3.

At pH ≈ 7, the potentiometric titrations show a deprotonation process. The fitting of the data is improved considerably by the insertion of a $(VO)_2L_2H_{-2}$ species into the model. This suggests that the hydrolytic processes transform VOL_2 complexes into the di-μ-hydroxo $(VO)_2L_2H_{-2}$ dimers, according to the principle established by Felcman and Fraústo da Silva.[25] Differently from the usual behaviour of the $V^{IV}O$ systems, a ferromagnetic interaction between the two $S = 1/2$ ions is observed with a distinctive EPR signal superimposed to the resonances of VOL_2. A forbidden signal at half field (ca. 1650 G) in the $\Delta M = \pm2$ region is also detected (see Discussion). The spectra recorded on an equimolar solution of $V^{IV}O$ and pzc, in both the $\Delta M = \pm1$ and $\Delta M = \pm2$ regions, are shown in Figures 4 and 5.

The possible configurations of a $[VO(\mu\text{-}OH)_2VO]^{2+}$ core in complexes consisting of two edge-sharing octahedrally coordinated $V^{IV}O$ ions are classified according to the orien-

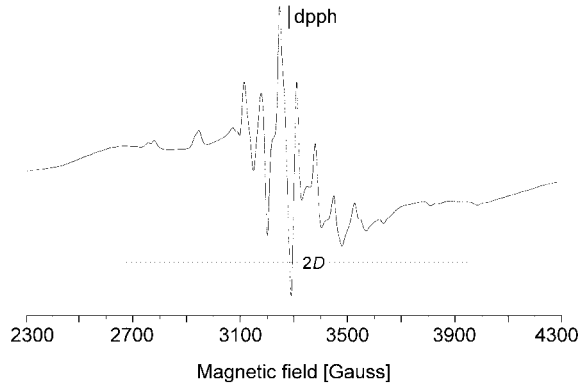


Figure 4. $\Delta M = \pm1$ region of the X-band anisotropic EPR spectrum recorded at 140 K and pH = 5.65 on an equimolar aqueous solution of $V^{IV}O$ and pzc with a concentration of 5×10^{-2} M.

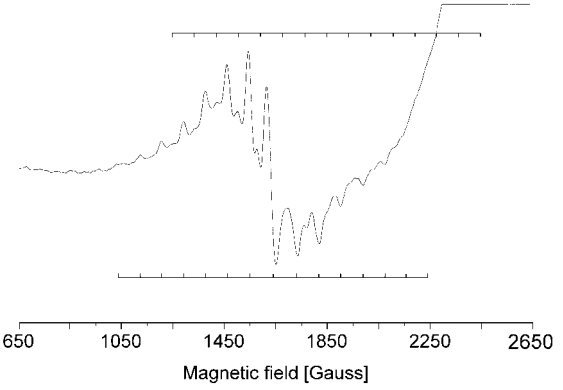
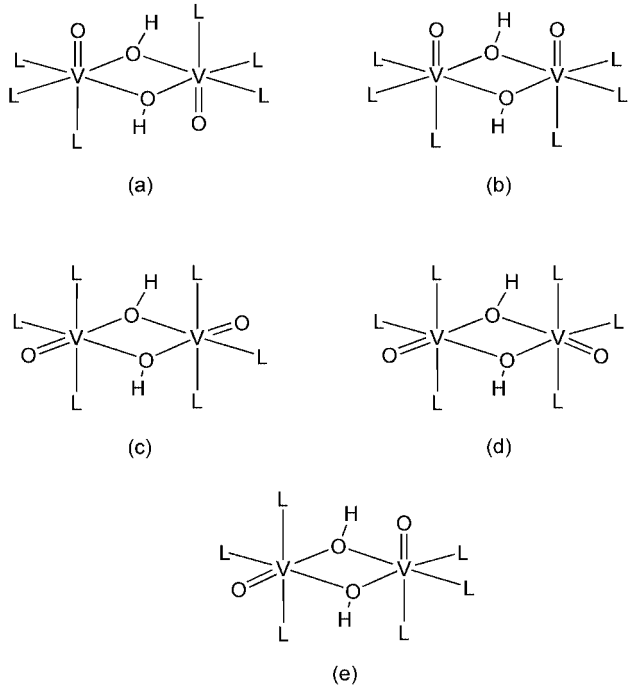


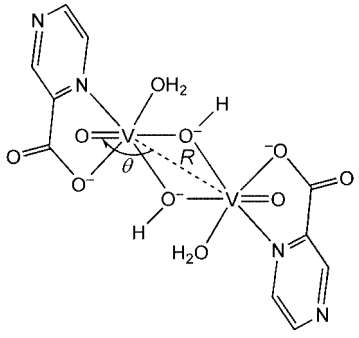
Figure 5. $\Delta M = \pm2$ region of the X-band anisotropic EPR spectrum recorded at 140 K and pH = 5.65 on an equimolar aqueous solution of $V^{IV}O$ and pzc with a concentration of 5×10^{-2} M.



Scheme 4. Possible arrangements of the $[VO(\mu\text{-}OH)_2VO]^{2+}$ core: (a) *anti*-orthogonal, (b) *syn*-orthogonal, (c) *anti*-coplanar, (d) *syn*-coplanar, and (e) twisted.

tation of the V=O group with respect to the plane defined by the two vanadium atoms and the two bridging oxygen atoms (orthogonal, coplanar and twisted) and the orientation of the two V=O bonds (*syn* or *anti*) (Scheme 4).[26]

The magnitude of the coupling constant in the $\Delta M = \pm 2$ region is nearly half of that expected for $A_{\parallel}$ in the monomeric species with the same equatorial donors. Values of about 84×10^{-4} cm^{-1} for the set [(N_{pyr}, COO^-); H_2O; OH^-] (*anti*-coplanar arrangement) and of about 80×10^{-4} cm^{-1} for [(N_{pyr}, COO^-); OH^-; OH^-] (*anti*- or *syn*-orthogonal arrangement) are expected. The experimental values, in the range $85–86 \times 10^{-4}$ cm^{-1} (Table 2), are consistent with the structure depicted in Scheme 5, where two OH^- ions bridge two metal ions in one equatorial and one axial position, with the remaining three equatorial sites occupied by the (N_{pyr}, COO^-) set and a H_2O molecule in an *anti*-coplanar arrangement.



Scheme 5. Structure of the dimeric complex $(VO)_2L_2H_{-2}$ formed by pzc. *R* is the distance between the two $V^{IV}O$ ions and θ the angle formed by the V=O and V–V directions.

Studies on the Solid Compounds

The solid compounds **1**, **2** and **3** were characterised by thermogravimetric, elemental, FT-IR and EPR analyses. Attempts to obtain solid compounds with reproducible stoichiometry with 5-OHpzc were unsuccessful.

Thermogravimetric and elemental analyses indicate a [VOL_2] composition for 5-Mepzc, and a [$VOL_2(H_2O)$] stoichiometry for pzc and 3-COOHpzc. The presence of a water molecule strongly bound to the metal ion in **2** and **3** is supported by the decomposition step at > 150 °C to yield the five-coordinate species [$VO(pzc)_2$] and [$VO(3\text{-}COOHpzc)_2$]. This temperature value is typical of vanadyl complexes containing equatorially coordinated water.[14e] On the contrary, the thermogravimetric analysis of **1** indicates the absence of water and the decomposition of the complex starts above 300 °C.

IR spectroscopy shows the presence of water in **2** and **3** and its absence in **1**. The V=O stretching frequency is normal for $V^{IV}O$ complexes. The separation between the asymmetrical (ν_{as}) and symmetrical (ν_s) stretching vibrations of the carboxylate group, $\Delta(\nu_{as} - \nu_s)$, for complexes **1**, **2** and **3**, in the range 212–243 cm^{-1}, suggests a monodentate coordination to the $V^{IV}O$ ion and allows a bridging behaviour to be ruled out.[27] In compound **3** the band at 1729 cm^{-1} indicates that the carboxylic group in position 3 of the aromatic ring is protonated (Table 3).

The solid compounds **1**–**3** were dissolved in an anhydrous weakly coordinating solvent (CH_3OH) or in a mixture of non-coordinating solvent ($CHCl_3$/toluene, 60:40, v:v) in order to study the geometry and the coordination mode of the ligands through EPR spectroscopy (Figure 6). Anisotropic spectra exhibit an axial symmetry with two *g* and two *A* values (Table 4). No traces of mono(chelated) or dimeric complexes are observed.

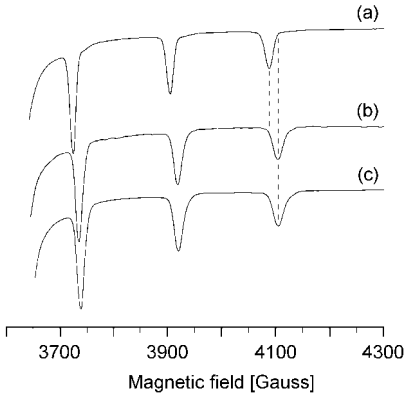


Figure 6. High-field region of the X-band anisotropic EPR spectra recorded at 140 K in CH_3OH. (a) [$VO(5\text{-}Mepzc)_2$] (**1**); (b) *cis*-[$VO(pzc)_2(H_2O)$] (**2**); and (c) *cis*-[$VO(3\text{-}COOHpzc)_2(H_2O)$] (**3**).

Table 4. EPR parameters of complexes **1**–**3** in CH_3OH.

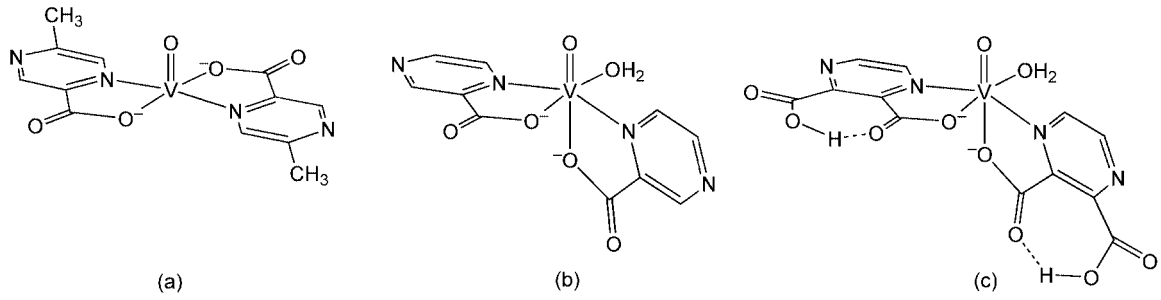
Complex	$g_{\parallel}$	$A_{\parallel}$[a]	$g_{\perp}$	$A_{\perp}$[a]
[$VO(5\text{-}Mepzc)_2$] (**1**)	1.947	163	1.982	59
cis-[$VO(pzc)_2(H_2O)$] (**2**)	1.944	168	1.985	60
cis-[$VO(3\text{-}COOHpzc)_2(H_2O)$] (**3**)	1.944	168	1.986	60

[a] $A_{\parallel}$ and $A_{\perp}$ measured in 10^{-4} cm^{-1} units.

Table 3. Selected IR parameters of the ligands and complexes **1**–**3**.[a]

Ligand/complex	ν_{as}(COOH)	ν_{as}(COO^-)	ν_s(COOH)	ν_s(COO^-)	$\Delta(\nu_{as} - \nu_s)$	ν(V=O)
5-Mepzc	1731 vs		1654 sh			
[$VO(5\text{-}Mepzc)_2$] (**1**)		1630 vs		1418 s	212	986 vs
pzc	1713 vs		1670 s			
cis-[$VO(pzc)_2(H_2O)$] (**2**)		1629 vs		1393 vs	236	984 vs
3-COOHpzc	1714 vs		1689 vs			
cis-[$VO(3\text{-}COOHpzc)_2(H_2O)$] (**3**)	1729 s	1632 vs		1389 s	243	986 vs

[a] ν and Δ values measured in cm^{-1}.



Scheme 6. Structure of the solid complexes **1** (a), **2** (b) and **3** (c).

The $A_{\parallel}$ value measured for the methyl derivative **1** is 163×10^{-4} cm^{-1}, indicative of an equatorial [(N_{pyr}, COO^-); (N_{pyr}, COO^-)] coordination mode. The value is comparable with those reported for [$V^{IV}O$(8-quinolinecarboxylato)$_2$] in a CH_2Cl_2/toluene mixture (161×10^{-4} cm^{-1})[14d] and for $V^{IV}O$-doped [$Ti^{IV}O$(8-quinolinecarboxylato)$_2$] (161×10^{-4} cm^{-1}).[14d] For the analogous complex formed by 2-pyridylacetate a value of 162×10^{-4} cm^{-1} was measured.[28] The coincidence of A_x and A_y values allows a distortion of the pentacoordinate square-pyramidal structure towards the trigonal bipyramid to be ruled out.[29]

The spectra of **2** and **3** are characterised by a larger hyperfine coupling constant (168×10^{-4} cm^{-1}) than for **1** (Table 4), because of the presence of weaker donors in the equatorial plane of the vanadyl ion. This clearly indicates that water replaces one of the two equatorially bound carboxylate ions, increasing the value of $A_{\parallel}$ by about 4×10^{-4} cm^{-1},[22,30] and that one ligand molecule switches its coordination mode from an (equatorial–equatorial) to an (equatorial–axial) arrangement. In the absence of single-crystal X-ray determinations, the three structures shown in Scheme 6 can be proposed.

The carboxylic group in position 3 of the pyrazine aromatic ring in **3** is protonated, similarly to the results obtained with the bis(chelated) complexes of Co^{II}[31] and Ni^{II}.[32,33] The structure is stabilised by an intramolecular hydrogen bond between the protonated carboxylic group and the coordinating deprotonated carboxylate ion in position 2 of the aromatic ring (Scheme 6). An analogous hydrogen bond is exhibited by *cis*-[$V^{IV}O$(HMDCI)$_2$(H_2O)],[24] formed by 4,5-dicarboxy-1-methylimidazole (H_2MDCI) similar to 3-COOHpzc. A further stabilisation of **2** and **3** could be provided by a network of intermolecular hydrogen bonds between the coordinated water molecules, as happens with the Co^{II} ion.[31]

Discussion

Stability of the *cis* and *trans* Isomers of Bis(chelated) $V^{IV}O$ Complexes

Few $V^{IV}O$ compounds with ($N_{aromatic}$, COO^-) coordination are known compared to those with (N_{imino}, O^-) coordination. A search in the Cambridge Structural Database[34] for monomeric vanadyl complexes formed by bidentate ligands with N,O donors yields 22 structures; among them, 18 do not exhibit water molecules coordinated to the $V^{IV}O$ ion and show a square-pyramidal geometry. Six-membered chelate rings characterise all the structures except [$V^{IV}O$(2-methyl-5-methylthio-8-hydroxyquinolato)$_2$],[35] [$V^{IV}O${2-[(–)-(1*S*,2*S*,5*R*)-menthylpyridine}$_2$][36] and [$V^{IV}O$(2-methyl-8-quinolinolato)$_2$].[37]

Rather surprisingly, the only four structures with the ($N_{aromatic}$, COO^-) donor set exhibit a water molecule bound to the $V^{IV}O$ ion. Two are characterised by a *cis* arrangement of the H_2O molecule with respect to the V=O bond: *cis*-[$V^{IV}O$(5-methoxycarbonylpicolinato)$_2$(H_2O)][14e] and *cis*-[$V^{IV}O$(1-methyl-4,5-dicarboxyimidazolato)$_2$(H_2O)].[24] In the other two, *trans*-[$V^{IV}O$(6-ethylpicolinato)$_2$(H_2O)][38] and *trans*-[$V^{IV}O$(2-quinolinecarboxylato)$_2$(H_2O)],[39] H_2O is *trans* to the V=O bond. This indicates that the ($N_{aromatic}$, COO^-) set favours the binding of water, probably for the high polarity of the carboxylate group, which makes the solvation of the complexes easier. In addition, other binary structures with the ($N_{aromatic}$, COO^-) donor set have been fully characterised in the solid state without single-crystal X-ray determination.[9,10,14c,14d,40–42]

Finally, three mixed complexes, in which one of the two bidentate donor sets is ($N_{aromatic}$, COO^-), have been described. One of them is *cis*-[VO(Hhpic-O,O)(Hhpic-O,N)(H_2O)], with H_2hpic = 3-hydroxy-2-pyridinecarboxylic acid,[43] where one of the two $Hhpic^-$ anions coordinates the vanadyl ion through the phenolate and carboxylate groups in the equatorial plane and the other one through the carboxylate group in *trans* position and the pyridine nitrogen atom in *cis* position with respect to the V=O bond, whereas the remaining equatorial site is occupied by a water molecule. The other two complexes are [$V^{IV}O$(dipic)(HDMCI)]$^-$ and *cis*-[$V^{IV}O$(acac)(HDMCI)(H_2O)], with H_2dipic = 2,6-pyridinedicarboxylic acid and Hacac = 2,4-pentanedione.[24] These last three examples highlight the preference of the ($N_{aromatic}$, COO^-) donor set to assume an orientation *cis* with respect to the V=O bond, with the aromatic nitrogen atom in the equatorial plane and the carboxylate oxygen atom in the axial position.

It is worth noting that the *cis* complexes are formed with more hydrophilic ligands (5-methoxycarbonylpicolinate,[14e] 4,5-dicarboxy-1-methylimidazolate,[24] picolinate,[9,14b,40] 3-hydroxy-2-pyridinecarboxylate[43]), whereas the *trans* structures are favoured by more hydrophobic ligands (6-methylpicolinate,[10,14c,41] 8-hydroxy-2-methylquinoline,[37] 6-ethylpicolinate[38]) and six-membered chelate rings (8-quinoline-

carboxylate,[14d] 2-pyridylacetate[28]). The results are confirmed by this study: the hydrophobic 5-methyl derivative forms the anhydrous pentacoordinate complex **1**, whereas the more hydrophilic pzc and 3-COOHpzc ligands form the *cis* complexes **2** and **3** with a water molecule coordinated in the equatorial plane of the $V^{IV}O$ ion.

The preference of a ligand for the *trans* or *cis* arrangement is not easily predictable. For instance, picolinate forms only the *cis* complex,[14b] 6-methylpicolinate the *trans* and *cis* isomers in comparable amounts,[14c] and 2-pyridylacetate only the *trans* species.[28] Generally, stronger ligands and six-membered chelate rings favour the *trans* isomer, as demonstrated by the comparison of carboxylates, pyrones and catechols,[44,45] and of oxalate and malonate[44] or picolinate[14b] and 2-pyridylacetate.[28]

For the four systems considered in this work, the amount of the *cis* isomer (**I** in Figure 7) increases in the order: 5-Mepzc < pzc < 5-OHpzc < 3-COOHpzc. With ligands yielding the same size and steric hindrance of the chelate ring, the order of stability does not follow the basicity of the donors, but the relative amount of the two isomers depends on the hydrophilicity of the species; in particular, the hydrophilicity of the complexes favours the *cis* isomer. Indeed, the *cis* arrangements are mainly formed by the two more hydrophilic ligands, 3-COOHpzc and 5-OHpzc, whereas the most hydrophobic, 5-Mepzc, gives almost exclusively the *trans* structure (Figure 7). The hydrophobicity of the complex hinders the approach and the coordination of a water molecule to the $V^{IV}O$ ion and, therefore, the formation of the *cis* complex: for instance, picolinate forms only the *cis* isomer,[14b] whereas the less hydrophilic 6-methyl derivative forms both the *trans* and *cis* complexes.[14c]

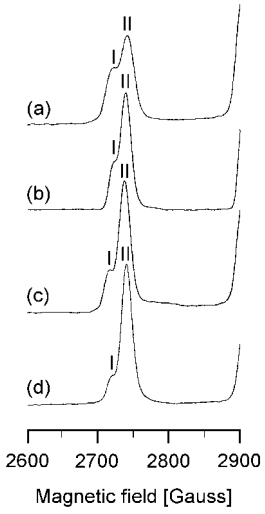


Figure 7. Low-field region of the X-band anisotropic EPR spectra of the bis(chelated) complexes formed by pzc, 5-Mepzc, 3-COOHpzc and 5-OHpzc recorded on aqueous solutions at 140 K with a $V^{IV}O$ concentration of 4 mM. (a) 3-COOHpzc, L/M = 10, pH = 5.05; (b) 5-OHpzc, L/M = 2, pH = 5.25; (c) pzc, L/M = 10, pH = 4.35; (d) 5-Mepzc, L/M = 5, pH = 5.00. **I** and **II** denote *cis*-VOL_2 and *trans*-VOL_2 complexes.

Magnetic Properties of the Hydroxo-Bridged $V^{IV}O$ Dimeric Complexes

A qualitative interpretation of the magnetic interactions in transition-metal dimers is given by the Goodenough–Kanamori rules,[46] based on the interactions between pairs of magnetic orbitals (the unpaired electron for $V^{IV}O$ generally resides in the d_{xy} orbital). The magnetic interaction of two ions with spin S_1 and S_2 is described by the Heisenberg Hamiltonian $\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2$, where J is the exchange coupling constant. If $S = 1/2$, as for $V^{IV}O$ dimers, the energy difference between the triplet ($S = 1$) and the singlet ($S = 0$) spin states is about J. Thus, if the J value is positive, the triplet state is more stable than the singlet one, the interaction is ferromagnetic and an EPR spectrum can be detected; in the opposite case, the singlet state is more stable, the interaction is antiferromagnetic and no EPR signal is observed. Plass demonstrated that for the two orthogonal configurations of the $[VO(\mu\text{-}OH)_2VO]^{2+}$ core (Scheme 4) either a direct interaction or a superexchange mechanism between the magnetic orbitals can be expected to be operative, yielding rather strong antiferromagnetic coupling.[26] However, the configuration of the core, the nature of the terminal ligands and the structural distortions can influence the exchange coupling constant.[47,48] It has been found that for certain combinations of the V–O–V angle and V···V distance, the value of J can become positive.[48]

In order to find examples of magnetic coupling between two $V^{IV}O$ ions in the literature, two searches have been performed on the Cambridge Structural Database.[34] The first, on the dimeric $[VO(\mu\text{-}OH)_2VO]^{2+}$ core, yielded six structures, four with an *anti*-orthogonal,[49] one with a *syn*-orthogonal[50] and one with a *syn*-coplanar arrangement.[51] All show antiferromagnetic behaviour with $-J$ values in the range 6–177 cm^{-1}. The second search, on the $[VO(\mu_2\text{-}OR)_2VO]^{2+}$ core, yielded 31 structures, 15 with an *anti*-orthogonal,[52] 10 with a *syn*-orthogonal,[53] 5 with an *anti*-coplanar[26,53j,54] and 1 with a twisted configuration.[26] Magnetic measurements are reported for 15 of them. The four structures with an *anti*-orthogonal and the seven with a *syn*-orthogonal arrangement show antiferromagnetic coupling with $-J$ values in the range 6–212 cm^{-1}. On the other hand, the six structures with an *anti*-coplanar and a twisted configuration display ferromagnetic coupling with J values in the range 3–56 cm^{-1}. This confirms the suggestions of Plass that for edge-shared dinuclear units, only the relative orientation of the vanadyl groups is necessary to qualitatively predict their magnetic behaviour in terms of antiferro- (*anti*- and *syn*-orthogonal and *syn*-coplanar) or ferromagnetic interactions (*anti*-coplanar and twisted) between the metal centres.[26]

A ferromagnetic interaction leads to a detectable EPR signal. For a system with tetragonal symmetry the anisotropic EPR spectrum consists of four bands, whose separation depends on the molecular interactions. The external lines, corresponding to the V=O orientation parallel to the magnetic field direction, are separated by $2D$, whereas the internal lines corresponding to the perpendicular orienta-

tion are separated by D, where D is the zero-field splitting. In the case of weak paramagnetic interaction the zero-field splitting has contributions of only dipolar origin and can be correlated to the distance between the two vanadium interacting centres (R) and to the angle formed by the V=O and V–V directions (θ) through the Stevens equation (1):[55]

$$D = 0.325 g^2 \frac{\left|1 - 3\cos^2\theta\right|}{R^3} \quad (1)$$

with D in cm^{-1} and R in Å. Usually two broad transitions in the $\Delta M = \pm 1$ region centred at $g \approx 2$ and a well-resolved ^{51}V hyperfine structure in the $\Delta M = \pm 2$ region at $g \approx 4$ are detectable.[56] If the symmetry of the complex is axial, two sets of 15 lines, partially overlapping, are observed in the forbidden $\Delta M = \pm 2$ region, with the magnitude of the coupling constant nearly half of that expected for $A_{\parallel}$ in the monomeric species with the same equatorial donors (Figure 5).

All four $(VO)_2L_2H_{-2}$ complexes formed by pzc, 5-Mepzc, 3-COOHpzc and 5-OHpzc exhibit a separation of the parallel components ($2D$) in the range 1312–1328 G between the high-field resonance at about 3990 G and the low-field resonance at about 2670 G, corresponding to a D value of about 660 G or 0.06 cm^{-1} (Table 2). In the literature, no agreement exists on the attribution of these transitions to the perpendicular or parallel components of the ***D*** tensor. In Figure 8, the D value derived from the Stevens equation is represented as a function of the θ angle for five R distances; the g value has been approximated to 2. For five of the six di-μ-hydroxo-bridged $V^{IV}O$ compounds reported in the literature, R is in the range 2.965–3.122 Å;[49,50] only the sixth compound is characterised by a higher value (3.45 Å), but this is due to the presence of a μ_2-squarato-O,O' bridging ligand, which keeps the metal ions distant.[51] Therefore, we believe that an estimate of about 2.9–3.1 Å for R is reasonable also for 2-pyrazinecarboxylic acid and its derivatives. For $R > 2.9$ Å, values higher than 0.11 cm^{-1} should result in $\cos^2\theta > 1$ and are not to be expected for D (Figure 8). This is a very important conclusion because it demonstrates that the separation measured on the experimental EPR spectrum cannot be attributed to the perpendicular components of the ***D*** tensor, to which a value of about 1320 G or 0.12 cm^{-1} would correspond.

From Figure 8 it is worth noting that if $D \approx 0.06$ cm^{-1} and R = 2.9–3.1 Å, only the angles in the range 27.2–32.7 and 147.3–152.8° satisfy the Stevens equation. These values are consistent with an *anti*-coplanar arrangement of the two $V^{IV}O$ ions (angles of 130.7 and 132.8° for the two *anti*-coplanar complexes $[\{V^{IV}O(Hsabhea)\}_2]\cdot 2CH_3OH$ and $[\{V^{IV}O(Hsabhea)\}_2]\cdot CH_3OH$, with H_3sabhea = *N*-salicylidene{2-[bis(2-hydroxyethyl)amino]ethyl}amine, were reported[26]), but not with an *anti*- or a *syn*-orthogonal configuration, for which much lower values of θ are expected (θ is in the range 101.0–111.4° for the five di-μ-hydroxo structures in the literature[49,50]).

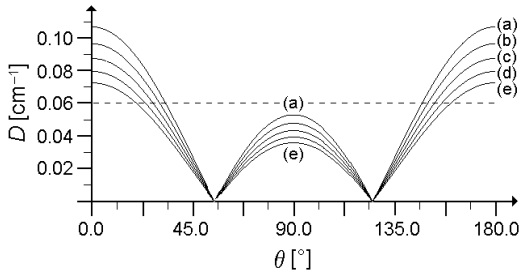


Figure 8. D value derived from the Stevens equation as a function of the θ angle: (a) R = 2.9 Å; (b) R = 3.0 Å; (c) R = 3.1 Å; (d) R = 3.2 Å; and (e) R = 3.3 Å. The g value has been approximated to 2.

In conclusion, an *anti*-coplanar arrangement with an aromatic nitrogen atom and a carboxylate oxygen atom, one water molecule and an OH^- ion in the equatorial plane and a second OH^- ion of another unit in the axial position of each $V^{IV}O$ ion is realised for the $(VO)_2L_2H_{-2}$ species formed by pzc, 5-Mepzc, 3-COOHpzc and 5-OHpzc (Scheme 5). These findings are supported by recent results[28] with hyphetri-COOH {4-[3,5-bis(2-hydroxyphenyl)-1,2,4-triazol-1-yl]benzoic acid} and hyphetri-SO_3H {4-[3,5-bis(2-hydroxyphenyl)-1,2,4-triazol-1-yl]benzenesulfonic acid}.[57] In weakly acidic aqueous solutions, they give $\Delta M = \pm 1$ (at $g \approx 2$) and $\Delta M = \pm 2$ (at $g \approx 4$) EPR signals analogous to those of pzc and its derivatives. Because they are tridentate chelating ligands, which occupy three equatorial positions of the $V^{IV}O$ ion with the donor set ($O^-_{aromatic}$, $N_{aromatic}$, $O^-_{aromatic}$), they enforce the formation of an *anti*-coplanar arrangement for the corresponding $(VO)_2L_2H_{-2}$ species with the two bridging OH^- ions in *cis* and *trans* positions with respect to the V=O bond.

Conclusions

2-Pyrazinecarboxylic acid and three of its derivatives (5-methyl-2-pyrazinecarboxylic, 2,3-pyrazinedicarboxylic and 5-hydroxy-2-pyrazinecarboxylic acids) coordinate the $V^{IV}O$ ion forming VOL, VOL_2 and $(VO)_2L_2H_{-2}$ species in acidic and neutral solutions. Bis(chelated) species are hexacoordinate and are characterised by a *cis*/*trans* isomerism, with the *trans* arrangement favoured with respect to the *cis* one. The application of the additivity rule[22] allows identification of the donors coordinated in the equatorial plane of the $V^{IV}O$ ion. The relative stability of the two isomers in aqueous solution is influenced by a number of factors, like the ligand bite, the size of the chelate ring, the basicity and the steric requirements of the ligands. Generally, large ligand bites, six-membered chelate rings and strong ligands favour the *trans* isomer.[44,45] However, these rules are only effective if applied to ligands with different bite, basicity and size of the chelate ring. Instead, if ligands of the same series are compared, like those derived from 2-pyrazinecarboxylic acid (same size of the chelate ring, comparable ligand bite and basicity), the hydrophilicity of the complexes becomes determinant. This conclusion is supported by the

solid-state structures because the hydrophobic 5-methyl derivative forms the pentacoordinate *trans* complex **1**, whereas the more hydrophilic pzc and 3-COOHpzc form the hexacoordinate *cis* compounds **2** and **3**, with a water molecule in the equatorial plane of the $V^{IV}O$ ion. The hydrophilicity, because of the presence of the polar carboxylate group, explains the reason why the only four monomeric $V^{IV}O$ complexes with a water molecule coordinated, among 22 structures found formed by bidentate ligands with an N,O coordination,[34] are characterised by an ($N_{aromatic}$, COO^-) donor set.

In weakly acidic solutions a $(VO)_2L_2H_{-2}$ species is detected by EPR spectroscopy and potentiometry. The rule established by Felcman and Fraústo da Silva suggests that the hydrolysis of a mono(chelated) $V^{IV}O$ complex with two adjacent equatorial sites occupied by water molecules gives a di-μ-hydroxo-bridged dimer,[25] but there are different possibilities for their geometrical arrangement (Scheme 4). Usually, these species are EPR-silent, as proved in several cases, for example with picolinic[14b] and 6-methylpicolinic acids.[14c] Plass demonstrated that an *anti*- and a *syn*-orthogonal configuration results in an antiferromagnetic coupling, whereas an *anti*-coplanar and a twisted arrangement give rise to a ferromagnetic coupling.[26] An *anti*-coplanar configuration for a ferromagnetically coupled $V^{IV}O$ complex can also be predicted through the Stevens equation.[55] Moreover, an analysis of this equation suggests that the signals present in the $\Delta M = \pm 1$ region of the EPR spectrum belong to the parallel components of the ***D*** tensor. These findings are supported by the value of the coupling constant in the $\Delta M = \pm 2$ region, which must be half of that expected for $A_{\parallel}$ in the monomeric species with the same equatorial donors. In this case, it allows the set [(N_{pyr}, COO^-); H_2O; OH^-], expected for an *anti*-coplanar arrangement, to be distinguished from [(N_{pyr}, COO^-); OH^-; OH^-], characteristic of an *anti*- or *syn*-orthogonal configuration. In conclusion, the theoretical and experimental results, compared with the data in the literature, suggest an *anti*-coplanar configuration for $(VO)_2L_2H_{-2}$ species, with two bridging OH^- ions in the equatorial and axial positions and the (N_{pyr}, COO^-) set and an H_2O molecule completing the coordination sphere of the $V^{IV}O$ ion (Scheme 5).

At the moment, the factors that favour the *anti*-coplanar configuration with respect to the *anti*- or *syn*-orthogonal are not clear to us. Although for bidentate ligands the simplest and more common *anti*- or *syn*-orthogonal arrangements of the $[VO(\mu\text{-}OH)_2VO]^{2+}$ core should be expected, this is not the case for 2-pyrazinecarboxylic acid and its derivatives. So, one of the next challenges in the chemistry of the $V^{IV}O$ ion is to try to understand the factors that stabilise each of the five configurations of the $[VO(\mu\text{-}OH)_2VO]^{2+}$ core and determine the ferromagnetic or antiferromagnetic coupling.

Experimental Section

Chemicals: All the ligands were Aldrich or Fluka products of puriss. quality. Their purity and their concentration in solution were determined by the Gran method.[58] $V^{IV}O$ solutions were prepared according to a procedure described in the literature.[59] All operations were performed under purified argon in order to avoid oxidation of the $V^{IV}O$ ion.

Potentiometric Measurements: The protonation constants of the ligands ($\log K$) and the stability constants of the $V^{IV}O$ complexes were determined by pH-potentiometric titrations of 2.0-mL samples. The ligand/metal molar ratio was in the range 1:1–10:1. The concentration of $V^{IV}O$ was 0.001 M. Measurements were carried out at 25 ± 0.1 °C and at a constant ionic strength of 0.1 M KNO_3 with a MOLSPIN pH-meter equipped with a digitally operated syringe (Molspin DSI 0.250 mL) controlled by a computer. The titrations were performed with a carbonate-free NaOH solution of known concentration (about 0.1 M) using a Russel CMAWL/S7 semimicro combined electrode, calibrated for hydrogen ion concentration by the method of Irving et al.[60] The number of experimental points was 100–150 for each titration curve. The reproducibility of the titration points included in the evaluation was within 0.005 pH units in the whole pH range examined (2–10). The stability constants of the complexes, reported as the logarithm of the overall formation constants $\beta_{pqr} = [VO_pL_qH_r]/[VO]^p[L]^q[H]^r$, where VO is the vanadyl ion, L is the deprotonated form of the ligand and H is the proton, were calculated with the aid of the SUPERQUAD program.[61] Standard deviations were calculated by assuming random errors. The conventional notation has been used. Negative indices for H in the formulas indicate either the dissociation of groups that do not deprotonate in the absence of $V^{IV}O$ coordination, or hydroxo ligands. Hydroxo complexes of $V^{IV}O$ were taken into account in the calculations. The following species were assumed: $[VO(OH)]^+$ ($\log\beta_{10-1} = -5.94$), $[(VO)_2(OH)_2]^{2+}$ ($\log\beta_{20-2} = -6.95$), with stability constants calculated from the data of Henry et al.[62] and corrected for the different ionic strengths by use of the Davies equation,[63] $[VO(OH)_3]^-$ ($\log\beta_{10-3} = -18.0$) and $[(VO)_2(OH)_5]^-$ ($\log\beta_{20-5} = -22.0$).[64]

***trans*-[VO(5-Mepzc)$_2$]:** $VOSO_4 \cdot 5H_2O$ (0.1265 g), dissolved in MeOH (5 mL), was added at room temperature to 5-Mepzc (0.1480 g), dissolved in MeOH (5 mL). The resulting solution was stirred at 50 °C. After 1 h, CH_3CN (20–30 mL) was added and the suspension was stirred at room temperature for 1 h. The dark brown solid was filtered under vacuum, washed with diethyl ether and dried under N_2. $C_{12}H_{10}N_4O_5V$ (341.18): calcd. C 42.25, H 2.95, N 16.42, V_2O_5 26.6; found C 41.56, H 3.21, N 16.87, V_2O_5 25.8.

***cis*-[VO(pzc)$_2$(H$_2$O)]:** Pzc (0.1316 g) was dissolved in MeOH (10 mL) by heating at 50 °C. $VOSO_4 \cdot 5H_2O$ (0.1265 g), dissolved in MeOH (5 mL), was added to the ligand. The mixture was stirred at 50 °C for 1 h. Subsequently, acetone (30 mL) was added and the suspension was stirred at room temperature for 1 h. The greenish solid was filtered under vacuum, washed with acetone and diethyl ether and dried under N_2. $C_{10}H_8N_4O_6V$ (331.14): calcd. C 36.27, H 2.43, N 16.92, H_2O 5.4, V_2O_5 27.5; found C 36.73, H 2.65, N 17.02, H_2O 6.0, V_2O_5 28.0.

***cis*-[VO(3-COOHpzc)$_2$(H$_2$O)]:** 3-COOHpzc (0.1480 g) was dissolved in MeOH (10 mL) at room temperature. $VOSO_4 \cdot 5H_2O$ (0.1265 g), dissolved in MeOH (5 mL), was added to the ligand. The solution was stirred at 50 °C for 1 h. Subsequently, diethyl ether (30 mL) was added and the suspension was stirred at room temperature for 1 h. The dark green solid was filtered under vacuum, washed with diethyl ether and dried under N_2. $C_{12}H_8N_4O_{10}V$ (419.16): calcd. C 34.39, H 1.92, N 13.37, H_2O 4.3, V_2O_5 21.7; found C 34.54, H 1.75, N, 13.07, H_2O 5.0, V_2O_5 21.2.

Spectroscopic and Analytical Measurements: Anisotropic EPR spectra were recorded on aqueous solutions with an X-band (9.15 GHz)

Varian E-9 spectrometer in the temperatures range 120–140 K. The spectra were simulated with the computer program Bruker WinEPR SimFonia. Infrared spectra (4000–600 cm^{-1}) were obtained with a JASCO FT-IR 480 Plus interferometer using KBr disks. Elemental analyses (C, H, N) were performed with a Perkin–Elmer 240 B analyser. The thermogravimetric studies, which allowed the determination of the H_2O and V_2O_5 content, were carried out with a Perkin–Elmer TGS-2 instrument under nitrogen.

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[15] In this work the *cis* nomenclature refers to the bis(chelated) complexes in which the two ligand molecules adopt an (equatorial–equatorial) and an (equatorial–axial) arrangement with respect to the V=O bond of the vanadyl ion; *cis* isomers are hexacoordinate with one solvent molecule coordinated in the fourth equatorial position; *trans* isomers are bis(chelated) complexes in which both ligand molecules adopt an (equatorial–equatorial) arrangement with respect to the V=O group; *trans* isomers can be pentacoordinate or hexacoordinate according to the absence or presence of a solvent molecule bound in the axial position.

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