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Potentiometric, Spectroscopic and DFT Study of the $V^{IV}O$ Complexes Formed by Di(pyridin-2-yl) Ligands

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The coordinating properties of a series of di(pyridin-2-yl) derivatives towards the $V^{IV}O^{2+}$ ion have been studied through the combined application of potentiometric and spectroscopic (electronic absorption and EPR spectroscopies) methods. In particular, di(pyridin-2-yl)amine (DPA), di(pyridin-2-yl)methane (DPM), di(pyridin-2-yl) ketone (DPK), di(pyridin-2-yl)methanol (DPMO), 2-acetylpyridine (2-AP) and 2-hydroxymethylpyridine (2-HMP), and two amino acid derivatives of di(pyridin-2-yl)methylamine (DPMA), namely *N*-glycyl-DPMA and *N*-histidyl-DPMA, have been examined. The stability constants of proton and $V^{IV}O$ complexes (logβ) were measured at 25 °C and at a constant ionic strength of 0.2 M (KCl). The results show that the simple di(pyridin-2-yl) derivatives having only pyridine nitrogen atoms form mono-chelated species with the (N_{pyr}, N_{pyr}) donor set, whereas those provided with carbonyl or hydroxy groups form mono- and bis-chelated complexes with (N_{pyr}, CO) or (N_{pyr}, O^-) coordination. The square pyramidal species with $2\times$(N_{pyr}, O^-) coordination exists in equilibrium with the octahedral isomer, which has an axially bound water molecule and is characterized by an anomalously low value of the ^{51}V hyperfine coupling constant along the z-axis (A_z). DFT calculations were used to optimize the geometry of the complexes and to predict the A_z values measured in the EPR spectra for the penta- and hexacoordinate complexes formed by DPK, DPMO, 2-AP and 2-HMP and for the $[VOLH_{-1}]^+$ and $[VOLH_{-2}]$ species formed by the amino acid derivatives of DPMA.

Introduction

Vanadium plays a number of roles in biological systems.[1] It is accumulated by tunicates,[2] *Pseudopotamilla occelata*,[3] and by some species of the mushroom genus *Amanita*.[4] Vanadium is also present in vanadium-dependent haloperoxidases[5] and nitrogenase,[6] and in human organisms it elicits a number of physiological responses, e.g. the inhibition of phosphate-metabolizing enzymes.[7] Moreover, most of its compounds show insulin-enhancing activity.[8]

The presence of vanadium in all these systems suggests its interaction with biomolecules, among which proteins and peptides have a special importance because of their high amount in the cellular environment and their possible interaction with the metal ions through a number of donor groups. The interaction of vanadium with different proteins and enzymes has been reported in the literature.[9]

Oligopeptides are the most closely related models for proteins and they can mimic specific metal ion-binding sites, e.g. GlyGlyHis for serum albumin.[10] Therefore, studies on synthetic models of vanadium–protein interactions can greatly contribute to the knowledge of its biological activity. Oligopeptides can interact with a metal ion through the terminal amino and carboxylate groups, intermediate peptide bonds and side-chain donors, which can play the role of "anchoring groups" and promote the deprotonation of the amide bond and its coordination in the $-N^-$ form.[11] Recently the role of the anchoring groups was studied with $V^{IV}O$ and it was found that phenolate O^-, alcoholate O^-, thiolate S^-, carboxylate COO^-, amino NH_2, and imidazole N are effective in promoting peptide amide deprotonation and coordination.[12,13] Many examples of $V^{IV}O$ complexes containing a V–N^-(amide) bond, both in solution and in the solid state, were characterized over the last years in the literature.[12–14]

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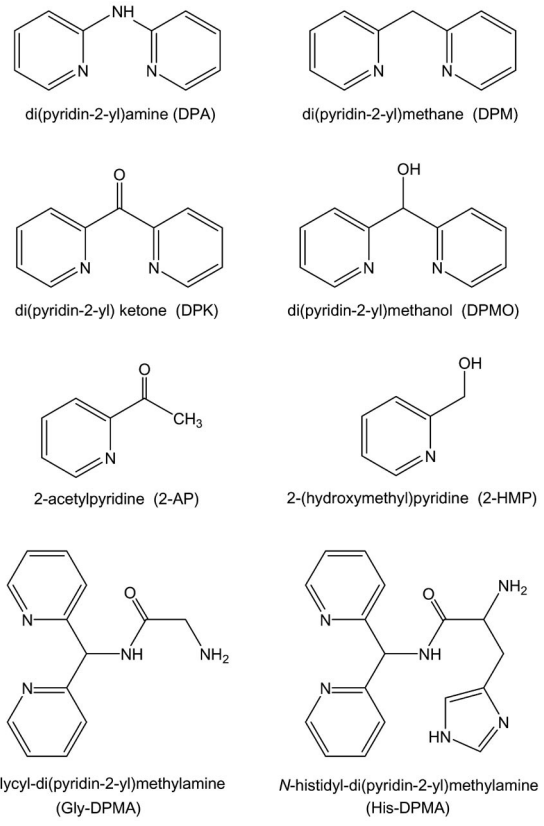
We recently demonstrated that the di(imidazol-2-yl) residue behaves as a good anchoring group, avoiding the hydrolysis and precipitation of vanadium hydroxide and allowing for the coordination of the amide nitrogen-N^-.[15] Pyridine nitrogen is known as a good donor group in vanadium coordination chemistry,[16] and therefore di(pyridin-2-yl) derivatives of amino acids could be good candidates to complex the $V^{IV}O$ ion and promote the coordination of an amide bond. Bis-chelated complexes of di(pyridin-2-yl)-methane have been prepared in the solid state with Cu^{II}, for which X-ray diffraction data shows the binding of four pyridine nitrogen atoms in the equatorial plane.[17] The complexation of Cu^{II}, Ni^{II} and Zn^{II} by *N*-prolyl-di(pyridin-2-yl)methylamine, and of Cu^{II} by *N*-glycyl- and *N*-histidyl-di(pyridin-2-yl)methylamine has been studied in aqueous solution.[18,19]

As a follow-up to our recent results obtained with di(imidazol-2-yl) ligands,[15] in this work we studied the $V^{IV}O$ complexation of two di(pyridin-2-yl) derivatives of amino acids, *N*-glycyl-di(pyridin-2-yl)methylamine (Gly-DPMA) and *N*-histidyl-di(pyridin-2-yl)methylamine (His-DPMA). Di(pyridin-2-yl)amine (DPA), di(pyridin-2-yl)methane (DPM), di(pyridin-2-yl) ketone (DPK), di(pyridin-2-yl)-methanol (DPMO), 2-acetylpyridine (2-AP) and 2-(hydroxymethyl)pyridine (2-HMP) were also studied as models. The structure of the ligands examined is reported in Scheme 1. The study was performed through the combined application of potentiometric and spectroscopic (electronic absorption and EPR spectroscopies) techniques. Density Functional Theory (DFT) calculations were used to obtain information on the structure of $V^{IV}O$ complexes and their EPR properties.



Scheme 1. Ligands.

Results and Discussion

Di(pyridin-2-yl)amine (DPA)

This ligand contains an amino nitrogen connecting the two pyridine rings and shows only the pK_a value of 7.04 attributable to the ammonium nitrogen; the two pyridine nitrogens are very acid and have pK_a < 1 (Table 1). DPA is soluble in an acidic aqueous solution where it exists in the protonated form; its solubility decreases at pH higher than 7 when it is present in the neutral form.

Table 1. Stability constants (logβ) of proton and $V^{IV}O$ complexes for DPA, DPM, DPK, DPMO, 2-AP and 2-HMP at 25.0 ± 0.1 °C and I = 0.20 M (KCl).[a]

Species	DPA	DPM	DPK	DPMO	2-AP	2-HMP
H_2L^{2+}	<8.0	7.72[b]	<3.9	<5.5	–	–
HL^+	7.04(1)	5.11[b]	2.91(3)	4.50(8)	3.02(5)	4.96(1)
pK_a (N_{pyr})	<1	2.61[b]	<1	<1	3.02	4.96
pK_a (N_{pyr})	<1	5.11[b]	2.91	4.50	–	–
pK_a (NH)	7.04	–	–	–	–	–
$[VOL]^{2+}$	5.30(11)	3.73(10)	2.87(7)	4.41(14)	2.07(12)	3.13(3)
$[VOLH_{-1}]^+$	–	–	–	0.84(10)	–	–1.42(22)
$[VOL_2]^{2+}$	10.21(12)	–	–	–	–	–
$[(VO)_2L_2H_{-2}]^{2+}$	–	1.23(14)	–	–	–	–
$[VOL_2H_{-2}]$	–	–	–0.82(5)	0.24(24)	–	–2.13(5)
pK(VOL)[c]	–	–	–	3.57	–	4.55

[a] The uncertainties (σ values) of the protonation and stability constants are given in parentheses. [b] Ref.[19] [c] pK(VOL) = logβ(VOL) – logβ($VOLH_{-1}$).

Potentiometric data indicate the formation of $[VOL]^{2+}$ and $[VOL_2]^{2+}$ (Table 1 and Figure S1 of Supporting Information); they survive until pH 6, whereas in neutral and alkaline solutions the predominant complexes are the hydrolytic products of the $V^{IV}O$ ion.

Anisotropic EPR spectra measured in frozen aqueous solutions with L/M = 5 show the presence of only one species (Table 2 and Figure 1) identified as the mono-chelated complex with two pyridine nitrogen atoms coordinated to the metal ion (Scheme 2). Increasing the pH of the solution results in the precipitation of the ligand and hydrolysis of the metal complex, with contemporary loss of the intensity of the EPR signals. This hinders the detection of the bis complex with 2×(N_{pyr}, N_{pyr}) coordination. In the case of 2,2′-bipyridine, which has the same donors but forms five-membered rather than six-membered rings, bis-chelated species are more stable and characterized by the presence of three nitrogen atoms in the equatorial plane and the fourth in the axial position.[20]

Table 2. EPR parameters of the $V^{IV}O$ complexes formed by DPA, DPM, DPK, DPMO, 2-AP and 2-HMP.[a]

Ligand	Species	g_z	A_z	Donor set
DPA	$[VOL]^{2+}$	1.946	168	$[(N_{pyr}, N_{pyr}); H_2O; H_2O]$
DPM	$[VOL]^{2+}$	1.952	168	$[(N_{pyr}, N_{pyr}); H_2O; H_2O]$
DPK	$[VOL]^{2+}$	1.951	167	$[(N_{pyr}, N_{pyr}); H_2O; H_2O]$
	$[VOL_2H_{-2}]$	1.952	152	$[(N_{pyr}, O^-); (N_{pyr}, O^-)]$
	trans-$[VOL_2{>}H_{-2}(H_2O)]$	1.959	143	$[(N_{pyr}, O^-); (N_{pyr}, O^-); H_2O_{ax}]$[b]
DPMO	$[VOL]^{2+}$	1.951	167	$[(N_{pyr}, N_{pyr}); H_2O; H_2O]$
	$[VOLH_{-1}]^+$	1.944	162	$[(N_{pyr}, O^-); H_2O; H_2O; H_2O_{ax}]$[b]
	$[VOL_2H_{-2}]$	1.954	151	$[(N_{pyr}, O^-); (N_{pyr}, O^-)]$
	trans-$[VOL_2H_{-2}(H_2O)]$	1.958	144	$[(N_{pyr}, O^-); (N_{pyr}, O^-); H_2O_{ax}]$[b]
2-AP	$[VOL]^{2+}$	1.946	173	$[(N_{pyr}, CO); H_2O; H_2O]$
	$[VOL_2]^{2+}$ [c]	1.951	162	$[(N_{pyr}, CO); (N_{pyr}, CO)]$
2-HMP	$[VOL]^{2+}$	1.940	174	$[N_{pyr}; H_2O; H_2O; H_2O]$
	$[VOLH_{-1}]^+$	1.947	163	$(N_{pyr}, O^-); H_2O; H_2O$
	$[VOL_2H_{-2}]$	1.956	152	$[(N_{pyr}, O^-); (N_{pyr}, O^-)]$

[a] A_z measured in 10^{-4} cm^{-1}. [b] Species having a water molecule coordinated in the axial position which causes an anomalous reduction of A_z. [c] Species not characterized by potentiometry.

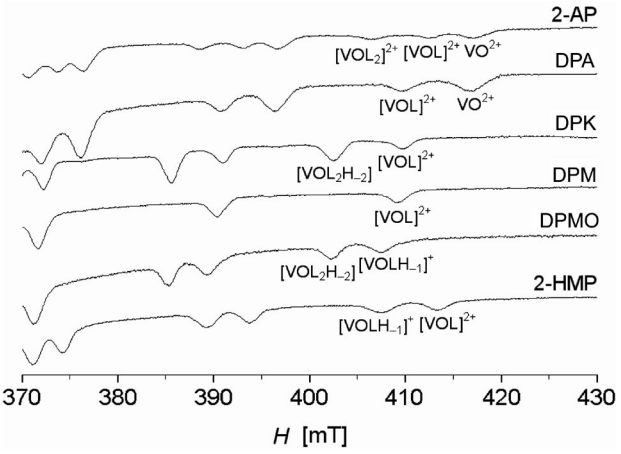
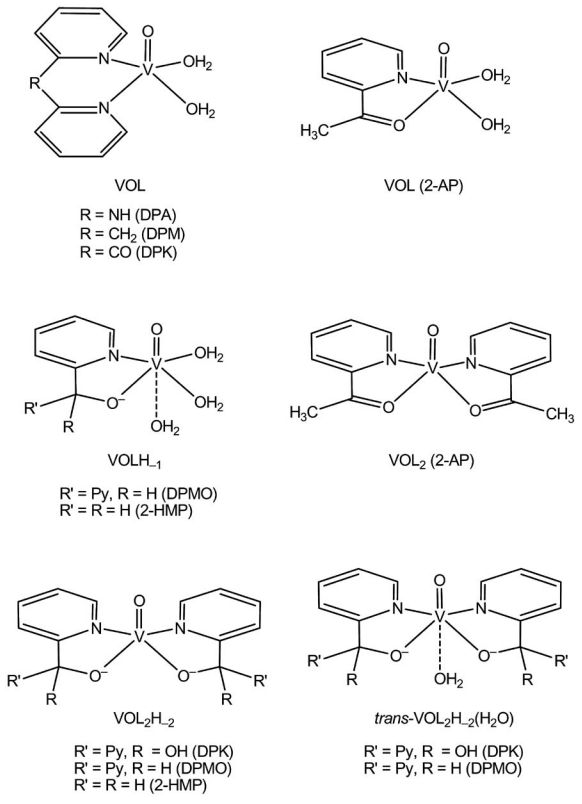


Figure 1. High-field region of the X-band anisotropic EPR spectra recorded in aqueous solutions at 120 K with a $V^{IV}O$ concentration of 2.5 mM and a ligand-to-metal molar ratio of 5:1: 2-AP, pH 4.30; DPA, 4.95; DPK, pH 3.25; DPM, pH 6.25; DPMO, pH 4.40; 2-HMP, pH 4.00. The coordination mode of the mono-chelated species ($[VOL]^{2+}$ or $[VOLH_{-1}]^+$) are: 2-AP, (N_{pyr}, CO); DPA, (N_{pyr}, N_{pyr}); DPK, (N_{pyr}, N_{pyr}); DPM, (N_{pyr}, N_{pyr}); DPMO, (N_{pyr}, O^-); 2-HMP, (N_{pyr}, O^-).



Scheme 2. Structure of the $V^{IV}O$ complexes.

Di(pyridin-2-yl)methane (DPM)

For di(pyridin-2-yl)methane the potentiometric measurements show two pK_a values, 2.61 and 5.11, assignable to the two pyridine nitrogen atoms.[19] Their higher basicity compared with that of DPA is due to the replacement of the amino nitrogen with a methylene group.

Potentiometric data suggest the formation of a mono-chelated complex $[VOL]^{2+}$, followed by an extensive hydrolysis at pH > 5 with formation of the EPR-silent dimeric species $[(VO)_2L_2H_{-2}]^{2+}$ and, at higher pH values, of $[(VO)_2(OH)_5]^-$ and $[VO(OH)_3]^-$ (Figure S2 of Supporting Information). The "basicity-adjusted" stability constant for the reaction $VO^{2+} + HL^+ \rightarrow [VOL]^{2+} + H^+$ is –1.38; for comparison, the value for the formation of $[VOL]^{2+}$ with di(imidazol-2-yl)methane is 0.33, almost two orders of magnitude higher.[15]

EPR spectra confirmed these results and in the low pH range a mono-chelated species $[VOL]^{2+}$ with (N_{pyr}, N_{pyr}) coordination is detected (Figure 1 and Scheme 2). At pH values higher than 6, anisotropic spectra show a continuous decrease of the hyperfine splitting constant A_z; the observed changes are, however, of low extent and cannot be due to the formation of the corresponding bis-chelated complex. This shift is explained supposing that the second ligand molecule is only weakly coordinated to the $V^{IV}O$ ion, due to low basicity of the pyridine nitrogen donors and to the steric hindrance between the two hydrogen atoms in position 3 of the two aromatic rings.[21]

Di(pyridin-2-yl) Ketone (DPK)

Di(pyridin-2-yl) ketone contains a carbonyl group connecting the two pyridine rings. The only measured pK_a value is 2.91 and is due to the deprotonation of the second pyridine nitrogen, the first having a too low pK_a value to be detected in aqueous solution.

Potentiometric data suggest the formation of the species $[VOL]^{2+}$ in the acidic pH range (Figure S3 of the Supporting Information). EPR spectra recorded on frozen solutions confirm this assumption and show the presence of a species having two pyridine nitrogen atoms coordinated in the equatorial plane of the metal ion (Figure 1 and Scheme 2).

By increasing the pH, two new species can be clearly distinguished in aqueous solution; they are present in the same relative amount in a wide pH range (Figure 2). For these complexes, having the same deprotonation degree, potentiometry suggests the stoichiometry $[VOL_2H_{-2}]$; this observation can be explained postulating the presence of two isomers in equilibrium with each other. Their EPR parameters are very similar to those of the analogous species formed by di(pyridin-2-yl)methanol, and different from those of the complexes formed by 2-acetylpyridine (Table 2); this indicates that one of the donors of DPK is not a simple carbonyl oxygen but, more likely, a negatively charged oxygen atom like that of a deprotonated hydroxy group.

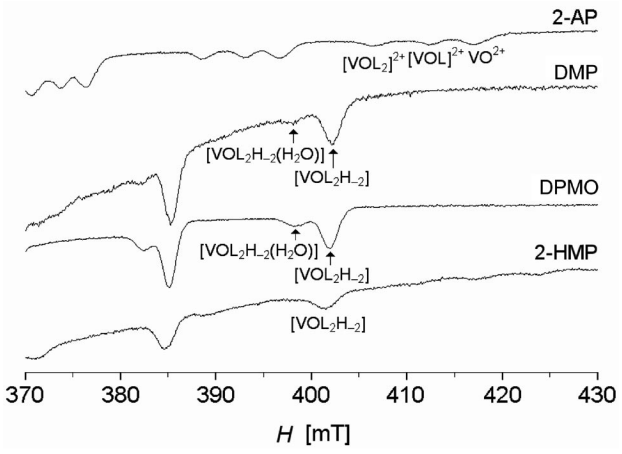
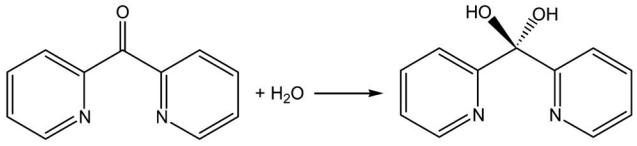


Figure 2. High-field region of the X-band anisotropic EPR spectra recorded in aqueous solutions at 120 K with a $V^{IV}O$ concentration of 2.5 mM and a ligand-to-metal molar ratio of 5:1: 2-AP, pH 4.30; DPK, pH 7.25; DPMO, pH, 7.45; 2-HMP, pH 6.20. The coordination modes of the bis-chelated species ($[VOL_2]^{2+}$, $[VOL_2H_{-2}]$ or $[VOL_2H_{-2}(H_2O)]$) are: 2-AP, 2×(N_{pyr}, CO); DPK, 2×(N_{pyr}, O^-); DPMO, 2×(N_{pyr}, O^-); 2-HMP, 2×(N_{pyr}, O^-).

The experimental data can be explained assuming that a water molecule adds to the carbonyl group originating a geminal diol in a metal-promoted hydration; this kind of reaction is well-documented in the literature and structures formed by the gem-diol derived from di(pyridin-2-yl) ketone are reported for Cr^{III}, Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} in aqueous solution,[22] and for Cr^{III}, Co^{II}, Co^{III}, Ni^{II} Cu^{II}, Ru^{II}, Pd^{II}, Pt^{II} and Au^{III} in the solid state.[23] To the best of our knowledge this is the first time that it is observed for the $V^{IV}O$ ion. Geminal diols usually are not stable, but can be generated from electron-deficient carbonyl compounds;[24] for example, in the presence of electron-attracting groups such as two pyridinium rings, the hydrate formation is observed.[25] Therefore, for DPK the two pyridine rings connected to the carbonyl group favour the hydration reaction with respect to 2-acetylpyridine (see below), and the formation of coordination compounds in the presence of the metal ion further stabilizes the geminal diol (Scheme 3).



Scheme 3. Hydration of a ketone to a geminal diol.

The formation of the hydration product justifies both the potentiometric data and the spectroscopic observations. In fact, potentiometry indicates the formation of the species $[VOL_2H_{-2}]$ which is, as a matter of fact, originated by the deprotonation of two hydroxy groups obtained after the addition of two water molecules to two ligand molecules $[VOL_2(H_2O)_2]^{2+} \rightarrow [VOL_2(OH)_2] + 2H^+$. It would be much more difficult to explain the formation of $[VOL_2H_{-2}]$ without considering the possibility of addition of a water molecule to the ligand.

Di(pyridin-2-yl)methanol (DPMO)

Di(pyridin-2-yl)methanol shows only one measurable pK_a value (4.50), which corresponds to the deprotonation of one of the two pyridine nitrogen atoms; the first pyridine nitrogen deprotonates with pK_a < 1, whilst the hydroxy group does not deprotonate in the absence of a metal ion (Table 1). The species distribution diagram is shown in Figure S4 of Supporting Information.

With DPMO the coordination starts in the acidic pH range with the formation of a species having EPR parameters not encountered with the previously examined ligands. In this pH region potentiometric data indicate the formation of two species of $[VOL]^{2+}$ and $[VOLH_{-1}]^+$ composition, whereas EPR spectra show the presence in solution of only one species with g_z 1.944 and an unusually low value of A_z 162×10^{-4} cm^{-1} (Figure 1). These parameters allow for ruling out the coordination mode (N_{pyr}, N_{pyr}) and support the formation of a species with the (N_{pyr}, O^-) donor set, analogous to that observed with 2-hydroxymethylpyridine (Scheme 2).

The stoichiometry $VOLH_{-1}$ is in agreement with the coordination of a deprotonated alcoholate group and the donor set (N_{pyr}, O^-); we can also suppose that $[VOL]^{2+}$ is, as a matter of fact, $VO(HLH_{-1})$ with the uncoordinated pyridine nitrogen in the protonated form and the deprotonated alco-

holate group coordinated to the metal ion; according to this interpretation, $[VOL]^{2+}$ and $[VOLH_{-1}]^{+}$ should have the same coordination mode, and consequently the same EPR parameters, differing only in the deprotonation degree of an uncoordinated pyridine nitrogen.

At higher pH values (from 5 to 10), potentiometry suggests the formation of a species of $[VOL_2H_{-2}]$ composition; according to the previous discussion, it is possible to advance the hypothesis that this is a bis-chelated species with $2\times(N_{pyr}, O^-)$ binding mode in which two deprotonated alcoholate groups are coordinated to the metal ion. In this pH range, the resonances of two species, in equilibrium with each other, can be distinguished by EPR spectroscopy (Figure 2). In this case too, this experimental observation can be interpreted on the basis of the presence of two isomers in aqueous solution, one characterized by A_z 151×10^{-4} cm^{-1} and another by A_z 144×10^{-4} cm^{-1}; interestingly, A_z values are comparable with those of the analogous species formed by DPK, confirming the hydration of ketone to give a geminal diol. An examination of such parameters allows one to affirm that for one of the two complexes (that having g_z 1.958 and A_z 144×10^{-4} cm^{-1}) an anomalous reduction of the ^{51}V hyperfine coupling constant along the z-axis is observed.

Usually, for a $V^{IV}O$ species the identification of the donors coordinated in the equatorial plane is possible through the application of the "additivity rule", which affirms that the value of the ^{51}V anisotropic hyperfine coupling constant along the z-axis in an EPR spectrum ($A_\parallel$ or A_z depending on the symmetry of the system, axial or rhombic) can be calculated from the sum of the contribution of each equatorial function [Equation (1)].[26,27]

$$A_z = \sum_{i=1}^{4} A_z\,(\text{donor } i) = A_z\,(\text{donor 1}) + A_z\,(\text{donor 2}) + A_z\,(\text{donor 3}) + A_z\,(\text{donor 4}) \quad (1)$$

For a $2\times(N_{pyr}, O^-)$ coordination, a value for A_z of 152.0×10^{-4} cm^{-1} is expected.[26] Usually, A_z experimentally falls in the range of ca. 3×10^{-4} cm^{-1} with respect to the prediction of the "additivity rule", but in some cases an anomalous reduction of its value has been observed.[14j,28] For the moment a univocal explanation of such a behaviour has not been found; Kabanos and co-workers explained the anomalous reduction observed in their complexes as due to the coordination of a negatively charged ligand in the axial position,[14j] which reduces the electric field gradient along the V=O bond decreasing the magnitude of the nuclear quadrupolar coupling constants and of A_z.[29] Recent observations indicate that an anomalous reduction of A_z could be caused by the axial coordination of a water or solvent molecule (see below).[30]

On the basis of these observations, the two isomers could be described as the square pyramidal species $[VOL_2H_{-2}]$, present in a larger amount, and the octahedral *trans*-$[VOL_2H_{-2}(H_2O)]$, present in a smaller amount (Scheme 2). The reduction of A_z for *trans*-$[VOL_2H_{-2}(H_2O)]$ is 5.7% with respect to the expected value.

Interestingly, a low value of A_z is also observed for the previously described mono-chelated species $[VOLH_{-1}]^{+}$ with (N_{pyr}, O^-) coordination; for this species the "additivity rule" predicts 167.2×10^{-4} cm^{-1} vs. 161.9×10^{-4} cm^{-1} experimental, corresponding to a reduction of 3.3%. This means that mono- and bis-chelated species with (N_{pyr}, O^-) coordination show an anomalous value of A_z and this can be attributed to the presence in both cases of a water molecule coordinated in the axial position.

In the discussion of the results obtained with DFT calculations (see below) it will be demonstrated that A_z values calculated for the species having a water molecule coordinated in the axial position are in very good agreement with the experimental values.

2-Acetylpyridine (2-AP)

The only deprotonable group present in the molecule is the pyridine nitrogen which has a pK_a value of 3.02. The ligand molecule does not contain any other deprotonable group and, for this reason, its $V^{IV}O$ complexes are not very stable.

With potentiometric measurements it is possible to calculate the thermodynamic stability constant of $[VOL]^{2+}$ species, but not of $[VOL_2]^{2+}$ (see Figure S5, Supporting Information). The value of the "basicity-adjusted" stability constant for the formation of $[VOL]^{2+}$ is –0.95: therefore, the closure of a five- instead of a six-membered chelated ring and the presence of an oxygen instead of nitrogen donor makes the (N_{pyr}, CO) donor set stronger than (N_{pyr}, N_{pyr}), for which the value is –1.38 (see above). However, the value of –0.95 is lower than that measured for the set (N_{imid}, N_{imid}) of di(imidazol-2-yl)methane (0.33);[15] therefore, the order of strength in $V^{IV}O$ ion binding is $(N_{imid}, N_{imid}) > (N_{pyr}, CO) > (N_{pyr}, N_{pyr})$.

EPR spectroscopy, however, allows for observing the formation of both the mono- and bis-chelated complexes with (N_{pyr}, CO) and $2\times(N_{pyr}, CO)$ coordination (Figures 1 and 2, Scheme 2). The spectroscopic parameters for such species are different from those measured for the complexes formed by DPK and this demonstrates that the two ligands behave in different way: DPK undergoes a hydration reaction to form complexes with (N_{pyr}, O^-) coordination, whereas for 2-AP this is inhibited by the presence of the electron-releasing methyl group[24] and the donor set is (N_{pyr}, CO).

The impossibility of calculating the stability constant for the bis-chelated species $[VOL_2]^{2+}$ through a pH-titration can be easily explained. Since the pK_a value of the ligand is rather low, the deprotonation of the second ligand molecule has no effect on the pH; in other words, at the pH value at which $[VOL_2]^{2+}$ forms the ligand is already deprotonated and, in the absence of a deprotonation process associated to its coordination, it is not possible to calculate a stability constant. In spite of the lack of thermodynamic data for the bis-chelated species, however, the spectroscopic data in aqueous solution are sufficient for the complete characterization of the system formed by 2-acetylpyridine.

2-(Hydroxymethyl)pyridine (2-HMP)

This ligand has only one pK_a value (4.96) which can be attributed to the pyridine nitrogen, whereas the hydroxy group does not undergo deprotonation in the measurable pH range. The hydroxy group can be deprotonated in the presence of the $V^{IV}O$ ion with contemporary formation of complexes with (N_{pyr}, O^-) coordination.

Potentiometric data can be fitted by assuming the formation of three species with $[VOL]^{2+}$, $[VOLH_{-1}]^+$ and $[VOL_2H_{-2}]$ stoichiometry (Figure 3). $[VOL]^{2+}$, observed in the acidic pH range, has the hydroxy group still protonated, for which the monodentate coordination of a pyridine nitrogen is postulated; $[VOLH_{-1}]^+$ and $[VOL_2H_{-2}]$, existing at pH higher than 4, are characterized by (N_{pyr}, O^-) and $2\times$(N_{pyr}, O^-) coordination.

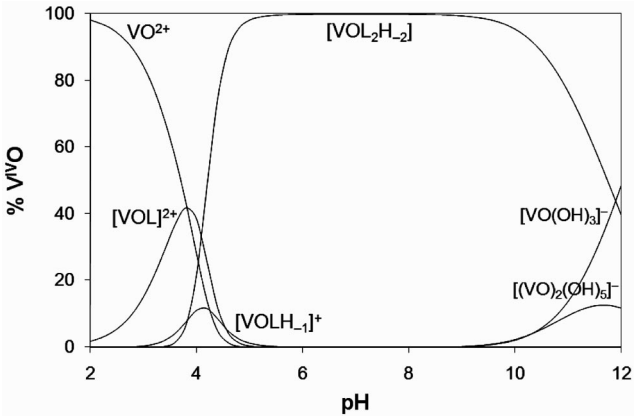


Figure 3. Species distribution for the $V^{IV}O$/2-HMP system as a function of pH with a ligand-to-metal molar ratio of 5:1 and a $V^{IV}O$ concentration of 2.5 mM.

Anisotropic EPR spectra (see Figures 1 and 2) confirm these observations and an examination of the spectral parameters of these two species shows that they are similar to those measured for DPMO. In particular, the mono-chelated complex with (N_{pyr}, O^-) coordination shows A_z 163×10^{-4} cm^{-1} in the case of 2-HMP and 162×10^{-4} cm^{-1} for DPMO, whereas for doubly chelated species with $2\times$(N_{pyr}, O^-) coordination an A_z value of 151×10^{-4} cm^{-1} is measured for both the ligands. The coincidence of the spectroscopic parameters indicates that the two ligands have, towards the $V^{IV}O$ ion, the same binding mode; the only difference is the presence of the hexacoordinate *trans*-$[VOL_2H_{-2}(H_2O)]$ species detected with DPMO but not with 2-HMP. This difference is probably due to the different solvation of the species formed by the two ligands.

N-Glycyl-di(pyridin-2-yl)methylamine (Gly-DPMA)

The ligand shows the pK_a values of 3.47 and 7.95, attributable to one of the two pyridine nitrogen atoms and to the terminal ammonium, respectively; the first pyridine nitrogen deprotonates with pK_a < 1 (Table 3).[19] Therefore, the fully protonated form of the ligand can be indicated as H_3L^{3+}.

Table 3. Stability constants (logβ) of proton and $V^{IV}O$ complexes for Gly-DPMA and His-DPMA at 25.0 ± 0.1 °C and I = 0.20 M (KCl).[a]

Species	Gly-DPMA	His-DPMA
H_4L^{4+}	–	<16.6[b]
H_3L^{3+}	<12.4[b]	15.65[b]
H_2L^{2+}	11.42[b]	12.74[b]
HL^+	7.95[b]	7.31[b]
pK_a(N_{pyr})	<1[b]	<1[b]
pK_a(N_{pyr})	3.47[b]	2.91[b]
pK_a(NH_2)	7.95[b]	7.31[b]
pK_a(N_{His})	–	5.43[b]
$[VOLH_2]^{4+}$	–	15.49(8)
$[VOLH]^{3+}$	10.96(4)	11.95(4)
$[VOLH_{-1}]^+$	1.57(5)	2.51(3)
$[VOLH_{-2}]$	–5.45(12)	–3.93(4)
pK($VOLH_{-1}$)[c]	7.02	6.44

[a] The uncertainties (σ values) of the protonation and stability constants are given in parentheses. [b] Ref.[19]. [c] pK($VOLH_{-1}$) = logβ($VOLH_{-1}$) – logβ($VOLH_{-2}$).

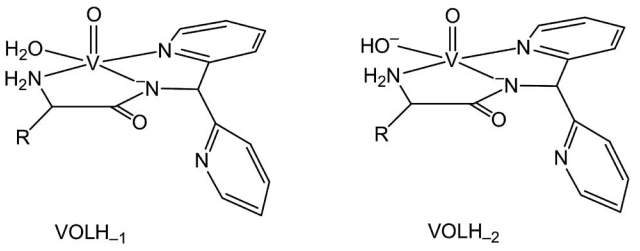
In the acidic pH range the EPR spectra can be interpreted assuming the formation of a mono-chelated species with (N_{pyr}, N_{pyr}) coordination; the spectroscopic parameters of this species are similar to those measured for the analogous species formed by DPA, DPM and DPK. If the A_z value for the coordination mode (N_{pyr}, N_{pyr}) is compared with that measured for di(imidazol-2-yl) residue (N_{im}, N_{im}) a small decrease can be observed ($167–169\times10^{-4}$ cm^{-1} vs. $169–170\times10^{-4}$ cm^{-1}).[15] A complete list of the EPR parameters for all the species formed is displayed in Table 4.

Table 4. EPR parameters of the $V^{IV}O$ complexes formed by Gly-DPMA and His-DPMA.[a]

Ligand	Species	g_z	A_z	Donors
Gly-DPMA	$[VOLH]^{3+}$	1.944	167	[(N_{pyr}, N_{pyr}); H_2O; H_2O]
	$[VOLH_{-1}]^+$	1.950	163	[(NH_2, N^-, N_{pyr}); H_2O]
	$[VOLH_{-2}]$	1.952	159	[(NH_2, N^-, N_{pyr}); OH^-]
His-DPMA	$[VOLH_2]^{4+}$	1.944	169	[(N_{pyr}, N_{pyr}); H_2O; H_2O]
	$[VOLH]^{3+}$	1.944	169	[(N_{pyr}, N_{pyr}); H_2O; H_2O]
	$[VOLH_{-1}]^+$	1.946	164	[(NH_2, N^-, N_{pyr}); H_2O]
	$[VOLH_{-2}]$	1.950	159	[(NH_2, N^-, N_{pyr}); OH^-]

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

At higher pH values, potentiometric data indicate the deprotonation of the terminal ammonium nitrogen which induces the deprotonation and coordination of the amide nitrogen with the formation of a stable five-membered chelated ring (Figure S6 of Supporting Information). The coordination of a pyridine nitrogen allows for the closure of a second five-membered chelated ring, whilst a water molecule occupies the fourth equatorial position; the stoichiometry for this species is $[VOLH_{-1}]^+$ (Scheme 4). In comparison with the amino acidic derivatives of di(imidazol-2-yl)-methylamine, an increase of the stability of this species which predominates in aqueous solution in the pH range 5–7 can be observed.[15] The hyperfine coupling constant A_z for this complex is 163×10^{-4} cm^{-1} comparable with the value of $163–165\times10^{-4}$ cm^{-1} measured for the corresponding species formed by di(imidazol-2-yl) derivatives.[15]



Scheme 4. Structure of the $[VOLH_{-1}]^+$ and $[VOLH_{-2}]$ complexes formed by Gly-DPMA (R = H), and His-DPMA (R = 4-CH_2-imidazole).

The water molecule coordinated in the equatorial plane of the metal ion undergoes a deprotonation process with a pK of 7.02, originating the corresponding mono-hydroxo complex, $[VOLH_{-2}]$. The structure of this complex is depicted in Scheme 4.

The A_z value measured for such a species, 159×10^{-4} cm^{-1}, is in good agreement with those observed for the di(imidazol-2-yl) derivatives.[15] The value of A_z predicted by the "additivity rule" is 159×10^{-4} cm^{-1} for $[VOLH_{-1}]^+$ and 155×10^{-4} cm^{-1} for $[VOLH_{-2}]$, if the contributions of 32.7 and 35.3×10^{-4} cm^{-1} are used for the amide-N$^-$ when the total equatorial charge of the $V^{IV}O$ ion is –1 ($VOLH_{-1}$) and –2 ($VOLH_{-2}$), respectively.[13] The two expected values are significantly higher than those measured: as discussed later, it is possible to predict the A_z value for the two species also by DFT methods, which give results comparable with those experimentally measured. However, by following what was done by Saladino and Larsen[31] for $V^{IV}O$ imidazole species after the fundamental work of Pecoraro and co-workers,[32] we studied through DFT calculations the value of ^{51}V A_z in $V^{IV}O$ pyridine complexes as a function of the orientation of the aromatic ring with respect to the V=O bond; we found that a dependence exists, and that the contribution of a pyridine nitrogen to A_z can be expressed by Equation (2)[33]

$$A_z(\text{pyr}) = 42.23 + 1.80 \times \sin(2\theta - 90) \quad (2)$$

where A_z is measured in 10^{-4} cm^{-1} and θ is the mean value of the two dihedral angles between V=O and the two N–C aromatic bonds of the equatorially coordinated pyridine rings. The values of θ for $[VOLH_{-1}]^+$ and $[VOLH_{-2}]$ can be found from the optimization of the structures by DFT methods and 65.9 and 65.4° result. With these data the "additivity rule" can be applied using 40.1 for amino-NH_2, 32.7 or 35.3 for amide-N$^-$, 45.6 for H_2O, 38.7 for OH^- and the values of 43.4×10^{-4} cm^{-1} for pyridine-N calculated with equation (2). The expected A_z values are in this case 161.8 for $[VOLH_{-1}]^+$ and 157.5×10^{-4} cm^{-1} for $[VOLH_{-2}]$, to be compared with those measured of 162.5 and 158.8×10^{-4} cm^{-1}.

N-Histidyl-di(pyridin-2-yl)methylamine (His-DPMA)

His-DPMA shows the pK_a values of 2.91, 5.43 and 7.31, attributable to one of the two pyridine atoms, to the imidazole nitrogen present in the side chain of the histidine residue and to the terminal ammonium, respectively; as observed with Gly-DPMA, the first pyridine nitrogen deprotonates with pK_a < 1.[19] Therefore, the completely protonated ligand can be written as H_4L^{4+}.

Because of the structural resemblance with Gly-DPMA, an analogous complexation scheme is expected with the differences derived by the possible interaction of the imidazole nitrogen atom present in the side chain with the $V^{IV}O$ ion. The diagram of species distribution is reported in Figure 4 with L/M = 3:1, whilst anisotropic EPR spectra recorded under the same experimental conditions are depicted in Figure 5.

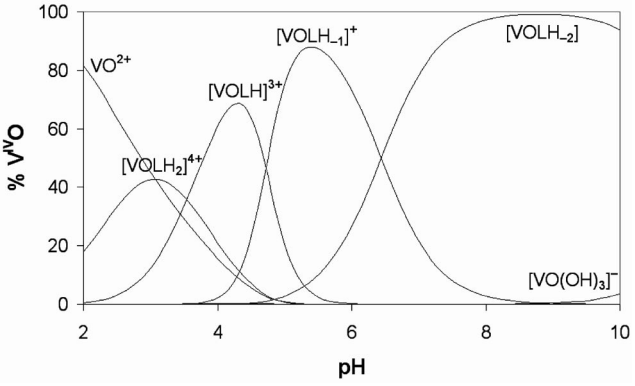


Figure 4. Species distribution for the $V^{IV}O$/His-DPMA system as a function of pH with a ligand-to-metal molar ratio of 3:1 and a $V^{IV}O$ concentration of 2.5 mM.

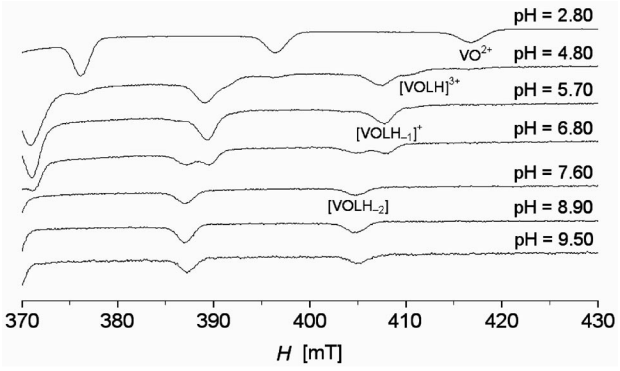


Figure 5. High-field region of the X-band anisotropic EPR spectra recorded at 120 K as a function of pH in an aqueous solution of the $V^{IV}O$/His-DPMA system with a ligand-to-metal molar ratio of 3:1 and a $V^{IV}O$ concentration of 2.5 mM.

Potentiometric titrations suggest the formation, in the acidic pH range, of two species with stoichiometry $[VOLH_2]^{4+}$ and $[VOLH]^{3+}$ which correspond to the same (N_{pyr}, N_{pyr}) coordination mode; these two species should have the uncoordinated ammonium group in the protonated form, and should differ only in the deprotonation degree of the imidazole nitrogen, protonated in the first and deprotonated in the second species.

An examination of the anisotropic EPR spectra measured on frozen aqueous solutions confirms that the complexes $[VOLH_2]^{4+}$ and $[VOLH]^{3+}$ have the same (N_{pyr}, N_{pyr})

binding mode (Figure 5); they are characterized by an A_z value of 169×10^{-4} cm^{-1} (Table 4).

After the deprotonation, amine nitrogen binds the metal ion promoting the deprotonation and coordination of the amide group, which closes the first five-membered chelated ring (Scheme 4); the binding of one of the two pyridine nitrogen atoms forms the second chelated ring, whereas a water molecule completes the equatorial coordination of $V^{IV}O$. This species is identified by potentiometry as $[VOLH_{-1}]^+$ and is confirmed by EPR measurements (Figure 5). It has a higher stability in comparison with the analogous species formed by Gly-DPMA (logβ of 2.51 and 1.57, respectively), probably because of the stabilizing effect of the imidazole nitrogen of the histidine residue.

As in the case of Gly-DPMA, the water molecule coordinated in the equatorial plane deprotonates originating the corresponding mono-hydroxo complex, $[VOLH_{-2}]$, which exists in solution in the pH range 7.0–9.5 (Figure 5). The p*K* for this deprotonation process is slightly lower than that measured for Gly-DPMA (6.44 vs. 7.02). The analogous p*K* value for *N*-glycyl-di(imidazol-2-yl)methylamine, *N*-α-glutamyl-di(imidazol-2-yl)methylamine and *N*-histidyl-di(imidazol-2-yl)methylamine is in the range 7.05–7.96.[15]

In this case too, A_z calculated for $[VOLH_{-1}]^+$ and $[VOLH_{-2}]$ by the "additivity rule" using a contribution of the pyridine nitrogen dependent on the aromatic ring orientation with respect to the V=O bond through Equation (2) (161.8 and 157.5×10^{-4} cm^{-1}, respectively) is in good agreement with the experimental values of 163.9 and 159.2×10^{-4} cm^{-1}. As will be discussed later, it is possible to predict the A_z values for both the species through DFT methods.

Optimization of the $V^{IV}O$ Structures

The geometry of the $[VOLH_{-1}]^+$ and $[VOLH_{-2}]$ complexes formed by Gly-DPMA and His-DPMA, and of $[VOL_2]$ and *trans*-$[VOL_2(H_2O)]$ species formed by DPK and DPMO was optimized performing DFT calculations with the Gaussian 03 software.[34]

Over the last years, it has been demonstrated that the use of DFT methods gives rather good results in the optimization of the geometries of transition-metal complexes, even if the optimization was usually performed in the gas phase instead of in solution.[35] In this work, the functional B3LYP,[36,37] which for many vanadium compounds allows a good agreement of the bond lengths and angles with the experimental X-ray structures to be reached, was used.[29,38] Spears suggested for $[V(CO)_6]^-$ the use of the 6-311g basis set for vanadium and of a polarization function with *d* character for the other elements,[38a] whereas Deligiannakis and Britt proposed that the simple 6-31g(d) set is enough to correctly simulate an experimental structure.[29] We recently demonstrated that the 6-311g basis set allows for finding a good agreement with the experimental bond length and angles for 24 representative $V^{IV}O$ complexes without causing a large increase in calculation time.[30]

As already done for the di(imidazolyl) derivatives,[15] the structures of the complexes $[VOLH_{-1}]^+$ and $[VOLH_{-2}]$ formed by Gly-DPMA and His-DPMA were optimized by replacing the non-coordinating pyridine ring with a hydrogen atom in order to speed up the time of simulation; the obtained ligand, *N*-glycyl-(pyridin-2-yl)methylamine, will be indicated by Gly-PMA. However, preliminary simulations at the level of theory B3LYP/sto-3g indicate that the second pyridine ring does not take part in the complexation, suggesting that strong steric constraints hinder its axial interaction with $V^{IV}O$; this is confirmed by the examination of the molecular models. The results of the simulations are summarized in Table 5 which also shows a comparison with similar structures reported in the literature;[14k,39–41] the optimized structures of the species $[VO(Gly\text{-}PMAH_{-1})(H_2O)]^+$ and $[VO(Gly\text{-}PMAH_{-1})(OH)]$, calculated at the B3LYP/6-311g level of theory, are shown in Figure 6.

The bond lengths V=O, V–NH_2, V–N^- and V–N_{pyr} for $[VO(Gly\text{-}PMAH_{-1})(OH)]$ are comparable with those of $[VO(Gly\text{-}L\text{-}Val)(phen)]\cdot H_2O$, characterized by a similar donor set [(NH_2, N^-, COO^-); (N_{pyr}, N_{pyr}^{ax})].[14k] For the V–OH bond a distance longer than that found for *cis*-$[VO(OH)(4,4'\text{-dtbipy})_2]BF_4\cdot 1.2H_2O$, where 4,4′-dtbipy is

Table 5. Details and structural parameters of the DFT calculations on the studied $V^{IV}O$ complexes and comparison with similar species reported in the literature.

Complex[a]	V=O	V–NH_2	V–N^-	V–N_{pyr}	V–OH[b]	V–O[c]	N–V–N	O–V–O	O=V–O_{ax}	θ[d]
$[VO(Gly\text{-}PMAH_{-1})(H_2O)]^+$	1.591	2.161	1.932	2.103	2.104	–	–	–	–	65.9
$[VO(Gly\text{-}PMAH_{-1})(OH)]$	1.611	2.155	1.992	2.123	1.864	–	–	–	–	65.4
$[VO(2\text{-}AP)_2]^{2+}$	1.568	–	–	2.111	–	2.028	148.4	144.3	–	102.1, 102.2
trans-$[VO(2\text{-}AP)_2(H_2O)]^{2+}$	1.583	–	–	2.142	2.267	2.054	169.6	160.3	180.0	96.7, 96.7
$[VO(2\text{-}HMPH_{-1})_2]$	1.610	–	–	2.114	–	1.912	152.1	131.9	–	101.6, 101.7
trans-$[VO(2\text{-}HMPH_{-1})_2(H_2O)]$	1.608	–	–	2.111	2.668	1.943	153.8	150.8	179.0	93.7, 96.4
$[VO(Gly\text{-}L\text{-}ValH_{-1})(phen)]$[e]	1.587	2.158	1.978	2.155	–	–	–	–	–	176.2
$[VO(2\text{-}mentholpyridineH_{-1})_2]$[f]	1.606	–	–	2.078	–	1.877	150.2	132.9	–	102.2, 102.2
$[VO(9\text{-}PF\text{-}9\text{-}olato)_2]$[g]	1.609	–	–	2.094[h]	–	1.889[h]	153.8	131.0	–	98.8, 105.1
trans-$[VO(6\text{-}etpic)_2(H_2O)]$[i]	1.571	–	–	2.150[h]	2.283	1.979[h,j]	167.8	156.7	177.0	102.0, 109.9

[a] Gly-PMA is *N*-glycyl-(pyridin-2-yl)methylamine, 2-AP is 2-acetylpyridine, 2-HMP is 2-(hydroxymethyl)pyridine, Gly-L-Val is glycyl-L-valinato, phen is 1,10-phenanthroline, 9-PF-9-olato is 9-(2-pyridyl)fluoren-9-olato and 6-etpic is 6-ethylpicolinato. [b] O belonging to an OH^- ion or to a H_2O molecule. [c] O belonging to the carbonyl of 2-AP or deprotonated alcoholic group of 2-HMP. [d] Mean value of the two dihedral angles between V=O and the two N–C aromatic bonds of the equatorially coordinated pyridine rings. [e] Ref.[14k] [f] Ref.[39] [g] Ref.[40] [h] Mean value. [i] Ref.[41] [j] O belonging to a carboxylate group.

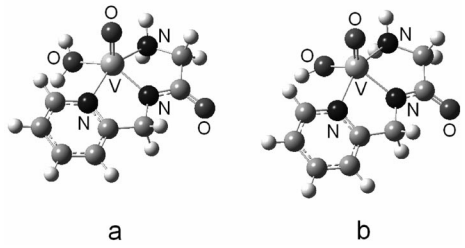


Figure 6. Simulated structures of the complexes [VO(Gly-PMAH$_{-1}$)-(H$_2$O)]$^+$ (a) and [VO(Gly –PMAH$_{-1}$)(OH)] (b) calculated by DFT methods at the B3LYP/6-311g level of theory (see Table 5). Gly-PMA is *N*-glycyl-(pyridyl-2-yl)methylamine.

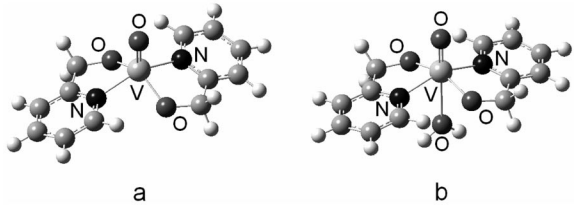


Figure 7. Simulated structures of the complexes [VO(2-HMPH$_{-1}$)$_2$] (a) and *trans*-[VO(2-HMPH$_{-1}$)$_2$(H$_2$O)] (b) calculated by DFT methods at the B3LYP/6-311g level of theory (see Table 5).

4,4′-di-*tert*-butyl-2,2′-bipyridine,[38b] is found. An important structural parameter, on which depends the value of the ^{51}V hyperfine coupling constant along the *z*-axis (A_z) through Equation (2) is the mean value of the dihedral angle θ, defined by the V=O and the aromatic N–C bonds, and chosen on the basis of the analogous definition for the coordination of an imidazole nitrogen.[32] From an examination of the data in Table 5, it can be noticed that for [VO(Gly-PMAH$_{-1}$)(OH)] the value is 65.4°.

For [VO(Gly-PMAH$_{-1}$)(H$_2$O)]$^+$, where a water molecule replaces an OH$^-$ ion, the V–N$^-$ bond becomes, as expected, shorter with increasing the length of the bond in *trans* position, whereas the V=O, V–NH$_2$ and V–N$_{pyr}$ distances don't undergo important variations. V–OH$_2$ (2.104 Å) is rather long compared with the values reported in the literature. The mean value of the dihedral angle θ is 65.9° (Table 5).

Concerning the doubly chelated complexes formed by DPK and DPMO, they exist in two isomeric forms, [VOL$_2$H$_{-2}$] and *trans*-[VOL$_2$H$_{-2}$(H$_2$O)] (see above); however, given that the second pyridine nitrogen does not coordinate the V^{IV}O ion, the simulations have been performed on the corresponding structures formed by 2-AP and 2-HMP. The possibility of an isomerism between a square pyramidal, pentacoordinated and an octahedral hexacoordinate species has been recently demonstrated for V^{IV}O complexes formed by 6-methylpicolinic acid and its derivatives with the perspective that this behaviour can be more diffuse than believed;[30] the data reported here confirm this hypothesis. The optimized structures of the species formed with 2-HMP are displayed in Figure 7.

A search in the literature for the square pyramidal structures with 2×(N$_{pyr}$, O$^-$) coordination mode yielded two hits,[42] which can be compared with the 2-HMP complexes; on the contrary, no structure with the 2×(N$_{pyr}$, CO) donor set is found. The only species characterized by X-ray diffraction analysis with an axially bound water which can be used as a comparison for the octahedral complexes is that formed by 6-ethylpicolinic acid, which however possesses a carboxylate rather than an alcoholate group bound to vanadium.[41]

The comparison between [VO(2-HMPH$_{-1}$)$_2$], [VO(2-mentholpyridineH$_{-1}$)$_2$],[39] and [VO(9-(2-pyridyl)fluoren-9-olato)$_2$]·0.5CH$_2$Cl$_2$[40] shows that the agreement is very good both for the distances and, mainly, for the bond angles: indeed, values for N–V–N and O–V–O angles of 152.1 and 131.9° are calculated vs. those experimental of 150.2 and 132.9° for [VO(2-mentholpyridineH$_{-1}$)$_2$] and of 153.8 and 131.0° for [VO(9-(2-pyridyl)fluoren-9-olato)$_2$]·0.5CH$_2$Cl$_2$. The calculated trigonality index τ [τ is defined as (β-α)/60, where β and α are the angles formed by the two pseudo-axial and two pseudo-equatorial donors, and is 1 for trigonal bipyramidal structures and 0 for square pyramidal][43] is 0.34 for [VO(2-HMPH$_{-1}$)$_2$], and 0.32 and 0.38 for [VO(2-mentholpyridineH$_{-1}$)$_2$] and [VO(9-(2-pyridyl)fluoren-9-olato)$_2$]·0.5CH$_2$Cl$_2$, respectively.

The results demonstrate that with DFT methods it is also possible to calculate well the bond angle between the oxo group and the axial water molecule, which is 179.0 for *trans*-[VO(2-HMPH$_{-1}$)$_2$(H$_2$O)] and 177.0° for *trans*-[VO(6-ethylpicolinato)$_2$(H$_2$O)].[41]

By going from the pentacoordinate structure of [VO(2-HMPH$_{-1}$)$_2$] to the hexacoordinate structure of *trans*-[VO(2-HMPH$_{-1}$)$_2$(H$_2$O)] the bond lengths remain almost unchanged (differences below 1.6%); concerning the bond angles, N–V–N does not change significantly (from 152.1 to 153.8°), and the only structural parameter that undergoes an important deformation is the O–V–O angle (from 131.9 to 150.8°). Therefore, the coordination of a water molecule in *trans* position to the V=O group results in the transformation of a structure distorted towards the trigonal bipyramid to a distorted octahedral with an arrangement of the oxo group and the four equatorial donors close to the square pyramid. This fact could have a significant effect on the value of A_z.

Prediction of the EPR Parameters

Many articles have been recently published on the possibility of predicting the ^{51}V hyperfine coupling constants in the EPR spectra of V^{IV}O species.[29,35h,44–47]

A DFT method for calculating the ***A*** tensor has been incorporated into Gaussian 03.[34] This method, unlike other programs like ADF, does not include relativistic effects or spin orbit coupling and uses Gaussian-type orbitals (GTOs).[48] Saladino and Larsen have shown that the best overall agreement with experimental ***A*** values can be obtained with the non-relativistic method and the half-and-half hybrid functionals.[46a] A_{iso} values calculated non-relativistically with half-and-half hybrid functionals deviate by

Table 6. EPR parameters calculated at the BHandHLYP/6-311g(d,p) level of theory for the $V^{IV}O$ complexes.[a]

Complex	A_{iso}^{calcd}	T_x^{calcd}	T_y^{calcd}	T_z^{calcd}	A_x^{calcd}	A_y^{calcd}	A_z^{calcd}	A_z^{exp}	$\%\|A_z\|$[b]
$[VO(Gly\text{-}PMAH_{-1})(H_2O)]^+$	–99.6	32.6	35.2	–67.8	–67.0	–64.4	–167.4	–162.5	+3.0
$[VO(Gly\text{-}PMAH_{-1})(OH)]$	–93.4	32.6	35.6	–68.2	–60.8	–57.8	–161.5	–158.8	+1.7
$[VO(2\text{-}AP)_2]^{2+}$	–97.9	30.9	37.1	–67.9	–67.0	–60.8	–165.8	–161.5	+2.7
trans-$[VO(2\text{-}AP)_2(H_2O)]^{2+}$[c]	–81.1	27.2	37.2	–64.4	–53.9	–43.9	–145.5	–	–
$[VO(2\text{-}HMP)_2]$	–83.2	30.9	37.0	–67.9	–52.3	–46.1	–151.1	–151.2	–0.1
trans-$[VO(2\text{-}HMP)_2(H_2O)]$	–76.9	28.9	38.5	–67.4	–48.0	–38.4	–144.3	–143.8	+0.3

[a] All the parameters given in 10^{-4} cm^{-1}. [b] Mean of the absolute percentage deviation from the experimental value: $100[(|A_z|^{calcd} - |A_z|^{exp})/|A_z|^{exp}]$. [c] Not existing structure.

about 10% from the experimental ones, whereas those calculated with the relativistic effects and pure generalized gradient correction functionals, such as BP86, deviate systematically by approximately 40%. The two authors ascribed to the improved performance of the half-and-half hybrid functionals for treating core shell spin polarization the difference in performance of the two methods.[46a]

We recently achieved consistent progress in the prediction of A_z with respect to the previous results, calculating A_z for 22 representative $V^{IV}O$ complexes with different charge, geometry and coordination mode through the use of the BHandHLYP (or BHandH) functional and 6-311g(d,p) basis set: deviations <5% and, often, <3% with respect to the experimental values are observed.[49] Particularly, excellent results have been obtained in the prediction of A_z for neutral complexes formed by ligands with the (N, O) donor set. Therefore, we believe that DFT methods can be rightfully used to predict A_z for a $V^{IV}O$ species.

The results of the simulations obtained on the structure of the complexes $[VO(Gly\text{-}PMAH_{-1})(H_2O)]^+$, $[VO(Gly\text{-}PMAH_{-1})(OH)]$, $[VO(2\text{-}AP)_2]^{2+}$, *trans*-$[VO(2\text{-}AP)_2(H_2O)]^{2+}$, $[VO(2\text{-}HMPH_{-1})_2]$ and *trans*-$[VO(2\text{-}HMPH_{-1})_2(H_2O)]$ are presented in Table 6.

It can be observed that the percentage deviation of the calculated A_z value for $[VO(Gly\text{-}PMAH_{-1})(H_2O)]^+$ and $[VO(Gly\text{-}PMAH_{-1})(OH)]$ is lower than 3% from the experimental value, supporting a $[(NH_2, N^-, N_{pyr}); H_2O]$ and $[(NH_2, N^-, N_{pyr}); OH^-]$ coordination.

The prediction of A_z for $[VO(2\text{-}AP)_2]^{2+}$ is correct, whereas it is worth noticing that the value of 145.5×10^{-4} cm^{-1} predicted for the non-existing *trans*-$[VO(2\text{-}AP)_2(H_2O)]^{2+}$ structure is comparable to that of the $V^{IV}O$ complexes formed by a series of eight amidrazone derivatives (from 146.9 to 149.1×10^{-4} cm^{-1}), for which the coordination $[(N_{imine}, CO); (N_{imine}, CO); O_{DMF}]$ and an octahedral coordination has been proposed.[28c]

The value of A_z for $[VO(2\text{-}HMPH_{-1})_2]$ and *trans*-$[VO(2\text{-}HMPH_{-1})_2(H_2O)]$ are in good agreement with those measured for the analogous species of DPK and DPMO, which have the same coordination mode (Table 2 and Scheme 2).

A comparison between A_z calculated for $[VO(2\text{-}AP)_2]^{2+}$, *trans*-$[VO(2\text{-}AP)_2(H_2O)]^{2+}$, $[VO(2\text{-}HMPH_{-1})_2]$ and *trans*-$[VO(2\text{-}HMPH_{-1})_2(H_2O)]$ shows that the wide range observed is mainly due to the variation of A_{iso} (from –76.9 to -97.9×10^{-4} cm^{-1}), whereas the T_z values change less (from –64.4 to -67.9×10^{-4} cm^{-1}).

DFT methods confirm that the presence of a water molecule in the axial position *trans* to the V=O bond can result in a decrease of the A_z value.[30] This seems to be in apparent contradiction with the "additivity rule" which affirms that ligands coordinated in the axial position don't contribute to the A_z value.[26] As a matter of fact, the presence of an axially bound ligand changes the geometry of a $V^{IV}O$ species from one square pyramidal with four ligands below the equatorial plane to one octahedral with the four ligands approaching the equatorial plane; this could yield a reduction of A_z. This hypothesis, however, is at the moment under examination.

Conclusions

The results demonstrate that ligands provided with the di(pyridin-2-yl)methyl residue are able to form $V^{IV}O$ complexes of moderate stability. In acidic aqueous solution such derivatives form mono-chelated species with (N_{pyr}, N_{pyr}) coordination; the corresponding bis complex is less stable and its formation is accompanied by the hydrolysis reactions of the $V^{IV}O$ ion. Therefore, the coordinating ability of the di(pyridin-2-yl)methyl moiety is lower than that shown by the di(imidazol-2-yl)methyl residue, which forms mono and bis six-membered chelated complexes with the (N_{imid}, N_{imid}) coordination.[15] The comparison of the strength of the latter donor set with (N_{pyr}, CO) and (N_{pyr}, O^-) forming five-membered chelated rings, shows that the order of efficiency in the $V^{IV}O$ binding is: $(N_{pyr}, O^-)^5 > (N_{imid}, N_{imid})^6 > (N_{pyr}, CO)^5 > (N_{pyr}, N_{pyr})^6$ (the superscript indicates the size of the chelated ring). However, when the di(pyridin-2-yl)methyl residue is connected to an amino acid residue it is able to anchor the metal ion in the acidic pH range favouring the deprotonation and coordination of the amide group.

In the case of di(pyridin-2-yl) ketone, the hydration of the carbonyl group to yield a geminal diol is observed.[22–25] Therefore for this ligand and its derivatives, this possibility both in the solid state and in aqueous solution must be always taken into account, with the consequence that the complexes could be the same as those formed by the corresponding alcohol and have a (N_{pyr}, O^-) rather than a (N_{pyr}, CO) coordination.

The results of the DFT calculations show that it is possible to predict with a good degree of accuracy both the

structure and the ^{51}V hyperfine coupling constants along the *z*-axis. This allows for distinguishing a penta- from a hexacoordinate complex having a water molecule *trans* to the V=O group. Interestingly, the octahedral species are countersigned by a value of A_z much lower than that predicted on the basis of the "additivity rule", attributable to the presence of a donor axially bound to the $V^{IV}O$ ion.[30] Therefore, DFT methods can be considered a powerful tool not only to optimize the coordination geometry of $V^{IV}O$ complexes but also to calculate the hyperfine coupling constant measured in an EPR spectrum.

Experimental Section

Ligands: The synthetic procedure for the preparation of the amino acid derivatives containing the di(pyridin-2-yl)methyl moiety has been described previously.[19] Di(pyridin-2-yl) ketone, di(pyridin-2-yl)amine, 2-acetylpyridine and (2-hydroxypyridyl)methanol were Aldrich products and were used as received. Di(pyridin-2-yl)methanol and di(pyridin-2-yl)methane were obtained from the reduction of di(pyridin-2-yl) ketone according to the established methods.[50,51] Their purity was checked by ^1H NMR and concentration was determined by potentiometric titration. $V^{IV}O$ solutions were prepared following literature methods.[52]

Potentiometric Measurements: The stability constants of proton and $V^{IV}O$ complexes were determined by pH-potentiometric titrations on 3–4 mL of sample. The ligand-to-metal molar ratio was between 1:1 and 10:1 and $V^{IV}O$ concentration was 0.001–0.004 M. Titrations were performed from pH 2.0 until precipitation or very extensive hydrolysis by adding carbonate-free KOH of known concentration (ca. 0.2 M KOH).[53] The pH was measured with a Metrohm 6.0234.100 combined electrode, calibrated for hydrogen ion concentration by the method of Irving et al.[54]

Measurements were carried out at 25.0 ± 0.1 °C and at a constant ionic strength of 0.2 M KCl with a MOLSPIN pH-meter and a MOL-ACS microburette (0.50 mL) controlled by a computer. Purified argon was bubbled through the samples to ensure the absence of oxygen. The number of experimental points was 50–70 for each titration curve and the reproducibility of the points included in the evaluation was within 0.005 pH unit in the whole pH range measured. The pH range examined, the total concentration of the ligand, and the ligand-to-metal ion molar ratio used in the potentiometric measurements are listed in Table 7.

The stability of the complexes, reported as the logarithm of the overall formation constant $\beta_{pqr} = [(VO)_pL_qH_r]/[VO]^p[L]^q[H]^r$, where VO stands for the $V^{IV}O^{2+}$ ion, L is the deprotonated form of the ligand and H is the proton, was calculated with the aid of the SUPERQUAD[55] and PSEQUAD programs.[56] Standard deviations were calculated by assuming random errors. The conventional notation has been used: negative indices for protons indicate either the dissociation of groups which do not deprotonate in the absence of $V^{IV}O$ coordination, or hydroxo ligands. Hydroxo complexes of $V^{IV}O$ were taken into account and 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.[57] and corrected for the different ionic strengths by use of the Davies equation,[58] $[VO(OH)_3]^-$ ($\log\beta_{10-3} = -18.0$) and $[(VO)_2(OH)_5]^-$ ($\log\beta_{20-5} = -22.0$).[59]

Spectroscopic Measurements: Anisotropic EPR spectra were recorded in aqueous solutions with an X-band (9.35 GHz) Bruker EMX spectrometer at 120 K. As usual for low-temperature measurements, a few drops of DMSO were added to the samples to ensure good glass formation. The spectra were simulated with the computer program Bruker WinEPR SimFonia.[60] Electronic spectra were recorded with Perkin–Elmer Lambda 25 or 35 spectrophotometers in the same concentration range as used for potentiometry. All operations were performed under a purified argon atmosphere in order to avoid oxidation of the $V^{IV}O$ ion.

Computational Details: All calculations presented in this paper were performed using the Gaussian 03 program (revision C.02)[34] and DFT methods.[61]

For the geometry optimization, the hybrid exchange-correlation functional B3LYP was employed.[36,37] The geometries were firstly pre-optimized at the B3LYP/sto-3g level and further optimized at the B3LYP/6-311g level of theory. For all the structures, minima were verified through frequency calculations.

The optimized structures were used to calculate the ^{51}V hyperfine coupling constants (A_{iso}, A_x, A_y and A_z) at the BHandHLYP/6-311g(d,p) level of theory; the BHandHLYP functional was incorporated in the Gaussian 03 software.

In the first-order approximation, the tensor $\boldsymbol{A}$ has one isotropic contribution deriving from the Fermi contact (A_{iso}) and another from the dipolar hyperfine interaction (tensor **T**): $\boldsymbol{A} = A_{iso}\mathbf{1} + \mathbf{T}$.[29,45,46,62] The values of the ^{51}V anisotropic hyperfine coupling constant along the *x*, *y* and *z* axes can be calculated by the equations: $A_x^{calcd} = A_{iso} + T_x$; $A_y^{calcd} = A_{iso} + T_y$; $A_z^{calcd} = A_{iso} + T_z$, with A_{iso}, T_x, T_y and T_z being read from the Gaussian 03 output.

The A_z value (as well as A_x and A_y) is negative, but in the literature is usually reported its absolute value and, therefore, the percentage deviation from the experimental value is calculated as: $100[(|A_z|^{calcd} - |A_z|^{exp})/|A_z|^{exp}]$ (Table 6).

Supporting Information (see also the footnote on the first page of this article): Species distribution as a function of pH for the systems formed by the $V^{IV}O$ ion and DPA, DPM, DPK, DPMO, 2-AP, Gly-DPMA (Figures S1–S6).

Table 7. pH range, total concentration of the ligand and ligand-to-metal ion molar ratio used in the potentiometric measurements.

Ligand	pH range	c_{Ligand} (M)	Ligand-to-$V^{IV}O$ ratio
DPA	3.0–5.0/5.6/6.8	2.0×10^{-3}	2.3/4.8/10.0
DPM	3.0–5.5	2.3×10^{-3}	2.3/4.5/9.0
DPK	2.4–6.0	$4.0 \times 10^{-3}/2.8 \times 10^{-3}$	1.4/2.8
DPMO	2.6–4.0	1.5×10^{-3}	1.0/2.1
2-AP	3.0–4.0	3.3×10^{-3}	0.9/1.8/3.6
2-HMP	3.0–5.0	3.7×10^{-3}	1.2/2.6/5.7
Gly-DPMA	2.5–4.2/9.9	$2.3 \times 10^{-3}/2.7 \times 10^{-3}$	1.0/4.3
His-DPMA	2.5–8.0/8.5/9.8/10.0	3.0×10^{-3}	3.0/3.1/3.9/4.8/5.5

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