

Structural, electron paramagnetic resonance and electron spin echo envelope modulation studies of oxovanadium(IV)–amidate compounds containing monoanionic axial ligands: effect on the ^{51}V -hyperfine coupling constants†

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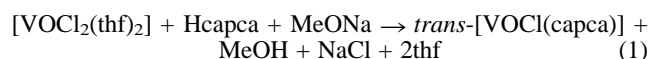
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Reaction of the amidate ligand *N*-{2-[(2-pyridylmethylene)amino]phenyl}pyridine-2-carboxamide (Hcapca) with $[\text{VOCl}_2(\text{thf})_2]$ and MeONa in 1:1:1 molar ratio in MeCN affords the compound *trans*- $[\text{VOCl}(\text{capca})]$ **1**, while reaction of **1** with NEt_4NCS , $\text{MeCO}_2\text{NHET}_3$ and imidazole yields the complexes *trans*- $[\text{VO}(\text{NCS})(\text{capca})]$ **2**, *trans*- $[\text{VO}(\text{MeCO}_2)(\text{capca})]$ **3** and *trans*- $[\text{VO}(\text{im})(\text{capca})]$ **4** respectively; the X-ray crystal structure of **1** is reported; Cw EPR studies of compounds **1**–**3** reveal a novel phenomenon of the reduction of their A_z components by ca. 10% compared to N_4 reference compounds.

The oxovanadium(IV) cation, $\text{V}^{\text{IV}}\text{O}^{2+}$, has been successfully employed as a spin probe in EPR¹ and electron spin echo envelope modulation (ESEEM)¹ studies of naturally occurring vanadoproteins and in proteins where the divalent cations (Mg^{2+} , Ca^{2+} , etc.) have been substituted by $\text{V}^{\text{IV}}\text{O}^{2+}$. More specifically, the z -component of the ^{51}V ($I = 7/2$) hyperfine coupling tensor A , has been extensively employed as a benchmark for the identification of the equatorial donor atom sets in oxovanadium(IV) complexes.^{1a,2}

Oxovanadium(IV) compounds have usually square pyramidal or octahedral geometry with a weak sixth ligand in axial position. To the best of our knowledge, there are only two other structurally characterized $\text{V}^{\text{IV}}\text{O}^{2+}$ species with a monoanionic ligand (Cl^-)³ in axial position and obviously the effect of the charged axial ligand on ^{51}V hyperfine coupling constants has not been systematically studied. The potentially tetradentate amidate ligand, *N*-{2-[(2-pyridylmethylene)amino]phenyl}pyridine-2-carboxamide (Hcapca), was chosen in an effort to force axial ligation of anionic as well as of neutral ligands. In this report, we describe the synthesis, the cw EPR, and ESEEM spectra of the oxovanadium(IV) compounds of the general formula *trans*- $[\text{V}^{\text{IV}}\text{OX}(\text{capca})]^{?/+}$ ($\text{X} = \text{Cl}^-$ **1**, SCN^- **2**, MeCO_2^- **3** and imidazole **4**) as well as the X-ray crystal structure of **1**·MeOH with the view to studying the effect of the charged axial ligands on the ^{51}V -hyperfine coupling constants and in particular on the parallel component, A_z .

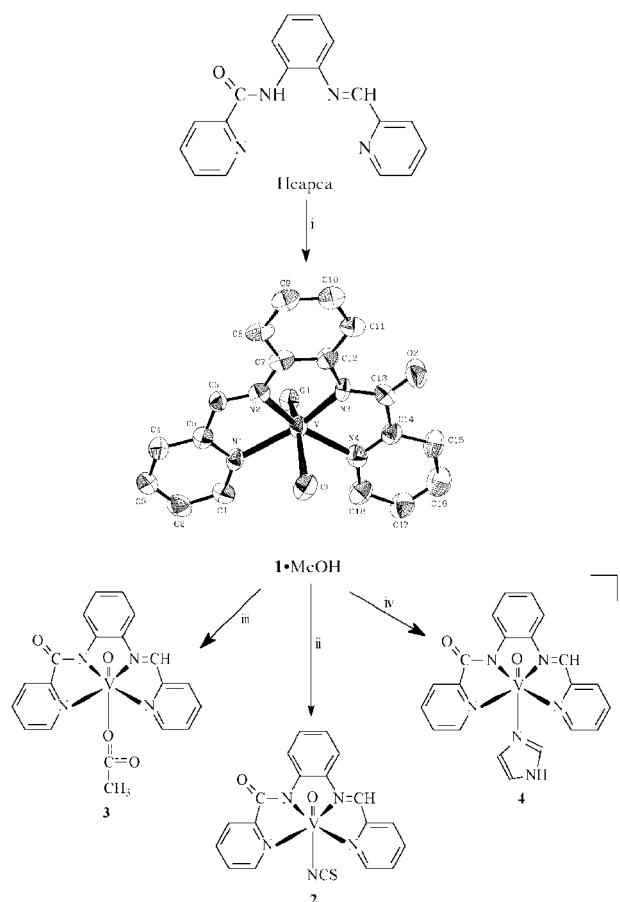
The mononuclear brick-red compound *trans*- $[\text{VOCl}(\text{capca})]$ **1** was prepared by refluxing a MeCN solution containing $[\text{VOCl}_2(\text{thf})_2]$ (3 mmol), Hcapca (3 mmol) and MeONa (3 mmol) for ca. 24 h [eqn. (1)]. The brick-red precipitate was Soxhlet extracted (CH_2Cl_2) to remove NaCl and to obtain **1**· CH_2Cl_2 .‡



† Electronic supplementary information (ESI) available: reference oxovanadium(IV) compounds. See <http://www.rsc.org/suppdata/cc/b0/b000399i/>

Crystals of **1**·MeOH suitable for X-ray structure analysis§ were obtained by vapour diffusion of diethyl ether into a concentrated MeOH solution (at 4 °C) of the complex. **2**, **3** and **4** were prepared according to Scheme 1.‡

The continuous wave (cw) EPR parameters of the four oxovanadium(IV) compounds (Table 1) were determined by computer simulation of the experimental cw EPR spectra. The cw EPR spectrum of **1**·MeOH is typical of a monomeric oxovanadium(IV) ($S = \frac{1}{2}$, $I = 7/2$) species with no evidence for



Scheme 1 Synthesis of the oxovanadium(IV) compounds **1** and **2**–**4** and X-ray crystal structure of **1**·MeOH. Reagents and conditions: i, MeCN, $[\text{VOCl}_2(\text{thf})_2]$, MeONa, reflux, argon; ii, MeOH, NEt_4NCS ; iii, MeCN, MeCO_2H , NEt_3 , 0 °C; iv, MeNO₂, imidazole. Selected interatomic distances (Å) for **1**·MeOH: V–O(1) 1.626(5), V–N(1) 2.171(7), V–N(2) 2.079(6), V–N(3) 2.010(7), V–N(4) 2.120(7), V–Cl 2.569(3).

Table 1 EPR parameters for the oxovanadium(IV) compounds **1**-MeOH, **2**, **3** and **4** in frozen MeNO₂ solutions (20 K) at X-band (microwave frequency 9.42 GHz, modulation amplitude 12.5 G, microwave power 3.2 mW)

Compound	g_x^a	g_y^a	g_z^a	10^{-4} cm^{-1}				
				g_{iso}^a	A_x^a	A_y^a	A_z^a	A_{iso}^a
1 -MeOH	1.981	1.979	1.947	1.969	53.0	49.0	145.0	82.3
2	1.981	1.979	1.947	1.969	52.0	48.0	148.0	82.7
3	1.984	1.980	1.949	1.971	52.0	45.0	144.5	80.5
4	1.980	1.978	1.946	1.968	58.0	55.0	162.0	91.7

^a Errors: g -values ± 0.002 , $A_{x,y,z}$ values $\pm 0.5 \times 10^{-4} \text{ cm}^{-1}$.

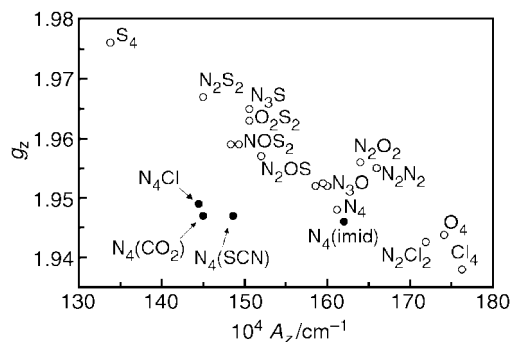


Fig. 1 A correlation plot of A_z vs. g_z for the $\text{V}^{\text{IV}}\text{O}^{2+}$ compounds **1**-MeOH and **2**-**4** (●) and a series of oxovanadium(IV) compounds (○) with various equatorial donor atoms.²

magnetic couplings between electron spins, *i.e.* line-broadening or splittings in the spectral features. ^{51}V ($S = \frac{1}{2}$, $I = 7/2$) EPR spectra of the oxovanadium(IV) compounds **2**, **3** and **4** are also typical of monomeric $\text{V}^{\text{IV}}\text{O}^{2+}$ compounds. The g and A tensors of **1**-MeOH and **2**-**4** were found to be rhombic (Table 1).

Fig. 1 (open circles) displays a correlation plot of g_z vs. A_z , for a series of known oxovanadium(IV) compounds with various equatorial donor atom sets.² The data lie approximately on a straight line with negative slope. This anti-correlation between g_z and A_z is well known and simply indicates that increased in-plane π - and σ -bonding results in decreased A_z values and increased g_z values.² Addition of the g_z and A_z values for compounds **1**-MeOH and **2**-**4** (filled circles) on the plot reveals that: (i) the points for compounds **1**-MeOH, **2** and **3** deviate substantially from the locus of the reference data. More specifically, compound **1**-MeOH⁴ has an A_z value of $145 \times 10^{-4} \text{ cm}^{-1}$, *ca.* 10% lower than the expected value of *ca.* $162 \times 10^{-4} \text{ cm}^{-1}$ for reference compounds⁵ with an N_4 equatorial donor atom set. A similar reduction of the A_z values by *ca.* 8–10% is also observed for compounds **2** and **3**, (ii) in all cases, the g_z values seem to be unaltered, (iii) the A_z value for compound **4**, with imidazole in axial position, falls on the main locus as expected. The shift of the points for **1**-MeOH, **2** and **3** relative to **4**, as well as relative to the reference data, implies that the physical mechanism which determines the A_z values in compounds **1**-MeOH, **2** and **3** is not the same as in the reference compounds. In the same context, it is noted that the $A_{x,y}$ values (Table 1) in compounds **1**-MeOH, **2** and **3** are also lower than those of compound **4**.

The equatorial ligands in compounds **1**-MeOH and **2**-**4** were studied by electron spin echo envelope modulation (ESEEM) spectroscopy.⁶ ESEEM is a pulsed EPR technique, eminently suited for measuring weak hyperfine couplings.⁶ Orientation-selective ESEEM spectra recorded across the EPR spectrum of compound **1**-MeOH, were dominated by two sets of sharp features at 3–5 and 7–9.5 MHz. According to numerical simulations, performed as described in ref. 7, the ESEEM spectra are assigned to ^{14}N ($I = 1$)-nuclei coupled to the electron spin $S = 1/2$. Two classes of almost isotropic ^{14}N -hyperfine couplings were resolved, with A_{iso} values of 5.2 and 6.1 MHz, respectively. These couplings are typical for ^{14}N ($I = 1$) atoms equatorially coordinated to $\text{V}^{\text{IV}}\text{O}^{2+}$.^{1d,e} The ESEEM spectra

recorded for **2**-**4** are comparable to those for **1**-MeOH, and this indicates that the equatorial coordination environment for compounds **2**-**4** is similar to the equatorial environment of **1**-MeOH, *i.e.* an N_4 donor-atom set for all complexes. Moreover, the ESEEM spectra show that in all four cases the ^{14}N ($I = 1$) hyperfine couplings are comparable, and this means that the bonding properties of the equatorial ligands in compounds **1**-MeOH and **2**-**4** are similar. Thus, the ESEEM spectra of compounds **1**-MeOH, **2** and **3** indicate that the reduction in their A_z values compared to N_4 reference complexes is not related to the nature of the equatorial ligands, but is rather due to the nature of the axial ligands.

In conclusion, a series of octahedral oxovanadium(IV) compounds, containing charged or neutral axial ligands, with the amidate molecule Hcapca was synthesized and structurally (**1**-MeOH) and spectroscopically characterized. The main effect of the monoanionic axial ligands on the A_z values of $\text{V}^{\text{IV}}\text{O}^{2+}$ compounds is their reduction by almost 10% compared to N_4 reference complexes. Thus, the present data reveal a novel phenomenon which bears strong relevance to the use of the A_z value as a predictive tool, in vanadoproteins, or $\text{V}^{\text{IV}}\text{O}^{2+}$ substituted proteins, *etc.* We are currently exploring analogous phenomena in $\text{V}^{\text{IV}}\text{O}^{2+}$ -compounds with various combinations of symmetries/charges of the ligands.

Notes and references

‡ The compounds analysed satisfactorily (C, H, N, V) as **1**-CH₂Cl₂, **1**-MeOH(crystals), **2**, **3** and **4**. Compound **2** was prepared by addition of NEt_4NCS (0.4 mmol) to a stirred suspension of **1**-CH₂Cl₂ (0.4 mmol) in MeOH (5 mL). Compounds **3** and **4** were prepared in a similar way, except that MeCN and MeNO₂ were used as solvents for the preparation of **3** and **4**, respectively.

§ *Crystal data*: **1**-MeOH, $\text{C}_{19}\text{H}_{17}\text{ClN}_4\text{O}_3\text{V}$, $M_r = 435.76$, monoclinic, space group $P2_1/a$, $a = 17.07(2)$, $b = 9.82(1)$, $c = 11.51(1)$ Å, $\beta = 94.03(4)^\circ$, $V = 1925(4)$ Å³, $Z = 4$, $D_c = 1.504 \text{ g cm}^{-3}$; $T = 298 \text{ K}$; no. of unique reflections 2457; no. of parameters 310; $R1/wR2$ [1544 reflections with $I > 2\sigma(I)$] 0.0663/0.1453. CCDC 182/1558. See <http://www.rsc.org/suppdata/cc/b0/b000399i/> for crystallographic files in .cif format.

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- There are two compounds in the literature (ref. 3) containing the unit *trans*-[V(=O)Cl] and having N_4 equatorial donor atom sets, namely: [VOCl(1-vinylimidazole)₄]⁺ and [VOCl(pyrazole)₄]⁺ with A_z values of 162 and $176 \times 10^{-4} \text{ cm}^{-1}$, respectively. The A_z value for compound [VOCl(pyrazole)₄]⁺ is characteristic of an equatorial donor set dominated by oxygens, most likely indicating decomposition of the complex in the solvent system (water-glycerine) used. The A_z value for [VOCl(1-vinylimidazole)₄]⁺ is in the expected range for an N_4 equatorial donor atom system.⁵
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