Synthesis, Physical Properties and *X*-Ray Crystal Structure of an Oxovanadium(IV) Complex of the Pendant-arm Macrocycle 6,13-Dimethyl-1,4,8,11-tetra-azacyclotetradecane-6,13-diamine†

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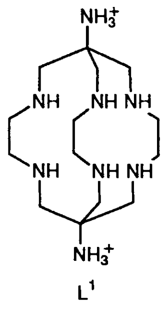
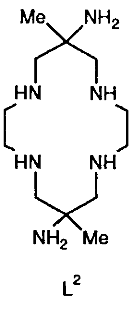
The pendant-arm macrocyclic hexa-amine 6,13-dimethyl-1,4,8,11-tetra-azacyclotetradecane-6,13-diamine (L^2) co-ordinates to the oxovanadium(IV) cation in a quinquedentate manner. The complex $[VO(L^2)][ClO_4]_2$ crystallises in the monoclinic space group $C2/c$, $a = 25.220(4)$, $b = 10.534(2)$, $c = 16.321(3)$ Å, $\beta = 94.53(1)°$. The vanadium atom is displaced by 0.397 Å above the macrocyclic plane of four nitrogens towards the oxo ligand, with a pendant amine occupying the *trans* site. Electron paramagnetic resonance and electronic spectra are consistent with the complex being a vanadyl penta-amine in solution as well as in the solid state.

The co-ordination chemistry of vanadium is dominated by the relatively stable oxovanadium(IV), or vanadyl, moiety.[1] Vanadyl complexes of many types of ligands have been reported, but few studies with saturated polyamines have appeared and there has been little structural characterisation of such complexes reported.[2–4] The stability of the vanadyl group has resulted in very few non-oxo vanadium(IV) complexes being reported. With polyamine ligands, there is one interesting example of a vanadium(IV) complex which does not contain a V=O bond, namely the complex of the macrobicyclic hexa-amine L^1 (1,8-diammonio-3,6,10,13,16,19-hexa-azabicyclo-[6.6.6]eicosane).[5,6] The encapsulating ability of the cage ligand L^1 results in protection of the vanadium(IV) centre from oxo ligand formation. The pendant-arm polyamine macrocycle L^2 (6,13-dimethyl-1,4,8,11-tetra-azacyclotetradecane-6,13-diamine) also has the potential to act as a sexidentate ligand,[7–11] with the two pendant primary amines occupying *trans* axial sites. Unlike the macrobicyclic polyamine L^1, L^2 commonly exhibits co-ordination ambivalence, and is able to act as a sexidentate, quinquedentate or quadridentate ligand, with no, one, or two primary amines respectively unbound.[7–11] As a continuation of studies of the complexation of L^2 to metal ions, we have investigated the chemistry with vanadium. The spectroscopic and electrochemical properties, and single crystal *X*-ray structure of an oxovanadium(IV) complex of L^2 are reported herein. Competition between the stable oxo ligand and the pendant primary amines for co-ordination to the vanadium centre is discussed.



L^1



L^2

Experimental

Syntheses.—Vanadium(III) acetylacetonate was obtained from Aldrich Chemicals, and L^2·6HCl was prepared as previously described.[8]

(6,13-Dimethyl-1,4,8,11-tetra-azacyclotetradecane-6,13-diamine)oxovanadium(IV) Perchlorate, $[VO(L^2)][ClO_4]_2$. To a solution of vanadium(III) acetylacetonate (0.5 g) in methanol (50 cm^3) was added dropwise a solution of L^2·6HCl (0.65 g) and triethylamine (1 cm^3) in methanol (30 cm^3). The solution was stirred at room temperature for 48 h. The resultant dark yellow solution was diluted with water (50 cm^3) and sorbed on a column (15 × 3 cm) of SP-Sephadex C-25 (Na$^+$ form) ion exchange resin. Washing the column with 0.2 mol dm^{-3} NaClO$_4$ solution removed uncomplexed vanadyl species, and the desired product was eluted as a purple band with 0.5 mol dm^{-3} NaClO$_4$ solution and concentrated on a rotary evaporator to *ca.* 20 cm^3 upon which the colour of the solution turned to green. Green crystals suitable for *X*-ray analysis formed on slow evaporation, and were collected, washed with ethanol, then diethyl ether, and dried in a vacuum desiccator (0.15 g, 20%). The filtrate yielded further crops on standing (Found: C, 27.3; H, 6.3; N, 15.4. Calc. for $C_{12}H_{30}Cl_2N_6O_9V$: C, 27.5; H, 5.8; N, 16.0%). Electronic spectrum (water): $\lambda_{max.}$ 675 (ε 15), 461 (ε 10), and 231 nm (ε 950 dm^3 mol^{-1} cm^{-1}). I.r. spectrum (KBr disc): ν(V=O) 960 cm^{-1}.

Physical Methods.—Electronic spectra were recorded on an Hitachi 150-20 spectrophotometer, and infrared spectra on a Nicolet MX-1 FT-IR spectrometer. Electrochemistry was performed as previously described,[8] in aqueous solution. Electron paramagnetic resonance spectra were run on a Varian E-9 spectrometer. The spectra were measured using *ca.* 10^{-3} mol dm^{-3} solutions of complex in water–dimethylformamide (2:1), with anisotropic spectra recorded at 77 K and isotropic spectra at room temperature. Diphenylpicrylhydrazyl (dpph) was employed as a reference.

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† (6,13-Dimethyl-1,4,8,11-tetra-azacyclotetradecane-6,13-diamine-$N^1N^4N^8N^{11}N'$)oxovanadium(IV) perchlorate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Positional co-ordinates (× 10^4) for $[VO(L^2)][ClO_4]_2$

Atom	*x*	*y*	*z*
V	3 305(1)	7 826(1)	4 159(1)
O(1)	2 721(1)	7 240(2)	4 040(1)
N(1)	3 512(1)	7 754(2)	2 943(1)
N(2)	3 097(1)	9 736(2)	3 990(1)
N(3)	4 118(1)	8 894(2)	4 187(1)
N(4)	3 338(1)	8 253(2)	5 406(1)
N(5)	3 764(1)	6 176(2)	4 304(1)
N(6)	3 427(1)	5 634(2)	5 912(2)
C(1)	3 887(1)	8 781(3)	2 743(2)
C(2)	4 000(1)	9 701(2)	3 452(1)
C(3)	3 522(1)	10 508(3)	3 649(2)
C(4)	2 906(1)	10 168(3)	4 786(2)
C(5)	3 259(1)	9 652(2)	5 496(2)
C(6)	3 791(1)	7 770(3)	5 957(2)
C(7)	3 920(1)	6 376(2)	5 856(2)
C(8)	4 143(1)	6 050(3)	5 038(2)
C(9)	4 026(1)	5 944(3)	3 526(2)
C(10)	3 686(1)	6 433(3)	2 800(2)
C(11)	4 456(1)	10 579(3)	3 262(2)
C(12)	4 356(1)	6 055(3)	6 532(2)
Cl(1)	4 435(1)	7 794(1)	653(1)
O(11)	4 490(1)	9 125(2)	561(2)
O(12)	4 777(1)	7 396(2)	1 346(2)
O(13)	4 586(1)	7 185(3)	−65(2)
O(14)	3 901(1)	7 504(2)	785(2)
Cl(2)	2 797(1)	3 512(1)	3 161(1)
O(21)	2 979(1)	3 968(2)	3 952(1)
O(22)	2 496(1)	2 382(2)	3 241(1)
O(23)	2 468(1)	4 451(2)	2 743(1)
O(24)	3 244(1)	3 268(2)	2 704(1)

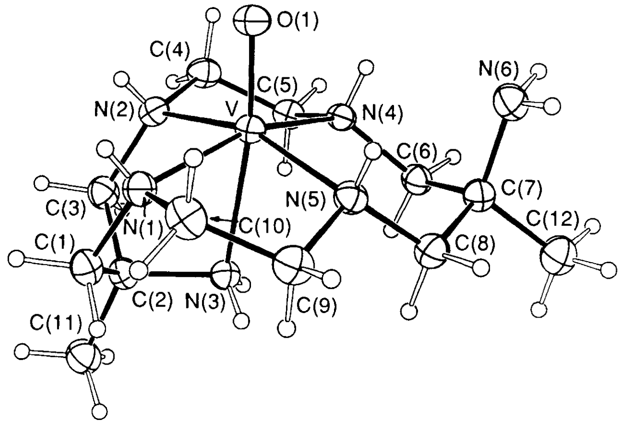


Figure 1. View of the cation $[VO(L^2)]^{2+}$

Structure Determination.—Crystal data. $[VO(L^2)][ClO_4]_2$, $C_{12}H_{30}Cl_2N_6O_9V$, M = 524.2, monoclinic, space group $C2/c$, a = 25.220(4), b = 10.534(2), c = 16.321(3) Å, β = 94.53(1)°, U = 4 322.4 Å^3, D_c (Z = 8) = 1.611 g cm^{-3}, $F(000)$ = 2 184, μ_{Mo} = 7.00 cm^{-1}. $A_{min.,max.}$ 1.08, 1.12, range of *hkl* −29 to 29, 0 to 12, 0 to 19, R = 0.030, R' = 0.035, residual extrema +0.27, −0.32 e Å^{-3}. Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections. Data were measured on an Enraf-Nonius CAD4-F four-circle diffractometer employing Mo-K_α radiation (0.7017 Å), graphite monochromator, and operating in the ω—θ scan mode. Data were reduced and Lorentz, polarization and decomposition and absorption corrections were carried out using the Enraf-Nonius Structure Determination Package. Of the 4 181 collected independent reflections not systematically absent, 3 048 with $I > 2\sigma(I)$ were considered observed and used in solution of the structure. The structure was solved by direct methods and refined by a full-matrix least-squares analysis using SHELX 76.[12] Hydrogen atoms were refined with isotropic thermal parameters and all other atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections for vanadium were taken from the International Tables,[13] and for all others the values supplied in SHELX 76 were used. Non-hydrogen atom positional co-ordinates are listed in Table 1. The atomic nomenclature for the cation is defined in an ORTEP[14] drawing in Figure 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Reaction of vanadium(III) acetylacetonate with L^2 in non-aqueous conditions produced the vanadyl species $[VO(L^2)]^{2+}$ with L^2 bound as a quinquedentate ligand, in modest yield. The reaction was found to work equally well in methanol or ethanol; however, if vanadyl sulphate was used as the precursor, no reaction occurred. The reaction product was initially eluted as a purple species, which upon rotary evaporation changed to green. Repeated attempts to isolate the purple compound, which displays electronic maxima at 513 nm (weak) and 269 nm (intense), were unsuccessful. It is highly unlikely that the purple intermediate is a vanadyl compound, as the electronic spectrum is not consistent with such a formulation (see below). It seems even less likely that the purple compound is a vanadium(III) polyamine, as these are known to be extremely air sensitive.[15] Further, electrochemical measurements, discussed below, indicate vanadium(III)–L^2 species are rapidly oxidized in aerated aqueous solution. The compound may be a non-oxo vanadium(IV) polyamine which slowly rearranges to the more stable green vanadyl penta-amine.

The electronic spectrum of green $[VO(L^2)]^{2+}$ in water was consistent with that of a vanadyl complex.[16] Moreover, the observation of two, and not three, visible maxima at 675 ($^2E \longleftarrow {}^2B_2$) and 461 nm ($^2B_1 \longleftarrow {}^2B_2$) is in accordance with co-ordination of the pendant primary amino group *trans* to the oxo ligand. The third expected transition ($^2A_1 \longleftarrow {}^2B_2$) is shifted to the ultraviolet as a result of an increased ligand field strength along the V=O axis direction and is obscured by an intense charge-transfer transition at 231 nm. The position of the two visible maxima are comparable with those reported for $VO(NCS)_5{}^{3-}$ (748 and 576 nm)[17] and particularly $VO(CN)_5{}^{3-}$ (694 and 418 nm).[18] The electronic spectrum was found to be insensitive to pH in the range 1 to 11, which indicates that the observed purple-to-green reaction is not a simple protonation/deprotonation process.

The frequency of the V=O vibration has been shown to be moderately sensitive to the co-ordination environment of the complex.[19] Specifically, co-ordination of molecules in the site *trans* to the oxo ligand results in a weakening of the V=O bonds such that these six-co-ordinate complexes possess V=O stretching frequencies at the lower end of the range observed for the vast array of vanadyl compounds (985 ± 50 cm^{-1}). The observation of a V=O resonance at 960 cm^{-1} is consistent with a six-co-ordinate vanadyl complex although this alone is not conclusive evidence for co-ordination of a pendant amino group.

Aqueous d.c. polarography identified a single, one-electron reduction of $[VO(L^2)]^{2+}$ at −0.87 V *vs.* Ag–AgCl. Cyclic voltammetry revealed that the cathodic wave (E_p −0.89 V) was essentially independent of scan rate (10—200 mV s^{-1}), indicating a rapid heterogeneous electron transfer. A similar observation was made on reoxidation, with a single anodic wave, again independent of scan rate, occurring at −0.66 V, with the anodic/cathodic current ratio *ca.* 0.9. The large separ-

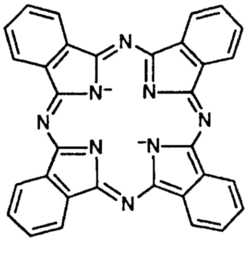
Table 2. Bond distances (Å) and angles (°) for $[VO(L^2)][ClO_4]_2$

O(1)–V	1.594(2)	N(1)–V	2.094(2)
N(2)–V	2.092(2)	N(3)–V	2.337(2)
N(4)–V	2.080(2)	N(5)–V	2.092(2)
C(1)–N(1)	1.491(4)	C(10)–N(1)	1.484(4)
C(3)–N(2)	1.487(4)	C(4)–N(2)	1.493(4)
C(2)–N(3)	1.481(3)	C(5)–N(4)	1.496(3)
C(6)–N(4)	1.487(3)	C(8)–N(5)	1.478(3)
C(9)–N(5)	1.496(4)	C(7)–N(6)	1.477(4)
C(2)–C(1)	1.519(4)	C(3)–C(2)	1.530(4)
C(11)–C(2)	1.527(4)	C(5)–C(4)	1.506(4)
C(7)–C(6)	1.516(4)	C(8)–C(7)	1.527(4)
C(12)–C(7)	1.534(4)	C(10)–C(9)	1.499(4)
O(11)–Cl(1)	1.419(2)	O(12)–Cl(1)	1.431(2)
O(13)–Cl(1)	1.415(2)	O(14)–Cl(1)	1.414(2)
O(21)–Cl(2)	1.419(2)	O(22)–Cl(2)	1.423(2)
O(23)–Cl(2)	1.430(2)	O(24)–Cl(2)	1.424(2)
N(1)–V–O(1)	99.6(1)	N(2)–V–O(1)	97.9(1)
N(2)–V–N(1)	89.3(1)	N(3)–V–O(1)	171.7(1)
N(3)–V–N(1)	75.6(1)	N(3)–V–N(2)	75.5(1)
N(4)–V–O(1)	99.7(1)	N(4)–V–N(1)	160.4(1)
N(4)–V–N(2)	84.9(1)	N(4)–V–N(3)	84.8(1)
N(5)–V–O(1)	101.0(1)	N(5)–V–N(1)	84.3(1)
N(5)–V–N(2)	160.9(1)	N(5)–V–N(3)	85.4(1)
N(5)–V–N(4)	95.2(1)	C(1)–N(1)–V	113.1(2)
C(10)–N(1)–V	106.4(2)	C(10)–N(1)–C(1)	116.4(2)
C(3)–N(2)–V	113.2(2)	C(4)–N(2)–V	105.8(2)
C(4)–N(2)–C(3)	116.8(2)	C(2)–N(3)–V	98.0(1)
C(5)–N(4)–V	108.3(1)	C(6)–N(4)–V	119.1(2)
C(6)–N(4)–C(5)	112.3(2)	C(8)–N(5)–V	118.8-2)
C(9)–N(5)–V	108.5(2)	C(9)–N(5)–C(8)	111.9(2)
C(2)–C(1)–N(1)	112.3(2)	C(1)–C(2)–N(3)	105.4(2)
C(3)–C(2)–N(3)	105.1(2)	C(3)–C(2)–C(1)	114.3(2)
C(11)–C(2)–N(3)	113.9(2)	C(11)–C(2)–C(1)	109.2(2)
C(11)–C(2)–C(3)	109.0(2)	C(2)–C(3)–N(2)	112.2(2)
C(5)–C(4)–N(2)	110.4(2)	C(4)–C(5)–N(4)	110.8(2)
C(7)–C(6)–N(4)	115.3(2)	C(6)–C(7)–N(6)	108.4(2)
C(8)–C(7)–N(6)	107.7(2)	C(8)–C(7)–C(6)	114.2(2)
C(12)–C(7)–N(6)	113.4(2)	C(12)–C(7)–C(6)	106.5(2)
C(12)–C(7)–C(8)	106.7(2)	C(7)–C(8)–N(5)	115.5(2)
C(10)–C(9)–N(5)	110.6(2)	C(9)–C(10)–N(1)	110.9(2)
O(12)–Cl(1)–O(11)	108.4(1)	O(13)–Cl(1)–O(11)	108.9(2)
O(13)–Cl(1)–O(12)	109.7(2)	O(14)–Cl(1)–O(11)	109.5(1)
O(14)–Cl(1)–O(12)	109.8(1)	O(14)–Cl(1)–O(13)	110.6(2)
O(22)–Cl(2)–O(21)	109.7(1)	O(23)–Cl(2)–O(21)	109.5(1)
O(23)–Cl(2)–O(22)	109.2(1)	O(24)–Cl(2)–O(21)	109.0(1)
O(24)–Cl(2)–O(22)	110.3(1)	O(24)–Cl(2)–O(23)	109.2(1)

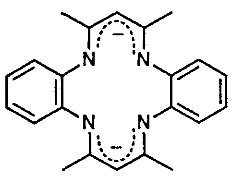
ation of the cathodic and anodic peak potentials (230 mV) coupled with the independence of the peak potentials to scan rate implies that the species reoxidized in the anodic sweep was the product of a rapid chemical reaction which follows the single-electron reduction. The pK_a of hydroxo/oxo-metal species can change markedly with oxidation state of the metal. Consequently, the most likely mechanism in this system is a reduction of the vanadyl pentamine to an oxopenta-amine-vanadium(III) species followed by rapid protonation of the oxo ligand (to form an hydroxo species). Oxidation of this species would proceed with a rapid following deprotonation to reform the original complex.

The single crystal *X*-ray structure of $[VO(L^2)][ClO_4]_2$ comprised the complex cation and two perchlorate anions, all located at general sites. There was no significant disorder of the perchlorate anions and the precision of the structure allowed definite location of all hydrogen atoms. Weak hydrogen-bonding interactions between perchlorate oxygens and co-ordinated amines (N $\cdots$ O 3.08—3.38 Å) connect cations and anions in sheets; the only moderately strong hydrogen bonding interaction is an intramolecular contact between the vanadyl oxygen and HN(4) [N $\cdots$ O 2.93, H $\cdots$ O, 2.16 Å]. Co-ordination of five of the six amine donors is apparent (Figure 1), with the oxo ligand occupying the sixth site and the unco-ordinated pendant amino group unprotonated. The configuration of the four secondary amines is the *trans*-I-(*RSRS*) form with all amine hydrogens on the same side of the N_4 plane.

The geometry of the complex cation is best described as a distorted octahedron with the vanadium centre being displaced above the plane of the four secondary nitrogens by 0.347 Å towards the oxo ligand. The V=O bond length [1.594(2) Å] is consistent with a vanadyl group.[1] The V–N(3) bond length [2.337(2) Å] is quite long and reflects the *trans* weakening effect of the oxo ligand in vanadyl complexes. This has also been observed recently in a vanadyl polyamino acid complex, where a tertiary amine *trans* to the vanadyl oxygen is longer (2.310 Å) than other V–N distances (average 2.14 Å).[4] The 'equatorial' V–N distances in $[VO(L^2)][ClO_4]_2$ (2.080—2.094 Å) are comparable with those observed in the structure of the $[V(L^1 - 2H)]^{4+}$ 'cage' complex.[5] Significantly, V–N distances to the two deprotonated secondary amines in the V^{IV} cage structure [2.063(3) Å] are shorter than the remaining four [V–N 2.096(5) Å]. This may reflect some V=N character due to donation of electron density from the deprotonated nitrogens into metal *d* orbitals. The greater affinity of the vanadyl group for electron-rich imine nitrogen donors over saturated amines in azamacrocyclic complexes is likewise reflected in V–N bond lengths in $[VO(L^3)]$ [2.026(7) Å][20] (H_2L^3 = phthalocyanine) and $[VO(L^4)]$ [2.031(6) Å][21] (H_2L^4 = 7,6-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetra-azacyclotetradecine). The displacement of the V centre from the N_4 plane in the structure of $[VO(L^2)]^{2+}$ (0.347 Å) is significantly less than those determined in the structures of the five-co-ordinate $[VO(L^3)]$ (0.575 Å) and $[VO(L^4)]$ (0.680 Å), but is comparable with the value in $[VO(CN)_5]^{3-}$ (0.37 Å).[22] The O(1)–V–N(3) angle is reduced to 171.7(1)°, with the pendant amino group being displaced toward C(2). This is most clearly seen by inspection of the angles N(3)–V–N(1,2) (75.6, 75.5°), which are much smaller than the corresponding angles N(3)–V–N(4,5) (84.8, 85.4°). This distortion is a result of ligand demands, that is the pendant amino group is displaced from the V=O axis so as to minimize intraligand strain. The analogous *trans* O–V–C angle in the structure of $[VO(CN)_5]^{3-}$ is much closer to linearity [177.9°], indicating that the distortion here is indeed due to steric strain rather than electronic effects. Non-hydrogen bond lengths and angles are given in Table 2. The structure of $[VO(L^2)][ClO_4]_2$ appears to be the first determined for vanadyl bound to a saturated penta-amine. The e.p.r. spectrum of $[VO(L^2)][ClO_4]_2$ at 77 K was consistent with a vanadyl complex possessing pseudo-axial symmetry.[23] Two sets (perpendicular and parallel to the V=O axis) of eight lines were observed (Figure 2) from coupling between the single electron and the ^{51}V nucleus ($I = \frac{7}{2}$). Spin-Hamiltonian parameters obtained from the anisotropic spectrum were $g_\perp = 2.001$, $g_\parallel = 1.970$, $A_\perp = 51.1$, and $A_\parallel =$



L^3



L^4

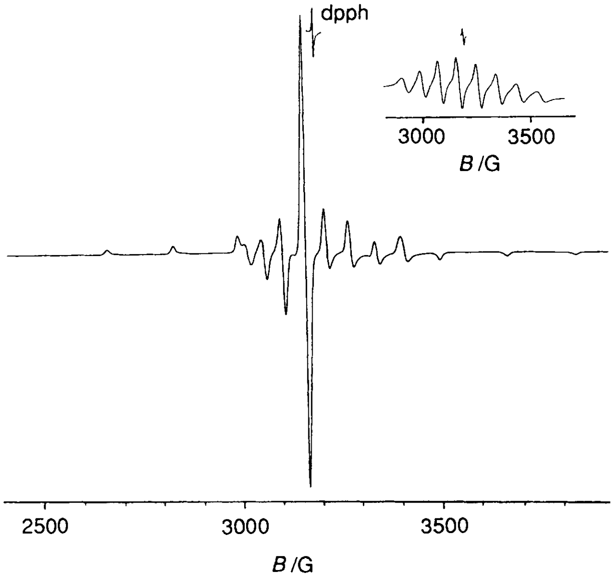


Figure 2. Electron paramagnetic resonance spectrum of $[VO(L^2)][ClO_4]_2$ at 77 K and (inset) 295 K in dimethylformamide–water (1:2)

151.1 × 10^{-4} cm^{-1}. The room-temperature spectrum yielded the isotropic values of $g_{iso} = 1.992$ and $A_{iso} = 82.5 \times 10^{-4}$ cm^{-1}. All spin-Hamiltonian parameters were in the range expected for axially asymmetric vanadyl complexes.[24]

The co-ordination of L^2 to the vanadyl cation has provided a unique opportunity to study, both structurally and spectroscopically, an oxovanadium(IV) penta-amine in solid state and solution. Previous characterizations of vanadyl penta-amines have relied almost solely upon i.r. and diffuse reflectance spectra to establish their structure.[2,3] The integrity of the compound addressed above appears to persist in both solid state and solution.

Acknowledgements

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