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A new unsymmetrical N,O-donor hexadentate ligand. Synthesis, structure and properties of its first vanadyl(IV) complex

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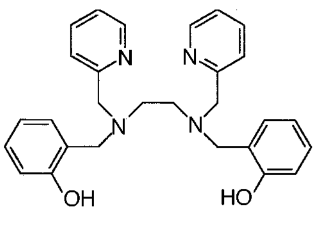
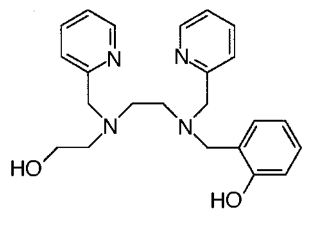
A new N,O-donor polyfunctional compound *N*-(2-hydroxybenzyl)-*N′*-(2-hydroxyethyl)-*N*,*N′*-bis(2-pyridylmethyl)-ethane-1,2-diamine (H_2bbpeten) and its first oxovanadium(IV) complex have been prepared in order to investigate the co-ordination chemistry of the unsymmetrical hexadentate ligand derived from an alkyldiamine containing phenolate-type, hydroxyethyl, and α-pyridyl pendant arms. The complex [$V^{IV}O$(Hbbpeten)]PF_6 **1** was characterized by elemental analyses, molar conductivity, IR, electronic and EPR spectroscopies, electrochemistry and X-ray diffraction methods. Spectroelectrochemistry in the UV/VIS spectral region has also been used to characterize the V^VO^{3+} analogue. The value $E_{\frac{1}{2}} = 0.427$ V *vs.* ferrocenium–ferrocene obtained from spectropotentiostatic data is consistent with cyclovoltammetric results. The electronic spectrum of the oxidized species shows two intense LMCT transitions in the 350–550 nm range, and solutions of [V^VO(Hbbpeten)]$^{2+}$ are stable on the time-scale of the experiments. A plot of $E_{\frac{1}{2}}$ *vs.* number of co-ordinated phenolates for **1** and structurally related complexes shows a fairly linear trend.

A considerable amount of research today reflects a growing interest in the importance of vanadium in biology.[1] It is an essential trace element of living plants and animals and has significant effects on normal growth.[2] While the vanadium requirement for mammals is at the nano- to pico-molar level, for several lower organisms it is considerably more pronounced.[2] It has been known since about 1910 that certain sessile marine organisms, sea squirts (*Ascidiae*) of the tunicate group, can accumulate vanadium in their 'blood cells' by a factor of 10^7 as compared to the surrounding sea-water.[3] Another vanadium-containing natural product, 'amavadin', can be isolated from mushrooms of the toadstool kind (genus *Amanita*).[4] Two enzymes have been isolated with a unique requirement for vanadium: (1) an alternative nitrogenase from several species of the nitrogen-fixing bacterium *Azotobacter*, which incorporates vanadium only (instead of molybdenum) into the corresponding cofactor when molybdenum is deficient or after genetic manipulation;[5] (2) a vanadium haloperoxidase, which has been isolated from several species of marine algae and from a terrestrial lichen, that catalyses the halogenation of organic substrates with the help of hydrogen peroxide.[6] Furthermore, it is well known that in the +3, +4 and +5 oxidation states, vanadium binds tightly to transferrins.[7]

To understand fully the role of vanadium in biological systems, the relationships between structure, spectroscopy and reactivity must be elucidated. To this end Neves *et al.*[8–11] have undertaken the synthesis and complete characterization of vanadium co-ordination compounds which have presumed structural and/or spectroscopic similarities to naturally occurring ones. In particular, we have started a new programme to investigate the co-ordination chemistry of unsymmetrical hexadentate ligands derived from alkyldiamines containing phenolate-type, hydroxyethyl, and α-pyridyl pendant arms. Here, we describe the preparation, structural, spectroscopic and electrochemical characterization of the co-ordination compound [$V^{IV}O$(Hbbpeten)]PF_6 with a new unsymmetric N_4O_2-donor (H_2(bbpeten). This ligand is structurally related to the symmetric H_2bbpen[9] in which one hydroxybenzyl has been replaced by a hydroxyethyl group. Interestingly, despite the similarities between these ligands (N_4O_2-donor set), their VO^{2+} complexes show significant structural differences.



H_2bbpen



H_2bbpeten

Experimental

Abbreviations

H_2bbpeten = *N*-(2-Hydroxybenzyl)-*N′*-(2-hydroxyethyl)-*N*,*N′*-bis(2-pyridylmethyl)ethane-1,2-diamine;H_2bbpen = *N*,*N′*-bis(2-hydroxybenzyl)-*N*,*N′*-bis(2-pyridylmethyl)ethane-1,2-diamine; H_2beten = *N*-(2-hydroxybenzyl)-*N′*-(2-hydroxyethyl)ethane-1,2-diamine; [$V^{IV}O$(tf)] = vanadium(IV)–transferrin; SCE = saturated calomel electrode; NHE = normal hydrogen electrode.

Materials

Salicylaldehyde, 2-(chloromethyl)pyridine hydrochloride, *N*-(2-hydroxyethyl)ethane-1,2-diamine, $VO(SO_4)\cdot 5H_2O$, $NaPF_6$, and tetra-*n*-butylammonium hexafluorophosphate were obtained from Aldrich. For the electrochemical, spectrochemical, and spectroscopic studies, high-purity solvents were used as received from Merck. High-purity argon was used to deoxygenate solutions. All other chemicals and solvents were reagent grade.

Syntheses

H_2beten·2HCl. This compound was obtained as an HCl salt from a condensation reaction of *N*-(2-hydroxyethyl)ethane-1,2-diamine (10.30 g, 99.04 mmol) and salicyladehyde (12.08 g,

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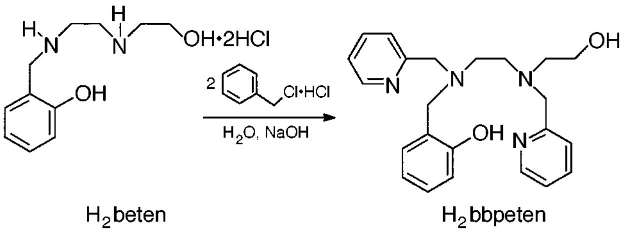


Scheme 1

99.04 mmol) followed by reduction with $NaBH_4$ (1.48 g, 39.00 mmol) in methanol as previously described.[12] Yield = 24.79 g (90.17%). IR (cm^{-1}): ν(N–H) 3273; ν(O–H) 3140; ν(C=N, C=C) 1599, 1512, 1458; δ(O–H) 1352; ν(C–O) 1274. ^{13}C NMR (D_2O): δ 157.59, 134.27, 134.20, 123.04, 119.23, 118.10, 58.97, 52.13, 49.89, 45.41 and 44.90 (Found: C, 41.13; H, 7.52; N, 8.93. Calc. for $C_{11}H_{24}Cl_2N_2O_4$: C, 41.38; H, 7.52; N, 8.78%).

H_2bbpeten. The unsymmetric compound was synthesized by nucleophilic substitution reaction of 2-(chloromethyl)pyridine hydrochloride (3.28 g, 20 mmol), previously neutralized with 4 mol dm^{-3} NaOH, with H_2beten•2HCl (2.83 g, 10 mmol), also previously neutralized with 4 mol dm^{-3} NaOH, in water (30 cm^3). Sodium hydroxide (4 mol dm^{-3}, 5 cm^3) was added very slowly to the stirred mixture in a cool bath according to the route in Scheme 1. It was extracted with eight 50 cm^3 portions of $CHCl_3$, and the extracts were combined, washed with sodium chloride solution, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography employing ethanol–water (3 : 1%) as eluent to afford 2.53 g (64.52%) of a yellow oil. IR (cm^{-1}): ν(O–H) 3250; ν(C=N, C=C) 1592, 1484, 1436; δ(O–H) 1368; ν(C–O) 1252. ^1H NMR ($CDCl_3$): δ 2.65 (6 H, $NCH_2C_6H_4$, CH_2OH), 3.80 (8 H, $NCH_2C_5H_4N$, NCH_2CH_2N), 7.25 (10 H, C_6H_4, C_5H_4N) and 8.50 (2 H, C_5H_4N); no proton shifts were observed for the OH groups (Found: C, 68.50; H, 7.45; N, 13.35. Calc. for $C_{23}H_{30}N_4O_3$: C, 67.31; H, 7.32; N, 13.66%).

[V^{IV}O(Hbbpeten)]PF_6 1. The co-ordination compound was prepared by refluxing a methanolic solution of $VO(SO_4)\cdot 5H_2O$ (0.25 g, 1 mmol) and H_2bbpeten (0.39 g, 1 mmol) with magnetic stirring for 1 h. To the reaction was added Et_3N (1 cm^3, 7.18 mmol) and $NaPF_6$ (0.17 g, 1 mmol), to yield a dark rose precipitate, which was recrystallized from acetonitrile–propan-2-ol (1 : 1) solution at room temperature. After a few days a microcrystalline solid was filtered off, washed with propan-2-ol and dried with diethyl ether. Yield: 0.28 g (47.25%) (Found: C, 45.83; H, 4.58; N, 9.09. Calc. for $C_{23}H_{27}F_6N_4O_3PV$: C, 45.78; H, 4.51; N, 9.29%). Crystals suitable for X-ray crystallography were obtained by slow evaporation of a acetonitrile–propan-2-ol (1 : 1) solution of the compound.

Physical measurements

Elemental analyses were performed on a Perkin-Elmer model 2400 instrument. Infrared spectra were obtained on a Perkin-Elmer model 781 spectrometer in KBr disc or film, ^{13}C and ^1H NMR spectra on a Bruker AC-200F spectrometer in D_2O or $CDCl_3$, EPR spectra at 298 and 77 K on a Bruker ESP 300E spectrometer and visible and NIR spectra in CH_3CN with a Perkin-Elmer Lambda 19 spectrometer. Molar conductivity was measured in CH_3CN (10^{-3} mol dm^{-3}) at 298 ± 0.1 K with a Digimed CD-21 instrument. Cyclic voltammetry experiments were performed with a Princeton Applied Research (PAR) 273 system in CH_3CN under argon at room temperature with 0.1 mol dm^{-3} [NBu^n_4][PF_6] as the supporting electrolyte. Cyclic voltammetry (CV) was carried out by using a standard three-component system consisting of a platinum-disc working electrode, a platinum-wire auxiliary electrode, and a SCE reference electrode. The ferrocenium–ferrocene couple was used to monitor the reference electrode and was observed at +0.205 V *versus* SCE. Spectropotentiostatic experiments were performed with the use of an optically transparent thin-layer cell constructed according to a procedure described elsewhere.[13] Potentials were applied to the cell by a potentiostat/galvanostat (PARC 263), and the spectra were collected with a Perkin-Elmer L19 spectrophotometer. The performance of the reference electrode was monitored before and after the experiments by measuring the ferrocene couple, which was found to have a value of +0.309 V *versus* SCE. Spectral changes were registered after equilibrium was established, following selected potential steps. We allowed 90 s between the recording of each spectrum, and the experiments were stopped when no further changes in the intensity of λ_{max} were observed for the oxidized species.

Crystallography

A pink prismatic crystal (0.10 × 0.25 × 0.50 mm) of [V^{IV}O(Hbbpeten)]PF_6 was mounted on a CAD-4 Nonius diffractometer. The cell parameters were obtained by a least-squares fit of 25 reflections ($8.57 < \theta < 15.31°$).

Crystal data. $C_{23}H_{27}F_6N_4O_3PV$, $M = 603.40$, triclinic, space group $P\bar{1}$, $a = 9.967(2)$, $b = 10.942(2)$, $c = 12.246(2)$ Å, $\alpha = 81.40(3)$, $\beta = 70.18(3)$, $\gamma = 85.13(3)°$, $U = 1241.5(4)$ Å^3, $Z = 2$.

The intensity data were collected by using an ω–2θ scan mode, with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å), a scan speed of 4–20° min^{-1}, and a scan range of (0.80 + 0.35 tan θ)°. No significant decline in intensities of three standard reflections was observed. The data were corrected for Lorentz-polarization effects. The number of measured reflections was 4600 in the range −11 to 11, −12 to 0, −14 to 14 with 4348 unique and 3428 with $I > 2\sigma(I)$ ($R_{int} = 0.0163$). A semiempirical absorption correction (based on ψ scans) was applied, with maximum and minimum transmission factors of 0.9999 and 0.9196. The structure was solved using SHELXS 86[14] and the atoms were refined anisotropically (on F^2) by full-matrix least squares using SHELXL 93[15] with 4348 reflections. The function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = [\sigma^2(F_o^2) + (0.0857P)^2 + 2.74P]^{-1}$ and $P = (2F_c^2 + F_o^2)/3$. All the hydrogen atoms were placed at calculated positions with isotropic displacement parameters 1.5 times those of their parent atoms. Maximum and minimum peaks in the final difference synthesis were 0.822 and −0.590 e Å^{-3}, respectively. The structure was refined to an R factor 0.0577 based on 3428 observed reflections with 346 refined parameters and $wR = 0.1533$.

CCDC reference number 186/818. A list of observed and calculated structure factors is available from one of the authors (I. V.).

Results and Discussion

Syntheses

The synthesis of the new unsymmetrical compound $H_s$bbpeten is conveniently carried out by treating 2-(chloromethyl)pyridine with the diamine H_2beten (Scheme 1). The characterization of H_2bbpeten was established unambiguously by elemental analysis, IR and ^1H NMR spectroscopies. It reacts in methanolic solution with $VO(SO_4)\cdot 5H_2O$ to form the stable monocationic [V^{IV}O(Hbbpeten)]$^+$ complex, which was isolated in good yield as the hexafluorophosphate salt **1**.

The IR spectrum of complex **1** is similar to that of free H_2bbpeten. It differs only in: (a) the appearance of a well defined band at 3564 cm^{-1} attributed to the ν(O–H) stretching of the primary alcohol which is not co-ordinated; (b) the band at 1364 cm^{-1}, attributed to the in-plane deformation δ(O–H) of the phenol, becomes less intense in relation to that observed for

Table 1 Selected bond distances (Å) and angles (°) for complex **1**

V–O(2)	1.598(3)	V–N(31)	2.123(3)
V–O(1)	1.912(3)	V–N(1)	2.214(3)
V–N(21)	2.112(3)	V–N(2)	2.324(3)
O(2)–V–O(1)	105.4(1)	N(21)–V–N(1)	79.5(1)
O(2)–V–N(21)	99.9(2)	N(31)–V–N(1)	92.2(1)
O(1)–V–N(21)	88.9(1)	O(2)–V–N(2)	166.5(1)
O(2)–V–N(31)	94.3(2)	O(1)–V–N(2)	85.1(1)
O(1)–V–N(31)	94.8(1)	N(21)–V–N(2)	88.6(1)
N(21)–V–N(31)	163.8(1)	N(31)–V–N(2)	76.0(1)
O(2)–V–N(1)	92.7(1)	N(1)–V–N(2)	78.4(1)
O(1)–V–N(1)	160.0(1)		

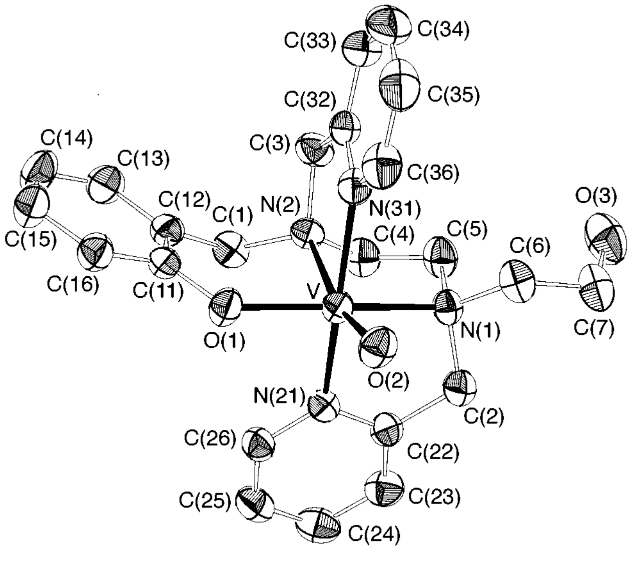
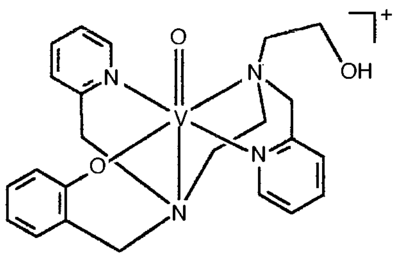


Fig. 1 Crystal structure of complex **1**, showing the atom-labelling scheme, at 50% probability

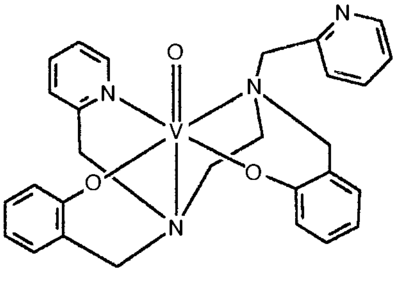
free H_2bbpeten; (c) the appearance of a band at 840 cm^{-1} attributed to the PF_6^- anion; (d) the appearance of a new band at 968 cm^{-1} attributed to the stretching ν(V=O). The molar conductivity of **1** in acetonitrile at 298 K is 145 Ω^{-1} cm^2 mol^{-1} which is consistent with a 1 : 1 electrolyte.[16]

Crystal and molecular structure of $[\mathrm{V^{IV}O(Hbbpeten)}]\mathrm{PF_6}$ 1

The structure of the co-ordination compound **1** consists of discrete mononuclear $[\mathrm{V^{IV}O(Hbbpeten)}]^+$ cations and unco-ordinated hexafluorophosphate anions in the asymmetric unit. An ORTEP[17] drawing of the complex cation with its atom-labelling scheme is shown in Fig. 1. Selected bond distances and angles are given in Table 1. The vanadium(IV) ion is in a distorted octahedral environment, in which one phenolate oxygen, one amine and two pyridyl nitrogen atoms in *trans* positions form the equatorial plane. The other amine nitrogen atom of the ethylenediamine backbone, in the *trans* position with respect to the terminal oxo group, and that oxo atom complete the co-ordination sphere of the vanadium while the hydroxyl group remains unco-ordinated.



$[\mathrm{VO(Hbbpeten)}]^+$



[VO(bbpen)]

Since the ligands H_2bbpeten and H_2bbpen[9] have similar N_4O_2-donor sets, it is useful to compare the structures of their $\mathrm{V^{IV}O^{2+}}$ complexes in order to gain insight concerning the spectroscopic properties of these complexes. The $[\mathrm{V^{IV}O(bbpen)}]$ co-ordination compound has been described as a synthetic analogue for $[\mathrm{V^{IV}O(tf)}]$.[9] While in $[\mathrm{V^{IV}O(bbpen)}]$ one pyridyl group of the ligand is pendant, in **1** the hydroxyethyl group of H_2bbpeten is not co-ordinated to the $\mathrm{V^{IV}}$. In the $[\mathrm{V^{IV}O(bbpen)}]$ two phenolate oxygens, one amine and one pyridyl nitrogen atom form the equatorial plane (N_2O_2 set), in contrast to the N_3O co-ordination observed in **1**. The co-ordination of the ethylenediamine backbone is identical in both complexes (*cis-trans* positions with respect to the V=O bond). The five-membered rings (VN_2C_2) with their usual skew conformation have N–C–C–N torsion angles of 56.0(5) and 54.2(4)° for **1** and $[\mathrm{V^{IV}O(bbpen)}]$, respectively. This form of co-ordination of the ethylenediamine group is unusual,[9,12b] since in other six-co-ordinated vanadyl complexes containing it, both diamine nitrogen atoms are co-ordinated *cis* rather than *cis–trans* to the V=O bond.[12a,18] This is probably due to the chelate ring strain in these co-ordination compounds, in which the five-membered ring VN_2C_2 formed with the ethylenediamine group is more flexible (two sp^3 C atoms) than the corresponding ring formed with the pyridyl group (one sp^2 and one sp^3 C atom) which requires smaller bite angles. The significantly smaller torsion angles N(2)–C(3)–C(32)–N(31) −6.7(6), N(1)–C(2)–C(22)–N(21) 27.3(6)° for **1** and 22.2(4)° in $[\mathrm{V^{IV}O(bbpen)}]$ demonstrate the ring strain caused by the rigidity of the pyridyl arms; these five-membered rings are closely planar, with the sum of the interior angles ranging between 530 and 540°. The remaining six-membered ring ($VONC_3$) formed by the pendant 2-hydroxybenzyl group in **1** adopts a distorted half-chair conformation with the torsion angle N(2)–C(1)–C(12)–C(11) of −55.8°. The V=O distance is short [1.598(3) Å], indicating the double-bond character typical of vanadyl(IV) complexes.[9,11] This value is slightly shorter compared to that [1.606(2) Å] in $[\mathrm{V^{IV}O(bbpen)}]$. As expected, the V–N (amine) bond distance of 2.324(3) Å *trans* to the V=O bond in **1** is 0.10 Å longer than that in the equatorial plane and is a consequence of the strong *trans* influence of the oxo group. A similar trend in these bond lengths has been observed in $[\mathrm{V^{IV}O(bbpen)}]$ [2.307(2) and 2.208(3) Å], but with longer V–N (amine) bonds in **1**. This fact can be associated with the higher rigidity of **1**, due to the presence of three five- and one six-membered rings compared to $[\mathrm{V^{IV}O(bbpen)}]$ which possesses two five- and two six-membered rings. In addition, the displacement of the V atom from the equatorial N_3O plane [0.296(1) Å] for the present co-ordination compound is significantly smaller compared with that of 0.345(2) Å in $[\mathrm{V^{IV}O(bbpen)}]$. The V–O (phenolate) [1.912(3) Å] bond distance in **1** compares very well with those in the bbpen co-ordination compound [average 1.923(2) Å]. However, the V–N (pyridine) [average 2.112(3) Å] bond distances in the equatorial plane of **1** are 0.052(3) Å shorter than that in $[\mathrm{V^{IV}O(bbpen)}]$ and are a reflection of the weak *trans* influence caused by the phenolate bond in the latter. From this information we can conclude that at least to some extent $[\mathrm{V^{IV}O}$-

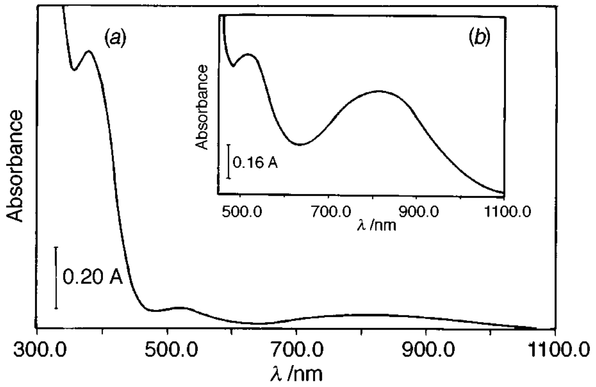


Fig. 2 Electronic spectra of complex **1** in CH_3CN, (*a*) 4×10^{-4}; (*b*) 10^{-3} mol dm^{-3}

(bbpen)] exhibits a higher degree of distortion in the equatorial plane compared to that of **1**.

The crystallographically independent hexafluorophosphate anion in the structure is ordered but shows significant distortions from a rigorous octahedral environment due to the high anisotropic thermal parameters of the F atoms. The P–F bonds range from 1.501(5) to 1.544(5) Å and F–P–F *cis* angles vary between 84.6(5) and 99.2(6)°. In addition, the distances between C(5) ··· O(3^{i}) (i 2 − *x*, 1 − *y*, −*z*) and C(23) ··· F(4^{ii}) (ii 2 − *x*, 1 − *y*, −1 − *z*) are 3.360(6) and 3.385(8) Å respectively, indicating C–H ··· O and C–H ··· F interactions involving hydrogen atoms on C(5) and C(23). The remaining bond lengths and angles for the ligand in **1** are as expected and will not be discussed further.

Electronic absorption and electron paramagnetic resonance spectra

The electronic spectra of complex **1** measured in CH_3CN in the visible region are displayed in Fig. 2 and reveals the following transitions at λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 844 (57), 760 (53), 516 (57) and 377 (1078). The values of λ_{max} of the lowest transitions that are overlapped in a very broad band were resolved by the regions of negative slope in the first derivative. According to Ballhausen and Gray,[19] the weak absorptions at 844 and 760 nm can be attributed to the d–d transitions $d_{xy} \longrightarrow d_{xz}$ and $d_{xy} \longrightarrow d_{yz}$, whereas that at 516 nm involves the $d_{x^2-y^2}$ orbital in compounds of low symmetry, as in [V^{IV}O(bbpen)] for which the corresponding transitions are observed at λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 925 (75), 870 (70) and 555 (125).[9] Consistent with the crystal data previously described, **1** is less distorted than [V^{IV}O(bbpen)]. The value of $10Dq = 19\,380$ cm^{-1} can be obtained directly from the transition at 516 nm. This value is somewhat higher than that for [V^{IV}O(bbpen)] (18 000 cm^{-1}) and most likely arises due to the distinct co-ordination environments in the equatorial plane of both compounds {N_3O for **1** and N_2O_2 for [V^{IV}O(bbpen)]}. The other absorption at 377 nm is tentatively assigned as a charge-transfer process as in [V^{IV}O(bbpen)].[9] The same positions of the absorption maxima were found in the reflectance spectra of a solid sample of **1**, which indicates that no ligand-dissociation processes occur in CH_3CN solution.

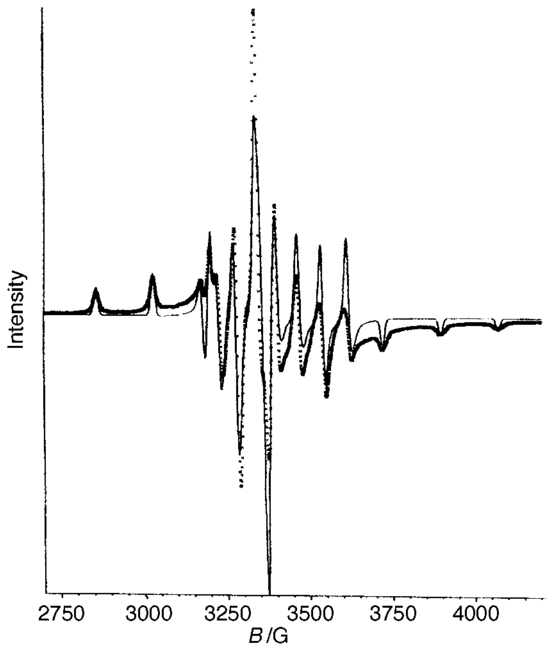


Fig. 3 X-Band EPR spectrum of complex **1** in CH_2Cl_2 at 77 K: (x) experimental spectrum; (——) simulated using the WINEPR SIMFONIA program, the molecular peak–peak linewidths referred to the *g* tensor axes of $\Delta B_x = 20.00$, $\Delta B_y = 12.00$, $\Delta B_z = 12.00$ G (G = 10^{-4} T) and a Gaussian line-shape function. The Hamiltonian parameters are $g_x = 1.9790$, $g_y = 1.9842$, $g_z = 1.9477$, $A_x = 57.10 \times 10^{-4}$, $A_y = 58.00 \times 10^{-4}$, $A_z = 159.00 \times 10^{-4}$ cm $^{-1}$

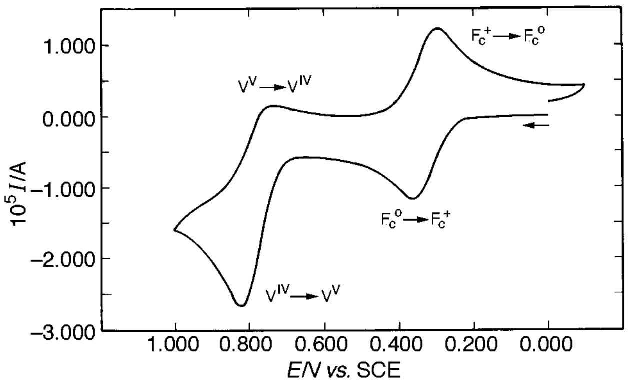


Fig. 4 Cyclic voltammogram of complex **1** in CH_3CN (0.1 mol dm^{-3} [NBu^n_4][PF_6]) at a platinum working electrode, scan rate 100 mV s^{-1}, under argon with two successive scans. Fc^0 = ferrocene

The X-band EPR spectrum of a frozen solution of complex **1** in CH_2Cl_2 together with the simulated spectrum is shown in Fig. 3. The Hamiltonian parameters obtained from the spectrum demonstrate the low-symmetry geometric structure in the molecule, as can be observed in other vanadyl complexes previously reported.[9,20] The rhombic distortion is consistent with X-ray diffraction data and the electronic absorption spectrum. However, this in-plane observable anisotropy, $|g_x - g_y| = 0.0052$, $|A_x - A_y| = 10^{-4}$ cm^{-1}, demonstrates that the distortions in **1** are somewhat less pronounced than those in [V^{IV}O(bbpen)], for which $|g_x - g_y| = 0.006$. Generally, ligands with a larger number of nitrogen donors form complexes with higher-energy $d_{xy} \longrightarrow d_{xz}$, d_{yz} and $d_{xy} \longrightarrow d_{x^2-y^2}$ transitions.[1] The higher values of the *g* parameters ($g_x = 1.9790$, $g_y = 1.9842$, $g_z = 1.9477$) for the present N_3O equatorial co-ordination are consistent with the more energetic d ⟶ d transitions found, compared to the values observed for [V^{IV}O(bbpen)] ($g_x = 1.9705$, $g_y = 1.9765$, $g_z = 1.9375$) which has an N_2O_2 equatorial co-ordination and consequently lower-energy d ⟶ d transitions.

Electrochemistry and spectroelectrochemistry

The cyclic voltammogram of complex **1** in CH_3CN at a scan rate of 100 m V s^{-1} (Fig. 4) shows a quasi-reversible redox couple at 0.695 V *versus* SCE (0.427 V *vs.* ferrocenium–ferrocene) which can be ascribed to the [V^VO(Hbbpeten)]$^{2+}$–[V^{IV}O(Hbbpeten)]$^+$ redox couple. As expected, this potential is anodically shifted by 0.537 and 1.187 V when compared with the $E_{\frac{1}{2}}$ values of [V^{IV}O(bbpen)] and [V^VO{(2-$OC_6H_4CH_2)_2N(CH_2)_2N(CH_2C_6H_4O$-2)}],[12] respectively, and clearly reflects the different

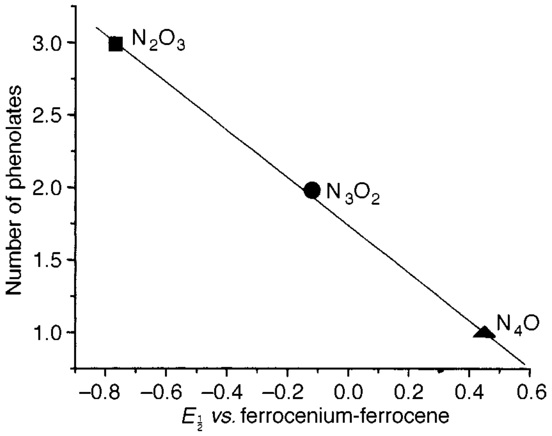


Fig. 5 Correlation between the number of bonded phenolates and the redox potential for the couple VO^{3+}–VO^{2+} with the co-ordination environment of the vanadyl ion in the complexes $[V^{IV}O(Hbbpeten)]^+$, $[V^{IV}O(bbpen)]$ and $[V^VO\{(2\text{-}OC_6H_4CH_2)N(CH_2)_2N(CH_2C_6H_4O\text{-}2)\}]$

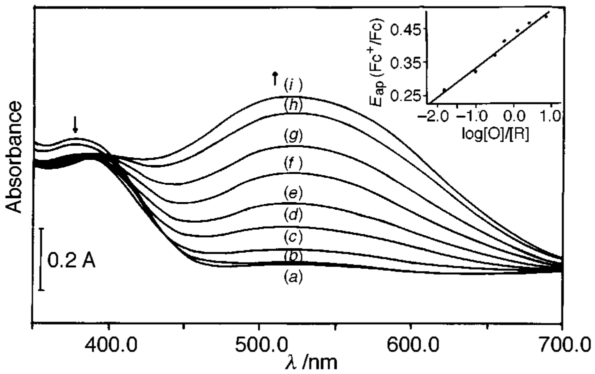


Fig. 6 Spectra recorded during a spectropotentiostatic experiment on 10^{-4} mol dm^{-3} $[V^{IV}O(Hbbpeten)]PF_6$ (0.1 mol dm^{-3} $[NBu^n_4][PF_6]$) in CH_3CN. Applied potentials in V *vs.* SCE are: (*a*) 0.00, (*b*) 0.57, (*c*) 0.62 (*d*) 0.67, (*e*) 0.71, (*f*) 0.74, (*g*) 0.76 (*h*) 0.78 and (*i*) 0.80

number of phenolate groups co-ordinated to the VO^{2+} moiety in these complexes.

A plot of $E_{\frac{1}{2}}$ *vs.* number of bonded phenolates (Fig. 5) for these co-ordination compounds exhibits a fairly linear trend. It is important to note that this trend can be used in the design of multidentate ligands for the stabilization of preferred oxidation states of vanadium.

We have used spectroelectrochemistry in the 350–700 nm region to examine the electronic absorption and redox properties of $[V^VO(Hbbpeten)]^{2+}$ generated in solution from co-ordination compound **1**. The spectral change for the reaction is shown in Fig. 6. The vanadium(v) complex exhibits maxima at 396 ($\varepsilon = 1770$) and 522 nm ($\varepsilon = 1950$ dm^3 mol^{-1} cm^{-1}). The lowest-energy band is assigned by analogy to other monooxo-vanadium(v) complexes,[9,21] as a phenolate-to-vanadium(v) charge-transfer transition. This band is blue shifted compared with the corresponding absorption of $[V^VO(bbpen)]^+$ ($\lambda = 582$ nm), while the molar absorption coefficient is approximately half that observed for $[V^VO(bbpen)]^+$. These data are in agreement with the presence of one co-ordinated phenolate in the oxidized species of **1**, two phenolates in $[V^VO(bbpen)]^+$, and three phenolates in $[V^VO\{(2\text{-}OC_6H_4CH_2)_2N(CH_2)_2\text{-}N(CH_2C_6H_4O\text{-}2)\}]$ ($\varepsilon = 6400$ dm^3 mol^{-1} cm^{-1}).[12]

The higher-energy band at 396 nm is also assigned by comparison with other reported vanadium(v) co-ordination compounds as being a LMCT process.[9,22] The maintenance of an isosbestic point in successive spectra strongly corroborates the presence of a single product throughout the course of the electrolysis. The $E_{\frac{1}{2}} = 0.416$ V *vs.* ferrocenium–ferrocene and $n = 0.9$ electron obtained from the Nernst plot are in good agreement with the CV results.

In conclusion, a $V^{IV}O^{2+}$ complex containing a novel polyfunctional ligand has been prepared and characterized structurally and spectroscopically. The accessibility of the oxidized species, evidenced by spectroelectrochemical studies, reveals that the $[V^VO(Hbbpeten)]^{2+}$ ion can be electrochemically generated in solution without changing the co-ordination sphere at the vanadium. Finally, the plot of $E_{\frac{1}{2}}$ *vs.* number of bonded phenolates (Fig. 5) reflects the importance of co-ordination compound **1** in this series of $bbpen^{2-}$ analogues, since it provides a useful method of designing multidentate ligands with bioinorganic relevance for the stabilization of preferred metal states.

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