DALTON
FULL PAPER

Synthesis and structure of vanadate esters of glycerol and propane-1,3-diol

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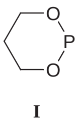
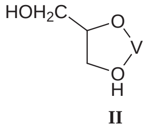
Complexes of the type [VO(L)(H_2gl)] and [VO(L)(Hpd)] have been synthesized in excellent yields by reacting bis(acetylacetonato)oxovanadium(IV) with H_2L in the presence of excess glycerol (H_3gl) and propane-1,3-diol (H_2pd) in methanol–acetone (hydroxyphenylmethylenehydrazones of 4-hydroxy-4-phenylbut-3-en-2-one, salicylaldehyde and 2-hydroxynaphthaldehyde are respectively abbreviated as H_2L^1, H_2L^2 and H_2L^3 and generally as H_2L). The crystal structures of [VO(L^2)(H_2gl)] and [VO(L^2)(Hpd)] have revealed tridentate ONO co-ordination by $[L^2]^{2-}$ while $[H_2gl]^-$ and $[Hpd]^-$ form five- and six-membered V(O,O) chelate rings respectively. In the distorted octahedral VO_5N co-ordination sphere the V–O (alkoxide) bond is 0.5–0.6 Å shorter than the V–O (alcoholic) bond which lies *trans* to the oxo oxygen atom. In [VO(L^2)(Hpd)] the lattice consists of dimers held together by O · · · N hydrogen bonding between the OH group of $[Hpd]^-$ in one molecule and the unco-ordinated $[L^2]^{2-}$ nitrogen in an adjacent molecule. In the [VO(L^2)(H_2gl)] lattice such dimers self-assemble into an infinite pattern *via* additional O · · · O hydrogen bonding between the unco-ordinated OH group of $[H_2gl]^-$ of one molecule with the co-ordinated alkoxidic oxygen of the adjacent molecule. In [VO(L)(H_2gl)] both the metal site and the $[H_2gl]^-$ ligand are chiral and the two equally abundant diastereoisomers are present in solution (^{1}H NMR). The ^{51}V chemical shifts are diagnostic of the alkoxidic chelate ring size: the shifts of [VO(L)(H_2gl)] being ≈30 ppm downfield from that of [VO(L)(Hpd)]. The complexes have low VO^{3+}–VO^{2+} reduction potentials.

It has been known for a long time that in the pentavalent state vanadium, like phosphorus, forms esters with alcohols.[1,2] The richness and importance of vanadate ester chemistry has emerged over the past 25 years.[3–14] Our interest lies in the design, isolation and characterization of esters incorporating V(O,O) chelation by polyhydric alcohols. Such species are very rare and a systematic quest for them has recently been initiated starting with ethane-1,2-diol.[15,16]

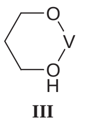
The present work concerns vanadate ester formation by the polyols glycerol and propane-1,3-diol. No vanadate ester of any kind has so far been reported for glycerol. In the case of 1,3-diols multinuclear esters incorporating oxo and alkoxo bridges are known but attempts to realise the six-membered V(O,O) chelation mode have failed.[17] In contrast the corresponding P(O,O) chelation mode **I** is well documented and is biologically very relevant as found in adenosine 3′,5′-phosphate.[18] Herein we report the first families of vanadate esters incorporating V(O,O) chelation by monoionized glycerol and propane-1,3-diol as in **II** and **III** respectively. Representative species have been structurally characterized and their solution properties scrutinized with the help of spectral and electrochemical tools. A collective examination of ^{51}V NMR spectra has revealed a correlation between alkoxidic chelate ring size and chemical shift.



I



II

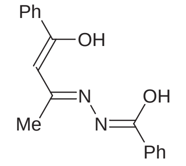


III

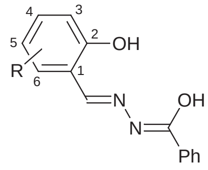
Results and Discussion

Synthesis

The case of glycerol (H_3gl) is considered first. Tridentate diacidic hydrazones (H_2L) have an excellent affinity for oxovanadium(V)[3,16,19,20] and three of these (H_2L^1, H_2L^2 and H_2L^3) have been used as coligands so as to block three co-ordination positions leaving two for possible polyol chelation.



H_2L^1



R = H, H_2L^2
R = 5,6-benzo, H_2L^3

The stoichiometric reaction of bis(acetylacetonato)oxovanadium(IV) with H_2L in methanol–acetone in air in the presence of excess H_3gl afforded dark coloured complexes of composition [VO(L)(H_2gl)] in excellent yields. Complexes of propane-1,3-diol (H_2pd) were prepared by replacing H_3gl by H_2pd in the above procedure and their composition is [VO(L)(Hpd)]. Characterization data for the two families are given in the Experimental section. These are the first vanadate esters of glycerol and the first 1,3-diol esters incorporating chelation modes **II** and **III**.

The complexes are insoluble in halogenocarbons but are soluble in dimethyl sulfoxide and all solution measurements were performed in this solvent. If the solvent is wet the complexes tend to undergo partial hydrolysis which could be suppressed by adding ≈5% of the relevant polyol. Most solution measurements were performed in dry dimethyl sulfoxide to which ≈2% free alcohol was added as a precaution to prevent hydrolysis.

All the complexes are electroactive at platinum and the quasi-reversible V^VO–$V^{IV}O$ couple occurs near −0.2 V *vs.* SCE. The oxovanadium(V) state is thus strongly stabilized by alkoxide co-ordination and this facilitates spontaneous $V^{IV}O \longrightarrow V^VO$ oxidation by aerial oxygen in the synthetic procedure.

Structure

The crystal structures of [VO(L^2)(H_2gl)] and [VO(L^2)(Hpd)] have been determined. Molecular views are shown in Figs. 1 and 2 and selected bond parameters are listed in Table 1.

[VO(L^2)(H_2gl)]. The chelation mode **II** is present and the ring

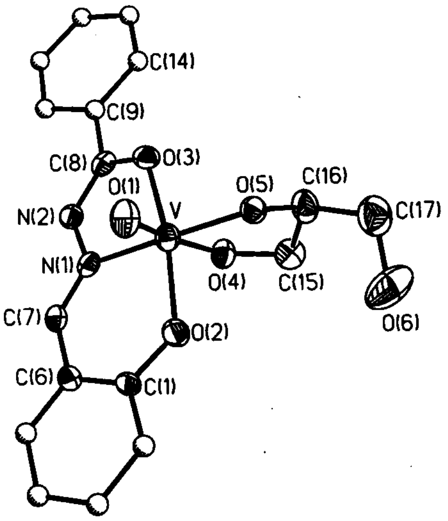


Fig. 1 Perspective view and atom labelling scheme of [VO(L^2)(H_2gl)]. All non-hydrogen atoms are represented by their 30% probability ellipsoids

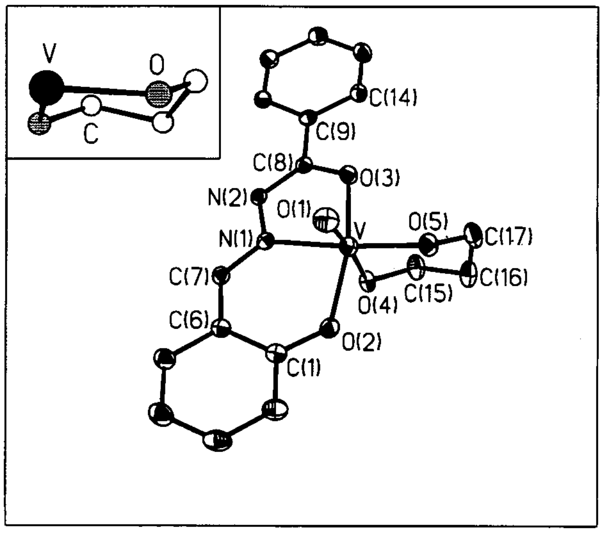
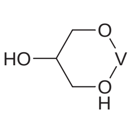


Fig. 2 Perspective view and atom labelling scheme of [VO(L^2)(Hpd)]; the inset shows the V(Hpd) chair. All non-hydrogen atoms in the structure are represented by their 30% probability ellipsoids

is non-planar. Very few metal complexes of glycerol have been structurally characterised.[21] The possible six-membered mode **IV** is not observed either in the solid state or in solution of the complexes (see below). Significantly the co-ordinated alkoxide group is derived from secondary and primary alcohol functions in **II** and **IV** respectively and it is therefore expected to be a better donor in the former case.



IV

Glycerol is prochiral and the co-ordinated $[H_2gl]^-$ ligand is chiral at C(16) (Fig. 1). Since the metal site in [VO(L^2)(H_2gl)] is also chiral, two diastereoisomers (each comprising of an enantiomeric pair) are possible. In Fig. 1 the configuration of $[H_2gl]^-$ is *S* while that of the metal site is *C*.[22] The crystal of [VO(L^2)(H_2gl)] examined by us is thus constituted of the *SC–RA* enantiomeric pair. In bulk samples the *RC–SA* diastereoisomer is also present and it makes an equal contribution to solution composition (see below).

The VO_5N co-ordination sphere is distorted octahedral, the metal atom is displaced by 0.33 Å towards the oxo atom O(1) away from the equatorial plane (mean deviation 0.04 Å) defined by O(2), N(1), O(3) and O(5). The $[L^2]^{2-}$ ligand is meridionally disposed and consists (excluding the pendent phenyl ring) of two nearly perfect (mean deviation <0.02 Å) planar segments mutually rotated around the N(1)–C(7) bond. The segments are C(8), N(1), N(2) and O(3) (plane A) and C(1)–C(7), O(2) (plane B). The dihedral angle between them is 17.4°. The metal atom does not lie on either of the planes, the displacement from the A and B planes being 0.16 Å and 0.63 Å. The chelate rings in the VL^2 fragment are thus non-planar, the six-membered ring being particularly so. The five V–O lengths (1.57–2.31 Å) follow the order O(1) (oxo) $\ll$ O(5) (alkoxide) < O(2) (phenolate) < O(3) (enolate) $\ll$ O(4) (alcoholic) reflecting the gradation of O $\longrightarrow$ V π-donation.

Table 1 Selected bond lengths (Å) and angles (°) for [VO(L^2)(H_2gl)] and [VO(L^2)(Hpd)]

	[VO(L^2)(H_2gl)]	[VO(L^2)(Hpd)]
V–O(1)	1.571(9)	1.589(2)
V–O(2)	1.870(8)	1.855(2)
V–O(3)	1.958(7)	1.957(2)
V–O(4)	2.308(8)	2.368(2)
V–O(5)	1.794(6)	1.766(2)
V–N(1)	2.091(9)	2.091(2)
O(1)–V–O(2)	99.9(4)	98.5(1)
O(1)–V–O(3)	97.5(4)	100.2(1)
O(1)–V–O(4)	175.2(4)	173.3(1)
O(1)–V–O(5)	102.3(4)	103.9(1)
O(1)–V–N(1)	99.5(3)	94.3(1)
O(2)–V–O(3)	154.0(4)	152.8(1)
O(2)–V–O(4)	84.8(3)	80.3(1)
O(2)–V–O(5)	100.5(3)	103.6(1)
O(2)–V–N(1)	83.1(3)	84.7(1)
O(3)–V–O(4)	78.0(3)	78.8(1)
O(3)–V–O(5)	94.4(3)	90.9(1)
O(3)–V–N(1)	75.1(3)	74.4(1)
O(4)–V–O(5)	76.7(3)	82.8(1)
O(4)–V–N(1)	80.9(3)	79.0(1)
O(5)–V–N(1)	156.9(4)	158.4(1)

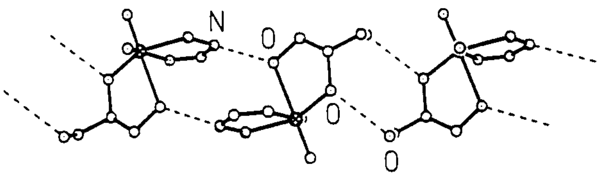


Fig. 3 The infinite hydrogen bonding in [VO(L^2)(H_2gl)]

In the lattice the molecules are assembled in an infinite hydrogen-bonded pattern (see Fig. 3, for clarity the VL fragment is shown only in part). The hydrogen bonds are of two types: N(2) ··· H–O(4) and O(5) ··· H–O(6), the corresponding distances between the terminal atoms being 2.708(17) Å and 2.862(16) Å respectively. Bonds of the former type generate dimers which are then aggregated into a chain by bonds of the latter type.

[VO(L^2)(Hpd)]. The six-membered chelation mode **III** is present and the ring has a distorted chair conformation (Fig. 2). In the case of phosphate esters the six-membered chelate **I** usually has a boat or twist conformation, the chair form being rare.[18]

The nature of the VO_5N co-ordination sphere and the trend of V–O lengths (Table 1) are similar to those in the glycerol complex. Here the A and B planes within the $[L^2]^{2-}$ ligand make a dihedral angle of 20.8°, the metal atom being displaced from the planes by 0.13 Å and 0.82 Å respectively. All the hydrogen atoms of the complex were directly located in Fourier-difference maps. The lattice consists of dimers (compare with Fig. 3) formed by intermolecular N(2) ··· H–O(4) hydrogen

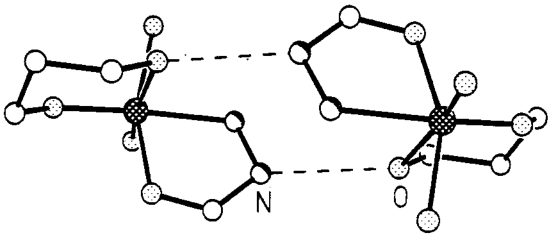


Fig. 4 Dimeric [VO(L^2)(Hpd)] formed by intermolecular hydrogen bonding

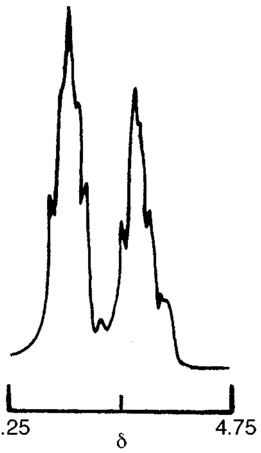


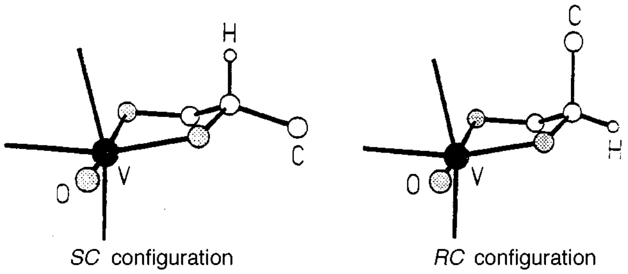
Fig. 5 Proton NMR spectrum of the methine proton of [H_2gl]$^-$ in [VO(L^2)(H_2gl)] in dry $(CD_3)_2SO$

bonding as highlighted in Fig. 4 [N(2)$\cdots$O(4) 2.865(5) Å, O(4)–H 0.93(6) Å, N(2)$\cdots$H 1.94(6) Å, N(2)$\cdots$H–O(4) 175(2)°]. The infinite chain (Fig. 3) in [VO(L^2)(H_2gl)] arises *via* self assembly of similar dimers promoted by O(5)$\cdots$O(6) hydrogen bonding.

Spectra

The V=O stretch is observed as a sharp and strong peak in the range 990–970 cm^{-1} consistent with six-co-ordination.[23] The hydrogen-bonded OH stretch occurs as a broad band near 3300 cm^{-1}. In solution the complexes display an intense band near 350 nm associated with a weaker one at 430 nm the latter is believed to be of O (alkoxidic) $\longrightarrow$ V LMCT origin.[7,14] This is consistent with the presence of strong O (alkoxidic) $\longrightarrow$ V π donation as reflected in bond distance data.

In dry $(CD_3)_2SO$ the methylene/methine ^1H resonances of the complexes are systematically shifted to lower field compared to those of the corresponding free alcohols, the shift of alkoxidic resonance being particularly large (≈2 ppm). The two distinct methine multiplets of [VO(L)(H_2gl)] near δ 5 (*e.g.* δ 4.96 and 5.11 in the case of $L = L^2$) have equal intensities and are assigned to the *SC–RA* and *RC–SA* diastereoisomers (the *SC* and *RC* configurations are depicted below). The ^1H spectrum showing the methine region in [VO(L^2)(H_2gl)] is depicted in Fig. 5.



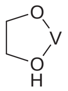
SC configuration

RC configuration

Table 2 The ^{51}V NMR spectral data * in dimethyl sulfoxide at 298 K

Compound	δ
[VO(L^1)(Hed)]	−467
[VO(L^2)(Hed)]	−512
[VO(L^3)(Hed)]	−514
[VO(L^1)(H_2gl)]	−465
[VO(L^2)(H_2gl)]	−509
[VO(L^3)(H_2gl)]	−510
[VO(L^1)(Hpd)]	−496
[VO(L^2)(Hpd)]	−538
[VO(L^3)(Hpd)]	−541

* $VOCl_3$ is used as external standard.



V

Alkoxidic ring size and ^{51}V chemical shifts

Each complex displays a sharp and single ^{51}V resonance in dry $(CD_3)_2SO$. Measurements were made for [VO(L)(H_2gl)], [VO(L)(Hpd)] as well as for [VO(L)(Hed)] (H_2ed = ethane-1,2-diol) incorporating the chelate ring **V**. Chemical shift data are listed in Table 2. For a given polyol ligand, the shifts of $[L^2]^{2-}$ and $[L^3]^{2-}$ complexes are nearly equal while that of $[L^1]^{2-}$ lies ≈40 ppm downfield.

For a given hydrazone ligand the chemical shift of [VO(L)(H_2gl)] is nearly equal to that of [VO(L)(Hed)]. In both cases the V(O,O) alkoxide–alcohol chelate rings are five-membered (modes **II** and **V**). In contrast [VO(L)(Hpd)] having the six-membered chelate ring **III** resonates ≈30 ppm upfield. The ^{51}V shifts are thus diagnostic of the V(O,O) chelate ring size in the present complexes. The observed trend appears to be of general significance and also applies to species where $[L]^{2-}$ is substituted by other O,N,O-chelating dianionic tridentate ligands.[24]

Conclusion

The first oxovanadium alkoxides of glycerol have been synthesized and characterized in the form of [VO(L)(H_2gl)] which incorporate the five-membered chelate ring **II**. The six-membered chelation mode (chair conformation) **III** in vanadate esters of propane-1,3-diol has also been realised for the first time as seen in [VO(L)(Hpd)]. Hydrogen bonding leads to self assembly in the crystalline state forming dimers in [VO(L^2)(Hpd)] and linear polymers in [VO(L^2)(H_2gl)].

In addition to the metal site the glycerol ligand in [VO(L)(H_2gl)] is also chiral and a diastereoisomeric pair occurs in solution. The ^{51}V chemical shifts are found to be diagnostic of the alkoxidic chelate ring size: the resonance of [VO(L)(H_2gl)] occurring ≈30 ppm downfield from that of [VO(L)(Hpd)] (for a given L ligand).

Experimental

Materials

The ligands H_2L^1[25] and H_2L^2[26] and bis(acetylacetonato)oxovanadium(IV)[27] were prepared by reported methods. Dimethyl sulfoxide was dried by a reported method[28] and tetraethylammonium perchlorate was obtained as before.[29] Deuteriated dimethyl sulfoxide was obtained from Aldrich. All other chemicals and solvents were of analytical grade and used as received.

Physical measurements

The ^{51}V NMR spectra were recorded on a Varian spectrometer

(78.8 MHz) at 25 °C, externally referenced to $VOCl_3$. Proton NMR spectra were recorded on a Bruker FT 300 MHz spectrometer, infrared spectra on a Perkin-Elmer 783 spectrophotometer and electronic spectra on a Hitachi 330 spectrophotometer. Electrochemical measurements were performed on a PAR model 370-4 system as described previously.[30] All potentials reported in this work are referenced to saturated calomel electrode (SCE) and are uncorrected for junction contribution. A Perkin-Elmer elemental analyser was used to collect microanalytical data (C, H and N).

Preparation of complexes

The [VO(L)(Hed)] complexes were prepared by a reported[16] procedure. The [VO(L)(H_2gl)] and [VO(L)(Hpd)] complexes were prepared by using a general method. Details are given below for two representative cases.

Oxo[(propane-1,2,3-triolato)(1−)-*O*^{1},*O*^{2}][salicylaldehyde hydroxyphenylmethylenehydrazonato(2−)]vanadium(v), [VO(L^2)(H_2gl)]. To a methanolic solution (15 cm^3) of $VO(acac)_2$ (0.10 g, 0.38 mmol) and H_2L^2 (0.09 g, 0.38 mmol) was added excess glycerol (1.22 g, 13.26 mmol, 1 cm^3). The mixture was warmed on a steam bath for 10 min and then left to evaporate at room temperature in air. The dark coloured crystalline complex that deposited was filtered, washed thoroughly with water and dried over P_4O_{10} *in vacuo*. Yield: 0.13 g (88%) (Found: C, 51.41; H, 4.42; N, 7.12. Calc. for $C_{17}H_{17}N_2O_6V$: C, 51.52; H, 4.29; N, 7.07%). IR (KBr, ν_{max}/cm^{-1}): 3400 (very br, OH); 975s (V=O). UV/VIS [dry Me_2SO, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 400 (sh) (5400), 330 (20 430). VO^{3+}–VO^{2+} couple [$E_{\frac{1}{2}}$/V(ΔE_p/mV)]: −0.24 (120). ^{1}H NMR [dry $(CD_3)_2SO$]: δ 3.62 (m, C*H*$_2$OH), 3.81 [m, C*H*$_2$O(H)V], 4.96 and 5.11 (m, C*H*OV), 6.8–8.0 (m, 9 H, aromatic), 9.04 (s, C*H*=N). [^{1}H NMR of H_3gl, 3.33 (m, 5 H, C*H*$_2$OH and C*H*OH)].

The following complexes were prepared using the same procedure as above.

[VO(L^1)(H_2gl)]. The reaction medium was acetone instead of methanol. Yield: 86% (Found: C, 55.15; H, 4.96; N, 6.37. Calc. for $C_{20}H_{21}N_2O_6V$: C, 55.04; H, 4.82; N, 6.42%). IR (KBr, ν_{max}/cm^{-1}): 3350 (very br, OH); 990s (V=O). UV/VIS [dry Me_2SO, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 445 (sh) (4680), 360 (10 200). VO^{3+}–VO^{2+} couple [$E_{\frac{1}{2}}$/V(ΔE_p/mV)]: −0.21 (150). ^{1}H NMR [dry $(CD_3)_2SO$]: δ 3.61 (m, C*H*$_2$OH), 3.84 [m, C*H*$_2$O(H)V], 4.95 and 5.14 (m, C*H*OV), 7.48–7.94 (m, 10 H, aromatic), 6.39 (s, C*H*=C), 3.38 (s, *Me*C=N).

[VO(L^3)(H_2gl)]. The reaction medium was acetone. Yield: 83% (Found: C, 56.41; H, 4.20; N, 6.37. Calc. for $C_{21}H_{19}N_2O_6V$: C, 56.50; H, 4.26; N, 6.28%). IR (KBr, ν_{max}/cm^{-1}): 3350 (very br, OH); 972s (V=O). UV/VIS [dry Me_2SO, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 430 (8260), 340 (22 370). VO^{3+}–VO^{2+} couple [$E_{\frac{1}{2}}$/V(ΔE_p/mV)]: −0.22 (140). ^{1}H NMR [dry $(CD_3)_2SO$]: δ 3.63 (m, C*H*$_2$OH), 3.85 [m, C*H*$_2$O(H)V], 4.97 and 5.14 (m, C*H*OV), 7.14–8.49 (m, 11 H, aromatic), 9.75 (s, C*H*=N).

[4-Hydroxy-4-phenylbut-3-en-2-one hydroxyphenylmethylene hydrazonato(2−)]oxo[(propane-1,3-diolato)(1−)-*O*^{1},*O*^{2}]-vanadium(v), [VO(L^1)(Hpd)]. An acetone solution (15 cm^3) of $VO(acac)_2$ (0.10 g, 0.37 mmol) and H_2L^1 (0.11 g, 0.37 mmol) was treated with propane-1,3-diol (1.05 g, 13.80 mmol, 1 cm^3). The mixture was warmed on a water-bath for 15 min and the resultant dark red solution was left to evaporate slowly at room temperature in air. A crystalline, dark coloured compound deposited and was filtered off, washed thoroughly with water and dried *in vacuo* over P_4O_{10}. Yield 0.14 g (90%) (Found: C, 57.10; H, 5.05; N, 6.60. Calc. for $C_{20}H_{21}N_2O_5V$: C, 57.14; H, 5.00; N, 6.67%). IR (KBr, ν_{max}/cm^{-1}): 3400 (very br, OH); 981s (V=O). UV/VIS [dry Me_2SO, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 450 (sh) (8250), 370 (13 560). VO^{3+}–VO^{2+} couple [$E_{\frac{1}{2}}$/V(ΔE_p/mV)]: −0.22 (140). ^{1}H NMR [dry $(CD_3)_2SO$]: δ 2.00 (m, CH_2C*H*$_2$$CH_2$), 3.68 [m, –C*H*$_2$O(H)V], 5.31 and 5.38 (m, C*H*$_2$OV), 7.34–7.97 (m, 10 H, aromatic), 6.36 (s, C*H*=C), 3.40 (s, *Me*C=N). [^{1}H NMR of H_2pd, 3.45 (q, 4 H, J_{HH} = 6.5, C*H*$_2$OH), 1.57 (qnt, 2 H, J_{HH} = 6.5 Hz, CH_2C*H*$_2$$CH_2$)].

The following complexes were prepared using the same procedure as above.

[VO(L^2)(Hpd)]. Methanol was used as the reaction medium in place of acetone. Yield: 88% (Found: C, 53.60; H, 4.54; N, 7.45. Calc. for $C_{17}H_{17}N_2O_5V$: C, 53.68; H, 4.47; N, 7.37%). IR (KBr, ν_{max}/cm^{-1}): 3220 (very br, OH); 974s (V=O). UV/VIS [dry Me_2SO, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 400 (sh) (6600), 330 (19 390). VO^{3+}–VO^{2+} couple [$E_{\frac{1}{2}}$/V(ΔE_p/mV)]: −0.23 (130). ^{1}H NMR [dry $(CD_3)_2SO$]: δ 2.06 (m, CH_2C*H*$_2$$CH_2$) 3.70 [m, –C*H*$_2$O(H)V], 5.43 and 5.55 (m, C*H*$_2$OV), 6.88–8.05 (m, 9 H, aromatic), 8.91 (s, C*H*=N).

[VO(L^3)(Hpd)]. Acetone was used as the reaction medium. Yield: 85% (Found: C, 58.70; H, 4.59; N, 6.56. Calc. for $C_{21}H_{19}N_2O_5V$: C, 58.60; H, 4.42; N, 6.51%). IR (KBr, ν_{max}/cm^{-1}): 3200 (very br, OH); 972s (V=O). UV/VIS [dry Me_2SO, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 425 (6730), 330 (17 840). VO^{3+}–VO^{2+} couple [$E_{\frac{1}{2}}$/V(ΔE_p/mV)]: −0.21 (140). ^{1}H NMR [dry $(CD_3)_2SO$]: δ 2.08 (m, CH_2C*H*$_2$$CH_2$), 3.64 [m, C*H*$_2$O(H)V] 5.38 and 5.52 (m, C*H*$_2$OV), 7.11–8.53 (m, 11 H, aromatic), 9.65 (s, C*H*=N).

Crystallography

Crystals of [VO(L^2)(H_2gl)] (0.3 × 0.2 × 0.3 mm) and [VO(L^2)(Hpd)] (0.3 × 0.4 × 0.3 mm) were grown by slow evaporation of methanolic solutions. For both complexes cell parameters were determined by a least-squares fit of 30 machine-centered reflections (2θ, 15–30°). Data were collected by the ω-scan method in the 2θ range 3–45° on a Siemens R3m/V diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Two check reflections measured after every 98 reflections showed no significant intensity reduction. Data were corrected for Lorentz and polarisation effects. An empirical absorption correction (transmission coefficients in the range 0.6–0.8) was performed on both sets of data on the basis of azimuthal scans[31] of six reflections. A total of 1187 and 1839 unique reflections [$I > 2\sigma(I)$] were taken as observed and used for the structure solution of [VO(L^2)(H_2gl)] and [VO(L^2)(Hpd)] respectively.

All calculations for data reduction, structure solution and refinement were done on a Micro VAX II computer with the program SHELXTL PLUS.[32] Perspective views were drawn using ORTEP.[33] Both the structures of [VO(L^2)(H_2gl)] and [VO(L^2)(Hpd)] were solved by direct methods and were refined by full-matrix least-squares procedures (final maximum and minimum shift/e.s.d.s in the range 0.001–0.000). In case of [VO(L^2)(H_2gl)] the metal atom, all nitrogen, oxygen and H_2gl^- carbon atoms as well as C(1), C(6), C(7) and C(8) atoms were made anisotropic and the rest refined isotropically and all hydrogen atoms were added in calculated positions (U = 0.08 Å^2). The ambiguity in the case of OH hydrogen atoms was resolved from consideration of hydrogen-bonding vectors. For [VO(L^2)(Hpd)] all non-hydrogen atoms were made anisotropic and the hydrogen atoms were directly located in Fourier-difference maps (fixed U value, 0.08 Å^2). Significant crystal data are listed in Table 3. Maximum, minimum difference peaks (e Å^{-3}) were 0.57, −0.41 and 0.29, −0.35 for [VO(L^2)(H_2gl)] and [VO(L^2)(Hpd)] respectively.

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Table 3 Crystallographic data for [VO(L^2)(H_2gl)] and [VO(L^2)(Hpd)]

	[VO(L^2)(H_2gl)]	[VO(L^2)(Hpd)]
Formula	$C_{17}H_{17}N_2O_6V$	$C_{17}H_{17}N_2O_5V$
M	396.3	380.3
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	7.888(4)	12.281(7)
b/Å	18.115(9)	8.089(2)
c/Å	12.678(8)	16.622(7)
β/°	107.42(5)	96.46(4)
U/Å^3	1728.3(17)	1640.8(12)
T/K	295	295
Z	4	4
μ(Mo-Kα)/cm^{-1}	6.11	6.37
Reflections measured	2635	2495
Independent reflections (R_{int})	2274 (0.036)	2152 (0.015)
R^a	0.0743	0.0337
R'^b	0.0786^c	0.0407^d

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ where $w = 1/[\sigma^2(|F|) + g|F|^2]$. [c] g in w, 0.0004. [d] g in w, 0.0002.

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