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FULL PAPER

Sugar vanadates: synthesis and characterisation of mannopyranoside and ribofuranoside esters incorporating VO^{3+}

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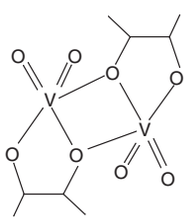
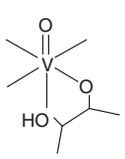
The sugars, methyl 4,6-di-*O*-methyl-α-D-mannopyranoside (H_2m) and methyl 5-*O*-methyl-β-D-ribofuranoside (H_2r) have been synthesized. These react smoothly with $[V^{IV}O(L)(H_2O)]$ in methanol in air affording the dark coloured vanadates $[V^{V}O(Hm)(L)]$ and $[V^{V}O(Hr)(L)]$ in excellent yields (L^{2-} = *N*-salicylideneglycinate). The crystal structure determination of $[V^{V}O(Hm)(L)]$ revealed five-membered chelation of VO^{3+} by the alcoholic and alkoxide oxygen atoms of the monoionised carbohydrate. The two atoms lie respectively *trans* to the oxo oxygen and aldimine nitrogen atoms. The five V–O bonds are unequal and span the range 1.57–2.37 Å. The asymmetric unit of the complex consists of two metrically similar molecules locked in carboxylate–alcohol O · · · O hydrogen bonding generating a macrocyclic cavity. In solution each ester displays a single ^{51}V resonance near δ −544. The ^{1}H NMR parameters of the alkoxidic and alcoholic CH protons and of OMe protons are consistent with the O,O-chelation mode for both the vanadates.

Ester formation with alcohols is a characteristic feature of both vanadium and phosphorus in the pentavalent state.[1–5] Thus vanadates can influence the activity of enzymes which are otherwise specific for sugar phosphates as in the inhibition of RNase[6,7] and ATPase[8] and the activation of glucose 6-phosphate dehydrogenase.[9] Such observations underline the potential importance of sugar vanadate chemistry which has so far been studied mostly in solution.[10–15] Very few authentic sugar vanadates have been isolated in the pure state and the structures of only a pair of these are known. Both contain VO_2^+ binucleated *via* alkoxide functions of diionised sugars[16,17] as in **1**.



1

This has prompted us to search for new types of sugar vanadates as a part of our general programme on oxovanadium alkoxides of polyols.[5] Herein we describe VO^{3+} species incorporating chelation of a hexose and a pentose sugar in their monoionised forms as in **2**. A tridentate salicylaldimine is used as a coligand. The complexes have been isolated in the solid state and a crystal structure determination for one has authenticated the binding mode **2**. Solution properties and structures are scrutinised.



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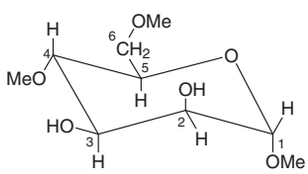
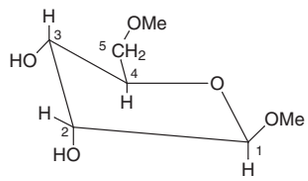
Results and discussion

The two sugar ligands used are methylated α-D-mannopyranoside (H_2m) **3** and β-D-ribofuranoside (H_2r) **4**. For their synthesis

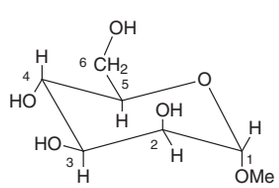


H_2m, **3**



H_2r, **4**

the parent glycoside such as **5** is converted into its isopropylidene derivative **6** followed by exhaustive methylation to **7** which affords **3** on hydrolysis. The Schiff base coligand H_2L **8** is formed *in situ via* condensation of salicylaldehyde with glycine.



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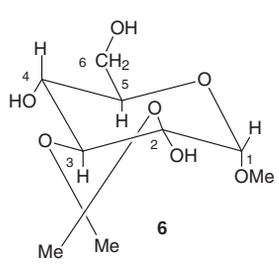

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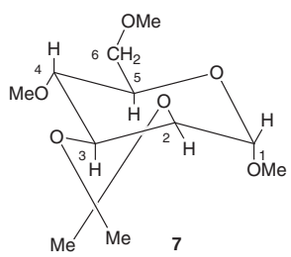

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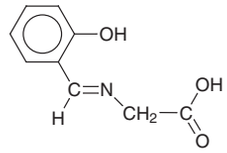


H_2L, **8**

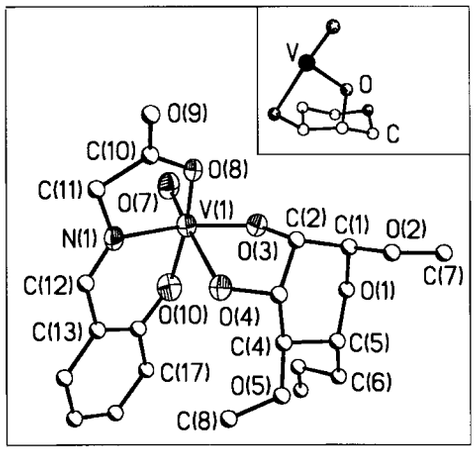


Fig. 1 Perspective view and atom-labeling scheme for molecule 1 in $[V^{V}O(Hm)(L)]\cdot\frac{1}{2}C_6H_6$ (solvent excluded); the alkoxide function is O3. The inset highlights the carbohydrate–VO^{3+} binding.

In each sugar ligand the two hydroxyl groups (one axial, one equatorial) are disposed in *cis* positions. This feature was designed to support chelation-stabilised ester formation in an environment where three of the VO^{3+} co-ordination sites are already engaged by the H_2L coligand. Model experiments with linear polyols helped us to arrive at this design strategy.[5]

Treatment of a solution of $[V^{IV}O(L)(H_2O)]$[18] in methanol in air with an excess of sugar ligands afforded the dark coloured esters $[V^{V}O(Hm)(L)]$ and $[V^{V}O(Hr)(L)]$ in excellent yields. The oxygen of air is believed to be the oxidant ($V^{IV}O \longrightarrow V^{V}O$) in this synthesis.

Characterisation data of the esters are listed in the Experimental section. The V=O stretch occurs as a sharp feature near 985 cm^{-1} suggesting six-co-ordination.[19,20] The sugar hydroxyl vibration is observed near 3200 cm^{-1}. Three carboxylate stretches occur in the range 1300–1700 cm^{-1} consistent with the monoco-ordination.[21] The dark red solutions of the complexes absorb at 500 nm (ε 300–500 $dm^3\ mol^{-1}\ cm^{-1}$) presumably due to a O^{-}(sugar)→V LMCT transition.[5,22] The stabilisation of the pentavalent state of the metal by the monoionised sugar ligand is reflected in the low VO^{3+}–VO^{2+} reduction potential (≈−0.30 V *vs*. SCE).

Structure

Only the mannopyranoside complex afforded good single crystals in the form of the benzene adduct $[V^{V}O(Hm)(L)]\cdot\frac{1}{2}C_6H_6$. Two metrically similar but crystallographically distinct molecules and a benzene molecule constitute the asymmetric unit. One of the molecules (molecule 1) is shown in Fig. 1 and selected bond parameters are listed in Table 1. The numbering of the corresponding atoms in molecules 1 and 2 are respectively *n* and *n* + 50, *e.g.* V(1)–O(3) and V(51)–O(53).

The carbohydrate ligand is bonded in the five-membered chelate mode **2**. The alcoholic hydrogen atoms H(4) and H(54) were directly observed in Fourier-difference maps. The alcoholic oxygen atoms O(4) and O(54) lie *trans* to the respective oxo oxygen atoms while the alkoxide oxygen atoms O(3) and O(53) lie *trans* to the respective Schiff base nitrogen atoms. In the carbohydrate framework, the alkoxide and alcohol functions occupy axial and equatorial positions respectively.

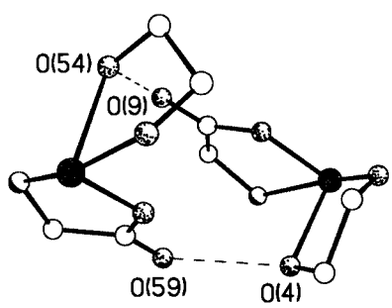
The salicylaldimine ligand binds in a meridional tridentate fashion. It consists of two excellently planar parts (mean deviation <0.02 Å), OC_6H_4CHN and CCO_2, the dihedral angles between them being 31.4 (molecule 1) and 27.7° (molecule 2).

The co-ordinated alkoxide, phenoxide and carboxylate oxygen atoms and the nitrogen atom constitute a good equatorial plane in each molecule. The metal atom is displaced from the plane by 0.34 (molecule 1) and 0.30 Å (molecule 2) towards the oxo oxygen atom. The five unequal V–O bond lengths spread over the range 1.57–2.37 Å following the order oxo < alkoxidic < phenoxidic < alcoholic. To achieve minimum competition for the same metal acceptor orbitals the weakly donating alcohol function rather than the strongly donating alkoxide function of the sugar ligand lies *trans* to the oxo oxygen atom and accordingly the V–O (alcoholic) bond is unusually long.

Table 1 Selected bond lengths (Å) and angles (°) for $[V^{V}O(Hm)(L)]\cdot\frac{1}{2}C_6H_6$

Molecule 1		Molecule 2	
V(1)–O(3)	1.799(7)	V(51)–O(53)	1.809(6)
V(1)–O(4)	2.366(8)	V(51)–O(54)	2.325(7)
V(1)–O(7)	1.571(7)	V(51)–O(57)	1.583(7)
V(1)–O(8)	1.970(7)	V(51)–O(58)	1.976(6)
V(1)–O(10)	1.858(7)	V(51)–O(60)	1.863(7)
V(1)–N(1)	2.072(8)	V(51)–N(51)	2.063(8)
C(2)–O(3)	1.409(11)	C(52)–O(53)	1.441(11)
C(3)–O(4)	1.433(12)	C(53)–O(54)	1.442(11)
O(3)–V(1)–O(4)	75.4(3)	O(53)–V(51)–O(54)	76.1(3)
O(3)–V(1)–O(7)	102.2(3)	O(53)–V(51)–O(57)	99.4(3)
O(3)–V(1)–O(8)	90.2(3)	O(53)–V(51)–O(58)	88.4(3)
O(3)–V(1)–O(10)	101.0(3)	O(53)–V(51)–O(60)	102.6(3)
O(4)–V(1)–O(7)	176.7(3)	O(54)–V(51)–O(57)	175.0(3)
O(4)–V(1)–O(8)	81.2(3)	O(54)–V(51)–O(58)	82.5(3)
O(4)–V(1)–O(10)	83.2(3)	O(54)–V(51)–O(60)	81.2(3)
O(7)–V(1)–O(8)	96.7(4)	O(57)–V(51)–O(58)	99.7(3)
O(7)–V(1)–O(10)	99.5(4)	O(57)–V(51)–O(60)	97.8(4)
O(8)–V(1)–O(10)	157.8(3)	O(58)–V(51)–O(60)	157.4(3)
O(3)–V(1)–N(1)	154.0(3)	O(53)–V(51)–N(51)	157.6(3)
O(4)–V(1)–N(1)	80.1(3)	O(54)–V(51)–N(51)	85.0(3)
O(7)–V(1)–N(1)	101.9(4)	O(57)–V(51)–N(51)	99.9(3)
O(8)–V(1)–N(1)	77.4(3)	O(58)–V(51)–N(51)	77.2(3)
O(10)–V(1)–N(1)	84.5(3)	O(60)–V(51)–N(51)	85.9(3)

Molecules 1 and 2 are linked into a supramolecular dimer *via* carboxylate–alcohol hydrogen bonds (O(4)···O(59) 2.698(12) and O((9)···O(54) 2.638(11) Å) as depicted in **9**. The average cavity diameter of the macrocycle so formed is 4.5 Å.



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NMR spectra and solution structure

Each ester displays a single sharp ^{51}V resonance near δ −544 suggesting the presence of a single species in solution in each case. The alkoxidic CH proton of the carbohydrate ligand occurs as an isolated ^{1}H signal shifted downfield by 1–2 ppm from the alcoholic CH proton.[5,23] The alcoholic OH signal occurring near δ 7 'disappears' upon shaking with D_2O.

In $[V^{V}O(Hm)(L)]$ the alkoxidic CH proton H(2) is involved in relatively weak[24] axial–equatorial (*a–e*) and equatorial–equatorial (*e–e*) couplings with H(3) and H(1) respectively resulting in a broad signal with ill resolved splittings. On the other hand the alcoholic CH proton H(3) is engaged in strong *a-a* coupling with H(4) in addition to the weaker *a–e* coupling with H(2) giving rise to a somewhat broad doublet of doublets.

The ^{1}H NMR spectrum of $[V^{V}O(Hr)(L)]$, Fig. 2, is consistent with the bonding mode **10** for the $[V^{V}(Hr)]$ fragment. Thus the alkoxidic CH proton H(3) occurs as a doublet of doublets

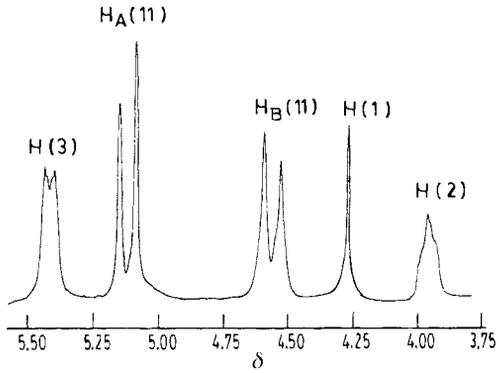
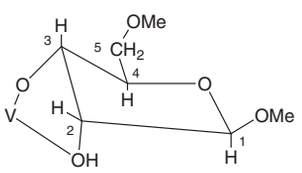
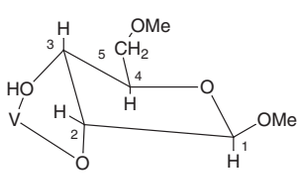


Fig. 2 The ^{1}H NMR spectrum (δ 4.0–5.5) of a fresh solution ($\approx 10^{-2}$ M) of [V^{V}O(Hr)(L)] in $(CD_3)_2SO$. For the numbering scheme see structure **4** (Hr fragment) and Fig. 1 (L fragment).

corresponding to *a*–*a* and *a*–*e* couplings with H(4) and H(2) respectively. The alcoholic CH proton H(2) (*a*–*e* couplings to H(1) and H(3)) occurs as an ill resolved multiplet. If the binding mode were **11** the spin–spin splitting pattern would have been just the opposite of the above.



10



11

The OMe chemical shifts of the ester lie close to those of the free sugars except where the OMe group is located adjacent to the alkoxide function. The latter applies to 1-OMe in [V^{V}O(Hm)(L)] and accordingly the signal is shifted downfield by ≈0.2 ppm. For [V^{V}O(Hr)(L)] none of the OMe signals is affected in this manner consistent with structure **10** (but not **11** where a shift of the 1-OMe would be expected).

Conclusion

Monoionised methyl 4,6-di-*O*-methyl-α-D-mannopyranoside and methyl 5-*O*-methyl-β-D-ribofuranoside have been successfully utilised to generate the sugar vanadates [V^{V}O(Hm)(L)] and [V^{V}O(Hr)(L)] incorporating VO^{3+} chelated by the sugar ligands *via* alkoxidic and alcoholic oxygen atoms. This binding mode persists in solution. Further studies on sugar vanadates are in progress.

Experimental

Materials

Methyl α-D-mannopyranoside and D-ribose were procured from Sigma Chemicals. Methyl β-D-ribofuranoside was prepared from D-ribose.[25] Tetraethylammonium perchlorate was prepared as before[26] and dimethylformamide was dried over P_4O_{10} followed by distillation in vacuum before use. All other chemicals and solvents were of analytical grade used as received.

Physical measurements

Spectra were measured with Perkin-Elmer 783 (IR), Hitachi 330 (UV/VIS) and Bruker FT 300 MHz (^{1}H NMR) spectrometers. ^{51}V NMR was recorded on a Varian spectrometer at 78.8 MHz with $VOCl_3$ as the external reference. The numbering scheme used for ^{1}H NMR is as in structures **3**, **4** and Fig. 1. Ligands **3** and **4** have nine and seven carbon atoms respectively. To retain an uniform numbering scheme for the L^{2-} ligand in the two esters no carbon atoms are numbered 8 and 9 in the ribose ester. Electrochemistry was performed on a PAR model 370–4 system as previously.[27]

Synthesis of sugar ligands

The synthesis was achieved by suitable modifications of general procedures available for protection by the isopropylidene group,[28] methylation[29] and hydrolysis.[30] The procedure described below is for the synthesis of methyl 4,6-di-*O*-methyl-α-D-mannopyranoside. Methyl 5-*O*-methyl-β-D-ribofuranoside was prepared similarly.

A dry dimethylformamide solution (30 cm^3) of methyl α-D-mannopyranoside **5** (5.00 g, 25.70 mmol) was treated with 2,2-dimethoxypropane (3.35 g, 32.17 mmol) and a catalytic amount of *p*-toluenesulfonic acid. The mixture was stirred for 24 h and then neutralised with triethylamine. Evaporation to dryness under reduced pressure followed by chromatography of the residue on a silica gel column (75 g, 60–120 mesh) using ethyl acetate as eluent afforded the methyl 2,3-*O*-isopropylidene-α-D-mannopyranoside **6**, which was isolated as a colourless solid upon removal of solvent. Yield : 2.75 g (46% on the basis of **5**) (Found: C, 51.22; H, 7.73. Calc. for $C_5H_9O_3$: C, 51.28; H, 7.68%). ^{1}H NMR [$CDCl_3$]: δ 4.79 (s, H(1)); 3.46 (s, 1-OMe), 1.48, 1.33 (s, CMe_2).

To a solution of compound **6** (2.75 g, 11.75 mmol) in dry dimethylformamide (30 cm^3) were added iodomethane (10.90 g, 76.80 mmol) and silver oxide (13.30 g, 57.60 mmol) and stirred for 12 h followed by addition of chloroform (150 cm^3) to quench the reaction. The solvent was removed and the sticky mass subjected to chromatography on a silica gel column (70 g, 60–120 mesh) using ethyl acetate–toluene (5 : 3) as the eluent. Upon removal of the solvent methyl 2,3-*O*-isopropylidene-4,6-di-*O*-methyl-α-D-mannopyranoside **7** was obtained as a white solid. Yield: 2.30 g (74% based on **6**) (Found : C, 54.90; H, 8.45. Calc. for $C_6H_{11}O_3$: C, 54.96; H, 8.40%). ^{1}H NMR [$CDCl_3$]: δ 4.78 (s, H(1)), 3.45 (s, 1-OMe), 3.44 (s, 4-OMe), 3.34 (s, 6-OMe), 1.48, 1.33 (s, CMe_2).

A solution of compound **7** (2.30 g, 8.78 mmol) in 30 cm^3 1 : 1 ethyl acetate–methanol was treated with *p*-toluenesulfonic acid to achieve 0.1 M acid, then stirred for 4 h at room temperature. Neutralisation with triethylamine followed by removal of the solvent under reduced pressure afforded a white residue which was chromatographed on a silica gel column (50 g, 60–120 mesh) using ethyl acetate–methanol (5 : 1) as eluent. After removal of the solvent the ligand methyl 4,6-di-*O*-methyl-α-D-mannopyranoside **3** was obtained. Yield: 1.36 g (70% based on **7**) (Found:C, 48.58; H, 8.17. Calc. for $C_3H_6O_2$: C, 48.64; H, 8.10%). ^{1}H NMR [$CDCl_3$]: δ 4.78 (s, H(1)), 3.46 (s, 1-OMe), 3.44 (s, 4-OMe), 3.35 (s, 6-OMe).

Preparation of complexes

The [V^{V}O(Hm)(L)] and [V^{V}O(Hr)(L)] complexes were prepared by using similar methods. Details are given below for the former.

[Methyl 4,6-di-*O*-methyl-α-D-mannopyranosidato)(1−)-*O*^{1},*O*^{2}]oxo[*N*-salicylideneglycinato(2−)]vanadium(V), [V^{V}O(Hm)(L)]. To a methanolic solution (15 cm^3) of [V^{IV}O(L)(H_2O)] (0.10 g, 0.38 mmol) was added H_2m (0.102 g, 0.46 mmol) and the mixture left to evaporate in air affording [V^{V}O(Hm)(L)] as a dark coloured solid. Yield:1.54 g (80%) (Found:C, 46.51; H, 5.10; N, 2.98. Calc. for $C_{18}H_{24}NO_{10}V$: C, 46.45; H, 5.16; N, 3.01%). UV/VIS [CH_2Cl_2, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 500(340) and 330(3840). IR (KBr, cm^{-1}): 985 (V=O), 1290 (CO_2, sym), 1615 (CO_2, asym), 1650 (CO_2, asym) and 3160 (very br, OH). ^{1}H NMR [$CDCl_3$]: δ 4.8 (s, H(1)), 5.42 (m, H(2)), 4.33 (dd, J = 4.1, 8.4, H(3)), 3.79 (m, H(4)), 3.46 (m, H(5), H(6)), 3.60 (s, 1-OMe), 3.38 (s, 4-OMe), 2.90 (s, 6-OMe), 7.41 (br, OH; 'disappears' on shaking with D_2O), 5.02 (d, J = 18.6, H_A(11)), 4.61

Table 2 Crystallographic data for $[V^{V}O(Hm)(L)]\cdot\frac{1}{2}C_6H_6$

Formula	$C_{21}H_{27}NO_{10}V$
M	504.37
Crystal size/mm	0.3 × 0.4 × 0.3
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	9.789(3)
b/Å	18.534(5)
c/Å	13.689(4)
β/°	91.64(2)
U/Å^3	2483(1)
Z	4
D_c/Mg m^{-3}	1.349
T/K	295
μ/mm^{-1}	0.452
Reflections collected	4381
Unique reflections (R_{int})	4060 (0.036)
Reflections with [$I > 2\sigma(I)$]	2828
Parameters refined	449
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0649, 0.1396
Maximum, minimum $\Delta\rho$/e Å^{-3}	0.457, −0.288

(d, J = 20, H_B(11)), 8.49 (s, H(12)), 7.50 (d, J = 7.2, H(14)), 6.96 (t, J = 8.4, H(15)), 7.59 (t, J = 9.9, H(16)) and 6.90 (d, J = 8.1, H(17)). ^{51}V NMR [$CDCl_3$]: δ −544. $E_{\frac{1}{2}}$(VO^{3+}–VO^{2+} couple) in CH_2Cl_2–CH_3CN(1 : 1): −0.25 V (irr).

Complex [$V^{V}O$(Hr)(L)]. Yield: 0.13 g (82%) (Found: C, 45.67; H, 4.70; N, 3.30. Calc. for $C_{16}H_{20}NO_9V$: C, 45.60; H, 4.75; N, 3.33%). UV/VIS [Me_2SO, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 500(516) and 340(4925). IR (KBr, cm^{-1}): 982 (V=O), 1305 (CO_2, sym), 1623 (CO_2, asym), 1700 (CO_2, asym) and 3130 (very br, OH). ^{1}H NMR [$(CD_3)_2SO$]: δ 4.27 (s, H(1)), 3.97 (m, H(2)), 5.42 (dd, J = 3.4, 8.2, H(3)), 3.34 (m, H(4), H(5)), 3.39 (s, 1-OMe), 3.33 (s, 5-OMe), 7.12 (d, J = 3.6, OH; 'disappears' on shaking with D_2O), 5.12 (d, J = 19.0, H_A(11)), 4.56 (d, J = 20.7, H_B(11)), 8.90 (s, H(12)), 7.62 (d, J = 7.2, H(14)), 7.02 (t, J = 7.2, H(15)), 7.70 (t, J = 6.9, H(16)) and 6.93 (d, J = 8.4, H(17)). ^{51}V NMR [$(CD_3)_2SO$]: δ −543. $E_{\frac{1}{2}}$(VO^{3+}–VO^{2+} couple) in Me_2SO: −0.28 V (irr).

Crystallography

Crystals of $[V^{V}O(Hm)(L)]\cdot\frac{1}{2}C_6H_6$ were grown by slow diffusion of hexane into benzene solution. Data were collected by the ω-scan technique on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ 0.71073 Å). Two check reflections displayed no intensity reduction. All calculations were done using the SHELXTL programs.[31] The structure was solved by direct methods and refined by full-matrix least squares on F^2. Data were corrected for Lorentz-polarisation effects and empirical absorption corrections were done on the basis of azimuthal scans of six reflections.[32] Metal, nitrogen, oxygen and all the carbohydrate carbon atoms were made anisotropic. A few of the hydrogens were directly located and the remaining included in calculated positions. Significant crystal data are listed in Table 2.

CCDC reference number 186/1492.

See http://www.rsc.org/suppdata/dt/1999/2537/ for crystallographic files in .cif format.

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References

1 D. C. Crans, R. A. Felty, O. P. Anderson and M. M. Miller, *Inorg. Chem.*, 1993, **32**, 247; D. C. Crans, R. A. Felty, H. Chen, H. Eckert and N. Das, *Inorg. Chem.*, 1994, **33**, 2427; W. J. Ray, D. C. Crans, J. Zheng, J. W. Brugner, H. Deng and M. Mahroof-Tahir, *J. Am. Chem. Soc.*, 1995, **117**, 6015; D. C. Crans, H. Chen and R. A. Felty, *J. Am. Chem. Soc.*, 1992, **114**, 4543.
2 M. J. Gresser and A. S. Tracey, *J. Am. Chem. Soc.*, 1986, **108**, 1935.
3 C. N. Caughlan, H. M. Smith and K. Watenpaugh, *Inorg. Chem.*, 1996, **5**, 2131; W. R. Scheidt, *Inorg. Chem.*, 1973, **12**, 1758; W. Priebsch and D. Rehder, *Inorg. Chem.*, 1990, **29**, 3013; D. Rehder, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 148.
4 C. J. Carrano, M. Mohan, S. H. Holmes, R. de la Rosa, A. Butler, J. M. Charnock and C. D. Garner, *Inorg. Chem.*, 1994, **33**, 646; G. Asgedom, A. Sreedhara, J. Kivikoski, J. Valkonen, E. Kolehmainen and C. P. Rao, *Inorg. Chem.*, 1996, **35**, 5674.
5 S. Mondal, S. P. Rath, K. K. Rajak and A. Chakravorty, *Inorg. Chem.*, 1998, **37**, 1713; S. P. Rath, K. K. Rajak, S. Mondal and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1998, 2097; S. Mondal, S. P. Rath, S. Dutta and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1996, 99; S. P. Rath, S. Mondal and A. Chakravorty, *Inorg. Chim. Acta*, 1997, **263**, 247.
6 R. N. Lindquist, L. J. Lynn, jun. and G. E. Lienhar, *J. Am. Chem. Soc.*, 1973, **95**, 8762.
7 B. Borah, C. W. Chen, W. Egan, M. Miller, A. Wlodawer and J. S. Cohen, *Biochemistry*, 1985, **24**, 2058.
8 *Vanadium in Biological System: Physiology and Biochemistry*, ed. N. D. Chasteen, Kluwer, Dordrecht, 1990.
9 A. F. Nour-Eldeen, M. M. Craig and M. J. Gresser, *J. Biol. Chem.*, 1985, **260**, 6836.
10 A. S. Tracey and M. J. Gresser, *Inorg. Chem.*, 1988, **27**, 2695.
11 C. F. G. C. Geraldes and M. M. C. A. Castro, *J. Inorg. Biochem.*, 1989, **35**, 79.
12 A. S. Tracey and C. H. Leon-Lai, *Inorg. Chem.*, 1991, **30**, 3200.
13 D. C. Crans, S. E. Harnung, E. Larsen, L. A. Theisen and I. Trabjerg, *Acta Chem. Scand.*, 1991, **45**, 456.
14 X. Zhang and A. S. Tracey, *Acta Chem. Scand.*, 1992, **46**, 1170.
15 J. Richter, D. Rehder, L. Wyns and A. Haikal, *Inorg. Chim. Acta*, 1995, **238**, 115; J. Richter and D. Rehder, *Z. Naturforsch., Teil B*, 1991, **46**, 1613; A. Sreedhara, C. P. Rao and B. J. Rao, *Carbohydr. Res.*, 1996, **289**, 39.
16 S. J. Angus-Dunne, R. J. Batchelor, A. S. Tracey and F. W. B. Einstein, *J. Am. Chem. Soc.*, 1995, **117**, 5292.
17 B. Zhang, S. Zhang and K. Wang, *J. Chem. Soc., Dalton Trans.*, 1996, 3257.
18 L. J. Theriot, G. O. Carlisle and H. J. Hu, *J. Inorg. Nucl. Chem.*, 1969, **31**, 2841.
19 C. J. Carrano and J. A. Bonadies, *J. Am. Chem. Soc.*, 1986, **108**, 4088; S. Holmes and C. J. Carrano, *Inorg. Chem.*, 1991, **30**, 1231; M. Mohan, S. M. Holmes, R. J. Butcher, J. P. Jasinski and C. J. Carrano, *Inorg. Chem.*, 1992, **31**, 2029.
20 S. Ooi, M. Nishigawa, K. Matasuto, H. Kuryoa and K. Saito, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 452.
21 B. Kavanagh, J. W. Steed and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1993, 327.
22 M. J. Clague, N. L Keder and A. Butler, *Inorg. Chem.*, 1993, **32**, 475; J. M. Arber, E. de Boer, C. D. Garner, S. S. Hasnain and R. Wever, *Biochemistry*, 1989, **28**, 7986.
23 A. A. Diamantis, J. M. Fredericksen, Md. A. Salam, M. R. Snow and R. T. Tiekink, *Aust. J. Chem.*, 1986, **39**, 1081.
24 I. L. Finar, *Organic Chemistry*, ELBS, Longman, Singapore, 1975, vol. 2, p. 300.
25 R. Barker and H. G. Fletcher, Jr., *J. Org. Chem.*, 1961 **26**, 4605.
26 D. T. Sawyer and J. L. Roberts, Jun., *Experimental Electrochemistry for Chemists*, Wiley, New York, 1974, p. 212.
27 G. K. Lahiri, S. Bhattacharya, B. K. Ghosh and A. Chakravorty, *Inorg. Chem.*, 1987, **26**, 4324.
28 G. M. Bebault and G. G. S. Dattow, *Can. J. Chem.*, 1972, **50**, 3373.
29 W. M. Ho, H. N. C. Wong, L. Navailles, C. Destrade, H. T. Naguyen and N. Isaert, *Tetrahedron*, 1995, **50**, 7373.
30 K. Takeo and M. Kawaguchi, *J. Carbohydr. Chem.*, 1993, **12**, 1045.
31 G. M. Sheldrick, SHELXTL, version 5.03, Siemens Analytical Instruments Inc., Madison, WI, 1994.
32 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

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