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Chemistry of oxovanadium(V) alkoxides: synthesis and structure of mononuclear complexes incorporating ethane-1,2-diol

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The reaction of [$V^{IV}O(L)(H_2O)$] with ethane-1,2-diol (H_2ed) in methanol in air afforded complexes of type [$V^VO(L)(Hed)$] in very good yields (H_2L^1 = *N*-salicylideneglycine, H_2L^2 = *N*-salicylidene-L-phenylalanine). The crystal structure of [$VO(L^2)(Hed)$] has revealed the presence of tridentate $[L^2]^{2-}$ and bidentate Hed^-. In the latter the alcoholic oxygen lies *trans* to the oxo atom. In the VO_5N co-ordination sphere the five vanadium–oxygen lengths follow the order: oxo < alkoxidic < phenoxidic < carboxylic < alcoholic. The absolute configuration of the complex is *CS*. The lattice consists of hydrogen-bonded (between alcoholic and carboxylic oxygen atoms) dimers having two-fold symmetry. The CD spectrum of [$VO(L^2)(Hed)$] has revealed the composite nature of the O(alkoxide) → V charge-transfer band in the visible region. In the ^1H NMR spectra of the complexes the four methylene protons of co-ordinated Hed^- are inequivalent. The [$V^VO(L)(Hed)$] complexes represent authentic examples of the very rare mononuclear oxovanadium species incorporating ethane-1,2-diol as a ligand.

The oxovanadium alkoxide motif, $V^VO(OR)$, has been known for many years,[1-3] but it is only recently that its chemistry is attracting significant attention.[4] The general upsurge in transition-metal alkoxide chemistry[5] is one reason, but more specific motivating factors include the prospect of realising new families of compounds,[6-11] potential utility as selective oxidants[12] and bioinorganic linkages to processes such as phosphorylation,[13] haloperoxidation[14] and insulin mimicking.[15]

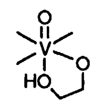
The present study concerns the binding of oxovanadium(V) to the simplest dihydric alcohol ethane-1,2-diol. Previous work[8,16-18] has revealed that alkoxide bridging is very facile and virtually all ethane-1,2-diol complexes isolated so far are binuclear, the crystal structure of one of which is known.[18] This has prompted us to search for rational ways of making mononuclear species incorporating ethane-1,2-diol.

Herein we report a couple of mononuclear complexes wherein the diol is chelated in the half-deprotonated form as in I. The structure of the chelates is probed with the help of single-crystal X-ray crystallography and ^1H NMR spectroscopy. Electronic and CD spectra as well as the electrochemistry of the compounds are reported. This work forms a part of our programs on oxovanadium chemistry.[19]

Results and Discussion

Synthesis and characterisation

Our strategy for realising mononuclear binding of the diol consists in blocking all co-ordination positions leaving just two for possible diol ligation. Since the oxo atom occupies one position, only three others require blocking in a six-co-ordinated situation. The tridentate blocking ligands used are the salicylaldimines of glycine and L-phenylalanine abbreviated as H_2L^1 and H_2L^2 respectively (general abbreviation H_2L). Upon treating [$V^{IV}O(L)(H_2O)$][7,10,19-22] with an excess of ethane-1,2-diol (H_2ed) in methanol at room temperature a dark red solution is formed. A deep brown crystalline solid of composition [$V^VO(L)(Hed)$] deposited in nearly quantitative yield upon keeping the solution in air. Oxygen in the air acts as an oxidant in this synthesis. In dimethyl sulfoxide solution a one-electron cyclic voltammetric reduction peak occurs at −0.32 V for [$VO(L^1)(Hed)$] and at −0.34 V for [$VO(L^2)(Hed)$] (*vs.* the saturated calomel electrode, SCE; platinum working electrode), due to metal reduction. Thus $[Hed]^-$ ligation brings about low metal reduction potentials making aerial oxidation of the metal site ($VO^{2+} \longrightarrow VO^{3+}$) facile.



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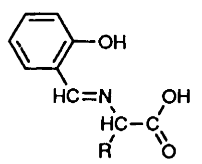

	R
H_2L^1	H
H_2L^2	CH_2Ph

The [$VO(L)(Hed)$] complexes are diamagnetic consistent with the vanadium(V) formulation. Selected spectral data are given in Table 1. The V=O stretch is observed as a strong and sharp band near 975 cm^{-1}. The presence of one symmetric (≈1320 cm^{-1}) and two asymmetric (≈1660 and ≈1630 cm^{-1}) stretching modes characterises monodentate carboxylate binding.[23] The O–H stretch of Hed^- appears as a relatively broad band around ≈3200 cm^{-1} suggesting its involvement in hydrogen bonding as is actually revealed by X-ray work (see below). Electronic and CD spectra (Table 1) of the complexes are discussed in a later section.

Crystal and molecular structure of [$VO(L^2)(Hed)$]

The complex belongs to the polar space group C_2 and the asymmetric unit consists of a single molecule. A molecular view is shown in Fig. 1 and selected bond parameters are listed in Table 2. All the eighteen hydrogen atoms (Fig. 1) in the complex were directly located in Fourier-difference maps.

The Hed^- ligand is chelated, the alkoxidic and alcoholic oxygen atoms lying *trans* to the azomethine nitrogen and oxo

Table 1 Infrared, electronic and CD spectral data

	IR data[a]/cm^{-1}				UV/VIS[b]	CD[b]
Compound	VO	$(CO_2^-)_{asym}$	$(CO_2^-)_{sym}$	OH	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	λ_{max}/nm ($\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1})
[VO(L^1)(Hed)]	978	1660, 1640	1315	3150	480 (456), 345 (5230)	—
[VO(L^2)(Hed)]	976	1670, 1640	1315	3200	495 (808), 345 (6220)	490 (63), 370 (−44) 350 (−18), 307 (152)

[a] In KBr discs. [b] In dry dimethyl sulfoxide.

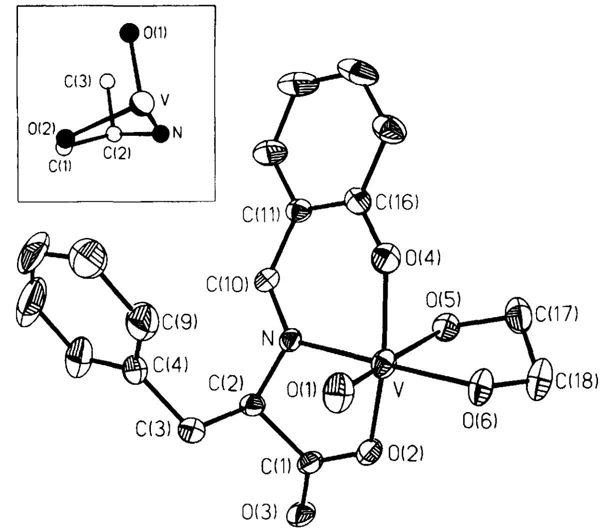

Fig. 1 An ORTEP[24] plot and atom-labelling scheme for [VO(L^2)(Hed)]. All non-hydrogen atoms are represented by their 30% probability ellipsoids. The *endo* configuration is shown inset

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

V–O(1)	1.584(4)	V–O(2)	1.948(3)
V–O(4)	1.859(3)	V–O(5)	2.331(4)
V–O(6)	1.787(4)	V–N	2.082(4)
O(2)–C(1)	1.293(6)	O(3)–C(1)	1.220(6)
O(4)–C(16)	1.333(7)	O(5)–C(17)	1.431(9)
O(6)–C(18)	1.421(7)		
O(1)–V–O(2)	97.9(2)	O(1)–V–O(4)	100.8(2)
O(1)–V–O(5)	177.5(2)	O(1)–V–O(6)	99.6(2)
O(2)–V–O(4)	155.1(2)	O(2)–V–O(5)	81.7(1)
O(2)–V–O(6)	94.0(2)	O(4)–V–O(5)	80.4(1)
O(4)–V–O(6)	99.0(2)	O(5)–V–O(6)	78.0(2)
O(1)–V–N	97.7(2)	O(2)–V–N	76.3(1)
O(4)–V–N	84.9(2)	O(5)–V–N	84.6(1)
O(6)–V–N	161.2(2)		

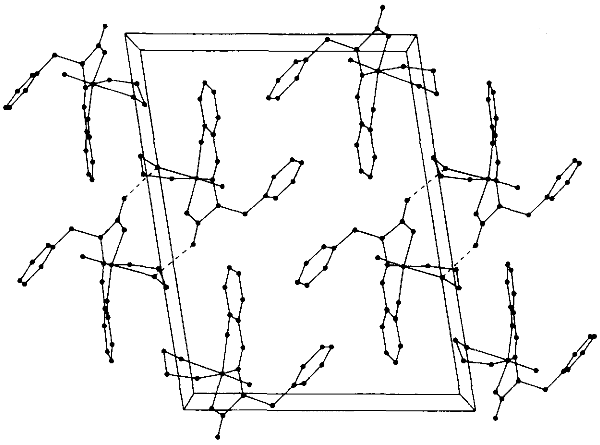

Fig. 2 Packing diagram of [VO(L^2)(Hed)] viewed down *b* axis revealing the O ··· O hydrogen bonding

oxygen respectively. The chelate is non-planar and the dimethylene bridge has a *gauche* configuration. The meridionally spanning tridentate [L^2]$^{2-}$ ligand has two excellently planar (mean deviation $\leqslant$ 0.03 Å) segments, CCO_2 and OC_6H_4CHN, intersecting along the N–C(2) bond (dihedral angle, 34.8°).

The undissociated alcoholic hydrogen of Hed$^-$ of one molecule is engaged in hydrogen bonding [O–H 0.93(5), H ··· O 2.26(5), O ··· O 2.760(10) Å; O–H ··· O 112.6(1.5)°] with the unco-ordinated carboxylate oxygen of a symmetry-related (C_2) neighbouring molecule. The [Hed]$^-$ of the latter molecule is in turn hydrogen bonded to the carboxylate oxygen of the former. The lattice consists of such doubly hydrogen-bridged dimers. A packing diagram (H atoms excluded) viewed down the *b* axis is shown in Fig. 2.

The VO_5N co-ordination sphere is a severely distorted octahedron in which the vanadium atom is displaced by 0.32 Å from the equatorial plane (mean deviation $\approx$ 0.05 Å) of O(2), O(4), O(6) and N towards the oxo oxygen. All the five vanadium–oxygen bonds have different lengths. The shortest is the bond to the oxo oxygen V=O(1), 1.584(4) Å and the longest is that to the glycolic hydroxyl oxygen V–O(5), 2.331(4) Å, which is *trans* to V=O(1). The remaining bond lengths follow the order: alkoxidic, V–O(6) < phenoxidic, V–O(4) < carboxylic, V–O(2) [1.787(4), 1.859(3) and 1.948(3) Å respectively]. In each of the three cases the oxygen function is monoanionic and the observed bond-length trend is believed to reflect the order of O→V donation (alkoxidic > phenoxidic > carboxylic). There is a parallel between the O–V length and acidity of the function concerned (carboxylic > phenolic > alcoholic). It is significant that the weak donor alcoholic rather than the strong donor alkoxidic oxygen of Hed$^-$ lies *trans* to the oxo oxygen. In this manner, competition between alkoxidic and oxo oxygen atoms for the same acceptor metal orbitals is avoided.

The signs of the atomic coordinates of [VO(L^2)(Hed)] were chosen so as to conform to the *S* configuration of the L-amino acid residue. Viewing the metal centre down the unique V=O axis, the priority sequence O(2) > O(5) > O(4) > N of the four atoms of the equator span clockwise corresponding to the absolute configuration *C* for the vanadium co-ordination sphere.[25] Here the V=O axis lies *endo* to the C(2)–C(3) bond (inset, Fig. 1). The complex thus has the *CS* configuration and we have no evidence for the presence of the *AS* diastereoisomer in which the V=O and C(2)–C(3) bonds would lie *exo*. The chiral selectivity imposed by the amino acid residue on the metal centre is similar to that observed in the quinolin-8-ol (Hhquin) complex [VO(L^2)(hquin)].[19]

Spectra

All spectral data were recorded in dimethyl sulfoxide in which the [VO(L)(Hed)] complexes have good solubility. We shall first consider the 500 MHz ^{1}H NMR spectra [dry $(CD_3)_2SO$ solvent]. Signals were assigned (Table 3) on the basis of intensity, spin–spin structure and chemical shift. The resonances of the [L]$^{2-}$ protons followed the same pattern as in [VO(L)(hquin)][19] with a characteristic large (0.5–1.0 ppm) high-field shift of the H(10) and H(12) signals of [VO(L^2)(Hed)] due to the ring current of the CH_2Ph phenyl group.

Table 3 Proton NMR spectral data[a] in $(CD_3)_2SO$

	δ(J/Hz)	
Proton	$[VO(L^1)(Hed)]$	$[VO(L^2)(Hed)]$
H(2)	4.56 (d,[b] 19.2), 5.07 (d,[b] 19.2)	4.64 (dd, 10.0, 5.0)
H(3)	—	3.30 (dd,[c] 13.0, 10.0) 3.47 (dd,[c] 13.0, 5.0)
H(5)–H(9)	—	7.22 (cm)
H(10)	8.86 (s)	7.89 (s)
H(12)	7.67 (d, 7.3)	Under H(5)–H(9), 7.22 (cm)
H(13)	7.01 (t, 7.2)	6.85 (t, 7.5)
H(14)	7.61 (t, 7.5)	7.52 (t, 7.7)
H(15)	6.89 (d, 8.2)	6.80 (d, 8.4)
H(17)	3.67 (cm), 3.73 (cm)	3.54 (cm), 3.65 (cm)
H(18)	4.90 (cm), 4.95 (cm)	4.79 (cm), 4.86 (cm)
H(5′)[d]	6.60 (s)[e]	6.62 (s)[e]

[a] The numbering system corresponds to that in Fig. 1, *e.g.* H(2) represents proton(s) attached to C(2); s = singlet; d = doublet; t = triplet; cm = complex multiplet. [b] The two H(2) protons are inequivalent. [c] The two H(3) protons are inequivalent. [d] Proton attached to O(5). [e] Broad.

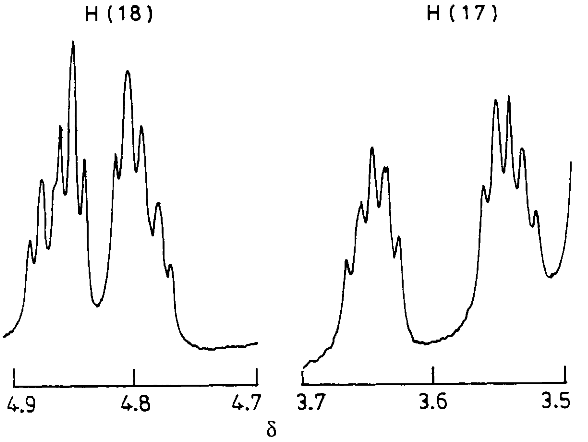

Fig. 3 Proton NMR spectra in $(CD_3)_2SO$ of the methylene protons of $[Hed]^-$ in $[VO(L^2)(Hed)]$

In the crystal structure of $[VO(L^2)(Hed)]$ all the four methylene protons of the Hed^- ligand are inequivalent. This situation persists in solution and we observe four distinct signals each of which is a complex multiplet. The case of $[VO(L^2)(Hed)]$ is displayed in Fig. 3. The pair of signals at lower field near δ 4.8 is due to the CH_2OV protons while those near δ 3.6 are assigned to the $CH_2O(H)V$ methylene protons.[6] The presence of the multiplet structure is a good indication that the rigidity of the chelate ring is retained to a considerable extent in solution. The alcoholic OH signal occurs as a broad resonance near δ 6.6.

The observation of the same set of signals as in Table 3 for every preperation of $[VO(L^2)(Hed)]$ shows that only the *CS* configuration of the complex (identified in the solid state) contributes to the solution composition. The *AS* diastereoisomer is a very minor constituent if it is formed at all.

The absorption and CD spectra of the complexes in the UV and visible region are collected in Table 1 and the spectra of $[VO(L^2)(Hed)]$ are shown in Fig. 4. They remained virtually unaffected upon addition of even a large excess ($\approx$0.8 mol dm^{-3}) of ethane-1,2-diol suggesting the absence of significant Hed^- dissociation. In the absorption spectrum an intense band occurs near 340 nm associated with a weaker shoulder near 490 nm. The latter is assigned to O (alkoxidic)$\rightarrow$V ligand-to-metal charge transfer (l.m.c.t.) excitation.[14] The presence of strong V$\leftarrow$O (alkoxide) donation is consistent with this assignment.

The CD spectrum of $[VO(L^2)(Hed)]$ consists of a well defined positive peak at 490 nm and a slightly weaker negative peak at 370 nm. Evidently the l.m.c.t. excitation has more than one component which are not resolved in the absorption spectrum. There is a weak negative shoulder at 350 nm and a strong positive peak at 307 nm. These probably correspond to the intraligand absorption peak at 345 nm.

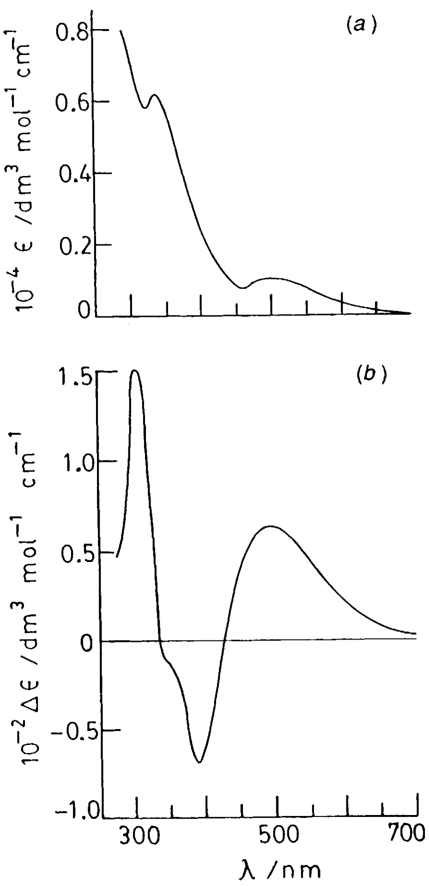

Fig. 4 Electronic (*a*) and CD spectra (*b*) of $[VO(L^2)(Hed)]$ in dimethyl sulfoxide solution

Conclusion

The rare mononuclear binding of ethane-1,2-diol to oxovanadium(v) has been realised in the form of [VO(L)(Hed)] complexes in which the motif **I** is present. The chirality of the amino acid residue in $[L^2]^{2-}$ controls the metal chirality and the observed configuration of $[VO(L^2)(Hed)]$ is exclusively *CS*. The rigidity of the Hed^- chelate ring is largely retained in solution and the four methylene protons give rise to four distinct ^1H NMR multiplets. The composite nature of the O (alkoxidic)$\rightarrow$V l.m.c.t. excitation is revealed in the CD spectrum of $[VO(L^2)(Hed)]$.

Table 4 Crystal data for [VO(L^2)(Hed)]

Formula	$C_{18}H_{18}NO_6V$
M	395.3
Crystal size/mm	0.16 × 0.36 × 0.58
Crystal system	Monoclinic
Space group	$C2$
a/Å	19.154(13)
b/Å	6.505(3)
c/Å	14.674(7)
β/°	99.10(5)
U/Å^3	1805.1
Z	4
D_c/g cm^{-3}	1.454
μ(Mo-Kα)/cm^{-1}	5.83
F(000)	816
Total number of reflections	2330
Number of unique reflections	2277
Number of observed reflections [$I > 3\sigma(I)$]	1618
g in $w = 1/[\sigma^2(\lvert F\rvert) + g\lvert F\rvert^2]$	0.001
Number of refined parameters	234
R^a	0.0380
R'^b	0.0482
Goodness of fit	1.11
Maximum and mean Δ/σ	0.046, 0.003
Data-to-parameter ratio	6.9:1
Maximum, minimum difference peaks/e Å^{-3}	0.31, −0.32

[a] $R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$. [b] $R' = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma w \lvert F_o\rvert^2]^{\frac{1}{2}}$.

Table 5 Atomic coordinates (× 10^4) for [VO(L^2)(Hed)]

Atom	x	y	z
V	−3 839(1)	0	−8 320(1)
N	−3 843(2)	−3 024(6)	−7 855(2)
O(1)	−4 069(2)	1 072(6)	−7 445(2)
O(2)	−4 766(2)	−1 024(6)	−8 873(2)
O(3)	−5 617(2)	−3 339(7)	−8 911(3)
O(4)	−2 866(2)	−155(7)	−7 958(2)
O(5)	−3 520(2)	−1 452(6)	−9 646(2)
O(6)	−3 873(2)	2 169(6)	−9 073(2)
C(1)	−5 030(2)	−2 696(8)	−8 596(3)
C(2)	−4 555(2)	−3 810(8)	−7 824(3)
C(3)	−4 787(2)	−3 258(9)	−6 887(3)
C(4)	−4 286(3)	−4 012(11)	−6 065(3)
C(5)	−4 318(4)	−5 975(14)	−5 732(5)
C(6)	−3 845(6)	−6 662(18)	−5 013(6)
C(7)	−3 320(6)	−5 341(30)	−4 591(5)
C(8)	−3 267(5)	−3 507(27)	−4 912(5)
C(9)	−3 755(3)	−2 761(15)	−5 656(4)
C(10)	−3 320(2)	−4 239(7)	−7 608(3)
C(11)	−2 592(2)	−3 666(8)	−7 604(3)
C(12)	−2 076(3)	−5 181(13)	−7 370(4)
C(13)	−1 372(3)	−4 724(15)	−7 359(4)
C(14)	−1 190(3)	−2 735(14)	−7 593(4)
C(15)	−1 683(3)	−1 250(11)	−7 813(3)
C(16)	−2 395(2)	−1 675(9)	−7 802(3)
C(17)	−3 262(3)	284(13)	−10 091(4)
C(18)	−3 775(4)	2 035(10)	−10 011(4)

Experimental

Materials

Electrochemical grade dry dimethyl sulfoxide, methanol and tetraethylammonium perchlorate were obtained as before.[26] All other chemicals and solvents were of analytical grade and used as received.

Physical measurements

Proton NMR spectra were recorded with a 500 MHz Bruker FT spectrometer, infrared spectra on a Perkin-Elmer 783 spectrophotometer, electronic spectra on a Hitachi 330 spectrophotometer, and CD spectra on a JASCO 500 spectropolarimeter. Electrochemical measurements were performed on a PAR model 370-4 system as previously.[27] All potentials reported in this work are uncorrected for junction contribution. A Perkin-Elmer elemental analyser was used to collect microanalytical data (C, H, N).

Preparations

The complexes reported were prepared by the same general method using [VO(L)(H_2O)][21] as the starting material.

(Ethane-1,2-diolato)oxo(*N*-salicylidene-L-phenylalaninato)-vanadium(V), [VO(L^2)(Hed)]. To a methanolic solution (15 cm^3) of [VO(L^2)(H_2O)] (0.10 g, 0.28 mmol) was added ethane-1,2-diol (1.11 g, 17.88 mmol; 1 cm^3). A dark red solution was formed which upon slow evaporation at room temperature in air afforded a crystalline, deep brown compound. It was filtered off, washed thoroughly with water and dried *in vacuo* over P_4O_{10}. Yield 0.10 g (90%) (Found: C, 54.65; H, 4.55; N, 3.50. Calc. for $C_{18}H_{18}NO_6V$: C, 54.70; H, 4.55; N, 3.55%).

The compound [VO(L^1)(Hed)] was prepared similarly in 86% yield (Found: C, 43.50; H, 4.05; N, 4.65. Calc. for $C_{11}H_{12}NO_6V$: C, 43.30; H, 3.95; N, 4.60%).

Crystal structure determination

Single crystals of [VO(L^2)(Hed)] (0.16 × 0.36 × 0.58 mm) were grown by slow evaporation of a methanolic solution. The cell parameters were determined by a least-squares fit of 30 machine-centred reflections (2θ 15–30°). Data were collected by the ω-scan method in the range 2θ 3–55° on a Siemens R3m/V diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Two check reflections measured after every 198 showed no significant intensity reduction during the 19.1 h of exposure to X-rays. Data were corrected for Lorentz and polarisation effects. An absorption correction was not performed since the absorption coefficient was small (5.83 cm^{-1}). Systematic absences led to the identification of the space group as either $C2$ or $C2/c$ and the structure was successfully solved only in $C2$. Of 2330 reflections, 2277 were unique and 1618 satisfying $I > 3.0\sigma(I)$ were used for structure solution.

All calculations for data reduction, structure solution, and refinement were done on a MicroVAX II computer with the program SHELXTL PLUS[28] and crystal-structure plots were drawn using ORTEP.[24] The structure was solved by direct methods and refined by full-matrix least-squares procedures. All non-hydrogen atoms were made anisotropic. All the hydrogen atoms were located in Fourier-difference maps. These were assigned a fixed $U = 0.08$ Å^2 and their coordinates were not refined. Significant crystal data are in Table 4, atomic coordinates in Table 5.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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