Non-planar Co-ordination of the Schiff-base Dianion *N,N'*-2,2-Dimethyltrimethylenebis[salicylideneiminate(2−)] to Vanadium†

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The Schiff-base dianion *N,N'*-2,2-dimethyltrimethylenebis[salicylideneiminate(2−)](salnptn) co-ordinates to vanadium(IV) to form [VO(salnptn)] whose crystal structure has been determined. The compound is polymeric in the solid state with $\cdots V{=}O \longrightarrow V{=}O \longrightarrow V{=}O \cdots$ chains, the salnptn donor atoms being coplanar and the salnptn framework umbrella-shaped. In the derivative [VO(OMe)(salnptn)], the crystal structure of which has also been determined, the OMe and the vanadyl oxygen are co-ordinated *cis* to each other, and the salnptn now occupies three equatorial and one axial co-ordination positions. Even *N,N'*-ethylenebis(salicylideneiminate) seems to behave analogously, though it is normally planar.

We have recently described a series of vanadium(IV) complexes of tetradentate dianionic Schiff bases.[1] It is now well established that vanadyl(IV) compounds with such ligands are essentially five-co-ordinate, but they fall into two classes, one of green compounds with ν(V=O) *ca.* 980 cm^{-1} in which the five-co-ordinate species are without obvious intermolecular interactions in the crystal, and another which are yellow-brown, with ν(V=O) *ca.* 880 cm^{-1} and which appear to 'polymerise' in the crystal, forming $\cdots V{=}O \longrightarrow V{=}O \longrightarrow V{=}O \cdots$ chains, though the O ⟶ V co-ordinate bond is rather long, *ca.* 2.2 Å compared with *ca.* 1.6 Å for V=O.[2]

Among the compounds we prepared was [VO(2-OC$_6$H$_4$-CH=NCH$_2$CMe$_2$CH$_2$N=CHC$_6$H$_4$O-2)][1] or [VO(salnptn)] which shows ν(V=O) at 871 cm^{-1} and is orange, suggesting a polymeric structure in the solid, but its solubility in organic solvents is nevertheless very high. Accordingly we undertook an X-ray crystal-structure analysis to determine whether the colour and IR data, or the solubility, is the more reliable indicator of the solid-state configuration.

Results and Discussion

The structure of [VO(salnptn)] (Fig. 1) shows that in the solid state it is indeed 'polymeric'. There is a chain of [VO(salnptn)] molecules arranged along a two-fold screw axis. Atom co-ordinates and bond dimensions are listed in Tables 1 and 2. Unlike the more usual tetradentate Schiff-base dianionic ligand salen, *N,N'*-ethylenebis(salicylideneiminate), this Schiff base is umbrella-shaped. However, the *N,N',O,O'* donor atoms are still essentially planar. The vanadium atom is above this plane by 0.299(3) Å, shifted towards its vanadyl oxygen atom. This kind of arrangement is typical of such species, pseudo-six-co-ordinate in the solid state. Indeed the comparable distance above the *N,N',O,O'* plane is 0.31 Å in the analogous propylene complex[3] and it is about half of that of unambiguously five-co-ordinate species such as [VO(salen)] (0.60 Å).[4]

The Schiff-base dianions are rotated by 180° with respect to each other in successive molecules in a chain, which is a very common feature of such $\cdots$V–O–V–O$\cdots$ chains.[5] The vanadyl–oxygen bond length is 1.627(4) Å, again similar to that in other 'polymeric' species, and longer than in [VO(salen)] (1.588 Å).[4] The other V–O chain separation is 2.245(4) Å, again normal. The V–O and V–N bond lengths to the Schiff-base anion are again very similar to those found elsewhere, so that the entire structure is really without any significant surprise.

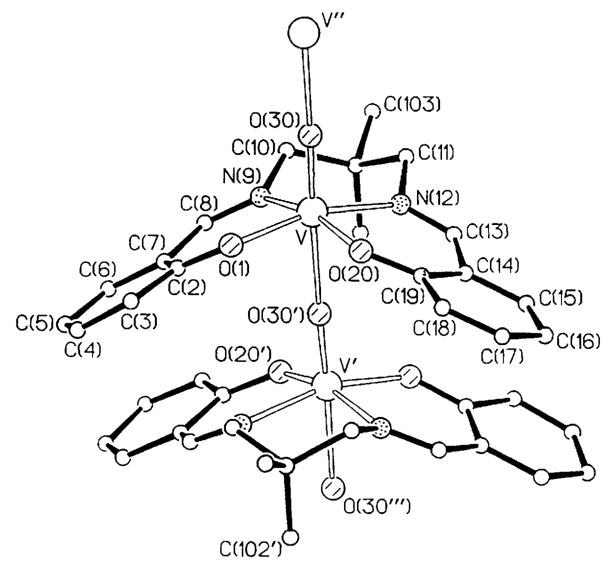

Fig. 1 View of a pair of molecules of [VO(salnptn)] in the $\cdots V{=}O \longrightarrow V{=}O \longrightarrow V{=}O \cdots$ polymeric chain structure. The atom numbering scheme is also shown

It has been known for some time that [VO(salen)] can be oxidised by air in the presence of perchloric acid to yield the salt [VO(salen)][ClO$_4$].[6,7] In the structure of this material there are very weak V–OClO$_3$ interactions *trans* to V=O, as judged by the V–OClO$_3$ separation [2.456(3) Å]. However, the analogue for [VO(salnptn)] has not been reported. Electrochemically, [VO(salnptn)] undergoes a reversible one-electron oxidation at 0.152 V *vs.* [Fe(η-C$_5$H$_5$)$_2$]–[Fe(η-C$_5$H$_5$)$_2$]$^+$ (+0.687 V *vs.*

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† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Final atomic coordinates (fractional × 10^4) for [VO(salnptn)] with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
V	2477.9(5)	3798(1)	45(1)
O(1)	2431(2)	4144(6)	1756(4)
C(2)	2839(3)	4893(8)	2683(6)
C(3)	2632(3)	5253(9)	3770(6)
C(4)	3031(4)	6132(10)	4742(6)
C(5)	3659(5)	6622(12)	4715(7)
C(6)	3871(4)	6196(11)	3697(7)
C(7)	3475(3)	5365(9)	2668(6)
C(8)	3763(3)	4877(9)	1677(6)
N(9)	3484(2)	4191(7)	643(5)
C(10)	3913(3)	3577(9)	−129(6)
C(101)	3765(3)	4286(9)	−1448(6)
C(102)	3803(3)	6249(8)	−1475(7)
C(103)	4272(4)	3488(12)	−2080(8)
C(11)	3108(3)	3619(9)	−2192(6)
N(12)	2537(2)	4246(7)	−1776(5)
C(13)	2077(3)	4927(9)	−2623(6)
C(14)	1440(3)	5351(8)	−2531(6)
C(15)	1020(4)	6126(10)	−3571(7)
C(16)	374(4)	6370(13)	−3634(9)
C(17)	126(4)	5818(11)	−2655(9)
C(18)	517(3)	5079(10)	−1632(7)
C(19)	1190(3)	4844(8)	−1529(6)
O(20)	1547(2)	4162(6)	−496(4)
O(30)	2514(2)	1701(5)	−30(4)

Table 2 Selected molecular dimensions in [VO(salnptn)]. Bond lengths in Å, angles in ° with e.s.d.s in parentheses

(*a*) About the V atom

V–O(1)	1.950(4)	V–O(20)	1.941(4)
V–N(9)	2.098(5)	V–O(30)	1.627(4)
V–N(12)	2.090(5)	V ··· O(30′)	2.245(4)
O(1)–V–N(9)	87.8(2)	N(12)–V–O(20)	88.5(2)
O(1)–V–N(12)	162.5(2)	O(1)–V–O(30)	101.6(2)
N(9)–V–N(12)	89.2(2)	N(9)–V–O(30)	96.0(2)
O(1)–V–O(20)	89.5(2)	N(12)–V–O(30)	95.8(2)
N(9)–V–O(20)	163.3(2)	O(20)–V–O(30)	100.7(2)
O(30)–V ··· O(30′)	174.9(2)	V ··· O(30′)–V′	176.2(2)

(*b*) Torsion angles in the salnptn ligand

O(1)–C(2)–C(7)–C(8)	−7.6(10)
C(2)–C(7)–C(8)–N(9)	9.8(11)
C(7)–C(8)–N(9)–C(10)	−171.0(6)
C(8)–N(9)–C(10)–C(101)	−125.4(6)
N(9)–C(10)–C(101)–C(11)	−66.5(7)
C(10)–C(101)–C(11)–N(12)	66.4(7)
C(101)–C(11)–N(12)–C(13)	127.8(6)
C(11)–N(12)–C(13)–C(14)	168.2(6)
N(12)–C(13)–C(14)–C(19)	−9.5(11)
C(13)–C(14)–C(19)–O(20)	10.6(10)

The primed atoms have coordinates: 0.5 − *x*, 0.5 + *y*, −*z*.

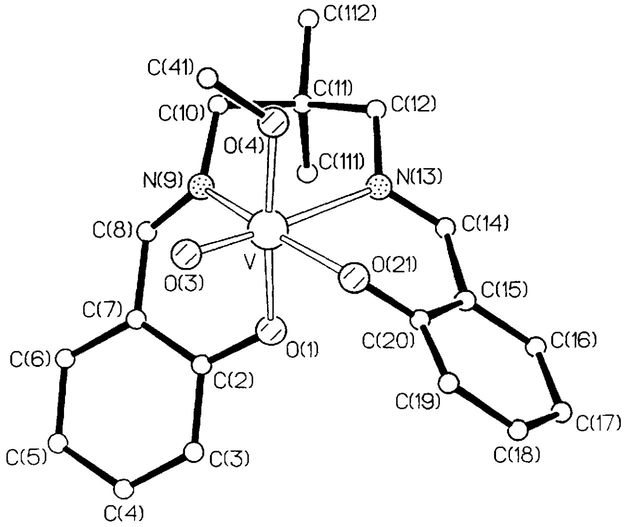


Fig. 2 A molecule of *cis*-[VO(OMe)(salnptn)], showing the atom numbering scheme

Table 3 Final atomic coordinates (fractional × 10^4) for *cis*-[VO(OMe)(salnptn)] with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
V	150.4(4)	1025.9(3)	1477.7(2)
O(1)	−1162(1)	1716(1)	1666.2(9)
C(2)	−1074(2)	2356(2)	2064(1)
C(3)	−1947(2)	2538(2)	2525(1)
C(4)	−1874(3)	3208(2)	2931(2)
C(5)	−937(3)	3727(2)	2904(2)
C(6)	−98(3)	3580(2)	2442(2)
C(7)	−145(2)	2892(2)	2024(1)
C(8)	684(2)	2798(2)	1493(1)
N(9)	841(2)	2141(1)	1160(1)
C(10)	1488(2)	2206(2)	527(1)
C(11)	712(3)	2145(2)	−88(1)
C(12)	238(3)	1285(2)	−167(2)
C(111)	−266(3)	2753(2)	−50(2)
C(112)	1462(4)	2317(3)	−712(2)
N(13)	−490(2)	1020(1)	391(1)
C(14)	−1479(3)	758(2)	238(1)
C(15)	−2275(2)	373(2)	701(1)
C(16)	−3396(3)	247(2)	494(2)
C(17)	−4171(3)	−163(2)	890(2)
C(18)	−3817(3)	−484(2)	1495(2)
C(19)	−2705(3)	−383(2)	1705(2)
C(20)	−1920(2)	62(2)	1328(1)
O(21)	−862(2)	149(1)	1558.1(9)
O(3)	676(2)	1084(1)	2216.0(9)
O(4)	1373(2)	528(1)	1089(1)
C(41)	2497(3)	459(2)	1376(2)

saturated calomel electrode), and we have now isolated and characterised [VO(salnptn)][BF_4] prepared by a chemical oxidative route.

We isolated, in the first place by accident, a species analysing for [VO(OMe)(salnptn)] from a solution of oxidised [VO(salnptn)] in methanol. Later we developed a logical synthesis starting from [VO(salnptn)][BF_4]·MeCN. Thus, [VO(salnptn)][BF_4]·MeCN reacts with LiOMe in MeOH to yield [VO(OMe)(salnptn)], which in turn reacts with acids such as $HClO_4$ to yield salts of $[VO(salnptn)]^+$.

The crystal-structure determination of [VO(OMe)(salnptn)] showed that V=O and V–OMe are unequivocally *cis* rather than *trans* as we had expected. The molecular structure is shown in Fig. 2, and atomic coordinates and selected bond lengths and angles are in Tables 3 and 4. The brown crystals contain isolated [VO(OMe)(salnptn)] molecules. The V=O and V–OMe separations [1.592(2) and 1.820(2) Å, respectively] are completely consistent with bond orders of two and one, as observed in comparable molecules,[4–6] but the geometry in the 'equatorial' plane, normal to V–O(3), is now quite different from that in [VO(salnptn)]. One nitrogen of salnptn is *trans* to the vanadyl oxygen and the corresponding V–N bond length [2.284(2) Å] is longer than the equatorial V–N bond [2.102(2) Å], presumably due to the *trans* influence of the oxygen. Similarly, V–O(1) *trans* to O(4) of the methoxide is long at [1.946(2) Å] compared to V–O(21) [1.874(2) Å]. Consequently, it would appear that the methoxide is also exercising some *trans* influence. The angle O(3)–V–N(13) is *ca.* 175° and the sum of the angles in the equatorial plane is *ca.* 360°, so its deviation from strict planarity is quite small.

Table 4 Selected molecular dimensions in *cis*-[VO(OMe)(salnptn)]. Bond lengths in Å, angles in ° with e.s.d.s in parentheses

(*a*) About the V atom			
V–O(1)	1.946(2)	V–O(21)	1.874(2)
V–N(9)	2.102(2)	V–O(3)	1.592(2)
V–N(13)	2.284(2)	V–O(4)	1.820(2)
O(1)–V–N(9)	81.4(1)	N(13)–V–O(3)	175.2(1)
O(1)–V–N(13)	85.7(1)	O(21)–V–O(3)	102.2(1)
N(9)–V–N(13)	81.1(1)	O(1)–V–O(4)	164.7(1)
O(1)–V–O(21)	86.3(1)	N(9)–V–O(4)	88.0(1)
N(9)–V–O(21)	160.2(1)	N(13)–V–O(4)	81.7(1)
N(13)–V–O(21)	82.6(1)	O(21)–V–O(4)	100.7(1)
O(1)–V–O(3)	95.3(1)	O(3)–V–O(4)	96.6(1)
N(9)–V–O(3)	94.3(1)		
(*b*) In the methoxy ligand			
O(4)–C(41)	1.436(4)	V–O(4)–C(41)	125.9(2)
(*c*) Torsion angles in the salnptn ligand			
O(1)–C(2)–C(7)–C(8)	6.5(4)		
C(2)–C(7)–C(8)–N(9)	−20.7(4)		
C(7)–C(8)–N(9)–C(10)	164.2(3)		
C(8)–N(9)–C(10)–C(11)	−105.0(3)		
N(9)–C(10)–C(11)–C(12)	−69.7(3)		
C(10)–C(11)–C(12)–N(13)	63.0(3)		
C(11)–C(12)–N(13)–C(14)	126.5(3)		
C(12)–N(13)–C(14)–C(15)	171.7(3)		
N(13)–C(14)–C(15)–C(20)	−16.8(4)		
C(14)–C(15)–C(20)–O(21)	4.9(4)		

This kind of co-ordination of a tetradentate dianionic Schiff-base derivative is unusual. It might be that the extra carbon in the backbone of H_2salnptn as compared to H_2salen enables this kind of co-ordination to occur. Indeed the angles and bond lengths of co-ordinated salnptn do not imply any great strain. One would not expect a salen homologue to be so easily obtainable, but we were able to prepare [VO(OMe)(salen)] by a method similar to that used for [VO(OMe)(salnptn)]. None of its physical data suggests that its structure is different, but we were unable to prepare crystals suitable for X-ray structure analysis. Nevertheless, NMR analysis shows that it is almost certainly *cis*.

The ^{1}H NMR spectra of H_2salen and H_2salnptn show equivalence of pairs of protons across an effective mirror plane. This is confirmed by the ^{13}C NMR spectra. In the compounds [VO(OMe)(salen)] and [VO(OMe)(salnptn)] this symmetry breaks down, even though it would be expected to be retained if the V=O and V–OMe bonds were *trans*. The spectra were assigned by careful consideration of chemical shifts and couplings, by two-dimensional ^{13}C–^{1}H correlations, and by ^{13}C DEPT to identify unequivocally quaternary non-hydrogen-bearing carbon atoms, CH, CH_2 and CH_3 groups. All this is shown in Tables 5 and 6.

Since the compound [VO(OMe)(salnptn)] is *cis* in the solid state, and since the NMR spectra indicate that this structure is retained in solution, the parallel between its spectra and those of [VO(OMe)(salen)] argue very strongly that the latter, too, is *cis* in solution, and, by extension, also in the solid state. This was a great surprise because the salen ligand is almost invariably flat. Very recently, and after this work was completed, it was reported that [$TiCl_2$(salen)] reacts with chiral α-hydroxy-carboxylic acids that give rise to an *O*,*O′* dianionic ligand, which forces the salen to adopt a helical configuration.[8] This was proved by X-ray crystallography, and adds to the examples of non-planar salen in [MoO_2(salen)],[9] [Cr(O_4C_2)(salen)]$^-$,[10] [Fe(O_4C_2)(salen)]$^-$ [10] and [Co(MeCOCHCOMe)(salen)][11] which are already described.

The driving force for the *cis* structure we assume to be the presence of two strongly π-bonding ligands, O^{2-} and OMe^-, within the same co-ordination sphere.[9,12] Such a circumstance, especially with two O^{2-} ligands, is well recognised to lead to *cis* co-ordination of the π bonders and the *cis* conformation in VO(OMe) groups has long been known.[13] The data suggest that we could use our systems to measure π-bonding abilities relative to that of O^{2-}. Of course, complexes such as [V(O)$_2$(salen)]$^-$ have yet to be prepared.

Experimental

Compounds were generally handled by standard Schlenk-tube techniques under dinitrogen, in dried solvents. Analyses were by the Department of Chemistry, University of Surrey. The IR spectra were obtained as Nujol mulls using a Perkin-Elmer 883 spectrometer and NMR spectra were determined in solution in CD_2Cl_2 with a JEOL GSX-270 spectrometer. The reference for ^{51}V shifts was $VOCl_3$. Cyclic voltammograms were run in acetonitrile using 0.2 mol dm^{-3} [NBu^n_4][BF_4] as supporting electrolyte in a conventional three-electrode cell fitted with a platinum working electrode. Compounds [VO(salnptn)] and [VO(salen)] were prepared as described elsewhere.[1]

[N,N′-2,2-*Dimethyltrimethylenebis*(*salicylideneiminato*)]-*oxovanadium Tetrafluoroborate–Acetonitrile* (1/1).—*Method A*. To a suspension of [VO(salnptn)] (2.5 g, 6.67 mmol) in MeCN (50 cm^3) was added HBF_4·Et_2O (1.10 g, 0.96 cm^3, 6.67 mmol). The orange solid dissolved immediately, giving a dark green solution. After stirring for 16 h in air, the solvent was removed *in vacuo* and the green residue was taken up in MeCN (20 cm^3) and filtered hot from a small residue. Cooling to −20 °C afforded dark green crystals (1.4 g, 2.8 mmol, 42%). Diethyl ether was added to the filtrate affording a further crop (0.9 g) (Found: C, 49.6; H, 4.6; N, 8.3. $C_{21}H_{23}BF_4N_3O_3V$ requires C, 50.1; H, 4.6; N, 8.3%). IR: 2267 ν(C≡N), 1057 ν(B–F), 997 cm^{-1} ν(V=O).

Method B. The same compound was made by treatment of *cis*-[VO(OMe)(salnptn)] (0.18 g, 0.45 mmol) with HBF_4·Et_2O (0.08 g, 0.45 mmol) in acetonitrile, in 57% yield.

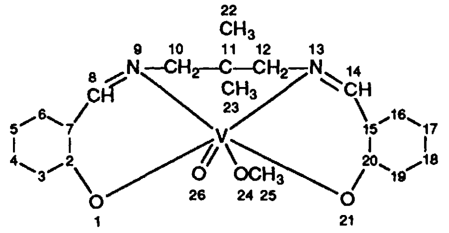
The perchlorate was prepared as an MeCN solvate (1 : 1) as in method A in 28% yield from reaction of [VO(salnptn)] (1.88 g, 5.0 mmol) with 60% $HClO_4$ (0.84 g, 5.0 mmol) in MeCN, and recrystallising from hot MeCN (Found: C, 48.4; H, 4.5; N, 7.5. $C_{21}H_{23}ClN_3O_7V$ requires C, 48.9; H, 4.5; N, 8.1%). IR: 2264 ν(C≡N), 1086 ν(Cl=O), 996 cm^{-1} ν(V=O).

[N,N′-2,2-*Dimethyltrimethylenebis*(*salicylideneiminato*)]-(*methoxo*)*oxovanadium*.—The compound [VO(salnptn)]-[BF_4]· MeCN (0.75 g, 1.5 mmol) was suspended in MeOH (20 cm^3) and solid lithium methoxide (0.06 g, 1.5 mmol) was added. The suspension immediately became dark red. After stirring for 3 h, the dark red product was filtered off, washed with methanol and diethyl ether, and dried *in vacuo*. Yield 82%. An analytically pure and crystallographically suitable sample was obtained by recrystallisation from MeCN (Found: C, 59.5; H, 5.40; N, 6.80. $C_{20}H_{23}N_2O_4V$ requires C, 59.1; H, 5.7; N, 6.9%). IR 951 cm^{-1} ν(V–O).

Solutions in CD_2Cl_2 are rather unstable and NMR data were obtained several times until the results were consistent. ^{51}V NMR: δ −503(s).

The salen homologue was prepared similarly, starting from either [{VO(salen)}$_2$(μ-F)][BF_4] (0.77 g, 1.0 mmol) or [VO-(salen)][ClO_4]·MeOH (0.93 g, 2.0 mmol) and LiOMe (0.08 g, 2.0 mmol), in 82% yield. Because it decomposed rapidly in hot acetonitrile, it was recrystallised from dichloromethane–methanol (Found: C, 55.6; H, 4.6; N, 7.7. $C_{17}H_{17}N_2O_4V$ requires C, 56.1; H, 4.70; N, 7.70%). IR: 947 cm^{-1} ν(V=O). Solutions in CD_2Cl_2 were not especially stable, and the NMR spectra had to be obtained as rapidly as possible. ^{51}V NMR: δ −513(s).

Table 5 Proton and ^{13}C NMR assignments for $H_2salnptn$ and [VO(OMe)(salnptn)]



	$H_2salnptn$			[VO(OMe)(salnptn)]			
	Atom	δ	*J*/Hz	Atom	δ	*J*/Hz	
(*a*) ^1H NMR assignments							
ABCD	3 (≡19)	6.98 (d)	(8.2)		6.44 (d)		
					6.77 (t)		
	4 (≡18)	7.32 (t)	(7.3, 7.6)		6.80 (d)		
				3, 4, 5, 6	6.93 (t)	*ca.* 8	2 × ABCD
	5 (≡17)	6.89 (t)	(7.3, 7.6)	16, 17, 18, 19	7.30 (t)		
					7.32 (d)		
	6 (≡16)	7.26 (d)	(7.6)		7.38 (d)		
					7.44 (d)		
	8 (≡14)	8.34 (s)		8, 14	8.045 (s)		
					8.315 (s)		
	10 (≡12)	3.49 (s)			3.04 (d)	12.5	
				10, 12	3.42 (d)	10.7	ABCD
					4.12 (d)	10.7	
					4.26 (d)	12.5	
				25	5.43 (s)		
	22 (≡23)	1.08 (s)		22, 23	0.575 (s)		
					1.050 (s)		
(*b*) ^{13}C NMR assignments							
	22, 23	24.7		22, 23	23.5		
					26.5		
	11	36.6		11	38.0 (quaternary)		
	10, 12	68.4		10, 12	73.1		
					73.6		
				25	75.0		
		117.3			117.5		
	3, 5, 7, 19	118.9			117.8		
		119.0			118.1		
				3, 5, 17, 19	120.3		
	4, 6, 16, 18	131.7		4, 6, 16, 18	132.5		
		132.6			133.6		
					133.9		
					135.7		
	8, 14	166.0		8, 14	162.7		
					163.0		
	2, 7, 15, 20	161.5		2, 7, 15, 20	172.0 (quaternary)		

Crystal-structure Analyses.—[VO(salnptn)]. *Crystal data*. $C_{19}H_{20}N_2O_3V$, $M = 375.3$, monoclinic, space group $P2_1/a$ (equiv. to no. 14), $a = 21.227(3)$, $b = 7.735(3)$, $c = 11.132(2)$ Å, $\beta = 104.170(14)°$, $U = 1772.1(8)$ Å^3, $Z = 4$, $D_c = 1.406$ g cm^{-3}, $F(000) = 780$, $\mu(\text{Mo-K}\alpha) = 5.6$ cm^{-1}, $\lambda(\text{Mo-K}\bar{\alpha}) = 0.710\,69$ Å.

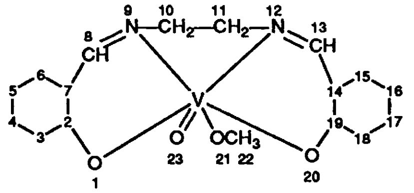
Crystals are thin, orange-yellow, elongated plates; most have extra side-growths. One, *ca.* 0.04 × 0.20 × 0.95 mm, was mounted on a glass fibre and, after photographic examination, was transferred to an Enraf–Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell parameters (by refinement from the settings of 25 reflections, θ in the range 10–12°, each centred in four orientations), and measurement of diffraction intensities (to θ_{max} 25°). There was no crystal deterioration.

After correction for Lorentz–polarisation effects, 3114 unique intensity data (1852 with $I > 2\sigma_I$) were input to the SHELX system[14] for an analytical absorption correction and for structure determination by the heavy-atom method. Refinement by full-matrix least-squares methods converged at $R = 0.091$ and $R' = 0.094$[14] for 2254 reflections (those with $I > \sigma_I$) weighted $w = (\sigma_F^2 + 0.004\,F^2)^{-1}$; the goodness-of-fit S was 1.23. All the non-hydrogen atoms were allowed anisotropic thermal parameters. Hydrogen atoms were included in idealised positions (the methyl groups in staggered orientations); their isotropic thermal parameters were refined freely. In a final difference map, the only peaks of significance (two at *ca.* 1.4 e Å^{-3}) were close to the V=O ⋯ V axis.

cis-[VO(OMe)(salnptn)]. *Crystal data*. $C_{20}H_{23}N_2O_4V$, $M = 406.4$, monoclinic, space group $B2_1/a$ (equiv. to no. 14), $a = 11.690(1)$, $b = 16.467(2)$, $c = 19.853(2)$ Å, $\beta = 90.009(8)°$, $U = 3821.5(7)$ Å^3, $Z = 8$, $D_c = 1.413$ g cm^{-3}, $F(000) = 1696$, $\mu(\text{Mo-K}\alpha) = 5.3$ cm^{-1}, $\lambda(\text{Mo-K}\bar{\alpha}) = 0.710\,69$ Å.

Crystals are very dark, well formed prisms. Photographic examination of one crystal, *ca.* 0.10 × 0.25 × 0.50 mm, mounted on a glass fibre, showed it to have monoclinic symmetry most conveniently described by a non-standard B-centred cell with a β angle very close to 90°. This was then

Table 6 Proton and ^{13}C NMR assignments for H_2salen and [VO(OMe)(salen)]



H_2salen Atom	δ	J/Hz	[VO(OMe)(salen)] Atom	δ	J/Hz	
(a) ^1H NMR assignments						
ABCD 3 (≡18)	6.9 (d)		3, 4, 5, 6	6.8 (t)	(6.7)	2 × ABCD
			15, 16, 17, 18	7.0 (q)	(6.6)	
4 (≡17)	7.3 (t)			7.5 (m)		
5 (≡16)	6.8 (t)					
6 (≡15)	7.2 (d)					
8 (≡13)	8.43 (s)		8, 13	8.32 (s),		
10 (≡11)	3.89 (s)			8.64 (s)		
			10, 11	3.4 (m)		ABCD
				3.9 (m)		
				4.0 (m)		
				4.3 (m)		
			22	5.1 (s)		
(b) ^{13}C NMR assignments						
			10, 11	58.7		
				61.4		
			22	74.2		
				118.1		
				118.7		
			3, 4, 5, 6	120.9		
			15, 16, 17, 18	132.0		
				134.1		
				134.2		
				136.0		
			7, 14	121.6 (quaternary)		
			8, 13	162.8		
				163.2		
			2, 19	169.7 (quaternary)		

transferred to the diffractometer for determination of accurate cell dimensions (using 25 reflections, θ in the range 10–11°, each centred in four orientations) and for measurement of diffraction intensities (to θ_{max} 25°).

In processing the data, corrections were applied for Lorentz–polarisation effects, absorption (by semi-empirical methods, from ψ-scan measurements) and to eliminate negative net intensities (by Bayesian statistical methods). There was no deterioration of the crystal during the data collection.

Of the 3350 unique reflections input to the SHELX system,[14] 843 had intensities $I > 2\sigma_I$. The complete structure was revealed in the E-map produced by the direct-methods routine TREF in SHELXS.[15] Refinement by full-matrix least-squares methods was smooth and rapid, converging with $R = 0.057$, $R' = 0.053$ and $S = 1.52$ for all 3350 reflections weighted $w = (\sigma_F{}^2 + 0.000\,30\ F^2)^{-1}$. Hydrogen atoms were included in idealised positions; in the methyl groups, these atoms were geometrically constrained. The isotropic thermal parameters of the hydrogen atoms were freely refined; all other atoms were allowed anisotropic thermal parameters.

In the final difference map, the principal peaks were *ca.* 0.35 e Å^{-3} and close to the V atom.

For both analyses, scattering factor curves for neutral atoms were taken from ref. 16. Computer programs used in the analyses have been noted above or in Table 4 of ref. 17, and were run on DEC MicroVAX-II or -3600 machines.

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

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