New Polymeric Compounds containing Vanadium–Oxygen Chains *

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The controlled protonation of complexes of tetradentate Schiff-base anions, L^{2-}, [VO(L)], has been found to yield $[V(OH_2)(L)]^{2+}$, $[V(L)OV(L)]^{2+}$, $[V(L)OV(L)OV(L)]^{2+}$ or $[V(L)OV(L)OV(L)OV(L)]^{2+}$, depending on reaction conditions. The crystal structures of two salts of the last where $L = N,N'$-ethylenebis(salicylideneiminate) have been determined, and compared with those of the known $[V(L)OV(L)O]^+$ and the new $[{V(L)OV(L)}_2]^{2+}$. These compounds are the first members of what appears to be an extensive family of compounds containing vanadium–oxygen chains.

We described recently a complex of vanadium, **1**, with the tetradentate Schiff-base dianion $(OC_6H_4CHNCH_2CH_2\text{-}NCHC_6H_4O)^{2-}$ which contains a unit we formulated as $[V^{IV}{=}O{\rightarrow}V^V{=}O]^+$.[1] We hoped to extend this to further derivatives, and the strategy we adopted was to attempt to remove oxygen from $V^{IV}{=}O$ or even $V^V{=}O$ compounds by protonation or by reaction with an oxygen-atom acceptor, hoping for polymerisation with an excess of the vanadyl species.

This strategy has been successful, and here we describe the synthesis and structure of two different salts containing chains $[V^{IV}{=}O{\rightarrow}V^{IV}\text{-}O\text{-}V^{IV}{\leftarrow}O{=}V^{IV}]^{2+}$ and of the dinuclear system $[V^{IV}\text{-}O\text{-}V^{IV}]^{2+}$, which may be considered to be the core of the tetranuclear units. Some of this work has already been described in a preliminary communication.[2]

Our work seemed to indicate that when an oxide ion is removed from a compound such as [VO(salen)],† leaving a hypothetical species V(salen)$^{2+}$ in the presence of more [VO(salen)], then the two vanadium moieties would aggregate to form chains $\{V_nO_{n-1}\}$, the value of n depending on the molar ratio of the two species. It is known that complexes $[VX_2(salen)]$ (X = Cl or Br) are obtained by reaction of [VO(salen)] with HX and the reaction is generally believed to proceed as shown [equation (1)].[3] This provides

$$[VO(salen)] \xrightarrow{2H^+} [V(OH_2)(salen)]^{2+} \xrightarrow{2X^-}$$
$$[VX_2(salen)] + H_2O \quad (1)$$
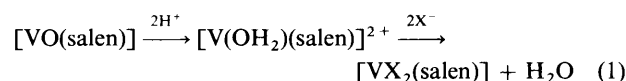
general support for our hypothesis of an aqua species as intermediate.

We hoped to prepare $[V(OH_2)(salen)]^{2+}$ using an acid with a poorly co-ordinating anion, $HBF_4 \cdot Et_2O$, and to use this acid and other oxygen-atom extractors to control the degree of polymerisation reaction outlined above. We also wished to determine whether dinuclear complexes analogous to $[V^{IV}O\text{-}(salen)V^VO(salen)]^+$ could be prepared using other Schiff-base derivatives.

† Schiff bases used in this work: N,N'-ethylenebis(salicylideneimine) or H_2salen; N,N'-2,2-dimethyltrimethylenebis(salicylideneimine) or H_2saldmtm; N,N'-trimethylenebis(salicylideneimine) or H_2saltm; N,N'-bis(2-hydroxynaphthylmethylene)ethylenediamine or H_2hnapen; N,N'-1,1-dimethylethylenebis(salicylideneimine) or H_2salibn.
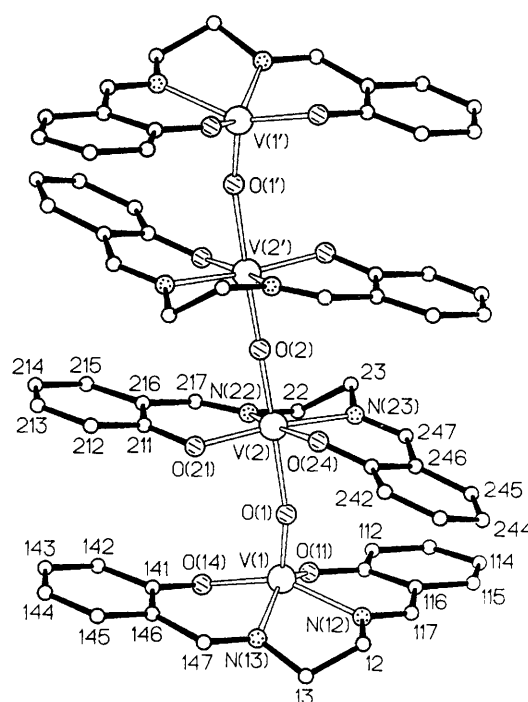

Fig. 1 Representation of the isolated cation in the structure of $[{V(salen)OV(salen)}_2O][BF_4]_2$ **2**. The atom numbering scheme is indicated; carbon atoms are labelled by their numbers only, *e.g.* C(143) is shown as 143

Results and Discussion

In initial experiments, we had hoped to extract the vanadyl oxygen atom from [VO(salen)] using $HBF_4 \cdot Et_2O$ (mole ratio 1:2) or trityl tetrafluoroborate. What we isolated was the salt $[V(salen)OV(salen)OV(salen)OV(salen)][BF_4]_2$ **2** which contains a linear $V^{IV}_4O_3$ system. This structure is unprecedented in vanadium chemistry, and is shown in Fig. 1. Atomic coordinates and bond lengths and angles are shown in Tables 1 and 2, respectively.

Another salt, **3**, containing this cation was obtained in the first place by reaction of $[VCl_2(salen)]$ and [VO(salen)] with $AgBPh_4$ in MeCN. We prepared it subsequently from the tetrafluoroborate salt and $NaBPh_4$. The crystal structure determination (Fig. 2, Tables 3 and 4) reveals that rather than containing isolated V_4O_3 units, the V_4O_3 units are linked by additional V–O interactions, the oxygen atoms involved being

Table 1 Final atomic coordinates ($\times 10^4$) for [{V(salen)OV(salen)}$_2$(μ-O)][BF$_4$]$_2$·2MeCN **2** with estimated standard deviations (e.s.d.s) in parentheses[a]

Atom	x	y	z	s.o.f.[a]	Atom	x	y	z	s.o.f.[a]
The [{V(salen)OV(salen)}$_2$(μ-O)]$^{2+}$ cation									
V(1)	3 200.0(5)	−3 467.1(4)	3 816.8(4)		V(2)	816.6(5)	−1 151.5(4)	1 255.1(4)	
O(11)	4 417(2)	−2 848(2)	4 552(2)		O(21)	1 548(2)	−2 103(2)	765(2)	
C(111)	4 230(3)	−2 317(3)	5 140(2)		C(211)	2 332(4)	−2 002(3)	216(3)	
C(112)	5 122(4)	−1 702(3)	5 376(3)		C(212)	2 206(4)	−2 517(3)	−475(3)	
C(113)	4 992(5)	−1 152(3)	5 993(3)		C(213)	3 045(5)	−2 443(4)	−1 019(3)	
C(114)	3 986(6)	−1 190(4)	6 390(3)		C(214)	4 015(6)	−1 886(5)	−887(4)	
C(115)	3 118(5)	−1 806(3)	6 187(3)		C(215)	4 154(5)	−1 375(4)	−221(3)	
C(116)	3 217(4)	−2 387(3)	5 561(3)		C(216)	3 289(4)	−1 404(3)	334(3)	
C(117)	2 350(4)	−3 081(3)	5 442(3)		C(217)	3 467(3)	−864(3)	1 033(3)	
N(12)	2 297(3)	−3 615(2)	4 859(2)		N(22)	2 688(3)	−752(2)	1 520(2)	
C(12)	1 359(4)	−4 306(3)	4 796(3)		C(22)	3 019(4)	−204(3)	2 232(3)	
C(13)	2 096(4)	−5 300(3)	4 695(3)		C(23)	1 611(4)	509(3)	2 087(3)	
N(13)	2 729(3)	−4 902(2)	3 944(2)		N(23)	713(3)	−207(2)	2 112(2)	
C(147)	2 895(4)	−5 432(3)	3 386(3)		C(247)	44(4)	−281(3)	2 701(3)	
C(146)	3 651(4)	−5 209(3)	2 737(3)		C(246)	−885(4)	−945(3)	2 776(3)	
C(145)	3 591(4)	−5 754(3)	2 068(3)		C(245)	−1 423(5)	−1 075(4)	3 542(3)	
C(144)	4 358(5)	−5 633(4)	1 484(3)		C(244)	−2 369(5)	−1 655(4)	3 591(4)	
C(143)	5 245(5)	−4 991(4)	1 568(3)		C(243)	−2 812(5)	−2 101(4)	2 886(4)	
C(142)	5 345(4)	−4 456(3)	2 228(3)		C(242)	−2 302(4)	−1 997(3)	2 129(3)	
C(141)	4 533(3)	−4 535(3)	2 809(3)		C(241)	−1 311(3)	−1 440(3)	2 084(3)	
O(14)	4 652(2)	−4 006(2)	3 435(2)		O(24)	−806(2)	−1 360(2)	1 359(2)	
O(1)	1 916(2)	−2 477(2)	2 731(2)		O(2)	0	0	0	
The BF$_4^-$ anion[b]									
B(30)	10 220(3)	−7 165(2)	−6 939(2)		F(31c)	9 850(3)	−6 293(2)	−6 687(2)	0.25
F(31a)	9 332(3)	−7 780(2)	−7 130(2)	0.25	F(32c)	9 829(3)	−6 758(2)	−8 003(2)	0.25
F(32a)	10 476(3)	−6 682(2)	−7 813(2)	0.25	F(33c)	11 666(3)	−7 699(2)	−6 410(2)	0.25
F(33a)	9 585(3)	−6 329(2)	−6 722(2)	0.25	F(34c)	9 536(3)	−7 910(2)	−6 656(2)	0.25
F(34a)	11 491(3)	−7 870(2)	−6 090(2)	0.25	F(31d)	11 234(3)	−7 186(2)	−6 062(2)	0.25
F(31b)	8 928(3)	−6 506(2)	−7 777(2)	0.25	F(32d)	8 984(3)	−6 277(2)	−7 324(2)	0.25
F(32b)	10 430(3)	−6 773(2)	−6 178(2)	0.25	F(33d)	9 931(3)	−8 163(2)	−6 671(2)	0.25
F(33b)	11 285(3)	−7 128(2)	−7 271(2)	0.25	F(34d)	10 732(3)	−7 034(2)	−7 700(2)	0.25
F(34b)	10 232(3)	−8 251(2)	−6 533(2)	0.25					
The disordered acetonitrile solvent molecule									
N(40a)	2 562(11)	2 351(8)	10 352(9)	0.5	C(41a)	192(13)	4 122(11)	9 240(12)	0.5
N(40b)	2 501(12)	2 575(10)	10 601(8)	0.5	C(41b)	369(12)	3 981(10)	8 770(9)	0.5
C(40)	1 577(7)	3 168(6)	9 848(6)						

[a] Site occupancy factor, if different from 1.0. [b] Each set of four fluorine atoms was refined with a common B atom, as a rigid idealised tetrahedral group.
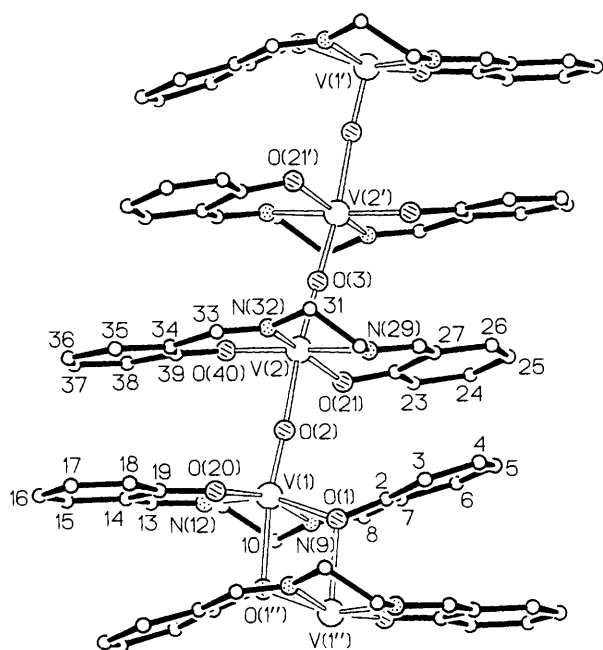

Fig. 2 Representation of the polymeric chain formed by cations in the structure of [{V(salen)OV(salen)}$_2$O][BPh$_4$]$_2$ **3**

part of the salen structures. Consequently, the cations are united to form an infinite chain. This is shown in comparative fashion in Fig. 3.

For both structures the V–O bond lengths in the chain are consistent with double bonds in the outermost two V–O links, multiple though not double bonds in the innermost two links, and single bonds in the remaining two links. For comparison, the V–O bonds to oxygen within the salen are about 1.9 Å, and this must connote a single bond. We write the basic chain in the form (V=O→V-O-V←O=V)$^{2+}$, which indicates that we are dealing with a V^{IV}=O moiety donating to a (V^{IV}-O-V^{IV})$^{2+}$ fragment which may be stable under certain circumstances.

In the family of complexes of tetradentate Schiff bases, H$_2$L, there is little difference between v(V=O) for [LV^{IV}=O] and [LV^V=O]$^+$.[3,4] In addition, those complexes with v(V=O) at 960 cm^{-1} or above are generally believed to be monomeric in the solid state, whereas those with v(V=O) at 880 cm^{-1} or below are believed to be stacked, ···V=O→V=O→···.[5] Our previous complex (V^{IV}=O→V^V=O)$^+$ **1** showed v(V=O) at 870 cm^{-1}, but, in contrast, our new complexes show v(V=O) at 945, 910 (for **2**) and 916 (for **3**) cm^{-1}. These values are very equivocal. However the two materials are very distinct in their properties. Similarly, the compounds both are paramagnetic with room-temperature moments corresponding to one unpaired electron per vanadium.

Such complexes are expected to hold the unpaired electrons in a d$_{xy}$ orbital at right-angles to the V–O chain.[6] This means that there should be no electron delocalisation along the chain.

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Table 2 Selected molecular dimensions in [{V(salen)OV(salen)}$_2$-(μ-O)][BF$_4$]$_2$·2MeCN **2**, bond lengths in Å, angles in ° with e.s.d.s in parentheses

(a) About the V atoms

V(1)–O(11)	1.890(2)	V(2)–O(21)	1.834(2)
V(1)–N(12)	2.042(3)	V(2)–N(22)	2.078(3)
V(1)–N(13)	2.029(3)	V(2)–N(23)	2.080(3)
V(1)–O(14)	1.901(2)	V(2)–O(24)	1.825(2)
V(1)–O(1)	1.625(2)	V(2)–O(2)	1.763(1)
		V(2)–O(1)	2.059(2)
O(11)–V(1)–N(12)	87.6(1)	O(21)–V(2)–N(22)	86.3(1)
O(11)–V(1)–N(13)	143.5(1)	O(21)–V(2)–N(23)	160.7(1)
N(12)–V(1)–N(13)	78.8(1)	N(22)–V(2)–N(23)	76.9(1)
O(11)–V(1)–O(14)	88.8(1)	O(21)–V(2)–O(24)	110.3(1)
N(12)–V(1)–O(14)	151.5(1)	N(22)–V(2)–O(24)	161.5(1)
N(13)–V(1)–O(14)	87.4(1)	N(23)–V(2)–O(24)	85.3(1)
O(11)–V(1)–O(1)	110.5(1)	O(21)–V(2)–O(2)	92.8(1)
N(12)–V(1)–O(1)	101.7(1)	N(22)–V(2)–O(2)	88.9(1)
N(13)–V(1)–O(1)	105.5(1)	N(23)–V(2)–O(2)	96.3(1)
O(14)–V(1)–O(1)	106.0(1)	O(24)–V(2)–O(2)	98.0(1)
		O(1)–V(2)–O(21)	86.2(1)
		O(1)–V(2)–N(22)	86.8(1)
		O(1)–V(2)–N(23)	83.4(1)
		O(1)–V(2)–O(24)	86.3(1)
		O(1)–V(2)–O(2)	175.6(1)
V(1)–O(1)–V(2)	162.2(1)	V(2)–O(2)–V(2')	180

(b) Torsion angles in the salen ligands

N(12)–C(12)–C(13)–N(13)	– 42.2(4)
N(22)–C(22)–C(23)–N(23)	46.6(4)

This is apparently not entirely true. The narrower [51]V EPR solid state signal we observed for the tetranuclear tetraphenylborate is consistent with more delocalisation in this case than in the tetrafluoroborate salt, but the mechanism is not clear. We have determined the magnetic susceptibility of the tetrafluoroborate down to 90 K. The crystals used were from the same crop as used for the structure determination. The plot of the data (Table 5) is a curve, the lowest part of which extrapolates linearly to $1/\chi = 0$ at $T = 0$ K, normal paramagnetic behaviour. However, there appears to be some antiferromagnetic effect operating above $ca.$ 150 K. We do not yet have comparable data for the tetraphenylborate.

We have already mentioned that the central unit of the V$_4$O$_3$ chains seems to be represented best by the formula [V^{IV}–O–V^{IV}]$^{2+}$, and it would be very useful to obtain this material as a salt. It might be accessible by careful protonation of [VO(salen)] with an amount of acid less than that necessary to protonate all the V=O to the moiety V(OH$_2$)$^{2+}$ which we have tentatively characterised in [V(H$_2$O)(salen)][BF$_4$] (see Experimental section). We have shown above how [{V(salen)}$_4$O$_3$]-[BF$_4$]$_2$ can be prepared in similar fashion, but with a ratio of HBF$_4$·Et$_2$O to vanadium of 1:2. When the ratio is 1:1 rather than 1:2 and the reaction is run at ambient temperature, the product analyses for [{V(salen)}$_2$O][BF$_4$]$_2$, which should contain the required cation. It has an effective magnetic moment of 1.7 μ$_B$ per V, consistent with a localised d^1–d^1 system.

Crystals for a crystal structure determination are as yet lacking. In addition, when the same reactants in the same proportions in the same solvent are heated to reflux temperature for 0.5 h the product appears to be [{V(salen)}$_3$-O$_2$][BF$_4$]$_2$, which can also be obtained by adding [VO(salen)] to the complex tentatively formulated as [{V(salen)}$_2$O][BF$_4$]$_2$. Though final crystallographic proof is still lacking for two of the three cases, we now have evidence for the first three members of what could be an infinite series, $viz.$ (V^{IV}–O–V^{IV})$^{2+}$, (V^{IV}=O→V^{IV}–O–V^{IV})$^{2+}$, (V^{IV}=O→V^{IV}–O–V^{IV}←O=V)$^{2+}$.

We have, as yet, no unequivocal evidence for [V(OH$_2$)-

(salen)][BF$_4$]$_2$, though we did isolate a compound analysing correctly for this species, as described in the Experimental section.

We obtained yet a further variant in these systems from the reaction of [VO(salen)] with HI. It was originally hoped that this would generate [VI$_2$(salen)].[7] We now have prepared this compound, but by an alternative route, but we also now know that iodide under these conditions reduces V^{IV} to V^{III}, and V^{III} to V^{II}.[8] The product from the HI reaction was first formulated by us as [{V(salen)}$_2$I$_3$], but X-ray structure analysis showed it to be rather different, namely [{[V(salen)]$_2$O}$_2$][I$_3$]$_2$ **4**, containing the unit [V^{IV}–O–V^{III}]$^+$, and this is shown in Fig. 4 with atomic coordinates and bond lengths and angles in Tables 6 and 7, and comparative data in Table 8.

This material has V(1)–O(1) 1.635(3) and V(2)–O(1) 2.006(3) Å, and it is extraordinary that comparable distances and angles in all four structures do not change significantly throughout the series, though formally we have V^{IV}=O donating to V^V, V^{IV} and to V^{III} in the different compounds. Where two of the structures exhibit a common feature, the geometrical properties seem to be very similar. This is not reflected in the values of v(V=O). Thus compound **1** has a single v(V=O) at 870 cm^{-1}, which is normally taken to imply a polymeric structure,[5] whereas **4** has a value of 970 cm^{-1}, which is supposed to indicate a mononuclear structure. Compounds **2** and **3** exhibit intermediate v(V=O) values.

The geometry of the salen interaction with vanadium seems to be similar throughout the series. Thus, in any six-co-ordinate environment, the vanadium lies approximately in the plane of the N,N',O,O' donor atoms. Where the co-ordination number is five, the vanadium is above the plane of these donors, moved by $ca.$ 0.3–0.5 Å towards the oxygen of the V–O double bond.

Although the links between the V(salen) end units which involve bridging V–O(salen) bonds are similar in **3** and **4** (Fig. 3), it is not clear why two such different structures are similarly linked, and it is not clear why such bonding occurs in **3** and **4** but not **2** (it is excluded in **1**, which, although there is an infinite chain of V$_2$O$_2$ units in the crystal, contains V=O not significantly interacting with the proximate vanadium in the next V$_2$O$_2$ unit). However, the differences between the structures are not restricted to this end interaction, but also involve differences in the packing of successive salen ligands within each cation.

The salens are grouped in pairs down the V–O–V chain, with the bridging pairs of methylenes on opposing sides of the chain. This can be seen most easily in **1**, where it is also evident that one pair of phenyl groups is eclipsed, whereas the other pair of phenyl groups is quite widely separated, with no superposition. In fact, in **2** a similar arrangement holds on either side of the centre of symmetry at O(2). Again, **4** shows this phenomenon in each half of the dimer, but also the second and third salens in the chain are forced to be opposed by the vanadium–oxygen interactions.

Compound **3** also has alternating salen arrangements, but there is much more overlap of the phenyl groups in **3** than in **2**. Since the bond lengths and angles in **2** and **3** are not very different, then this difference must be ascribed to the anions in the lattice, BPh$_4$$^-$ in **3** and BF$_4$$^-$ in **2**. We presume that crystal packing forces caused by the presence of the bulky BPh$_4$$^-$ ion as compared to the BF$_4$$^-$ ion are sufficient to cause the individual tetranuclear units to interact, and also to force more phenyl ring overlap within the individual tetranuclear species. It will require study of the influence of a range of anions to bear this out. A comparison of the arrangements of the various salen ligands looking approximately along the vanadium–oxygen chain is shown in Fig. 5.

These compounds are all indefinitely stable under dinitrogen in the solid state. However, we showed that [{V(salen)-O}$_2$][ClO$_4$] is substantially dissociated in solution to give [VO(salen)] and [VO(salen)]$^+$. The same may be true of two homologues described in the Experimental section, but we do not yet know. However, the EPR spectrum of [{V(salen)}$_4$-
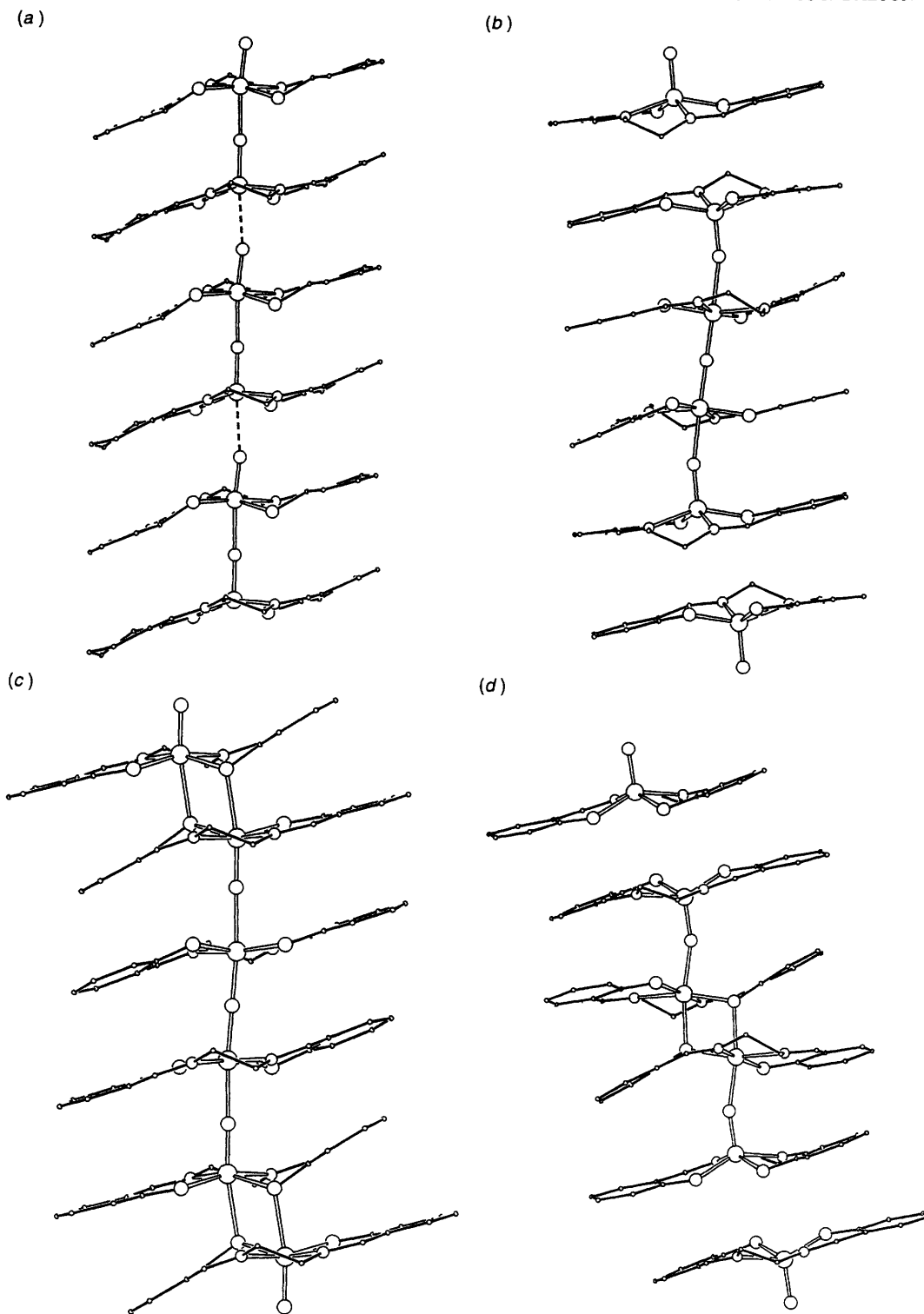
(a)   (b)

(c)   (d)

Fig. 3 The linear packing arrangements in [{V(salen)O}₂][I₅] **1** (a), [{V(salen)OV(salen)}₂O][BF₄]₂ **2** (b), [{V(salen)OV(salen)}₂O][BPh₄]₂ **3** (c) and [{[V(salen)]₂O}₂][I₃]₂ **4** (d)

O₃][BF₄]₂ dissolved in acetonitrile exhibits a signal characteristic of [VO(salen)] and of intensity corresponding to 2 equivalents. Addition of water caused this intensity to increase to correspond to ca. 4 equivalents. It is tempting to infer that the tetranuclear species dissociates to give [VO(salen)] and [{V(salen)}₂O]²⁺. Addition of [PPh₄]Br to the acetonitrile solution affords 3 equivalents of [VO(salen)] and 1 equivalent of [VBr₂(salen)].

We have attempted to prepare trifluoromethanesulfonate (triflate) salts analogous to the tetrafluoroborate salts by

treating [VO(salen)] with CF₃SO₃H in various ratios. We have isolated [{V(salen)}₄O₃][CF₃SO₃]₂ using a 2:1 ratio of [VO(salen)] to acid, but when higher acid ratios were used only small yields of the Vᵛ species [VO(salen)]CF₃SO₃ could be isolated even in the absence of O₂. However, we were able to prepare [V(salen)(CF₃SO₃)₂] by treatment of [VO(salen)] with CF₃SO₃SiMe₃ in CH₂Cl₂. This new compound has substantial conductivity in nitromethane (Λ_M 77 ohm⁻¹ cm² mol⁻¹), even higher than that of its iodide analogue (30.6 ohm⁻¹ cm² mol⁻¹).

Table 3 Final atomic coordinates ($\times 10^4$) for [{V(salen)OV(salen)}$_2$(μ-O)][BPh$_4$]$_2$·2MeCN **3** with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
The [{V(salen)OV(salen)}$_2$(μ-O)]$^{2+}$ cation							
V(1)	3821.0(4)	4681.6(4)	4688.7(3)	V(2)	1227.4(4)	4838.4(4)	4893.7(3)
O(1)	4596(2)	5160(1)	5462(1)	O(21)	1371(2)	5912(1)	4687(1)
C(2)	4186(2)	5805(2)	5703(2)	C(22)	1165(2)	6585(2)	4968(2)
C(3)	4220(3)	5830(3)	6327(2)	C(23)	946(3)	7295(2)	4620(2)
C(4)	3880(3)	6504(3)	6594(2)	C(24)	769(3)	8008(3)	4906(2)
C(5)	3520(3)	7168(3)	6239(2)	C(25)	817(3)	8037(3)	5526(3)
C(6)	3453(3)	7148(3)	5620(2)	C(26)	1031(3)	7346(3)	5875(2)
C(7)	3761(3)	6462(2)	5332(2)	C(27)	1209(3)	6600(2)	5602(2)
C(8)	3668(3)	6479(2)	4677(2)	C(28)	1537(3)	5917(2)	5986(2)
N(9)	3750(2)	5852(2)	4345(1)	N(29)	1701(2)	5202(2)	5793(1)
C(10)	3651(3)	5906(2)	3680(2)	C(30)	2085(3)	4561(2)	6232(2)
C(11)	3048(3)	5180(2)	3405(2)	C(31)	1498(3)	3810(2)	6026(2)
N(12)	3433(2)	4460(2)	3764(1)	N(32)	1449(2)	3741(2)	5367(1)
C(13)	3467(3)	3772(3)	3491(2)	C(33)	1580(3)	3039(2)	5137(2)
C(14)	3785(3)	3023(2)	3780(2)	C(34)	1500(3)	2871(2)	4500(2)
C(15)	3792(3)	2340(3)	3394(2)	C(35)	1662(3)	2076(3)	4317(2)
C(16)	4063(4)	1585(3)	3635(3)	C(36)	1516(3)	1868(3)	3716(2)
C(17)	4304(3)	1494(3)	4261(3)	C(37)	1185(3)	2444(3)	3271(2)
C(18)	4312(3)	2148(2)	4653(2)	C(38)	1025(3)	3237(3)	3433(2)
C(19)	4068(3)	2930(2)	4421(2)	C(39)	1171(3)	3458(2)	4047(2)
O(20)	4143(2)	3548(1)	4813(1)	O(40)	990(2)	4214(1)	4202(1)
O(2)	2727(2)	4709(1)	4858(1)	O(3)	0	5000	5000
The BPh$_4^-$ anion							
B(5)	7573(3)	4412(3)	1600(2)	C(71)	8030(3)	3482(2)	1647(2)
C(51)	7447(3)	4752(2)	892(2)	C(72)	8064(3)	3015(2)	2174(2)
C(52)	6584(3)	4660(2)	455(2)	C(73)	8508(3)	2255(2)	2255(2)
C(53)	6484(4)	4917(3)	−150(2)	C(74)	8923(3)	1923(3)	1801(2)
C(54)	7249(4)	5276(3)	−341(2)	C(75)	8886(3)	2343(3)	1273(2)
C(55)	8125(4)	5389(3)	79(2)	C(76)	8447(3)	3111(2)	1193(2)
C(56)	8211(3)	5130(3)	676(2)	C(81)	8371(3)	5008(2)	2060(2)
C(61)	6489(3)	4401(2)	1786(2)	C(82)	8288(3)	5854(2)	2040(2)
C(62)	6058(3)	5068(3)	2027(2)	C(83)	8941(4)	6373(3)	2408(2)
C(63)	5096(3)	5076(3)	2115(2)	C(84)	9743(3)	6067(3)	2804(2)
C(64)	4498(3)	4412(3)	1972(2)	C(85)	9862(3)	5239(3)	2847(2)
C(65)	4878(3)	3737(3)	1745(2)	C(86)	9192(3)	4732(2)	2484(2)
C(66)	5841(3)	3734(3)	1651(2)				
The MeCN solvent molecule							
N(90)	2162(6)	3047(5)	1749(5)	C(92)	832(6)	4170(5)	1473(4)
C(91)	1551(7)	3567(6)	1635(4)				
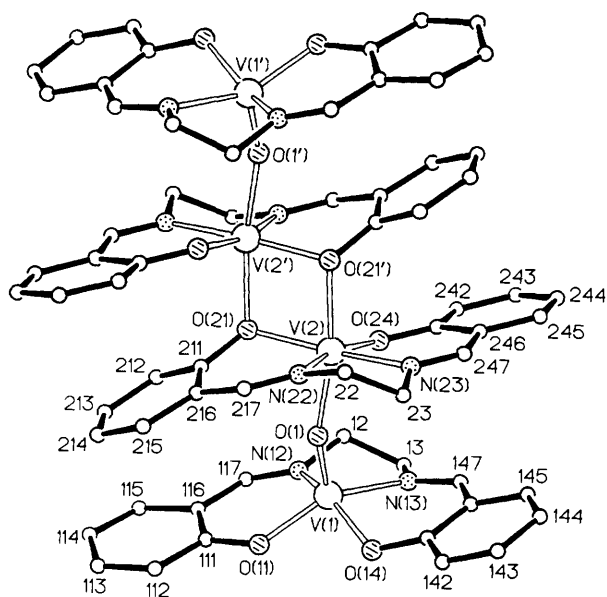
Fig. 4 Representation of the cation in the structure of [{[V-(salen)]$_2$O}$_2$][I$_3$]$_2$ **4**

We have also attempted, with some success, to prepare analogous polymeric derivatives using other Schiff bases, in particular H$_2$saldmtm, which has a 2,2-dimethylpropane-1,3-diyl backbone rather than a 1,2-ethanediyl backbone as in H$_2$salen. We were able to prepare [VO(saldmtm)], [V(saldmtm)(CF$_3$SO$_3$)$_2$], [{[V(saldmtm)]$_2$O}$_2$][I$_3$]$_2$ and [{V-(saldmtm)O}$_2$][I$_3$]. An ion similar to the last was prepared using the Schiff base H$_2$hnapen (2-HOC$_{10}$H$_6$CHNCH$_2$)$_2$. No tetranuclear or aqua species could be unequivocally identified.

Experimental

Compounds [VO(L)] (L = Schiff base) were prepared as described in the literature[3] or by us as described in refs. 7 and 9 or by the new method described for [VO(salen)] which involves extremely mild conditions but gives a methanol solvate. Other reagents and solvents were used as received from commercial suppliers. All manipulations were carried out under N$_2$.

Magnetic moments were generally measured at 20 °C by the Faraday method. The error is generally ±0.1 μ_B. The temperature dependence of the magnetic properties of [{V(salen)}$_4$O$_3$][BF$_4$]$_2$ was investigated by Professor L. Larkworthy, University of Surrey, using a Gouy balance. EPR spectra were obtained by Dr. D. J. Lowe as solids or solutions, as described, using a Bruker ER200D spectrometer. IR spectra were obtained as Nujol mulls or in dispersion in KBr, using Perkin-Elmer 883 and Digilab 324FT-IR spectrometers.
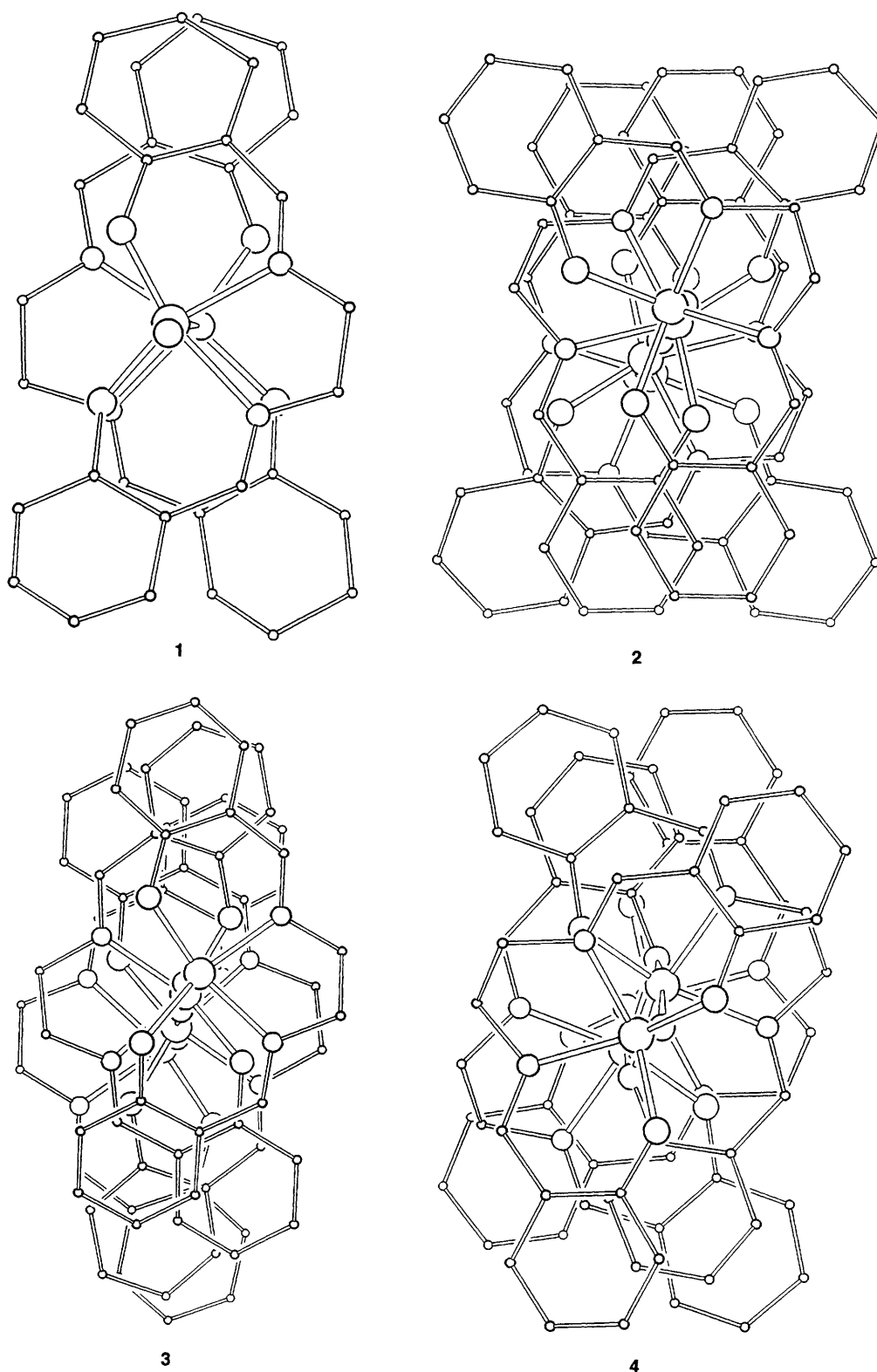
Fig. 5 Views of the cation species in 1–4 demonstrating the varied relative arrangements of the salen ligands

Solution conductivities were obtained with a Portland Electronics Ltd. conductivity bridge. Analyses were by Mr. C. J. Macdonald, NFL, using a Perkin-Elmer 2400 C,H,N analyser, or by Butterworth Analytical Laboratories Ltd.

Syntheses.—N,N'-*Ethylenebis(salicylideneiminato)oxo-vanadium*(IV)–*methanol* (1/1). Solutions of N,N'-bis(salicyl-idene)ethylenediamine (0.53 g, 2 mmol) in dichloromethane (10

cm^3) and oxobis(pentane-2,4-dionato)vanadium(IV) (0.53 g, 2 mmol) in dichloromethane (10 cm^3) were mixed and methanol (20 cm^3) added. Crystals slowly formed in the solution; after 15 h its volume was reduced to 20 cm^3 *in vacuo* and the green crystals filtered off and washed with methanol and diethyl ether, yield 0.59 g, 81% (Found: C, 55.3; H, 4.7; N, 7.7. $C_{17}H_{18}N_2O_4V$ requires C, 55.9; H, 4.9; N, 7.7%), μ_{eff} 1.75 μ_B. IR: 972 cm^{-1} [v(V=O)].

Aqua[N,N'-*ethylenebis(salicylideneiminato)*]*vanadium*(IV) *bis(tetrafluoroborate)*. To [VO(salen)] (7.3 g, 22 mmol) suspended in MeCN (80 cm³) was added HBF₄·Et₂O (7.5 g, 47 mmol). The mixture immediately turned black, and was stirred for 30 min. Then slow addition of Et₂O (100 cm³) produced dark blue crystals, which were filtered off, washed with Et₂O

Table 4 Selected dimensions in [{V(salen)OV(salen)}₂(μ-O)][BPh₄]₂·2MeCN **3**, bond lengths in Å, angles in ° with e.s.d.s in parentheses

(a) About the V atoms

V(1)–O(1)	1.994(2)	V(2)–O(21)	1.846(2)
V(1)–N(9)	2.068(3)	V(2)–N(29)	2.063(3)
V(1)–N(12)	2.051(3)	V(2)–N(32)	2.081(3)
V(1)–O(20)	1.926(2)	V(2)–O(40)	1.824(2)
V(1)–O(2)	1.627(2)	V(2)–O(2)	2.095(2)
V(1)–O(1″)	2.289(2)	V(2)–O(3)	1.775(1)
O(1)–V(1)–N(9)	85.9(1)	O(21)–V(2)–N(29)	86.2(1)
O(1)–V(1)–N(12)	157.1(1)	O(21)–V(2)–N(32)	160.7(1)
N(9)–V(1)–N(12)	79.1(1)	N(29)–V(2)–N(32)	77.1(1)
O(1)–V(1)–O(20)	101.0(1)	O(21)–V(2)–O(40)	109.9(1)
N(9)–V(1)–O(20)	161.5(1)	N(29)–V(2)–O(40)	161.6(1)
N(12)–V(1)–O(20)	88.7(1)	N(32)–V(2)–O(40)	85.4(1)
O(1)–V(1)–O(2)	98.6(1)	O(21)–V(2)–O(2)	86.1(1)
N(9)–V(1)–O(2)	94.7(1)	N(29)–V(2)–O(2)	86.8(1)
N(12)–V(1)–O(2)	99.8(1)	N(32)–V(2)–O(2)	83.5(1)
O(20)–V(1)–O(2)	101.1(1)	O(40)–V(2)–O(2)	85.5(1)
O(1)–V(1)–O(1″)	73.8(1)	O(21)–V(2)–O(3)	92.4(1)
N(9)–V(1)–O(1″)	79.4(1)	N(29)–V(2)–O(3)	87.2(1)
N(12)–V(1)–O(1″)	86.4(1)	N(32)–V(2)–O(3)	96.3(1)
O(20)–V(1)–O(1″)	86.1(1)	O(40)–V(2)–O(3)	100.5(1)
O(2)–V(1)–O(1″)	170.6(1)	O(2)–V(2)–O(3)	173.9(1)
V(1)–O(2)–V(2)	168.3(1)	V(2)–O(3)–V(2′)	180

(b) Torsion angles in the salen ligands

N(9)–C(10)–C(11)–N(12)	−45.3(4)
N(29)–C(30)–C(31)–N(32)	46.2(4)

and dried *in vacuo*, yield 10.4 g, 90% (Found: C, 37.6; H, 3.7; N, 5.8. C₁₆H₁₆B₂F₈N₂O₃V requires C, 37.7; H, 3.1; N, 5.5%). IR: 3300 [ν(OH)], 1050 (vbr) cm⁻¹ [ν(BF)], no band assignable to ν(V=O), μ_eff = 1.73 μ_B.

μ-*Oxo-bis*{[N,N'-*ethylenebis(salicylideneiminato)*]*vanadium*-(IV)} *bis(tetrafluoroborate)*. To [VO(salen)] (1.0 g, 3.0 mmol) in MeCN (30 cm³) was added HBF₄·Et₂O (0.05 g, 3.0 mmol). The black solution was stirred for 30 min, and careful addition of Et₂O (60 cm³) produced a black precipitate. After storage at −20 °C for 14 h, the product was filtered off, washed with Et₂O (10 cm³) and dried *in vacuo*, yield 0.86 g, 70% (Found: C, 45.8; H, 3.5; N, 7.4. C₃₂H₂₈B₂F₈N₄O₅V₂ requires C, 46.6; H, 3.4; N, 6.8%), μ_eff = 1.70 μ_B per V. IR: 1050 [ν(BF)] and 955 cm⁻¹ [ν(V=O)].

Bis(μ-*oxo*)*tris*{[N,N'-*ethylenebis(salicylideneiminato)*]-*vanadium*(IV)} *bis(tetrafluoroborate)-acetonitrile* (1/1). To [VO(salen)] (1.3 g, 4.0 mmol) dissolved in MeCN (40 cm³) was added HBF₄·Et₂O (0.67 g, 4.0 mmol). The black mixture was heated under reflux for 10 min, and cooled. After addition of Et₂O (60 cm³) and allowing to stand 14 h at −20 °C, a black

Table 5 Magnetic susceptibility* of [{V(salen)}₄O₃][BF₄]₂ **2** as a function of temperature

μ_eff/μ_B	10⁶ χ_A/ emu	T/K
1.53	990	294
1.46	1153	232
1.44	1290	200
1.41	1478	168
1.39	1764	136
1.36	1975	117
1.35	2197	104
1.33	2463	90

* A ligand susceptibility correction of −213 × 10⁶ emu was applied. μ_eff = 2.828 (χ_A T)^½.

Table 6 Final atomic coordinates (× 10⁴) for [{V(salen)OV(salen)}₂][I₃]₂·2MeCN, with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
The [{V(salen)OV(salen)}₂]²⁺ cation							
V(1)	4 718.9(7)	10 286.9(6)	3 369.9(5)	V(2)	5 568.3(7)	9 482.2(6)	1 215.0(5)
O(11)	4 238(3)	11 789(2)	3 492(2)	O(21)	4 292(3)	10 943(2)	165(2)
C(111)	3 135(5)	12 790(4)	2 971(3)	C(211)	4 141(5)	11 973(3)	314(3)
C(112)	3 183(6)	13 824(4)	2 949(4)	C(212)	2 897(6)	12 877(4)	114(3)
C(113)	2 061(7)	14 871(4)	2 440(4)	C(213)	2 744(7)	13 956(4)	185(4)
C(114)	868(6)	14 934(5)	1 942(5)	C(214)	3 818(8)	14 126(5)	430(4)
C(115)	795(5)	13 942(5)	1 979(4)	C(215)	5 043(7)	13 224(5)	664(4)
C(116)	1 926(5)	12 855(4)	2 477(3)	C(216)	5 247(5)	12 114(4)	638(3)
C(117)	1 795(5)	11 850(4)	2 469(3)	C(217)	6 582(5)	11 170(4)	957(3)
N(12)	2 757(3)	10 806(3)	2 789(3)	N(22)	6 891(3)	10 101(3)	1 234(3)
C(12)	2 485(5)	9 843(4)	2 687(4)	C(22)	8 274(5)	9 190(4)	1 567(4)
C(13)	3 409(5)	8 863(4)	3 632(4)	C(23)	8 469(5)	8 244(4)	2 436(4)
N(13)	4 701(4)	8 792(3)	3 871(3)	N(23)	7 349(3)	8 032(3)	2 109(3)
C(147)	5 758(5)	7 804(4)	4 330(3)	C(247)	7 547(4)	7 005(4)	2 387(3)
C(146)	7 061(5)	7 654(3)	4 710(3)	C(246)	6 549(5)	6 670(4)	2 220(3)
C(145)	8 149(6)	6 521(4)	5 051(4)	C(245)	6 941(6)	5 483(4)	2 528(4)
C(144)	9 398(6)	6 331(5)	5 456(4)	C(244)	6 014(8)	5 139(5)	2 438(5)
C(143)	9 606(5)	7 250(5)	5 578(4)	C(243)	4 689(7)	5 948(5)	2 053(4)
C(142)	8 571(5)	8 352(4)	5 277(4)	C(242)	4 279(5)	7 101(4)	1 750(4)
C(141)	7 277(4)	8 578(4)	4 826(3)	C(241)	5 190(5)	7 493(3)	1 806(3)
O(14)	6 296(3)	9 678(2)	4 535(2)	O(24)	4 758(3)	8 615(2)	1 509(2)
O(1)	5 203(3)	10 151(2)	2 376(2)				
The triiodide anions							
I(1)	0	0	0	I(3)	5 000	5 000	5 000
I(2)	−771.6(4)	2 405.0(3)	−106.1(3)	I(4)	7 790.8(5)	3 363.0(5)	5 606.9(4)
The acetonitrile molecule							
N(3)	9 204(11)	1 012(14)	3 083(10)	C(31)	7 161(9)	1 609(8)	3 562(6)
C(3)	8 342(10)	1 237(9)	3 327(7)				

solid was filtered off, washed with MeCN and Et$_2$O, and dried *in vacuo*, yield 0.40 g, 25% (Found: C, 49.5; H, 3.8; N, 8.0. C$_{50}$H$_{45}$B$_2$F$_8$N$_7$O$_8$V$_3$ requires C, 50.0; H, 3.8; N, 8.2%), μ$_{eff}$ = 1.7 μ$_B$ per V. IR: 1050 [v(BF)] and 950 cm^{-1} [v(V=O)].

Tris(μ-oxo)tetrakis{[N,N'-ethylenebis(salicylideneiminato)]-vanadium(IV)} bis(tetrafluoroborate)-acetonitrile (1/2), **2**. To [VO(salen)] (1.7 g, 5.0 mmol) in MeCN (70 cm^3) was added HBF$_4$·Et$_2$O (0.42 g, 2.5 mmol). The black mixture was heated to reflux, filtered hot and then cooled. Black crystals deposited overnight. These were filtered off, washed with MeCN and Et$_2$O, and dried *in vacuo*, yield 1.0 g, 50% (Found: C, 52.4; H, 4.0; N, 8.5. C$_{68}$H$_{62}$B$_2$F$_8$N$_{10}$O$_{11}$V$_4$ requires C, 51.9; H, 4.0; N, 8.9%), μ$_{eff}$ = 1.53 μ$_B$ per V. IR: 1050 [v(BF)] and 945, 910 cm^{-1} [v(V=O)], Λ$_M$ 120 ohm^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3}, MeNO$_2$). Alternatively,

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Table 7 Selected dimensions in [{V(salen)OV(salen)}$_2$][I$_3$]$_2$·2MeCN **4**, bond lengths in Å, angles in ° with e.s.d.s in parentheses

(a) About the V atoms

V(1)–O(11)	1.883(3)	V(2)–O(21)	1.949(3)
V(1)–N(12)	2.041(3)	V(2)–N(22)	2.090(3)
V(1)–N(13)	2.044(3)	V(2)–N(23)	2.069(4)
V(1)–O(14)	1.910(3)	V(2)–O(24)	1.882(3)
V(1)–O(1)	1.635(3)	V(2)–O(1)	2.006(3)
		V(2)–O(21')	2.106(3)
O(11)–V(1)–N(12)	87.9(1)	O(21)–V(2)–N(22)	84.5(1)
O(11)–V(1)–N(13)	145.6(1)	O(21)–V(2)–N(23)	160.2(1)
N(12)–V(1)–N(13)	78.1(1)	N(22)–V(2)–N(23)	78.3(1)
O(11)–V(1)–O(14)	90.0(1)	O(21)–V(2)–O(24)	110.7(1)
N(12)–V(1)–O(14)	149.4(1)	N(22)–V(2)–O(24)	164.6(1)
N(13)–V(1)–O(14)	86.7(1)	N(23)–V(2)–O(24)	87.0(1)
O(11)–V(1)–O(1)	108.7(1)	O(1)–V(2)–O(21)	93.0(1)
N(12)–V(1)–O(1)	104.3(1)	O(1)–V(2)–N(22)	88.6(1)
N(13)–V(1)–O(1)	105.2(1)	O(1)–V(2)–N(23)	96.3(1)
O(14)–V(1)–O(1)	105.3(1)	O(1)–V(2)–O(24)	88.2(1)
		O(1)–V(2)–O(21')	170.4(1)
V(1)–O(1)–V(2)	156.0(2)	O(21)–V(2)–O(21')	77.4(1)
		N(22)–V(2)–O(21')	90.7(1)
		N(23)–V(2)–O(21')	92.9(1)
		O(24)–V(2)–O(21')	95.0(1)

(b) Torsion angles in the salen ligands

N(12)–C(12)–C(13)–N(13)	−41.8(5)
N(22)–C(22)–C(23)–N(23)	45.8(5)

(c) In the anions

I(1)–I(2)	2.9104(3)	I(3)–I(4)	2.902(1)

[VO(salen)] (2.1 g, 6.3 mmol) in MeCN (40 cm^3) was heated under reflux with Ph$_3$CBF$_4$ (1.1 g, 3.3 mmol) for 10 min. Black crystals formed after addition of Et$_2$O (60 cm^3) to the cooled solution. These were recrystallised from MeCN, yield 0.9 g, 40%.

Tris(μ-oxo)tetrakis{[N,N'-1,1-dimethylethylenebis(salicyl-ideneiminato)]vanadium(IV)} bis(tetrafluoroborate). To [VO-(salibn)] (1.47 g, 4.1 mmol) in acetonitrile (20 °C) at 50 °C was added HBF$_4$·Et$_2$O (0.33 g, 2.0 mmol) dissolved in acetonitrile (10 cm^3). The resulting black mixture was stirred for 30 min, cooled and Et$_2$O (3 × 3 cm^3) added to give a black precipitate, which was filtered off, washed with Et$_2$O, and dried *in vacuo*, yield 0.9 g, 28% (Found: C, 53.1; H, 4.5; N, 6.8. C$_{72}$H$_{72}$B$_2$F$_8$N$_8$O$_{11}$V$_4$ requires C, 54.0; H, 4.5; N, 7.0%), μ$_{eff}$ = 1.67 μ$_B$ per V. IR: 1050 [v(BF)] and 955 cm^{-1} [v(V=O)].

Tris(μ-oxo)tetrakis{[N,N'-ethylenebis(salicylideneiminato)]-vanadium(IV)} bis(tetraphenylborate)-acetonitrile (1/2), **3**. To [VCl$_2$(salen)] (0.86 g, 2.2 mmol) suspended in MeCN (20 cm^3) was added AgBPh$_4$ (1.9 g, 4.4 mmol). The mixture was stirred at 20 °C for 45 min, and the grey precipitate filtered off. Addition of Et$_2$O (20 cm^3) to the green solution produced after 6 d at −20 °C shiny black crystals, which were filtered off, washed with small quantities of MeCN and Et$_2$O and dried *in vacuo*, yield 40 mg, 0.3% (Found: C, 66.4; H, 4.7; N, 6.0. C$_{116}$H$_{102}$B$_2$N$_{10}$O$_{11}$V$_4$ requires C, 68.4; H, 5.0; N, 6.9%), μ$_{eff}$ = 1.56 μ$_B$ per V. IR: 916 cm^{-1} [v(V=O)].

Tris(μ-oxo)tetrakis{[N,N'-ethylenebis(salicylideneiminato)]-vanadium(IV)} bis(trifluoromethanesulfonate). To [VO(salen)] (2.0 g, 6.0 mmol) dissolved in MeCN (60 cm^3) was added CF$_3$SO$_3$H (0.45 g, 3.0 mmol). The black mixture was heated under reflux for 10 min, filtered hot, and allowed to cool at −20 °C for 5 d. Black crystals were filtered off, washed with MeCN and Et$_2$O, and dried *in vacuo*, yield 1.9 g, 78% (Found: C, 49.1; H, 3.5; N, 7.0. C$_{66}$H$_{56}$F$_6$N$_8$O$_{17}$S$_2$V$_4$ requires C, 49.1; H, 3.5; N, 6.9%), μ$_{eff}$ = 1.56 μ$_B$ per V, Λ$_M$ = 99 ohm^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3}, MeNO$_2$). IR: 970 cm^{-1} [v(V=O)].

N,N'-Ethylenebis(salicylideneiminato)bis(trifluoromethane-sulfonato)vanadium(IV). This was prepared in a way similar to that used for the diiodo analogue from [VO(salen)] (0.56 g, 1.6 mmol) and Me$_3$SiOSO$_2$CF$_3$ (0.8 cm^3, 0.92 g, 4 mmol) in dichloromethane (40 cm^3). After 1 h dark blue crystals were filtered off, washed with CH$_2$Cl$_2$ and hexane and dried *in vacuo*, yield 0.96 g, 93% (Found: C, 35.2; H, 2.2; N, 4.0. C$_{18}$H$_{14}$F$_6$N$_2$O$_8$S$_2$V requires C, 35.1; H, 2.3; N, 4.6%), μ$_{eff}$ = 1.90 μ$_B$ per V, Λ$_M$ = 77 ohm^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3}, MeNO$_2$). IR: no band assignable to v(V=O).

Table 8 Comparison of molecular dimensions (lengths in Å, angles in °) and properties of [{V(salen)O}$_2$][I$_5$] **1**, [{V(salen)}$_4$O$_3$][BF$_4$]$_2$ **2**, [{V(salen)}$_4$O$_3$][BPh$_4$]$_2$ **3** and [{[V(salen)]$_2$O}$_2$][I$_3$]$_2$ **4**. The atom numbering scheme relates to that of complex **2**, Fig. 1, but is applied to all the structures

Complex	1	2	3	4
V(1)–O(1)	1.67(5)	1.625(2)	1.627(2)	1.635(3)
O(1)–V(2)	2.06(5)	2.059(2)	2.095(2)	2.006(3)
V(2)–O(2)	1.58(3)	1.763(1)	1.775(1)	2.106(3)^a
V(1)–O″	2.41(4)^b	—	2.289(2)^c	—
V(1)···V(1″)	—	—	3.430(1)	—
V(2)···V(2′)	—	—	—	3.167(1)
V(1)–O(1)–V(2)	162(3)	162.2(1)	168.3(1)	156.0(2)
O(1)–V(2)–O(2)	166(2)	175.6(1)	173.9(1)	170.4(1)^a
V(2)–O(2)–V(2′)	165(2)^d	180	180	—
O(1)–V(1)–O″	173(2)^b	—	170.6(1)^c	—
Distance of V atom from salen N$_2$O$_2$ mean plane				
V(1)	0.39(2)	0.544(2)	0.304(1)	0.539(2)
V(2)	0.16(6)	0.141(1)	0.150(1)	0.051(2)
v(V=O)/cm^{-1} (solid state)	870	945, 910	916	970
μ$_{eff}$/μ$_B$ per V (solid state)	0.8 (295 K)	1.53 (294 K)	1.56 (300 K)	2.4 (295 K)
EPR, *g* values (solid state)		1.98 (vbr, singlet)	1.98 (narrower singlet)	

^{a} O(2) is of a salen ligand, *viz.* O(21') in Fig. 4. ^{b} O″ is O(2) of the molecule below [see Fig. 3(*a*)]. ^{c} O″ is of a salen ligand in the molecule below, *viz.* O(1″) in Fig. 2. ^{d} V(2′) is V(1) of the next molecule up [see Fig. 3(*a*)].

Table 9 Crystallographic details for compounds 2–4

Complex	2	3	4
Crystal data			
Elemental formula	$C_{64}H_{56}B_2F_8N_8O_{11}V_4 \cdot 2C_2H_3N$	$C_{112}H_{96}B_2N_8O_{11}V_4 \cdot 2C_2H_3N$	$C_{64}H_{56}I_6N_8O_{10}V_4 \cdot 2C_2H_3N$
M	1572.7	2037.5	2144.5
Crystal system	Triclinic	Monoclinic	Triclinic
Space group (no.)	$P\bar{1}$ (no. 2)	$P2_1/n$ (equiv. to no. 14)	$P\bar{1}$ (no. 2)
$a/\text{Å}$	10.511(1)	13.783(1)	12.035(1)
$b/\text{Å}$	13.349(1)	16.459(1)	13.421(1)
$c/\text{Å}$	14.831(1)	22.232(3)	13.947(1)
$\alpha/°$	70.489(9)	90	82.183(5)
$\beta/°$	109.413(7)	101.638(8)	104.427(6)
$\gamma/°$	79.442(7)	90	63.941(6)
$U/\text{Å}^3$	1745.7(3)	4939.7(8)	1880.3(3)
Z	1	2	1
$D_c/\text{g cm}^{-3}$	1.496	1.370	1.894
$F(000)$	802	2116	1030
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	5.9	4.2	29.6
Experimental details			
Crystal colour, shape	Very dark, thick needles	Very dark, truncated square pyramids	Black, long fine needles
Crystal size (mm)	ca. 0.20 × 0.25 × 0.40	0.17 × 0.21 × 0.26	0.12 × 0.21 × 0.16
On diffractometer:			
θ range of centred reflections	10–11	10–12	10–11
θ_{max} for intensities (°)	25	23	25
no. unique reflections	6138	8683	6613
no. observed reflections (with $I > 2\sigma_I$)	5047	5637	5388
In processing data, corrections for:			
Lorentz-polarisation	Yes	Yes	Yes
deterioration (overall)	Yes (9.7%)	Yes (14%)	Yes (0.4%)
absorption	Yes	Yes	Yes
negative intensities	Yes	Yes	No
Structure determination	Direct methods (SHELXS/TREF in $P1$)	Heavy-atom method (SHELX)	Automated Patterson methods (SHELXS/ATT)
Refinement:			
Final R	0.053	0.071	0.049
R_w^{10}	0.053	0.063	0.047
R_g^{10}	0.050	0.066	0.050
no. reflections	6138	7343 (with $I > \sigma_I$)	6613
weighting scheme, w	1 (unit weights)	$(\sigma_F^2 + 0.000\ 43\ F^2)^{-1}$	σ_F^{-2}
Difference map peaks:			
height (e Å^{-3})	ca. 0.6	ca. 0.9	ca. 2.0; ca. 1.0
location	In anion region	Close to V–O chain bond	Near I_3^-; near V

N,N'-2,2-*Dimethyltrimethylenebis(salicylideneiminato)bis(trifluoromethanesulfonato)vanadium*(IV). This was similarly made from [VO(saldmtm)] (0.9 g, 2.4 mmol) and $Me_3SiOSO_2CF_3$ (1.2 cm^3, 6 mmol) in dichloromethane (60 cm^3) as dark blue crystals, yield 1.09 g, 69% (Found: C, 38.1; H, 3.0; N, 4.1. $C_{21}H_{20}F_6N_2O_8S_2V$ requires C, 38.4; H, 3.0; N, 4.3%), μ_{eff} = 1.80 μ_B per V, Λ_M = 92 ohm^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3}, $MeNO_2$). IR: no band assignable to $\nu(V=O)$.

$Bis(\mu\text{-}oxo\text{-}bis\{[N,N'\text{-}ethylenebis(salicylideneaminato)]\text{-}vanadium\})\ bis(triiodide)$, 4. Gaseous HI [generated from I_2 (1.9 g, 7.5 mmol) and boiling tetralin (70 cm^3)] was bubbled through a green suspension of [VO(salen)] (2.0 g, 6.0 mmol) in MeCN (50 cm^3). The suspension gradually turned black, and iodine was observed to accumulate in a guard wash bottle placed after the reaction vessel. After all the iodine to generate HI had been added, N_2 was swept through the system for 1 h. The mixture was heated to reflux for 20 min, and then filtered hot. The filtrate at 20 °C for 5 d produced large shiny black crystals, which were filtered off, washed with Et_2O and dried in vacuo, yield 2.3 g, 75% (Found: C, 36.7; H, 2.7; I, 36.2; N, 5.8. $C_{64}H_{56}I_6N_8O_{10}V_4$ requires C, 37.3; H, 2.7; I, 36.9; N, 5.4%), μ_{eff} = 2.42 μ_B per V, Λ_N(acetonitrile) = 342 ohm^{-1} cm^2 mol^{-1}. IR: 970 cm^{-1} [$\nu(V=O)$].

$Bis[\mu\text{-}oxo\text{-}bis\{[N,N'\text{-}2,2\text{-}dimethyltrimethylenebis(salicylideneiminato)]vanadium\}\ bis(triiodide)$. Gaseous HI (ca. 11 mmol) [generated from I_2 (1.4 g, 5.5 mmol) and boiling tetralin] was passed into a solution of [VO(saldmtm)] (1.9 g, 5.0 mmol)

during ca. 20 min. A brown material crystallised, which was filtered off, washed with MeCN and Et_2O, and dried in vacuo, yield 1.25 g, 45% (Found: C, 40.3; H, 3.7; N, 4.7. $C_{76}H_{80}I_6N_8O_{10}V_4$ requires C, 40.9; H, 3.6; N, 5.0%), μ_{eff} = 2.36 μ_B. IR: 905 cm^{-1} [$\nu(V=O)$].

$Bis\{N,N'\text{-}2,2\text{-}dimethyltrimethylenebis(salicylideneiminato)\}\text{-}oxovanadium\}$ triiodide. A solution of [VO(saldmtm)] (3.7 g, 10.0 mmol) in MeCN (200 cm^3) was placed in the bottom of a Soxhlet extractor and I_2 (2.0 g, 8.0 mmol) extracted into it during 45 min. Upon cooling the pot to room temperature, crystallisation commenced. After 1 d at -20 °C, the product was filtered off, washed with MeCN (40 cm^3) and Et_2O (25 cm^3) and dried in vacuo, yield 2.3 g, 41% (Found: C, 40.5; H, 2.8; N, 4.6. $C_{38}H_{40}I_3N_4O_6V_2$ requires C, 40.3; H, 3.6; N, 5.0%), μ_{eff} = 1.0 ± 0.1 μ_B per V. IR: 890 cm^{-1} [$\nu(V=O)$].

$Bis\{[N,N'\text{-}2,2\text{-}dimethyltrimethylenebis(salicylideneiminato)]\text{-}oxovanadium\}$ pentaiodide. Recrystallisation of the triiodide (0.92 g, 2.5 mmol) from acetonitrile (50 cm^3) in the presence of I_2 (0.20 g, 0.78 mmol) yielded the pentaiodide, also obtainable by direct reaction of [VO(saldmtm)] and I_2.

$Bis\{[N,N'\text{-}bis(2\text{-}hydroxynaphthylmethylene)ethylenediaminato]oxovanadium\}$ triiodide. This was prepared similarly to the saldmtm triiodide described above, using [VO(hnapen)] (2.65 g, 6.1 mmol) and I_2 (2.0 g, 7.9 mmol) in MeCN (200 cm^3), yield ca. 50% (Found: C, 44.2; H, 2.5; N, 4.0. $C_{48}H_{36}I_3N_4O_6V_2$ requires C, 46.2; H, 2.9; N, 4.5%), μ_{eff} = 0.9 μ_B per V. IR: 852 cm^{-1} [$\nu(V=O)$].

Crystal Structure Analyses of Complexes **2–4**.—Crystal data and experimental details of the three samples are in Table 9. Crystals of each sample were mounted on glass fibres and photographed before transferring to our Enraf-Nonius CAD4 diffractometer [with monochromated radiation, λ(Mo-Kα) = 0.710 69 Å] for determination of accurate cell parameters (by refinement from the settings of 25 reflections, each centred in four orientations) and for measurement of diffraction intensities (by the ω–θ scan method).

During processing, the intensities were corrected as indicated in Table 9; the absorption corrections were by semi-empirical ψ-scan methods, and Bayesian statistical methods were used to remove negative net intensities. The structures were determined by a variety of methods in the SHELX system,[10,11] and refinement was by least-squares methods with final R factors[10] as shown in Table 9. Hydrogen atoms were included in idealised positions in the salen ligands in each structure and in the anion of **3**. In the MeCN solvent molecule of **4** the three hydrogen atoms were refined with geometrical constraints; these atoms were not included in **2** and **3**. The thermal parameters of all the hydrogen atoms were refined independently. All the non-hydrogen atoms in **3** and **4**, and all those of the cation of **2**, were allowed anisotropic thermal parameters. In **2** the anion is disordered in several orientations about a common boron atom, and the acetonitrile solvent molecule is disordered in two orientations sharing a common centre carbon atom position. In the final difference maps there were residual peaks of significance in each structure, but none suggesting additional moieties in the lattice.

Scattering factor curves for neutral atoms, in each analysis, were taken from ref. 12. Computer programs used in the analyses have been noted above and in Table 4 of ref. 13, and were run on a DEC MicroVAX II computer in this Laboratory.

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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