Crystal and Molecular Structure of the Compound [(salen)VOVO(salen)][I_5]·MeCN [salen = *N,N'*-ethylenebis(salicylideneiminate)]† and the Preparation of Similar Complexes with Other Schiff-base Ligands

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The oxidation of [VO(salen)] [salen = *N,N'*-ethylenebis(salicylideneiminate)] with iodine produces a mixed vanadium(IV)–vanadium(V) species containing [(salen)VOVO(salen)]$^+$ and the counter ion I_5^-, as determined by X-ray crystal-structure analysis. The oxidation of related vanadyl Schiff-base complexes produces similar species. Magnetic and spectroscopic properties of these new complexes are described.

We recently described the reaction of [VO(salen)] [salen = *N,N'*-ethylenebis(salicylideneiminate) dianion] with iodine.[1] This was an attempt to prepare the unknown [VI_2(salen)], in which we planned to replace the iodide ligands by hydrazine or substituted hydrazine groups. Instead of this product we obtained black crystals containing varying quantities of iodine; after recrystallisation from acetonitrile we obtained crystals which analysed for [{VO(salen)}$_2$]I_5·MeCN. The present report describes the molecular structure of these crystals as determined by X-ray diffraction, and the results of our attempts to prepare other salts of the [{VO(salen)}$_2$]$^+$ cation and similar complexes using [VO(salpn)] and [VO(salphen)] as starting materials in place of [VO(salen)] [salpn = *N,N'*-trimethylenebis(salicylideneiminate) dianion; salphen = *N,N'-o*-phenylenebis(salicylideneiminate) dianion]. We also describe magnetic and spectroscopic measurements on these complexes.

Results and Discussion

Structure of [{VO(salen)}$_2$][I_5]·MeCN.—The preparation of a complex of stoichiometry [{VO(salen)}$_2$][I_5]·MeCN, with a magnetic moment of 1.6 ± 0.2 μ_B and a band in the IR spectrum assignable to ν(V=O) at 880 cm^{-1}, has been described,[1] along with its use as a source of nitrogen-ligand complexes of vanadium.

X-Ray diffraction studies showed that it is composed of discrete [(salen)V^{IV}–O–V^{V}O(salen)]$^+$ cations, I_5^- anions, and disordered solvent, MeCN, molecules (Fig. 1). Atomic coordinates are given in Table 1, and selected molecular dimensions in Table 2.

The cations are stacked parallel to the *b* axis of the crystal. There are four distinct V–O distances, and V ··· V distances of 3.682(14) and 3.962(14) Å alternate along the column. Each V atom is surrounded 'equatorially' by the four co-ordinating atoms of a salen ligand, and has an oxo O atom each side of this plane. The arrangement about V(1) is distorted octahedral, with the metal atom lying only 0.16 Å from the mean plane of the salen O and N atoms; the apical vanadyl O atoms are 1.58(3) and 2.06(5) Å from V(1). Atom V(2), however, lies 0.39 Å from its salen co-ordinating plane, and O(62) is 1.67(5) Å beyond the V atom which thus has a typical square-pyramidal co-ordination pattern; the O atom in the sixth site of the 'octahedron' is 2.41(4) Å from V(2) and, we suggest, is not formally bonding. The cations are, thus, discrete bimetallic complex units with the form: [V^{IV}(salen)=O→V^{V}(salen)=O]. This is, we believe, the first example of an oxo-bridged mixed vanadyl(IV)–vanadyl(V) complex in which the two V atoms are distinct. In most bimetallic vanadium complexes previously recorded, whether V^{III}–V^{III}, V^{IV}–V^{IV}, V^{IV}–V^{V} or V^{V}–V^{V}, there is little difference, if any, in the V–O bond lengths and in the co-ordination pattern about each metal. The V^{IV}=O separations are 1.67(5) Å, slightly longer than for isolated V^{IV}=O systems {*cf.* 1.59 Å in [V^{IV}O(salen)] itself},[2] but comparable to the value reported for [{VO(salpn)}$_n$] in which each V^{IV}=O system is a ligand upon the next in a polymeric chain.[3] The free, presumably V^{V}=O, unit has a separation of 1.58(3) Å which is quite reasonable and comparable to that in [VO(salen)]$^+$.[4,5] It is difficult to find comparable structures to assess the other axial separations. Thus, 2.06(5) Å for O→V^{V} is of the order observed for H_2O→V^{IV} in [$VO(H_2O)_4(SO_4)$]·H_2O, *ca.* 2.04 and 2.223(5) Å,[6] but the 2.41(4) Å that we observe for O ··· V^{IV} between cations is considerably longer, even than the distance 2.310(5) Å in [VO(salen)(H_2O)]$^+$,[4] and we suggest that this O ··· V represents a non-bonding distance; a similar arrangement is found in [VO(salen)]ClO_4 where one of the perchlorate O atoms 'associates' with the cation, V ··· O 2.456(3) Å.[5]

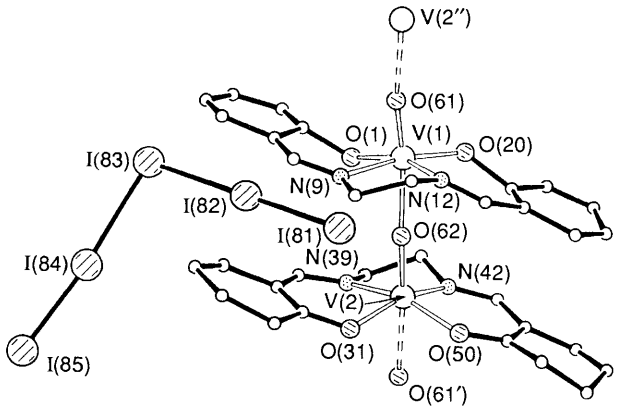

Fig. 1 View of the cation and anion in [(salen)VOVO(salen)][I_5]·MeCN

† Bis[*N,N*-ethylenebis(salicylideneiminato)]-1κ^4*N,N',O,O'*; 2κ^4*N''*,*N''',O''O'''*-μ-oxo-oxo-1κ*O*-divanadium pentaiodide–acetonitrile (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Final atomic coordinates (fractional × 10^4) for [(salen)VOVO(salen)][I_5]·MeCN with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
The cation							
V(1)	9 011(5)	6 600(12)	4 922(6)	V(2)	8 998(5)	1 785(14)	5 105(5)
O(61)	8 948(14)	8 671(43)	4 899(27)	O(62)	8 990(21)	3 971(65)	5 167(23)
O(1)	8 523(15)	6 034(61)	4 341(22)	O(31)	8 496(13)	1 233(52)	5 770(18)
C(2)	8 060(22)	7 032(95)	4 261(28)	C(32)	8 046(19)	1 802(78)	5 736(24)
C(3)	7 866(21)	7 095(89)	3 640(27)	C(33)	7 780(23)	1 929(97)	6 309(30)
C(4)	7 403(25)	7 560(98)	3 586(33)	C(34)	7 287(27)	2 979(114)	6 352(37)
C(5)	7 148(22)	7 826(88)	4 068(27)	C(35)	7 034(20)	3 369(78)	5 706(25)
C(6)	7 297(22)	7 859(90)	4 694(29)	C(36)	7 301(21)	2 944(86)	5 205(29)
C(7)	7 795(22)	7 201(85)	4 834(27)	C(37)	7 813(26)	2 119(104)	5 123(32)
C(8)	7 975(20)	7 066(83)	5 474(26)	C(38)	8 013(20)	1 937(80)	4 505(26)
N(9)	8 418(18)	6 589(68)	5 628(23)	N(39)	8 472(16)	1 592(63)	4 409(22)
C(10)	8 557(22)	6 528(95)	6 276(29)	C(40)	8 649(20)	1 189(79)	3 710(25)
C(11)	9 090(19)	7 175(87)	6 386(26)	C(41)	9 177(21)	1 859(95)	3 716(27)
N(12)	9 372(16)	6 695(64)	5 837(21)	N(42)	9 430(14)	1 360(53)	4 292(19)
C(13)	9 792(27)	5 901(108)	5 866(37)	C(43)	9 894(23)	814(96)	4 204(32)
C(14)	10 157(28)	5 269(112)	5 414(35)	C(44)	10 152(20)	371(73)	4 799(26)
C(15)	10 643(23)	4 520(90)	5 649(33)	C(45)	10 635(18)	−538(68)	4 686(25)
C(16)	10 938(27)	4 011(87)	5 067(30)	C(46)	10 933(26)	−785(84)	5 197(31)
C(17)	10 822(25)	4 263(98)	4 379(34)	C(47)	10 741(30)	−898(124)	5 889(42)
C(18)	10 372(19)	4 912(78)	4 234(26)	C(48)	10 307(29)	261(116)	5 970(39)
C(19)	10 041(24)	5 331(106)	4 756(34)	C(49)	9 983(17)	501(74)	5 435(23)
O(20)	9 601(16)	6 435(60)	4 536(20)	O(50)	9 530(13)	969(49)	5 639(17)
The anion							
I(81)	8 407(2)	7 205(10)	8 210(3)	I(84)	6 010(2)	4 885(7)	7 219(2)
I(82)	7 521(2)	7 667(7)	7 492(3)	I(85)	5 400(3)	2 218(10)	7 656(3)
I(83)	6 608(2)	8 074(9)	6 671(3)				
Disordered MeCN solvent molecule							
C(71)	4 985(51)	6 805(171)	2 352(58)	C(73)	5 641(23)	8 148(89)	2 368(29)
C(72)	5 323(23)	6 893(88)	2 323(28)	C(74)	6 011(39)	8 168(132)	2 212(47)

Atoms C(71) and C(74) have site occupancies of 0.5.

In five-co-ordinate species of the type [VO(ligand)] the vanadium atom is generally displaced out of the plane of the four donor atoms of the ligand towards the axial oxygen, by as much as 0.6 Å.[7] This is observed similarly in our vanadium(IV) moiety (see above).

The V–O(salen) bonds in vanadium(IV) complexes are normally *ca.* 0.1 Å longer than those in vanadium(V) complexes, *viz.* 1.92 and 1.81 Å respectively. Our values are not far removed from these dimensions and confirm our formulation of the dimeric cation. It has been noted that V–N(salen) distances are little affected by the vanadium oxidation state; in our cation, however, we find that the V–N distances about V(2) are rather shorter than those about the 'harder' V(1).

The dimensions in the salen ligands are not very precise, but none varies greatly from expected values. The pair of ligands have an approximately parallel, stepped-ring conformation. It is the stacking of some of the phenyl groups of these ligands that controls the packing of the cations in columns. The normals to the ring planes of C(14)–C(19) and C(44)–C(49) are virtually parallel, and the overlapping rings are *ca.* 3.46 and 3.51 Å apart, within and between cations respectively. The rings of C(2)–C(7) and C(32)–C(37) are not quite overlapping and the normals to these planes are 10(2)° apart; there are several atom–atom contacts at normal van der Waals distances between these planes, but the phenyl rings cannot be described as 'stacked'. This alignment of ligands brings O(61) into an apical pseudo-octahedral site of V(2) of an adjacent cation, but, as noted above, at the non-bonding V · · · O distance of 2.41(4) Å.

The I_5^- anions in our crystals are V-shaped, having two almost linear I_3 moieties at an angle of 98.2(2)° and with a common apical I atom. The four I–I bonds are all different, with the outer pairs much shorter than those about I(83); it appears that two I_2 molecules are bound to a central I^- ion, but the bond lengths suggest unequal delocalisation of electrons in the two arms. Several I_5^- ions with similar I–I bond differences have been observed. Often this anion has short contacts with other iodine moieties to form planar networks, or with other iodine or sulphur groups to link into organic molecules. The angle at the central I atom shows a range of values, from 85.5 to 100.2°, presumably depending on the interactions with other groups. The only short contacts our anion has are with the methylene and phenyl C–H groups of neighbouring salen ligands; the shortest I · · · C and I · · · H distances are 3.62(7) and 2.94 Å.

The dimensions of our I_5^- anion accord with those reported for [NMe_4][I_5][8] and elsewhere.[9]

Preparation of Similar Complexes.—In attempts to prepare analogues of [{VO(salen)}$_2$][I_5] using other Schiff bases, [VO(salpn)] and [VO(salphen)] were treated with I_2 in acetonitrile, yielding the similar salts [{VO(salpn)}$_2$][I_5] and [{VO(salphen)}$_2$][I_3]. These were characterised by analysis and by their magnetic moments (one unpaired electron per two vanadium atoms) and IR spectra, ν(V=O) at 870 cm^{-1} as for [{VO(salen)}$_2$][I_5].

It was desirable also to prepare salts of [{VO(salen)}$_2$]$^+$ using anions other than I_5^-. Treatment of [VO(salen)] with $HClO_4$ or HPF_6 in acetonitrile in air yielded [VO(salen)]X (X = ClO_4 or PF_6)[5] and mixing those isolated vanadium(V) salts with [VO(salen)] yielded the binuclear complexes [{VO(salen)}$_2$]$^+X^-$, which again had ν(V=O) at 870 cm^{-1} and one unpaired electron per two vanadium atoms. These preparations were useful insofar as the 'parent' mononuclear cations were available for spectroscopic purposes (see later).

An attempt was also made to prepare [{VO(salen)}$_2$]BF_4 by

Table 2 Selected molecular dimensions (bond lengths in Å, angles in °) in [(salen)VOVO(salen)][I_5]·MeCN with e.s.d.s in parentheses

(*a*) About the V atoms

V(1)–O(61)	1.58(3)	V(2)–O(62)	1.67(5)
V(1)–O(1)	1.82(4)	V(2)–O(31)	1.95(4)
V(1)–N(9)	2.14(5)	V(2)–N(39)	2.01(5)
V(1)–N(12)	2.10(4)	V(2)–N(42)	2.04(4)
V(1)–O(20)	1.77(4)	V(2)–O(50)	1.90(4)
V(1)–O(62)	2.06(5)	V(2)···O(61′)	2.41(4)
O(61)–V(1)–O(1)	98.1(21)	O(62)–V(2)–O(31)	98.8(22)
O(61)–V(1)–N(9)	86.8(20)	O(62)–V(2)–N(39)	96.7(23)
O(1)–V(1)–N(9)	84.2(19)	O(31)–V(2)–N(39)	89.3(17)
O(61)–V(1)–N(12)	92.4(19)	O(62)–V(2)–N(42)	103.0(22)
O(1)–V(1)–N(12)	156.6(19)	O(31)–V(2)–N(42)	156.4(17)
N(9)–V(1)–N(12)	75.4(18)	N(39)–V(2)–N(42)	79.4(17)
O(61)–V(1)–O(20)	98.8(21)	O(62)–V(2)–O(50)	107.0(22)
O(1)–V(1)–O(20)	109.8(20)	O(31)–V(2)–O(50)	92.9(15)
N(9)–V(1)–O(20)	163.7(20)	N(39)–V(2)–O(50)	155.5(19)
N(12)–V(1)–O(20)	89.0(18)	N(42)–V(2)–O(50)	89.2(16)
O(61)–V(1)–O(62)	165.5(20)	O(61′)···V(2)–O(62)	173.1(21)
O(1)–V(1)–O(62)	84.7(21)	O(61′)···V(2)–O(31)	82.6(15)
N(9)–V(1)–O(62)	79.3(21)	O(61′)···V(2)–N(39)	76.5(17)
N(12)–V(1)–O(62)	80.3(20)	O(61′)···V(2)–N(42)	74.6(15)
O(20)–V(1)–O(62)	93.6(22)	O(61′)···V(2)–O(50)	79.6(15)
V(1)–O(61)···V(2″)	165.0(22)	V(1)–O(62)–V(2)	161.6(30)

(*b*) In the I_5^- anion

I(81)–I(82)	2.812(7)	I(81)–I(82)–I(83)	177.0(3)
I(82)–I(83)	2.983(8)	I(82)–I(83)–I(84)	98.2(2)
I(83)–I(84)	3.115(8)	I(83)–I(84)–I(85)	174.6(3)
I(84)–I(85)	2.754(9)		

Primes indicate symmetry-related positions: ′ $x, y-1, z$; ″ $x, y+1, z$.

treatment of [VO(salen)] with 0.5 mol equivalent of trityl tetrafluoroborate in acetonitrile, and crystallising with diethyl ether. The product obtained however analysed for [{V(salen)}$_4$O$_3$][BF_4]$_2$·2MeCN, apparently containing four V^{IV} and three O atoms. Its magnetic moment was 3.2 ±0.1 μ_B, and its IR spectrum was different from both those of mononuclear and dinuclear complexes, having bands assignable to ν(V=O) at 940 and 910 cm^{-1}.

Spin Localisation in Dinuclear and Tetranuclear Cations.—In an attempt to find whether the one unpaired electron in the dinuclear cation [{VO(salen)}$_2$]$^+$ is localised over one vanadium atom or delocalised, a 1:100 by weight mixture of [{VO(salen)}$_2$]ClO_4 and [VO(salen)]ClO_4 was recrystallised from acetonitrile–diethyl ether, ground very finely and examined in the solid state by ESR spectrometry. This gave a simple eight-line spectrum showing that the unpaired electron is localised on one vanadium atom in the solid state.

The magnetic moment of [{V(salen)}$_4$O$_3$][BF_4]$_2$ corresponds to the spin-only value for two electrons, suggesting that there is spin pairing of the two electrons on V^{IV} atoms in this structure, and by inference localisation of the unpaired electrons on the others. This may be because the unpaired electron in simple vanadyl compounds like [VO(salen)] is held [10] to reside in the d_{xy} orbital (*z* being the V=O bond direction). and there would be no overlap between these orbitals on adjacent vanadium atoms.

Robin and Day [11] proposed a classification scheme for compounds containing metals in more than one oxidation state. Class I systems are defined as those with metal ions in sites of very different symmetry and ligand-field strength, and there is no delocalisation of unpaired electrons, while Class III systems have metals on identical sites with complete delocalisation (Class II systems are intermediate). Our dinuclear cations clearly fit into Class I, although the principal ligands are chemically the same, and the bridging oxygen atom might have been expected to facilitate electron interchange. On such grounds a Class II behaviour might have been expected.

State of Association of Cations in Solution.—The electrochemistry of [V^{IV}O(salen)] in acetonitrile solution has been investigated in considerable detail.[5] This showed that the compound undergoes a reversible one-electron oxidation. There was no evidence of an intermediate V^{IV}–V^V species. Nevertheless, having isolated a solid V^{IV}–V^V species, we attempted to detect it in solution by other techniques.

ESR spectrometry. ESR spectra of salts of the dinuclear cations in acetonitrile solution at 10^{-3}–10^{-2} mol dm^{-3} at room temperature also show simple eight-line spectra. This is consistent with the dinuclear complexes existing in solution but the unpaired electron being localised; however, it is also consistent with there being complete dissociation of the complexes to mononuclear vanadium-(IV) and -(V) species in solution. In order to distinguish between these possibilities, solution UV–VIS and IR spectrometric studies were undertaken.

Visible–ultraviolet spectrometry. The UV–VIS spectra of the following solutions (all in acetonitrile) were examined in the region 400–700 nm: [VO(salen)], 10^{-3} mol dm^{-3}, **A**; [VO(salen)]ClO_4, 10^{-3} mol dm^{-3}, **B**; a 1:1 mixture of [VO(salen)], 2×10^{-3} mol dm^{-3} and [VO(salen)]ClO_4, 2×10^{-3} mol dm^{-3}, **C**; [{VO(salen)}$_2$]ClO_4, 10^{-3} mol dm^{-3}, **D**; and [{VO(salen)}$_2$][I_5], 10^{-3} mol dm^{-3}, **E**. The spectra of **C** and **D** were found to be identical, *i.e.* the same solution species is obtained whether one starts from a mixture of appropriate mononuclear complexes or from the binuclear adduct. The spectrum of **C** or **D** is almost exactly the superposition of the spectra of **A** and **B**. This is consistent with complete localisation of the unpaired electron in a Robin and Day Class I system, but also with complete dissociation of multinuclear species in solution so that a solution containing complexes of V^{IV} and V^V is a simple mixture of mononuclear species. (The spectrum of **E** shows enhanced general absorption over that of **D**, presumably because of the presence of the I_5^- ion.) Similar results (**A** + **B** = **C** or **D**) were obtained when the conductivities of the same solutions were measured.

Solution infrared spectra. Solution spectra in acetonitrile solution were examined in the 1000–800 cm^{-1} region where ν(V=O) occurs. The strongest band in this region, which may be assigned to ν(V=O), occurred at 981 cm^{-1} in the spectra of [VO(salen)], [{VO(salen)}$_2$][I_5] and also [{VO(salen)}$_2$]ClO_4 and [VO(salen)]ClO_4 though here it was partly obscured by the intense band due to ν(Cl=O) in the perchlorate ligand centred at 1040 cm^{-1}.

In contrast, the bands assigned to ν(V=O) in solid-state spectra occurred at quite different wavenumbers (870 cm^{-1}) for [{VO(salen)}$_2$][I_5] and [{VO(salen)}$_2$]ClO_4 from those for [VO(salen)] and [VO(salen)]ClO_4 (both at 981 cm^{-1}).[5] Thus the difference in ν(V=O) in the solid state between mononuclear and dinuclear cations is absent in solution, and the spectra suggest that the dinuclear cations are dissociated in solution to the vanadium-(IV) and -(V) mononuclear species [which fortuitously have the same ν(V=O) at 981 cm^{-1}].[5]

Experimental

General.—Reactions were carried out in dried solvents under nitrogen. Microanalyses were performed by Mr. C. J. Macdonald of this Laboratory. Magnetic susceptibilities were measured by the Faraday method at 20 °C, and additional data on [(salen)VOVO(salen)][I_5]·MeCN at low temperatures were obtained by Dr. L. F. Larkworthy at the University of Surrey. Infrared spectra were obtained using a Perkin-Elmer 882 instrument, UV–VIS spectra by a Perkin-Elmer 550S machine and ESR spectra by Dr. D. J. Lowe of this Laboratory on a Bruker ER200 D-SRC spectrometer.

Preparation of Complexes.—The complex [(salen)VOVO(salen)][I_5]·MeCN was prepared as described.[1] Crystals for X-ray analysis were obtained by slow recrystallisation of the crude product twice from acetonitrile.

The complex [(salen)VOVO(salen)][I_7]·MeCN was prepared in a similar way but using [VO(salen)] (2.5 g, 7.5 mmol) and iodine (4.0 g, 16.0 mmol). The black needles that crystallised were much shorter than those of the pentaiodide but their IR spectra were identical (Found: C, 25.4; H, 1.6; N, 3.7. $C_{34}H_{31}I_7N_5O_6V_2$ requires C, 25.6; H, 1.8; N, 4.3%).

Reaction of [(salen)VOVO(salen)]$^+$ *with* $NaBPh_4$. The dinuclear pentaiodide (1.2 g, 1 mmol) was stirred in methanol (20 cm^3) and $NaBPh_4$ (0.7 g, 2 mmol) added. An iodine colour developed in solution and the black needles became a blue powder that was filtered off and washed with methanol and diethyl ether. It analysed as the known [{VO(salen)}$_2$Na]-BPh_4[7] (Found: C, 67.1; H, 4.9; N, 5.5. $C_{56}H_{48}BN_4NaO_6V_2$ requires C, 66.7; H, 4.7; N, 5.5%), μ_{eff} = 1.9 μ_B per V.

[(salpn)VOVO(salpn)][I_5]. The complex [VO(salpn)] (1.4 g, 5 mmol), prepared as described,[3] was heated to reflux in acetonitrile (100 cm^3). Unlike [VO(salen)], the polymeric [VO(salpn)] was almost insoluble. Iodine (1.88 g, 7.5 mmol) was added and the mixture heated under reflux overnight, then filtered at reflux temperature leaving [VO(salpn)] (*ca.* 0.7 g). The hot solution deposited blackish green crystals (1.0 g, 0.75 mmol) of the product on cooling to room temperature (Found: C, 30.9; H, 2.4; N, 4.0. $C_{34}H_{32}I_5N_4O_6V_2$ requires C, 30.7; H, 2.4; N, 4.1%), $\mu_{eff} = 1.8 \pm 0.2\ \mu_B$.

[(salphen)VOVO(salphen)][I_3]. The complex [VO(salphen)] (3.0 g, 8 mmol), prepared as described,[1] was heated to reflux in acetonitrile (450 cm^3). Iodine (2.1 g, 8.0 mmol) was added, giving a green suspension which was refluxed for 1 h then filtered at reflux temperature. The hot solution very slowly deposited green crystals (0.3 g) over 1 week after cooling to room temperature (Found: C, 41.7; H, 2.4; N, 4.6. $C_{40}H_{23}I_3N_4O_6V_2$ requires C, 42.0; H, 2.4; N, 4.9%), $\mu_{eff} = 1.8 \pm 0.2\ \mu_B$.

[(salen)VOVO(salen)]ClO_4·MeCN. Approximately equimolar quantities of [VO(salen)] (0.20 g, 0.6 mmol) and [VO(salen)]ClO_4·MeOH (0.30 g, 0.65 mmol) were heated to reflux temperature for 10 min in acetonitrile (30 cm^3) and allowed to cool to 20 °C. Diethyl ether (45 cm^3) was added and the mixture was set aside overnight giving dark green crystals (0.3 g, 0.37 mmol) (Found: C, 50.3; H, 3.9; N, 8.5. $C_{34}H_{31}ClN_5O_{10}V_2$ requires C, 50.6; H, 3.8; N, 8.7%), $\mu_{eff} = 2.0 \pm 0.2\ \mu_B$ at 20 °C.

The corresponding hexafluorophosphate was made similarly (Found: C, 47.9; H, 3.5; N, 7.7. $C_{34}H_{31}F_6N_5O_6PV_2$ requires C, 47.9; H, 3.6; N, 8.2), $\mu_{eff} = 1.8 \pm 0.2\ \mu_B$ at 20 °C.

[{V(salen)}$_4O_3$][BF_4]$_2$·2MeCN. The complex [VO(salen)] (2.5 g, 7.5 mmol) and trityl tetrafluoroborate (1.3 g, 4.0 mmol) were heated to reflux temperature in acetonitrile (40 cm^3) for 10 min, then cooled to 20 °C. Addition of diethyl ether gave a black precipitate which was recrystallised from a small quantity of acetonitrile as black needles (1.0 g, 0.9 mmol) (Found: C, 51.9; H, 3.9; N, 8.7. $C_{68}H_{62}B_2F_8N_{10}O_{11}V_4$ requires C, 51.9; H, 3.9; N, 8.9%), $\mu_{eff} = 3.2 \pm 0.1\ \mu_B$ at 20 °C.

Crystal Structure Analysis of [(salen)VOVO(salen)][I_5]·MeCN.—*Crystal data.* $C_{32}H_{28}I_5N_4O_6V_2$·C_2H_3N, M = 1342.1, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 26.840(4), b = 7.607(2), c = 20.347(6) Å, U = 4154.1 Å^3, Z = 4, D_c = 2.146 g cm^{-3}, $F(000)$ = 2516, μ(Mo-Kα) = 41.6 cm^{-1}, λ(Mo-K$\bar{\alpha}$) = 0.710 69 Å.

Crystals are virtually black, very fine, long needles. The sample was recrystallised twice from acetonitrile and many crystals were mounted, in air, on glass fibres for photographic examination; most crystals were not single, or showed very streaky diffraction spots or an alternative lattice superimposed on the main lattice. Finally an acceptable crystal was found and transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for determination of cell parameters (from 25 reflections, each centred in four orientations, with θ in the range 8.8–11.0°), and measurement of diffraction intensities (to θ_{max} = 20°, the limit of observable data).

During processing, corrections were made for Lorentz and polarisation effects, crystal deterioration (17% overall), and absorption (from the shape and size, *viz.* 0.04 × 0.05 × 0.40 mm, of the crystal). Of the 2050 unique data entered into the SHELX program system,[12] 1424 had $I \geqslant 2\sigma_I$ and were used in the structure analysis.

The unexpected structure was determined eventually from Patterson and (many) trial-and-error methods. Refinement by full-matrix least-squares methods was terminated with R = 0.086 and R' = 0.099[12] for the 1424 observed data, weighted equally. Only the I and V atoms were allowed anisotropic thermal parameters; the other non-hydrogen atoms were refined isotropically. Hydrogen atoms were included in idealised positions, with all parameters riding on those of their bonded C atoms. The thermal parameters of all atoms are not considered reliable, and the bond dimensions in the salen ligands are not very precise. However, we are certain that the overall structure is sound. A solvent, MeCN, molecule was identified in the crystal, disordered in overlapping sites; the orientations of the two molecules have not been fully resolved. In the final difference map, the nine largest peaks, 0.9–1.6 e Å^{-3}, were all close to the I_5^- anion.

Scattering factors for neutral atoms were taken from ref. 13. Computer programs used in this analysis have been noted in ref. 12 and in Table 4 of ref. 14, and were run on the MicroVAX II machine 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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