# The Preparation and Structure of [VI$_2$(salen)]·CH$_2$Cl$_2$ [salen = *N,N'*-ethylenebis(salicylideneiminate)(2−)] and of Some Homologues of Related Schiff Bases†

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The elusive [VI$_2$(salen)] [salen = *N,N'*-ethylenebis(salicylideneiminate)(2−)] and some of its homologues have been successfully prepared. The structure of [VI$_2$(salen)]·CH$_2$Cl$_2$ has been determined by X-ray crystallography, and the conformation is *trans*-octahedral, as expected, with long V–I separations. The complex is air-stable in the solid state, but appears to be moisture-sensitive in solution, and undergoes autoredox reactions ($V^{IV} \longrightarrow V^{III}$, $I^- \longrightarrow I_2$) in ionising solvents.

We have been interested in developing nitrogen-fixing systems based upon vanadium but with ligand donor sets akin to the oxygen-containing nitrogen-fixing systems developed by Shilov and co-workers.[1] We chose to investigate Schiff-base ligands in moieties such as V(salen) [H$_2$salen = *N,N'*-ethylenebis(salicylideneimine)], hoping to synthesise [V$^{II}$(salen)] and also species such as [V(NHNH$_2$)(salen)] containing reduced dinitrogen residues. For this purpose we required compounds [VX$_2$(salen)] (X = Cl, Br or I) and specifically [VI$_2$(salen)] because iodide should be a particularly good leaving group in metathetical reactions. However, this compound has not been reported hitherto.

## Results and Discussion

The compounds [VX$_2$(salen)] (X = Cl or Br) are obtainable by a variety of methods.[2] For example, [VO(salen)] reacts with hydrogen chloride in acetonitrile to yield [VCl$_2$(salen)] in a series of two protonations followed by loss of water and coordination of chloride. Alternatively, SOCl$_2$ or PCl$_5$ in benzene can effect the change.[3] Similarly, PPh$_3$Br$_2$ and [VO(salen)] yield [VBr$_2$(salen)].[4]

We attempted similar experiments to prepare the diiodide. However, reaction of [VO(salen)] with PPh$_3$I$_2$ gives [V(salen)(OPPh$_3$)I]I.[5] Direct reaction of [VO(salen)] with I$_2$ gives [V$^{IV}$(salen)OV$^{V}$(salen)O][I$_5$],[6] the structure of which was ascertained by X-ray analysis. Finally, treatment of [VO(salen)] with HI in CH$_2$Cl$_2$ causes reduction of vanadium, and formation of I$_2$, and we have isolated and structurally characterised [{V$^{III}$(salen)OV$^{IV}$(salen)}$_2$][I$_3$]$_2$.[7]

We finally obtained the desired compound in almost quantitative yield by reaction of [VO(salen)] with Me$_3$SiI (1 : 2) in CH$_2$Cl$_2$. The black crystalline material was isolated as a 1 : 1 solvate with CH$_2$Cl$_2$, and subsequently we obtained [VI$_2$(salen)]·C$_2$H$_4$Cl$_2$. The complexes [VI$_2$(acac)$_2$] (acac = acetylacetonate) and [VI$_2$L'] [where H$_2$L' is the Schiff base *N,N'*-2,2-dimethyltrimethylenebis(salicylideneimine), *N,N'*-1,1-dimethylethylenebis(salicylideneimine) or *N,N'*-ethylenebis(α-methylsalicylideneimine)] were obtained by similar reactions. These compounds are all paramagnetic, with appropriate spin-only magnetic moments at room temperature.

Comparable reactions of [VO(salen)] with Me$_3$SiBr or Me$_3$SiCl yielded [VBr$_2$(salen)] or [VCl$_2$(salen)] in almost quantitative yields, but we observed no reaction of [VO(salen)] with Me$_3$SiN$_3$ under similar conditions.

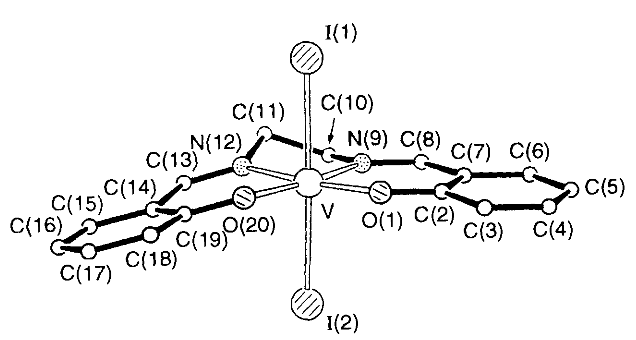

**Fig. 1** Representation of the structure of [VI$_2$(salen)], showing the atomic numbering scheme

In order to confirm that we had indeed obtained [VI$_2$(salen)], and because C,H,N analyses are not very informative, we undertook an X-ray crystal structure analysis. The structure is presented in Fig. 1, and selected bond lengths and angles are in Table 1 and atom coordinates are in Table 2. The molecule presents the hoped-for octahedral structure with *trans* iodides, and the salen constituting the equatorial plane. The salen itself is not exactly planar, but the vanadium atom lies within 0.013 Å of the good mean plane defined by the two oxygen and two nitrogen donors of the salen. The mean plane [O(1)–N(9)] of one salicylideneimine group, is almost parallel to the N$_2$O$_2$ plane, while the normal to the mean plane [N(12)–O(20)] of the other salicylideneimine group is *ca.* 15° to the normal of the N$_2$O$_2$ plane. Each benzo group has one neighbouring, overlapping, centrosymmetrically related ring at normal van der Waals stacking distances (3.4–3.6 Å); on the opposite side, in each case, there is a Cl atom of a solvent molecule lying above the ring, at distances of 3.65 and 3.76 Å. These intermolecular distances do not suggest strong packing interactions and the salen ligand retains a relatively flat conformation. The V–O and V–N separations [1.787(2), 1.811(2) Å and 2.070(3), 2.085(2) Å, respectively] are of the same magnitudes as those found in other V$^{IV}$(salen) compounds.[8] However, the V–I separations present more of a problem.

To our knowledge, there are four literature reports of molecular structures in which V–I separations are quoted, and none is strictly comparable to ours. These are as follows: [{V$^{IV}$I(C$_5$H$_5$)$_2$}$_2${V(C$_5$H$_5$)(NO)}$_2$O$_4$], 2.653(2);[9]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

**Table 1** Molecular dimensions (bond lengths in Å, angles in °) in *trans*-[$VI_2$(salen)]$CH_2Cl_2$ with estimated standard deviations (e.s.d.s) in parentheses

(*a*) About the V atom

| | | | |
|---|---|---|---|
| V–I(1) | 2.779(1) | V–N(9) | 2.070(3) |
| V–I(2) | 2.747(1) | V–N(12) | 2.085(2) |
| V–O(1) | 1.787(2) | V–O(20) | 1.811(2) |
| I(1)–V–I(2) | 175.11(2) | O(1)–V–N(12) | 163.0(1) |
| I(1)–V–O(1) | 91.6(1) | N(9)–V–N(12) | 77.7(1) |
| I(2)–V–O(1) | 91.9(1) | I(1)–V–O(20) | 91.4(1) |
| I(1)–V–N(9) | 89.3(1) | I(2)–V–O(20) | 90.4(1) |
| I(2)–V–N(9) | 87.6(1) | O(1)–V–O(20) | 111.4(1) |
| O(1)–V–N(9) | 85.2(1) | N(9)–V–O(20) | 163.3(1) |
| I(1)–V–N(12) | 88.3(1) | N(12)–V–O(20) | 85.6(1) |
| I(2)–V–N(12) | 87.2(1) | | |

(*b*) In the salen ligand

| | | | |
|---|---|---|---|
| O(1)–C(2) | 1.330(3) | C(11)–N(12) | 1.458(4) |
| C(2)–C(3) | 1.400(4) | N(12)–C(13) | 1.290(4) |
| C(2)–C(7) | 1.391(4) | C(13)–C(14) | 1.427(5) |
| C(3)–C(4) | 1.387(4) | C(14)–C(15) | 1.412(5) |
| C(4)–C(5) | 1.390(5) | C(14)–C(19) | 1.405(4) |
| C(5)–C(6) | 1.376(5) | C(15)–C(16) | 1.367(6) |
| C(6)–C(7) | 1.407(4) | C(16)–C(17) | 1.391(6) |
| C(7)–C(8) | 1.417(4) | C(17)–C(18) | 1.370(5) |
| C(8)–N(9) | 1.292(4) | C(18)–C(19) | 1.402(4) |
| N(9)–C(10) | 1.472(4) | C(19)–O(20) | 1.329(4) |
| C(10)–C(11) | 1.506(5) | | |
| V–O(1)–C(2) | 140.7(2) | C(10)–C(11)–N(12) | 108.3(3) |
| O(1)–C(2)–C(3) | 119.6(3) | V–N(12)–C(11) | 115.3(2) |
| O(1)–C(2)–C(7) | 119.2(3) | V–N(12)–C(13) | 125.6(2) |
| C(3)–C(2)–C(7) | 121.2(3) | C(11)–N(12)–C(13) | 119.1(3) |
| C(2)–C(3)–C(4) | 118.7(3) | N(12)–C(13)–C(14) | 125.7(3) |
| C(3)–C(4)–C(5) | 120.9(3) | C(13)–C(14)–C(15) | 119.3(3) |
| C(4)–C(5)–C(6) | 120.2(3) | C(13)–C(14)–C(19) | 121.8(3) |
| C(5)–C(6)–C(7) | 120.3(3) | C(15)–C(14)–C(19) | 118.6(3) |
| C(2)–C(7)–C(6) | 118.8(3) | C(14)–C(15)–C(16) | 120.8(3) |
| C(2)–C(7)–C(8) | 122.3(3) | C(15)–C(16)–C(17) | 119.9(3) |
| C(6)–C(7)–C(8) | 118.9(3) | C(16)–C(17)–C(18) | 120.9(3) |
| C(7)–C(8)–N(9) | 125.5(3) | C(17)–C(18)–C(19) | 119.9(3) |
| V–N(9)–C(8) | 126.9(2) | C(14)–C(19)–C(18) | 119.8(3) |
| V–N(9)–C(10) | 116.6(2) | C(14)–C(19)–O(20) | 120.2(3) |
| C(8)–N(9)–C(10) | 116.3(3) | C(18)–C(19)–O(20) | 120.0(3) |
| N(9)–C(10)–C(11) | 109.0(3) | V–O(20)–C(19) | 137.2(2) |

(*c*) Torsion angles in the salen ligand

| | |
|---|---|
| O(1)–C(2)–C(7)–C(8) | −1.9(5) |
| C(2)–C(7)–C(8)–N(9) | −0.5(5) |
| C(7)–C(8)–N(9)–C(10) | −172.9(3) |
| C(8)–N(9)–C(10)–C(11) | −158.4(3) |
| N(9)–C(10)–C(11)–N(12) | −38.4(4) |
| C(10)–C(11)–N(12)–C(13) | −143.8(3) |
| C(11)–N(12)–C(13)–C(14) | −173.5(3) |
| N(12)–C(13)–C(14)–C(19) | 7.2(5) |
| C(13)–C(14)–C(19)–O(20) | −4.8(5) |

(*d*) In the dichloromethane molecule

| | | | |
|---|---|---|---|
| C(30)–Cl(31) | 1.739(5) | C(30)–Cl(32) | 1.761(5) |
| Cl(31)–C(30)–Cl(32) | 112.4(3) | | |

**Table 2** Final atomic coordinates (fractional × $10^4$) for *trans*-[$VI_2$(salen)]·$CH_2Cl_2$ with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| V | 402.9(7) | 2150.8(3) | −23.0(3) |
| I(1) | 3235.7(3) | 1155.6(1) | 143.6(2) |
| I(2) | −2410.7(3) | 3049.9(1) | −309.0(1) |
| O(1) | −623(3) | 2264(1) | 1117(1) |
| C(2) | −1839(4) | 1966(2) | 1709(2) |
| C(3) | −2327(4) | 2307(2) | 2569(2) |
| C(4) | −3605(5) | 1990(2) | 3175(2) |
| C(5) | −4396(5) | 1349(2) | 2936(2) |
| C(6) | −3932(5) | 1025(2) | 2086(2) |
| C(7) | −2639(4) | 1332(2) | 1456(2) |
| C(8) | −2245(4) | 1002(2) | 582(2) |
| N(9) | −1147(4) | 1243(2) | −67(2) |
| C(10) | −1106(6) | 871(2) | −931(2) |
| C(11) | 663(6) | 986(2) | −1557(2) |
| N(12) | 1111(4) | 1755(2) | −1340(2) |
| C(13) | 1882(5) | 2131(2) | −1955(2) |
| C(14) | 2560(4) | 2854(2) | −1845(2) |
| C(15) | 3334(5) | 3208(2) | −2581(2) |
| C(16) | 4114(5) | 3873(2) | −2501(2) |
| C(17) | 4196(5) | 4196(2) | −1690(3) |
| C(18) | 3472(5) | 3867(2) | −963(2) |
| C(19) | 2626(4) | 3195(2) | −1029(2) |
| O(20) | 1930(3) | 2873(1) | −323(1) |
| The dichloromethane solvent molecule | | | |
| C(30) | −13(8) | 4297(3) | 1319(3) |
| Cl(31) | −1101(2) | 4330.4(6) | 2413.3(8) |
| Cl(32) | 1041(2) | 5129.7(8) | 1077.3(9) |

[{$V^{IV}(C_5Me_5)I_2\}_2O$], 2.618(2) and 2.614(1);[10] [$V^{III}I(C_9H_7)_2$], 2.794(1);[11] and [$V^{IV}(C_5H_5)I_3$], 2.562(5), 2.601(5) and 2.5441(1) Å.[12,*] In our vanadium(IV) compound, the V–I separations are 2.779(1) and 2.747(1) Å, considerably longer than in the other vanadium(IV) compounds, and are of the same order as in the very different iodobis(indenyl)vanadium(III).[11] It might have been expected to be shorter. The sum of vanadium(IV) and iodine(−I) ionic radii is (0.60 + 2.16) = 2.76 Å. The $V^{IV}$–I covalent bond (a radius for $V^{IV}$ was inferred from our structural data) should be 1.24 + 1.33 = 2.57 Å.[13] Consequently, the V–I separations in our compound imply a high degree of ionic character.

This situation is reminiscent of the complex [$FeI_2$([16]ane-$S_4$)] ([16]ane$S_4$ = 1,5,9,13-tetrathiacyclohexadecane), which can, with equal justification, be formulated as [Fe([16]ane$S_4$)]-$I_2$.[14] Like the iron compound, [$VI_2$(salen)] possesses a far from negligible molar conductivity in $MeNO_2$ (≈30 ohm$^{-1}$ cm$^2$ mol$^{-1}$) even when we took every reasonable precaution to exclude air and moisture. A fully dissociated 1:1 electrolyte might be expected to have a conductivity *ca.* four times this value.[15] In contrast, [$VCl_2$(salen)] and [$VBr_2$(salen)] are non-conductors in this solvent.

We conclude that the V–I bonds in [$VI_2$(salen)] are substantially ionic in character and that iodide should be the good leaving group we have looked for. In such circumstances, one might expect that recrystallisation of [$VI_2$(salen)] from tetrahydrofuran (thf) or MeCN (= L) should give new species [$VL_2$(salen)]$I_2$. In fact, the product obtained from thf appeared to be the known [VI(thf)(salen)][5] on one occasion, though this was not reproducible. From MeCN we consistently obtained [{V(salen)OV(salen)}$_2$][$I_3$]$_2$·2MeCN. This was prepared by us in earlier work and unequivocally characterised by X-ray structure analysis.[7] The identity of the product was confirmed by X-ray oscillation and zero-layer Weissenberg photographs.

It is evident from these observations that solutions of [$VI_2$(salen)] are exceedingly sensitive to moisture and that when iodide and the $V^{IV}$(salen) moiety come together, then reduction to vanadium(III) occurs. This may well limit the value for synthetic purposes of [$VI_2$(salen)] in ionising solvents.

We have obtained the EPR spectra of all the compounds [$VX_2$(salen)] (X = Cl, Br or I) in solution in the non-ionising solvent dichloromethane at ambient temperature. The *g* and *A*

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[*] *Note added at proof:* There is now a further example, [$VI_2(MeOCH_2CH_2OMe)_2$], with mean V–I 2.808(2) Å (F. Calderazzo, G. E. de Benedetto, G. Pampalonc, C. M. Mössmer, J. Strähle and K. Wurst, *J. Organomet. Chem.*, 1993, **451**, 73).

values we obtained in the characteristic eight-line spectra were: $g$ = 1.952 (lit.,[16] 1.950) and $A$ = 82 × $10^{-4}$ $cm^{-1}$ (lit.,[16] 76 × $10^{-4}$) (X = Cl), $g$ = 1.968 (lit.,[16] 1.955) and $A$ =79 × $10^{-4}$ $cm^{-1}$ (lit.,[16] 80 × $10^{-4}$) (X = Br) and $g$ =1.997 ± 0.002, $A$ = 71 × $10^{-4}$ $cm^{-1}$ (X = I). These $g$ values suggest increasing electron delocalisation in the sequence Cl < Br < I, and the $A$ values greater unpaired electron density on the vanadium in the opposite sequence. These data are self-consistent, though this is no more than a qualitative analysis. It is not what one might expect were [$VI_2$(salen)] completely ionic.

## Experimental

Reactions were generally carried out using standard Schlenk techniques in dried solvents under $N_2$. The C,H,N analyses were undertaken by Mr. C. J. Macdonald of the Nitrogen Fixation Laboratory using a Perkin Elmer 2400 analyser and iodine analyses were by Butterworth Analytical Laboratories. Infrared spectra were obtained using a Perkin Elmer 883 spectrometer, as Nujol mulls. The EPR spectra at room temperature in solution in dichloromethane were obtained on a Bruker ESP 300 spectrometer, courtesy of Dr. D. J. Lowe. Conductivities were obtained using a Portland Electronics Bridge and magnetic moments in the solid state at 20 °C were determined by the Faraday method using $Hg[Co(NCS)_4]$ as standard and making the usual diamagnetic corrections using Pascal's constants.

The new Schiff base *N*,*N'*-2,2-dimethyltrimethylenebis(salicylideneimine) and its $V^{IV}O$ derivative were prepared as described below. Other Schiff bases and [VO(salen)] and its homologues were prepared analogously. Trimethylsilyl compounds and [$VO(acac)_2$] were purchased from Aldrich, and used without further purification.

*Syntheses*.—N,N'-2,2-*Dimethyltrimethylenebis*(*salicylideneimine*). Salicylaldehyde (9.76 g, 80 mmol) was added slowly to a solution of 2,2-dimethyl-1,3-diaminopropane (4.09 g, 40 mmol) in methanol (80 $cm^3$) at the boiling point. Yellow crystals formed immediately; the solution was boiled for 10 min and then set aside to cool. After 1 d yellow crystals (10.8 g, 87%) were filtered off, washed with methanol and diethyl ether and dried in air (Found: C, 73.2; H, 6.2; N, 8.6. $C_{19}H_{22}N_2O_2$ requires C, 73.5; H, 7.1; N, 9.0%).

[N,N'-2,2-*Dimethyltrimethylenebis*(*salicylideneiminato*)]-*oxovanadium*(IV). The complex [$VO(acac)_2$] (4.35 g, 16.4 mmol) was added to acetonitrile (150 $cm^3$) and the mixture heated to reflux and filtered hot leaving a small residue. 2,2-Dimethylpropylene-*N*,*N'*-bis(salicylideneimine) (5.07 g, 16.4 mmol) was added to the hot filtrate using a Soxhlet extractor. The mixture was kept at reflux temperature for 30 min, then cooled. After 1 d orange-red crystals (3.28 g, 54%) were filtered off, washed with cold acetonitrile and diethyl ether, and dried *in vacuo* (Found: C, 60.4; H, 5.4; N, 7.5. $C_{19}H_{20}N_2O_3V$ requires C, 60.8; H, 5.3; N, 7.4%. Magnetic moment = 1.87 $\mu_B$.

[N,N'-*Ethylenebis*(*salicylideneiminato*)]*diiodovanadium*(IV) -*dichloromethane* (1/1). To a solution of [VO(salen)] (1.67 g, 5.0 mmol) in $CH_2Cl_2$ (100 $cm^3$) was added by syringe $Me_3SiI$ (1.4 $cm^3$, 2.0 g, 10.0 mmol). The dark brown solution was set aside at −20 °C. After 6 d, black crystals (3.20 g, 97%) were filtered off, washed with $CH_2Cl_2$ and $Et_2O$ and dried *in vacuo* (Found: C, 30.8; H, 2.00; I, 37.4; N, 3.90. $C_{17}H_{16}Cl_2I_2N_2O_2V$ requires C, 31.1; H, 2.45; I, 38.7; N, 4.25%). Magnetic moment = 1.80 ± 0.05 $\mu_B$. $\Lambda_M$ = 30.6 $ohm^{-1}$ $cm^2$ $mol^{-1}$ ($10^{-3}$ mol $dm^{-3}$, $MeNO_2$).

Using a similar method, the 1/1 solvate with $C_2H_4Cl_2$-1,2 was also obtained (Found: C, 32.3; H, 2.3; N, 4.3. $C_{18}H_{18}Cl_2I_2N_2O_2V$ requires C, 32.3; H, 2.7; N, 4.2%). Yield ≈ 80%.

[N,N'-2,2-*Dimethyltrimethylenebis*(*salicylideneiminato*)]-*diiodovanadium*. This was prepared in 75% yield from the appropriate oxovanadium(IV) compound and $Me_3SiI$ in a similar way (Found: C, 37.1; H, 3.3; I, 40.5; N, 4.7. $C_{19}H_{20}I_2N_2O_2V$ requires C, 37.2; H, 3.3; I, 41.4; N, 4.6%). Magnetic moment = 1.75 $\mu_B$. $\Lambda_M$ = 41.5 $ohm^{-1}$ $cm^2$ $mol^{-1}$ ($10^{-3}$ mol $dm^{-3}$, $MeNO_2$).

*Diiodo*-[N,N'-1,1-*dimethylethylenebis*(*salicylideneiminato*)]-*vanadium–dichloromethane* (1/1). This was prepared as above in 70% yield (Found: C, 33.6; H, 2.7; I. 37.2; N, 4.0. $C_{19}H_{20}Cl_2I_2N_2O_2V$ requires C, 33.3; H, 2.95; I, 37.1; N, 4.1%). Magnetic moment = 1.72 $\mu_B$. $\Lambda_M$ = 30.2 $ohm^{-1}$ $cm^2$ $mol^{-1}$ ($10^{-3}$ mol $dm^{-3}$, $MeNO_2$).

[N,N'-*Ethylenebis*($\alpha$-*methylsalicylideneiminato*)]*diiodovanadium*. This was prepared as above in ≈80% yield (Found: C, 36.2; H, 3.0; I, 38.6; N, 4.2. $C_{18}H_{18}I_2N_2O_2V$ requires C, 36.1; H, 3.0; I, 42.4; N, 4.7%). Magnetic moment = 1.87 $\mu_B$. $\Lambda_M$ = 37.2 $ohm^{-1}$ $cm^2$ $mol^{-1}$ ($10^{-3}$ mol $dm^{-3}$, $MeNO_2$).

The known compounds [$VCl_2$(salen)] and [$VBr_2$(salen)] were prepared similarly in *ca.* 95% yield from [VO(salen)] and $Me_3SiCl$ or $Me_3SiBr$, respectively. The authenticity was confirmed by C,H,N analyses and by comparison of IR spectra with those of authentic samples (Found: C, 49.3; H, 3.20; N, 7.05. $C_{16}H_{14}Cl_2N_2O_2V$ requires C, 49.5; H, 3.65; N, 7.20. Found: C, 39.7; H, 2.65; N, 5.65. $C_{16}H_{14}Br_2N_2O_2V$ requires C, 40.3; H, 2.95; N, 5.85%).

*Bis*(*acetylacetonato*)*diiodovanadium–dichloromethane* (1/1). This was prepared in similar fashion in 80% yield from [$VO(acac)_2$] and $Me_3SiI$. It was recrystallised from $CH_2Cl_2$–$Et_2O$ (Found: C, 22.4; H, 3.1; I, 46.7; N, 0.0. $C_{11}H_{16}Cl_2I_2O_4V$ requires C, 22.4; H, 2.75; I, 43.2; N, 0.0%). $\Lambda_M$ = 35.9 $ohm^{-1}$ $cm^2$ $mol^{-1}$ ($10^{-3}$ mol $dm^{-3}$, $MeNO_2$). The magnetic moment in the solid could not be determined because the sample loses weight on the magnetic balance, even under $N_2$.

*Crystal Structure Determination of* [$VI_2$(salen)]·$CH_2Cl_2$.—*Crystal data.* $C_{16}H_{14}I_2N_2O_2V{\cdot}CH_2Cl_2$, $M$ = 656.0, triclinic, space group $A\bar{1}$ (equivalent to no. 2; preferred to $P\bar{1}$, conforming to photographic orientation), $a$ = 7.6378(6), $b$ = 17.731(2), $c$ = 16.113(1) Å, $\alpha$ = 95.816(7), $\beta$ = 75.172(5), $\gamma$ = 85.960(8)°, $U$ = 2088.0 $Å^3$, $Z$ = 4, $D_c$ = 2.087 g $cm^{-3}$, $F(000)$ = 1244, $\mu$(Mo-K$\alpha$) = 36.6 $cm^{-1}$, $\lambda$(Mo-K$\bar{\alpha}$) = 0.710 69 Å.

The crystals were isolated directly from the dilute reaction solution. They were air-stable, black and opaque with a metallic shine. Most were single with many well-formed faces and edges, and *ca.* 0.5 mm long. One of the crystals (*ca.* 0.21 × 0.33 × 0.40 mm) was mounted on a glass fibre. Preliminary oscillation and Weissenberg photographs showed the crystal to diffract well and gave approximate unit-cell dimensions and the symmetry of the crystal.

After transferring the crystal to our Enraf-Nonius CAD4 diffractometer (with monochromated molybdenum radiation), accurate cell dimensions were determined using 25 strong reflections with $10 < \theta < 11°$, each centred in four orientations. Diffraction intensities were measured to $\theta_{max}$ = 27°. Corrections were made for Lorentz–polarisation effects, slight deterioration (overall *ca.* 2.7%), absorption (by semi-empirical $\psi$-scan methods) and to ensure no negative intensities (by Bayesian statistics). The complete set of 4552 unique reflections was entered into the SHELX program system.[17]

The structure was determined using the heavy-atom method, based on the vanadium and two iodine atoms, which were found manually in a Patterson map. The remaining atoms were located from electron-density and Fourier difference maps. During refinement by full-matrix least-squares methods, all the non-hydrogen atoms were allowed anisotropic thermal parameters and the hydrogen atoms were included in idealised positions with independent isotropic thermal parameters. At convergence, $R$ = 0.029, $R'$ = 0.037, and goodness-of-fit =2.44 for all 4552 reflections weighted $w = (\sigma_F^2 + 0.000\,36F^2)^{-1}$. In the final difference map the only peak of significance (*ca.* 1.0 e $Å^{-3}$) lay close to the solvent molecule; no other peaks exceeded 0.4 e $Å^{-3}$.

Scattering factors were taken from ref. 18. The computer programs which were used are listed in Table 4 of ref. 19 and were all run on the MicroVAX II machine in this Laboratory.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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