Reactions of Vanadium(IV) Halide Complexes containing Schiff-base Ligands with Hydrazines; Preparation and Structure of [*N,N'*-Ethylenebis(salicylideneiminato)]bis-(phenylhydrazine)vanadium(III) Iodide†

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The complexes $[VX_2L]$ [L = *N,N'*-ethylenebis(salicylideneiminate)(salen) or *N,N'*-1,2-phenylenebis-(salicylideneiminate)(salphen), X = Cl or Br] have been prepared by established routes, but attempts to prepare the iodo-analogue led to other products, including $[(salen)V(\mu\text{-}O)VO(salen)][I_5]$. It is not possible to prepare hydrazine or hydrazide complexes directly from the dihalides, but $[V(NH_2NHPh)_2(salen)]I$ was synthesised by an indirect route, and its structure determined by X-ray analysis. The phenylhydrazines are bound end-on. Several other new vanadium-(III) and (IV) species are described.

The realisation that a vanadium-based nitrogenase can be generated by micro-organisms which normally produce the molybdenum nitrogenase has stimulated reasearch into vanadium systems which fix nitrogen.[1] It is already known that vanadium(II)–pyrocatechol mixtures reduce dinitrogen to ammonia in aqueous alcoholic media in a restricted pH range near 10,[2] and several heterogeneous vanadium-containing nitrogen-fixing systems are known. No nitrogen-containing intermediates have been isolated from such systems, although it has been shown that polynuclear species are present in the vanadium(II)–catechol systems, and when a fixing solution is quenched in acid a small amount of hydrazine is formed. To date, only one stable vanadium dinitrogen complex has been characterised.[3]

We have been attempting to synthesise vanadium complexes containing dinitrogen and partially reduced dinitrogen species, and we describe here some researches based upon complexes containing Schiff bases. Stable vanadyl(IV) compounds of this kind are well known, and may be converted into $[VX_2L]$ (X = Cl or Br, L = Schiff-base dianion) by the action of $SOCl_2$[4] or PPh_3Br_2,[5] respectively. As Schiff bases, we selected H_2salen [*N,N'*-ethylenebis(salicylideneimine)] and H_2salphen [*N,N'*-1,2-phenylenebis(salicylideneimine)] for which, compounds $[VX_2L]$ are known for X = Cl or Br, but not for X = I. We also report some new reactions of $[VO(acac)_2]$ (acac = pentane-2,4-dionate).

Results and Discussion

The characterisation of the new complexes is summarised in Table 1.

(*i*) *Halogenation of* [VOL].—Although we were able to prepare $[VX_2L]$ (X = Cl or Br, L = salen or salphen) by the published routes,[4,5] reaction of [VO(salen)] with PPh_3I_2 gave $[VI(salen)(OPPh_3)]I$. The use of 1 molar equivalent of iodine yielded a complex in the form of black needles, which analysed approximately for VOI_2(salen). Recrystallised from MeCN at −20 °C they yielded similar crystals which were shown by X-ray structure analysis to be $[(salen)V(\mu\text{-}O)VO(salen)][I_5]\cdot$MeCN. This complex is a 1 : 1 electrolyte in MeCN and $MeNO_2$ and has a magnetic moment of 0.8 ± 0.1 μ_B per vanadium atom. It shows ν(V=O) in its IR spectrum at 880 cm^{-1}, in the region normally assigned to ν(V=O→V). The use of an excess of iodine in the preparative reaction gives the related salt $[(salen)V(\mu\text{-}O)VO(salen)][I_7]$. The structure of this cation, which contains both bridging and terminal oxygen atoms and, formally, both V^{IV} and V^{V}, will be discussed elsewhere.[6]

The complexes $[VX_2L]$ react with Li(OMe) in MeOH to yield $[V(OMe)_2L]$, of expected properties, which are immediately reconverted into [VOL] by water.

(*ii*) *Reactions of Halides with Hydrazines.*—The reaction of $[VX_2L]$ with hydrazines is solvent-dependent. In methanol or ethanol, $[VX_2L]$ (X = Cl or Br, L = salen or salphen) produce complexes VXL·2ROH (R = Me or Et). The complexes have solid-state magnetic moments at 293 K of *ca.* 2.8 μ_B, consistent with the presence of two unpaired electrons. We therefore formulate these species as vanadium(III) monohalogeno-complexes containing one co-ordinated alcohol molecule. There is ample precedent for co-ordinated alcohol in vanadium chemistry.[7] The hydrazines clearly function here as reducing agents rather than as ligands.

In non-protic solvents, such as MeCN, the products of the reactions with hydrazines or substituted hydrazines are dinuclear species of the formulae $[(VXL)_2]$. These have magnetic moments in the solid state of *ca.* 2.5 μ_B, somewhat lower than the spin-only value, and suggestive of some spin pairing. The materials show low conductances in MeCN and $MeNO_2$. The complex $[\{VCl(salen)\}_2]$, prepared from $[VCl_3(thf)_3]$ (thf = tetrahydrofuran) and Na_2(salen), has been shown[8] to contain a double halide bridge, and a sample prepared according to this literature method was found to be identical to our product. In our systems the hydrazines are clearly acting as reducing agents, and we were able to synthesise $[\{VX(salen)\}_2]$ employing $AlEt_2(OEt)$ in their stead.

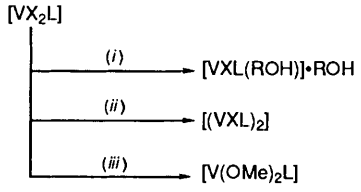
The complexes $[\{VClL\}_2]$ are converted into [VClL(ROH)]·ROH on warming in the alcohol under reflux for 5 min. The converse reaction is not so facile. Heating [VCl(salen)(MeOH)]·MeOH in thf under reflux for 15 h gave $[\{VCl(salen)\}_2]$, but the salphen analogue yielded [VCl(salphen)(MeOH)] under the same conditions.

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

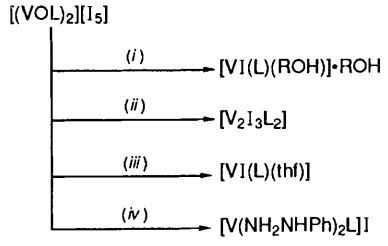
Table 1 Analyses and other physical data for new complexes

Complex		Colour	Yield(%)	Analysis[a] (%) C	H	N	Min.μ_B[b] 293 K
1	[VCl(salen)(MeOH)]·MeOH	Yellow	70	51.4(51.7)	5.3(5.2)	6.4(6.7)	2.79
2	[VCl(salen)(EtOH)]·EtOH	Yellow	60	53.7(54.1)	6.4(5.8)	6.1(6.3)	
3	[VBr(salen)(MeOH)]·MeOH	Yellow-brown	75	47.0(46.9)	4.8(4.8)	5.9(6.1)	2.69
4	[VBr(salen)(EtOH)]·EtOH	Yellow-brown	65	48.4(49.2)	5.7(5.3)	5.5(5.7)	
5	[VCl(salphen)(MeOH)]·MeOH	Yellow	65	56.5(56.7)	5.2(4.7)	6.0(6.0)	2.79
6	[VBr(salphen)(MeOH)]·MeOH	Brown	60	51.7(51.9)	4.8(4.3)	5.5(5.5)	2.81
7	$[\{VCl(salen)\}_2]$	Yellow	60	54.8(54.4)	3.3(3.9)	7.9(7.9)	2.47
8	$[\{VBr(salen)\}_2]$	Yellow	70	48.2(48.4)	3.3(3.5)	6.9(7.1)	2.55
9	$[\{VCl(salphen)\}_2]$	Yellow	90	58.9(59.9)	3.7(3.5)	6.5(7.0)	
10	$[\{VBr(salphen)\}_2]$	Yellow	95	52.8(53.9)	3.4(3.1)	6.6(6.5)	
11	$[V(OMe)_2(salen)]$	Red	70	55.3(55.5)	5.5(5.8)	7.1(6.8)	1.95
12	$[V(OMe)_2(salphen)]$	Red	70	61.8(61.8)	4.8(4.7)	6.8(6.1)	1.92
13	$[VI(salen)(OPPh_3)]I$	Brown	60	48.1(48.0)	3.3(3.4)	3.5(3.3)	2.19
14	$[V(salen)(OPPh_3)(MeOH)]I\cdot MeOH$	Yellow	55	54.6(55.0)	4.8(4.7)	3.8(3.6)	2.95
15	$[(salen)V(\mu\text{-}O)VO(salen)][I_5]\cdot MeCN$	Black	>70	30.3(30.4)	2.2(2.3)	4.7(5.2)	1.6
16[c]	[VI(salen)(MeOH)]·MeOH	Brown	64	42.0(42.5)	4.2(4.3)	5.3(5.5)	2.79
17[c]	[VI(salen)(EtOH)]·EtOH	Brown	60	44.2(44.7)	4.9(4.9)	5.2(5.2)	2.83
18[c]	$[VI(NMeNMe_2)(salen)]$[d]	Brown	25	43.9(44.1)	4.1(4.4)	10.2(10.8)	1.93
19[c]	[VI(salen)(thf)]	Yellow	80	46.3(46.5)	4.0(4.3)	5.7(5.4)	2.59
20[c]	$[V(NH_2NHPh)_2(salen)]I$[e]	Red	80	50.9(50.9)	4.5(4.4)	12.7(12.7)	2.84
21	$[VOI(acac)(OPPh_3)]$	Brown	60	47.5(48.0)	4.0(3.9)		2.05
22	$[\{VO(OEt)(acac)\}_2]$	Blue	75	40.0(39.8)	6.3(5.7)		1.62
23	$[\{VO(OMe)(acac)\}_2]$	Blue	75	36.5(36.5)	5.0(5.1)		1.57

[a] Required values in parentheses. [b] Per vanadium atom. [c] Yields calculated on basis of two vanadium atoms in complex **15** being reducible. [d] Iodine: 23.3 (24.5)%. [e] Iodine: 18.3 (19.2)%.



Scheme 1 Reactions of vanadium(IV) chlorides and bromides. X = Cl or Br, L = salen or salphen. (*i*) $PhNHNH_2$, ROH(R = Me or Et); (*ii*) $PhNHNH_2$, MeCN; (*iii*) Li(OMe), MeOH



Scheme 2 Reactions of $[(VOL)_2][I_5]$ (L = salen). (*i*) $PhNHNH_2$, ROH(R = Me or Et); (*ii*) $PhNHNH_2$, MeCN; (*iii*) $AlEt_2(OEt)$, thf; (*iv*) $AlEt_2(OEt)$, $PhNHNH_2$, MeCN

The reactions of the iodo-species that we isolated with hydrazines in alcohols are similar to those of the chloro- and bromo-species. Thus, $[(salen)V(\mu\text{-}O)VO(salen)][I_5]$ and phenylhydrazine gave [VI(salen)(ROH)]·ROH, and $[VI(salen)(OPPh_3)]I$ and phenylhydrazine in methanol produce the vanadium(III) complex formulated as $[V(salen)(OPPh_3)(MeOH)]I\cdot MeOH$, which may be regarded as a derivative of [VX(salen)(ROH)]·ROH. In contrast, the reactions of iodo-species with hydrazines in non-protic solvents are altogether different. Thus, $[(salen)V(\mu\text{-}O)VO(salen)][I_5]$ with phenylhydrazine or *N*-phenyl-*N'*-(trimethylsilyl)hydrazine in MeCN gives black crystals analysing for $V_2I_3(salen)_2$. These were not further characterised. Trimethyl(trimethylsilyl)hydrazine gave a product formulated as $[V(NMeNMe_2)(salen)]I$, but we were unable to obtain crystals suitable for X-ray analysis. An alternative reductant, $AlEt_2(OEt)$, and $[(salen)V(\mu\text{-}O)VO(salen)][I_5]$ yielded a precipitate of [VI(salen)(thf)] in thf, but in acetonitrile a red solution was obtained and addition of phenylhydrazine gave $[V(NH_2NHPh)_2(salen)]I$, characterised by X-ray structure analysis. The reaction Schemes 1 and 2 summarise the reactions of vanadium halides with hydrazines.

(*iii*) *The Structure of* $[V(NH_2NHPh)_2(salen)]I$.—In the crystal the cationic complex $[V(NH_2NHPh)_2(salen)]^+$ and the iodide anion both lie on two-fold symmetry axes. The V atom has six-fold, roughly octahedral co-ordination, with the salen ligating atoms forming the equatorial plane, and the hydrazine ligands in the apical sites, Fig. 1. The two-fold axis lies in the equatorial plane. Atomic coordinates are listed in Table 2 and molecular dimensions in Table 3.

The salen ligand is formed of two almost parallel planes connected through the central *gauche* N–C–C–N link. None of the atoms O(1) to C(8) in this ligand is far removed from their mean plane [maximum deviation of 0.12 Å for N(8)] and the normal of this plane makes an angle of 28.9(1)° with the normal to the equatorial N_2O_2 mean plane. The V–O and V–N co-ordination dimensions in the equatorial plane are quite characteristic of vanadium salen complexes.

In the apical sites the hydrazine ligands are bound end-on through the NH_2 group to the V atom with the N(20)–V–N(20′) angle 170.5(2)°. The angles about N(20) show a tetrahedral arrangement, with V–N(20)–N(21) 110.8(3)°, as expected from sp^3-hybridised orbitals at N(20). The V–N(hydrazine) separations of 2.170(4) Å are those to be expected of a V^{III}–N co-ordinate bond and the N–N distance in the hydrazines, 1.434(6), is consistent with a single bond and similar to those recorded for $[VCl(NNMePh)(NH_2NMePh)_2]^+$ which shows side-on co-ordination of the hydrazine ligands.[9] The hydrogen atom H(21) of the NHPh group is directed back towards the salen ligand and appears to form weak, bifurcated, hydrogen bonds with O(1) and the anion I.

A much stronger hydrogen bond is formed between H(20b) and a related anion; here the H ··· I distance is short at 2.66(5) Å and the N–H ··· I arrangement is essentially linear. The second hydrogen atom of the NH_2 group is, unusually, not involved in any hydrogen bonds. The cations and anions are

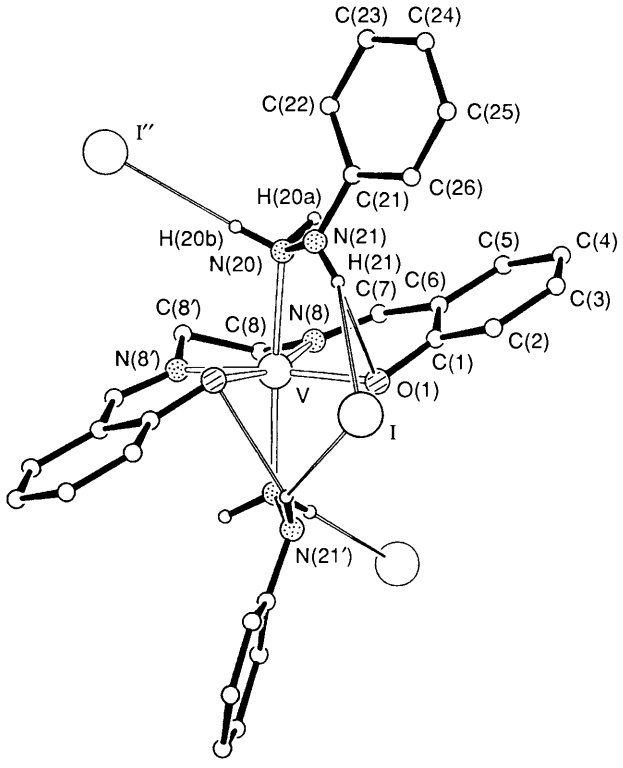


Fig. 1 View of the cation $[V(NH_2NHPh)_2(salen)]^+$ and the iodide anions connected to it through hydrogen bonds (marked with thin bonds). The atom-numbering scheme is shown; symmetry relations, noted by primes, are detailed in Table 3.

Table 2 Final atomic coordinates (fractional × 10^4) for $[V(NH_2NHPh)_2(salen)]I$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
V	0	5657.8(9)	2500
O(1)	1035(4)	4752(3)	2974(1)
C(1)	1164(6)	4863(5)	3495(2)
C(2)	1307(6)	3900(6)	3808(2)
C(3)	1474(6)	4005(6)	4349(3)
C(4)	1529(7)	5038(8)	4587(3)
C(5)	1391(6)	5991(6)	4291(3)
C(6)	1170(6)	5925(5)	3739(2)
C(7)	1013(6)	6968(5)	3440(3)
N(8)	640(5)	7028(3)	2958(2)
C(8)	621(7)	8130(4)	2690(2)
N(20)	−1813(5)	5506(4)	3022(2)
H(20a)	−1739(59)	5931(47)	3373(22)
H(20b)	−2669(60)	5773(42)	2870(22)
N(21)	−2071(6)	4347(4)	3154(2)
H(21)	−1336(52)	3964(40)	3089(19)
C(21)	−2757(6)	4098(5)	3625(2)
C(22)	−3796(6)	4790(5)	3832(2)
C(23)	−4496(7)	4469(6)	4293(3)
C(24)	−4172(9)	3466(7)	4539(3)
C(25)	−3147(8)	2774(6)	4328(3)
C(26)	−2439(7)	3086(5)	3876(2)
I	0	1753.6(4)	2500

thus connected through weak and strong hydrogen bonds in a two-dimensional network in the crystal. Interactions in the third dimension are at normal van der Waals distances.

(*iv*) *Reactions of* $[VO(acac)_2]$.—Our experiments with $[VO(acac)_2]$ were not fruitful. Attempts to prepare $[VX_2(acac)_2]$ using PPh_3X_2 (X = Br or I) produced $[VOBr_2(OPPh_3)_2]$ (as previously reported)[5] and the new compound $[VOI(acac)(OPPh_3)]$, respectively. The complex $[VO(acac)_2]$ with hydrazines in alcohols (ROH) yields the known blue, crystalline $[\{VO(OR)(acac)\}_2]$,[10] which regenerates $[VO(acac)_2]$ upon reaction with Hacac in CH_2Cl_2. These reactions were not pursued.

Table 3 Molecular dimensions (bond lengths in Å, angles in °) in $[V(NH_2NHPh)_2(salen)]I$ with e.s.d.s in parentheses

(*a*) Around the V atom

V–O(1)	1.881(3)	V–N(20)	2.170(4)
V–N(8)	2.082(5)		
O(1)–V–O(1′)	110.4(2)	N(8)–V–N(8′)	77.6(2)
O(1)–V–N(8)	86.6(2)	N(8)–V–N(20)	87.6(2)
O(1)–V–N(8′)	161.6(2)	N(8)–V–N(20′)	99.9(2)
O(1)–V–N(20)	88.8(2)	N(20)–V–N(20′)	170.5(2)
O(1)–V–N(20′)	85.8(2)		

(*b*) In the salen ligand

O(1)–C(1)	1.329(6)	C(5)–C(6)	1.410(7)
C(1)–C(2)	1.394(7)	C(6)–C(7)	1.455(8)
C(1)–C(6)	1.400(7)	C(7)–N(8)	1.270(7)
C(2)–C(3)	1.380(8)	N(8)–C(8)	1.471(6)
C(3)–C(4)	1.364(9)	C(8)–C(8′)	1.515(11)
C(4)–C(5)	1.359(8)		
V–O(1)–C(1)	128.4(3)	C(1)–C(6)–C(5)	119.0(6)
O(1)–C(1)–C(2)	119.3(5)	C(1)–C(6)–C(7)	122.3(5)
O(1)–C(1)–C(6)	121.6(5)	C(5)–C(6)–C(7)	118.7(6)
C(2)–C(1)–C(6)	119.1(5)	C(6)–C(7)–N(8)	124.9(5)
C(1)–C(2)–C(3)	119.8(6)	V–N(8)–C(7)	124.7(4)
C(2)–C(3)–C(4)	121.4(6)	V–N(8)–C(8)	115.7(4)
C(3)–C(4)–C(5)	119.9(6)	C(7)–N(8)–C(8)	119.6(5)
C(4)–C(5)–C(6)	120.8(6)	N(8)–C(8)–C(8′)	107.5(4)

(*c*) In the hydrazine ligand

N(20)–H(20a)	1.02(6)	C(21)–C(26)	1.389(7)
N(20)–H(20b)	0.95(6)	C(22)–C(23)	1.393(8)
N(20)–N(21)	1.434(6)	C(23)–C(24)	1.375(9)
N(21)–H(21)	0.85(5)	C(24)–C(25)	1.377(9)
N(21)–C(21)	1.385(7)	C(25)–C(26)	1.372(8)
C(21)–C(22)	1.382(7)		
V–N(20)–H(20a)	115.6(32)	N(21)–C(21)–C(22)	122.0(6)
V–N(20)–H(20b)	113.6(32)	N(21)–C(21)–C(26)	118.3(5)
V–N(20)–N(21)	110.8(3)	C(22)–C(21)–C(26)	119.5(5)
H(20a)–N(20)–H(20b)	104.1(44)	C(21)–C(22)–C(23)	119.5(6)
H(20a)–N(20)–N(21)	106.4(31)	C(22)–C(23)–C(24)	120.5(6)
H(20b)–N(20)–N(21)	105.5(31)	C(23)–C(24)–C(25)	119.8(6)
N(20)–N(21)–H(21)	109.1(33)	C(24)–C(25)–C(26)	120.3(6)
N(20)–N(21)–C(21)	119.0(5)	C(21)–C(26)–C(25)	120.4(6)
H(21)–N(21)–C(21)	115.9(34)		

(*d*) In the hydrogen bonds

N(20) · · · I″	3.608(5)	N(21) · · · I	4.001(5)
H(20b) · · · I″	2.66(5)	H(21) · · · O(1)	2.45(5)
N(21) · · · O(1)	3.013(6)	H(21) · · · I	3.26(5)
N(20)–H(20b) · · · I″	173(4)	N(21)–H(21) · · · I	147(4)
N(21)–H(21) · · · O(1)	125(4)		

Primed atoms are related by the symmetry operations; ′ $-x, y, \frac{1}{2}-z$ and ″ $x-\frac{1}{2}, \frac{1}{2}+y, \frac{1}{2}-z$

Conclusion

The compounds $[VI_2L]$ are not obtainable by parallel routes to those which are successful for $[VCl_2L]$ and $[VBr_2L]$. However, novel vanadium-(IV) and (V) species are produced by reactions with I_2. A bis(phenylhydrazine) derivative of vanadium(III) with end-on hydrazine co-ordination was obtained, but in general hydrazines reduce vanadium(IV) materials without incorporation of the hydrazine. The iodide–vanadium systems seem to

differ from the chloride and bromide systems, presumably because I^- is a good leaving group. The bis(phenylhydrazine) complex seems an appropriate material from which to synthesise diazenide and hydrazine derivatives of vanadium.

Experimental

General.—Solvents were dried and distilled before use and all reactions carried out under a dry dinitrogen atmosphere. Infrared spectra were recorded on a Perkin-Elmer 883 instrument as Nujol mulls and magnetic susceptibilities were measured at 293 K by the Faraday method. Microanalyses were by Mr. C. J. Macdonald (Nitrogen Fixation Laboratory) or by Butterworth Laboratories. The complexes [VO(salen)],[8] $[VCl_2(salen)]$,[4] $[VBr_2(salen)]$,[5] [VO(salphen)],[8] $[VCl_2(salphen)]$[4] and $[VBr_2(salphen)]$[5] were prepared by literature methods. Analyses, yields, and other physical data are presented in Table 1.

Reactions of Vanadium(IV) *Dihalides with Hydrazines in Alcohols:*[VCl(salen)(MeOH)]·MeOH **1.**—A suspension of $[VCl_2(salen)]$ (1.95 g, 5 mmol) in methanol (25 cm^3) was stirred at room temperature and phenylhydrazine (0.54 g, 5 mmol) added dropwise. There was immediate gas evolution and a clear dark red solution formed. This was warmed to 50 °C, and filtered leaving no residue. On cooling, yellow *crystals* (1.4 g) precipitated, which were washed with methanol and diethyl ether and dried *in vacuo*. The same compound was obtained when *p*-nitrophenylhydrazine or hydrazine hydrate was used instead of phenylhydrazine.

Other compounds synthesised similarly were [VCl(salen)(EtOH)]·EtOH **2**, [VBr(salen)(MeOH)]·MeOH **3**, [VBr(salen)(EtOH)]·EtOH **4** and [VX(salphen)(MeOH)]·MeOH (X = Cl, **5**; or Br, **6**).

Reactions of Vanadium(IV) *Dihalides with Hydrazines or Silyl-substituted Hydrazines in Non-protic Solvents:*$[\{VCl(salen)\}_2]$ **7.**—A suspension of $[VCl_2(salen)]$ (1.95 g, 5 mmol) was stirred in acetonitrile (50 cm^3) at 20 °C. Phenylhydrazine (1.08 g, 10 mmol) was added and the black precipitate turned golden-yellow over 30 min. Triethylamine (2 cm^3) (to cause triethylamine hydrochloride rather than phenylhydrazine hydrochloride to form) was added; the colour of the *precipitate* did not change but its bulk lessened. After 10 min it was filtered off and washed with acetonitrile and diethyl ether. Yield 1.0 g.

Other compounds prepared similarly were $[\{VBr(salen)\}_2]$ **8** and $[\{VX(salphen)\}_2]$ (X = Cl, **9**; or Br, **10**). For these preparations various silylated hydrazines were used, generally initially at −20 °C, and no triethylamine was added.

$[V(OMe)_2(salen)]$ **11.**—A suspension of $[VCl_2(salen)]$ (3.9 g, 10 mmol) in methanol (50 cm^3) was stirred at 20 °C. Lithium methoxide (0.76 g, 20 mmol) was added and the black suspension became a red crystalline *precipitate*; it was filtered off and washed with methanol and ether. Yield 2.0 g. A similar reaction starting with $[VCl_2(salphen)]$ gave $[V(OMe)_2(salphen)]$ **12.**

$[VI(salen)(OPPh_3)]I$ **13.**—Triphenylphosphine diiodide was made by mixing solutions containing equimolar quantities of triphenylphosphine and iodine in acetonitrile at 20 °C. The yellow precipitate was filtered off and washed with acetonitrile and diethyl ether. The compound [VO(salen)] (3.3 g, 10 mmol) and triphenylphosphine diiodide (5.2 g, 10 mmol) were heated to reflux temperature in acetonitrile (100 cm^3) and filtered hot; on cooling overnight 6.0 g of brown crystals separated. These were again recrystallised from acetonitrile giving 5.1 g of product, which was washed with acetonitrile and ether and dried *in vacuo*.

$[V(salen)(OPPh_3)(MeOH)]I$·MeOH **14.**—Compound **13** (2.6 g, 3.1 mmol) in a suspension in methanol (50 cm^3) was stirred at room temperature and phenylhydrazine (0.4 g, 3.7 mmol) added dropwise. There was immediate gas evolution and a clear dark brown solution formed. This was filtered at 50 °C leaving no residue. On cooling, brown *crystals* (1.3 g) precipitated; they were washed with methanol and diethyl ether and dried *in vacuo*.

$[(salen)V(\mu\text{-}O)VO(salen)][I_5]$·MeCN.—The compound [VO(salen)] (5.0 g, 15 mmol) was heated under reflux in acetonitrile (375 cm^3) and filtered hot. Iodine (3.05 g, 12 mmol) was extracted into the hot solution during 1 h by use of a Soxhlet apparatus. The solution became black. It was allowed to cool overnight to room temperature when black *needles* (5.6 g) crystallised; they were washed with acetonitrile and diethyl ether and dried *in vacuo*. Recrystallisation of a small portion from acetonitrile gave longer black needles suitable for X-ray structure analysis.

[VI(salen)(MeOH)]·MeOH] **16.**—Compound **15** (2.95 g, 2.2 mmol) in suspension in methanol (80 cm^3) was stirred at room temperature and phenylhydrazine (0.54 g, 5.0 mmol) added dropwise. There was immediate gas evolution and a red-brown solution formed; it was filtered at 40 °C leaving no residue. The volume of the solution was reduced *in vacuo* to 20 cm^3 and it was cooled to −20 °C. Brown *crystals* were washed with methanol and diethyl ether and dried *in vacuo*. Yield 1.6 g, 3.2 mmol.

The complex [VI(salen)(EtOH)]·EtOH **17** was synthesised similarly.

$[VI(NMeNMe_2)(salen)]$ **18.**—Compound **15** (1.14 g, 0.85 mmol) was stirred in suspension at 0 °C in MeCN (20 cm^3). The compound $Me_2NNMe(SiMe_3)$ (2 cm^3) was added giving an immediate red colour. The solution was allowed to warm to 20 °C then diethyl ether (20 cm^3) was added. The mixture was filtered immediately and kept at −20 °C for 5 d. Brown *crystals* precipitated (0.2 g, 0.4 mmol); they were washed with MeCN–diethyl ether (1:1) and then with ether and dried *in vacuo*.

[VI(salen)(thf)] **19.**—Compound **15** (3.0 g, 2.2 mmol) was stirred in thf (80 cm^3) at 20 °C giving a black suspension. Diethylaluminium ethoxide (20 cm^3, 25% in toluene, 32 mmol) was added and the *suspension* turned yellow-brown over 3 d; it was filtered off and washed with thf and hexane.

$[V(NH_2NHPh)_2(salen)]I$ **20.**—Compound **15** (3.0 g, 2.2 mmol) was stirred in acetonitrile (80 cm^3) at 20 °C giving a black suspension. Diethylaluminium ethoxide (20 cm^3, 25% in toluene, 32 mmol) was added, giving a clear dark red solution. Phenylhydrazine (2 cm^3) was added and solvent slowly removed *in vacuo* until crystallisation began; diethyl ether (150 cm^3) was added and the mixture was set aside at −20 °C. The dark red crystals (2.3 g, 3.5 mmol) that precipitated were washed with acetonitrile–diethyl ether (1:1) then with diethyl ether and dried *in vacuo*. Crystals suitable for X-ray analysis were obtained from MeCN solution by addition of diethyl ether.

$[VOI(acac)(OPPh_3)]$ **21.**—Oxobis(pentane-2,4-dionato)-vanadium (1.34 g, 5 mmol) was added to PPh_3I_2 (2.6 g, 5 mmol) in acetonitrile (50 cm^3). The mixture was heated briefly to 60 °C, filtered hot, and set aside to cool. Brown *crystals* separated; these were recrystallised from MeCN. Yield 1.6 g, 3 mmol.

$[\{VO(OEt)(acac)\}_2]$ **22.**—Oxobis(pentane-2,4-dionato)-vanadium (4.0 g, 15 mmol) was stirred in absolute ethanol (50 cm^3) at 20 °C. The compound $N_2H_4{\cdot}H_2O$ (0.75 g, 15 mmol) was added and the turquoise suspension turned dull blue. After 2 h the blue powder was filtered off, washed with diethyl ether, and recrystallised from dichloromethane–hexane as blue *crystals*. Yield 2.4 g, 5.6 mmol. $[\{VO(OMe)(acac)\}_2]$ **23** was prepared similarly.

Reaction of [(salen)V(μ-O)VO(salen)][I_5] *with Phenylhydrazine in Acetonitrile.*—Compound **15** (2.6 g, 2 mmol) was suspended in acetonitrile (100 cm^3) and treated with phenylhydrazine (0.5 g, 4.6 mmol) giving a black solution which was filtered at 60 °C and then set aside for 3 d at −20 °C. Black *crystals* formed. They were washed with MeCN and diethyl ether and dried *in vacuo*. Yield 0.65 g [Found: C, 37.7; H, 2.5; N, 5.4. [V_2I_3(salen)$_2$] requires C, 37.8; H, 2.8; N, 5.5%]. Magnetic moment calculated on this basis in the solid state (293 K) = 2.40 μ_B per vanadium atom.

Crystal Structure Analysis of [V(NH_2NHPh)$_2$(salen)]I.—*Crystal data* $C_{28}H_{30}IN_6O_2V$, M = 660.4, orthorhombic, space group *Pbcn* (no. 60), a = 9.462(1), b = 11.846(1), c = 25.238(2) Å, U = 2828.9 $Å^3$, Z = 4, D_c = 1.550 g cm^{-3}, F(000) = 1328, μ(Mo-Kα) = 14.5 cm^{-1}, λ(Mo-K$\bar{\alpha}$) = 0.710 69 Å.

Crystals are small, translucent, red plates. One, *ca.* 0.12 × 0.10 × 0.04 mm, was mounted in air on a glass fibre. After preliminary photographs, it was transferred to our Enraf-Nonius CAD4 diffractometer for determination of accurate cell dimensions (from 25 reflections with θ *ca.* 10.5°, each centred in four orientations) and measurement of diffraction intensities (to θ_{max} = 20°). During processing, the intensities were corrected for Lorentz-polarisation effects, absorption (from ψ-scan measurements), and to eliminate negative intensities (by Bayesian statistics); from the monitoring of two reflections throughout the data collection, no deterioration of the crystal was observed.

Of the 1320 independent reflections input to the SHELX program[11] system, 919 have $I > 2\sigma_I$. The structure was determined by the heavy-atom method, and refined by full-matrix least-squares methods, allowing all non-hydrogen atoms anisotropic thermal parameters. The three hydrogen atoms on the N atoms of the hydrazine ligand were identified from difference maps and were refined independently with isotropic thermal parameters; the remaining hydrogen atoms were included in idealised positions and set to ride on their bonded C atoms. Refinement converged with R = 0.049 and R_g = 0.034[11] for all 1320 data weighted $w = \sigma_F^{-2}$. In a final difference map there were no peaks of significance; all features were between −0.33 and +0.35 e $Å^{-3}$.

Scattering-factor curves for C, H, N, O, V and I^- were taken from ref. 12. Computer programs (in addition to SHELX) used in this analysis have been listed in Table 4 of ref. 13 and were run on the MicroVAX II in this Laboratory.

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

References

1 R. L. Robson, R. R. Eady, T. H. Richardson, R. W. Miller, M. Hawkins and J. R. Postgate, *Nature (London)*, 1986, **322**, 388.
2 N. P. Luneva, L. A. Nikonova and A. E. Shilov, *Kinet. Katal.*, 1980, **21**, 1041.
3 J. J. H. Edema, A. Meetsma and S. Gambarotta, *J. Am. Chem. Soc.*, 1989, **111**, 6878.
4 M. Pasquali, F. Marchetti and C. Floriani, *Inorg. Chem.*, 1979, **18**, 2401.
5 K. P. Callahan and P. J. Durand, *Inorg. Chem.*, 1980, **19**, 3211.
6 A. Hills, D. L. Hughes, G. J. Leigh and J. R. Sanders, *J. Chem. Soc., Dalton Trans.*, 1991, 61.
7 F. A. Cotton, S. A. Duraj, L. E. Manzer and W. J. Roth, *J. Am. Chem. Soc.*, 1985, **107**, 3850.
8 M. Mazzanti, S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *Inorg. Chem.*, 1986, **25**, 2308.
9 J. Bultitude, L. F. Larkworthy, D. C. Povey, G. W. Smith, J. R. Dilworth and G. J. Leigh, *J. Chem. Soc., Chem. Commun.*, 1986, 1748.
10 M. M. Musiani, F. Milani, R. Graziani, M. Vidali, V. Casellato and P. A. Vigato, *Inorg. Chim. Acta*, 1982, **61**, 115.
11 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.
12 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.
13 S. N. Anderson, R. L. Richards and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1986, 245.

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