New compounds of tetradentate Schiff bases with vanadium(IV) and vanadium(V) †

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A new range of potentially tetradentate proligands, H_2L, derived from aromatic aldehydes and ketones and aliphatic diamines has been prepared. Their vanadyl(IV) and vanadyl(V) complexes [VO(L)] and [VO(L)]$^+$, and also some adducts [VO(L)→VO(L)]$^+$, have been synthesized. The structures of four selected complexes have been determined and it is shown that these must be a result of both steric and electronic factors that make prediction of conformation and stacking difficult. The adducts [VO(L)→VO(L)]$^+$ have structures that persist in solution in dichloromethane, where they can undergo redox chemistry, but they apparently dissociate into their component complexes in the donor solvent acetonitrile.

Introduction

The family of Schiff bases derived from diamines (especially ethane-1,2-diamine) and phenolic aldehydes, H_2L, has proved to be the source of versatile ligands for many transition metals including vanadium(IV) and vanadium(V).[1] They normally form the basis of square pyramidal or octahedral complexes in which the four Schiff base donor atoms, two oxygen atoms and two nitrogen atoms, co-ordinate in an approximately planar manner. Most of these complexes are vanadyl complexes, [VO(L)] and [VO(L)]$^+$, generally five-co-ordinate due to the strong *trans* influence of the doubly bonded oxygen. However, although the vanadium(V) complexes to be discussed in this paper are always five-co-ordinate in the solid state, the reported vanadium(IV) complexes may not be. Some are stacked up in the crystal in infinite chains, . . . V=O→V=O→V=O . . ., depending upon the Schiff base. Some are green and have v(V=O) at *ca.* 980 cm^{-1} and are mononuclear in the solid state, and others are orange-to-chocolate brown and polynuclear and have v(V=O) at *ca.* 860 cm^{-1}. Our new compounds generally show this pattern. Why some compounds stack and others do not has not been established.[2]

These vanadium(IV) and vanadium(V) complexes always give[3] rise to solid state adducts of the form [V^{IV}=O→V^V=O]$^+$, whatever the nature of the tetradentate Schiff-base anion. The adduct derived from H_2salen [*N,N'*-bis(salicylidene)ethane-1,2-diamine] dissociates into its component complexes in solution in MeCN.[3]

We have recently published[4] a description of some new Schiff bases and their vanadyl(IV) complexes. This paper expands that study to further homologous Schiff bases and their vanadyl(V) complexes, and also to some of the related vanadyl(IV)/vanadyl(V) adducts. None of the new systems carries extra potential donors to the vanadium in its substituents.

Results

Schiff bases, H_2L, and their oxovanadium(IV) complexes, [VO(L)]

The new Schiff bases are detailed in Table 1. They fall into three

classes, those where the substituents in the aromatic rings are varied, those where the nature of the bridge between the aromatic rings is varied, and those where both are varied. The compounds were characterised solely by IR and NMR spectroscopy because the method of synthesis is well established and the bases were effectively characterised subsequently as their vanadyl(IV) derivatives (Table 2). These derivatives were generally synthesized by heating oxobis(pentane-2,4-dionato)-vanadium(IV) and the Schiff base in an appropriate solvent to reflux, except for that of H_2(hap-1,3-pn) (see Experimental section and Table 2, and also the footnote to Table 1 for an explanation of the designations of the Schiff bases).

Why these complexes, [VO(L)], are either mononuclear and green or linearly polymeric and brown in the solid state, depending upon L, has been rationalised in terms of electronic properties.[5] A plot of v(V=O), apparently always determined in the same medium, against the sum of appropriate Hammett σ factors was shown to be linear for four complexes. The range of v(V=O) was 978–983 cm^{-1} with an error on each value of ±1 cm^{-1}. The value of v(V=O) was correlated with the charge on vanadium and the consequent acceptor ability of the complex, the more electron deficient the vanadium the greater is the drive towards solid state polymerisation.[5] In solution rather than in the solid state all the complexes are green and therefore presumably monomeric. We have now made a similar plot for our mononuclear complexes in the solid state, and find no linear correlation for eight compounds with a range of v(V=O) of more than 30 cm^{-1}. We conclude that control of the solid-state structure is unlikely to be simply electronic.

In at least three cases we have been able to isolate two forms of complex with the same Schiff base, though unfortunately we have not been able to characterise both structurally. This is the first time such isomerism has been seen with tetradentate L, though there are reports of similar behaviour in other Schiff base systems.[6] The data seem to confirm that in the substituted salen derivatives the monomeric form is favoured unless strong electron-withdrawing groups are present. An extension of the dimethylene chain to trimethylene also appears to favour polymer formation. In the hope of confirming this postulate, the crystal structure of the chocolate brown compound [VO{salnptn(3-OMe)$_2$}] was obtained. This is a species of which a green form may also be prepared. On drying these brown crystals they turned green reversibly, but otherwise the material seemed little changed. The brown crystals (Fig. 1)

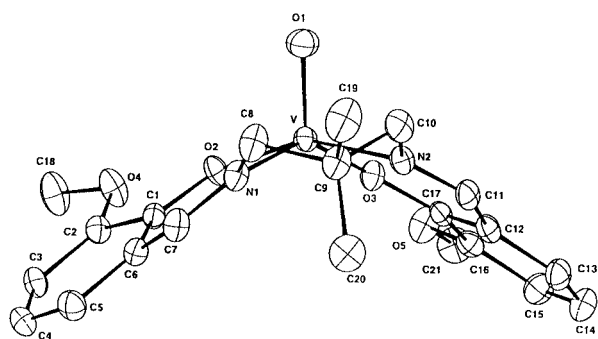† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4437/

Table 1 New tetradentate Schiff bases[a]

Amine	Aldehyde/ketone	Abbreviated symbol	Yield (%)
$NH_2CH_2CH_2NH_2$	$2\text{-}OH\text{-}3\text{-}OMeC_6H_3CHO$	$H_2\{salen(3\text{-}OMe)_2\}$	95
$NH_2CH_2CH_2NH_2$	$2\text{-}OH\text{-}5\text{-}OMeC_6H_3CHO$	$H_2\{salen(5\text{-}OMe)_2\}$	95
$NH_2CH_2CH_2NH_2$	$2\text{-}OH\text{-}5\text{-}MeC_6H_3CHO$	$H_2\{salen(5\text{-}Me)_2\}$	73
$NH_2CH_2CH_2NH_2$	$2,3\text{-}(OH)_2C_6H_3CHO$	$H_2\{salen(3\text{-}OH)_2\}$	81
$NH_2CHMeCH_2NH_2$	$2\text{-}OHC_6H_4CHO$	$H_2(sal\text{-}1,2\text{-}pn)$	98
$NH_2CHMeCH_2NH_2$	$2\text{-}OH\text{-}3\text{-}OMeC_6H_3CHO$	$H_2\{sal\text{-}1,2\text{-}pn(3\text{-}OMe)_2\}$	88
$NH_2CHMeCH_2NH_2$	$2\text{-}OH\text{-}5\text{-}BrC_6H_3CHO$	$H_2\{sal\text{-}1,2\text{-}pn(5\text{-}Br)_2\}$	73
$NH_2CH_2CH_2CH_2NH_2$	$2\text{-}OHC_6H_4CHO$	$H_2(sal\text{-}1,3\text{-}pn)$	61
$NH_2CH_2CH_2CH_2NH_2$	$2\text{-}OH\text{-}5\text{-}BrC_6H_3CHO$	$H_2\{sal\text{-}1,3\text{-}pn(5\text{-}Br)_2\}$	54
$NH_2CH_2CH_2CH_2NH_2$	$2\text{-}OH\text{-}3\text{-}OMeC_6H_3CHO$	$H_2\{sal\text{-}1,3\text{-}pn(3\text{-}OMe)_2\}$	47
$NH_2CH_2CMe_2CH_2NH_2$	$2\text{-}OHC_6H_4CHO$	$H_2(salnptn)$	92
$NH_2CH_2CMe_2CH_2NH_2$	$2\text{-}OH\text{-}5\text{-}BrC_6H_3CHO$	$H_2\{salnptn(5\text{-}Br)_2\}$	35
$NH_2CMe_2CH_2NH_2$	$2\text{-}OHC_6H_4CHO$	$H_2(salibn)$	92
$NH_2CH_2CH_2NH_2$	$2\text{-}OHC_6H_4C(Me)O$	$H_2(hapen)$	93
$NH_2CH_2CH_2NH_2$	$2\text{-}OH\text{-}4\text{-}OMeC_6H_3C(Me)O$	$H_2\{hapen(4\text{-}OMe)_2\}$	93
$NH_2CHMeCH_2NH_2$	$2\text{-}OHC_6H_4C(Me)O$	$H_2(hap\text{-}1,2\text{-}pn)$	77
$NH_2CH_2CH_2CH_2NH_2$	$2\text{-}OHC_6H_4C(Me)O$	$H_2(hap\text{-}1,3\text{-}pn)$	86

[a] $H_2(salen) = 1,2\text{-}C_6H_4(OH)CH=NCH_2CH_2N=CHC_6H_4(OH)\text{-}1,2$; additional substituents in the aromatic rings are indicated here and elsewhere directly by 5-Me, 3-OMe, *etc.*; $H_2(sal\text{-}1,2\text{-}pn) = 1,2\text{-}C_6H_4(OH)CH=NCMeHCH_2N=CHC_6H_4(OH)\text{-}1,2$; $H_2(sal\text{-}1,3\text{-}pn) = 1,2\text{-}C_6H_4(OH)CH=NCH_2\text{-}CH_2CH_2N=CHC_6H_4(OH)\text{-}1,2$; $H_2(salnptn) = 1,2\text{-}C_6H_4(OH)CH=NCH_2CMe_2CH_2N=CHC_6H_4(OH)\text{-}1,2$; $H_2(salibn) = 1,2\text{-}C_6H_4(OH)CH=NCH_2CH_2\text{-}CHMeN=CHC_6H_4(OH)\text{-}1,2$; $H_2(hapen) = 1,2\text{-}C_6H_4(OH)CMe=NCH_2CH_2N=CMeC_6H_4(OH)\text{-}1,2$; $H_2(hap\text{-}1,2\text{-}pn) = 1,2\text{-}C_6H_4(OH)CMe=NCHMe\text{-}CH_2N=CMeC_6H_4(OH)\text{-}1,2$; $H_2(hap\text{-}1,3\text{-}pn) = 1,2\text{-}C_6H_4(OH)CMe=NCH_2CH_2CH_2N=CMeC_6H_4(OH)\text{-}1,2$.

Table 2 New vanadyl(IV) complexes

Compound	Yield (%)	$\tilde{\nu}(V=O)/cm^{-1}$	Colour	Preparative solvent	Analysis CHN (%) (Calc.)
$[VO\{salen(5\text{-}Me)_2\}]$	92	959	Green	MeOH	59.8(59.8); 4.9(5.0); 7.7(7.8)
$[VO\{salen(3\text{-}OH)_2\}]$	80	970	Green	MeCN	52.5(52.6); 3.7(3.9); 7.8(7.7)
$[VO\{sal\text{-}1,2\text{-}pn(3\text{-}OMe)_2\}]\cdot H_2O$	76	987	Green	MeOH	52.9(53.6); 4.8(5.2); 6.4(6.6)
$[VO\{salen\text{-}1,2\text{-}pn(5\text{-}Br)_2\}]$	70	980	Green	MeOH/MeCN	40.4(40.4); 2.6(2.8); 5.4(5.6)
$[VO\{sal\text{-}1,2\text{-}pn(5\text{-}Br)_2\}]$	77	865	Orange	MeOH	39.6(40.4); 2.7(2.8); 5.3(5.6)
$[VO(sal\text{-}1,3\text{-}pn)]$	85	862	Orange	MeCN	Not analysed
$[VO\{sal\text{-}1,3\text{-}pn(5\text{-}Br)_2\}]\cdot 0.5CH_2Cl_2$	76	872	Orange	CH_2Cl_2	39.8(40.4); 2.6(3.1); 5.4(5.4)
$[VO\{sal\text{-}1,3\text{-}pn(3\text{-}OMe)_2\}]$	84	861	Orange	MeCN	Not analysed
$[VO(salibn)]$	81	991	Turquoise	MeOH	Not analysed
$[VO\{salnptn(3\text{-}OMe)_2\}]$	66	986, 860	Orange-brown	MeCN	57.9(57.9); 5.6(5.6); 6.7(6.4)
$[VO\{salnptn(5\text{-}Br)_2\}]$	91	962	Orange	MeCN	42.7(42.8); 3.3(3.4); 5.1(5.3)
$[VO\{hapen(4\text{-}OMe)_2\}]$	93	978	Green	MeOH	57.0(57.0); 5.3(5.3); 6.5(6.5)
$[VO(hap\text{-}1,2\text{-}pn)]\cdot MeOH$	83	989, 973	Green	MeOH	58.7(59.0); 5.9(5.9); 6.9(6.8)
$[VO(hap\text{-}1,3\text{-}pn)]$	15–39	842	Orange	MeOH	62.1(60.8); 5.9(5.4); 7.4(7.5)

Fig. 1 Molecular structure of $[VO\{salnptn(3\text{-}OMe)_2\}]$.

Table 3 A comparison of the dimensions of the two vanadyl(IV) salnptn derivatives

Dimension (Å or °)	$[VO\{salnptn\text{-}(3\text{-}OMe)_2\}]$	$[VO(salnptn)]$[6]
V–O(1)	1.583(3)	1.627(4)
V–O(2), V–O(3)	1.950(3), 1.951(3)	1.950(4), 1.941(4)
V–N(1), V–N(2)	2.075(4), 2.085(3)	2.098(5), 2.090(5)
O(1)···V′	Not aligned	2.245(4)
Above O(2)O(3)N(1)N(2) plane	0.530(2)	0.299(3)
O(1)–V–O(2)	106.1(2)	101.6(2)
O(1)–V–O(3)	111.5(2)	100.7(2)
O(1)–V–N(1)	104.0(2)	96.0(2)
O(1)–V–N(2)	99.4(2)	95.8(2)

contain isolated molecules, and this thus constitutes the first example of a brown or orange mononuclear isomer. We cannot say whether the green form is also monomeric. Table 3 gives some selected dimensions for this molecule as well as those for the analogous compound $[VO(salnptn)]$,[7] without any ring substituents. These parameters are very similar to those reported for homologous materials.[6]

The dimethylmethylene group inserted into the Schiff-base backbone causes the salnptn$(3\text{-}OMe)_2(2-)$ ligand to distort and the consequent umbrella shape might impose the mononuclear structure. However, the vanadyl oxygen is also more exposed on the other side of the N_2O_2 plane and this might therefore have the opposite effect. The parent salnptn$(2-)$ compound without the substituents in the aromatic rings is actually polymeric, though its local dimensions (Table 3) are not very different from those of the salnptn$(3\text{-}OMe)_2(2-)$ monomeric species. The only significant differences concern the V=O bond lengths, where the donor vanadyl length is longer in the polymeric structure and the displacement of the vanadium from the N_2O_2 plane is less. It seems unlikely that the cause of the structural difference between the two compounds is purely steric, although the successive Schiff bases along the polymeric chain of the salnptn$(2-)$ derivative adopt the usual transoid

Table 4 Salts containing new cations of the type [VO(L)]$^+$

Compound	Yield (%), Colour	$\tilde{\nu}$(V=O)/cm^{-1}	Analysis, CHN (%) (Calc.)
[VO{salen(3-OH)$_2$}][ClO$_4$]^a	54, dark green	978	—
[VO{salen(3-OH)$_2$}][PF$_6$]·2H$_2$O·0.5MeCN ^{b}	62, dark green	975	36.4(36.0); 3.3(3.6); 6.0(6.2)
[VO{salen(5-OMe)$_2$}][ClO$_4$]·MeOH·0.5HClO$_4$^{c}	75, green	941	40.2(39.7); 3.7(3.9); 4.9(4.9)
[VO{salen(5-OMe)$_2$}][CF$_3$SO$_3$]·MeOH ^{d}	21, green	971	41.7(41.8); 3.8(3.9); 4.6(4.9)
[VO{salen(5-Me)$_2$}][PF$_6$]^e	20, black	960	—

^{a} [VO{salen(3-OH)$_2$}] (0.66 g, 1.80 mmol) in acetonitrile (20 cm^3), perchloric acid (0.12 cm^3, 1.80 mmol), insoluble powder. ^{b} [VO{salen(3-OH)$_2$}] (1.54 g, 4.20 mmol) in acetonitrile (30 cm^3), hexafluorophosphoric acid (0.4 cm^3, 4.20 mmol), insoluble powder. ^{c} [VO{salen(5-OMe)$_2$}] (0.37 g, 0.93 mmol) in acetonitrile (30 cm^3), perchloric acid (0.12 cm^3, 1.86 cm^3). ^{1}H NMR (360 MHz, CD$_3$CN); δ 2.43 (s, br, 4 H, 2 × CH$_2$), 3.84 (s, 6 H, 2 × OMe), 6.99 (s, br, 2 H, aryl), 7.37 (s, br, 4 H, aryl) and 8.90 (s, br, 2 H, 2 × CH). The product is diamagnetic in the solid state. ^{d} [VO{salen(5-OMe)$_2$}] (1.02 g, 2.60 mmol) in acetonitrile (70 cm^3), trifluoromethanesulfonic acid (0.23 cm^3, 2.60 mmol). ^{1}H NMR (400 MHz, CD$_3$CN) δ 3.87 (s, 10 H), 7.03 (s, 2 H), 7.43 (s, br, 4 H) and 8.95 (s, br, 2 H); ^{19}F (377 MHz, CD$_3$CN) δ −79.6 (s); ^{51}V (131.5 MHz, CD$_3$CN) δ −570.2 ($\Delta\nu_{1/2} \approx 1200$ Hz). ^{e} [VO{salen(5-Me)$_2$}] (0.7 g, 1.90 mmol) in acetonitrile (100 cm^3), hexafluorophosphoric acid (0.3 cm^3, 3.4 mmol). ^{1}H NMR (250 MHz, CD$_3$CN) δ 2.28 (s, 6 H, 2 × CH$_3$), 3.92–4.08 (m, 4 H, 2 × CH$_2$), 6.75 (d, 2 H, J 8.41, aryl), 6.98 (s, 2 H, aryl), 7.48 (d, 2 H, J 7.54, aryl), 8.21 (s, br, 2 H, 2 × CH); ^{19}F (282 MHz, acetone-d$_6$) δ −78.56 (d, J_{FP} 706.4 Hz); ^{51}V (131.5 MHz, acetone-d$_6$) δ −570.7 ($\Delta\nu_{1/2} \approx 530$ Hz).

arrangement that might be expected to reduce steric interactions between adjacent Schiff bases.

Oxovanadium(V) and dinuclear oxovanadium(IV)/oxovanadium(V) complexes

Complexes [VO(L)]$^+$ (L = tetradentate Schiff base dianion). The types of product obtained from the reaction of oxovanadium(IV) tetradentate Schiff base complexes with acids in air comprise [VO(L)]$^+$, which will be discussed now, the dinuclear salts [(L)V^{IV}OV^{V}O(L)]$^+$, which will be described below, and [VO(L)(solvent)]$^+$ and [(L)OV^{V}FV^{V}O(L)]$^+$ which will be described elsewhere.[8]

Some salts with five-co-ordinate cations [VO(L)]$^+$ are listed in Table 4. In many other cases the products of such reactions actually contain co-ordinated methanol, and these are not discussed here. As might be expected, neither [VO{salen(5-X)$_2$}] (X = Cl or Br) is rapidly oxidised (see below) and neither [VO{salen(3,5-X$_2$)$_2$}] (X = Cl or Br) nor [VO{salnptn(5-Br)$_2$}] is oxidised by perchloric acid in air though the compound with X = Cl seems to generate a green (mononuclear?) form that reverts to orange upon standing. That with X = Br decomposes. In addition, [VO{salnptn(5-Br)$_2$}] does not react with perchloric acid in acetonitrile, and the complete absence of reactivity is attributed in part to the longer bridge of the Schiff base. Similarly, [VO(sal-1,2-pn)] appears also to be very slow to oxidise under these conditions, and no clean product could be isolated.

There are a few unexpected observations. For example, [VO{salen(5-OMe)$_2$}] reacts with perchloric acid in acetonitrile to give a diamagnetic green powder which shows an absorption band at 941 cm^{-1} in its IR spectrum which may be assigned to ν(V=O), and a broad absorption band for perchlorate at 1107 cm^{-1}. The value for ν(V=O) is much lower than is generally expected of mononuclear vanadium(V) perchlorate salts, and can be understood if the vanadyl oxygen is involved in a hydrogen-bonding network, which is unlikely, or if there is a group co-ordinated *trans* to V=O. We have no evidence to suggest that acetonitrile can co-ordinate to this site in our compounds. Indeed, the only molecule we found that can do so consistently is methanol,[8] though alcohols and water are known to bind to similar sites in related compounds.

Oxidation reactions can occur in air in the presence of acids other than perchloric acid. For example, [VO{salen(3-OH)$_2$}] reacts in acetonitrile with hexafluorophosphoric acid. The reaction of [VO(salen)] with trifluoromethanesulfonic (triflic) acid is known to give [VO(salen)][CF$_3$SO$_3$]·MeOH, as a black crystalline solid after recrystallisation from methanol.[9] Likewise, [VO{salen(5-OMe)$_2$}] reacts with triflic acid at room temperature to give [VO{salen(5-OMe)$_2$}][CF$_3$SO$_3$]·MeOH as small dark green, elongated needles, in low yield and not suitable for structure analysis. It is not known whether methanol

in these materials is co-ordinated to vanadium, or if it is present as solvent of crystallisation.

Oxovanadium(IV)/oxovanadium(V) complexes, [V^{IV}O(L)→V^{V}O(L)]$^+$. *(a) Preparations.* If compounds [VO(L)] are slow to oxidise, or if the oxidising agent is relatively weak, then it is possible to isolate a mixed oxidation state adduct {V^{IV}O→V^{V}O}$^+$. For example, we showed that [VO(salen)] is oxidised by iodine in acetonitrile at reflux to give [V(salen)O→V(salen)O][I$_5$]·MeCN as black needles after recrystallisation from acetonitrile.[3]

We have now obtained several more such dinuclear products after oxidation with iodine (see Experimental section and Table 5). Reactions between iodine and oxovanadium(IV) tetradentate Schiff base complexes were carried out either in acetonitrile or in dichloromethane. In many cases reactions were repeated since different ratios of oxovanadium(IV) tetradentate Schiff base complexes to iodine gave different polyiodide anions in the products. All these compounds are dark solids which show ν(V=O) in the range 859–918 cm^{-1}. Tables 5 and 6 summarise the results. Neither [VO{salen(3-OH)$_2$}], nor [VO{salen(3,5-Cl$_2$)$_2$}] nor [VO{sal-1,3-pn(5-Br)$_2$}] is oxidised by iodine under the reaction conditions employed, but the green [VO{salen(3,5-Cl$_2$)$_2$}] changes to the orange polymeric form on stirring with iodine at room temperature.

However, in addition to the compounds [VO(L)]$^+$ discussed above, dinuclear compounds can also be obtained by air oxidation in the presence of acids. A further route to these dinuclear complexes is by cocrystallisation of a vanadium(IV) and a vanadium(V) species (see below). All these materials are detailed in Table 6. For example, [VO{salen(5-Cl)$_2$}] reacts with perchloric acid in acetonitrile in air to give the mixed oxidation-state dinuclear product [{salen(5-Cl)$_2$}V^{IV}O→V^{V}O{salen(5-Cl)$_2$}][ClO$_4$] as a dark green powder. These dinuclear products are insoluble in acetonitrile and they readily precipitate from solution. In methanol, this dinuclear species appears to "dissociate" to give a light green powder from a blue supernatant liquid. The light green powder (ν(V=O) at 974 cm^{-1}) is the V^{IV} starting material. A dark blue microcrystalline solid was isolated from the filtrate after storage at −20 °C for several weeks, and clearly this is [VO{salen(5-Cl)$_2$}][ClO$_4$]. X-Ray diffraction studies[8] showed a crystal of this material to contain the vanadium(V) mononuclear salt [VO{salen(5-Cl)$_2$}(MeOH)][ClO$_4$], but the co-ordinated methanol is very labile.

Similarly, [VO{salen(5-Br)$_2$}] reacts with perchloric acid to give the mixed-oxidation-state dinuclear salt, [{salen(5-Br)$_2$}V^{IV}O→V^{V}O{salen(5-Br)$_2$}][ClO$_4$], as a dark green insoluble powder. Microanalyses and the IR spectrum are consistent with the formulation [{VO{salen(5-Br)$_2$}}$_2$][ClO$_4$]·0.5MeCN. The reaction of the complex [VO{salen(5-Br)$_2$}] with trifluoromethanesulfonic acid over six days at room temperature in

Table 5 New compounds prepared by iodine oxidation and containing the dinuclear cations [{VO(L)}$_2$]$^+$

Compound	Yield (%), Colour	ṽ(V=O)^a/cm^{-1} V^{IV}/V^V adduct	V^V parent	Analysis, CHN (%) (Calc.)
[{VO{salen(5-OMe)$_2$}}$_2$][I$_3$]·2CH$_2$Cl$_2$^{c}	82, green	870	973	34.1(34.1); 2.8(2.7); 4.2(4.2)
[{VO{salen(5-Me)$_2$}}$_2$][I$_3$]^d	56, black	872	959	38.7(39.2); 3.1(3.3); 4.8(5.1)
[{VO{salen(5-Br)$_2$}}$_2$][I$_5$]^e	83, brown	918	970	23.8(23.8); 1.4(1.5); 3.4(3.5)
[{VO{salen(3-OMe)$_2$}}$_2$][I$_3$]·0.5MeCN^f	59, green	859	991^b	37.2(37.4); 3.1(3.2); 5.4(5.3)
[{VO(hapen)}$_2$][I$_5$]·MeCN·Et$_2$O^g	60, black	909	991	34.8(34.3); 2.9(3.4); 4.5(4.8)
[{VO(salibn)}$_2$][I$_3$]·0.5MeCN^h	94, black	888	991	39.7(39.5); 3.3(3.4); 5.9(5.6)
[{VO(hap-1,2-pn)}$_2$][I$_5$]·CH$_2$Cl$_2$^{i}	52, black	865	989, 973	30.6(30.6); 2.7(2.7); 3.7(3.6)
[{VO{salen-1,3-pn(3-OMe)$_2$}}$_2$][I$_3$]·CH$_2$Cl$_2$^{j}	82, brown	893	861	36.7(36.6); 3.1(3.3); 4.3(4.4)
[{VO(sal-1,2-pn)}$_2$][I$_3$]^k	74, brown	882	986, 972	38.0(38.0); 2.9(3.0); 5.5(5.2)
[{VO{sal-1,2-pn(5-Br)$_2$}}$_2$][I$_3$]^l	79, khaki	866	980	29.4(29.4); 1.9(2.0); 3.9(4.0)

^{a} KBr disc, unless otherwise indicated. ^{b} Nujol mull. ^{c} [VO{salen(5-OMe)$_2$}] (0.82 g, 2.1 mmol), iodine (0.40 g, 1.6 mmol). ^{d} [VO{salen(5-Me)$_2$] (0.66 g, 1.8 mmol), iodine (0.46 g, 1.8 mmol). MS (FAB): m/z = 722, [M]$^+$, 3.7%, based on m/z = 154, 100%. ^{e} [VO{salen(5-Br)$_2$}] (1.06 g, 2.10 mmol), iodine (0.41 g, 1.6 mmol). ^{f} [VO{salen(3-OMe)$_2$}] (1.07 g, 2.7 mmol), iodine (1.35 g, 1.36 mmol). ^{g} [VO(hapen)] (0.65 g, 1.8 mmol), iodine (0.46 g, 1.8 mmol). ^{h} [VO(salibn)] (0.48 g, 1.3 mmol), iodine (0.17 g, 0.66 mmol). ^{i} [VO(hap-1,2-pn)] (0.69 g, 1.83 mmol), iodine (0.34 g, 1.36 mmol). ^{j} [VO{sal-1,3-pn(3-OMe)$_2$}] (0.96 g, 2.3 mmol), iodine (0.48 g, 1.9 mmol). MS (FAB): [M]$^+$, 1.8%, based on m/z = 154, 100%. ^{k} [VO(sal-1,2-pn)] (0.52 g, 1.5 mmol), iodine (0.29 g, 1.13 mmol). ^{l} [{VO{sal-1,2-pn(5-Br)$_2$}}] (1.06 g, 2.10 mmol), iodine (0.41 g, 1.60 mmol).

Table 6 Products containing cations of the form [{VO(L)}{VO(L′)}]$^+$ or [{VO(L)}$_2$]$^+$ prepared by acid oxidation or cocrystallisation

Compound	Yield (%), Colour	ṽ(V=O)^a/cm^{-1} V^{IV}/V^V adduct	V^{IV}parent/ V^V parent	Analysis CNH (%) (Calc.)
[{VO{salen(5-Cl)$_2$}}$_2$][ClO$_4$]^c	43, green	898	972	42.0(42.5); 2.7(2.7); 6.7(6.2)
[{VO{salen(5-Cl)$_2$}}$_2$][BF$_4$]·0.5HBF$_4$^{d}	60, green	902	972	40.8(43.1); 2.6(2.7); 6.2(6.3)
[{VO{salen(5-Br)$_2$}}$_2$][ClO$_4$]·0.5MeCN^e	50, green	903^b	970	35.5(36.0); 2.2(2.3); 5.7(5.7)
[{VO{salen(5-Br)$_2$}}$_2$][BF$_4$]·0.5HBF$_4$^{f}	59, green	896	965	34.0(34.0); 2.1(2.2); 5.0(5.0)
[{VO{salen(5-Br)$_2$}}$_2$][SO$_3$CF$_3$]·0.5CF$_3$SO$_3$H^g	52, green	928	970	33.3(33.3); 2.0(2.0); 4.7(4.6)
[{VO(salen)}{VO(salnptn)}][BF$_4$]^h	82, black	910, 874	989/997	Not analysed
[{VO(salnptn)}{VO(salen)}][ClO$_4$]^i	68, black	862	872/980	51.8(52.2); 4.3(4.3); 7.8(7.6)
[{VO{salen(5-Me)$_2$}}$_2$][ClO$_4$]^j	66, green	935	959/983	52.0(52.6); 4.3(4.4); 6.5(6.8)
[{VO(salibn)}$_2$][ClO$_4$]·2CHCl$_3$^{k}	55, green	916	991	42.1(42.1); 3.5(3.5); 5.2(5.1)

^{a} KBr disc, unless otherwise indicated. ^{b} Nujol mull. ^{c} [VO{salen(5-Cl)$_2$}] (0.63 g, 1.60 mmol), HClO$_4$ (0.2 cm^3), CH$_3$CN (40 cm^3), 6 d. ^{d} [VO{salen(5-Cl)$_2$}] (0.86 g, 2.13 mmol), HBF$_4$·Et$_2$O (0.3 cm^3), CH$_3$CN (30 cm^3), 1 d. ^{e} [VO{salen(5-Br)$_2$}] (2.20 g, 4.48 mmol), HClO$_4$ (0.6 cm^3), CH$_3$CN (100 cm^3), 6 d. ^{f} [VO{salen(5-Br)$_2$}] (1.47 g, 2.99 mmol), HBF$_4$·Et$_2$O (0.4 cm^3), CH$_3$CN (50 cm^3), 1 d. ^{g} [VO{salen(5-Br)$_2$}] (2.65 g, 5.40 mmol), CH$_3$SO$_3$H (0.5 cm^3), CH$_3$CN (60 cm^3), 6 d. ^{h} [VO(salen)] (0.46 g, 1.38 mmol), [VO(salnptn)][BF$_4$] (0.64 g, 1.37 mmol), CH$_2$Cl$_2$ (180 cm^3), 3 d at −20 °C. ^{i} [VO(salen)]-[ClO$_4$] (1.41 g, 3.25 mmol), [VO(salnptn)] (1.22 g, 3.25 mmol), CH$_3$CN (60 cm^3), 3 weeks at −20 °C. ^{j} [VO{salen(5-Me)$_2$}] (0.30 g, 0.83 mmol), [VO{salen(5-Me)$_2$}][ClO$_4$] (0.38 g, 0.83 mmol), CH$_2$Cl$_2$ (60 cm^3), 7 d at −20 °C. ^{k} [VO(salibn)] (0.73 g, 2.02 mmol), [VO(salibn)][ClO$_4$] (0.93 g, 2.01 mmol), CH$_3$CN (50 cm^3), 3 weeks at −20 °C, see Experimental.

acetonitrile gives the dark green, mixed-oxidation-state, dinuclear salt in 52% yield. Both [V^{IV}O{salen(5-X)$_2$}] (X = Br or Cl) react relatively rapidly (24 h) with tetrafluoroboric acid–diethyl ether in acetonitrile to give dark green powders, [{VO{salen(5-X)$_2$}}$_2$][BF$_4$]. In methanol or tetrahydrofuran these give the fluoro-bridged [{VO{salen(5-X)$_2$}}$_2$(μ-F)][BF$_4$], to be described elsewhere, and the vanadium(IV) starting materials, eqn. (1).

$$[\{VO\{salen(5\text{-}Cl)_2\}\}_2][BF_4] \xrightarrow{\text{MeOH}}$$

$$[\{VO\{salen(5\text{-}Cl)_2\}\}_2(\mu\text{-}F)][BF_4] + [VO\{salen(5\text{-}Cl)_2\}] \quad (1)$$

blue crystals   green powder
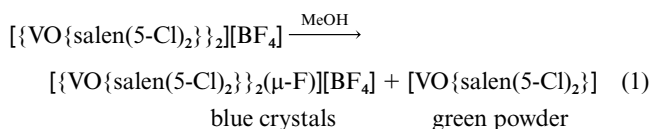
The alternative preparation of these mixed-oxidation-state adducts, by crystallising a mixture of the salt [V^{V}O(L)]X (X = BF$_4$ or ClO$_4$) and one equivalent of [V^{IV}O(L)], is not always successful. Where the two starting materials have different solubilities in the reaction solvent the least soluble material often precipitates first and no dinuclear species can be isolated. This happens with the vanadium(IV) hapen(2−) and vanadium(V) salen(2−) derivatives. However, [VO{salen(5-Me)$_2$}(MeOH)][ClO$_4$] and [VO{salen(5-Me)$_2$}] give the mixed-oxidation-state dinuclear product as a dark green crystalline solid. X-Ray diffraction studies show the presence of a dinuclear cation [{VO{salen(5-Me)$_2$}}$_2$]$^+$ (Fig. 2 and Table 7)
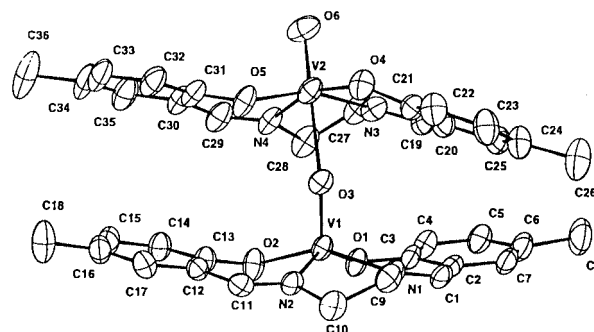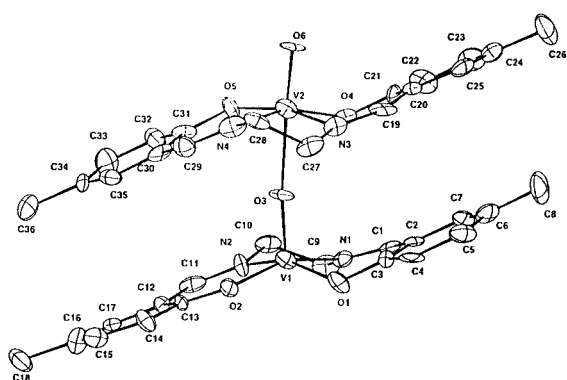

Fig. 2 Molecular structure of [{VO{salen(5-Me)$_2$}}$_2$][ClO$_4$] (perchlorate ion is omitted).

with {salen(5-Me)$_2$}$^{2-}$ units in the equatorial planes and rotated by about 180° with respect to each other.

This strategy was adapted to produce dinuclear salts with two different Schiff base dianions (Tables 5, 6). The Schiff base dianions were carefully selected to ensure comparable solubilities and little steric repulsion. A dinuclear salt was obtained from [VO(salnptn)] and [VO(salen)][ClO$_4$] as a black microcrystalline solid. The IR spectrum of this product shows v(V=O) at 862 cm^{-1}, and a broad absorption band at 1092 cm^{-1} for perchlorate. Microanalyses of the black solid are consistent with a formulation of [(salnptn)V^{IV}O→V^{V}O(salen)][ClO$_4$]. The

Table 7 Selected dimensions of structurally characterised complexes [{VO(L)}₂]⁺

Dimension (Å or °)	[{VO{salen(5-Me)₂}}₂][I₃]	[{VO(sal-1,2-pn)}₂][I₃]	[{VO{salen(5-Me)₂}}₂][ClO₄]
V(1)–O(3)	1.608(11)	1.63(2)	1.598(3)
V(2)–O(3)	2.127(10)	2.18(2)	2.230(3)
V(1)···O(6′)	2.360(10)	—	—
V(2)–O(6)	1.588(10)	1.59(3)	1.580(4)
V(1)–O(1), V(1)–O(2)	1.910(14), 1.891(12)	1.89(3), 1.90(2)	1.901(3), 1.896(3)
V(2)–O(4), V(2)–O(5)	1.836(12), 1.797(13)	1.78(3), 1.80(2)	1.812(3), 1.836(3)
V(1)–N(1), V(1)–N(2)	2.04(2), 2.02(2)	1.96(3), 1.93(4)	2.047(4), 2.046(4)
V(2)–N(3), V(2)–N(4)	2.07(2), 2.11(2)	2.10(3), 2.05(3)	2.073(4), 2.069(4)
V(1) above O(2)O(3)N(1)N(2) plane	0.383(7)	0.541(16)	0.542(2)
V(2) above O(4)O(5)N(3)N(4) plane	0.241(7)	0.251(14)	0.272(2)
V(1)–O(3)–V(2)	172.6(8)	161.3(14)	159.7(2)
O(3)–V(2)–O(6)	169.3(8)	174.5(12)	171.6(2)
O(3)–V(1)···O(6′)	168.0(8)	—	—
V(2)–O(6)···V(1″)	172.3(7)	—	—

Fig. 3 Molecular structure of [{VO{salen(5-Me)₂}}₂][I₃] (triiodide anion is omitted).

band at 862 cm⁻¹ is not very different from v(V=O) observed in [VO(salnptn)], which is about 20 cm⁻¹ lower than the comparable absorption observed for [{VO(salen)}₂][ClO₄]. It seems that [VO(salnptn)] is a better donor to [VO(salen)]⁺ than is [VO(salen)], perhaps due to the projection of the vanadyl group from the N₂O₂ plane. An isomer was obtained from [VO(salen)] and [VO(salnptn)][BF₄] in acetonitrile. The black microcrystalline solid shows v(V=O) at 874 and 910 cm⁻¹, and a strong absorption band at 1060 cm⁻¹ assignable to tetrafluoroborate. We formulate this as [(salen)VO→VO(salnptn)]-[BF₄], though we could obtain no crystals suitable for X-ray studies.

*(b) Structures.* The crystal of [{VO{salen(5-Me)₂}}₂][I₃] contains a dinuclear cation [{salen(5-Me)₂}V^IV=O→V^V=O-{salen(5-Me)₂}]⁺ (Fig. 3 and Table 7) with a structure having features similar to those reported for the salen homologue and with the cationic units stacked linearly. The vanadium atoms carry the Schiff bases rotated about 180° with respect to each other in the transoid arrangement, as expected. The central V(1)–O(3)–V(2) angle of 172.6(8)° is considerably more "linear" than the comparable angle in [{VO(salen)}₂]-[I₅]·MeCN.[3] The V(2)–O(3) bond distance [2.127(10) Å] is similar to the distances in the [V=O→V=O] links in polymeric oxovanadium(IV) tetradentate Schiff base complexes such as [VO(sal-1,3-pn)][2] and [VO(salnptn)],[7] 2.213(9) and 2.245(4) Å, respectively. The distance between the neighbouring dinuclear cations in the structure, V(1)···O(6′), is 2.360(10) Å, which is non-bonding and slightly shorter than in [{VO(salen)}₂]-[I₅]·MeCN.[3]

In contrast, the X-ray diffraction study of [{VO{salen(5-Me)₂}}₂][ClO₄] shows the presence of a dinuclear [{VO-{salen(5-Me)₂}}₂]⁺ cation (Fig. 2 and Table 7) with {salen-(5-Me)₂}²⁻ units in the equatorial planes and again rotated by about 180° with respect to each other. The V(1)–O(3)–V(2)

Complex	Formula	E_1/V	E_2/V	ΔE/mV[b]
1	[VO(salen)]	0.58	0.68	100
2	[VO(sal-1,2-pn)]	0.55	0.67	120
3	[VO{salen(5-OMe)₂}]	0.48	0.64	160
4	[VO(salibn)]	0.59	0.69	100
5	[VO(salnptn)]	0.64	0.77	130
6	[VO{salen(5-Me)₂}]	0.50	0.67	170
7	[{VO{salen(5-Me)₂}}₂][ClO₄]	0.52	0.65	130
8	[VO{salen(5-Me)₂}][ClO₄]	0.52	0.65	130

[a] Potentials measured from cyclic voltammograms, in CH₂Cl₂ at a platinum disk electrode. [b] $\Delta E = E_2 - E_1$ in mV.
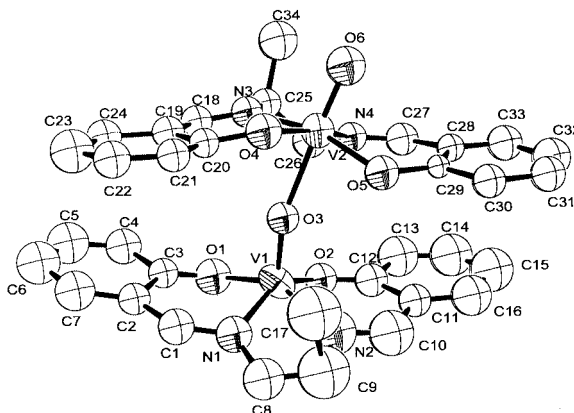
Fig. 4 Molecular structure of [{VO(sal-1,2-pn)}₂][I₃] (triiodide anion is omitted).

angle of 159.7(2)° is considerably less linear than in the triiodide, and the cationic units are no longer stacked linearly.

The dark brown, dinuclear [{VO(sal-1,2-pn)}₂][I₃] was recrystallised from acetonitrile. The rather small crystals did not yield a structure of the highest quality, but the principal features are quite clear and as expected (Fig. 4 and Table 7). The central V(1)–O(3)–V(2) angle is 161.3(14)° and there is no linear association between neighbouring cations.

(c) Electrochemical studies. In order to investigate the effects of the Schiff base substituents on the oxidation potential of [VO(L)] voltammetric experiments were carried out on compounds **1–6**. At a platinum electrode, in CH₂Cl₂ with [NBu₄]-[PF₆] as supporting electrolyte, each complex shows *two* distinct reversible oxidation waves; Fig. 5 shows the cyclic voltammogram of **6** as a representative example. The potentials recorded in Table 8 (E_1 and E_2 are the potentials for the first and second oxidation waves, respectively) were estimated from
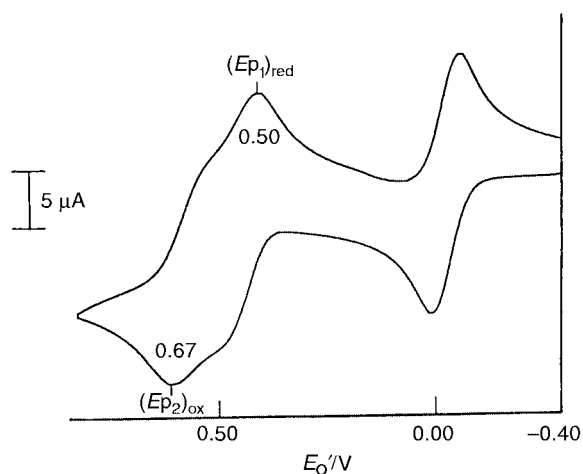
Fig. 5 Cyclic voltammogram of [VO{salen(5-Me)$_2$}] **6** in dichloromethane. The reversible one-electron oxidation wave of [Fe(η^5-C$_5$Me$_5$)$_2$] is centred at −0.09 V.

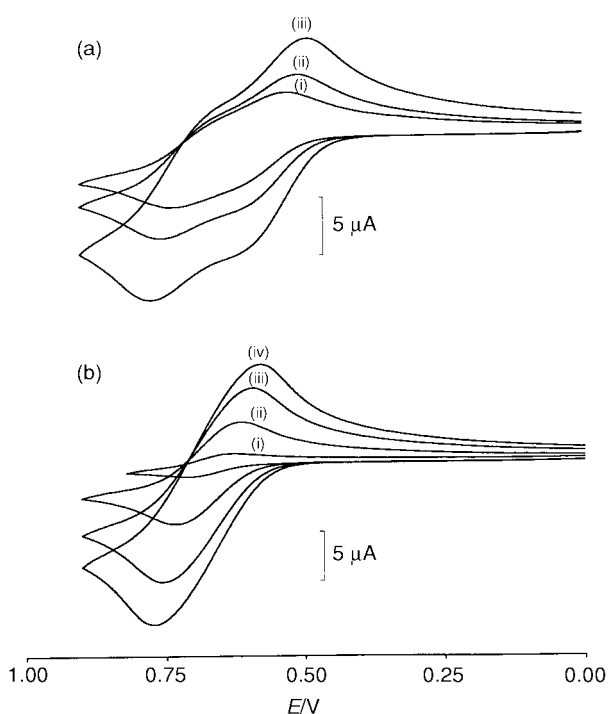**Fig. 6** Cyclic voltammogramms for [VO(salen)] **1** in CH$_2$Cl$_2$ using [NBu$_4$][PF$_6$] (a) and [NBu$_4$][BF$_4$] (b) as supporting electrolytes.

cyclic voltammograms where the relative concentrations of the complex and [Fe(η-C$_5$Me$_5$)$_2$], the internal potential standard, were adjusted so that their oxidation waves were equal in height, implying equal peak currents. The peak-to-peak separation (δE in mV) for the oxidation wave of [Fe(η-C$_5$Me$_5$)$_2$] was then assumed to be equal to that for each of the two waves of the complex, allowing the potentials for the individual waves to be estimated from $(E_{p1})_{red}$ + 0.5 δE for the first oxidation wave and $(E_{p2})_{ox}$ − 0.5 δE for the second. {In these expressions $(E_{p1})_{red}$ is the reduction peak potential for the first wave and $(E_{p2})_{ox}$ is the oxidation peak potential for the second wave (Fig. 5)}. In the case of [VO(salen)] **1** the two oxidation potentials were also determined using differential pulse voltammetry, giving values of 0.59 and 0.66 V consistent with the data from cyclic voltammetry.

The observation of two oxidation waves is very different from the results of previous voltammetric studies of [VO(salen)] **1**[3,10–12] which have invariably shown that **1** is oxidised to the monocation [VO(salen)]$^+$ in a fully reversible one-electron step, in either MeCN or CH$_2$Cl$_2$. We have therefore repeated our

study under conditions more similar to those previously used in order to establish the source of this apparent contradiction. The voltammetry reported in ref. 12 for **1** in CH$_2$Cl$_2$ was carried out using a sample concentration of 0.2 × 10^{-3} mol dm^{-3} in the presence of 0.1 mol dm^{-3} [NBu$_4$][BF$_4$] as supporting electrolyte. Under our experimental conditions the CV of **1** shows two waves at sample concentrations from 1.0 × 10^{-3} to 3.0 × 10^{-3} mol dm^{-3} with little change in the separation between the two waves (Fig. 6a). Remarkably, however, the replacement of [NBu$_4$][PF$_6$] by [NBu$_4$][BF$_4$] as the supporting electrolyte leads to the observation of only one oxidation wave at sample concentrations from 0.2 × 10^{-3} to 3.0 × 10^{-3} mol dm^{-3} (Fig. 6b). A solvent effect is also apparent in that the two waves are not observed with either supporting electrolyte salt in MeCN. Indeed, it is necessary only to add 1 cm^3 of MeCN to an electrochemical cell containing 25 cm^3 of a 1.0 × 10^{-3} mol dm^{-3} solution of **1** in CH$_2$Cl$_2$ (with [NBu$_4$][PF$_6$] as supporting electrolyte) for the two waves at 0.58 and 0.68 V to be replaced immediately by one, centred at 0.59 V.

For one ligand, {salen(5-Me)$_2$}$^{2-}$, voltammetric studies were also carried out on the V^{IV}/V^V adduct [{VO{salen(5-Me)$_2$}}$_2$][ClO$_4$] **7** and on the vanadium(v) complex [VO{salen(5-Me)$_2$}][ClO$_4$] **8**, again in CH$_2$Cl$_2$ with [NBu$_4$][PF$_6$] as supporting electrolyte. In both cases two waves were again observed (one oxidation and one reduction for **7** and two reductions for **8**), at potentials virtually identical to those for the two oxidation waves of neutral [VO{salen(5-Me)$_2$}] **6**.

Discussion

Two major questions arise from these studies. The first is what controls the arrangement of Schiff base residues in these compounds and the way the individual units align themselves within the crystal? In every example that we have isolated, whether dinuclear (as described here) or tetranuclear (as described elsewhere),[13] successive Schiff-base residues along a vanadium chain are transoid. However, the triiodide(1−) analogue of our pentaiodide(1−) salt[3] was prepared by Tsuchida and co-workers,[10] by reducing [(salen)V^{IV}OV^{IV}(salen)]$^{2+}$ electrochemically in acetonitrile to [(salen)V^{IV}OV^{III}(salen)]$^+$ (which we showed[13] to have the transoid arrangement), then exposing the reduced product to dioxygen, and finally adding tetrabutylammonium triiodide. The crystal of the triiodide[10] contains two crystallographically independent cationic molecules per asymmetric unit, one with the two Schiff base dianions transoid and the other where they are cisoid. Furthermore, the structure of [{VO(salen)}$_2$][ClO$_4$] reported in the same publications[10] contains only cisoid arrangements of the Schiff bases. Neither of these two salts shows linear stacking, and the only obvious variable is the cation.

The bond angles and atom separations in [{VO(salen)}$_2$][I$_5$]·MeCN (transoid),[3] [{VO(salen)$_2$}$_2$][I$_3$] (cisoid and transoid),[11] and [{VO(salen)}$_2$][ClO$_4$]·MeCN (cisoid)[10] are all rather similar and certainly do not change significantly with conformation. Nevertheless, the values of v(V=O) (880, 981, and 870 cm^{-1}) are anion dependent, even though there is no obvious anion–cation interaction. The cause of the different rotational arrangements of the salen(2−) and also of the different stacking arrangements of the cationic units is not evident. We showed recently[13] that a change of anion from [BF$_4$]$^-$ to [BPh$_4$]$^-$ determines whether the units {V$_4$(salen)$_4$O$_3$}$^{2-}$ in the corresponding salts stack end to end in the solid state or not, and again there are no obvious anion–cation interactions. Crystal packing forces and non-bonding interactions appear to have a much greater influence on determining detailed structure than might be expected. In addition to the salen derivatives discussed above, the salen(5-Me)$_2$ derivative perchlorate described here is transoid and not stacked up in the crystal whereas the transoid triiodide is not stacked.

As discussed above, the neutral compounds [V^{IV}O(L)] also

show the mononuclear/polynuclear stacking dichotomy, and here there can be no anion dependence. We are unable to rationalise these phenomena.

The second question concerns the persistence of dinuclear structures in solution. It has previously been assumed that [VO(salen)] and [VO(salen)]$^+$ are mononuclear in solution. However, the voltammetric behaviour observed under our experimental conditions (two reversible waves separated by *ca.* 100–170 mV) is typical of dinuclear species in which there is weak communication between the two metal centres. Thus, the simplest explanation for the observed electrochemistry is summarised in Scheme 1, *i.e.* where the units are associated

$$[\{VO(L)\}_2] \xrightleftharpoons{-e^-} [\{VO(L)\}_2]^+ \xrightleftharpoons{-e^-} [\{VO(L)\}_2]^+$$
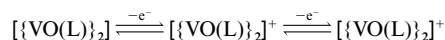
Scheme 1

(which is certainly the case for complex **7** in the solid state). This interpretation does seem to contradict the spectroscopic and structural findings described above which imply that the two end-members of this redox series are mononuclear, at least in the solid state. However, association of the mononuclear units is likely to be weak (and certainly disrupted by replacing CH$_2$Cl$_2$ by the better donor solvent MeCN) and subtle effects involving, for example, ion pairing differences in the presence of [NBu$_4$][PF$_6$] and [NBu$_4$][BF$_4$] may be adequate to account for the observed electrochemistry. An alternative rationalisation for the electrochemical results, in which association occurs on oxidation of mononuclear [VO(L)] to yield the V^{IV}/V^V adducts as soon as the vanadium(V) species is produced and in which subsequent oxidation of the vanadium(IV) partner yields mononuclear [V^{V}O(L)]$^+$ (as in Scheme 2), would require fast

$$2\,[VO(L)] \xrightleftharpoons{-e^-} [\{VO(L)\}_2]^+ \xrightleftharpoons{-e^-} 2\,[VO(L)]^+$$
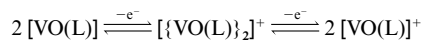
Scheme 2

association/dissociation on the voltammetric timescale. More detailed electrochemical studies are required in order to define this system more clearly; it appears to be more complex than previously recognised.

Experimental

All reactions were carried out under dinitrogen, using standard Schlenk techniques unless otherwise stated. Solvents used were dried and distilled under dinitrogen as follows; acetonitrile over calcium hydride, dichloromethane and chloroform pre-dried over calcium chloride and distilled over calcium hydride, diethyl ether and tetrahydrofuran were pre-dried over sodium wire and distilled over a sodium potassium alloy, and methanol was distilled over magnesium methoxide. Oxobis(pentane-2,4-dionato)vanadium(IV)[14] and reported Schiff bases were prepared using standard literature methods. The IR spectra were obtained from dispersions in potassium bromide or Nujol mulls using a Perkin-Elmer model 1710 FTIR spectrophotometer. Carbon, nitrogen and hydrogen analyses were carried out by Ms. Nicola Walker at the University of Surrey on a Leenan CE 440 Elemental Analyser. Mass spectra were recorded by Dr Ali Abdul Sada on a VG Autospec spectrometer for Electron Impact spectra (EI source at 70 eV) and on a Kratos MS80RF for Fast Atom Bombardment spectra (FAB source at 80 kV, with xenon gas and a matrix of 3-nitrobenzyl alcohol). The ^{1}H and ^{19}F NMR spectra were recorded on a Bruker Advance DPX300 spectrometer, ^{51}V spectra on Bruker AMX500 or ACP250 spectrometers (operating frequencies 131.5 and 66 MHz, respectively); solvents were supplied by the Cambridge Isotope Laboratories. Magnetic moments were recorded in the solid state, at room temperature using a Johnson Matthey susceptibility balance with MnCl$_2$ in a sealed tube as calibrant.

Diamagnetic corrections were based on a value of -182×10^{-6} cgs units for N,N'-bis(salicylidene)ethane-1,2-diamine, and appropriate corrections to this value were calculated using Pascal constants.

Electrochemical studies were carried out using an EG&G model 273 potentiostat in conjunction with a three-electrode cell. For cyclic voltammetry and differential pulse voltammetry the auxiliary electrode was a platinum wire and the working electrode was a platinum disc. The reference was a standard calomel electrode (SCE) separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. Solutions in CH$_2$Cl$_2$ were 0.1×10^{-3} mol dm^{-3} in the test compound and 0.1 mol dm^{-3} in [NBu$_4$][PF$_6$] as the supporting electrolyte. The potentials for the neutral compounds **1**–**6** (Table 8) were calibrated using [Fe(η^5-C$_5$Me$_5$)$_2$] as an internal potential standard. The potentials of the cations **7** and **8** were calibrated using [Fe(η^5-C$_5$H$_4$COMe)$_2$], given that each cation would otherwise be chemically reduced in the cell by [Fe(η^5-C$_5$Me$_5$)$_2$]. Under the conditions used, $E^{\circ\prime}$ for the one-electron oxidations of [Fe(η^5-C$_5$Me$_5$)$_2$] and [Fe(η^5-C$_5$H$_4$COMe)$_2$] are -0.09 and $+0.97$ V, respectively.

The crystal structure analyses were all carried out at room temperature using an Enraf-Nonius CAD4 diffractometer and monochromated Mo-Kα radiation (0.71073 Å). The structures were refined on all F^2 using the SHELX 93 program.[15] For [VO\{salen(5-Me)$_2$\}$_2$][I$_3$], data were collected only as far as 22° because there were no significant data above this limit. Since the absolute configuration has been correctly assigned there seemed no point in collecting Friedel equivalents. For [\{VO(sal-1,2-pn)\}$_2$][I$_3$] the crystal was very small and no dimension was greater than 0.1 mm. Absorption effects were considered to be minimal, and only the V and I atoms were refined anisotropically. Diffraction was weak, and though the structure is quite clear, detailed analysis of dimensions seems inadvisable. Details of the structure determinations are shown in Table 9.

CCDC reference number 186/1723.

See http://www.rsc.org/suppdata/dt/1999/4437/ for crystallographic files in .cif format.

Preparation of Schiff bases, H$_2$L

The Schiff bases used in this study were usually prepared by reaction of the aldehyde and the amine in methanol, and are listed in Table 1. The synthesis of Schiff base H$_2$\{salen(5-Me)$_2$\} is described below as an example. With the exception of H$_2$\{sal-1,2-pn(3-OMe)$_2$\}, which was an oil, all the compounds are yellow crystalline solids. They were characterised by IR and ^{1}H NMR spectroscopies.

H$_2$\{salen(5-Me)$_2$\}. 5-Methylsalicylaldehyde was prepared in 20% yield following the literature method.[16] The aldehyde (5.60 g, 0.04 mol) was dissolved in ethanol (200 cm^3) and ethane-1,2-diamine (1.40 cm^3, 0.02 mol) added. The bright yellow solution was stirred for 2 h at room temperature, and the Schiff base filtered off and washed with diethyl ether (50 cm^3). Yield: 4.40 g, 73%. IR (KBr disc, cm^{-1}): 1639s, 1493s, 1367s, 1233s, 1041s and 824s. ^{1}H NMR (300 MHz, ^{1}H, acetone-d$_6$): δ 2.22 (s, 6 H, 2 × CH$_3$), 3.96 (s, 4 H, 2 × CH$_2$), 6.61 (s, 2 H, aryl), 7.09–7.14 (m, 4 H, aryl) and 8.47 (s, 2 H, 2 × CH).

Preparation of vanadyl(IV) Schiff base complexes, [VO(L)]

These complexes were prepared by ligand exchange of oxobis(pentane-2,4-dionato)vanadium(IV) with the appropriate Schiff base. The exception was [VO(hap-1,3-pn)], which could also be prepared by reaction of H$_2$(hap-1,3-pn) with vanadyl(IV) sulfate hydrate in the presence of triethylamine as a proton acceptor. Furthermore, since we were unable to isolate H$_2$\{sal-1,2-pn(3-OMe)$_2$\}, [VO\{sal-1,2-pn(3-OMe)$_2$\}] was prepared by a one-pot synthesis, detailed below, together with the syntheses of [VO\{salen(5-Me)$_2$\}] (a typical example),

Table 9 Crystal data and structure refinement

	[VO{salnptn(3-OMe)$_2$}]	[{VO{salen(5-Me)$_2$}}$_2$][I$_3$]	[{VO{salen(5-Me)$_2$}}$_2$][ClO$_4$]	[{VO(sal-1,2-pn)}$_2$][I$_3$]
Empirical formula	C$_{21}$H$_{24}$N$_2$O$_5$V	C$_{36}$H$_{36}$I$_3$N$_4$O$_6$V$_2$	C$_{36}$H$_{36}$ClN$_4$O$_{10}$V$_2$	C$_{34}$H$_{32}$I$_3$N$_4$O$_6$V$_2$
Formula weight	435.4	551.6	822.0	1075.2
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (non-standard no. 14)	$P2_1$ (no. 4)	$P2_1/n$ (non-standard no. 14)	$P2_1/c$ (no. 14)
a/Å	8.682(3)	7.625(3)	15.157(5)	13.712(5)
b/Å	17.520(3)	17.769(5)	10.378(2)	13.666(3)
c/Å	13.600(3)	14.628(7)	23.576(5)	21.310(8)
β/°	107.35(2)	93.51(4)	93.33(2)	108.11(3)
V/Å^3	1974.6(9)	1978.2(13)	3702(2)	3795(2)
Z	4	4	4	4
μ/mm^{-1}	0.54	2.86	0.64	2.98
Reflections collected	3703	2720	6744	4865
Independent reflections	3470 [R(int) = 0.0314]	2511 [R(int) = 0.0550]	6492 [R(int) = 0.0965]	4643 [R(int) = 0.1609]
Reflections with $I > 2\sigma_I$	2757	1799	3683	1514
Final $R1$, $wR2$ [$I > 2\sigma_I$]	0.068, 0.181	0.051, 0.095	0.075, 0.180	0.122, 0.234
(all data)	0.085, 0.203	0.084, 0.109	0.136, 0.223	0.307, 0.336

and of both isomeric forms of [VO{sal-1,2-pn(5-Br)$_2$}], [VO{salnptn(3-OMe)$_2$}], and [VO{salen(3,5-Cl)$_2$}]. For details of all the new products, see Table 2. Other compounds [VO(L)] mentioned in the text have been described previously.[2,3,5]

[VO{salen(5-Me)$_2$}]. The compound H$_2${salen(5-Me)$_2$} (2.76 g, 9.32 mmol) was dissolved in methanol (80 cm^3) and oxobis(pentane-2,4-dionato)vanadium(IV) (2.47 g, 9.32 mmol) added. The solution was heated to reflux for 2 h and filtered hot. After cooling, a green solid was isolated from the brown supernatant liquid and washed with diethyl ether (50 cm^3). Yield: 3.13 g, 92%. IR (KBr disc, cm^{-1}): 1622s, 1538s, 1469s, 1293s and 959s ν(V=O). Solid state magnetic susceptibility: μ_{eff} = 1.60 ± 0.2 μ_B.

[VO(hap-1,3-pn)]. *(a) From vanadyl(IV) sulfate.* The compound H$_2$(hap-1,3-pn) (0.93 g, 3.0 mmol) was dissolved in methanol (40 cm^3), and triethylamine (0.97 cm^3, 0.35 mol) added. This mixture was then added dropwise to a warmed methanol solution (100 cm^3) of vanadyl(IV) sulfate hydrate (0.49 g, 3.0 mmol). The solution was stirred in air for 20 min and then filtered. An orange-yellow solid was filtered off from an olive green supernatant liquid and washed with cold methanol (40 cm^3). Yield: 0.16 g, 15%. IR (KBr disc, cm^{-1}): 843s ν(V=O). MS (EI): m/z = 375, [M]$^+$, 100%. MS (FAB): m/z = 375, [M]$^+$, 66%, based on m/z = 119, 100%.

(b) From oxobis(pentane-2,4-dionato)vanadium(IV). The compound H$_2$(hap-1,3-pn) (3.80 g, 12.2 mmol) was dissolved in methanol (50 cm^3) and sodium (0.70 g, 0.03 mol) added to form the sodium salt Na$_2$(hap-1,3-pn) *in situ*. Oxobis-(pentane-2,4-dionato)vanadium(IV) (3.20 g, 0.01 mol) was then added and the brown solution left stirring at room temperature for 3.5 h. The orange solid formed was filtered off and washed with diethyl ether (40 cm^3). Yield: 1.79 g, 39%. IR (KBr disc, cm^{-1}): 842s ν(V=O). MS (FAB): m/z = 375, [M]$^+$, 66%, based on m/z = 119, 100%.

[VO{salnptn(3-OMe)$_2$}]. The compound H$_2${salnptn-(3-OMe)$_2$} (1.20 g, 3.24 mmol) was dissolved in acetonitrile (100 cm^3) and oxobis(pentane-2,4-dionato)vanadium(IV) (0.85 g, 3.21 mmol) added. The suspension was heated under reflux for 2 h to give a green-brown solution, which was filtered hot through Celite. The solution was then stored at -20 °C for 3 d. The chocolate brown crystals formed were filtered off and washed with diethyl ether (30 cm^3). Yield: 0.93 g, 66%. IR (KBr disc, cm^{-1}): 986s and 860s ν(V=O). The absorption band at 860 cm^{-1} is *ca.* 90% of the intensity of the band at 986 cm^{-1}. MS (EI): m/z = 435, [M]$^+$, 100%.

[VO{sal-1,2-pn(3-OMe)}$_2$]. The compound 3-methoxy-salicylaldehyde (4.0 g, 13.2 mmol) was dissolved in methanol

(80 cm^3) to afford a yellow solution. Propane-1,2-diamine (1.12 cm^3, 13.2 mmol) was added but no Schiff base was isolated. Oxobis(pentane-2,4-dionato)vanadium(IV) (3.5 g, 0.01 mol) was added, and the suspension heated under reflux for 1 h. A green solid was filtered off and washed with diethyl ether (60 cm^3). Yield: 4.10 g, 76%. IR (KBr disc, cm^{-1}): 987s ν(V=O). Solid state magnetic susceptibility: μ_{eff} 1.77 ± 0.2 μ_B.

The following preparations of isomeric pairs of compounds illustrate the relative ease of interconversion.

[VO{salen(3,5-Cl)$_2$}]. *Mononuclear isomer.* Oxobis(pentane-2,4-dionato)vanadium(IV) (3.41 g, 12.9 mmol) in acetonitrile (30 cm^3) was added to an acetonitrile solution (30 cm^3) of H$_2${salen(3,5-Cl)$_2$} (5.23 g, 12.9 mmol). The reaction mixture was heated under reflux for 20 min, and the green solid formed was filtered off whilst the solution was still hot. The solid was washed with acetonitrile (30 cm^3), and diethyl ether (10 cm^3). Further washing with diethyl ether changed the green solid to an orange brown solid. Yield: 5.82 g, 96%. IR (KBr disc, cm^{-1}): 992s, ν(V=O). Found: C, 40.9; H, 1.9; N, 5.8. C$_{16}$H$_{10}$Cl$_4$N$_2$O$_3$V requires C, 40.8; H, 2.1; N, 6.0%. MS (FAB): m/z = 471, [M]$^+$, 10%, based on m/z = 154, 100%. Solid state magnetic susceptibility: μ_{eff} = 1.65 ± 0.2 μ_B.

Polynuclear isomer. An acetonitrile solution (30 cm^3) of oxobis(pentane-2,4-dionato)vanadium(IV) (4.11 g, 15.5 mmol) was added to an acetonitrile solution (50 cm^3) of H$_2${salen-(3,5-Cl)$_2$} (6.30 g, 15.5 mmol). A green solid was formed after heating under reflux for 20 min. Continued heating gave an orange solid, which was filtered off and washed with cold acetonitrile (20 cm^3) and diethyl ether (40 cm^3). Yield: 7.09 g, 97%. IR (KBr disc, cm^{-1}): 867s, ν(V=O). MS (EI): m/z = 471, [M]$^+$, 100%.

[VO{sal-1,2-pn(5-Br)$_2$}]. *Polynuclear isomer.* The compound H$_2${sal-1,2-pn(5-Br)$_2$} (2.26 g, 5.14 mmol) was suspended in methanol (60 cm^3) and oxobis(pentane-2,4-dionato)-vanadium(IV) (1.36 g, 5.13 mmol) added. An orange suspension was formed and stirred for 2 h at room temperature. The orange solid was filtered off and washed with diethyl ether (60 cm^3). Yield: 2.0 g, 77%. IR (KBr disc, cm^{-1}): 865s ν(V=O). MS (EI): m/z = 505, [M]$^+$, 100%.

Mononuclear isomer. The compound H$_2${sal-1,2-pn(5-Br)$_2$} (2.80 g, 6.03 mmol) was suspended in methanol (80 cm^3) and oxobis(pentane-2,4-dionato)vanadium(IV) (1.6 g, 6.03 mmol) added. The suspension was heated under reflux for 1.5 h to give an orange solid with some green impurity. This could not be removed by washing with cold methanol or diethyl ether. On washing with acetonitrile an insoluble bottle-green product instantly formed. This was filtered off and washed with diethyl ether (50 cm^3). Yield: 2.25 g, 70%. IR (KBr disc, cm^{-1}): 980s ν(V=O). MS (EI): m/z = 505 [M]$^+$, 100%.

Preparation of salts of vanadyl(V) Schiff base complexes, [VO(L)]⁺, by reactions with acids in air

Some new salts of this kind are listed in Table 4, and some typical preparations are given below. The inclusion of additional molecules of solvent or acid in some of the formulations below has not been everywhere confirmed, but this phenomenon has often been found in compounds of this type. These materials presumably all contain five-co-ordinate vanadium(V), and compounds prepared similarly but containing co-ordinated solvent and thus six-co-ordinate vanadium(V) will be described elsewhere.

[VO{salen(5-Br)$_2$}][CF$_3$SO$_3$]. The complex [VO{salen-(5-Br)$_2$}] (2.65 g, 5.40 mmol) was suspended in acetonitrile (60 cm³) and triflic acid (0.50 cm³, 5.7 mmol) added to give an immediate change to dark green. The suspension was stirred at room temperature for 6 d, and the green solid formed filtered off and washed with diethyl ether (40 cm³). Yield: 1.69 g, 52%. IR (KBr disc, cm⁻¹): 928s v(V=O), 826s, 700s, 690s and 639s. Found: C, 33.4; H, 2.0; N, 4.7. C$_{33}$H$_{24}$Br$_4$F$_3$N$_4$O$_9$SV requires C, 35.0; H, 2.1; N, 5.0%.

[VO(salibn)][CF$_3$SO$_3$]. The complex [VO(salibn)] (1.94 g, 5.37 mmol) was dissolved in acetonitrile (60 cm³) to afford a green-blue solution. Trifluoromethanesulfonic acid (0.47 cm³, 5.31 mmol) was added, and a change to deep blue occurred immediately. The solution was stirred for 22 h and layered with diethyl ether. A dark blue crystalline solid was isolated. Yield: 1.59 g, 56% IR (KBr disc, cm⁻¹): 964s v(V=O). Found: C, 42.1; H, 3.7; N, 5.1. C$_{19}$H$_{20}$F$_3$N$_2$O$_7$SV requires C, 44.5; H, 3.9; N, 5.5%. NMR: ¹H (400 MHz, CD$_3$CN) δ 1.66 (s, br, 6 H, 2 × CH$_3$), 4.15 (s, br, 1 H, CH), 4.39 (s, br, 1 H, CH), 7.13 (m, 2 H, aryl), 7.34 (m, 2 H, aryl), 7.89 (s, br, 2 H, aryl), 8.02 (m, 2 H, aryl), 9.05 (s, 1 H, CH) and 9.11 (s, 1 H, CH); ¹⁹F (376 MHz, CD$_3$CN) δ −79.581s; ⁵¹V (131.5 MHz, CD$_3$CN) δ −586.3s ($\Delta v_{1/2} \approx 200$ Hz).

Preparation of salts of adducts [VO(L)→VO(L)]⁺

Compounds prepared by iodine oxidation are listed in Table 5, and those by oxidation in the presence of acids, or by co-crystallisation, Table 6.

(a) Reactions with iodine. A specimen protocol is given. The other products are listed in Table 5.

[{VO{salen(3-OMe)$_2$}}$_2$][I$_3$]·0.5MeCN. The complex [VO{salen(3-OMe)$_2$}] (1.07 g, 2.73 mmol) was dissolved in acetonitrile (50 cm³) and iodine (0.35 g, 1.4 mmol) added. The solution was heated under reflux for 7 h, and then cooled to room temperature over a period of several hours. The green solid was filtered off and washed with diethyl ether (30 cm³). Yield: 0.95 g, 59%. IR (KBr disc, cm⁻¹): 1618s, 1560m, 1262s, 1085s, 859s v(V−O) and 802s.

(b) Reactions with acids in air. The following examples illustrate the general method.

[{VO{salen(5-Cl)$_2$}}$_2$][ClO$_4$]. The complex [VO{salen-(5-Cl)$_2$}] (0.63 g, 1.60 mmol) was suspended in acetonitrile (40 cm³) and perchloric acid (0.2 cm³, 3.20 mmol) was added. The dark green solution was stirred at room temperature for 6 d. A dark green solid was filtered off and washed with diethyl ether (30 cm³). Yield: 0.30 g, 43%. IR (KBr disc, cm⁻¹): 1094s (br) v(Cl−O) and 898s v(V−O). MS (FAB): $m/z = 401$, [M]⁺, 24%, based on $m/z = 55$, 100%.

[{VO{salen(5-Cl)$_2$}}$_2$][BF$_4$]·0.5HBF$_4$. The complex [VO-{salen(5-Cl)$_2$}] (0.86 g, 2.13 mmol) was suspended in aceto-nitrile (30 cm³), and tetrafluoroboric acid–diethyl ether (0.31 cm³, 2.11 mmol) added. After 24 h at room temperature, a dark green solid was filtered off and washed with diethyl ether (30

cm³). The initial filtrate was layered with diethyl ether to yield a further crop of the dark green solid. Yield: 0.60 g, 60%. IR (KBr disc, cm⁻¹): 902s, v(V=O).

(c) Cocrystallisation of vanadium(IV) and vanadium(V) species. For details of further compounds prepared by this method see Table 6.

[{VO{salen(5-Me)$_2$}}$_2$][ClO$_4$]. The complex [VO{salen(5-Me)$_2$}][ClO$_4$] (0.38 g, 0.83 mmol) was dissolved in acetonitrile (60 cm³), [VO{salen(5-Me)$_2$}] (0.30 g, 0.83 mmol) then added and the suspension heated under reflux for 1.5 h. The solution was reduced to dryness, dichloromethane (60 cm³) added, and the dark green solution heated under reflux for 2 h. Green crystals were isolated by layering the filtrate with diethyl ether and storing at −20 °C for 7 d. Yield: 0.45 g, 66%. IR (KBr disc, cm⁻¹): 1623s, 1547s, 1276s, 1255s, 1093s (br), 935s and 829s.

[{VO(salibn)}$_2$][ClO$_4$]·2CHCl$_3$. The complex [VO(salibn)] (1.0 g, 2.8 mmol) was dissolved in acetonitrile (50 cm³), and perchloric acid (0.36 cm³, 5.5 mmol) added to give an immediate change to dark blue. The solution was stirred at room temperature for 5 d, filtered through Celite and reduced to dryness. The crude [VO(salibn)][ClO$_4$] was used without further purification or characterisation; 0.93 g (2.01 mmol) was dissolved in acetonitrile (50 cm³) and [VO(salibn)] (0.73 g, 2.02 mmol) added. The solution was reduced to dryness and chloroform (150 cm³) added to give a dark solution, from which a green powder was isolated after storage at −20 °C for 3 w. This was then filtered off and washed with diethyl ether (30 cm³). Yield: 1.13 g, 55%. IR (KBr disc, cm⁻¹): 1615s, 1543s, 1446s, 1298s, 1272s, 1098s, 916s, 820s, 805s and 755s.

[{VO(salen)}{VO(salnptn)}][BF$_4$]. The complex [VO(salen)] (0.46 g, 1.4 mmol) was dissolved in acetonitrile (100 cm³), [VO(salnptn)][BF$_4$] (0.64 g, 1.4 mmol) added and the solution heated under reflux for 1.5 h. The solution was reduced to dryness and the residue taken up in dichloromethane (180 cm³). This solution was then stored at −20 °C for 3 d. A black crystalline solid was filtered off and washed with diethyl ether (30 cm³). Yield: 0.90 g, 82%. IR (KBr disc, cm⁻¹): 1611s, 1546s, 1446s, 1272s, 1060s (br), 910 and 874s.

[{VO(salnptn)}{VO(salen)}][ClO$_4$]·0.5MeCN. The complex [VO(salen)][ClO$_4$] (1.41 g, 3.3 mmol) was dissolved in acetonitrile (100 cm³) to afford a blue solution; [VO(salnptn)] (1.22 g, 3.3 mmol) was added, and the solution heated to reflux for 2.5 h. The solution was then cooled to room temperature and kept at −20 °C for several weeks. A black crystalline solid was isolated and washed with diethyl ether (30 cm³). Yield: 1.83 g, 68%. IR (KBr disc, cm⁻¹): 1612s, 1545s, 1447s, 1304s, 1092s (br), 862s and 764s.

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