Novel Binuclear Vanadium(v)–Schiff Base Cations containing Single Fluorine Bridges and the Structure of Difluorodioxovanadate(1−)†

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The complex [VO(salen)] [H_2salen = *N,N'*-ethylenebis(salicylideneimine)] reacted with $HBF_4 \cdot Et_2O$ in air to produce the novel linear species [{VO(salen)}$_2$(μ-F)]$^+$, the structure of which has been determined as its BF_4^- and $[VO_2F_2]^-$ salts. The perchlorate and triflate ($O_3SCF_3^-$) salts have been characterised spectroscopically and analytically, as well as the tetrafluoroborate homologues from salicylaldehyde and 2-methylpropylenediamine, and from ethylenediamine and 3-methoxysalicylaldehyde. The $[VO_2F_2]^-$ is mononuclear in the above salt, as well as in $[PPh_4][VO_2F_2]$, compared to a polynuclear form found in $[NH_4][VO_2F_2]$. The mononuclear anion was also fully characterised by ^{19}F and ^{51}V NMR spectroscopy.

We have recently described a family of new vanadium–oxygen species which also contain Schiff bases, which owe their existence to the ability of compounds such as [VO(salen)] [H_2salen = *N,N'*-ethylenebis(salicylideneimine)] to act as an oxygen donor towards other vanadium species.[1] Included in the range of new species identified are [{[V(salen)]$_2$O}$_2$O]$^{2+}$ which we have prepared as two different salts of different crystal and molecular structures (the tetrafluoroborate and the tetraphenylborate),[1,2] [(salen)VOVO(salen)][I_5][3] (containing V^{IV} and V^V), and [{(salen)VOV(salen)}$_2$][I_3]$_2$ (which contains V^{IV} and V^{III}).[2,4] The persistent structural motif in all these materials is $V{=}O{\rightarrow}V$.

In the solid state, compounds [VO(L)] (L = Schiff-base dianion) may be polymeric, due to the $V^{IV}{=}O{\rightarrow}V^{IV}$ interaction, or monomeric, depending on the Schiff base, in no obviously rational fashion.[5,6] However, we were able to synthesise [V^{IV}(salen)O$\rightarrow V^V$(salen)O]$^+$ by direct crystallisation of a mixture of [VO(salen)] and [VO(salen)][ClO_4].[3] To explore these interactions further we required a range of complexes [VO(L)]$^+$ (L = Schiff-base dianion), and since [VO(salen)][ClO_4] in the solid state shows a definite perchlorate–vanadium interaction[7] we decided to synthesise the corresponding tetrafluoroborate.

The protonation of [VO(salen)] has been studied in some detail.[7] For example, reaction with anhydrous HCl in solution in anhydrous acetonitrile in the presence of air yields [VCl_2(salen)]. The corresponding reaction with $HClO_4$ produces [VO(salen)][ClO_4]. When air was excluded from the $HClO_4$ reaction the product was a 1 : 1 mixture of [VO(salen)]$^+$ and a vanadium(III) species. Protonation of the vanadyl oxygen to yield something such as V^{III}(H_2salen) was suggested to occur.[7] In the circumstances it seemed reasonable to attempt the reaction of [VO(salen)] with $HBF_4 \cdot Et_2O$ in air to produce [VO(salen)][BF_4], rather than ion exchange with [VO(salen)][ClO_4]. However, the product we obtained was rather different.

Results and Discussion

The black crystalline product from the reaction of [VO(salen)] with $HBF_4 \cdot Et_2O$ in acetonitrile in air is diamagnetic, consistent with the presence of vanadium(v). The IR spectrum contained a band at 1049 cm^{-1} due to the tetrafluoroborate and one at 953 cm^{-1}, assigned to ν(V=O), but at significantly lower wavenumber than that previously reported for [VO(salen)]$^+$ (981 cm^{-1}).[7]

The analysis of the product (C,H,N,F) could not be easily rationalised. Although the values for C, H and N were consistent with the structure eventually determined by X-ray analysis, the analysis for F was never more than *ca.* 80% of the required value, despite repeated attempts to improve it. We feel that this must be due to the method of analysis (combustion microanalysis) and that the observed value must be an artefact.

The X-ray analysis showed that the crystal contains two independent cations (Fig. 1), and that the overall formula is [{VO(salen)}$_2$(μ-F)][BF_4]. It could not be determined unambiguously whether the μ-F might not be μ-O, and in view of the microanalytical data which suggested that only four fluorine atoms were present we had some hesitation initially about its identity. However, the formulation requires a 1− anion, and the ^{19}F NMR spectrum (see below) is unambiguous, as were further preparative data.

In order to confirm the bridging fluoride, we prepared [VO(salen)][ClO_4] and [VO(salen)][O_3SCF_3] by reaction of [VO(salen)] in air with $HClO_4$ and CF_3SO_3H (triflic acid), respectively. Both salts were recrystallised as 1 : 1 methanol solvates. The IR spectra were as expected with ν(V=O) at 984 (perchlorate) and 978 cm^{-1} (triflate), and *ca.* 30 cm^{-1} to higher wavenumber than the value for the new fluoro-bridged material. Reaction with 0.5 molar equivalent of [NBu^n_4]F yielded black crystalline materials analysing for [{VO(salen)}$_2$(μ-F)]X (X = ClO_4 or O_3SCF_3). In both cases, ν(V=O) was found at 953 cm^{-1}. Single-crystal X-ray photographs showed that the perchlorate is isostructural with the tetrafluoroborate obtained previously.

The ^{51}V NMR spectra of [VO(salen)][O_3SCF_3] shows a single broad peak ($\Delta\nu_{\frac{1}{2}}$ *ca.* 250 Hz) at δ −598.5 with respect to $VOCl_3$. The comparable [{VO(salen)}$_2$(μ-F)][O_3SCF_3] shows an even broader resonance, at δ −587.5. Comparison of the ^{19}F NMR spectra of all three dinuclear salts shows a broad band at δ −137, assignable to the bridging fluoride, as well as signals arising from the appropriate anions. The presence of the bridging fluoride, in the solid state and in solution, has thus been demonstrated unequivocally.

The structure of [{VO(salen)}$_2$(μ-F)][BF_4] (Fig. 1) shows an almost linear OVFVO system, the VFV angles being 172.0(2) and 173.5(2)° in the two independent cations. The conformations of the salen residues, which are rotated by *ca.* 180° with respect

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: mmHg ≈ 133 Pa.

to each other, are as expected, and the bond lengths are similar to those found in the related V–O–V complexes. However, rather unexpectedly, the vanadium atoms are moved out of the equatorial N_2O_2 plane of the co-ordination octahedra towards the outer oxygen atoms by *ca.* 0.22 Å. In related species, six-co-ordinate vanadium tends to be closer to the N_2O_2 plane,[3] so this suggests that the V–F interactions are rather weak. Selected bond lengths and angles are shown in Table 1, and Table 2 lists the atomic coordinates. There are no strictly comparable structures in the literature, so the V–F separations observed here (mean 2.055 Å), shorter than those seen elsewhere (2.2–2.3 Å),[8-10] do not necessarily mean that the V–F binding is stronger. The other structures described are often polymeric species, sometimes with multiple fluorine bridges, *viz.* $[V_3O_3F_{12}]^{3-}$,[8] $[V_2O_2F_8(H_2O)]^{2-}$,[8] $[VO_2F_2]^-$[9] and $[VOF_5]^{2-}$.[10]

Table 1 Selected molecular dimensions (lengths in Å, angles in °) in $[\{VO(salen)\}_2(\mu\text{-}F)][BF_4]$ with estimated standard deviations (e.s.d.s) in parentheses

(*a*) About the V atoms*

x =	a	b	c	d
V(1*x*)–O(1*x*)	1.832(4)	1.809(4)	1.837(4)	1.823(4)
V(1*x*)–N(9*x*)	2.058(5)	2.098(5)	2.071(5)	2.104(5)
V(1*x*)–N(12*x*)	2.095(5)	2.057(5)	2.117(5)	2.049(5)
V(1*x*)–O(20*x*)	1.830(4)	1.831(4)	1.811(4)	1.846(4)
V(1*x*)–O(21*x*)	1.590(4)	1.604(4)	1.587(4)	1.591(4)
V(1*x*)–F(22*xx*′)	2.041(3)	2.078(3)	2.058(3)	2.042(3)
O(1*x*)–V(1*x*)–N(9*x*)	87.0(2)	86.4(2)	86.0(2)	85.7(2)
O(1*x*)–V(1*x*)–N(12*x*)	157.4(2)	161.5(2)	159.0(2)	160.3(2)
N(9*x*)–V(1*x*)–N(12*x*)	76.8(2)	77.4(2)	76.6(2)	76.3(2)
O(1*x*)–V(1*x*)–O(20*x*)	107.5(2)	107.0(2)	108.8(2)	108.8(2)
N(9*x*)–V(1*x*)–O(20*x*)	161.6(2)	158.6(2)	158.4(2)	157.1(2)
N(12*x*)–V(1*x*)–O(20*x*)	85.9(2)	86.3(2)	85.3(2)	86.1(2)
O(1*x*)–V(1*x*)–O(21*x*)	97.7(2)	101.2(2)	98.3(2)	99.6(2)
N(9*x*)–V(1*x*)–O(21*x*)	89.1(2)	95.4(2)	90.8(2)	96.6(2)
N(12*x*)–V(1*x*)–O(21*x*)	97.8(2)	89.2(2)	93.8(2)	90.6(2)
O(20*x*)–V(1*x*)–O(21*x*)	99.6(2)	98.2(2)	102.1(2)	98.3(2)
O(1*x*)–V(1*x*)–F(22*xx*′)	83.9(2)	87.1(2)	83.7(2)	85.9(2)
N(9*x*)–V(1*x*)–F(22*xx*′)	83.7(2)	79.4(2)	80.6(2)	79.5(2)
N(12*x*)–V(1*x*)–F(22*xx*′)	78.8(2)	81.3(2)	81.8(2)	82.9(2)
O(20*x*)–V(1*x*)–F(22*xx*′)	86.7(2)	84.5(2)	85.4(2)	83.8(2)
O(21*x*)–V(1*x*)–F(22*xx*′)	172.6(2)	170.0(2)	171.0(2)	173.0(2)
V(1*x*)–F(22*xx*′)–V(1*x*′)	172.0(2)		173.5(2)	

(*b*) In the $[BF_4^-]$ ions

B(3)–F(31)	1.343(11)	B(4)–F(41)	1.369(13)
B(3)–F(32)	1.356(11)	B(4)–F(42)	1.342(13)
B(3)–F(33)	1.345(10)	B(4)–F(43)	1.324(11)
B(3)–F(34)	1.369(10)	B(4)–F(44)	1.344(11)
F(31)–B(3)–F(32)	108.6(8)	F(41)–B(4)–F(42)	106.0(8)
F(31)–B(3)–F(33)	112.1(7)	F(41)–B(4)–F(43)	108.9(8)
F(32)–B(3)–F(33)	108.2(8)	F(42)–B(4)–F(43)	111.7(9)
F(31)–B(3)–F(34)	111.1(8)	F(41)–B(4)–F(44)	109.3(9)
F(32)–B(3)–F(34)	105.5(7)	F(42)–B(4)–F(44)	108.6(8)
F(33)–B(3)–F(34)	111.0(8)	F(43)–B(4)–F(44)	112.2(8)

* If *x* = a then *x*′ = b, if *x* = c then *x*′ = d (*cf.* Fig. 1).

In contrast, the V=O separations observed here (mean 1.593 Å) are close to the usual range of values, *cf.* [VO(salen)] 1.588,[5] $[VO(salen)][ClO_4]$ 1.576 Å,[7] but perhaps at the longer end, and this is at least consistent with the observed values of ν(V=O). It would appear that F co-ordinated *trans* to O does weaken the V=O bond, in part because of competition with O for the d_{xz} and d_{yz} orbitals, and in part due to σ-electron donation.

Since fluoride is apparently one of the few donor atoms capable of binding to $[VO(salen)]^+$, we attempted to synthesise [VO(F)(salen)] by reaction of $[VO(salen)][ClO_4]$ with 1 molar equivalent of $[NBu^n{}_4]F$. The salt $[\{VO(salen)\}_2(\mu\text{-}F)][ClO_4]$ was isolated in rather lower yield than when only 0.5 molar equivalent was employed, and with 2 molar equivalents the yield was reduced to 45%. In contrast, the reaction with $[VO(salen)][O_3SCF_3]$ with 1 equivalent of fluoride gave a poorly soluble product which formed cubic crystals which appeared to be a salt of $[\{VO(salen)\}_2(\mu\text{-}F)]^+$ from its IR spectrum, but not the triflate salt. This was confirmed by characteristic resonances in the ^{19}F and ^{51}V NMR spectra, but in addition there was a triplet (1 : 2 : 1) signal at δ −596.6 in the ^{51}V spectrum and an octet in the ^{19}F spectrum at δ −34.5, the couplings of the two being 275 Hz. This is consistent with a species containing a VF_2 moiety, but we required an X-ray analysis to prove this was $[VO_2F_2]^-$, even though there were no obvious peaks in the IR spectrum assignable to ν(V=O), apart from the band at 953 cm^{-1} already believed to arise from $[\{VO(salen)\}_2(\mu\text{-}F)]^+$.

In order to check the conversion of $[VO(salen)]^+$ into $[VO_2F_2]^-$ we monitored the ^{51}V NMR spectra of mixtures of $[VO(salen)][O_3SCF_3]$ and $[NBu^n{}_4]F{\cdot}H_2O$ in MeCN in different molar ratios. At a molar ratio of 1 : 0 a single signal at δ −599 assignable to $[VO(salen)]^+$ was observed. With a ratio of 1 : 0.5 the $[VO(salen)]^+$ resonance was still observed, but with an intensity only *ca.* 40% of that of a new peak at δ −587, which we had assigned previously to $[\{VO(salen)\}_2(\mu\text{-}F)]^+$. At a 1 : 1 ratio the peak at δ −599 was still evident but now the intensity was *ca.* 6% of that at δ −587, which had also broadened considerably. In addition, there were two new peaks, each of intensity *ca.* 20% of that of the main δ −587 peak, at δ −592 and −596 and a very weak resonance at δ −556. Finally, at a ratio of 1 : 2 an intense peak at δ −595 ppm occurred, with minor peaks (< 6% relative intensity at the best) at δ −556,

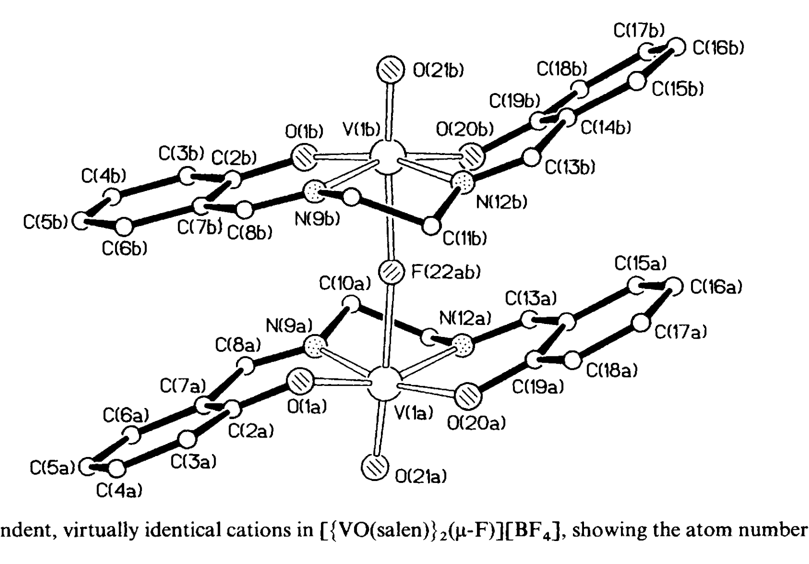

Fig. 1 One of the two independent, virtually identical cations in $[\{VO(salen)\}_2(\mu\text{-}F)][BF_4]$, showing the atom numbering scheme

Table 2 Final atomic coordinates (fractional × 10^4) for $[\{VO(salen)\}_2(\mu\text{-}F)][BF_4]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
V(1a)	3 651.8(7)	1 063.6(4)	−423.9(3)	V(1c)	11 217.6(7)	1 145.7(4)	2 241.6(3)
O(1a)	2 913(3)	1 319(2)	−833(1)	O(1c)	11 426(3)	882(1)	2 780(1)
C(2a)	2 951(4)	1 775(3)	−994(2)	C(2c)	11 720(4)	427(3)	2 877(2)
C(3a)	2 703(4)	1 852(3)	−1 425(2)	C(3c)	12 251(5)	364(3)	3 236(2)
C(4a)	2 745(5)	2 319(3)	−1 595(3)	C(4c)	12 528(5)	−113(3)	3 338(2)
C(5a)	2 983(6)	2 723(3)	−1 353(3)	C(5c)	12 275(5)	−521(3)	3 100(3)
C(6a)	3 203(5)	2 648(3)	−926(3)	C(6c)	11 735(4)	−460(2)	2 751(2)
C(7a)	3 187(4)	2 181(3)	−737(2)	C(7c)	11 454(4)	14(2)	2 628(2)
C(8a)	3 345(4)	2 122(3)	−272(2)	C(8c)	10 850(4)	63(3)	2 277(2)
N(9a)	3 462(3)	1 710(2)	−82(2)	N(9c)	10 638(3)	472(2)	2 098(2)
C(10a)	3 574(4)	1 687(2)	387(2)	C(10c)	9 970(4)	478(2)	1 759(2)
C(11a)	4 295(4)	1 318(2)	470(2)	C(11c)	10 286(5)	833(2)	1 423(2)
N(12a)	4 107(3)	885(2)	196(2)	N(12c)	10 568(3)	1 285(2)	1 649(2)
C(13a)	4 097(4)	447(3)	362(2)	C(13c)	10 380(4)	1 711(3)	1 487(2)
C(14a)	3 893(4)	−4(3)	129(2)	C(14c)	10 603(4)	2 175(3)	1 675(2)
C(15a)	3 828(4)	−450(3)	355(2)	C(15c)	10 331(4)	2 605(3)	1 463(2)
C(16a)	3 628(5)	−883(3)	143(3)	C(16c)	10 502(5)	3 066(3)	1 632(3)
C(17a)	3 485(5)	−885(3)	−292(3)	C(17c)	10 945(5)	3 105(3)	2 022(3)
C(18a)	3 561(4)	−449(3)	−525(2)	C(18c)	11 218(4)	2 685(3)	2 237(2)
C(19a)	3 754(4)	−8(3)	−319(2)	C(19c)	11 055(4)	2 217(3)	2 068(2)
O(20a)	3 822(3)	408(1)	−552(1)	O(20c)	11 354(3)	1 813(1)	2 268(1)
O(21a)	4 534(3)	1 288(1)	−611(1)	O(21c)	12 094(2)	975(1)	2 013(1)
F(22ab)	2 526(2)	848(1)	−127(1)	F(22cd)	9 992(2)	1 276(1)	2 487(1)
V(1b)	1 377.1(7)	727.2(4)	213.6(3)	V(1d)	8 745.0(7)	1 443.9(4)	2 665.3(3)
O(1b)	1 326(3)	1 392(1)	291(1)	O(1d)	8 583(3)	776(2)	2 710(1)
C(2b)	1 175(4)	1 794(2)	56(2)	C(2d)	8 990(4)	404(3)	2 902(2)
C(3b)	1 284(4)	2 257(3)	240(2)	C(3d)	8 864(4)	−90(3)	2 775(2)
C(4b)	1 118(5)	2 677(3)	5(3)	C(4d)	9 259(5)	−474(3)	2 995(3)
C(5b)	832(5)	2 642(3)	−414(3)	C(5d)	9 789(5)	−377(3)	3 350(3)
C(6b)	738(5)	2 192(3)	−610(2)	C(6d)	9 917(4)	103(3)	3 489(2)
C(7b)	910(4)	1 758(2)	−376(2)	C(7d)	9 521(4)	498(3)	3 271(2)
C(8b)	771(4)	1 289(3)	−584(2)	C(8d)	9 648(4)	984(3)	3 436(2)
N(9b)	883(3)	860(2)	−409(2)	N(9d)	9 343(3)	1 390(2)	3 276(2)
C(10b)	696(4)	410(2)	−660(2)	C(10d)	9 529(5)	1 870(2)	3 479(2)
C(11b)	1 398(4)	36(2)	−553(2)	C(11d)	9 878(4)	2 203(2)	3 124(2)
N(12b)	1 488(3)	44(2)	−78(2)	N(12d)	9 264(3)	2 136(2)	2 761(2)
C(13b)	1 560(4)	−358(2)	138(2)	C(13d)	9 054(4)	2 520(3)	2 537(2)
C(14b)	1 700(4)	−373(2)	602(2)	C(14d)	8 547(4)	2 510(3)	2 146(2)
C(15b)	1 625(5)	−829(3)	818(3)	C(15d)	8 313(4)	2 961(3)	1 954(3)
C(16b)	1 815(5)	−870(3)	1 252(3)	C(16d)	7 925(5)	2 960(3)	1 558(3)
C(17b)	2 124(5)	−463(3)	1 473(2)	C(17d)	7 791(5)	2 519(4)	1 342(2)
C(18b)	2 230(4)	−10(3)	1 270(2)	C(18d)	8 019(4)	2 068(3)	1 519(2)
C(19b)	2 008(4)	40(2)	838(2)	C(19d)	8 382(4)	2 061(3)	1 932(2)
O(20b)	2 098(3)	481(1)	634(1)	O(20d)	8 627(3)	1 627(2)	2 092(1)
O(21b)	464(3)	556(1)	418(1)	O(21d)	7 822(3)	1 631(2)	2 835(1)
B(3)	1 332(7)	3 327(3)	5 416(3)	B(4)	4 628(8)	1 218(4)	3 118(3)
F(31)	1 139(4)	3 439(2)	5 004(2)	F(41)	3 925(4)	1 318(2)	2 859(2)
F(32)	2 152(3)	3 140(2)	5 430(2)	F(42)	5 316(4)	1 182(2)	2 851(2)
F(33)	1 301(3)	3 728(2)	5 675(1)	F(43)	4 724(4)	1 585(2)	3 399(2)
F(34)	804(3)	2 957(2)	5 569(1)	F(44)	4 509(3)	779(2)	3 314(1)

−586 and −588. Independent measurements enable us to assign the peak at δ −595 or −596 to $[VO_2F_2]^-$. Further increase in the ratio of fluoride to vanadium did not afford much change to the ^{51}V NMR spectrum, the peak at δ 596 being the only significant one observable.

The ^{19}F NMR spectra of these mixtures were also monitored. Starting with pure $[VO(salen)][O_3SCF_3]$ and the single characteristic singlet with ^{13}C satellites (δ −79.8) we observed the growth of a peak attributable to $[\{VO(salen)\}_2(\mu\text{-}F)]^+$ (δ −137.2) together with a very weak resonance at δ −152.1, as $[NBu^n{}_4]F{\cdot}H_2O$ was added. This last, which we assign to BF_4^-, seems to arise from the glass, from which boron was leached as increasing amounts of fluoride were added. Finally, in a 1:3 mixture of $[VO(salen)][O_3SCF_3]$ and $[NBu^n{}_4]F{\cdot}H_2O$, peaks assignable to $CF_3SO_3^-$ and the minor resonance at δ −152.1 occurred.

Now the resonance assignable to $[NBu^n{}_4]F{\cdot}H_2O$ alone in MeCN is observed at δ −114.9 (together with the minor one at δ −152.1, assigned to $[BF_4]^-$). Consequently neither the resonance of F^- nor that of $[VO_2F_2]^-$ is observed for these mixtures where they might be expected. Examination of the ^{19}F NMR spectrum of a 1:1 mixture of $[PPh_4][VO_2F_2]$ and $[NBu^n{}_4]F{\cdot}H_2O$ also failed to show these resonances, though there was a broad resonance at about δ −60 and another at *ca.* δ −127. We conclude that the fluoride in $[VO_2F_2]^-$ is exchanging rapidly with F^- in solution. There was no sign of resolution of fluorine resonances, even at −40 °C.

We believe that these observations establish that the sequence $[VO(salen)]^+ \longrightarrow [\{VO(salen)\}_2(\mu\text{-}F)_2]^+ \longrightarrow [VO_2F_2]^-$ occurs, and that clearly both fluoride and water are necessary to effect this conversion. However, there are other minor species involved, and we have not been able to identify these. In addition, there may be species in the sequence beyond $[VO_2F_2]^-$, but we have not pursued them.

The mononuclear tetrahedral ion $[VO_2F_2]^-$ has already been posited in the salts $[PPh_4][VO_2F_2]$ and $[AsPh_4][VO_2F_2]$.[11] The ^{51}V and ^{19}F NMR spectra of these species[12] are exceedingly similar to those we have assigned using the formulation $[\{VO(salen)\}_2(\mu\text{-}F)][VO_2F_2]$ for our new compound. The structure of the ammonium salt[9] formulated as $[NH_4][VO_2F_2]$ revealed that $[VO_2F_2]^-$ is polymeric in the solid state (if not in solution), with an oxygen and a fluorine bridge between each pair of vanadium atoms, giving essentially six-co-ordination. However, our analysis of $[\{VO(salen)\}_2(\mu\text{-}F)][VO_2F_2]$ suggested an alternative mononuclear structure for $[VO_2F_2]^-$, consistent with that inferred from the IR spectra of the $[PPh_4]^+$ and $[AsPh_4]^+$ salts.[11]

Crystals of $[\{VO(salen)\}_2(\mu\text{-}F)][VO_2F_2]$ are isostructural with those of the tetrafluoroborate described above, and the cation structures are essentially identical. Bond lengths and angles are listed in Table 3, and atomic coordinates in Table 4. In the crystal the anions are disordered so that there is no preferred orientation of V–O and V–F bonds. The mean V–(O,F) bond length is 1.681(7) Å, which falls between the values expected for V=O and V–F. There are short V–(O,F) • • • H–C contacts, as in the tetrafluoroborate structure, and the same kind of interactions probably occur. Clearly the form of $[VO_2F_2]^-$ contained in this crystal is new and mononuclear, rather than polymeric as established in $[NH_4][VO_2F_2]$.[9] Since we were not able to refine the structure to give individual V–O and V–F bond lengths in the anion, we undertook a structural analysis of $[PPh_4][VO_2F_2]$, already proposed to contain tetrahedral $[VO_2F_2]^-$.[11]

The IR spectrum of $[PPh_4][VO_2F_2]$ (Nujol mull) shows a strong band at 959 cm^{-1} (*cf.* 953 cm^{-1} for the OVFVO salt) assignable to ν(V=O) with a shoulder at 995 cm^{-1} (in retrospect, also present in the spectrum of the OVFVO salt). We assign ν(V–F) to bands at 665 and 631 cm^{-1} (*cf.* 658 and 629 cm^{-1} for the OVFVO salt). The IR, ^{19}F and ^{51}V NMR spectra were essentially the same as those already reported.[11,12] The X-ray analysis revealed monomeric $[VO_2F_2]^-$, in complete orientational disorder (Fig. 2). Bond lengths and angles and atomic coordinates are in Tables 5 and 6, respectively. The refinement reached convergence with six independent fluorine atoms around each vanadium in an anion. The $[PPh_4]^+$ cation refined very clearly, so that we conclude that this disorder, as shown in Fig. 2, is real and not some artefact. The anion is situated on an axis of $\bar{4}$ symmetry, so that effective equivalence of O and F was to be expected, but the situation is even more complex and unexpected. No V=O and V–F bond lengths, or corresponding angles, can be inferred.

Table 3 Selected molecular dimensions (lengths in Å, angles in °) in $[\{VO(salen)\}_2(\mu\text{-}F)][VO_2F_2]$ with e.s.d.s in parenthees

(*a*) About the V atoms *

x =	a	b	c	d
V(1*x*)–O(1*x*)	1.832(5)	1.816(5)	1.834(4)	1.827(5)
V(1*x*)–N(9*x*)	2.060(6)	2.088(6)	2.075(6)	2.098(5)
V(1*x*)–N(12*x*)	2.108(6)	2.063(5)	2.106(6)	2.066(6)
V(1*x*)–O(20*x*)	1.837(5)	1.843(5)	1.818(5)	1.840(4)
V(1*x*)–O(21*x*)	1.596(5)	1.590(5)	1.599(5)	1.590(5)
V(1*x*)–F(22*xx*′)	2.036(4)	2.079(4)	2.070(4)	2.044(4)
O(1*x*)–V(1*x*)–N(9*x*)	86.5(2)	86.7(2)	85.9(2)	85.4(2)
O(1*x*)–V(1*x*)–N(12*x*)	158.0(2)	160.6(2)	159.1(2)	160.5(2)
N(9*x*)–V(1*x*)–N(12*x*)	77.5(2)	76.9(2)	76.8(2)	77.5(2)
O(1*x*)–V(1*x*)–O(20*x*)	107.6(2)	107.2(2)	108.1(2)	108.2(2)
N(9*x*)–V(1*x*)–O(20*x*)	162.0(2)	158.3(2)	158.9(2)	157.8(2)
N(12*x*)–V(1*x*)–O(20*x*)	85.9(2)	85.9(2)	85.8(2)	85.5(2)
O(1*x*)–V(1*x*)–O(21*x*)	98.0(2)	101.7(2)	98.4(2)	100.7(2)
N(9*x*)–V(1*x*)–O(21*x*)	89.1(2)	95.4(2)	90.7(2)	96.1(2)
N(12*x*)–V(1*x*)–O(21*x*)	96.6(2)	90.2(2)	93.6(2)	90.6(2)
O(20*x*)–V(1*x*)–O(21*x*)	99.6(2)	97.9(2)	102.4(2)	98.3(2)
O(1*x*)–V(1*x*)–F(22*xx*′)	84.4(2)	86.6(2)	84.3(2)	85.4(2)
N(9*x*)–V(1*x*)–F(22*xx*′)	83.1(2)	80.1(2)	80.2(2)	79.0(2)
N(12*x*)–V(1*x*)–F(22*xx*′)	78.9(2)	80.5(2)	81.2(2)	82.1(2)
O(20*x*)–V(1*x*)–F(22*xx*′)	87.2(2)	84.1(2)	85.5(2)	84.5(2)
O(21*x*)–V(1*x*)–F(22*xx*′)	171.7(2)	170.4(2)	170.3(2)	171.9(2)
V(1*x*)–F(22*xx*′)–V(1*x*′)	173.9(2)		173.9(2)	

(*b*) In the $[VO_2F_2]^-$ ions

V(3)–F/O(31)	1.686(5)	V(4)–F/O(41)	1.719(7)
V(3)–F/O(32)	1.662(7)	V(4)–F/O(42)	1.696(6)
V(3)–F/O(33)	1.670(5)	V(4)–F/O(43)	1.668(6)
V(3)–F/O(34)	1.699(6)	V(4)–F/O(44)	1.649(5)
F/O(31)–V(3)–F/O(32)	109.5(4)	F/O(41)–V(4)–F/O(42)	108.9(3)
F/O(31)–V(3)–F/O(33)	109.5(3)	F/O(41)–V(4)–F/O(43)	109.8(3)
F/O(32)–V(3)–F/O(33)	108.7(3)	F/O(42)–V(4)–F/O(43)	110.2(3)
F/O(31)–V(3)–F/O(34)	109.8(3)	F/O(41)–V(4)–F/O(44)	110.0(3)
F/O(32)–V(3)–F/O(34)	108.1(3)	F/O(42)–V(4)–F/O(44)	108.2(3)
F/O(33)–V(3)–F/O(34)	111.1(3)	F/O(43)–V(4)–F/O(44)	109.8(3)

* If *x* = a then *x*′ = b, if *x* = c then *x*′ = d (*cf.* Fig. 1).

Conclusion

We have shown that monofluoride bridges can form in vanadium(V) compounds to produce chains OVFVO, which are analogous to some of the monooxide-bridged chains we have already described. However, we do not yet know whether such chains can be extended to vanadium-(IV) and -(III) chemistry. Similar compounds can be obtained from at least two further Schiff bases in addition to H_2salen, as detailed in the Experimental section. The chain is stable in the solid state and in solution, so that fluoride is a reasonably strong donor to vanadium(V). An excess of fluoride seems capable of forcing the displacement of salen residues from vanadium(V), which is rather unexpected. The behaviour described in this paper should not be assumed to be characteristic of all tetradentate Schiff-base complexes, and variations are currently being explored. In addition, it is likely that the oxygen atoms of the OVFVO chain can act as donors to further metal atoms. This is also under study.

We have confirmed that $[VO_2F_2]^-$ can indeed exist as a monomeric, presumably tetrahedral species, as well as in the polymeric form already described. Disorder problems prevented us from determining the detailed structure, but the NMR spectra make its characterisation sure. Such orientational disorder should be characteristic of many oxofluoro-anions, but it is not considered necessary to carry out further studies on the current system to obtain more structural data.

Experimental

Reactions were all carried out under dinitrogen using standard

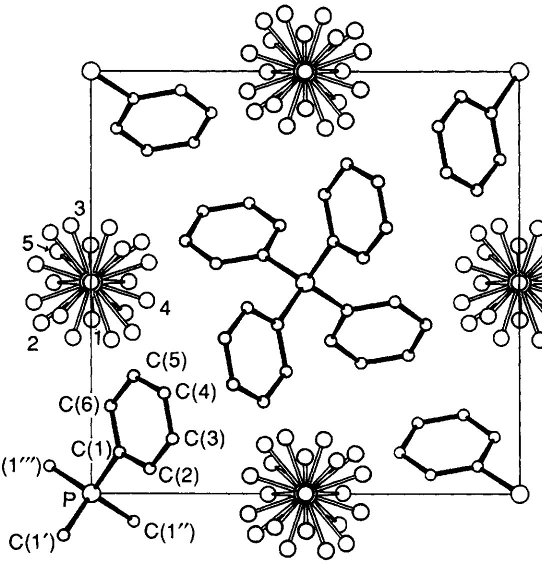

Fig. 2 Projection down the *c* axis of a cell of $[PPh_4][VO_2F_2]$. The P atom lies at the origin from which the *a* axis goes up the page and the *b* axis to the right across the page. In the anion the number of the oxygen/fluorine atom is indicated; O/F(6) lies directly above the V atom

Table 4 Final atomic coordinates (fractional × 10^4) for $[\{VO(salen)\}_2(\mu\text{-}F)][VO_2F_2]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
V(1a)	3 599.5(8)	1 097.4(4)	−397.2(4)	V(1c)	11 341.6(8)	1 170.5(4)	2 302.8(4)
O(1a)	2 853(3)	1 360(2)	−792(1)	O(1c)	11 553(3)	910(2)	2 834(1)
C(2a)	2 895(5)	1 811(3)	−954(2)	C(2c)	11 877(5)	466(3)	2 926(2)
C(3a)	2 643(6)	1 892(3)	−1 372(3)	C(3c)	12 413(5)	397(3)	3 279(3)
C(4a)	2 661(6)	2 350(4)	−1 547(3)	C(4c)	12 720(5)	−65(3)	3 384(3)
C(5a)	2 928(7)	2 739(4)	−1 303(4)	C(5c)	12 496(5)	−472(3)	3 139(3)
C(6a)	3 161(6)	2 683(3)	−881(4)	C(6c)	11 961(5)	−413(3)	2 796(3)
C(7a)	3 137(5)	2 212(3)	−706(3)	C(7c)	11 650(5)	48(3)	2 680(2)
C(8a)	3 309(5)	2 149(3)	−251(3)	C(8c)	11 046(5)	98(3)	2 333(2)
N(9a)	3 439(4)	1 740(2)	−59(2)	N(9c)	10 800(4)	494(2)	2 155(2)
C(10a)	3 579(6)	1 715(3)	404(2)	C(10c)	10 134(5)	492(3)	1 818(3)
C(11a)	4 279(6)	1 345(3)	475(3)	C(11c)	10 432(6)	851(3)	1 486(2)
N(12a)	4 097(4)	914(2)	211(2)	N(12c)	10 702(4)	1 303(2)	1 718(2)
C(13a)	4 109(5)	481(3)	368(2)	C(13c)	10 493(5)	1 724(3)	1 563(2)
C(14a)	3 911(5)	37(3)	138(3)	C(14c)	10 691(5)	2 188(3)	1 753(3)
C(15a)	3 903(5)	−407(3)	363(3)	C(15c)	10 425(6)	2 616(3)	1 534(3)
C(16a)	3 717(6)	−846(3)	156(3)	C(16c)	10 582(7)	3 070(4)	1 696(3)
C(17a)	3 522(5)	−837(3)	−277(3)	C(17c)	11 016(6)	3 111(3)	2 086(3)
C(18a)	3 539(5)	−402(3)	−505(3)	C(18c)	11 299(5)	2 699(3)	2 303(3)
C(19a)	3 728(5)	34(3)	−295(3)	C(19c)	11 145(5)	2 232(3)	2 136(2)
O(20a)	3 743(3)	445(2)	−529(1)	O(20c)	11 446(3)	1 834(2)	2 341(1)
O(21a)	4 484(3)	1 311(2)	−589(1)	O(21c)	12 234(3)	1 016(2)	2 077(2)
F(22ab)	2 492(3)	899(1)	−84(1)	F(22cd)	10 095(2)	1 276(1)	2 535(1)
V(1b)	1 378.4(8)	764.2(4)	273.9(3)	V(1d)	8 836.3(8)	1 418.3(4)	2 704.9(4)
O(1b)	1 306(3)	1 425(2)	345(1)	O(1d)	8 713(3)	752(2)	2 729(1)
C(2b)	1 155(5)	1 818(3)	98(2)	C(2d)	9 125(5)	391(3)	2 928(2)
C(3b)	1 292(5)	2 280(3)	267(3)	C(3d)	9 010(5)	−99(3)	2 791(3)
C(4b)	1 111(6)	2 685(3)	27(3)	C(4d)	9 408(6)	−478(3)	3 002(3)
C(5b)	800(6)	2 647(3)	−386(3)	C(5d)	9 937(6)	−386(3)	3 355(3)
C(6b)	673(6)	2 192(3)	−553(3)	C(6d)	10 050(5)	84(3)	3 494(3)
C(7b)	864(5)	1 768(3)	−316(2)	C(7d)	9 653(5)	475(3)	3 288(2)
C(8b)	687(5)	1 290(3)	−505(2)	C(8d)	9 752(5)	961(3)	3 462(2)
N(9b)	821(4)	875(2)	−328(2)	N(9d)	9 423(4)	1 351(2)	3 308(2)
C(10b)	622(5)	419(3)	−559(2)	C(10d)	9 599(6)	1 831(3)	3 519(2)
C(11b)	1 366(5)	76(3)	−480(2)	C(11d)	9 938(6)	2 165(3)	3 173(2)
N(12b)	1 518(4)	90(2)	−18(2)	N(12d)	9 335(4)	2 113(2)	2 806(2)
C(13b)	1 622(4)	−306(3)	200(2)	C(13d)	9 123(5)	2 490(3)	2 579(2)
C(14b)	1 813(5)	−324(3)	657(2)	C(14d)	8 628(5)	2 479(3)	2 197(2)
C(15b)	1 770(5)	−774(3)	871(3)	C(15d)	8 380(5)	2 922(3)	2 008(3)
C(16b)	1 998(6)	−799(4)	1 289(3)	C(16d)	7 984(5)	2 918(3)	1 612(3)
C(17b)	2 286(5)	−390(3)	1 509(3)	C(17d)	7 826(6)	2 486(4)	1 404(3)
C(18b)	2 356(5)	58(3)	1 299(2)	C(18d)	8 063(5)	2 049(3)	1 582(2)
C(19b)	2 094(5)	96(3)	872(2)	C(19d)	8 459(5)	2 038(3)	1 976(2)
O(20b)	2 152(3)	532(2)	677(1)	O(20d)	8 713(3)	1 612(2)	2 144(1)
O(21b)	507(3)	583(2)	498(1)	O(21d)	7 912(3)	1 590(2)	2 877(2)
V(3)	1 369(1)	3 379.9(5)	5 491.4(4)	V(4)	4 774(1)	1 188.1(5)	3 161.4(4)
F/O(31)	1 173(5)	3 537(2)	4 978(2)	F/O(41)	3 904(4)	1 345(2)	2 844(2)
F/O(32)	2 363(4)	3 145(2)	5 532(2)	F/O(42)	5 650(4)	1 083(2)	2 845(2)
F/O(33)	1 306(4)	3 878(2)	5 801(2)	F/O(43)	4 986(4)	1 642(2)	3 505(2)
F/O(34)	646(4)	2 945(2)	5 650(2)	F/O(44)	4 557(4)	680(2)	3 427(2)

Schlenk techniques unless otherwise stated. Microanalyses were undertaken by M. Patel, University of Sussex, or C. J. Macdonald of this Laboratory on a Perkin-Elmer 2400 analyser except where stated otherwise. The IR spectra were obtained as Nujol mulls using a Perkin-Elmer 883 spectrometer, and UV spectra as solutions in dichloromethane or acetonitrile using a Perkin-Elmer 5505 spectrometer. Proton and ^{51}V NMR spectra were obtained on Bruker AMX500 or JEOL GSX270 machines, using $SiMe_4$ and $VOCl_3$, respectively, as external standards, ^{19}F NMR spectra on Bruker WP80 or JEOL GSX270 spectrometers with $CFCl_3$ as external reference. The Bruker measurements were courtesy of Dr. T. Avent, University of Sussex. 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 with Pascal's constants.

All the chemicals were obtained either from Aldrich or BDH Chemicals, and generally used without further purification. When working with Schlenk techniques, solvents were dried and freshly distilled before use. The compounds H_2salen and [VO(salen)] were prepared as described elsewhere.[13]

Nitromethane, used for conductivity measurements, was purified by refluxing it for 1 h over ground CaH_2 at 50 mmHg, then fractionating it at 50 mmHg (b.p. 36 °C) using a Vigreux column and collecting the middle fraction over molecular sieves (4A). By this method, the conductivity of the solvent was reduced from 1.31 to 0.11 μS cm^{-1}.

μ-Fluoro-bis{[N,N′-*ethylenebis(salicylideneiminato)*]*oxovanadium} Tetrafluoroborate.*—To a suspension of [VO(salen)] (1.0 g, 3.0 mmol) in acetonitrile (50 cm^3) was added *via* syringe tetrafluoroboric acid, $HBF_4{\cdot}Et_2O$ (0.49 g, 3.0 mmol, 0.42 cm^3). The green solid dissolved immediately yielding a dark blue-black solution. After stirring overnight in air, the solvent was removed to dryness with a rotary evaporator and the remaining solid dissolved in boiling methanol (150 cm^3), leaving a small residue which was filtered off. The dark blue-black filtrate was allowed to cool and set aside at −20 °C for

Table 5 Selected molecular dimensions (lengths in Å, angles in °) in $[PPh_4][VO_2F_2]$ with e.s.d.s in parentheses

(*a*) In the tetraphenylphosphonium ion			
P–C(1)	1.793(7)	C(3)–C(4)	1.344(13)
C(1)–C(2)	1.393(11)	C(4)–C(5)	1.379(14)
C(1)–C(6)	1.372(9)	C(5)–C(6)	1.389(13)
C(2)–C(3)	1.363(12)		
C(1)–P–C(1′)	107.3(3)	C(1)–C(2)–C(3)	120.0(7)
C(1)–P–C(1″)	110.6(3)	C(2)–C(3)–C(4)	120.4(9)
P–C(1)–C(2)	117.7(5)	C(3)–C(4)–C(5)	120.8(9)
P–C(1)–C(6)	122.3(6)	C(4)–C(5)–C(6)	119.9(7)
C(2)–C(1)–C(6)	119.9(7)	C(1)–C(6)–C(5)	119.0(7)
(*b*) In the difluorodioxovanadate(V) ion			
V–F/O(1)	1.66(4)	V–F/O(4)	1.69(6)
V–F/O(2)	1.87(7)	V–F/O(5)	1.68(4)
V–F/O(3)	1.76(6)	V–F/O(6)	1.73(5)

In the disordered anion, there are several possible (approximately regular) VO_2F_2 tetrahedra; the only one with crystallographic $\bar{4}$ symmetry involves the F/O(5) atoms: F/O(5)–V–F/O(5′) 102.2(22), F/O(5)–V–F/O(5″) 113.2(22).

Table 6 Final atomic coordinates (fractional × 10^4) for $[PPh_4]$-$[VO_2F_2]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
P	0	0	0
C(1)	656(5)	987(5)	1488(11)
C(2)	1361(6)	595(6)	2868(11)
C(3)	1887(8)	1312(8)	4027(12)
C(4)	1698(7)	2395(7)	3893(16)
C(5)	988(6)	2804(6)	2562(18)
C(6)	453(5)	2091(5)	1350(13)
V	0	5000	−2500
F/O(1)	12(32)	4120(27)	−730(51)
F/O(2)	−1175(64)	4042(51)	−2109(101)
F/O(3)	−473(85)	6346(38)	−2112(98)
F/O(4)	1298(47)	4573(88)	−2862(101)
F/O(5)	−789(32)	5730(39)	−3981(65)
F/O(6)	0	5000	−4918(71)

There is extensive disorder amongst the fluorine/oxygen atoms of the $[VO_2F_2]^-$ anions.

7 d. The black, crystalline product (0.254 g, 0.33 mmol, 22%) was filtered off, washed with MeOH and diethyl ether and dried in air. More product (0.186 g, 0.24 mmol, 16%) was obtained by removing *ca.* 50 cm^3 solvent from the filtrate, layering the rest with ether (50 cm^3) and leaving the mixture at −20 °C for 2 d (Found: C, 49.4; H, 3.20; F, 9.55; N, 7.10. $C_{32}H_{28}BF_5N_4O_6V_2$ requires C, 49.8; H, 3.65; F, 12.3; N, 7.25%). UV (MeCN): λ_{max} 570 nm. IR (Nujol mull): ν_{max} 1625s (C=N), 1598s (aromatic C$\overset{\cdots}{-}$C), 1553s (aromatic C$\overset{\cdots}{-}$C), 1277s (phenyl C–O), 1049s (br) (BF_4), 953s (V=O) and 757s cm^{-1} (aromatic C–H). NMR (CD_3CN): ^1H (500 MHz), δ 3.92 (1 H, m), 4.10 (1 H, m), 6.81 (1 H, d, *J* 8.1), 6.95 (1 H, t, *J* 7.4), 7.26 (1 H, d, *J* 7.7), 7.63 (1 H, t, *J* 7.4 Hz) and 8.30 (1 H, s); ^{51}V (500 MHz), δ −587.6 (s, $\Delta\nu_{\frac{1}{2}} \approx 450$ Hz); (270 MHz), δ −587.4 (430 Hz); ^{19}F (80 MHz), δ −152.2 (s) and −136.9 (s, br); (270 MHz), δ −152.2 and −137.2.

Similar methods were used to prepare the following compounds.

μ-*Fluoro-bis*{[N,N′-2-*methylpropylenebis*(*salicylideneiminato*)]*oxovanadium*} *tetrafluoroborate*. Yield 48% (Found: C, 51.8; H, 4.4; N, 6.8. $C_{36}H_{36}BF_5N_4O_6V_2$ requires C, 52.1; H, 4.3; N, 6.8%). IR (Nujol mull): ν_{max} 1620s (C=N), 1596s (aromatic C$\overset{\cdots}{-}$C), 1276s (phenyl C–O), 1072s (br) (BF_4), 952s (V=O) and 759s cm^{-1} (aromatic C–H). NMR (270 MHz, CD_3CN): ^1H, δ 1.27 (3 H, s), 1.66 (3 H, s), 3.90 (2 H, m), 6.62 (1 H, t, *J* 7.4), 6.78 (2 H, m), 6.94 (1 H, d, *J* 8.0), 7.18 (2 H, t, *J* 7.4), 7.56 (2 H, m), 7.76 (1 H, t, *J* 7.4 Hz), 8.13 (1 H, s) and 8.25 (1 H, s); ^{51}V, δ −576.1 (s, $\Delta\nu_{\frac{1}{2}} \approx 550$ Hz); ^{19}F, δ −152.2 (s) and −136.2 (s).

μ-*Fluoro-bis*{[N,N′-*ethylenebis*(3-*methoxysalicylideneiminato*)]*oxovanadium*} *tetrafluoroborate*. Yield 39% (Found: C, 47.8; H, 4.2; N, 6.1. $C_{36}H_{36}BF_5N_4O_{10}V_2$ requires C, 48.4; H, 4.0; N, 6.3%). IR (Nujol mull): ν_{max} 1618s (C=N), 1597s (aromatic C$\overset{\cdots}{-}$C), 1279s (phenyl C–O), 1055s (br) (BF_4), 951s (V=O) and 756s cm^{-1} (aromatic C–H). NMR (270 MHz, CD_3CN): ^1H, δ 3.84 (1 H, m), 3.91 (3 H, s), 4.10 (1 H, m), 6.95 (2 H, m), 7.15 (1 H, d, *J* 6.4 Hz) and 8.30 (2 H, s); ^{51}V, −568.1 (s, $\Delta\nu_{\frac{1}{2}} \approx 750$ Hz); ^{19}F −152.2 (s) and −138.4 (s).

μ-*Fluoro-bis*{[N,N′-*ethylenebis*(*salicylideneiminato*]*oxovanadium*} *Perchlorate*.—To stirred solutions of [VO(salen)]-[ClO_4]·MeOH (0.46 g, 1.0 mmol) in acetonitrile (15 cm^3) were quickly added 1 mol dm^{-3} [NBu_4]F solutions in thf [0.5 (1), 1 (2) and 2 cm^3 (3), respectively] and stirring stopped immediately. The colour changed from dark blue to violet, the intensity of the final colour depending on the amount of fluoride added. From solutions 1 and 2 crystals started to precipitate immediately. After leaving the mixtures at −20 °C overnight, the black, crystalline products [0.35 g, 0.45 mmol, 89% (1); 0.26 g, 0.33 mmol, 66% (2)] were filtered off, washed with MeCN and diethyl ether and dried in air.

From solution 3 crystals did not precipitate directly. The solvent was removed on the rotary evaporator and the residue dissolved in boiling methanol (150 cm^3). After leaving the mixture at −20 °C for 6 d, the black crystalline product (0.18 g, 0.23 mmol, 46%) was filtered off, washed with methanol and diethyl ether and dried in air [Found: (1) C, 49.0; H, 3.45; N, 7.45. (2) C, 48.6; H, 3.25; N, 7.25. (3) C, 48.6; H, 3.35; N, 6.80. $C_{32}H_{28}ClFN_4O_{10}V_2$ requires C, 49.0; H, 3.60; N, 7.15%]. IR (Nujol mull): ν_{max} 1628s (C=N), 1597s (aromatic C$\overset{\cdots}{-}$C), 1552s (aromatic C$\overset{\cdots}{-}$C), 1275s (phenyl C–O), 1100s (br) (ClO_4), 952s (V=O) and 757 cm^{-1} (aromatic C–H).

[N,N′-*Ethylenebis*(*salicylideneiminato*)]*oxovanadium Triflate–Methanol* (1/1).—To a suspension of [VO(salen)] (2.67 g, 8.0 mmol) in MeCN (*ca.* 100 cm^3), was added *via* syringe, triflic acid (1.20 g, 8.0 mmol, 0.71 cm^3). The green suspension immediately gave a blue-black solution. After stirring overnight in air, the solvent was removed on the rotary evaporator, and the residue redissolved in hot methanol (20 cm^3). After filtering, diethyl ether (60 cm^3) was added and the solution set aside at −20 °C. Five days later the black crystalline product (1.90 g, 3.69 mmol, 46%) was filtered off, washed with MeOH–Et_2O (1 : 5) and diethyl ether and dried in air (Found: C, 41.4; H, 2.90; N, 5.55. $C_{18}H_{18}F_3N_2O_7SV$ requires C, 42.0; H, 3.55; N, 5.45%). UV (MeCN): λ_{max} 560 nm. IR (Nujol mull): ν_{max} 3383m (br) (MeOH), 1618s (C=N), 1597s, (aromatic C$\overset{\cdots}{-}$C), 1556s (aromatic C$\overset{\cdots}{-}$C), 1300–1200s (br) (CF_3SO_3), 1031s (CF_3SO_3), 978s (V=O), 769s (aromatic C–H), 634s (CF_3SO_3), 571m (CF_3SO_3) and 521m cm^{-1} (CF_3SO_3). NMR (CD_3CN): ^1H (500 MHz), δ 4.22 (1 H, m), 4.45 (1 H, s, br), 7.08 (1 H, d, *J* 8.3), 7.28 (1 H, t, *J* 7.5), 7.82 (1 H, s, br), 7.91 (1 H, d, *J* 7.8 Hz) and 9.07 (1 H, s); ^{51}V (500 MHz), δ −598.5 (s, $\Delta\nu_{\frac{1}{2}} \approx 250$ Hz); ^{19}F (80 MHz), δ −79.8 (s).

μ-*Fluoro-bis*{[N,N′-*ethylenebis*(*salicylideneiminato*)]*oxovanadium*} *Triflate*.—To a dark blue solution of [VO(salen)]-[O_3SCF_3]·MeOH (1.03 g, 2.0 mmol) in acetonitrile (25 cm^3) was added a 1 mol dm^{-3} [NBu_4]F solution in thf (1.0 cm^3), whereupon the colour changed slightly to blue-violet. After 16 h the solvent was removed on the rotary evaporator and the black residue was dissolved in boiling methanol (60 cm^3). After

Table 7 Crystal data and details of crystal structure analyses

	[{VO(salen)}$_2$(μ-F)][BF$_4$]	[{VO(salen)}$_2$(μ-F)][VO$_2$F$_2$]	[PPh$_4$][VO$_2$F$_2$]
Elemental formula	$C_{32}H_{28}BF_5N_4O_6V_2$	$C_{32}H_{28}F_3N_4O_8V_3$	$C_{24}H_{20}F_2O_2PV$
M	772.3	806.4	460.3
Crystal colour, shape	Very dark brown, tapered prisms	Well formed, shiny black prisms	Pale yellow, flat needles
Crystal size/mm	0.08 × 0.12 × 0.48	0.17 × 0.17 × 0.43	0.55 × 0.21 × 0.024
Crystal system	Orthorhombic	Orthorhombic	Tetragonal
Space group (no.)	*Pcab* (equiv. to no. 61)	*Pcab* (equiv. to no. 61)	$I\bar{4}$ (no. 82)
a/Å	15.3427(8)	15.377(1)	12.1895(9)
b/Å	26.955(3)	27.244(3)	
c/Å	30.894(2)	31.247(4)	7.1423(8)
U/Å^3	12 776	13 090	1061.2
Z	16	16	2
D_c/g cm^{-3}	1.606	1.637	1.441
F(000)	6272	6528	472
μ(Mo-Kα)/cm^{-1}	6.4	8.8	5.6
θ Range for cell parameter determination/°	10–11	12–13	12–13
θ_{max} for intensity measurements/°	20	22	20
Total unique reflections	5942	7999	511
No. of 'observed' data (with $I > 2\sigma_I$)	3528	4158	367
Structure determination	Direct methods[15] (SHELXS/TREF)	Isostructural with [BF$_4$]$^-$ salt	Since $Z = 2$, then V and P atoms must be on special positions
R	0.086	0.083	0.071
R'[14]	0.061	0.065	0.070
R_g[14]	0.051	0.062	0.074
No. of reflections in refinement	5942	6184 ($I > \sigma_I$)	511
Weighting scheme	σ_F^{-2}	$(\sigma_F^2 + 0.0005F^2)^{-1}$	$(\sigma_F^2 + 0.0123F^2)^{-1}$

leaving the solution for 6 d at −20 °C, the black crystalline product (0.675 g, 0.81 mmol, 81%) was filtered off, washed with MeOH and diethyl ether and dried in air (Found: C, 46.7; H, 2.80; N, 6.80. $C_{33}H_{28}F_4N_4O_9SV_2$ requires C, 47.5; H, 3.35; N, 6.70%). IR (Nujol mull): ν_{max} 1627s (C=N), 1597s (aromatic C$\overset{\cdots}{-}$C), 1554s (aromatic C$\overset{\cdots}{-}$C), 1300–1230s (br) (CF_3SO_3), 1032s (CF_3SO_3), 953s (V=O), 757s (aromatic C–H), 637s (CF_3SO_3), 571m (CF_3SO_3) and 517m cm^{-1} (CF_3SO_3). NMR (CD_3CN): ^{1}H (500 MHz), δ 3.92 (1 H, m), 4.10 (1 H, m), 6.81 (1 H, d, *J* 8.2), 6.94 (1 H, t, *J* 7.4), 7.26 (1 H, d, *J* 7.7), 7.63 (1 H, t, *J* 7.7 Hz) and 8.30 (1 H, s); ^{51}V (500 MHz), δ −587.5 (s, $\Delta\nu_{\frac{1}{2}} \approx 450$ Hz); ^{19}F (80 MHz), δ −137.3 (s, br) and −80.0 (s).

μ-Fluoro-bis{*N,N′-ethylenebis(salicylideneiminato)oxovanadium*} *Difluorodioxovanadate*.—Into a stirred solution of [VO(salen)][O_3SCF_3]·MeOH (0.257 g, 0.5 mmol) in acetonitrile (7 cm^3) was syringed quickly a 1 mol dm^{-3} [NBu$_4$]F solution in thf (0.5 cm^3) and stirring stopped immediately. After 2 d at room temperature, black shiny cubic crystals (0.093 g, 0.115 mmol, 69%) were filtered off, washed with MeCN and diethyl ether and dried in air (Found: C, 47.6; H, 3.10; N, 6.95. $C_{32}H_{28}F_3N_4O_8V_3$ requires C, 47.7; H, 3.50; N, 6.95%). IR (Nujol mull): ν_{max} 1627s (C=N), 1597s (aromatic C$\overset{\cdots}{-}$C), 1552s (aromatic C$\overset{\cdots}{-}$C), 1275s (phenyl C–O), 991 (sh) (V=O), 963 (sh) (V=O), 953s (V=O), 757s (aromatic C–H), 658s (V–F) and 629m cm^{-1} (V–F). NMR (CD_3CN): ^{1}H (500 MHz), δ 3.93 (1 H, m), 4.10 (1 H, m), 6.81 (1 H, d, *J* 8.1), 6.95 (1 H, t, *J* 7.5), 7.26 (1 H, d, *J* 7.5), 7.63 (1 H, t, *J* 7.3 Hz) and 8.30 (1 H, s); ^{51}V (500 MHz), δ −596.6 (t, *J* 273 Hz) and −587.9 (s, $\Delta\nu_{\frac{1}{2}} \approx 450$ Hz); ^{19}F (80 MHz), δ −137.1 (s, br) and −34.5 (oct, *J* 278 Hz).

Tetraphenylphosphonium Difluorodioxovanadate.[11]—Sodium metavanadate, $NaVO_3$ (0.610 g, 5.0 mmol), was dissolved in HF (1%, aqueous, 50 cm^3) in a polyethylene beaker. Over 2 h the solid first turned orange, then red and finally dissolved giving a yellow solution. Upon addition of a hot, saturated solution of tetraphenylphosphonium chloride in water (300 cm^3), and filtering after 20 min, pale yellow needles started to form. After 24 h at room temperature the product (1.60 g, 3.5 mmol, 70%) was filtered off, washed with water, dried in air, washed with diethyl ether and dried over P_4O_{10} (Found: C, 62.4; H, 4.30; N, 0.0. $C_{24}H_{20}F_2O_2PV$ requires C, 62.6; H, 4.40; N, 0.0%). IR (Nujol mull): ν_{max} 1585m (aromatic C$\overset{\cdots}{-}$C), 1483s (aromatic C$\overset{\cdots}{-}$C), 1436s (P–Ph), 995 (sh) (V=O), 959s (V=O), 724s (aromatic C–H), 690s (aromatic C–H), 665s (V–F) and 631s cm^{-1} (V–F). NMR (CD_3CN): ^{51}V (500 MHz), δ −596.0 (t, *J* 250 Hz); ^{19}F (80 MHz), δ −35 (oct, *J* 273 Hz).

Crystal Structure Analyses.—The analyses of the three samples followed very similar procedures. That for one complex is described here; crystal data and refinement results for the three samples are summarised in Table 7.

A crystal of [{VO(salen)}$_2$(μ-F)][BF$_4$] was mounted in air on a glass fibre and, after photographic examination, was transferred to our Enraf–Nonius CAD4 diffractometer [with monochromated radiation, λ(Mo-Kα) = 0.710 69 Å] for determination of accurate cell dimensions (from the settings of 25 reflections, θ = 10–11°, each centred in four orientations) and measurement of diffraction intensities to $\theta_{max} = 20°$. Intensities were corrected for Lorentz-polarisation effects and absorption (by semiempirical ψ-scan methods) and were adjusted (by Bayesian statistical methods) to remove negative net intensities.

These data were entered into the SHELX program system[14] for structure determination[15] and refinement (by large-block-matrix least-squares methods). All the non-hydrogen atoms were allowed anisotropic thermal parameters; hydrogen atoms were included in idealised positions with isotropic thermal parameters riding on those of the parent carbon atoms. In the final difference map there were no peaks of significance.

Scattering factor curves for neutral atoms were taken from ref. 16. Computer programs have been noted above and in Table 4 of ref. 17, and were run on the DEC MicroVAX II computer in this Laboratory.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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