DOI: 10.1002/ejic.200701156

Complexes of Vanadium(V) Oxide Trifluoride with Nitrogen and Oxygen Donor Ligands: Coordination Chemistry and Some Fluorination Reactions

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Keywords: Vanadium complexes / Oxide-fluorides

[$VOF_3(MeCN)$], obtained by dissolving VOF_3 in dry acetonitrile, is a useful synthon for the preparation of complexes of the oxide-fluoride, and the reaction with 2,2′-bipyridyl, 1,10-phenanthroline, $Me_2N(CH_2)_2NMe_2$ and $Ph_2P(O)CH_2P(O)Ph_2$ (L–L), or Ph_3PO, Me_3PO, Ph_3AsO, pyridine and pyridine *N*-oxide (L), produces the complexes [VOF_3(L–L)] or [$VOF_3(L)_2$] respectively. These were characterised by microanalysis, IR, UV/Vis and multinuclear NMR [^{51}V, $^{19}F\{^1H\}$, $^{31}P\{^1H\}$, ^1H] spectroscopy, the data showing them to be six-coordinate with *trans* F–V–F units and the neutral ligands *trans* to O and F, respectively. X-ray crystal structures of [VOF_3(1,10-phenanthroline)], [$VOF_3(Ph_3PO)_2$] and [$VOF_3(pyNO)_2$] confirm the geometry, although the first two exhibit O/F disorder *trans* to the neutral ligand. Unstable complexes with ether and thioether ligands including [$VOF_3\{MeO(CH_2)_2OMe\}$], [$VOF_3\{MeS(CH_2)_2SMe\}$] and [VOF_3(15-crown-5)] are also described; these decompose rapidly even in the solid state, with fluorination of the ligands. The [$VOF_3(Ph_3AsO)_2$] also decomposes in solution to a mixture of products including Ph_3AsF_2 and [$V_6O_{12}F_4(Ph_3AsO)_2(Ph_2AsO_2)_2$] identified crystallographically. Comparisons with complexes of $VOCl_3$ are also described.

Introduction

The majority of the coordination chemistry with neutral ligands in both the d- and p-blocks is based upon the metal chlorides, bromides or iodides,[1] and the corresponding chemistry of metal fluorides has been relatively little investigated. This is despite the wide variety of oxidation states found in metal fluorides and the quite different electronic properties conferred upon the metal by the small and very electronegative fluoride. In the last few years significant progress has been made with the synthesis and characterisation of organometallic[2] and low-valent metal fluoride complexes,[3] but for the early d-block metals in particular, the neutral ligand coordination chemistry mostly involves scattered and often quite old reports of individual complexes, and with limited characterisation. The chemistry of high-valent vanadium is dominated by oxido-species, including the oxide halides VO_2X (X = F or Cl) and VOX_3 (X = F, Cl or Br).[1,4] Complexes of $VOCl_3$ with a variety of hard mono- (L) and bidentate (L–L), *N*- and O-donor ligands have been prepared; mostly they are intensely coloured five- ([$VOCl_3L$]) or six-coordinate ([$VOCl_3L_2$] or [$VOCl_3$(L–L)]), highly moisture-sensitive and the vanadium is easily reduced to lower oxidation states.[5–8] Very recently we have reported the first examples with soft thioether ligands, [$VOCl_3\{RS(CH_2)_2SR\}$], [$VOCl_3(\kappa^2\text{-}[9]aneS_3)$] and [$VOCl_2(\kappa^3\text{-}[9]aneS_3)$][$SbCl_6$].[9]

The oxide trifluoride, VOF_3, is a yellow solid which, unlike the molecular (C_{3v}) $VOCl_3$ and $VOBr_3$, is polymeric with a dinuclear $OF_2V(\mu\text{-}F)_2VOF_2$ core linked by long F-bridges into a polymer with distorted six-coordinate vanadium centres.[10] Its coordination chemistry with neutral ligands is little explored,[11–13] and none of the few reported complexes have been studied in any detail. There is a large amount of work on the oxidofluoridovanadates(V) including [VO_2F_2]$^-$, [VOF_4]$^-$ and [$VOF_4(H_2O)$]$^-$, which are known as mononuclear species with large organic cations, but in the alkali-metal salts are often fluoride-bridged oligomers.[14–19]

Here we report the synthesis, spectroscopic and structural characterisation of a range of VOF_3 complexes. In addition to their inherent interest, there is renewed interest in using early d-block metal complexes in olefin oligomerisation catalysis, where the choice of metal and co-ligands seems to have a marked influence (presently poorly understood) on the polymer chain length.[20] VOF_3 has also been used to couple electron-rich aromatic units, e.g. stilbenes into phenanthrenes or *N*-arylbenzylamines to phenanthridines.[21]

Results and Discussion

The complexes of VOF_3 are generally less sensitive to hydrolysis than those of $VOCl_3$ and the solids do not appear

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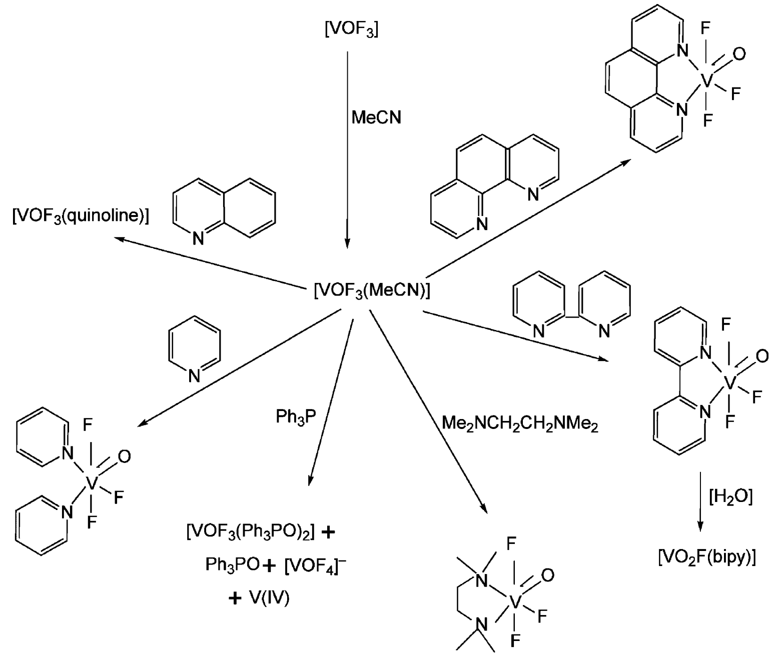
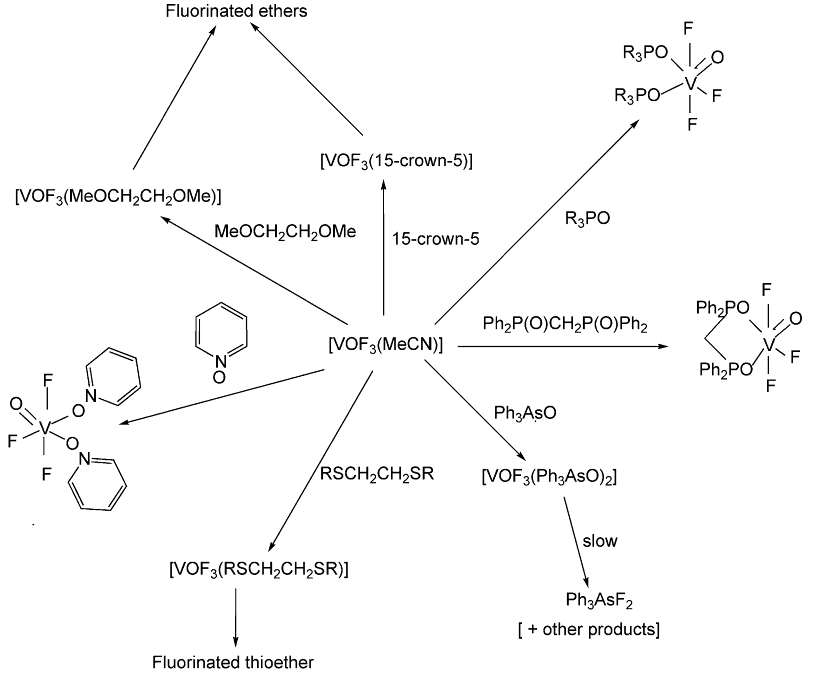
to be affected by exposure to light (in marked contrast to many of the chloride analogues).[5] All syntheses were carried out in dry solvents under dinitrogen. Although the complexes can be made in pyrex glass vessels and handled in *dry* chlorinated solvents – VOF_3 does not react with CH_2Cl_2 on a preparative timescale[22] – crystals grown for X-ray studies from $MeCN/CH_2Cl_2$ or CH_2Cl_2/Et_2O over a period of several weeks were sometimes found to contain chlorido ligands obviously derived from slow reaction with the solvent.

VOF_3 is slightly soluble in chlorocarbons, for example in CH_2Cl_2 it exhibits a ^{51}V NMR resonance at $\delta = -714$ (relative to $VOCl_3$ at $\delta = 0$ ppm). It dissolves easily in dry THF to give a yellow solution ($\delta = -761$ ppm) from which a sticky yellow solid can be isolated on evaporation, but this decomposes quite quickly into a green oil (vide infra) and is not a useful synthon. In dry MeCN, VOF_3 produces a yellow solution from which a yellow powder is obtained on removing the solvent in vacuo. The solid is moisture-sensitive, turns brown on exposure to air, decomposes in MeCN



Scheme 1.



Scheme 2.

solution in a few days, and turns green, although the pure dry solid can be kept for weeks without decomposition. The composition approximates to [VOF$_3$(MeCN)], but as previously observed,[13] it is sometimes rather deficient in nitrile. The IR spectrum shows one strong υ(CN) mode at 2335 cm^{-1}, a strong combination band υ(CC) + δ(CH$_3$) at 2297 cm^{-1}, υ(VO) at 1029 cm^{-1} and several υ(VF) modes at 720–583 cm^{-1}. In CD$_2$Cl$_2$ solution it exhibits δ(^{51}V) at –792 ppm and the shift is unaffected by adding MeCN to the solution. The ^{19}F{^{1}H} NMR spectrum at 295 K is a broad singlet δ = 215, which broadens on cooling and then splits below 240 K into two resonances in approximate ratio 2:1 at δ = 195, 218 ppm. The ^{1}H NMR spectrum at 295 K shows a singlet at δ = 2.10 but on cooling to 240 K the solution shows resonances due to coordinated (δ = 2.45 ppm) and free (δ = 2.01 ppm) nitrile. The complex is probably five-coordinate in solution and partially dissociated, but attempts to obtain a crystalline sample have been unsuccessful and it is possible the solid may be polymeric. The exclusive formation of a 1:1 complex in this system contrasts with that of VOCl$_3$ where both 1:1 and 1:2 complexes are known.[23] However, the freshly prepared dry MeCN solution of VOF$_3$ provides the most convenient solution synthon for the preparation of a range of complexes in high yields (Schemes 1 and 2). The presence of moisture in these reactions leads to oxidofluoridovanadate(V) anions, readily identified in the NMR spectra. These anions are [VO$_2$F$_2$]$^-$ δ(^{51}V) = –596.4 (t) J = 273 Hz, δ(^{19}F{^{1}H}) = –29.2 (8 lines) and [VOF$_4$]$^-$ δ(^{51}V) = –793.9 (quintet) J = 91 Hz, δ(^{19}F{^{1}H}) = +123.0 (8 lines). In passing we note that for several of the complexes described below, including [VOF$_3$(L)$_2$] (L = Ph$_3$PO, Ph$_3$AsO, L$_2$ = MeO(CH$_2$)$_2$OMe) the ^{51}V NMR resonances show some evidence of ^{51}V-^{19}F couplings, although these are not sufficiently well resolved to aid stereochemical assignments. The ^{19}F NMR spectra are typically broad lines due to unresolved couplings and the effect of the ^{51}V quadrupole (^{51}V, 99.75%, I = 7/2, Q = –0.052 × 10^{-28} m^2, Ξ = 26.289 MHz, R_c = 2150).

Nitrogen Donor Ligands

The reaction of 2,2′-bipyridyl or 1,10-phenanthroline with VOF$_3$ in MeCN afforded the bright yellow [VOF$_3$(L–L)] complexes (Scheme 1). The dry solids appear airstable and exhibit single strong υ(VO) modes at 973 (bipy) and 978 (phen) cm^{-1} typical of six-coordinate V^V species, and in solution in CH$_2$Cl$_2$ each complex contains two ^{19}F NMR resonances in the ratio 1:2, and a single ^{51}V NMR resonance, consistent with the presence of a single isomer (Table 1 summarises key data, full details are in the Experimental Section). The complex ^{1}H NMR spectra show that this is the unsymmetrical form shown in Scheme 1, and this was confirmed by an X-ray study of [VOF$_3$(1,10-phenanthroline)]. The structure of deep orange-yellow crystals grown from MeCN solution is shown in Figure 1. The structure reveals a distorted octahedral geometry with the axial F–V–F unit bent (162.1°) towards the neutral ligand with an N–V–N angle of 74.6(1)°. The molecule has crystal-

Table 1. Selected spectroscopic data.

Complex	υ(V=O)[a] [cm^{-1}]	δ (^{51}V)[b] [ppm]	δ (^{19}F)[c] [ppm]	δ (^{19}F)[d] [ppm]
[VOF$_3$(2,2′-bipy)]	973	–734.5	173.1 (F), 163.7 (2 F)	–
[VOF$_3$(1,10-phen)]	978	–737	175.5 (F), 164.0 (2 F)	–
[VOF$_3$(py)$_2$]	982	–748	184.8 (F), 170.2 (2 F)	–
[VOF$_3${Me$_2$N(CH$_2$)$_2$NMe$_2$}]	973	–684	161.8 (2 F), 157.9 (F)	–
[VOF$_3$(MeCN)]	1025	–788	230 (br)	220.3 (F), 191.8 (2 F) 190 K
[VOF$_3$(quin)]	1016	–607	122 (br)	–
[VOF$_3$(OPPh$_3$)$_2$]	977	–778.5	191 (br)	188.1 (F), 177.0 (2 F) 243 K
[VOF$_3$(OAsPh$_3$)$_2$]	995	–751	157 (br)	168.2 (F), 156.1 (2 F) 273 K
[VOF$_3${Ph$_2$P(O)CH$_2$P(O)Ph$_2$}]	982	–753.5	203.3 (F), 169.2 (2 F)	–
[VOF$_3$(OPMe$_3$)$_2$]	956	–765	not observed	172.5 (F), 154.8 (2 F) 223 K
[VOF$_3$(pyNO)$_2$]	957	–716	167 (br)	148.2 (F), 145.2 (2 F) 223 K
[VOF$_3${MeO(CH$_2$)$_2$OMe}][e]	978	–754	186 (br)	194.5 (F), 182.7 (2 F) 243 K
[VOF$_3$(15-crown-5)][e]	991	–756	184 (vbr)	184.0 (F), 176.3 (2 F) 243 K
[VOF$_3${MeS(CH$_2$)$_2$SMe}][e]	995	–684.5	181 (br)	191.0 (F), 167.6 (2 F) 243 K
[VOF$_3$(Me$_2$S)$_2$] [e]	995	–671 (223 K)	187 (br)	176.3 (F), 166.1 (2 F) 223 K
[Ph$_4$As][VOF$_4$]	1018	–793.9 (q) J = 91 Hz	+123 (8 lines)	–
[Ph$_4$As][VO$_2$F$_2$]	960 (br)	–594.4 (t) J = 273 Hz	–29.2 (8 lines)	–

[a] Nujol mull. [b] 295 K in CH$_2$Cl$_2$ solution relative to neat VOCl$_3$. [c] 295 K in CH$_2$Cl$_2$ solution relative to CFCl$_3$. [d] Data at temperature specified. [e] Measured on freshly prepared materials (see text).

lographic twofold symmetry and there is disorder in the VF/VO bonds *trans* to the nitrogen which precludes detailed bond length comparisons, although the bond lengths are clearly much as expected. O/F disorder is a common problem in the X-ray structures of transition metal oxide-fluorides (including $[VO_2F_2]^-$).[19]

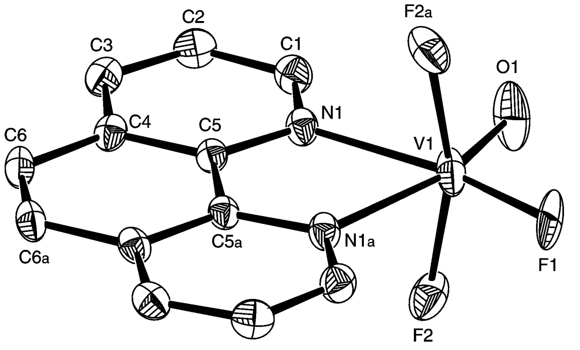


Figure 1. Structure of $[VOF_3(1,10\text{-phenanthroline})]\cdot0.5MeCN$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The molecule has crystallographic twofold symmetry passing through V1 and bisecting the C5–C5a bond. There is disorder involving O1 and F1 and in the Figure O1a and F1a have been omitted (see text). Symmetry operation: *a* = 1 – *x*, 1/2 – *y*, *z*. Selected bond lengths [Å] and angles [°]: V1–F2 1.7998(15), V1–N1 2.2039(19); F2–V1–F2a 162.05(9); N1–V1–N1a 74.60(10).

The very similar spectroscopic data leads to a similar structural assignment for [VOF_3(2,2′-bipyridyl)], and this isomer was also the form found in the corresponding [$VOCl_3$(L–L)] (L–L = 2,2′-bipyridyl or 1,10-phenanthroline).[5] Attempts to grow X-ray quality crystals of [VOF_3(2,2′-bipyridyl)] were unsuccessful, although in one attempt some dark orange crystals were isolated from a solution of the complex in MeCN/Et_2O and structure solution revealed these to be [VO_2F(2,2′-bipyridyl)] which must have formed by hydrolysis. The structure of [VO_2F(2,2′-bipyridyl)] which is a weakly oxygen-bridged dimer, has been reported previously,[24] the compound being synthesised from 2,2′-bipyridyl and V_2O_5 in HF/H_2O/EtOH solution.[11] Our structure is in excellent agreement with that reported and will not be discussed further, but it does show the interconversion of the two V^V oxide-fluoride moieties.

The reaction of VOF_3 with pyridine in MeCN/CH_2Cl_2 under rigorously anhydrous conditions produces a yellow solution from which pale yellow, solid [$VOF_3(py)_2$] may be isolated by precipitation with hexane. Traces of water instantly discharge the colour, and impure cream [pyH][VOF_4] can be isolated from the hydrolysed solution. The spectroscopic properties of [$VOF_3(py)_2$] are very similar to those of the diimine complexes, in particular the υ(VO) mode at 982 cm^{-1} and the ^{51}V and ^{19}F chemical shifts (Table 1), leading to assignment of the same geometric isomer. In solution at low temperatures, the ^1H NMR shows a number of weak extra features some assignable to free pyridine, and there is an extra, weak ^{51}V resonance at –774 possibly due to formation of some [VOF_3(py)] by dissociation. Both [$VOCl_3(py)_n$] (*n* = 1 or 2) were isolated in the corresponding chloride system.[5] From VOF_3 in MeCN with $Me_2N(CH_2)_2NMe_2$ under rigorously anhydrous conditions [$VOF_3\{Me_2N(CH_2)_2NMe_2\}$] was obtained as a pale yellow powder, poorly soluble in MeCN or CH_2Cl_2, and in contrast to the diimine complexes, very moisture sensitive. Brief exposure to air converts the yellow powder to a yellow-green oil, and in solution it is very readily hydrolysed to $[VOF_4]^-$. The υ(VO) and υ(VF) IR stretches are very similar to those in the diimine complexes suggesting the same isomer is present. In the ^{19}F NMR spectrum whilst the chemical shift of the axial fluorines is little changed, that of the $F_{trans\mathrm{N}}$ is ca. 20 ppm to high frequency of those in the diimine complexes.

In contrast the reaction of VOF_3 with quinoline in a 1:2 molar ratio in MeCN produced the yellow 1:1 complex, [VOF_3(quinoline)]. The solid exhibits υ(VO) at 1016 cm^{-1} suggesting a five-coordinate vanadium centre in the solid. In solution the complex exhibits a broad ^{51}V NMR resonance at δ = –607 and a very broad ^{19}F resonance at δ = +122 ppm. Unfortunately the complex was too poorly soluble for low-temperature NMR studies.

Oxygen Donor Ligands

The complexes with phosphane oxides are robust, and are stable for weeks in the solid state if protected from moisture. The reaction of VOF_3 with Ph_3PO or Me_3PO in MeCN in either a 1:1 or 1:2 molar ratio gave the deep yellow [$VOF_3(R_3PO)_2$] (R = Me or Ph) complexes, which exhibit single υ(VO) and several υ(VF) stretches, and two υ(PO) stretches (Experimental Section). The geometry present was confirmed by an X-ray structure of [$VOF_3(Ph_3PO)_2$] (Figure 2) which shows a distorted octahedron, with *trans*-fluorines and the phosphane oxides mutually *cis*. The molecule has crystallographic twofold symmetry and again the O/F *trans* to the neutral ligands are disordered. In solution in CH_2Cl_2 at 295 K the NMR spectra of [$VOF_3(Ph_3PO)_2$] shows a single $\delta(^{51}V)$ and broad singlet $\delta(^{19}F)$ resonances, indicative of exchange, but on cooling the latter split into two resonances separated by ca. 10 ppm with relative intensities 1:2, consistent with the solid-state structure. The $^{31}P\{^1H\}$ NMR resonance is also a broad singlet at room temperature, but at 223 K shows two singlets due to $P_{trans\mathrm{F}}$ and $P_{trans\mathrm{O}}$ as expected. The NMR spectra of [$VOF_3(Me_3PO)_2$] are generally similar, as is the behaviour on lowering the temperature (Table 1), and the complex is clearly isostructural. Interestingly, whilst $VOCl_3$ forms [$VOCl_3(Me_3PO)_2$], with Ph_3PO the product is five-coordinate, [$VOCl_3(Ph_3PO)$].[5] The diphosphane dioxide, $Ph_2P(O)CH_2P(O)Ph_2$ forms yellow [$VOF_3\{Ph_2P(O)CH_2P(O)Ph_2\}$] which exhibited two well separated υ(PO) vibrations in the IR spectrum at 1148 and 1064 cm^{-1}, a single ^{51}V NMR resonance, two broad $^{31}P\{^1H\}$ resonances and two ^{19}F resonances (1:2 ratio) in CH_2Cl_2 solution at 295 K consistent with the same isomer as found with the monodentates (Scheme 2). On cooling the solution the resonances sharpen and at 223 K the phosphorus NMR spectrum shows two doublets with $^{2}J_{PP}$ = 13 Hz.

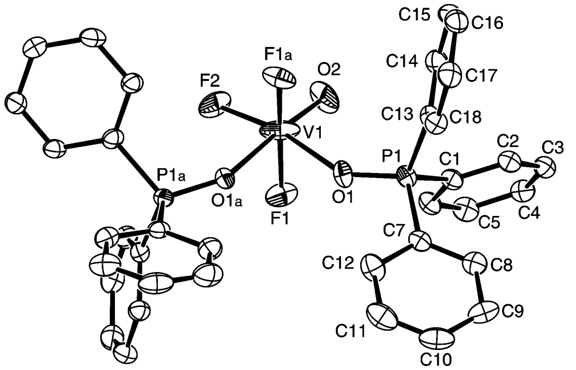


Figure 2. Structure of [$VOF_3(Ph_3PO)_2$] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The molecule has crystallographic twofold symmetry. There is disorder involving O2 and F2 and in the Figure O2a and F2a have been omitted (see text). Symmetry operation: $a = -x, -y, z$. Selected bond lengths [Å] and angles [°]: P1–O1 1.509(2); V1–O1 2.135(2); V1–F1 1.7924(18); O1–V1–O1a 79.86(12); F1–V1–F1a 165.76(13); V1–O1–P1 144.43(14).

The reaction of [$VOF_3(MeCN)$] with Ph_3AsO in MeCN/CH_2Cl_2 produced deep yellow [$VOF_3(Ph_3AsO)_2$] which had very similar spectroscopic properties to the phosphane oxide analogue, and is assigned a similar geometry. The complex is less stable and a solution of [$VOF_3(Ph_3AsO)_2$] in CH_2Cl_2 refrigerated for two weeks deposited colourless crystals, which were identified by a crystal structure determination as Ph_3AsF_2, showing fluorination of the arsane oxide is possible in this system (VO_2F may be the other product but this was not identified).The conversion of R_3AsO to R_3AsCl_2 is achieved by a number of *p*-block halides including $GeCl_4$, $COCl_2$, $AsCl_3$ and PCl_3,[25–27] but the only prior report of conversion of Ph_3AsO to Ph_3AsF_2 is using aqueous HF.[28] The X-ray structure confirms the identity of the product and is in good agreement with the literature data.[29] A solution of [$VOF_3(Ph_3AsO)_2$] in MeCN slowly darkened when stirred at room temperature for several days, and the ^{51}V NMR spectrum showed the loss of the resonance due to the arsane oxide complex, and several new resonances in the region δ = –450 to –600 ppm. Clearly a number of decomposition products containing V^{V} are present. A small amount of crystals deposited from this solution when refrigerated for one week, the molecular structure of which is shown in Figure 3. The elemental composition is [$V_6O_{12}F_4(Ph_3AsO)_2(Ph_2AsO_2)_2$]. The pale yellow colour of the crystals is consistent with V^{V} rather than a lower oxidation state or a mixed valence material, and the bond lengths are reasonable on this basis. Although distinction of bridging F and O is difficult, the pattern V–O(terminal) < V–O(V)(bridging) < V–F(bridging) is plausible and fits the proposed oxidation state. The data quality was mediocre with only about 50% of the reflections "observed" and disorder in the phenyl rings showing as very elongated displacement ellipsoids of the C atoms, and for this reason the structure is not discussed in detail.[30] Figure 3 shows a centrosymmetric dimeric molecule with a Ph_3AsO ligand bonded to V1 and two bridging (O,O′) diphenylarsinate-(1–) ligands ($Ph_2AsO_2^{-}$) which must arise from cleavage of a phenyl group and oxygen transfer to arsenic in Ph_3AsO. The ^{51}V NMR spectrum obtained from the same batch of crystals shows three broad resonances at δ = –485, –496 and –516 ppm which are probably of the cluster (and a number of much weaker resonances to lower frequency due to other products). Insufficient crystals were obtained for a more detailed spectroscopic study. In contrast the ^{31}P{^{1}H} and ^{51}V NMR spectra of "aged" solutions of [$VOF_3(Ph_3PO)_2$] showed only some free Ph_3PO in addition to the starting complex.

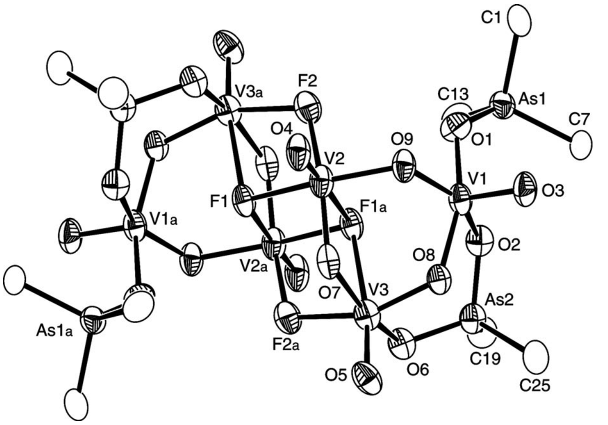


Figure 3. Structure of the reaction product from a MeCN solution of [$VOF_3(Ph_3AsO)_2$]. The diagram shows [$V_6O_{12}F_4(Ph_3AsO)_2(Ph_2AsO_2)_2$]·2MeCN with all C atoms except the *ipso* omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level and C atoms are shown as boundary ellipsoids. The centrosymmetric dimer is linked through the bridging F1 and F2. Symmetry operation: $a = -x, -y, -z$. Selected bond lengths [Å] and angles [°]: V–O(terminal) 1.581(7)–1.590(7); V–O(V)(bridging) 1.766(8)–1.885(7); V–F(bridging) 1.971(6)–2.358(6); As1–O1 1.686(7); As2–O2 1.695(7); As2–O6 1.685(7); V1–O1–As1 129.7(4).

The reaction of pyridine *N*-oxide with VOF_3 in MeCN gave deep orange-yellow crystals of [$VOF_3(pyNO)_2$]. The IR spectrum of this complex, particularly the υ(VO) at 957 cm^{-1} and the presence of two υ(NO) bands, indicate a six-coordinate complex with *cis*-pyridine *N*-oxide ligands. This is confirmed by the crystal structure (Figure 4, Table 2), and in contrast to the other complexes in this work, this complex with no crystallographic symmetry appears to be free of the O/F disorder problem. The molecule reveals a distorted octahedron about the vanadium with the *trans* F–V–F = 160.6(1)° bent towards the neutral ligands, and with the pyridine *N*-oxide ligands *trans* to V=O and one V–F. The bond lengths about the vanadium centre are much as expected with d(V=O) = 1.622(2) Å, $d(\text{V–F})_{trans\text{F}}$ = 1.815(2), 1.800(2) Å, and $d(\text{V–F})_{trans\text{PyNO}}$ = 1.771(2) Å. The d(V–O) involving the neutral ligands are longer at 2.179(2), and 2.041(2) Å, the longer bond of the two being *trans* to the oxido ligand, showing the expected greater *trans* influence. In solution the NMR spectroscopic data are consistent with fast ligand exchange at room temperature as found in the phosphane oxides, but on cooling the solution the data (Table 1) become consistent with the solid state geometry.

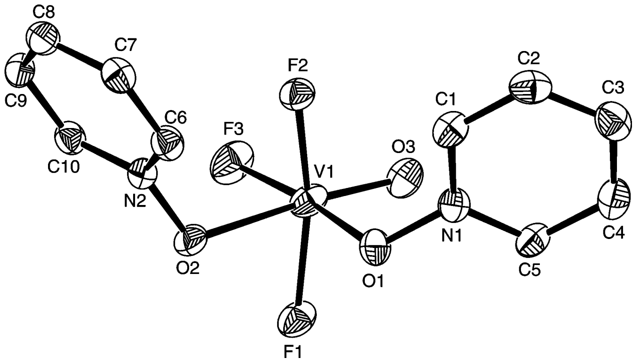


Figure 4. Structure of [VOF_3(pyridine *N*-oxide)$_2$]$\cdot xH_2O$ showing the atom numbering scheme. The solvate water is omitted, displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for [VOF_3(pyridine *N*-oxide)$_2$]$\cdot xH_2O$.

V1–F1	1.8002(19)	V1–O1	2.041(2)
V1–F2	1.8148(18)	V1–O2	2.179(2)
V1–F3	1.7708(19)	V1–O3	1.622(2)
O1–N1	1.354(3)	O2–N2	1.344(3)
F1–V1–F2	160.59(9)	O1–V1–O2	81.43(9)
F1–V1–F3	94.08(9)	O3–V1–O1	90.86(10)
F2–V1–F3	91.39(9)	O2–V1–O3	172.19(9)
F1–V1–O1	85.40(9)	F2–V1–O1	85.71(8)
F1–V1–O2	78.41(8)	F2–V1–O2	83.22(8)
F1–V1–O3	99.84(10)	F2–V1–O3	97.52(10)
F3–V1–O1	169.04(10)	F3–V1–O3	100.01(11)
F3–V1–O2	87.74(9)	N1–O1–V1	116.63(16)
N2–O2–V1	117.79(16)		

The addition of 1 mol-equiv. of $MeO(CH_2)_2OMe$ to a solution of VOF_3 in dry MeCN, followed by concentration to a small volume in vacuo precipitated a pale yellow powder, but this darkened rapidly and became dark green in less than 12 h. The freshly prepared material exhibits a $\delta(^{51}V)$ resonance at –754 and in the IR spectrum υ(VO) at 978 and υ(VF) at 628, 600 (sh) cm^{-1}, which are reasonable values for [VOF_3{$MeO(CH_2)_2OMe$}]. The [$VOCl_3${$MeO(CH_2)_2OMe$}][5] is extremely moisture sensitive, but stable when dry, and the rapid decomposition of the fluoride complex is due to fluorination of the ether (C–H to C–F conversion) and reduction to V^{IV}.[31] Similar behaviour was observed on reaction of VOF_3 with 15-crown-5 (Table 1) and THF (vide supra) in that the initial products were yellow powders but these also turned into green oils in a few hours.

Sulfur Donor Ligands

We were unable to isolate complexes from the reaction of thioethers including Me_2S, $RS(CH_2)_2SR$, (R = Me, Et or *i*Pr) with VOF_3 in MeCN solution, and the solutions turned green in a few hours due to reduction of the vanadium. However, the reaction of [VOF_3(MeCN)] with one mol-equiv. of $MeS(CH_2)_2SMe$ in anhydrous CH_2Cl_2, followed by concentration in vacuo, led to a fawn solid. The solid turns green over a few hours (vide infra), but the freshly prepared sample exhibited υ(VO) at 995 cm^{-1} and υ(VF) at 654 and 568(br) cm^{-1}, and had a diffuse reflectance UV/Vis spectrum similar to the other VOF_3 adducts in this work leading to the provisional identification as [VOF_3{$MeS(CH_2)_2SMe$}]. In solution the complex is very readily hydrolysed to $[VOF_4]^-$, but under rigorously anhydrous conditions in CH_2Cl_2 it exhibits a $\delta(^{51}V)$ resonance at δ = –685.5 ppm and a broad ^{19}F resonance at δ = 181 ppm. On cooling the solution to 243 K the ^{19}F resonance splits into two at δ = 191.0 (F) and 167.5 (2 F). The vanadium chemical shift which is ca. 50 ppm to high frequency of those in most complexes with N- or O-donors is characteristic of the presence of the softer S-donor.[9] Similar complexes are formed by $EtS(CH_2)_2SEt$ [$\delta(^{51}V)$ = –681 ppm] and *i*PrS(CH$_2$)$_2$S*i*Pr [$\delta(^{51}V)$ = –684 ppm], but these decompose more rapidly and will not be discussed further. The reaction of VOF_3 in MeCN with Me_2S rapidly deposits a greenish-blue solid, but again reaction using [VOF_3(MeCN)] in CH_2Cl_2 is more successful, producing a straw coloured powder after removal of the solvent in vacuo. The solid exhibits υ(VO) at 993 cm^{-1} and υ(VF) at 649, and 570 cm^{-1} and in freshly prepared CH_2Cl_2 solution at 223 K has $\delta(^{51}V)$ = –670 ppm and $\delta(^{19}F)$ = 176.3 (F) and 166.1 (2 F). On warming above 243 K the vanadium resonance is lost and the fluorine resonances collapse into a broad feature at $\delta \approx 187$ ppm, suggesting the formulation as [$VOF_3(Me_2S)_2$] which is reversibly dissociating thioether at room temperature.

The $^{19}F\{^1H\}$ NMR spectra of the decomposed samples of [VOF_3{$RS(CH_2)_2SR$}] or from in situ reactions of [VOF_3(MeCN)] with $RS(CH_2)_2SR$ or Me_2S show sharp resonances in the region δ = –150 to –180 ppm where alkyl CF resonances are expected, and corresponding ^1H NMR resonances at $\delta \approx 4.5$–5.8 ppm, and it seems likely that as in the reactions with ether ligands (vide supra)[31] fluorination of the carbon skeletons on the thioethers occurs. We have not attempted to isolate or probe the organic products in more detail (cf. ref.[32]). Me_2Se also reduced VOF_3 in MeCN to a blue solution and a blue-green precipitate formed rapidly. The only V^V species present in the solution was small amounts of $[VOF_4]^-$.

Phosphorus and Arsenic Ligands

The addition of an MeCN solution of VOF_3 to a solution of PPh_3 or $AsPh_3$ in MeCN or CH_2Cl_2 produced an immediate colour change from pale yellow to blue-green, and in situ UV/Vis spectra were typical of a VO^{2+} species ($E_{max} \approx 14700$ cm^{-1}).[33] However, examination of the solutions by ^{51}V and, where appropriate, $^{31}P\{^1H\}$ NMR spectroscopy, identified varying amounts of other products including [$VOF_3(OEPh_3)_2$] (E = P or As) and $[VOF_4]^-$. There was no evidence that V^V complexes of the group 15 donor ligands were formed; a similar result was observed in the case of $VOCl_3$.[5]

Conclusions

The results described above constitute the first detailed study of the coordination chemistry of an early 3d metal oxide-fluoride, specifically of VOF_3. They reveal that the oxide-fluoride is a strong Lewis acid forming stable complexes with neutral N-donors and some O-donor ligands. Comparison with complexes of $VOCl_3$[5,9] with the same ligands reveals considerable similarities, although those of the oxide-fluoride are more resistant to reduction and hydrolysis. In the majority of cases the same isomer (with the neutral ligands *trans* to one F/Cl and the O) seems to be present in both series of six-coordinate complexes. Both oxide trihalides are reduced by phosphorus, arsenic or selenium ligands. The ^{51}V chemical shifts show a low frequency shift of around 600–700 ppm between corresponding six-coordinate complexes of $VOCl_3$ and VOF_3, although the υ(VO) stretches in the IR spectra show only small and irregular variations. The solid state UV/Vis spectra of the VOF_3 adducts are little different to those of VOF_3 itself, indicating either that replacing the fluoride bridges in the parent oxide-fluoride, by hard N- or O-donors has little effect on the orbital energies, or more likely that the charge transfer (CT) transitions involving the neutral ligands are of relatively low intensities, and the $F \rightarrow V$ and $O \rightarrow V$ transitions dominate the spectra. For tetrahedral $VOCl_3$ formation of five- or six-coordinate complexes results in significant low energy shifts in the CT transitions, although again band energies vary only slightly with the neutral ligands present.[5] There are some notable differences between complexes of the two oxide halides, e.g. the $[VOF_3(OEPh_3)_2]$ (E = P or As) are six-coordinate whereas $VOCl_3$ forms only five-coordinate 1:1 complexes with these ligands, although both give six-coordinate $[VOX_3(OPMe_3)_2]$. Marked differences occur in the decomposition of the ether and thioether complexes of VOF_3 by fluorination of the ligands, whereas the ether complexes of $VOCl_3$ are not chlorinated and the thioethers oxidise at S under certain conditions.[5,9]

Experimental Section

VOF_3 was obtained from Aldrich and used as received. All reactions were conducted under anhydrous conditions under dry dinitrogen using standard vacuum line, Schlenk and glove-box techniques. Solvents were dried by distillation from CaH_2 (CH_2Cl_2), P_4O_{10} (MeCN), Na/benzophenone ketyl (hexane, THF and diethyl ether). 2,2′-Bipyridyl, 1,10-phenanthroline, Ph_3PO, Ph_3AsO and pyridine *N*-oxide were dried by heating in vacuo, Me_3PO was freshly sublimed in vacuo. 15-Crown-5 was dried by refluxing with excess $SOCl_2$, followed by vacuum drying at 60 °C. 1,2-Bis(methoxy)ethane was dried by distillation from Na pellets. Quinoline, pyridine and $Me_2N(CH_2)_2NMe_2$ were refluxed over BaO and freshly distilled. Thioethers were distilled and stored over molecular sieves.

^{51}V NMR spectra were recorded in 10 mm o.d. tubes from dry MeCN or CH_2Cl_2 solutions containing 5% of the deuterated analogue as lock, using a Bruker DPX400 operating at 105.2 MHz, and referenced to external neat $VOCl_3$ (δ = 0 ppm). $^{19}F\{^1H\}$ NMR spectra were also recorded with a Bruker DPX400 and are referenced to $CFCl_3$. Other physical measurements were made as described.[5,9] Analytical data were obtained from the microanalytical laboratory of Strathclyde University. $[Ph_4P][VO_2F_2]$ was made following the method in ref.[19] but using 5% aqueous HF. It was found to contain ca. 10% $[Ph_4P][VOF_4]$ (by ^{19}F NMR) but because only the NMR spectroscopic data were required for comparison purposes, purification was not attempted.

$[VOF_3(MeCN)]$: VOF_3 (0.248 g, 2.0 mmol) was dissolved in MeCN (15 mL) and stirred for 20 min. The yellow solution was taken to dryness in vacuo, producing a fine pale yellow powder, which turns brown on contact with moist air. Yield 0.30 g, 91%. $C_2H_3F_3NOV$ (165.0): calcd. C 14.6, H 1.8, N 8.5; found C 14.0, H 2.0, N 8.0. ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ = 2.10 (s) ppm; (240 K): δ = 2.45 (s), 2.01 (s) ppm. $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = 230 (vbr) ppm; (190 K): 220.3 (s, F), 191.8 (s, 2 F) ppm. ^{51}V (CH_2Cl_2/CD_2Cl_2, 295 K): δ = –788 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 2335 (s, CN), 2297 (s, υCC +δCH_3), 1029 (vs, VO), 717 (s,VF), 660 (vs, VF), 580 (s, VF) cm^{-1}. UV/Vis E_{max}/cm^{-1} (*dr* diluted with $BaSO_4$): 29400, 23800 (sh).

$[VOF_3(2,2'\text{-bipy})]$: VOF_3 (0.124 g, 1.0 mmol) was dissolved in MeCN (15 mL) and a solution of 2,2′-bipyridyl (0.16 g, 1.0 mmol) in MeCN (5 mL) was added. The pale yellow solution was stirred for 30 min, then concentrated in vacuo to 5 mL and the deep yellow solid filtered off, rinsed with hexane and dried in vacuo. Yield 0.23 g, 80%. $C_{10}H_8F_3N_2OV$ (280.1): calcd. C 42.9, H 2.9, N 10.0; found C 43.4, H 2.9, N 10.3. ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ = 9.40 (d, *J* = 10 Hz, 1 H), 8.63 (d, *J* = 10 Hz, 1 H), 8.27 (m, 2 H), 8.15 (d, *J* = 10 Hz, 1 H), 8.05 (d, *J* ≈ 10 Hz, 1 H), 7.77 (m, 1 H), 7.56 (m, 1 H) ppm. $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = 173.1 (vbr, F), 163.7 (s, 2 F) ppm. ^{51}V (CH_2Cl_2/CD_2Cl_2, 295 K): δ = –734.5 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 973 (vs, VO), 660 (s, VF), 624 (vs, VF), 558 (s, VF) cm^{-1}. UV/Vis E_{max}/cm^{-1} (*dr* diluted with $BaSO_4$): 34500, 27400.

$[VOF_3(1,10\text{-phen})]$: Preparation similar to $[VOF_3(2,2'\text{-bipy})]$; orange yellow solid. Yield 75%. $C_{12}H_8F_3N_2OV$ (304.1): calcd. C 47.4, H 2.7, N 9.2; found C 47.5, H 2.6, N 10.0. ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ = 9.66 (d, *J* = 8 Hz, 1 H), 8.92 (d, *J* = 8 Hz, 1 H), 8.72 (d, *J* = 9 Hz, 1 H), 8.51 (d, *J* = 8 Hz, 1 H), 8.07 (s, 2 H), 8.08 (m, 1 H), 7.85 (dd, 1 H) ppm. $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = 175.5 (vbr, F), 164.0 (s, 2 F) ppm. ^{51}V (CH_2Cl_2/CD_2Cl_2, 295 K): δ = –736.7 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 978 (vs, VO), 657 (s, VF), 625 (vs, VF), 567 (s, VF) cm^{-1}. UV/Vis E_{max}/cm^{-1} (*dr* diluted with $BaSO_4$): 30300, 24400 (sh).

$[VOF_3\{Me_2N(CH_2)_2NMe_2\}]$: VOF_3 (0.124 g, 1.0 mmol) was dissolved in MeCN (15 mL) and a solution of $Me_2N(CH_2)_2NMe_2$ (0.116 g, 1.0 mmol) in CH_2Cl_2 (15 mL) added at 0 °C. The pale-green yellow solution was stirred for 30 min, the solvents removed in vacuo, and the residue extracted with CH_2Cl_2 (20 mL). The solution was filtered to remove some white solid, concentrated to 5 mL and hexane (5 mL) added to precipitate a pale yellow powder. This was filtered off and dried in vacuo. Yield 0.11 g, 45%. $C_6H_{16}F_3N_2OV \cdot 0.5CH_2Cl_2$ (282.5): calcd. C 27.6, H 6.1, N 9.9; found C 27.1, H 7.1, N 10.3. ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ = 2.27 (s, 3 H), 2.43 (s, 3 H), 3.03 (m, 2 H) ppm. $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = 161.8 (s, 2 F), 157.9 (s, F) ppm. ^{51}V (CH_2Cl_2/CD_2Cl_2, 295 K): δ = –684 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 973 (vs, VO), 654 (sh, VF), 620 (s, vbr, VF), 572 (vs, VF) cm^{-1}. UV/Vis E_{max}/cm^{-1} (*dr* diluted with $BaSO_4$): 28740.

$[VOF_3(pyridine)_2]$: VOF_3 (0.248 g, 2.0 mmol) was dissolved in MeCN (15 mL) and pyridine (0.32 g, 4.0 mmol) in CH_2Cl_2 (5 mL) added and the mixture stirred for 20 min. The clear solution was concentrated to 5 mL and on addition of hexane (5 mL) a pale yellow solid was precipitated, which was filtered off, rinsed with hexane, and dried in vacuo. Pale yellow powder. Yield 0.30 g, 53%. $C_{10}H_{10}F_3N_2OV{\cdot}CH_2Cl_2$ (367.1): calcd. C 36.0, H 3.3, N 7.6; found C 36.1, H 3.3, N 7.7. ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ = 7.4–8.8 (m) ppm; (233 K): δ = 7.54 (m, 4 H), 7.95–8.01 (m, 2 H), 8.50 (s, 2 H), 9.00 (s, 2 H) ppm. ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): δ = 184.8 (s, F), 170.2 (s, 2 F) ppm. ^{51}V (CH_2Cl_2/CD_2Cl_2, 295 K): δ = –748.0 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 982 (vs, VO), 637 (s, VF), 560 (vs, VF) cm^{-1}. UV/Vis E_{max}/cm^{-1} (*dr* diluted with $BaSO_4$): 31250, 27700(sh).

[VOF_3(quinoline)]: VOF_3 (0.248 g, 2.0 mmol) was dissolved in MeCN (15 mL) and quinoline (0.52 g, 4.0 mmol) added and the mixture stirred for 20 min. The yellow solution was concentrated to 5 mL and the solid which precipitated, filtered off and rinsed with hexane, and dried in vacuo. Yellow powder. Yield 0.31 g, 61%. $C_9H_7F_3NOV$ (253.1): calcd. C 42.7, H 2.8, N 5.5; found C 42.3, H 3.2, N 5.5. ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ = 7.62 (s), 7.69 (s), 7.86 (s), 8.00 (s), 8.27 (s), 8.41 (s), 9.0 (s) ppm. ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): δ = 121.6 (s) ppm; (253 K): δ = 118.6 (br) ppm. ^{51}V (CH_2Cl_2/CD_2Cl_2, 295 K): δ = –607.1 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 1016 (vs, VO), 653 (s, VF), 629 (vs, VF), 585 (s, VF) cm^{-1}. UV/Vis E_{max}/cm^{-1} (*dr* diluted with $BaSO_4$): 32500, 26600 (sh).

[$VOF_3(Ph_3PO)_2$]: VOF_3 (0.124 g, 1.0 mmol) was dissolved in MeCN (15 mL) and a solution of Ph_3PO (0.56 g, 2.0 mmol) in CH_2Cl_2 (10 mL) added. The pale yellow solution was stirred for 30 min, then concentrated in vacuo to 5 mL and allowed to stand for 1 h. The yellow solid was filtered off, rinsed with hexane and dried in vacuo. Yield 0.46 g, 67%. $C_{36}H_{30}F_3O_3P_2V{\cdot}2CH_2Cl_2$ (850.0): calcd. C 53.6, H 4.0; found C 54.4, H 4.1. ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ = 7.4–7.7 (m, Ph) ppm. ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): δ = 191 (vbr) ppm; (273 K): δ = 194.3 (s, F), 183.5 (s, 2 F); (243 K): δ = 188.1 (s, F), 177.0 (s, 2 F) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 295 K): δ = 48.6 (s) ppm; (223 K): δ = 48.8 (s, P), 43.3 (s, P) ppm. ^{51}V (CH_2Cl_2/CD_2Cl_2, 295 K): δ = –778.5 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 1148 (s, PO), 1064 (vs, PO), 977 (vs, VO), 645 (s, VF), 629 (vs, VF) cm^{-1}. UV/Vis E_{max}/cm^{-1} (*dr* diluted with $BaSO_4$): 33900, 28100.

[$VOF_3(Me_3PO)_2$]: VOF_3 (0.124 g, 1.0 mmol) was dissolved in MeCN (15 mL) and a solution of Me_3PO (0.184 g, 2.0 mmol) in CH_2Cl_2 (5 mL) added. The pale yellow solution was stirred for 30 min, then concentrated in vacuo to 5 mL and allowed to stand for 1 h. The yellow solid was filtered off, rinsed with hexane and dried in vacuo. Yield 0.27 g, 88%. $C_6H_{18}F_3O_3P_2V{\cdot}0.5CH_2Cl_2$ (350.5): calcd. C 22.4, H 5.5; found C 22.4, H 5.9. ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ = 1.7 (br, s) ppm; (223 K): δ = 1.94 (d, $^2J_{PH}$ = 14 Hz), 1.85 (d, $^2J_{PH}$ = 14 Hz) ppm. ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): no resonance; (273 K): δ = 163.7 (s), 181.5 (s) ppm; (223 K): δ = 154.8 (s), 172.5 (s) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 295 K): δ = 69.0 (br, s) ppm; (253 K): δ = 67.5 (s) ppm; (223 K): δ = 68.7 (s), 72.2 (s) ppm. ^{51}V (CH_2Cl_2/CD_2Cl_2, 295 K): δ = –765.0 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 1136 (s, VO), 1090 (vs, PO), 956 (vs, VO), 641 (s, VF), 607 (vs, VF), 573 (s, VF) cm^{-1}. UV/Vis E_{max}/cm^{-1} (*dr* diluted with $BaSO_4$): 29800.

[$VOF_3\{Ph_2P(O)CH_2P(O)Ph_2\}$]: VOF_3 (0.124 g, 1.0 mmol) was dissolved in MeCN (15 mL) and a solution of $Ph_2P(O)CH_2P(O)Ph_2$ (0.42 g, 1.0 mmol) in CH_2Cl_2 (10 mL) added. The pale yellow solution was stirred for 30 min, then concentrated in vacuo to 5 mL, and the pale yellow solid filtered off, rinsed with hexane and dried in vacuo. Yield 0.35 g, 65%. $C_{25}H_{22}F_3O_3P_2V$ (540.3): calcd. C 55.6, H 4.1; found C 55.0, H 3.7. ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ = 3.67 (br, 1 H, CH_2), 7.30–7.62 (m, 10 H, Ph) ppm. ^{19}F{^{1}H} (CD_2Cl_2, 295 K): δ = 169.2 (s, 2 F), 203.3 (s, F) ppm; (223 K): δ = 160.0 (s, 2 F), 195.5 (s, F) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 295 K): δ = 43.2 (br, s, P), 31.3 (br, s, P) ppm; (253 K): δ = 44.4 (s, P), 31.7 (s, P) ppm; (223 K): δ = 45.3 (d, $^2J_{PP}$ = 13 Hz, P), 32.5 (d, P) ppm. ^{51}V (CH_2Cl_2/CD_2Cl_2, 295 K): δ = –753.5 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 1148 (s, PO), 1084 (s, PO), 982 (vs, VO), 680 (s, VF), 628 (vs, VF) cm^{-1}. UV/Vis E_{max}/cm^{-1} (*dr* diluted with $BaSO_4$): 31600, 27780.

[$VOF_3(Ph_3AsO)_2$]: VOF_3 (0.124 g, 1.0 mmol) was dissolved in MeCN (15 mL) and a solution of Ph_3AsO (0.64 g, 2.0 mmol) in CH_2Cl_2 (5 mL) added. The deep yellow solution was stirred for 30 min, then concentrated in vacuo to 5 mL and allowed to stand for 1 h. The yellow solid was filtered off, rinsed with hexane and dried in vacuo. Yield 0.35 g, 46%. $C_{36}H_{30}As_2F_3O_3V$ (768.2): calcd. C 56.3, H 3.9; found C 55.9, H 3.7. ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ = 7.4–7.7 (m, Ph) ppm. ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): δ = 156.8 ppm; (273 K): δ = 168.2 (F), 156.1 (2 F) ppm. ^{51}V (CH_2Cl_2/CD_2Cl_2, 295 K): δ = –751.2 (s) ppm; (223 K): δ = –751.6 (ill-defined multiplet) ppm. IR (Nujol): $\tilde{\nu}$ = 995 (vs, VO), 845 (m, AsO), 815 (br, AsO), 680 (s, VF), 660 (vs, VF), 632 (sh, VF) cm^{-1}. UV/Vis E_{max}/cm^{-1} (*dr* diluted with $BaSO_4$): 34000, 28900, 25300 (sh).

[$VOF_3\{MeS(CH_2)_2SMe\}$]: [VOF_3(MeCN)] (0.16 g, 1.0 mmol) was dissolved in dry CH_2Cl_2 (20 mL) and $MeS(CH_2)_2SMe$ (0.12 g, 1.0 mmol) syringed in with vigorous stirring. The initially orange solution turned pale yellow and a fawn solid formed. After 10 min the solution was concentrated in vacuo to 5 mL, and the solid filtered off and dried in vacuo. Yield 0.21 g, 75%. The solid turns brownish green in a few hours, precluding microanalytical measurements. ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ = 2.6 (s, 3 H), 3.0 (s, 2 H) ppm. ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): δ = 181 (br) ppm; (243 K): δ = 191.0 (F), 167.6 (2 F) ppm. ^{51}V (CH_2Cl_2/CD_2Cl_2, 295 K): δ = –684.5 ppm. IR (Nujol): $\tilde{\nu}$ = 995 (vs, VO), 654 (s, VF), 568 (br, vs, VF) cm^{-1}. UV/Vis E_{max}/cm^{-1} (*dr* diluted with $BaSO_4$): 32500, 27400 (sh).

[VOF_3(pyridine *N*-oxide)$_2$]: VOF_3 (0.248 g, 2.0 mmol) was dissolved in MeCN (15 mL) and pyridine *N*-oxide (0.38 g, 4.0 mmol) in CH_2Cl_2 (5 mL) added and the mixture stirred for 20 min. The yellow solution was concentrated to 5 mL and hexane (10 mL) added to precipitate a yellow solid. After 1 h the solid was separated by decantation of the solvent and dried in vacuo. Yellow powder. Yield 0.42 g, 67%. $C_{10}H_{10}F_3N_2O_3V{\cdot}0.5CH_2Cl_2$ (356.5): calcd. C 35.4, H 3.1, N 7.9; found C 34.8, H 3.4, N 8.3. ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ = 7.39 (s, 2 H), 8.29 (br, 3 H) ppm. ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): δ = 167.0 (br, s) ppm; (223 K): δ = 145.2 (s, 2 F), 148.2 (s, F) ppm. ^{51}V (CH_2Cl_2/CD_2Cl_2, 295 K): δ = –716 (s) ppm; (243 K): δ = –708.0 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 1225 (s, NO), 1204 (s, NO), 957 (vs, VO), 615 (s,vbr, VF), 581 (vs, VF), 556 (vs, VF) cm^{-1}. UV/Vis E_{max}/cm^{-1} (*dr* diluted with $BaSO_4$): 33300, 26600 (sh).

X-ray Crystallography: Details of the crystallographic data collection and refinement parameters are given in Table 3. Crystals of [VOF_3(1,10-phen)]$\cdot$0.5MeCN, [$VOF_3(Ph_3PO)_2$] and [VOF_3(pyridine *N*-oxide)$_2$]$\cdot x H_2O$ were obtained by cooling MeCN solutions of the complexes in the freezer (–20 °C) for one week. A few crystals of [$V_6O_{12}F_4(Ph_3AsO)_2(Ph_2AsO_2)_2$] deposited from a solution of [$VOF_3(Ph_3AsO)_2$] in MeCN refrigerated for one week, and crystals of Ph_3AsF_2 were obtained by layering a CH_2Cl_2 solution of [$VOF_3(Ph_3AsO)_2$] with diethyl ether. Data collection used a Nonius Kappa CCD diffractometer fitted with monochromated (confocal mirror) Mo-K_α X-radiation (λ = 0.71073 Å) and the crystals held at 120 K in a nitrogen gas stream. Structure solution and refinement were straightforward.[34,35] with H atoms being placed in geometrically calculated positions using the default C–H distance.

Table 3. Crystallographic parameters.[a]

Compound	[VOF$_3$(1,10-phen)]·0.5MeCN	[VOF$_3$(Ph$_3$PO)$_2$]	[VOF$_3$(pyNO)$_2$]·xH$_2$O
Formula	$C_{13}H_{9.5}F_3N_{2.5}OV$	$C_{36}H_{30}F_3O_3P_2V$	$C_{10}H_{10.7}F_3N_2O_{3.35}V$
M	324.67	680.48	320.45
Crystal system	tetragonal	orthorhombic	triclinic
Space group	$I4_1/a$ (no. 88)	$Fdd2$ (no. 43)	$P\bar{1}$ (no. 2)
a [Å]	9.179(2)	18.664(3)	6.581(2)
b [Å]	9.179(2)	33.310(6)	7.441(2)
c [Å]	30.516(7)	9.9297(15)	12.632(4)
α [°]	90	90	99.353(16)
β [°]	90	90	90.731(16)
γ [°]	90	90	92.144(12)
V [Å^3]	2571.2(10)	6173.1(18)	609.8(3)
Z	8	8	2
μ(Mo-K_α) [mm^{-1}]	0.806	0.480	0.861
F(000)	1304	2800	323
Total number of reflections	8090	8758	9446
R_{int}	0.038	0.038	0.044
Unique reflections	1474	3233	2815
No. of parameters, restraints	108, 2	214, 3	178, 0
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.044, 0.093	0.045, 0.085	0.051, 0.095
R_1, wR_2 [all data]	0.054, 0.098	0.054, 0.090	0.068, 0.103

[a] Common items: temperature = 120 K; wavelength (Mo-K_α) = 0.71073 Å; θ(max) = 27.5°. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

[VOF$_3$(1,10-phen)]·0.5MeCN showed the V on a twofold axis forcing O/F disorder on the model. Initially treated as four isotropic F atoms, the shorter V–F1 was treated as the likely disordered atom and inspection of the peaks in the difference electron-density map close to F1 showed the two largest peaks about 1.6 and 1.75 Å from the V1. These were interpreted as V1–O1 and V1–F1 respectively with site occupancies of 0.5. Loosely constraining these distances (SHELXL DFIX) followed by least-squares refinement allowed convergence although not surprisingly there were large correlation coefficients between the O1 and F1 parameters. The same approach was followed for [VOF$_3$(Ph$_3$PO)$_2$] where again the molecule had twofold crystallographic symmetry with the disordered O2/F2 *trans* to the phosphane oxide ligand. Bond lengths and angles involving these disordered atoms should be treated with caution and even the other atoms, although the atomic displacement ellipsoids seem normal, are at least in principle subject to the same disorder. The molecule of [VOF$_3$(pyridine *N*-oxide)$_2$]·xH$_2$O has no crystallographic symmetry and thus the O position can be established from the V1–O3 distance. The V–O and V–F distances are better determined and are broadly in line with those proposed for the disordered structures discussed above. The H atoms on the partial water molecule O4 (x = 0.35) were not located, but support comes from the potential H-bonded distances O4···F3 [2.852(4) Å] and O4···O2′ [2.355(4) Å]. Selected bond lengths and angles are given in Table 2 and the captions to Figures 1, 2 and 3.

CCDC-664748 (for phen), -664749 (for Ph$_3$PO), -664750 (for pyNO) and -664751 (for Ph$_3$AsO) contain supplementary crystallographic data. Data for Ph$_3$AsF$_2$ (CCDC-664752) are also included. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We thank the Engineering and Physical Sciences Research Council (EPSRC) for support and Prof. E. G. Hope for discussions and for providing the data in ref.[31]

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[30] $[V_6O_{12}F_4(Ph_3AsO)_2(Ph_2AsO_2)_2]\cdot 2MeCN$. Formula $C_{64}H_{56}As_4F_4N_2O_{18}V_6$, $M = 1822.43$, triclinic: $a = 9.850(2)$, $b = 14.119(3)$, $c = 14.229(3)$ Å, $\alpha = 102.999(12)$, $\beta = 98.994(12)$, $\gamma = 109.744(12)°$, $V = 1755.6(6)$ Å^3. Space group $P\bar{1}$ (no. 2), $Z = 1$, $T = 120$ K, $\mu(\text{Mo-}K_{\alpha}) = 2.716$ mm^{-1}. Reflections measured: 26846, unique reflections: 8022, $R_{\text{int}} = 0.135$. Least squares parameters: 427, $R1 = 0.113$, $wR2 = 0.168$ [4315 reflections $I > 2\sigma(I)$].
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Received: October 25, 2007