New compounds containing the *triangulo*-trichlorotrivanadium(II) moiety†

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The complex $[\mathrm{VCl_2(tmen)_2}]$ (tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine) changes spontaneously into a *triangulo*-trinuclear species $[\mathrm{V_3(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)_2(tmen)_3}]^+$ in solution in tetrahydrofuran upon addition of salts of suitable counter ions. The apical (μ_3) chlorides can be replaced by methoxide, and the tmen by diphosphines. Several related materials, all containing the *triangulo*-$\mathrm{V_3X_3}$ (X = Cl or Br) motif, were characterised by mass spectroscopy, X-ray diffraction and other techniques. These clusters are antiferromagnetic both in solution and in the solid state. Thermogravimetric analysis of *trans*-$[\mathrm{VCl_2(tmen)_2}]$ and of $[\mathrm{V(MeOH)_6}]\mathrm{Cl_2}$ implied the formation of similar *triangulo*-$\mathrm{V_3Cl_3}$ species, which appear to be of common occurrence in vanadium(II) chemistry.

We have recently been working on the chemistry of vanadium,[1] inspired partly by the work of Gambarotta and co-workers[2] who described the first dinitrogen complex of vanadium that is stable at room temperature, and partly by the discovery of the vanadium-containing nitrogenases.[3] We needed to synthesize the dinitrogen complex $[\{\overline{\mathrm{V(C_6H_4CH_2N}}\mathrm{Me_2})_2(\mathrm{C_5H_5N})\}_2(\mu\text{-}\mathrm{N_2})]$ by the reaction of $\mathrm{Li(C_6H_4CH_2\text{-}1\text{-}NMe_2\text{-}2)}$ with $[\mathrm{VCl_2(tmen)_2}]$ (tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine) under $\mathrm{N_2}$, and had difficulty in obtaining reproducible results, despite following the prescribed procedure[2] as closely as we could. We satisfied ourselves that the problem did not arise from the lithium salt, which was recommended[2] to be freshly sublimed, but which is nevertheless quite stable over considerable periods, and concluded that the problem unexpectedly concerns the well defined vanadium complex. The work described here shows that this is probably the case. Some of these results have been published in preliminary form.[4]

Results and Discussion

Preparative studies

In our search for suitable vanadium(II) starting materials to synthesize vanadium–dinitrogen complexes we attempted to prepare $[\mathrm{VI_2(tmen)_2}]$ by the reaction of the corresponding dichloride with $\mathrm{SiMe_3I}$ in tetrahydrofuran (thf).[4] Although the product analysed (C, H, N) precisely for the required material, an admittedly incomplete X-ray analysis (due to poor-quality crystals) showed that our product was actually $[\mathrm{V_3(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)_2(tmen)_3}]\mathrm{I}$ **A**,[5] which has percentage contents of C, H and N the same as those of the diiodide to the second decimal place! Apart from our surprise at this extraordinary coincidence, we also wondered how the trinuclear cation had arisen. It was not new, having been isolated in salts from the reactions of $[\mathrm{VCl_2(tmen)_2}]$ with $\mathrm{NaNPh_2}$[6] and of the former complex with $[\mathrm{VCl_3(thf)_3}]$.[7] Its appearance was ascribed to disproportionations and halide abstractions.

The trinuclear vanadium cation is bluish green (turquoise), whereas the starting $[\mathrm{VCl_2(tmen)_2}]$ is a beautiful clear blue. During the preparation of complex **A** we observed that upon heating the reaction mixture in thf to boiling it turned reversibly turquoise. Upon cooling to −20 °C the blue colour reappeared. This suggested the equilibrium (1) (see experimental section).

$$3[\mathrm{VCl_2(tmen)_2}] \rightleftharpoons [\mathrm{V_3Cl_5(tmen)_3}]^+ + \mathrm{Cl^-} + 3\mathrm{tmen} \quad (1)$$

Addition of a cold thf solution of $\mathrm{Na[BPh_4]}$ to a cold thf solution of the dichloride also provoked a colour change to green. On cooling this mixture to −20 °C the blue dichloride crystallised out, whereas at room temperature the addition of hexane allowed turquoise $[\mathrm{V_3Cl_5(tmen)_3}][\mathrm{BPh_4}]$ **B**, of which the structure was determined (Fig. 1 and Table 1), to crystallise. The way in which the tetraphenylborate provokes this change is not obvious. The isolated tetraphenylborate salt was apparently unchanged in solution in thf at any temperature between −20 °C and the boiling point, but upon addition of both extra chloride as the benzyltri-*n*-butylammonium salt and of extra

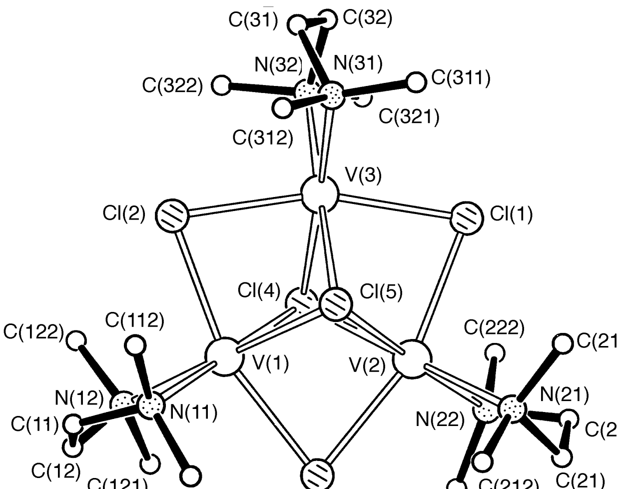

Fig. 1 Structure of the *triangulo*-trivanadium(II) cation in complex **B**, showing the atom numbering scheme

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† *Non-SI unit employed:* $\mu_\mathrm{B} \approx 9.27 \times 10^{-24}\ \mathrm{J\ T^{-1}}$.

Table 1 Selected molecular dimensions in $[V_3Cl_5(tmen)_3][BPh_4]$ **B** (bond lengths in Å, angles in °) with estimated standard deviations (e.s.d.s) in parentheses; angles marked with an asterisk have e.s.d.s less than 0.05°

About the vanadium atoms

V(1)···V(2)	3.155(1)	V(2)···V(3)	3.136(1)
V(1)···V(3)	3.134(1)		
V(1)–Cl(2)	2.482(1)	V(2)–Cl(5)	2.497(1)
V(1)–Cl(3)	2.507(1)	V(2)–N(21)	2.216(3)
V(1)–Cl(4)	2.524(1)	V(2)–N(22)	2.213(3)
V(1)–Cl(5)	2.515(1)	V(3)–Cl(1)	2.499(1)
V(1)–N(11)	2.220(3)	V(3)–Cl(2)	2.501(1)
V(1)–N(12)	2.217(3)	V(3)–Cl(4)	2.532(1)
V(2)–Cl(1)	2.505(1)	V(3)–Cl(5)	2.510(1)
V(2)–Cl(3)	2.504(1)	V(3)–N(31)	2.206(3)
V(2)–Cl(4)	2.537(1)	V(3)–N(32)	2.214(3)
V(2)···V(1)···V(3)	59.8*	V(1)···V(3)···V(2)	60.4*
V(1)···V(2)···V(3)	59.8*		
Cl(2)–V(1)–Cl(3)	162.0*	Cl(4)–V(2)–N(21)	178.3(1)
Cl(2)–V(1)–Cl(4)	84.0*	Cl(5)–V(2)–N(21)	93.7(1)
Cl(3)–V(1)–Cl(4)	83.0*	Cl(1)–V(2)–N(22)	95.3(1)
Cl(2)–V(1)–Cl(5)	84.0*	Cl(3)–V(2)–N(22)	97.4(1)
Cl(3)–V(1)–Cl(5)	83.2*	Cl(4)–V(2)–N(22)	95.5(1)
Cl(4)–V(1)–Cl(5)	87.9*	Cl(5)–V(2)–N(22)	176.4(1)
Cl(2)–V(1)–N(11)	96.1(1)	N(21)–V(2)–N(22)	82.8(1)
Cl(3)–V(1)–N(11)	97.6(1)	Cl(1)–V(3)–Cl(2)	162.4*
Cl(4)–V(1)–N(11)	176.8(1)	Cl(1)–V(3)–Cl(4)	83.3*
Cl(5)–V(1)–N(11)	95.3(1)	Cl(2)–V(3)–Cl(4)	83.4*
Cl(2)–V(1)–N(12)	96.5(1)	Cl(1)–V(3)–Cl(5)	84.3*
Cl(3)–V(1)–N(12)	96.8(1)	Cl(2)–V(3)–Cl(5)	83.7*
Cl(4)–V(1)–N(12)	94.5(1)	Cl(4)–V(3)–Cl(5)	87.8*
Cl(5)–V(1)–N(12)	177.6(1)	Cl(1)–V(3)–N(31)	98.3(1)
N(11)–V(1)–N(12)	82.3(1)	Cl(2)–V(3)–N(31)	95.4(1)
Cl(1)–V(2)–Cl(3)	161.8*	Cl(4)–V(3)–N(31)	177.7(1)
Cl(1)–V(2)–Cl(4)	83.1*	Cl(5)–V(3)–N(31)	94.1(1)
Cl(3)–V(2)–Cl(4)	82.8*	Cl(1)–V(3)–N(32)	95.8(1)
Cl(1)–V(2)–Cl(5)	84.5*	Cl(2)–V(3)–N(32)	96.8(1)
Cl(3)–V(2)–Cl(5)	83.6*	Cl(4)–V(3)–N(32)	95.0(1)
Cl(4)–V(2)–Cl(5)	88.0*	Cl(5)–V(3)–N(32)	177.2(1)
Cl(1)–V(2)–N(21)	97.0(1)	N(31)–V(3)–N(32)	83.2(1)
Cl(3)–V(2)–N(21)	97.4(1)		
V(2)–Cl(1)–V(3)	77.6*	V(2)–Cl(4)–V(3)	76.4*
V(1)–Cl(2)–V(3)	77.9*	V(1)–Cl(5)–V(2)	78.0*
V(1)–Cl(3)–V(2)	78.0*	V(1)–Cl(5)–V(3)	77.2*
V(1)–Cl(4)–V(2)	77.1*	V(2)–Cl(5)–V(3)	77.5*
V(1)–Cl(4)–V(3)	76.6*		

Torsion angles in the tmen ligands

N(11)–C(11)–C(12)–N(12)	−39.3(9)
N(21)–C(21)–C(22)–N(22)	−60.8(4)
N(31)–C(31)–C(32)–N(32)	59.8(5)

tmen, blue crystals of the dichloride were formed upon cooling. The trinuclear compound has a magnetic moment in solution in $[^2H_8]$ thf of 2.14 μ_B per vanadium atom, considerably less than the spin-only value, indicating coupling between the vanadium atoms. Solid-state magnetic susceptibility measurements on the corresponding iodide between 113 and 293 K showed that it is antiferromagnetic in the solid state, with a surprisingly high Neel temperature of 230 K (Fig. 2).

This particular trinuclear structure was, at the time, the sole example with a *triangulo*-V_3Cl_3 basis and we have yet to discover the mechanism of formation. However, it is known that $[VCl_2(tmen)_2]$ is formed from the reaction of dinuclear vanadium(II) species such as $[V_2Cl_3(thf)_6]^+$ with tmen.[8] This suggests that there may well be a series of equilibria (2) involving

$$[VCl_2(tmen)_2] \rightleftharpoons [V_2Cl_4(tmen)_2] \rightleftharpoons [V_3Cl_5(tmen)_3]^+ \quad (2)$$

all three states of aggregation. There are precedents for the binuclear species in copper,[9] chromium[10] and iron[12] chemistry, and the reaction of a binuclear compound with a mononuclear one may well be the route to the trinuclear. We have attempted to exploit this to synthesize mixed-metal species.[11]

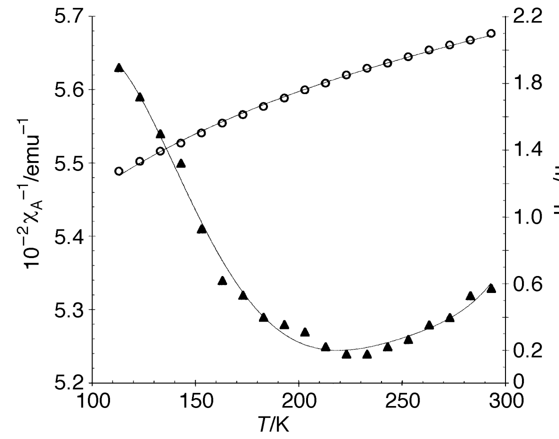

Fig. 2 Plot of the inverse of the atomic magnetic susceptibility (▲) and effective magnetic moment (○) *versus* temperature for $[V_3Cl_5(tmen)_3]I$ **A**

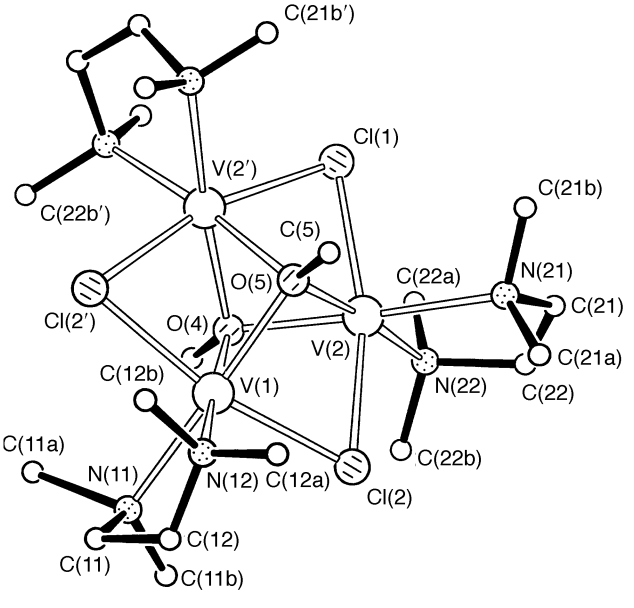

Fig. 3 View of the $[V_3(\mu\text{-}Cl)_3(\mu_3\text{-}OMe)_2(tmen)_3]^+$ cation in the co-crystallised iodide salts **C** and **D**

We showed subsequently using thermogravimetric analysis that $[VCl_2(tmen)_2]$ loses weight on heating under N_2 to about 215 °C, corresponding to the loss of one molecule of tmen, and implying an empirical formula for the product consistent with both the tri- and bi-nuclear formulations. At this stage the residue is turquoise. By about 430 °C another tmen molecule has been lost, and the residue above *ca.* 600 °C corresponds to VCl (or conceivably VO_2 if the material had scavenged oxygen).[11] Parallel behaviour was observed upon heating *in vacuo* and the turquoise solid obtained at 180 °C analysed for $[VCl_2(tmen)]$.[12] We also studied some other vanadium(II) species. Though there was no strong indication of stable species $[VCl_2(py)_2]$ (py = pyridine) upon heating $[VCl_2(py)_4]$,[13,14] $[V(MeOH)_6]Cl_2$[15] does appear to form stable $VCl_2(MeOH)_2$ (compare with the reports in refs. 14 and 16). The final weight loss always corresponds to the formation of VCl (or VO_2), though we were unable to characterise this species by chemical means.

It is tempting to infer that all the vanadium species VCl_2(monodentate ligand)$_2$ are actually polynuclear. That this may be so was shown by an attempt to synthesize $[VI_2(tmen)_2]$ from the compound $VCl_2(EtOH)_2$[17] which is antiferromagnetic in the solid state, implying some kind of polynuclear interaction. Treatment of this last material with KI in methanol {expected to generate $[V(MeOH)_6]I_2$}, followed by tmen in thf, produced not $[VI_2(tmen)_2]$ but crystals containing the two cationic species

$[V_3(\mu\text{-}Cl)_3(\mu_3\text{-}OMe)_2(tmen)_3]^+$ **C** and $[V_3(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)(\mu_3\text{-}OMe)(tmen)_3]^+$ **D** (Fig. 3, Table 2). This result also showed that it is possible to replace the apical chlorides of the cluster by methoxides, but hardly constitutes a rational synthesis of such materials. This we now developed.

Table 2 Selected molecular dimensions (length in Å, angles in °) in $[V_3Cl_3(OMe)_2(tmen)_3]I$ **C** with $[V_3Cl_4(OMe)(tmen)_3]I\cdot MeOH$ **D**

About the vanadium atoms

V(1) · · · V(2)	2.999(4)	V(2) · · · V(2′)	3.008(6)
V(1)–Cl(2)	2.491(4)	V(2)–Cl(1)	2.512(5)
		V(2)–Cl(2)	2.489(5)
V(1)–O(4)	2.142(13)	V(2)–O(4)	2.136(10)
V(1)–O(5)	2.149(14)	V(2)–O(5)	2.125(10)
V(1)–N(11)	2.263(17)	V(2)–N(21)	2.298(16)
V(1)–N(12)	2.242(18)	V(2)–N(22)	2.271(16)
V(2) · · · V(1) · · · V(2′)	60.2(1)	V(1) · · · V(2) · · · V(2′)	59.9(1)
Cl(2)–V(1)–Cl(2′)	166.0(2)	Cl(1)–V(2)–Cl(2)	166.0(2)
Cl(2)–V(1)–O(4)	84.4(1)	Cl(1)–V(2)–O(4)	83.1(3)
		Cl(2)–V(2)–O(4)	84.6(3)
Cl(2)–V(1)–O(5)	84.2(1)	Cl(1)–V(2)–O(5)	85.0(3)
		Cl(2)–V(2)–O(5)	84.8(3)
O(4)–V(1)–O(5)	71.1(5)	O(4)–V(2)–O(5)	71.7(5)
Cl(2)–V(1)–N(11)	95.5(1)	Cl(1)–V(2)–N(21)	96.2(6)
		Cl(2)–V(2)–N(21)	95.3(5)
O(4)–V(1)–N(11)	104.4(6)	O(4)–V(2)–N(21)	173.4(7)
O(5)–V(1)–N(11)	175.5(6)	O(5)–V(2)–N(21)	101.8(7)
Cl(2)–V(1)–N(12)	95.3(1)	Cl(1)–V(2)–N(22)	96.0(4)
		Cl(2)–V(2)–N(22)	93.2(4)
O(4)–V(1)–N(12)	176.3(6)	O(4)–V(2)–N(22)	102.5(5)
O(5)–V(1)–N(12)	105.2(6)	O(5)–V(2)–N(22)	173.9(6)
N(11)–V(1)–N(12)	79.3(6)	N(21)–V(2)–N(22)	84.1(7)
V(2)–Cl(1)–V(2′)	73.6(2)	V(1)–Cl(2)–V(2)	74.1(1)

In the methoxo ligands

O(4)–C(4)	1.414(24)	O(5)–C(5)	1.417(30)
V(1)–O(4)–V(2)	89.0(4)	V(1)–O(5)–V(2)	89.1(5)
V(2)–O(4)–V(2′)	89.5(6)	V(2)–O(5)–V(2′)	90.1(6)
V(1)–O(4)–C(4)	125.4(13)	V(1)–O(5)–C(5)	125.0(17)
V(2)–O(4)–C(4)	126.0(6)	V(2)–O(5)–C(5)	126.0(9)

Torsion angles in the tmen ligands

N(11)–C(11)–C(12)–N(12)	66(2)
N(21)–C(21)–C(22)–N(22)	47(5)

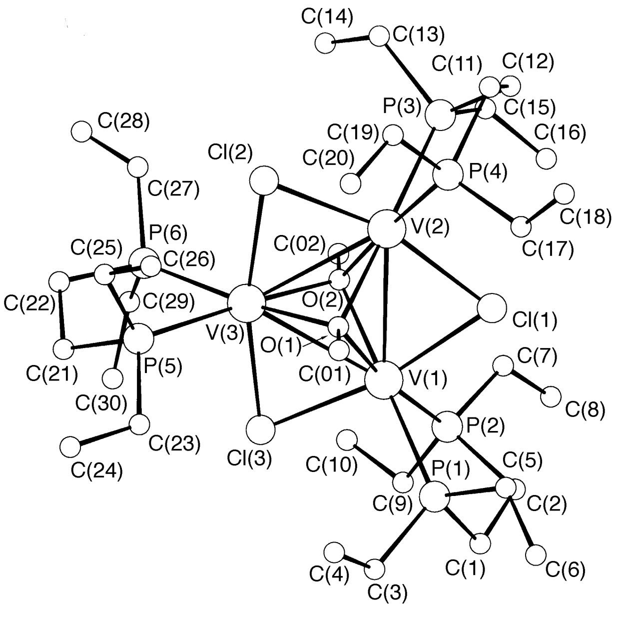

Fig. 4 A CAMERON[18] plot of the molecular structure of one of the crystallographically independent cations in the crystal of **F**, $[V_3(\mu\text{-}Cl)_3(\mu_3\text{-}OMe)_2(depe)_3]^+$, showing the atom labelling scheme

Table 3 Selected bond lengths (Å) and angles (°) for one of the crystallographically independent molecules in $[V_3Cl_3(OMe)_2(depe)_3][BPh_4]$ **F**

About the V atoms

V(1)–V(2)	2.961(4)	V(2)–V(3)	2.982(4)
V(1)–V(3)	2.950(4)		
V(1)–Cl(1)	2.455(6)	V(2)–Cl(2)	2.480(5)
V(1)–Cl(3)	2.484(5)	V(2)–Cl(1)	2.478(5)
V(1)–O(1)	2.114(11)	V(2)–O(1)	2.071(12)
V(1)–O(2)	2.100(11)	V(2)–O(2)	2.119(11)
V(1)–P(1)	2.525(6)	V(2)–P(3)	2.525(6)
V(1)–P(2)	2.521(6)	V(2)–P(4)	2.538(6)
V(3)–O(1)	2.098(12)	V(3)–Cl(2)	2.466(6)
V(3)–O(2)	2.103(11)	V(3)–Cl(3)	2.505(5)
V(3)–P(5)	2.524(6)	O(2)–C(01)	1.42(2)
V(3)–P(6)	2.538(6)	O(1)–C(02)	1.39(2)

About V(2) and some Cl ligands in the cation (the angles about the other V and Cl atoms are very similar)

Cl(1)–V(2)–Cl(2)	164.6(2)	O(1)–V(2)–Cl(1)	85.0(3)
O(1)–V(2)–P(3)	103.1(4)	O(1)–V(2)–Cl(2)	84.8(3)
O(2)–V(2)–P(4)	106.1(4)	O(2)–V(2)–Cl(1)	83.7(3)
O(2)–V(2)–Cl(2)	82.1(3)	O(1)–V(2)–O(2)	71.1(5)
Cl(1)–V(2)–P(3)	95.7(2)	Cl(2)–V(2)–P(3)	97.9(2)
O(2)–V(2)–P(3)	174.2(4)	Cl(1)–V(2)–P(4)	92.3(2)
Cl(2)–V(2)–P(4)	97.4(2)	O(1)–V(2)–P(4)	176.3(4)
P(3)–V(2)–P(4)	79.7(2)	C(02)–O(1)–V(2)	126.2(11)
C(01)–O(2)–V(2)	123.2(10)	V(2)–O(1)–V(3)	91.3(5)
V(2)–O(1)–V(1)	90.1(5)	V(2)–O(2)–V(1)	89.1(4)
V(3)–O(2)–V(2)	89.8(4)	V(1)–Cl(1)–V(2)	73.8(2)
V(3)–Cl(2)–V(2)	74.1(2)		

The reaction of $[VCl_2(tmen)_2]$ with $Na[BPh_4]$ in methanol produced a heavy white precipitate, which contained both tmen and tetraphenylborate. From the filtrate we isolated in low yield a crystalline compound formulated as $[V_3Cl_3(OMe)_2(tmen)_3][BPh_4]\cdot 2MeOH$ **E**. No extra tmen had been added and no attempt was made to optimise the yield. There was no indication of the formation of a pentamethoxo complex. However, reaction of $[V_3Cl_5(tmen)_3][BPh_4]$ with depe $(Et_2PCH_2CH_2PEt_2)$ in methanol gave a good yield of $[V_3Cl_3(OMe)_2(depe)_3][BPh_4]$ **F**, characterised by X-ray analysis (Fig. 4 and Table 3), as well as $(H_2tmen)(OMe)[BPh_4]$ and some of the known $[VCl_2(depe)_2]$.[19] The trinuclear nature was confirmed by positive ion FAB mass spectroscopy. The addition of more depe increased the yield of the mononuclear species at the expense of the trinuclear complex.

The effective magnetic moment per vanadium atom in a solution of the deep green-blue crystals of complex **F** in $[^2H_8]$thf is within the range 2.25–1.90 μ_B, decreasing with temperature between 323 and 172 K. The magnetic susceptibility also decreases with temperature. This may be due to antiferromagnetic coupling, as observed for both $[V_3Cl_3(OMe)_2(tmen)_3]I$ **C** in solution and for the depe complex **F** in the solid state (Fig. 5). Presumably there is a superexchange interaction between the vanadium atoms, mediated by the bridging chloride and/or methoxide ligands, because the metal–metal separations obtained from the X-ray analysis (see below) are too large to allow extensive direct interactions. Nevertheless, there is a difference between chloride and methoxide in that the Neel temperature in the methoxide case appears to be below liquid-nitrogen temperature, indicating stronger antiferromagnetic coupling in the pentachloro cation.

The isolation of $[VCl_2(depe)_2]$ from the reaction mixture that also generates the trinuclear species is consistent with the proposition that the driving force for the formation of the trinuclear species is the bulk of the bidentate ligand. There are no examples of three tmen molecules co-ordinated to a single first-transition-series metal(II) ion, whereas corresponding derivatives of ethane-1,2-diamine are common. Substituted amines are usually somewhat weaker complexing agents than unsubstituted amines. Other experiments showed that *N,N,N′*-

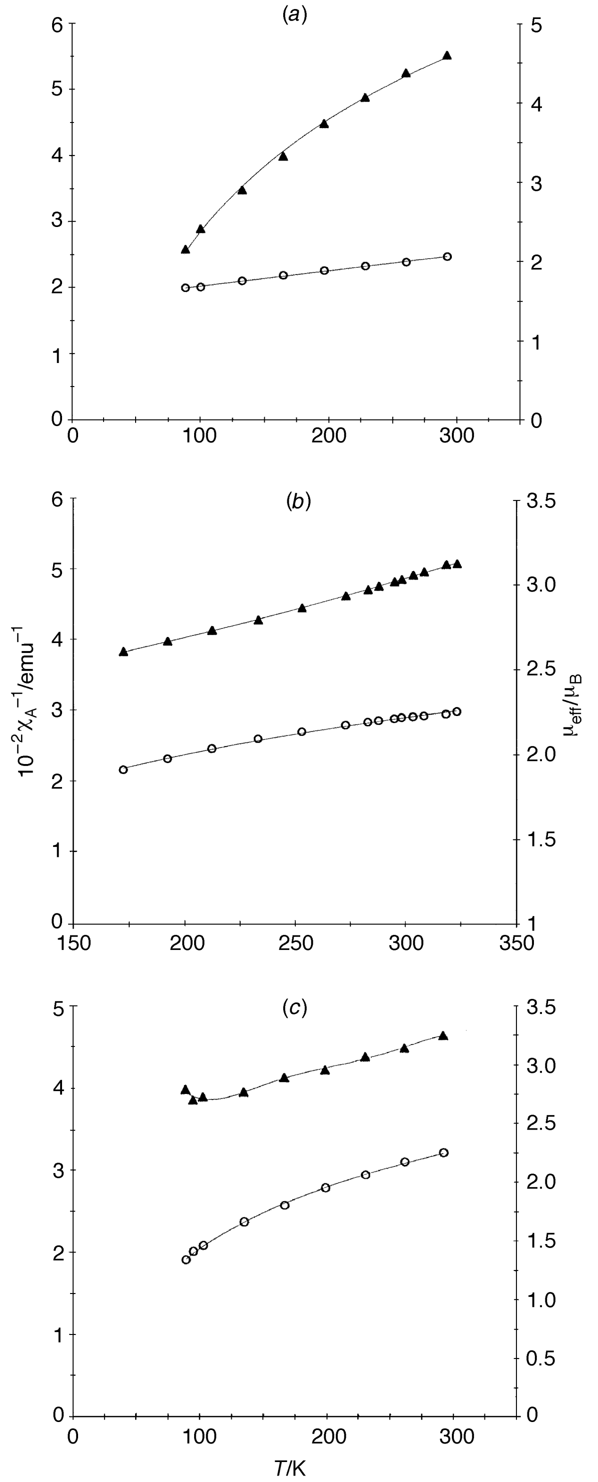

Fig. 5 Plot of the inverse of the atomic magnetic susceptibility (▲) and effective magnetic moment (○) *versus* temperature for (*a*) $[V_3Cl_3(OMe)_2(tmen)_3]I$ **C** in the solid state and for $[V_3Cl_3(OMe)_2(depe)_3][BPh_4]$ **F** in solution (*b*) and in the solid state (*c*)

trimethylethane-1,2-diamine and *N,N′*-dimethylethane-1,2-diamine (dmen) form mononuclear vanadium(II) adducts (see Experimental section) that have no tendency to form spontaneously trinuclear species.[5,11] Presumably depe as a ligand to vanadium(II) is less sterically demanding than tmen, but more demanding than the other two diamines.

We have also prepared and characterised the related complex $[V_3Br_3(OEt)_2(tmen)_3]^+$ as the tetraphenylborate salt **G**, but have not, as yet, explored its chemistry. For this we required the new complex $[VBr_2(tmen)_2]$ **H**, prepared as described in the Experimental section. We also characterised this structurally, and the data are presented in Fig. 6 and Table 4. The *trans* structure and magnetic properties are very similar to those demonstrated for the isostructural $[VCl_2(tmen)_2]$.[8]

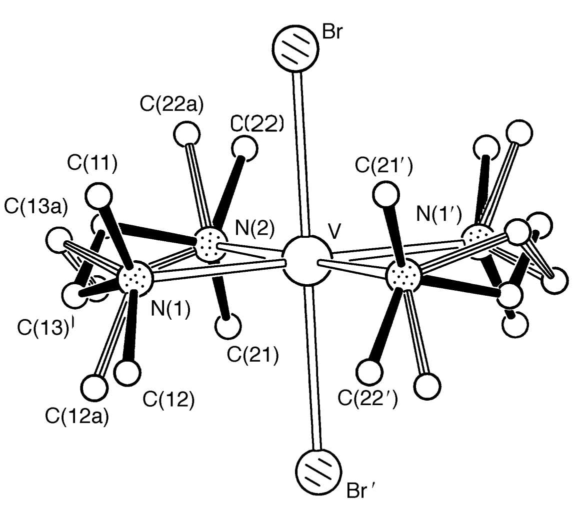

Fig. 6 View of the molecular structure of *trans*-$[VBr_2(tmen)_2]$ **H**, with the atom numbering scheme. The vanadium atom lies on a centre of symmetry. The alternative sites for the tmen ligands are indicated

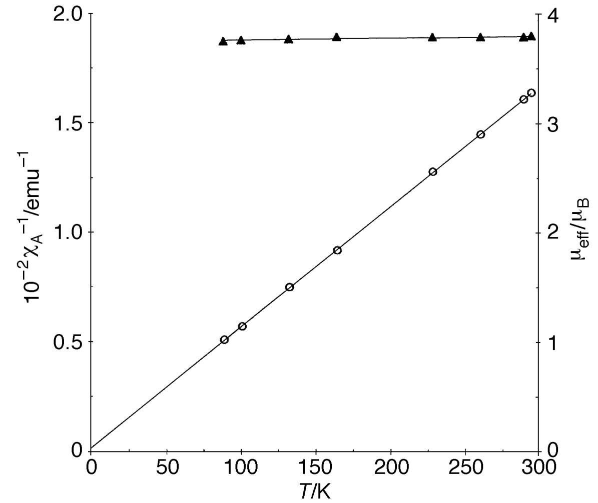

Fig. 7 Plot of the magnetic moment (▲) and reciprocal magnetic susceptibility (○) *versus* temperature for *trans*-$[VBr_2(tmen)_2]$ **H**, showing Curie-type behaviour

Table 4 Selected interatomic distances (Å) and angles (°) for *trans*-$[VBr_2(tmen)_2]$ **H**

V–Br	2.565(1)		
V–N(1)	2.313(7)	V–N(2)	2.324(7)
Br–V–N(1)	89.9(2)	Br–V–N(2)	90.1(2)
N(1)–V–N(2)	81.0(3)		

A plot of the reciprocal of the atomic susceptibility of vanadium in $[VBr_2(tmen)_2]$ against absolute temperature (Fig. 7) is a straight line which passes through the origin upon extrapolation. The complex therefore follows the Curie law with $\theta = 0$, and $\mu_{eff} = 3.8\mu_B$, independent of temperature between 89 and 259 K. As expected, this is close to the expected spin-only value, and is consistent with a mononuclear formulation.

Structural studies

Comparative structural data for the three trinuclear complexes described here are presented in Table 5. In each case the V · · · V separation is too long for there to be significant direct metal–

Table 5 Comparison of mean principal dimensions (lengths in Å, angles in °) in the *triangulo*-V_3Cl_3 complexes

Complex	**B**	**C/D**	**F**
V···V	3.142(7)	3.002(4)	2.965(9)
$V-Cl_{eq}$	2.500(4)	2.496(7)	2.475(5)
$V-Cl_{ax}/O$	2.519(6)	2.136(5)	2.101(7)
V−N/P	2.214(2)	2.270(11)	2.531(3)
$Cl_{ax}/O\cdots Cl_{ax}/O$	3.497(1)	2.496(19)	
$Cl_{eq}-V-Cl_{eq}$	162.1(2)	166.0(0)	166.3(5)
$Cl_{ax}/O-V-Cl_{ax}/O$	87.9(6)	71.4(4)	70.9(5)
N/P−V−N/P	82.8(3)	81.3(24)	79.8(2)
$Cl_{eq}-V-Cl_{ax}/O$	83.6(2)	84.3(1)	84.7(3)
Cl_{eq}−V−N/P	96.7(3)	95.4(2)	94.4(2)
N/P−V−Cl_{ax}/O (*trans*)	177.3(3)	174.9(7)	174.5(4)
N/P−V−Cl_{ax}/O (*cis*)	94.7(3)	103.5(8)	104.5(4)
$V-Cl_{eq}-V$	77.8(1)	74.0(2)	73.6(3)
$V-Cl_{ax}/O-V$	77.1(2)	89.3(2)	89.7(5)

metal interactions. They are also consistent with depe being less demanding sterically than tmen. The metal–metal separations are also paralleled by the $V-Cl_{eq}$ separations. The depe compound appears to be the most compact of the three, though it should be noted that the data sets were not all collected at the same temperature.

Compared to the corresponding starting materials $[VCl_2(tmen)_2]$[8] and $[VCl_2(depe)_2]$,[19] the $V-Cl_{eq}$ separations are all increased, from 2.487(1) Å in the former and from 2.444(2) Å in the latter. The changes are larger for the tmen complexes. Similarly, the V–N separations decreases, from 2.319(1) Å, but the decrease in the phosphine case is less, from a mean of 2.558(2) Å. What this means in any absolute sense is not clear, but the greater readjustments in the case of the tmen complexes are consistent with a comparatively greater driving force for their formation. Consistent with this, the addition of $Na[BPh_4]$ to a purple methanolic solution of $[VCl_2(depe)_2]$ at room temperature does not produce a trinuclear complex and unreacted starting material was isolated.[11]

The replacement of the capping chlorides by methoxides has a significant effect on the overall topology of the *triangulo* structure, increasing the $Cl_{eq}-V-Cl_{eq}$ angles and decreasing the $V-Cl_{eq}-V$ angles. The V−(μ_3-O) bonds are shorter than the corresponding V−(μ_3-Cl) bonds. Consequently the core of the *triangulo*-methoxide ions is 'flatter' than that in the V_2Cl_5 species and the distortion of the octahedral geometry about each vanadium is altered. As the trinuclear core becomes more compact the tmen ligands are pushed away from their vanadium partners. This may mean that the tmen ligands are more labile in the methoxide complexes, and this we are hoping to test.

Comparative structural data for the complexes $[VX_2(tmen)_2]$ (X = Cl or Br) are presented in Table 6. It is evident that there is very little difference between the structures. There is considerable disorder in the ethylene bridges in both compounds, but the vanadium–nitrogen bond lengths are the same, as are the N−V−N bite angles. The V−Br separation [2.656(1) Å] differs from the V−Cl separation [2.487(1) Å] by the difference between the halide ionic radii (0.15 Å) so that there are probably no unusual electronic or steric pressures at work.

Experimental

All operations were carried out under an inert atmosphere in a dinitrogen-filled dry-box (Faircrest Engineering, Croydon) or using standard Schlenk techniques. Solvents were dried by standard procedures and distilled under N_2 prior to use.

The commercial products diethylaluminium ethoxide (25% solution in toluene), sodium tetraphenylborate, trimethylsilyl iodide, vanadium tribromide and vanadium trichloride (Aldrich) were used without further purification. 1,2-[Bis(diethylphosphino)]ethane (depe) was prepared by published methods.[20] *N,N,N′,N′*-Tetramethylethane-1,2-diamine (tmen) was refluxed over molten sodium for *ca.* 1 h and then distilled under N_2. The complexes $[VCl_2(tmen)_2]$ and $VCl_2(EtOH)_2$ were prepared as described.[8,17]

Table 6 Mean dimensions (lengths in Å, angles in °) in $[VX_2(tmen)_2]$ (X = Cl or Br)

C	$[VCl_2(tmen)_2]$[8]	$[VBr_2(tmen)_2]$
V−X	2.487(1)	2.656(1)
V−N	2.319(1)	2.318(6)
N−V−N	81.44(7)	81.0(3)
X−V−N	89.96(1)	90.0(1)

Microanalyses were by Mr. Colin Macdonald (Nitrogen Fixation Laboratory) or Ms. Nicola Walker (Department of Chemistry, University of Surrey), using Perkin-Elmer 2400 and Leeman CE 440 CHN elemental analysers, respectively. Chlorine and iodine contents were determined by Butterworth Laboratories (Teddington, Middlesex), while vanadium analyses were performed by Southern Science (Sussex Laboratory), by inductively coupled plasma optical emission spectroscopy.

The NMR solvents, supplied by Goss Scientific Instruments, were dried over molecular sieves before use and kept under dinitrogen in Schlenk tubes equipped with grease-free taps. Spectra were obtained in the appropriate deuteriated solvents using JEOL GSX-270 equipment. Tetramethylsilane was used as reference for ^1H NMR spectra. The IR data were recorded on a Perkin-Elmer 883 instrument, from Nujol mulls prepared under dinitrogen and spread on KBr plates. Conductivity measurements were carried out in tetrahydrofuran, nitromethane, or dichloromethane solutions (*ca.* 10^{-3} mol dm^{-3}) using a V-shaped cell (cell constant = 1.54) connected to a Portland Electronics bridge. Mass spectra were recorded by Dr. A. Abdul Sada (University of Sussex) on a VG Autospec spectrometer (Fisons Instruments) equipped with a CsI gun at 25 kV [secondary ion (SIMS) technique] or on a Kratos MS80RF machine with xenon at 8 kV [fast atom bombardment (FAB) technique]. In both cases 3-nitrobenzyl alcohol was used as the matrix.

Thermogravimetric analyses were run on Perkin-Elmer TGA7 equipment using N_2 as the purging gas in the temperature range 20–800 °C, with the collaboration of Dr. Steve Armes and Mr. Stuart Lascelles, University of Sussex.

Magnetic susceptibility determinations were carried out in solution by variable-temperature NMR spectroscopy using the Evans method[21] with tetramethylsilane as the marker molecule. Samples were carefully weighed under N_2, dissolved in the appropriate solvent mixture (deuteriated solvent + marker) in a glove-box, and transferred to the outer tube of the coaxial NMR tube system. Spectra were recorded in the temperature range −100 to 50 °C (173–323 K) for $[^2H_8]$thf solutions. Two resonance lines were normally produced by each magnetically distinct proton of the solvent/marker molecules. Diamagnetic corrections were made using Pascal's constants.[22] Measurements in the solid state for the same samples were carried out at the University of Surrey, using a Newport variable-temperature Gouy balance over the range 90–295 K. The field strength was calibrated by measurements on $Hg[Co(NCS)_4]$ and $[Ni(NH_2CH_2CH_2NH_2)_3][S_2O_3]$; the temperature scale was checked with $CuSO_4\cdot 5H_2O$. Corrections were applied for the diamagnetism of the sample tubes.

Syntheses

$[V_3Cl_5(tmen)_3]I$ A. To a light blue solution of $[VCl_2(tmen)_2]$ (5.5 g, 15.5 mmol) in thf–tmen (20 : 1, 200 cm^3) kept under reflux was added an excess of trimethylsilyl iodide (9.1 g, 6.5 cm^3, 45.7 mmol) by syringe, producing an immediate precipitation of a bright bluish green powder. At that temperature (*ca.* 70 °C) the mother-liquor was light green. The suspension was concentrated by solvent distillation at atmospheric pressure to a final volume of 80 cm^3 and then filtered at room temperature. The green solid was washed with thf (100 cm^3) and hexane (80 cm^3) and dried for 4 h *in vacuo*. Yield: 1.5 g (36%). The filtrate (plus thf washings) was light blue at room temperature, but when heated again under reflux showed the same change to light green and produced once more a small amount of the green powder (*ca.* 0.1 g isolated) upon concentration. Allowing the system to cool again to 20 °C reversibly restored the blue colour to the mixture.

The bluish green $[V_3Cl_5(tmen)_3]I$ **A** was also prepared from $[V_2(\mu\text{-}Cl)_3(thf)_6][AlEt_2Cl_2]$ (3.8 g, 4.8 mmol) in refluxing thf, after addition of a large excess of tmen (8.0 cm^3, 6.2 g, 53.0 mmol) and $SiMe_3I$ (3.0 cm^3, 4.2 g, 21.0 mmol). The yield was similar (32%) (Found: C, 26.6; H, 6.2; Cl, 21.1; N, 10.1. $C_{18}H_{48}Cl_5IN_6V_3$ requires C, 26.8; H, 6.0; Cl, 22.0; N, 10.4%). Conductivity in nitromethane solution, $\Lambda_m = 97 \pm 8$ μS cm^2 mol^{-1} (1:1 electrolyte).[23] Note that the required values for $[VI_2(tmen)_2]$, $C_{12}H_{32}I_2N_4V$ are: C, 26.8; H, 6.0; N, 10.4%.

$[V_3Cl_5(tmen)_3][BPh_4]\cdot thf$ B. A light blue solution of $[VCl_2(tmen)_2]$ (1.2 g, 3.5 mmol) in thf (60 cm^3) was slowly mixed with $Na[BPh_4]$ (0.40 g, 1.2 mmol, dissolved in 15 cm^3 thf). Immediately after addition a turquoise (light bluish green) solution was produced. The reaction mixture was concentrated to *ca.* 30 cm^3 *in vacuo*, filtered through Celite to eliminate sodium chloride and carefully layered with hexane (20 cm^3). Thin green needles started to crystallise soon after the addition of hexane. The mixture was then allowed to stand at room temperature for 3 d to give turquoise crystals (needle-like + thick plates) which were filtered off, washed with thf (5 cm^3) and hexane (20 cm^3) and dried *in vacuo* for *ca.* 8 h. Yield: 0.6 g (54%). Both forms gave very similar microanalytical results (Found: C, 51.6; H, 7.25; Cl, 16.2; N, 7.8. $C_{42}H_{68}BCl_5N_6V_3\cdot thf$ requires C, 51.6; H, 7.15; Cl, 16.6; N, 7.9%). Positive-ion FAB mass spectrum: *m/z* 678 {42%, $[V_3Cl_5(tmen)_3]^+$}.

This product sometimes crystallises without the solvating thf; the reason may be minor changes in the composition of the crystallisation mixture (concentration of the solution and slightly different thf–hexane proportion) (Found: C, 50.4; H, 7.0; N, 8.5. $C_{42}H_{68}BCl_5N_6V_3$ requires C, 50.5; H, 6.9; N, 8.4%).

$[V_3Cl_3(\mu_3\text{-}OMe)_2(tmen)_3]I$ C and $[V_3Cl_3(\mu_3\text{-}Cl)(\mu_3\text{-}OMe)(tmen)_3]I\cdot MeOH$ D. The ethanol adduct $VCl_2(EtOH)_2$ (1.9 g, 8.9 mmol) was dissolved in methanol (70 cm^3) forming a purple solution to which precisely 2 equivalents of potassium iodide (3.0 g, 17.8 mmol) in methanol (30 cm^3) were added. A white precipitate, presumed to be KCl, formed immediately but the mixture was left to stir for 3 h. The white solid was then filtered off but, on filtration, more white powder began to form. Complete removal of the salt proved extremely difficult, therefore the solution was evacuated to dryness yielding a mixture of two solids, one purple and one white. Tetrahydrofuran (50 cm^3) was added to this, forming a bright green solution instantly. The white powder was insoluble in thf and was filtered off successfully. The compound tmen (5.0 cm^3, 33 mmol) was then added to the green solution forming a deep red solution with immediate precipitation of another white solid. The mixture was left to stir overnight. The precipitate was filtered off and analysed as $(H_2tmen)I_3\cdot MeOH$ (Found: C, 20.9; H, 5.4; N, 7.6. $C_7H_{22}I_2N_{20}$ requires C, 20.8; H, 5.0; N, 6.9%). Magnetic moment measurements carried out on this white solid showed it to be diamagnetic. The red solution was taken to dryness giving a red-brown powder mixed with crystals (58% yield), which were washed with diethyl ether and dried *in vacuo*. The powder was used for analysis, which suggested considerable contamination with $(H_2tmen)I_2$ (Found: C, 27.3; H, 6.75; N, 9.2; V, 17.5. $C_{20}H_{54}Cl_3IN_6O_2V_3$ **C** requires C, 30.3; H, 6.8; N, 10.6; V, 19.3. $C_{19}H_{51}Cl_4IN_6OV_3$ **D** requires C, 28.5; H, 6.4; N, 10.5; V, 19.2%). μ_{eff} (solid state) 2.06 (293) and 1.66 μ_B (89 K). The crystals were subjected to X-ray analysis, as described below.

$[V_3Cl_3(OMe)_2(tmen)_3][BPh_4]\cdot 2MeOH$ E. The complex $[VCl_2(tmen)_2]$ (2.0 g, 5.6 mmol) was completely dissolved in methanol (40 cm^3, purple solution) and then mixed with a colourless solution of $Na[BPh_4]$ (0.6 g, 1.8 mmol) in methanol (5.0 cm^3). There was no significant change of colour in the mother-liquor after the addition, but a heavy precipitation of a bluish white powder was observed. The mixture was allowed to react for 30 min and then concentrated *in vacuo* to *ca.* 20 cm^3 and filtered. The filtrate was a clean purple solution, which was left at room temperature for 3 d. The bluish white powder (probably a mixture of $(H_2tmen)(OMe)[BPh_4]$ and **E**) was washed with methanol (20 cm^3), dried for 1 h *in vacuo* and analysed by IR and ^1H NMR spectroscopies. $[H_2tmen][OMe][BPh_4]$: ^1H NMR ($[^2H_8]$thf): δ 2.19 (s, 12 H, NCH_3), 2.42 (s, 4 H, NCH_2), 6.75, 6.89 and 7.32 (t, t, m, 20 H, C_6H_5). From the filtrate a light purplish blue crystalline solid was formed. This was then filtered off, washed with methanol (30 cm^3) and dried *in vacuo* for 2 h. Yield: 0.3 g (16%) (Found: C, 52.8; H, 7.7; N, 7.8. $C_{44}H_{74}BCl_3N_6O_2V_3\cdot 2MeOH$ requires C, 52.4; H, 7.85; N, 8.0%).

$[V_3Cl_3(OMe)_2(depe)_3][BPh_4]\cdot MeOH$ F. The complex $[V_3Cl_5(tmen)_3][BPh_4]$ (2.3 g, 2.3 mmol) was suspended in methanol (90 cm^3) at room temperature. To this suspension was added depe (1.6 cm^3, 1.4 g, 6.8 mmol) producing a purple solution with some green solid in suspension. The reaction was carried out for about 20 h in a glove-box and the mixture was then filtered, giving a deep greenish blue powder (1.2 g, 41% yield) and a purple filtrate. {The yield can be increased by careful solvent evaporation from the filtrate, to about half of the initial volume, and standing at room temperature for some days. If the filtrate is cooled to −20 °C instead of being left at room temperature, a mixture of **F**, $(H_2tmen)(OMe)[BPh_4]$ and $[VCl_2(depe)_2]$ is obtained.} The powder was washed with methanol (90 cm^3) and the blue washings were collected and cooled to −20 °C for 2 d to produce small deep greenish blue prisms of $[V_3Cl_3(OMe)_2(depe)_3][BPh_4]\cdot MeOH$ (Found: C, 53.0; H, 8.05; N, 0.0. $C_{56}H_{98}BCl_3O_2P_6V_3\cdot MeOH$ requires C, 53.0; H, 8.0; N, 0.0%). From the purple filtrate, colourless crystals of $(H_2tmen)(OMe)[BPh_4]$ (Found: C, 79.2; H, 8.35; N, 6.2. $C_{31}H_{41}BN_2O$ requires C, 79.5; H, 8.85; N, 6.0%) and purple needles of $[VCl_2(depe)_2]$ (Found: C, 45.0; H, 9.0; N, 0.0. $C_{20}H_{48}Cl_2P_4V$ requires C, 45.0; H, 9.05; N, 0.0%) were isolated by fractional crystallisation. Mass spectra (positive ion FAB), *m/z* 937 {3, $[V_3Cl_3(OMe)_2(depe)_3]^+$}; {SIMS) for $[VCl_2(depe)_2]$}, *m/z* 533 (100%).

$[V_3Br_3(OEt)_2(tmen)_3][BPh_4]$ G. This compound was synthesized from $[VBr_2(tmen)_2]$ **H** which is itself attainable by two routes.

(*a*) The compound VBr_3 (5.0 g, 0.02 mmol) was heated in thf (40 cm^3) under reflux for 24 h. This generates $[VBr_3(thf)_3]$. Diethylaluminium ethoxide (10 cm^3, 0.07 mmol, 25% w/w in toluene) was then added to the red suspension of $[VBr_3(thf)_3]$ which formed a green solution upon stirring at room temperature for 4 d. Upon reducing the volume slightly *in vacuo* green crystals of $[V_2Br_3(thf)_6][AlEt_2Br_2]$ appeared. These were filtered off and suspended in thf (100 cm^3). The amine tmen (2.9 cm^3) was then added and the mixture heated under reflux for 1 h. After cooling, the mixture was stored at 4 °C for 12 h, yielding blue crystals of $[VBr_2(tmen)_2]$ which were washed with diethyl ether and dried *in vacuo*. Yield 59% (Found: C, 31.8; H, 6.85; N, 11.9. $C_{12}H_{32}Br_2N_4V$ requires C, 32.5; H, 7.3; N, 12.6%).

(*b*) Purple crystals of $VBr_2(EtOH)_2$ (5.0 g) were heated at 100 °C *in vacuo* to remove as much of the ethanol as possible, though the IR spectrum indicated that some alcohol was retained in the final product. Freshly distilled thf (40 cm^3) was added to this powder to produce a green solution, to which tmen (8.0 cm^3, 61 mmol) was added. This gave a light blue suspension in a green solution. After heating for 1 h under reflux the mixture was held at 4 °C for 12 h. The resulting mixture of blue crystals and powder was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield 72% (Found: C, 32.6; H, 7.3; N, 12.7; V, 11.4. $C_{12}H_{32}Br_2N_4V$ requires C, 32.5; H, 7.3; N, 12.6; V, 11.5%). The green filtrate was used for further work as detailed below.

The required material (**G**) was then prepared as follows: to the green filtrate from (*b*) above estimated to contain [VBr$_2$-(tmen)$_2$] equivalent to (0.55 g, 1.24 mmol) in thf (60 cm^3) was added Na[BPh$_4$] (0.43 g, 1.26 mmol). Heating to reflux for 1 h produced a white precipitate in a red solution. After filtration, the filtrate was allowed to stand for 1 week, yielding a brown crystalline solid that was filtered off and dried *in vacuo* (Found: C, 48.2; H, 7.0; N, 7.0. $C_{46}H_{78}BBr_3N_6O_2V_3$ requires C, 48.0; H, 6.85; N, 7.3%). μ_{eff} (solid state) 1.65 μ_B at 295 K, 1.27 μ_B at 89 K. A further red material that precipitated from the filtrate was not investigated.

[VCl$_2$(dmen)$_2$]. *N,N′*-Dimethylethane-1,2-diamine (2.9 cm^3, 27 mmol) was added with stirring to a green solution of VCl$_2$(EtOH)$_2$ (2.82 g) in thf (100 cm^3). A pink precipitate separated from a purple solution. After stirring for 30 min, the solid was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield 87% (Found: C, 32.3; H, 8.3; N, 18.6; V, 16.7. $C_8H_{24}Cl_2N_4V$ requires C, 32.2; H, 8.1; N, 18.8; V, 17.1%). μ_{eff} (solid state, independent of temperature 87–295 K) 3.83 μ_B.

[VBr$_2$(dmen)$_2$]. This complex was prepared similarly as a lilac solid in 81% yield from VBr$_2$(thf)$_2$ (2.36 g) and dmen (1.70 cm^3, 16.0 mmol) (Found: C, 24.4; H, 6.25; N, 14.5; V, 13.2. $C_8H_{24}Br_2N_4V$ requires C, 24.0; H, 6.55; N, 14.1; V, 12.7%). μ_{eff} (solid state, independent of temperature 87–295 K) 3.77 μ_B.

[VI$_2$(dmen)$_2$]·CH$_2$Cl$_2$. Trimethylsilyl iodide (2.1 cm^3, 14.8 mmol) was added to a stirred pink suspension of [VCl$_2$(dmen)$_2$] (2.14 g, 7.2 mmol) in dichloromethane (100 cm^3). The mixture formed a deep purple precipitate, and was heated to reflux for 14 h. The precipitate was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield 82% (Found: C, 17.7; H, 4.65; N, 10.3; V, 12.5. $C_8H_{24}I_2N_4V{\cdot}CH_2Cl_2$ requires C, 19.1; H, 4.6; N, 9.9; V, 9.0%). μ_{eff} (solid state, independent of temperature 87–295 K) 3.48 μ_B.

X-Ray crystallographic analyses

Crystal data for the four complexes are summarised in Table 7, in which some of the experimental details and results are also listed. The analyses followed similar procedures; that for complex **B** is described below, and the variations for the other analyses follow.

[V$_3$Cl$_5$(tmen)$_3$][BPh$_4$] B. Crystals were large, thick green plates which had to be cut to a suitable size. Five air-sensitive fragments were sealed inside capillary tubes in a glove-box, and were examined photographically for crystal quality and determination of approximate unit cell dimensions. One (*ca.* 0.30 × 0.45 × 0.50 mm) was then mounted on an Enraf-Nonius CAD4 diffractometer (with monochromated radiation); accurate cell parameters and the orientation matrix (from the settings of 25 representative reflections in the range $12 < \theta < 14°$, each centred in four orientations) were determined.

Diffraction intensities were measured to $\theta_{max} = 25°$. The intensities of three representative reflections were monitored throughout the data collection, and a plot of those intensities against time showed an overall crystal decomposition of 7.7%. During processing, data were corrected for Lorentz-polarisation effects and decomposition, and negative intensities were eliminated by Bayesian statistical methods. No absorption correction was applied. 8838 Unique reflections were entered into the SHELX system.[24]

The structure was solved by direct methods using SHELXS[26] (which showed all the non-hydrogen atoms), and refined in the SHELXN[24] program. All the hydrogen atoms, including the methyl H atoms in the tmen ligands, were located from difference maps. No structural disorder was detected.

All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the methylene groups and the phenyl rings were fixed in idealised positions, and the coordinates of the methyl hydrogen atoms were refined with geometrical constraints; the isotropic thermal parameters of all the hydrogen atoms were refined freely. The final refinement cycles, by large-block-matrix least-squares methods, were based on all 8838 reflections and 689 parameters.

Scattering-factor curves for neutral atoms were taken from ref. 27. Computer programs used in this analysis have been noted above or listed in ref. 28 and were run on a DEC MicroVAX II machine at the Nitrogen Fixation Laboratory.

[V$_3$Cl$_3$(OMe)$_2$(tmen)$_3$]I C with [V$_3$Cl$_4$(OMe)(tmen)$_3$]I·MeOH D. Crystals were long, very dark square prisms. Several were mounted in sealed Lindemann capillaries and, after photographic examination, one was transferred to the CAD4 diffractometer for determination of accurate cell parameters (from the settings of 25 reflections, $\theta = 10$–$11°$) and for measurement of diffraction intensities.

The intensities were corrected for Lorentz-polarisation effects, slight deterioration (3% overall), absorption (by semi-empirical ψ-scan methods) and to remove negative net intensities (by Bayesian statistical methods). The space group was determined to be *Pmnb* (or *P*2$_1$*nb*) but it was noted that several of the systematically absent reflections had small but significant intensities suggesting some not-totally-random disorder in the crystal.

The structure of complex **C** was solved by direct methods, using the TREF (direct methods) routines of SHELXS.[26] The [V$_3$Cl$_3$(OMe)$_2$(tmen)$_3$]$^+$ cation lies about a mirror plane of symmetry which passes through one V atom, V(1); the tmen ligand of this V atom lies in one orientation or its mirror image, with N(11) and N(12) lying on (or very close to) the mirror plane. Refinement by full-matrix least-squares methods and successive difference maps showed disorder in the crystal and a minor component, believed to be [V$_3$Cl$_4$(OMe)(tmen)$_3$]I·MeOH **D**, occupying *ca.* 17% of the sites in the crystal. No hydrogen atoms were included in the refinement. All the atoms (except the carbon atoms of a tmen ligand disordered about a mirror plane, and the atoms of the partially occupied methanol molecule) were allowed anisotropic thermal parameters. In the final difference map the principal peaks, *ca.* 1.0 e Å^{-3}, were located close to the major iodide position.

In the major component the iodide anion I(1) lies close to and straight out from a μ_3-OMe ligand, with I(1) ··· C(5) 3.58(3) Å and O(5)–C(5) ··· I(1) 180(2)°. In the minor component, that methoxy group is replaced by a μ_3-Cl group [not resolved from O(5)], the iodide anion, as I(2), moves in toward the cation and a space is left for a solvent, MeOH, molecule which is hydrogen bonded to the iodide: O(7) ··· I(2) 3.62(13) Å and C(7)–O(7) ··· I(2) 102(7)°.

[V$_3$Cl$_3$(OMe)$_2$(depe)$_3$][BPh$_4$] F. Crystals were small, short greenish blue prisms (air-sensitive). Several were quickly transferred to a drop of oil under the microscope; one, *ca.* 0.20 × 0.20 × 0.05 mm, was selected, collected on a glass fibre and mounted on a CAD4 diffractometer where it was cooled to 173 K to minimise structural disorder and crystal decomposition. After the determination of the cell parameters, the diffraction intensities were measured to $\theta_{max} = 20°$; further collection (to $\theta = 25°$) was not possible because of the weak diffraction from the crystal.

The structure was solved by automated Patterson routines in SHELXS,[26] which revealed two crystallographically independ-

Table 7 Crystal data and details of the crystallographic analyses

	$[V_3Cl_5(tmen)_3][BPh_4]$ **B**	$[V_3Cl_3(OMe)_2(tmen)_3]I$, **C** and $[V_3Cl_4(OMe)(tmen)_3]I{\cdot}MeOH$ **D**	$[V_3Cl_3(OMe)_2(depe)_3][BPh_4]$ **F**	*trans*-$[VBr_2(tmen)_2]$ **H**
Formula	$C_{42}H_{68}BCl_5N_6V_3$	$C_{20}H_{54}Cl_3IN_6O_2V_3$ (83%) and $C_{19}H_{51}Cl_4IN_6OV_3{\cdot}CH_4O$ (17%)	$C_{52}H_{98}BCl_3O_2P_6V_3$	$C_{12}H_{32}Br_2N_4V$
M	998.0	796.8 and 833.2	1259.1	443.2
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1/n$ (equivalent to no. 14)	*Pmnb* (equivalent to no. 62)	*Pbca* (no. 61)	$P2_1/n$ (equivalent to no. 14)
a/Å	19.619(1)	13.633(1)	24.184(5)	8.006(4)
b/Å	21.566(2)	14.454(2)	27.431(7)	13.037(9)
c/Å	12.050(1)	17.963(3)	39.465(6)	9.014(8)
β/°	99.252(5)			100.42(5)
U/Å	5032.3(7)	3539.7(8)	26 181(10)	925.4(2)
Z	4	4	16	2
D_c/g cm^{-3}	1.317	1.495	1.28	1.590
F(000)	2084	1632 (for 83% **C** + 17% **D**)	10 640	450
μ(Mo-Kα)/cm^{-1}	8.3	18.8	7.3	47.9
λ(Mo-Kα)/Å	0.710 69	0.710 69	0.710 73	0.710 73
θ_{max} for data collection/°	25	22.5	20	26
Crystal degradation (%)	7.7	3.0	<2.0	10
No. unique reflections	8838	2424	12 158	2036
‘Observed’ reflections ($I > 2\sigma_I$)	6192	1314	5592	1810
Final *R*	0.063	0.088	0.099	0.062
Final weighted *R*	0.067 (R_g[24])	0.093 (R_w[24])	0.201 ($wR2$[25])	0.062/0.078 (R_w[24])
No. reflections used	All 8838	1314 (with $I > 2\sigma_I$)	5592 (with $I > 2\sigma_I$)	1160 (with $I > 3\sigma_I$)
Weighting scheme, w^{-1}	$\sigma_F^2 + 0.001\,72F^2$	$\sigma_F^2 + 0.0193F^2$	$\sigma^2(F_o^2) + (0.078P)^2 + 146.2P$ $P = (F_o^2 + 2F_c^2)/3$	$\sigma(F^2) + (0.6F)^2 + 6$
Highest peaks in difference map/e Å^{-3}	0.5, close to a tmen ligand	1.0, close to major iodide	0.6, close to V atoms	1.2, by V and Br atoms

ent ion pairs with no significant differences in the corresponding bond distances and angles. Refinement was by full-matrix least-squares methods on the intensities (F^2) of all independent reflections using SHELXL 93.[25] The non-hydrogen atoms in the cations were refined anisotropically, but the B and C atoms of the tetraphenylborate anions were treated isotropically with the phenyl groups as rigid bodies of idealised D_{6h} symmetry. The H atoms were included in riding mode with U_{iso} (H) equal to $1.2U_{eq}$ (C) or $1.5U_{eq}$ (C) for methyl groups.

At the completion of the refinement cycles the final $R1$[28] indices were 0.099 and 0.217 for the 'observed' reflections and all data (938 parameters), respectively. These high R factors are a consequence of weak diffraction.

[VBr$_2$(tmen)$_2$] H. A single crystal (0.7 × 0.7 × 0.4 mm) prepared from VBr$_2$(EtOH)$_2$ and tmen was mounted under dinitrogen in a Lindemann capillary and examined on a CAD-4 diffractometer. The heavy atoms were located by Patterson methods and the remaining atoms by Fourier methods. The disordered atoms of the ethylene bridges were resolved only with difficulty, and finally the isotropic refinement converged to $R = 0.22$ with 50% occupancy assigned to two different orientations of each bridge. An absorption correction was then made using DIFABS,[29] when R decreased to 0.097. Anisotropic treatment of the non-hydrogen atoms and full-matrix least-squares methods were used in the final stages of refinement.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/388.

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