ELSEVIER

www.elsevier.nl/locate/ica

Inorganica Chimica Acta 319 (2001) 147–158

Inorganica Chimica Acta

The synthesis of *triangulo*-trimetal complexes containing both iron(II) and vanadium(II)

David J. Evans [b], Peter B. Hitchcock [a], G. Jeffery Leigh [a,*], Brian K. Nicholson [c], Antonio C. Niedwieski [d], Fábio S. Nunes [d], Jaísa F. Soares [d]

[a] *School of Chemistry, Physics and Environmental Science, University of Sussex, Falmer, Brighton BN1 9QJ, UK*
[b] *Department of Biological Chemistry, John Innes Centre, Norwich Research Park, Colney, Norwich NR4 7UH, UK*
[c] *Chemistry Department, University of Waikato, Hamilton, New Zealand*
[d] *Departamento de Química, Universidade Federal do Paraná, Centro Politécnico, 81531-990 Curitiba PR, Brazil*

Received 9 February 2001; accepted 2 April 2001

Abstract

Reactions between a variety of vanadium(II) and iron(II) starting materials in tetrahydrofuran (thf) solution afforded di-, tri-, and tetra-nuclear complexes containing thf or *N,N,N′,N′*-tetramethylethylenediamine (tmen) as ligands. Most products were ionic and contained the two metals in different structural units, cation or anion. Trinuclear clusters formulated as $[V_{3-x}Fe_xCl_5(tmen)_3][BPh_4](x = 0–3)$ were obtained and characterised by C, H, N and metal analyses, ^1H NMR, Mössbauer, and positive ion FAB and electrospray mass spectroscopies, and magnetic moment measurements in solution. We characterised fully by low-temperature single-crystal X-ray diffraction analysis the mixed-metal *triangulo*-complex salt $[V_2Fe(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)_2(tmen)_3][BPh_4]$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structures; Iron(II) complexes; Vanadium(II) complexes; *Triangulo*-trimetal complexes

---

1. Introduction

Iron and either molybdenum or vanadium are present in the putative active sites of the two most common nitrogenases [1,2]. In addition, it is evident that polymetal species are probably involved in the reduction of N_2 by some chemical systems [2]. Despite what is known about nitrogenase active centres and what is surmised about these chemical nitrogen-fixing systems, there are no examples of synthetic pre-formed metal clusters or assemblies that react with dinitrogen. This persuaded us that it would be worthwhile to try to prepare simple mixed-metal cluster complexes, related to some we had already characterized [3] but containing both iron and vanadium, that might, under appropriate conditions, react with dinitrogen.

One complex we intended to use as starting material was $[VCl_2(tmen)_2]$ (tmen = *N,N,N′,N′*-tetramethylethane-1,2-diamine) [4], but we found [5]that it changes spontaneously but reversibly under very mild conditions to a trinuclear complex, $[V_3(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)_2(tmen)_3]^+$ [5]. It seems reasonable to assume that the reaction of a mononuclear compound with a dinuclear material might be involved in its formation. Recent synthetic and mechanistic studies of this reaction support our hypothesis [6a]. A related reaction route might therefore allow us to prepare trinuclear mixed iron–vanadium clusters. We have already shown that the reaction of iron(II) chloride with tmen forms interconvertible complexes *trans*-$[FeCl_2(tmen)_2]$, $[\{FeCl(tmen)\}_2(\mu\text{-}Cl)_2]$, and $[Fe_3(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)_2(tmen)_3]^+$ [6]. We now describe efforts to synthesise mixed trinuclear species $[M_3(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)_2(tmen)_3]^+$ where M may be both iron or vanadium. To achieve this we used a selection of mono- and di-nuclear species of iron and vanadium as starting materials.

---

* Corresponding author. Tel.: +44-1273-606755; fax: +44-1273-67849.

E-mail address: g.j.leigh@sussex.ac.uk (G.J. Leigh).

PII: S0020-1693(01)00450-9

2. Results and discussion

2.1. Reactions involving $[Fe_2(\mu\text{-}Cl)_3(thf)_6][SnCl_5(thf)]$

This material [7] contains a $\{M_2(\mu\text{-}X)_3\}^+$ (X = Cl or Br) core, frequently encountered in first-row transition metal ion chemistry [8]. Its reactions with the V^{II} species are fast, giving a remarkable succession of colours for 15–20 min. It transpires that the products formed are determined by the redox chemistry of the Sn^{IV}/V^{II} pair.

Reactions of the diiron salt in thf at room temperature with $[VCl_2(tmen)_2]$ [4] (proportion 2Fe:1V) or with $[V_2Cl_3(thf)_6][BPh_4]$ [9] (1Fe:1V) produce air-sensitive magenta solutions. This colour is characteristic of vanadium(III)-thf adducts [10]. When concentrated under vacuum and kept at −20°C for 4–6 days, both solutions yielded air-sensitive red crystals and a white powder. Fractional recrystallisation over a period of 3 months gave the following products: paramagnetic pink or purple (**1**) and bright green (**2**) well-formed crystals, a colourless diamagnetic crystalline solid (**3**), and a white powder (**4**). The products were all isolated in very small amounts and frequently as mixtures that were hand-separated.

Materials (**1**) had analyses consistent with the empirical formula $[VCl_3(thf)_3]$, though their colour ranged from pink to purple. Probably they are formed in the oxidation of V^{II} by the Sn^{IV}. It has been noted that $[VCl_3(thf)_3]$ is not reduced by $SnCl_2$ in tetrahydrofuran (thf), though $FeCl_3$ is [7]. Our results imply that the opposite process, reduction of Sn^{IV} by V^{II}, is spontaneous. The order of magnitudes of decreasing reducing power of the various redox couples in thf appears to be $V^{II}/V^{III} > Sn^{II}/Sn^{IV} > Fe^{II}/Fe^{III}$. We were not able to obtain $[Fe_2(\mu\text{-}Cl)_3(thf)_6][BPh_4]$ from the $[SnCl_5(thf)]^-$ salt by metathesis using $Na[BPh_4]$ and so we were not able to carry out reactions that were not complicated by the oxidising effect of Sn^{IV} on V^{II}.

We formulate the bright green product **2** as $[V_2^{II}Cl_3(thf)_6][SnCl_5(thf)]$, consistent with the microanalysis (see Section 4), though this contains a potentially reactive V^{II}/Sn^{IV} couple. Nevertheless, the analysis favours this formulation rather than $[V^{III}Cl_2(thf)_4]$-$[Sn^{IV}Cl_5(thf)]$, which has also been described. Surprisingly, this solid has been stated to be bright-green, an unexpected colour for a V^{III}–thf complex, though it was never characterised structurally [7].

The microanalysis of **3** is consistent with the formulation '$Sn(BPh_4)_2$', but the ^1H NMR spectrum in CD_2Cl_2 (Fig. 1) also reveals a pair of resonances assignable to thf protons. The proportion $[BPh_4]^-$: thf is 1.00:0.75, as judged by spectrum integration. This thf appears to be lattice solvent which is easily lost upon drying, when the crystals become opaque and white. The ^{13}C NMR spectrum, obtained from the same diluted dichloromethane solution used for the ^1H NMR analysis, showed only traces of thf at δ ca. 25 and 67,

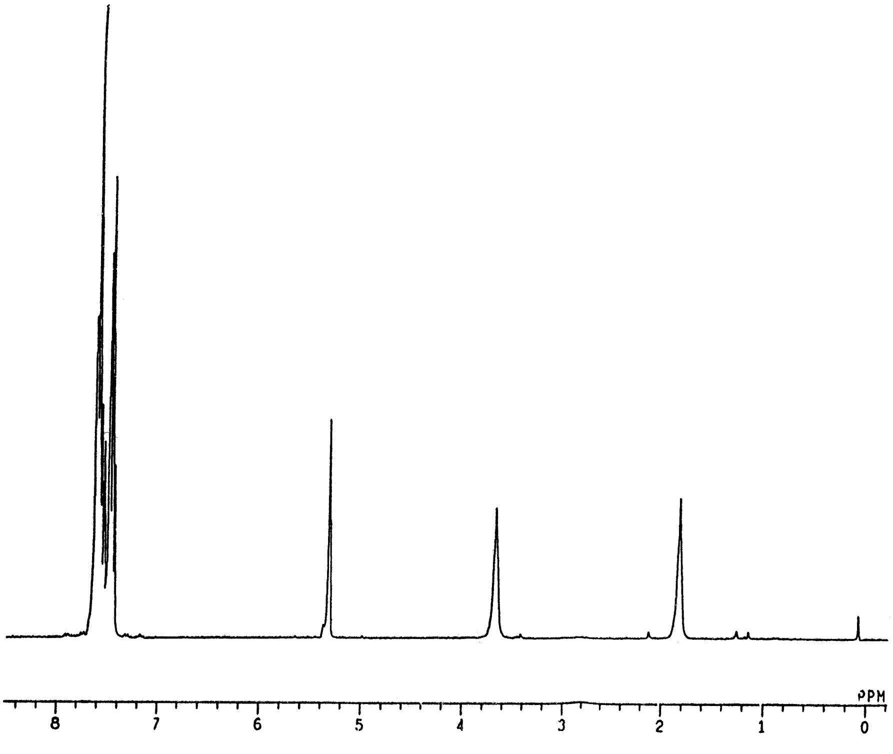

Fig. 1. ^1H NMR spectrum of '$Sn(BPh_4)_2 \cdot x$thf' (**3**) in CD_2Cl_2 (δ-scale, 270 MHz). The spectrum was recorded from −40 to 120 ppm but no signals were found outside the range 0→10 ppm.

Table 1
^{57}Fe Mössbauer parameters for complexes **5**–**7** and for $[Fe_3Cl_5(tmen)_3][BPh_4]$ (recorded at 77 K, referenced against iron foil at 298 K)

Compound	δ [a] (mm s^{-1})	q.s. [a] (mm s^{-1})	Γ [a,b] (mm s^{-1})	% Total area/constraint applied [a,c]
$[V_3Cl_5(tmen)_3]_2[FeCl_4]$ (**5**)	1.03 (1)	2.57 (1)	0.28 (1)	100
$[Fe_3Cl_5(tmen)_3][BPh_4]$ (Ref. [6])	1.14 (1)	2.00 (1)	0.22 (1)	100
$[M_3Cl_5(tmen)_3][BPh_4]$ (**6**, sample 1)	1.12 (1), 1.13 (1), 1.13 (1)	2.58 (7), 2.20 (3), 1.86 (4)	0.17 (4), 0.15 (4), 0.15 (2)	18, 49, 33
$[M_3Cl_5(tmen)_3][BPh_4]$ (**6**, sample 2)	1.12 (1), 1.14 (1), 1.13 (1)	2.43 (1), 2.12 (1), 1.83 (1)	0.13 (1), 0.14 (1), 0.13 (1)	17/1, 54/3, 34/2
$[V_2FeCl_5(tmen)_3][BPh_4]$ (**6**, sample 3)	1.106(3)	2.258(7)	0.190(6)	100
$[FeCl_2(dppe)]$ (Ref. [18] and this work)	0.74 (1)	2.55 (1)	0.17 (1)	100
$[V_3Cl_5(tmen)_3]_2[FeCl_4(dppe)]$ (**7**)	0.89 (1)	2.32 (1)	0.27 (1)	100

[a] Numbers in parenthesis correspond to the experimental error in the last significant figure(s).

[b] Half-width at half maxima.

[c] See text.

together with very intense phenyl carbon resonances in the anion (δ 125–140). No clear evidence was found in either ^{1}H or ^{13}C NMR spectra for π-complex formation between parallel phenyl rings of two $[BPh_4]^-$ anions and the metal(II) cation [11]. Compound **4** was identified as the well known tetranuclear compex $[Fe_4Cl_8(thf)_6]$, formed frequently from thf solutions of iron(II) chloride [12].

The following balanced equation can be written for this reaction.

$$2[V_2Cl_3(thf)_6][BPh_4] + 2[Fe_2Cl_3(thf)_6][SnCl_5(thf)]$$
$$\rightarrow 2[VCl_3(thf)_3] + [V_2Cl_3(thf)_6][SnCl_5(thf)] + \text{‘}Sn(BPh_4)_2\text{’}$$
$$+ [Fe_4Cl_8(thf)_6]$$

Apparently no hoped-for bimetallic Fe/V species was generated in this system.

2.2. Reactions involving $[Fe_4Cl_8(thf)_6]$

Because of the very long Fe···Fe distances in the crystals of this compound, it may dissociate in solution [12b], producing reactive dinuclear intermediates capable of reacting with mononuclear vanadium materials. When a thf suspension of this complex reacted with $[VCl_2(tmen)_2]$ (atomic ratio 1.1 Fe: 1V), a powder (**5**) resembling $[V_3Cl_5(tmen)_3]I^5$ in colour (turquoise), habit, and solubility was formed. A plausible formulation, consistent with the microanalysis, is $[V_3Cl_5(tmen)_3]_2$-$[FeCl_4]$. The $\{Fe^{II}Cl_x(thf)_y\}$ units generated from $[Fe_4Cl_8(thf)_6]$ in solution might have accepted chloride from $[VCl_2(tmen)_2]$, triggering the formation of the trinuclear vanadium core [5].

The large line widths in the solid state ^{57}Fe Mössbauer spectra of **5** (Table 1) suggested that the sample was contaminated with iron-containing impurities, but the isomer shift and quadrupole splitting are typical of high-spin iron(II) and consistent with reported values of $[FeCl_4]^{2-}$ in a number of different salts [13] at 77–80 K (i.s. 1.00–1.06 mm s^{-1}; q.s. 2.62–3.07 mm s^{-1}). The low solubility of the product in organic solvents made its purification difficult.

Six moles of V^{II} complex should interact with one mole of Fe^{II} complex to form (**5**), but the atom proportions used in the reaction were approximately 1:1. Consistent with the presence of an excess of iron(II) in the reaction mixture, $[\{FeCl(tmen)\}_2(\mu\text{-}Cl)_2]$ [6b] was obtained as a by-product. No attempt was made to isolate any $[FeCl_2(tmen)_2]$ [6b] or to determine the yields of the Fe–tmen complexes, but the formation of $[\{FeCl(tmen)\}_2(\mu\text{-}Cl)_2]$ implies that tmen has been lost from the vanadium starting material, as expected if the trinuclear vanadium cation is generated [5]. Again, no bimetallic trinuclear complex appeared to have been formed.

To test whether $[Fe_4Cl_8(thf)_6]$ can generate mononuclear species capable of reacting with dinuclear $[V_2Cl_3(thf)_6][BPh_4]$, the two complexes were allowed to react in refluxing thf (1Fe:1V atom ratio) in the presence of tmen. Upon the addition of the amine, the boiling solution changed from light to deep green. Filtration, concentration under vacuum and cooling to −20°C for 5 days did not afford any solid, suggesting that $[MCl_2(tmen)_2]$ ($M = V^{II}$ or Fe^{II}) and $[\{FeCl(tmen)\}_2(\mu\text{-}Cl)_2]$, which normally crystallise under these conditions, were probably not formed. Long deep-green needles (**6**) (sample 1) were obtained after slow diffusion of hexane into the thf solution at room temperature. The product contained Fe and V, in the atomic proportion 1.5:1 (V:Fe), but C, H, N analysis was consistent with the rather less precise formulation $[V_{3-x}Fe_xCl_5(tmen)_3][BPh_4]$, $x = 0$–3 (see Section 4). The analytical data and our previous results [5,6] with single-metal systems are consistent with the conclusion that trinuclear cations had been formed, but possibly in a mixture containing all combinations of the two metals within the defined stoichiometry.

2.3. Reactions involving $[\{FeCl(tmen)\}_2(\mu\text{-}Cl)_2]$

When solutions of this complex and of $[VCl_2(tmen)_2]$ in thf (Fe/V atomic ratio 1:1) were mixed at room temperature, no reaction was observed even after stirring for 20–24 h. However, the addition of a solution of $Na[BPh_4]$ in thf (Fe/V metal:tetraphenylborate 3:1) caused an immediate change from blue to grass-green. A very fine suspension of a white powder (probably NaCl) was filtered off, leaving a clear green solution. Layering with a small amount of hexane afforded large deep green prisms which were again formulated as $[V_{3-x}Fe_xCl_5(tmen)_3][BPh_4]$ ($x = 0–3$) (**6**, sample 2), based on C, H, N and metal analyses.

This preparation was perfectly reproducible. Slightly different crystallisation conditions (solvent proportions and solution concentration) produced distinct crystal shapes (thick plates, needles or long prisms), but the habit of all crystals in a given batch was normally the same. Sometimes the crystals contained thf. The batches all had similar compositions, as shown by the data reported in Section 4. Crystals of **6** suitable for a good X-ray analysis (sample 3) were finally isolated after a new preparation from $[\{FeCl(tmen)\}_2(\mu\text{-}Cl)_2]$, $[VCl_2(tmen)_2]$ and $Na[BPh_4]$ in thf (Fe:V atomic ratio 1.6:1; Fe + V:$[BPh_4]^-$ 3:1) at room temperature. The crystals again contained both Fe and V. Our problem was to demonstrate whether these materials **6** contained distinct cocrystallised tri-iron and trivanadium species, or whether they were the sought-after mixed-metal trinuclear species.

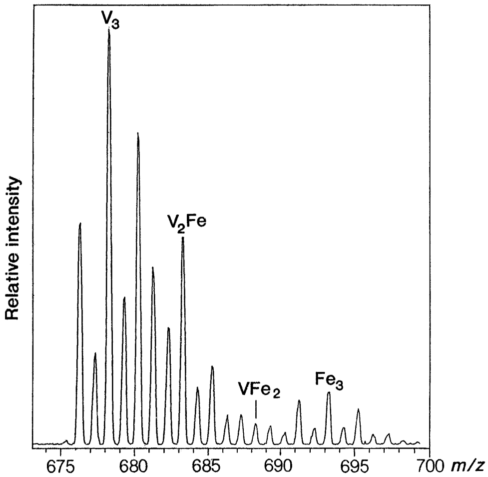

Fig. 2. The parent cation region of the ESMS of **6**. The peaks correspond to a mixture of all species $[V_{3-x}Fe_xCl_5(tmen)_3]^+$, $x = 0–3$. Analysis is complicated by overlapping isotope patterns, but the peaks at *m/z* 678, 683, 688 and 693 are characteristic of the V_3, V_2Fe, VFe_2 and Fe_3 combinations, respectively.

2.4. Physical studies of the *triangulo*-trimetal species

2.4.1. Mass spectroscopy

Electrospray mass spectrometry (ESMS) is a mild technique ideally suited for characterising ions in solution. When a solution of **6**, sample 2, in 1,2-$C_2H_4Cl_2$ was injected, a clean spectrum was obtained which showed no significant signals other than a complicated envelope of peaks between *m/z* 675 and 695, Fig. 2. These arise from the isotopomers associated with all of the species $[V_{3-x}Fe_xCl_5(tmen)_3]^+$, $x = 0–3$, showing that the sample contains mixed-metal cores, and is not simply a mixture of the V_3 and Fe_3 materials. ESMS cannot be used as a quantitative technique under these conditions, and the relative intensities of peaks in the pattern were not completely reproducible. The signal strengths also consistently varied with time during a single injection, with the V-rich species being more dominant in the early part of the acquisition and the Fe-rich ones later, for reasons that are not apparent. However, it is clear that all mixed species are present in **6**, sample 2, in solution.

When the experiment was repeated using MeCN as solvent and mobile phase, spectra were less clean with many peaks at lower masses suggesting fragmentation of the M_3 aggregates, but the mixed V/Fe parent ions were still detectable. If the mass spectrometer was not thoroughly flushed, then peaks assignable to $[M_3Cl_{5-n}(OH)_n(tmen)_3]^+$ or to $[M_3Cl_{5-n}(OEt)_n(tmen)_3]^+$ were found, indicating reactivity with H_2O or EtOH, respectively, lingering in the tubing. The V-rich species dominated this type of process, suggesting either that they undergo Cl^-/OR^- exchange more readily, or that the OR^- adducts are less stable for the Fe-rich aggregates. In fact, related *triangulo*-alkoxotrivanadium species have been structurally characterized [5b], but none of their iron analogues is known.

In the FAB mass spectra of **6**, samples 1 and 2, the 'molecular' ion for $[V_3Cl_5(tmen)_3]^+$ (*m/z* 678) was always present. We also always observed a peak at *m/z* 553, which we have accounted for previously [6b] by a reaction between the 'all-iron' trinuclear cation and the alcohol matrix (3-nitrobenzylalcohol) used for sample preparation. This fragment, possibly $\{(Htmen)_2[BPh_4]\}^+$, was also observed when the all-iron cation was submitted to FAB-MS analysis, but never arose from the all-vanadium cation. The *m/z* 678 and 553 fragments were also observed when a ground single prismatic crystal of **6**, sample 2, was submitted for MS-FAB analysis, and this supports the hypothesis of co-crystallisation. No evidence was found in the FAB^+ spectra for mixed-metal cations with the $\{V_2Fe\}$ and $\{VFe_2\}$ cores.

The FAB-MS is a much harsher technique and the ablation process may be inducing selective reaction of the Fe-containing species with the matrix (c.f. the re-

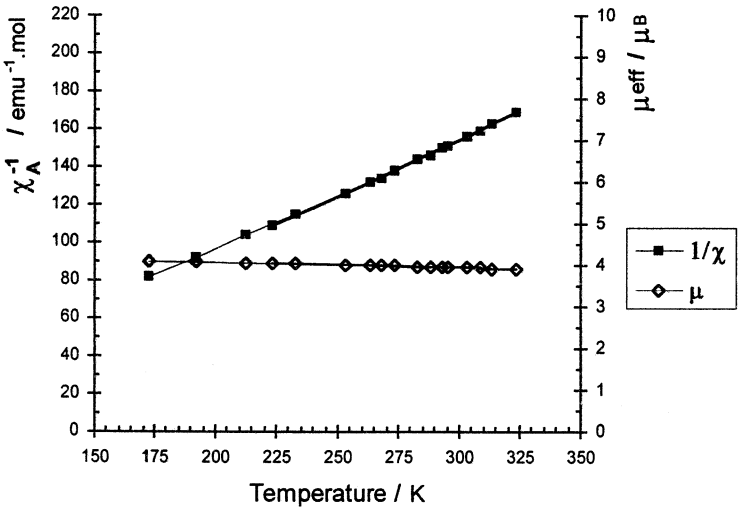

Fig. 3. Plot of the reciprocal of the atomic magnetic susceptibility (χ_A^{-1}) and effective magnetic moment (μ_{eff}) versus absolute temperature (T) for $[M_3Cl_5(tmen)_3][BPh_4]$ ($M = V^{II}$ and Fe^{II}) (**6**) sample 2. Diamagnetic correction: 1.985×10^{-4} emu atom^{-1} M^{II}. The observed changes were reversible with the increase or decrease in temperature.

sults discussed in the previous paragraphs). Another possibility is that composition varies with phase, since ESMS samples are from solution whereas FAB-MS samples are from the solid, but the ESMS results are more consistent with the Mössbauer and X-ray crystallography results which both involve the solid state.

2.4.2. Mössbauer spectroscopy

The Mössbauer parameters obtained from spectra of samples 1, 2 and 3 of **6** at 77 K are shown in Table 1.

The Mössbauer spectrum of of **6**, samples 1 and 2, (Table 1) were convincingly deconvoluted as three quadrupole doublets, which we assign to $\{Fe_3\}$, $\{Fe_2V\}$ and $\{FeV_2\}$ aggregates. The isomer shifts are all very similar to the value obtained for $[Fe_3Cl_5(tmen)_3][BPh_4]$, indicating high-spin iron(II) nuclei in trimetallic cations [6b]. The areas of the three Mössbauer doublets quoted in Table 1 are in the proportions 1:3:2, with no constraints applied to the analysis. Because the probable components of the products differ only in the V/Fe ratio, these areas reflect the number of iron nuclei in the different complexes. The complexes $[Fe_3Cl_5(tmen)_3][BPh_4]$ and $[V_3Cl_5(tmen)_3][BPh_4]$ are isostructural and have remarkably similar dimensions [5,6], and should cocrystallise with few packing problems. Similar trinuclear cations such as $[V_3Cl_3(OMe)_2(tmen)_3]^+$ and $[V_3Cl_4(OMe)(tmen)_3]^+$ also cocrystallise [5].

Complex **6**, sample 3, has similar Mössbauer parameters to those of samples 1 and 2. However, only a single species seemed to be present, giving rise to a single quadrupole doublet. Thus sample 3 was the most likely to contain a single mixed-metal species. Microanalysis implied the presence of the trinuclear cation and tetraphenylborate, but also of protonated tmen (see below). Clearly the three samples are similar but not of exactly the same composition. They are all likely to contain more or less mixed-metal cations.

For our preferred curve fitting, (i) the relative intensities of the signals in the non-constrained spectrum (sample 1) are compatible with the areas in the constrained spectrum of sample 2; (ii) the baseline deviations from zero are small and random in all cases; and (iii) the final χ^2 value, which reflects the overall quality of the fitting model, was equally low for both the constrained and the non-constrained models. The fits are only consistent with the hypothesis that **6**, samples 1, 2, and 3, are crystallographic mixtures of Fe^{II}-containing trinuclear cations differing only in the relative amounts of iron they contain, and that in sample 3 one such species, not the tri-iron species, is clearly predominant.

2.4.3. NMR spectroscopy

The product **6**, sample 2, and the homonuclear clusters $[V_3Cl_5(tmen)_3][BPh_4]$ and $[Fe_3Cl_5(tmen)_3][BPh_4]$ are not diamagnetic and therefore they do not produce well-resolved ^1H NMR spectra. However, each spectrum is characteristic and can be used to distinguish the complexes in solution. When crystals of the homonuclear iron and vanadium clusters were mixed, the ^1H NMR spectrum of their solution in $[^2H_8]$-thf was remarkably similar to that obtained from **6**. This also supports the hypothesis that **6** is a crystalline mixture of trinuclear species.

2.4.4. Magnetic properties

The magnetic behaviour of the product **6**, sample 2 was analysed in $[^2H_8]$-thf solution by the Evans method [14] in the temperature range + 50 to − 100°C (323–

173 K) (Fig. 3). In order to simplify the analysis of the data, it was assumed that the sample used was an equimolar mixture of [Fe_3Cl_5(tmen)$_3$][BPh_4] and [V_3Cl_5(tmen)$_3$][BPh_4].

The tris(vanadium(II)) complex is known to be *antiferromagnetic* [5] and the tris(iron(II)) analogue *ferromagnetic* [6b]. In the all-vanadium complex, the effective magnetic moment per metal ion at 20–25°C is lower than the 'spin-only' value of $3.87\mu_B$ and decreases with decrease of temperature [5]. For the trinuclear iron compound, the effective magnetic moment is compatible with the 'spin-only' value of $4.90\mu_B$ per metal atom at 20–25°C and *increases* with the decrease of the temperature. If we assume that no intermolecular interaction occurs in solution, and that the magnetic field generated by the complexes in the mixture has the same nature and intensity as those produced in the pure samples, an 'average molecule' of [M_3Cl_5(tmen)$_3$][BPh_4] would then be expected to show a magnetic moment intermediate between the two extremes. This seems to be the behaviour shown in Fig. 3.

The measured μ_{eff} per metal atom is $3.95\mu_B$ at 22°C, slightly higher than the 'spin-only' value for three unpaired electrons per metal ion (as expected for an 'average' species) and it increases slowly as the temperature was lowered. Neither the very low μ_{eff} characteristic of the 'all-vanadium' trinuclear complexes [5] nor the high values given by the $\{Fe_3Cl_5\}^+$ core [6b] were obtained, nor a temperature-dependence characteristic of either. The experimental evidence is consistent with the hypothesis of a mixture and possibly of heterometal clusters.

*2.5. The X-ray diffraction analysis of [M_3Cl_5(tmen)$_3$][BPh_4] ($M = Fe^{II}$ and/or V^{II}) (**6**)*

A single crystal analysis of **6**, sample 2, carried out at room temperature, revealed a highly disordered structure. Although the presence of *triangulo*-trinuclear cations was evident the structure could not be refined satisfactorily and, of course, there was no possibility of distinguishing between iron and vanadium in the three equivalent sites.

Single crystal X-ray diffraction analysis at 173 K of **6**, sample 3, confirmed that the unit cell contained co-crystallised [V_2FeCl_5(tmen)$_3$]$^+$ and [Htmen···thf]$^+$ as tetraphenylborate salts (Fig. 4). This formulation agrees well with the microanalytical data (see Section 4). The presence of two V^{II} and one Fe^{II} centres disordered equally over the metal positions in the cation was strongly indicated by the final occupancy factors calculated for these sites during structure refinement. The best molecular model to agree with the experimental structure factors was clearly consistent with each metal site having an occupancy factor of 2/3 for vanadium and 1/3 for iron. No alternative model, such as the ones provided by the $\{V_3\}$, $\{VFe_2\}$ or $\{Fe_3\}$ combinations, was as satisfactory. This result, together with the overall quality of the X-ray data and final refinement parameters presented in Table 2 points to a confident structural characterisation of the mixed-metal species [V_2FeCl_5(tmen)$_3$]$^+$.

The cation contains the normal $\{M_3Cl_3\}$ planar six-membered ring found in other trinuclear complexes [5,6,15,16], capped by two chlorine atoms so that each metal atom has approximately octahedral coordination, completed by the nitrogen atoms of a chelating tmen.

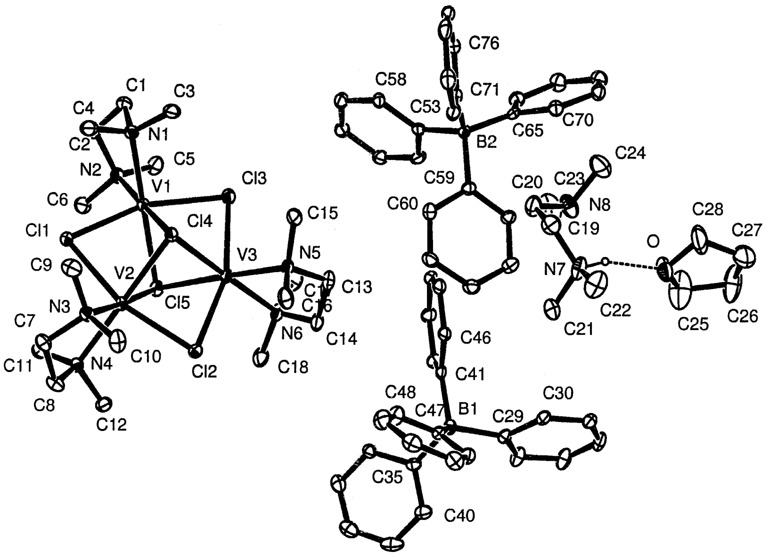

Fig. 4. ORTEP plot of the unit cell contents in [V_2FeCl_5(tmen)$_3$][Htmen···thf][BPh_4]$_2$ (complex **6**, sample 3). The metal sites in the *triangulo*-complex are labelled V(1), V(2) and V(3), corresponding to the major site occupancy, but they actually contain two V^{II} and one Fe^{II} centres disordered equally over the three positions (see text). Occupancies are $2/3V + 1/3Fe$.

Table 2
Crystal data and structure refinement for $[V_2FeCl_5(tmen)_3]$-$[Htmen{\cdots}thf][BPh_4]_2$

Empirical formula	$C_{76}H_{113}B_2Cl_5FeN_8OV_2$
Formula weight	1527.34
Temperature of data collection (K)	173(2)
Wavelength (Mo Kα) (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$ (no. 14)
Unit cell dimensions	
a (Å)	18.0273(4)
b (Å)	13.8745(2)
c (Å)	32.5746(5)
β (°)	94.277(5)
V (Å^3)	8124.9(2)
Z	4
Absorption coefficient (mm^{-1})	0.61
θ Range for data collection (°)	3.70–21.95
Reflections collected	39516
Independent reflections	9837 [$R_{int} = 0.062$]
Reflections with $I > 2\sigma(I)$	8127
Completeness to $\theta = 21.95°$ (%)	99.4
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.068$, $wR_2 = 0.147$
R indices (all data)	$R_1 = 0.084$, $wR_2 = 0.153$

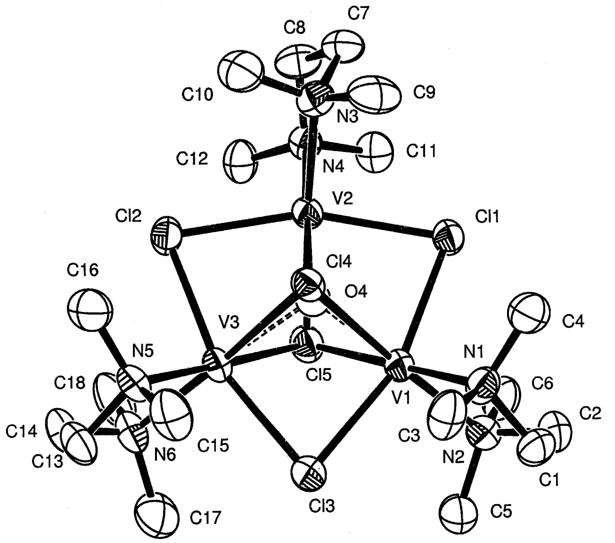

Fig. 5. View of the trinuclear cation in $[V_2FeCl_5(tmen)_3]$-$[Htmen{\cdots}thf][BPh_4]_2$ (product **6**, sample 3), showing the *triangulo* arrangement of the metal sites and the alternative capping groups. Occupancies are: 0.91 Cl(4) and 0.09 OH.

Chlorine atoms Cl(4) and Cl(5) are removed by − 1.762(3) and 1.795(2) Å, respectively, from the least-squares plane defined by the metal atoms. There is some replacement (9%) of Cl(4) by an OH (Fig. 5). In the $[Htmen{\cdots}thf]^+$ moiety, the protonated amine is hydrogen-bonded to the oxygen atom of thf (N(7)···O distance 2.678 Å). Selected bond lengths and angles are shown in Table 3. Table 4 compares the principal mean dimensions with the corresponding values for $[V_3Cl_5(tmen)_3]^+$ and $[Fe_3Cl_5(tmen)_3]^+$ [5,6]. The average bond lengths and angles in **6** are not very different from the dimensions of the two homonuclear cations.

2.6. Other preparative studies

2.6.1. Reactions involving $[FeCl_2(dppe)]$

An X-ray crystallographic distinction between iron and vanadium in a trinuclear cluster might be easier were they bound to different ligands. This approach has been used by others to help distinguish the different metal sites in the crystal structure of the trinuclear $[CpMn(FeCp')_2(\mu\text{-}CO)_2(\mu\text{-}NO)]$ ($Cp = C_5H_5$ and $Cp' = C_5H_4CH_3$) [17].

The complex $[FeCl_2(dppe)]$ ($dppe = Ph_2PCH_2CH_2PPh_2$) [18] was described as tetrahedral [19] by analogy with the structurally characterised $[FeCl_2(dippe)]$ [20] and $[Fe(CH_2Ph)_2(dippe)]$ [21] ($dippe = Pr^i_2PCH_2CH_2PPr^i_2$). We have now shown that $[FeCl_2(dppe)]$ can be obtained pure and in high yield (> 80%) from a fast reaction between $FeCl_2$ and dppe in boiling thf (see Section 4).

When white $[FeCl_2(dppe)]$ was allowed to react with an equimolar amount of the light blue $[VCl_2(tmen)_2]$ in thf, a familiar change to turquoise was observed in the reaction mixture, and a turquoise powder (**7**) was isolated. This colour is characteristic of $[V_3Cl_5(tmen)_3]^+$ [5]. The product was insoluble in ethers and only slightly soluble in dichloromethane, and could not be recrystallised. All this, and the microanalysis, suggested

Table 3
Selected bond lengths (Å) and bond angles (°) for $[V_2FeCl_5(tmen)_3]$-$[Htmen{\cdots}thf][BPh_4]_2$ (**6**, sample 3)

Bonding and non-bonding distances about the metal centres			
V(1)···V(2)	3.1771(14)	V(1)···V(3)	3.1578(13)
V(2)···V(3)	3.1586(14)		
V(1)–N(1)	2.212(5)	V(1)–N(2)	2.224(5)
V(1)–Cl(3)	2.4772(19)	V(1)–Cl(1)	2.4816(18)
V(1)–Cl(4)	2.553(3)	V(1)–Cl(5)	2.5621(19)
V(2)–N(3)	2.190(5)	V(2)–N(4)	2.200(5)
V(2)–Cl(1)	2.4938(19)	V(2)–Cl(2)	2.4942(19)
V(2)–Cl(4)	2.536(2)	V(2)–Cl(5)	2.5760(19)
V(3)–N(5)	2.199(5)	V(3)–N(6)	2.210(5)
V(3)–Cl(3)	2.500(2)	V(3)–Cl(2)	2.5016(19)
V(3)–Cl(4)	2.525(2)	V(3)–Cl(5)	2.5459(18)
Angles about the metal centres			
V(1)···V(2)···V(3)	59.79(3)	V(1)···V(3)···V(2)	60.40(3)
N(1)–V(1)–N(2)	83.74(19)	Cl(3)–V(1)–Cl(1)	161.20(7)
N(1)–V(1)–Cl(1)	97.24(14)	N(2)–V(1)–Cl(1)	95.40(14)
N(1)–V(1)–Cl(3)	97.06(14)	N(2)–V(1)–Cl(3)	98.24(14)
N(3)–V(2)–N(4)	82.93(18)	Cl(2)–V(2)–Cl(1)	160.7(17)
N(3)–V(2)–Cl(1)	94.62(15)	N(4)–V(2)–Cl(1)	97.82(14)
N(3)–V(2)–Cl(2)	100.50(15)	N(4)–V(2)–Cl(2)	95.88(14)
N(5)–V(3)–N(6)	83.23(19)	Cl(2)–V(3)–Cl(3)	161.33(7)
N(5)–V(3)–Cl(2)	95.95(15)	N(6)–V(3)–Cl(2)	95.39(16)
N(5)–V(3)–Cl(3)	98.34(15)	N(6)–V(3)–Cl(3)	98.16(16)

Standard deviations in parentheses.

Table 4
Principal mean dimensions in trinuclear cations

Mean dimensions	Complex		
	$[V_3Cl_5(tmen)_3]^+$ (Ref. [5])	$[Fe_3Cl_5(tmen)_3]^+$ (Ref. [6b])	$[V_2FeCl_5(tmen)_3]^+$ (**6**, sample 3)
$M–Cl_{equatorial}$ (Å)	2.500(4)	2.490(8)	2.491(9)
$M–Cl_{capping}$ (Å)	2.519(6)	2.566(12)	2.550(17)
M···M (Å)	3.142(7)	3.235(8)	3.164(9)
M–N (Å)	2.214(2)	2.194(5)	2.206(11)
$Cl_{equatorial}–M–Cl_{equatorial}$ (°)	162.1(2)	158.9(2)	161.1(3)
$M–Cl_{equatorial}–M$ (°)	77.8(1)	81.0(4)	78.8(4)
$Cl_{capping}–M–Cl_{capping}$ (°)	87.9(1)	86.5(3)	88.4(4)
N–M–N (°)	82.8(3)	83.9(5)	83.3(3)

that a cluster similar to $[V_3Cl_5(tmen)_3]^+$ [5] had been formed. The FAB-MS spectrum (*m*/*z* 678) confirmed the presence of $[V_3Cl_5(tmen)_3]^+$ in the solid. The Mössbauer spectrum (Table 1) was consistent with the presence of a high-spin iron(II) species as in $[FeCl_2(dppe)]$ [18,19], but the larger isomer shift implies a higher coordination number. The impure product 7 did not appear to contain the required mixed-metal cluster.

Finally, the reaction between $[V_2Cl_3(thf)_6][AlCl_2Et_2]^9$ and $[FeCl_2(dppe)]$ (V^{II}:Fe^{II} 1:2) in the presence of tmen and $Na[BPh_4]$ (V/Fe metal:amine:$[BPh_4]^-$ proportion 3:3:1) was expected to yield a product such as $[\{Fe(dppe)\}_2\{V(tmen)\}Cl_5][BPh_4]$. However, the amine displaced the phosphine from the iron, and pure dppe was isolated from the reaction mixture. The metal-containing green semi-crystalline product, isolated in small amount, produced a FAB-MS spectrum very similar to that of **6**, implying the formation of $\{Fe_3\}$- and $\{V_3\}$-*triangulo* complexes, and similar mixed-metal cores.

3. Conclusions

The difficulties of complete characterisation of the mixed-metal complexes suggest that a more reliable entry into the chemistry of these heterobimetallic species needs to be found. However, our data leave little doubt that mixed-metal trinuclear clusters *triangulo*-$[M_3Cl_5(L\text{-}\kappa^2)_3]^+$ (M = both Fe and V) have been prepared, and the material with two vanadiums and one iron has been well characterised. Tmen seems to be a good ligand for vanadium, although it is not electron-rich and it frequently gives rise to crystallographic disorder at room temperature. In spite of that, its role as a leaving molecule during the assembly of the tris-V^{II} and tris-Fe^{II} cations is clearly important [5,6]. Alternative neutral ligands have not yet been identified. As for V-starting materials other than $[VCl_2(tmen)_2]$ and $[V_2Cl_3(thf)_6]^+$, we have yet to explore possibilities such as $[V(MeOH)_6]Cl_2$ [22] and other V^{II}-complexes with alcohols. Complexes such as '$VCl_2(EtOH)_2$' [23] may be even more useful because the many complexes 'VCl_2L_2' may really be trinuclear [5,6].

These complexes were investigated principally to model the active-site cluster of vanadium nitrogenases, though they have so far exhibited no dinitrogen chemistry. ESMS data support the presence of the mixed-metal complexes in **6** and the crystallography is best interpreted in such terms. However, these preparative pathways cannot be used reliably to obtain pure hetero-bimetallic products. They are clearly mixed Fe/V species. To the best of our knowledge, the materials described here are the only examples of clusters containing both iron and vanadium in the same structural unit, apart from some vanadium–iron–sulfur clusters. However, vanadium–oxygen clusters have been reported to show a singular and unexpected dinitrogen chemistry [24]. The preparation of iron–vanadium clusters with similar dinitrogen chemistry remains one of our principal objectives.

4. Experimental

All operations were carried out under an inert atmosphere in a dinitrogen-filled drybox (Faircrest Engineering, Croydon) or with standard Schlenk techniques. Solvents were dried by standard procedures [25] and distilled under N_2 prior to use.

The commercial products diethylaluminium ethoxide (25% solution in toluene), 1,2-bis(diphenylphosphino)ethane (dppe), iron(II) chloride, iron(III) chloride, sodium tetraphenylborate, tin(II) chloride and vanadium(III) chloride (Aldrich) were used without further purification. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine was refluxed over molten sodium for ca. 1 h and then distilled under N_2. $[VCl_3(thf)_3]$ [10a], *trans*-$[VCl_2(tmen)_2]$ [4], $[Fe_2Cl_3(thf)_6][SnCl_5(thf)]$ [7] and $[V_2Cl_3(thf)_6][BPh_4]$ [9] were prepared by published methods. $[Fe_4Cl_8(thf)_6]$ [12] was obtained as a by-product during the preparation of $[Fe_2Cl_3(thf)_6]$-$[SnCl_5(thf)]$, as described below. $[\{FeCl(tmen)\}_2((\text{-}Cl)_2]$

was prepared from an equimolar mixture of anhydrous $FeCl_2$ and tmen in refluxing thf [6b].

Microanalyses were performed by Mr Colin McDonald (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. Vanadium, iron and tin analyses were performed by Southern Science (Sussex Laboratory), by ICP-OES.

NMR solvents, supplied by Goss Scientific Instruments, were dried over molecular sieve before use and kept under dinitrogen in Schlenk tubes equipped with grease-free taps. NMR spectra were obtained in the appropriated deuterated solvents using JEOL GSX-270 equipment. The operating frequencies for the observation of ^1H and ^{13}C were 270.2 and 67.9 MHz, respectively. Tetramethylsilane was used as reference. IR data were recorded on a Perkin Elmer 883 instrument, from Nujol mulls prepared under dinitrogen and spread on KBr plates.

Electrospray mass spectra were recorded on VG Platform II mass spectrometer. The most suitable mobile phase was found to be 1,2-$C_2H_4Cl_2$. The lines of the instrument were first flushed with dry ethanol, and then overnight with carefully dried 1,2-$C_2H_4Cl_2$ which was stored under Ar. Samples, made up under Ar in the same solvent, were injected via a Rheodyne valve with a 10^{-6} dm^{-3} sample loop. The nebuliser tip was at 3500 V and 60°C, with dinitrogen used as a drying and nebulising gas. The skimmer cones were maintained at 20 V to minimise fragmentation. Spectra were assigned from m/z values and isotope distribution patterns that were simulated using the ISOTOPE program [26].

FAB mass spectra were recorded by Dr A. Abdul Sada (School of Chemistry, Physics and Environmental Sciences, University of Sussex), on a VG Autospec spectrometer (Fisons Instruments), equipped with a CsI gun at 25 kV (SIMS technique) or on a Kratos MS80RF machine with xenon at 8 kV (FAB technique). In both cases, 3-nitrobenzyl alcohol was used as the matrix.

Mössbauer data were recorded at 77 K by Mrs. J. Elaine Barclay, using an ES-Technology MS105 spectrometer with a 25 mCi ^{57}Co source in a rhodium matrix. Spectra were referenced against iron foil at 298 K. Samples were pure solids or mixtures with boron nitride (ca. 50% w/w), ground to fine powders and then transferred to the aluminium sample holders in the glove box. The program used for spectra fitting and parameter calculation was ATMOSFIT 4, written by Dr Ian Morrison (University of Essex).

Magnetic moment and magnetic susceptibility measurements were carried out in solution by variable-temperature NMR spectroscopy using the Evans method [14]. Corrections for the diamagnetism of the ligands were applied by the use of Pascal constants [27]. No solid-state magnetochemistry measurements were made.

4.1. Preparation of [$Fe_2Cl_3(thf)_6$][$SnCl_5(thf)$] and [$Fe_4Cl_8(thf)_6$]

Anhydrous $SnCl_2$ (4.1 g, 21.6 mmol) was added to a yellow solution of $FeCl_3$ (7.0 g, 43.2 mmol) in 200 cm^3 of thf. The mixture was stirred for 4h, filtered through Celite and allowed to stand at room temperature for 3 days. Colourless crystals of [$Fe_4Cl_8(thf)_6$] were then filtered off, washed with thf (60 cm^3) and dried for 2 h. Yield: 3.3 g. The pale yellow filtrate was cooled to −20°C for 2 d to produce small light yellow needles of [$Fe_2Cl_3(thf)_6$][$SnCl_5(thf)$]. These were washed with 50 cm^3 of cold thf (−20°C) and dried for 2 h under vacuum. Yield: 4.6 g. Total yield, based on iron content: 53%. *Anal.* Found for [$Fe_4Cl_8(thf)_6$]: C, 30.6; H, 5.30; N, 0.0. $C_{24}H_{48}Cl_8Fe_4O_6$ requires: C, 30.7; H, 5.16; N, 0.0%. *Anal.* Found for [$Fe_2Cl_3(thf)_6$][$SnCl_5(thf)$]: C, 32.6; H, 5.65; N, 0.0. $C_{28}H_{56}Cl_8Fe_2O_7Sn$ requires: C, 33.0; H, 5.55; N, 0.0%.

4.2. Preparation of [$FeCl_2(dppe)$]

Anhydrous $FeCl_2$ (1.0 g, 7.9 mmol) and dppe (3.3 g, 8.3 mmol) were suspended in thf (70 cm^3) and heated under reflux. After ca. 15 min, the light pink suspension changed to a clear light yellow solution and after 35 min to a very heavy white suspension. The mixture was heated a further 2 h and was filtered hot, giving a greenish–white powder and a light yellow filtrate. The solid was then washed with thf (40 cm^3) and thf/hexane (1:3, 45 cm^3) and dried under vacuum. A second crop of the product was recovered by filtration from the mother liquor after 3 days at room temperature. Yield: 3.5 g (83%). *Anal.* Found: C, 59.3; H, 4.60; N, 0.0. $C_{26}H_{24}Cl_2FeP_2$ requires: C, 59.5; H, 4.60; N, 0.0%. Mössbauer parameters are presented in Table 1.

4.3. Reaction between [$Fe_2Cl_3(thf)_6$][$SnCl_5(thf)$] and [$V_2Cl_3(thf)_6$][BPh_4]

The V^{II}-starting material (1.1 g, 1.1 mmol) was completely dissolved in thf (20 cm^3) and the bright green solution added slowly to a light yellow suspension of the Fe^{II}-starting material (1.1 g, 1.1 mmol) in thf (30 cm^3). The colour changed to lemon yellow, light brown, reddish brown and finally to magenta in ca. 15 min. The mixture was stirred for 1.5 h, concentrated to ca. 30 cm^3 under vacuum, filtered and stored at −20°C. Four days later, 0.1 g of a pink crystalline material (**1**, sample 1) was filtered off, washed with cold thf (3 cm^3) and dried for 30 min. The filtrate was further concentrated to ca. 20 cm^3, left at room temperature for 4 more days and filtered to give 0.1 g of a white powder

(**4**) which was washed with thf (5 × 2 cm^3) and dried. The filtrate (plus washings) was layered with hexane (35 cm^3) and was allowed to stand at room temperature for two weeks. When it was filtered, a mixture (less than 0.1 g) of bright green needles (**2**) and plum-coloured short prisms (**1**, sample 2) was isolated. The magenta filtrate was cooled to −20°C for 3 months; another mixture (less than 0.1 g) of colourless (**3**) and deep purple (**1**, sample 3) thick plates was then filtered off and washed with cold thf (10 cm^3, 0°C). The colourless crystals turned white upon drying and the orange filtrate was discarded. *Anal.* Found (%) for **1**, sample 1: C, 38.3; H, 6.70; for **1**, sample 2: C, 38.4; H: 6.65; for **1**, sample 3: C, 38.3; H, 6.75. $[VCl_3(thf)_3]$ requires: C, 38.6; H, 6.50%. *Anal.* Found for **2** (%): C, 32.5; H, 5.60. $[V(II)_2Cl_3(thf)_6][SnCl_5(thf)]$ requires: C, 33.3; H, 5.60%. *Anal.* Found for **3** (%): C, 76.9; H, 5.35. $Sn(BPh_4)_2$ requires: C, 76.1; H, 5.30%. $Sn(BPh_4)_2 \times thf$ requires: C, 75.2; H, 5.80%. *Anal.* Found for **4** (%): C, 29.1; H, 5.20; N, 0.0; Fe, 23.8; Sn, 0.0; V, 0.5. $[Fe_4Cl_8(thf)_6]$ requires: C, 30.7; H, 5.15; N. 0.0; Fe, 23.7; Sn, 0.0; V, 0.0%.

4.4. Reaction between $[Fe_4Cl_8(thf)_6]$ and $[VCl_2(tmen)_2]$

Tetrahydrofuran (160 cm^3) was added to the mixture of $[Fe_4Cl_8(thf)_6]$ (2.4 g, 2.6 mmol) and $[VCl_2(tmen)_2]$ (3.3 g, 9.2 mmol), producing a suspension which was stirred for ca. 20 h at room temperature. A large amount of a turquoise powder (**5**) was formed, which was insoluble in the mother liquor even after heating for 3 h under reflux. The mixture was filtered hot; the powder was washed with thf (60 cm^3) and dried for 2 h under vacuum. Yield: 2.0 g, 46% based on the total metal content. From the filtrate, concentrated to ca. 90 cm^3 and kept at −20°C for 5 days, ca. 0.1 g of $[\{FeCl(tmen)\}_2(m\text{-}Cl)_2]$ was isolated. *Anal.* Found for 5 (%): C, 27.4; H, 6.30; N, 10.0. $[V_3Cl_5(tmen)_3]_2[FeCl_4]$ ($C_{36}H_{96}Cl_{14}FeN_{12}V_6$) requires: C, 27.8; H, 6.25; N, 10.8%.

4.5. Reaction between $[Fe_4Cl_8(thf)_6]$, $[V_2Cl_3(thf)_6](BPh_4)$ and tmen

A mixture of $[V_2Cl_3(thf)_6](BPh_4)$ (1.5 g, 1.5 mmol) and $[Fe_4Cl_8(thf)_6]$ (0.7 g, 0.75 mmol) in thf (120 cm^3) was stirred for 1 h at room temperature and under reflux for 2 h when everything dissolved. Then tmen (3 cm^3, 2.3 g, 19.9 mmol) was added, producing a deep green solution which was kept under reflux for further 30 min and then filtered. A small amount of a fine black powder was discarded. The filtrate was concentrated under vacuum to ca. 25 cm^3, layered with hexane (20 cm^3) and left at room temperature for 3 days. Shiny deep green needles (**6**, sample 1) were filtered off, washed with thf/hexane (1:2, 100 cm^3) and dried. Yield: 0.6 g (30%). Found for **6**, sample 1(%): C, 50.0; H, 6.90; N, 8.15; Fe, 5.95; V: 9.0%; ratio V/Fe 1.5. The calculated values are presented below with the data for **6**, sample 2. IR (cm^{-1}, Nujol mull): 1770 (w); 1824 (w); 1880 (w); 1958 (w); 1580 (m); n(B-aryl) at 1426 (s); n(C–N) at 1002 (m) and 1018 (s); d(C–H aromatic, out-of-plane) at 708 (s), 734 (s) and 748 (s); n(M–N) at 442 (m), 470 (m) and 498 (m).

4.6. Reaction between $[\{FeCl(tmen)\}_2(\mu\text{-}Cl)_2]$, $[VCl_2(tmen)_2]$ and $Na[BPh_4]$

Solutions of $[\{FeCl(tmen)\}_2(\mu\text{-}Cl)_2]$ (1.4 g, 2.9 mmol) and $[VCl_2(tmen)_2]$ (1.0 g, 2.9 mmol) in thf (35 cm^3) were mixed at room temperature. No significant change of colour was observed, even after stirring for ca. 20 h. A colourless solution of $Na[BPh_4]$ (1.0 g, 2.9 mmol) in thf (10 cm^3) was then added to the reaction mixture, which changed immediately to a dark grass-green fine suspension. The mixture was stirred for further 20 h and filtered, giving a green filtrate and a small amount of a grey residue (discarded). The filtrate was concentrated under vacuum to ca. 50 cm^3 and then layered with hexane (30 cm^3). Slow diffusion of the hexane layer into the thf solution produced large deep green thick prisms which were filtered off after 5 days, washed with thf/hexane 1:1 (80 cm^3) and dried. Yield: 2.27 g, 77%, based on the average molecular weight of an equimolar mixture of the $\{V_3\}$, $\{V_2Fe\}$, $\{VFe_2\}$ and $\{Fe_3\}$ trinuclear complexes (**6**, sample 2). The product was then recrystallised twice from thf/hexane mixtures (2:1); the yield of each recrystallisation step was 65–70%. Deep green needles or long prisms of **6**, sample 2, were also obtained under slightly different crystallisation conditions; no analytical technique unequivocally distinguished one type of crystal from the other two. The product is very soluble in thf and CH_2Cl_2, and insoluble in diethyl ether, hexane and toluene and it reacts with acetone and methanol. Found for a representative sample of **6**, sample 2: C, 49.9; H, 6.95; N, 8.25; Fe, 9.0; V, 5.7%; ratio V/Fe 0.7. The metal contents of five preparations (each analysis carried out in duplicate or triplicate) were in the range 4–10% w/w (for Fe) and 5–11% w/w (for V), the ratio V/Fe ranging from ca. 2:1 to ca. 1:2. *Anal.* Calc. for an equimolar mixture of the tetraphenylborate salts of $[V_3Cl_5(tmen)_3]^+$, $[V_2FeCl_5(tmen)_3]^+$, $[VFe_2Cl_5(tmen)_3]^+$ and $[Fe_3Cl_5(tmen)_3]^+$: C, 50.2; H, 6.85; N, 8.35; Fe, V, 8%.

FAB-MS results obtained for **6**, sample 2 (*m*/*z*, relative intensity): 678 $[V_3Cl_5(tmen)_3]^+$ (17%); 553 (residue from $[Fe_3Cl_5(tmen)_3]^+$ possibly $\{(Htmen)_2[BPh_4]\}^+$, 5%); 439 (8%); 269(7%); 117 $\{Htmen\}^+$ (100%); 72 $\{Me_2NCH_2CH_2\}^+$ (93%); 58 $\{Me_2NCH_2\}^+$ (88%). IR (Nujol mull, cm^{-1}): 1958 (w); 1875 (w); 1815 (w); 1765 (w); 1581 (s); n(B-aryl) at 1424 (s); n(C–N) at 1003 (m) and 1018 (s); d(C–H aromatic, out-of-plane) at 708 (s);

735 (s) and 749 (s); n(M–N) at 441 (m); 469 (m) and 497 (m).

Product **6** was sometimes isolated with lattice solvent and needed to be filtered carefully to prevent the crystals from becoming opaque on washing and drying. Analytical data for such a solvate. *Anal.* Found: C, 51.8; H, 7.40; N. 7.75. Calc. for $[M_3Cl_5(tmen)_3](BPh_4)(thf$, as an equimolar mixture of the $\{V_3\}$, $\{Fe_3\}$, $\{V_2Fe\}$ and $\{VFe_2\}$ solvates: C, 51.3; H, 7.10; N, 7.80%.

The preparation of **6**, sample 3, was carried out essentially as described above, from 1.3 g (2.7 mmol) of $[\{FeCl(tmen)\}_2(\mu\text{-}Cl)_2]$, 1.2 g (3.4 mmol) of $[VCl_2(tmen)_2]$ and 0.95 g (2.8 mmol) of $Na[BPh_4]$, all dissolved in thf (Fe/V proportion 1.6:1; metal/tetraphenylborate 3:1). The reaction mixture was stirred at room temperature for 20 h, filtered through Celite and layered with hexane (thf/hexane proportion 1.5:1). Green prisms were filtered off after 3 days at room temperature and were analysed for C, H, N, Fe and V contents. *Anal.* Found for **6**, sample 3: C, 60.2; H, 7.44; N, 7.66, total metal content: 10.3% (5.6% V; 4.7% Fe). Calc. for $[V_2FeCl_5(tmeda)_3][tmedaH\cdots thf][BPh_4]_2$, $C_{76}H_{113}B_2Cl_5FeN_8OV_2$: C, 60.4; H, 7.54; N, 7.41%, total metal content: 10.4% (6.7% V; 3.7% Fe).

4.7. Reaction between $[FeCl_2(dppe)]$ and $[VCl_2(tmen)_2]$

A light blue solution of the V(II)-starting material (0.5 g, 1.4 mmol) in thf (20 cm^3) was mixed with a white suspension of $[FeCl_2(dppe)]$ (0.7 g, 1.4 mmol) in thf (30 cm^3). The mixture changed immediately to a turquoise suspension of **7**, which was stirred for ca. 20 h and then filtered. The solid (0.4 g) was washed with thf (2 cm^3) and hexane (20 cm^3) and dried under vacuum. The filtrate (light purple) was discarded. The product was insoluble in thf, diethyl ether and hexane, and only slightly soluble in dichloromethane. *Anal.* Found for **7**: C, 36.5; H, 6.05; N, 7.95. $[V_3Cl_5(tmen)_3]_2[FeCl_4(dppe)]$ requires: C, 38.1; H, 6.20; N, 8.60%. FAB-MS (m/z, relative intensity): 882 (9%); 852 (0.5%); 678 $[V_3Cl_5(tmen)_3]^+$ (9%); 479 (7%); 147 (39%); 110 (100%); 72 (26%); 67 (40%).

*4.8. X-ray diffraction analysis of $[V_2FeCl_5(tmen)_3][Htmen\cdots thf][BPh_4]_2$ (**6**, sample 3)*

A long, green, air-sensitive prism, ca. 0.25 × 0.15 × 0.10 mm^3 was mounted on a glass fibre and cooled on a Nonius Kappa CCD area detector diffractometer. No deterioration correction was necessary and no absorption correction was applied. All the non-hydrogen atoms were allowed anisotropic thermal parameters. Refinement was by full-matrix least-square methods on F^2. Programs used: WINGX and SHELXL-97 [28]. For details, see Table 2.

Acknowledgements

We acknowledge the financial support from the Brazilian Research Council (CNPq) and the British Council to J.S. de S., and from the BBSRC.

References

[1] (a) R.L. Robson, R.R. Eady, T.H. Richardson, R.W. Miller, M. Hawkins, J.R. Postgate, Nature (London) 322 (1986) 388;
(b) R.R. Eady, G.J. Leigh, J. Chem. Soc., Dalton Trans. (1994) 2739.

[2] (a) N.P. Luneva, S.A. Mironova, A.E. Shilov, M.Yu. Antipin, Y.T. Struchkov, Angew. Chem., Int. Ed. Engl. 32 (1993) 1178;
(b) T.A. Bazhenova, A.E. Shilov, Coord. Chem. Rev. 144 (1995) 69;
(c) A.E. Shilov, Cattech. 3 (1999) 72.

[3] D.L. Hughes, G.J. Leigh, J.R. Sanders, J.S. de Souza, J. Chem. Soc., Chem. Commun. (1996) 1985.

[4] J.J.H. Edema, W. Stauthamer, F. van Bolhuis, S. Gambarotta, W.J.J. Smeets, A.L. Spek, Inorg. Chem. 29 (1990) 1302.

[5] (a) D.L. Hughes, L.F. Larkworthy, G.J. Leigh, C.J. McGarry, J.R. Sanders, G.W. Smith, J.S. de Souza, J. Chem. Soc., Chem. Commun. (1994) 2137;
(b) P.B. Hitchcock, D.L. Hughes, L.F. Larkworthy, G.J. Leigh, C.J. Marmion, J.R. Sanders, G.W. Smith, J.S. de Souza, J. Chem. Soc., Dalton Trans. (1997) 1127.

[6] (a) A.C. Niedwieski, A.R. Raimondi, D.L. Hughes, G.J. Leigh, F.S. Nunes, J.F. Soares, in: F.O. Pedrosa, M. Hungria, M.G. Yates, W.E. Newton (Eds.), Nitrogen Fixation: from Molecules to Crop Productivity, Kluwer Academic, New York, 2000, p. 62 and unpublished data;
(b) S.C. Davies, D.L. Hughes, G.J. Leigh, J.R. Sanders, J.S. de Souza, J. Chem. Soc., Dalton Trans. (1997) 1981.

[7] Z. Janas, P. Sobota, T. Lis, J. Chem. Soc., Dalton Trans. (1991) 2429.

[8] P. Sobota, Polyhedron 11 (1992) 715.

[9] J.A.M. Canich, F.A. Cotton, S.A. Duraj, W.J. Roth, Polyhedron 6 (1987) 1433.

[10] (a) L.E. Manzer, Inorg. Synth. 21 (1982) 138;
(b) P. Sobota, J. Ejfler, S. Szafert, K. Szczegot, W. Sawka-Dobrowolska, J. Chem. Soc., Dalton Trans. (1993) 2353.

[11] (a) R.J. Haines, A.L. du Preez, J. Am. Chem. Soc. 93 (1971) 2820;
(b) G.J. Kruger, A.L. du Preez, R.J. Haines, J. Chem. Soc., Dalton Trans. (1974) 1302;
(c) R.J. Haines, A.L. du Preez, J. Organomet. Chem. 84 (1975) 357;
(d) J.R. Sanders, J. Chem. Soc., Dalton Trans. (1973) 743.

[12] (a) V.K. Bels'kii, V.M. Ishchenko, G.M. Bulychev, A.N. Protskii, G.L. Soloveichik, O.G. Ellert, Z.M. Seifulina, Yu.V. Rakitin, V.M. Novotortsev, Inorg. Chim. Acta 96 (1985) 123;
(b) F.A. Cotton, R.L. Luck, K.-A. Son, Inorg. Chim. Acta 179 (1991) 11.

[13] E. Slade, A. Houlton, J. Silver, D.J. Evans, G.J. Leigh, J. Chem. Soc., Dalton Trans. (1993) 1217.

[14] (a) D.F. Evans, J. Chem. Soc. (1959) 2003;
(b) D.F. Evans, G.V. Fazakerley, R.F. Phillips, J. Chem. Soc. A (1971) 1931;
(c) D.F. Evans, T.A. James, J. Chem. Soc., Dalton Trans. (1979) 723.

[15] (a) J.J.H. Edema, A. Meetsma, S. Gambarotta, J. Chem. Soc., Chem. Commun. (1990) 951;

(b) J.J.H. Edema, R. Duchateau, S. Gambarotta, C. Bensimon, Inorg. Chem. 30 (1991) 3585.

[16] (a) P. Sobota, J. Utko, S. Szafert, Z. Janas and T. Glowiak, J. Chem. Soc., Dalton Trans. (1996) 3469;
(b) D.A. Handley, P.B. Hitchcock, G.J. Leigh, Inorg. Chim. Acta (in press).

[17] M.E. Barr, A. Bjarnason, L.F. Dahl, Organometallics 13 (1994) 1981.

[18] R.A. Henderson, J. Chem. Soc., Dalton Trans. (1988) 509.

[19] J.E. Barclay, G.J. Leigh, A. Houlton, J. Silver, J. Chem. Soc., Dalton Trans. (1988) 2865.

[20] A.R. Hermes, G.S. Girolami, Inorg. Chem. 7 (1988) 1775.

[21] A.R. Hermes, G.S. Girolami, Organometallics 6 (1987) 763.

[22] F.A. Cotton, S.A. Duraj, L.E. Manzer, W.J. Roth, J. Am. Chem. Soc. 107 (1985) 3850.

[23] L.F. Larkworthy, M.W. O'Donoghue, Inorg. Chim. Acta 71 (1983) 81.

[24] N.P. Luneva, L.A. Nikonova, A.E. Shilov, Kinet. Catal. 21 (1980) 1041.

[25] P.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, 3rd edn., Pergamon, New York, 1988.

[26] L.J. Arnold, J. Chem. Educ. 69 (1992) 811.

[27] A. Earnshaw, Introduction to Magnetochemistry, Academic Press, London, 1968, p. 4.

[28] G.M. Sheldrick, SHELX-97, Program for the refinement of crystal structures, University of Göttingen, 1997.