Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

N,N,N′,N′-Tetramethylethane-1,2-diaminium tri-μ-chloro-bis[(*N,N,N′,N′*-tetramethylethane-1,2-diamine)vanadium(II)] tetraphenylborate tetrahydrofuran solvate

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Received 1 June 2004
Accepted 21 June 2004
Online 26 June 2004

Key indicators

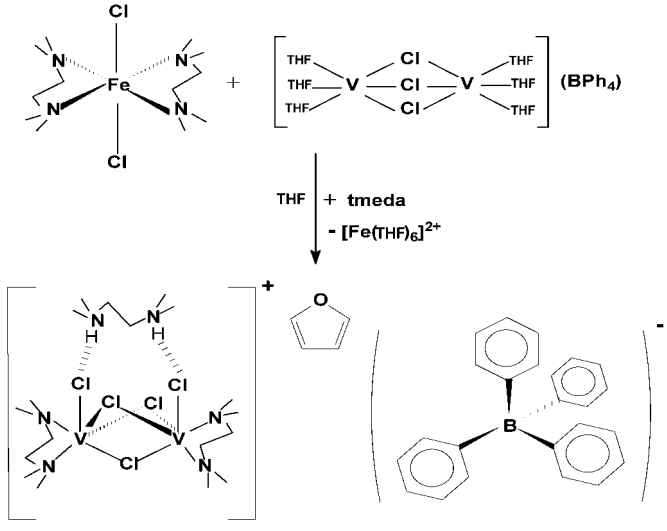
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.046
wR factor = 0.118
Data-to-parameter ratio = 15.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title complex, $(C_6H_{18}N_2)[V_2Cl_5(C_6H_{16}N_2)_2](C_{24}H_{20}B)\cdot C_4H_8O$, was prepared by the reaction of $[V_2Cl_3(THF)_6](BPh_4)$ with $[FeCl_2(tmeda)_2]$ in the presence of one equivalent of tmeda (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) in methanol. The crystal structure shows the tmeda to be coordinated to the vanadium core groups. The exchange of the diamine from iron to vanadium sheds new light on the mechanism of self-assembly of *triangulo* trinuclear complexes.

Comment

Vanadium and iron trinuclear complexes have been studied as potential functional models of the reducing site of vanadium–nitrogenase (Luneva *et al.*, 1982; Shilov, 1987). The trinuclear complex $[V_3(\mu\text{-Cl})_3(\mu_3\text{-Cl})_2(tmeda)_3](BPh_4)$ is the only product isolated from the reaction of $[V_2Cl_3(THF)_6](BPh_4)$ with excess *N,N,N′,N′*-tetramethylethylenediamine (tmeda) in THF, through a mechanism which probably involves partial breakage of the binuclear complex into a mononuclear species, such as *trans*-$[VCl_2(tmeda)_2]$, which then reacts, in a further step, with the intact molecules of the binuclear complex (Niedwieski, Hitchcock *et al.*, 2003). Indeed, this mechanism seems to be effective, as we succeeded in isolating the homometallic complex $[V_3(\mu\text{-Cl})_3(\mu_3\text{-Cl})_2(tmeda)_3](BPh_4)$ from the reaction between the mononuclear blue complex $[VCl_2(tmeda)_2]$ and the green binuclear compound $[V_2Cl_3(THF)_6](BPh_4)$, in the presence of tmeda (molar ratio of 1:1:1) in refluxing THF (Niedwieski, Hitchcock *et al.*, 2003; Niedwieski, Leigh *et al.*, 2003).



(I)

Two preparative routes have been reported for the trinuclear species, $[M_3(\mu\text{-Cl})_3(\mu_3\text{-Cl})_2(tmeda)_3]^+$ (where M = V, Ti,

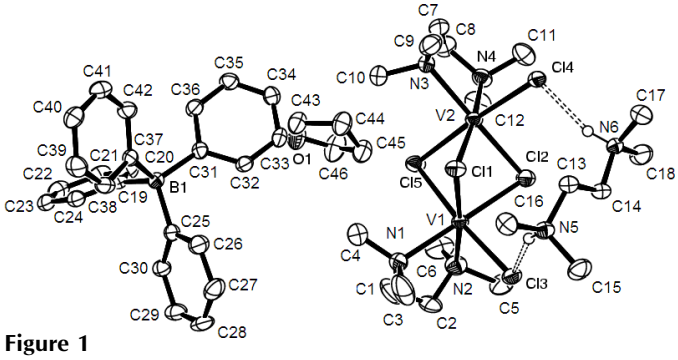


Figure 1
View of the title complex, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 20% probability level. Dashed lines indicate hydrogen bonds. H atoms have been omitted. Only the major disorder component is shown.

Fe, Co or Ni). The first has been described as involving a disproportionation (Edema *et al.*, 1990; Edema *et al.*, 1991). The second appears to involve halide and perhaps diamine dissociation (Hughes *et al.*, 1994; Hitchcock *et al.*, 1997).

The third route, presented here, in an attempt to prepare mixed-metal *triangulo* complexes, might allow better control of the reaction pathway than the other approaches used exclusively to synthesize homometallic compounds, avoiding the formation of undesired redox reaction products. In an attempt to synthesize the heterometallic complex $[V_2Fe(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)_2(tmeda)_3](BPh_4)$ from the reaction between $[V_2Cl_3(THF)_6](BPh_4)$, $[FeCl_2(tmeda)_2]$ and tmeda (1:1:1 ratio) we, in fact, isolated complex (I).

An *ORTEP* view of (I) shows two hexacoordinated vanadium(II) centres, each one bound to one tmeda molecule and four chlorides (Fig. 1). It is interesting to note that the chloride ligands originally linked to the iron(II) are now coordinated to the vanadium centres. The crystallographic environment is very similar to that seen in the homometallic $[M_3(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)_2(tmeda)_3](BPh_4)$ (M = V or Fe) (Hughes *et al.*, 1994; Davies *et al.*, 1997) and also expected for the mixed V and Fe complex $[V_2Fe(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)_2(tmeda)_3](BPh_4)$. On the other hand, a key step in the mechanism of self-assembly is definitely the transfer of tmeda from the iron starting material $[FeCl_2(tmeda)_2]$ to the binuclear vanadium fragment.

Selected bond distances and angles are listed in Table 1. Each vanadium centre has an octahedral environment, with three bridging and one terminal chloride ligands. The former distances lie in the range 2.4899 (10)–2.5121 (11) Å; the latter are 2.4785 (10) and 2.4843 (11) Å. The structure shows that the uncoordinated diamine was in the correct position to coordinate the iron(II) ion and close the *triangulo* trinuclear structure. Hydrogen bonds exist for Cl3···H5 and Cl4···H6, with distances of 2.15 (4) and 2.12 (4) Å, respectively.

Experimental

All operations were carried out under an inert atmosphere using standard Schlenk techniques. The solvent was dried by a standard procedure and distilled twice under N_2 prior to use (Perrin & Armarego, 1997). Liquid tmeda was refluxed over sodium and distilled twice under N_2. The starting material, $[V_2Cl_3(THF)_6](BPh4)$, was prepared as described (Bouma *et al.*, 1984). $[FeCl_2(tmeda)_2]$ was prepared according to Davies *et al.* (1997). For the preparation of complex (I), $[FeCl_2(tmeda)_2]$ (0.95 g, 2.64 mmol) was dissolved in 25 ml of methanol. To the resulting yellow solution, 0.40 ml (2.64 mmol) of tmeda and 2.53 g (2.64 mmol) of $[V_2Cl_3(THF)_6](BPh_4)$ dissolved in 35 ml of methanol were added. 65 ml of hexane was then slowly layered over the dark-green solution, affording pale-green needles. Recrystallization from THF and hexane (1:3) produced prismatic green crystals suitable for X-ray analysis (yield 44%).

Crystal data

$(C_6H_{18}N_2)[V_2Cl_5(C_6H_{16}N_2)_2]\cdot(C_{24}H_{20}B)\cdot C_4H_8O$
M_r = 1021.08
Triclinic, $P\overline{1}$
a = 9.3902 (17) Å
b = 14.9426 (13) Å
c = 19.455 (4) Å
α = 102.125 (14)°
β = 98.065 (17)°
γ = 92.267 (11)°
V = 2635.8 (8) Å^3
Z = 2
D_x = 1.287 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 7.3–10°
μ = 0.65 mm^{-1}
T = 173 (2) K
Prism, green
0.3 × 0.3 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.88, T_{max} = 0.94
9241 measured reflections
9241 independent reflections
6586 reflections with $I > 2\sigma(I)$
θ_{max} = 25.0°
$h = 0 \rightarrow 11$
$k = -17 \rightarrow 17$
$l = -23 \rightarrow 22$
2 standard reflections
frequency: 60 min
intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.118
S = 0.98
9241 reflections
586 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 1.5496P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

V1—N2	2.247 (3)	V2—N3	2.246 (3)
V1—N1	2.257 (3)	V2—N4	2.264 (3)
V1—Cl3	2.4843 (11)	V2—Cl4	2.4785 (10)
V1—Cl5	2.4882 (11)	V2—Cl5	2.4899 (10)
V1—Cl1	2.5056 (11)	V2—Cl2	2.4932 (11)
V1—Cl2	2.5121 (11)	V2—Cl1	2.5014 (11)
V1···V2	3.0901 (10)		
N2—V1—N1	81.65 (12)	N3—V2—N4	82.04 (11)
N2—V1—Cl3	91.86 (9)	N3—V2—Cl4	89.51 (8)
N1—V1—Cl3	91.59 (8)	N4—V2—Cl4	92.50 (8)
N2—V1—Cl5	92.17 (9)	N3—V2—Cl5	93.73 (8)
N1—V1—Cl5	93.13 (8)	N4—V2—Cl5	91.45 (8)
Cl3—V1—Cl5	174.20 (4)	Cl4—V2—Cl5	175.20 (4)
N2—V1—Cl1	173.87 (9)	N3—V2—Cl2	176.48 (8)
N1—V1—Cl1	94.11 (9)	N4—V2—Cl2	94.53 (9)
Cl3—V1—Cl1	92.69 (4)	Cl4—V2—Cl2	91.45 (4)
Cl5—V1—Cl1	83.61 (4)	Cl5—V2—Cl2	85.52 (4)
N2—V1—Cl2	96.09 (9)	N3—V2—Cl1	94.82 (8)
N1—V1—Cl2	177.12 (8)	N4—V2—Cl1	174.04 (8)
Cl3—V1—Cl2	90.27 (4)	Cl4—V2—Cl1	92.55 (4)
Cl5—V1—Cl2	85.15 (4)	Cl5—V2—Cl1	83.66 (4)
Cl1—V1—Cl2	88.00 (4)	Cl2—V2—Cl1	88.52 (4)

The H atoms attached to N5 and N6 were located in a difference map and refined freely. Other H atoms were placed in idealized positions and refined using a riding model, with C—H = 0.95–0.99 Å and with $U_{iso}(H) = 1.3U_{eq}(C)$. Atoms C1, C2, C5 and C6 are disordered over two sites. Refined occupancy factors for the two components are 0.564:0.436(13).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

This work was supported by the Brazilian PRONEX Program (contract No. 41.96.0884.00). We thank Professor G. J. Leigh for helpful discussions and Dr Peter B. Hitchcock (CPES, University of Sussex, England) for the crystal structure data.

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