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Key indicators

Single-crystal X-ray study
T = 295 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.056
wR factor = 0.174
Data-to-parameter ratio = 17.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

A trigonal prismatic coordination geometry for vanadium in bis(2-oxidonaphthalene-1-carbaldehyde benzoylhydrazonato)vanadium(IV) dichloromethane hexane hemisolvate

The V^{IV} atom in the title compound, $[\text{V}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_4)_2] \cdot \text{CH}_2\text{Cl}_2 \cdot 0.5\text{C}_6\text{H}_{14}$, which crystallizes as a dichloromethane hexane hemisolvate, exists in a trigonal prismatic geometry. The hexane molecule lies across an inversion center and both solvent molecules are disordered.

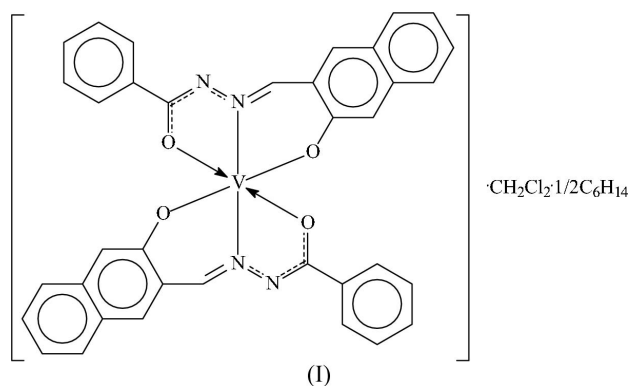
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Comment

Six-coordinate compounds almost invariably prefer to adopt octahedral over trigonal prismatic geometry, and some metal ions adopt octahedral geometry almost exclusively. Authenticated examples of trigonal prismatic complexes, particularly of the first-row transition metals, are exceedingly rare (Cambridge Structural Database, Version 5.26; Allen, 2002). The first example (for a first-row metal) is tris(dithiobenzil)vanadium (Eisenberg *et al.*, 1966; Eisenberg & Gray, 1967); the chelating effect of the three $(\text{C}_6\text{H}_5)_2\text{C}_2\text{S}_2$ ligands is believed to be responsible for stabilizing the trigonal prismatic coordination. A similar effect is probably responsible for the existence of this coordination geometry in the tris(5,6-dihydro-1,4-dithiin-2,3-dithiolato)vanadate monoanion (Welch *et al.*, 1988). Interestingly, $(\text{CH}_3)_3\text{SiN}(\text{VCl}_3(2,2'-\text{C}_{10}\text{H}_8\text{N}_2))$ (Schweda *et al.*, 1985) shows that a thiol chelate is not a critical requirement for the manifestation of such a geometry. Our interest in attempting to synthesize a trigonal prismatic vanadium compound comes from yet another early report on bis(acetylacetonate benzoylhydrazonato)vanadium(IV); this compound was obtained by reacting oxovanadium(IV) bis(acetylacetonate) with benzoylhydrazine (Diamantis *et al.*, 1976). The present report follows previous reports on the hydrazonates of vanadium (Gao *et al.*, 2005; Huo, Gao, Liu, Zhao, & Ng, 2004; Huo, Gao, Liu, Li & Ng, 2004).



The bis-*O,N,O'*-chelated vanadium(IV) complex, (I), crystallizes as a dichloromethane hexane hemisolvate (Fig. 1); the geometry is unambiguously trigonal prismatic (Fig. 2).

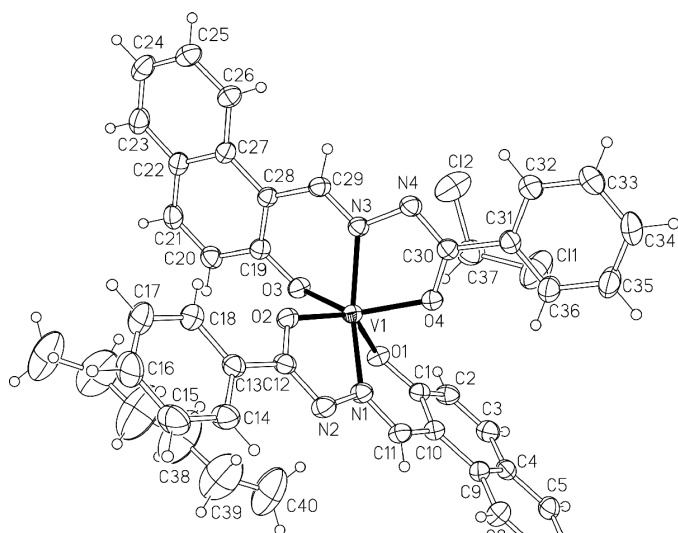


Figure 1
ORTEP plot (Johnson, 1976) of the asymmetric unit of (1), together with the second half of the hexane molecule. Displacement ellipsoids are drawn at the 30% probability level and H atoms are drawn as spheres of arbitrary radii. Only the major components of the disordered solvent molecules are shown.

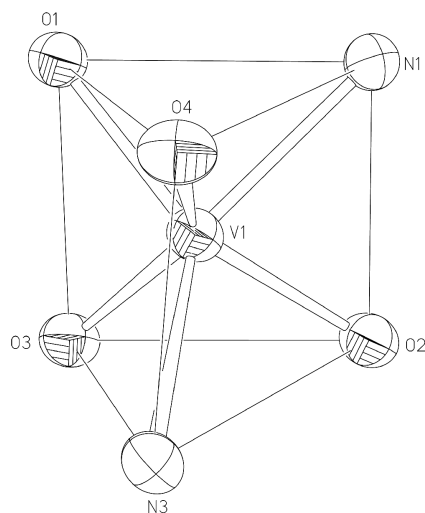


Figure 2
Trigonal bipyramidal geometry of the V atom.

Chelation by the two planar anionic groups leads to the formation of five- and six-membered rings. Bond dimensions involving the V atom are similar to those found in the reported acetylacetonate benzoylhydrazine analog (Diamantis *et al.*, 1976). The present compound probably does not pack efficiently owing to the naphthyl fused ring, and the voids in the crystal structure are readily filled by the disordered solvent molecules.

Experimental

An ethanol solution (15 ml) of $\text{VO}(\text{acac})_2$ (0.27 g, 1 mmol) was added to an ethanol solution (15 ml) of 2-hydroxynaphthalene-1-carbaldehyde benzoylhydrazone (0.64 g, 2 mmol). The resulting mixture was refluxed for 1 h. The brown product formed was collected and

dissolved in dichloromethane. Crystals were obtained by the diffusion of hexane into the filtered solution. Analysis calculated for $\text{C}_{40}\text{H}_{33}\text{Cl}_2\text{N}_4\text{O}_4\text{V}$: C 63.55, H 4.41, N 7.43%; found: C 63.47, H 4.44, N 7.39%.

Crystal data

$[\text{V}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_4)_2] \cdot \text{CH}_2\text{Cl}_2 \cdot 0.5\text{C}_6\text{H}_{14}$
 $M_r = 755.54$
 Triclinic, $P\bar{1}$
 $a = 12.598$ (3) Å
 $b = 13.021$ (3) Å
 $c = 13.652$ (3) Å
 $\alpha = 116.04$ (3)°
 $\beta = 101.84$ (3)°
 $\gamma = 106.21$ (3)°
 $V = 1787.2$ (6) Å³

$Z = 2$
 $D_x = 1.404$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 15371 reflections
 $\theta = 3.0$ – 27.5 °
 $\mu = 0.48$ mm⁻¹
 $T = 295$ (2) K
 Prism, black
 $0.38 \times 0.26 \times 0.18$ mm

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\text{min}} = 0.758$, $T_{\text{max}} = 0.919$
 17362 measured reflections

8039 independent reflections
 5896 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 27.5$ °
 $h = -15 \rightarrow 16$
 $k = -16 \rightarrow 16$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.174$
 $S = 1.05$
 8039 reflections
 474 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1036P)^2 + 0.4047P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.88$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.94$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

V1–O1	1.904 (2)	V1–O4	1.910 (2)
V1–O2	1.917 (2)	V1–N1	2.043 (2)
V1–O3	1.906 (2)	V1–N3	2.061 (2)
O1–V1–O2	136.38 (8)	O2–V1–N3	87.80 (8)
O1–V1–O3	82.56 (8)	O3–V1–O4	137.24 (9)
O1–V1–O4	87.17 (9)	O3–V1–N1	132.15 (9)
O1–V1–N1	82.30 (9)	O3–V1–N3	82.57 (9)
O1–V1–N3	131.90 (9)	O4–V1–N1	86.78 (9)
O2–V1–O3	86.62 (9)	O4–V1–N3	73.94 (8)
O2–V1–O4	126.63 (9)	N1–V1–N3	138.06 (9)
O2–V1–N1	74.24 (8)		

The dichloromethane and hexane molecules are disordered. The C atom of the dichloromethane molecule is disordered over two positions and the disorder was treated by restraining the C–Cl distance to 1.790 (5) Å and the Cl···Cl distance to 2.92 (1) Å; a relatively tight restraint was used to avoid a large difference in the C–Cl distances. The occupancy of the two disordered positions C37/C37' refined to 0.815 (12)/0.185(12). The centrosymmetric hexane molecule is disordered over two orientations and their occupancies refined to 0.741 (13) and 0.259 (13); the C–C bond lengths were restrained to 1.54 (1) Å and the C···C distances to 2.51 (1) Å. The displacement parameters of the minor component atoms were set equal to those of the major component atoms. H atoms were placed in calculated positions, with C–H = 0.93 (aromatic), 0.96 (methylene) or 0.97 Å (methyl), and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (aromatic/methylene) or $1.5U_{\text{eq}}(\text{C})$ (methyl), and included in the final cycles of refinement in a riding model.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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