

Craig C. McLauchlan* and
Kenneth J. McDonaldDepartment of Chemistry, Illinois State University,
Campus Box 4160, Normal, IL 61790-4160, USA

Correspondence e-mail: mclauchlan@ilstu.edu

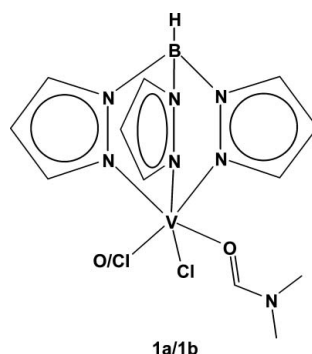
Key indicators

Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(C-C) = 0.006$ Å
Disorder in main residue
 R factor = 0.049
 wR factor = 0.134
Data-to-parameter ratio = 17.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Cocrystallization of dichloro(*N,N*-dimethyl-
formamide)[hydrotris(pyrazol-1-yl)borato]-
vanadium(III) with its partially oxidized
analog chloro(*N,N*-dimethylformamide)-
[hydrotris(pyrazol-1-yl)borato]oxovanadium(IV)Received 9 January 2006
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The components dichloro(*N,N*-dimethylformamide)[hydrotris(pyrazol-1-yl)borato]vanadium(III), [TpVCl₂(DMF)], and its partially oxidized analog chloro(*N,N*-dimethylformamide)-[hydrotris(pyrazol-1-yl)borato]oxovanadium(IV), [TpVOCl(DMF)], cocrystallize in an approximately 1:1 ratio, viz. [V(C₉H₁₀BN₆)Cl₂(C₃H₆NO)][V(C₉H₁₀BN₆)ClO(C₃H₆NO)]. The components both exist in the solid state with disorder of the Cl/O site and with V in a pseudo-octahedral coordination geometry. The complexes each have three pyrazole units of the hydrotris(pyrazol-1-yl)borate ligand bound to one 'face' of the vanadium center and one chloro, one oxo/chloro, and one oxo-bound *N,N*-dimethylformamide ligand bound to the other face.

Comment

In the course of our continuing investigations of vanadium complexes with tridentate ligands, we have synthesized a number of complexes with the scorpionate ligand hydrotris(pyrazol-1-yl)borate, Tp⁻. Many complexes between Tp⁻ and V have been reported by Carrano and co-workers (Kime-Hunt *et al.*, 1989; Mohan *et al.*, 1992; Mokry *et al.*, 1994; Dean, Bond *et al.*, 1996; Dean *et al.*, 1996*a,b*; Otieno *et al.*, 1996), including one of the title complexes TpVCl₂(DMF) (1a), where DMF is *N,N*-dimethylformamide. Recently we reported a hydrolysis product of 1a, TpVOCl(pzH), isolated in our efforts to crystallize compound 1a in acetone under aerobic conditions (McLauchlan & McDonald, 2005). We report the structure of a cocrystal of complex 1a with its oxidized analogue TpVOCl(DMF), 1b.



Displacement ellipsoid plots of the asymmetric unit of TpVCl₂(DMF) and TpVOCl(DMF) are shown in Fig. 1. The materials cocrystallize such that the primary difference is the substitution of an O atom (O1A) for a Cl atom (Cl1) in the two

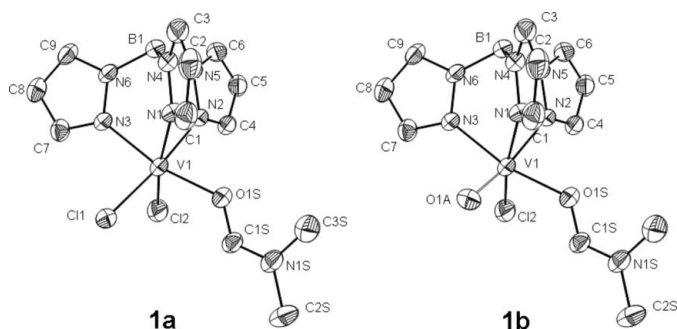


Figure 1
Displacement ellipsoid plots (50%) of the asymmetric unit of $\text{TpVCl}_2(\text{DMF})$, 1a, and $\text{TpVOCl}(\text{DMF})$, 1b. H atoms have been omitted for clarity. Note that the molecules are identical save for the Cl1 and O1A atoms.

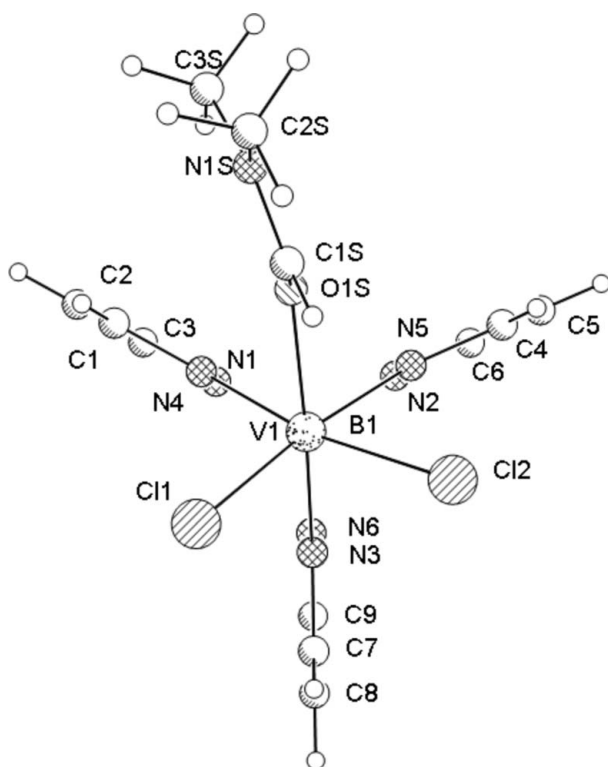


Figure 2
 $\text{TpVCl}_2(\text{DMF})$, 1a, viewed along $\text{V} \cdots \text{B}$ illustrating the canting of the DMF plane relative to the opposing pyrazole ring. The mean planes are inclined by $23.7(2)^\circ$ relative to one another.

structures, much like the $\text{MoO}_x\text{Cl}_{3-x}(\text{PR}_3)_3$ disorder reported by Parkin (1992). In both compounds, the vanadium center possesses pseudo-octahedral geometry, with three pyrazole units of the Tp bound to one 'face' of the vanadium center and one chloro ligand, one chloro/oxo ligand and an oxo-bound *N,N*-dimethylformamide ligand bound to the other face. In 1a, a non-crystallographic pseudo-mirror plane is present in the molecule as 1a ideally has C_s symmetry. However, a canting of the DMF ligand out of the ideal plane [the DMF plane is inclined by $23.7(2)^\circ$ to the opposing pyrazole plane] reduces the symmetry of the molecule, allowing a chiral crystal structure (Fig. 2). Compound 1b lacks a mirror plane and is also chiral. $\text{TpVCl}_2(\text{DMF})$ was originally reported by Mohan *et al.*

(1992) to contain a dichloromethane solvent molecule as well, although no structural characterization was reported. No solvent molecule was located in the difference map in our study.

The structure can be modeled with the appropriate molecular formula $\text{TpVCl}_2(\text{DMF})$, but slight improvements in the reliability indices and, more notably, displacement ellipsoids of the chlorides are noted with modeling of cocrystallization with a partially oxidized (*ca* 47%) species, $\text{TpVOCl}(\text{DMF})$ (see below). This oxidation is likely due to growth of the crystals in air, as oxidation of 1a in solution has been noted by Otieno *et al.* (1996). The overall formulation of the crystal, then, is $\text{TpVCl}_{1.53}\text{O}_{0.47}(\text{DMF})$. These values are consistent with average values of 1.4:1 Cl/V obtained using energy dispersive analysis by X-rays on several crystals. X-ray diffraction studies on other crystals showed some variability in the percent oxidation of the structure. No evidence for a supercell was found in any of the data collections.

Selected bond lengths and angles for complexes 1a and 1b are displayed in Table 1. V–N bond lengths range from 2.109 (3) to 2.181 (3) Å and interligand angles range from $81.7(1)$ to $100.6(1)^\circ$. These bond lengths and angles are typical of structurally characterized complexes of V with $^{3,5-R^2}\text{Tp}$, where *R* = H, methyl or isopropyl groups in the 3- and 5-positions on the pyrazole rings (Kime-Hunt *et al.*, 1989; Heimer & Cleland, 1990; Mokry *et al.*, 1994; Malinak *et al.*, 1995; Scheuer *et al.*, 1995; Dean, Bond *et al.*, 1996; Dean *et al.*, 1996*a,b*; Otieno *et al.*, 1996; Collison *et al.*, 1997; Herberhold *et al.*, 1998; Rehder *et al.*, 1998; Kosugi *et al.*, 1999; Hauser *et al.*, 2002; McLauchlan & McDonald, 2005). V–Cl bond lengths are slightly shorter than typical, with an average distance of 2.261 (2) Å, and the V=O bond distance is slightly longer than typical for these complexes at 1.741 (8) Å (Collison *et al.*, 1993; Kosugi *et al.*, 1999; Kime-Hunt *et al.*, 1989; Heimer & Cleland, 1990), providing further evidence of the disorder between the co-crystallized species.

Experimental

$\text{TpVCl}_2(\text{DMF})$ was prepared according to the procedure of Mohan *et al.* (1992). Magnetic susceptibility, IR spectra, and UV/vis spectra on the bulk material are consistent with those previously reported (Mohan *et al.*, 1992). Light-green prismatic crystals [m.p. 456 (1) K] suitable for X-ray analysis were prepared by evaporation of an acetone solution of $\text{TpVCl}_2(\text{DMF})$ in aerobic conditions. Samples of crystals were analyzed for elemental content on an EDS-equipped Hitachi S3500 SEM to afford an average 1.4:1 Cl/V ratio.

Crystal data

$[\text{V}(\text{C}_9\text{H}_{10}\text{BN}_6)\text{Cl}_2(\text{C}_3\text{H}_6\text{NO})]$
 $[\text{V}(\text{C}_9\text{H}_{10}\text{BN}_6)\text{ClO}(\text{C}_3\text{H}_6\text{NO})]$
 $M_r = 797.66$
 Orthorhombic, $P2_12_12_1$
 $a = 8.6005(5)$ Å
 $b = 13.7002(10)$ Å
 $c = 14.8204(13)$ Å
 $V = 1746.3(2)$ Å³
 $Z = 2$

$D_x = 1.517$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5892 reflections
 $\theta = 4.1$ – 27.5°
 $\mu = 0.82$ mm⁻¹
 $T = 100(2)$ K
 Prism, light green
 $0.19 \times 0.12 \times 0.06$ mm

Data collection

Oxford Diffraction Xcalibur3 CCD diffractometer
 φ and ω scans
 Absorption correction: numerical (Clark & Reid, 1995)
 $T_{\min} = 0.812$, $T_{\max} = 0.901$
 15979 measured reflections

3987 independent reflections
 3370 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$
 $\theta_{\max} = 27.5^\circ$
 $h = -11 \rightarrow 11$
 $k = -16 \rightarrow 17$
 $l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.134$
 $S = 1.10$
 3987 reflections
 229 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0723P)^2 + 0.5753P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.58 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983),
 1714 Friedel pairs
 Flack parameter: 0.07 (3)

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cl1–V1	2.234 (2)	N2–V1	2.181 (3)
O1A–V1	1.741 (8)	N3–V1	2.109 (3)
Cl2–V1	2.2872 (13)	O1S–V1	2.019 (2)
N1–V1	2.121 (3)		
O1S–V1–N3	166.77 (11)	N1–V1–Cl1	100.56 (10)
O1S–V1–N1	83.92 (10)	N2–V1–Cl1	173.41 (9)
N3–V1–N1	84.43 (11)	O1S–V1–Cl2	93.35 (8)
O1S–V1–N2	89.47 (10)	N3–V1–Cl2	96.79 (8)
N3–V1–N2	82.65 (10)	N1–V1–Cl2	168.16 (9)
N1–V1–N2	81.71 (11)	N2–V1–Cl2	86.76 (8)
O1S–V1–Cl1	96.90 (9)	Cl1–V1–Cl2	91.20 (7)
N3–V1–Cl1	91.38 (9)		

H atoms were positioned geometrically (B–H = 1.00, C–H = 0.95–0.98 \AA) and refined using a riding model with fixed individual displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{B,C})$ and $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$]. As previously noted, the structure solution can be modeled with the appropriate molecular formula $\text{TpVCl}_2(\text{DMF})$ resulting in a reliability index of 0.073. The displacement ellipsoid of Cl1, however, was unusually large [$U_{\text{eq}} = 0.0796(7) \text{\AA}^2$ for Cl1 versus $0.0529(4) \text{\AA}^2$ for Cl2] and the V–Cl1 bond length was unusually short [2.179 (3) \AA], attracting our attention. Subsequently both Cl atoms were modeled for disorder with an O atom. Each Cl/O disorder was refined independently. The occupancies of one Cl/O pair refined to 92:8 and, as such, Cl2 was modeled as 100% Cl in subsequent refinement cycles. The remaining Cl1/O1A pair occupancies were allowed to continue to vary freely and settled at the 53 (1):47 (1) ratio reported in the comment. We have collected data on more than one of these crystals and note a variability in the oxygen content of the crystals.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduc-

tion: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

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