

Chloro[hydrotris(pyrazol-1-yl)borato]oxo-(1*H*-pyrazole)vanadium(IV)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

The title compound,  $[V(C_9H_{10}BN_6)ClO(C_3H_4N_2)]$  or  $TpVOCl(pzH)$ , exists in the solid state as discrete molecules with  $V^{IV}$  in a pseudo-octahedral coordination geometry. The complex has three pyrazole units of the  $Tp$  ligand bound to one 'face' of the vanadium center and chloro, oxo and pyrazole ligands bound to the other face. Bond lengths and angles are typical of structurally characterized complexes of known complexes of vanadium with substituted  $Tp$  ligands.

Received 3 October 2005

Accepted 18 October 2005

Online 27 October 2005

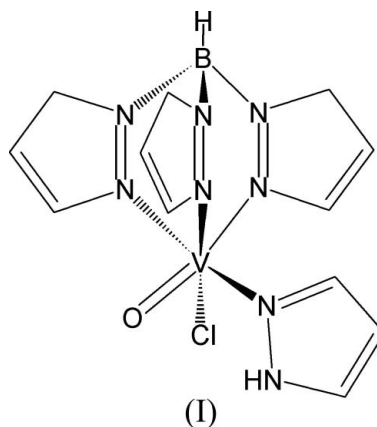
## Key indicators

Single-crystal X-ray study  
 $T = 100$  K  
Mean  $\sigma(C-C) = 0.005$  Å  
 $R$  factor = 0.073  
 $wR$  factor = 0.126  
Data-to-parameter ratio = 17.0

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

## Comment

In the course of our 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 *et al.*, 1996, 1996*a,b*; Otieno *et al.*, 1996), including the complex  $TpVCl_2(DMF)$ , (II), which, suprisingly, involves exposure of the vanadium(III) starting complex to air to drive the reaction (Kime-Hunt *et al.*, 1989; Mohan *et al.*, 1992). Typically,  $V^{III}$  oxidizes quickly to  $V^{IV}$  or  $V^V$  when exposed to air. However, complex (II) is a remarkably air-stable material; it can remain exposed for months and remain green, but it is very air-sensitive when it is in solution.



Upon stirring complex (II) in solution under aerobic conditions, Otieno *et al.* (1996) reported that the complex turned blue. This blue species was believed to be the oxidized product  $TpVOCl(DMF)$ . In our efforts to crystallize compound (II) from acetone (McDonald & McLauchlan, 2005) under aerobic conditions we also isolated the title compound,  $TpVOCl(pzH)$ , (I), as blue crystals. Complex (I) was expected to be  $TpVOCl(DMF)$ , as the crystals were blue and isolated in air in moist acetone, but instead a hydrolysis

product was isolated. This hydrolysis of the scorpionate ligand is similar to that noted with hydrotris(pyrazolyl)borates; hydrolysis has been noted before with hydrotris(3,5-dimethylpyrazolyl)borate ( $\text{Tp}^{\text{Me}_2}$ ) and hydrotris(3,5-diisopropylpyrazolyl)borate ( $\text{Tp}^{\text{iPr}_2}$ ) complexes with vanadium (Kime-Hunt *et al.*, 1989, Collison *et al.*, 1993, Kosugi *et al.*, 1999).

A displacement ellipsoid plot of (I) is shown in Fig. 1. The vanadium center possesses pseudo-octahedral geometry, with three pyrazole units of the Tp ligand bound to one 'face' of the vanadium center and chloro, oxo, and pyrazole ligands bound to the other face. This octahedral geometry has been reported to be unusual for  $\text{V}^{\text{IV}}$  complexes (Kosugi *et al.*, 1999). However,  $\text{Tp}^{\text{R}^2}\text{VOClX}$  complexes for  $X = \text{benzoate}$ , chloride, acetonitrile, and pyridine, as well as the  $\text{Tp}^{\text{R}^2}\text{VOX}_2$  complex with  $X = N,N$ -dipropyldithiocarbamate, have all been structurally characterized (Kosugi *et al.*, 1999; Kime-Hunt *et al.*, 1989; Heimer & Cleland, 1990). Each of these reports, however, involves the more structurally bulky  $\text{Tp}^{\text{Me}_2}$  or  $\text{Tp}^{\text{iPr}_2}$  groups. The  $\text{V}-\text{N}(\text{pzH})$  bond lengths range from 2.100 (3) to 2.273 (3) Å and interligand angles range from 80.3 (1) to 100.0 (1)°. These bond lengths and angles are typical of structurally characterized complexes of known complexes of V with  $\text{Tp}^{\text{R}^2}$  (Kime-Hunt *et al.*, 1989; Heiner & Cleland, 1990; Mokry *et al.*, 1994; Malinak *et al.*, 1995; Dean *et al.*, 1996, 1996*a,b*; Otieno *et al.*, 1996; Rehder *et al.*, 1998; Kosugi *et al.*, 1999; Hauser *et al.*, 2002).

### Experimental

Blue prismatic crystals of the title compound,  $\text{TpVOCl}(\text{pzH})$ , were prepared by evaporation of a moist acetone solution of  $\text{TpVCl}_2(\text{DMF})$  in aerobic conditions.  $\text{TpVCl}_2(\text{DMF})$  was prepared according to the procedure of Mohan *et al.* (1992).

#### Crystal data

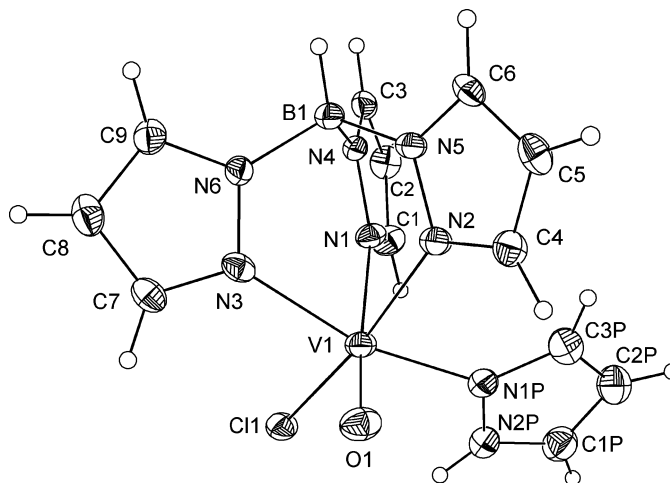
$[\text{V}(\text{C}_9\text{H}_{10}\text{BN}_6)\text{ClO}(\text{C}_3\text{H}_4\text{N}_2)]$	$D_x = 1.583 \text{ Mg m}^{-3}$
$M_r = 383.51$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 7083 reflections
$a = 8.3295 (5) \text{ \AA}$	$\theta = 4.0\text{--}28.5^\circ$
$b = 12.6110 (8) \text{ \AA}$	$\mu = 0.80 \text{ mm}^{-1}$
$c = 15.3711 (12) \text{ \AA}$	$T = 100 (2) \text{ K}$
$\beta = 94.642 (6)^\circ$	Prism, blue
$V = 1609.34 (19) \text{ \AA}^3$	$0.07 \times 0.05 \times 0.02 \text{ mm}$
$Z = 4$	

#### Data collection

Oxford Diffraction Xcalibur3 diffractometer equipped with a CCD detector	3685 independent reflections
$\varphi$ and $\omega$ scans	3483 reflections with $I > 2\sigma(I)$
Absorption correction: analytical (Clark & Reid, 1995)	$R_{\text{int}} = 0.060$
$T_{\text{min}} = 0.901$ , $T_{\text{max}} = 0.962$	$\theta_{\text{max}} = 27.5^\circ$
23290 measured reflections	$h = -10 \rightarrow 10$
	$k = -16 \rightarrow 16$
	$l = -19 \rightarrow 19$

#### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0298P)^2 + 3.4547P]$
$R[F^2 > 2\sigma(F^2)] = 0.074$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.126$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.24$	$\Delta\rho_{\text{max}} = 0.71 \text{ e \AA}^{-3}$
3685 reflections	$\Delta\rho_{\text{min}} = -0.62 \text{ e \AA}^{-3}$
217 parameters	
H-atom parameters constrained	



**Figure 1**  
Displacement ellipsoid plot, at the 50% probability level, of (I).

**Table 1**

Selected geometric parameters (Å, °).

$\text{Cl1}-\text{V1}$	2.3708 (10)	$\text{N2}-\text{V1}$	2.100 (3)
$\text{N1}-\text{V1}$	2.273 (3)	$\text{N3}-\text{V1}$	2.101 (3)
$\text{N1P}-\text{V1}$	2.133 (3)	$\text{O1}-\text{V1}$	1.609 (3)
$\text{O1}-\text{V1}-\text{N2}$	93.40 (12)	$\text{N3}-\text{V1}-\text{N1}$	80.81 (11)
$\text{O1}-\text{V1}-\text{N3}$	100.02 (13)	$\text{N1P}-\text{V1}-\text{N1}$	80.29 (11)
$\text{N2}-\text{V1}-\text{N3}$	85.41 (11)	$\text{O1}-\text{V1}-\text{Cl1}$	98.55 (10)
$\text{O1}-\text{V1}-\text{N1P}$	98.67 (13)	$\text{N2}-\text{V1}-\text{Cl1}$	167.98 (8)
$\text{N2}-\text{V1}-\text{N1P}$	90.56 (11)	$\text{N3}-\text{V1}-\text{Cl1}$	91.19 (8)
$\text{N3}-\text{V1}-\text{N1P}$	161.07 (11)	$\text{N1P}-\text{V1}-\text{Cl1}$	88.94 (9)
$\text{O1}-\text{V1}-\text{N1}$	174.28 (12)	$\text{N1}-\text{V1}-\text{Cl1}$	87.08 (8)
$\text{N2}-\text{V1}-\text{N1}$	81.00 (11)		

H atoms were positioned geometrically ( $\text{B}-\text{H} = 1.00$ ,  $\text{N}-\text{H} = 0.88$  and  $\text{C}-\text{H} = 0.95 \text{ \AA}$ ) and refined using a riding model with fixed individual displacement parameters [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{B,C,N})$ ].

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2004); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This research was supported by Illinois State University, the National Institutes of Health (1 R25 GM073603-01), and the Illinois Board of Higher Education. CCM thanks Dr A. A. Narducci Sarjeant of Johns Hopkins University for experimental assistance and helpful discussions.

### References

- Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* **A51**, 887–897.  
 Collison, D., Eardley, D. R., Mabbs, F. E., Powell, A. K. & Turner, S. S. (1993). *Inorg. Chem.* **32**, 664–671.  
 Dean, N. S., Bond, M. R., O'Conner, C. J. & Carrano, C. J. (1996). *Inorg. Chem.* **35**, 7643–7648.  
 Dean, N. S., Mokry, L. M., Bond, M. R., O'Conner, C. J. & Carrano, C. J. (1996*a*). *Inorg. Chem.* **35**, 2818–2825.  
 Dean, N. S., Mokry, L. M., Bond, M. R., O'Conner, C. J. & Carrano, C. J. (1996*b*). *Inorg. Chem.* **35**, 3541–3547.  
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

- Hauser, C., Bill, E. & Holm, R. H. (2002). *Inorg. Chem.* **41**, 1615–1624.
- Heimer, N. E. & Cleland, W. E. Jr (1990). *Acta Cryst.* **C46**, 2049–2051.
- Kime-Hunt, E., Spartalian, K., DeRusha, M., Nunn, C. M. & Carrano, C. J. (1989). *Inorg. Chem.* **28**, 4392–4399.
- Kosugi, M., Hikichi, S., Akita, M. & Moroza, Y. (1999). *Inorg. Chem.* **38**, 2567–2578.
- McDonald, K. J. & McLauchlan, C. C. (2005). In preparation.
- Malinak, S., Demadis, K. D. & Coucouvanis, D. (1995). *J. Am. Chem. Soc.* **117**, 3126–3133.
- Mohan, M., Holmes, S. H., Butcher, R. J., Jasinski, J. P. & Carrano, C. J. (1992). *Inorg. Chem.* **31**, 2029–2034.
- Mokry, L. M., Thompson, J., Bond, M. R., Otieno, T., Mohan, M. & Carrano, C. J. (1994). *Inorg. Chem.* **33**, 2705–2706.
- Otieno, T., Mokry, L. M., Bond, M. R. & Carrano, C. J. (1996). *Inorg. Chem.* **35**, 850–856.
- Oxford Diffraction (2004). *Xcalibur CCD system* (Version 1.171.21 beta), including *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Rehder, D., Gailus, H. & Schmidt, H. (1998). *Acta Cryst.* **C54**, 1590–1592.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.