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A potential synthon for models of vanadium haloperoxidase: (3,5-dimethylpyrazole)-bis[2-hydroxy-2-methylbutanoato(1–)]-oxovanadium(IV)

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.054
wR factor = 0.144
Data-to-parameter ratio = 18.7

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

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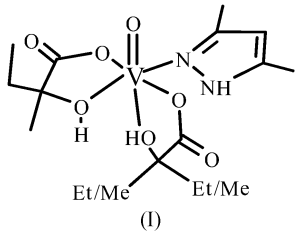
The crystal structure of the title compound, $[VO(C_5H_9O_3)_2(C_5H_8N_2)]$, has been obtained from single-crystal X-ray diffraction data measured at 150 K. The title compound provides a potential synthon for complexes that model V-containing haloperoxidases. The complex is pseudo-octahedral and the metal–oxo bond length is 1.595 (2) Å.

Comment

In support of our ongoing research programme into the bio-inorganic chemistry of vanadium, the crystal structure of the title compound, (I) (Fig. 1), has been determined to characterize this potential synthon for complexes that model the active site of V-containing haloperoxidases. The heteroleptic oxovanadium(IV) VO^{2+} complex (μ_{eff} = 1.67 BM) is coordinated by two 2-hydroxy-2-methylbutanoate ligands and a 3,5-dimethylpyrazole ligand. The complex has pseudo-octahedral coordination geometry, with the axial oxo group *trans* to the hydroxy donor atom of one of the hydroxy acid chelates [O1—V1—O2 = 172.12 (9)°]. The V atom lies 0.338 (1) Å above the plane defined by atoms O3, O5, O6 and N1, toward the oxo group.



(I)

Protonation of the hydroxy groups is indicated by a close contact distance of 2.522 (3) Å between O5 and O4 on a nearby complex at $(\frac{1}{2}-x, \frac{1}{2}-y, -z)$, and a distance of 2.611 (3) Å between O2 and O7 on another complex at $(1-x, y, \frac{1}{2}-z)$. A further hydrogen-bond interaction occurs between N2 and O6 on the neighbouring complex at $(1-x, y, \frac{1}{2}-z)$, with a donor–acceptor distance of 2.902 (3) Å. The V1—O2 bond length is 2.209 (2) Å and is significantly longer than the V1—O5 metal-to-hydroxy donor distance of 2.023 (2) Å for the second 2-hydroxy-2-methylbutanoate ligand, located exclusively in the equatorial plane. The difference in bond lengths presumably reflects the *trans* influence of the axial oxo group. Similar bond-length differences *trans* and equatorial to a vanadium oxo group are found for similar complexes reported in the literature. A VO^{3+} complex described by Mondal *et al.* (1998) has an oxo–metal to *trans* hydroxy donor atom distance of 2.312 Å. In a square-pyramidal VO^{2+}

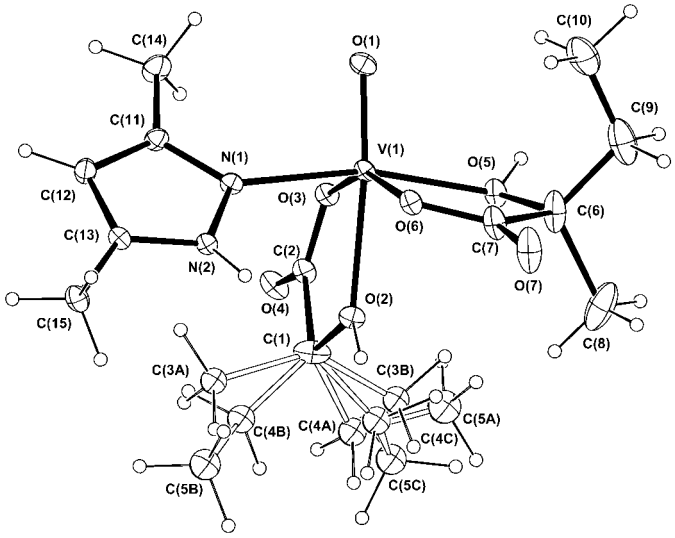


Figure 1
*ORTEP*II (Johnson, 1976; Hall *et al.*, 1999) projection of (I), with displacement ellipsoids shown at the 20% probability level.

complex related to (I), there is an equatorial hydroxy donor-to-metal distance of 1.987 (2) Å (Barr-David *et al.*, 1992).

The axial *tert*-α-hydroxy acid is enantiomerically disordered, with populations for the two isomers refined and then fixed at 0.75 (*R* isomer in the asymmetric unit) and 0.25 (*S* isomer in the asymmetric unit). The ethyl residue of the predominant enantiomer is further disordered over two orientations, with site occupancies of 0.55 and 0.2. The hydroxy acid ligand located exclusively in the equatorial plane has an *S* configuration at C6 in the asymmetric unit.

The V1—N1 bond length [2.112 (2) Å] in (I) is very close to the V—N$^{\varepsilon}$ (H486) bond length (2.11 Å) found in the crystal structure of the V-haloperoxidase obtained from *Ascophyllum nodosum* (Weyand *et al.*, 1999). The VO^{2+} motif of (I), together with the oxygen-rich coordination sphere and the single V—N(pyrazole) bond, may be a suitable precursor for model complexes of the active site of V-haloperoxidases.

Experimental

Crystals were isolated from a dichloromethane solution (1.5 ml) containing one equivalent of [hydrotris(3,5-dimethylpyrazolyl)-borato](pentane-2,4-dionato)oxovanadium(IV) (Beddoes *et al.*, 1990) and six equivalents of 2-hydroxy-2-methylbutanoic acid. After 30 min, the colour of the solution changed from blue to grey to yellow–brown. The solution was left standing in air for four weeks to afford dark-blue crystals of (I), suitable for crystal structure analysis.

Crystal data

$[VO(C_5H_9O_3)_2(C_5H_8N_2)]$
M_r = 397.32
Monoclinic, *C*2/*c*
a = 20.990 (10) Å
b = 10.140 (5) Å
c = 20.240 (10) Å
β = 114.215 (7)°
V = 3929 (3) Å^3
Z = 8
D_x = 1.343 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 1023 reflections
θ = 2.8–27.7°
μ = 0.54 mm^{-1}
T = 150 (2) K
Prismatic, blue
0.46 × 0.28 × 0.19 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.817, T_{max} = 0.904
18 722 measured reflections
4642 independent reflections
3825 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 28.3°
h = −27 → 25
k = −13 → 13
l = −26 → 26

Refinement

Refinement on F^2
$R(F)$ = 0.054
$wR(F^2)$ = 0.144
S = 1.49
4641 reflections
248 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 5P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.75 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5O···O4^{i}	0.89 (2)	1.64 (2)	2.522 (3)	171 (5)
O2—H2O···O7^{ii}	0.872 (19)	1.74 (2)	2.611 (3)	178 (4)
N2—H2N···O6^{ii}	0.82 (4)	2.10 (4)	2.902 (3)	165 (3)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{3}{2} - y, -z$; (ii) $1 - x, y, \frac{1}{2} - z$.

One of the two hydroxycarboxylate ligands is enantiomerically disordered, with the ligand sites being a mixture of both enantiomers, having populations refined and then fixed at 0.75 and 0.25. The ethyl residue of one of the enantiomers is further disordered over two sites with occupancies of 0.55 and 0.2. The structure solution in the non-centrosymmetric space group *Cc* has two complex molecules in the asymmetric unit, one of which has ligands that are the same enantiomer, whereas in the second complex, the ligands are racemic. Significant residual peaks between 1 and 1.84 in the vicinity of the ethyl and methyl residues in the *Cc* solution could not be rationally modelled as disorder. Additionally, the Flack parameter (Flack, 1983; Bernardinelli & Flack, 1985; Flack & Bernardinelli, 1999, 2000) refines to 0.48 (4) for the *Cc* model. Consequently, the disordered centrosymmetic solution was selected as providing the best model for the structure.

In general, the non-H-atom sites were modelled with anisotropic displacement parameters, and a riding model was used for the H atoms. The disordered non-H-atom sites were modelled with isotropic displacement parameters. The hydroxy atoms H2O and H5O, and the pyrazole atom H2N, were located and modelled with isotropic displacement parameters. Weak distance restraints were required for the hydroxy H-atom sites. Distance restraints were applied to the disordered residues, and the displacement parameters for atoms C4*A* and C4*C* were constrained to be the same, as were those of C3*A* and C3*B*.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT* and *XPREP* (Bruker, 2001); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *TEXSAN for Windows* (Molecular Structure Corporation, 1997), *Xtal*3.6 (Hall *et al.*, 1999), *ORTEP*II (Johnson, 1976) and *WinGX* (Farrugia, 1999).

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