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Di-μ-dioxo-bis({1-[phenyl(2-pyridyl-κN)-methylene]-2-(pyrrolidin-1-ylthiocarbonyl-κS)-hydrazinato-κN^1}oxovanadium(V))

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Key indicators

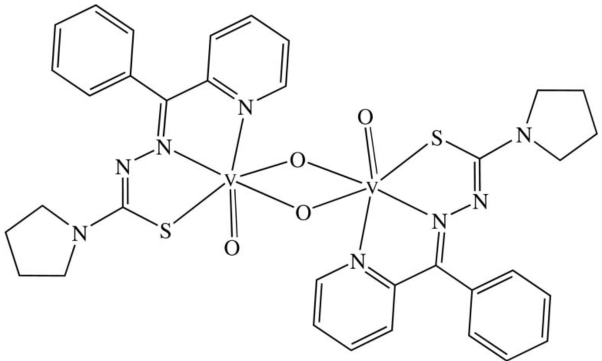
Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.005 Å
R factor = 0.051
wR factor = 0.120
Data-to-parameter ratio = 15.6

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

In the title centrosymmetric binuclear complex, $[V_2(C_{17}H_{17}N_4S)_2O_4]$, pairs of V atoms are linked by two oxo bridges. The coordination geometry at each V^V atom is distorted octahedral, involving a pyridine N atom, a thiolate S atom, an azomethine N atom from the 1-[phenyl(2-pyridyl)methylene]-2-(pyrrolidin-1-ylthiocarbonyl)hydrazine(−) ligand, and one terminal O and 2 bridging O atoms. The crystal structure is stabilized by weak intermolecular C—H···O interactions.

Comment

The chemistry of vanadium-containing complexes has been driven by its presence in biological systems. Oxovanadium(IV) and vanadate(V) are the main species present in solution under physiological conditions. The coordination chemistry of vanadium has received considerable attention since the discovery of vanadyl bromoperoxidase, from marine brown algae *Ascophyllum nodosum*. Since then several vanadium-containing enzymes have been isolated and characterized. Thus vanadium has gained status as an important element by catalysing both peroxidase and nitrogenase processes in biological systems. The title complex, (I), is a result of our attempts to synthesize a model complex from 2-benzoylpyridine pyrrolidine-1-carbothiohydrazine (HBpypTsc) and vanadium, which resulted in an unusal μ-oxo-bridged structure. The structures of HBpypTsc (Sreekanth & Kurup, 2004) and its Cu^{II} (Sreekanth & Kurup, 2003), Fe^{III} (Sreekanth & Kurup, 2004), Au^{III} (Sreekanth *et al.*, 2004), and Mn^{II} (Sreekanth *et al.*, 2006) complexes have been reported previously.



(I)

The asymmetric unit of (I) consists of one half of the $[V_2(C_{17}H_{17}N_4S)_2O_4]$ molecule; the other half is related by an inversion centre which is at the centre of the V1—O1—V1^i—O1^i ring [symmetry code: (i) $-x, -y, 1 - z$]. The coordination geometry at each V^V atom is distorted octahedral (Fig. 1), in which the equatorial plane is formed by two bridging dioxo O atoms, an azomethine N and a terminal O atom while the axial

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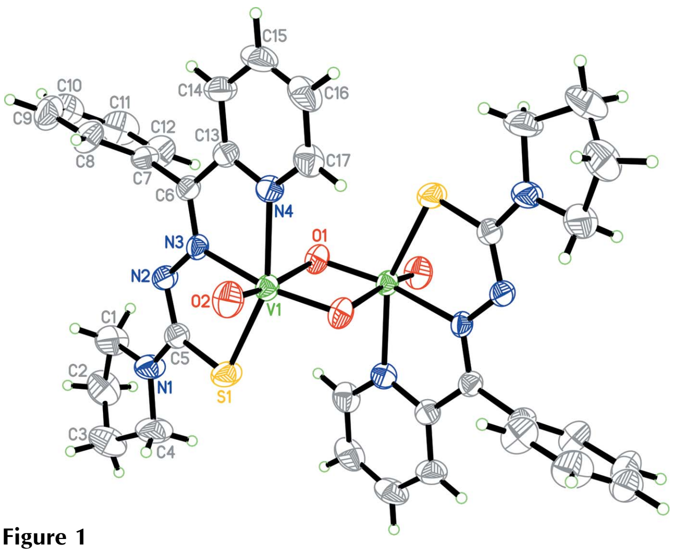

Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atomic numbering. The unlabelled atoms are related by the symmetry operator (−*x*, −*y*, 1 − *z*).

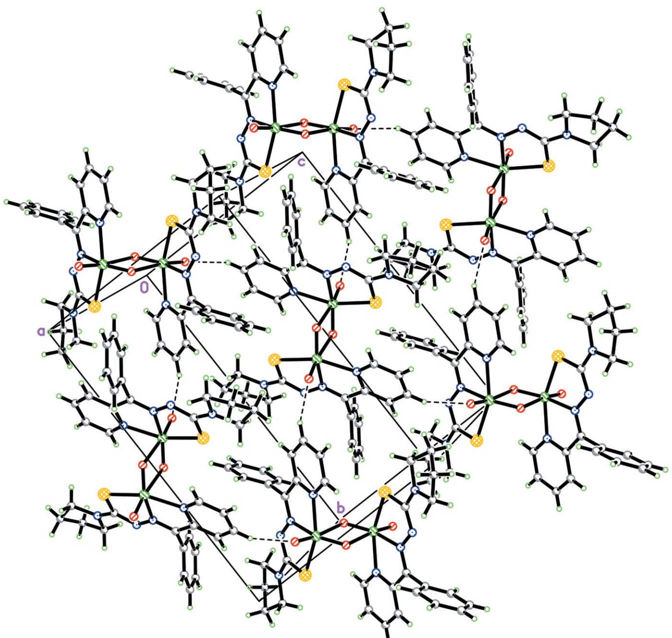

Figure 2
The crystal packing of (I), showing weak intermolecular C—H···O interactions as dashed lines.

coordination sites are occupied by a thiolate S atom and a pyridine N atom from a 1-[phenyl(2-pyridyl)methylene]-2-(pyrrolidin-1-ylthiocarbonyl)hydrazine(−) ligand. Selected bond lengths and angles are listed in Table 1. The intramolecular V···V distance is 3.169 (1) Å. Bond lengths and angles in the ligands have normal values (Allen *et al.*, 1987) and the pyridinyl rings are essentially planar. The pyrrolidine ring (N1/C1–C4) adopts an envelope conformation, with puckering parameters q_2 = 0.346 (5) Å and ω = 87.4 (7)° (Cremer & Pople, 1975); the r.m.s. deviation for atoms C1/C3/C4/N1 is 0.041 (4) Å, while atom C2 forms the flap, 0.522 (5) Å from this plane. The atoms in the methylidine-1-pyrrolidinecarbothiohydrazide unit are essentially planar (r.m.s. deviation = 0.088 Å). The phenyl ring substituent is twisted with respect to the V1/N3/C6/C13/N4/C7 plane, as reflected in the N3—C6—C7—C12 torsion angle, indicating a (−)synclinal conformation. The dihedral angle between the methylidine-1-pyrrolidinecarbothiohydrazide plane and phenyl ring is 71.72 (18)°. The tridentate ligands are *trans* to each other. The crystal structure is stabilized by intermolecular weak C—H···O interactions (Fig. 2 and Table 2).

Experimental

Vanadyl acetylacetonate (Aldrich) was used as received. The ligand HBpypTsc was synthesized by the procedure discussed elsewhere (Sreekanth & Kurup, 2004). All solvents were distilled before use. The title compound was synthesized by stirring a solution of the ligand HBpypTsc (1 mmol) in chloroform (20 ml) while adding a solution of vanadylacetyl acetonate (1 mmol) over a period of 1 h. The solution turned orange; it was filtered and allowed to stand for 6 d, giving X-ray quality single crystals of (I). Analysis calculated (found) (%): C 52.10 (52.04), H 4.32 (4.37), N 14.27 (14.28).

Crystal data

$[V_2(C_{17}H_{17}N_4S)_2O_4]$
M_r = 784.71
Monoclinic, $P2_1/c$
a = 10.3912 (8) Å
b = 17.4103 (14) Å
c = 11.0953 (7) Å
β = 118.877 (5)°
V = 1757.7 (2) Å^3
Z = 2
D_x = 1.483 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.70 mm^{-1}
T = 297 (2) K
Slab, light brown
0.52 × 0.44 × 0.18 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{\min}$ = 0.701, $T_{\max}$ = 0.881
9824 measured reflections
3801 independent reflections
3129 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.026
$\theta_{\max}$ = 27.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.120
S = 1.16
3801 reflections
243 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + 1.5976P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.41 e Å^{-3}
$\Delta\rho_{\min}$ = −0.30 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

V1—O2	1.612 (2)	V1—N3	2.184 (2)
V1—O1^i	1.6702 (19)	V1—O1	2.354 (2)
V1—N4	2.117 (2)	V1—S1	2.3899 (9)
O2—V1—O1^i	106.01 (11)	N4—V1—O1	82.77 (8)
O2—V1—N4	90.21 (11)	N3—V1—O1	74.30 (7)
O2—V1—N3	102.39 (10)	O2—V1—S1	96.26 (9)
O1^i—V1—N3	151.59 (9)	N4—V1—S1	151.20 (7)
N4—V1—N3	73.93 (9)	N3—V1—S1	77.27 (6)
O2—V1—O1	172.83 (10)	O1—V1—S1	89.25 (6)
O1^i—V1—O1	77.42 (9)	V1^i—O1—V1	102.59 (9)
N3—N2—C5—N1	−177.8 (2)	N3—C6—C7—C12	−73.8 (4)

Symmetry code: (i) −*x*, −*y*, −*z* + 1.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10*A*···O2^{ii}	0.93	2.44	3.278 (5)	149
C15—H15*A*···O2^{iii}	0.93	2.44	3.302 (4)	154

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

H atoms were placed in calculated positions, with C—H = 0.93–0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *APEX2* (Bruker, 2005); cell refinement and data reduction: *SAINT* (Bruker, 2005); program(s) used to solve and refine structure: *SHELXTL* (Sheldrick, 1998); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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