H atoms were refined with anisotropic displacement parameters. Refinement using all data (676) produced final residuals of $R = 0.033$, $wR = 0.042$. There is some disorder in the —CF_3 groups, which have three different orientations with occupancies of 0.453, 0.391 and 0.174. These were determined by fixing the displacement parameters to one value and allowing the occupancies to refine, then taking the average occupancy for the group, fixing it at that number then letting the displacement parameters refine. The *NRCCAD* diffractometer control program (Le Page, White & Gabe, 1986) was used for data collection and the *NRCVAX* system (Gabe, Le Page, Charland, Lee & White, 1989) was used for all computations.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71793 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1031]

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Oxobis(*N*-oxopyridine-2-thiolato-*N*,*O*)vanadium(IV)

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Abstract

The title compound, oxobis(pyridine-2-thiolato *N*-oxide-*N*,*O*)vanadium(IV), $[V(C_5H_4NOS)_2O]$, contains vanadium in a distorted square-pyramidal coordination geometry with a multiply bonded O atom at the apex and a basal plane defined by a *cis* S_2O_2 group of donor atoms from the organic ligands. The V—O basal distances are 1.952 (3) and 1.961 (3) Å, the V—S basal distances are 2.386 (2) and 2.361 (1) Å and the axial V═O distance is 1.593 (3) Å.

Comment

The conjugate base of 1-hydroxypyridine-2-thione (or its tautomer 2-pyridinethiol *N*-oxide) forms a variety of metal derivatives which have received extensive attention as a consequence of their antifungal and antibacterial activity (Pansy, Stander, Koerber & Donovick, 1953; Chandler & Segel, 1978; Box, Shanga, Sanghvi & Sugden, 1980; Bennett, Gannon & Onyekweln, 1982). The synthesis and characterization of several transition-metal and rare earth complexes with this ligand have been described (Robinson, 1964; Hodge, Nordquest & Blinn, 1972; West & Frank, 1979; Davidson, Preston & Russo, 1983). These authors have indicated that the formation of metal-ion complexes occurs with both the *N*-oxide O atom and the S atom serving as donors. The determination of the structures of the phenylbismuth, Zn and Ni complexes has confirmed these results (Curry & Jandacek, 1972; Barnett, Kretschmar & Hartman, 1977; Chen, Hu, Wu, Weng & Kang, 1991). Recently we reported the thermal behaviour of a number of first-row transition-metal complexes (Higes-Rolando, Pérez-Florindo &

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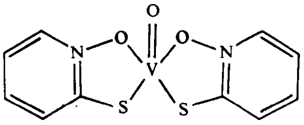
Valenzuela-Calahorro, 1991). The order of thermal stability seems to be determined by the structure of these coordination compounds. In order to explore the relationship between the structure and properties of such compounds further, the crystal structure of bis(*N*-oxopyridine-2-thiolato)oxovanadium(IV), (I), has been studied and is reported in this paper.



(I)

The title complex crystallizes as discrete monomers. The geometry of the molecule may be described as a flattened square pyramid in which the V atom is coordinated to a terminal O atom and two *N*-oxopyridine-2-thiolate ligands through the O and S atoms of each forming two five-membered rings. The two chelate rings are found to have a *cis* configuration. The whole molecule thus exhibits *pseudo*-C_s symmetry with the σ plane passing through the V—O(3) bond and the midpoints of S(1)···S(2) and O(1)···O(2).

The V—O(3) distance [1.593 (3) Å] is consistent with the presence of a V=O double bond [*i.e.* an oxovanadium(IV) moiety] and is close to the average distance of 1.598 Å found by Mayer (1988) for a substantial number of oxovanadium(IV) complexes. The V atom lies 0.642 Å above the O(1)–O(2)–S(1)–S(2) least-squares plane [the maximum deviation from which is found for O(1), 0.052 Å] towards the oxo ligand. The V—O(3) bond is tilted slightly relative to the normal to the basal plane, with which it makes an angle of 1.1°. The V—S bond lengths [2.361 (1) and 2.386 (2) Å] are slightly longer than those observed in bis[tris(*tert*-butoxo)silylthiolato]-oxovanadium(IV) (average 2.333 Å), which is the only other structurally characterized oxovanadium(IV) complex having a [(VO)S_2O_2] donor set of ligands (Preuss, Steidel & Exner, 1990), but are similar or slightly smaller than those reported for other [(VO)S_4] complexes; for example, V—S(dithiolate) = 2.378 Å (Money, Huffman & Christou, 1985) and 2.374 Å (Collison, Mabbs, Temperley, Christou & Huffman, 1988), V—S(thione) = 2.424 Å (Bristow, McAvilley, Clegg & Collison, 1989) and V—S(dithiocarbamate) = 2.402 Å (Henrick, Raston & White, 1976). The basal V—O bonds, averaging 1.956 Å, are not significantly different and fall within the usual range observed in vanadium(IV) complexes (Holloway & Melnick, 1985; Vilas Boas & Costa Pessoa, 1987; Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989).

The two five-membered chelate rings show an envelope conformation, the V atom being 0.504 and 0.561 Å out of the planes through O(1)–N(1)–C(5)–S(1) and O(2)–N(2)–C(10)–S(2), respectively. The V—O—N angles (average 119.3°) are much larger than the V—S—C angles (average 95.6°) as there is a difference in the orbitals used in the bonding of the O and S atoms: the O donor atoms are sp^2 hybridized, while the bonding orbitals of the S donor atoms are of mainly *p* character. The organic ligands are essentially planar with maximum mean-plane deviations observed for the S atoms [S(1) −0.063, S(2) −0.022 Å]. The N—O distances (average 1.347 Å) are appreciably shorter than those of 1.388 Å found in Me_3NO, where no π bonding can occur (Caron, Palenik, Goldish & Donohue, 1964). The C—S distances (average 1.710 Å) are also significantly shorter than the sum of the covalent radii for C and S atoms (1.81 Å; Pauling, 1960). These data indicate the presence of some double-bond character in the N—O bonds as well as in the C—S bonds.

Within the crystal packing the shortest intermolecular distances are found between neighbouring molecules related by inversion centres. The shortest V···V distance is 5.216 Å. The nearest intermolecular approach to the V atom is made by an S atom at distance of 4.376 Å. The shortest intermolecular contact (for non-H atoms) is 3.320 Å between C(4) and C(8^i) [symmetry code: (i) $-x$, $-y$, $-z$].

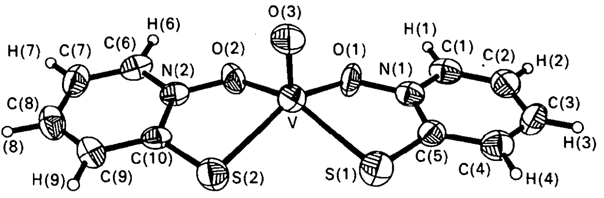


Fig. 1. *XP* routine *SHELXTL-Plus* plot of the molecule showing the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level. H atoms are plotted with arbitrary radii.

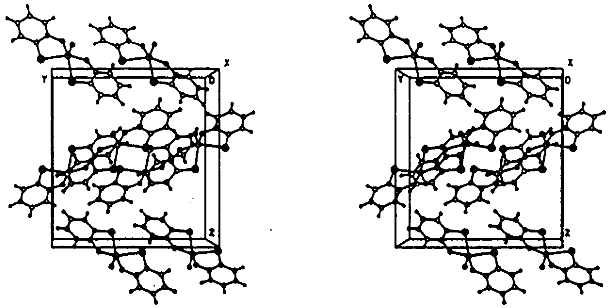


Fig. 2. Stereoview of the molecular packing in the unit cell.

Experimental

Diffraction-quality crystals of the title compound were obtained in a test tube by the reaction of an aqueous 0.025 *M* solution of the sodium salt of 1-hydroxypyridine-2-thione in a gel medium (tetramethoxysilane, 5% in water) with a supernatant 0.025 *M* solution of vanadium(III) chloride.

Crystal data

$[V(C_5H_4NOS)_2O]$
$M_r = 319.2$
Orthorhombic
Pbca
$a = 11.227\ (2)$ Å
$b = 14.155\ (5)$ Å
$c = 15.476\ (3)$ Å
$V = 2459.4\ (11)$ Å^3
$Z = 8$
$D_x = 1.726$ Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 7\text{–}20°$
$\mu = 1.107$ mm^{-1}
$T = 293\ (3)$ K
Bipyramid
0.33 × 0.30 × 0.22 mm
Violet

Data collection

Stoe Siemens AED-2 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (8 reflections, $\Delta\psi = 10°$)
$T_{\min} = 0.486$, $T_{\max} = 0.556$
3927 measured reflections
3893 independent reflections

2262 observed reflections $[F_o > 4\sigma(F_o)]$
$R_{\text{int}} = 0.024$
$\theta_{\max} = 27.5°$
$h = -3 \rightarrow 13$
$k = -3 \rightarrow 13$
$l = -3 \rightarrow 13$
4 standard reflections frequency: 120 min intensity variation: insignificant

Refinement

Refinement on *F*
$R = 0.054$
$wR = 0.030$
$S = 1.54$
2262 reflections
163 parameters
$w = 1/[\sigma^2(F_o) + 0.0001(F_o)^2]$
$(\Delta/\sigma)_{\max} = 0.004$

$\Delta\rho_{\max} = 1.56$ e Å^{-3} (near V)
$\Delta\rho_{\min} = -0.97$ e Å^{-3} [near C(10)]
Extinction correction: none
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1989)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	U_{eq}
V	0.1618 (1)	0.0972 (1)	0.0819 (1)	0.0401 (3)
S(1)	0.2435 (1)	0.1231 (1)	−0.0584 (1)	0.0498 (5)
S(2)	0.1711 (1)	−0.0681 (1)	0.0625 (1)	0.0485 (5)
O(1)	0.0675 (3)	0.2082 (2)	0.0516 (2)	0.0443 (13)
O(2)	0.0222 (3)	0.0641 (2)	0.1517 (2)	0.0437 (13)
O(3)	0.2646 (3)	0.1249 (2)	0.1482 (2)	0.0537 (13)
N(1)	0.1045 (4)	0.2648 (2)	−0.0130 (3)	0.0352 (17)
N(2)	0.0124 (3)	−0.0244 (3)	0.1831 (2)	0.0332 (16)
C(1)	0.0478 (4)	0.3489 (3)	−0.0213 (3)	0.0420 (21)
C(2)	0.0809 (5)	0.4093 (3)	−0.0858 (3)	0.0524 (21)
C(3)	0.1704 (5)	0.3859 (3)	−0.1421 (3)	0.0507 (22)
C(4)	0.2252 (4)	0.2986 (3)	−0.1342 (3)	0.0484 (21)
C(5)	0.1901 (4)	0.2353 (3)	−0.0697 (3)	0.0359 (18)
C(6)	−0.0649 (4)	−0.0398 (3)	0.2483 (3)	0.0382 (20)
C(7)	−0.0773 (5)	−0.1280 (3)	0.2828 (3)	0.0486 (21)
C(8)	−0.0084 (5)	−0.2011 (3)	0.2498 (3)	0.0468 (23)
C(9)	0.0687 (5)	−0.1853 (3)	0.1825 (3)	0.0427 (22)
C(10)	0.0791 (4)	−0.0945 (3)	0.1474 (3)	0.0349 (17)

Table 2. *Selected geometric parameters* (Å, °)

V—O(1)	1.952 (3)	N(2)—C(6)	1.348 (6)
V—O(2)	1.961 (3)	N(2)—C(10)	1.361 (6)
V—O(3)	1.593 (3)	C(1)—C(2)	1.365 (7)
V—S(1)	2.386 (2)	C(2)—C(3)	1.371 (7)
V—S(2)	2.361 (1)	C(3)—C(4)	1.387 (7)
S(1)—C(5)	1.707 (4)	C(4)—C(5)	1.397 (7)
S(2)—C(10)	1.712 (4)	C(6)—C(7)	1.366 (7)
O(1)—N(1)	1.346 (5)	C(7)—C(8)	1.390 (7)
O(2)—N(2)	1.348 (5)	C(8)—C(9)	1.372 (7)
N(1)—C(1)	1.356 (6)	C(9)—C(10)	1.401 (7)
N(1)—C(5)	1.367 (6)		
O(3)—V—S(1)	105.6 (1)	O(2)—N(2)—C(6)	118.2 (4)
O(3)—V—S(2)	107.1 (1)	O(2)—N(2)—C(10)	119.1 (4)
O(3)—V—O(1)	110.5 (1)	C(6)—N(2)—C(10)	122.7 (4)
O(3)—V—O(2)	106.5 (1)	S(1)—C(5)—N(1)	117.7 (5)
S(1)—V—S(2)	91.1 (1)	S(1)—C(5)—C(4)	124.8 (4)
S(1)—V—O(1)	82.3 (1)	S(2)—C(10)—N(2)	119.0 (4)
S(1)—V—O(2)	147.7 (1)	S(2)—C(10)—C(9)	123.2 (4)
S(2)—V—O(1)	142.3 (1)	N(1)—C(1)—C(2)	119.4 (4)
S(2)—V—O(2)	82.5 (1)	N(1)—C(5)—C(4)	117.5 (4)
O(1)—V—O(2)	83.7 (1)	N(2)—C(6)—C(7)	120.4 (4)
V—S(1)—C(5)	95.8 (2)	N(2)—C(10)—C(9)	117.8 (4)
V—S(2)—C(10)	95.3 (2)	C(1)—C(2)—C(3)	120.8 (4)
V—O(1)—N(1)	119.4 (2)	C(2)—C(3)—C(4)	119.1 (4)
V—O(2)—N(2)	119.1 (2)	C(3)—C(4)—C(5)	120.6 (4)
O(1)—N(1)—C(1)	116.6 (4)	C(6)—C(7)—C(8)	118.7 (4)
O(1)—N(1)—C(5)	120.8 (3)	C(7)—C(8)—C(9)	120.6 (4)
C(1)—N(1)—C(5)	122.5 (4)	C(8)—C(9)—C(10)	119.7 (4)

Intensity data were collected with minimum and maximum measuring times of 0.45 and 3.0 s, respectively, with a scan range of 2.00° plus *Kα* separation. Friedel pairs were measured at $-\omega$. Stationary-counter background measurements were made at the beginning and end of the scan. Intensities were corrected for Lorentz-polarization. The atomic coordinates of the V and S atoms were determined from a Patterson map using the *SHELXTL-Plus* program (Sheldrick, 1989). The remaining non-H atoms were located from subsequent Fourier maps. The positions of the H atoms were generated from assumed geometries, checked in Fourier maps and included in the calculations with estimated isotropic displacement parameters without refinement (riding model). All calculations were performed on a MicroVAX 2000 computer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1029). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Octadecacarbonylhexaosmium Chloroform Solvate

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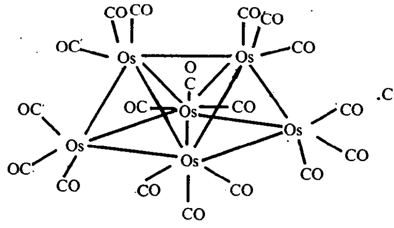
Abstract

The hexaosmium clusters in octadecacarbonyl-1κ^3C,2κ^3C,3κ^3C,4κ^3C,5κ^3C,6κ^3C-hexaosmium–chloroform (1/1), [$Os_6(CO)_{18}$].$CHCl_3$, have essentially the same internal geometry as in unsolvated $Os_6(CO)_{18}$ but participate in O···H and O···Cl contacts with the chloroform solvate molecules.

Comment

The structure of the title compound (I) consists of bicapped tetrahedral Os_4 clusters within molecules of $Os_6(CO)_{18}$, each of which interacts with molecules of the chloroform solvate through O···H contacts [O(9)···H(1S^{ii}) = 2.65 (3), O(16)···H(1S^{iii}) = 2.55 (3) Å] and O···Cl contacts [O(9)···Cl(3^{i}) = 3.010 (19) Å; symmetry codes: (i) $-1 + x, y, z$; (ii) $1 - x, -y, -z$; (iii) $1 - x, -y, 1 - z$]. The Os···Os distances within the Os_4 tetrahedron range from 2.7395 (11) to 2.8159 (12) Å, while those involving the μ_3-capping Os atoms average 2.808 (18) Å; these values are similar to those of the unsolvated molecule (Mason, Thomas & Mingos, 1973). The Os—C—O angles range from 169.6 (16) to 179.6 (17)°.



(I)

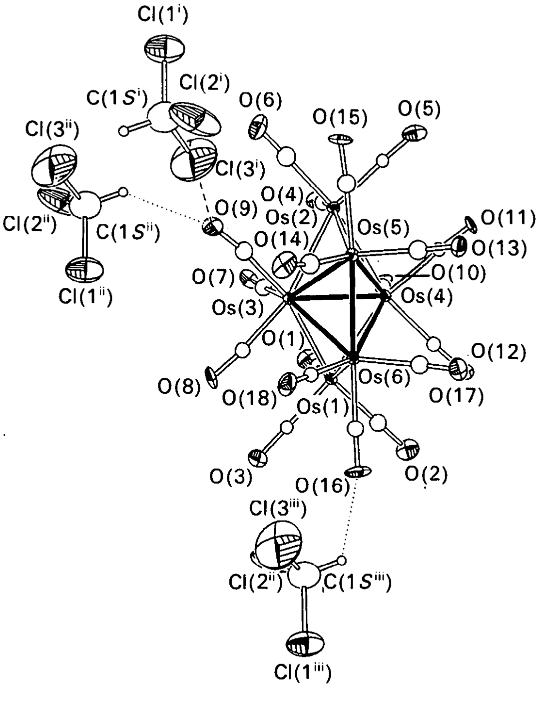


Fig. 1. One $Os_6(CO)_{18}$ molecule and the $CHCl_3$ solvate molecules with which it interacts are shown. The C atoms of the carbonyl groups bear the same numbers as the corresponding O atoms. The central Os_4 tetrahedron is indicated by solid bonds, O···H interactions by dotted lines and the Cl···O interaction by a dashed line. Displacement ellipsoids are shown at the 50% level for Os, Cl and O atoms. [Symmetry codes: (i) $-1 + x, y, z$; (ii) $1 - x, -y, -z$; (iii) $1 - x, -y, 1 - z$.]