

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1136). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Clearfield, A., Warner, D. K., Saldarriaga-Molina, C. H., Ropal, R. & Bernal, I. (1975). *Can. J. Chem.* **53**, 1622–1629.
- Collman, J. P., Hegedus, L. S., Norton, J. R. & Finke, R. G. (1987). *Principles and Applications of Organotransition Metal Chemistry*, pp. 577–617. California: University of Science Books.
- Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
- Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–S83.
- Prout, K., Cameron, T. S., Forder, R. A., Critchley, S. R., Denton, B. & Rees, G. V. (1974). *Acta Cryst.* **B30**, 2290–2304.
- Sheldrick, G. M. (1991). *SHELXTL-Plus. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
- Solovchik, G. L., Arkhireeva, T. M., Bel'skii, V. K. & Bulychov, B. M. (1988). *Metalloorg. Khim.* **1**, 226–230.

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An Oxovanadium(IV) Complex Chelated by Dipyrindyl Sulfide

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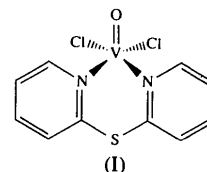
Abstract

The complex (di-2-pyridyl sulfide-*N,N'*)dichlorooxovanadium(IV), $[\text{VOCl}_2(\text{C}_{10}\text{H}_8\text{N}_2\text{S})]$, was prepared by the reaction of VCl_3 and sodium 2-mercaptopyridine *N*-oxide in ethanol solution under an atmosphere of argon. The N atoms of the dipyrindyl sulfide ligand and the two chloride ligands coordinate to the oxovanadium(IV) ion, to give a complex with square-pyramidal geometry. The

dipyrindyl sulfide ligand forms a folded six-membered chelate ring with a larger N—V—N bite angle than that formed by 2,2'-bipyridyl.

Comment

Pyridines have been utilized widely in the synthesis of transition metal complexes because of their σ/π -bonding capability. An additional and significant effect on the geometry of the complex formed is expected when multidentate polypyridines are used. 2,2'-Bipyridine (bpy) is one such ligand (Holloway & Melnik, 1985), and gives rise to a five-membered chelate ring. Ligands of the type py—X—py (bpyX; X = O or S) give six-membered chelate rings, modifying the metal–nitrogen bonding. Many vanadium complexes of bpy have been synthesized and characterized by X-ray crystallography (Boas & Pessoa, 1987), whereas vanadium complexes of bpyX are few. Here we report the structure of the title complex, (I).



The structure of the the title complex, (I), is shown in Fig. 1. The mononuclear vanadium(IV) center is ligated by an O, two Cl and two N atoms. The V—O bond distance [1.573 (2) Å] is typical for vanadium complexes having a terminal oxo group (Nugent & Mayer, 1988). The N—V—N, O—V—Cl, O—V—N and Cl—V—N bond angles indicate a typical square-pyramidal VOCl_2N_2 core with the oxo ligand occupying the apical site. The V atom lies 0.52 Å above the plane formed by the two Cl and two N atoms. The O atom of the sodium 2-mercaptopyridine *N*-oxide used in the synthesis of (I) is a likely source of the terminal oxo ligand, while the presence of vanadium may promote the ligand-coupling reaction which results in the formation of the bpyS ligand, an unexpected product of the reaction. The bpyS ligand is not planar, and the six-membered chelate ring has a folded boat-like conformation. In the chelate ring the N—V—N, V—N—C, N—C—S and C—S—C bond angles, and the V—N, N—C and C—S bond lengths all fall within the range of usual values; hence the six-membered ring is not strained. The N(1)—V(1)—N(2) bond angle is larger than that found for the rigid five-membered chelate ring formed by bpy in the oxovanadium(IV) complex $[\text{VO}(\text{bpy})(\text{N-methoxyiminodiacetate})]$ [77.4 (2)°] (de C. T. Carrondo, Duarte, Silva & da Silva, 1991). The V—N bond lengths in the title complex are longer than those in $[\text{VO}(\text{bpy})(\text{N-methoxyiminodiacetate})]$ [2.088 (4), 2.094 (4) Å]. These results show that the

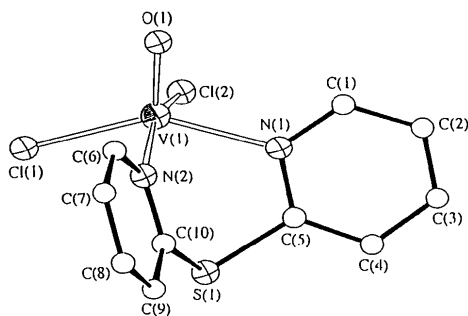


Fig. 1. An ORTEP (Johnson, 1976) view of [VOCl₂(C₁₀H₈N₂S)] with numbering scheme and displacement ellipsoids at the 30% probability level. H atoms are omitted for clarity.

folded six-membered chelating mode of the bpyS ligand results in an unstrained chelate ring. This ligand may prove useful in the synthesis of new transition metal complexes.

Neither ligand coordination nor attractive interactions with other vanadyl groups are indicated in the crystal packing. This is accounted for by the steric hindrance of the pyridine rings. A V=O...V=O interaction has been found in some oxovanadium compounds (Mathew, Carty & Palenik, 1970; Farmer & Urbach, 1974; Hills, Hughes, Leigh & Prieto-Alcón, 1993). The distances between intermolecular pyridine rings (*circa* 3.9–4.0 Å) indicate no π - π stacking interaction between them in the crystal structure.

Experimental

The title complex was prepared by the reaction of equimolar amounts of VCl₃ and sodium 2-mercaptopyridine *N*-oxide in ethanol solution under an argon atmosphere using standard Schlenk techniques. After stirring for 2 h, diethyl ether was allowed to diffuse into the green solution obtained. Green crystals were formed after six months.

Crystal data

[VOCl₂(C₁₀H₈N₂S)]

$M_r = 326.09$

Triclinic

$P\bar{1}$

$a = 7.847(2) \text{ \AA}$

$b = 12.691(3) \text{ \AA}$

$c = 7.395(2) \text{ \AA}$

$\alpha = 101.77(2)^\circ$

$\beta = 116.20(2)^\circ$

$\gamma = 74.31(2)^\circ$

$V = 633.2(3) \text{ \AA}^3$

$Z = 2$

$D_x = 1.710 \text{ Mg m}^{-3}$

Data collection

Rigaku AFC-5R diffractometer

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 11.5\text{--}16.6^\circ$

$\mu = 1.326 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Plate

$0.25 \times 0.25 \times 0.20 \text{ mm}$

Green

$R_{\text{int}} = 0.026$

$\theta_{\text{max}} = 27.5^\circ$

ω - 2θ scans

Absorption correction:

none

3129 measured reflections

2917 independent reflections

1923 observed reflections

$[I > 3\sigma(I)]$

$h = 0 \rightarrow 10$

$k = -15 \rightarrow 15$

$l = -8 \rightarrow 8$

3 standard reflections

monitored every 150

reflections

intensity decay: 4.5%

Refinement

Refinement on F

$R = 0.035$

$wR = 0.040$

$S = 1.20$

1923 reflections

186 parameters

H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.000225F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.08$

$\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
V(1)	0.21741 (8)	0.25220 (5)	0.56366 (8)	2.56 (2)
Cl(1)	0.2204 (1)	0.07135 (7)	0.4329 (1)	3.69 (4)
Cl(2)	0.0999 (1)	0.31037 (7)	0.2444 (1)	3.44 (4)
S(1)	0.6610 (1)	0.21148 (7)	0.6877 (1)	3.17 (4)
O(1)	0.0424 (3)	0.2999 (2)	0.6270 (4)	4.0 (1)
N(1)	0.3718 (4)	0.3814 (2)	0.6735 (4)	2.8 (1)
N(2)	0.4233 (4)	0.1900 (2)	0.8389 (4)	2.6 (1)
C(1)	0.2900 (6)	0.4883 (3)	0.6935 (6)	3.4 (2)
C(2)	0.3930 (7)	0.5692 (3)	0.7506 (6)	4.0 (2)
C(3)	0.5863 (7)	0.5415 (3)	0.7891 (6)	4.2 (2)
C(4)	0.6750 (6)	0.4322 (3)	0.7747 (6)	3.5 (2)
C(5)	0.5634 (5)	0.3548 (3)	0.7168 (5)	2.7 (1)
C(6)	0.3779 (6)	0.1649 (3)	0.9765 (5)	3.1 (2)
C(7)	0.5160 (6)	0.1195 (3)	1.1501 (6)	3.5 (2)
C(8)	0.7078 (6)	0.0984 (3)	1.1820 (6)	3.8 (2)
C(9)	0.7578 (6)	0.1250 (3)	1.0428 (5)	3.2 (2)
C(10)	0.6110 (5)	0.1715 (3)	0.8738 (5)	2.6 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

V(1)—Cl(1)	2.300 (1)	N(2)—C(10)	1.339 (4)
V(1)—Cl(2)	2.322 (1)	C(1)—C(2)	1.364 (5)
V(1)—O(1)	1.573 (2)	C(2)—C(3)	1.370 (6)
V(1)—N(1)	2.116 (3)	C(3)—C(4)	1.379 (6)
V(1)—N(2)	2.107 (3)	C(4)—C(5)	1.371 (5)
S(1)—C(5)	1.781 (3)	C(6)—C(7)	1.375 (5)
S(1)—C(10)	1.782 (3)	C(7)—C(8)	1.373 (6)
N(1)—C(1)	1.344 (4)	C(8)—C(9)	1.378 (5)
N(1)—C(5)	1.350 (4)	C(9)—C(10)	1.378 (5)
N(2)—C(6)	1.333 (4)		
Cl(1)—V(1)—Cl(2)	91.98 (4)	C(6)—N(2)—C(10)	118.3 (3)
Cl(1)—V(1)—O(1)	110.5 (1)	N(1)—C(1)—C(2)	122.2 (4)
Cl(1)—V(1)—N(1)	146.31 (8)	C(1)—C(2)—C(3)	119.9 (4)
Cl(1)—V(1)—N(2)	86.00 (8)	C(2)—C(3)—C(4)	119.7 (4)
Cl(2)—V(1)—O(1)	103.3 (1)	C(3)—C(4)—C(5)	118.1 (4)
Cl(2)—V(1)—N(1)	86.86 (8)	S(1)—C(5)—N(1)	115.3 (2)
Cl(2)—V(1)—N(2)	157.93 (8)	S(1)—C(5)—C(4)	122.0 (3)
O(1)—V(1)—N(1)	102.4 (1)	N(1)—C(5)—C(4)	122.7 (3)
O(1)—V(1)—N(2)	98.0 (1)	N(2)—C(6)—C(7)	122.4 (4)
N(1)—V(1)—N(2)	82.8 (1)	C(6)—C(7)—C(8)	118.7 (4)
C(5)—S(1)—C(10)	97.2 (1)	C(7)—C(8)—C(9)	119.7 (4)
V(1)—N(1)—C(1)	124.3 (2)	C(8)—C(9)—C(10)	118.1 (4)
V(1)—N(1)—C(5)	117.6 (2)	S(1)—C(10)—N(2)	115.8 (2)
C(1)—N(1)—C(5)	118.0 (3)	S(1)—C(10)—C(9)	121.5 (3)
V(1)—N(2)—C(6)	124.1 (2)	N(2)—C(10)—C(9)	122.7 (3)
V(1)—N(2)—C(10)	117.6 (2)		

Weak reflections with $I < 10.0\sigma(I)$ were scanned a second time and the counts were accumulated to assure good counting statistics. The structure was solved by direct methods using *MITHRIL* (Gilmore, 1984) in the *TEXSAN* package (Molecular Structure Corporation, 1989). H atoms were placed in calculated positions ($C-H = 1.08 \text{ \AA}$).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, and a packing diagram have been deposited with the IUCr (Reference: AS1119). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Boas, V. L. & Pessoa, J. C. (1987). *Vanadium. Comprehensive Coordination Chemistry*, Vol. 3, edited by G. Wilkinson, R. D. Gillard & J. A. McCleverty, pp. 453–583. Oxford: Pergamon Press.
- Carrondo, M. A. A. F. de C. T., Duarte, M. T. L. S., Silva, J. A. L. & da Silva, J. J. R. F. (1991). *Polyhedron*, **10**, 73–77.
- Farmer, R. L. & Urbach, F. L. (1974). *Inorg. Chem.* **13**, 587–592.
- Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
- Hills, A., Hughes, D. L., Leigh, G. J. & Prieto-Alcón, R. (1993). *J. Chem. Soc. Dalton Trans.* pp. 3609–3617.
- Holloway, C. E. & Melnik, M. (1985). *Inorg. Chem. Rev.* **7**, 75–159.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.
- Mathew, M., Carty, A. J. & Palenik, G. J. (1970). *J. Am. Chem. Soc.* **92**, 3197–3198.
- Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Nugent, W. A. & Mayer, J. M. (1988). *Metal-Ligand Multiple Bonds*. New York: Wiley Interscience.

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Bis(η^5 -indenyl)tetrakis(μ -iodo)dimolybdenum($Mo-Mo$)

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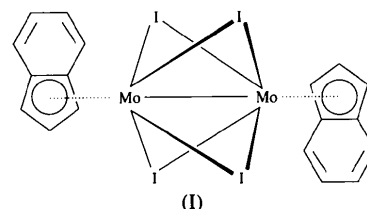
Abstract

The title compound, $[Mo_2(I)_4(C_9H_7)_2]$, is synthesized by the reaction of $MoI_3(thf)_3$ ($thf = \text{tetrahydrofuran}$) and sodium indenyl, followed by the further reaction of an intermediate product with tetraphenylphospho-

nium iodide to form tetraphenylphosphonium indenyl-triiodomolybdate. The title compound forms from the latter compound by loss of tetraphenylphosphonium iodide. The product is a tetra- μ -iodo-bridged dinuclear molybdenum complex with two terminal indenyl ligands. The indenyl groups are η^5 -bonded to the Mo atoms. The molecule sits on a crystallographic inversion center and has non-crystallographic symmetry C_{2h} . The metal-metal distance is $2.720(4) \text{ \AA}$.

Comment

The title compound, (I), was obtained from an attempt to grow crystals of tetraphenylphosphonium indenyl-triiodomolybdate, whose structure at present remains unknown.



Although crystals of the title compound were found to be poorly formed and give only weak X-ray diffraction peaks with broad and irregular profiles, the structural analysis was carried out in order to identify the product and permit the synthetic program to move forward. Since techniques are now commonly available for carrying out analyses on problematic samples (Sheldrick, 1993), a meaningful refinement and useful analysis turned out to be possible.

The title compound crystallizes with one half-molecule per asymmetric unit. The molecule sits across a crystallographic inversion center. The indenyl groups occupy terminal positions and are η^5 -bonded to the Mo atoms through the five-membered rings of the indenyls, as can be seen in Fig. 1. The Mo—C distances lie in the range $2.18(2)$ – $2.41(2) \text{ \AA}$. The local twofold axis of the indenyl group bisects a projection of the planar $Mo_2(\mu-I)$ systems. That is, if the molecule is viewed from end to end, the long axes of the indenyl groups are seen superposed with the bisector of opposite pairs of I—Mo—I bond angles. The overall symmetry of the dinuclear complex, including noncrystallographic symmetry, is thus C_{2h} . The mirror plane of the chemical point group runs longitudinally through the two indenyl ligands and bisects the I—Mo—I angles. Neighboring molecules form weak but energetically favorable packing interactions. Each terminal indenyl group of one molecule is related by a crystallographic inversion center to an indenyl group of another molecule, in such a way that the two groups are almost eclipsed. The interplanar distance is $3.41(1) \text{ \AA}$, which is almost identical to the stacking distance in graphite (Pauling, 1960). This indicates a weak van der Waals attraction, which is