Table 3. *Torsion angles* (°)

Cl(1)—Cu—N(1)—C(1N1)	62·5 (8)	Cl(1)—Cu—N(7)—C(7N2)	61·2 (8)
Cl(1)—Cu—N(1)—C(1N2)	−61·5 (7)	Cl(2)—Cu—N(7)—C(6)	−71·2 (7)
Cl(1)—Cu—N(1)—C(2)	−179·4 (7)	Cl(2)—Cu—N(7)—C(7N1)	49·8 (8)
Cl(2)—Cu—N(1)—C(1N1)	−46·9 (8)	Cl(2)—Cu—N(7)—C(7N2)	170·1 (8)
Cl(2)—Cu—N(1)—C(1N2)	−170·9 (7)	N(1)—Cu—N(7)—C(6)	65·6 (12)
Cl(2)—Cu—N(1)—C(2)	71·2 (7)	N(1)—Cu—N(7)—C(7N1)	−173·4 (9)
O(4)—Cu—N(1)—C(1N1)	−136·5 (8)	N(1)—Cu—N(7)—C(7N2)	−53·1 (13)
O(4)—Cu—N(1)—C(1N2)	99·5 (7)	O(4)—Cu—N(7)—C(6)	18·6 (7)
O(4)—Cu—N(1)—C(2)	−18·4 (7)	O(4)—Cu—N(7)—C(7N1)	139·6 (9)
N(7)—Cu—N(1)—C(1N1)	176·7 (9)	O(4)—Cu—N(7)—C(7N2)	−100·1 (8)
N(7)—Cu—N(1)—C(1N2)	52·6 (12)	Cu—N(1)—C(2)—C(3)	44·9 (11)
N(7)—Cu—N(1)—C(2)	−65·2 (11)	C(1N1)—N(1)—C(2)—C(3)	165·6 (10)
Cl(1)—Cu—O(4)—C(3)	71·0 (11)	C(1N2)—N(1)—C(2)—C(3)	−72·0 (12)
Cl(1)—Cu—O(4)—C(5)	−66·7 (12)	N(1)—C(2)—C(3)—O(4)	−53·6 (12)
Cl(2)—Cu—O(4)—C(3)	−112·3 (7)	C(2)—C(3)—O(4)—Cu	37·6 (11)
Cl(2)—Cu—O(4)—C(5)	110·1 (8)	C(2)—C(3)—O(4)—C(5)	174·6 (10)
N(1)—Cu—O(4)—C(3)	−11·6 (8)	Cu—O(4)—C(5)—C(6)	−39·2 (11)
N(1)—Cu—O(4)—C(5)	−149·2 (8)	C(3)—O(4)—C(5)—C(6)	−176·4 (10)
N(7)—Cu—O(4)—C(3)	149·3 (8)	O(4)—C(5)—C(6)—N(7)	56·0 (12)
N(7)—Cu—O(4)—C(5)	11·7 (8)	C(5)—C(6)—N(7)—Cu	−47·6 (11)
Cl(1)—Cu—N(7)—C(6)	179·8 (7)	C(5)—C(6)—N(7)—C(7N1)	−169·4 (11)
Cl(1)—Cu—N(7)—C(7N1)	−59·1 (8)	C(5)—C(6)—N(7)—C(7N2)	71·7 (13)

parameters for all non-H atoms, H atoms in fixed, calculated positions, secondary-extinction parameter refined to 0·0017 (7) × 10^{-4}. At final convergence, $R = 0{\cdot}0753$, $wR = 0{\cdot}1021$, $S = 1{\cdot}161$ for 128 parameters, max. shift/e.s.d. in final cycle 0·02, max. and min. residues in final difference Fourier synthesis 0·84, −0·90 e Å^{-3} respectively. The weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}000214F^2$ gave satisfactory agreement analyses. Scattering factors were inlaid (Sheldrick, 1976) except for Cu (Cromer & Mann, 1968). Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, while selected bond lengths, angles and torsion angles appear in Tables 2 and 3.* The atom-numbering scheme for the molecule is shown in Fig. 1, which was generated using *ORTEP* (Mallinson & Muir, 1985). Molecular geometry calculations were performed using *CALC* (Gould & Taylor, 1985). The high *R* values reflect the poor quality of the crystal, which was the best that could be obtained.

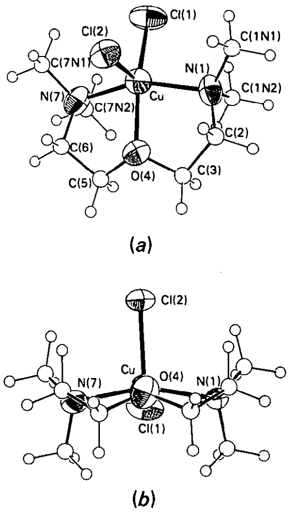

Fig. 1. (*a*) A general view of the molecule showing atom-numbering scheme. (*b*) A view parallel to the mean basal plane defined by Cl(1), N(1), N(7) and O(4). In both views thermal ellipsoids are drawn at the 30% probability level, excepting those of C and H which have artificial radii of 0·10 and 0·15 Å respectively for clarity.

We thank the SERC for funding towards the purchase of a diffractometer.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and details of least-squares mean planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51105 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1988). C**44**, 1834–1836

Structure of Di-μ-thio-bis[(diethyldithiophosphinato)thiotungsten(V)]

By Hartmut Wunderlich

Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf, Universitätsstrasse 1,
D-4000 *Düsseldorf, Federal Republic of Germany*

(*Received* 11 *September* 1987; *accepted* 31 *May* 1988)

Abstract. $[W_2S_4\{(C_2H_5)_2PS_2\}_2]$, $M_r = 802{\cdot}4$, monoclinic, $P2_1/c$, $a = 12{\cdot}059\ (3)$, $b = 12{\cdot}691\ (2)$, $c = 14{\cdot}697\ (4)$ Å, $\beta = 101{\cdot}25\ (2)°$, $V = 2206\ (1)$ Å^3, $Z = 4$, $D_m = 2{\cdot}41$, $D_x = 2{\cdot}42$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71073$ Å, $\mu = 12{\cdot}02$ mm^{-1}, $F(000) = 1496$, room temperature, $R = 0{\cdot}037$ for 4877 observed reflections

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and 182 parameters. Intensities corrected by empirical absorption correction. The complex contains two pentacoordinated W atoms bridged by two S atoms. The configuration of the terminal S atoms is *syn*. There are three different W—S distances with averaged lengths of 2·114 (2) (terminal), 2·320 (2) (bridging), and 2·470 (2) Å (to ligands). The W—W distance of 2·807 (1) Å can be regarded as a single bond. The coordination of the W atoms is distorted square-pyramidal.

Experimental. The preparation of the compound has been reported by Keck, Kuchen, Mathow, Meyer, Mootz & Wunderlich (1981) and yielded well shaped crystals of intensive red color. Photographs showed monoclinic symmetry and systematic absences of the unique space group $P2_1/c$ [fully reduced mesh, cell choice 1, *International Tables for Crystallography* (1983)]. $D_m = 2{\cdot}41$ Mg m^{-3} was determined by flotation, giving $Z = 4$ formula units per cell. A crystal shaped almost as a regular triangle (edges 0·35, thickness 0·1 mm) was used for the determination of the lattice parameters (15 reflections, $33 < 2\theta < 40°$, Mo $K\alpha$, Syntex $P2_1$, crystal monochromator) and for the data collection. The intensities of all 6408 symmetry-independent reflections up to $(\sin\theta)/\lambda = 0{\cdot}704$ Å^{-1} were measured with an ω scan of 0·7° and variable speeds between 0·7 and 58·6° min^{-1}. The indices ranged from 0 to $h = 16$, $k = 17$ and from $l = -20$ to 20. Three standard reflections ($11\bar{1}$, $\bar{3},7,\overline{10}$, $\bar{6}7\bar{4}$) measured every 200 reflections did not vary significantly. For an empirical absorption correction a ψ scan with increments of 12° for 13 reflections was performed and resulted in max. and min. transmissions of 0·933 and 0·357, respectively. By a ψ scan (10 steps of 1°) of a few selected weak reflections marked with errors tremendous effects of multiple reflection could be evidenced. Thus, the background intensities were corrected for asymmetry (Wunderlich, 1986) and 49 reflections showing $F_o \gg F_c$ had to be eliminated in a later stage. The final set of data contained 4877 unique observed ($F > 4\sigma_F$) and 1482 unobserved reflections.

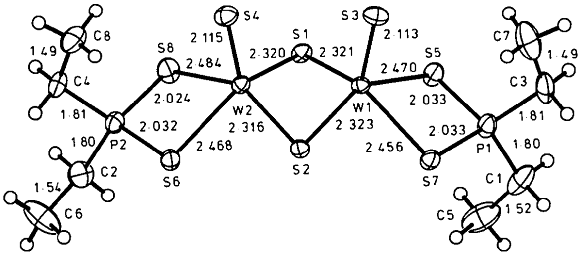

Fig. 1. Crystal structure of the title complex with displacement ellipsoids of 25% probability and bond lengths (Å). The e.s.d.'s are: W—S 0·002, P—S 0·003, P—C 0·01 and C—C 0·01–0·02 Å. The radius of the calculated H atoms was set to 0·15 Å.

Table 1. *Atomic positions and equivalent isotropic displacement parameters* (Å^2 × 10^2) *of the non-*H *atoms with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}(U_{11}a^{*2}a^2 + 2U_{12}a^*b^*ab\cos\gamma + \ldots).$$

	x	y	z	$U_{\rm eq}$
W1	0·19336 (2)	0·53657 (2)	0·75750 (2)	3·34 (1)
W2	0·27238 (2)	0·38560 (2)	0·64589 (2)	3·55 (1)
S1	0·1183 (2)	0·4969 (1)	0·6037 (1)	4·29 (5)
S2	0·3787 (1)	0·4810 (1)	0·7665 (1)	3·85 (5)
S3	0·1174 (2)	0·4359 (2)	0·8422 (1)	5·58 (7)
S4	0·2186 (2)	0·2472 (2)	0·7047 (1)	5·50 (7)
S5	0·0619 (2)	0·6868 (2)	0·7216 (1)	5·26 (6)
S6	0·4634 (2)	0·3501 (2)	0·6164 (1)	4·74 (6)
S7	0·2920 (2)	0·6737 (2)	0·8605 (1)	4·83 (6)
S8	0·2328 (2)	0·3512 (2)	0·4762 (1)	5·89 (7)
P1	0·1495 (2)	0·7631 (2)	0·8347 (1)	5·45 (7)
P2	0·3919 (2)	0·2944 (2)	0·4888 (1)	4·84 (6)
C1	0·1778 (10)	0·8987 (7)	0·8107 (7)	8·7 (4)
C2	0·4596 (8)	0·3445 (8)	0·3990 (5)	6·9 (3)
C3	0·0775 (8)	0·7680 (9)	0·9319 (6)	7·7 (4)
C4	0·3986 (8)	0·1523 (7)	0·4819 (6)	6·8 (3)
C5	0·2357 (12)	0·9169 (10)	0·7294 (8)	11·3 (5)
C6	0·5831 (10)	0·3092 (12)	0·4085 (8)	11·6 (6)
C7	0·0451 (11)	0·6646 (11)	0·9673 (7)	11·3 (6)
C8	0·3512 (10)	0·0891 (7)	0·5507 (6)	7·7 (4)

Table 2. *Bond angles* (°) *at the* W *atoms* (*e.s.d.'s are* 0·1°)

S3—W1—S1	108·1	S4—W2—S1	108·7
S3—W1—S2	107·8	S4—W2—S2	106·8
S3—W1—S5	105·0	S4—W2—S6	107·0
S3—W1—S7	106·2	S4—W2—S8	104·5
S1—W1—S2	100·2	S1—W2—S2	100·4
S1—W1—S5	81·2	S1—W2—S6	142·3
S1—W1—S7	143·5	S1—W2—S8	81·4
S2—W1—S5	144·8	S2—W2—S6	80·4
S2—W1—S7	80·5	S2—W2—S8	146·0
S5—W1—S7	78·4	S6—W2—S8	78·2

Initial coordinates of the W atoms were obtained from the Patterson function; the structure was completed in the usual way. All H atoms were constructed and used as fixed-atom contributions during the final refinement on F (182 parameters) converging at $S = 1{\cdot}59$ with all $\Delta/\sigma < 0{\cdot}05$. The isotropic extinction parameter was refined to 3·6 (1) × 10^{-6}, weights were derived from $1/w = \sigma_F{}^2 + cF_o{}^2$ with c refined to 0·00009. Atomic scattering factors including corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974); $R = 0{\cdot}037$ (0·055) and $wR = 0{\cdot}035$ (0·037) for the observed (all) data. Residual electron densities were in the range from −1·5 to +1·3 e Å^{-3}. The final parameters of the non-H atoms are given in Table 1.* The U_{ii} values of the C atoms range up to 0·17 Å^2 probably reflecting insufficient absorption correction and further

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* Lists of anisotropic displacement parameters, calculated H-atom positions, bond angles, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51089 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

data errors. All calculations were carried out with the program system *SHELXTL* (Sheldrick, 1983).

Bond lengths of the complex are shown in Fig. 1, main bond angles are given in Table 2. From these the distortion from an ideal square-pyramidal coordination of the W atoms with the terminal S atoms in axial position can be seen. The four S atoms forming the base of the two pyramids are planar within 0·05 Å. The axes W1—S3 and W2—S4 of the pyramids are tilted by 18·9°. The torsion angle S3—W1—W2—S4 is −1·0 (1)° which means that the two terminal S atoms are in an exact *syn* configuration as already postulated by spectroscopy (Keck, Kuchen & Mathow, 1986). There are three groups of W—S distances, and the C—C distances are shortened by large displacement parameters caused by the data errors. The complex is close to the point symmetry *m* with atoms W1, W2, S3, S4, P1, P2, C1 to C5, and C7 planar within 0·09 Å. Atoms C6 and C8 deviate 0·18 and 1·18 Å, respectively, from this least-squares plane.

Related literature. Crystal structures of two modifications of $W_2S_4[S_2P(OEt)_2]_2$ have been reported (Drew, Hobson, Mumba, Rice & Turp, 1987) and reveal similar geometries although the comparison is limited by the low accuracy of these structures. The main core *syn*-$W_2S_2(\mu\text{-}S)_2^{2+}$ itself has been characterized in several crystal structures as in $[N(C_2H_5)_2]_2W_2S_2(\mu\text{-}S)_2(S_4)_2$ (Cohen & Stiefel, 1985, and literature cited therein).

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Acta Cryst. (1988). C**44**, 1836–1838

Structure of *mer*-Trichlorotris(pyridyl)osmium(III)

BY ALEXANDER J. BLAKE, GRAHAM A. HEATH,* GRAHAM SMITH AND LESLEY J. YELLOWLEES

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland

AND DAVID W. A. SHARP

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

(*Received* 8 *December* 1987; *accepted* 3 *June* 1988)

Abstract. $[OsCl_3(C_5H_5N)_3]$, $M_r = 533{\cdot}86$, monoclinic, $P2_1/n$, $a = 9{\cdot}0837\,(20)$, $b = 12{\cdot}521\,(4)$, $c = 15{\cdot}550\,(3)$ Å, $\beta = 91{\cdot}170\,(17)°$, $V = 1768{\cdot}3$ Å^3, $Z = 4$, $D_x = 2{\cdot}005$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71073$ Å, $\mu = 7{\cdot}678$ mm^{-1}, $F(000) = 1012$, $T = 298$ K, $R = 0{\cdot}0199$ for 2356 unique observed reflections. The Os occupies an octahedral environment, coordinated by three chloride and three pyridyl ligands in a meridional arrangement. The reaction mechanism which leads to this product involves the stepwise substitution of chloride ligands in $[OsCl_6]^{2-}$ by pyridine: the first bound pyridine directs the substitution of the *trans* Cl by the second, thereby ensuring the meridional rather than the facial isomer of $OsCl_3(py)_3$. The mutually *trans* Os—N and Os—Cl distances are 2·086 (3) and 2·3761 (10) Å respectively, compared with 2·090 (4), 2·097 (4) Å for the *trans* Os—N bonds and 2·3569 (11), 2·3590 (11) Å for the *trans* Os—Cl bonds. The pyridyl ligands are twisted out of the mean $OsN_3Cl(3)$ plane by 52·6 (3), 48·6 (3) and 43·5 (3)°: the limiting contacts appear to involve the Cl and α-H atoms, at distances of about 2·8 Å.

Experimental. Compound prepared by electroreduction of $[Pr_4N]_2[OsCl_6]$ in pyridine at room temperature and recrystallized from chloroform/diethyl ether (Heath, Sharp, Smith & Yellowlees, 1988). Dark red crystal, 0·28 × 0·32 × 0·40 mm, AED2 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radia-

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[*] Present address: Research School of Chemistry, Australian National University, GPO Box 4, Canberra ACT 2601, Australia.

0108-2701/88/101836-03$03.00