

C(7)	-0.09003 (44)	0.35437 (23)	0.09000 (23)	0.0365 (14)
C(9)	0.12241 (43)	0.34131 (25)	0.18838 (24)	0.0398 (15)
C(2)	-0.33513 (48)	0.60541 (24)	-0.04292 (24)	0.0402 (15)
C(3)	-0.36395 (44)	0.52598 (24)	-0.06278 (23)	0.0370 (14)
C(11)	-0.47909 (47)	0.50277 (28)	-0.13040 (27)	0.0498 (16)
C(8)	0.00983 (44)	0.30496 (26)	0.13722 (24)	0.0397 (15)
C(1)	-0.22470 (46)	0.62522 (26)	0.01712 (25)	0.0419 (15)
O(1)	0.0	0.82136 (29)	0.25000	0.0729 (20)

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Structure of Dimethyl(phenyl)phosphonium Tris(1,2-benzenedithiolato)tungsten(V)

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Abstract

The reaction of $[\text{WCl}_4(\text{PMe}_2\text{Ph})_3]$ with $\text{C}_6\text{H}_4(\text{SH})_2$ -1,2 in toluene gives dark brown $[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_2(\text{PMe}_2\text{Ph})_2]$, which on standing in solution gives deep green $[\text{PHMe}_2\text{Ph}][\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$. The X-ray structure of $[\text{PHMe}_2\text{Ph}][\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$ shows the tungsten to be coordinated by three $(\text{C}_6\text{H}_4\text{S}_2-1,2)^{2-}$ ligands with an average W—S distance of 2.386 (6) Å in a geometry which is halfway between octahedral and trigonal prismatic.

Comment

While dithiolate hydride complexes of molybdenum are well established, *e.g.* $[\text{MoH}_2(\text{C}_6\text{H}_4\text{S}_2-1,2)-(\text{PMe}_2\text{Ph})_2]$ (Lazarowych & Morris, 1987) and $[\text{MoH}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{3-}$ (Sellmann & Zapf, 1985), analogues of tungsten have proved elusive (Sellmann, Kern & Moll, 1991). As part of our investigation into the chemistry of molybdenum and tungsten hydrides with sulfur co-ligands (Burrow, Hills, Hughes, Lane, Morris & Richards, 1991), we have examined the reactions of $\text{C}_6\text{H}_4(\text{SH})_2$ -1,2 with the complex $[\text{WCl}_4(\text{PMe}_2\text{Ph})_3]$ in the hope of finding a route to new complexes of this type. The reaction



$[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_2(\text{PMe}_2\text{Ph})_2]$ + unidentified products produced a dark oil which, from $\text{CH}_2\text{Cl}_2/\text{MeOH}$, gave a dark brown complex formulated as $[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_2(\text{PMe}_2\text{Ph})_2]$ on the basis of ^1H and ^{31}P NMR spectral data [$\delta^{31}\text{P}$ -135.2 versus $\text{P}(\text{OMe})_3$]. A similar complex of molybdenum, *cis*- $[\text{Mo}(\text{C}_6\text{H}_4\text{S}_2-1,2)_2(\text{PMe}_2\text{Ph})_2]$, is known (Lazarowych & Morris, 1990). When a solution of $[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_2(\text{PMe}_2\text{Ph})_2]$ was allowed to stand, crystals of the

Table 2. Geometric parameters (Å, °)

Cu(1)—Cl(2)	2.255 (2)	C(3)—C(11)	1.497 (6)
Cu(1)—N(2)	2.035 (4)	Cu(1)—Cl(1)	2.274 (2)
Cu(1)—Cl(2a)	2.754 (2)	Cu(1)—N(1)	2.001 (3)
N(2)—C(6)	1.351 (5)	Cl(2)—Cu(1a)	2.754 (2)
N(1)—C(5)	1.349 (5)	N(2)—C(10)	1.338 (5)
C(6)—C(5)	1.483 (5)	N(1)—C(1)	1.364 (5)
C(5)—C(4)	1.380 (5)	C(6)—C(7)	1.388 (6)
C(3)—C(4)	1.402 (5)	C(12)—C(8)	1.482 (6)
C(7)—C(8)	1.398 (6)	C(10)—C(9)	1.391 (6)
C(9)—C(8)	1.388 (5)	C(2)—C(1)	1.370 (6)
C(2)—C(3)	1.393 (6)		
Cl(2)—Cu(1)—Cl(1)	93.9 (1)	N(2)—Cu(1)—N(1)	80.2 (1)
Cl(1)—Cu(1)—N(2)	152.5 (1)	Cl(1)—Cu(1)—Cl(2a)	109.5 (1)
Cl(1)—Cu(1)—N(1)	93.7 (1)	N(1)—Cu(1)—Cl(2a)	86.4 (1)
Cl(2)—Cu(1)—Cl(2a)	87.4 (1)	Cu(1)—N(2)—C(6)	114.4 (2)
N(2)—Cu(1)—Cl(2a)	96.9 (1)	C(6)—N(2)—C(10)	118.3 (3)
Cu(1)—Cl(2)—Cu(1a)	91.7 (1)	Cu(1)—N(1)—C(1)	126.0 (3)
Cu(1)—N(2)—C(10)	127.3 (3)	N(2)—C(6)—C(5)	115.1 (3)
Cu(1)—N(1)—C(5)	116.5 (2)	C(5)—C(6)—C(7)	122.8 (3)
C(5)—N(1)—C(1)	117.5 (3)	N(2)—C(10)—C(9)	122.5 (3)
N(2)—C(6)—C(7)	122.1 (3)	N(1)—C(5)—C(6)	113.6 (3)
N(1)—C(5)—C(4)	122.1 (3)	C(6)—C(5)—C(4)	124.3 (3)
C(6)—C(7)—C(8)	119.7 (3)	C(5)—C(4)—C(3)	120.9 (4)
C(4)—C(3)—C(2)	116.3 (3)	C(10)—C(9)—C(8)	119.8 (4)
C(2)—C(3)—C(11)	121.7 (4)	C(3)—C(2)—C(1)	120.5 (4)
C(12)—C(8)—C(9)	122.5 (4)	C(4)—C(3)—C(11)	122.0 (4)
N(1)—C(1)—C(2)	122.7 (4)	C(12)—C(8)—C(7)	120.1 (4)
Cl(2)—Cu(1)—N(2)	94.8 (1)	C(7)—C(8)—C(9)	117.4 (4)
Cl(2)—Cu(1)—N(1)	171.5 (1)		

The complex was prepared by addition of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1 mmol) to a solution containing 4,4'-dimethyl-2,2'-bipyridine (1 mmol) in freshly distilled ethanol. The resulting solution was refluxed and a green microcrystalline solid formed when the reaction mixture was cooled. The complex was recrystallized from acetonitrile.

SHELXTL/PC software (Sheldrick, 1991) was used to solve and refine the structure and collect data. Water H atoms were located from difference Fourier maps.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and geometry, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71122 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1026]

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Sheldrick, G. M. (1991). *SHELXTL/PC*. Version 4.2. Siemens Analytical X-ray, Instruments, Inc., Madison, Wisconsin, USA.

green paramagnetic complex $[\text{PHMe}_2\text{Ph}][\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$ deposited in low yield after several days. This complex anion has also been obtained as its NMe_4^+ salt (Sellmann, Kern & Moll, 1991) and its $[\text{Co}(\text{C}_5\text{H}_5)_2]^+$ salt (Burrow & Morris, 1992) but has not been structurally characterized.

The three dithiolate ligands in the anion are arranged in a propeller form around the W atom whose coordination geometry may be described as halfway between octahedral and trigonal prismatic (Fig. 1). In this respect it falls into the well established pattern for a range of dithiolate complexes. In particular the structure of the dianion $[\text{Mo}\{\text{S}_2\text{C}_2(\text{CN})_2\}_3]^{2-}$ (Brown & Stiefel, 1970) is very similar to that of $[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^-$. In the structure of the latter anion (Fig. 1), the two triangles defined by the S(11), S(31), S(21) and S(32), S(22), S(12) atoms are twisted from the eclipsed trigonal-prismatic stereochemistry by an angle α of 33° ; the corresponding angle in $[\text{Mo}\{\text{S}_2\text{C}_2(\text{CN})_2\}_3]^{2-}$ is 27° . An octahedral complex would have a value for α of 60° , as is found in the uncharged complex $[\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3]$ (Smith, Schrauzer, Mayweg & Heinrich, 1965).

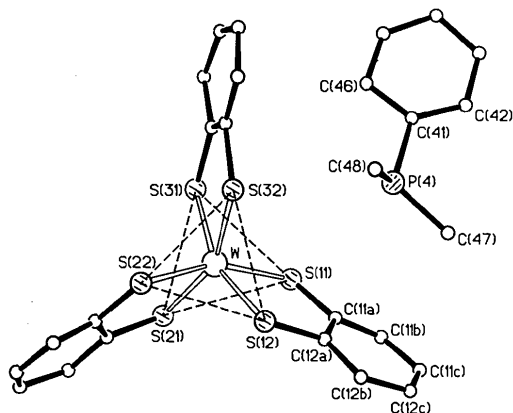


Fig. 1. Molecular structure of the complex $[\text{PHMe}_2\text{Ph}][\text{W}(\text{C}_6\text{H}_4\text{S}_2)_3]$. The cation shown is at $(x, y, z - 1)$ with respect to the coordinates of Table 1.

The average W—S distance [$2.368(6) \text{ \AA}$] and chelate bite angle [$81.9(6)^\circ$] in $[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^-$ are close to those of $[\text{Mo}\{\text{S}_2\text{C}_2(\text{CN})_2\}_3]^{2-}$ [$2.386(13) \text{ \AA}$ and $82(1)^\circ$, respectively]. Other parameters of the structure of $[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^-$ are unexceptional.

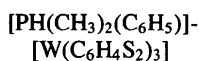
The reason for the deviation of the geometry of tris(dithiolate) complexes of early transition metals in high oxidation states from trigonal prismatic has received much attention (Martin & Takats, 1989). In a formally d^0 $[\text{M}(\text{S}_2)_3]$ ($M = \text{metal}$, $\text{S}_2 = \text{dithiolate}$)

unit, trigonal-prismatic geometry allows a more favourable bonding situation than does octahedral geometry (Martin & Takats, 1989). However, a number of factors can induce twisting away from trigonal-prismatic geometry, so that twisting occurs even in the formally d^0 complex $[\text{W}(\text{OCH}_2\text{CH}_2\text{O})_3]$ (Scherle & Schröder, 1974). Among those factors suggested are the constraints of chelate bite size, proper matching of ligand and metal orbital energies, the symmetry and ligand π -orbitals and ligand field stabilization energies, as well as the charge of the complex. Inter-donor-atom bonding has also been suggested, but seems less likely to be an important factor (Martin & Takats, 1989).

The unsaturated ligands in $[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^-$ and $[\text{Mo}\{\text{S}_2\text{C}_2(\text{CN})_2\}_3]^{2-}$ might be expected to favour trigonal-prismatic geometry by virtue of favourable π -bonding interactions (Martin & Takats, 1989). Although X-ray evidence is not available, the uncharged complexes $[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$ and $[\text{W}(\text{CH}_3\text{C}_6\text{H}_3\text{S}_2-3,4)_3]$ appear to have the trigonal-prismatic geometry expected on this basis (Stiefel, Eisenberg, Rosenberg & Gray, 1966). Any favourable π interaction present in these complexes appears to be disrupted by the addition of an electron to the system as occurs in the series $[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{n-}$ ($n = 0, 1$) discussed here, and in the series $[\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3]^{n-}$ ($n = 0, 1$) (Brown & Stiefel, 1970; Smith, Schrauzer, Rosenberg & Gray, 1965), so that twisting of the anion is observed in each case. Departure from the trigonal-prismatic geometry presumably would also be seen along the series $[\text{Mo}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{n-}$ ($n = 0, 1, 2, 3$) (Sellmann & Zapf, 1985) for which X-ray data are not available.

In crystals of $[\text{PHMe}_2\text{Ph}][\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$, we note additional factors which might influence the geometry of the anion. The phosphonium cation has a tetrahedral arrangement about the P atom (Fig. 1). Allowing for a P—H distance of 1.42 \AA , the H atom is estimated to be 2.69 \AA from S(11) in the anion at $(x, y, 1 + z)$. P(4) is $4.03(1) \text{ \AA}$ from S(11) and $4.02(1) \text{ \AA}$ from S(32) in this anion, but the P—H bond vector is directed more towards S(11) in an arrangement indicating a weak P—H \cdots S(11) hydrogen bond. This insertion of the cation between two of the dithiolate 'blades' and the hydrogen-bonding interaction may be further contributory factors in the twisting of the ligands from the trigonal-prismatic geometry. Symmetry-related cations lie in the clefts between the other pairs of 'blades' and make normal van der Waals contacts with the $(\text{C}_6\text{H}_4\text{S}_2-1,2)^{2-}$ ring atoms.

Note added in proof. Since this work was completed, the structure of the title anion has been reported, but with the $(\text{NMe}_4)^+$ cation (Knoch, Sellmann & Kern, 1992).

Experimental*Crystal data*

$$M_r = 743.7$$

Orthorhombic

 $P2_12_12_1$

$$a = 12.928 (2) \text{ \AA}$$

$$b = 14.814 (2) \text{ \AA}$$

$$c = 15.028 (3) \text{ \AA}$$

$$V = 2878.1 (8) \text{ \AA}^3$$

$$Z = 4$$

$$D_x = 1.716 \text{ Mg m}^{-3}$$

Mo $K\alpha$ radiation

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

Cell parameters from 25 reflections

$$\theta = 10\text{--}11^\circ$$

$$\mu = 4.59 \text{ mm}^{-1}$$

$$T = 293 \text{ K}$$

Wedge shaped

$$0.57 \times 0.42 \times 0.40 \text{ mm}$$

Very dark green

Data collection

Enraf-Nonius CAD-4 diffractometer

 ω - θ scans

Absorption correction: empirical

$$T_{\min} = 0.21, T_{\max} = 0.35$$

3856 measured reflections

1822 independent reflections

1319 observed reflections

$$[I > 2\sigma(I)]$$

*Refinement*Refinement on F^2

$$\text{Final } R = 0.078$$

$$wR = 0.064$$

1822 reflections

177 parameters

H-atom parameters not refined

$$w = \sigma^{-2}(F)$$

$$R_{\text{int}} = 0.12$$

$$\theta_{\text{max}} = 17.5^\circ$$

$$h = -10 \rightarrow 10$$

$$k = 0 \rightarrow 12$$

$$l = -12 \rightarrow 12$$

2 standard reflections

frequency: 167 min

intensity variation: none

$$(\Delta/\sigma)_{\text{max}} = 0.33$$

$$\Delta\rho_{\text{max}} = 2.0 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -2.1 \text{ e \AA}^{-3}$$

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters (\AA^2)
$$U_{\text{iso}} \text{ for C atoms; } U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j \text{ for W, S and P atoms.}$$

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
W	0.21161 (9)	0.20314 (9)	0.18683 (8)	0.084 (1)
S(11)	0.3281 (5)	0.2813 (7)	0.0919 (4)	0.099 (4)
C(11a)	0.2746 (17)	0.2980 (18)	-0.0067 (14)	0.074 (7)
C(11b)	0.3246 (17)	0.3494 (17)	-0.0706 (16)	0.082 (9)
C(11c)	0.2807 (21)	0.3644 (20)	-0.1542 (16)	0.107 (9)
C(12c)	0.1800 (20)	0.3375 (20)	-0.1717 (19)	0.117 (11)
C(12b)	0.1242 (21)	0.2932 (22)	-0.1045 (17)	0.113 (10)
C(12a)	0.1721 (16)	0.2705 (17)	-0.0233 (15)	0.075 (8)
S(12)	0.1043 (6)	0.2152 (7)	0.0591 (5)	0.110 (4)
S(21)	0.2032 (7)	0.3350 (6)	0.2740 (5)	0.122 (4)
C(21a)	0.0920 (26)	0.3260 (22)	0.3342 (23)	0.133 (13)
C(21b)	0.0641 (32)	0.3964 (28)	0.3922 (29)	0.186 (18)
C(21c)	-0.0233 (31)	0.3908 (28)	0.4469 (27)	0.164 (15)
C(22c)	-0.0857 (29)	0.3157 (30)	0.4316 (27)	0.186 (16)
C(22b)	-0.0718 (27)	0.2447 (28)	0.3717 (26)	0.170 (16)
C(22a)	0.0282 (24)	0.2519 (22)	0.3327 (21)	0.109 (11)
S(22)	0.0568 (6)	0.1676 (7)	0.2626 (6)	0.114 (5)
S(31)	0.3614 (7)	0.1718 (7)	0.2742 (6)	0.127 (5)
C(31a)	0.3972 (24)	0.0616 (22)	0.2588 (20)	0.103 (10)
C(31b)	0.4876 (25)	0.0289 (25)	0.3043 (26)	0.151 (13)
C(31c)	0.5057 (30)	-0.0626 (25)	0.2821 (23)	0.153 (15)

C(32c)	0.4485 (31)	-0.1241 (30)	0.2296 (26)	0.192 (18)
C(32b)	0.3506 (31)	-0.0943 (28)	0.1962 (33)	0.195 (17)
C(32a)	0.3359 (31)	-0.0010 (27)	0.2128 (30)	0.176 (17)
S(32)	0.2237 (8)	0.0477 (7)	0.1595 (6)	0.123 (4)
P(4)	0.3883 (8)	0.0680 (7)	0.9334 (7)	0.125 (5)
C(41)	0.5201 (29)	0.0231 (27)	0.9467 (23)	0.147 (14)
C(42)	0.5948 (32)	0.0225 (32)	0.8770 (27)	0.177 (17)
C(43)	0.6914 (35)	-0.0203 (29)	0.8876 (29)	0.177 (16)
C(44)	0.7122 (36)	-0.0605 (33)	0.9710 (30)	0.207 (18)
C(45)	0.6347 (29)	-0.0514 (34)	1.0377 (31)	0.201 (18)
C(46)	0.5335 (24)	-0.0141 (22)	1.0315 (21)	0.113 (11)
C(47)	0.3810 (23)	0.1366 (23)	0.8331 (22)	0.122 (11)
C(48)	0.2977 (31)	-0.0181 (25)	0.9338 (23)	0.151 (13)
H(4)	0.3646	0.1243	1.0072	

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

Coordination sphere of the W atom			
W—S(11)	2.376 (7)	W—S(12)	2.375 (8)
W—S(21)	2.355 (9)	W—S(22)	2.362 (8)
W—S(31)	2.385 (9)	W—S(32)	2.344 (10)
S(11)—W—S(12)	81.3 (2)	S(11)—W—S(21)	87.7 (3)
S(11)—W—S(22)	159.3 (3)	S(11)—W—S(31)	84.9 (3)
S(11)—W—S(32)	109.3 (3)	S(12)—W—S(21)	111.1 (3)
S(12)—W—S(22)	84.9 (3)	S(12)—W—S(31)	159.0 (3)
S(12)—W—S(32)	88.3 (4)	S(21)—W—S(22)	83.0 (3)
S(21)—W—S(31)	83.8 (3)	S(21)—W—S(32)	156.3 (3)
S(22)—W—S(31)	112.3 (3)	S(22)—W—S(32)	85.5 (3)
S(31)—W—S(32)	81.4 (3)		
1,2-Benzenedithiolato ligands			
S(11)—C(11a)	1.65 (2)	C(22a)—S(22)	1.68 (3)
C(12a)—S(12)	1.73 (2)	C(31)—C(31a)	1.71 (3)
S(21)—C(21a)	1.70 (3)	C(32a)—S(32)	1.81 (4)
W—S(11)—C(11a)	110.2 (8)	W—S(22)—C(22a)	108.9 (11)
W—S(12)—C(12a)	108.6 (8)	W—S(31)—C(31a)	109.3 (12)
W—S(21)—C(21a)	105.6 (12)	W—S(32)—C(32a)	111.6 (12)
Dimethyl(phenyl)phosphonium cation			
P(4)—C(41)	1.84 (4)	P(4)—C(48)	1.73 (4)
P(4)—C(47)	1.82 (3)		
C(41)—P(4)—C(47)	109.8 (15)	C(47)—P(4)—C(48)	112.2 (16)
C(41)—P(4)—C(48)	111.1 (18)		
Estimated hydrogen-bond dimensions			
P(4)—H(4)	1.42	P(4)···S(32 ⁱ)	4.019 (13)
P(4)···S(11 ⁱ)	4.032 (14)	H(4)···S(32 ⁱ)	3.14
H(4)···S(11 ⁱ)	2.69		
P(4)—H(4)···S(11 ⁱ)	156	C(11a)—S(11)···H(4 ⁱⁱ)	77.3
W—S(11)···H(4 ⁱⁱ)	88.5		

Symmetry codes: (i) $x, y, 1 + z$; (ii) $x, y, z - 1$.

Diffraction data were measured to the limit of observable intensities, viz. $\theta_{\text{max}} = 17.5^\circ$, for $\pm h, +k, \pm l$ reflections. Equivalent reflections were merged giving a data set comprising $\pm h, +k, +l$ reflections. The W atom was located by the Patterson method and subsequent electron density and difference Fourier syntheses yielded the positions of all non-H atoms. In the final cycles of refinement, the W, P and S atoms were given anisotropic thermal parameters and the C atoms were refined isotropically. H atoms were not included and C—C bond lengths in the aromatic rings were restrained to $1.395 \pm 0.02 \text{ \AA}$. After the final cycles of refinement, the structure of the opposite enantiomer at $-x, -y, -z$ was refined with the same data set and gave much higher R factors ($R = 0.093, wR = 0.079$). Computer programs used in this analysis were *SHELX76* (Sheldrick, 1976) and those noted in Anderson, Richards & Hughes (1986), and were run on a MicroVAX II computer in the Nitrogen Fixation Laboratory.

We thank NATO for a collaborative research grant to RHM and RLR.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71095 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1035]

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Structure of $[(C_2H_5)_2NH_2]_3BiCl_6$

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Abstract

In diethylammonium hexachlorobismuthate(III) the Bi atoms form a slightly distorted cubic *I* arrangement, *i.e.* they occupy the corners and the midpoint (owing to the *c*-glide plane) of the pseudo-cubic

rhombohedral unit cell defined by the transformation $a'_1 = -\frac{1}{3}a_1 + \frac{1}{3}a_2 + \frac{1}{3}c$, $a'_2 = -\frac{1}{3}a_1 - \frac{2}{3}a_2 + \frac{1}{3}c$, $a'_3 = \frac{2}{3}a_1 + \frac{1}{3}a_2 + \frac{1}{3}c$; each Bi atom is surrounded octahedrally by six Cl atoms. The octahedron occurs in two different orientations according to the *c*-glide plane. The centres of the organic groups are close to the midpoints of the edges and the faces of the *I*-centred cubic cell. The isolated octahedra are connected to form a three-dimensional framework by hydrogen bonding *via* three symmetrically equivalent atoms Cl(1), which form an octahedral face. The other three Cl(2) atoms are not involved in the bonding scheme. Each octahedron is surrounded by six $(C_2H_5)_2NH_2$ groups. The two H atoms connected to the N atom bridge to different octahedra; a third H atom connected to a non-methyl C atom also bridges to Cl(1), thus completing a distorted tetrahedral environment for Cl(1), set up by three H and one Bi atom. The distance Bi—Cl for the hydrogen bonded Cl(1) is 2.875 Å; it is diminished for Cl(2) to 2.587 Å.

Comment

The present investigation is part of a series of studies on the influence of organic cations on heavy-metal halogenides. The structure was originally solved by

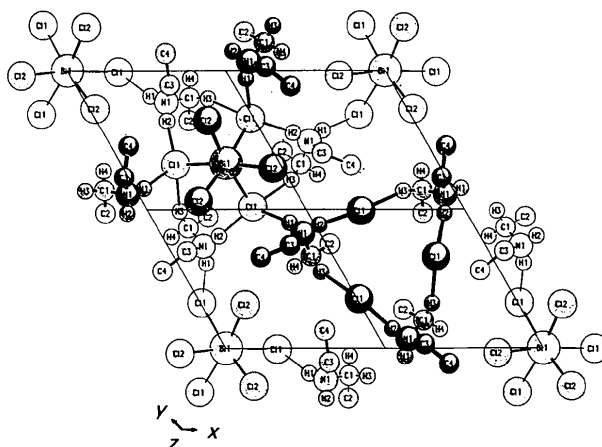


Fig. 1. Projection of part of the unit cell along *c*.

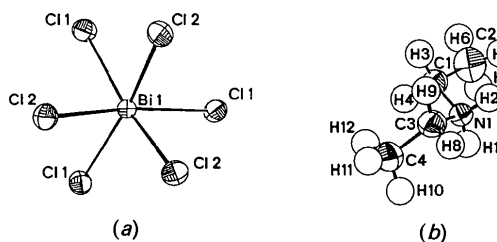


Fig. 2. Displacement ellipsoids for (a) the $BiCl_6$ octahedron and (b) the $(C_2H_5)_2NH_2$ group.