Crystal and Molecular Structure of Bromobis-(π-cyclopentadienyl)(tribromostannyl)molybdenum(IV)

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The crystal and molecular structure of the title compound has been determined by three-dimensional *X*-ray methods with intensity measurements from a linear diffractometer (orthorhombic, $a = 14{\cdot}05$, $b = 12{\cdot}30$, $c = 8{\cdot}82$ Å, space group *Pnma* or $Pna2_1$, $Z = 4$), and refined by least squares to *R* 0·056 for 601 independent reflections. The tin atom forms four bonds directed towards the corners of a distorted tetrahedron with Sn–Mo 2·691 and mean Sn–Br, 2·505 Å. The tin co-ordination polyhedron is completed by a much longer bromine contact (3·411 Å) to give a very distorted trigonal bipyramid.

The Sn–Mo–Br bond angle is 80·2° and the Mo–Br bond length is 2·605 Å. The π-cyclopentadienyl rings are not well determined.

THE preceding paper[1] describes the preparation and properties of the complexes $(\pi\text{-}C_5H_5)_2M(SnX_3)X$ (M = Mo or W, X = Cl or Br). We have determined the crystal structure of one of these $(\pi\text{-}C_5H_5)$ $2Mo(SnBr_3)Br$.†

EXPERIMENTAL

Crystal Data.—$C_{10}H_{10}Br_4MoSn$, $M = 664{\cdot}5$, Orthorhombic, $a = 14{\cdot}05 \pm 0{\cdot}01$, $b = 12{\cdot}30 \pm 0{\cdot}01$, $c = 8{\cdot}82 \pm 0{\cdot}01$ Å, $U = 1524$ Å^3, $D_m = 2{\cdot}85$ (by flotation), $Z = 4$, $D_c = 2{\cdot}895$. Mo-K_α radiation $\lambda = 0{\cdot}7107$ Å, μ(Mo-K_α) = 117 cm^{-1}. Space group *Pnma* (C_{2h}^{16}, No. 62) or $Pna2_1$ (C_{2v}^{9}, No. 33).

From a crystal of dimensions 0·1 × 0·1 × 0·1 mm, 601 independent reflections with $I > 3\sigma$ were measured on a Hilger and Watts linear diffractometer. The measurements were corrected for Lorentz and polarization effects but not for absorption.

The three-dimensional unsharpened Patterson function computed from these data indicated that the molybdenum, tin, and two bromine atoms lie in the mirror plane at $y = \frac{1}{4}$, of the space group *Pnma* and that the remaining pair of bromine atoms are at sites related by the mirror plane. An F_o synthesis phased on the heavy-atom positions in space group *Pnma* showed clearly the positions of the remaining carbon atoms. The trial structure was refined by the full-matrix least-squares method, with isotropic temperature factors for all atoms.

After computing four cycles with unit weights, followed by two cycles with the following weighting function applied: $w = [1 + (||50F_o| - 2500||)/2000]^{-1}$, convergence was reached at *R* 0·126. Three further refinement cycles were computed with a full-matrix, anisotropic temperature factors for all atoms and with the weighting function unchanged. The final *R* value was 0·056.

The observed structure amplitude and structure factors calculated from the atomic parameters in Table 1 are listed in Supplementary Publication No. SUP 20393 (5 pp., 1 microfiche).‡ All calculations were carried out on the Oxford University KDF 9 computer with programs developed by Rollett *et al.*[2] Atomic scattering amplitudes were those for neutral atoms given in ref. 3. Those of molybdenum(0), tin(0), and bromine(0) were corrected for the real part of the anomalous dispersion.

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† The structure of $(\pi\text{-}C_5H_5)_2Mo(SnCl_3)Cl$ has also been examined by three dimensional *X*-ray methods. The molecular structure has no features that are significantly different from the bromide except that the location of the atoms of the $(\pi\text{-}C_5H_5)$ rings is even more uncertain. It is our intention not to publish the details of the chloro-structure.

‡ For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[1] M. L. H. Green, A. H. Lynch, and M. G. Swanwick, preceding paper.

[2] J. S. Rollett, O. J. R. Hodder, and G. Ford, unpublished work.

[3] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962, pp. 209 *et seq.*

RESULTS AND DISCUSSION

The crystals contain isolated $(\pi\text{-}C_5H_5)_2Mo(SnBr_3)Br$ molecules constrained to lie about the mirror planes of space group *Pnma* (Figure 1). The mirror plane contains the Br•Mo•SnBr group and relates the remaining pair of bromine atoms and the pair of π-cyclopentadienyl groups.

TABLE 1

Atomic parameters (× 10^4 Å^2) * with standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn(1)	1258(2)	2500	2212(3)	269(1)	381(1)	251(1)		31(2)	
Mo(1)	1709(2)	2500	−751(4)	197(2)	280(2)	267(2)		43(3)	
Br(1)	2742(4)	2500	3785(7)	430(3)	1609(6)	405(4)		−283(5)	
Br(3)	−140(4)	2500	−947(8)	223(2)	1922(7)	858(5)		−228(6)	
Br(2)	393(3)	4040(3)	3475(5)	742(3)	588(2)	680(3)	−365(4)	288(4)	377(4)
C(1)	2042(41)	4333(32)	108(51)	2173(52)	357(27)	915(34)	382(44)	−891(69)	−1545(62)
C(2)	2810(31)	3851(37)	−326(79)	793(30)	665(32)	1056(67)	405(25)	−556(71)	−845(51)
C(3)	2730(28)	3635(23)	−1939(64)	744(26)	80(16)	2012(61)	−615(47)	1882(65)	−748(35)
C(4)	1759(34)	3930(27)	−2355(59)	1425(35)	169(18)	1350(41)	1127(51)	106(66)	−479(47)
C(5)	1440(26)	4399(26)	−918(64)	753(26)	345(20)	1591(50)	−950(56)	1525(57)	255(39)

* The temperature factor is in the form: $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{23}klb^*c^* + U_{13}hla^*c^* + U_{12}hka^*b^*)]$.

The anisotropic temperature factors of atoms of the π-cyclopentadienyl group are unsatisfactory. They could be interpreted in terms of a large in-plane libration, but an equally reasonable interpretation would be that either the π-cyclopentadienyl groups are disordered or that the apparent mirror plane is, in fact, not there so that the structure would be better described in space group $Pna2_1$. The present work does not enable us to distinguish between these alternatives. It is necessary, therefore, to treat the detail of the observed dimensions and orientation of the π-cyclopentadienyl groups with some scepticism. The anisotropic temperature factors of the heavy atoms suggest that the proposed model is a good representation of this part of the structure.

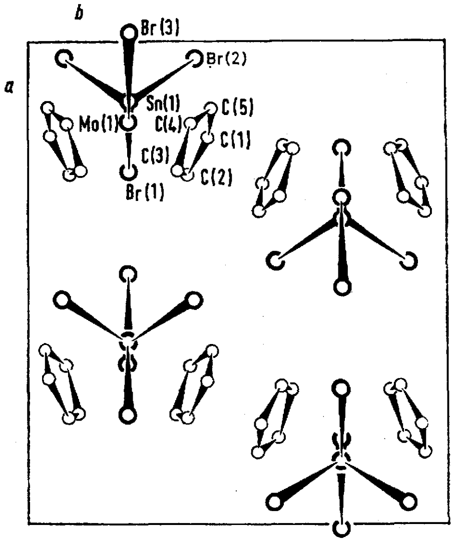

FIGURE 1 The crystal structure projected down the c axis

In Figure 2 the molecule is shown projected on the best plane of a π-cyclopentadienyl group and the interatomic distances and interbond angles are given in Table 2. In the molecule the environment of the tin atom is approximately tetrahedral but with a fifth long contact from Br(3) (the bromine atom bonded to the molybdenum) to tin, in a direction not inconsistent with a bonding interaction. The environment of the tin atom is closely analogous to that found in the Mo^{II} complex $(bipy)(OC)_3ClMo[Sn(Me)Cl_2]$ (bipy = 2,2′-bipyridyl)[4] in which the tin is five-co-ordinate trigonal bipyramidal; in this complex Sn–Mo is 2·75 Å, Sn–Cl(apical) and Sn–Cl(equatorial) are 2·43 and 2·35 Å respectively and are significantly different, and Sn–Cl(apical, bridging) at 2·81 Å is much larger. In the present work Mo–Sn is shorter (2·69 Å) as is to be expected for Mo^{IV}. Three of the Sn–Br bond lengths are equivalent (mean 2·505 Å) and indicate strong bonds, but the fifth contact to tin

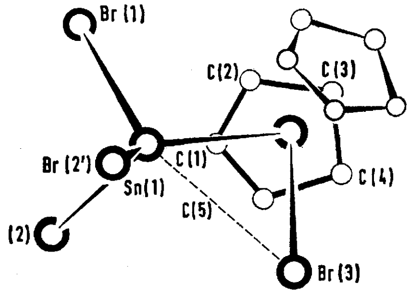

FIGURE 2 The molecule of $(\pi\text{-}C_5H_5)_2Mo(SnBr_3)Br$ seen projected on the plane of one of the cyclopentadienyl rings

TABLE 2

Interatomic distances (Å) and interbond angles (°)

(*a*) Distances

Sn(1)–Mo(1)	2·691(4)	C(1)–C(2)	1·30(9)
Sn(1)–Br(1)	2·503(8)	C(2)–C(3)	1·44(9)
Sn(1)–Br(2)	2·509(5)	C(3)–C(4)	1·44(7)
		C(4)–C(5)	1·47(7)
Mo(1)–Br(3)	2·605(9)	C(5)–C(1)	1·24(8)

(*b*) Angles

Mo(1)–Sn(1)–Br(1)	109·9(2)	C(1)–C(2)–C(3)	109(5)
Mo(1)–Sn(1)–Br(2)	123·0(2)	C(2)–C(3)–C(4)	105(5)
Br(1)–Sn(1)–Br(2)	99·1(2)	C(3)–C(4)–C(5)	101(4)
Br(2)–Sn(1)–Br(2′)	98·0(2)	C(4)–C(5)–C(1)	113(5)
		C(5)–C(1)–C(2)	111(5)
Sn(1)–Mo(1)–Br(3)	80·16(2)		

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[4] M. Elder, W. A. G. Graham, D. Hall, and R. Kummer, *J. Amer. Chem. Soc.*, 1968, **90**, 2186.

Sn · · · Br(3), is rather long, 3·411 Å. The Sn–Mo–Br(3) bond angle (80·2°) is only slightly smaller than the corresponding angles in the similar complexes[5] of d^2 metals $(\pi\text{-}C_5H_5)_2MoCl_2$ (81·6°) and $[(\pi\text{-}C_5H_5)_2ReBr_2]^+BF_4^-$ (82·1°). The bromine atom Br(3) is 4·402 Å away from the mirror-plane-related bromine atoms Br(2) and Br(2′). The angles Mo–Sn–Br(2) (123·0°) are enlarged from the expected tetrahedral angles and the angles Br(2)–Sn–Br(1) (99·1°), correspondingly reduced. This distortion cannot be reasonably explained in terms of Br(2) · · · Br(3) repulsions because this non-bonded contact is well in excess of the sum of the van der Waals radii, 3·90 Å. The angle Br(1)–Sn · · · Br(3) is 152°. It is therefore reasonable to assume that the long Sn–Br(3) contact represents a bonding interaction and that the bonding at the tin atom is best described in terms of four strong essentially σ bonds plus a fifth much weaker bond in which the tin atom of the $Mo(SnBr_3)$ group acts as either a π or possibly σ acceptor to the bromine lone-pair electrons. This fifth contact may be analogous to an n–π^* interaction in an electron-donor–electron-acceptor molecular complex. The five bonds form a distorted trigonal-bipyramidal co-ordination polyhedron about the tin, Figure 2.

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[1/2250 *Received, 29th November,* 1971]

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[5] J. C. Green, M. L. H. Green, and C. K. Prout, *J.C.S. Chem. Comm.*, 1972, 421.