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THE CRYSTAL STRUCTURE OF BROMOTRIS(TETRACARBONYL-COBALT)TIN(IV)

R. D. BALL and D. HALL*.

Chemistry Department, University of Alberta, Edmonton, Alberta (Canada)

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SUMMARY

Crystals of $BrSn[Co(CO)_4]_3$ are hexagonal, $a = 10.20$, $c = 11.81$ Å, space group $P6_3$. The molecule comprises a central tin atom, surrounded tetrahedrally by the bromine atom and three $Co(CO)_4$ groups. The Sn–Co bond length is 2.60 Å.

INTRODUCTION

As part of an investigation into the ability of Group IVB elements to form cobalt carbonyl cluster compounds[1], tin was found to give compounds of type $R–Sn[Co(CO)_4]_3$ (R = halogen) which appear not to contain a cobalt–cobalt bond. To confirm this deduction and to elucidate details of the geometry, the crystal structure of $BrSn[Co(CO)_4]_3$ has been determined.

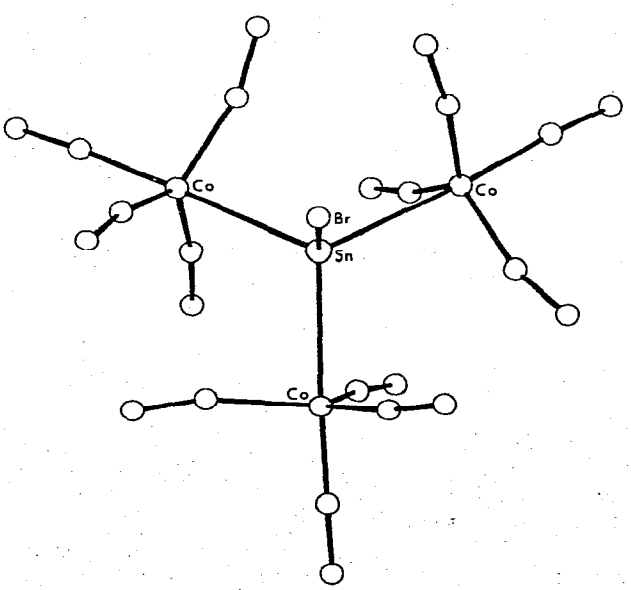

Fig. 1. The $BrSn[Co(CO)_4]_3$ molecule.

* Present address: Chemistry Department, University of Auckland, New Zealand.

EXPERIMENTAL

Dark red hexagonal needles of $BrSn[Co(CO)_4]_3$ were supplied by Dr. W. A. G. Graham. Crystal Data: $C_{12}O_{12}BrCo_4Sn$, $M=711.5$, hexagonal, $a=10.20(1)$, $c=11.81(2)$, $U=1064$ Å^3. Diffraction symmetry $6/m$, systematic absences in $00l$ for l odd, space group $P6_3$. D_m (by flotation) 2.20 g·cm^{-3}, $Z=2$, $D_c=2.22$ g·cm^{-3}. Mo-K_α radiation, $\lambda=0.71069$ Å, $u=52.8$ cm^{-1}.

Intensity data were obtained by visual measurements from Weissenberg photographs about each of the crystal axes, and were corrected for absorption. Individual layers were correlated by least squares[2], to give a unique set of 339 data.

The Sn and Br atoms are required by symmetry to occupy positions of type $(\frac{1}{3}, \frac{2}{3}, z)$. The z coordinate of Sn was taken as zero to define the origin, and that of the

TABLE 1

ATOM COORDINATES AND THERMAL PARAMETERS[a]

Atom	*x/a*	*y/b*	*z/c*	B(Å^2)
Sn	0.6666	0.3333	0.50	
Br	0.6666	0.3333	0.7131(8)	
Co	0.4023(6)	0.2908(6)	0.4421(6)	
C(1)	0.2361(72)	0.2651(65)	0.4020(44)	8.2(1.3)
O(1)	0.1121(61)	0.2201(51)	0.3731(40)	10.9(1.2)
C(2)	0.4659(50)	0.4791(64)	0.4772(50)	7.5(1.2)
O(2)	0.5057(38)	0.6113(38)	0.4866(38)	8.8(8)
C(3)	0.4286(44)	0.2390(47)	0.3141(39)	4.3(8)
O(3)	0.4508(34)	0.1804(35)	0.2261(35)	6.9(8)
C(4)	0.3186(59)	0.1668(59)	0.5563(39)	5.6(1.1)
O(4)	0.2747(50)	0.0767(50)	0.6304(45)	10.4(1.1)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Sn	132(10)	132(10)	69(4)	66(5)	0	0
Br	396(34)	396(34)	56(7)	198(17)	0	0
Co	117(8)	143(8)	82(5)	58(7)	25(6)	9(6)

[a] For anisotropic parameters $f=f_0\cdot\exp-(h^2\cdot B_{11}+k^2\cdot B_{22}+l^2\cdot B_{33}+2h\cdot k\cdot B_{12}+2h\cdot l\cdot B_{13}+2k\cdot l\cdot B_{23})$.

TABLE 2

BOND LENGTHS (Å) AND BOND ANGLES (°)

Sn–Br	2.520(5)	Co–Sn–Co	112.5(2)
Sn–Co	2.602(6)	Co–Sn–Br	104.8(2)
Co–C(1)	1.74(6)	Sn–Co–C(1)	176(4)
Co–C(2)	1.81(6)	Sn–Co–C(2)	86(4)
Co–C(3)	1.71(5)	Sn–Co–C(3)	86(3)
Co–C(4)	1.73(5)	Sn–Co–C(4)	89(3)
C(1)–O(1)	1.19(8)		
C(2)–O(2)	1.17(7)		
C(3)–O(3)	1.20(6)		
C(4)–O(4)	1.25(7)		

Br obtained from a Patterson function, together with the general coordinates of the Co atom. The remaining atoms were located on a difference synthesis. Structure factors were calculated using scattering factors as given by Cromer and Waber[3], with a real dispersion correction[4] applied to those for Sn, Br and Co.

Full matrix least squares refinement, assuming anisotropic thermal motion for the Sn, Br and Co atoms, isotropic motion for the lighter atoms, returned a final R of 0.085. Atomic coordinates and thermal parameters are listed in Table 1, and bond lengths and angles in Table 2. Tables of observed and calculated structure factors may be obtained from the authors.

DISCUSSION

The molecule may be described in terms of a central tin atom, to which the bromine atom and three $Co(CO)_4$ groups are bonded, the geometry about Sn being approximately tetrahedral. There is no bond between cobalt atoms (Co–Co = 4.32 Å), and the structure is thus essentially as previously predicted[1]. The molecular symmetry is C_3, by space group requirement, but is not C_{3v} as was previously assumed in consideration of the IR spectrum in cyclohexane solution[1]. The lower symmetry appears to arise from the necessity to avoid repulsive interaction between carbonyl groups, the same repulsions being evidenced in the details of angles about the tin atom, *i.e.* the Co–Sn–Co angles at 112.5° are significantly greater than the Br–Sn–Co angles of 104.8°.

The Sn–Co bond length has not been previously reported, but the observed value of 2.60 Å is consistent with the sum of the covalent radii (Sn 1.39 Å[5]; Co 1.225 Å[6]). The Sn–Br bond length of 2.52 Å is similar to that (2.51 Å) observed in (4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)dimethyltin(IV) bromide[7], and is within the range of earlier reported values (2.44–2.55 Å)[8] for Sn–Br bonds. The Co–C and C–O bond lengths appear to be normal, within their somewhat higher errors. Bond angles involving the carbonyl groups are again as are commonly observed, including the three Sn–Co–C angles to equatorial carbonyls, which are all slightly less than 90°.

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