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THE CRYSTAL STRUCTURE OF BIS(2,4-PENTANEDIONATO)(HEPTACARBONYLDICOBALT)TIN(IV)

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SUMMARY

The crystal structure of $(C_5H_7O_2)_2SnCo_2(CO)_7$ has been determined. The crystals are orthorhombic, $a=13.88$, $b=29.34$, $c=11.53$ Å, space group *Pbca*. The molecule comprises a tin atom to which two acetylacetonate ligands and a bidentate $Co_2(CO)_7$ group are coordinated. The latter group may be described as two $Co(CO)_3$ groups connected by a direct Co–Co bond (of length 2.63 Å), and bridged by a further carbonyl group.

INTRODUCTION

Direct reaction between tin halides and dicobalt octacarbonyl[1] yields compounds such as $BrSn[Co(CO)_4]_3$, which contains discrete $Co(CO)_4$ groups[2]. However, reaction with bis(2,4-pentanedionato)dichlorotin gives among other products $(C_5H_7O_2)_2SnCo_2(CO)_7$, for which mass and IR spectra indicate a direct Co–Co bond[3]. X-ray analysis of this compound has been undertaken to confirm its structure.

EXPERIMENTAL

Red needle-shaped crystals were supplied by Dr. W. A. G. Graham, and were recrystallised from THF. Crystal Data: $C_{17}H_{14}O_{11}Co_2Sn$, mol. wt. 634.8, orthorhombic, $a=13.88(1)$, $b=29.34(2)$, $c=11.53(1)$ Å, $U=4698$ Å^3, space group *Pbca*. D_m (by flotation) 1.80, $Z=4$, D_c 1.80 g·cm^{-3}. Mo-K_α radiation, $\lambda=0.71069$ Å, $\mu=24.6$ cm^{-1}. Cell dimensions were determined from precession photographs by the method of Patterson and Love[4]. Intensities of layers $0kl$–$11kl$ were collected using a Pailred diffractometer, with single crystal monochromatised Mo-K_α radiation. The ω-scan procedure was used, and background counted before and after each reflection. No absorption correction was applied. A unique data set of 1408 reflections was obtained, for which $I>2\sigma(I)$.

The expected array of tin and cobalt atoms was revealed from a Patterson synthesis, and the light atom positions were obtained from a subsequent difference synthesis. The structure was refined by full-matrix least squares, the scattering factors

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being those of Cromer and Waber[5], with real and imaginary dispersion corrections[6] to those for Sn and Co. With all atoms assumed to have isotropic motion, R converged at 0.086. With the tin and cobalt atoms permitted anisotropic motion, and the two non-methyl hydrogens included in calculated positions, R converged at 0.059. A table

TABLE 1

FINAL ATOMIC POSITIONAL AND THERMAL PARAMETERS[a]

Atom	x	y	z	$B(\AA^2)$
Sn	0.2380(1)	0.1142(1)	0.1020(1)	4.4[b]
Co1	0.1317(2)	0.1639(1)	−0.0287(2)	4.4[b]
Co2	0.2994(2)	0.1348(1)	−0.1036(2)	4.6[b]
C1	0.1695(4)	0.1235(6)	−0.1433(16)	5.8(0.5)
O1	0.1316(9)	0.0997(5)	−0.2169(12)	7.8(0.4)
C2	0.0796(16)	0.1976(8)	−0.1350(20)	8.3(0.6)
O2	0.0409(16)	0.2179(6)	−0.2088(15)	11.1(0.5)
C3	0.0345(16)	0.1349(7)	0.0295(18)	7.3(0.5)
O3	−0.0338(11)	0.1167(5)	0.0621(13)	8.7(0.4)
C4	0.1606(15)	0.2108(8)	0.0537(19)	7.8(0.6)
O4	0.1851(10)	0.2438(6)	0.1067(14)	10.0(0.4)
C5	0.3830(15)	0.1702(7)	−0.0366(18)	6.8(0.5)
O5	0.4401(11)	0.1963(5)	0.0025(12)	8.3(0.4)
C6	0.3465(14)	0.0817(7)	−0.1068(18)	7.0(0.5)
O6	0.3787(11)	0.0439(5)	−0.1120(13)	9.4(0.4)
C7	0.3228(16)	0.1563(8)	−0.2409(21)	8.3(0.6)
O7	0.3348(12)	0.1684(6)	−0.3361(15)	10.8(0.5)
O8	0.1776(8)	0.0487(4)	0.0602(9)	5.1(0.3)
O9	0.3532(7)	0.0763(4)	0.1665(10)	5.1(0.3)
O10	0.3070(8)	0.1647(4)	0.2041(10)	5.5(0.3)
O11	0.1606(11)	0.1006(3)	0.2532(10)	5.2(0.3)
C8	0.1683(12)	0.1201(6)	0.3568(15)	5.4(0.4)
C9	0.0946(13)	0.0983(7)	0.4427(17)	6.7(0.5)
C10	0.2265(13)	0.1544(6)	0.3801(16)	6.2(0.4)
C11	0.2893(14)	0.1769(7)	0.3122(18)	6.3(0.5)
C12	0.3531(14)	0.2171(7)	0.3545(17)	7.0(0.5)
C13	0.3599(12)	0.0338(6)	0.1890(14)	4.9(0.4)
C14	0.4498(12)	0.0181(6)	0.2518(17)	5.7(0.4)
C15	0.2868(12)	0.0004(6)	0.1609(15)	5.4(0.4)
C16	0.2071(12)	0.0106(6)	0.0990(16)	5.0(0.4)
C17	0.1436(13)	−0.0310(6)	0.0623(15)	6.2(0.5)
H1	0.2280	0.1650	0.4630	7.8
H2	0.3040	−0.0100	−0.0610	6.1

[a] Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

[b] These values of B are the equivalent isotropic thermal parameters corresponding to the anisotropic thermal vibration tensors having the following components (× 10^{-5}):

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co1	672(17)	102(4)	844(25)	28(6)	19(16)	10(9)
Sn	721(9)	109(2)	719(10)	6(3)	6(3)	27(5)
Co2	708(17)	138(4)	691(22)	62(6)	47(18)	24(10)

TABLE 2

INTRAMOLECULAR DISTANCES[a]

Atoms	*Distances*(Å)	*Atoms*	*Distances* (Å)
Sn-Co1	2.564(3)	O8-C16	1.27(2)
Sn-Co2	2.591(3)	O9-C13	1.28(2)
Sn-O8	2.15(1)	C15-C13	1.35(2)
Sn-O9	2.09(1)	C15-C16	1.45(2)
Sn-O10	2.12(1)	C16-C17	1.56(2)
Sn-O11	2.09(1)	C13-C14	1.51(2)
Co1-Co2	2.626(4)	O10-C11	1.32(2)
Co1-C1	1.85(2)	O11-C8	1.33(2)
Co1-C2	1.73(2)	C10-C8	1.32(2)
Co1-C3	1.73(2)	C10-C11	1.34(2)
Co1-C4	1.72(2)	C8-C9	1.56(2)
		C11-C12	1.56(2)
Co2-C1	1.89(2)		
Co2-C5	1.74(2)		
Co2-C6	1.69(2)		
Co2-C7	1.74(2)		
C1-O1	1.22(2)		
C2-O2	1.17(2)		
C3-O3	1.15(2)		
C4-O4	1.19(2)		
C5-O5	1.19(2)		
C6-O6	1.20(2)		
C7-O7	1.17(2)		

[a] Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

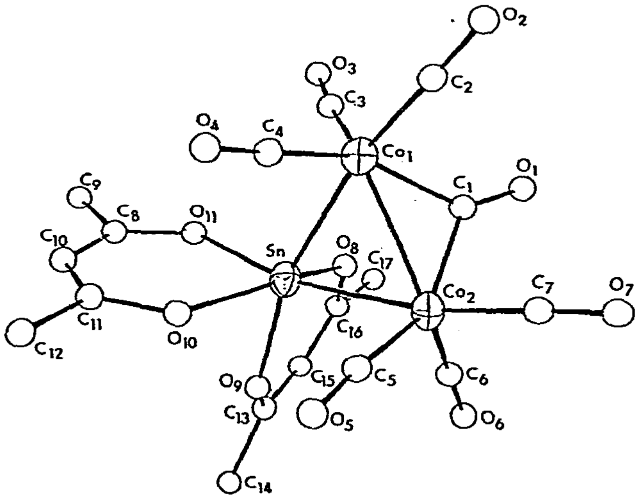

Fig. 1. The $\mathrm{Acac_2SnCo_2(CO)_7}$ molecule.

TABLE 3

Intramolecular angles[a,b]

Atoms	*Angles*(°)	*Atoms*	*Angles*(°)
Sn–Co1–Co2	59.88(9)	Sn–O8–C16	126(1.0)
Sn–Co2–Co1	58.88(8)	O8–C16–C17	114(1.5)
Co1–Sn–Co2	61.24(9)	O8–C16–C15	130(1.6)
		C16–C15–C13	123(1.7)
Co1–Sn–O8	98.7(3)	C15–C13–O9	124.(1.6)
Co1–Sn–O9	162.6(3)	C14–C13–O9	117(1.5)
Co1–Sn–O10	100.9(3)	Sn–O9–C13	131(1.0)
Co1–Sn–O11	107.7(3)		
Co2–Sn–O8	97.6(3)		
Co2–Sn–O9	101.4(3)	Sn–O10–C11	129(1.2)
Co2–Sn–O10	101.3(3)	O10–C11–C12	133(1.7)
Co2–Sn–O11	168.2(3)	O10–C11–C10	123(1.9)
O8–Sn–O9	84.4(4)	C11–C10–C8	131(2.0)
O8–Sn–O10	157.6(4)	C10–C8–O11	124(1.8)
O8–Sn–O11	79.4(4)	O11–C8–C9	110(1.5)
O9–Sn–O10	80.2(4)	Sn–O11–C8	129(1.1)
O9–Sn–O11	89.7(4)		
O10–Sn–O11	84.4(4)		
Co1–C1–Co2	89.2(9)		
Sn–Co1–C1	83.9(6)	Co1–C1–O1	138(1.5)
Sn–Co1–C2	168.6(7)	Co1–C2–O2	176(2.1)
Sn–Co1–C3	86.6(7)	Co1–C3–O3	175(2.0)
Sn–Co1–C4	89.7(7)	Co1–C4–O4	176(2.0)
Sn–Co2–C1	82.4(5)	Co2–C1–O1	133(1.5)
Sn–Co2–C5	87.3(7)	Co2–C5–O5	175(1.9)
Sn–Co2–C6	86.1(7)	Co2–C6–O6	178(2.0)
Sn–Co2–C7	168.9(7)	Co2–C7–O7	175(2.2)
C4–Co1–C3	111(1)	C5–Co2–C6	108(1)
C4–Co1–C2	92(1)	C5–Co2–C7	94(1)
C3–Co1–C2	103(1)	C6–Co2–C7	104(1)
C1–Co1–C3	100.6(9)	C1–Co2–C6	101.7(9)
C1–Co1–C4	147.2(9)	C1–Co2–C5	148.1(9)
C1–Co1–C2	88.7(9)	C1–Co2–C7	91.2(9)

Angles in chelate rings

Atoms	*Angles*(°)	*Atoms*	*Angles*(°)
Sn–O8–C16	125.5(1.1)	Sn–O10–C11	128.9(1.2)
O8–C16–C15	130.0(1.6)	O10–C11–C10	122.6(1.9)
C16–C15–C13	123.1(1.7)	C11–C10–C8	130.8(2.0)
C15–C13–O9	123.9(1.6)	C10–C8–O11	124.1(1.8)
C13–O9–Sn	130.7(1.0)	C8–O11–Sn	128.8(1.1)

[a] Numbers in parentheses are estimated standard deviations occurring in the last digits listed. [b] Dihedral angle between planes defined by Co1–C1–Co2 and Co1–Sn–Co2 = 113.0°.

of observed and calculated amplitudes is available from the authors. The atom coordinates and thermal parameters are listed in Table 1, bond lengths in Table 2, bond angles in Table 3. The molecule is depicted in Fig. 1.

DISCUSSION

The molecule may be described as a six-coordinate tin atom with two acetylacetonato groups and a $Co_2(CO)_7$ group, each functioning as a bidentate ligand. The two cobalt atoms form a direct bond, length 2.626 Å, and this bond is bridged by the carbonyl C_1–O_1. The tin and cobalt atoms form a near-equilateral triangle. The contrast with $BrSn[Co(CO)_4]_3$ is apparent, the latter compound containing four-coordinate tin and discrete $Co(CO)_4$ groups, with the angle Co–Sn–Co approximately tetrahedral[2]. In the present compound this angle is 61.2°, but the strain imposed is evidenced by the fact that the Co–Co bond length is considerably larger than the range of values, 2.43–2.55 Å, observed in other cobalt carbonyl cluster compounds[7]. The only instance of a Co–Co bond comparable in length with that presently observed is in $SCo_3(CO)_9$ [8], in which compound an unpaired electron is thought to occupy an antibonding metal orbital.

The two Sn–Co bond lengths are somewhat shorter than was observed in $BrSn[Co(CO)_4]_3$, and in terms of the least squares error differ from one another significantly. There is no apparent explanation for this in the geometry of the molecule, and it is then likely that the actual errors are greater than has been indicated. The variation in bond length between C_{13}–C_{15} and C_{15}–C_{16}, in contrast to the similarity between C_8–C_{10} and C_{10}–C_{11}, suggests the same conclusion. Other dimensions of the molecule appear to be normal.

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