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CRYSTAL STRUCTURE OF CHLOROTRIS(TETRACARBONYLCOBALT)-TIN, $ClSn[Co(CO)_4]_3$

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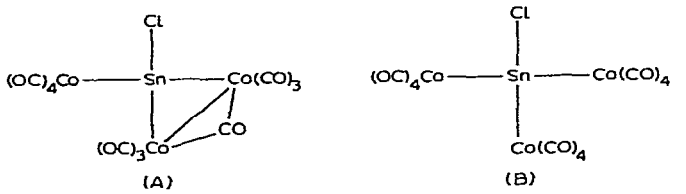
SUMMARY

The molecular structure of the title compound is unequivocally established by X-ray crystallography. The coordination of Co atoms is trigonal-bipyramidal, whereas that of Sn atom being distorted tetrahedral. The mean Sn–Co distance is 2.60 Å. The Sn–Cl bond length (2.54 Å) is definitely greater than the sum of covalent radii (2.39 Å.)

INTRODUCTION

Graham *et al.*[1] have studied the reaction of $SnCl_4$ with $Co_2(CO)_8$ and isolated the solid dark red compound (I) which on the basis of its mass spectrum was assigned the structure (A) containing Co–Co bond and the bridged CO-group although the symmetrical structure (B) seems to be more natural:



In view of our previous investigations of tin–transition metal bond distances[2,3] we undertook the X-ray study of (I) to elucidate its molecular structure and to determine the Sn–Co bond length.

RESULTS AND DISCUSSION

The plate-like crystals of (I) are orthorhombic: $a = 8.36 \pm 0.01$, $b = 16.08 \pm 0.01$, $c = 16.20 \pm 0.01$ Å, $V = 2074$ Å^3, $d_m = 2.00$ g·cm^{-3}, $Z = 4$ belonging to the space group $P2_1/c$. The intensities of ca. 650 independent non-zero reflections were estimated visually disregarding absorption corrections. An equi-inclination Weissenberg goniometer was used with unfiltered iron radiation. The structure was resolved by the heavy-atom technique and refined by the full-matrix least-squares method with

individual isotropic temperature factors to $R=0.12_2$ with an overall temperature factor $B=5.2$ Å. The standard deviations are: Sn–Co 0.01, Sn–Cl 0.01_5, Co–C 0.03, C–O 0.05 Å, CoSnCo 0.3, CoSnCl 0.5, SnCoC 0.9, CCoC 1.9, CoCO 1.7°. The final atomic coordinates and isotropic temperature factors B_j in Å^2 are given in Table 1.

The molecular geometry is shown in Fig. 1. According to the present X-ray study the compound (I) seems to have the symmetrical structure (B). Similar molecular

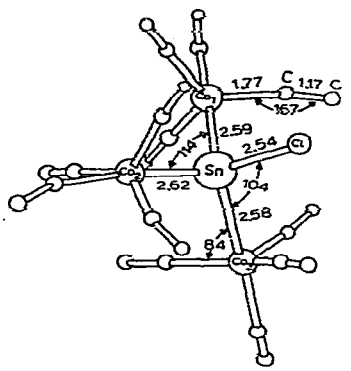


Fig. 1.

structure has been established independently[4] for analogous bromo-derivative, $BrSn[Co(CO)_4]_3$. The tin atom has distorted tetrahedral coordination. Due to steric factors the CoSnCo angles (average 114°) are increased and the ClSnCo angles (average 104°) are decreased as compared to the ideal value. A similar distortion is found, in the analogous molecule of $ClSn[Mn(CO)_5]_3$(II)(av. MnSnMn 116°, av. ClSnMn 101°)[5]. The Sn–Cl bond length (2.54 Å) is definitely greater than that found in (II) (2.43 Å) and also than the sum of the single bonded covalent radii (2.39 Å). This lengthening is probably caused by polar character of the Sn–Cl bond in (I).

The coordination of Co atoms is distorted trigonal-bipyramidal. The equa-

TABLE 1

Atom	x	y	z	B	Atom	x	y	z	B
Sn	0.0500	0.2346	0.3641	3.6	C(11)	0.355	0.133	0.609	4.8
Co(1)	−0.0716	0.1209	0.2492	3.6	C(12)	0.342	0.276	0.509	4.6
Co(2)	−0.1709	0.3446	0.3792	3.6	O(1)	0.264	0.113	0.229	6.5
Co(3)	0.2444	0.1785	0.5091	3.8	O(2)	−0.218	0.002	0.112	5.7
Cl	0.2428	0.3176	0.2976	3.9	O(3)	−0.316	0.248	0.162	4.9
C(1)	0.140	0.124	0.246	7.6	O(4)	−0.136	0.025	0.391	5.2
C(2)	−0.158	0.041	0.174	4.2	O(5)	−0.140	0.406	0.214	4.0
C(3)	−0.199	0.203	0.197	4.5	O(6)	−0.383	0.202	0.390	4.0
C(4)	−0.091	0.068	0.342	7.0	O(7)	−0.425	0.463	0.391	4.9
C(5)	−0.139	0.390	0.286	4.7	O(8)	0.058	0.407	0.544	5.8
C(6)	−0.301	0.262	0.393	5.1	O(9)	0.356	0.047	0.412	5.7
C(7)	−0.313	0.419	0.394	6.3	O(10)	−0.070	0.154	0.548	6.5
C(8)	−0.040	0.375	0.484	5.2	O(11)	0.444	0.110	0.375	4.5
C(9)	0.300	0.101	0.446	7.0	O(12)	0.440	0.333	0.532	5.0
C(10)	0.047	0.164	0.530						

torial CCoC angles vary from 113° to 132°. Equatorial CO-groups are deflected from apical CO-groups towards the Sn atom so as the average values of SnCoC (equatorial) angles are less than 90° [80.9, 88.7 and 82.9 for Co(1), Co(2) and Co(3) respectively]. The mean bond lengths are: 1.77 Å for Co–C and 1.17 Å for C–O and the CoCO angles vary from 160° to 175°.

The Sn–Co bond lengths are found to be 2.58, 2.59 and 2.62 Å. A similar difference though strange for tetrahedral Sn atom, is found also for Sn–Mn bond distances in (II): 2.720, 2.746 and 2.753 Å in one independent molecule and 2.703, 2.745 and 2.758 Å in another. The average Sn–Co bond length (2.60 Å) is somewhat shorter than the value (2.66 Å) found previously[3] in $(OC)_4CoSn(C_6H_5)_2Mn(CO)_5$ and definitely less than the sum of single bonded covalent radii (2.75 Å)[6,7].

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