Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE CRYSTAL STRUCTURE OF TRIBROMOTRIINDIUMTETRACOBALT PENTADECACARBONYL

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(Received November 5th, 1969)

SUMMARY

The crystal structure of $Br_3In_3Co_4(CO)_{15}$ has been determined using three-dimensional X-ray diffractometer data. The crystals are in space group $P2_1/c$, $a = 14.25$, $b = 17.62$, $c = 16.87$ Å, $\beta = 133.2°$. The structure was solved by Patterson methods and refined by least squares to $R = 0.072$. The molecule comprises a six-membered ring of alternate indium and bromine atoms, with each indium bonded to a separate cobalt-tetracarbonyl group, and all three indium atoms bonded to the cobalt of a single cobalt-tricarbonyl group.

INTRODUCTION

A valuable preparative method for compounds involving bonds between a transition metal and a main group metal has been the insertion reaction involving a main group halide of low oxidation state and a dinuclear metal carbonyl. A typical example is the reaction between InBr and $Co_2(CO)_8$ in tetrahydrofuran (THF) solution[1], which gave the product $BrIn[Co(CO)_4]_2 \cdot THF$, in which the solvent molecule is apparently coordinated to the indium atom. When the same reaction was carried out in benzene a different product resulted, which was assigned the formula $In_3Br_3Co_4(CO)_{16}$. The structure of this compound was far from obvious, and its crystal structure has consequently been determined. As a result the correct molecular formula has been established as $In_3Br_3Co_4(CO)_{15}$[2].

EXPERIMENTAL

Orange needle-shaped crystals of hexagonal cross-section were supplied by Dr. W. A. G. Graham. Cell parameters were obtained from Weissenberg and precession photographs, and errors estimated by the method of Patterson and Love[3], as $a = 14.25 \pm 0.01$, $b = 17.62 \pm 0.02$, $c = 16.87 \pm 0.02$ Å, $\beta = 133.2 \pm 0.5°$. The space group is $P2_1/c$, $d_0 = 2.69$ g/cm^3, $d_c = 2.64$ g/cm^3 for 2 molecules of $In_3Br_3Co_4(CO)_{15}$ per cell. A more convenient cell was that with dimensions $a = 21.26$, $b = 17.62$, $c = 16.87$, $\beta = 99.3°$, space group $B2_1/c$, 4 molecules per cell, and this was used throughout the determination and for reference in this paper.

Reciprocal lattice levels *hk*0–*hk*11 were scanned using a Pailred automated diffractometer, which employed Mo $K\alpha$ radiation, monochromatised from the [111] face of a silicon crystal. The ω-scan procedure was used, and background counted

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before and after each reflection scan. For the layers $l=0$–3 the equivalent forms hkl and $h\bar{k}l$ were collected; as these showed no significant variation only the unique data were collected thereafter. Fourteen $hk0$ reflections were remeasured after each layer, as the crystal showed some signs of decomposition. For each, the intensity I_t after collection of the tth layer corresponded well with the expression $\log(I_t/I_0) = -0.0088t_t$, where t_t is the time in days after collection of the zero layer, and intensities were correspondingly corrected. No absorption corrections were considered necessary: the linear absorption coefficient for Mo $K\alpha$ radiation is 84 cm^{-1}, the crystal was of hexagonal section, mean radius 0.01 cm.

An observation was regarded as significant if $I > 0$ and $\sigma_I/I < 0.5$, where $I = T - t \cdot B$, $\sigma_I = (T + t^2 \cdot B)^{\frac{1}{2}}$, T being the scan count, B the total background count and t the ratio of scan time to total background time. A total data set of 1920 observed reflections was thus obtained, from 4514 reflections scanned.

The Patterson function was somewhat complex because of the large number of heavy atoms, but after some trials a set of peaks was recognised as being consistent with the Harker and Cross vectors corresponding to two heavy atoms. A vector superposition procedure then revealed all ten heavy atoms, and an initial R index of 0.24 refined by least squares to 0.17. A difference Fourier synthesis then revealed the carbonyl atoms, and continued refinement, assuming anisotropic thermal motion for the heavy atoms, isotropic motion for the carbon and oxygen atoms, converged at $R=0.072$. The weighting factor was of the form $1/w = 1 + [(F_o - b)/a]^2$, with $a=73$, $b=129$. These values were chosen so that $\langle w \cdot (F_o - F_c)^2 \rangle$ was invariant with $|F|$. Attempted anisotropic refinement of the light atoms led to their parameters assuming unreal values, and was not continued.

RESULTS AND DISCUSSION

Atom coordinates are listed in Table 1, and thermal parameters in Table 2. Bond lengths and angles are listed in Tables 3 and 4, respectively, and the molecule is portrayed in Fig. 1. A stereo-diagram of the molecular packing is shown in Fig. 2. Observed and calculated structure factors are listed in Table 5.

The three indium and three bromine atoms alternate to form a six-membered ring, in a chair conformation. Each indium is separately bonded to the cobalt of a $Co(CO)_4$ group, and all three indiums are bonded to the fourth cobalt atom, which is situated directly below the centre of the triangle formed by the indiums (see Fig. 1). This "capping" cobalt atom has three carbonyls attached to it. The indium–indium separations range from 3.292 to 3.356 Å, and no interaction between them is indicated. (The In–Br bond length in In_2Br_6 was reported[4] as 2.56 Å, whence the covalent radius for indium may be deduced as 1.42 Å.) Bonds may then be assumed corresponding to those indicated in Fig. 1, and assuming that the bromines each contribute 3 electrons to the ring bonding system, all atoms acquire an inert gas configuration.

Four of the six In–Co bond lengths are within error of the mean value, 2.58 Å, but the other two, In(1)–Co(2) at 2.532 Å and In(2)–Co(1) at 2.63 Å differ by ten times the standard deviation (σ). If the covalent radii are assumed as 1.42 Å for indium (see above) and 1.23 Å for cobalt [estimated from the non-carbonyl bridged Co–Co separation of 2.45 Å in $Co_2(CO)_4(tert\text{-}BuC_2H)_2(C_2H_2)$[5]] the expected value for a Co–In single bond is 2.65 Å. Again, four of the six In–Br bonds agree well with the

TABLE 1: ATOM COORDINATES

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
In(1)	0.1203(1)	0.1252(1)	0.3838(2)	C(23)	0.041(2)	−0.007(2)	0.402(3)
In(2)	0.0473(1)	0.2913(1)	0.3997(2)	O(23)	−0.015(2)	0.001(2)	0.402(2)
In(3)	0.1766(1)	0.2793(1)	0.3120(2)	C(24)	0.173(2)	0.005(2)	0.490(3)
Br(1)	0.0796(2)	0.1892(2)	0.5156(3)	O(24)	0.211(2)	0.018(2)	0.544(2)
Br(2)	0.1574(2)	0.3716(2)	0.4332(3)	C(31)	−0.112(2)	0.441(2)	0.435(3)
Br(3)	0.2431(2)	0.1768(2)	0.4099(3)	O(31)	−0.154(1)	0.479(2)	0.442(2)
Co(1)	0.0666(2)	0.2143(3)	0.2748(3)	C(32)	−0.088(2)	0.325(2)	0.342(3)
Co(2)	0.1219(2)	−0.0172(3)	0.4041(4)	O(32)	−0.116(1)	0.296(2)	0.285(2)
Co(3)	−0.0470(2)	0.3788(3)	0.4172(3)	C(33)	−0.035(2)	0.340(2)	0.517(3)
Co(4)	0.2512(2)	0.3464(3)	0.2296(4)	O(33)	−0.030(2)	0.323(2)	0.578(3)
C(11)	0.038(2)	0.296(3)	0.224(3)	C(34)	−0.000(2)	0.450(3)	0.384(3)
O(11)	0.018(1)	0.349(2)	0.190(2)	O(34)	0.028(2)	0.502(2)	0.359(2)
C(12)	0.096(2)	0.161(2)	0.203(3)	C(41)	0.303(3)	0.389(3)	0.172(4)
O(12)	0.116(1)	0.126(2)	0.154(2)	O(41)	0.339(2)	0.410(2)	0.130(3)
C(13)	−0.006(1)	0.165(2)	0.278(2)	C(42)	0.301(2)	0.354(3)	0.321(3)
O(13)	−0.052(1)	0.128(2)	0.280(2)	O(42)	0.333(2)	0.359(2)	0.380(2)
C(21)	0.122(2)	−0.119(3)	0.422(3)	C(43)	0.247(2)	0.259(3)	0.176(3)
O(21)	0.120(2)	−0.180(2)	0.433(2)	O(43)	0.248(2)	0.203(3)	0.145(3)
C(22)	0.151(3)	−0.018(3)	0.311(4)	C(44)	0.189(2)	0.413(3)	0.210(3)
O(22)	0.175(2)	−0.023(3)	0.253(3)	O(44)	0.146(2)	0.457(2)	0.201(2)

TABLE 2: THERMAL PARAMETERS (Å^2)

Anisotropic atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
In(1)	0.049(2)	0.034(1)	0.068(3)	0.000(1)	0.006(1)	0.004(1)
In(2)	0.048(1)	0.036(1)	0.061(2)	−0.001(1)	0.011(1)	−0.006(1)
In(3)	0.040(2)	0.038(1)	0.074(3)	−0.001(1)	0.009(1)	0.003(1)
Br(1)	0.096(3)	0.051(3)	0.058(4)	0.014(2)	0.019(3)	0.007(2)
Br(2)	0.053(2)	0.050(2)	0.096(5)	−0.014(2)	0.015(2)	−0.024(3)
Br(3)	0.038(2)	0.052(2)	0.119(4)	0.002(2)	−0.007(2)	0.024(3)
Co(1)	0.037(2)	0.036(2)	0.052(4)	0.002(2)	0.005(2)	−0.004(2)
Co(2)	0.060(3)	0.037(3)	0.071(5)	−0.004(2)	0.007(3)	−0.006(3)
Co(3)	0.041(3)	0.038(3)	0.075(5)	0.002(2)	0.009(3)	−0.002(3)
Co(4)	0.039(3)	0.057(3)	0.084(5)	0.000(2)	0.013(3)	0.016(3)

Isotropic atom	B	Atom	B	Atom	B
C(11)	5.8(1)	C(23)	5.3(9)	C(34)	6.8(11)
O(11)	6.6(7)	O(23)	6.9(7)	O(34)	8.8(9)
C(12)	5.4(9)	C(24)	5.6(9)	C(41)	8.0(13)
O(12)	7.5(8)	O(24)	7.9(8)	O(41)	9.5(10)
C(13)	3.7(7)	C(31)	5.3(9)	C(42)	6.4(11)
O(13)	5.9(6)	O(31)	6.8(7)	O(42)	7.4(8)
C(21)	7.4(12)	C(32)	4.4(8)	C(43)	6.6(11)
O(21)	9.2(9)	O(32)	6.8(7)	O(43)	10.7(11)
C(22)	8.1(13)	C(33)	5.9(10)	C(44)	6.8(11)
O(22)	11.2(12)	O(33)	8.0(8)	O(44)	9.1(9)

TABLE 3

BOND LENGTHS (Å)

In(1)-Br(1)	2.800(6)	Co(2)-C(21)	1.82(6)
In(1)-Br(3)	2.732(4)	Co(2)-C(22)	1.81(7)
In(1)-Co(1)	2.573(5)	Co(2)-C(23)	1.72(4)
In(1)-Co(2)	2.532(5)	Co(2)-C(24)	1.73(5)
In(2)-Br(1)	2.696(5)	C(21)-O(21)	1.10(5)
In(2)-Br(2)	2.716(4)	C(22)-O(22)	1.20(6)
In(2)-Co(1)	2.637(6)	C(23)-O(23)	1.20(4)
In(2)-Co(3)	2.585(5)	C(24)-O(24)	1.16(5)
In(3)-Br(3)	2.710(5)	Co(3)-C(31)	1.83(4)
In(3)-Br(2)	2.735(5)	Co(3)-C(32)	1.73(4)
In(3)-Co(1)	2.591(5)	Co(3)-C(33)	1.83(6)
In(3)-Co(4)	2.582(6)	Co(3)-C(34)	1.76(5)
Co(1)-C(11)	1.74(5)	C(31)-O(31)	1.13(4)
Co(1)-C(12)	1.76(5)	C(32)-O(32)	1.18(4)
Co(1)-C(13)	1.78(4)	C(33)-O(33)	1.09(5)
C(11)-O(11)	1.16(5)	C(34)-O(34)	1.21(5)
C(12)-O(12)	1.17(5)	Co(4)-C(43)	1.79(5)
C(13)-O(13)	1.17(4)	Co(4)-C(42)	1.75(5)
		Co(4)-C(41)	1.76(6)
		Co(4)-C(44)	1.76(5)
		C(43)-O(43)	1.13(5)
		C(42)-O(42)	1.15(5)
		C(41)-O(41)	1.19(6)
		C(44)-O(44)	1.19(5)

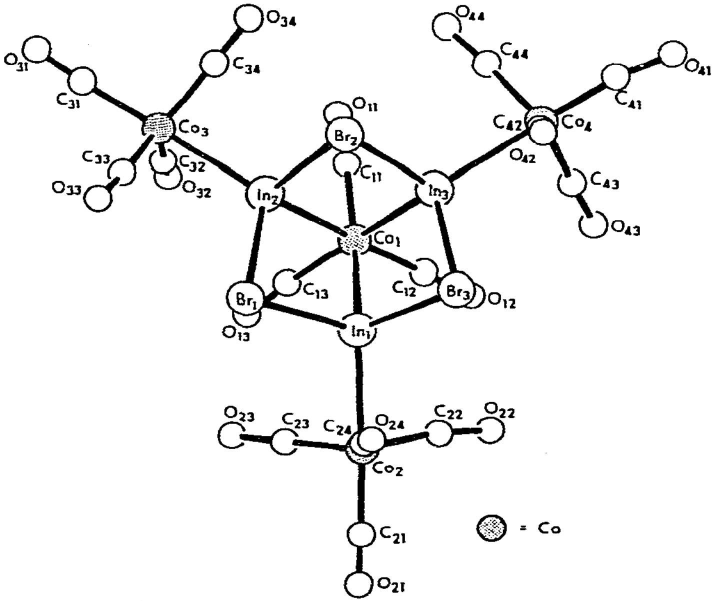

Fig. 1. The $In_3Br_3Co_4(CO)_{15}$ molecule.

TABLE 4

BOND ANGLES (°)

Co(1)–In(1)–Co(2)	134.5(2)	In(1)–Co(2)–C(21)	178(2)
Br(1)–In(1)–Br(3)	98.3(2)	In(1)–Co(2)–C(22)	83(2)
Br(1)–In(1)–Co(1)	101.0(2)	In(1)–Co(2)–C(23)	85(1)
Br(1)–In(1)–Co(2)	106.6(2)	In(1)–Co(2)–C(24)	83(1)
Br(3)–In(1)–Co(1)	102.5(2)	C(21)–Co(2)–C(22)	99(2)
Br(3)–In(1)–Co(2)	108.4(2)	C(21)–Co(2)–C(23)	94(2)
Co(1)–In(2)–Co(3)	129.0(2)	C(21)–Co(2)–C(24)	95(2)
Br(1)–In(2)–Br(2)	94.8(2)	C(22)–Co(2)–C(23)	118(2)
Br(1)–In(2)–Co(1)	102.1(2)	C(23)–Co(2)–C(24)	118(2)
Br(1)–In(2)–Co(3)	114.9(2)	C(24)–Co(2)–C(22)	120(2)
Br(2)–In(2)–Co(1)	101.5(2)	In(2)–Co(3)–C(31)	177(1)
Br(2)–In(2)–Co(3)	108.8(2)	In(2)–Co(3)–C(32)	84(1)
Co(1)–In(3)–Co(4)	132.6(2)	In(2)–Co(3)–C(33)	84(1)
Br(2)–In(3)–Br(3)	92.6(2)	In(2)–Co(3)–C(34)	84(2)
Br(2)–In(3)–Co(1)	102.2(2)	C(31)–Co(3)–C(32)	99(2)
Br(2)–In(3)–Co(4)	109.3(2)	C(31)–Co(3)–C(33)	93(2)
Br(3)–In(3)–Co(1)	102.6(2)	C(31)–Co(3)–C(34)	97(2)
Br(3)–In(3)–Co(4)	110.2(2)	C(32)–Co(3)–C(33)	118(2)
In(1)–Br(1)–In(2)	75.0(1)	C(33)–Co(3)–C(34)	125(2)
In(2)–Br(2)–In(3)	76.0(1)	C(34)–Co(3)–C(32)	114(2)
In(3)–Br(3)–In(1)	74.5(1)		
In(1)–Co(1)–In(2)	79.9(2)	In(3)–Co(4)–C(41)	178(2)
In(2)–Co(1)–In(3)	79.9(2)	In(3)–Co(4)–C(42)	83(2)
In(3)–Co(1)–In(1)	79.1(2)	In(3)–Co(4)–C(43)	84(2)
In(1)–Co(1)–C(11)	162(2)	In(3)–Co(4)–C(44)	84(2)
In(1)–Co(1)–C(12)	91(1)	C(41)–Co(4)–C(42)	98(2)
In(1)–Co(1)–C(13)	88(1)	C(41)–Co(4)–C(43)	94(2)
In(2)–Co(1)–C(11)	84(2)	C(41)–Co(4)–C(44)	97(2)
In(2)–Co(1)–C(12)	168(1)	C(42)–Co(4)–C(43)	120(2)
In(2)–Co(1)–C(13)	88(2)	C(43)–Co(4)–C(44)	119(2)
In(3)–Co(1)–C(11)	89(1)	C(44)–Co(4)–C(42)	117(2)
In(3)–Co(1)–C(12)	90(1)		
In(3)–Co(1)–C(13)	164(1)		
C(11)–Co(1)–C(12)	103(2)		
C(12)–Co(1)–C(13)	100(2)		
C(13)–Co(1)–C(11)	101(2)		
Co(1)–C(11)–O(11)	178(4)	Co(3)–C(31)–O(31)	176(4)
Co(1)–C(12)–O(12)	178(4)	Co(3)–C(32)–O(32)	172(4)
Co(1)–C(13)–O(13)	175(3)	Co(3)–C(33)–O(33)	173(4)
Co(2)–C(21)–O(21)	178(5)	Co(3)–C(34)–O(34)	175(5)
Co(2)–C(22)–O(22)	173(5)	Co(4)–C(41)–O(41)	175(5)
Co(2)–C(23)–O(23)	179(4)	Co(4)–C(42)–O(42)	180(5)
Co(2)–C(24)–O(24)	174(4)	Co(4)–C(43)–O(43)	172(5)
		Co(4)–C(44)–O(44)	175(5)

mean of 2.727 Å, but two, *viz.* In(1)–Br(1) at 2.800 Å and In(2)–Br(1) at 2.696 Å, differ significantly (by 12σ and 6σ respectively). All of these bonds are considerably longer than the value of 2.56 Å observed in In_2Br_6.

No satisfactory explanation can be put forward for these individual large deviations from equality for the lengths of what appear to be equivalent bonds, but

(continued p. 210)

TABLE 5

OBSERVED AND CALCULATED STRUCTURE FACTORS (× 10)

H	K	FO	FC
L = 0			
[illegible]	[illegible]	[illegible]	[illegible]

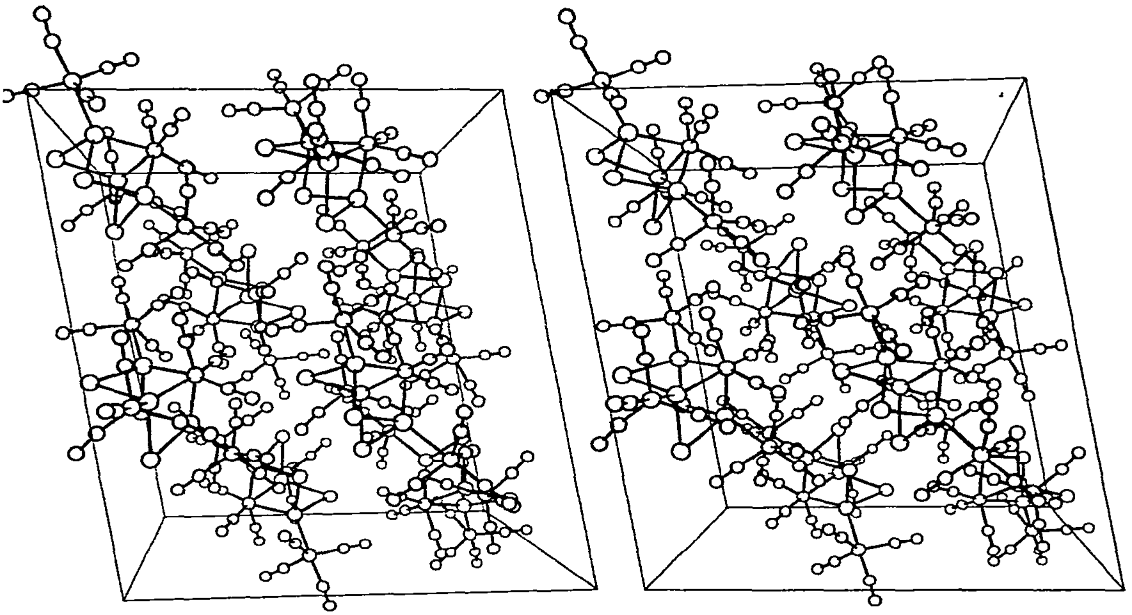

Fig. 2. A stereodiagram of the structure.

the general trends, *i.e.* shorter than normal In–Co and longer than normal In–Br bonds, may be correlated with the bond angles about the indium atom. These show some variation, but the extreme angle types are cobalt–indium–cobalt at *ca.* 132° and bromine–indium–bromine at *ca.* 94°. Bent[6] has demonstrated that in compounds of type X_2MY_2, where M uses sp^3 hybrid orbitals and X is more electronegative than Y, *p* character is increased in the M–X bonds with decreasing X–M–X angle and increased M–X bond length, and vice versa with respect to Y. Similar trends have recently been observed[7] in the structure of $Cl_2Ge[\pi\text{-}C_5H_5Fe(CO)_2]_2$. It is of course likely that in the present molecule, influences other than electronegativity may be involved; ,in particular the strain introduced by the necessity for Co(1) to make bonding contact with all three indiums. The In–Co(1)–In angles are consequently *ca.* 80°, and the octahedron of ligands about this atom is thus considerably distorted.

The fourteen independent Co–C and C–O bonds show mean lengths of 1.77 and 1.16 Å, with internal standard deviations of 0.035 Å in each case. These error estimates are less than the average of the least squares estimates, which gives confidence that these latter are not underestimates. There is no discernible difference between the dimensions associated with the apical $Co(CO)_3$ group and the three $Co(CO)_4$ groups. In all cases the Co–C–O angle is within a few degrees of 180°, as is normal. In the $Co(CO)_4$ groups the equatorial carbonyl groups show the normal repulsion from the terminal carbonyl, such that the In–Co–C angles range from 83–85°. It can be seen from Fig. 1. that the group involving Co(3) is rotated with respect to the indium–bromine ring rather differently from the other two, but as there are no unusually short non-bonded intramolecular contacts in either case, (minimum value, O(13)···O(23) of 3.06 Å), it appears that the difference must arise from packing requirements.

There are various oxygen–oxygen intermolecular contacts of 3.1–3.2 Å, but no closer approaches, and the molecular packing, as shown in Fig. 2, appears in no way remarkable.

ACKNOWLEDGEMENT

Financial support from the National Research Council of Canada is gratefully acknowledged.

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