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

THE CRYSTAL STRUCTURE OF TETRAETHYLAMMONIUM DIBROMOBIS(TETRACARBONYLCOBALT)INDATE(III)

P. D. CRADWICK*
Chemistry Department, University of Alberta, Edmonton, Alberta (Canada)
(Received September 15th, 1970)

SUMMARY

The crystal structure of $Et_4N^+[Br_2Co_2(CO)_8In]^-$ has been determined using three dimensional X-ray diffractometer data. The crystals are in space group $P2_1/n$, $a=17.63$, $b=18.56$, $c=16.47$ Å, $\beta=104.7°$. The structure was solved by Patterson methods and refined by least squares to $R=0.113$. The anion is tetrahedral about the indium atom with the cobalt moieties in the normal trigonal bipyramidal configuration. There are two independent molecules in the asymmetric unit which are related by a non-crystallographic *c* glide.

INTRODUCTION

The compound tetraethylammonium dibromobis(tetracarbonylcobalt)indate(III), $Et_4N^+[Br_2Co_2(CO)_8In]^-$ has been prepared by the insertion reaction between InBr and $Co_2(CO)_8$ in the presence of tetraethylammonium chloride[1], and the crystal structure has been determined as a contribution to a study of the products of such reactions. The structure of the chemically related compound $In_3Br_3Co_4(CO)_{15}$ has been described previously[2].

EXPERIMENTAL

Yellow needle-shaped crystals of square 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 $a=17.63\pm0.02$, $b=18.56\pm0.03$, $c=16.47\pm0.02$ Å, $\beta=104.7\pm0.5°$. The space group is $P2_1/n$, $d_o=2.05$ g/cm^3, $d_c=2.0$ g/cm^3 for 8 molecules of $Et_4N^+[Br_2Co_2(CO)_8In]^-$ per cell, requiring 2 molecules per asymmetric unit.

Reciprocal lattice levels $h0l$–$h11l$ were scanned using a Pailred automated diffractometer, which employed MoK_α radiation, monochromatised from the [111] face of a silicon crystal. Details of the procedure have been described previously[2]. The crystal was sealed in a Lindemann glass capillary during data collection as it proved to be unstable in the atmosphere. No absorption corrections were applied;

* Present address: Chemistry Department, University of Glasgow, Glasgow (Scotland).

TABLE 1

FINAL ATOMIC COORDINATES AND TEMPERATURE FACTORS (Å^2)

Atom	x	y	z	B
In 1	0.4755(3)	0.4604(3)	0.7324(3)	4.5(2)
Br 1	0.5301(4)	0.4754(4)	0.8910(5)	6.5(2)
Br 2	0.3563(5)	0.3794(4)	0.7202(5)	6.8(3)
Co 1	0.4268(6)	0.5852(6)	0.6652(7)	6.3(3)
Co 2	0.5805(7)	0.3812(7)	0.6882(8)	6.9(3)
In 2	0.5017(3)	0.0721(3)	0.2339(3)	4.6(2)
Br 11	0.5851(4)	0.0535(4)	0.3849(5)	6.7(2)
Br 12	0.4382(7)	0.1942(5)	0.2448(5)	8.0(3)
Co 11	0.5960(6)	0.0911(5)	0.1369(6)	4.9(3)
Co 12	0.3921(9)	−0.0228(8)	0.2001(8)	5.8(3)
O 21	0.538(3)	0.274(3)	0.785(3)	10(2)
C 21	0.560(5)	0.331(6)	0.763(6)	14(3)
O 22	0.684(4)	0.483(3)	0.780(4)	13(2)
C 22	0.647(7)	0.438(7)	0.717(7)	17(4)
O 23	0.703(6)	0.302(5)	0.638(6)	22(4)
C 23	0.654(8)	0.303(7)	0.643(8)	20(6)
O 24	0.482(4)	0.405(4)	0.531(5)	16(2)
C 24	0.534(6)	0.403(5)	0.602(7)	12(3)
O 11	0.388(3)	0.717(4)	0.600(4)	13(3)
C 11	0.395(4)	0.664(5)	0.611(4)	5(2)
O 12	0.356(3)	0.595(3)	0.803(4)	11(2)
C 12	0.378(5)	0.594(4)	0.741(6)	9(3)
O 13	0.589(3)	0.612(2)	0.698(3)	7(2)
C 13	0.524(5)	0.609(4)	0.696(4)	6(2)
O 14	0.330(3)	0.492(3)	0.532(3)	11(2)
C 14	0.379(3)	0.534(3)	0.575(3)	3(2)
O 111	0.681(3)	0.130(3)	0.022(4)	8(2)
C 111	0.659(4)	0.104(4)	0.078(5)	8(2)
O 112	0.643(3)	0.221(3)	0.244(4)	12(2)
C 112	0.629(3)	0.170(4)	0.207(4)	4(2)
O 113	0.675(3)	−0.035(3)	0.209(3)	8(2)
C 113	0.638(4)	0.020(4)	0.173(4)	6(2)
O 114	0.455(2)	0.081(2)	0.010(3)	7(1)
C 114	0.511(5)	0.092(4)	0.075(5)	9(2)
O 121	0.394(4)	−0.001(3)	0.361(4)	12(2)
C 121	0.369(10)	0.003(10)	0.294(13)	29(9)
O 122	0.508(3)	−0.107(3)	0.161(3)	10(2)
C 122	0.454(5)	−0.072(5)	0.180(4)	8(2)
O 123	0.274(3)	−0.134(3)	0.169(3)	9(2)
C 123	0.332(7)	−0.087(7)	0.198(7)	17(4)
O 124	0.301(3)	0.077(3)	0.085(3)	7(1)
C 124	0.344(4)	0.034(5)	0.140(5)	8(2)
N 1	0.352(4)	0.171(4)	0.510(4)	7(2)
NC 1	0.421(6)	0.136(5)	0.515(5)	10(3)
NC 2	0.292(5)	0.121(4)	0.496(4)	7(2)
NC 3	0.347(7)	0.224(9)	0.588(10)	27(6)
NC 4	0.367(7)	0.272(8)	0.456(9)	25(5)
C 1	0.494(6)	0.175(6)	0.517(6)	15(4)
C 2	0.206(4)	0.151(4)	0.501(4)	6(2)
C 3	0.366(5)	0.163(5)	0.659(5)	11(3)

(Continued)

TABLE 1 (*continued*)

Atom	x	y	z	B
C 4	0.301(5)	0.200(5)	0.385(6)	14(3)
N 2	0.344(3)	0.325(3)	0.977(3)	3(1)
NC 5	0.322(4)	0.248(4)	0.987(4)	7(2)
NC 6	0.278(4)	0.366(4)	0.920(4)	7(2)
NC 7	0.351(3)	0.352(3)	1.075(3)	4(2)
NC8	0.429(3)	0.335(3)	0.956(3)	3(2)
C 5	0.318(3)	0.210(3)	0.892(3)	4(2)
C 6	0.304(3)	0.448(3)	0.934(3)	3(1)
C 7	0.268(4)	0.354(4)	1.090(4)	8(2)
C 8	0.493(4)	0.291(4)	1.047(4)	8(2)

TABLE 2

INTRAMOLECULAR DISTANCES (Å)

In 1–Br 1	2.561(9)	C 11–O 11	1.02(12)
In 1–Br 2	2.586(10)	C 12–O 12	1.18(11)
In 1–Co 1	2.638(12)	C 13–O 13	1.16(10)
In 1–Co 2	2.644(14)	C 14–O 14	1.24(8)
In 2–Br 11	2.576(9)	C 21–O 21	1.28(12)
In 2–Br 12	2.582(10)	C 22–O 22	1.43(14)
In 2–Co 11	2.637(12)	C 23–O 23	0.91(18)
In 2–Co 12	2.596(14)	C 24–O 24	1.30(14)
Co 1–C 11	1.75(8)	C 111–O 111	1.16(10)
Co 1–C 12	1.71(9)	C 112–O 112	1.13(9)
Co 1–C 13	1.74(8)	C 113–O 113	1.27(9)
Co 1–C 14	1.80(5)	C 114–O 114	1.28(10)
Co 2–C 21	1.67(10)	C 121–O 121	1.09(22)
Co 2–C 22	1.46(13)	C 122–O 122	1.29(11)
Co 2–C 23	2.22(14)	C 123–O 123	1.36(14)
Co 2–C 24	1.50(12)	C 124–O 124	1.31(10)
Co 11–C 111	1.69(8)		
Co 11–C 112	1.87(7)		
Co 11–C 113	1.58(8)		
Co 11–C 114	1.60(9)		
Co 12–C 121	1.74(21)		
Co 12–C 122	1.54(9)		
Co 12–C 123	1.61(13)		
Co 12–C 124	1.58(8)		
N 1–NC 1	1.39(12)	N 2–NC 5	1.52(9)
N 1–NC 2	1.40(10)	N 2–NC 6	1.52(9)
N 1–NC 3	1.66(17)	N 2–NC 7	1.67(7)
N 1–NC 4	2.14(16)	N 2–NC 8	1.53(8)
NC 1–C 1	2.52(13)	NC 5–C 5	1.70(8)
NC 2–C 2	1.66(11)	NC 6–C 6	1.61(9)
NC 3–C 3	1.61(19)	NC 7–C 7	1.58(10)
NC 4–C 4	2.00(17)	NC 8–C 8	1.65(9)

TABLE 3

BOND ANGLES

Atoms	Angle (°)	Atoms	Angle (°)
Br 1–In 1–Br 2	103.5(3)	In 2–Co 11–C 113	89(3)
Co 1–In 1–Co 2	124.3(4)	In 2–Co 11–C 114	75(3)
Br 1–In 1–Co 1	109.2(4)	In 2–Co 12–C 121	89(7)
Br 1–In 1–Co 2	103.4(4)	In 2–Co 12–C 122	85(3)
Br 2–In 1–Co 1	108.0(4)	In 2–Co 12–C 123	171(4)
Br 2–In 1–Co 2	106.5(4)	In 2–Co 12–C 124	86(3)
Br 11–In 2–Br 12	102.1(3)		
Co 11–In 2–Co 12	122.6(4)	Co 1–C 11–O 11	161(8)
Br 11–In 2–Co 11	107.6(3)	Co 1–C 12–O 12	168(8)
Br 11–In 2–Co 12	108.7(4)	Co 1–C 13–O 13	161(7)
Br 12–In 2–Co 11	106.7(3)	Co 1–C 14–O 14	158(5)
Br 12–In 2–Co 12	107.4(4)	Co 2–C 21–O 21	125(6)
		Co 2–C 22–O 22	154(10)
In 1–Co 1–C 11	174(3)	Co 2–C 23–O 23	136(13)
In 1–Co 1–C 12	88(3)	Co 2–C 24–O 24	163(9)
In 1–Co 1–C 13	85(3)	Co 11–C 111–O 111	155(7)
In 1–Co 1–C 14	85(2)	Co 11–C 112–O 112	172(6)
In 1–Co 2–C 21	79(3)	Co 11–C 113–O 113	174(6)
In 1–Co 2–C 22	89(5)	Co 11–C 114–O 114	161(7)
In 1–Co 2–C 23	171(4)	Co 12–C 121–O 121	138(16)
In 1–Co 2–C 24	82(4)	Co 12–C 122–O 122	174(7)
In 2–Co 11–C 111	178(3)	Co 12–C 123–O 123	162(10)
In 2–Co 11–C 112	83(2)	Co 12–C 124–O 124	176(7)
NC 1–N 1–NC 2	110(7)	NC 5–N 2–NC 6	111(5)
NC 1–N 1–NC 3	119(8)	NC 5–N 2–NC 7	98(4)
NC 1–N 1–NC 4	104(6)	NC 5–N 2–NC 8	114(4)
NC 2–N 1–NC 3	109(7)	NC 6–N 2–NC 7	108(4)
NC 2–N 1–NC 4	134(6)	NC 6–N 2–NC 8	123(5)
NC 3–N 1– NC 4	80(7)	NC 7–N 2–NC 8	99(4)
N 1–NC 1–C 1	122(8)	N 2–NC 5–C 5	104(5)
N 1–NC 2–C 2	117(6)	N 2–NC 6–C 6	104(5)
N 1–NC 3–C 3	95(9)	N 2–NC 7–C 7	109(5)
N 1–NC 4–C 4	62(5)	N 2–NC 8–C 8	116(5)

the linear absorption coefficient for MoK_α radiation is 66 cm^{-1}, the mean cross-sectional radius of the crystal was 0.06 mm. A total data set of 898 observed reflections were obtained for which the maximum θ value was 0.3, implying a resolution no better than 0.9 Å.

The Patterson function was complicated by the large number of heavy atoms and also by the non-crystallographic c glide relating the two molecules in the asymmetric unit. This relationship became apparent on inspection of the $h0l$ zone in which the $l=2n+1$ reflections were noticeably weaker than those with $l=2n$. A systematic analysis of the Harker section followed by vector superposition procedures ultimately revealed the ten heavy atoms of both anions, and an initial structure factor calculation

gave an R factor of 0.45, which refined by least squares to 0.22. A difference Fourier synthesis revealed the positions of the carbonyl atoms and further least squares refinement reduced the R factor to 0.15. The cation atoms were found from a new difference synthesis and despite the fact that the geometry about some atoms appeared unreasonable, all were included in the refinement, which led to a final R of 0.113 for the observed data. Although there was some indication of anisotropic motion for the heavy atoms from the difference syntheses isotropic temperature factors were retained throughout in deference to the quantity of observed data.

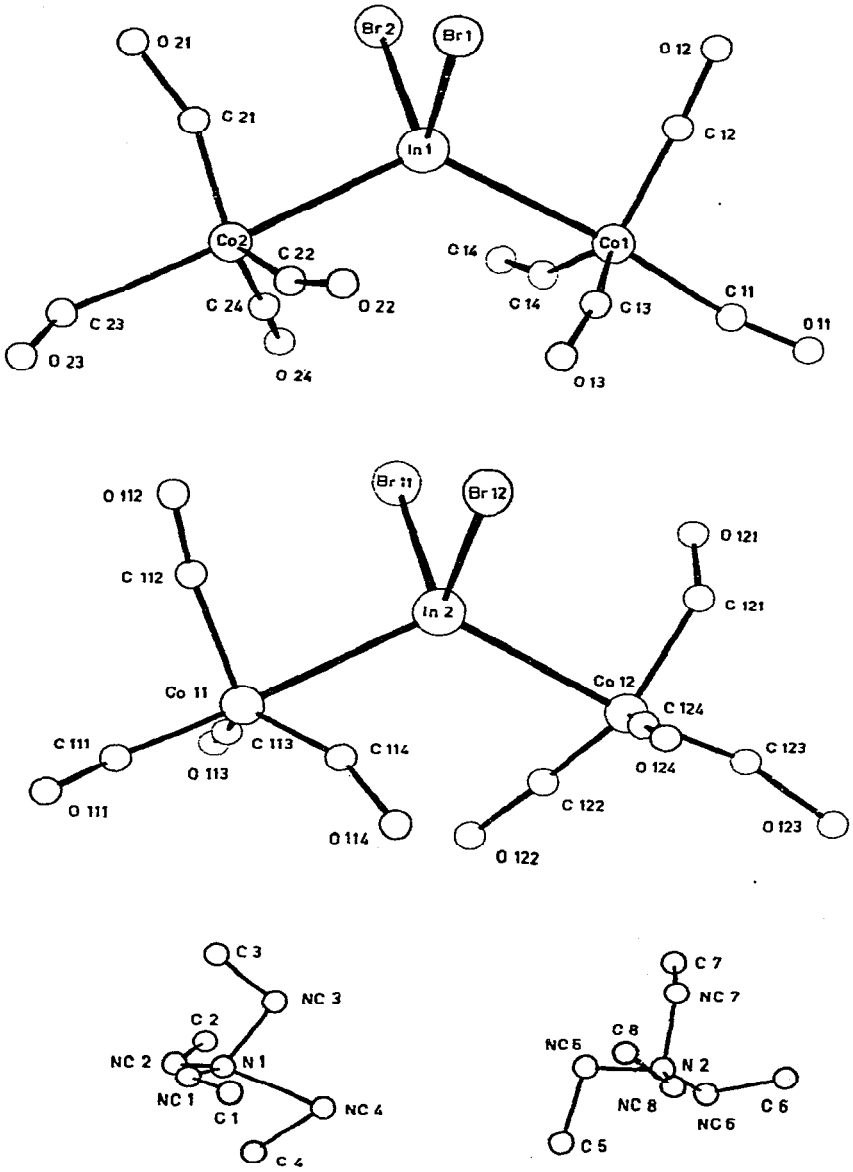

Fig. 1. The anions and cations of $Et_4N^+[Br_2Co_2(CO)_8In]^-$.

TABLE 4

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10)
Unobserved data are marked with an asterisk.

(Table continued)

TABLE 4 (*continued*)

Early stages of the refinement utilized the observed data only, with unit weights, but at the stage where the light atoms were included, the unobserved data were introduced. These reflections were given values and standard deviations recommended by Hamilton[4], where Imin was estimated from the local background for each reflection. A weighting scheme[5] of the form $\sigma = [T + t^2 \cdot B + (0.03\ I)^2]^{\frac{1}{2}}$, was then used for the observed reflections, and the unobserved data were further downweighted by 25%. At convergence the standard deviation of a reflection of unit weight was 1.14. The final R factor including unobserved data was 0.257.

RESULTS

Atom coordinates and thermal parameters are listed in Table 1, bond lengths and angles in Tables 2 and 3 respectively, and the unobserved and calculated structure factors in Table 4. Fig. 1 shows the structure of the anions and the cations and a stereo-diagram of the molecular packing is shown in Fig. 2.

The geometry about the indium atoms is essentially tetrahedral, although some bond angles show considerable distortion from the ideal value of 109°; in particular, the Br–In–Br angles are 102.1° and 103.5° whereas the Co–In–Co angles

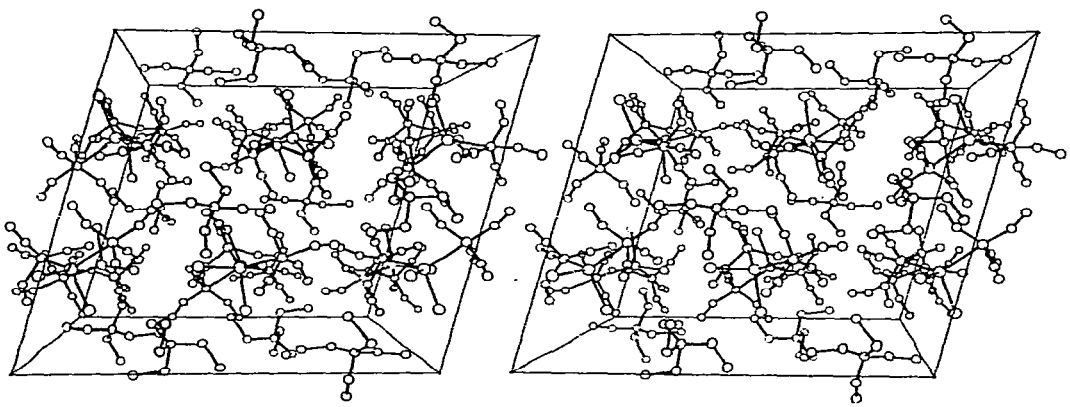

Fig. 2. A stereodiagram of the structure.

are 122.6° and 124.3°. Steric repulsion between the cobalt tetracarbonyl groups is no doubt largely responsible for the latter distortion,and the resultant strain is then minimised by a change in hybridisation giving rise to the decrease of the Br–In–Br angles. The range of In–Co bond lengths is 2.596–2.644 Å, with the mean, 2.652 Å, agreeing with 2.65 Å predicted from the covalent radii of these atoms[2]. Similarly the range of In–Br bond lengths is 2.561–2.586 Å, and the mean 2.575 Å, is in good agreement with the value observed in In_2Br_6 of 2.56 Å[6]. The geometry about the Co atoms is the expected trigonal bipyramid, and the equatorial carbonyl groups all show the normal repulsion from the terminal carbonyl such that the In–Co–C angles range from 75°–89°. This range is considerably larger than that observed in related compounds[2], which probably reflects the relative inaccuracy in the positions of the light atoms. The dimensions of the Et_4N^+ cations are particularly improbable, and almost certainly indicate that these ions are ordered within the crystal to a limited extent only, as has been observed in other structures[7,8]. This lack of order, with its

associated cut-off of data at low θ, imposes an essential restriction on the precision of a structure analysis.

The ions pack in what appears to be an electrostatically favourable manner, at least if it is assumed that the ion charges are centred on the N and In atoms respectively. A feature of the structure is that the crystallographically independent but chemically equivalent ions have a relationship which is very near that of a *c* glide, operation, and undoubtedly the consequent interactions between parameters imposed a further difficulty upon their determinations.

ACKNOWLEDGEMENT

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

REFERENCES

1 D. PATMORE, *Ph.D. Thesis*, University of Alberta, (1968).
2 P. D. CRADWICK AND D. HALL, *J. Organometal. Chem.*, 22 (1970) 203.
3 A. L. PATTERSON AND W. E. LOVE, *Amer. Mineral.*, 45 (1960) 325.
4 W. C. HAMILTON, *Acta Crystallogr.*, 8 (1955) 185.
5 B. G. DE BOOR, A. ZALKIN AND D. H. TEMPLETON, *Inorg. Chem.*, 7 (1968) 2288.
6 V. SCHOMAKER AND D. P. STEVENSON, *J. Amer. Chem. Soc.*, 64 (1942) 2514.
7 D. S. BROWN, F. W. B. EINSTEIN AND D. G. TUCK, *Inorg. Chem.*, 8 (1969) 14.
8 C. H. SCHWALKE AND W. N. LIPSCOMBE, *J. Amer. Chem. Soc.*, 91 (1969) 194.