Table 3. *Angles* (°) *between selected planes* (*e.s.d.'s* 0·5–1·0°)

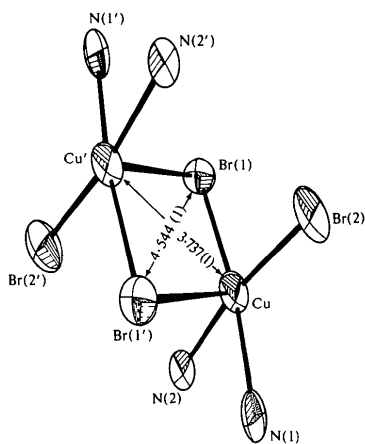|		Angles (°) to planes			
Plane	Defined by	1	2	3	4
1	Cu, Br(1), Br(2)				
2	Cu, N(1), N(2)	3·1			
3	Cu, N(1), N(2), O(1), O(2), C(1), C(2)	8·5	5·8		
4	C(3) through C(8)	66·8	67·9	67·0	
5	C(9) through C(14)	30·6	33·6	39·0	65·7

Fig. 2. Enlarged view of the coordination around Cu.

ligand-field geometry around Cu is a distorted, elongated square pyramid, the equatorial plane of which is defined by the two N atoms of the bidentate diphenylethanedione dioxime ligand [Cu–N 1·987 (5) and 2·007 (5) Å], and by the two Br atoms [Cu–Br 2·358 (1) and 2·351 (1) Å]. Br(2) is bonded to one Cu atom only, whereas Br(1) acts as a bridge between the two Cu atoms and forms the apex of the coordination pyramid of the adjacent Cu' [Cu'–Br(1) 3·427 (1) Å]. The Cu–Cu' distance is 3·737 (1) Å. Table 3 contains information about the angles between selected planes of a monomer and reveals, in particular, the large tilt of the phenyl groups with respect to the mean plane through Cu and the chelating part of the organic ligand.

Compared with the previously studied analogous di-μ-bromo-bis[bromo(2,3-butanedione dioxime)copper(II)] dimer (Endres, 1978), the apical Cu–Br distance of 3·427 Å in the present dimer (*vs* 2·883 Å in the former) and the Cu–Cu contact of 3·737 Å (*vs* 3·599 Å) are considerably longer. The equatorial Cu–Br separations, by contrast, are substantially shorter here, 2·358 and 2·351 Å *vs* 2·387 and 2·372 Å. Also, the Cu–Br–Cu bridge angle of only 78·1° is considerably smaller than in the former dimer (85·59°). The oxime H atoms do not form H bridges between dimers, as in the 2,3-butanedione dioxime compound (Endres, 1978), nor do such bridges contribute to link the two halves of a dimer.

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Structure of Methylammonium Hexabromoindate(III) Monobromide

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Abstract. $4[NH_3(CH_3)]^+ . [InBr_6]^{3-} . Br^-$, $M_r = 802·4$, monoclinic, $P2_1/c$, $a = 16·838$ (6), $b = 7·722$ (2), $c = 20·864$ (6) Å, $\beta = 128·67$ (2)°, $V = 2118$ (1) Å³, $\rho = 2·516$ Mg m⁻³, $Z = 4$, Mo $K\bar{\alpha}$ radiation, $\lambda = 0·71069$ Å, $\mu = 15·08$ mm⁻¹; $R = 0·038$ for 1558 unique reflections. The crystal structure is isomorphous with that of $(CH_3NH_3)_4InCl_7$, consisting of $CH_3NH_3^+$ cations, and Br^- and octahedral $InBr_6^{3-}$

anions (In—Br 2·670 Å). The Br⁻ ions are probably hydrogen bonded to the cations; other examples of similar lattices are discussed briefly.

Introduction. Crystals of the title compound are colourless parallelepipeds elongated along **b**. A crystal 0·26 × 0·08 × 0·05 mm was mounted on a four-circle computer-controlled Syntex $P2_1$ diffractometer for intensity collection. The determination of cell dimensions, space group and other computations are described elsewhere (Khan, Steevensz, Tuck, Noltes & Corfield, 1980). 4167 reflections ($2\theta \le 50°$; hkl, $hk\bar{l}$) were measured and reduced to 1558 unique observed [$I > 3\sigma(I)$] reflections. The results were corrected for Lorentz and polarization effects, and an analytical absorption correction was also applied; the minimum and maximum corrections were 1·91 and 3·25 respectively.

A Patterson synthesis showed that the title compound is isomorphous with $(CH_3NH_3)_4InCl_7$ (Schlimper & Ziegler, 1972), and the initial atomic coordinates were assumed from the latter structure, with Br replacing Cl. The structure was refined anisotropically by full-matrix least-squares methods to $R = 0·040$. H atoms could not be located at this stage, and an attempt to use them in idealized positions did not lead to a successful refinement of their temperature factors. The refinement was therefore continued without the H atoms and yielded a final $R = 0·038$, $R_w = 0·045$. Weights derived from counting statistics were used in the final cycles. The maximum shift/error in the final cycle was 0·01, and the final difference map was devoid of any significant features. The final coordinates are

Table 1. *Atomic coordinates for* $(CH_3NH_3)_4InBr_7$, *with standard deviations in parentheses*

	x	y	z	U_{eq} ($Å^2 \times 10^3$)*
In(1)	0	0	0	27·5 (8)
In(2)	0·5	0	0	27·6 (8)
Br(1)	0·1318 (1)	0·2404 (3)	0·1056 (1)	46 (1)
Br(2)	0·1219 (1)	−0·2479 (2)	0·1055 (1)	46 (1)
Br(3)	0·6383 (1)	−0·2250 (2)	0·0261 (1)	44 (1)
Br(4)	0	0·3858 (5)	0·75	73 (3)
Br(5)	−0·0951 (1)	0·0105 (3)	0·0656 (1)	47 (1)
Br(6)	0·5988 (1)	0·0135 (3)	0·1621 (1)	44 (1)
Br(7)	0·6130 (1)	0·2606 (2)	0·0140 (1)	41 (1)
Br(8)	0·5	0·3861 (5)	0·25	75 (3)
N(1)	0·927 (1)	0·499 (2)	0·565 (1)	58 (11)
N(2)	0·428 (1)	0·525 (2)	0·864 (1)	50 (10)
N(3)	0·158 (1)	−0·062 (3)	0·273 (1)	75 (15)
N(4)	0·339 (1)	−0·068 (3)	0·617 (1)	72 (12)
C(1)	0·318 (2)	0·477 (2)	0·793 (1)	60 (14)
C(2)	0·817 (2)	0·506 (3)	0·520 (2)	77 (19)
C(3)	0·140 (2)	0·112 (4)	0·285 (1)	77 (23)
C(4)	0·367 (2)	0·112 (3)	0·648 (1)	66 (18)

* U_{eq} is calculated from the refined anisotropic thermal parameters (deposited) ($U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$).

Table 2. *Interatomic distances (Å) and angles (°), with e.s.d.'s in parentheses*

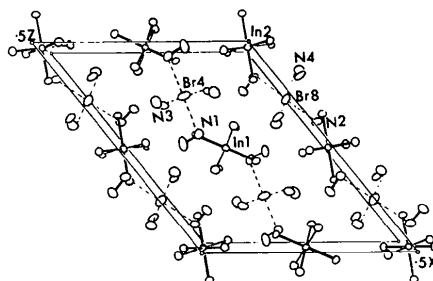|				
In(1)—Br(1)	2·668 (2)		In(2)—Br(3)	2·674 (2)
In(1)—Br(2)	2·660 (2)		In(2)—Br(6)	2·680 (2)
In(1)—Br(5)	2·681 (2)		In(2)—Br(7)	2·658 (2)
N(1)—C(2)	1·46 (3)		N(3)—C(3)	1·42 (3)
N(2)—C(1)	1·53 (3)		N(4)—C(4)	1·48 (3)
Br(4)···N(1)	3·35 (1)		Br(8)···N(2)	3·35 (1)
Br(4)···N(3)	3·46 (2)		Br(8)···N(4)	3·42 (1)
Br(1)—In(1)—Br(2)	90·2 (1)		Br(3)—In(2)—Br(6)	89·6 (1)
Br(1)—In(1)—Br(5)	90·6 (1)		Br(3)—In(2)—Br(7)	89·8 (1)
Br(2)—In(1)—Br(5)	89·9 (1)		Br(6)—In(2)—Br(7)	89·7 (1)

Fig. 1. Packing diagram for $(CH_3NH_3)_4InBr_7$. The atoms are drawn as 50% probability ellipsoids, and hydrogen bonds are indicated by broken lines.

given in Table 1,* with important distances and angles in Table 2. Fig. 1 shows the packing, and illustrates the probable hydrogen-bonding network. The atomic numbering is the same as that used by Schlimper & Ziegler (1972). Scattering factors (including the anomalous-dispersion terms) were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The crystal structures of a number of anionic and neutral In^{III} chloride complexes have been reviewed by Contreras, Einstein, Gilbert & Tuck (1977). The species include coordination numbers of four, five and six, and some six-coordinate complexes of the type $[InCl_n(H_2O)_{6-n}]^{(n-3)-}$. Many of the compounds were originally reported by Ekeley & Potratz (1936); others were prepared later, and tentative structures assigned on the basis of vibrational spectroscopy (Gislason, Lloyd & Tuck, 1971). The conclusions of this study, that the anionic complexes are (tetrahedral) $InCl_4^-$, $InCl_5^{2-}$ or (octahedral) $InCl_6^{3-}$ species, have been confirmed by subsequent crystallographic results.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35732 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The present work was undertaken for two reasons. Firstly, no accurate In^{III}–Br lengths have been reported; secondly, the title compound has the stoichiometry (cation$^+$)$_4$InBr$_7$, which raises obvious problems about the coordination number at In in the presumed anionic complex. The compound is one of two reported to have this stoichiometry, the cations being $(CH_3)_3NH^+$ and $(CH_3)_2NH_2^+$ (Gislason, Lloyd & Tuck, 1971).

The present structural results show that the only In^{III} species present in the solid state is the $InBr_6^{3-}$ anion, which has the expected regular octahedral stereochemistry. The lattice contains two independent $InBr_6^{3-}$ units, which yield essentially identical bond distances and angles, the average In–Br length being 2·670 Å, and the Br–In–Br angles for all pairs of *trans* ligands are 180°. The In–Br bond is *ca* 0·15 Å longer than In–Cl in $InCl_6^{3-}$, for which two concordant values of 2·521 Å (Contreras, Einstein, Gilbert & Tuck, 1977) and 2·523 Å (Schlimper & Ziegler, 1972) have been reported. A similar increase is evident from the older electron diffraction studies of (dimeric) gaseous In_2Cl_6 and In_2Br_6, where the In–X distances for four-coordinate In are 2·46 and 2·58 Å (average) respectively (Brode, 1940; Stevenson & Schomaker, 1942). In terms of the effect of coordination number on In–X length, the present value for In–Br in $InBr_6^{3-}$ is *ca* 0·23 Å longer than that found for the analogous bond in tetrahedral $InBr_4^-$ (2·442 Å) (M. Khan & D. G. Tuck, unpublished results); this increase is similar to that noted earlier for In–Cl bonds (Contreras, Einstein, Gilbert & Tuck, 1977).

The presence of an extra Br$^-$ ion in the lattice raises an intriguing problem. The classical example of such behaviour is $(NH_4)_3SiF_7$, shown to involve a structure of $3NH_4^+ + SiF_6^{2-} + F^-$ (Hoard & Williams, 1942), and it may be significant that the corresponding alkali-metal hexafluorosilicate salts have the expected M_2SiF_6 stoichiometry, and that $(NH_4)_2SiF_6$ also exists (Wells, 1975). Schlimper & Ziegler (1972) showed that $(CH_3NH_3)_4InCl_7$ consists of $4(CH_3NH_3)^+ + InCl_6^{3-} + Cl^-$, and it is therefore reasonable to assume that the same structure also holds for $[(CH_3)_2NH_2]_4InCl_7$ (Gislason, Lloyd & Tuck, 1971) although with the $(CH_3)_3NH^+$ cation, the stable species has the conventional $C_3^+InCl_6$ stoichiometry. Finally, spectroscopic results imply a structural analogy between $[(CH_3)_2NH_2]_4InBr_7$ and the title compound. There are therefore at least five cases in which the lattice incorporates a halide ion which is not interacting directly with the MX_6^{n-} anion. Given the nature of the cations involved in these compounds, it seems reasonable to suggest that the incorporation of the halide anion into the lattice serves to give extra stabilization by the hydrogen-bonding interaction $\geqslant N^+$–H$\cdots X^-$. In the present case, the average N–Br distance of 3·40 Å is close to the N^+–H$\cdots$Br distances of 3·30 and 3·44 Å, in 11-aminoundecanoic acid.HBr.0·5H$_2$O (Sim, 1955) in keeping with this proposal. Similarly, the N–F distances in $(NH_4)_3SiF_7$ (2·90 Å) are only slightly longer than those reported for $\geqslant N^+$–H$\cdots F^-$ in NH_4F and related simple salts (Pimentel & McClellan, 1960), and the $\geqslant N^+$–H$\cdots$Cl distances in $(CH_3NH_3)_4InCl_7$ (3·22 ± 0·05 Å) are well within the range found in a variety of hydrogen-bonded systems in salts of quaternary organic nitrogen cations (Pimentel & McLellan, 1960).* Further work is required to obtain the structural data necessary for a proper understanding of these and similar structures.

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* The distance is actually stated as 2·23 Å in the paper by Schlimper & Ziegler (1972), but calculations with their atomic coordinates show that this is a misprint, and that the larger value given above is correct.

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