

dans les plans (10 $\bar{1}$). La Fig. 2 représente la projection sur la plan *ac* de ces enchaînements.

Le Tableau 2 donne les principales distances interatomiques et angles de liaison de l'arrangement de $\text{CuCr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$.

La Fig. 3 donne les mêmes informations en ce qui concerne les molécules d'eau et leurs voisins. Ces molécules d'eau appartiennent à la classe 1, type *D* de Ferraris & Franchini-Angela (1972): le cation Cu^{2+} auquel l'oxygène *O(W)* est lié se situe approximativement sur la bissectrice des orbitales libres de cet oxygène, c'est-à-dire sur la bissectrice extérieure des liaisons oxygène-hydrogène. Les valeurs des angles $\text{H}-\text{O}(W)-\text{H}$ sont particulièrement élevées (129 et 121°) par rapport à la valeur moyenne de ce type d'angles (107,8° selon Ferraris & Franchini-Angela). Des valeurs comparables ont cependant été obtenues par Yuen & Collin (1974) pour le diphosphate Na_6Cu

$(\text{P}_2\text{O}_7)_2 \cdot 16\text{H}_2\text{O}$. Les autres distances et angles indiqués par la Fig. 3 sont tout à fait habituels dans ce genre de composé.

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Potassium Diaquatetabromoindate(III)

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Abstract. $\text{K}[\text{InBr}_4(\text{H}_2\text{O})_2]$, monoclinic, $P2_1/c$, $a = 6.852$ (15), $b = 11.984$ (8), $c = 6.996$ (6) Å, $\beta = 113.38$ (5)°, $Z = 2$. The final $R = 0.046$ for 2016 independent reflections with $I > 3\sigma I$. The salt contains discrete $[\text{InBr}_4(\text{H}_2\text{O})_2]^-$ anions and disordered K^+ cations lying in a general symmetry site with a 50% occupation probability. The $[\text{InBr}_4(\text{H}_2\text{O})_2]^-$ octahedral ion is a tetrabromo-*trans*-diaqua complex of In^{III} in which the In–O distance is 2.261 (6) Å and the In–Br distances are 2.606 (1) and 2.621 (1) Å.

Introduction. $\text{K}[\text{InBr}_4(\text{H}_2\text{O})_2]$ was prepared by slow evaporation of aqueous solutions of InBr_3 and reagent-grade KCl , in appropriate molecular ratio as established by Wignacourt (1979) in the ternary solubility diagram $\text{InBr}_3\text{--KBr--H}_2\text{O}$. The compound being highly hygroscopic, a small crystal, coated with Nujol, was mounted in a quartz capillary. The cell parameters were determined by a least-squares procedure from setting angles of 25 reflections measured on a Philips PW 1100 automatic four-circle diffractometer, with graphite-monochromatized $\text{Mo } K\alpha$ radiation ($\lambda = 0.7107$ Å). The intensities of 3309 reflections with $3 < \theta < 30^\circ$

were collected by the ω - 2θ scan technique with a $0.03^\circ \text{ s}^{-1}$ scanning speed and a 1.30° scan width. The background was measured for half the scan time at each end of the scan. The intensities of three periodically monitored reflections displayed no significant variations. The systematic extinctions for reflections with l odd for $h0l$, and k odd for $0k0$ defined the space group as $P2_1/c$. The intensities were corrected for Lorentz and polarization effects. An attempt to correct for absorption ($\mu = 18.53 \text{ mm}^{-1}$) failed because the Nujol coat made it impossible to measure the crystal dimensions. The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971); 350 reflections with $|I(E)| > 1.20$ were included in the phase-determining process with sixteen sets of starting phases. The *E* map corresponding to the solution with the best figure of merit (ABSFOM maximum) revealed the positions of four atoms in the asymmetric unit: one In, two Br, and one O. A difference map showed the existence of two peaks (corresponding to a general position in $P2_1/c$) whereas one was expected for the remaining K atom; the refinement of the occupation probabilities led to a 50% ratio for each position. Atomic and thermal parameters were refined by full-matrix least-

Table 1. *Final positional parameters [for In, Br(1), Br(2) $\times 10^5$, for O, K $\times 10^4$] and equivalent isotropic thermal parameters, with their e.s.d.'s*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
In	100000	100000	100000	1.9
Br(1)	79670 (3)	85202 (6)	71425 (12)	2.7
Br(2)	65924 (14)	112370 (7)	87100 (14)	3.5
O	9082 (10)	9224 (4)	12471 (9)	3.3
K	7169 (5)	940 (2)	3862 (4)	2.1

squares methods. The final *R* and *R*_w [*w* = 1/ $\sigma^2(F_o)$] were 0.046 and 0.058 respectively.* Scattering factors were taken from Cromer & Waber (1965) and anomalous-dispersion corrections were applied for K⁺, In, Br and O. The refined coordinates are listed in Table 1.

Discussion. The ionic packing with the atom numbering is shown in Fig. 1. Intraionic bond lengths and angles are given in Fig. 2, interionic distances in Table 2. The present work establishes that the [InBr₄(H₂O)₂]⁻ anion has *trans* stereochemistry, which is found for the first time in the octahedral aquahalogenoindates. The structures of [InCl₃(H₂O)₃](dioxane)₃ (Whitlow & Gabe, 1975) and [InCl₄(H₂O)₂](S₄N₃) (Ziegler, Schlimper, Nuber, Weiss & Ertl, 1975) both showed that the O atoms were located in *cis* positions (*trans* to Cl

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34904 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

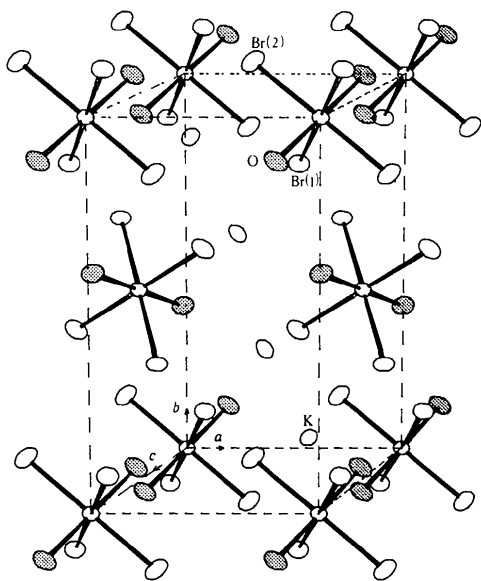


Fig. 1. Atom numbering and ionic packing with 50% probability thermal ellipsoids (Nowogrocki, 1977).

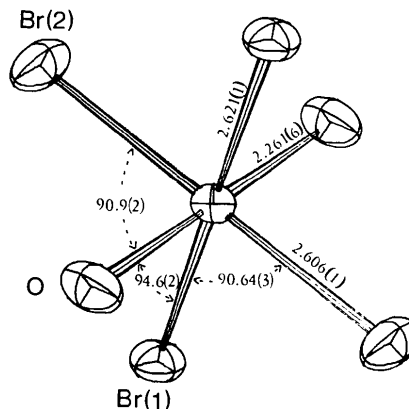


Fig. 2. Interatomic distances (Å) and angles (°) in the [InBr₄(H₂O)₂]⁻ anion.

Table 2. *Interatomic distances (Å) about the K⁺ cation, with their e.s.d.'s*

Coding of equivalent positions: (1) *x, y, z*; (2) $\bar{x}, \bar{y}, \bar{z}$; (3) $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$; (4) $x, \frac{1}{2} - y, \frac{1}{2} + z$. Br(2) 4/011 means that Br(2) is in position (4), translated by 0*a*, 1*b*, 1*c*.

K ⁺ 1/000			
	O	1/011	2.812 (7)
	O	2/212	2.826 (7)
	Br(1)	2/111	3.366 (3)
	Br(2)	4/011	3.403 (3)
	Br(2)	1/011	3.485 (3)
	Br(2)	1/010	3.584 (3)
	Br(1)	1/010	3.602 (3)
	Br(2)	2/111	3.606 (3)
	Br(1)	2/211	3.726 (4)

atoms) as in K₂[InCl₅H₂O] (Wignacourt, Mairesse & Barbier, 1976). Furthermore, the [InCl₄(urea)₂]⁻ anion was also proposed to have the *cis* stereochemistry (Tuck & Woodhouse, 1964), the difference from [InBr₄(H₂O)₂]⁻ probably being due to the larger size of the halogen ligand.

The octahedral [InBr₄(H₂O)₂]⁻ ion is slightly distorted both in bond lengths and angles. The In—Br distances obtained, when compared with the 2.57 Å reported by Brode (1940) in InBr, presumably indicate the covalent bonding in this complex. The In—O distance is in good agreement with those observed in the above-mentioned aquachloroindates.

It is not easy to determine the K⁺ coordination number: each ion is surrounded (Table 2) by two O atoms at about 2.80 Å, and six Br atoms between 3.36 and 3.60 Å; but we also find another at about 3.73 Å.

As the experimental conditions did not enable us to find the H atom positions, no conclusion can be drawn about the possible existence of hydrogen bonding. Nevertheless, we note that the Br(1) 4/010 atom (coding in Table 2) lies 3.363 Å from the O 1/000 atom, while the sum of their van der Waals radii is 3.42 Å.

The thermal motion of the $[\text{InBr}_4(\text{H}_2\text{O})_2]^-$ anion does not fit with the values resulting from a rigid-body analysis by the TLS method (Schomaker & Trueblood, 1968). The corrected bond distances obtained by Busing & Levy's (1964) method, considering the riding motion of the O and Br atoms upon the heavier In, are $\text{In}-\text{Br}(1) = 2.627$, $\text{In}-\text{Br}(2) = 2.611$ and $\text{In}-\text{O} = 2.272 \text{ \AA}$.

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Rubidium Tribromomanganate

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Abstract. RbMnBr_3 , hexagonal, $P6_3/mmc$, $a = 7.56$ (2), $c = 6.35$ (2) \AA , $D_o = 3.97$, $D_x = 4.01 \text{ Mg m}^{-3}$, $Z = 2$. The unit cell accommodates two close-packed layers of composition RbBr_3 stacked perpendicular to $[001]$. Mn ions are located between these layers, being octahedrally coordinated by Br ions. The structure is isomorphous with that of CsNiCl_3 .

Introduction. Complex halides of composition $X\text{MnY}_3$, where X represents an alkali ion and Y a halogen ion, usually have structures based on close-packed layers of composition XY_3 with the Mn ions located between the layers such that they are coordinated octahedrally by Y ions. In these structures the XY_3 layers are parallel to the (001) faces of a hexagonal cell and can be of three types (A , B or C) according to the position of the cross-section of the unit cell in the layer.

The structure of CsMnBr_3 (Goodyear & Kennedy, 1972) has the layer sequence $BABA \dots$, giving a structure which is isomorphous with that of CsNiCl_3 . On the other hand, the structure of RbMnCl_3 (Goodyear, Steigmann & Ali, 1977) has the six-layer sequence $BCBACA \dots$, whilst that of CsMnCl_3 (Goodyear & Kennedy, 1973) is based on a nine-layer sequence, $BABACACBC \dots$

The material examined in this work was prepared by heating a stoichiometric mixture of RbBr and MnBr_2 in

an evacuated silica tube until molten and then cooling the sample at a rate of 5 K h^{-1} . Pink crystals of RbMnBr_3 were formed which were unstable in the presence of water vapour. Consequently, the crystals selected for X-ray examination were enclosed in sealed Lindemann-glass capillary tubes.

The cell dimensions were determined from α_1 – α_2 doublet separations on zero-layer Weissenberg photographs taken with $\text{Cu K}\alpha$ radiation and the observed density indicated $Z = 2$. It was evident at this stage that the structure was almost certainly isomorphous with that of CsMnBr_3 .

Intensities were collected from equi-inclination photographs taken about c with $\text{Mo K}\alpha$ radiation. The intensities of 105 symmetrically independent reflexions were measured on layer lines 0–5 with accurately timed film exposures; 67 reflexions were too weak to be observed. The systematically absent reflexions were all of the type hhl with $l = 2n + 1$, consistent with the space group $P6_3/mmc$ of CsMnBr_3 . The observed data were corrected for the Lorentz–polarization factor and for absorption by assuming the crystal to be cylindrical with a mean $\mu r = 1.1$.

In the initial cycle of least-squares refinement, positional parameters suggested by the CsMnBr_3 structure were assumed and each atom was assigned an individual isotropic temperature factor of 1.5 \AA^2 . After