The thermal motion of the $[InBr_4(H_2O)_2]^-$ 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 In—Br(1) = 2·627, In—Br(2) = 2·611 and In—O = 2·272 Å.

References

BRODE, H. (1940). *Ann. Phys. (Leipzig)*, **37**, 344–364.

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

NOWOGROCKI, G. (1977). Unpublished program from *ORTEP* (C. K. JOHNSON), written for a Hewlett Packard 9825 computer.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

TUCK, D. G. & WOODHOUSE, E. J. (1964). *Chem. Ind.* pp. 1363–1364.

WHITLOW, S. H. & GABE, E. J. (1975). *Acta Cryst.* B**31**, 2534–2536.

WIGNACOURT, J. P. (1979). Unpublished data.

WIGNACOURT, J. P., MAIRESSE, G. & BARBIER, P. (1976). *Cryst. Struct. Commun.* **5**, 293–296.

ZIEGLER, M. L., SCHLIMPER, H. V., NUBER, B., WEISS, J. & ERTL, G. (1975). *Z. Anorg. Allg. Chem.* **415**, 193–201.

Rubidium Tribromomanganate

BY J. GOODYEAR, E. M. ALI AND H. H. SUTHERLAND

Physics Department, The University, Hull HU6 7RX, England

Abstract. $RbMnBr_3$, hexagonal, $P6_3/mmc$, $a = 7·56$ (2), $c = 6·35$ (2) Å, $D_o = 3·97$, $D_x = 4·01$ 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 $XMnY_3$, 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 $BABA$ ..., 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 $BCBACA$ ..., whilst that of $CsMnCl_3$ (Goodyear & Kennedy, 1973) is based on a nine-layer sequence, $BABACACBC$ ....

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 a_1–a_2 doublet separations on zero-layer Weissenberg photographs taken with 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 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 Å^2. After

Table 1. *Final atomic parameters (origin at centre* $\bar{3}m1$)

	Equipoint	x	y	z	B (Å^2)
Mn	2(a)	0	0	0	1·00 (15)
Rb	2(d)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	1·32 (15)
Br	6(h)	0·1650 (10)	0·3300 (20)	$\frac{1}{4}$	1·32 (9)

Table 2. *Selected bond lengths* (Å)

	Multi-plicity		Location of atoms
Mn—Br octahedron			Mn at (000)
Mn—Br(i)	3 ⎫	2·681 (12)	Rb at ($\frac{1}{3}\frac{2}{3}\frac{3}{4}$)
Mn—Br(ii)	3 ⎬		Br(i), Br(ii), Br(iii) at heights
Br(i)—Br(i)	3 ⎫	3·742 (25)	$z = \frac{1}{4}, -\frac{1}{4}$ and $\frac{3}{4}$,
Br(ii)—Br(ii)	3 ⎬		respectively.
Br(i)—Br(ii)	6	3·840 (12)	
Rb—Br distances			
Rb—Br(i)	6	3·780 (10)	
Rb—Br(ii)	3 ⎫	3·865 (12)	
Rb—Br(iii)	3 ⎬		

refinement, $R = \sum||F_o| - |F_c||/\sum|F_o|$ reduced to 6·6%. At this stage, the shift in each atomic parameter was $<0\cdot03\sigma$ and the calculated structure factors for the unobserved reflexions were all less than the minimum observable value. Scattering factors for Rb$^+$, Mn^{2+} and Br$^-$ were taken from *International Tables for X-ray Crystallography* (1974).

The final atomic parameters and some selected bond lengths are given in Tables 1 and 2, respectively.*

Discussion. The Rb and Br ions form an approximate hexagonally close-packed array such that each Rb ion has 12 nearest Br neighbours. The Mn ions occupy the octahedral sites formed by the Br ions and the Mn—Br octahedra share opposite faces to form chains of composition $(MnBr_3)_n^{n-}$, parallel to [001].

Because of the mutual repulsion of adjacent Mn^{2+} ions in the face-sharing octahedra, each octahedron is trigonally distorted. Consequently, the Br(i)—Br(i) and Br(ii)—Br(ii) edges are each significantly shorter than the Br(i)—Br(ii) edge and the Br(i)—Mn—Br(i) and Br(ii)—Mn—Br(ii) angles are each 88·5° whilst the Br(i)—Mn—Br(ii) angle is 91·5°.

The dimensions of the octahedron are very similar to those of the MnBr$_6$ octahedron in CsMnBr$_3$. In each structure the Mn—Br length is 2·68 Å and the mean Br—Br distance 3·79 Å.

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34955 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

GOODYEAR, J. & KENNEDY, D. J. (1972). *Acta Cryst.* B28, 1640–1641.

GOODYEAR, J. & KENNEDY, D. J. (1973). *Acta Cryst.* B29, 744–748.

GOODYEAR, J., STEIGMANN, G. A. & ALI, E. M. (1977). *Acta Cryst.* B33, 256–258.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Struktur ternärer *I*-tetragonaler Boride: $(B_{12})_4C_2Ti_{1.86}$ und $(B_{12})_4C_2V_{1.29}$

VON E. AMBERGER UND H. P. GERSTER

Institut für Anorganische Chemie der Universität München, Meiserstrasse 1, D-8000 München 2, Bundesrepublik Deutschland

Abstract. $(B_{12})_4C_2Ti_{1.86}$, tetragonal, $P4_2/nnm$, $a = 8\cdot876$ (1), $c = 5\cdot062$ (1) Å, $V = 398\cdot80$ (17) Å^3, $Z = 1$, $D_x = 2\cdot631$ (5), $D_m = 2\cdot63$ (1) Mg m^{-3}; single-crystal counter data, $R_w = 0\cdot049$ for 172 observed independent reflexions. $(B_{12})_4C_2V_{1.29}$, tetragonal, $P4_2/nnm$, $a = 8\cdot857$ (9), $c = 5\cdot070$ (12) Å, $V = 397\cdot72$ (1·75) Å^3, $Z = 1$, $D_x = 2\cdot54$ (1), $D_m = 2\cdot55$ (1) Mg m^{-3}; Weissenberg method; $R_w = 0\cdot096$ for 123 observed independent reflexions of a twinned crystal.

Einleitung. Hoard, Hughes & Sands (1958) beschrieben erstmals die Struktur des sogenannten *I*-tetragonalen Bors. Diese Struktur bildet sich originär nur durch Einbau von Fremdatomen. Das zeigten