

## Structural Differences between $\text{RbMnCl}_3$ and $\text{RbMnBr}_3$

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### Abstract

The crystal structures of  $\text{RbMnCl}_3$  and  $\text{RbMnBr}_3$  were determined to be hexagonal  $P6_3/mmc$ . The differences between these two structures are that in  $\text{RbMnCl}_3$  there are six close-packed layers while there are two close-packed layers in  $\text{RbMnBr}_3$ . Moreover, in the latter structure the Mn-Br octahedra share opposite faces to form infinite chains of composition  $(\text{MnBr}_3)$  parallel to the *c*-axis, while in the  $\text{RbMnCl}_3$  structure such an infinite chain does not exist. The reasons put forward to account for these differences are that the cation/anion ratio in  $\text{RbMnCl}_3$  is too large to permit the formation of infinite chains of Mn-Cl face sharing octahedra. The second reason is a polarisation effect: the extra polarisation of the bromine compared with the chlorine makes  $\text{RbMnBr}_3$  isomorphous with  $\text{CsNiCl}_3$ , which has two close-packed layers, while  $\text{RbMnCl}_3$  is not.

### 1. Introduction

Many complex chlorides and bromides of composition  $\text{XMCl}_3$  and  $\text{XMBr}_3$ , where X represents an alkali ion and M a metal in the first transition series, have structures which are based on hexagonally close-packed layers of composition  $\text{XCl}_3$  and  $\text{XBr}_3$ , with M ions situated between the layers, being octahedrally coordinated by Cl or Br ions. In such structures the  $\text{XCl}_3$  and  $\text{XBr}_3$  layers are of three types (A, B or C) according to the position of the cross section of the hexagonal cell (see Fig. 2).

These materials are very hygroscopic and must be prepared by allowing  $\text{RbX}$  and  $\text{Mn}_2\text{X}$  (where X is a Cl or Br atom) to react in a sealed evacuated silica tube. The final products must be stored in a moisture-free atmosphere once removed from the silica tube. The apparatus used to prepare the compounds is shown in Fig. 1. It was fitted onto a two-stage oil vapour diffusion pump employed to evacuate the system. Stoichiometric amounts of  $\text{RbX}$  and  $\text{MnX}_2 \cdot 4\text{H}_2\text{O}$  were placed in the silica tube, a constriction being made in the neck of the tube to facilitate sealing at a later stage and also to prevent the solid ingredients being sucked into the vapour trap, and then cooled by liquid nitrogen incorporated into the system. A pressure of less than  $2 \times 10^{-5}$  Torr (1 Torr  $\equiv$  133 Pa) was required to prevent the formation of oxides and hydroxides.

The temperature of the sample was slowly raised to  $120^\circ\text{C}$  and kept constant until all the water of crystallisation had been driven off. The temperature was

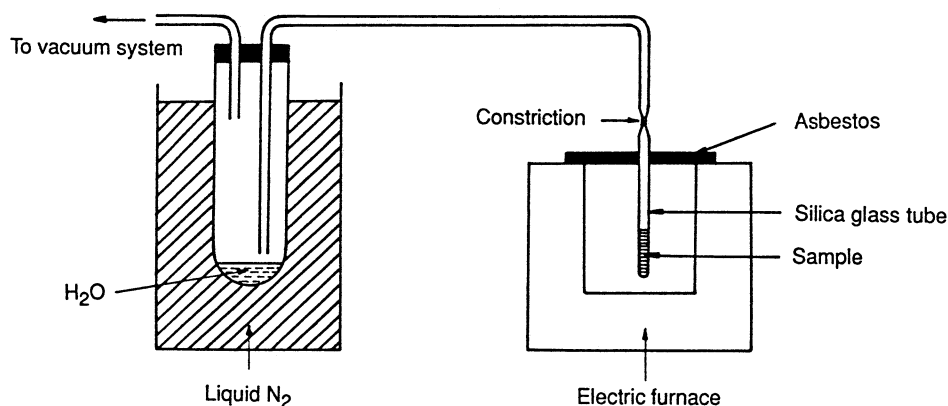


Fig. 1. Apparatus used for preparation of crystals.

then raised slowly to about  $650^{\circ}\text{C}$  when both compounds melted and mixed together. The silica tube was then sealed at the constriction and cooled in another electric furnace at the rate of about  $10^{\circ}\text{C}$  per hour. In order to cool the furnace at this rate the input current to the furnace windings was slowly reduced by variac wound down by a suitably geared electric motor. In this way the sample was cooled to room temperature. The vacuum surrounding the compound ensured that the crystals would keep indefinitely.

Crystals were chosen from a crushed bulk of sample using a low power ( $\times 35$ ) polarising microscope. A suitable crystal fulfills the criterion that when placed on the microscope stage, rotated between the crossed polarisers and illuminated with parallel white light, it shows complete extinction over the whole crystal at a certain position, repeating every  $90^{\circ}$  of rotation. The crystals must also be small and approximately cylindrical in shape in order to reduce and correct for absorption of the incident X-ray beam. In practice, rectangular crystals of the appropriate size were elected, typically  $0.27\text{ mm}$  in length and  $0.135\text{ mm}$  in width and thickness.

The crystal selected for X-ray examination was mounted in a Lindemann glass-tube of  $0.3\text{ mm}$  diameter sealed at one end. A small plug of  $\text{P}_2\text{O}_5$  was put on the other end and mounted on the goniometer head by means of black wax to completely seal the specimen.

## 2. Determination of Unit Cell Dimensions

Oscillation and Weissenberg photographs were taken about the  $a$ -axis with  $\text{Cu K}\alpha$  radiation. The unit cell dimensions were determined from  $\alpha_1$ - $\alpha_2$  doublet separations on a zero layer Weissenberg photograph, taken with  $\text{Cu K}\alpha$  radiation, using the method of Main and Woolfson (1963). The unit cell parameters for the compounds  $\text{RbMnCl}_3$  and  $\text{RbMnBr}_3$  were determined to be (see Goodyear *et al.* 1977, 1980):

	$a$ (Å)	$c$ (Å)
$\text{RbMnCl}_3$	$7.16(1)$	$17.83(4)$
$\text{RbMnBr}_3$	$7.56(2)$	$6.35(2)$

The macroscopic density of the material was determined by weighing the sample in air and in toluene. For  $\text{RbMnCl}_3$ , the observed density was found to be  $D = 3.09 \text{ g cm}^{-3}$ . By assigning six molecules of  $\text{RbMnCl}_3$  to the unit cell the calculated density was  $3.11 \text{ g cm}^{-3}$ . In  $\text{RbMnBr}_3$  agreement between the observed ( $3.97 \text{ g cm}^{-3}$ ) and calculated ( $4.01 \text{ g cm}^{-3}$ ) density was obtained by assigning two molecules of  $\text{RbMnBr}_3$  to the unit cell.

### 3. Intensity Data Collection

Intensity data were collected from equi-inclination Weissenberg photographs taken about the  $a$ -axis with  $\text{Mo K}\alpha$  radiation. The intensities of symmetrically independent reflections were measured both visually and with a flying spot microdensitometer on layer lines 0–6 from accurately timed film exposures. The systematically absent reflections were of the type  $hhl$  with  $l = 2n + 1$ ; hence the space group must be either  $P6_3mc$  or  $P\bar{6}2c$  or  $P6_3/mmc$ . The latter, which is centro-symmetric was chosen since it is the space group of  $\text{CsNiCl}_3$ . The observed data were corrected for the Lorentz polarisation factor and for absorption using factors given by Bond (1959) for a cylindrical specimen. A computer program was used to apply these corrections. The linear absorption coefficient  $\mu$  used in the absorption correction program was calculated from the mass absorption coefficients of the constituent elements, taken from the 'International Tables for X-ray Crystallography' (1962).

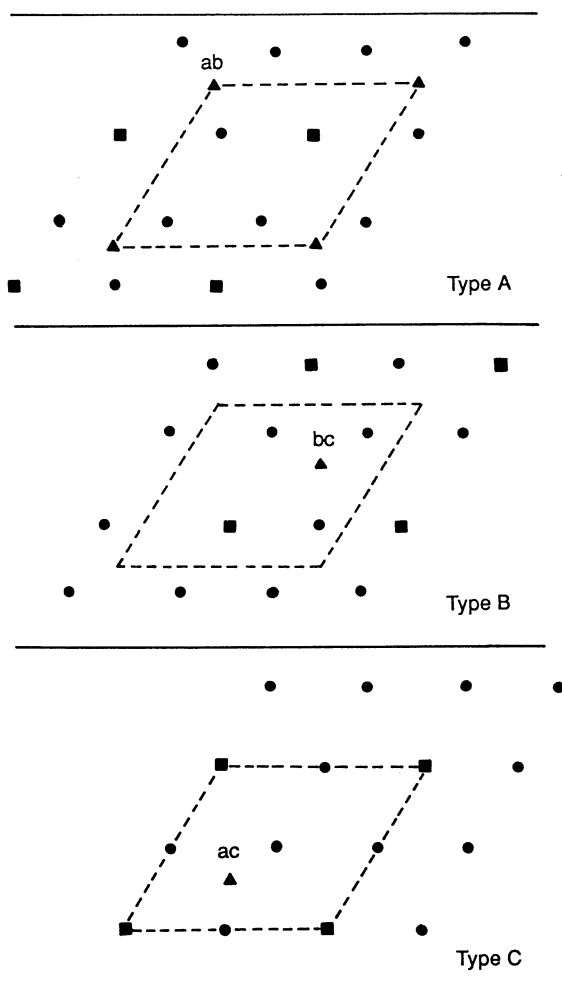
### 4. Structural Analysis

#### (a) $\text{RbMnCl}_3$

Previous work by Kestigian *et al.* (1967) using powder diffractometry indicated a hexagonal cell for  $\text{RbMnCl}_3$  with  $a = 7.164 \text{ \AA}$  and  $c = 17.79 \text{ \AA}$ , in agreement with the present data. The initial structure was determined by considering a stacking sequence of  $\text{RbCl}_3$  which would explain a  $c$ -parameter of the order of  $18 \text{ \AA}$ . In the  $\text{CsMnCl}_3$  structure (Goodyear and Kennedy 1973) the  $c$ -parameter is of the order of  $27 \text{ \AA}$  and accommodates nine close-packed layers, indicating a layer separation of about  $3 \text{ \AA}$ , and thus suggesting six layers in the unit cell of  $\text{RbMnCl}_3$ . This is also consistent with the assignment of six molecules per unit cell.

Since each Rb atom must be in contact with 12 Cl atoms there are three possible positions of a layer in relation to the outline of the unit cell, these correspond to the types A, B and C of Fig. 2. The stacking sequence of a six-layer structure would then be BCBCA....

In  $\text{RbMnCl}_3$ -type complex halides with  $\text{RbCl}_3$  close-packed layers, the Mn atoms have to occupy octahedral holes between six Cl atoms. It can be seen in Fig. 2 that only certain positions are possible for the Mn atom in contact with either side of an A, B or C layer, if they are to have only 12 Cl atoms as nearest neighbours. These positions are indicated by triangles in Fig. 2.



**Fig. 2.** Close-packed  $\text{XCl}_3$  ( $\text{XBr}_3$ ) layers classified according to the position of the unit cell (dashed lines). The circles and squares represent Cl (Br) and X (Rb) atoms respectively. The triangles show the octahedral sites for the M (Mn) atoms between different pairs of layers; ab, bc and ac are the sites between A and B, B and C, and A and C respectively.

The structure was refined in the space group  $P6_3/mmc$  using a three-dimensional least squares refinement program. The weighting scheme used in the refinement was

$$w = (a + |F_o| + c|F_o|^2)^{-1},$$

where  $a = 2F_{\min}$  and  $c = 2/F_{\max}$  and where  $F_{\min}$  and  $F_{\max}$  are the minimum and maximum observed intensities. Several cycles of least squares refinement reduced the reliability factor,  $R = (\Sigma |F_o| - |F_c|) / \Sigma |F_o|$ , to 16% at which stage it was apparent that the two strongest reflections, 110 and 220, were suffering from extinction because their intensities were roughly proportional to  $|F|$

Table 1. Initial and final atomic parameters for RbMnCl<sub>3</sub>

Space group is *P*6<sub>3</sub>/*mmc* with origin at  $\bar{3}m1$ . Standard deviations given in parentheses

Equipoint		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
(a) Initial parameters					
Mn(1)	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{6}$	1.50
Mn(2)	2(a)	0	0	0	1.50
Rb(1)	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	$-\frac{1}{12}$	1.50
Rb(2)	2(b)	0	0	$\frac{1}{4}$	1.50
Cl(1)	12(k)	$\frac{1}{6}$	$-\frac{1}{6}$	$\frac{1}{12}$	1.50
Cl(2)	6(h)	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{4}$	1.50
(b) Final parameters					
Mn(1)	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	0.1603(15)	1.32(49)
Mn(2)	2(a)	0	0	0	1.40(84)
Rb(1)	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	-0.0888(13)	3.57 44
Rb(2)	2(b)	0	0	$\frac{1}{4}$	2.70(63)
Cl(1)	12(k)	0.1616(79)	-0.1616(79)	0.0820(15)	1.84(38)
Cl(2)	6(h)	0.4928(74)	-0.4928(74)	$\frac{1}{4}$	1.00(53)

Table 2. Observed and calculated structure factors for RbMnCl<sub>3</sub>

Space group *P*6<sub>3</sub>/*mmc*. \* Corrected for extinction

<i>K</i>	<i>L</i>	<i>F</i> <sub>0</sub>	<i>F</i> <sub>c</sub>	<i>K</i>	<i>L</i>	<i>F</i> <sub>0</sub>	<i>F</i> <sub>c</sub>	<i>K</i>	<i>L</i>	<i>F</i> <sub>0</sub>	<i>F</i> <sub>c</sub>	<i>K</i>	<i>L</i>	<i>F</i> <sub>0</sub>	<i>F</i> <sub>c</sub>
<i>H</i> = 0															
0	6	262	283	4	2	85	82	3	5	45	48	-1	8	51	58
0	12	291	295	4	3	134	123	3	7	59	53	-1	9	46	35
0	18	94	92	4	4	144	159	3	8	52	44	-1	11	36	42
0	24	59	91	4	5	96	96	3	9	43	40	3	0	71	100
1	3	62	57	4	7	87	89	3	11	41	41	<i>H</i> = 4			
1	4	100	120	4	8	130	121	3	16	45	42	-2	6	170	158
1	5	81	72	4	9	108	111	4	0	110	118	-2	12	211	216
1	7	89	81	4	10	50	60	4	12	64	64	-1	3	43	35
1	8	78	64	4	14	53	53	5	4	29	50	-1	4	100	78
1	9	59	62	4	15	54	49	5	5	30	33	-1	5	68	48
1	11	59	55	4	16	84	90	5	7	38	36	-1	7	58	53
1	16	56	57	5	4	53	59	<i>H</i> = 2				-1	8	48	44
2	1	55	60	5	5	65	43	-1	4	36	23	-1	9	43	40
2	2	122	142	5	7	35	46	-1	6	27	22	-1	11	47	41
2	3	203	210	5	8	49	36	-1	8	24	43	4	0	162	149
2	4	232	247	6	0	161	191	-1	12	91	109	<i>H</i> = 5			
2	5	150	147	6	6	92	85	2	0	327*	364	-2	4	70	60
2	7	143	133	6	12	129	131	2	6	155	158	-2	5	31	35
2	8	175	171	<i>H</i> = 1				2	12	245	216	-2	7	48	38
2	9	172	160	1	0	257*	220	3	3	45	39	-2	8	34	31
2	10	84	82	1	4	39	23	3	4	41	60	-2	9	37	43
2	13	37	42	1	6	22	22	4	2	46	61	-2	11	35	40
2	14	74	67	1	8	50	43	4	3	72	88	-1	12	53	63
2	15	65	65	2	3	32	25	4	4	101	118	<i>H</i> = 6			
2	16	128	114	2	4	99	103	4	5	58	70	-2	3	89	88
2	17	61	53	2	5	66	65	4	7	47	64	-2	4	144	118
2	19	57	40	2	7	70	72	4	8	57	93	-2	5	73	70
2	20	67	63	2	8	60	58	4	9	49	82	-2	7	61	64
2	21	61	60	2	9	39	35	5	0	56	66	-2	8	92	93
3	0	145	175	2	11	36	42	<i>H</i> = 3				-2	9	77	82
3	6	40	22	2	16	58	50	-1	4	104	103	-1	4	47	50
3	12	110	89	3	3	34	35	-1	5	63	65	-1	5	39	34
				3	4	68	80	-1	7	68	72	-1	7	41	36

rather than to  $|F|^2$ . They were corrected for primary extinction by the relation (Darwin 1922)

$$I_c = \frac{I_o}{(\tanh mq)/mq},$$

where  $I_c$  and  $I_o$  are the calculated and observed intensities,  $q$  is the amplitude of the radiation reflected by a single phase of atoms and  $m$  is the succession. The quantity  $q$  equals  $2Ne^2d^2F/mc^2$  in which  $N$  is the number of unit cells in unit volume,  $d$  is the spacing of the planes,  $F$  is the structure factor, and  $e$  and  $c$  have their usual meanings. After correction by primary extinction, the final value of  $R$  was 11.8%.

In the last cycle of refinement the shifts in the positional parameters were less than 1/50 of a standard deviation and for the isotropic temperature terms the shifts were less than 1/15 of a standard deviation. The initial and final position parameters are given in Table 1. The rather large standard deviation in the  $x$  and  $y$  coordinates of the two Cl atoms can be attributed to inadequate correction for absorption due to the irregular shape of the crystal. The calculated structure factors for each unobserved reflection were less than the minimum observable value. The observed and calculated structure factors in the final cycle are given in Table 2. For the structure factor calculations the atomic scattering factors for  $Rb^+$ ,  $Mn^{2+}$  and  $Cl^-$  were taken from 'International Tables for X-ray Crystallography' (1962).

In the structure Mn(1)-Cl octahedra are linked in pairs by sharing octahedral faces through common Cl(2) ions. Consequently these octahedra are trigonally distorted because of the mutual repulsion of the two neighbouring Mn ions.

**Table 3. Bondlengths (Å) for  $RbMnCl_3$**

Standard deviations are given in parentheses

Multiplicity			Location of atoms			
Mn(1)–Cl octahedron:						
Mn–Cl(1 <sup>i</sup> )	2 · 55(8)	3	Mn(1)	$\frac{1}{3}$	$\frac{2}{3}$	$z$
Mn–Cl(2 <sup>i</sup> )	2 · 54(7)	3	Mn(2)	0	0	0
Cl(1 <sup>i</sup> )–Cl(1 <sup>ii</sup> )	3 · 69(17)	3	Rb(1)	$\frac{1}{3}$	$\frac{2}{3}$	0
Cl(1 <sup>i</sup> )–Cl(2 <sup>i</sup> )	3 · 63(4)	6	Rb(2)	0	0	$\frac{1}{4}$
Cl(2 <sup>i</sup> )–Cl(2 <sup>ii</sup> )	3 · 43(16)	3	Cl(1 <sup>i</sup> )	$x$	$2x$	$z$
			Cl(1 <sup>ii</sup> )	$x$	$1-x$	$z$
Mn(2)–Cl octahedron:						
Mn–Cl(1 <sup>i</sup> )	2 · 48(8)	6	Cl(1 <sup>iii</sup> )	$x$	$\bar{x}$	$z$
Cl(1 <sup>i</sup> )–Cl(1 <sup>iii</sup> )	3 · 47(17)	6	Cl(1 <sup>iv</sup> )	$2x$	$x$	$\bar{z}$
Cl(1 <sup>i</sup> )–Cl(1 <sup>iv</sup> )	3 · 54(7)	6	Cl(2 <sup>i</sup> )	$1-2x$	$1-x$	$\frac{1}{4}$
			Cl(2 <sup>ii</sup> )	$x$	$1-x$	$\frac{1}{4}$
			Cl(2 <sup>iii</sup> )	$2x-1$	$x$	$-\frac{1}{4}$
Rb(1)–Cl distances:						
Rb–Cl(1 <sup>i</sup> )	3 · 72(6)	3				
Rb–Cl(1 <sup>iv</sup> )	3 · 58(1)	6				
Rb–Cl(2 <sup>iii</sup> )	3 · 59(6)	3				
Rb(2)–Cl distances:						
Rb–Cl(1 <sup>i</sup> )	3 · 60(6)	6				
Rb–Cl(2 <sup>i</sup> )	3 · 58(1)	6				

This accounts for the relatively short Cl(2<sup>i</sup>)-Cl(2<sup>ii</sup>) bondlength of 3.43 Å and a Cl(2<sup>i</sup>)-Mn(1)-Cl(2<sup>ii</sup>) angle of only 85° compared with 91° and 92° respectively for the Cl(1<sup>i</sup>)-Mn(1)-Cl(2<sup>i</sup>) and Cl(1<sup>i</sup>)-Mn(1)-Cl(1<sup>ii</sup>) angles. On the other hand, each vertex of a Mn(2)-Cl octahedron is shared with a neighbouring Mn(1)-Cl octahedron and the former is much more regular, the Cl-Cl bondlengths ranging from 3.47 to 3.54 Å and the Cl-Mn(2)-Cl angles from 89° to 91°. The bondlengths for RbMnCl<sub>3</sub> are listed in Table 3.

**Table 4. Initial and final atomic parameters for RbMnBr<sub>3</sub>**  
Origin is at centre  $\bar{3}m1$ . Standard deviations in parentheses

Equipoint		x	y	z	B (Å <sup>2</sup> )
(a) Initial parameters					
Mn	2a	0	0	0	1.5
Rb	2d	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	1.5
Br	6h	0.156	0.312	$\frac{1}{4}$	1.5
(b) Final parameters					
Mn	2a	0	0	0	1.00(15)
Rb	2d	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	1.32(15)
Br	6h	0.1650(10)	0.3300(20)	$\frac{1}{4}$	1.32(9)

**Table 5. Observed and calculated structure factors for RbMnBr<sub>3</sub>**

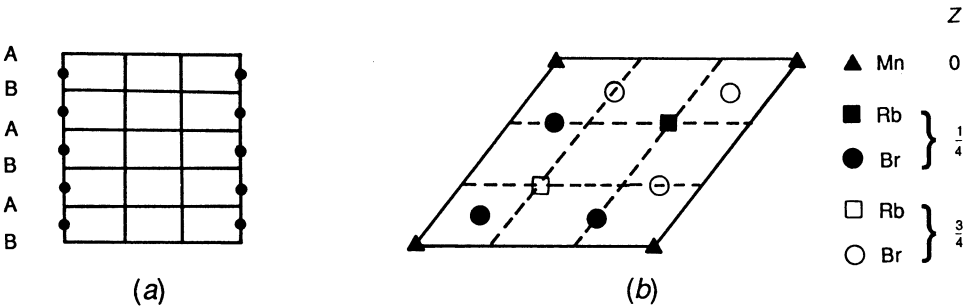
H	K	F <sub>0</sub>	F <sub>c</sub>	H	K	F <sub>0</sub>	F <sub>c</sub>	H	K	F <sub>0</sub>	F <sub>c</sub>	H	K	F <sub>0</sub>	F <sub>c</sub>
L = 0				L = 1								L = 2			
2	0	106	103	2	0	66	64	3	2	26	31	4	0	49	54
3	0	72	62	4	0	45	46	4	2	114	112	5	0	12	13
4	0	73	69	8	0	24	22	5	2	13	15	6	0	141	141
6	0	188	183	10	0	13	14	6	2	73	77	9	0	15	16
7	0	33	26	2	1	14	13	7	2	25	27	10	0	10	14
8	0	34	34	3	1	25	24	8	2	61	62	1	1	15	11
1	1	13	15	5	1	22	18	10	2	32	31	3	1	39	42
3	1	56	57	4	2	40	38	3	3	50	50	4	1	36	35
4	1	45	48	6	2	24	26	4	3	28	37	2	2	206	205
5	1	29	37	6	4	18	19	4	4	106	100	3	2	24	28
6	1	25	25	L = 2				5	4	15	14	4	2	47	45
9	1	17	21	2	0	172	182	6	4	58	58	5	2	30	27
2	2	277	283	3	0	22	25	8	4	36	35	6	2	33	31
3	2	46	47	4	0	141	136	L = 3				8	2	76	75
4	2	68	59	5	0	43	43	1	0	13	14	4	3	14	11
5	2	33	35	6	0	133	121	2	0	46	50	5	3	23	25
6	2	35	39	7	0	20	17	4	0	40	41	6	3	19	19
8	2	104	96	8	0	69	67	8	0	25	20	4	4	124	120
4	3	17	13	10	0	42	41	2	1	9	11	8	4	11	12
5	3	31	31	1	1	75	83	3	1	21	21	10	4	35	32
6	3	22	25	2	1	61	56	L = 4				L = 5			
4	4	152	151	3	1	25	23	5	1	23	16	2	0	29	37
5	4	31	23	4	1	19	20	4	2	39	33	4	0	28	31
6	4	33	29	5	1	19	20	6	2	14	23	8	0	19	16
7	4	14	17	7	1	33	32	6	4	20	17	3	1	15	16
8	4	15	15	8	1	26	23	L = 4				4	2	27	25
6	6	61	67	2	2	179	177	2	0	71	67	6	2	18	19
								3	0	46	23	6	4	12	13

(b) *RbMnBr<sub>3</sub>*

The initial structure was assumed to be isomorphous with *CsNiCl<sub>3</sub>* whose unit cell consists of two hexagonally close-packed *CsCl<sub>3</sub>* layers with Ni octahedrally coordinated by Cl ions. The position parameters of *CsNiCl<sub>3</sub>* were assumed and an individual temperature factor of 12·5 Å<sup>2</sup> was assigned to each atom.

Several cycles of least squares refinement reduced the reliability factor from 23·6% to 6·6% at which stage an interlayer scaling of the calculated to the observed structure factor was carried out. After a further few cycles the refinement ceased and the reliability factor *R* decreased slightly to 6·5%. At this stage the shifts in the atomic parameters were all less than 1/50 of a standard deviation and for the isotropic temperature terms the shifts were less than 1/60 of a standard deviation. Furthermore, the calculated structure factors of the 67 unobserved reflections were all less than the minimum observable value. The initial and final atomic parameters are given in Table 4, and the structure factors in the last cycle in Table 5.

The *RbBr<sub>3</sub>* layers are of three types (A, B or C) according to the position of the cross section of the hexagonal cell (see Fig. 2). The stacking sequence of



**Fig. 3.** (a) An *a*-axis projection of the *RbMnBr<sub>3</sub>* or *CsNiCl<sub>3</sub>* structure. The unit cell consists of an A and B layer. The stacking sequence is AB·AB. (b) A *c*-axis projection of *RbMnBr<sub>3</sub>* or *CsNiCl<sub>3</sub>* structure. The *z* parameter is given as a fraction of the *c*-axis value, the triangle can be either Mn<sup>2+</sup> or Ni<sup>2+</sup> and the circles either Cl<sup>−</sup> or Br<sup>−</sup>.

**Table 6. Bondlengths (Å) for *RbMnBr<sub>3</sub>***  
Standard deviations are given in parentheses

Multiplicity			Location of atoms
Mn–Br octahedron:			Mn at (000)
Mn–Br(i)	3	2·681(12)	Rb at ( $\frac{2}{3}$ , $\frac{1}{3}$ , $\frac{1}{4}$ )
Mn–Br(ii)	3		Br(i) at height $z = \frac{1}{4}$
Br(i)–Br(i)	3	3·742(25)	Br(ii) at height $z = -\frac{1}{4}$
Br(ii)–Br(ii)	3		Br(iii) at height $z = \frac{3}{4}$
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		



$\text{RbMnBr}_3$  would then be BABA... which is shown in Fig. 3*a*. In the close-packed array of  $\text{RbBr}_3$  layers, only one quarter of the octahedral sites are bounded exclusively by Br atoms and each of these must be occupied by an Mn atom in order to obtain the correct compositional formula. The triangles in Fig. 2 indicate these sites in the unit cell between different pairs of layers; for example, that labelled *ab* in such a site between A and B type layers. Fig. 3*b* is a *c*-axis projection of the  $\text{RbMnBr}_3$  structure, where Rb and Br atoms form an approximate hexagonal close-packed array such that each Rb atom has 12 nearest Br neighbours.

In  $\text{RbMnBr}_3$  the Mn–Br octahedra share opposite faces to form infinite chains of composition  $(\text{MnBr}_3)$  parallel to the *c*-axis. The infinite chains are held together by the Rb atoms. The repulsion of successive  $\text{Mn}^{2+}$  ions in the chains causes the trigonal distortion of the octahedra and consequently the Br atoms in the shared faces are brought closer together, thereby making the Br(1)–Mn–Br(1) and Br(2)–Mn–Br(2) angles less than  $90^\circ$  and the Br(1)–Mn–Br(2) angles correspondingly greater. Bondlengths are given in Table 6.

## 5. Discussion and Conclusions

The difference between the crystal structure of  $\text{RbMnCl}_3$  and  $\text{RbMnBr}_3$  is that in  $\text{RbMnCl}_3$  we have six close-packed layers while there are only two in  $\text{RbMnBr}_3$ . Moreover, in the latter structure the Mn–Br octahedra share opposite faces to form infinite chains of composition  $(\text{MnBr}_3)$  parallel to the *c*-axis, while in the  $\text{RbMnCl}_3$  structure that infinite chain does not exist. The reason put forward to account for this difference is the cation/anion ratio and the polarisation effect.

The unit cell dimensions of  $\text{RbMnBr}_3$  suggest that its structure might be isomorphous with that of  $\text{CsNiCl}_3$ , as shown by the following:

	<i>a</i> (Å)	<i>c</i> (Å)
$\text{RbMnBr}_3$	7.56(2)	6.35(2)
$\text{CsNiCl}_3$	7.17	5.941
$\text{RbMnCl}_3$	7.16(1)	17.83(4)

The structure of  $\text{CsNiCl}_3$  consists of two hexagonally close-packed layers in the sequence BABA... along the *c*-axis, with each layer approximately 3 Å wide. The unit cell dimensions of  $\text{RbMnCl}_3$  suggest that the structure of this compound should have a six-layer sequence,  $c = 17.83(4) \text{ Å} \approx 6 \times 3 \text{ Å}$ .

The second reason for the difference between the two structures can be considered as a cation/anion ratio effect:

$$\text{CsNiCl}_3 : \quad \text{Ni–Cl} = 2.43 \text{ Å}, \quad r_{\text{Cl}} = 1.81 \text{ Å}, \quad r_{\text{Ni}} = 0.62 \text{ Å}, \quad r_{\text{Ni}}/r_{\text{Cl}} = 0.34.$$

$$\text{RbMnBr}_3 : \quad \text{Mn–Br} = 2.68 \text{ Å}, \quad r_{\text{Br}} = 1.96 \text{ Å}, \quad r_{\text{Mn}} = 0.72 \text{ Å}, \quad r_{\text{Mn}}/r_{\text{Br}} = 0.37.$$

$$\text{RbMnCl}_3 : \quad \text{Mn–Cl} = 2.51 \text{ Å}, \quad r_{\text{Cl}} = 1.81 \text{ Å}, \quad r_{\text{Mn}} = 0.72 \text{ Å}, \quad r_{\text{Mn}}/r_{\text{Cl}} = 0.40.$$

Hence it can be concluded that the cation/anion ratio in  $\text{RbMnCl}_3$  is too large to permit the formation of infinite chains of Mn–Cl face-sharing octahedra, and so we find the compounds  $\text{CsNiCl}_3$  and  $\text{RbMnBr}_3$  are isomorphous while  $\text{RbMnCl}_3$  is a modification of the  $\text{CsNiCl}_3$  structure.

The third reason is polarisation, where an anion has its electron cloud distorted by a cation. The polarising power of a cation varies directly as its charge and inversely as its radius. Hence, polarisation in a cation increases as its size decreases. The  $\text{Mn}^{2+}$  ion with a relatively large ionic radius (0.72 Å) has a smaller polarisation effect than other transition metal ions.

The polarisability of an ion measures the ease with which the electron cloud can be distorted, and is determined from the refractive index; it is directly proportional to the size of the anion. Hence, the bromine anion with radius 1.96 Å has a larger polarisation effect than the chlorine anion with radius 1.81 Å. The extra polarisation by the bromine ion must be large enough to compensate for the decrease in polarisation of the  $\text{Mn}^{2+}$  ion compared with other transition metal ions. Hence, we find that  $\text{RbMnBr}_3$  is isomorphous with  $\text{CsNiCl}_3$ , while  $\text{RbMnCl}_3$  is not.

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