Acta Cryst. (1978). B34, 2617–2618

Trirubidium Heptachlorodimanganate

By J. Goodyear, E. M. Ali and H. H. Sutherland

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

(*Received* 7 *April* 1978; *accepted* 2 *May* 1978)

Abstract. $Rb_3Mn_2Cl_7$, tetragonal, $I4/mmm$, a = 5·05 (1), c = 26·14 (5) Å, D_o = 3·05, D_x = 3·06 g cm^{-3}, Z = 2. The final R was 0·080 for 98 visually estimated data. Mn ions are octahedrally coordinated by Cl ions. Each MnCl octahedron shares five vertices with neighbouring octahedra to form slices of perovskite-type structure, two unit cells thick, parallel to (100), alternate slices being displaced a distance $a/\sqrt{2}$ in the [110] direction. Cl ions at the unshared vertices are linked to the Rb(1) ions in the adjacent slice of perovskite structure such that each Rb(1) ion is coordinated by nine Cl ions. The Rb(2) ions lie within the slices and each is coordinated by 12 Cl ions. The structure is strictly isomorphous with that of $Sr_3Ti_2O_7$.

Introduction. $Rb_2Mn_2Cl_7$ has previously been examined by Seifert & Koknat (1965) using an X-ray powder technique. They found a body-centred tetragonal cell with a = 5·059 (5) and c = 26·146 (10) Å and, on the basis of these data and an observed density of 3·04 g cm^{-3}, proposed a structure for the compound which was, in fact, isomorphous with that of $Sr_3Ti_2O_7$ (Ruddlesden & Popper, 1958).

The material studied in this work was prepared by heating stoichiometric amounts of RbCl and $MnCl_2$ in an evacuated silica tube until molten and then cooling the sample at the rate of 5 °C h^{-1}. Because of the very hygroscopic nature of the compound, the crystal selected for X-ray examination was mounted in a sealed Lindemann-glass tube.

Unit-cell dimensions were determined from α_1–α_2 doublet separations on a zero-layer Weissenberg photograph taken about a with Cu $K\alpha$ (λ_{α_1} = 1·54051 Å) radiation. These and the observed density agreed, within experimental error, with the data given by Seifert & Koknat (1965).

Intensity data were collected from Weissenberg equi-inclination photographs taken about the a axis with Mo $K\alpha$ radiation. The intensities of 98 symmetrically independent reflections were measured visually on layer lines 0–4 from accurately timed film exposures. The systematically absent reflections were all of the type $h + k + l = 2n + 1$, consistent with $I4/mmm$, the space group of $Sr_3Ti_2O_7$. These data were corrected for the Lorentz–polarization factor and for absorption; for the latter the crystal was assumed to be cylindrical with a mean μr value of 0·9.

Isomorphism with $Sr_3Ti_2O_7$ would require an axial ratio of about 5:1 and an a parameter equal to twice the Mn—Cl bond length in an $MnCl_6$ octahedron. In the structure of Rb_2MnCl_4, Goodyear, Ali & Steigmann (1977) found the mean value of the latter to be 2·52 Å, which is indeed very nearly $a/2$. It was thus assumed at the outset that the two structures were isomorphous.

In the initial cycle of least-squares refinement idealized atomic positional parameters were used and an individual isotropic temperature factor of 2·0 Å^2 was assigned to each atom. After several cycles the residual, $R = \sum||F_o| - |F_c||/\sum |F_o|$, reduced to 8·0% at which stage the shifts in atomic parameters were all <0·025σ and the calculated structure factors for the 56 unobserved reflections were all less than the minimum observable value. For the structure factor calculations the atomic scattering factors for Rb$^+$, Mn^{2+} and Cl$^-$ 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. This work forms part of an investigation of the structures of compounds in the system RbCl/$MnCl_2$. It has shown that $Rb_3Mn_2Cl_7$ is strictly isomorphous with $Sr_3Ti_2O_7$.

Table 1. *Final atomic parameters (origin at centre 4/mmm)*

	Equipoint	x	y	z	B (Å^2)
Mn	4(e)	0	0	0·4014 (8)	2·03 (44)
Rb(1)	4(e)	0	0	0·1833 (6)	2·47 (30)
Rb(2)	2(a)	0	0	0	2·69 (46)
Cl(1)	2(b)	0	0	½	2·73 (115)
Cl(2)	4(e)	0	0	0·3076 (12)	2·15 (80)
Cl(3)	8(g)	0	½	0·0961 (10)	2·88 (52)

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33588 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond lengths* (Å)

		Multiplicity
Mn—Cl octahedron		
Mn—Cl(1)	2·577 (21)	1
Mn—Cl(2^{ii})	2·452 (38)	1
Mn—Cl(3^{i})	2·526 (5)	4
Cl(1)—Cl(3^{i})	3·562 (19)	4
Cl(2^{ii})—Cl(3^{i})	3·565 (29)	4
Cl(3^{i})—Cl(3^{ii})	3·571 (7)	4
Rb—Cl distances		
Rb(1)—Cl(2^{i})	3·249 (36)	1
Rb(1)—Cl(2^{ii})	3·579 (7)	4
Rb(1)—Cl(3^{i})	3·402 (21)	4
Rb(2)—Cl(1)	3·571 (7)	4
Rb(2)—Cl(3^{i})	3·562 (19)	8

Location of atoms			
Mn	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}-z$
Cl(1)	$\frac{1}{2}$	$\frac{1}{2}$	0
Cl(2^{i})	0	0	z
Cl(2^{ii})	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}-z$
Cl(3^{i})	0	$\frac{1}{2}$	z
Cl(3^{ii})	$\frac{1}{2}$	0	z
Rb(1)	0	0	z
Rb(2)	0	0	0

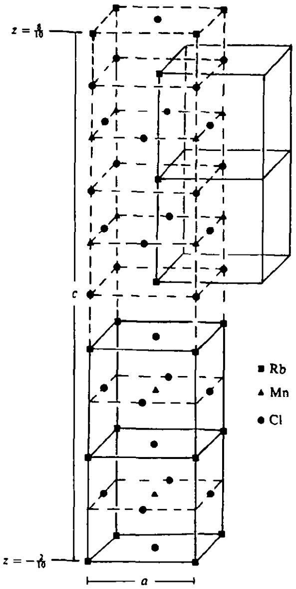

Fig. 1. The contents of one unit cell of the $Rb_3Mn_2Cl_7$ structure; double perovskite-type unit cells are shown as full lines.

The structure is related to that of perovskite in rather a simple way. Although a unit cell of perovskite-type structure would have the composition $RbMnCl_3$, a single slice two unit cells thick has the composition $Rb_3Mn_2Cl_7$. The structure can be regarded as consisting of such slices stacked perpendicular to the c axis, alternate slices being displaced a distance $a/\sqrt{2}$ in the [110] direction (see Fig. 1), giving an idealized axial ratio of 5:1. The structure of Rb_2MnCl_4 (Goodyear, Ali & Steigmann, 1977) was also found to be similarly related to perovskite, but in this case the slices were one unit cell thick.

The Rb(2) ions are located in the middle of the double perovskite layers and so each is surrounded by 12 Cl ions, whilst Rb(1) ions are situated on the surfaces of the slices and have the unusual coordination of nine Cl ions. As one might expect, the Rb(2)—Cl distances are fairly uniform (3·56–3·57 Å) whilst, because of the unsymmetrical nature of the coordination group around Rb(1), the Rb(1)—Cl distances range from 3·25 to 3·58 Å. In the structure of Rb_2MnCl_4, where every Rb ion is coordinated by nine Cl ions, the Rb—Cl distances varied from 3·24 to 3·57 Å.

The Mn ions lie at the centres of the perovskite unit cells and are hence octahedrally coordinated by Cl ions. Distortion in the $MnCl_6$ octahedron is mainly due to the mutual repulsion along [001] of neighbouring Mn ions in the double perovskite layers. For this reason the Cl(2^{ii})—Mn—Cl(3^{i}) angle is 91·5° whilst Cl(1)—Mn—Cl(3^{i}) is 88·5°. On the other hand, the Cl(3^{i})—Mn—Cl(3^{ii}) angle is very nearly 90°. The average Mn—Cl and Cl—Cl bond lengths are 2·52 and 3·57 Å, respectively, agreeing to within 0·01 Å with the values found in Rb_2MnCl_4.

References

Goodyear, J., Ali, E. M. & Steigmann, G. A. (1977). *Acta Cryst.* B**33**, 2932–2933.

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

Ruddlesden, S. N. & Popper, P. (1958). *Acta Cryst.* **11**, 54–55.

Seifert, H. J. & Koknat, F. W. (1965). *Z. Anorg. Allg. Chem.* **341**, 269–280.