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Rubidium Trichloromanganate

BY J. GOODYEAR, G. A. STEIGMANN AND E. M. ALI

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

Abstract. $RbMnCl_3$, hexagonal, $P6_3/mmc$, $a = 7.16$ (1), $c = 17.83$ (4) Å, $D_o = 3.09$, $D_x = 3.11$ g cm^{-3}, $Z = 6$. The unit cell accommodates six close-packed layers of composition $RbCl_3$ with Mn ions situated between the layers, being octahedrally coordinated by Cl ions. The structure differs from that of $CsMnCl_3$ in that it has a six-layer, rather than nine-layer, stacking sequence.

Introduction. Many complex chlorides of composition $XMCl_3$, 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 XCl_3 with the M ions situated between the layers, being octahedrally coordinated by Cl ions. In such structures the XCl_3 layers are of three types (A, B or C) according to the position of the cross-section of the hexagonal cell (see Fig. 1). The structure of $CsNiCl_3$ consists of layers in the sequence $BABA$---, whilst that of $CsMnCl_3$ (Goodyear & Kennedy, 1973) has the nine-layer sequence $BABACACBC$---. The unit-cell dimensions of $RbMnCl_3$ suggested that the crystal structure of this compound should have a six-layer sequence.

The material was prepared by heating stoichiometric amounts of $RbCl$ and $MnCl_2$ in an evacuated silica tube until molten and then cooling the sample to room temperature at about 5°C h^{-1}. Orange crystals were formed, most of which were intimately twinned and unsuitable for single-crystal study. After much searching a single crystal was found which, although of unfavourable shape, permitted a Weissenberg study to be made of the crystal structure. Because of the very hygroscopic nature of the material, the selected crystal was mounted in a sealed Lindemann glass tube containing phosphorus pentoxide.

The dimensions of the unit cell were determined from $\alpha_1-\alpha_2$ doublet separations on a zero-layer Weissenberg photograph taken with Cu $K\alpha$ radiation. The volume of the unit cell and the observed density indicated six formula units per cell, which is what would be required for a six-layer structure.

Intensity data were collected from equi-inclination photographs taken about the a axis with Mo $K\alpha$ radiation. The intensities of 125 symmetrically independent reflexions were measured, both visually and with a flying-spot microdensitometer, on layer lines 0–6 from accurately timed film exposures. The systematically absent reflexions were of the type hhl with $l = 2n + 1$, and about 250 reflexions were too weak to be observed. The observed data were corrected for the Lorentz–polarization factor and a very approximate correction was made for absorption by assuming the crystal to be cylindrical in shape with a μr value of 0.8. Because of the relatively small range in the magnitudes of the observed structure factors, each reflexion was given unit weight in the refinement procedure.

Initially, the structure was assumed to consist of the six-layer stacking sequence $BCBACA$---. The idealized positional parameters suggested the space group $P6_3/mmc$, consistent with the absent reflexions. Several cycles of least-squares refinement reduced the residual, $R = \Sigma |F_o| - |F_c| / \Sigma |F_o|$, to 16%, at which stage it was apparent that the two strongest reflexions, 110 and 220, were suffering from extinction. The latter were then removed from the refinement and after they were corrected for 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 $\frac{1}{50}$ of a standard deviation and for the isotropic temperature terms the shifts were less than $\frac{1}{15}$ of a standard deviation. Furthermore, the calculated structure factor for each

unobserved reflexion was less than the minimum observable value and an electron density projection along the *a* axis did not reveal any spurious peaks. 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).

The final atomic parameters are given in Table 1 and some selected bond lengths are listed in Table 2.* The rather large standard deviations in the *x* and *y* coordinates of the two Cl atoms are attributable to the inadequate correction for absorption, due to the irregular shape of the crystal.

Discussion. This work forms part of an investigation of the structures of compounds in the system $RbCl/MnCl_2$. Previous work by Kestigian, Croft & Leipziger (1967) using powder diffractometry indicated a hexagonal cell for $RbMnCl_3$ with $a = 7\cdot164$ and $c = 17\cdot79_8$ Å, in agreement with the present data.

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. This accounts for the relatively short $Cl(2^i)$–$Cl(2^{ii})$ bond length of $3\cdot43$ Å and a $Cl(2^i)$–$Mn(1)$–$Cl(2^{ii})$ angle of only $85°$ compared with 91 and $92°$, respectively, for the $Cl(1^i)$–$Mn(1)$–$Cl(2^i)$ and $Cl(1^i)$–$Mn(1)$–$Cl(1^{ii})$ 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 thereby much more regular, the Cl–Cl bond lengths ranging from $3\cdot47$ to $3\cdot54$ Å and the Cl–Mn(2)–Cl angles from 89 to $91°$.

The average Mn–Cl and Cl–Cl bond lengths for the whole structure are respectively $2\cdot51$ and $3\cdot55$ Å, somewhat shorter than the corresponding values ($2\cdot54$ and $3\cdot60$ Å) for the $CsMnCl_3$ structure.

Finally, the structure was refined in the non-centred space group $P6_3mc$ to test whether Rb(2) and Cl(2) do in fact actually lie on the same plane at $z = \frac{1}{4}$. In this space group Mn(2) was placed at the origin, Rb(1) and

Mn(1) were each located in two sets at equipoint 2(*b*) and Cl(1) in two sets at 6(*c*). Because of the greater number of refinable parameters, the value of *R* decreased somewhat to $10\cdot3\%$ but the final shifts in the atomic parameters were much greater than in the case of refinement in $P6_3/mmc$. The final parameters in the non-centred space group are given in Table 3, where it will be seen that Rb(2) has moved about two standard
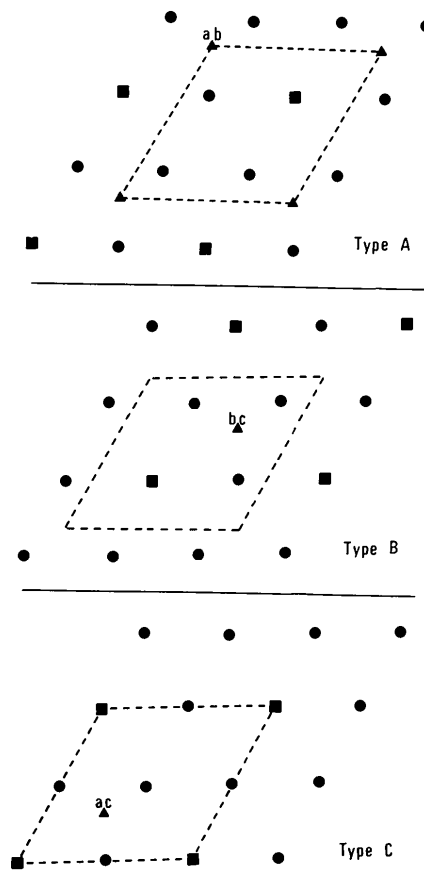

Fig. 1. Close-packed XCl_3 layers classified according to the position of the unit cell (broken line). The circles and squares represent Cl and X(Rb) atoms respectively. The triangles show the octahedral sites for the M(Mn) atoms between different pairs of layers; *ab*, *bc* and *ac* are the sites between *A* and *B*, *B* and *C*, *A* and *C* respectively.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32049 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

	Equipoint	x	y	z	B (Å²)
Mn(1)	4(*f*)	$\frac{1}{3}$	$\frac{2}{3}$	$0\cdot1603$ (15)	$1\cdot32$ (49)
Mn(2)	2(*a*)	0	0	0	$1\cdot40$ (84)
Rb(1)	4(*f*)	$\frac{1}{3}$	$\frac{2}{3}$	$-0\cdot0888$ (13)	$3\cdot57$ (44)
Rb(2)	2(*b*)	0	0	$\frac{1}{4}$	$2\cdot70$ (63)
Cl(1)	12(*k*)	$0\cdot1616$ (79)	$-0\cdot1616$ (79)	$0\cdot0820$ (15)	$1\cdot84$ (38)
Cl(2)	6(*h*)	$0\cdot4928$ (74)	$-0\cdot4928$ (74)	$\frac{1}{4}$	$1\cdot00$ (53)

Table 2. *Selected bond lengths* (Å)

		Multiplicity	Location of atoms			
Mn(1)—Cl octahedron						
Mn—Cl(1^i)	2.55 (8)	3	Mn(1)	$\frac{1}{3}$	$\frac{2}{3}$	z
Mn—Cl(2^i)	2.54 (7)	3	Mn(2)	0	0	0
Cl(1^i)—Cl(1^{ii})	3.69 (17)	3	Rb(1)	$\frac{1}{3}$	$\frac{2}{3}$	z
Cl(1^i)—Cl(2^i)	3.63 (4)	6	Rb(2)	0	0	$\frac{1}{4}$
Cl(2^i)—Cl(2^{ii})	3.43 (16)	3	Cl(1^i)	x	$2x$	z
			Cl(1^{ii})	x	$1-x$	z
Mn(2)—Cl octahedron			Cl(1^{iii})	x	$\bar{x}$	z
Mn—Cl(1^i)	2.48 (8)	6	Cl(1^{iv})	$2x$	x	$\bar{z}$
Cl(1^i)—Cl(1^{iii})	3.47 (17)	6	Cl(2^i)	$1-2x$	$1-x$	$\frac{1}{4}$
Cl(1^i)—Cl(1^{iv})	3.54 (7)	6	Cl(2^{ii})	x	$1-x$	$\frac{1}{4}$
			Cl(2^{iii})	$2x-1$	x	$-\frac{1}{4}$
Rb(1)—Cl distances						
Rb—Cl(1^i)	3.72 (6)	3				
Rb—Cl(1^{iv})	3.58 (1)	6				
Rb—Cl(2^{iii})	3.59 (6)	3				
Rb(2)—Cl distances						
Rb—Cl(1^i)	3.60 (6)	6				
Rb—Cl(2^i)	3.58 (1)	6				

Table 3. *Final atomic parameters in space group* $P6_3mc$ *(origin on* 6_3*)*

	Equipoint	x	y	z	B (Å^2)
Mn(1')	2(b)	$\frac{1}{3}$	$\frac{2}{3}$	0.1588 (17)	1.14 (54)
Mn(1'')	2(b)	$\frac{2}{3}$	$\frac{2}{3}$	0.3366 (18)	1.03 (52)
Mn(2)	2(a)	0	0	0	1.72 (50)
Rb(1')	2(b)	$\frac{1}{3}$	$\frac{2}{3}$	−0.0871 (14)	2.99 (43)
Rb(1'')	2(b)	$\frac{1}{3}$	$\frac{2}{3}$	0.5889 (13)	2.68 (41)
Rb(2)	2(a)	0	0	0.2555 (25)	2.08 (32)
Cl(1')	6(c)	0.1712 (92)	−0.1712 (92)	0.0809 (16)	1.67 (38)
Cl(1'')	6(c)	−0.1537 (60)	0.1537 (60)	−0.0835 (17)	1.71 (43)
Cl(2)	6(c)	0.4928 (44)	−0.4928 (44)	0.2485 (42)	0.75 (27)

deviations from the $z = \frac{1}{4}$ plane and Cl(2) less than one standard deviation. A disadvantage of the non-centred space group becomes evident when one calculates bond lengths and angles; for it is found that the Mn(2)—Cl octahedron is just as distorted as the face-sharing Mn(1')—Cl and Mn(1'')—Cl octahedra, and the degree of distortion is physically inconsistent with the way in which the octahedra are linked in the structure. For this reason it has been concluded that $P6_3/mmc$ is the correct space group.

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