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The Structure of Manganese Methylammonium Trichloride Dihydrate, a Member of the CsMnCl₃.2H₂O Family, at Room Temperature

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Abstract

$CH_6N^+.Mn^{2+}.3Cl^-.2H_2O$ is monoclinic, $P2_1/c$, with $a = 7.774\ (6)$, $b = 9.122\ (4)$, $c = 11.457\ (8)$ Å, $\beta = 91.41\ (6)°$, $Z = 4$. It is isotypic with $CsMnCl_3.2H_2O$, *i.e.*, it forms infinite linear chains of corner-linked $MnCl_4(H_2O)_2$ octahedra. The linkage of adjacent octahedra takes place *via* Cl atoms. The two water molecules are *cis*. The orthorhombic symmetry of the Cs salt is reduced by the non-spherical $CH_3NH_3^+$ cation. The structure was refined to $R = 0.039$. All H atoms but one on the methyl group were located. Each water molecule takes part in one interchain and one intrachain O–H···Cl hydrogen bond. Only one N–H···Cl hydrogen bond is formed. A structural phase transition with a doubling of a takes place at 188.5 K.

Introduction

Different crystalline phases were obtained from aqueous solutions of CH_3NH_3Cl and $MnCl_2$ when we undertook crystal-growth experiments with variable molar ratios of the starting materials. With a 2:1 ratio, the only result was $(CH_3NH_3)_2MnCl_4$, which belongs to the family of perovskite-like layer structures of general formula $(C_nH_{2n+1}NH_3)_2MCl_4$. A 1:2 ratio, however, yielded a sequence of different crystalline phases. It started with $(CH_3NH_3)_2MnCl_4$, followed by faint-pink crystals of long prismatic shape. Last in the sequence were crystals of $MnCl_2.4H_2O$. Observation of the second phase with a polarizing microscope indicated low symmetry. The crystals were only slightly hygroscopic but efflorescent. Chemical analysis revealed the formula $CH_3NH_3MnCl_3.2H_2O$ and X-ray photographs showed a strong relationship with $CsMnCl_3.2H_2O$ (Jensen, Andersen & Rasmussen, 1962), though the symmetry was lower. The Cs compound has recently been of interest, mainly due to its linear-chain antiferromagnetism at low temperatures which made it a kind of guinea-pig in the field of low-dimensional phenomena (Smith & Friedberg, 1968; Skalyo, Shirane, Friedberg & Kobayashi, 1970; Kopinga, 1977). Therefore, it seemed worthwhile to solve the structure of the title compound, which, in contrast to the Cs compound, has the additional possibility of hydrogen bonding between the $CH_3NH_3^+$ cations and the chains.

Experimental

Crystals of $CH_3NH_3MnCl_3.2H_2O$ suitable for X-ray work were grown by evaporation from an aqueous solution of CH_3NH_3Cl and $MnCl_2$ in a molar ratio of 1:2. To guarantee a constant humidity the crystals had to be sealed in a capillary. Preliminary Weissenberg and precession photographs revealed the Laue group $2/m$ and from the systematic extinctions ($h0l$: $l = 2n +$ 1; $0k0$: $k = 2n + 1$) the space group $P2_1/c$ could be assigned unambiguously. A prismatic crystal $0.15 \times 0.3 \times 0.6$ mm was used on a Syntex $P2_1$ autodiffractometer with Mo $K\alpha_1$ radiation to determine the crystal data and to collect the intensities. The lattice constants were obtained by least squares from 14 reflexions lying in the range $15 < 2\theta < 27.8°$. The values are listed in Table 1 with some other crystal data. Intensities were collected at room temperature by the θ–2θ technique up to $\sin \theta/\lambda = 0.596$ Å^{-1} with a variable scan speed of 3.0–$29.3°$ min^{-1}. Two standards, checked periodically, indicated no significant change in the intensities. The measurement of reflexions having $0 \le h \le 9$, $0 \le k \le 10$, $-13 \le l \le 13$ gave 1671 reflexions, 1431 of which had $I > 1.96\sigma(I)$. No absorption correction was applied.

The structure was solved by Patterson and Fourier techniques. After refinement with anisotropic temperature factors, all H atoms, with the exception of one belonging to the methyl group, could be located from a difference map. Refinement was by least squares minimizing $\sum w(|F_o| - |F_c|)^2$ with anisotropic temperature factors for all non-hydrogen atoms. H atoms were given a constant isotropic temperature factor of U $= 0.07$ Å^2 and were not varied in the final cycles. Complex neutral scattering factors and unit weights were employed (*International Tables for X-ray Crystallography*, 1974). 10 reflexions, suspected to be strongly influenced by extinction, were removed from the data set. The final $R_w = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| =$ 0.039 for 1436 reflexions with $F_o > 3\sigma(F_o)$ and 73 parameters. Table 2 lists the final positional parameters.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35070 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Crystal data

$CH_3NH_3MnCl_3.2H_2O$	$M_r = 229.39$
$a = 7.774$ (6) Å	$P2_1/c$
$b = 9.122$ (4)	$Z = 4$
$c = 11.457$ (8)	λ(Mo $K\alpha_1$) = 0.70926 Å
$\beta = 91.41$ (6)°	μ(Mo $K\alpha_1$) = 2.60 mm^{-1}
$V = 812.2$ (9) Å^3	$D_c = 1.88$ Mg m^{-3}
$F(000) = 460$	$T = 292$ K

Table 2. Final positional parameters ($\times 10^4$; for H $\times 10^3$) with e.s.d.'s in parentheses

	x	y	z
C	4734 (8)	2704 (6)	3780 (6)
H(41)	419 (8)	340 (7)	339 (6)
H(42)	554 (8)	289 (7)	440 (6)
N	5639 (5)	1650 (5)	3057 (4)
H(31)	476 (8)	130 (7)	250 (6)
H(32)	580 (8)	66 (7)	352 (6)
H(33)	633 (8)	210 (7)	269 (6)
Mn	378 (1)	0 (1)	2502 (1)
Cl(1)	7315 (1)	4139 (1)	1074 (1)
Cl(2)	2582 (1)	4028 (1)	6157 (1)
Cl(3)	9857 (1)	2495 (1)	3481 (1)
O(1)	−1679 (4)	9291 (4)	3689 (3)
H(11)	−197 (8)	828 (7)	367 (6)
H(12)	−162 (8)	955 (7)	435 (6)
O(2)	−1677 (4)	687 (4)	1239 (3)
H(21)	−202 (8)	15 (7)	67 (6)
H(22)	−183 (8)	155 (7)	97 (6)

Discussion

The main features of the structure may be seen from Figs. 1 and 2. It consists of linear chains running parallel to b. The chain itself consists of $MnCl_4(H_2O)_2$ octahedra, which are corner-linked to each other *via* Cl bridges. The basal plane of the octahedron consists of two Cl atoms and two *cis* water molecules. In adjacent octahedra the water molecules are on opposite sides of the chain. The octahedra are rather distorted, Table 3. Bond lengths and angles are normal. As expected, the
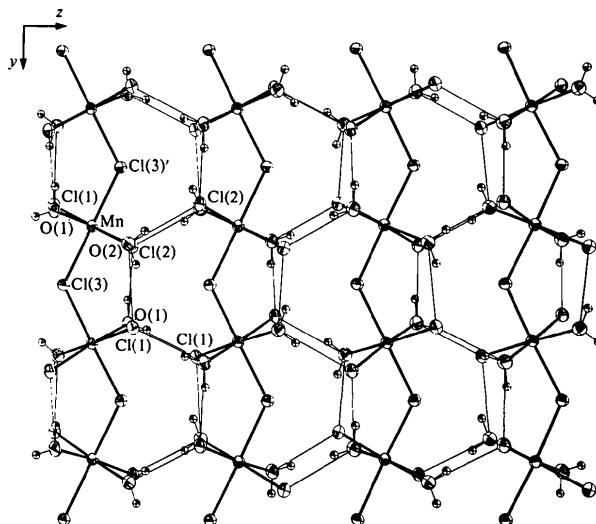

Fig. 1. *ORTEP* plot (Johnson, 1965) of $CH_3NH_3MnCl_3.2H_2O$ showing chains of corner-linked $MnCl_4(H_2O)_2$ octahedra (thick lines) running along the y direction. Thin lines indicate intrachain and interchain hydrogen bonds forming a hydrogen-bonded layer. The $CH_3NH_3^+$ ions separate these layers from each other but have been omitted for clarity. Cl(3) and Cl(3)' are symmetrically equivalent, but have different bond lengths to Mn.
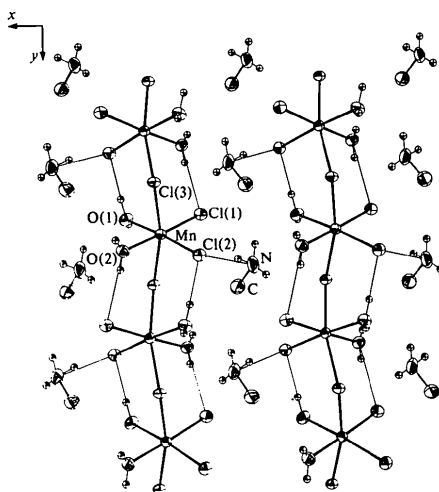
Fig. 2. *ORTEP* plot (Johnson, 1965) of $CH_3NH_3MnCl_3.2H_2O$ showing two hydrogen-bonded layers (*cf.* Fig. 1) separated by $CH_3NH_3^+$ ions. Thick lines are normal bonds, while thin lines are hydrogen bonds. Each $CH_3NH_3^+$ ion forms only one hydrogen bond. The H atoms of the methyl group have been omitted for clarity.

bonds between Mn and the bridging Cl atoms are longer (2·574 and 2·552 Å) than the bonds to the terminal Cl atoms (2·520 and 2·495 Å).

The chains are folded into a gentle zigzag configuration which is due to extensive hydrogen bonding (Fig. 1, Table 4). Each water molecule takes part in two O—H···Cl hydrogen bonds, the first of which is intrachain and is responsible for the folding of the chain. The second is interchain and links neighbouring chains in the z direction. This one is also responsible for the closer packing of the chains in this direction than in the x direction ($c/2 = 5·73$, $a = 7·77$ Å), giving the structure some two-dimensional character. Taking the O···Cl distances as a measure, the hydrogen bonds seem to be of different strengths. Their lengths are in good agreement with accepted values (Joesten & Schaad, 1974). The angles at the H atoms within a hydrogen bond indicate that three of the bonds are considerably bent and only one (I) seems to be nearly straight. The values of the Cl···O···Cl angles match the H—O—H angles of the water molecule quite well. The water molecules and the corresponding Cl···O···Cl planes are inclined by 12(6) and 20(6)°. The hydrogen-bonding system corresponds to that calculated for a-RbMnCl$_3$.2H$_2$O, which is also isotypic with the title compound. The calculation (El Saffar, 1970) used an electrostatic model (Baur, 1965) and yielded H atom positions on the basis of heavy-atom coordinates.

In the x direction the hydrogen-bonded layers are separated from each other by the $CH_3NH_3^+$ cations (Fig. 2). In this direction we find a fairly strong

Table 3. *Distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

(*a*) Bond distances and angles describing the octahedral coordination sphere of Mn

Mn—O(1)	2·221 (4)	O(2)—Mn—Cl(2)	89·5 (1)
Mn—O(2)	2·219 (4)	O(2)—Mn—Cl(1)	178·2 (1)
Mn—Cl(1)	2·520 (2)	O(2)—Mn—Cl(3)	85·6 (1)
Mn—Cl(2)	2·495 (2)	O(2)—Mn—Cl(3)′	85·2 (1)
Mn—Cl(3)	2·552 (2)	Cl(1)—Mn—Cl(2)	91·3 (1)
Mn—Cl(3)′	2·574 (2)	Cl(1)—Mn—Cl(3)	92·8 (1)
		Cl(1)—Mn—Cl(3)′	96·3 (1)
O(1)—Mn—O(2)	87·9 (1)	Cl(2)—Mn—Cl(3)	95·1 (1)
O(1)—Mn—Cl(2)	175·9 (1)	Cl(2)—Mn—Cl(3)′	94·2 (1)
O(1)—Mn—Cl(1)	91·4 (1)	Cl(3)—Mn—Cl(3)′	166·8 (1)
O(1)—Mn—Cl(3)	88·0 (1)	Mn—Cl(3)—Mn	127·57 (7)
O(1)—Mn—Cl(3)′	82·4 (1)		

(*b*) Contact distances within the octahedron

O(1)···O(2)	3·082 (5)	O(2)···Cl(3)′	3·254 (4)
O(1)···Cl(1)	3·400 (4)	Cl(1)···Cl(2)	3·585 (3)
O(1)···Cl(3)	3·324 (4)	Cl(1)···Cl(3)	3·673 (2)
O(1)···Cl(3)′	3·168 (4)	Cl(1)···Cl(3)′	3·904 (3)
O(2)···Cl(2)	3·325 (4)	Cl(2)···Cl(3)	3·724 (2)
O(2)···Cl(3)	3·250 (4)	Cl(2)···Cl(3)′	3·713 (2)

(*c*) Bond distances and angles within the $CH_3NH_3^+$ group and the water molecules (the missing methyl H atom could not be located)

N—C	1·461 (8)		
N—H(31)	0·98 (6)	H(31)—N—C	105 (4)
N—H(32)	1·06 (7)	H(32)—N—C	109 (4)
N—H(33)	0·80 (7)	H(33)—N—C	108 (5)
C—H(41)	0·88 (7)	H(41)—C—N	114 (4)
C—H(42)	0·95 (7)	H(42)—C—N	103 (4)
O(1)—H(11)	0·95 (7)		
O(1)—H(12)	0·79 (7)	H(11)—O(1)—H(12)	108 (6)
O(2)—H(21)	0·85 (7)		
O(2)—H(22)	0·85 (7)	H(21)—O(2)—H(22)	103 (6)

(*d*) Short contacts involving C and N

N···O(1)	3·070 (6)	N···Cl(1)	3·487 (5)
N···O(2)	3·111 (6)	N···Cl(3)	3·392 (5)
N···Cl(1)	3·409 (5)	C···Cl(2)	3·450 (7)

[N···Cl(2) 3·243 Å], slightly bent [N—H(31)···Cl(2) 168°] hydrogen bond. However, this is the only ammonium H atom which takes part in a hydrogen bond. All other short distances involving the $CH_3NH_3^+$ cations are van der Waals contacts (Table 3*d*).

In comparison with CsMnCl$_3$.2H$_2$O, we find for the methylammonium compound that the hydrogen-bonded layers are considerably more widely separated. On the other hand, the introduction of the methyl-ammonium group has no obvious pronounced influence on the dimensions of the layer itself. This can be seen by comparison of the lattice constants (CsMnCl$_3$.2H$_2$O: $a = 9·060$, $b = 7·285$, $c = 11·455$ Å; Jensen, Andersen & Rasmussen, 1962).

The same relation is found for Mn···Mn distances, these being of importance for the magnetic interactions. It is in the x direction that we find the widest separation of neighbouring Mn atoms: 7·774 (6) Å.

Table 4. *Distances* (Å) *and angles* (°) *in hydrogen bonds*

E.s.d.'s in parentheses refer to the last significant figure. Hydrogen bonds (I) and (III) are intrachain, and (II) and (IV) are interchain.

(I)		(III)	
$O(1)\cdots Cl(2)$	3·114 (4)	$O(2)\cdots Cl(1)$	3·249 (4)
$O(1)-H(11)$	0·95 (7)	$O(2)-H(22)$	0·85 (7)
$H(11)\cdots Cl(2)$	2·17 (7)	$H(22)\cdots Cl(1)$	2·46 (7)
$O(1)-H(11)\cdots Cl(2)$	174 (6)	$O(2)-H(22)\cdots Cl(1)$	155 (6)

(II)		(IV)	
$O(1)\cdots Cl(1)$	3·199 (4)	$O(2)\cdots Cl(2)$	3·198 (4)
$O(1)-H(12)$	0·79 (7)	$O(2)-H(21)$	0·85 (7)
$H(12)\cdots Cl(1)$	2·47 (7)	$H(21)\cdots Cl(2)$	2·36 (7)
$O(1)-H(12)\cdots Cl(1)$	153 (6)	$O(2)-H(21)\cdots Cl(2)$	141 (3)
$Cl(1)\cdots O(1)\cdots Cl(2)$	109·1 (1)	$Cl(1)\cdots O(2)\cdots Cl(2)$	111·2 (1)

Angle between planes H–O–H and		Angle between planes H–O–H and	
$X\cdots O\cdots X$	20 (6)°	$X\cdots O\cdots X$	12 (6)°

(V)

$N\cdots Cl(2)$	3·243 (5)
$N-H(31)$	0·98 (7)
$H(31)\cdots Cl(2)$	2·28 (6)
$N-H(31)\cdots Cl(2)$	168 (6)

Along the chain we find 4·599 (2) Å and along the z axis 5·769 (5) Å.

That $CH_3NH_3MnCl_3 \cdot 2H_2O$ is isotypic with $CsMnCl_3 \cdot 2H_2O$ and with α-$RbMnCl_3 \cdot 2H_2O$ (Jensen, 1967) becomes clear by comparison of the coordinates. This is accomplished by reflecting the coordinates of the Cs compound across a mirror plane at $y = \frac{1}{4}$ and by applying the transformation matrix

$$\begin{pmatrix} 0 & 1 & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The space group $P2_1/c$ is a maximal *translation-engleiche* subgroup (index 2) of *Pcca* (Neubüser & Wondratschek, 1966), which is the space group of the Cs compound. This symmetry reduction leaves the centres of symmetry unchanged. It is achieved by

replacing Cs^+, which in *Pcca* occupies a site [4(d)] with point symmetry 2, by the non-spherical $CH_3NH_3^+$ ion and thus destroying the twofold axes.

Comparison of the geometries of the octahedra in $CH_3NH_3MnCl_3 \cdot 2H_2O$, $CsMnCl_3 \cdot 2H_2O$ and α-$RbMnCl_3 \cdot 2H_2O$ shows that the Mn–O distance in the former is considerably longer than those in the alkali salts [2·230 and 2·234 Å compared with 2·08 (Cs) and 2·177 Å (Rb)]. We believe that this fact reflects the rather labile coordination geometry in these soft materials where hydrogen bonding and packing conditions have an important influence.

At 188·5 ($\pm$1) K, $CH_3NH_3MnCl_3 \cdot 2H_2O$ undergoes a structural phase transition, as has been confirmed by DSC measurements and X-ray photographs. The latter indicate that the low-temperature phase is a super-structure of the room-temperature phase with doubling of a and orthorhombic symmetry. One can speculate that this results from a reorientation of the methyl-ammonium groups by formation of additional $N-H\cdots Cl$ hydrogen bonds by the H atoms not yet involved in bonding. A programme of further investigations is intended.

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