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Methylammonium Trichloromanganate(II) Dihydrate

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Abstract. $[NH_3CH_3][MnCl_3].2H_2O$, monoclinic, $P2_1/c$, $a = 7{\cdot}803$ (4), $b = 9{\cdot}151$ (5), $c = 11{\cdot}486$ (7) Å, $\beta = 91{\cdot}37$ (4)°, $\rho_c = 1{\cdot}859$ Mg m^{-3}, $Z = 4$; $R = 0{\cdot}040$, $R_w = 0{\cdot}034$ for 1445 reflections. The salt contains *cis*-$[MnCl_4(H_2O)_2]$ octahedral moieties which form monobridged infinite chains parallel to **b**. The bridging Mn–Cl–Mn angle is 127·58 (5)°. Mn–Cl distances range from 2·502 (1) to 2·583 (2) Å. Mn–O distances are 2·225 (2) and 2·235 (2) Å. Each water molecule hydrogen bonds to a chloride ion on an adjacent octahedron in the chain and to a chloride ion on an adjacent chain. This latter ties the chains together in sheets in the *bc* plane.

Introduction. Crystals of $[NH_3CH_3][MnCl_3].2H_2O$ were grown by the evaporation of a 95% ethanol solution containing a 1:1 molar ratio of the amine hydrochloride and $MnCl_2.4H_2O$. The compound crystallizes as pale-pink monoclinic needles. Systematic X-ray extinctions ($h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$) define the space group $P2_1/c$.

Lattice constants were determined from 12 accurately centered high-angle reflections. Intensity data were collected on an automatic Picker diffractometer with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). A θ–2θ step-scan technique was used with 20 steps deg^{-1} and 3 s step^{-1}. Background was measured before and after each scan. A total of 1445 unique reflections ($2\theta < 45°$) were obtained. No crystal decomposition occurred during data collection. The data were corrected for absorption ($\mu = 2{\cdot}58$ mm^{-1}), and errors assigned by the relationship $\sigma^2(I) = \sigma^2_{stat} + c^2I^2$, where $\sigma^2(I)$ is the estimated variance in intensity, σ_{stat} is the error determined from the counting statistics during data collection, c is a constant set equal to 0·03, and I is the intensity of the reflection.

Initial positions for the Mn atoms were determined from a Patterson synthesis. The remaining atomic positions were determined either from the Patterson map or from later electron density and electron density difference maps. All atomic positions and anisotropic thermal parameters for non-hydrogen atoms were refined using full-matrix least-squares methods. The thermal parameters for the H atoms were fixed at $B = 4{\cdot}0$ Å^2. The scattering-factor tables listed in *International Tables for X-ray Crystallography* (1962) were used for calculating structure factors. The final residual indices were $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{\frac{1}{2}} = 0{\cdot}034$ and $R = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}040$, where F_o and F_c are the observed and calculated structure factors and $w = 1/\sigma^2$ is the weight assigned to the reflections.* All reflections were included in the final

* Lists of structure factors and anisotropic thermal parameters and a full list of interatomic distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36048 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic parameters for* $[NH_3CH_3][MnCl_3].2H_2O$

	x	y	z	U_{eq}* (Å^2)
Mn	0·03798 (5)	0·99997 (5)	0·25022 (4)	0·0238 (3)
Cl(1)	0·01444 (9)	0·74959 (7)	0·15184 (6)	0·0276 (5)
Cl(2)	0·25818 (9)	0·09699 (8)	0·11553 (6)	0·0307 (6)
Cl(3)	0·73163 (10)	0·41377 (8)	0·10758 (6)	0·0324 (6)
O(1)	0·8313 (3)	0·0690 (3)	0·1238 (2)	0·036 (2)
O(2)	0·1672 (3)	0·4299 (3)	0·1306 (2)	0·036 (2)
N	0·5647 (4)	0·1656 (4)	0·3066 (3)	0·053 (2)
C	0·4765 (5)	0·2704 (5)	0·3767 (4)	0·055 (3)
HO(1)	0·168 (6)	0·462 (5)	0·064 (4)	0·051
HO(2)	0·181 (6)	0·344 (5)	0·117 (4)	0·051
HO(3)	0·832 (6)	0·158 (5)	0·105 (4)	0·051
HO(4)	0·807 (6)	0·023 (5)	0·064 (4)	0·051
HN(1)	0·612 (6)	0·206 (5)	0·245 (4)	0·051
HN(2)	0·580 (6)	0·097 (5)	0·358 (4)	0·051
HN(3)	0·502 (6)	0·109 (5)	0·259 (4)	0·051
HC(1)	0·401 (6)	0·235 (5)	0·389 (5)	0·051
HC(2)	0·420 (6)	0·333 (5)	0·329 (4)	0·051
HC(3)	0·544 (5)	0·315 (5)	0·421 (4)	0·051

* Calculated for the non-hydrogen atoms from the anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$ as $U_{eq} = [a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ac(\cos\beta)\beta_{13}]/6\pi^2$. U_{eq} for H atoms was set equal to 0·051 ($B_{eq} = 4{\cdot}0$).

Table 2. *Manganese–manganese interatomic distances*

		Description
Mn–Mn^{i}	4·613 (3) Å	Shortest distance along the chain
Mn–Mn^{ii}	5·765 (4)	Shortest distance between chains
Mn–Mn^{iii}	7·803 (4)	Shortest distance between hydrogen-bonded planes of chains

Symmetry code: (i) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $-x, 2 - y, -z$; (iii) $1 + x, y, z$.

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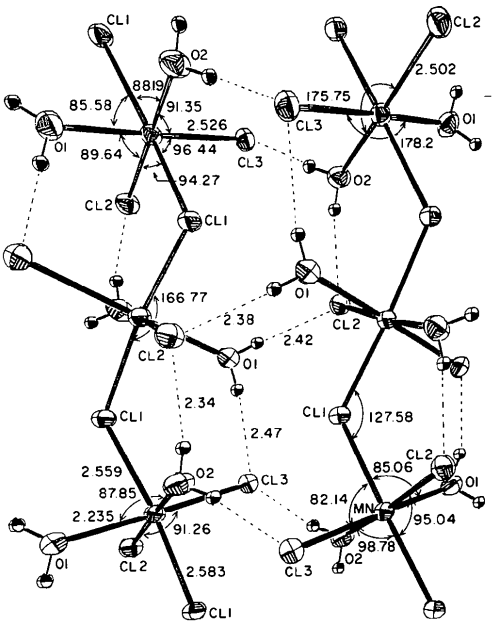

Fig. 1. The hydrogen-bonded plane of chains in $[NH_3CH_3][MnCl_3].2H_2O$. The chains which run in the **b** direction are hydrogen bonded together in the **c** direction. E.s.d.'s are 0·001–0·002 Å and 0·02–0·08° for intrachain distances and angles, and 0·05 Å for hydrogen-bonding distances (broken lines).

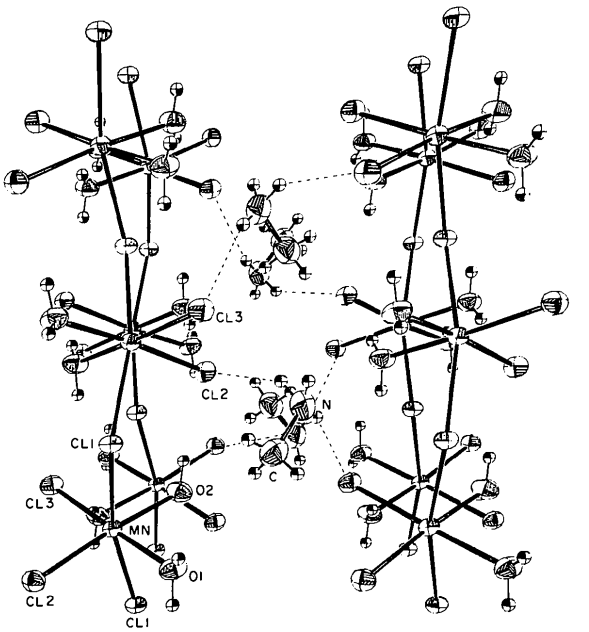

Fig. 2. A view of $[NH_3CH_3][MnCl_3].2H_2O$ showing the position of the $[NH_3CH_3]^+$ ions between the hydrogen-bonded planes of chains.

refinement. The final atomic parameters are given in Table 1 and pertinent interatomic distances and angles are given in Table 2 and Fig. 1. Computer programs used were from a local library (Anderson, 1971; Caputo, 1976).

Discussion. The salt has a structure with infinite chains of corner-sharing *cis*-$[MnCl_4(H_2O)_2]$ octahedra running parallel to **b**, as shown in Fig. 1. Adjacent chains are hydrogen bonded together in the **c** direction to form sheets. This salt is isostructural to $Cs[MnCl_3].2H_2O$, both in the chain geometry and the hydrogen-bonding configuration in the sheet (Jensen, Anderson & Rasmussen, 1962). Both $Cs[MnCl_3].2H_2O$ and the isomorphous α-$Rb[MnCl_3].2H_2O$ (Jensen, 1967) belong to space group *Pcca*. $[NH_3CH_3][MnCl_3].2H_2O$ was also assigned to this space group on the basis of apparent systematic extinctions before a more accurate measurement of the β angle indicated that the structure was monoclinic. The methylammonium ions hydrogen bond adjacent sheets together *via* Cl···H–N–H···Cl paths (Fig. 2). This hydrogen bonding is the reason for the distortion from an orthorhombic system, the sheets having moved with respect to each other along the **c** direction.

The chain axis for α-$Rb[MnCl_3].2H_2O$ and $Cs[MnCl_3].2H_2O$ is the *a* axis with repeat distances of 9·005 and 9·060 Å respectively. Hydrogen bonding is parallel to **c**, which has a unit-cell length of 11·340 and 11·455 Å respectively. The corresponding distances for $[NH_3CH_3][MnCl_3].2H_2O$ are 9·151 and 11·486 Å. As can be seen, the basic structure experiences a gradual expansion along the chain and hydrogen-bonding directions as the size of the cation increases. The corresponding Mn–Mn distances also become larger as one goes from the α-Rb (4·538 Å), to the Cs (4·56 Å) and methylammonium salt (4·613 Å).

The *b* axis runs perpendicular to the hydrogen-bonded planes of chains in the α-Rb and Cs salts and has unit values of 7·055 and 7·285 Å. The equivalent distance $a^* = 7·801$ Å in the methylammonium salt would be expected to be larger to accommodate packing of the larger cation between the hydrogen-bonded planes.

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