Acta Cryst. (1981). B**37**, 1618–1619

Dimethylammonium Trichloromanganate(II) Dihydrate

BY RUTH E. CAPUTO AND ROGER D. WILLETT

Department of Chemistry, Washington State University, Pullman, Washington 99164, *USA*

(*Received* 30 *July* 1980; *accepted* 9 *March* 1981)

Abstract. $[NH_2(CH_3)_2][MnCl_3].2H_2O$, orthorhombic, *Cmca*, $a = 17{\cdot}156\ (9)$, $b = 12{\cdot}000\ (6)$, $c = 9{\cdot}313\ (4)$ Å, $\rho_c = 1{\cdot}686$ Mg m^{-3}, $Z = 8$; $R = 0{\cdot}057$, $R_w = 0{\cdot}051$ for 881 reflections. The salt contains *cis*-$[MnCl_4(H_2O)_2]$ octahedra which form mono-bridged infinite chains parallel to **c**. The bridging angle is 127·60 (6)°. The Mn—O distance is 2·201 (4) Å and the Mn—Cl distances range from 2·516 (1) to 2·625 (2) Å. Each water molecule forms one hydrogen bond within and one hydrogen bond between chains. The latter tie the chains together in sheets in the *bc* plane.

Introduction. Pale-pink orthorhombic crystals of $[NH_2(CH_3)_2][MnCl_3].2H_2O$ were grown by the evaporation of a 95% ethanol solution containing a 1 : 1 molar ratio of the amine hydrochloride and $MnCl_2.4H_2O$. Systematic extinctions (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$; and $hk0$, $h = 2n + 1$) define the space group *Cmca*. Lattice constants were determined from 12 accurately centered high-angle reflections. Intensity data were collected on an automated 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 881 unique reflections ($2\theta < 50°$) were obtained. No crystal decomposition occurred during data collection. The data were corrected for absorption ($\mu = 2{\cdot}212$ mm^{-1}), and errors assigned by the relationship $\sigma^2(I) = \sigma^2_{\rm stat} + c^2I^2$, where $\sigma^2(I)$ is the estimated variance in intensity, $\sigma_{\rm stat}$ is the error determined from the counting statistics during data collection, c is a constant set equal to 0·05, 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 $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0{\cdot}051$ and $R = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}057$, where F_o and F_c are the observed and calculated structure factors and $w = 1/\sigma^2$ is the weight assigned to the reflection.* All reflections were included in the final refinement. Final atomic parameters for the compound are given in Table 1 and pertinent interatomic distances and angles are given in Table 2 and Fig. 1. Computer

Table 1. *Atomic parameters for* $[NH_2(CH_3)_2]$-$[MnCl_3].2H_2O$

	x	y	z	U_{eq}* (Å^2)
Mn	0·0	0·23520 (7)	0·21429 (9)	0·0243 (5)
Cl(1)	0·0	0·34530 (12)	0·45216 (14)	0·0262 (8)
Cl(2)	0·10866 (7)	0·10961 (9)	0·29616 (11)	0·0342 (7)
O	0·0877 (3)	0·1469 (3)	0·6323 (4)	0·043 (2)
N	0·1621 (3)	0·0	0·0	0·038 (3)
C	0·2097 (4)	0·4032 (6)	0·4489 (7)	0·065 (4)
HO(1)	0·084 (5)	0·407 (6)	0·141 (8)	0·051
HO(2)	0·113 (4)	0·139 (6)	0·548 (7)	0·051
HN	0·117 (4)	0·041 (5)	0·072 (6)	0·051
HC(1)	0·162 (4)	0·333 (5)	0·419 (7)	0·051
HC(2)	0·259 (4)	0·423 (5)	0·377 (7)	0·051
HC(3)	0·241 (4)	0·126 (5)	0·029 (7)	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 $U_{eq} = (a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33})/6\pi^2$. 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$^{\rm i}$	4·670 (2) Å	Shortest distance along the chain
Mn—Mn$^{\rm ii}$	6·037 (3)	Shortest distance between chains
Mn—Mn$^{\rm ii}$	8·604 (4)	Shortest distance between hydrogen-bonded planes of chains

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

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* 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 36049 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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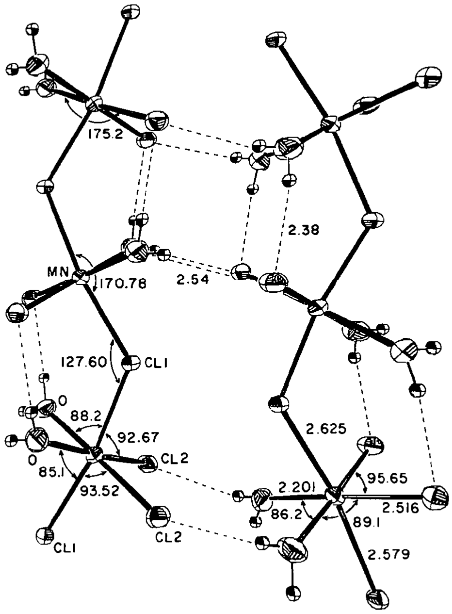

Fig. 1. The hydrogen-bonded plane of chains in $[NH_2(CH_3)_2][MnCl_3].2H_2O$. The chains which run in the **c** direction are hydrogen bonded together in the **b** direction. E.s.d.'s are 0·001–0·004 Å and 0·04–0·1° for intrachain distances and angles, and 0·07 Å for hydrogen-bonding distances (broken lines).

programs used were from a local library (Anderson, 1971; Caputo, 1976).

Discussion. As seen in Fig. 1, the structure of $[NH_2(CH_3)_2][MnCl_3].2H_2O$ consists of chains of corner-sharing *cis*-$[MnCl_4(H_2O)_2]$ octahedra running parallel to **c** which are hydrogen bonded in the **b** direction. The ammonium groups separate the planes of hydrogen-bonded chains, as shown in Fig. 2. No hydrogen bonding between these planes occurs.

The structure has strong similarities to that of $[NH_3CH_3][MnCl_3].2H_2O$, which also contains chains of corner-sharing *cis*-$[MnCl_4(H_2O)_2]$ octahedra (Caputo & Willett, 1981). In the methylammonium salt, the Mn—Cl(1)—Mn—Cl(1)—Mn backbones of the chains run parallel to each other. This is not the case for the dimethylammonium salt, as seen in Fig. 1. Here, the Cl(1) atoms on adjacent chains are tipped toward or away from each other. The O atoms are *cis* in both structures, but their positions relative to the hydrogen-bonded plane of chains are different. The manner in which the chains are hydrogen bonded together has been radically altered as a result of these changes.

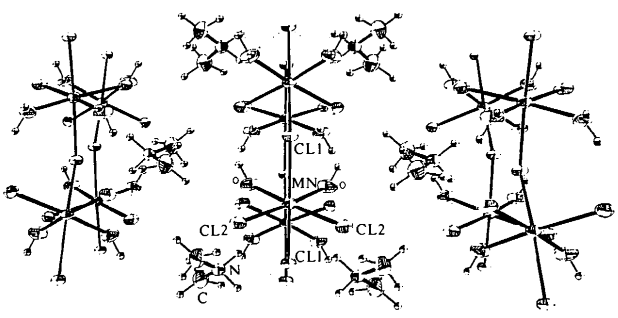

Fig. 2. A view of $[NH_2(CH_3)_2][MnCl_3].2H_2O$ showing the positions of the $[NH_2(CH_3)_2]^+$ ions between hydrogen-bonded planes of chains.

The change in the relative positions of the Mn—Cl(1)—Mn—Cl(1)—Mn chains can be rationalized if hydrogen bonding of the dimethylammonium ion is examined. Each N—H is close to a Cl(1) atom. The Cl(1) atoms on different chains have tipped toward each other to accommodate the two N—H's of the dimethylammonium group. The other changes are a result of the altered arrangement in the backbone of the chains.

If the two structures are compared, an increase in the repeat distances along the chain and hydrogen-bonding directions is seen to accompany the increase in cation size. In the methylammonium salt the repeat distance along the chain is 9·151 Å. The repeat distance in the dimethylammonium salt is 9·313 Å, significantly larger. The lattice parameter in the direction of hydrogen bonding is also larger, 12·000 compared to 11·486 Å. The Mn—Cl(1) bonds are longer in the dimethylammonium salt, and the Cl(1)—Mn—Cl(1) angle has opened up from 166·77 to 170·78°. Both changes would contribute to a longer repeat distance along the chain. A more interesting feature, perhaps, is the constancy of the Mn—Cl(1)—Mn angle which is 127·58 and 127·60° for $[NH_3CH_3][MnCl_3].2H_2O$ and $[NH_2(CH_3)_2][MnCl_3].2H_2O$ respectively.

References

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