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Trimethylammonium Manganese(II) Chloride Dihydrate

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$[(CH_3)_3NH]MnCl_3.2H_2O$, $M=257.45$, orthorhombic, *Pnma*, $a=16.779$ (3), $b=7.434$ (1), $c=8.227$ (1) Å, $V=1026.2$ Å^3, $\varrho_o=1.67$ (1) (by flotation in a mixture of CCl_4 and CH_2I_2), $\varrho_c=1.666$ g cm^{-3}, $Z=4$, Mo $K\alpha_1$ radiation, $\lambda=0.70926$ Å, μ(Mo $K\alpha)=19.13$ cm^{-1}, $F(000)=516$, final $R=0.051$ (all reflections) for the Caputo and Willett data set and 0.029 (observed reflections) for the Muir data set. The structure is comprised of infinite chains of edge-sharing $MnCl_4(OH_2)_2$ octahedra separated by the trimethylammonium ions and discrete Cl ions. It is, in fact, identical with that of the analogous Co compound with minor modifications produced by the difference in ionic radii of the two metal ions.

Introduction

Single crystals of $[(CH_3)_3NH]MnCl_3.2H_2O$ were prepared by evaporating an aqueous solution containing equimolar amounts of $[(CH_3)_3NH]Cl$ and $MnCl_2.4H_2O$. Pink crystals form as prisms extended along **b**, bounded principally by {201}, {100}, {210}, and {320}. Preliminary analysis of crystals mounted on a GE Single Crystal Orienter and by Weissenberg photographs showed systematically absent reflections in the 0*kl* zone when $k+l=2n+1$ and in the *hk*0 zone when $h=2n+1$, indicating space groups *Pnma* or *Pna2₁*. The centrosymmetric *Pnma* was shown by subsequent analysis to be correct. Elemental analyses of 5.68 N, 13.99 C, and 5.57% H were obtained for the compound. The theoretical composition includes 5.44 N, 13.99 C, and 5.49% H.

Two data sets were collected and refined simultaneously and independently of each other. Both data sets were of extremely high quality. However, since the Muir data set was more extensive than the Caputo and Willett data set and gave a superior refinement (although based on a set of 'observed' reflections rather than a complete data set), the results of the Muir refinement are reported.

The Caputo and Willett data set was collected from a crystal $0.23 \times 0.19 \times 0.28$ mm on an automated Picker four-circle diffractometer using Zr-filtered Mo $K\alpha$ radiation. The computer programs used for centering and data collection were those written for the Oak Ridge computer-controlled X-ray diffractometer, after which the automation system had been patterned. A least-squares analysis of the reciprocal-lattice coordinates of 12 accurately centered reflections was used to obtain the lattice parameters and to provide an orientation matrix for use in data collection (Busing, Ellison, Levy, King & Roseberry, 1968). A θ–2θ scan was employed during data collection with a scan width

of 2·0°, where 20 steps were made per degree and each step was counted for 4·0 s. Collecting over an angle range of 5 to 45° in 2θ produced 976 unique reflections. Three peaks were used as standards and were remeasured every 20 reflections to check decomposition and possible movement of the crystal. No systematic deviations from counting statistics were observed. Lorentz–polarization corrections were made on the data and weights assigned to individual reflections as follows: $\sigma^2(I) = \sigma_{stat}^2 + c^2 I^2$ where $\sigma^2(I)$ is the estimated variance in intensity, c is a constant assigned a value of 0·03, I is the intensity of the reflection, and σ_{stat} is the error determined from the counting statistics during data collection. Absorption corrections using a linear absorption coefficient of 2·069 mm^{-1} were applied, with $T_{max} = 0·71$ and $T_{min} = 0·69$ (Wehe, Busing & Levy, 1962). Scattering factors (*International Tables for X-ray Crystallography*, 1968) for Mn^{2+}, Cl$^-$, N, C, O, and H were used. All atomic positions and anisotropic thermal parameters for non-hydrogen atoms were refined by full-matrix least squares, the weighted $R\{= [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}, \ w = 1/\sigma^2(F)\}$ being minimized (Busing, Martin & Levy, 1962). The thermal parameters for H were fixed at 4·0 Å^2. A final weighted R of 0·038 and unweighted $R[= \sum ||F_o| - |F_c||/\sum|F_o|]$ of 0·051 were obtained including all reflections with a 'goodness of fit' of 1·46.*

For the Muir intensity-data collection a well formed crystal of maximum dimensions 0·22 mm was chosen and its 11 faces were identified and accurately measured for absorption corrections. Accurate cell parameters were determined by a least-squares fit to the setting angles of 12 reflections in the range $45 \le 2\theta \le 50°$ measured with unfiltered Mo $K\alpha_1$ radiation ($\lambda = 0·70926$ Å) on a Picker FACS-I diffractometer in the temperature range 24·9 to 25·4°C. Data were collected with Zr-filtered Mo $K\alpha$ radiation, a θ–2θ scan over a range of 1·2° plus the α_1–α_2 divergence, and a scan rate of 1° (in 2θ) min^{-1} with backgrounds measured for 10 s at each end of the scan. The 2θ range was $2 \le 2\theta \le 55°$.

* A list of structure factors for both data sets and atomic parameters for the Caputo and Willett set have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31779 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Three standard reflections (020,011,201) were monitored after every 100 data reflections and used to scale the data. Variations in the scale factor were less than ± 2·5% during the entire data collection. Data whose intensities were such that one–four attenuators were automatically inserted by the Picker software were remeasured at lower mA settings along with the standard reflections. Absorption corrections were applied to the data, with $T_{max} = 0·77$ and $T_{min} = 0·66$. Intensity measurements were obtained for 1336 reflections, of which 1110 had intensities that exceeded their own standard deviations and were included in subsequent data analysis.

Because of the similarity between the lattice parameters and space group of the title compound and of the analogous Co compound, structural refinement was begun with the Co compound parameters. A structure factor calculation based on these atoms with isotropic temperature factors and with two cycles of refinement yielded an R of 0·058 and a weighted R of 0·062. Subsequent full-matrix least-squares refinement with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms reduced R to 0·029 and the weighted R to 0·022. The weighting scheme used was $w = 1/\sigma_F^2$, where σ_F was derived from counting statistics only. Neutral-atom scattering factors (Cromer & Mann, 1968) were used, except for Mn^{2+}, and were corrected for anomalous dispersion (Cromer & Liberman, 1970). In the

Table 1. *Fractional coordinates and temperature factors*

	x	y	z	U_{iso}
Mn	0·0	0·0	0·0	
Cl(1)	−0·10180 (3)	0·25	−0·00067 (8)	
Cl(2)	0·10193 (4)	0·25	−0·06443 (9)	
Cl(3)	−0·08918 (4)	0·25	0·49798 (9)	
O	0·0227 (1)	0·0380 (2)	0·2594 (2)	
N	0·1828 (2)	0·25	0·3110 (3)	
C(1)	0·1674 (2)	0·25	0·4874 (4)	
C(2)	0·2257 (2)	0·0844 (3)	0·2593 (4)	
H(O1)	0·038 (2)	−0·044 (3)	0·316 (3)	0·039 (7)
H(O2)	−0·012 (2)	0·084 (5)	0·313 (4)	0·074 (11)
H(11)	0·218 (2)	0·25	0·546 (4)	0·043 (9)
H(12)	0·139 (2)	0·147 (3)	0·511 (3)	0·046 (7)
H(21)	0·238 (2)	0·098 (3)	0·150 (4)	0·046 (7)
H(22)	0·196 (2)	−0·026 (4)	0·285 (3)	0·052 (7)
H(23)	0·274 (2)	0·086 (4)	0·303 (3)	0·055 (8)
H(N)	0·137 (2)	0·25	0·257 (4)	0·049 (10)

Table 1 (*cont.*)

Anisotropic temperature factors ($\times 10^5$) of the form $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	173 (2)	629 (7)	650 (6)	24 (4)	−21 (3)	−39 (5)
Cl(1)	142 (2)	689 (11)	1076 (9)	0	40 (6)	0
Cl(2)	166 (2)	811 (11)	997 (12)	0	39 (4)	0
Cl(3)	261 (2)	1000 (11)	779 (9)	0	24 (6)	0
O	252 (6)	918 (25)	671 (20)	79 (53)	7 (8)	29 (19)
N	159 (8)	1047 (46)	1050 (41)	0	−134 (16)	0
C(1)	288 (14)	1493 (71)	971 (53)	0	−32 (23)	0
C(2)	248 (10)	1268 (46)	1461 (50)	63 (9)	−24 (18)	−268 (72)

final cycle the average parameter shifted by 0·015 of its e.s.d. value [maximum 0·11 for z for H(O2)]. All the H atoms appeared in a difference Fourier map at heights ranging from 0·53 to 0·72 e Å^{-3}, compared with the highest peak of 0·31 e Å^{-3} observed in a final difference Fourier map including all atoms. The r.m.s. deviation of an observation of unit weight is 0·68. The intensities of seven strong reflections, included in the refinement, were ~5% lower than their calculated values. This seemed related to residual uncertainties in the attenuator calibration when three or four attenuators were inserted rather than to extinction, and so no extinction correction was attempted.

The atomic coordinates and thermal parameters are given in Table 1.* The atoms are named by reference to the analogous Co compound (Losee, McElearney, Shankle, Carlin, Cresswell & Robinson, 1973).

Discussion

In recent years, the magnetic properties of linear chain systems containing Mn^{II} have been studied extensively (Ackerman, Cole & Holt, 1974; Hone & Richards, 1974). In particular, $(CH_3)_4MnCl_3$ and $CsMnCl_3.2H_2O$ have been used as model systems for studying properties of one-dimensional exchange-coupled systems. The present work was done in an effort to expand further the number of systems available for this type of inquiry.

The basic features of the structure, Fig. 1 (Johnson, 1965), are infinite chains of edge-sharing $MnCl_4(OH_2)_2$ octahedra with bridging Cl atoms and *trans* O atoms. The chains run parallel to **b** and are hydrogen bonded together along **c** through the Cl ions which are located between chains. The trimethylammonium groups lie between the planes of hydrogen-bonded chains. Bond
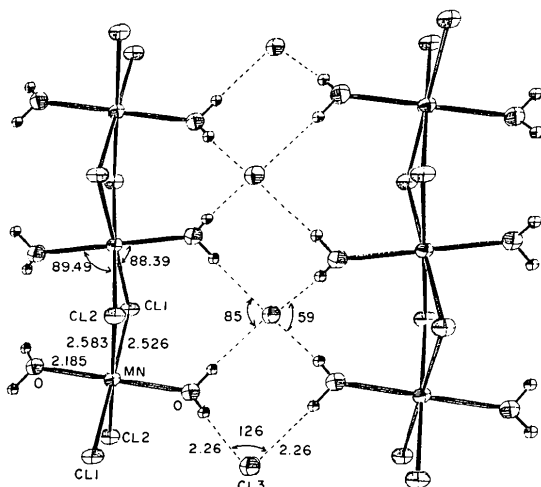
* See previous footnote.

Fig. 1. The hydrogen-bonded plane of chains in $[(CH_3)_3NH]MnCl_3.2H_2O$. The chains which run along **b** are hydrogen bonded together in the **c** direction.

angles and bond distances with the corresponding estimated standard deviations are given in Table 2. This compound is isostructural with the analogous Co compound (Losee et al., 1973). The lattice parameters for the Co compound are $a = 16·671$, $b = 7·273$, and $c = 8·113$ Å. These are significantly smaller than those for the Mn compound, as would be expected from the decrease in crystal ionic radius going from Mn^{II} to

Table 2. *Selected bond lengths (Å) and angles (°) and their e.s.d.'s*

Mn···Mn	3·7170 (5)	Mn——Cl(1)——Mn	94·83 (2)
Mn——O	2·1859 (8)	Mn——Cl(2)——Mn	92·13 (2)
Mn——Cl(1)	2·5241 (4)	Cl(1)—Mn——Cl(2)	85·28 (2)
Mn——Cl(2)	2·5807 (5)	O——Mn——Cl(1)	88·50 (4)
Mn···Cl(3)	4·7413 (5)	O——Mn——Cl(2)	89·54 (4)
O——H(O1)	0·81 (3)	Mn——O——H(O1)	121 (2)
O——H(O2)	0·81 (3)	Mn——O——H(O2)	118 (2)
Cl(3)—H(O1)	2·34 (2)	H(O1)-O——H(O2)	104 (4)
Cl(3)—H(O2)	2·35 (3)	O——H(O1)-Cl(3)	159 (3)
		O——H(O2)-Cl(3)	167 (3)

Co^{II}. The dihedral angle between adjacent MnCl$_4$ planes is 16·20°, compared with a value of 15·58° for the analogous Co compound.

Recently, a short account of the magnetic susceptibility of the Mn^{II} salt has been published (Merchant, McElearney, Shankle & Carlin, 1974). The magnetic behavior was interpreted in terms of a collection of one-dimensional linear chains, with weak antiferromagnetic coupling along the chain as well as between chains. This is consistent with the structural results. The bridging Mn–Cl–Mn angles of 94·83 and 92·13° are in the range where ferro- and antiferromagnetic superexchange contributions are expected to roughly cancel each other. As in the Co^{II} salt, the hydrogen-bonding network provides a superexchange mechanism between chains.

The positional parameters for the two studies of the Mn compound agree very well – only one positional parameter for the non-hydrogen atoms differs by more than twice the joint standard deviation, defined as $\sigma(\text{joint}) = [\sigma^2(M) + \sigma^2(CW)]^{1/2}$, where CW refers to the data of Caputo and Willett and M refers to the Muir data set. The thermal parameters differ by less than three times the joint standard deviation, except for two anisotropic 'cross terms', for which there are significant sign differences.

In order to compare further the two data sets on the title compound, a δ_p half-normal probability plot was prepared, using X_i calculated with *International Tables for X-ray Crystallography* (1974). Values of δ_{p_i} were calculated as

$$\delta_{p_i} = \frac{\text{CW parameter}(i) - \text{M parameter}(i)}{\sigma(\text{joint})} .$$

Fig. 2 shows the plot for 74 of the 76 parameters. The remaining two are off scale, due to the change in sign of the anisotropic 'cross terms'. It can be seen from the plot that the first 60 parameters, corresponding

to X_i less than 1·3, form a relatively linear plot, with zero intercept, and a slope of 1·30. If it is assumed that there is an equal error distribution in both sets of e.s.d.'s, then in both cases the e.s.d.'s have been underestimated by a factor of 1·3. The remaining points on the plot seem to belong to a different distribution with a slope of 1·6. These latter points include mainly H atom parameters.

The good agreement between the results of the two studies of the title compound indicates that the determinations of the overall structure are probably correct. This is confirmed by the half-normal probability plot, subject to the observation that the standard deviations may be slightly underestimated.

Fig. 2. Half-normal probability plot of 76 δ_{pi} derived from the comparison of the atom parameters from the Caputo and Willett data set and the Muir data set.

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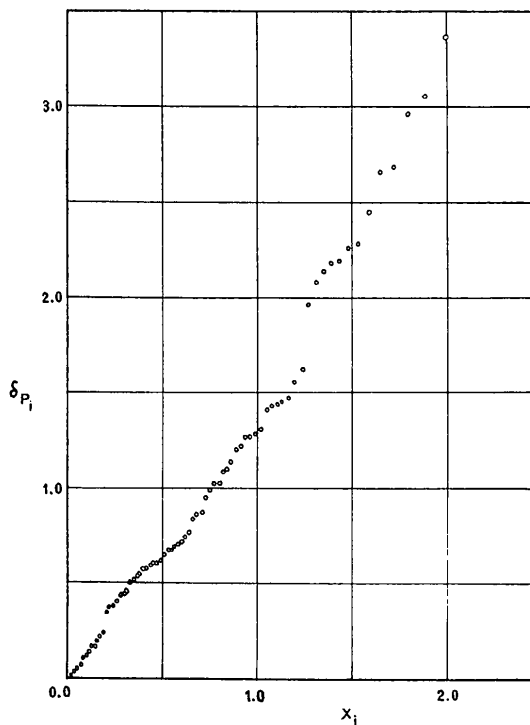WEHE, D. J., BUSING, W. R. & LEVY, H. A. (1962). *ORABS*. Oak Ridge National Laboratory Report ORNL-TM-229.