

(A_{1g}) is also expected to be observed in the Raman spectrum. There is only one other band observed in the spectrum at 194 cm^{-1} . This appears rather low for an octahedral Ga—Cl stretching vibration but in the absence of any strong band we tentatively ascribe it to this mode.

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Diethylenetriammonium Tetrachloromanganate(II) Chloride

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Abstract. $[(\text{NH}_3\text{CH}_2\text{CH}_2)_2\text{NH}_2\text{Cl}]\text{MnCl}_4 \cdot \text{C}_4\text{H}_{16}\text{N}_3^{3+} \cdot \text{Cl}^- \cdot \text{MnCl}_4^{2-}$, orthorhombic, *Pnma*, $a = 7.116$ (1), $b = 24.629$ (6), $c = 7.201$ (2) Å, $Z = 4$, $D_c = 1.78\text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å. Final $R = 0.051$ for a total of 1794 independent reflections. The compound is isostructural with the analogous Cu^{II} salt [Ferguson & Zaslow (1971). *Acta Cryst.* **B27**, 849–852; Greenhough & Ladd (1977). *Acta Cryst.* **B33**, 1266–1269] consisting of a laminar network of corner-sharing MnCl_6 octahedra. The bridging Mn—Cl distances are 2.5681 (5) and 2.5749 (6) Å while the terminal Mn—Cl distance is significantly shorter at 2.4978 (4) Å. The terminal NH_3^+ moieties hydrogen bond to chloride ions in the laminar network, while the NH_2^+ moiety hydrogen bonds to the lattice chloride ion.

Introduction. Crystals of $[(\text{NH}_3\text{CH}_2\text{CH}_2)_2\text{NH}_2\text{Cl}]\text{MnCl}_4$ grow as flat pink plates from ethanolic solutions of equimolar mixtures of the ammonium chloride salt and $\text{MnCl}_4 \cdot 4\text{H}_2\text{O}$.

Weissenberg and precession photographs exhibited *mmm* symmetry with systematic absences $0kl$, $k + l = 2n + 1$ and $hk0$, $h = 2n + 1$, indicating the space group *Pnma*. A crystal approximately $0.055 \times 0.037 \times 0.118$ mm was selected and data were collected on a Picker diffractometer using a θ – 2θ scan technique with

Zr-filtered Mo $K\alpha$ radiation. A scan range of 1.6° with $0.05^\circ/\text{step}$ and 3 s/step was used with 30 s background measurements before and after each scan. A total of 1794 independent reflections were measured at room temperature. Absorption corrections were applied ($\mu = 2.106\text{ mm}^{-1}$) with transmission factors ranging from 0.35 to 0.48. The unit-cell size and probable space group (*Pnma*) matched closely the Cu analog. Refinement was initiated using the coordinates from the structure of the Cu analog and rapidly converged. H atoms were found on a difference density map and included in the final refinement. A value of $R_1 (= \sum |F_o| - |F_c| / \sum |F_o|) = 0.051$ (0.038 for $|F| > 3\sigma$) was obtained and $R_3 \{ = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2} \} = 0.044$ where $w = 1/\sigma^2$ with $\sigma^2(I) = TC + 2.56 BK + (0.04)^2 I^2$ where TC = total counts, BK = total background counts, and $I = TC - 1.6BK$. The standard error of an observation of unit weight was 1.34. Final parameters are listed in Table 1 and pertinent distances and angles are given in Table 2.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35947 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional ($\times 10^5$ for non-H atoms; $\times 10^3$ for H) and thermal parameters with e.s.d.'s in parentheses

B_{eq} for non-H atoms is calculated from the refined anisotropic β_{ij} 's according to Willis & Pryor (1975). For H atoms the final refined isotropic B values are listed.

	x	y	z	B_{eq}/B (\AA^2)
Mn	0	0	0	1.31 (3)
Cl(1)	1215 (9)	10049 (2)	4514 (8)	2.06 (3)
Cl(2)	28501 (8)	-1159 (2)	21514 (7)	1.97 (3)
Cl(3)	44426 (13)	25000	53334 (11)	2.24 (3)
N(1)	1195 (43)	25000	54272 (40)	1.84 (10)
N(2)	-3332 (36)	9889 (8)	48500 (33)	2.26 (10)
C(1)	-6174 (38)	19898 (9)	45970 (34)	2.00 (10)
C(2)	3141 (38)	15182 (9)	56014 (37)	2.18 (10)
H(1)	142 (11)	250	528 (9)	2.8 (16)
H(2)	-13 (7)	250	668 (8)	0.9 (9)
H(3)	-37 (5)	198 (1)	323 (6)	0.9 (6)
H(4)	-186 (8)	200 (2)	483 (6)	1.9 (8)
H(5)	170 (6)	154 (2)	536 (5)	1.1 (7)
H(6)	5 (5)	153 (1)	691 (5)	1.0 (6)
H(7)	-146 (7)	95 (2)	497 (5)	1.7 (8)
H(8)	26 (7)	70 (2)	546 (7)	2.7 (10)
H(9)	-10 (8)	98 (2)	352 (9)	2.7 (11)

Table 2. Interatomic distances (\AA) and angles ($^\circ$)

Mn—Cl(1)	2.4978 (4)	Cl(1)—Mn—Cl(2)	90.24 (2)
Mn—Cl(2)	2.5681 (5)	Cl(2)—Mn—Cl(2 ⁱ)	91.349 (4)
Mn—Cl(2 ⁱ)	2.5749 (6)	Mn—Cl(2)—Mn ⁱ	159.64 (2)
N(1)—C(1)	1.487 (3)	C(1 ⁱⁱ)—N(1)—C(1)	115.3 (3)
C(1)—C(2)	1.520 (3)	N(1)—C(1)—C(2)	107.5 (2)
C(2)—N(2)	1.485 (3)	C(1)—C(2)—N(2)	111.3 (2)
N(2)—Cl(1)	3.184 (2)	C(2)—N(2)—Cl(1)	108.7 (2)
N(2)—Cl(2 ⁱⁱⁱ)	3.239 (2)	C(2)—N(2)—Cl(2 ⁱⁱⁱ)	103.1 (2)
N(2)—Cl(1)	3.242 (3)	C(2)—N(2)—Cl(1)	108.9 (2)
N(1)—Cl(3)	3.077 (3)	C(1)—N(1)—Cl(3)	110.1 (2)
N(1)—Cl(3 ^{iv})	3.091 (3)	C(1)—N(1)—Cl(3 ^{iv})	105.2 (2)
N(1)—H(1)	0.93 (8)	C(2)—H(6)	0.96 (4)
N(1)—H(2)	0.92 (6)	N(2)—H(7)	0.91 (5)
C(1)—H(3)	1.00 (4)	N(2)—H(8)	0.93 (5)
C(1)—H(4)	0.90 (5)	N(2)—H(9)	0.97 (6)
C(2)—H(5)	1.00 (4)		

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

Scattering factors were taken from *International Tables for X-ray Crystallography* (1968). Computer programs used were from a local program library (Anderson, 1971; Caputo, 1976).

Discussion. The structure assumes the familiar two-dimensional layer of corner-shared MnCl_6 octahedra, with adjacent layers separated by the organic cations (see Fig. 1). The Mn octahedra are compressed, with the bridging Mn—Cl distances 0.070 to 0.077 \AA longer than the terminal Mn—Cl distance (2.5789 and

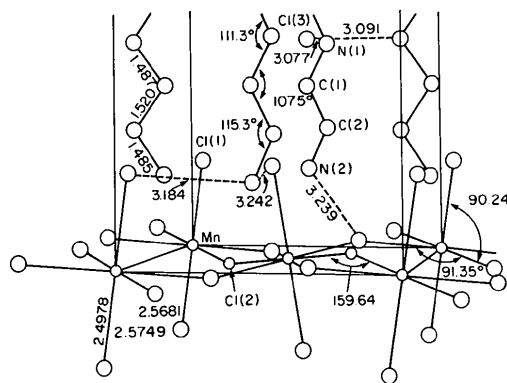


Fig. 1. The structure of diethylenetriammonium tetrachloromanganate(II) chloride. The b axis is vertical with the mirror plane perpendicular to this axis going through atoms N(1) and Cl(3).

2.5681 \AA vs 2.4978 \AA). The bridging Mn—Cl—Mn angle between octahedra is 159.64 (2) $^\circ$. This is the smallest such angle reported to date for the layered Mn^{2+} salts. This is a result of a twist of the octahedra around the normal to the layer, making the projection of the Mn—Cl—Mn bridge onto the ac plane non-linear.

The geometry of the $(\text{H}_2\text{dien})^{3+}$ ion is identical to that in the Cu^{2+} salt. The middle NH_2 group is strongly hydrogen bonded to the lattice chloride, Cl(3), with short linear N—H...Cl bonds with N—Cl distances of 3.077 and 3.091 \AA . Each terminal NH_3^+ group hydrogen bonds to one axial chloride (3.239 \AA) and two equatorial chlorides (3.184 and 3.242 \AA). The hydrogen bonding locks the cation very rigidly into the lattice.

The twist of the octahedra is also present in the Cu^{2+} salt and may be the source of anomalous magnetic anisotropy found in that salt (Losee & Hatfield, 1974) and in the analogous triethylenetetraammonium salt, $(\text{C}_6\text{H}_{22}\text{Cl}_2\text{N}_2)\text{CuCl}_4$ (Losee, Hatfield & Bernal, 1975).

The space group for the salt herein described is the same as for the room-temperature phase of $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$, di(methylammonium) tetrachloromanganate(II) (Kind, Plesko & Roos, 1978). The in-layer lattice constants are substantially larger (7.17 and 7.36 \AA) (Crowley, 1980) for the latter salt, although it should have the usual perovskite-type layer structure for compounds of this general formula and thus be analogous to the structure determined in this paper. This would indicate that the lattice chloride ion, instead of expanding the structure, actually causes it to contract due to the tightness of the hydrogen bonding between the central NH_2 group and the chloride ion.

Salts of the type $(\text{RNH}_3)_2\text{MX}_4$ and $(\text{NH}_3\text{-RNH}_3)\text{MX}_4$ are generally characterized by the existence of structural phase transitions, often slightly above room temperature (Arend, Tichy, Baberschke & Rys,

1976). These are usually associated with the onset of disorder of the cations in the structure (Kind *et al.*, 1979). A DTA scan of this salt revealed no evidence of a similar transition. Apparently the multiple hydrogen-bonding possibilities for the $-\text{NH}_3^+$ moieties allow disorder of the organic chain, but the hydrogen bonding to the lattice chloride is so restrictive that it prohibits such motion.

The MnCl_6 octahedra are tipped away from the normal to the layer by 7.5° . This tilt has been associated with the weak ferromagnetic behavior of these salts, as evidenced by the existence of a small residual magnetic moment in the magnetically ordered state and the onset of hysteresis behavior at the magnetic phase-transition temperature, T_N (Groenendijk, van Duyneveldt & Willett, 1979). Preliminary a.c. susceptibility measurements were made on a Hartshorn bridge at Iowa State University over the temperature range 30–50 K. This is the region anticipated for the onset of three-dimensional ordering. The existence of the sharp peak in the susceptibility at 43 K is characteristic of a weak ferromagnetic system. Thus, the existence of spin canting is confirmed in this salt, consistent with the small canting of the spin moment in the direction of the tilt of the terminal Mn–Cl bond away from the normal to the layer.

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o,o'-Dibromodibenzyl Ether

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Abstract. $\text{C}_{14}\text{H}_{12}\text{Br}_2\text{O}$, $M_r = 356.06$, monoclinic, $P2_1/c$, $a = 12.222(2)$, $b = 10.157(3)$, $c = 13.183(2)$ Å, $\beta = 125.86(1)^\circ$; $Z = 4$, $D_c = 1.783$ Mg m^{-3} . The structure was solved by heavy-atom techniques and refined by least squares, using 936 observed data and anisotropic temperature factors, to $R = 0.044$. The two halves of the molecule are not related by symmetry. Molecules of *o,o'*-dibromodibenzyl ether are approximately planar with both Br atoms on the same side of the molecule.

Introduction. Many tricyclic compounds show psychotropic activity (Chang, 1979). Useful precursors to

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these potential drugs contain *ortho*-bromo substituted phenyl rings separated by one or more atoms (Chang, 1979). These latter materials provide a vehicle for the study of the effects of intramolecular interactions on the configuration about the central atoms. The two-atom separation case has been the study of several investigations (Corey, 1979 and references therein). To extend these studies to the three-atom separation case the structure of the title compound was investigated.

Crystals were prepared by V. Chang (Chang, 1979). An approximately spherical crystal with a diameter of 0.22 mm was mounted on a Syntex $P2_1$ diffractometer and a total of 1865 intensities were measured using Mo

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