

Structure of β -Bis(ethylammonium) Tetrachloromanganate(II): A Neutron Refinement

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Abstract. β -(C₂H₅NH₃)₂MnCl₄, orthorhombic, *Abma*, $T = 294$ K, $a = 7.355$ (3), $b = 7.260$ (3), $c = 22.10$ (1) Å, $Z = 4$, $\lambda = 1.0327$ Å. The MnCl₆-octahedra layer adopts the $a^-a^-c^0$ tilt system; the ethylammonium group is disordered; the hydrogen-bonding scheme is a superposition of two symmetry-related schemes.

Introduction. β -(C₂H₅NH₃)₂MnCl₄ belongs to a group of compounds (C_nH_{2n+1}NH₃)₂MCl₄ with $M = \text{Mn, Cd, Fe, Cu}$ which form perovskite-like layer structures derivable from the K₂NiF₄ structure type. Because of reorientations of the alkylammonium groups (influenced by N—H...Cl hydrogen bonds, hereinafter abbreviated h.b.) and changes of the tilt systems of the octahedra layer, these compounds generally exhibit several structural phase transitions (de Jongh & Miedema, 1974; Chapuis, Arend & Kind, 1975; Heger, Mullen & Knorr, 1975, 1976; Seliger, Blinc, Kind & Arend, 1976; Chapuis, Kind & Arend, 1976; Depmeier, 1976, 1977; Depmeier, Felsche & Wildermuth, 1977; Chapuis, 1977). The title compound (hereinafter called β C2Mn) is the room-temperature form of (C₂H₅NH₃)₂MnCl₄ and has already been the subject of an X-ray study (Depmeier, 1976), which showed the general features of the structure, *i.e.* the topology, the most important bond lengths and angles of the non-hydrogen atoms, the tilt system of the octahedra layer and the disorder of the ethylammonium group. However, the important question of the H positions (especially of those attached to N) could not be answered (in fact a h.b. scheme was assumed which later turned out to be wrong). Other X-ray work on the γ phase at 126 K (Depmeier, 1977) resolved the N—H positions and, together with first results of this neutron work, explained the mechanism of the $\gamma \rightarrow \beta$ phase transition. This paper now reports the results of the neutron work on β C2Mn.

Crystals suitable for neutron work were obtained by slow evaporation of a solution of MnCl₂ and C₂H₅NH₃Cl (molar ratio 1:2) in a mixture of water

and ethanol. A crystal, 9.4 × 8.2 × 1.9 mm, was chosen and enclosed in a thin-walled Al tube to protect it from humidity. The cell dimensions and intensities were measured on the four-circle diffractometer P32 at the FR2 reactor at the Kernforschungszentrum Karlsruhe. The temperature was 294 K and neutrons of 1.0327 Å from a Cu(311) monochromator were used. Data were collected by the ω -scan technique up to $(\sin \theta)/\lambda = 0.65$ Å⁻¹ yielding 629 unique reflexions of which 499 had $I > 2\sigma(I)$ and were classed as observed. 130 reflexions with $I < 2\sigma(I)$ were given half the intensity of the weakest observed reflexion. A transmission factor for (C₂H₅NH₃)₂MnCl₄ was measured by the attenuation of the monochromatic beam. With $\mu = 2.32$ cm⁻¹ an absorption correction was applied to the measured intensities (Prewitt, 1965). The structure was refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$ with anisotropic temperature factors for all atoms. Neutron scattering lengths were $b(\text{Mn}) = -0.387$, $b(\text{Cl}) = 0.958$, $b(\text{N}) = 0.940$, $b(\text{C}) = 0.665$, $b(\text{H}) = -0.374 \times 10^{-12}$ cm (Willis, 1973). Unit weights were used. Because of the disorder of the ethylammonium group and the relatively small number of reflexions, the refinement was seriously affected by correlation problems. For this reason some coordinates [$x, y(\text{H}12)$; $x(\text{H}22)$; $y(\text{H}23)$] were taken from difference maps and held invariant. The disorder is typical for this type of structure (*e.g.* Willett & Riedel, 1975; Depmeier, 1976; Depmeier & Mason, 1978) and is responsible for some bond lengths [*e.g.* C(1)—C(2)] and some anisotropic temperature factor coefficients not being consistent with the expected values. However, the most important parts of the structure are clear. The final R ($= \sum \Delta / \sum |F_o|$) was 0.088 for 629 reflexions and 110 parameters.* The *SHELX* program was used throughout the refinement.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33319 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. Fig. 1 shows an *ORTEP* plot (Johnson, 1965) of β C2Mn around $z = 0.5$. The corner-sharing MnCl_6 octahedra belong to one octahedra layer with net charge 2-. Below and above the layer, cavities are formed by eight Cl atoms in which the RNH_3^+ ions are situated and fixed by $\text{N}\cdots\text{Cl}$ h.b.'s. (For clarity the *ORTEP* plot shows only one of two symmetry-related $\text{C}_2\text{H}_5\text{NH}_3$ groups of occupancy factor 0.5. The two groups are related by a mirror plane perpendicular to y passing through the Mn atoms.) Thus, neutral strata are formed which stack on each other.

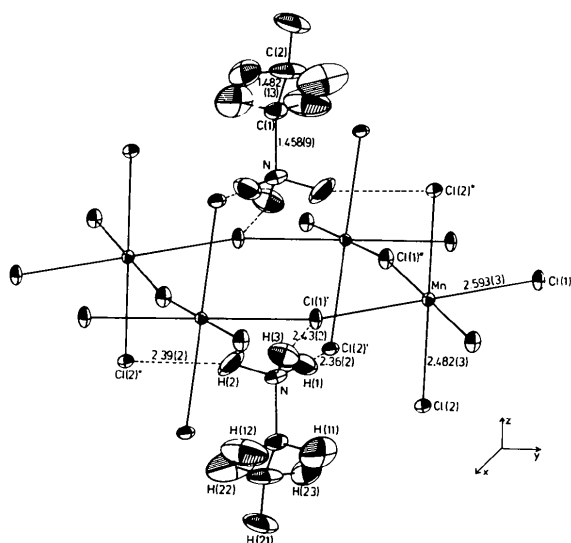


Fig. 1. *ORTEP* plot (20% probability) of β -($\text{C}_2\text{H}_5\text{NH}_3$) $_2\text{MnCl}_4$ around $z = 0.5$. On each side of the octahedra layer only one of two symmetry-related ethylammonium groups is shown.

Table 1. Final positional parameters ($\times 10^4$)

The second-row values are the X-ray data of Depmeier (1976) (e.s.d.'s in parentheses).

	x	y	z
Mn	0	0	0
Cl(1)	7500	7500	5102 (1)
Cl(2)	397 (4)	-243 (25)	1112 (1)
N	4828 (6)	12 (38)	1016 (2)
H(1)	4840 (20)	0	1008 (5)
H(2)	3573 (25)	-328 (197)	980 (7)
H(3)	4854 (52)	1519 (28)	943 (11)
C(1)	5517 (30)	-564 (35)	711 (7)
H(11)	5564 (10)	-400 (8)	1614 (3)
H(12)	5560 (40)	-470 (50)	1620 (10)
C(2)	5509 (75)	-1768 (39)	1664 (13)
H(21)	6920	0	1617 (8)
H(22)	4515 (22)	465 (19)	2111 (4)
H(23)	4560 (15)	610 (50)	2100 (10)
H(31)	5122 (37)	287 (102)	2535 (7)
H(32)	4250	1728 (36)	2082 (14)
H(33)	3455 (40)	-440	2119 (12)

Table 1 lists the positional parameters; the second row of values of the non-hydrogen atoms are the X-ray results (Depmeier, 1976). The neutron and X-ray results are nearly identical; only the y coordinates of Cl(2) and C(2) differ appreciably. For Cl(2) this is because it was located on the mirror plane at $y = 0$ in the X-ray work.

From the values of Table 1 the bond lengths and angles of Table 2 have been calculated. Again the second row of values are the X-ray results. There is one striking difference between the X-ray and neutron work: $\text{Mn}-\text{Cl}(2)$ is 2.466 (3) in the former and 2.482 (3) Å in the latter. Again this is because of the different location of Cl(2) in the two studies. On comparing these values with related compounds (Table 4 of Depmeier, 1977) the neutron result seems more reliable. The differences in the $\text{N}-\text{C}(1)$ and $\text{C}(1)-\text{C}(2)$ distances should be attributed to the dynamical disorder and do not have physical meaning.

The major aim of this work was to elucidate the hydrogen-bonding scheme and the corresponding distances and angles. These are listed in Table 3. In this table the second column contains the X-ray results for γ -($\text{C}_2\text{H}_5\text{NH}_3$) $_2\text{MnCl}_4$ (Depmeier, 1977). This table

Table 2. Bond lengths (Å) and angles ($^\circ$), with e.s.d.'s in parentheses

$\text{Mn}-\text{Cl}(1)$	2.593 (3)	$\text{C}(2)-\text{C}(1)-\text{N}$	113 (1)
$\text{Mn}-\text{Cl}(2)$	2.591 (1)	$\text{H}(3)-\text{N}-\text{H}(1)$	110 (5)
$\text{N}-\text{C}(1)$	2.466 (1)	$\text{H}(2)-\text{N}-\text{H}(1)$	105 (9)
$\text{C}(1)-\text{C}(2)$	1.458 (9)	$\text{H}(2)-\text{N}-\text{H}(3)$	109 (3)
	1.49 (3)	$\text{C}(1)-\text{N}-\text{H}(1)$	112 (3)
	1.482 (13)	$\text{C}(1)-\text{N}-\text{H}(2)$	109 (2)
	1.52 (4)	$\text{C}(1)-\text{N}-\text{H}(3)$	111 (2)
$\text{N}-\text{H}(1)$	0.96 (4)	$\text{H}(11)-\text{C}(1)-\text{H}(12)$	108 (3)
$\text{N}-\text{H}(2)$	1.11 (3)	$\text{H}(11)-\text{C}(1)-\text{N}$	107 (2)
$\text{N}-\text{H}(3)$	0.94 (2)	$\text{H}(11)-\text{C}(1)-\text{C}(2)$	109 (2)
$\text{C}(1)-\text{H}(11)$	1.00 (3)	$\text{H}(12)-\text{C}(1)-\text{N}$	108 (1)
$\text{C}(1)-\text{H}(12)$	1.04 (1)	$\text{H}(12)-\text{C}(1)-\text{C}(2)$	112 (1)
$\text{C}(2)-\text{H}(21)$	1.05 (2)	$\text{H}(21)-\text{C}(2)-\text{H}(22)$	106 (4)
$\text{C}(2)-\text{H}(22)$	0.94 (3)	$\text{H}(21)-\text{C}(2)-\text{H}(23)$	103 (4)
$\text{C}(2)-\text{H}(23)$	1.02 (3)	$\text{H}(22)-\text{C}(2)-\text{H}(23)$	118 (2)
$\text{Cl}(1)'\text{-Mn}-\text{Cl}(1)''$	91.2 (1)	$\text{C}(1)-\text{C}(2)-\text{H}(21)$	113 (3)
$\text{Cl}(1)'\text{-Mn}-\text{Cl}(1)'''$	88.8 (1)	$\text{C}(1)-\text{C}(2)-\text{H}(22)$	118 (2)
$\text{Cl}(1)'\text{-Mn}-\text{Cl}(2)''$	87.0 (1)	$\text{C}(1)-\text{C}(2)-\text{H}(23)$	98 (2)
$\text{Cl}(1)''\text{-Mn}-\text{Cl}(2)'''$	92.7 (1)		

Table 3. Distances (Å) and angles ($^\circ$) defining the hydrogen-bonding systems of β - and γ -($\text{C}_2\text{H}_5\text{NH}_3$) $_2\text{-MnCl}_4$

	β	γ
$\text{H}(1)\cdots\text{Cl}(2)'$	2.36 (4)	2.35 (6)
$\text{N}\cdots\text{Cl}(2)'$	3.271 (6)	3.25 (1)
$\text{H}(2)\cdots\text{Cl}(2)''$	2.39 (4)	2.48 (6)
$\text{N}\cdots\text{Cl}(2)''$	3.455 (6)	3.35 (1)
$\text{H}(3)\cdots\text{Cl}(1)'$	2.43 (4)	2.30 (6)
$\text{N}\cdots\text{Cl}(1)'$	3.357 (6)	3.26 (1)
$\text{N}-\text{H}(1)\cdots\text{Cl}(2)'$	160 (10)	157 (4)
$\text{N}-\text{H}(2)\cdots\text{Cl}(2)''$	162 (10)	156 (4)
$\text{N}-\text{H}(3)\cdots\text{Cl}(1)'$	162 (10)	158 (4)

clearly shows the differences between the two phases regarding the h.b. distances and angles. In contrast to the γ phase the ethylammonium group is disordered in β C2Mn and so is the h.b. scheme. It is the superposition of two orientations. In both of them two h.b.'s run to axial Cl atoms, one to a bridging Cl. This scheme may be designated *aab*, replacing the term 'monoclinic' (Chapuis, Kind & Arend, 1976); correspondingly the term 'orthorhombic h.b. scheme' may be replaced by *abb*; the reason for this new designation is the fact that a 'monoclinic' orientation of the h.b. scheme does not correspond to the symmetry of the structure in cases where n of the general formula is not equal to 1.

The octahedra layer is puckered and this may be described by specifying the tilt system as $a^-a^-c^0$ (Glazer, 1972; Depmeier, 1977). The tilt angle about the pseudotetragonal a axes is 5° . The four Cl(1) atoms surrounding the central Mn do not form a regular square but a rectangle with $\text{Cl}(1)-\text{Cl}(1)'' = 3.630$ (3.591 Å) and $\text{Cl}(1)'\text{-Cl}(1)'' = 3.705$ (3.706 Å). The values in brackets refer to the γ phase and these values clearly show that the $\gamma \rightarrow \beta$ phase transition mainly affects b [$a_\beta - a_\gamma = 0.03$, $b_\beta - b_\gamma = 0.109$ Å, cf. also Fig. 6 of Depmeier, Felsche & Wildermuth (1977)]. This effect should be attributed to the stronger N—H(3)···Cl(1) h.b. in the γ phase.* The main

* This correlation between h.b. strength and lattice constants seems to be a valuable tool to explain phase transitions in compounds $(\text{C}_n\text{H}_{2n+1}\text{NH}_2)_2\text{MnCl}_4$ with $n > 3$ where single crystals are not available at the moment.

differences between the γ and the β phases have been discussed (Depmeier, 1977).

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2:3 Complex of Rubidium and 7,7,8,8-Tetracyanoquinodimethane

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Abstract. $\text{Rb}_2(\text{C}_{12}\text{H}_4\text{N}_4)_3$, monoclinic, $a = 7.297$ (1), $b = 10.392$ (1), $c = 21.444$ (2) Å, $\beta = 97.45$ (1)°, $Z = 2$, $U = 1612.3$ Å³, $F(000) = 772$, $\mu(\text{Mo}) = 32.6$ cm⁻¹; systematic absences: $h0l$ absent for l odd, $0k0$ for k odd; space group $P2_1/c$. The final R_w is 0.063 for 2750 observed reflexions. Inspection of Weissenberg photographs showed the compound to be isomorphous with Cs_2TCNQ_3 .

Introduction. As part of a series of crystal structure determinations of TCNQ complexes to study the phase transitions common to most of these salts, the crystal structures of two modifications of RbTCNQ were determined in our laboratory (Hoekstra, Spoelder & Vos, 1972; van Bodegom, de Boer & Vos, 1977). The structure determination of a third modification was carried out by Shirota & Kobayashi (1973). Recently