The Crystal Structure of γ-Bis(ethylammonium) Tetrachloromanganate(II) at 126 K and its γ → β Phase Transition

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γ-Bis(ethylammonium) tetrachloromanganate(II), stable below 225 K, is orthorhombic, space group *Pbca*, with $a = 7.325$ (8), $b = 7.151$ (11), $c = 22.035$ (19) Å, $Z = 4$. Refinement for 1329 reflexions with $I > 1.96\sigma(I)$ measured at 126 K converged to $R = 0.040$ and $R_w = 0.047$. The perovskite-like layer of corner-sharing $MnCl_6$ octahedra shows an a^-a^-c tilt system; the ethylammonium group takes one of the two orientations of the β form. The hydrogen bonding involves two axial Cl(2) atoms and one equatorial Cl(1) atom as acceptors. The phase transition is accomplished by a change of the tilt system ($a^-a^-c \rightarrow a^-a^-c^0$) and by orientation switching of the ethylammonium group.

Introduction

The title compound (C2MNLT) is one of a group of compounds, with the general formula $(C_nH_{2n+1}NH_3)_2MCl_4$ (M = Mn, Cd, Fe), which belong to the K_2NiF_4 structure type. An important feature of their structure is the existence of perovskite-like layers of corner-sharing MCl_6 octahedra. For charge balance $(C_nH_{2n+1}NH_3)^+$ ions are attached to each side of these layers by N–H···Cl hydrogen bonds, the alkyl groups pointing away from the layer. Thus neutral strata are formed which have only van der Waals contacts (*e.g.* Depmeier, 1976).

These compounds are subject to a number of phase transitions, which may be due to changes in the tilt system of the octahedra layers and/or to reorientations of the alkylammonium groups, the reason for the latter being changes of the N–H···Cl hydrogen-bonding system.

To elucidate the mechanisms of the phase transitions much recent work has been done (de Jongh & Miedema, 1974; Depmeier, Felsche & Wildermuth, 1977). Up to now mainly the methyl compounds and their phase transitions have been studied in detail (Chapuis, Arend & Kind, 1975; Chapuis, Kind & Arend, 1976; Seliger, Blinc, Kind & Arend, 1976; Heger, Mullen & Knorr, 1975, 1976). We started our investigations on the ethyl and propyl compounds with M = Mn in order to show the influence of the alkyl chain length on the phase transition. This is the first single-crystal work on a phase transition of a $(C_nH_{2n+1}NH_3)_2MnCl_4$ compound with $n > 1$. An X-ray analysis has been reported for β-$(C_2H_5NH_3)_2MnCl_4$ (Depmeier, 1976);* neutron single-crystal measure-

* Fig. 2 of Depmeier (1976) has to be modified: the angles 91° and 89° should be interchanged; the angle 89·8° should be 90·2°; and the hydrogen bonds are not correct. See this paper for discussion.

ments of γ- and β-$(C_2H_5NH_3)_2MnCl_4$ are still under evaluation (Depmeier & Heger, 1977). Differential scanning calorimetric (DSC) results for phase transitions of compounds $(C_nH_{2n+1}NH_3)_2MnCl_4$ with $n = 1–17$ have also been reported (Bocanegra, Tello, Arriandiaga & Arend, 1975; Vacatello & Corradini, 1973, 1974; Depmeier, Felsche & Wildermuth, 1977).

Experimental

Suitable crystals were grown by evaporation of a solution of $C_2H_5NH_3Cl$ and $MnCl_2$ (Merck) in a mixture of water and ethanol. From preliminary photographs (Huber low-temperature device 153) approximate cell dimensions were obtained. Only a few reflexions with $h + l$ odd (210, 610, 430), which are forbidden for *Abma* [β-$(C_2H_5NH_3)_2MnCl_4$], indicated a change in the space-group symmetry and thus a phase transition. As, on the whole, only weak reflexions disobeyed the *Abma* extinction rules it was not until the end of the data collection that the space group could be determined definitely as *Pbca*, which was also confirmed by the successful refinement.

A crystal $0.5 \times 0.4 \times 0.2$ mm was sealed in a Lindemann capillary to protect it from moisture. A Syntex $P2_1$ diffractometer with a LT-1 cooling device was used to determine accurate cell dimensions and to

Table 1. *Crystal data*

γ-$(C_2H_5NH_3)_2MnCl_4$	
$a = 7.325$ (8) Å	$M_r = 288.86$
$b = 7.151$ (11)	$\lambda(\text{Mo }K\alpha) = 0.7107$ Å
$c = 22.035$ (19)	$\mu = 19.11$ cm^{-1}
$V = 1154$ Å^3	$D_x = 1.66$ g cm^{-3}
$F(000) = 588$	(for $Z = 4$)
	$D_o = 1.67$ (295 K)

collect the data with Mo $K\alpha$ radiation from a graphite monochromator. The temperature was held at 126 K and a reference reflexion (117) was measured after every 50 reflexions and showed no significant change. The ω–2θ scan method was used up to $\sin \theta/\lambda = 0.704$ Å^{-1}. This gave 1990 unique reflexions of which 1334 had $I > 1.96\sigma(I)$ and were regarded as observed. The unobserved reflexions were ignored. No absorption correction was applied. Table 1 gives crystal data.

Structure determination and refinement

Systematic extinctions $0kl$: $k = 2n + 1$, $h0l$: $l = 2n + 1$, $hk0$: $h = 2n + 1$ led to space group *Pbca*. The distribution of normalized structure factors was clearly centric. The room-temperature coordinates of Mn, Cl, N and C were used as a starting point. After refinement of these coordinates the H atoms could be seen on a difference map. The structure was refined by full-matrix least squares minimizing $\Sigma w(F_o - F_c)^2$ with aniso-tropic temperature factors for Mn, Cl, N and C and isotropic for H atoms attached to N atoms. H atoms attached to C atoms were constrained to geometrically ideal positions and had an invariant isotropic tem-perature factor equivalent to that of the attached C atom. Complex scattering factors for C, H, N, Mn^{2+} and Cl$^-$ were employed (*International Tables for X-ray Crystallography*, 1974) and weights were $w = 3.01/[\sigma^2(F) + 0.005F^2]$. The final R_w $(= \Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_o|)$ was 0.047 and $R = 0.040$ for 1329 reflexions and 64 parameters. Five reflexions were omitted, three of which were suspected to be affected by extinction. In the last cycle no shift/e.s.d. >0.01 occurred and a final difference map showed no remarkable peak or hole. For all calculations the *SHELX* system (Sheldrick, 1976) was used. The final

parameters are given in Table 2 and the bond angles not contained in Fig. 1 are given in Table 3.*

Table 3. *Bond angles* (°) *not included in Fig.* 1

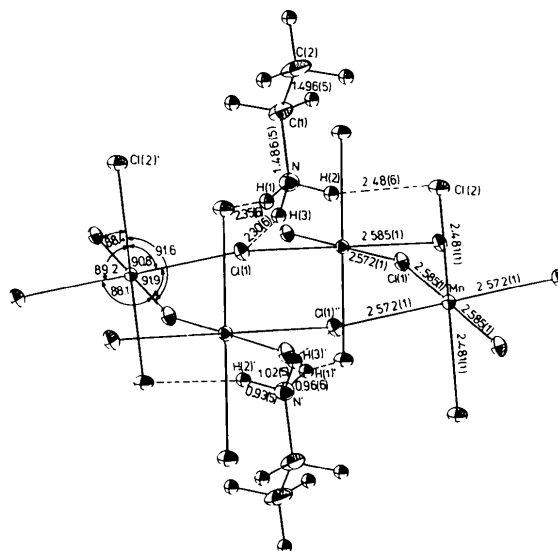| C(2)–C(1)–N | 111.3 (3) | H(1)–N–H(2) | 103 (4) |
C(1)–N–H(1)	119 (3)	H(1)–N–H(3)	100 (4)
C(1)–N–H(2)	113 (3)	H(2)–N–H(3)	101 (4)
C(1)–N–H(3)	119 (3)		

Fig. 1. A view of the structure around $z = 0.5$ showing the atom designation, important bond lengths (Å) and angles (°). The e.s.d.'s of the Cl–Mn–Cl angles are less than 0.1°.

Table 2. *Final positional and thermal parameters with estimated standard deviations in parentheses*

H atoms attached to C were fixed at geometrically ideal positions. Anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \cdots + 2U_{12}a^*b^*hk)]$, and isotropic of the form $\exp(-8\pi^2 U \sin^2 \theta/\lambda^2)$; U_{ij} and U are in Å^2. All parameters are multiplied by 10^4.

	x	y	z	U_{11} (or U)	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn	0 (0)	0 (0)	0 (0)	92 (3)	84 (3)	97 (3)	3 (2)	−4 (2)	−2 (2)
Cl(1)	7311 (1)	7314 (1)	5113 (0)	120 (3)	108 (3)	155 (4)	−2 (2)	−11 (2)	27 (2)
Cl(2)	413 (1)	−134 (1)	1117 (0)	156 (4)	201 (4)	97 (4)	−1 (2)	−2 (2)	1 (3)
N	4835 (4)	198 (4)	1036 (1)	154 (13)	190 (12)	138 (12)	−5 (10)	19 (9)	4 (10)
H(1)	3575 (85)	−43 (56)	945 (23)	311 (135)					
H(2)	4953 (59)	1464 (68)	949 (21)	250 (116)					
H(3)	5430 (73)	−371 (68)	662 (23)	310 (130)					
C(1)	5562 (5)	−299 (5)	1645 (2)	218 (16)	293 (16)	160 (14)	−3 (13)	−19 (12)	88 (14)
H(4)	5507	−1799	1700	128					
H(5)	6961	166	1678	128					
C(2)	4473 (6)	601 (6)	2139 (2)	346 (20)	427 (21)	134 (15)	−15 (15)	2 (14)	116 (18)
H(6)	5034	213	2574	170					
H(7)	3072	138	2111	170					
H(8)	4526	2102	2088	170					

Structure description

The structure may be described in terms of three items: (a) the octahedra layer, (b) the ethylammonium group, (c) the hydrogen bonding. The most important distances and angles may be taken from Fig. 1, which is an *ORTEP* plot (Johnson, 1965) of part of the structure around $z = 0.5$.

The perovskite-like layer is formed by $MnCl_6$ octahedra, each of which is connected to four others by bridging $Cl(1)$ atoms. Thus, each $Cl(1)$ belongs to two octahedra. The two $Cl(2)$ atoms remain free and belong to only one octahedron. This layer is far from possessing its highest possible symmetry. In fact, the symmetry is lowered by distortions of the single octahedra and by tilting of the layer as a whole. There is a marked compression of $Mn-Cl(2)$ [2·481 (1) Å] compared with $Mn-Cl(1)$ [2·585 (1) and 2·572 (1) Å]. This compression has been observed for all other comparable Mn compounds (Table 4). $Mn-Cl(2)$ is not perpendicular to the plane of the bridging $Cl(1)$ atoms. The $Mn-Cl(1)-Mn$ bridges are neither symmetrical nor linear. Each bridge involves two different distances (2·585 and 2·572 Å); the angle $Mn-Cl(1)-Mn$ is 166°. This non-linearity is due to a puckering of the octahedra layer, which may be described in a way similar to that of Glazer (1972) for perovskites, *i.e.* for corner-sharing octahedra, which are linked three-dimensionally. In this notation tilts are broken into their components with respect to the cubic axes of the aristotype (Megaw, 1973). Thus, *a* means a certain tilt angle in the *x* direction, *b* a certain tilt angle in the *y* direction. If some tilt angles are equal they are denoted by identical letters.

Superscripts + and − distinguish between *in phase* and *in antiphase* tilting of successive octahedra in a given direction. A superscript zero means a tilt angle of

0°. Applied to our two-dimensional case of corner-sharing octahedra the symbol corresponding to the direction perpendicular to the layer needs no + or − superscript, but a zero should be used when the tilt angle is 0°. Fig. 2 shows that $Cl(1)$ atoms which lie on zigzag lines parallel to *y* have identical *z* coordinates (0·0113 or 0·9887). In fact, they are related by the *b* glide. This means that there are identical tilt angles for the octahedra with respect to the pseudotetragonal axes x_p and y_p. In addition, the octahedra are tilted about the *z* direction. This tilt angle of 8·8° (171·2°) is marked by a double arc in Fig. 2. The tilt angle for the other directions may be calculated to be 5·55°, if the
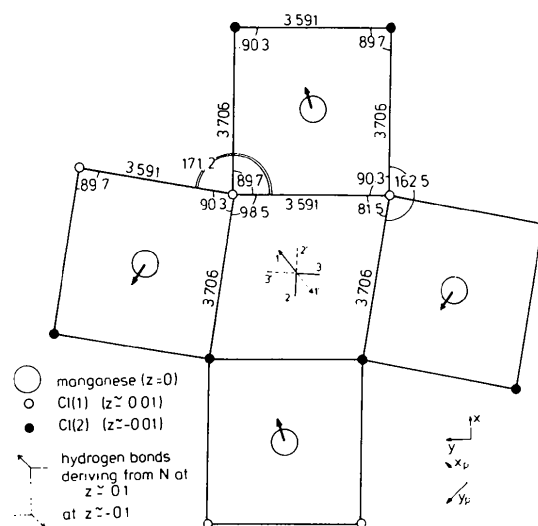

Fig. 2. Coordination of the Mn atoms at $z = 0.0$ showing distances (Å) and angles (°) between corner-sharing $Cl(1)$ atoms only. E.s.d.'s are 0·001 Å for distances and 0·1° for angles. The double arc denotes the complementary angle to the *c* tilt angle of 8·8°. Bold arrows indicate $Cl(2)$ at $z \sim 0.1$.

Table 4. $Mn-Cl$ *bond lengths* (Å) *for some* K_2NiF_4-*type structures* (*chlorine derivatives*)

C2 denotes $(C_2H_5NH_3)_2MnCl_4$ (analogously C1 and C3).

	Radiation used (X = X-ray, N = neutron)	$Mn-Cl(1)$ (bridging Cl)	$Mn-Cl(2)$ (terminal Cl)	Temperature (K)
β-C2[a]	X	2·591 (0)	2·466 (3)	295
β-C2[b]	N	2·593 (0)	2·482 (3)	295
γ-C2[c]	X	2·585 (1) 2·572 (1)	2·481 (1)	126
δ-C3[d]	X	2·629 (5)	2·475 (10)	295
δ-C3[e]	N	2·600 (0)	2·485 (2)	180
$|NH_3(CH_2)_3NH_3|MnCl_4^f$	N	2·584 (3)	2·491 (3)	295
α-C1[g]	N	2·56 (1)	2·50 (2)	404
β-C1[g]	N	2·57 (2)	2·51 (3)	293
γ-C1[h]	N	2·556 (3) 2·578 (3)	2·499 (3)	188

(a) Depmeier (1976). (b) Depmeier & Heger (1977). (c) This work. (d) Peterson & Willett (1972). (e) Depmeier & Mason (1977). (f) Willett & Riedel (1975). (g) Heger, Mullen & Knorr (1975). (h) Heger, Mullen & Knorr (1976).

parallelograms of Cl(1) atoms are assumed to be squares. Thus, the tilt system for C2MNLT may be described as a^-a^-c.

The ethylammonium group is situated in a relatively large hole and this may be the reason for its large thermal vibration despite the low temperature used. The high thermal parameters may also be responsible for the unexpected short C(1)—C(2) distance of 1·496 (5) Å. The C—N distance of 1·486 Å is comparable with that in other related compounds.

The hydrogen bonding involves two strong bonds, N—H(1)···Cl(2) [2·35 Å, ∠N—H···Cl = 157 (4)°, N···Cl = 3·25 Å] and N—H(3)···Cl(1) [2·30 Å, 158 (4)°, N···Cl = 3·26 Å], while the third, N—H(2)···Cl(2) [2·48 Å, 156 (4)°, N···Cl = 3·35 Å], is less strong. The N···Cl(1)″ distance of 3·34 Å is shorter than the N···Cl(2) distance of the N—H(2)···Cl(2) hydrogen bond (henceforth h.b.) although it is not involved in a h.b. from above the layer (Fig. 1). This example shows that it can be dangerous to assume a h.b. from donor–acceptor distances only. The ethyl group takes the favourable staggered conformation with respect to the hydrogen bonding. There is no disorder in C2MNLT.

Discussion of the structure and the γ → β phase transition

Discussion of the differences between the structures of C2MNLT and β-(C₂H₅NH₃)₂MnCl₄ (C2MNRT) may help to explain the mechanism of the γ → β phase transition. The results for C2MNRT originate from

Depmeier (1976) and Depmeier & Heger (1977), the latter being neutron results. The most important differences are (see also Table 4 and Figs. 2 and 3):

— The C₂H₅NH₃ group is ordered for C2MNLT, but disordered for C2MNRT.

— In as far as X-ray results can be compared with neutron results, the following is valid: For C2MNLT the N—H(3)···Cl(1) h.b. is much shorter, N—H(1)···Cl(2) is almost equal and N—H(2)···Cl(2) becomes longer than for C2MNRT.

— The tilting system of the octahedron layer in C2MNLT is a^-a^-c in contrast to C2MNRT, where it is $a^-a^-c^0$.

— The geometry of the Cl(1) environment of Mn in C2MNLT is a parallelogram instead of a rectangle. This means two Mn—Cl(1) bond lengths for C2MNLT, but one for C2MNRT.

— The angle Mn—Cl(1)—Mn is smaller for C2MNLT (166·0°) than for C2MNRT (171·6°).

These differences may be explained by the special features of the two phases. For C2MNLT and C2MNRT the —NH₃ residue is situated in a box of eight Cl atoms which are all possible acceptors for N—H···Cl h.b.'s. In each case the box is distorted, thus favouring some Cl atoms as h.b. acceptors and discriminating against others. Distortion of the box forces the formation of a special h.b. system; conversely, a certain h.b. system forces a special distortion. Both effects appear to operate. Chapuis, Kind & Arend (1976) developed a notation to describe the various h.b. systems for this type of compound. Two cases had to be distinguished: (I) Two h.b.'s run to bridging Cl(1), and one to an axial Cl(2) atom. (II) One h.b. runs to a bridging Cl(1), and two to axial Cl(2) atoms. Because of the symmetry of the corresponding compounds, the former was called 'orthorhombic' and the latter 'monoclinic'. From our results there is some evidence that, in contrast to the results for (CH₃NH₃)₂MCl₄ (M = Cd, Mn), an 'orthorhombic' configuration is impossible (or at least unfavourable) for (CₙH₂ₙ₊₁NH₃)₂MCl₄ with n > 1. This becomes evident from Fig. 4, which shows schematically MCl₆ octahedra with an —NH₃ residue taking the 'orthorhombic' configuration. Two ethyl-group orientations, (I) and (II), are distinguished. (I) is the average (non-split) position of C(1) and C(2) for

β-(C₂H₅NH₃)₂MnCl₄   γ-(C₂H₅NH₃)₂MnCl₄

ᵇ   Mn at z=0·0 with Cl(2) above the layer
○   Cl(1) at z=0·01
●   Cl(1) at z=−0·01
↖   Cl(1) shift
↘   hydrogen bond to Cl(1)
⊣   hydrogen bonds to Cl(2)
↱   NH₃ group above the layer
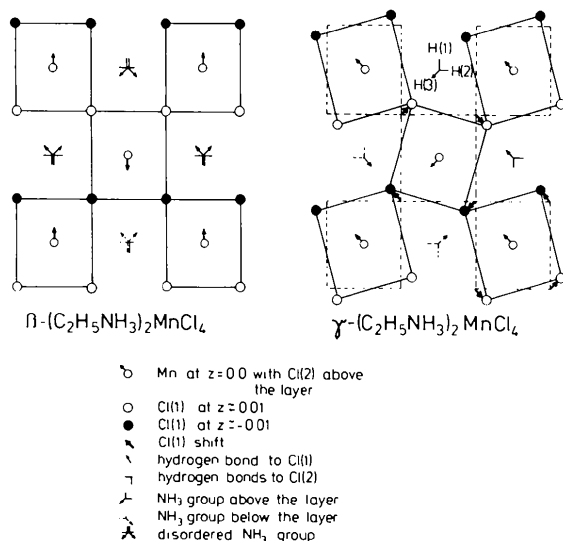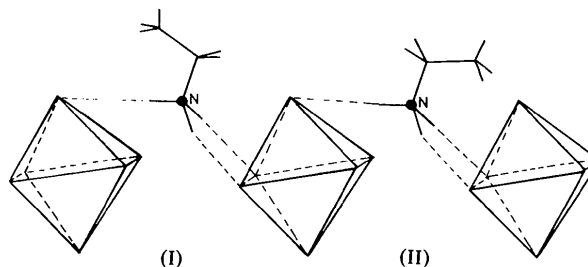↴   NH₃ group below the layer
⅄   disordered NH₃ group

Fig. 3. Schematic drawing of the essential difference between C2MNLT and C2MNRT. For clarity the differences due to the interaction of the hydrogen bonding and the octahedra layer are exaggerated.

(I)   (II)

Fig. 4. The incompatibility of an alkylammonium group (n > 1) for

C2MNRT (Depmeier, 1976) and $(C_3H_7NH_3)_2MnCl_4$ (Peterson & Willett, 1972). In this position the alkyl-ammonium groups are assumed to be on a mirror plane. Both (I) and (II) are unfavourable, because for (I) the H atoms at C(1) and N are not staggered, as would be expected for an unrestricted alkylammonium group, whereas in (II) the cation is staggered [but this orientation is sterically hindered by the interaction of the H atoms attached to C(2) and the axial Cl(2)]. As a consequence one may assume that any staggered $C_nH_{2n+1}NH_3$ group with $n > 1$ should take an orientation such as that in Fig. 1, i.e. a 'monoclinic' $-NH_3$ group orientation with the H(3), N and C atoms on a non-crystallographic mirror plane. This ordered orientation has been found for the title compound. It has been found disordered as a superposition of two such orientations for C2MNRT (Depmeier & Heger, 1977), δ-$(C_3H_7NH_3)_2MnCl_4$ (Depmeier & Mason, 1977) and $(NH_3CH_2CH_2NH_3)MCl_4$ ($M = Mn$, Fe) (Willett & Riedel, 1975), which are all neutron diffraction results.

Fig. 3 shows schematically the structural features of C2MNRT and C2MNLT. C2MNRT possesses disordered $C_2H_5NH_3$ groups. There are short $H(1)\cdots Cl(2)$ h.b.'s which attract alternately the vertices of b-glide-related $MnCl_6$ octahedra. This attraction causes a puckering of the planes of the bridging Cl(1) atoms and the puckering can be described as $a^-a^-c^0$. The puckering is supported by the disordered $H(3)\cdots Cl(1)$ h.b.'s which elevate the affected Cl(1) atoms and, furthermore, cause a distortion of the Cl(1) squares to give a rectangle. The $H(2)\cdots Cl(2)$ h.b.'s do not cause any puckering, because, since they are disordered and thus operate in opposite directions, they cancel.

In C2MNLT only one 'monoclinic' configuration of the $C_2H_5NH_3$ group is retained and this one-sided arrangement accounts for some of the geometric properties of this phase.

The $H(1)\cdots Cl(2)$ h.b. retains its strength and direction and thus the a^-a^- component of the puckering is retained. The $H(3)\cdots Cl(1)$ h.b., however, is much stronger and directed towards one Cl(1). Each Cl(1) atom which is elevated by the a^-a^- component of puckering is attracted by one $H(3)\cdots Cl(1)$ h.b. and so this puckering is supported. In addition, however, each symmetry-related $H(3)\cdots Cl(1)$ h.b. pointing to one particular octahedron causes an attraction on the corresponding Cl(1) atom and, as a consequence, the octahedron is rotated as a whole. Alternating octahedra are rotated conversely. This rotation can be described as a c tilt and the whole tilting system may thus be described as a^-a^-c. By the one-sided attraction the rectangles are slightly distorted to give parallelograms, thus accounting for two different Mn–Cl(1) bonds. Moreover, the additional c tilt causes the Mn–Cl(1)–Mn angle to decrease. The weak $H(2)\cdots Cl(2)$ h.b.'s, which are distorted in C2MNRT and thus have no influence upon the puckering, are now polar and pull all Cl(2) atoms of one octahedron layer in one direction. Cl(2) atoms of successive layers are pulled in opposite directions. This bond causes an additional distortion of the octahedra, as may be seen by the Cl(1)–Mn–Cl(2) angles (Fig. 1), and supplies only a small contribution to the puckering scheme.

Fig. 5, a heat capacity versus temperature curve from a DSC run (DSC 2, Perkin Elmer), shows that the transition has a preliminary region where the heat capacity rises, followed by the transition itself. After the transition the heat capacity is lower than before. We interpret this curve as follows: With increasing temperature, approaching the transition temperature of 225 K, more and more octahedra and ethylammonium groups take a 'wrong' orientation. When 'right' and 'wrong' orientations have equal probability the transition occurs. After the transition no additional disorder can occur and so the heat capacity is lower than before the transition. Thus, the $\gamma \to \beta$ phase transition can be regarded as being of the orientation-switching type.

From the group-theoretical point of view the space group of C2MNLT is a maximal klassengleiche subgroup of the space group of C2MNRT ($Abma = Cmca$) (Neubüser & Wondratschek, 1966).

Fig. 5. A heat capacity versus temperature curve for the $\gamma \to \beta$ phase transition of $(C_2H_5NH_3)_2MnCl_4$.

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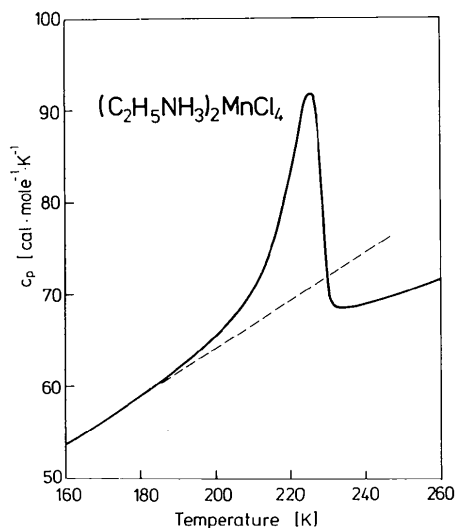CHAPUIS, G., KIND, R. & AREND, H. (1976). *Phys. Stat. Sol. (a),* **36**, 285–295.

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The Crystal and Molecular Structure of 1,3,4,6-Tetra-O-acetyl-2,5-O-methylene-D-mannitol: The Solid State Conformation of a 1,3-Dioxepane Ring

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$C_{15}H_{22}O_{10}$, monoclinic, $a = 10\cdot000$, $b = 12\cdot526$, $c = 8\cdot193$ Å, $\gamma = 113\cdot79°$. Space group $P2_1$, 1338 independent reflexions, $R = 0\cdot06$. The structure was solved with the tangent formula. The seven-membered ring is in the twist-chair conformation with the two O atoms in positions that relieve the main transannular interactions.

Introduction

There is little experimental information available about the conformations of unsubstituted seven-membered rings since pseudorotation is extremely facile. Strain-minimization calculations (Bocian, Picket, Rounds & Strauss, 1975) have predicted two pseudorotation families, the boat and chair, separated by an inversion barrier of $\sim$34 kJ mol^{-1}. Each family has two extreme conformations; one is twisted (*e.g.* a twist-chair) with C_2 symmetry, the other is not twisted and has C_s
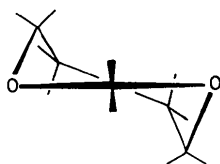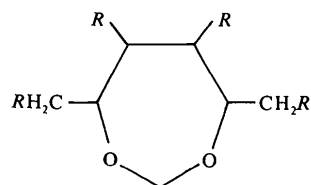
symmetry. The calculations indicate that while the boat and twist-boat conformations have almost equal energy, the twist-chair is $\sim$2 kJ mol^{-1} more stable than the chair, and $\sim$4 kJ mol^{-1} more stable than the boat conformation.

The conformations of a number of substituted 1,3-dioxepane rings have been investigated in solution by ^{1}H NMR (Grindley & Szarek, 1974) where it was concluded that the principal conformation is a twist-chair with the C_2 axis through the acetal C atom (Fig. 1). Presented here is the crystal structure of a closely related compound, 1,3,4,6-tetra-O-acetyl-2,5-O-methylene-D-mannitol (I).

Fig. 1. Idealized C_5O_2 ring in the twist-chair conformation, showing C_2 symmetry.

(I) $R = CH_3COO$