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The Crystal Structure of Bis(*n*-butylammonium) Tetrachloromanganate(II), (*n*-C$_4$H$_9$NH$_3$)$_2$MnCl$_4$, at 294 K

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Abstract

Bis(*n*-butylammonium) tetrachloromanganate(II), 2C$_4$H$_{12}$N$^+$.MnCl$_4^{2-}$, [NH$_3$C$_4$H$_9$]$_2$[MnCl$_4$], crystallizes in a perovskite-type layer structure with $a = 7\cdot3356$ (6), $b = 7\cdot2512$ (8), $c = 31\cdot880$ (6) Å, space group *Abma*, $Z = 4$. Its structure has been refined to $R = 0\cdot049$ ($R_w = 0\cdot041$) with 516 independent reflexions. The N—H⋯Cl hydrogen-bonding system and the butylammonium groups are disordered as in the room-temperature phases of the ethyl and propyl homologues. The butylammonium chain, however, has a different conformation: N—C(1)—C(2)—C(3) are all-*trans*, but the terminal C(4) is *gauche*.

Introduction

In recent years, much work has been done on the structures, phase transitions, lattice dynamics and two-dimensional magnetism of the K$_2$NiF$_4$-type compounds (C$_n$H$_{2n+1}$NH$_3$)$_2$*M*Cl$_4$ with *M* = Mn, Cd, Fe, Cu, Pd (see, *e.g.*, Arend, Huber, Mischgofsky & Richter-van Leeuwen, 1978, and literature cited therein). All these compounds undergo structural phase transitions, up to as many as five in (C$_3$H$_7$NH$_3$)$_2$MnCl$_4$. This particular compound shows commensurate and incommensurate superstructures at various temperatures (Depmeier, Felsche & Wildermuth, 1977). In a recent work (Depmeier, 1979, hereafter D79) it has been reported that the propyl compound in the series (C$_n$H$_{2n+1}$NH$_3$)$_2$MnCl$_4$ with *n* = 1–10 exhibits some unique properties, *e.g.* it has the largest distortion of the MnCl$_6$ octahedra and the highest transition temperature to a fully disordered state. A possible reason for these characteristics was given on the basis of packing modes of the different alkyl chains. In the initial stages of D79 it was known from single-crystal structure determinations (Peterson & Willett, 1972; Depmeier, 1976; Depmeier & Mason, 1978; Depmeier & Heger, 1978) that the ethyl and propyl compounds have some important structural features in common; in particular, both compounds have the same hydrogen-

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bonding system. For the other members of the series with n up to 9, however, only powder data were available. Consequently, it was desirable to show at least for one higher homologue of the propyl compound that it also has the same basic structural features. This report describes the structure of the room-temperature phase of (n-$C_4H_9NH_3)_2MnCl_4$ (C4Mn).

The preparation of this type of compound has been described (Arend, Huber, Mischgofsky & Richter-van Leeuwen, 1978).

In the course of a re-examination of the batches used for the powder work of D79, small crystals of C4Mn were found, which were platelet-shaped and frequently twinned. Owing to their sensitivity to touch and to moisture, they were sealed in thin-walled capillaries. Preliminary Weissenberg and precession photographs revealed that the space group *Abma* and lattice constants were in agreement with the values obtained from the powder photographs.

A crystal $0.20 \times 0.18 \times 0.21$ mm (crystal volume 0.2480×10^{-2} mm^3) was used on a Syntex $P2_1$ auto-diffractometer with Cu $K\alpha$ radiation. Lattice constants were obtained by least-squares refinements from 16 high-angle reflexions lying in the range $80 \le 2\theta \le 90°$. The values are listed in Table 1 with other crystal data. Intensities were collected at 294 K by the θ–2θ scan technique up to $2\theta = 110°$ with scan speed 2–10° min^{-1}. Three periodically checked standards showed no significant change of intensities. The reflexions from the quadrants $(+h,+k,+l)$ and $(+h,+k,-l)$ were averaged and gave 589 unique reflexions, 454 of which had $I > 3\sigma(I)$. Backgrounds were obtained according to the Lehmann–Larsen algorithm (Schwarzenbach, 1977). The data were corrected for absorption [μ(Cu $K\alpha$) = 12.25 mm^{-1}] by the Gaussian integration method. Absorption factors ranged from 2.624 to 4.105.

The structure was solved by using the Mn and Cl positions of δ-$(C_3H_7NH_3)_2MnCl_4$ (Depmeier & Mason, 1978). Subsequent difference maps and refinement cycles revealed the positions of atoms N to C(3) on the mirror plane. After further isotropic refinement the terminal C(4) could be found in a general position near the mirror plane as a relatively flat peak in the difference map. This map already showed disorder of the butylammonium chain. The structure was refined by a full-matrix least-squares procedure minimizing $\sum w(|F_o| - |F_c|)^2$ with anisotropic temperature factors for all atoms. Complex scattering factors were used for

C^0, N^0, Cl^- and Mn^{2+} (*International Tables for X-ray Crystallography*, 1974). No H atoms could be located unambiguously in the final difference map and they were not included in the structure factor calculation. Regions of positive electron density around the N atom, however, indicated the expected disordered hydrogen-bonding system. As in the ethyl and propyl homologues (Depmeier, 1976) the butylammonium group was refined by splitting these atoms in two mirror-related positions with an occupancy factor of 0.5. The final R_w = $\sum w^{1/2}\Delta/w^{1/2}|F_o|$ was 0.041 and R was 0.049 for 516 reflexions with $F > 3\sigma(F)$ and 61 parameters. Reflexion 002 was considered to be affected by extinction and omitted from the calculation. Weights were $w = 1/\sigma^2(F)$ with $\sigma(F)$ derived from counting statistics. Table 2 lists the final positional and population parameters and Table 3 the bond distances and angles.*

Discussion

Fig. 1 shows an *ORTEP* plot (Johnson, 1965) of C4Mn around $z = 0.5$. The corner-sharing MnCl$_6$ octahedra belong to one perovskite-like layer of charge $(-2)_n$ which is sandwiched between layers of butyl-ammonium cations. These are fixed to the layers of octahedra by N–H$\cdots$Cl hydrogen bonds shown as dotted lines in Fig. 1. The hydrogen-bonding system is

Table 2. *Final positional parameters* $(\times 10^4)$ *with e.s.d.'s in parentheses, and population parameters*

	x	y	z	Population parameter
Mn	0	0	0	1.0
Cl(1)	7500	2500	68 (1)	1.0
Cl(2)	376 (2)	0	769 (1)	1.0
N	−164 (9)	254 (37)	4299 (2)	0.5
C(1)	556 (16)	429 (26)	3888 (4)	0.5
C(2)	−365 (31)	−563 (32)	3534 (6)	0.5
C(3)	494 (43)	−275 (61)	3122 (6)	0.5
C(4)	−520 (69)	1123 (70)	2874 (20)	0.5

Table 1. *Crystal data*

$(C_4H_9NH_3)_2MnCl_4$	$M_r = 344.92$
$a = 7.3356$ (6) Å	*Abma*
$b = 7.2512$ (8)	$Z = 4$
$c = 31.880$ (6)	λ(Cu $K\alpha$) = 1.54178 Å
$V = 1695.8$ Å^3	μ(Cu $K\alpha$) = 12.25 mm^{-1}
$F(000) = 716$	$D_c = 1.35$ Mg m^{-3}

Table 3. *Bond lengths* (Å) *and angles* (°) *including possible hydrogen bonds*

Mn–Cl(1)	2.588 (0)	N–Cl(1)	3.25
Mn–Cl(2)	2.468 (2)	N–Cl(2)	3.28
N–C(1)	1.418 (16)		
C(1)–C(2)	1.499 (27)	N–C(1)–C(2)	119.0 (1.5)
C(2)–C(3)	1.474 (33)	C(1)–C(2)–C(3)	114.3 (2.2)
C(3)–C(4)	1.485 (64)	C(2)–C(3)–C(4)	111.0 (3.7)

disordered and consists of two mirror-related systems. The mirror plane in Fig. 1 is perpendicular to b and passes through Cl(2)', Mn', Mn" and Cl(2)". In one position Cl(1), Cl(2)" and Cl(2)''' are involved in hydrogen bonds, whereas in the other the mirror-related Cl atoms are involved. This means that Cl(2)" is involved in both hydrogen-bonding systems. The mirror plane affects not only the hydrogen bonds, but also the butylammonium groups. For clarity only one mirror-related butylammonium group (of site occupancy factor 0·5) on each side of the layer of octahedra is shown.

Each butylammonium layer has a net charge of $(-1)_n$. Thus neutral layers are formed which stack on top of each other. The influence of the packing of these layers on the properties of the corresponding compound has been discussed in D79.

Fig. 1 shows also that the octahedra are far from ideal. The bonds from the central Mn atom to the bridging Cl(1) and to the terminal Cl(2) atoms are different in length: 2·588 (0) for Mn–Cl(1) and 2·468 (2) Å for Mn–Cl(2). These values are in good agreement with those found in similar compounds [(cf. Table 4 of Depmeier, 1977); note that the Mn–Cl(1) value for C4Mn is much closer to that of the ethyl compound than to that of the propyl compound – this difference is also discussed in D79].

By means of the hydrogen bonding the layer of octahedra is puckered and the symmetry of an octahedron itself is further reduced to orthorhombic (left side of
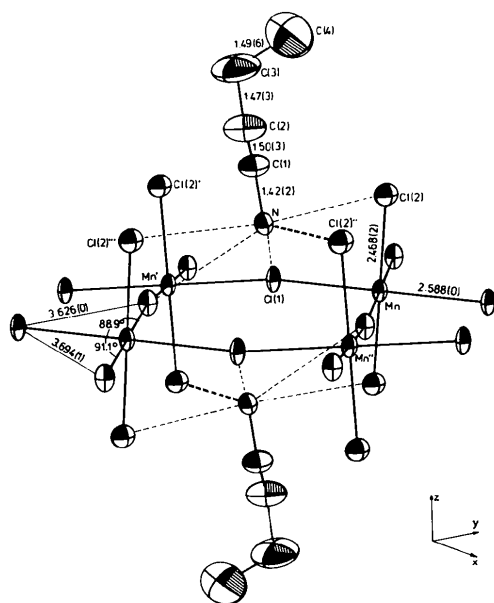
Fig. 1). The value for the octahedron distortion angle $(91·1°) - \Omega$ in D79 – is shown in the figure. For clarity the angle $(166·5°)$ which describes the washboard-like puckering of the layer of octahedra – ψ in D79 – is not shown. Both values agree well with those of the room-temperature phase of $(C_2H_5NH_3)_2MnCl_4$, but less well with those of the propyl compound (cf. Table 2 of D79).

The most striking feature of the butylammonium group is that the terminal methyl group C(4) is *gauche*. Fig. 2 (ORTEP; Johnson, 1965) illustrates the conformation of this group. The dihedral angle C(1)–C(2)–C(3)–C(4) is 100 (8)°. This value, however, is affected by the relatively high degree of thermal disorder in the butyl residue and, therefore, is not exact. The other dihedral angle, N–C(1)–C(2)–C(3), is 180°, indicating the *trans* conformation of this part of the chain. The high degree of thermal disorder is also responsible for the apparently shortened N–C and C–C single bonds. The neighbourhood of terminal methyl groups was seen to play an important role as mentioned in D79. It was claimed that some of the special properties of the propyl compound result from efficient packing, which is less satisfactory in C4Mn. Fig. 3 shows the packing of the terminal methyl groups together with the adjacent C(3) methylene groups of two neighbouring layers. The methyl groups are at $z = 0·71$ and 0·79, respectively. As already mentioned, the butylammonium groups as a whole are disordered. The disorder is evident in Fig. 3 which shows mirror planes perpendicular to y and passing almost through the C(3) methylene groups. For a chosen methyl group on one side of the mirror plane (labelled I) some calculated distances to neighbouring groups are given. With a van der Waals radius of 2·0 Å for a methyl group, distances smaller than about 4·0 Å

Fig. 1. ORTEP plot (Johnson, 1965) showing a part of a layer of octahedra with butylammonium ions attached by N–H···Cl hydrogen bonds (dotted lines). On each side only one butyl-ammonium group is shown. The other is produced by the mirror plane passing through Cl(2)', Mn', Mn" and Cl(2)". Some important distances and angles are given.
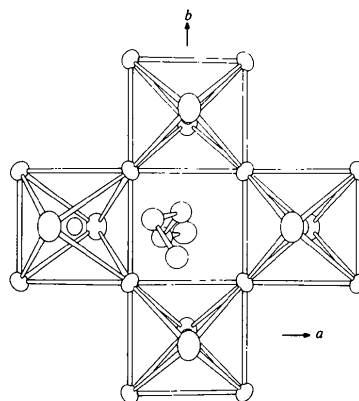

Fig. 2. Projection of the structure of C4Mn along c emphasizing the conformation of the butylammonium group. Only one disordered n-butylammonium chain is shown. The Mn and Cl atoms were drawn with 50% probability thermal ellipsoids by ORTEP (Johnson, 1965) whereas the N and C atoms were drawn to an arbitrary scale.
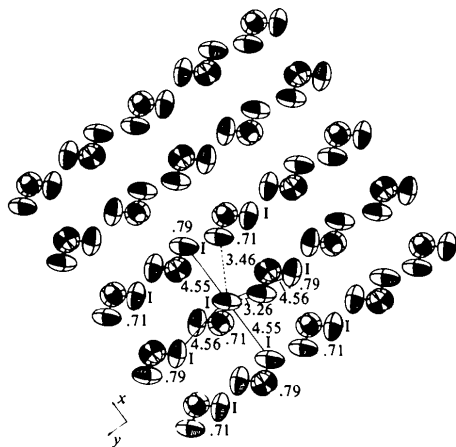
Fig. 3. The packing of the layers.

are impossible (dotted lines in Fig. 3). It is convincing from Fig. 3 that there is strong correlation, be it dynamic or static, between the positions of the terminal methyl groups in the y as well as in the x direction. Each methyl group has four neighbours belonging to the adjacent layer at distances of approximately 4·5 Å. Thus, the packing is rather loose. With the arguments given in D79 this kind of neighbourhood results in a stability less than in $(C_2H_5NH_3)_2MnCl_4$ or $(C_3H_7NH_3)_2MnCl_4$.

DTA measurements have shown that C4Mn undergoes some structural phase transitions at lower temperatures. It should be of interest to see whether the all-*trans* conformation is reached at some lower temperature. This work is in progress.

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The Crystal Structure of a Dickite:*N*-Methylformamide Intercalate [Al₂Si₂O₅(OH)₄. HCONHCH₃]

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Abstract

The structure of the intercalate has been solved with film-scanned data. The final R is 9·4%. The organic molecules are regularly ordered, the threefold hydrogen bonds from the clay OH groups to the amide O atom found in the formamide intercalate being retained. The remaining part of the *N*-methylformamide molecule rotates with respect to the OH groups since there is no hydrogen bonding from the N atom to these OH groups. There are no hydrogen bonds from the amide to the SiO₄ tetrahedra of the neighbouring layer.

The organic molecules themselves are non-planar (at the N atom). The stacking of the octahedral (AlO₆) part of the clay layers upon the SiO₄ tetrahedra is different from that previously found for dickite itself and the dickite:formamide intercalate.

Introduction

Recently there has been considerable interest in intercalates, *i.e.* materials in which molecules are inserted between the sheets of a basically unchanged host material. These guest species are often small organic