A Study of the Crystal Structure of $(CH_3NH_3)_2MnCl_4$ by Neutron Diffraction at 188 ± 1 K

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The structure has been determined from three-dimensional neutron diffraction data collected at 188 K. There are four formulae in a unit cell of dimensions $a = b = 7.23$, $c = 19.32$ Å. Despite the tetragonal axial symmetry, there are significant deviations towards orthorhombic symmetry in some intensities. The present structure is based on orthorhombic symmetry with space group *Pccn*, and has been refined by several cycles of full-matrix least squares to a final *R* of 4.8%. The structure shows two features: pseudosymmetry and short hydrogen bonds. These features are discussed in relation to the twinning. Explanations of the twinning are suggested. The transformation is considered to result from ordered arrangements (order–disorder) of H atoms and slight displacements (displacive) of the other atoms from the closest-packing positions. The structure is held together by an extensive system of hydrogen bonds. This phase transition is compared with that of the tetragonal form of $(CH_3NH_3)_2CdCl_4$.

Introduction

The present study is an extension of studies made in this Institute on $(CH_3NH_3)_2MnCl_4$. The importance of knowing details of the phase transition at 188 K is shown by the increasing interest in two features: (1) the tetragonal–orthorhombic–monoclinic phase-transition series and (2) a comparison of the cation arrangements (especially the H atoms) in the high- and low-temperature phases. The structure at 188 K has been studied by Heger, Mullen & Knorr (1976). They have reported that the structure appears to be tetragonal in space group $P4_22_12/ncm$. However, the existence of the tetragonal phase at this low temperature has been questioned, particularly by Petzelt (1975). Moreover, reflexion criteria in the orthorhombic space group *Pccn* are the same as in the tetragonal space group $P4_22_12/ncm$. The possibility of an orthorhombic pseudotetragonal crystal must therefore be considered. The present analysis indicates that the structure at 188 K is orthorhombic (pseudotetragonal) in space group *Pccn*. The higher apparent symmetry arises because of disorder or from a type of twinning which gives a similar diffraction pattern. These possibilities are considered below.

Experimental

Unit cell and space group

$(CH_3NH_3)_2MnCl_4$ at 188 K is orthorhombic (pseudotetragonal). The unit-cell dimensions are $a = b = 7.23$, $c = 19.32$ Å. There are four formula units per cell, giving a calculated density (D_x) of 1.68 g cm^{-3}.

The crystal was cooled by a stream of N_2 gas (Knorr, Jahn & Heger, 1974).

In spite of this tetragonal axial symmetry, the distribution of the intensities is distinctly orthorhombic. In order to emphasize the orthorhombic symmetry, it was concluded that the crystal was twinned. Support for this conclusion comes from the irregularities of the intensities of the reflexions of type *hk*0: 110, 130 absent; 350 weak; 220, 440 very strong; and 240 strong. The relation between the twin pairs can be described either as a reflexion across (110) or as a rotation about the normal to this plane, so that the *a* and *b* axes of one twin component coincide with the *b* and *a* axes, respectively, of the other. Because of the equality of the *a* and *b* axes, no splitting is observed and the *hkl* reflexions of one component overlap with the *khl* reflexions of the other. This means that the weak reflexions transform to the difference structure and the strong reflexions transform to the average structure.

Extinctions show that reflexions occur as follows: *hkl*: no conditions; *hk*0: $h + k = 2n$; 0*kl*: $l = 2n$. These conditions together with the true diffraction symmetry imply that the space-group symmetry is $P2_12_12/ccn$ (D_{2h}^{10}). The refinement was successfully carried out in *Pccn* and this is considered to be the true space group for this low-temperature transformation.

Intensity data

The neutron intensity data were measured on a P32 neutron diffractometer at the FR2 reactor in Karlsruhe. The neutron wavelength was 1.0327 Å. The crystals used were irregular platelets on (001). The same intensity data (measured by G. Heger) have been used in this work. The intensity data were collected up

to $\sin \theta/\lambda = 0.48$ Å^{-1}. 183 independent reflexions were measured.

Structure determination and refinement

The structure was determined from a three-dimensional Patterson synthesis, which could easily be interpreted on the basis of the space group $Pccn$. From the peaks surrounding the origin, the vectors arising from the Mn and Cl atoms could be identified.

A three-dimensional Fourier synthesis, with all reflexions, gave the coordinates of the N and C atoms and improved the coordinates for the Cl atoms. Three cycles with isotropic temperature factors reduced R to 18.9%. At this stage a three-dimensional $F_o - F_c$ map was calculated to obtain information on the positions of the H atoms. The positions of all H atoms attached to C and N were clearly revealed. The inclusion of the H atoms in the structure factor calculations reduced R to 8.9%.

Five cycles of least-squares refinement with anisotropic temperature factors for H atoms only and unit weight reduced R to 5.6%.

For the final cycles of refinement a Cruickshank (1965) weighting scheme $[w = 1/(A + B|F_o| + C|F_o|^2)]$ reduced R to 4.8%. R is defined as $\Sigma ||F_o| - |F_c||/\Sigma |F_o|$.

All computations were performed with the X-RAY 67 system of programs (Stewart, 1967) modified at the university of Tübingen. The scattering lengths for all atoms were taken from Bacon (1962): $b_{Mn} = -0.387$, $b_{Cl} = 0.99$, $b_N = 0.94$, $b_C = 0.665$ and $b_H = -0.374$ (all $\times 10^{-12}$ cm). Final positional and thermal parameters are listed in Table 1.* The projection of the crystal structure along the z axis is shown in Fig. 1.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32315 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
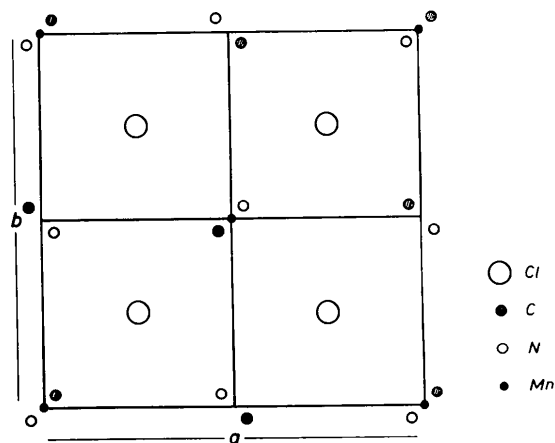

Fig. 1. Projection of the unit cell on (100). H atoms have been omitted.

Results and discussion

It is worth noting that for tetragonal symmetry (Heger, Mullen & Knorr, 1976) both the C and N atoms of the (CH_3NH_3) group would have to occupy the site $8(i)$ (point symmetry m). The observed intensity completely refutes this possibility, since there is no indication that reflexions with $h + k = 2n$ are particularly strong, as required by occupancy of this special position. Therefore it was necessary for both C and N to be placed in eight-fold general sets of the type $8(e)$ $[\pm(x,y,z); \pm\frac{1}{2} + x, y, \frac{1}{2} - z)$ and $\pm(x,\frac{1}{2} + y,\frac{1}{2} - z)]$ in space group $Pccn$.

The transition from $Abma$ to $Pccn$ was obtained by separating the Cl and H atoms. Bond lengths and angles are given in Table 2. The bond distances and angles are all quite normal and need no special comment. The details of the coordination of the C and N atoms are shown in Fig. 2.

The structure is held together by an extensive system of hydrogen bonds. The H atom arrangements, as

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Table 1. *Atomic parameters (all $\times 10^4$, except B)*

Positional parameters are given as fractions of the lattice translations. Anisotropic and isotropic temperature factors correspond to $T = \exp[-(\beta_{11}h^2 + \beta\beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ and $T = \exp(-B\sin^2\theta/\lambda^2)$ respectively. Estimated standard deviations are given in parentheses.

	x	y	z	B		x	y	z	B
Mn	0	0	0	1.022 (7)	Cl(3)	276 (9)	301 (1)	1279 (5)	1.792 (6)
Cl(1)	2500	2500	−175 (6)	0.984 (4)	C	342 (2)	284 (2)	3126 (3)	2.844 (8)
Cl(2)	7500	2500	8 (9)	1.859 (8)	N	−275 (1)	−156 (5)	3846 (12)	1.402 (1)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
H(1)	350 (8)	574 (4)	4185 (1)	139 (2)	415 (1)	−29	166 (3)	3 (5)	−54 (1)
H(2)	−1556 (8)	49 (6)	3922 (4)	82 (14)	224	33 (5)	42 (4)	21 (1)	23 (1)
H(3)	398 (1)	−1489	3904 (2)	471 (4)	172 (1)	33 (3)	439 (4)	38 (9)	58 (3)
H(4)	1510 (1)	−21 (5)	3007 (17)	1676	578 (1)	42 (6)	245 (1)	227 (1)	32 (3)
H(5)	23 (1)	1742 (8)	3049 (26)	379 (5)	204 (6)	43 (21)	−33 (2)	14 (6)	78 (32)
H(6)	−232 (12)	−622 (10)	2776 (9)	354 (14)	1025 (33)	45 (5)	66 (8)	91 (3)	−143 (25)

viewed along [100] and [001], are shown in Figs. 3 and 4.

Data for the hydrogen bonds are summarized in Table 3. The average H $\cdots$ Cl distance of 2·6 Å is 0·4 Å less than the sum of the van der Waals radii (3·0 Å), and this can be taken as evidence for a hydrogen bond. The packing is determined by H $\cdots$ H, C $\cdots$ H and N $\cdots$ H contacts (Table 4). The shortest non-bonding
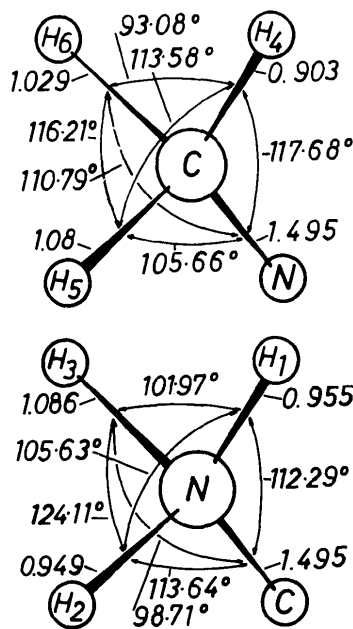

Fig. 2. Angles and interatomic distances (Å) around the C and N atoms.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with standard deviations in parentheses*

Mn–Cl(1)	2·579 (1)	C–H(5)	1·089 (1)
Mn–Cl(2)	2·556	C–H(6)	1·029 (2)
Mn–Cl(3)	2·489 (2)	N–H(1)	0·955 (5)
C–N	1·495 (3)	N–H(2)	0·949 (8)
C–H(4)	0·903 (1)	N–H(3)	1·086 (5)

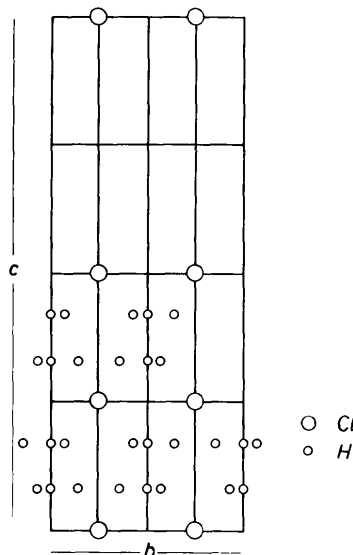|	
Cl(1)–Mn–Cl(2)	90·05 (0)
Cl(1)–Mn–Cl(3)	90·72 (0·3)
Cl(2)–Mn–Cl(3)	90·64 (0·4)
Mn–Cl(1)–Mn	146·91 (0·4)
Mn–Cl(2)–Mn	179·31 (0·5)
H(4)–C–H(5)	113·58 (4·5)
H(4)–C–H(6)	93·08 (4·5)
H(5)–C–H(6)	116·21 (2·1)
H(1)–N–H(2)	105·63 (5·1)
H(1)–N–H(3)	101·97 (5·2)
H(2)–N–H(3)	124·11 (5·5)
N–C–H(21)	117·68 (4·0)
N–C–H(5)	105·66 (1·6)
N–C–H(6)	110·79 (1·9)
C–N–H(1)	112·29 (3·9)
C–N–H(2)	113·64 (3·3)
C–N–H(3)	98·71 (2·9)

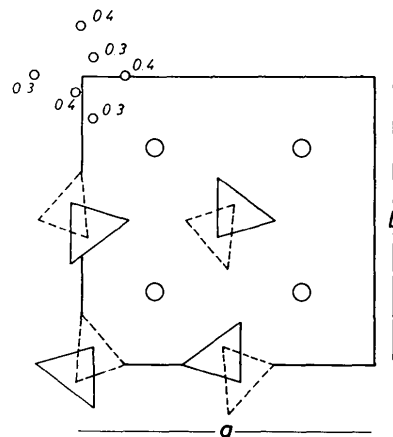

Fig. 3. The array of H atoms viewed along [100].

Fig. 4. H atoms viewed along [001]. The numbers represent the z coordinate for each H atom.

Table 3. H $\cdots$ Cl *distances* (Å) *and angles* (°)

H(1) $\cdots$ Cl(1)^i	2·42 (5)	N–H(1)–Cl(1)^i	165·94 (5)
H(1) $\cdots$ Cl(2)^i	2·95 (5)	N–H(1)–Cl(2)^i	107·43 (5)
H(2) $\cdots$ Cl(2)^i	2·82 (4)	N–H(2)–Cl(2)^i	176·59 (3)
H(2) $\cdots$ Cl(3)^{ii}	2·33 (7)	N–H(2)–Cl(3)^i	155·98 (3)
H(3) $\cdots$ Cl(2)^{iii}	2·69 (3)	N–H(3)–Cl(2)^{ii}	125·07 (2)
H(3) $\cdots$ Cl(3)^{iii}	2·39 (8)	N–H(3)–Cl(3)^{iii}	138·81 (6)
H(4) $\cdots$ Cl(3)^v	3·01 (1)	C–H(4)–Cl(3)^v	108·42 (2)
H(5) $\cdots$ Cl(3)^{iv}	2·89 (1)	C–H(5)–Cl(3)^{iv}	144·72 (1)
H(6) $\cdots$ Cl(3)^{vi}	2·99 (1)	C–H(6)–Cl(3)^{vi}	116·30 (1)

Symmetry code

(i)	$\frac{1}{2} - x, y, \frac{1}{2} + z$	(iv)	$-x, \frac{1}{2} + y, \frac{1}{2} - z$
(ii)	$x - \frac{1}{2}, -y, \frac{1}{2} - z$	(v)	$\frac{1}{2} + x, -y, \frac{1}{2} - z$
(iii)	$-x, y - \frac{1}{2}, \frac{1}{2} - z$	(vi)	x, y, z

H $\cdots$ H distances within the CH_3 and NH_3 groups have a mean value of 1·5 Å. None of intermolecular H $\cdots$ H distances are significantly smaller than the sum of the accepted van der Waals radii (2·4 Å).

The C $\cdots$ H and N $\cdots$ H distances are appreciably shorter than the sum of the van der Waals radii (Pauling, 1960). The short distances are essential features of the structural packing, and this may account for the frequency with which twinning occurs. Evidently minimum energy is attained in the crystal by maximizing the number of bonds at the expense of bond strength.

The interesting feature of this orthorhombic structure is its pseudotetragonal appearance. This character of the diffraction pattern can be qualitatively explained as follows: (1) It was noticed that the major faces of the crystals developed are (110) and (001). The directions of the cell axes are along [001], [110] and [$\bar{1}$10]. It seems quite reasonable to conclude that in these crystals, the crystal habit is influenced very strongly by the pseudocell rather than the true crystallographic cell. (2) The homogeneity of the basal sections (optical examination) and the similarity between 0kl and h0l reflexions indicate an identical molecular arrangement in the

projection along a and b. If the planes of the (CH_3NH_3) molecule are inclined to a or b at $45°$, and as the axes a and b are of the same length, then for both projections the cell will look almost identical. Such an inclination is confirmed by the fact that the reflexion from the (220) plane is the strongest and the reflexion from the (440) plane is quite strong. This arrangement is that obtained at the end of the refinement (Fig. 5). (3) There are unusual interesting features about the distribution of the intensities of the reflexions of the type $hk0$: a slight but remarkable non-uniformity of the $uu0$ reflexions is observed, distinguishing them from the $gg0$ reflexions ($u = $ odd, $g = $ even). Such effects are never observed with untwinned crystals. They confirm the presence of twinning and indicate a slight disorientation of the individuals making up the twins. The study of the structure showed that the orientation of the molecule (CH_3NH_3) is nearly parallel to the plane (110). The H triangles are alternately oriented so as to give a tetragonal appearance when viewed parallel to c. For the twinned structure, the H atoms would contribute to each $gg0$, but only one third of them to each $uu0$, both sets now having tetragonal symmetry. This is not the case when the crystal is untwinned, when all the H atoms would contribute alike to each $gg0$ and $uu0$. As already indicated, the appearance of pseudotetragonal symmetry is a result of the occurrence of twinning. In other words, the orthorhombic, rather than tetragonal, symmetry of this structure is because of the arrangement of the H atoms.

Table 4. *Distances involving H atoms* (Å)

H(1)$\cdots$H(2)	1·51 (9)	H(4)$\cdots$H(5)	1·67 (9)	
H(1)$\cdots$H(3)	1·58 (4)	H(4)$\cdots$H(6)	1·47 (11)	
H(2)$\cdots$H(3)	1·79 (9)	H(5)$\cdots$H(6)	1·79 (0)	
H(1)$\cdots$H(4)	2·465 (7)	C$\cdots$H(1)	2·057 (3)	
H(1)$\cdots$H(5)	2·364 (3)	C$\cdots$H(2)	2·068 (6)	
H(1)$\cdots$H(6)	2·888 (3)	C$\cdots$H(3)	1·977 (13)	
H(2)$\cdots$H(4)	2·836 (12)	N$\cdots$H(4)	2·075 (9)	
H(2)$\cdots$H(5)	2·376 (4)	N$\cdots$H(5)	2·074 (1)	
H(2)$\cdots$H(6)	2·460 (4)	N$\cdots$H(6)	2·095 (1)	
H(3)$\cdots$H(4)	2·186 (7)			
H(3)$\cdots$H(5)	2·874 (3)			
H(3)$\cdots$H(6)	2·313 (3)			

Twinning

The above considerations suggest that twinning of the orthorhombic (pseudotetragonal) crystal by reflexion across (110) might bring about the required tetragonal symmetry of the reflexion. The approximately equal values of the two components suggest that multiple twinning occurs. The important fact to be emphasized is that the twin plane is almost a symmetry plane of the structure. This appears to be an example of 'twinning by pseudomerohedry' (Friedel, 1905), *i.e.* a multiple lattice simulates a symmetry higher than that of the lattice. The orthorhombic twin implies perfectly ordered domains of very small cells, for which the space group $Pccn$ applies. A report on twinning will be presented elsewhere together with the study of the structure at room temperature (Mikhail, 1977).
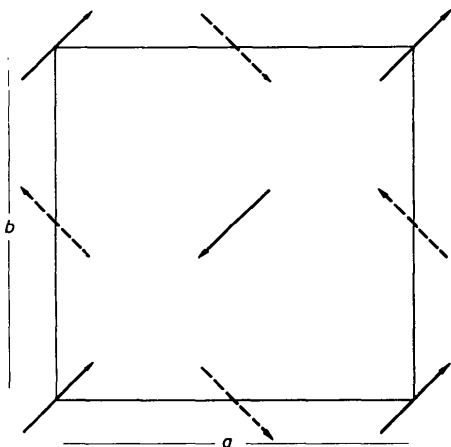

Fig. 5. The arrangement of the organic molecule. The lengths of the arrows represent the lengths of the molecules. Broken lines correspond to a half translation along c.

The relation between the phase transformation and twinning

The phase transformation at 256·9 K is derived from the room-temperature phase by ordering of the H atoms in such a way that $a = b$, while c is common. Whereas the H atoms undergo a disorder–order trans-

formation, the other atoms undergo a displacive transition from one ordered arrangement to another. The discontinuity results from an adjustment of the H atoms to positions which are midway between the positions satisfying the stable configurations of each half of the twin. The function of the twinning is to minimize the overall shape changes that occur in the macroscopic crystal on the transformation from orthorhombic to monoclinic symmetry.

It is interesting to compare the structure of this phase transition with that of $(CH_3NH_3)_2CdCl_4$ (Chapuis, Arend & Kind, 1975). Comparison of the above results with the corresponding table in Chapuis et al. shows certain similarities (however, these are not very great). $(CH_3NH_3)_2CdCl_4$ shows evidence of disorder of some of the H atoms, but $(CH_3NH_3)_2MnCl_4$, as noted above, shows no disorder at all. Thus the tetragonal symmetry of the crystals with Cd could be because of a random distribution, while in the Mn compound it is a result of twinning. An alternative explanation of why $(CH_3NH_3)_2CdCl_4$ shows disorder and $(CH_3NH_3)_2MnCl_4$ does not may be related to the fast rotation of CH_3 groups, as well as to a small but real rotation of NH_3 groups. This condition in the structure of $(CH_3NH_3)_2CdCl_4$ would further reduce the possibility of twinning.

We conclude that either (CH_3NH_3) as a whole or the H atoms alone are important factors in allowing or preventing the introduction of the disordered or twinned state.

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A Study of the Crystal Structure of $(CH_3NH_3)_2MnCl_4$ by Neutron Diffraction at 404 K

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The 404 K phase transition in $(CH_3NH_3)_2MnCl_4$ involves a change from the face-centred orthorhombic room-temperature structure to a tetragonal structure, space group $I4/m$, with $a = b = 5.119, c = 19.48$ Å and $Z = 4$. This high-temperature cell is related to the orthorhombic cell by $a_{tet} = |110|/2$ and $c_{tet} = c_{orth}$. The crystal structure has been determined by neutron diffraction (wavelength 1.0346 Å). Full-matrix least-squares refinement resulted in a final R of 5.6% for 133 reflexions. The $(CH_3NH_3)^+$ cation shows orientational disorder and is arranged in zigzags in order to retain tetragonal symmetry. The crystal is governed by the behaviour of the (CH_3NH_3) group which gives rise to the hydrogen-bond system in the structure. The intramolecular hydrogen bonds may be considered as principally responsible for the twisting of the $MnCl_6$ octahedra. A weak $C-H \cdots Cl$ bifurcated hydrogen bond is present.

Introduction

This work is part of a systematic study of $(C_nH_{2n-1}NH_3)_2MCl_4$, where $M = $ Mn, Fe or Cu. The study of $(CH_3NH_3)_2MnCl_4$ has previously been at-

tempted by Foster & Naida (1968) and Peterson & Willet (1972). On the basis of the indexing of powder photographs, the unit cell was believed to be tetragonal, similar to that of α-Cs_2MnCl_4. The existence of the phase transition has been established by optical obser-