Tetramethylammonium Manganese(II) Tribromide (TMMB) at 235 and 115 K*

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Abstract. $C_4H_{12}NMnBr_3$, hexagonal; at 235 K: $P6_3/m$, $a = 9 \cdot 4142$ (33), $c = 6 \cdot 7768$ (16) Å, $V = 520 \cdot 17$ (26) Å^3, $Z = 2$, $D_x = 2 \cdot 35$ g cm^{-3}, μ(Mo $K\alpha$) $= 125 \cdot 5$ cm^{-1}; at 115 K: $P6_3$, $a = 9 \cdot 3563$ (30), $c = 6 \cdot 7657$ (12) Å, $V = 512 \cdot 95$ (23) Å^3. The phase change at $\sim$143 K is associated with partial ordering of the cations, but it leaves almost unchanged the dimensions of the anion chains (face-linked octahedra).

Introduction. Crystals of the title compound were prepared as in Putnik, Cole & Holt (1976). They are somewhat hygroscopic, but are stable indefinitely in a stream of N_2 in which one was mounted with the LT-1 attachment of a Syntex $P2_1$ diffractometer. Cell constants were determined from the centred positions of 15 reflections (with e.s.d.'s from the least-squares fit) at a range of temperatures from $+5$ to $-158\,^{\circ}$C (Table 1 and Fig. 1). Temperatures were measured with a thermocouple at the crystal position. Data for $+h$, $+k$ and $+l$ were collected at 235 K to $2\theta = 60^{\circ}$ (graphite-monochromatized Mo $K\alpha$ radiation) with $\omega/2\theta$ scans, at rates (2θ) between 1 and $29 \cdot 3^{\circ}$ min^{-1}, depending on the intensity of a 2 s pre-scan. The scan range was $\pm 0 \cdot 65^{\circ}$ in 2θ around the α_1 and α_2 positions. Three standard reflections showed no significant change in intensity during collection. After correction for Lorentz, polarization and absorption effects, 433 reflections were considered observed and used in the

refinement. The systematic absence $00l$, $l \neq 3n$ indicates space groups $P6_3$ or $P6_3/m$; these give site symmetry of either 3 or $\bar{3}$ at Mn. Two similar compounds, the Mn chloride (Morosin & Graeber, 1967) and the Ni bromide (Stucky, d'Agostino &
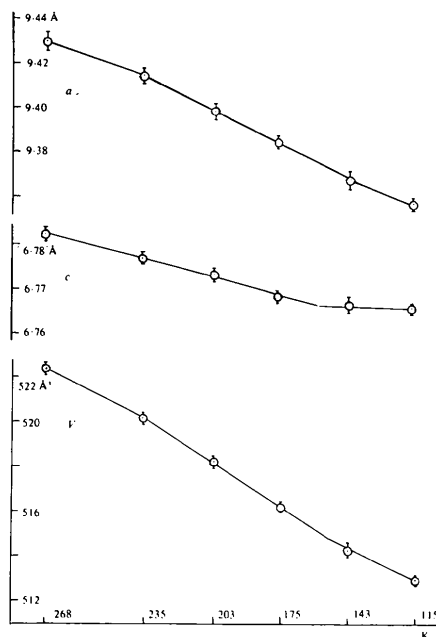

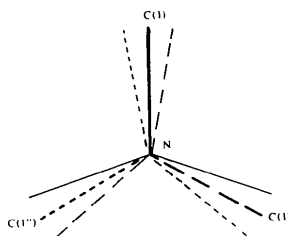Fig. 1. The variation of cell constants with temperature. Error bars cover $\pm 1\sigma$.

Table 1. *Cell constants at various temperatures with e.s.d.'s in parentheses*

T(K)	a(Å)	c(Å)	V(Å^3)
268	9·4299 (45)	6·7821 (17)	522·38 (33)
235	9·4142 (33)	6·7768 (16)	520·17 (26)
203	9·3982 (37)	6·7732 (15)	518·22 (28)
175	9·3845 (27)	6·7684 (13)	516·21 (22)
143	9·3672 (45)	6·7666 (18)	514·33 (34)
115	9·3563 (30)	6·7657 (12)	512·95 (23)

Fig. 2. The disordered $(CH_3)_4N^+$ ion at 235 K, showing the $z = 0 \cdot 25$ level. Each type of line represents the C–N bonds of one pair of orientations, with thick lines showing C atoms at $\frac{1}{3}$ occupancy, thin lines those at $\frac{1}{6}$ occupancy.

McPherson, 1966), reported respectively as $P6_3/m$ and $P6_3$, provided initial coordinates, and showed that the major distinction between 6_3 and $6_3/m$ was likely to be in the cation order or disorder. Initial refinement in $P6_3$ with Br and Mn only, and anisotropic temperature factors, gave $R = 0.090$. This showed no appreciable deviation from centrosymmetry, and so $P6_3/m$ was adopted. On a difference synthesis, the N atom was visible in the expected position $(\frac{1}{3},\frac{2}{3},\frac{1}{4})$ and refinement with it gave $R = 0.069$. Two peaks could be attributed to C atoms, but neither lay on the $(\frac{1}{3},\frac{2}{3},z)$ line, as expected. Instead, one (height 138) lay off the line at $z = 0.08$ (and 0.42) while another (height 268) was level with N at $z = 0.25$. This suggested a complex disorder (Fig. 2) in which each peak at $z = 0.25$ is made up of a central $\frac{1}{3}$ weight C atom, and two edge $\frac{1}{6}$ weight atoms, while the peaks at 0.08 and 0.42 are single, of weight $\frac{1}{3}$. In refinement, one atom was placed on each of the peaks with appropriate occupancy. Final refinement gave $R = 0.052$, with a virtually blank difference map (maximum peak height $40 \simeq \frac{1}{3}$ e Å^{-3}). A weighting scheme was used, with $w = 1.0$, or $(\sin\theta/\lambda)/0.6$ for reflections with $\sin\theta/\lambda < 0.6$.

At 115 K (the lowest accessible temperature with the LT-1), scans through reflections showed no splitting of peaks and no deviation of the cell angles from 90 and 120°. Examination of reciprocal space between reflections showed some scattering, which was very irregular and streaked, and of very low intensity compared to the primary peaks. It was concluded that there was possibly some disorder, but no systematic cell enlarge-

ment. (Unfortunately a full low-temperature photographic study was not feasible.) A full monoclinic data set $(\pm h,+k,+l)$ was collected to $2\theta = 60°$ under identical conditions to those used at 235 K. However, averaging of the sets of three equivalent reflections showed that there were no significant deviations from $6/m$ Laue symmetry, with an index of agreement of 0.038 (including unobserved reflections). This set (432 observed reflections) was therefore used in the refinement. In $P6_3$ it gave $R = 0.049$ on Mn, Br and N (anisotropic temperature factors). In a Fourier synthesis, a peak lay on the $\frac{1}{3},\frac{2}{3},z$ axis both above and below N (heights 133 and 144 at $z = 0.08$ and 0.45). Insertion of an ordered set of atoms (with the axial C atom at 0.45), refinement and confirmation of the hand (as that with slightly lower R) gave $R = 0.026$. This used the same weighting scheme as before. A final difference synthesis was again almost blank, though a peak (height 65) remained at $\frac{1}{3},\frac{2}{3},0.08$. A further indication of problems with the $(\text{CH}_3)_4\text{N}^+$ ion came from the high temperature factor of C(2) (off the $\frac{1}{3},\frac{2}{3},z$ line). Insertion of C atoms at lower occupancy with the opposite arrangement, however, produced no significant improvement. Further, the arrangement of the heavy atoms did not depart appreciably from centrosymmetry. The space group was therefore changed to $P6_3/m$, with a similar (but disordered) orientation of the $(\text{CH}_3)_4\text{N}^+$ ion. Refinement gave $R = 0.028$. The most reasonable deduction is that the structure is indeed noncentrosymmetric, although the deviation from centrosymmetry of the heavy atoms is small. It is

Table 2. *Atomic coordinates* $(\times 10^4)$ *and temperature factors* $(\times 10^3)$, *with e.s.d.'s in parentheses*

Anisotropic temperature factors are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* \dots)]$.

(a) 235 K

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	0	0	5000	35.1	35.1	21.0 (11)	17.5 (4)	0.0	0.0
Br	1542 (1)	2577 (1)	7500	42.4 (6)	31.3 (5)	33.3 (5)	12.5 (4)	0.0	0.0
N(1)	3333	6667	2500	39	39	31 (7)	20 (2)	0	0
C(1)	1575 (32)	6229 (42)	2500	34 (12)	82 (20)	218 (50)	29 (13)	0	0
C(2)	2441 (66)	6303 (52)	560 (100)	153 (50)	45 (20)	177 (49)	−3 (25)	−104 (42)	20 (28)

(b) 115 K, space group $P6_3/m$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	0	0	5000	26.61	26.61	18.06 (8)	13.31 (3)	0.00	0.00
Br	1592.06 (10)	2583.57 (10)	7500	31.3 (5)	22.99 (4)	24.63 (3)	9.42 (3)	0.00	0.00
N(1)	6667	3333	−2500	25.0	25.0	20.5 (4)	12.5 (2)	0.0	0.0
C(1)	1680 (3)	6290 (3)	2106 (10)	162 (2)	213 (2)	763 (9)	76 (2)	−273 (4)	8 (5)
C(2)	3333	6667	4636 (6)	330	330	124 (3)	165 (2)	0	0

(c) 115 K, space group $P6_3$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	0	0	5000	26.4	26.4	17.9 (6)	13.2 (2)	0.0	0.0
Br	1592.3 (7)	2583.4 (7)	7516.0 (131)	31.1 (3)	23.2 (3)	24.6 (2)	9.4 (2)	2.4 (14)	3.9 (15)
N(1)	3333	6667	2431 (56)	24	24	19 (5)	12 (1)	0	0
C(1)	1664 (21)	6305 (20)	2166 (62)	68 (9)	74 (8)	344 (47)	34 (7)	−122 (19)	3 (17)
C(2)	3333	6667	4669 (50)	238	238	49 (14)	119 (19)	0	0

	x	y	z	$U(\text{Å}^2)$
C(22)	3333	6667	193 (162)	63

Table 3. *Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

	115K ($P6_3$)	115K ($P6_3/m$)	235K ($P6_3/m$)
Mn—Br	2·712 (6)	2·7046 (5)	2·7097 (13)
	2·697 (6)		
Br—Mn—Br	84·8 (2)	85·12 (2)	85·04 (5)
	94·9 (2)	94·88 (2)	94·96 (5)
	85·4 (2)		180·0
	179·6 (2)	180·0	
Mn—Br—Mn	77·30 (3)	77·30 (3)	77·40 (4)
N—C(1)	1·51 (5)	1·429 (3)	1·49 (5)
N—C(2)	1·43 (3)	1·443 (4)	1·50 (6)
C(1)—N—C(2)	97 (2)	100·7 (3)	108 (2)
C(1)—N—C(2)	118 (2)		(120)

also probable that the low-temperature crystals are subject to considerable disorder, and contain a significant proportion of crystallites reversed in polarity compared to the bulk of the crystal. The results of both refinements are included in the tables. Scattering factors (Mn^{2+}, Br^-, C and N) were from *International Tables for X-ray Crystallography* (1974) (with anomalous dispersion for Mn and Br), all in the analytical form. Computing was with the XRAY 76 system (Stewart, 1976) on a Burroughs B6700 computer. Table 2 contains final atomic coordinates, Table 3 the bond lengths and angles.*

Discussion. The title compound is structurally similar to a number of compounds of formula ABX_3 whose significance lies in the cooperative magnetic interactions between metal atoms in chains of face-linked octahedra (Ackerman, Cole & Holt, 1974; Putnik & Holt, 1977). This has major effects on the magnetic properties, and on the optical spectrum in the visible region.

Examination of TMMB showed that the line width of its EPR signal (in the 55° orientation) undergoes a discontinuous decrease from 138 to 114 G in a 5° temperature range about 143 K (Putnik, Garrett & Holt, 1978). In addition, a splitting appears in the electronic absorption bands below 143 K which becomes quite distinct by 80 K. For $^6A(S) \rightarrow ^4T_1(P)$, this splitting is in excess of 500 cm^{-1} (Putnik, Cole & Holt, 1976). This phenomenon is not observed in either the electronic absorption spectrum (Day & Dubicki, 1973) or the EPR spectrum of TMMC (Putnik, Garrett & Holt, 1978). The present study was undertaken to obtain information on the corresponding phase change.

The plots of cell constants with temperature (Fig. 1) show breaks corresponding to the phase change, though their magnitude is small compared to those in TMMC, which undergoes both a cell expansion and a

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* Lists of structure factors at 235 and 115 K have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33407 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
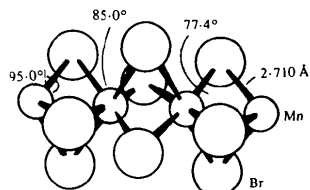

Fig. 3. Dimensions in the anionic chain.

change of symmetry (Peercy & Morosin, 1971). The difference presumably arises because the Br^- ions allow more space for the cations. This small change is confirmed in the structural results. The major effect is the ordering of the cation. At 235 K it is highly disordered and must approximate closely to a sphere. By 115 K it has taken up an ordered position on the threefold axis, and it appears that the $MnBr_6$ octahedra have very slightly distorted mirror symmetry.

As for most of the corresponding compounds, the chain is slightly elongated, with Br—Mn—Br angles of 84–85° between adjoining octahedra (Fig. 3). This value hardly changes from 235 to 115 K and is very similar to that in the corresponding chloride (Morosin & Graeber, 1967) and the Ni bromide (Stucky et al., 1966). One would not expect the ordering of the cation to affect the magnetic and electronic properties of Mn^{2+} ions, and indeed it does not in TMMC. It is remarkable, however, that the very slight distortion in the $MnBr_6$ octahedra generates such large effects in the optical and EPR spectra. There is perhaps some factor of the microenvironment of the Mn^{2+} which is not detectable by the X-ray technique which accounts for the observed phenomena. We are attempting to shed further light on this problem through Raman and broad-line NMR experiments.

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