depend on the metal—equatorial ligand distances. This is in agreement with the concept of the equatorial—axial interactions of the ligands (Gažo, Boča, Jóna, Kabešová, Macašková, Šima, Pelikán & Valach, 1982).

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Acta Cryst. (1991). C**47**, 1208–1210

Structure of Tetramethylammonium Tribromocadmate in the Ferroelectric Phase

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(*Received* 1 *November* 1990; *accepted* 19 *December* 1990)

Abstract. $[N(CH_3)_4][CdBr_3]$, $M_r = 426{\cdot}2$, hexagonal, $P6_1$, $a = 9{\cdot}257\,(4)$, $c = 20{\cdot}900\,(5)$ Å, $V = 1551\,(1)$ Å^3, $Z = 6$, $D_x = 2{\cdot}738$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 135{\cdot}27$ cm^{-1}, $F(000) = 1176$, $T = 133$ K, final $R = 0{\cdot}041$ for 1610 independent reflections. The cell dimension is tripled along the c axis in comparison with the structure in the room-temperature phase. $N(CH_3)_4$ groups are ordered. H-atom positions were not determined.

Introduction. $N(CH_3)_4MX_3$-type compounds (M = Mn, Ni, Cd, ...; X = Cl, Br, I) have been widely studied as quasi-one-dimensional magnetic systems. $N(CH_3)_4CdBr_3$ is the only compound which has been known to exhibit ferroelectric activity; spontaneous polarization along the c axis is observed below 156 K (Gesi, 1990). The crystal structure at room temperature (space group $P6_3/m$; $Z = 2$) consists of infinite linear chains formed by face-shared $CdBr_6$ octahedra and of orientationally disordered $N(CH_3)_4$ groups (Asahi, Hasebe & Gesi, 1990). Most $N(CH_3)_4MX_3$-type compounds have such a structure at room temperature (Morosin & Graeber, 1967; Morosin, 1972). The ferroelectric phase is expected to be an ordered phase as suggested by several authors (Daoud, 1976; Venu, Sastry & Ramakrishna, 1987). The present paper reports the structure in the ferroelectric phase at 133 K.

Experimental. Single crystals were grown by the evaporation method from aqueous solution. D_m not measured. Spherical specimen with radius 0·10 mm, Rigaku AFC-5 diffractometer, graphite-monochromated Mo $K\alpha$ radiation; scan mode θ–2θ, scan speed 10° min^{-1} in θ, scan width $(1{\cdot}5 + 0{\cdot}5\tan\theta)^\circ$; cell dimensions from 24 reflections, $7{\cdot}7 < \theta < 8{\cdot}9^\circ$; Lorentz and polarization corrections; absorption corrections, min. and max. transmission coefficients 0·154 and 0·197; $\sin\theta/\lambda < 0{\cdot}904$ Å^{-1} ($0 \le h \le 16$, $0 \le k \le 16$, $0 \le l \le 37$ and $-16 \le h \le 0$, $-16 \le k \le 0$, $0 \le l \le 37$); four standard reflections ($\bar{2}16$, 026, 0,0,12, 231) monitored every 150 reflections, no significant variation; 7430 reflections measured, 3293 unique reflections [$R_{\rm int} = 0{\cdot}042$ based on F for 1871 unique reflections with $F > \sigma(F)$], of which 1613 with $F > 3\sigma(F)$ were used in refinement. The positional parameters of Cd, Br and N atoms in the room-temperature phase (Asahi *et al.*, 1990) were used as the starting parameters; C atoms found by Fourier synthesis; atomic scattering factors for Cd^{2+}, Br^-, N and C and dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV); full-matrix least-squares refinement with anisotropic thermal parameters (total of 81 parameters varied). At the final stage of refinement, three reflections (230, 0,0,12 and 203) were removed because of the possibility of extinction effects. $R = 0{\cdot}041$, $wR =$

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Table 1. *Positional parameters and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\sum_i\sum_j B_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cd	0·0023 (2)	0·0221 (1)	0·0	1·14
Br(1)	0·0858 (1)	0·2786 (1)	0·08923 (9)	1·12
Br(2)	−0·2771 (2)	−0·1391 (1)	0·07630 (9)	1·25
Br(3)	0·1600 (2)	−0·0867 (1)	0·08426 (10)	1·17
N	0·6595 (17)	0·3484 (15)	0·0849 (9)	1·26
C(1)	0·6341 (20)	0·2309 (21)	0·0291 (8)	2·77
C(2)	0·8270 (16)	0·5057 (16)	0·0794 (10)	2·52
C(3)	0·5212 (16)	0·3906 (15)	0·0867 (12)	2·63
C(4)	0·6511 (22)	0·2636 (21)	0·1464 (9)	3·05

Table 2. *Bond lengths* (Å) *and angles* (°) *at* 133 K *with e.s.d.'s in parentheses*

Cd—Br(1)	2·807 (2)	Cd^i—Br(1)	2·760 (2)
Cd—Br(2)	2·757 (2)	Cd^i—Br(2)	2·799 (2)
Cd—Br(3)	2·778 (2)	Cd^i—Br(3)	2·791 (3)
N—C(1)	1·53 (3)	N—C(3)	1·51 (3)
N—C(2)	1·51 (2)	N—C(4)	1·49 (3)

Br(1)—Cd—Br(2)	81·99 (5)	Br(3)—Cd—Br(1^{ii})	94·30 (7)
Br(1)—Cd—Br(3)	85·03 (5)	Cd—Br(1)—Cd^i	77·62 (4)
Br(2)—Cd—Br(3)	87·58 (5)	Cd—Br(2)—Cd^i	77·78 (4)
Br(1)—Cd^i—Br(2)	82·08 (5)	Cd—Br(3)—Cd^i	77·58 (6)
Br(1)—Cd^i—Br(3)	85·68 (5)	C(1)—N—C(2)	110 (1)
Br(2)—Cd^i—Br(3)	86·51 (5)	C(1)—N—C(3)	111 (2)
Br(1)—Cd—Br(1^{ii})	96·95 (5)	C(1)—N—C(4)	110 (1)
Br(1)—Cd—Br(2^{ii})	96·19 (7)	C(2)—N—C(3)	110 (1)
Br(2)—Cd—Br(2^{ii})	96·06 (7)	C(2)—N—C(4)	109 (1)
Br(2)—Cd—Br(3^{ii})	95·46 (5)	C(3)—N—C(4)	107 (2)
Br(3)—Cd—Br(3^{ii})	92·42 (7)		

Symmetry code: (i) $x-y, x, z+\frac{1}{6}$; (ii) $y, -x+y, z-\frac{1}{6}$.

0·037, $S = 0·64$, $w = [\sigma^2(F_o)]^{-1}$, $(\Delta/\sigma)_{max} = 0·006$; $(\Delta\rho)_{max} = 1·1$, $(\Delta\rho)_{min} = -1·3$ e Å^{-3}. H atoms could not be found. Computer programs *UNICS*3 (Sakurai & Kobayashi, 1979).

Discussion. Final atomic parameters are given in Table 1.† Bond lengths and angles are listed in Table 2. The crystal structure is shown in Figs. 1 and 2.

According to the Landau theory of second-order phase transition, space group $P6_1$ cannot be induced from $P6_3/m$ by the modulation with wavevector $\mathbf{q} = \mathbf{c}^*/3$. Thus the phase transition is of the first order. In the room-temperature phase, Cd^{2+} is at the origin and three Br^- ions form a regular triangle in the mirror plane at $z = \frac{1}{4}$. In the ferroelectric phase, all atoms take general positions: Cd^{2+} deviates from the c axis and triangles of Br^- ions are deformed. Spontaneous polarization is due to the displacements of ions along the c axis. Since the z parameter of Cd^{2+} is fixed at 0·0 in the analysis, relative displacements of Br^- ions to Cd^{2+} can be estimated by $(z - 1/12)$: the average of $(z - 1/12)$ over three ions is −0·00007 (5). The contribution to the spontaneous polarization is calculated to be about one fourth of the observed value $2·7 \times 10^{-4}$ C m^{-2} (Gesi, 1990) when point charge is assumed for each ion.

$N(CH_3)_4$ groups are ordered in the ferroelectric phase. In the room-temperature phase, $N(CH_3)_4$ groups are associated with site symmetry of $\bar{6}$ ($3/m$) and necessarily disordered. In the structure analysis (Asahi *et al.*, 1990), we adopted a model proposed by Morosin & Graeber (1967): an N—C bond coincides with the threefold rotation axis of the site and the group takes two configurations related to each other by the mirror plane. Another type of model has been proposed theoretically by Jewess (1982): a mirror plane of the $N(CH_3)_4$ group coincides with the mirror plane of the site and the group takes three configurations related to each other by the threefold rotation axis. Configuration of the $N(CH_3)_4$ group in the ferroelectric phase corresponds to one of the

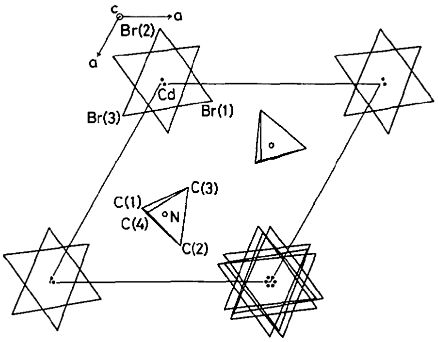

Fig. 1. The **c** projection of the structure of $N(CH_3)_4CdBr_3$ ($0 \le z < \frac{1}{3}$). Only the right-lower corner shows the projection of the region with $0 \le z \le 1$.

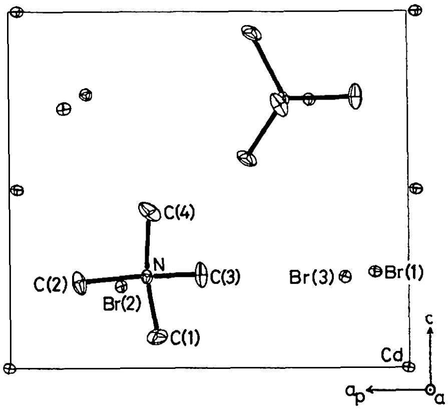

Fig. 2. The **a** projection of the structure of $N(CH_3)_4CdBr_3$ ($0 \le z \le \frac{1}{3}$).

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53856 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

configurations of the latter model. This correspondence suggests the possibility of disorder in the latter type in the room-temperature phase.

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Acta Cryst. (1991). C**47**, 1210–1212

Structure of *p*-(*N*,*N*-Dimethylamino)phenyl 1,2,4-Triazol-1-yl Ketone *p*-Nitrophenylhydrazone

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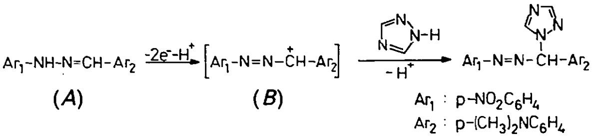
(*Received* 2 *April* 1990; *accepted* 13 *August* 1990)

Abstract. $C_{17}H_{17}N_7O_2$, $M_r = 351{\cdot}37$, triclinic, $P\bar{1}$, $a = 11{\cdot}361\ (5)$, $b = 10{\cdot}327\ (3)$, $c = 7{\cdot}763\ (3)$ Å, $\alpha = 80{\cdot}47\ (1)$, $\beta = 104{\cdot}95\ (4)$, $\gamma = 104{\cdot}89\ (3)°$, $V = 845{\cdot}6\ (6)$ Å^3, $Z = 2$, $F(000) = 368$, $D_x = 1{\cdot}380$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}90$ mm^{-1}, room temperature, $R = 0{\cdot}058$ for 1281 observed reflections. The best plane of the five-membered triazole ring lies almost perpendicular to the best planes of two benzene rings. The symmetry-related molecules are linked together by two N—H···N hydrogen bonds forming dimers.

Introduction. The title compound was prepared by electrochemical oxidation of *p*-(*N*,*N*-dimethylamino)-benzaldehyde *p*-nitrophenylhydrazone (*A*) in the presence of 1,2,4-triazole (Gunić & Tabaković, 1988). It was concluded that the electrochemical oxidation of (*A*) in the presence of heteroaromatic bases occurs through the formation of cation (*B*), which is attacked by base as a nucleophile. This excluded the possibility of annelation of the heteroaromatics through nitrilimine as an intermediate. 1,2,4-Triazole can attack the cation (*B*) with all five positions according to its behaviour towards electrophiles (Potts, 1961). On the basis of high-resolution mass spectral and NMR data the structure of the product isolated was assigned as *N*,*N*-dimethyl-*p*-[(*p*-nitrophenylazo)(1,2,4-triazol-1-yl)methyl]aniline. It is the purpose of the present paper to correct the proposed structure on the basis of crystal structure analysis.



Experimental. The title compound crystallizes as red transparent prisms. A crystal of dimensions 0·32 × 0·68 × 0·84 mm was selected for X-ray analysis and mounted on a Philips PW1100 diffractometer. The refined lattice parameters, $a = 11{\cdot}361\ (5)$, $b = 10{\cdot}327\ (3)$, $c = 7{\cdot}763\ (3)$ Å, $\alpha = 80{\cdot}47\ (1)$, $\beta = 104{\cdot}95\ (4)$ and $\gamma = 104{\cdot}89\ (3)°$, were obtained by a least-squares procedure from the setting angles of 13 reflections with $8 < \theta < 12°$. Intensities were collected with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). Scan range $2 < \theta < 30°$, ω scan, h −15 to 15, k −12 to 13, l 0 to 8. A standard reflection was measured every hour and remained constant throughout the measurement. A total of 1583 reflections were collected of which 1568 were unique ($R_{\rm int}$

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