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Structure of Tetramethylammonium Tetraiodozincate in the Monoclinic Phase

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Abstract. $[N(CH_3)_4]_2ZnI_4$, $M_r = 721{\cdot}2$, monoclinic, $P12_1/c1$, $a = 9{\cdot}612\,(9)$, $b = 16{\cdot}656\,(15)$, $c = 13{\cdot}222\,(18)$ Å, $\beta = 90{\cdot}15\,(4)°$, $V = 2117\,(4)$ Å^3, $Z = 4$, $D_x = 2{\cdot}263$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu = 70{\cdot}74$ cm^{-1}, $F(000) = 1312$, $T = 250$ K, final $R = 0{\cdot}051$ for 1704 unique reflections with $F > 3\sigma(F)$. The structure is characterized by the counterclockwise rotations on axes along [010] of all ions from the basic room-temperature structure.

Introduction. $[N(CH_3)_4]_2ZnI_4$ is one of the members of $[N(CH_3)_4]_2MX_4$-type compounds. The highest-temperature phases are of the β-K_2SO_4-type structure with space group *Pmcn* in common (Wiesner, Srivastava, Kennard, DiVaira & Lingafelter, 1967). The setting of the crystal axes chosen by Sawada, Shiroishi, Yamamoto, Takashige & Matsuo (1978) is adopted in this paper. The crystal undergoes successive phase transitions at about 260 and 220 K (Werk, Chapuis & Schmid, 1987). These phases are denoted as I, II (monoclinic, $b = b_0$) and III (ferroelectric, $Pbc2_1$, $b = 2b_0$) in the order of decreasing temperature, where b_0 is the cell dimension in phase I. Crystal structures of phases I and III have been reported: in phase III the distortion with respect to the basic room-temperature structure is mainly due to rotations of the ZnI_4 tetrahedra (Werk, Chapuis & Perret, 1987). Most of the isomorphous compounds, $[N(CH_3)_4]_2MCl_4$ with M = Zn, Co, Ni, Fe, Mn and Cu, exhibit many modulated phases with modulation along [001] (Gesi, 1986). The title compound is especially of interest because of the modulation along [010]. This type of modulation has been reported only in two other compounds $[N(CH_3)_4]_2CuBr_4$ (Hasebe, Mashiyama, Tanisaki & Gesi, 1982) and $[N(CH_3)_4]_2CdI_4$ (Werk & Chapuis, 1988). The present paper reports the structure in phase II.

Experimental. Single crystals of $[N(CH_3)_4]_2ZnI_4$ were grown by the slow evaporation method from an aqueous solution containing an excess of ZnI_2 without acidification (Gesi & Perret, 1988). D_m was not determined. A spherical specimen with radius 0·112 mm was mounted on an automatic four-circle diffractometer (Rigaku AFC-5), graphite-monochromated Mo $K\alpha$ radiation. Temperature of the sample kept at 250 ± 0·3 K by controlled nitrogen gas flow. Cell dimensions from 24 reflections, $8{\cdot}9 < \theta < 11{\cdot}2°$; the ω-mode up to $(\sin\theta)/\lambda < 0{\cdot}538$ Å^{-1} ($0 \leq h \leq 10$, $0 \leq k \leq 17$, $-14 \leq l \leq 14$), scan speed 10° min^{-1} in θ, scan width $1{\cdot}9° + 0{\cdot}5° \tan\theta$; three standard reflections (511, 163 and 136) monitored every 150 reflections, no significant variation detected. 3074 reflections measured, 2876 unique reflections; $R_{\text{int}} = 0{\cdot}02$ based on F. After absorption, Lorentz and polarization corrections, 1704 unique reflections with $F > 3\sigma(F)$ were used for the analysis. Min., max. transmission coefficients 0·325, 0·335.

When the single crystal was cooled down to phase II, a single peak of Bragg reflection split into two due to the formation of monoclinic domains with (001) in common. Because of the small deviation of angle β

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Table 1. *Positional parameters and equivalent isotropic thermal parameters* ($Å^2 \times 10^2$) *at* 250 K *with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Zn	0·2593 (4)	0·4068 (1)	0·2550 (2)	5·0
I(1)	0·2386 (3)	0·3992 (1)	0·0583 (1)	7·1
I(2)	0·2693 (4)	0·5537 (1)	0·3195 (1)	9·5
I(3)	0·0421 (2)	0·3373 (1)	0·3326 (2)	9·7
I(4)	0·4859 (2)	0·3323 (1)	0·3136 (1)	9·0
N(1)	0·241 (2)	0·100 (1)	0·151 (1)	6·4
C(1)	0·309 (3)	0·094 (2)	0·258 (2)	12·9
C(2)	0·233 (10)	0·027 (2)	0·096 (3)	21·4
C(3)	0·326 (4)	0·162 (3)	0·097 (4)	20·3
C(4)	0·119 (4)	0·137 (3)	0·145 (3)	20·8
N(2)	0·251 (3)	0·836 (1)	0·474 (1)	5·5
C(5)	0·264 (5)	0·752 (1)	0·439 (2)	11·5
C(6)	0·195 (4)	0·894 (2)	0·394 (2)	10·9
C(7)	0·378 (3)	0·863 (2)	0·516 (4)	16·3
C(8)	0·156 (4)	0·837 (2)	0·566 (3)	13·9

Table 2. *Bond lengths* (Å) *and angles* (°) *at* 250 K *with e.s.d.'s in parentheses*

Zn—I(1)	2·611 (5)	N(1)—C(3)	1·49 (5)
Zn—I(2)	2·592 (5)	N(1)—C(4)	1·34 (6)
Zn—I(3)	2·601 (4)	N(2)—C(5)	1·49 (6)
Zn—I(4)	2·622 (4)	N(2)—C(6)	1·53 (4)
N(1)—C(1)	1·56 (4)	N(2)—C(7)	1·41 (6)
N(1)—C(2)	1·42 (10)	N(2)—C(8)	1·52 (5)
I(1)—Zn—I(2)	112·1 (2)	I(2)—Zn—I(3)	108·6 (2)
I(1)—Zn—I(3)	108·2 (2)	I(2)—Zn—I(4)	108·6 (2)
I(1)—Zn—I(4)	109·4 (2)	I(3)—Zn—I(4)	109·9 (2)
C(1)—N(1)—C(2)	116 (4)	C(5)—N(2)—C(6)	114 (3)
C(1)—N(1)—C(3)	104 (3)	C(5)—N(2)—C(7)	110 (3)
C(1)—N(1)—C(4)	117 (3)	C(5)—N(2)—C(8)	108 (3)
C(2)—N(1)—C(3)	112 (5)	C(6)—N(2)—C(7)	112 (3)
C(2)—N(1)—C(4)	108 (5)	C(6)—N(2)—C(8)	110 (2)
C(3)—N(1)—C(4)	97 (3)	C(7)—N(2)—C(8)	102 (3)

from 90°, each measured intensity contains contributions from hkl reflection of the first domain and that of $h\bar{k}\bar{l}$ of the second. If the volume fraction of the first domain to the total volume is denoted by x, then the measured intensity can be expressed as follows:

$$I = xF^2(hkl) + (1 - x)F^2(h\bar{k}\bar{l}).$$

The block-diagonal-matrix least-squares program of *UNICS*3 (Sakurai & Kobayashi, 1979) was rewritten to include the volume fraction x as a parameter.

The positional parameters of non-H atoms obtained for the isomorphous $[N(CH_3)_4]_2ZnBr_4$ (Asahi, Hasebe & Gesi, 1988) were used as the starting parameters. The least-squares refinement with anisotropic thermal parameters (a total of 138 parameters varied), minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o)]^{-1}$, gave the results: $R = 0{\cdot}051$, $wR = 0{\cdot}043$, $S = 0{\cdot}83$ and $(\Delta/\sigma)_{max} < 0{\cdot}1$. The volume fraction x was 0·482 (3). A difference Fourier synthesis was not made. Atomic scattering factors for neutral atoms, dispersion corrections for Zn and I were taken from *International Tables for X-ray Crystallography* (1974).

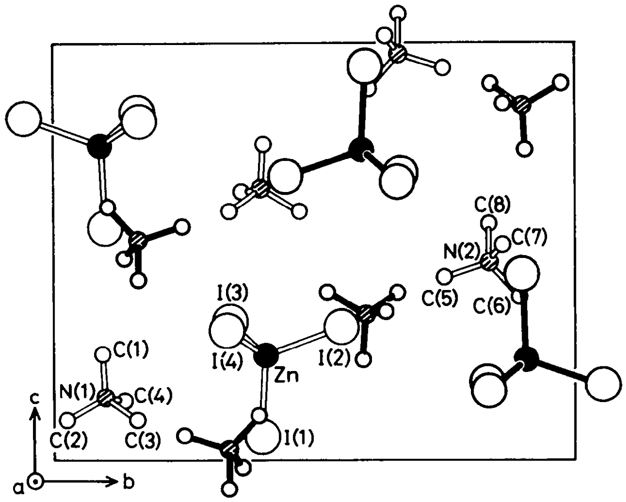

Fig. 1. The *a* projection of the structure of $[N(CH_3)_4]_2ZnI_4$.

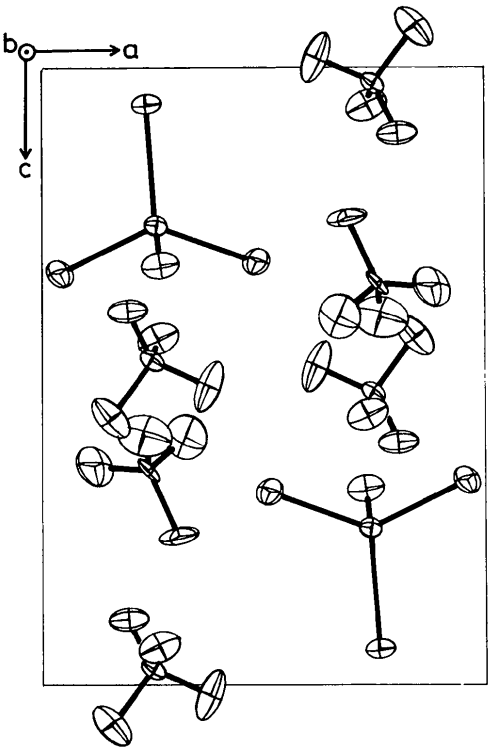

Fig. 2. Arrangement of ions projected along the *b* axis. Because of overlapping, the following four ions are not drawn: two ZnI_4's derived by *c*- and *n*-glide from the tabulated arrangement, and $N(1)(CH_3)_4$ of the tabulated one and that derived by inversion.

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

The structure shown in Fig. 1 was induced by the second-order phase transition through the loss of the mirror plane m_x which exists in phase I. Three kinds of displacements are relevant for each tetrahedral ion: a translation along [100], a rotation on an axis along [010] and that on an axis along [001]. For the less-distorted ZnI_4 tetrahedron, values of the displacements were estimated to be 0·089 (4) Å, 4·2 (1)° and 1·1 (1)° respectively. For the first value, the displacement of Zn was taken, the second was defined as the b projection of the angle between the I(1)—Zn direction and the c^* direction, and the third the c projection of the angle between the I(3)—I(4) direction and [100]. The displacements of two kinds of $N(CH_3)_4$ tetrahedra were not estimated because of their large distortion. The characteristic feature in Fig. 1 is the counterclockwise rotations of all ions along [010]. This feature has been reported in $[N(CH_3)_4]_2ZnBr_4$ (Asahi *et al.*, 1988), $[N(CH_3)_4]_2MnBr_4$ (Hasebe, Asahi & Gesi, 1990) and $[N(CH_3)_4]_2MnCl_4$ (Mashiyama & Koshiji, 1989). As is seen from Figs. 1 and 2, rotational displacements of $N(CH_3)_4$ tetrahedra are larger than those of ZnI_4 tetrahedra. This result is in contrast with that in phase III reported by Werk, Chapuis & Perret (1987).

The thermal parameters of the C atoms are very large. It suggests the possibility of disorder in $N(CH_3)_4$ ions in phase I. A study of the structure in phase I is now in progress in order to investigate the mechanism of the phase transition.

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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 52350 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of the Conducting Salts of Ethylenedithiotetrathiafulvalene (EDTTTF) and Methylenedithiotetrathiafulvalene (MDTTTF): (EDTTTF)I_3 and (MDTTTF)I_3

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Abstract. (I): 2-(2-Dithiolylidene)-5,6-dihydrodithiolo[4,5-*b*]dithiinium triiodide, $C_8H_6S_6^+.I_3^-$, M_r = 675·2, monoclinic, $P2_1/c$, $a = 15{\cdot}307\,(2)$, $b = 9{\cdot}622\,(1)$, $c = 12{\cdot}013\,(1)$ Å, $\beta = 110{\cdot}69\,(1)°$, $V = 1655{\cdot}0\,(4)$ Å^3, $Z = 4$, $D_m = 2{\cdot}74$, $D_x = 2{\cdot}709$ g cm^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 62{\cdot}80$ cm^{-1}, $F(000) = 1228$, $T = 296\,(2)$ K. (II) 2-(2-Dithiolylidene)-dithiolo[4,5-*d*]dithiolium triiodide, $C_7H_4S_6^+.I_3^-$, M_r =

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