

Structural Analysis of the Orthorhombic Room- and Low-Temperature Phases of $[\text{N}(\text{CH}_3)_4]_2\text{ZnI}_4$

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Abstract

Bis(tetramethylammonium) tetraiodozincate (TMA- ZnI_4) exhibits two successive structural transitions of first and second order at 218 and 255 K, respectively. The crystal structures of phase I (room temperature) and of phase III (150 K) have been determined by X-ray diffraction. The high-temperature phase I has a $\beta\text{-K}_2\text{SO}_4$ -type structure with an orientational disorder of the TMA groups. In phase III, the crystal structure is commensurately modulated by an ordered displacement of the rigid ZnI_4 tetrahedra and TMA groups. The modulation direction is perpendicular to the pseudohexagonal axis, an orientation which is specific to this compound. Crystal data of phase I: $M_r = 691.0$, $Pm\bar{c}n$, $a = 9.639(9)$, $b = 16.722(4)$, $c = 13.254(6)$ Å, $V = 2163(3)$ Å³, $Z = 4$, $D_x = 2.24$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 70.2$ cm⁻¹, $F(000) = 1312$, $R = 0.045$ for 1276 observed reflections. Crystal data of phase III: $M_r = 721.28$, $Pbc2_1$, $a = 9.574(3)$, $b = 33.020(6)$, $c = 13.106(3)$ Å, $V = 4143(3)$ Å³, $Z = 8$, $D_x = 2.31$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 71.01$ cm⁻¹, $F(000) = 2624$, $R = 0.041$ for 2886 observed reflections.

1. Introduction

A considerable number of compounds of the type $[\text{N}(\text{CH}_3)_4]_2\text{BX}_4$ have been the subject of recent studies (Axe, 1986). They belong to the $A_2\text{BX}_4$ family whose members undergo a series of ferroic and displacive phase transitions and show similar behaviour. All compounds under consideration adopt the same normal (high-temperature) structure of the $\beta\text{-K}_2\text{SO}_4$ type. This structure is pseudohexagonal with the space group $Pm\bar{c}n$. It is customary to choose c to describe the pseudohexagonal axis.

A variety of successive phase transitions which may lead to commensurate or incommensurate structures take place in these compounds. In general, the

wavevector of the modulation is along the c^* direction. Most of them have been united in a common pressure–temperature diagram (Gesi, 1986) describing their sequence of phase transitions.

In contrast, the newly discovered compounds $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ (Hasebe, Mashiyama & Tanisaki, 1985; Gesi, 1982), $[\text{N}(\text{CH}_3)_4]_2\text{CdI}_4$ (Kallel, Bats & Daoud, 1981; Werk & Chapuis, 1988) and $[\text{N}(\text{CH}_3)_4]_2\text{ZnI}_4$ (henceforth TMA- ZnI_4) (Werk, Chapuis & Perret, 1987) exhibit a sequence of transitions which does not follow this general phase diagram, since they develop modulations perpendicular to the pseudohexagonal axis in the b^* direction. This common feature constitutes a new subgroup of phases of the TMA- BX_4 family.

In TMA- CuBr_4 the modulation wavevector of the incommensurate phase is $\mathbf{q} = (\frac{1}{2} - \delta)\mathbf{b}^*$. On lowering the temperature, a lock-in transition results in a ferroelectric commensurate phase with $\delta = 0$ and space group $Pbc2_1$. On further cooling, another commensurate structure with space group $P12_1/c1$ is found (Hasebe, Mashiyama & Tanisaki, 1982). Structural analyses of the normal and the lock-in phases have been reported (Trouelan, Lefebvre & Derollez, 1984; Hasebe *et al.*, 1985). The thermodynamics of the phase-transition sequences have been studied by Lopez-Echarri, Ruiz-Larrea & Tello (1988).

At normal pressure, the title compound TMA- ZnI_4 exhibits two phase transitions below room temperature. Besides the normal phase (I), a ferroelastic phase (II) (Hasebe, Asahi & Gesi, 1990) is found which transforms into a commensurate phase (III). Studies of the dielectric properties (Gesi & Perret, 1988) indicate that phase III is of the so-called improper ferroelectric type. This term is used to indicate that the ferroelectric state does not disappear with decreasing temperature. This is in contrast to the other TMA- BX_4 -type ferroelectrics in which the ferroelectric state exists only in a limited temperature range.

We report in this paper a study of TMA-ZnI₄ with modulations along the **b*** direction. In particular, we present analyses obtained from differential scanning calorimetry (DSC), optical microscopy and single-crystal X-ray studies. The structures of the phases I and III are reported. As previously observed for other β -K₂SO₄-type compounds, the normal phase was found to be disordered (Rb₂ZnCl₄, Itoh, Hinasada, Daika, Ando & Nakamura, 1986; Rb₂ZnBr₄, de Pater, Axe & Currat, 1979; TMA-CuBr₄, Hasebe *et al.*, 1985; and others). In TMA-ZnI₄ an order-disorder process was associated with the structural transition from phase I to III.

2. Experimental

Synthesis. Transparent crystals of TMA-ZnI₄ were grown by evaporation at room temperature of an aqueous hypophosphorous acid solution containing (CH₃)₄N⁺.I⁻ and ZnI₂ in the molar ratio 1:10. Single-crystal X-ray studies confirmed the identity of the compound.

DSC and polarized-light microscopy. Calorimetric studies have shown that TMA-ZnI₄ undergoes two phase transitions at 255 and 218 K (Arend, 1986; M. L. Werk, unpublished results). Both transitions were reversible. The peak-shape anomalies indicate that the transitions are of second and first order, respectively.

This finding is in agreement with results obtained using polarized-light microscopy (Werk, Chapuis & Schmid, 1987). Observations on (100)-cut platelets of TMA-ZnI₄ at room temperature showed the orthorhombic phase I optically monodomain. The second-order phase transition from phase I to phase II is accompanied by the appearance of unstable, narrow ferroelastic domains. In phase II, the birefringence increased continuously with decreasing temperature. The occurrence of domains strongly indicated a symmetry reduction, probably from orthorhombic to monoclinic. The transition from phase II to phase III is characterized by a sharp decrease in birefringence and a return to optical homogeneity. This transition behaviour was reversible with a hysteresis of about 5°.

X-ray diffraction. At room temperature, the intensity distribution of single-crystal photographs indicated the presence of the normal β -K₂SO₄-type structure. The space group is *Pmcn* if we postulate a centre of symmetry as confirmed later by refinement. In phase III, below 220 K, commensurate superstructure reflections appeared which result in a doubling of the lattice parameter *b*. This phase is orthorhombic and the systematic absences indicate the diffraction symbol *Pbc**. Packing considerations and the assumption that phase III is a minor distortion of phase I favoured the polar space group *Pbc*2₁.

Spontaneous polarization effects observed by pyroelectric charge measurements (Gesi & Perret, 1988) confirmed the polar character of phase III.

Data collection. X-ray measurements were carried out on an Enraf-Nonius CAD-4 four-circle diffractometer. Intensities of phases I and III were each measured on a different specimen. Phase III was identified by the appearance of the superstructure reflections. During the measurement of phase III the crystal was cooled to \approx 150 K by an open stream of nitrogen gas. The temperature was controlled by a thermocouple positioned a few millimeters from the crystal. Temperature fluctuations at the thermocouple were less than 1°. Experimental details of the measurements are given in Table 1.

2.1. Structure refinement

All calculations were performed with the *XRAY72* system of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) Atomic scattering factors for neutral atoms were taken from Cromer & Mann (1968) and the dispersion corrections were those of Cromer & Liberman (1970).

Normal phase (phase I). The structure of the normal phase was refined with the starting parameters for the Zn and I atoms of the isomorphous compound TMA-ZnCl₄ (Wiesner, Srivastava, Kennard, Di Vaira & Lingafelter, 1967). Difference Fourier maps revealed all C and N atoms. Refinements were carried out by full-matrix least squares, including anisotropic displacement parameters for all atoms. In the final cycles, an extinction parameter was also refined. In the refinement, the C atoms exhibited large anisotropic thermal parameters *U*_{ij}. This result indicates an orientational disorder of the NC₄ tetrahedra rather than thermal displacements. Only *U*_{ij} of the C(21) atom and the N atoms have smaller values. This suggests a rotational disorder of the NC₄ tetrahedra which deviates from the average orientation. A model was introduced with disordered NC₄ tetrahedra symmetrically distributed on two equivalent positions. The anisotropic refinement is also indicative of a displacement of the ZnI₄ tetrahedra, but too small to justify atomic separation.

Phase III. During intensity measurements of phase III, significant variations of the intensity-control reflections were observed owing to technical problems. The data were scaled correspondingly. Refinement was started from the positional parameters for the Zn and I atoms obtained for the normal phase and transformed to the base vectors of the superstructure cell.

The remaining coordinates for the N and C atoms were obtained from a difference Fourier map. Refinement of the enantiomorph-polarity parameter (Flack, 1983) was used to determine the orientation

Table 1. Data on the structure determinations of $[N(CH_3)_4]_2ZnI_4$

	Phase I	Phase III
Temperature (K)	293	150
Space group	<i>Pmcn</i>	<i>Pbc</i> ₂
<i>a</i> (Å)	9.668 (9)	9.574 (3)
<i>b</i> (Å)	16.765 (4)	33.020 (6)
<i>c</i> (Å)	13.303 (6)	13.106 (3)
<i>V</i> (Å ³)	2156 (3)	4143 (3)
<i>Z</i>	4	8
<i>D_x</i> (g cm ⁻³)	2.24	2.31
<i>F</i> (000)	1312	2624
λ (Mo <i>K</i> α) (Å)	0.7107	0.7107
Monochromator	Graphite	Graphite
No. of reflections used for lattice parameters	15	20
θ range for lattice parameters (°)	10–20	10–24
Scan width	(0.65 + 0.34tan θ)°	(0.8 + 0.34tan θ)°
Scan speed (° min ⁻¹)	Variable, 2–10	Variable, 1.65–10
Scan mode	$\omega/2\theta$	ω
Range of <i>hkl</i>	0 ≤ <i>h</i> ≤ 13 0 ≤ <i>k</i> ≤ 23 –18 ≤ <i>l</i> ≤ 18	–10 ≤ <i>h</i> ≤ 10 –35 ≤ <i>k</i> ≤ 35 0 ≤ <i>l</i> ≤ 14
Orientation control reflections (period)	3 (every 70 reflections)	3 (every 100 reflections)
Intensity control reflections (period)	3 (every 70 reflections)	3 (every 60 min)
(sin θ/λ) _{max} (Å ⁻¹)	0.7050	0.5493
Collected reflections	5837	6051
Non-equivalent reflections	3273	3028
Reflections with <i>I</i> > 3 σ (<i>I</i>)	1276	2886
μ (Mo <i>K</i> α) (cm ⁻¹)	70.2	71.01
Crystal faces	(010), (0 $\bar{1}$ 0), (20 $\bar{1}$) ($\bar{1}$ 00), ($\bar{1}$ 1 $\bar{1}$ 3), (1 $\bar{1}$ 13)	{100}, {010}, {001}
Approximate crystal dimensions (mm)	0.21 × 0.25 × 0.24	0.44 × 0.15 × 0.15
Min./max. transmission	0.188/0.303	0.349/0.408
<i>R</i> _{int}	—	0.028
Reflections used	All	All
Extinction correction	Yes	No
<i>R</i>	0.045	0.041
<i>wR</i>	0.060	0.045
Weight function	1/ σ^2 (<i>F</i>)	1/ σ^2 (<i>F</i>)
Max. shift/e.s.d. in final least-squares cycle	—	0.075
No. of parameters		
Variables	136	465
Soft restrictions	0	208

of the polar axis. Anisotropic displacement parameters were assigned to all atoms. The origin of the coordinate system along *c* was fixed using the method of Flack & Schwarzenbach (1988).

In the final refinement cycles, H-atom positions were calculated assuming N—CH₃ tetrahedra with ideal cubic symmetry and a C—H bond length of 1 Å. The resulting H-atom coordinates were refined using distances and rigid-bond restraints (Schwarzenbach & Didisheim, 1987). H-atom displacements were assumed to be isotropic. The weight of each restraint corresponded to the reciprocal value of the standard deviation for the prescribed rigid bond. Assumed e.s.d.'s for rigid-bond restraints were N—C = 0.0 and C—H = 0.0; distances were restrained such that C—H = 1. In the last step it was multiplied by ten in order to release the constraints. Because of limitations of the available computer memory, the least-squares matrix was subdivided into four blocks. One block included the atom parameters of the ZnI₄ tetrahedra and each of the remaining blocks contained one TMA group.

Table 2. Fractional atomic coordinates ($\times 10^4$), population factors (*pp*) and equivalent isotropic displacement parameters (Å² $\times 10^4$)

E.s.d.'s are given in parentheses. $U_{eq} = \frac{1}{3}\text{trace}U$.					
	<i>x</i>	<i>y</i>	<i>z</i>	<i>pp</i>	<i>U</i> _{eq}
(a) Normal phase I					
Zn	2500	4073.8 (7)	2541.3 (8)		674 (7)
I(1)	2500	3989 (5)	580.8 (5)		970 (6)
I(2)	2500	5538.7 (5)	3183 (7)		1173 (7)
I(3)	284.1 (8)	3363.3 (5)	3225.6 (5)		1214 (6)
N(1)	2500	1005 (6)	1516 (6)		76 (3)
C(11)	1910 (30)	910 (20)	2520 (10)	0.5	1600 (100)
C(12)	3320 (50)	1660 (20)	1320 (40)	0.5	1900 (200)
C(13)	3020 (20)	210 (10)	1080 (20)	0.5	1500 (100)
C(14)	1220 (40)	1250 (30)	1000 (30)	0.5	2400 (300)
N(2)	2500	8341 (5)	4749 (6)		710 (30)
C(21)	2500	7543 (9)	4380 (10)		1570 (900)
C(22)	1040 (30)	8530 (10)	5030 (30)	0.5	1700 (200)
C(23)	3220 (30)	8340 (20)	5680 (20)	0.5	1600 (200)
C(24)	3010 (20)	8920 (10)	4000 (10)	0.5	1100 (100)
(b) Phase III					
Zn(1)	2044 (2)	2031.9 (6)	2176 (2)		280 (9)
I(11)	2448 (1)	1973.8 (4)	199.6 (9)		342 (7)
I(12)	1633 (1)	2773.8 (3)	2773 (1)		404 (7)
I(13)	–166 (1)	1593.4 (3)	2642 (1)		382 (7)
I(14)	4264 (1)	1749.0 (4)	3104 (1)		412 (7)
Zn(2)	3785 (2)	2984.0 (6)	7069 (2)		293 (9)
I(21)	7246 (1)	2994.0 (4)	9071.9 (8)		332 (7)
I(22)	7204 (1)	2245.3 (3)	6389 (1)		465 (7)
I(23)	5320 (1)	3408.5 (4)	6321 (1)		442 (7)
I(24)	9780 (1)	3301.1 (4)	6499 (1)		405 (7)
N(1)	7950 (10)	4500 (4)	8090 (10)		330 (40)
C(11)	7530 (20)	4900 (6)	8520 (20)		900 (100)
H(111)	8100 (100)	4960 (20)	9140 (60)		900 (300)
H(112)	7700 (100)	5115 (8)	7990 (50)		1700 (300)
H(113)	6520 (40)	4890 (20)	8700 (100)		600 (200)
C(12)	9470 (20)	4450 (6)	8240 (20)		800 (100)
H(121)	9980 (30)	4610 (30)	7700 (70)		900 (200)
H(122)	9740 (40)	4560 (40)	8930 (50)		900 (200)
H(123)	9720 (40)	4157 (9)	8230 (100)		900 (200)
C(13)	7220 (20)	4177 (7)	8600 (20)		900 (100)
H(131)	6200 (30)	4190 (30)	8430 (80)		600 (200)
H(132)	7600 (100)	3910 (6)	8370 (80)		1800 (300)
H(133)	7300 (100)	4200 (30)	9360 (20)		800 (200)
C(14)	7570 (20)	4484 (7)	6960 (10)		640 (90)
H(141)	7700 (100)	4200 (10)	6700 (30)		900 (200)
H(142)	6570 (40)	4560 (30)	6870 (20)		600 (200)
H(143)	8170 (90)	4680 (30)	6580 (20)		800 (200)
N(2)	2170 (20)	487 (4)	1140 (10)		390 (50)
C(21)	3250 (20)	813 (6)	1250 (20)		730 (90)
H(211)	3960 (80)	730 (20)	1770 (80)		900 (200)
H(212)	3700 (100)	860 (30)	580 (30)		700 (200)
H(213)	2790 (40)	1070 (10)	1500 (100)		800 (200)
C(22)	2870 (20)	103 (6)	780 (20)		620 (90)
H(221)	3200 (100)	140 (10)	50 (30)		500 (200)
H(222)	3700 (80)	50 (20)	1210 (60)		900 (200)
H(223)	2200 (60)	–128 (9)	830 (80)		600 (200)
C(23)	1080 (30)	623 (9)	390 (20)		1100 (100)
H(231)	600 (100)	380 (10)	100 (100)		1700 (300)
H(232)	400 (100)	810 (40)	730 (40)		1400 (300)
H(233)	1540 (40)	770 (40)	–190 (60)		900 (200)
C(24)	1510 (20)	423 (6)	2140 (10)		670 (90)
H(241)	1200 (100)	690 (10)	2420 (50)		700 (200)
H(242)	700 (80)	240 (30)	2060 (30)		900 (200)
H(243)	2210 (50)	300 (40)	2620 (30)		800 (200)
N(3)	2490 (10)	4210 (4)	4380 (10)		310 (40)
C(31)	1670 (20)	4252 (6)	5330 (10)		540 (80)
H(311)	1950 (80)	4040 (20)	5820 (30)		600 (200)
H(312)	650 (20)	4220 (30)	5170 (20)		600 (200)
H(313)	1840 (90)	4520 (10)	5640 (50)		600 (200)
C(32)	2380 (20)	3790 (6)	4000 (10)		560 (80)
H(321)	1410 (50)	3740 (10)	3740 (90)		700 (200)
H(322)	2600 (100)	3599 (6)	4580 (80)		600 (200)
H(323)	3070 (90)	3750 (10)	3440 (70)		700 (200)
C(33)	1880 (20)	4499 (5)	3600 (10)		420 (70)
H(331)	2420 (70)	4480 (20)	2950 (30)		400 (100)
H(332)	1950 (90)	4782 (6)	3870 (40)		600 (100)
H(333)	880 (30)	4430 (20)	3480 (50)		300 (100)
C(34)	3960 (20)	4318 (6)	4540 (10)		450 (60)
H(341)	4030 (30)	4610 (10)	4770 (70)		600 (100)
H(342)	4500 (30)	4280 (30)	3890 (30)		400 (100)
H(343)	4370 (40)	4140 (20)	5080 (60)		400 (100)
N(4)	7200 (10)	821 (4)	4840 (10)		320 (40)
C(41)	7220 (20)	1260 (6)	5150 (10)		490 (60)

Table 2 (cont.)

	x	y	z	pp	U _{eq}
H(411)	7790 (90)	1290 (10)	5780 (50)		400 (100)
H(412)	6240 (30)	1350 (10)	5280 (80)		500 (100)
H(413)	7600 (100)	1425 (7)	4590 (40)		700 (200)
C(42)	6630 (20)	570 (5)	5670 (10)		390 (60)
H(421)	5680 (50)	670 (20)	5860 (50)		400 (100)
H(422)	7260 (60)	580 (20)	6280 (30)		400 (100)
H(423)	6550 (90)	282 (8)	5440 (30)		500 (100)
C(43)	6330 (20)	778 (5)	3890 (10)		490 (70)
H(431)	6350 (90)	490 (9)	3650 (50)		400 (100)
H(432)	6720 (70)	960 (20)	3340 (30)		600 (100)
H(433)	5350 (30)	860 (30)	4040 (30)		700 (200)
C(44)	8660 (20)	690 (5)	4640 (10)		440 (60)
H(441)	9060 (40)	860 (20)	4080 (60)		500 (100)
H(442)	8670 (30)	400 (10)	4440 (80)		500 (100)
H(443)	9230 (30)	730 (30)	5270 (30)		600 (200)

Symmetry transformations: $x, y, z; -x + \frac{1}{2}, -y - \frac{1}{4}, \frac{1}{2} + z; -x + \frac{1}{2}, y + \frac{1}{2}, z; x, \frac{1}{2} - y, z + \frac{1}{2}$.

Final values of the reliability factors were $R = 0.041$, $wR = 0.045$. The maximum shift/e.s.d. after the final least-squares cycle was 0.075. In the final difference Fourier map the residual maxima were $2.1 e \text{ \AA}^{-3}$, at a distance of 0.89 Å from I.

Final atomic positional and equivalent isotropic displacement parameters of phases I and III are listed in Tables 2(a) and 2(b). Tables 3(a) and 3(b) list important distances for the two phases.*

3. Results and discussion

Crystal structure of the normal phase. The structure of the normal phase shows that TMA-ZnI₄ indeed belongs to the A_2BX_4 family. Structural units are isolated NC₄ tetrahedra and ZnI₄ tetrahedra. Several descriptions of normal K₂SO₄-type structures can be found in the literature (Axe, 1986, and references cited therein). The disordered arrangement of the tetrahedra seems to be an important characteristic feature of these compounds (Wiesner *et al.*, 1967; Matsunaga, 1982; Hasebe *et al.*, 1985; Perret, Godefroy & Arend, 1987).

Figs. 1 and 2 show the contents of the unit cell of TMA-ZnI₄ projected onto (001). In the ideal structure, all tetrahedra are located on planes normal to **a**. At $x = \frac{1}{4}$, the ZnI₄ tetrahedra point downwards along $-c$ and at $x = \frac{3}{4}$ they point upwards along $+c$. The NC₄ tetrahedra at $x = \frac{1}{4}$ and $x = \frac{3}{4}$ are arranged alternately. The tetrahedra are located on mirror planes. Furthermore, all tetrahedra can be considered to lie on four different layers normal to **c**. Two layers at $z = \frac{1}{4}$ and $z = \frac{3}{4}$ are occupied by ZnI₄ and NC₄ tetrahedra. The remaining layers at $z = 0$ and $z = \frac{1}{2}$ contain only NC₄ tetrahedra.

* Lists of structure factors, anisotropic atomic displacement parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52337 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

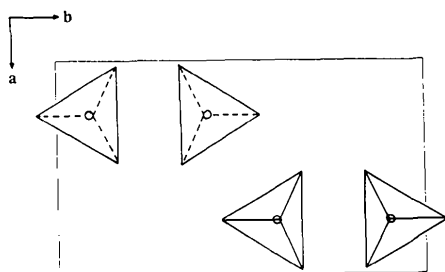
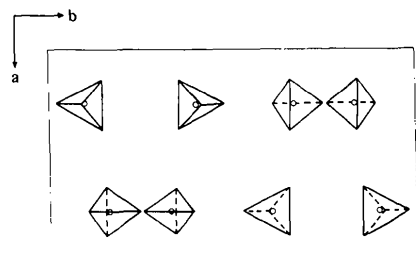
Table 3. Selected interatomic distances (Å) and bond angles (°) with e.s.d.'s in parentheses

Bond lengths for phase I are given without and with (second column) corrections for thermal motion.

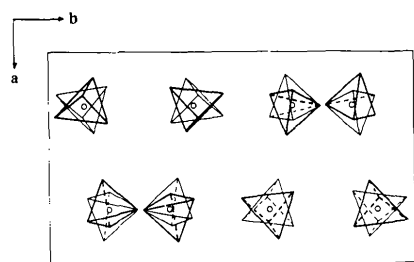
(a) Normal phase I					
Zn—I(1)	2.602 (2)	2.623	I(1)—Zn—I(2)	112.28 (5)	
I(2)	2.593 (2)	2.622	I(1)	I(3)	108.82 (4)
I(3)	2.607 (2)	2.639	I(2)	I(3)	108.44 (4)
N(1)—C(11)	1.45 (2)	1.55	C(11)—N(1)—C(12)	119 (2)	
C(12)	1.38 (4)	1.48	C(11)	C(13)	112 (1)
C(13)	1.53 (2)	1.63	C(11)	C(14)	97 (2)
C(14)	1.46 (4)	1.59	C(12)	C(13)	115 (2)
			C(12)	C(14)	100 (3)
			C(13)	C(14)	110 (2)
N(2)—C(21)	1.42 (2)	1.49	C(21)—N(2)—C(22)	107 (1)	
C(22)	1.49 (3)	1.58	C(21)	C(23)	107 (1)
C(23)	1.42 (3)	1.51	C(21)	C(24)	113 (1)
C(24)	1.48 (2)	1.51	C(22)	C(23)	104 (2)
			C(22)	C(24)	110 (1)
			C(23)	C(24)	115 (1)
(b) Phase III					
Zn(1)—I(11)	2.626 (3)		I(11)—Zn(1)—I(12)	112.80 (9)	
I(12)	2.601 (2)		I(11)	I(13)	107.86 (9)
I(13)	2.635 (2)		I(11)	I(14)	108.17 (8)
I(14)	2.621 (3)		I(11)	I(13)	109.05 (8)
			I(12)	I(14)	108.61 (9)
			I(13)	I(14)	110.35 (9)
Zn(2)—I(21)	2.628 (3)		I(21)—Zn(2)—I(22)	110.51 (8)	
I(22)	2.602 (2)		I(21)	I(23)	109.25 (9)
I(23)	2.615 (3)		I(21)	I(24)	108.85 (9)
I(24)	2.629 (3)		I(22)	I(23)	108.88 (9)
			I(22)	I(24)	109.51 (9)
			I(23)	I(24)	109.83 (8)
N(1)—C(11)	1.46 (2)		C(11)—N(1)—C(12)	108 (1)	
C(12)	1.49 (2)		C(11)	C(13)	111 (1)
C(13)	1.51 (2)		C(11)	C(14)	109 (1)
C(14)	1.51 (3)		C(12)	C(13)	109 (1)
			C(12)	C(14)	109 (1)
			C(13)	C(14)	110 (1)
N(2)—C(21)	1.47 (2)		C(21)—N(2)—C(22)	110 (1)	
C(22)	1.48 (2)		C(21)	C(23)	109 (1)
C(23)	1.48 (2)		C(21)	C(24)	110 (1)
C(24)	1.51 (2)		C(22)	C(23)	111 (1)
			C(22)	C(24)	108 (1)
			C(23)	C(24)	108 (1)
N(3)—C(31)	1.50 (2)		C(31)—N(3)—C(32)	110 (1)	
C(32)	1.47 (2)		C(31)	C(33)	108 (1)
C(33)	1.51 (2)		C(31)	C(34)	109 (1)
C(34)	1.48 (2)		C(32)	C(33)	110 (1)
			C(32)	C(34)	108 (1)
			C(33)	C(34)	110 (1)
N(4)—C(41)	1.49 (2)		C(41)—N(4)—C(42)	108 (1)	
C(42)	1.48 (2)		C(41)	C(43)	111 (1)
C(43)	1.44 (3)		C(41)	C(44)	109 (1)
C(44)	1.52 (2)		C(42)	C(43)	110 (1)
			C(42)	C(44)	111 (1)
			C(43)	C(44)	108 (1)

In the final model adopted for the structure refinement, each NC₄ tetrahedron is displaced from the mirror plane of the space group *Pmcn*. The tetrahedra are essentially rotated about directions parallel to the **b** and **c** axes which cross their centres of gravity. It is not known whether the disorder is static or dynamic.

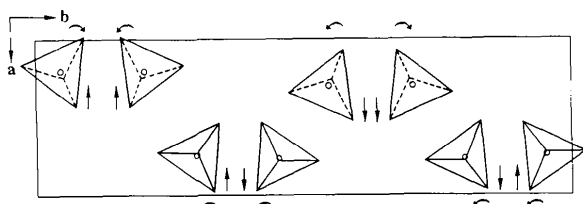
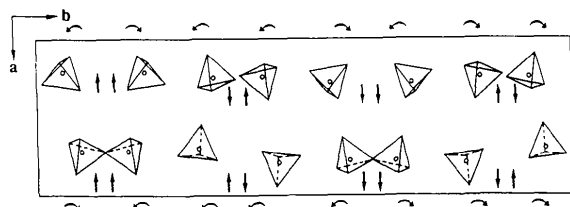
For all atoms of phase I (Table 2), the values are given with and without correction for thermal motion (Schomaker & Trueblood, 1968). In phase I, the Zn—I distances are shorter than in phase III, but become equal after correction for thermal motion.

Fig. 1. Phase I, ZnI_4 tetrahedra.

(a)



(b)

Fig. 2. (a) Phase I, NC_4 tetrahedra, calculated average structure.
(b) Phase I, NC_4 tetrahedra, refined positions.Fig. 3. Phase III, ZnI_4 tetrahedra. Rotations and translations of the rigid tetrahedra are indicated by arrows.Fig. 4. Phase III, NC_4 tetrahedra with displacements of the rigid tetrahedra.Table 4. Displacements of the tetrahedra from the ideal structure with symmetry $Pm\bar{c}n$ for phase III

	Zn(1)	Zn(2)	N(1)	N(2)	N(3)	N(4)
T_x	-0.046	-0.012	-0.033	-0.001	-0.030	-0.045
R_x	7	3	25	28	22	15
R_i	6	6	13	3	5	18

Notes: T_x = translation (relative units) of the cations along the a axis. R_i = rotation ($^\circ$) about an axis parallel to i .

3.1. Analysis of the displacements in the low-temperature phase III

In phase III, the ZnI_4 and NC_4 tetrahedra are alternately displaced. Along the b direction two tetrahedra, which are equivalent in the normal phase, show an antiphase displacement in the superstructure. This leads to the doubling of the b lattice constant and a transformation of the mirror plane of phase I into a glide plane (Figs. 3 and 4). A macroscopic dipole moment is created and the compound becomes ferroelectric (Gesi & Perret, 1988). Table 3 shows that all the tetrahedra are quite regular. The deviations of their bond lengths and angles are much smaller than the displacements of the tetrahedra out of the mirror planes (Table 4). This confirms that the commensurate modulation of phase III consists mainly of displacements of rigid tetrahedral units. Their orientations characterize the different phases.

In order to discuss the structural change, the orientations of the tetrahedra in phase III will be compared with the ideal structure. Starting from the average structure, the modulated phase III results from the combination of three motions given in Table 4. Because the tetrahedra are nearly rigid, their translational displacements are represented by the displacements of the cations. The largest displacements are rotations of the tetrahedra about the b and c directions. In addition, there is a small translation of the tetrahedra along the a direction.

The reason for the occurrence of the structural instability leading from phase I to phase III is not yet clear. Based on a semi-microscopic model, Janssen (1986) gives an explanation for the various commensurate and incommensurate modulated structures of the $\beta\text{-K}_2\text{SO}_4$ type and in particular of TMA-BX_4 compounds. The model is based on the competition of interactions between tetrahedra giving rise to a so-called 'structural frustration'. Janssen's (1986) approach was first formulated for structures with a modulation wavevector along the c direction. We believe, however, that the same mechanism may also be applied to the title compound.

Starting from the common basic structure, the model postulates displacive modulations of rigid tetrahedral units. In the basic structure, each NC_4 tetrahedron has a pair of equivalent ZnI_4 tetrahedra as first neighbours with the distance $a/2$ parallel to a in the ab plane. Intertetrahedral interactions favour

the approach of one corner of the NC₄ tetrahedron to the Zn ion of one of the two nearest ZnI₄ tetrahedra. These forces are antagonistic to the inter-tetrahedral repulsion forces, causing the tetrahedra to move to an equilibrium orientation. Fig. 5 shows an *ab* layer at $z = 0.25$. NC₄ and ZnI₄ tetrahedra are displaced by rotations of equal sign about an axis parallel to *c*, such that all corners of the NC₄ tetrahedron point towards a face of the neighbouring ZnI₄ tetrahedron. This configuration forms pseudo-hexagonal rings of NC₄ and ZnI₄ tetrahedra. All tetrahedra forming a ring are rotated in the same direction about *c* and commonly shifted parallel to *a*. Neighbouring rings along *b* are rotated and shifted in the opposite directions. This is in contrast to compounds exhibiting modulations along *c*, where the tetrahedra of an *ab* layer are all displaced in a unique way. In phase III, the NC₄ tetrahedra perpendicular to *c* at $z = 0.0$ and $z = 0.5$ are also displaced to an equilibrium position where corners of ZnI₄ tetrahedra point towards faces of neighbouring NC₄ tetrahedra.

In this structure, the displacements are essentially rotations of rigid tetrahedra. This behaviour is common to most of the other *A₂BX₄* compounds (Hogervorst, 1986; Colla, 1988). Since the rotation of the tetrahedra is an obvious aspect of the structural phase transition, it has been chosen as the structural order parameter by Janssen (1986). We believe that the displacements of TMA-ZnI₄ may also support this order parameter. But the specific orientation of the tetrahedra makes TMA-ZnI₄ a remarkable case. In compounds exhibiting modulations along *c*, the tetrahedra pointing upwards along +*c* and downwards along -*c* are rotated in the opposite direction about *c*. Thus the orientation of the tetrahedra determined by the vertex parallel to *c* was considered to control the sign of the rotation. This coincidence does not appear in TMA-ZnI₄.

The above-mentioned choice of tetrahedra rotations as an order parameter may help to explain the existence of modulated phases. An understanding

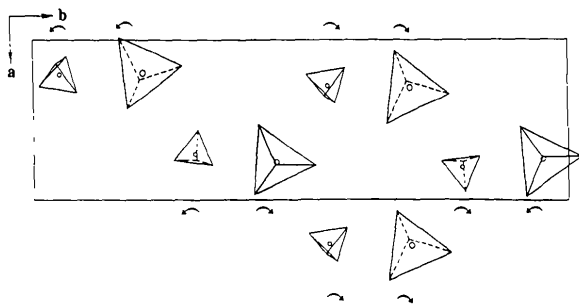


Fig. 5. Phase III, ZnI₄ tetrahedra and NC₄ tetrahedra, layer at $z = 0.25$.

of a modulation parallel to *b* or *c* requires additional mechanisms which favour one of the modulation directions for the different compounds before a final conclusion can be obtained.

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