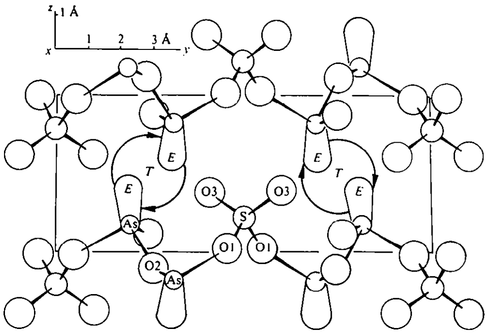

Fig. 1. Projection orthogonale de la structure sur le plan (100). Les tunnels T sont formés par des interactions entre paires E (E–E ~ 2,82 Å) parallèlement aux axes hélicoïdaux ($z = \frac{1}{2}$) et perpendiculaires au plan de la figure.

atomes d'oxygène (O···O ~ 2,9 Å). La distance entre deux paires de deux tunnels voisines est par contre très grande.

Ces considération ouvrent des perspectives aussi bien dans la possibilité de réaliser des intercalations moléculaires ou ioniques entre les feuillets que dans la probabilité d'être en présence d'un matériau à conduction électronique, par le biais des tunnels. Il paraît donc envisageable d'obtenir des matériaux intercalés ayant des propriétés de conduction mixte. Nous orientons actuellement nos recherches dans cette voie.

Références

Almin, K. E. & Westgren, A. (1942). *Ark. Kemi, Mineral. Geol.* **B15**, 22–29.
Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Douglade, J. & Mercier, R. (1982). *Acta Cryst.* **38**, 720–723.
Frueh, A. J. (1951). *Am. Mineral.* **36**, 833–837.
Galy, J., Meunier, G., Andersson, S. & Åström, A. (1975). *J. Solid State Chem.* **13**, 142–159.
International Tables for X-ray Crystallography (1967). Tome II, pp. 302–303. Birmingham: Kynoch Press.
Mercier, R. (1975). *Rev. Chim. Minér.* **12**, 508–517.
Mercier, R., Sourisseau, C. & Lucazeau, G. (1977). *J. Raman Spectrosc.* **6**(4), 195–203.
Pertlik, F. (1975). *Monatsh. Chem.* **106**, 755–762.
Sheldrick, G. M. (1976). *SHELX* 76. Programme pour la détermination des structures. Univ. Cambridge, Angleterre.

Acta Cryst. (1982). B**38**, 898–900

Structure of Ammonium Tetrachlorozincate in the Ferroelectric Phase

By H. Matsunaga, K. Itoh and E. Nakamura

Faculty of Science, Hiroshima University, Hiroshima 730, *Japan*

(*Received* 29 *July* 1981; *accepted* 22 *September* 1981)

Abstract. $(NH_4)_2]ZnCl_4]$, 223 K, orthorhombic, $P2_1cn$, $a = 7{\cdot}184\ (1)$, $b = 12{\cdot}568\ (2)$, $c = 27{\cdot}838\ (3)$ Å, $U = 2513{\cdot}5\ (7)$ Å^3, $Z = 12$, $D_c = 1{\cdot}929$ Mg m^{-3}; $R = 0{\cdot}038$ for 2192 reflexions observed on an automatic four-circle diffractometer (Cu $K\alpha$ radiation). The structure is isostructural with room-temperature K_2ZnCl_4. The distortion of $ZnCl_4$ tetrahedra in the ferroelectric phase is smaller than that in the room-temperature phase.

Introduction. Ferroelectric activity in $(NH_4)_2[ZnCl_4]$ below 266 K was reported by Belobrova, Moskalev, Bizukina, Milul & Aleksandrova (1980). Recently, we have found two other phase transitions at 319 and 406 K and confirmed that the phases below 406 K show satellite reflexions (Matsunaga & Nakamura, 1981). The phases observed are phase I (normal, $c = c_o$), phase II (paraelectric, $c = 4c_o$), phase III (antiferroelectric, $c = 4c_o$) and phase IV (ferroelectric, $c = 3c_o$) in descending order of temperature. In order to clarify the mechanism of the successive phase transitions of this compound, details of the structure at each phase are desired. The structure at room temperature (phase III) has already been determined by Mikhail (1980). In this paper we report the structure of the ferroelectric phase (phase IV).

Single crystals were grown by slow evaporation of an aqueous solution of NH_4Cl and $ZnCl_2$ in the molar ratio 2:1. A specimen, spherical in shape (0·75 mm in diameter), was prepared and coated with epoxy-type resin because of its deliquescence. Bragg reflexions were observed by a computer-controlled Rigaku AFC-5 automatic four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation. The temperature of the specimen was controlled at 223 ± 0·5 K by a stream of cold nitrogen gas. The orientation

0567-7408/82/030898-03$01.00

Table 1. *Final atomic coordinates* ($\times10^4$) *and equivalent isotropic thermal parameters* (Å^2 $\times10^4$), $\exp(-8\pi^2 U_{eq}\sin^2\theta/\lambda^2)$, *where* $U_{eq} = (U_1U_2U_3)^{1/3}$; U_i $(i = 1,2,3)$ *are the mean-square amplitudes along the principal axes of the thermal vibration ellipsoids*

	x	y	z	U_{eq}
N(1)	2724 (13)	6811 (6)	1723 (2)	300 (29)
N(2)	2307 (13)	6854 (5)	5043 (2)	289 (24)
N(3)	2803 (12)	6771 (6)	8385 (2)	289 (27)
N(4)	2869 (13)	4020 (7)	2887 (3)	391 (31)
N(5)	2480 (16)	4051 (7)	6206 (3)	427 (40)
N(6)	2330 (17)	3942 (7)	9548 (3)	446 (33)
Zn(1)	2500	4225 (1)	925·4 (3)	279 (3)
Zn(2)	2565 (2)	4271 (1)	4255·9 (4)	277 (3)
Zn(3)	2651 (2)	4213 (1)	7573·6 (4)	290 (3)
Cl(1)	2336 (5)	4181 (2)	1726 (1)	327 (11)
Cl(2)	1896 (4)	5861 (2)	629 (1)	302 (10)
Cl(3)	428 (4)	3059 (2)	608 (1)	329 (9)
Cl(4)	5322 (4)	3734 (2)	635 (1)	373 (9)
Cl(5)	3122 (4)	4288 (2)	5049 (1)	280 (8)
Cl(6)	2038 (4)	5889 (2)	3932 (1)	272 (8)
Cl(7)	231 (4)	3175 (2)	4051 (1)	358 (9)
Cl(8)	5201 (3)	3632 (2)	3887 (1)	285 (7)
Cl(9)	2348 (5)	4158 (2)	8371 (1)	322 (11)
Cl(10)	3272 (4)	5847 (2)	7268 (1)	276 (8)
Cl(11)	−25 (4)	3671 (2)	7220 (1)	312 (8)
Cl(12)	4919 (4)	3076 (2)	7333 (1)	381 (9)

matrix and the cell parameters were determined by least-squares calculation based on 25 reflexions.

Integrated intensity data were collected with the ω–2θ scanning mode. The primary-beam intensity was measured by a monitoring counter to make a correction for each Bragg intensity. The scanning speed was 8° min^{-1} and the scanning range $\Delta\omega$ was varied according to the relation $\Delta\omega = 1{\cdot}3° + 0{\cdot}5° \tan\theta$. 2488 independent reflexions were measured within the range $\theta < 65{\cdot}0°$; of these, 2192 with $|F_o| > 3\sigma(|F_o|)$ were used for the least-squares calculations. Systematic absences were found for $hk0$: $h + k = 2n + 1$, $h0l$: $l = 2n + 1$, indicating $Pmcn$ or $P2_1cn$ as possible space groups. Owing to the ferroelectric activity in this phase, the latter was adopted. The data were corrected for absorption because of the large absorption effect ($\mu r \simeq 5{\cdot}70$). The atomic parameters of room-temperature K_2ZnCl_4 (Mikhail & Peters, 1979), which was expected to be isostructural with this compound, were employed for the initial parameters in the least-squares calculation. Neutral-atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The atomic parameters of non-H atoms were refined by the block-diagonal least-squares calculation with the program *UNICS* (1967). The refinement with anisotropic thermal parameters converged with discrepancy factors $R = 0{\cdot}038$ and $R_2 = 0{\cdot}040$ respectively, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

Table 2. *Bond lengths* (Å) *and angles* (°) *for* $ZnCl_4$ *tetrahedra and* N—Cl *distances within* 3·7 Å

Zn(1)—Cl(1)	2·233 (2)	Cl(1)—Zn(1)—Cl(2)	112·1 (1)
—Cl(2)	2·257 (2)	Cl(1)—Zn(1)—Cl(3)	109·8 (1)
—Cl(3)	2·268 (3)	Cl(1)—Zn(1)—Cl(4)	113·4 (1)
—Cl(4)	2·268 (3)	Cl(2)—Zn(1)—Cl(3)	108·6 (1)
		Cl(2)—Zn(1)—Cl(4)	106·8 (1)
		Cl(3)—Zn(1)—Cl(4)	105·8 (1)
Zn(2)—Cl(5)	2·245 (2)	Cl(5)—Zn(2)—Cl(6)	114·5 (1)
—Cl(6)	2·257 (2)	Cl(5)—Zn(2)—Cl(7)	112·9 (1)
—Cl(7)	2·244 (3)	Cl(5)—Zn(2)—Cl(8)	107·2 (1)
—Cl(8)	2·299 (3)	Cl(6)—Zn(2)—Cl(7)	109·0 (1)
		Cl(6)—Zn(2)—Cl(8)	106·0 (1)
		Cl(7)—Zn(2)—Cl(8)	106·7 (1)
Zn(3)—Cl(9)	2·230 (2)	Cl(9)—Zn(3)—Cl(10)	114·8 (1)
—Cl(10)	2·267 (2)	Cl(9)—Zn(3)—Cl(11)	109·9 (1)
—Cl(11)	2·265 (3)	Cl(9)—Zn(3)—Cl(12)	110·1 (1)
—Cl(12)	2·268 (3)	Cl(10)—Zn(3)—Cl(11)	106·1 (1)
		Cl(10)—Zn(3)—Cl(12)	108·6 (1)
		Cl(11)—Zn(3)—Cl(12)	107·0 (1)
N(1)—Cl(1)	3·318 (8)	N(4)—Cl(1)	3·261 (8)
—Cl(2)	3·324 (7)	—Cl(8)	3·286 (8)
—Cl(7^{iii})	3·290 (8)	—Cl($10^{\mathrm{ii}-a+b+c}$)	3·335 (10)
—Cl($8^{\mathrm{iii}-a}$)	3·377 (8)	—Cl($11^{\mathrm{ii}+b+c}$)	3·286 (10)
—Cl($9^{\mathrm{ii}+b+c}$)	3·548 (10)	—Cl($12^{\mathrm{iv}-c}$)	3·389 (9)
—Cl($10^{\mathrm{iv}+b-c}$)	3·334 (8)		
—Cl($11^{\mathrm{ii}+b+c}$)	3·413 (8)		
—Cl($12^{\mathrm{ii}-a+b+c}$)	3·314 (8)		
N(2)—Cl($2^{\mathrm{iv}+b}$)	3·317 (7)	N(5)—Cl(3^{iv})	3·461 (10)
—Cl(3^{iii})	3·256 (8)	—Cl(5)	3·267 (8)
—Cl($4^{\mathrm{iii}-a}$)	3·343 (8)	—Cl($6^{\mathrm{ii}+b+c}$)	3·298 (12)
—Cl(6)	3·278 (7)	—Cl($8^{\mathrm{ii}-a+b+c}$)	3·351 (10)
—Cl($5^{\mathrm{ii}-a+b+c}$)	3·341 (9)	—Cl(11)	3·380 (9)
—Cl(6)	3·327 (7)		
—Cl($7^{\mathrm{ii}+b+c}$)	3·284 (8)		
—Cl($8^{\mathrm{ii}-a+b+c}$)	3·396 (8)		
N(3)—Cl($1^{\mathrm{ii}+b+c}$)	3·483 (9)	N(6)—Cl($2^{\mathrm{ii}+b+c}$)	3·326 (12)
—Cl($3^{\mathrm{ii}+b+c}$)	3·388 (8)	—Cl($3^{\mathrm{i}+c}$)	3·435 (9)
—Cl($4^{\mathrm{ii}-a+b+c}$)	3·322 (8)	—Cl($4^{\mathrm{ii}-a+b+c}$)	3·297 (10)
—Cl($6^{\mathrm{iv}+b}$)	3·358 (7)	—Cl(7^{iv})	3·357 (10)
—Cl(9)	3·300 (7)	—Cl(9)	3·289 (8)
—Cl(10)	3·334 (7)		
—Cl($11^{\mathrm{iii}+c}$)	3·312 (8)		
—Cl($12^{\mathrm{iii}-a+c}$)	3·313 (8)		

Symmetry code: (i + c) $x, y, 1 + z$; (ii + b + c) $\frac{1}{2} + x, 1 - y, 1 - z$; (ii − a + b + c) $-\frac{1}{2} + x, 1 - y, 1 - z$; (iii) $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii − a) $-\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii + c) $\frac{1}{2} + x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii − a + c) $-\frac{1}{2} + x, \frac{1}{2} + y, \frac{3}{2} - z$; (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv + b) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (iv − c) $x, \frac{1}{2} - y, -\frac{1}{2} + z$; (iv + b − c) $x, \frac{3}{2} - y, -\frac{1}{2} + z$.

The final atomic parameters and their e.s.d.'s are listed in Table 1* and bond lengths and angles in Table 2. A final difference Fourier map showed irregular maxima of 0·8 e Å^{-3} near Zn, but no peaks >0·3 e Å^{-3} in remaining places. The location of the H atoms could not be determined.

Discussion. Projections of the structure down the *a* and *b* axes are shown in Fig. 1 together with labelling of the non-H atoms.

The structure determined here is basically isostructural with that of K_2ZnCl_4 at room temperature

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36416 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

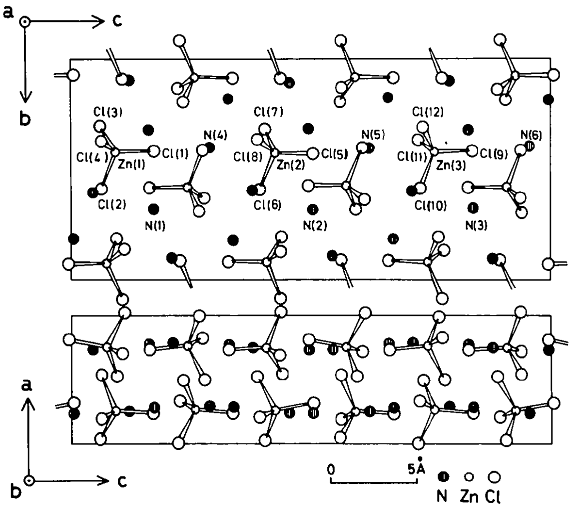

Fig. 1. Arrangement of the atoms viewed along **a** and **b**.

(Mikhail & Peters, 1979), and has a long period of $c = 3c_0$ compared with the structure of the normal phase as in K_2ZnCl_4. It is worth noting, however, that there is a marked difference between $(NH_4)_2[ZnCl_4]$ and K_2ZnCl_4 in the distribution of satellite reflexions based on the structure of the normal phase. In $(NH_4)_2[ZnCl_4]$ many satellite reflexions are observed in the (0*kl*) plane, whereas they are hardly found in the same plane in K_2ZnCl_4 (Itoh, Kataoka, Matsunaga & Nakamura, 1980).

The bond lengths of Zn—Cl, which range from 2·230 to 2·299 Å (mean 2·258 Å), are close to those of $ZnCl_4$ tetrahedra in $Li_2ZnCl_4.2H_2O$ (Jacobi & Brehler, 1969), $ZnCl_2.\frac{4}{3}H_2O$ (Follner & Brehler, 1970), Na_2ZnCl_4 (van Loon & Visser, 1977) and K_2ZnCl_4 (Mikhail & Peters, 1979). The present results show that the maximum differences of Zn—Cl bond lengths in each $ZnCl_4$ tetrahedron are 0·035, 0·038 and 0·055 Å (mean 0·043 Å), while corresponding values in the room-temperature phase (Mikhail, 1980) range from 0·065 to 0·234 Å (mean 0·159 Å). The maximum differences of the Cl—Zn—Cl bond angles in the respective $ZnCl_4$ tetrahedra are 7·6, 8·5 and 8·7° in the present work, whereas they are 13·1, 4·7, 11 and 8·7° in the room-temperature phase (Mikhail, 1980). These facts show that, in the ferroelectric phase, $ZnCl_4$ tetrahedra are less distorted than those in the room-temperature phase. The coordination numbers for the NH_4^+ ions are 8 [N(1), N(2), N(3)] and 5 [N(4), N(5), N(6)], while they are 5, 6, 7 and 8 in the room-temperature phase. These facts suggest that the arrangement of the $ZnCl_4$ tetrahedra and NH_4^+ ions in the ferroelectric phase is more regular than that in the room-temperature phase.

References

Belobrova, I. A., Moskalev, A. K., Bizukina, N. V., Milul, S. V. & Aleksandrova, I. P. (1980). *Solid State Commun.* **33**, 1101–1102.

Follner, H. & Brehler, B. (1970). *Acta Cryst.* B**26**, 1679–1682.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Itoh, K., Kataoka, T., Matsunaga, H. & Nakamura, E. (1980). *J. Phys. Soc. Jpn*, **48**, 1039–1040.

Jacobi, H. & Brehler, B. (1969). *Z. Kristallogr.* **128**, 390–405.

Loon, C. J. J. van & Visser, D. (1977). *Acta Cryst.* B**33**, 188–190.

Matsunaga, H. & Nakamura, E. (1981). *J. Phys. Soc. Jpn*, **50**, 2789–2790.

Mikhail, I. (1980). *Acta Cryst.* B**36**, 2126–2128.

Mikhail, I. & Peters, K. (1979). *Acta Cryst.* B**35**, 1200–1201.

UNICS (1967). *Universal Crystallographic Computation Program System*, edited by T. Sakurai. Tokyo: The Crystallographic Society of Japan.

Acta Cryst. (1982). B**38**, 900–903

Structure of Mercury(II) Iodide Nitrate

By Kenneth Persson and Bertil Holmberg

Physical Chemistry 1, *Chemical Center, University of Lund, POB* 704, *S*-220 07 *Lund* 7, *Sweden*

(*Received* 30 *June* 1981; *accepted* 23 *September* 1981)

Abstract. $HgINO_3$, M_r = 389·53, orthorhombic, *Pnma*, *a* = 7·3850 (26), *b* = 5·2567 (29), *c* = 12·5277 (69) Å, *Z* = 4, and D_x = 5·32 Mg m^{-3}. The structure was refined anisotropically from single-crystal diffractometer data to an *R* value of 0·044 for 610 independent reflexions. An $(HgI^+)_n$ zigzag chain passes through the structure parallel to the *a* axis. In this chain, Hg is coordinated to two I atoms with an I—Hg—I angle of 158·66°, and the I atoms coordinate two Hg atoms with an Hg—I—Hg angle of 90·25°. The

0567-7408/82/030900-04$01.00