En conclusion, la détermination de la structure cristalline de $Na_3PO_4.8H_2O$ nous a permis d'émettre une hypothèse de réarrangement lors du passage de l'octahydrate aux complexes hydratés de formule $Na_3PO_4.\frac{1}{n}NaY.xH_2O$ (par exemple $Na_3PO_4.\frac{1}{4}NaOH.$-$12H_2O$ ou $Na_3PO_4.\frac{1}{5}NaCl.11H_2O$).

Le réarrangement ne peut être étudié pour les complexes hydratés de formule $nNa_3PO_4.NaY.xH_2O$; en effet, contrairement aux sels de structure hexagonale, ceux-ci lors de leur dégradation thermique, ne présentent pas l'octahydrate comme intermédiaire.

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Twinning by Pseudomerohedry in Ammonium Tetrachlorozincate(II), $(NH_4)_2[ZnCl_4]$. A Reinvestigation of the Crystal Structure at Room Temperature

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Abstract. $M_r = 243{\cdot}3$, monoclinic, Pc, $a = 12{\cdot}620\,(2)$, $b = 7{\cdot}211\,(8)$, $c = 37{\cdot}098\,(6)$ Å, $\beta = 90{\cdot}00\,(2)°$, $V = 3376{\cdot}0$ Å^3, $Z = 16$, $D_x = 1{\cdot}92$ Mg m^{-3}, $\mu = 4{\cdot}18$ mm^{-1}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $F(000) = 1920$. Crystals of $(NH_4)_2[ZnCl_4]$ exhibit twinning by pseudomerohedry. The apparent *mmm* symmetry is caused by twinning and by the pseudo-orthorhombic symmetry of the lattice. Due to the pseudosymmetry an erroneous space group, namely $P2_1cn$, has been assigned to $(NH_4)_2[ZnCl_4]$ in the literature. Intensity measurements on several crystals of $(NH_4)_2[ZnCl_4]$ at room temperature clearly prove monoclinic symmetry. The correct space group is Pc. A complete structure refinement is applied to a twinned crystal. The refined volume fraction of the smaller crystal in the twin is 0·033 (1). The final weighted R factor is 4·0% for all 8084 independent reflections. The spread in Zn—Cl bond lengths (2·182 to 2·306 Å) and in Cl—Zn—Cl angles (104·5 to 114·3°) is smaller than found by Mikhail [*Acta Cryst.* (1980), B**36**, 2126–2128] who refined the structure in $P2_1cn$. The twin factor of the crystal used by Mikhail appears to be about 0·32.

Introduction. Several papers on the successive phase transitions in $(NH_4)_2[ZnCl_4]$ have been published (Belobrova, Moskalev, Bizukina, Misul & Aleksandrova, 1980; Matsunaga & Nakamura, 1981; Smolensky, Siny, Prokhorova, Kuzminov & Mikvabia, 1981; Kucharczyk, Warczewski & Broda, 1981). Using average values of the transition temperatures one can denote at least the following three phases. Phase (I) ($T > 400$ K) is a presumably orthorhombic phase with $c = c_o \simeq 9{\cdot}3$ Å. Phase (II) ($270 < T < 400$ K) has a superstructure with $c = 4c_o$. It is subdivided by Matsunaga & Nakamura (1981) into a paraelectric phase ($319 < T < 406$ K) and an antiferroelectric phase ($270 < T < 319$ K). Phase (III) ($T < 270$ K) is a ferroelectric phase having $c = 3c_o$. The crystal structure of the orthorhombic phase (III) has been published by Alexandrov, Kruglik & Misul (1981) and independently by Matsunaga, Itoh & Nakamura (1982). Recently, papers on the room-temperature phase (II) have been published by Mikhail (1980) and by Warczewski (1980). Both authors adopted the orthorhombic space group $P2_1cn$. Earlier attempts at an analysis of this phase (van Koningsveld, Warczewski & de Wolff, 1975) had made us doubt whether the actual symmetry is really orthorhombic. This induced us to reinvestigate the crystal structure of $(NH_4)_2[ZnCl_4]$ at room temperature.

Experimental. Clear, colourless crystals were obtained by slow evaporation at room temperature of an aqueous solution of NH_4Cl and $ZnCl_2$ (Marignac, 1857). The freshly prepared crystals were ground to spheres with a diameter of 0·3 mm or less. These were enclosed in thin-walled capillaries. Preliminary Weissenberg and precession photographs revealed no incommensurate reflections, no streaks and no other anomalies. The cell dimensions were taken from

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Warczewski (1980). Intensities were collected with a Nonius CAD-4 diffractometer using graphite-monochromated Mo *Kα* radiation. From a provisional inspection of the data set the systematic extinctions ($h0l$ for l = odd) were obvious but several $hk0$ reflections for $(h+k)$ = odd were significantly different from zero. The monoclinic symmetry of the apparently orthorhombic crystals was proven by accurately measuring six general reflections from several crystals. For each of these six, intensities were collected for all eight combinations ($\pm h, \pm k, \pm l$). There was good agreement between the intensities of hkl, $\bar{h}\bar{k}l$, $\bar{h}\bar{k}\bar{l}$ and $hk\bar{l}$ (average I_1) and also among the other four reflections (average I_2). An example is given in Table 1, which shows very large and significant differences between I_1 and I_2. Hence, the possible space groups are $P1\frac{2}{c}1$ or $P1c1$. The polar space group $P1c1$ was chosen because Mikhail's (1980) results proved the absence of a twofold axis along **b**. The Bijvoet differences of the six reflections selected were in the same order of magnitude as the differences between the intensities of $\bar{h}\bar{k}l$ and hkl. Therefore, these reflections were not seriously affected by anomalous dispersion.

Twinning. From Table 1 it is seen that the difference between I_1 and I_2 is dependent on the crystal chosen. For a twinned crystal the observed intensities I_1 and I_2 are derived from the values for a hypothetical untwinned crystal, J_1 and J_2, by the relationships (Britton, 1972):

$$\begin{aligned} I_1 &= (1-\alpha)J_1 + \alpha J_2 \\ I_2 &= \alpha J_1 + (1-\alpha)J_2 \end{aligned} \qquad (1)$$

where α is the volume fraction of the smaller twin mate (the twin factor). If Q is defined with the observed intensities:

$$Q = |I_1 - I_2|/(I_1 + I_2), \qquad (2)$$

then, with (1), Q can be rewritten:

$$Q = (1-2\alpha)|J_1 - J_2|/(J_1 + J_2). \qquad (3)$$

If Q values for the same reflection in different crystals are considered, equation (3) shows that twinning reveals itself in a linear relationship between Q and α. Equation (3) is graphically represented, for all six reflections from nine crystals, in Fig. 1. The position of the point $\alpha = 0$ is not known. However, it should be close to crystal 8 because I_2 of the 317 reflection from this crystal is very low (see Table 1). If crystal 8 is assumed to be a perfect crystal ($\alpha = 0$), the $\bar{\alpha}$ value of each of the other crystals is the weighted average of six α values which can then be obtained with equation (3). The ensuing value of the twin factor of crystal 9, used for the structure determination, is $\bar{\alpha} = 0{\cdot}025$ (3) (Table 2). Q values for Mikhail's (1980) crystal (*Mi*) are calculated from his observed structure factors (F_o) by:

$$Q = |2F_o^2/(i_1 + i_2) - 1|,$$

where $i_{1,2}$ are the observed values $I_{1,2}$ from our experiment after correction for the continuous factors. From Table 2 it is seen that the twin factor for the *Mi* crystal can be estimated to be about 0·32. If straight lines are drawn from the origin to the points representing the Q values for crystal 8, the linear relationship between Q and α for each reflection is obvious and proves the twinning of the crystals. The twins are most probably related by a lost symmetry element from $P2_1cn$: a mirror plane perpendicular to the c axis or, equivalently, a twofold axis along the a axis.

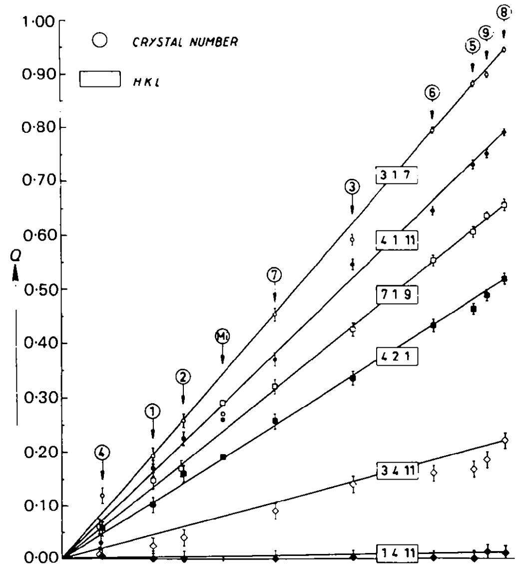

Fig. 1. Q *versus* $(1-2\alpha)$ for nine $(NH_4)_2[ZnCl_4]$ crystals. The calculated data for the *Mi* crystal are added.

Table 1. *Measured intensities of the* 317 *reflection in three* $(NH_4)_2[ZnCl_4]$ *crystals*

Crystal number	317	$\bar{3}\bar{1}\bar{7}$	$3\bar{1}7$	$\bar{3}1\bar{7}$	I_1	$31\bar{7}$	$\bar{3}\bar{1}7$	$3\bar{1}\bar{7}$	$\bar{3}17$	I_2
4	351	343	341	324	*340*	268	250	276	274	*267*
7	278	262	247	245	*258*	682	695	684	678	*685*
8	679	625	661	621	*647*	17	19	20	19	*19*

Table 2. *Q values and* α *values* (*relative to crystal* 8) *of crystals* 8, 9 *and Mikhail's crystal*

Standard deviations are calculated (using the method of propagation of errors) assuming a σ of 2% in I_1 and I_2.

	Mi		9		8	
hkl	*Q*	α	*Q*	α	*Q*	α
421	0·19	0·32	0·488 (11)	0·027 (14)	0·516 (10)	0
719	0·29	0·28	0·635 (8)	0·015 (9)	0·654 (8)	0
4,1,11	0·26	0·33	0·751 (6)	0·024 (5)	0·789 (5)	0
317	0·27	0·35	0·897 (3)	0·024 (2)	0·943 (2)	0
$\bar{\alpha}$		0·32		0·025 (3)		0

Data collection and refinement. A nearly spherical crystal (radius 0·12 mm) (crystal 9), 8112 independent reflections, $2° < 2\theta < 56°$, ω-scan mode, scan angle $\Delta\omega = (0{\cdot}80 + 0{\cdot}35\mathrm{tg}\,\theta)°$, intensities measured with 2% accuracy or for a maximum counting time of 120 s; inspection of diffractometer output showed a very asymmetric background for 28 reflections due to unfavourable geometrical measuring conditions, these were omitted during refinement; of the 8084 remaining reflections 3875 had $I > \sigma(I)$; spherical absorption correction [$\mu(\mathrm{Mo}\,K\alpha) = 4{\cdot}12\ \mathrm{mm}^{-1}$], computed values of the transmission coefficient in the range 1·99 to 2·08; atomic positional parameters of Mikhail (1980),* suitably transformed, used as initial values of the eight independent molecules for the twin refinement in *Pc*. If $[x_i]$ are the positional parameters of one part of the twin and the twin operation is represented by the matrix $[T_{ij}]$, the coordinates of the twin mate of the crystal (with reference to the axes of the untwinned fraction) are given by $[x_i'] = [T_{ij}][x_i]$. Similarly, the anisotropic temperature factors U'_{ij} of the twinned fraction are given by

$$U'_{ij} = \sum_{k=1}^{3}\sum_{l=1}^{3}[T_{ik}][T_{jl}]U_{ij}$$

(Hawthorne, 1974). These equations were applied as linear constraints in the refinement cycles. The twin factor was refined using the constraint:

$$\sum_{j=1}^{p}\alpha_j = 1,$$

where p is the number of twinned fractions.† In this way standard least-squares programs can easily be extended. Least-squares twin refinement carried out on the Leiden University IBM 370–158 computer (program written by Mrs Elisabeth W. M. Rutten-Keulemans), scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974), function minimized was $\sum w(\Delta F)^2$ [with $w = (\sigma_F)^{-2}$, the standard deviation in F_o, and $\Delta F = |F_o| - |F_c|$ with $F_c = \{(1-\alpha)F_c^2[x_i] + \alpha F_c^2[x_i']\}^{\frac{1}{2}}$].

Individual isotropic full-matrix refinement of the Zn, Cl and N atoms converged to $R = 11{\cdot}0\%$ and $R_w = 11{\cdot}9\%$ for 3875 reflections. The twin factor was $\alpha = 0{\cdot}059$ (4). Inspection of the correlation matrix showed the strongest correlations (up to 0·93) between the parameters of Zn and Cl in the tetrahedra (numbered by the Zn index) 1 and 7, 2 and 8, 3 and 6, and 4 and 5 and between the y parameters of pairs of N atoms. Blocked full-matrix refinement, with the Zn(1)-, Zn(3)-, Zn(6)- and Zn(7)$\mathrm{Cl_4}$ tetrahedra in block 1, the remaining $\mathrm{ZnCl_4}$ tetrahedra in block 2 and the N atoms in block 3, and anisotropic temperature factors for Zn and Cl resulted in $R = 3{\cdot}4\%$ and $R_w = 3{\cdot}8\%$ for 3576 reflections with $I > 2\sigma(I)$. The twin factor was 0·034 (2). The R_w factor for the enantiomeric structure at this point was 4·1%. The value of 3·8% is significantly lower and thereby confirms the correctness of the structure as well as the enantiomorph chosen. A difference Fourier synthesis gave indications where protons might be located. These positions were idealized (N—H = 0·94 Å; H—N—H = 109·46°). H atoms were assigned the fixed isotropic thermal parameters of the attached N atoms; in further refinement cycles a riding model was employed. Anisotropic refinement of the N atoms resulted in a non-positive-definite value of the temperature factor for N(7) and N(13). This may be caused by errors in the absorption correction due to non-sphericity of the crystal. It was decided to refine the N atoms isotropically in the last cycles. The final unweighted and weighted R indices are $R = 3{\cdot}5$ and $R_w = 3{\cdot}6\%$ for the 3875 reflections only and $R = 9{\cdot}6$ and $R_w = 4{\cdot}0\%$ for all 8084 reflections. The final twin-factor is 0·033 (1) for both refinements. This value agrees closely with the above-predicted value of at least 0·025 (3) (see Table 2).

Discussion. All crystals measured exhibit twinning by pseudomerohedry with obliquity (within an error of 0·02°) equal to zero (Catti & Ferraris, 1976). The twinning ranges from a small amount to nearly equal fractions of the individual crystals in the twin. Attempts to observe the domain structure with a polarization microscope failed. However, the observed linear relationship between Q and α implies that the domains must be larger than the mosaic blocks. The observed large spread of α for different crystals points to an even more macroscopic size of the domains. Because of the rather high value of $\bar{\alpha}$ (see Table 2), the apparent *mmm* diffraction symmetry in the *Mi* crystal makes it plausible that an erroneous space group has been determined for that crystal.

A projection of the structure along the *a* axis and the labelling of the atoms are given in Fig. 2. The final atomic parameters of the non-hydrogen atoms are listed in Table 3. Interatomic distances and angles involving the heavy atoms are given in Table 4.* A comparison with the structural data, published by Mikhail (1980), on the same room-temperature phase (II) and with the data published by Alexandrov, Kruglik & Misul (1981) and very recently by Matsunaga, Itoh &

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* There is a misprint in the z value of Cl(5); the correct value seems to be $z = 1{\cdot}1223$.

† In our case: $\alpha_1 = \alpha$; $\alpha_2 = 1 - \alpha$ (or α_1, α_2 interchanged depending on which twin mate is predominant).

* Lists of structure factors, anisotropic thermal parameters, H-atom positional parameters and N—Cl distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38102 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Nakamura (1982), both on the low-temperature phase (III), is given in Table 5. The improvement of the structure reported here compared to the structure given by Mikhail is evident.*

The crystal consists of rows of $ZnCl_4$ tetrahedra and NH_4^+ ions. In each row there is a pseudotranslation of $\frac{1}{4}\mathbf{c}$. This explains the weakness of all *hkl* reflections for $l = 4n + 2$. In addition there is a non-crystallographic pseudo glide plane perpendicular to **a** with a translation of $(m/8)\mathbf{c}$ (with $m = \pm 1, \pm 3$) between the tetrahedra (numbered by the Zn index) 1 (2) and 3′, 1 (2) and 4′, 3 (4) and 2′ and 3 (4) and 1′, where the primed numbers indicate '*c*-repeated' tetrahedra (see Fig. 1). This non-crystallographic symmetry accounts for the observation that all 0*kl* reflections for $l = 8n + 4$ are weak. Each tetrahedron in one row is related with a tetrahedron in another row by a pseudo diagonal glide plane: 1 with 5, 2 with 6, 3 with 7 and 4 with 8. Apart from the N atoms, the most significant deviations from the pseudo diagonal glide plane are between the Cl atoms bonded to Zn(1) and those to Zn(5). A distance of 0·65 Å, measured along the *y* axis, would exist between the Cl(52) atom and the '*n*-repeated' Cl(12)

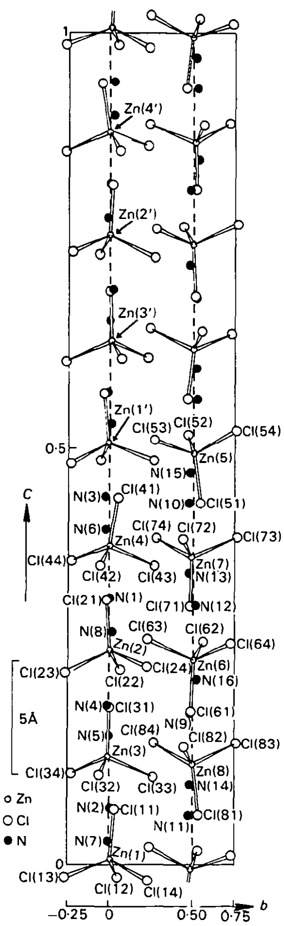

Fig. 2. Projection of the room-temperature structure of $(NH_4)_2[ZnCl_4]$ along the *a* axis.

Table 3. *Positional parameters* ($\times 10^4$) *and equivalent isotropic temperature factors of the non-hydrogen atoms*

$B_{eq} = \frac{8}{3}\pi^2$ trace $\tilde{\mathbf{U}}$. *B* values are given for N atoms.

	x	*y*	*z*	B_{eq}, *B* (Å^2)
Zn(1)	2870	83 (2)	60·0	2·39 (4)
Zn(2)	2856 (1)	7 (2)	2558·2 (4)	2·33 (4)
Zn(3)	6338 (1)	−72 (2)	1302·7 (4)	2·52 (4)
Zn(4)	6351 (1)	11 (2)	3811·6 (4)	2·60 (4)
Zn(5)	7843 (1)	5036 (2)	4938·5 (5)	2·39 (4)
Zn(6)	7860 (1)	5051 (2)	2443·7 (4)	2·39 (4)
Zn(7)	1332 (1)	4900 (2)	3683·5 (2)	2·61 (4)
Zn(8)	1343 (1)	5005 (2)	1195·2 (5)	2·63 (4)
Cl(11)	2976 (3)	360 (6)	667 (1)	4·79 (10)
Cl(12)	1233 (3)	532 (8)	−152 (1)	5·48 (13)
Cl(13)	3465 (4)	−2650 (5)	−148 (1)	5·86 (13)
Cl(14)	3924 (3)	2336 (6)	−187 (1)	5·88 (11)
Cl(21)	2909 (3)	−182 (7)	3166 (1)	6·03 (14)
Cl(22)	1230 (3)	632 (6)	2332 (1)	3·71 (9)
Cl(23)	3398 (3)	−2701 (5)	2295 (1)	3·45 (8)
Cl(24)	3974 (3)	2251 (5)	2370 (1)	4·91 (11)
Cl(31)	6265 (4)	−37 (7)	1890 (1)	5·89 (13)
Cl(32)	7983 (3)	−628 (7)	1082 (1)	5·03 (11)
Cl(33)	5802 (3)	2620 (6)	1055 (1)	4·83 (11)
Cl(34)	5260 (3)	−2283 (5)	1095 (1)	5·14 (12)
Cl(41)	6350 (3)	503 (6)	4400 (1)	4·47 (10)
Cl(42)	7973 (3)	−588 (6)	3585 (1)	4·03 (9)
Cl(43)	5744 (3)	2676 (5)	3537 (1)	3·93 (9)
Cl(44)	5255 (3)	−2294 (5)	3642 (1)	4·60 (10)
Cl(51)	7881 (3)	5429 (7)	4330 (1)	4·89 (11)
Cl(52)	6221 (3)	4642 (7)	5167 (1)	4·87 (10)
Cl(53)	8870 (3)	2647 (6)	5102 (1)	6·03 (12)
Cl(54)	8464 (3)	7609 (5)	5215 (1)	4·74 (11)
Cl(61)	7911 (3)	4926 (7)	1830 (1)	6·41 (16)
Cl(62)	6220 (2)	5628 (6)	2661 (1)	3·53 (9)
Cl(63)	8405 (3)	2348 (5)	2694 (1)	4·04 (10)
Cl(64)	8990 (3)	7266 (6)	2642 (1)	5·03 (11)
Cl(71)	1301 (3)	4848 (7)	3091 (1)	5·81 (13)
Cl(72)	2984 (3)	4384 (6)	3905 (1)	4·40 (10)
Cl(73)	812 (3)	7643 (6)	3911 (1)	4·51 (10)
Cl(74)	220 (3)	2810 (6)	3914 (1)	4·77 (9)
Cl(81)	1285 (3)	5342 (6)	603 (1)	5·24 (11)
Cl(82)	2992 (3)	4493 (7)	1410 (1)	4·62 (11)
Cl(83)	754 (3)	7628 (6)	1456 (1)	4·97 (11)
Cl(84)	268 (3)	2703 (6)	1380 (1)	5·38 (12)
N(1)	386 (7)	58 (12)	3179 (2)	3·4 (2)
N(2)	338 (7)	109 (11)	681 (2)	3·0 (2)
N(3)	8920 (7)	−282 (14)	4410 (3)	3·1 (2)
N(4)	8886 (7)	−192 (12)	1912 (2)	3·6 (2)
N(5)	3003 (7)	−22 (13)	1544 (3)	4·3 (2)
N(6)	3058 (9)	−245 (16)	4016 (3)	6·1 (4)
N(7)	6085 (7)	−96 (12)	296 (2)	3·8 (2)
N(8)	5920 (6)	163 (9)	2781 (2)	3·6 (2)
N(9)	5342 (6)	4856 (11)	1815 (2)	2·9 (2)
N(10)	5236 (7)	4744 (14)	4333 (3)	3·0 (2)
N(11)	4004 (6)	4720 (11)	591 (2)	2·4 (2)
N(12)	3907 (7)	5200 (12)	3093 (2)	3·2 (2)
N(13)	8038 (7)	4712 (13)	3478 (3)	4·5 (2)
N(14)	7902 (6)	4860 (9)	963 (2)	3·7 (2)
N(15)	1025 (7)	4806 (13)	4697 (3)	4·0 (2)
N(16)	1017 (7)	5266 (13)	2215 (3)	4·3 (2)

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* *Note added in proof:* Very recently Matsunaga (1982) also concluded that the space group was *Pc* at room temperature. The possibility of twinning, however, was not mentioned. He kindly provided me with the F_o values of the reflections used in Fig. 1. The ensuing value of $\bar{\alpha}$ in his crystal is 0·034. The remarkable short average Zn(1)—Cl and Zn(4)—Cl distances he found were not observed in my analysis and might be caused by neglecting the twinning.

atom. This explains the anomalous B_{22} value* of 35·6 Å^2 for Cl(2) reported by Mikhail (1980). The pseudo glide planes, described above, and the *c* glide plane induce pseudo inversion centres. This may explain the strong correlations observed during the refinement.

This discussion is a reminder to regard with caution unexpected geometrical results and anomalous temperature factors.

A detailed comparsion of the modulation parameters in $(NH_4)_2[ZnCl_4]$ with those in other $A_2[ZnX_4]$-type structures [A = K, Rb, $N(CH_3)_4$; X = Cl, Br] will appear in the near future as part of a thesis of A. C. R. Hogervorst from our laboratory.

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Table 4. *Bond lengths* (Å) *and angles* (°) *in the* $ZnCl_4$ *tetrahedra*

Average e.s.d.'s: Zn—Cl: 0·004 Å, Cl—Zn—Cl: 0·2°.

Zn(1)—Cl(11)	2·264	Cl(11)—Zn(1)—Cl(12)	113·1
—Cl(12)	2·234	Cl(11)—Zn(1)—Cl(13)	113·5
—Cl(13)	2·246	Cl(11)—Zn(1)—Cl(14)	107·5
—Cl(14)	2·291	Cl(12)—Zn(1)—Cl(13)	108·4
		Cl(12)—Zn(1)—Cl(14)	107·0
		Cl(13)—Zn(1)—Cl(14)	106·9
Zn(2)—Cl(21)	2·260	Cl(21)—Zn(2)—Cl(22)	114·1
—Cl(22)	2·262	Cl(21)—Zn(2)—Cl(23)	111·5
—Cl(23)	2·288	Cl(21)—Zn(2)—Cl(24)	109·5
—Cl(24)	2·257	Cl(22)—Zn(2)—Cl(23)	106·5
		Cl(22)—Zn(2)—Cl(24)	108·0
		Cl(23)—Zn(2)—Cl(24)	107·0
Zn(3)—Cl(31)	2·182	Cl(31)—Zn(3)—Cl(32)	113·7
—Cl(32)	2·267	Cl(31)—Zn(3)—Cl(33)	112·7
—Cl(33)	2·251	Cl(31)—Zn(3)—Cl(34)	109·1
—Cl(34)	2·234	Cl(32)—Zn(3)—Cl(33)	106·3
		Cl(32)—Zn(3)—Cl(34)	107·9
		Cl(33)—Zn(3)—Cl(34)	106·9
Zn(4)—Cl(41)	2·211	Cl(41)—Zn(4)—Cl(42)	113·5
—Cl(42)	2·254	Cl(41)—Zn(4)—Cl(43)	107·6
—Cl(43)	2·306	Cl(41)—Zn(4)—Cl(44)	113·2
—Cl(44)	2·251	Cl(42)—Zn(4)—Cl(43)	107·2
		Cl(42)—Zn(4)—Cl(44)	108·2
		Cl(43)—Zn(4)—Cl(44)	106·7
Zn(5)—Cl(51)	2·277	Cl(51)—Zn(5)—Cl(52)	114·3
—Cl(52)	2·235	Cl(51)—Zn(5)—Cl(53)	110·6
—Cl(53)	2·239	Cl(51)—Zn(5)—Cl(54)	109·9
—Cl(54)	2·260	Cl(52)—Zn(5)—Cl(53)	109·3
		Cl(52)—Zn(5)—Cl(54)	104·5
		Cl(53)—Zn(5)—Cl(54)	108·0
Zn(6)—Cl(61)	2·278	Cl(61)—Zn(6)—Cl(62)	112·9
—Cl(62)	2·260	Cl(61)—Zn(6)—Cl(63)	111·5
—Cl(63)	2·265	Cl(61)—Zn(6)—Cl(64)	109·5
—Cl(64)	2·264	Cl(62)—Zn(6)—Cl(63)	106·9
		Cl(62)—Zn(6)—Cl(64)	109·4
		Cl(63)—Zn(6)—Cl(64)	106·4
Zn(7)—Cl(71)	2·200	Cl(71)—Zn(7)—Cl(72)	112·1
—Cl(72)	2·273	Cl(71)—Zn(7)—Cl(73)	112·7
—Cl(73)	2·248	Cl(71)—Zn(7)—Cl(74)	111·1
—Cl(74)	2·229	Cl(72)—Zn(7)—Cl(73)	106·0
		Cl(72)—Zn(7)—Cl(74)	109·1
		Cl(73)—Zn(7)—Cl(74)	105·5
Zn(8)—Cl(81)	2·211	Cl(81)—Zn(8)—Cl(82)	113·5
—Cl(82)	2·258	Cl(81)—Zn(8)—Cl(83)	108·8
—Cl(83)	2·251	Cl(81)—Zn(8)—Cl(84)	111·3
—Cl(84)	2·250	Cl(82)—Zn(8)—Cl(83)	106·9
		Cl(82)—Zn(8)—Cl(84)	109·1
		Cl(83)—Zn(8)—Cl(84)	106·8

Table 5. *Comparison of structural data of* $(NH_4)_2[ZnCl_4]$ *as published by different authors*

	Phase (III)		Phase (II)	
	Alexandrov *et al.* (1981)	Matsunaga *et al.* (1982)	Mikhail (1980)	This report
Space group	$Pc2_1n$	$Pc2_1n$	$P2_1cn$	Pc
Z	12	12	16	16
a (Å)	12·568	12·568	12·643	12·620
b (Å)	7·179	7·184	7·221	7·211
c (Å)	27·838	27·838	37·172	37·098
β (°)				90·00
Range of Zn—Cl distances (Å)	2·222—2·298	2·230—2·299	2·11—2·40	2·182—2·306
Range of Zn—Cl angles (°)	104·6—114·8	105·8—114·8	104·2—117·6	104·5—114·3
Range of max. differences in Zn—Cl distances in each tetrahedron (Å) (mean value)	0·012—0·065 (0·045)	0·035—0·055 (0·043)	0·065—0·234 (0·159)	0·018—0·095 (0·056)
Range of max. differences in Cl—Zn—Cl angles in each tetrahedron	8·0—10·2	7·6—8·7	4·7—13·1	6·5—9·8

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* The thermal parameters deposited are undoubtedly values of *B* and not of *β*, as they are called.