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## References

ANDERSSON, S. & HYDE, B. G. (1974). *J. Solid State Chem.* **9**, 92–101.

CHEVREL, R., SERGENT, M., SEEBER, B., FISCHER, Ø., GRÜTTNER, A. & YVON, K. (1979). *Mater. Res. Bull.* **14**, 567–577.

FISCHER, Ø. (1978). *Appl. Phys.* **16**, 1–28.

GRÜTTNER, A., YVON, K., CHEVREL, M., POTEL, M., SERGENT, M. & SEEBER, B. (1979). *Acta Cryst.* B**35**, 285–292.

HÖNLE, W., VON SCHNERING, H. G., LIPKA, A. & YVON, K. (1980). *J. Less-Common Met.* In the press.

*International Tables for X-ray Crystallography* (1969). Vol. I, 3rd ed. Birmingham: Kynoch Press.

KLEPP, K. & BOLLER, H. (1979). *Monatsh. Chem.* **110**, 677–684.

MAREZIO, M., DERNIER, P. D., REMEIKA, J. P., CORENZWIT, E. & MATTHIAS, B. T. (1973). *Mater. Res. Bull.* **8**, 657–668.

POTEL, M., CHEVREL, R., SERGENT, M., DECROUX, M. & FISCHER, Ø. (1979). *C. R. Acad. Sci. Sér. C*, **288**, 429–432.

SEEBER, B., DECROUX, M., FISCHER, Ø., CHEVREL, R., SERGENT, M. & GRÜTTNER, A. (1979). *Solid State Commun.* **29**, 419–423.

YVON, K. (1978). *Solid State Commun.* **25**, 327–331.

YVON, K. (1979). *Current Topics in Materials Science*, Vol. 3, ch. 2, edited by E. KALDIS. Amsterdam: North-Holland.

YVON, K. & PAOLI, A. (1977). *Solid State Commun.* **24**, 41–45.

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# Structure of Ammonium Tetrachlorozincate(II)

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**Abstract.** $(NH_4)_2[ZnCl_4]$, orthorhombic, $Pna2_1$, $Z = 16$, $a = 37{\cdot}172$ (3), $b = 7{\cdot}221$ (3), $c = 12{\cdot}643$ (4) Å, $\rho$(calc) = 1·904 Mg m$^{-3}$. The structure was solved by direct methods and refined by least squares ($R = 0{\cdot}057$) with 1452 reflections measured on an automatic four-circle diffractometer (Mo $K\alpha$ radiation). It consists of isolated $ZnCl_4$ tetrahedra connected by $NH_4$ groups which exhibit a wide range of coordination numbers and geometries.

**Introduction.** Since X-ray diffraction patterns taken for $A_2[ZnCl_4]$, where $A$ = Cs, Rb, K and $NH_4$, exhibit pronounced differences (Jacobi, 1970), the information available on the isostructural Co compound (Vermin, Verschoor & IJdo, 1976) and $K_2[ZnCl_4]$ is insufficient to allow a detailed comparison between the members of the series. We felt it appropriate to undertake a complete crystal structure analysis of $(NH_4)_2[ZnCl_4]$, in order to confirm the characterization of the anion and to study further the physical properties of these compounds.

Clear, colourless crystals were obtained by slow evaporation of an aqueous solution of $NH_4Cl$ and $ZnCl_2$ in the ratio 2:1. Since they are deliquescent, the freshly prepared crystals were enclosed in thin-walled capillaries. Preliminary X-ray photographs showed additional reflexions corresponding to a cell with a quadruple $a$ axis, while those at $h = \pm 0{\cdot}5$ are completely absent. This investigation differs from that of $K_2[ZnCl_4]$ (Mikhail & Peters, 1979) in which satellite reflections at $a = \pm\frac{1}{3}$ occur.

A crystal of dimensions 0·16 × 0·20 × 0·18 mm was optically centred on a Syntex $P1$ four-circle diffractometer. The orientation matrix and the cell parameters were determined on the basis of 15 reflections.

The linear absorption coefficient $\mu$ for Mo $K\alpha$ radiation was calculated to be 4·12 $\mu$m$^{-1}$.

The intensities of 1736 *hkl* reflections were measured according to the $\omega$-scan technique (Mo $K\alpha$, graphite monochromator) using a scan range of 1° and a scan speed between 0·5 and 24·0° min$^{-1}$ depending on the intensity of the measured reflections. In the range $3{\cdot}0° < 2\theta < 55{\cdot}0°$, 1452 *hkl* reflections with $I > 1{\cdot}96(I)$ were obtained for the structure refinement. For the evaluation, the *XTL* system (Syntex, Nova 1200) was employed. An absorption correction was applied to all intensities, based on $\Psi$-scan measurement.

The structure was solved by the direct method with the *MULTAN* program system (Germain, Main &

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Woolfson, 1971). The phases of 320 reflections were determined and on the resulting $E$ map approximate positions of the Zn atoms could be determined. A three-dimensional Fourier synthesis gave the coordinates of the Cl and K atoms and improved the coordinates for the Zn atoms. The parameters of the complete structure were refined by least squares to $R = 0{\cdot}109$. Further refinement with anisotropic thermal parameters yielded final index values of 0·057 and 0·072 for $R$ and $R_w$ respectively; $R = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$, $R_w = \sum w^{1/2}(\lvert F_o\rvert - \lvert F_c\rvert)/\sum w^{1/2}F_o$, where $w = 1/\sigma^2$.*

The final atomic parameters and their estimated standard deviations are listed in Table 1. The corresponding bond lengths and angles are given in Table 2.

Table 1. *Final atomic coordinates* ($\times 10^4$)

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| Zn(1) | 62 (2) | 7557 (6) | 7871 |
| Zn(2) | 2444 (2) | 2549 (6) | 12888 (3) |
| Zn(3) | −1308 (3) | 2576 (6) | 6391 (1) |
| Zn(4) | 1190 (3) | 2527 (6) | 6338 (1) |
| Cl(1) | 665 (4) | 7870 (1) | 7968 (8) |
| Cl(2) | −189 (6) | 7702 (6) | 6272 (7) |
| Cl(3) | −138 (4) | 4961 (3) | 8652 (4) |
| Cl(4) | −173 (4) | 9811 (4) | 8721 (5) |
| Cl(5) | 2669 (4) | 3286 (8) | 12223 (4) |
| Cl(6) | −1850 (5) | 7607 (8) | 7896 (9) |
| Cl(7) | 2299 (4) | 4781 (9) | 8427 (5) |
| Cl(8) | 2377 (5) | −381 (3) | 8945 (4) |
| Cl(9) | −1913 (6) | 2560 (3) | 6233 (4) |
| Cl(10) | 1103 (4) | 7086 (8) | 2988 (4) |
| Cl(11) | 1084 (4) | 90 (1) | 10857 (5) |
| Cl(12) | 1072 (4) | 5106 (1) | 10221 (3) |
| Cl(13) | 594 (4) | 2985 (4) | 6381 (1) |
| Cl(14) | 1420 (4) | 1970 (1) | 8002 (4) |
| Cl(15) | 1473 (3) | 5207 (7) | 5804 (4) |
| Cl(16) | 1357 (4) | 10219 (1) | 5206 (4) |
| N(1) | 1849 (4) | 2668 (3) | 10357 (2) |
| N(2) | 643 (9) | 7280 (5) | 5330 (9) |
| N(3) | −951 (9) | 7375 (2) | 7948 (2) |
| N(4) | 1609 (1) | 7896 (4) | 8057 (7) |
| N(5) | 527 (7) | 2371 (4) | 8925 (9) |
| N(6) | 1938 (3) | 7478 (5) | 3988 (8) |
| N(7) | 2218 (8) | 3122 (7) | 6140 (2) |
| N(8) | −281 (9) | 2606 (7) | 5954 (4) |

Table 2. *Interatomic distances* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| Zn(1)–Cl(1) | 2·253 (17) | Zn(3)–Cl(9) | 2·26 (2) |
| –Cl(2) | 2·23 (2) | –Cl(10) | 2·17 (2) |
| –Cl(3) | 2·250 (18) | –Cl(11) | 2·202 (17) |
| –Cl(4) | 2·138 (19) | –Cl(12) | 2·404 (18) |
| Zn(2)–Cl(5) | 2·33 (2) | Zn(4)–Cl(13) | 2·24 (2) |
| –Cl(6) | 2·211 (19) | –Cl(14) | 2·30 (2) |
| –Cl(7) | 2·317 (16) | –Cl(15) | 2·305 (14) |
| –Cl(8) | 2·11 (2) | –Cl(16) | 2·283 (18) |
| N(1)–Cl(5) | 3·29 (6) | N(5)–Cl(1) | 3·50 (5) |
| –Cl(6) | 3·24 (5) | –Cl(2) | 3·23 (7) |
| –Cl(7) | 3·32 (56) | –Cl(3) | 3·12 (6) |
| –Cl(8) | 3·45 (5) | –Cl(4) | 3·20 (6) |
| –Cl(11) | 3·45 (5) | –Cl(11) | 3·61 (7) |
| –Cl(12) | 3·38 (5) | –Cl(12) | 3·28 (6) |
| –Cl(14) | 3·40 (5) | –Cl(13) | 3·24 (8) |
| | | –Cl(14) | 3·53 (6) |
| N(2)–Cl(1) | 3·38 (5) | N(6)–Cl(5) | 3·23 (5) |
| –Cl(2) | 3·31 (5) | –Cl(7) | 3·35 (4) |
| –Cl(3) | 3·24 (5) | –Cl(8) | 3·28 (4) |
| –Cl(4) | 3·39 (4) | –Cl(9) | 3·48 (6) |
| –Cl(10) | 3·42 (5) | –Cl(10) | 3·37 (4) |
| –Cl(13) | 3·39 (4) | –Cl(15) | 3·32 (4) |
| –Cl(15) | 3·50 (5) | –Cl(16) | 3·31 (4) |
| –Cl(16) | 3·41 (4) | | |
| N(3)–Cl(2) | 3·55 (4) | N(7)–Cl(5) | 3·53 (3) |
| –Cl(3) | 3·60 (4) | –Cl(7) | 3·14 (4) |
| –Cl(4) | 3·52 (4) | –Cl(8) | 3·33 (4) |
| –Cl(6) | 3·35 (4) | –Cl(9) | 3·27 (3) |
| –Cl(10) | 3·27 (3) | –Cl(15) | 3·18 (3) |
| –Cl(11) | 3·25 (4) | | |
| N(4)–Cl(1) | 3·51 (8) | N(8)–Cl(2) | 3·58 (3) |
| –Cl(5) | 3·58 (8) | –Cl(2) | 3·65 (3) |
| –Cl(7) | 3·43 (8) | –Cl(11) | 3·56 (4) |
| –Cl(8) | 3·31 (8) | –Cl(12) | 3·50 (4) |
| –Cl(14) | 3·05 (7) | –Cl(13) | 3·32 (4) |
| –Cl(15) | 3·50 (7) | | |
| Cl(1)–Zn(1)–Cl(2) | 117·6 (8) | Cl(9)–Zn(3)–Cl(10) | 115·5 (8) |
| Cl(1)–Zn(1)–Cl(3) | 112·9 (7) | Cl(9)–Zn(3)–Cl(11) | 110·3 (8) |
| Cl(1)–Zn(1)–Cl(4) | 107·4 (8) | Cl(9)–Zn(3)–Cl(12) | 108·3 (8) |
| Cl(2)–Zn(1)–Cl(3) | 107·5 (7) | Cl(10)–Zn(3)–Cl(11) | 104·5 (7) |
| Cl(2)–Zn(1)–Cl(4) | 104·5 (8) | Cl(10)–Zn(3)–Cl(12) | 111·5 (7) |
| Cl(3)–Zn(1)–Cl(4) | 106·1 (7) | Cl(11)–Zn(3)–Cl(12) | 106·4 (7) |
| Cl(5)–Zn(2)–Cl(6) | 112·0 (8) | Cl(13)–Zn(4)–Cl(14) | 111·7 (8) |
| Cl(5)–Zn(2)–Cl(7) | 108·3 (7) | Cl(13)–Zn(4)–Cl(15) | 109·7 (7) |
| Cl(5)–Zn(2)–Cl(8) | 107·4 (8) | Cl(13)–Zn(4)–Cl(16) | 112·9 (8) |
| Cl(6)–Zn(2)–Cl(7) | 111·4 (8) | Cl(14)–Zn(4)–Cl(15) | 104·2 (7) |
| Cl(6)–Zn(2)–Cl(8) | 110·3 (8) | Cl(14)–Zn(4)–Cl(16) | 110·1 (7) |
| Cl(7)–Zn(2)–Cl(8) | 107·3 (8) | Cl(15)–Zn(4)–Cl(16) | 107·8 (7) |

**Discussion.** The structure is shown in Fig. 1. It consists of isolated $ZnCl_4$ tetrahedra connected by ammonium groups. The structure of this series can also be related to certain silicates in which the anions form isolated tetrahedra. The values of the Zn–Cl distances found here are closely comparable with those observed in $Li_2[ZnCl_4].2H_2O$ (Jacobi & Brehler, 1969), $Li[ZnCl_3].3H_2O$ (Jacobi, 1969), $ZnCl_2.\frac{4}{3}H_2O$ (Follner & Brehler, 1970) and $K_2[ZnCl_4]$ (Mikhail & Peters, 1979).

Participation of Cl atoms in hydrogen bonds with the protons of $NH_4^+$ contributes to the distortion from tetrahedral symmetry about the Zn atom and to the differences in the Zn–Cl bond lengths. The N–Cl distances range from 3·047 to 3·648 Å (average 3·374 Å). Such changes in N–Cl distances appear to arise partly because of the specific packing forces in the crystal and partly because of the different orientations of the $ZnCl_4$ tetrahedra. The N–Cl coordination varies from five to eight; the coordination polyhedron is a distorted trigonal bipyramid for fivefold coordination, a distorted octahedron for sixfold coordination, a distorted pentagonal bipyramid or irregular for sevenfold coordination and a distorted square antiprism for

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35278 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

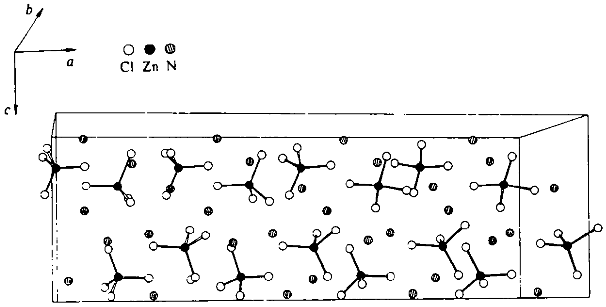

Fig. 1. Arrangement of the atoms viewed along the *b* axis.

eightfold coordination. With the Zn—Cl tetrahedra the 5 and 7 polyhedra share one face, one vertex and two edges and the 6 and 8 polyhedra share two vertices and two edges.

The main structural differences between the $K^+$ and $NH_4^+$ compounds lie in the details of the coordination about the cation. Even though the differences in the details of coordination mean that $(NH_4)_2[ZnCl_4]$ cannot be considered strictly isostructural with $K_2[ZnCl_4]$ and its isotypes, the similarities in coordination and in the basic arrangement of the structural elements are greater than those necessarily implied by the term 'isopuntal'.

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### References

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

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Jacobi, H. (1969). *Naturwissenschaften*, **56**, 368.

Jacobi, H. (1970). *Z. Kristallogr.* **129**, 434–435.

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

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

Vermin, W. J., Verschoor, G. C. & IJdo, D. J. W. (1976). *Acta Cryst.* B**32**, 3325–3328.

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# Structure of a Lead Apatite $Pb_9(PO_4)_6$

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**Abstract.** $Pb_9(PO_4)_6$, hexagonal, $P6_3/m$, $a = 9{\cdot}826$ (4), $c = 7{\cdot}357$ (3) Å, $Z = 1$. Crystals were grown from the melt of a product prepared by a hydrothermal reaction of $Pb(CH_3COO)_2.3H_2O$ and $K_2HPO_4$ at 473 K. Structure refinement was carried out by the full-matrix least-squares method to $R = 0{\cdot}043$ with 490 independent X-ray reflection data. This crystal is of an apatite structure type and is deficient in Pb at the Pb(1) site, with the OH group missing.

**Introduction.** Several reports exist on compounds of the lead apatite group. Bhatnagar (1971) synthesized $Pb_9(PO_4)_6$ and $Pb_{10}(PO_4)_6X_2$ ($X$ = OH, F, Cl), and independently Engel (1973) precipitated $Pb_{10}(OH)_2(PO_4)_6$, $Pb_{10}O(PO_4)_6$ and $Pb_8M_2(PO_4)_6$ ($M$ = Na, K, Rb, Tl). Brixner, Bierstedt, Jeap & Barkley (1973) reported on the ferroelastic phase transition of monoclinic $\alpha$-$Pb_3(PO_4)_2$ to hexagonal $\beta$-$Pb_3(PO_4)_2$.

In the course of our series of studies on apatite group compounds we obtained single crystals of $Pb_9(PO_4)_6$ and determined its crystal structure.

Powdery lead hydroxyapatite was prepared by a hydrothermal reaction of $Pb(CH_3COO)_2.3H_2O$ and $K_2HPO_4$ at 473 K for 1 week. This hydroxyapatite was fused at 1363 K and cooled to room temperature, yielding single crystals of a lead phosphate. The crystals are transparent, pale yellow in colour and prismatic in shape with diameters of 0·1–0·2 mm and lengths of 0·2–0·8 mm.

The product was identified to be an apatite from the

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