Acta Cryst. (1977). B**33**, 259–260

Ammonium Dilead Chloride

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(*Received* 23 *July* 1976; *accepted* 20 *August* 1976)

Abstract. $NH_4Pb_2Cl_5$, monoclinic, $P2_1/c$, $a = 9{\cdot}018$ (3), $b = 7{\cdot}981$ (6), $c = 12{\cdot}502$ (4)Å, $\beta = 90{\cdot}09$ (2)°, $Z = 4$, $D_c = 4{\cdot}50$ g cm^{-3}. $NH_4Pb_2Cl_5$ adopts the same structure as PbU_2Se_5. This structure could be assigned to a number of other halides in the series AB_2X_5 with A = K, Rb, Tl or NH_4; B = Pb or Sr and X = Cl or Br.

Introduction. Jansen (1968) reported the unit-cell dimensions of a series of compounds AB_2X_5, with A = K, Rb or NH_4; B = Pb or Sr and X = Cl or Br. In this series a tetragonal modification with $I4/mcm$ symmetry occurs (Powell & Tasker, 1937) which is an ordered version of the Cr_5B_3 (*anti*-) type structure (Bertaut & Blum, 1953). The other modification gave powder X-ray diagrams which could be indexed on the basis of an orthorhombic unit cell (Jansen, 1968). The systematic extinctions $hk0$: $h = 2n$ and $00l$: $l = 2n$, however, do not fit an orthorhombic space group. The lattice constants of this modification are comparable with those of U_3Se_5 (Moseley, Brown & Whittaker, 1972), if the difference between the ionic radii of Se^{2-}, and Cl^- and Br^- is taken into account. Cation substitutions in the U_3Se_5 structure lead to a structure with *Pnma* symmetry (Jeitschko & Donohue, 1975) and to one with $P2_1/c$ symmetry (Potel, Brochu & Padiou, 1975). In order to distinguish between the two possibilities it is sufficient to look for the occurrence of reflexions $0kl$: $k + l = 2n + 1$, which are forbidden in *Pnma*. In this way $P2_1/c$ symmetry could be assigned to this modification.

A single crystal prepared by Jansen from an aqueous solution of NH_4Cl and $PbCl_2$ was used for determining the structure. The crystal was approximately rectangular with dimensions 27 × 24 × 138 μm. It was mounted along its c axis on an Enraf–Nonius three-circle single-crystal diffractometer. The precise unit-cell parameters were determined on a single-crystal diffractometer at 20 °C, with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å).

Intensities were recorded by the θ–2θ scan method for all reflexions between 5 and 35° with positive and negative h. Monochromatic (graphite) Mo $K\alpha$ radiation was used for measuring intensities. Background intensities were determined at $\theta \pm \frac{1}{2}\Delta$ with $\Delta = 0{\cdot}45 + 0{\cdot}5 \tan\theta$; 3347 reflexions were measured. The standard deviations, $\sigma(I)$, were calculated from counting statistics. Nearly half the reflexions had $I < 2\sigma(I)$ and were considered non-significant. Absorption corrections were applied with a computer program written by de Graaff (1973). The transmission factors ranged between 0·37 and 0·46 ($\mu = 380$ cm^{-1}). Together with the absorption corrections new standard deviations were computed, taking into account the inaccuracy of the absorption correction and the attenuation factors, leaving 1835 independent observed reflexions.

The intensities were reduced to F values and a Wilson (1942) plot was calculated, yielding approximate values for the scale factor and the initial overall isotropic thermal parameter B.

All crystallographic calculations were carried out on the Leiden University IBM 370/158 computer, with a set of computer programs written or modified by Rutten-Keulemans and de Graaff. Atomic scattering

Table 1. *Positional parameters* (× 10^4) (*space group* $P2_1/c$) *and thermal parameters* (Å^2 × 10^4)

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
NH_4*	60 (16)	594 (21)	8334 (13)						
Pb(1)	4953 (1)	9905 (1)	1744 (1)	256 (4)	277 (5)	239 (5)	−33 (8)	−30 (9)	−38 (7)
Pb(2)	2490 (1)	9365 (1)	4937 (1)	189 (4)	239 (4)	256 (6)	−20 (8)	29 (9)	−40 (6)
Cl(1)	397 (7)	3230 (8)	779 (6)	241 (27)	275 (30)	477 (42)	−34 (47)	216 (59)	−58 (52)
Cl(2)	4580 (7)	3344 (7)	948 (5)	315 (30)	207 (28)	347 (37)	15 (46)	148 (50)	−54 (51)
Cl(3)	2775 (8)	1544 (9)	3120 (5)	465 (37)	355 (37)	269 (39)	273 (59)	96 (56)	148 (56)
Cl(4)	2838 (6)	5423 (7)	4990 (5)	236 (25)	273 (30)	219 (33)	59 (40)	−24 (45)	−69 (43)
Cl(5)	2715 (7)	6857 (8)	2197 (5)	283 (29)	322 (31)	306 (37)	47 (50)	110 (56)	−74 (49)

* NH_4 has an isotropic temperature factor of 0·7 (2) Å^2.

factors for N, H, Pb and Cl were taken from Cromer & Mann (1968) and used after correction for the real part of the anomalous dispersion $\Delta f'$. The function minimized during the least-squares refinement was $\Sigma\, w_F(|F_o| - |F_c|)^2$, with the weighting scheme $w_F = 1/\sigma^2_F$. The starting positional parameters were derived from the U_3Se_5 structure. A three-dimensional Patterson synthesis proved this to be the correct model.

A few cycles of full-matrix refinement of positional parameters and individual anisotropic thermal parameters, for all atoms except H, led to convergence at $R_F = \Sigma\, ||F_o| - |F_c|| / \Sigma F_o = 0{\cdot}0796$ and $R_{wF} = [w(|F_o| - |F_c|)^2/\Sigma\, wF_o^2]^{1/2} = 0{\cdot}0714$. Introduction of the imaginary part of the anomalous dispersion of Mo $K\alpha$ for the Pb atoms led to $R_F = 0{\cdot}0783$ and $R_{wF} = 0{\cdot}0696$.

At this stage an extinction correction (Zachariasen, 1967) was applied. This led to $R_F = 0{\cdot}0773$ and $R_{wF} = 0{\cdot}0686$. A final difference Fourier synthesis gave no significant peaks. A refinement based on the 1468 strongest reflexions led, after extinction correction, to $R_F = 0{\cdot}0481$ and $R_{wF} = 0{\cdot}0489$. Final positional and thermal parameters are listed in Table 1.*

Table 2. *Interionic distances* (Å)

NH_4–Cl(1)	3·27 (2)	Pb(1)–Cl(4)	2·975 (9)
NH_4–Cl(1)	3·34 (2)	Pb(1)–Cl(4)	2·915 (9)
NH_4–Cl(3)	3·57 (2)	Pb(1)–Cl(5)	3·21 (1)
NH_4–Cl(3)	3·36 (2)	Pb(1)–Cl(5)	2·93 (1)
NH_4–Cl(4)	3·36 (2)	Pb(2)–Cl(1)	2·90 (1)
NH_4–Cl(4)	3·35 (2)	Pb(2)–Cl(1)	2·89 (1)
NH_4–Cl(5)	3·29 (2)	Pb(2)–Cl(2)	2·98 (1)
NH_4–Cl(5)	3·40 (2)	Pb(2)–Cl(2)	2·91 (1)
Pb(1)–Cl(2)	2·94 (1)	Pb(2)–Cl(3)	2·87 (1)
Pb(1)–Cl(2)	3·17 (1)	Pb(2)–Cl(4)	3·16 (1)
Pb(1)–Cl(3)	2·92 (1)	Pb(2)–Cl(5)	3·00 (1)
Pb(1)–Cl(3)	3·38 (1)		

Discussion. Interionic distances and their estimated standard deviations (e.s.d.'s) are presented in Table 2. Apart from the similarity to the ordered U_3Se_5 structure, as with PbU_2Se_5 (Potel, Brochu & Padiou, 1975), the structure of $NH_4Pb_2Cl_5$ may also be compared with that of $(NH_4)_3ZnCl_5$ (Klug & Alexander, 1944), in which there are tetrahedral holes occupied by additional Zn. It was possible to assign the $NH_4Pb_2Cl_5$ structure to a number of other halides. The lattice constants of these compounds are listed in Table 3. Owing to the slight deviation of the monoclinic angle from 90° it was impossible to determine the magnitude of this deviation on the basis of powder diagrams.

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Table 3. *Lattice constants of compounds* AB_2X_5 (Å)

Compounds with $P2_1/c$ symmetry.

Compound	*a*	*b*	*c*	*β*	Reference
KPb_2Cl_5	8·877	7·939	12·511	90	Jansen (1968)
$RbPb_2Cl_5$	9·002	8·010	12·550	90	
$NH_4Pb_2Cl_5$	9·018 (3)	7·981 (6)	12·502 (4)	90·09 (2)	This work
	9·035	7·967	12·491	90	Jansen (1968)
$TlPb_2Cl_5$	8·950 (4)	7·886 (3)	12·568 (4)	90	This work
KPb_2Br_5	9·265	8·376	13·065	90	Jansen (1968)
$NH_4Pb_2Br_5$	9·394	8·414	13·052	90	
$TlPb_2Br_5$	9·304 (4)	8·336 (3)	13·004 (5)	90	This work
KSr_2Cl_5	8·881	7·855	12·665	90	Jansen (1968)
$RbSr_2Cl_5$	9·011	7·927	12·686	90	
$NH_4Sr_2Cl_5$	9·013	7·897	12·650	90	

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32051 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.