

particulier pour les oxygènes de liaison O(L1) et O(L2). Ceci s'explique par le fait que la forme β que nous étudions est métastable à température ordinaire. Il suffit d'un faible apport d'énergie thermique pour que la structure se réorganise en donnant la forme α . Les valeurs des paramètres d'agitation thermique rendent compte de ce manque de stabilité.

Les ellipsoïdes de vibration de O(L1) et O(L2) sont très étirés. Les axes principaux de plus grande dimension forment des angles de 105° et 92° avec les directions correspondantes. Les valeurs très faibles des distances P–O(L) dans les tétraèdres PO₄ s'expliquent également par le fait que ces oxygènes sont peu localisés.

Par ailleurs, il convient de remarquer que cette structure est totalement originale. En effet, Schultz (1974), a effectué une comparaison entre les paramètres de maille de la forme keatite de la silice ($a = 7,46$, $c = 8,61$ Å, groupe spatial $P4_12_12$) et différents polyphosphates (Be,Zn,Cd). Il pensait que Cd(PO₃)₂ β pouvait avoir une structure dérivée de celle de la keatite par remplacement de cations. Le présent travail montre qu'il n'en est rien: les atomes de cadmium sont en coordination octaédrique et non tétraédrique. Nous avons par ailleurs calculé la fonction de Patterson théorique pour la keatite afin de la comparer à celle de Cd(PO₃)₂ β ; cela met en évidence le fait qu'il n'existe aucune corrélation entre les deux structures, malgré la similitude des paramètres de maille.

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Crystal Structure of [Co(NH₃)₆][Pb₄Cl₁₁], and Relationship with the Chlorolead Structural Moieties in NH₄[Pb₂Cl₅] and PbCl₂

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Abstract

[Co(NH₃)₆][Pb₄Cl₁₁] crystallizes in the monoclinic space group $C2/c$, with $a = 20.658$ (3), $b = 7.762$ (2), $c = 16.171$ (1) Å, $\beta = 114.58$ (1) $^\circ$, and $Z = 4$. The structure has been refined to an R of 0.063 for 2193 observed [$|F_o| > 3\sigma(F_o)$] reflections. Two crystallographically independent Pb atoms are present and show distorted trigonal-prismatic coordination by Cl, with one additional Cl atom above one of the rectangular faces of the prism. The prisms share corners thereby

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Références

- AVERBUCH-POUCHOT, M. T. & DURIF, A. (1972). *Z. Kristallogr.* **135**, 318–319.
- AVERBUCH-POUCHOT, M. T., DURIF, A. & GUITEL, J. C. (1976a). *Acta Cryst.* B32, 1533–1535.
- AVERBUCH-POUCHOT, M. T., DURIF, A. & GUITEL, J. C. (1976b). *Acta Cryst.* B32, 1894–1896.
- AVERBUCH-POUCHOT, M. T., DURIF, A. & TORDJMAN, I. (1973). *Cryst. Struct. Commun.* **2**, 89–90.
- BAGIEU-BEUCHER, M., GUITEL, J. C., TORDJMAN, I. & DURIF, A. (1974). *Bull. Soc. Fr. Minéral. Cristallogr.* **97**, 481–484.
- BEUCHER, M. & GRENIER, J. C. (1968). *Mater. Res. Bull.* **3**, 643–648.
- BEUCHER, M. & TORDJMAN, I. (1968). *Bull. Soc. Fr. Minéral. Cristallogr.* **91**, 207.
- BROWN, J. J. & HUMMEL, F. A. (1964). *J. Electrochem. Soc.* **111**, 660–665.
- LAÜGT, M., BAGIEU-BEUCHER, M. & GRENIER, J. C. (1972). *C. R. Acad. Sci. Sér. C*, **275**, 1283–1285.
- LAÜGT, M., DURIF, A. & AVERBUCH-POUCHOT, M. T. (1973). *Bull. Soc. Fr. Minéral. Cristallogr.* **96**, 383–385.
- LAÜGT, M., GUITEL, J. C., TORDJMAN, I. & BASSI, G. (1972). *Acta Cryst.* B28, 201–208.
- NORD, A. G. & BÖRJE-LINDBERG, K. (1975). *Acta Chem. Scand. Sér. A*, **29**, 1–6.
- PREWITT, C. T. (1966). *SFLS-5*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- SCHULTZ, E. (1974). Dissertation, Kiel.
- TORDJMAN, I., BEUCHER, M., GUITEL, J. C. & BASSI, G. (1968). *Bull. Soc. Fr. Minéral. Cristallogr.* **91**, 344–349.

forming a three-dimensional network, which is held together by [Co(NH₃)₆]³⁺ cations. The anionic moiety and the cations are linked by N–H...Cl bridges. The coordination of Pb by Cl is similar to that in NH₄[Pb₂Cl₅] and PbCl₂.

Introduction

Only a few structures of chloroplumbates(II) have been determined. Two coordination types of Cl atoms

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around Pb are observed: octahedral, in $[\text{Co}(\text{NH}_3)_6]_2[\text{Pb}_2\text{Cl}_{10}]$ (Haupt & Huber, unpublished) or $[\text{Co}(\text{en})_3]_2[\text{Pb}_2\text{Cl}_9]\text{Cl} \cdot 3\text{H}_2\text{O}$ (Haupt & Huber, 1978), and trigonal prismatic in $\text{NH}_4[\text{Pb}_2\text{Cl}_5]$ (Keller, 1976). The last has a smaller Pb:Cl ratio than the first two compounds. A similar coordination of Pb was found in PbCl_2 (Nozik, Fykin & Muradyan, 1976). The present X-ray study was undertaken to determine the structure of $[\text{Co}(\text{NH}_3)_6][\text{Pb}_4\text{Cl}_{11}]$, another chloroplumbate(II) with a low Pb:Cl ratio but with a large cation, and also to compare it with the known structures of chloroplumbates(II) having other Pb:Cl ratios.

Experimental

Suitable red single crystals were obtained by reacting $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and PbCl_2 in aqueous solution (Ephraim & Mosimann, 1923). White crystals of $\text{NH}_4[\text{Pb}_2\text{Cl}_5]$ were prepared from NH_4Cl and PbCl_2 in water (Jansen, 1968). Preliminary precession and Weissenberg photographs of $[\text{Co}(\text{NH}_3)_6][\text{Pb}_4\text{Cl}_{11}]$ indicated a monoclinic lattice with systematic absences (hkl , $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$) consistent with the space groups $C2/c$ and Cc . Since the statistics of the normalized structure factors suggested a space group with a centre of symmetry, $C2/c$ was adopted. The choice was confirmed by the successful structure analysis. A summary of crystal data is given in Table 1. The crystal used for data collection had a plate-like form and dimensions $0.03 \times 0.50 \times 0.20$ mm. The intensity measurements were made on a Hilger &

Table 1. *Crystal data*

Numbers in parentheses here and throughout the paper give the estimated standard deviations on the least significant digits.

$[\text{Co}(\text{NH}_3)_6][\text{Pb}_4\text{Cl}_{11}]$	FW 1379.9
$a = 20.658(3) \text{ \AA}$	Space group $C2/c$
$b = 7.762(2)$	$D_m = 3.91 \text{ Mg m}^{-3}$
$c = 16.171(1)$	$D_c = 3.89$ for $Z = 4$
$\beta = 114.58(1)^\circ$	$\mu(\text{Mo } K\alpha) = 29.267 \text{ mm}^{-1}$
$V = 2358.00 \text{ \AA}^3$	$F(000) = 2400$

Table 3. Pb—Cl distances (\AA) in $[\text{Co}(\text{NH}_3)_6][\text{Pb}_4\text{Cl}_{11}]$, $\text{NH}_4[\text{Pb}_2\text{Cl}_5]$ and PbCl_2

. See Figs. 2 and 3 for numbering of atoms.

	$[\text{Co}(\text{NH}_3)_6][\text{Pb}_4\text{Cl}_{11}]$		$\text{NH}_4[\text{Pb}_2\text{Cl}_5]$		PbCl_2^*
	Pb(1)	Pb(2)	Pb(1)	Pb(2)	
Pb—Cl(1)	2.908 (5)	2.991 (5)	2.911 (7)	2.917 (8)	3.072 (1)
Pb—Cl(2)	3.007 (5)	2.950 (5)	2.918 (9)	2.966 (8)	2.873 (1)
Pb—Cl(3)	2.931 (5)	2.940 (8)	2.940 (8)	2.895 (9)	2.873 (1)
Pb—Cl(4)	2.882 (6)	2.964 (7)	2.964 (7)	2.870 (8)	3.072 (1)
Pb—Cl(5)	2.929 (6)	3.228 (6)	3.158 (6)	2.895 (8)	2.850 (1)
Pb—Cl(6)	3.055 (5)	2.984 (5)	2.922 (7)	2.960 (8)	3.067 (1)
Pb—Cl(7)	3.155 (7)	2.927 (7)	3.217 (8)	3.162 (6)	3.076 (2)

* Calculated from the atomic parameters of Nozik, Fykin & Muradyan (1976).

Watts four-circle diffractometer controlled by a PDP-8I computer (Mo $K\alpha$ radiation, $\lambda = 0.70926 \text{ \AA}$, graphite monochromator and scintillation counter). Cell dimensions and the orientation matrix were determined by least squares from the angular settings of 23 reflections. A complete set of symmetry-independent reflections was collected within the angular range $2 \leq 2\theta \leq 30.8^\circ$ in an $\omega-2\theta$ scan mode with 70 steps [scan width $\Delta 2\theta = (1.34 + 0.34 \text{ tg } \theta)^\circ$ from background to background], an ω step rate of $0.01^\circ \text{ s}^{-1}$ and a 2θ step rate of $0.02^\circ \text{ s}^{-1}$. Backgrounds were measured at each end of the scan range for 7 s. Four standard reflections showed no significant change in intensity. The intensities were corrected for background and then reduced after correction for the Lorentz effect and absorption. Of the 2629 independent reflections measured, 436 were unobserved and not included in the refinement.

Structure determination and refinement

The structure was solved by direct methods with *SHELX* (Sheldrick, 1976). 173 phase relations were generated from eight starting reflections selected by hand, and five *E* maps were calculated. The best of the *E* maps showed the positions of the three heavy atoms: two crystallographically independent Pb atoms in general positions and the Co atom in a special position.

Table 2. *Positional parameters* ($\times 10^4$) for $[\text{Co}(\text{NH}_3)_6][\text{Pb}_4\text{Cl}_{11}]$

	<i>x</i>	<i>y</i>	<i>z</i>
Pb(1)	7524 (1)	-103 (1)	943 (1)
Pb(2)	6493 (1)	-306 (1)	2848 (1)
Cl(1)	0	5243 (11)	2500
Cl(2)	7182 (3)	3716 (6)	536 (3)
Cl(3)	6593 (3)	2172 (6)	4307 (3)
Cl(4)	7425 (3)	2403 (6)	2670 (3)
Cl(5)	5991 (3)	-47 (6)	925 (3)
Cl(6)	1064 (3)	1087 (6)	2907 (3)
Co	5000	5000	0
N(1)	5024 (10)	3425 (15)	950 (8)
N(2)	4037 (3)	4227 (18)	-789 (8)
N(3)	4634 (8)	6824 (13)	536 (10)

Table 4. Cl—Pb—Cl bond angles ($^{\circ}$) in $[\text{Co}(\text{NH}_3)_6][\text{Pb}_4\text{Cl}_{11}]$, $\text{NH}_4[\text{Pb}_2\text{Cl}_5]$ and PbCl_2

See Figs. 2 and 3 for numbering of atoms.

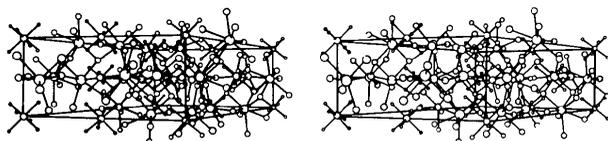
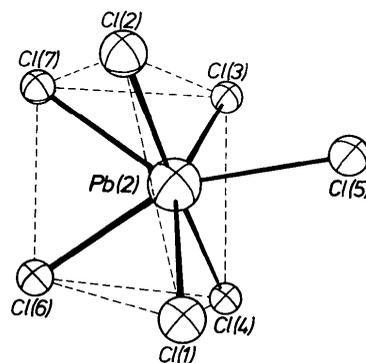
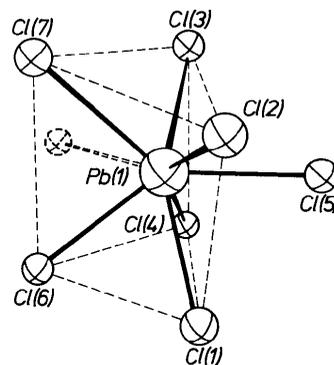
	$[\text{Co}(\text{NH}_3)_6][\text{Pb}_4\text{Cl}_{11}]$		$\text{NH}_4[\text{Pb}_2\text{Cl}_5]$		PbCl_2^*
	Pb(1)	Pb(2)	Pb(1)	Pb(2)	
Cl(1)—Pb—Cl(2)	75.5 (1)	84.8 (2)	92.0 (2)	76.1 (2)	74.38 (3)
Cl(1)—Pb—Cl(3)	157.0 (2)	139.2 (2)	149.0 (2)	155.9 (2)	152.25 (4)
Cl(1)—Pb—Cl(4)	84.7 (2)	82.5 (2)	84.4 (2)	84.9 (2)	94.57 (3)
Cl(1)—Pb—Cl(5)	78.4 (2)	66.8 (1)	75.8 (2)	81.2 (2)	77.50 (3)
Cl(1)—Pb—Cl(6)	64.7 (1)	74.7 (1)	69.4 (2)	76.3 (2)	69.76 (3)
Cl(1)—Pb—Cl(7)	122.7 (2)	135.5 (2)	137.0 (2)	123.1 (2)	131.32 (4)
Cl(2)—Pb—Cl(3)	97.3 (2)	97.2 (2)	89.2 (2)	103.2 (2)	103.53 (4)
Cl(2)—Pb—Cl(4)	147.6 (2)	153.9 (2)	145.0 (2)	159.8 (2)	152.25 (4)
Cl(2)—Pb—Cl(5)	72.5 (1)	74.7 (1)	72.7 (2)	83.7 (2)	75.29 (3)
Cl(2)—Pb—Cl(6)	108.8 (1)	120.6 (2)	78.9 (2)	103.5 (2)	126.40 (4)
Cl(2)—Pb—Cl(7)	74.2 (1)	80.7 (2)	74.5 (2)	70.1 (2)	69.79 (3)
Cl(3)—Pb—Cl(4)	90.8 (2)	78.4 (2)	77.2 (2)	91.1 (2)	78.38 (3)
Cl(3)—Pb—Cl(5)	78.6 (2)	74.5 (1)	75.0 (2)	74.8 (2)	75.29 (3)
Cl(3)—Pb—Cl(6)	157.0 (2)	133.8 (2)	140.9 (2)	126.2 (2)	126.40 (4)
Cl(3)—Pb—Cl(7)	74.5 (1)	84.5 (2)	72.9 (2)	77.7 (2)	69.79 (3)
Cl(4)—Pb—Cl(5)	78.4 (2)	79.4 (1)	72.7 (2)	86.6 (2)	77.50 (3)
Cl(4)—Pb—Cl(6)	84.8 (2)	77.5 (1)	130.7 (2)	78.3 (2)	69.76 (3)
Cl(4)—Pb—Cl(7)	138.1 (2)	123.8 (2)	129.2 (2)	127.7 (2)	131.32 (4)
Cl(5)—Pb—Cl(6)	140.6 (2)	137.1 (1)	133.7 (2)	153.8 (2)	130.73 (4)
Cl(5)—Pb—Cl(7)	133.6 (2)	144.9 (2)	133.7 (2)	136.1 (2)	121.83 (4)
Cl(6)—Pb—Cl(7)	81.0 (1)	77.2 (2)	68.0 (2)	69.0 (2)	107.44 (4)

* Calculated from the atomic parameters of Nozik, Fykin & Muradyan (1976).

Further refinement with these atoms and a subsequent difference map revealed the positions of the remaining non-hydrogen atoms. In the final refinement the H atoms were refined as rigid groups and were constrained at 0.85 Å from the respective N atoms, their positions being dictated by the geometry of the $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion. The refinement converged to $R = \sum |F_o - F_c| / \sum |F_o| = 0.063$.* The final parameters of the heavy atoms are given in Table 2. Bond lengths and angles are given in Tables 3 and 4. Scattering factors were taken from Cromer & Mann (1968), Doyle & Turner (1968), and Stewart, Davidson & Simpson (1965). Corrections for the real and imaginary components of the anomalous dispersion were included.

Fig. 1 shows the arrangement of the anionic and cationic components in the unit cell. Figs. 2 and 3 are perspective views of the coordination unit of one Pb atom and the seven nearest Cl ligands in $[\text{Co}(\text{NH}_3)_6]$ -

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34028 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.


 Fig. 1. Unit cell of $[\text{Co}(\text{NH}_3)_6][\text{Pb}_4\text{Cl}_{11}]$ (ORTEP, Johnson, 1965).

 Fig. 2. Perspective view of the arrangement of Cl atoms around Pb in $[\text{Co}(\text{NH}_3)_6][\text{Pb}_4\text{Cl}_{11}]$.

 Fig. 3. Perspective view of the arrangement of Cl atoms around Pb in $\text{NH}_4[\text{Pb}_2\text{Cl}_5]$.

$[\text{Pb}_4\text{Cl}_{11}]$ and $\text{NH}_4[\text{Pb}_2\text{Cl}_5]$ respectively; the numbering scheme is also shown.

The structure of $\text{NH}_4[\text{Pb}_2\text{Cl}_5]$ was solved by Patterson and Fourier methods with *SHELX* (Sheldrick, 1976) and refined to $R = \sum |F_o - F_c| / \sum |F_o| = 0.072$ for 1566 observed $[|F_o| > 3\sigma(F_o)]$ reflections.

Results

$[\text{Co}(\text{NH}_3)_6]^{3+}$ cations, showing the known octahedral arrangement of NH_3 ligands around the central atom, and a Cl-bridged three-dimensional chloroplumbate(II) ion exist in the structure. Between these units hydrogen bonding has to be assumed, because an appreciable proportion of the distances between Cl ligands of the anionic species and N atoms of the cation (3.149–3.896 Å) lie in the range 3.11–3.41 Å, which is considered as characteristic for N–H–Cl bridges (Veal & Hodgson, 1972).

The anionic unit is composed of two crystallographically independent Pb atoms coordinated by seven Cl atoms with Pb–Cl distances of 2.908 (5)–3.228 (6) Å. The Cl arrangement shown in Fig. 2 corresponds to a distorted trigonal prism with Cl(5) above one of the rectangular faces of the prism. Above one of the other two rectangular faces of the prism around Pb(1) there is another Cl atom, but at a distance of 3.478 (6) Å; therefore, this should not be considered as part of the coordination sphere of Pb, since, at most, only a very weak interaction might be assumed. The prisms are connected through common corners thereby forming a three-dimensional network.

The coordination geometry of Cl around Pb in $[\text{Co}(\text{NH}_3)_6][\text{Pb}_4\text{Cl}_{11}]$ is very similar to the arrangement of Cl and Pb in PbCl_2 , the structure of which has recently been redetermined by neutron diffraction (Nozik, Fykin & Muradyan, 1976). From the positional parameters given in that paper we calculated Pb–Cl distances and Cl–Pb–Cl angles for comparison; these are shown in Tables 3 and 4, together with the corresponding distances and angles in $\text{NH}_4[\text{Pb}_2\text{Cl}_5]$. These were calculated from the positional parameters obtained from a determination and refinement of the structure of this compound, which was investigated independently by Keller (1976). The positional parameters he reported were essentially in accordance with ours; these, therefore, are not repeated here. In $\text{NH}_4[\text{Pb}_2\text{Cl}_5]$ also, seven Cl ligands are found in the range 2.870 (8)–3.217 (8) Å from Pb. The arrangement is shown in Fig. 3. Keller (1976) has already pointed out that the coordination around Pb in

$\text{NH}_4[\text{Pb}_2\text{Cl}_5]$ and $\text{Ti}[\text{Pb}_2\text{Cl}_5]$ corresponds to that in PbCl_2 . In $\text{NH}_4[\text{Pb}_2\text{Cl}_5]$, distances between N and Cl also lie in the range of 3.11–3.41 Å, so that hydrogen bonding between the NH_4^+ cation and the anionic chloroplumbate(II) layers has to be assumed.

In $\text{NH}_4[\text{Pb}_2\text{Cl}_5]$, structural units of six Pb atoms together with their trigonal-prismatic Cl environment can be distinguished; the Pb atoms lie at the corners of three tetrahedra, which have common faces. The Pb units form layers with common edges along *z* and common edges and faces alternating along *y*. The arrangement of the Pb atoms resembles that in $\text{Pb}_6\text{O}(\text{OH})_6(\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ (Spiro, Templeton & Zalkin, 1969), though in this compound the Pb_6 units are isolated with Pb–Pb distances of 3.440 (5)–4.086 (6) Å. In the Pb units of $\text{NH}_4[\text{Pb}_2\text{Cl}_5]$ the Pb–Pb distances are comparable with those in PbCl_2 , where the shortest Pb–Pb distance is 4.501 Å. Two Pb–Pb distances are shorter [4.352 (2) and 4.405 (1) Å]. The NH_4^+ cations lie between the chloroplumbate(II) layers.

From the structures of PbCl_2 and chloroplumbates, it is apparent that, in cases with a stoichiometric Pb:Cl ratio <1:3, the arrangement of Cl is (distorted) trigonal prismatic with an additional Cl ligand above a rectangular face of the prism (and two more-distant Cl atoms above the other two rectangular faces). However, with a Pb:Cl ratio >1:3 the geometry of Cl around Pb is octahedral, for example in $[\text{Co}(\text{en})_3]_2[\text{Pb}_2\text{Cl}_9] \cdot \text{Cl} \cdot 3\text{H}_2\text{O}$ (Haupt & Huber, 1978).

References

- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
 EPHRAIM, F. & MOSIMANN, P. (1923). *Helv. Chim. Acta*, **6**, 1112–1132.
 HAUPT, H. J. & HUBER, F. (1978). *Z. Anorg. Allg. Chem.* **442**, 31–40.
 JANSEN, P. W. J. (1968). *Recl Trav. Chim. Pays-Bas*, **87**, 1021–1024.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 KELLER, H.-L. (1976). *Z. Naturforsch. Teil B*, **31**, 885.
 NOZIK, YU. Z., FYKIN, L. E. & MURADYAN, L. A. (1976). *Kristallografiya*, **21**, 76–79.
 SHELDRIK, G. M. (1976). Personal communication.
 SPIRO, T. G., TEMPLETON, D. H. & ZALKIN, A. (1969). *Inorg. Chem.* **8**, 856–861.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 VEAL, J. T. & HODGSON, D. J. (1972). *Inorg. Chem.* **11**, 597–600.