

# The Crystal Structure of $\text{Pb}_2\text{Cl}_6[\text{NH}_3(\text{CH}_2)_2\text{NH}_3]$

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Crystals of a lead(II) chloride ethylenediamine complex of formula  $\text{Pb}_2\text{Cl}_6[\text{NH}_3(\text{CH}_2)_2\text{NH}_3]$  are orthorhombic, space group  $Pbcm$  with  $a = 9.402(3)$ ,  $b = 16.068(4)$ ,  $c = 16.887(15)$  Å and  $Z = 8$ . The structure was refined by full-matrix least-squares methods based on 1950 observed reflections to  $R = 0.031$ . The lead atoms, Pb(1), Pb(2), Pb(3), are each eight-coordinated. The coordination polyhedra may be described as distorted bicapped trigonal prisms around the atoms Pb(1) and Pb(3) and as a square antiprism around Pb(2). The polyhedra are linked by sharing faces to infinite layers running parallel to the  $bc$ -plane. The ethylenediammonium ions, located between the layers, are linked *via* hydrogen bonds to the chloride ions.

The present study of the crystal chemistry of  $\text{Pb}_2\text{Cl}_6[\text{NH}_3(\text{CH}_2)_2\text{NH}_3]$  is part of a research program at our division on negatively charged polynuclear halide complexes of heavy metals in the solid state. It seems reasonable to expect isolated, infinite linear or two-dimensional complexes if the additional cations, necessary to obtain electroneutrality, are large. Such large cations, e.g.  $\text{NH}_3^+(\text{CH}_2)_2\text{NH}_3^+$ , are preferably found among organic compounds.

## EXPERIMENTAL

Crystals of the actual compound were prepared by crystallization of stoichiometric quantities of  $\text{PbCl}_2$  and  $\text{NH}_2(\text{CH}_2)_2\text{NH}_2$  from HCl (1:1) solution. The product consisted of colourless plates.

Preliminary Weissenberg photographs indicated orthorhombic symmetry. The conditions limiting possible reflections were  $0kl$ :  $k = 2n$  and  $h0l$ :  $l = 2n$ , indicating either space group  $Pbcm$  (No. 57) or  $Pbc2_1$  (No. 29\*).

\* Orientation different from that given in the International Tables.

The density,  $3.63 \text{ g cm}^{-3}$ , was measured by flotation. The unit-cell dimensions, determined from least-squares refinement of the settings of 15 reflections measured on a single-crystal diffractometer, were  $a = 9.402(3)$  Å,  $b = 16.068(4)$  Å and  $c = 16.887(15)$  Å. The volume  $V = 2551.0 \text{ Å}^3$ . Assuming  $Z = 8$  the value of the calculated density was  $3.58 \text{ g cm}^{-3}$ .

A single crystal with the dimension  $0.20 \times 0.15 \times 0.08 \text{ mm}$  was used for collecting intensity data on a computer-controlled, four-circle diffractometer (Enraf-Nonius CAD-4) with MoK $\alpha$  radiation and a graphite monochromator. The  $\omega$ - $2\theta$  scan technique was used with a peak scan interval  $\Delta\omega = 0.90^\circ + 0.50^\circ \tan \theta$  and background scans for 1/4 of the peak scan time. A total of 3836 independent reflections was recorded. 1885 reflections with  $I < 3\sigma(I)$  were considered not significantly different from the background and were excluded from the refinement. The values of  $\sigma(I)$  were based on counting statistics. The intensities of two standard reflections, 1 10 6, 1  $\bar{1}$  0 6, were measured

Table 1. Atomic coordinates with standard deviations in parentheses.

| Atom  | X/a         | Y/b           | Z/c           |
|-------|-------------|---------------|---------------|
| Pb(1) | 0.13687(5)  | 0.00219(3)    | 0.08276(2)    |
| Pb(2) | 0.03767(6)  | $\frac{1}{4}$ | 0             |
| Pb(3) | -0.08234(8) | 0.17649(4)    | $\frac{1}{4}$ |
| Cl(1) | 0.2063(4)   | 0.3926(2)     | 0.0517(2)     |
| Cl(2) | 0.8600(3)   | 0.1086(2)     | 0.0664(2)     |
| Cl(3) | 0.5839(3)   | 0.4709(2)     | 0.0957(2)     |
| Cl(4) | 0.1966(3)   | 0.1807(2)     | 0.1408(2)     |
| Cl(5) | 0.8706(3)   | 0.3164(1)     | 0.1421(2)     |
| Cl(6) | 0.0469(3)   | 0.0076(2)     | $\frac{1}{4}$ |
| Cl(7) | 0.6259(5)   | 0.1555(3)     | $\frac{1}{4}$ |
| N(1)  | 0.5227(12)  | 0.1514(5)     | 0.0625(6)     |
| N(2)  | 0.1774(14)  | 0.3645(8)     | $\frac{1}{4}$ |
| N(3)  | 0.5759(17)  | 0.3632(10)    | $\frac{1}{4}$ |
| C(1)  | 0.5326(16)  | 0.2433(7)     | 0.0436(7)     |
| C(2)  | 0.3246(17)  | 0.4045(9)     | $\frac{1}{4}$ |
| C(3)  | 0.4261(20)  | 0.3319(11)    | $\frac{1}{4}$ |

Table 2. Thermal parameters. The form of the anisotropic temperature factor is  $\exp[-(\hbar^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23} + 2hl\beta_{13})]$ . The  $\beta_{ij}$  values are multiplied by  $10^6$  for the Pb and Cl atoms and by  $10^4$  for the N and C atoms.

| Atom  | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|-------|--------------|--------------|--------------|--------------|--------------|--------------|
| Pb(1) | 671(5)       | 366(2)       | 193(1)       | 121(3)       | -18(3)       | 23(2)        |
| Pb(2) | 572(6)       | 184(2)       | 239(2)       | 0            | 0            | -11(2)       |
| Pb(3) | 813(8)       | 168(2)       | 435(3)       | 3(4)         | 0            | 0            |
| Cl(1) | 1164(40)     | 217(10)      | 181(10)      | -181(17)     | -125(18)     | 39(8)        |
| Cl(2) | 540(28)      | 187(9)       | 272(11)      | -7(14)       | 6(16)        | -9(8)        |
| Cl(3) | 578(28)      | 243(10)      | 277(12)      | -37(15)      | 15(16)       | 58(9)        |
| Cl(4) | 641(31)      | 265(10)      | 190(10)      | -28(15)      | -38(15)      | 4(8)         |
| Cl(5) | 776(32)      | 152(8)       | 198(10)      | 44(14)       | 62(16)       | 16(7)        |
| Cl(6) | 1386(63)     | 132(12)      | 165(12)      | -14(26)      | 0            | 0            |
| Cl(7) | 650(48)      | 293(16)      | 234(15)      | -26(24)      | 0            | 0            |
| N(1)  | 95(13)       | 18(3)        | 25(4)        | -5(6)        | 1(6)         | 4(3)         |
| N(2)  | 57(15)       | 23(5)        | 17(5)        | 5(7)         | 0            | 0            |
| N(3)  | 75(18)       | 49(7)        | 11(5)        | -5(11)       | 0            | 0            |
| C(1)  | 165(20)      | 20(4)        | 26(5)        | -22(9)       | -11(9)       | 4(4)         |
| C(2)  | 61(18)       | 22(6)        | 16(5)        | 2(9)         | 0            | 0            |
| C(3)  | 65(21)       | 33(7)        | 31(8)        | 14(11)       | 0            | 0            |

Table 3. Selected interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses.

|                    |          |  |          |
|--------------------|----------|--|----------|
|                    |          | Square antiprism around Pb(2)                |          |
| Pb(1) - Pb(1)      | 3.800(2) | Pb(2) - 2 Cl(1)                              | 2.920(3) |
| Pb(1) - Pb(2)      | 4.322(1) | Pb(2) - 2 Cl(4)                              | 3.021(4) |
| Pb(1) - Pb(3)      | 4.480(2) | Pb(2) - 2 Cl(2)                              | 3.035(3) |
|                    |          | Pb(2) - 2 Cl(5)                              | 3.060(4) |
|                    |          | Bicapped trigonal prism around Pb(3)         |          |
| Pb(1) - Cl(1)      | 2.905(4) | Pb(3) - Cl(7)                                | 2.764(5) |
| Pb(1) - Cl(1)      | 3.713(4) | Pb(3) - 2 Cl(5)                              | 2.927(3) |
| Pb(1) - Cl(2)      | 3.085(4) | Pb(3) - Cl(6)                                | 2.973(4) |
| Pb(1) - Cl(2)      | 3.127(3) | Pb(3) - 2 Cl(4)                              | 3.207(3) |
| Pb(1) - Cl(3)      | 2.682(3) | Pb(3) - 2 Cl(2)                              | 3.331(4) |
| Pb(1) - Cl(4)      | 3.083(3) |  |          |
| Pb(1) - Cl(5)      | 3.150(2) |  |          |
| Pb(1) - Cl(6)      | 2.949(3) |  |          |
|                    |          | In the ethylenediammonium ions               |          |
| C(1) - C(1')       | 1.49(2)  | C(2) - C(3)                                  | 1.51(2)  |
| C(1) - N(1)        | 1.51(1)  | C(2) - N(2)                                  | 1.53(2)  |
|                    |          | C(3) - N(3)                                  | 1.50(3)  |
|                    |          | Interatomic N - Cl distances less than 3.3 Å |          |
| N(1) - Cl(2)       | 3.25(1)  | N(2) - Cl(6)                                 | 3.12(1)  |
| N(1) - Cl(3)       | 3.12(1)  | N(3) - 2 Cl(3)                               | 3.13(1)  |
|                    |          | Angles in the ethylenediammonium ions        |          |
| C(1) - C(1) - N(1) | 110(1)   |  |          |
| C(3) - C(2) - N(2) | 104(1)   |  |          |
| C(2) - C(3) - N(3) | 110(1)   |  |          |

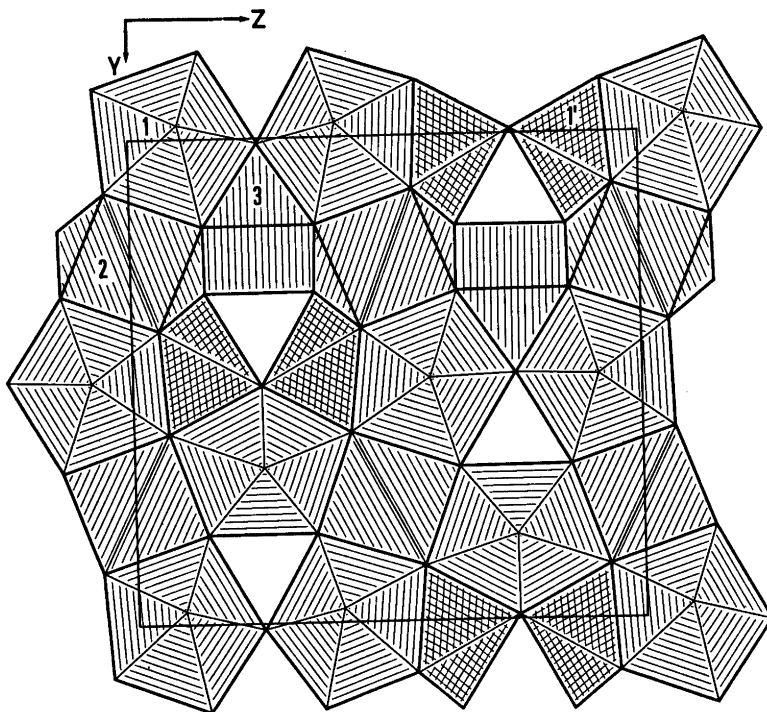


Fig. 1. Projection of a repetition unit of one  $(\text{Pb}_2\text{Cl}_6^{2-})_n$ -layer on the  $bc$ -plane. The positions of the chlorine atoms correspond to the intersections of the lines. The Pb(1) polyhedra are shaded with lines parallel to the heavy lines showing their edges. The Pb(1') polyhedra are shaded by crossing lines. The antiprisms around Pb(2) are indicated by shading lines parallel to a face diagonal of the square face. The shading lines of the polyhedra of Pb(3) are parallel to the  $b$ -axis. One polyhedron of each kind is numbered according to the lead atom in the drawing.

after every 50 reflections to check the stability of the crystal and the electronics.

The fluctuations in the intensities of the standard reflections were random and less than 8%. The intensities were corrected for Lorentz, polarization and absorption effects [ $\mu(\text{MoK}\alpha) = 275 \text{ cm}^{-1}$ ]; the transmission factors varied from 0.069 to 0.213.

#### STRUCTURE DETERMINATION AND REFINEMENT

Assuming the centrosymmetric space group  $Pbcm$ , the positions of the lead atoms were deduced from a three-dimensional vector map. Two of the lead atoms of the asymmetric part of the unit cell occupy special positions. The positions of all other non-hydrogen atoms were obtained from successive difference Fourier syntheses. The positions so obtained were refined by least-squares calculations using an

isotropic temperature factors for all atoms. At this stage the  $R$  factor was 0.032. The presence of secondary extinction effects in the intensity data was investigated by including an isotropic extinction parameter in the calculations; the refined value of this parameter being  $g = 0.14(2) \times 10^4$ . The refinement converged to  $R = 0.031$  and  $R_w = 0.037$  (1951 independent reflections). The goodness of fit,  $S$ , was 1.16. The weights  $w_i$  were calculated according to  $w_i^{-1} = \sigma^2(F_o^2) + 0.00028|F_o|^2$ . As a reasonable structure was obtained in this way, space group  $Pbc2_1$  was not further considered.

The atomic scattering factors were those given by Doyle and Turner.<sup>1</sup> The final positional and thermal parameters are given in Tables 1 and 2. A list of observed and calculated structure factors is available on request to the Division of Inorganic Chemistry 2.

Selected interatomic distances and angles are presented in Table 3.

All computations were made on the UNIVAC 1108 computer in Lund. A short account of the program system has been given by Stålhandske.<sup>2</sup>

## DESCRIPTION AND DISCUSSION

The crystal structure of  $\text{Pb}_2\text{Cl}_6[\text{NH}_3(\text{CH}_2)_2\text{NH}_3]_n$  is built up of identical layers  $(\text{Pb}_2\text{Cl}_6^{2-})_n$  perpendicular to the  $a$ -axis and ions  $\text{NH}_3^+(\text{CH}_2)_2\text{NH}_3^+$  between them. The repetition unit of such a layer projected on the  $bc$ -plane is shown in Fig. 1. Each lead atom coordinates eight chlorine atoms (Tables 1, 3). The coordination polyhedra may be described as distorted bicapped trigonal prisms around the atoms Pb(1) and Pb(3) and as a square antiprism around Pb(2). The point symmetries of the sites of the lead atoms are  $I$ ,  $2$  and  $m$  for Pb(1), Pb(2), and Pb(3), respectively. Except for the contacts of the polyhedra of Pb(1) and the centro-symmetrically related ones, Pb(1'), all coordination polyhedra are linked by sharing triangular faces (Fig. 1).

The Pb(1) atoms occur in pairs in the structure related by a centre of symmetry at 0,0,0 and the distance between them is 3.800(1) Å. The bicapped triangular prism around Pb(1) has one nearly square, strictly planar face, which is shared by the corresponding Pb(1') prism. The coulombic repulsion between the Pb(1) atoms may explain the remarkably long Pb(1)–Cl(1) distance of 3.713(2) Å. The two short distances Pb(1)–Cl(3), 2.682(2) Å, and Pb(3)–Cl(7), 2.764(2) Å, can be explained by considering that each of the atoms Cl(3) and Cl(7) only forms one coordinative bond while the other chlorine atoms form three or four bonds. The lead-chlorine distances are in good agreement with the value 2.75(4) Å found in bis-thiourea-lead(II) chloride reported by Nardelli and Fava.<sup>3</sup> The remaining lead-chlorine distances are fairly close to the value reported as a mean for  $\text{PbCl}_2$ .<sup>4,5</sup>

The positively charged ethylenediamine ions  $\text{NH}_3^+(\text{CH}_2)_2\text{NH}_3^+$  connect subsequent  $(\text{Pb}_2\text{Cl}_6^{2-})_n$ -layers by means of N–H...Cl hydrogen bonds. The two ethylenediammonium ions I, II in the asymmetric part of the unit cell occur in the *trans* conformation. The non-hydrogen atoms of ion I, including the carbon

atoms C(2) and C(3) (Table 1), are strictly coplanar, being situated in the mirror plane  $z = \frac{1}{2}$ . The ions of this kind extend along the  $a$ -axis and their projections on the  $bc$ -plane fall within the non-shaded triangular areas in Fig. 1. The atoms within the ion II are related by the two-fold axis running along  $x, \frac{1}{2}, 0$ . The ion contains the carbon atoms C(1) and C(1') and is only approximately planar. These ions are approximately parallel to the plane of the  $(\text{Pb}_2\text{Cl}_6^{2-})_n$ -layers. The bond distances and angles within the ethylenediamine ions (Table 3) agree with those reported by Jamet-Delcroix<sup>6</sup> but for the angle C(3)–C(2)–N(2), 104(1)°, which is significantly smaller than for crystalline ethylenediamine, 114.50(2)°. The nitrogen-chlorine (N–H...Cl) distances less than 3.3 Å are given in Table 3. Both ions I and II are in contact with two adjacent layers  $(\text{Pb}_2\text{Cl}_6^{2-})_n$  via hydrogen bonds.

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