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# The first salt of an isolated pentachloroplumbate(II) trianion

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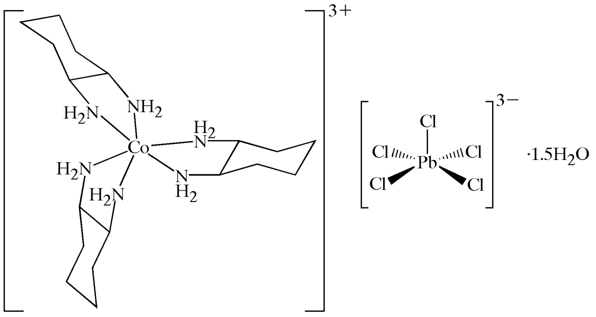
The title compound, tris(cyclohexane-1,2-diamine-$\kappa^2N,N'$)-cobalt pentachloroplumbate sesquihydrate, $[Co(C_6H_{14}N_2)_3][PbCl_5]\cdot1.5H_2O$, crystallizes in the monoclinic space group $C2/c$, with a tricationic cobalt complex, a pentachloroplumbate trianion, one water molecule in a general position and a second water molecule on a crystallographic twofold axis. The compound is the first example of an isolated $[PbCl_5]^{3-}$ moiety; the Pb atom is coordinated in a square-pyramidal fashion, with four longer bonds to Cl atoms in the basal plane and a shorter distance to the apex. The ionic constituents and the solvent molecules form a three-dimensional network of hydrogen bonds.

## Comment

Pentachlorometallates containing isolated $[MCl_5]^{n-}$ anions have been documented for both main group ($M$ = In, Tl, Ge, Sn and Sb) and transition metals ($M$ = V, Mn, Fe, Cu, Pt and Hg). For these elements, the Cambridge Structural Database (CSD; Version of August 2005; Allen, 2002) contains at least one error-free example, without disorder, for which three-dimensional atomic coordinates are available. The prototypic $[PbCl_5]^{3-}$ anion, presumably a simple building block, has not yet been structurally characterized; we communicate here the synthesis and first X-ray diffraction study of such a pentachloroplumbate. In the context of a systematic comparison of homo- and heterochiral crystals, we performed a cocrystallization experiment on tris(*trans*-cyclohexane-1,2-diamine)-cobalt trichloride, $[Co(chxn)_3]Cl_3$, and $PbCl_2$ in aqueous solution. The tricationic cobalt species represented the enantiomeric mixture of the thermodynamically stable isomers, namely the $\Delta$ configured complex of the ($R$,$R$)-diamine and its $\Lambda$-($S$,$S$) mirror image (Kalf *et al.*, 2002). From a solution containing both starting materials, a red crystalline product precipitates according to equation (1) below.

$$[Co(chxn)_3]Cl_3\cdot2H_2O + PbCl_2 \xrightarrow[H_2O]{} \underset{(I)}{[Co(chxn)_3]PbCl_5\cdot1.5H_2O} \quad (1)$$

Single-crystal X-ray diffraction analysis showed that the solid (I) contains the expected complex cations (Fig. 1) and isolated $[PbCl_5]^{3-}$ (Fig. 2) anions. To the best of our knowledge, the latter moiety has not yet been documented in the solid. Earlier reports on 'pentachloroplumbates' do not refer to structures with isolated $[PbCl_5]^{3-}$ building blocks but rather to compounds with chains of corner-sharing octahedra (Mousdis *et al.*, 1998; Ng, 2000). We note that the formation of (I) necessarily competes with reprecipitation of lead(II) chloride, which is only sparingly soluble in cold water.



(I)

Fig. 2 shows that our pentachloroplumbate anion adopts an essentially square-pyramidal geometry, with a shorter apical bond and four longer coordination distances to the chloro substituents in the tetragonal plane (Table 1). The metal atom lies 0.0368 (4) Å above this plane, in the direction of the apical ligand. Building blocks of an extended solid cannot be considered 'isolated' in a strict sense. In the present case, however, this description of the anion as being 'isolated' rather than being part of an extended moiety is justified; additional neighbors of the central Pb atom are located at much longer distances and involve two C-bonded H atoms at 3.287 (3) and 3.485 (3) Å, as well as a water O atom at

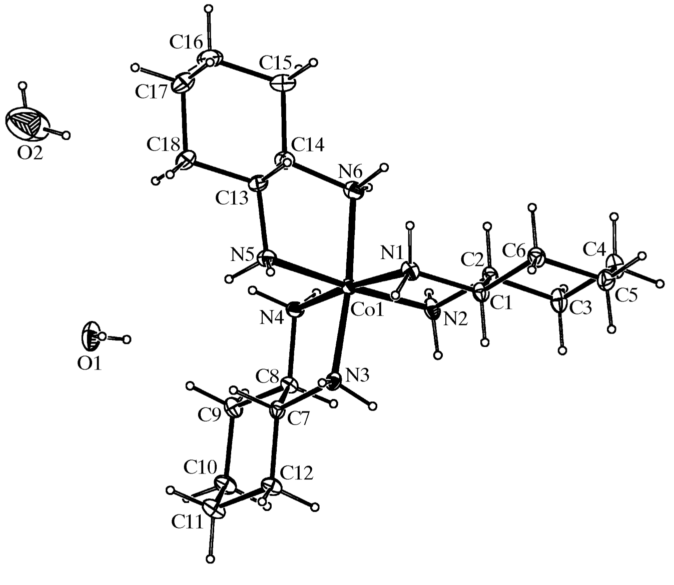


**Figure 1**
A displacement ellipsoid plot [*PLATON* (Spek, 2003); 50% probability, with H atoms of arbitrary radii] of the cation and the solvent water molecules in (I). The solvent molecule associated with atom O2 is located on a crystallographic twofold axis in space group $C2/c$.

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3.5487 (17) Å. Solid (I) contains a cation, an anion, a water molecule in a general position of the space group *C*2/*c* and an additional water molecule on the twofold crystallographic axis; the compound is a sesquihydrate.

All potential hydrogen-bond donors, *viz.* six NH and three symmetrically independent OH groups, are involved in moderate-to-weak hydrogen bonding, the acceptor atoms being either the plumbate Cl or the hydrate O atoms. Table 2 summarizes the hydrogen-bond geometry.

To which structures should the new $[PbCl_5]^{3-}$ anion be compared? The apical $Pb^{II}-Cl$ distance is almost as short as those in chloro complexes of $Pb^{IV}$ (Olafsson *et al.*, 2000; Cashin *et al.*, 2002), whereas the longer bonds in the base closely match the mean Pb—Cl distance for more than 200 structures in the CSD; for 202 error-free observations of Pb—Cl distances, the mean value is 2.873 Å and the median is 2.864 Å. The distances and angles in the structurally characterized pentachloroantimonates cover a wide range. Several $[SbCl_5]^{2-}$ groups in the literature (Zaleski & Pietraszko, 1995; Li *et al.*, 1995; Derwahl *et al.*, 1996; Ohta & Yamashita, 1997) not only adopt a square-pyramidal geometry but also match the metal–halide distance pattern of one shorter apical and four longer bonds. However, in these antimonates, the metal atom and the apical ligand are situated on opposite faces of the square plane, whereas in our pentachloroplumbate, the metal is slightly displaced towards the apex.

In crystalline (I), loss of crystal water occurs at 443 K and decomposition starts at *ca* 553 K. We have no direct evidence about the species present in solution, but $^{207}Pb$ NMR data provide some insight; an aqueous solution of tris(cyclohexanediamine)cobalt pentachloroplumbate shows a signal at −2224 p.p.m. This single resonance shifts to −1902 p.p.m. upon addition of LiCl (5 equivalents), *i.e.* when the Cl/Pb ratio is increased. Under the same conditions, a saturated solution of $PbCl_2$, with a lower Cl/Pb ratio, shows a resonance at −2383 p.p.m. The 'hydrated $Pb^{2+}$ cation' is found at *ca* −2800 p.p.m. (Harrison *et al.*, 1983). These numbers, which will surely depend on concentration or supersaturation and should not be overinterpreted, are in agreement with the presence of $Pb^{2+}$ cations with variable numbers of solvent water molecules and chloride ions in the coordination environment.

Originally, our interest in homo- and heterochiral crystals had induced us to perform reaction (1), and we conclude our short report with the negative outcome of a closely related experiment. Our new pentachloroplumbate (I) exists in the form of racemic crystals. Their formation is obviously preferred over the statistically less popular (Jacques *et al.*, 1994) crystallization alternative, namely a conglomerate, whereas the nitrate of the same cationic complex shows spontaneous resolution (Morooka *et al.*, 1991). We therefore expected that the enantiomerically pure cobalt complex as a starting material would enforce a chiral space group and hence an independent second example of a solid of the chemical composition $[Co(chxn)_3]PbCl_5$, with the pentachloroplumbate in a different packing environment. However, when aqueous solutions of enantiomerically pure $[Co(chxn)_3]Cl_3$ and $PbCl_2$ were mixed and evaporated under the same conditions, no precipitation of an analogous, necessarily homochiral, compound was observed; after prolonged evaporation, $PbCl_2$ reprecipitated. We conclude that the competition between (I) and lead chloride is a close one, and that the formation of further pentachloroplumbate derivatives will not be trivial.

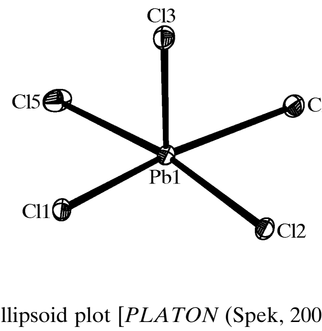

**Figure 2**
A displacement ellipsoid plot [*PLATON* (Spek, 2003); 50% probability] of the pentachloroplumbate anion in (I).

## Experimental

From a solution containing $[Co(chxn)_3]Cl_3\cdot 2H_2O$ and $PbCl_2$, the red crystalline product precipitates according to equation (1) (see *Comment*). $[Co(chxn)_3]Cl_3\cdot 2H_2O$ (0.5 mmol, 0.272 g) [for the synthesis and structure of this compound, see Kalf *et al.* (2002)] and $PbCl_2$ (0.5 mmol, 0.139 g) were dissolved separately in water (10 ml each) at 318 K. The orange-coloured mixture was stirred for 30 min at 318 K and then allowed to cool to room temperature; after 2 d, precipitation of large red crystals of $[Co(chxn)_3]PbCl_5\cdot 1.5H_2O$ began (yield 89%). The saturated solution should not be exposed to low temperatures; cooling of a saturated solution of (I) to 279 K resulted in the formation of $PbCl_2$. Analysis calculated for $C_{36}H_{90}Cl_{10}Co_2N_{12}O_3Pb_2$: C 26.59, H 5.58, N 10.34%; found: C 26.23, H 5.98, N 10.17%.

*Crystal data*

$[Co(C_6H_{14}N_2)_3][PbCl_5]\cdot 1.5H_2O$
$M_r$ = 812.97
Monoclinic, *C*2/*c*
$a$ = 27.066 (2) Å
$b$ = 12.4657 (11) Å
$c$ = 21.3066 (19) Å
$\beta$ = 125.889 (1)°
$V$ = 5824.0 (8) $Å^3$
$Z$ = 8
$D_x$ = 1.854 Mg $m^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 6549 reflections
$\theta$ = 2.5–29.8°
$\mu$ = 6.83 $mm^{-1}$
$T$ = 110 (2) K
Fragment, red
0.39 × 0.28 × 0.17 mm

*Data collection*

Bruker SMART CCD area-detector diffractometer
$\omega$ scans
Absorption correction: analytical (*PLATON*; Spek, 2003)
$T_{min}$ = 0.084, $T_{max}$ = 0.357
42820 measured reflections
8402 independent reflections
6901 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.066
$\theta_{max}$ = 30.0°
$h = -37 \rightarrow 38$
$k = -17 \rightarrow 17$
$l = -29 \rightarrow 29$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.048
$S$ = 1.01
8402 reflections
294 parameters
$w = 1/[\sigma^2(F_o^2) + (0.007P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.46 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.19 e $Å^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Pb1—Cl3 | 2.6211 (7) | Pb1—Cl5 | 2.8748 (8) |
| Pb1—Cl1 | 2.8241 (7) | Pb1—Cl4 | 2.8863 (7) |
| Pb1—Cl2 | 2.8677 (7) | | |
| | | | |
| Cl3—Pb1—Cl1 | 90.01 (2) | Cl2—Pb1—Cl5 | 171.57 (2) |
| Cl3—Pb1—Cl2 | 98.06 (2) | Cl3—Pb1—Cl4 | 87.25 (2) |
| Cl1—Pb1—Cl2 | 86.51 (2) | Cl1—Pb1—Cl4 | 166.97 (2) |
| Cl3—Pb1—Cl5 | 88.76 (2) | Cl2—Pb1—Cl4 | 81.27 (2) |
| Cl1—Pb1—Cl5 | 88.56 (2) | Cl5—Pb1—Cl4 | 104.11 (2) |

**Table 2**
Hydrogen-bond geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*A*···O1$^{i}$ | 0.92 | 2.06 | 2.931 (4) | 157 |
| N1—H1*B*···Cl5$^{i}$ | 0.92 | 2.60 | 3.399 (3) | 146 |
| N2—H2*A*···Cl5$^{ii}$ | 0.92 | 2.77 | 3.592 (3) | 149 |
| N2—H2*B*···Cl2$^{iii}$ | 0.92 | 2.73 | 3.416 (3) | 133 |
| N2—H2*B*···Cl4$^{iii}$ | 0.92 | 2.76 | 3.527 (3) | 141 |
| N3—H3*A*···Cl5$^{ii}$ | 0.92 | 2.35 | 3.265 (3) | 175 |
| N3—H3*B*···Cl1$^{i}$ | 0.92 | 2.36 | 3.190 (2) | 150 |
| N4—H4*A*···Cl4 | 0.92 | 2.66 | 3.466 (3) | 146 |
| N4—H4*B*···Cl4$^{iii}$ | 0.92 | 2.47 | 3.246 (2) | 143 |
| N5—H5*A*···Cl3 | 0.92 | 2.94 | 3.854 (2) | 170 |
| N5—H5*B*···Cl1$^{i}$ | 0.92 | 2.60 | 3.300 (3) | 134 |
| N6—H6*A*···O1$^{i}$ | 0.92 | 2.01 | 2.901 (3) | 163 |
| N6—H6*B*···Cl2$^{iii}$ | 0.92 | 2.42 | 3.241 (3) | 149 |
| O1—H1O···Cl2$^{i}$ | 0.80 | 2.36 | 3.109 (3) | 158 |
| O1—H2O···Cl1$^{i}$ | 0.80 | 2.38 | 3.122 (2) | 153 |
| O2—H3O···Cl4$^{iv}$ | 0.80 | 2.55 | 3.2845 (19) | 154 |

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x, -y+1, z-\frac{1}{2}$; (iii) $-x, -y+1, -z$; (iv) $-x, y, -z+\frac{1}{2}$.

All H atoms were introduced in idealized positions (C—H = 0.98 Å, N—H = 0.92 Å and O—H = 0.80 Å) and treated as riding.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1278). Services for accessing these data are described at the back of the journal.

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