

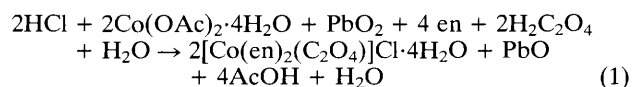
A Novel, Polymeric Clathrate of the Pentachlorodiplumbate Anion: the Preparation and Crystal Structure of $[\text{Co}(\text{N-methylethylenediamine})_2(\text{C}_2\text{O}_4)]\text{Pb}_2\text{Cl}_5 \cdot 2\text{H}_2\text{O}$ (1)

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When $\text{MeNH}[\text{CH}_2]_2\text{NH}_2$ was used in conjunction with the synthetic procedure to prepare $[\text{Co}(\text{en})_2(\text{C}_2\text{O}_4)]\text{Cl} \cdot 4\text{H}_2\text{O}$ (en = $\text{NH}_2[\text{CH}_2]_2\text{NH}_2$), the novel title compound **1** was isolated.

We have used the efficient, one-pot synthesis [reaction (1); en = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$] of Jordan and Froebe^{1a} to prepare the oxalate **2** the structure of which we have determined.^{1b} Surprisingly, then, when we changed the amine to $\text{MeNH}[\text{CH}_2]_2\text{NH}_2$ (*N*-Me-en), crystals were obtained which were much more insoluble than related halides previously examined. Their composition and molecular structure were quite a surprise since the reaction conditions were identical with those used in reaction (1).^{1a}



Red prisms[†] were obtained from reaction (1) with *N*-Me-en replacing en, which initially, we took for the desired product; however, their density indicated something considerably heavier than the chloride was present. Microprobe analysis

was used to determine the relative amounts of heavy elements: Co, Cl and Pb (1 : 5 : 2) were found (Found: C, 10.2; H, 2.6; N, 6.0; Pb: 46.4. $\text{Pb}_2\text{CoCl}_5\text{O}_6\text{N}_4\text{C}_8\text{H}_{24}$ requires C, 10.4; H, 2.6; N, 6.1; Pb, 44.9%).

The structure of the product **1** was determined by X-ray crystallography.[†] The cations are present in the lattice in

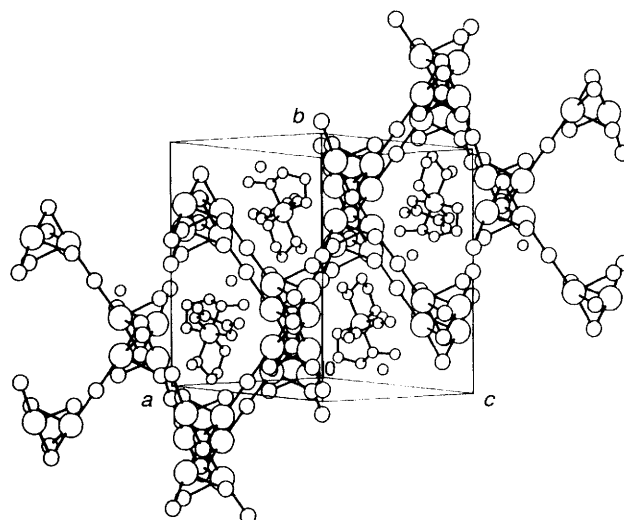


Fig. 1 Packing (PLUTO) of cations, anions and waters in the unit cell. For more details see text. Note that the cations and the waters of crystallization are in cages formed by the infinitely polymerized $-(\text{Pb}_2\text{Cl}_5^-)_n$ -units. Also note the orientation of the oxalato ligand oxygens with respect to the Pb anions.

[†] Crystal data for $\text{Pb}_2\text{CoCl}_5\text{O}_6\text{N}_4\text{C}_8\text{H}_{24}$; monoclinic, $P2_1/n$, $Z = 4$, $a = 10.532(2)$, $b = 15.126(5)$, $c = 14.564(3)$ Å, $\beta = 109.10(2)^\circ$, $V = 2192.44$ Å³, $2\theta_{\text{max}}(\text{Mo-K}\alpha) = 50^\circ$. Number of reflections measured: 4991; number of unique reflections (averaged): 3822; number of data with $I(hkl) \geq 3.0\sigma(I)$: 2373; number of variables: 238; number of atoms: 48; $\mu = 168.278$ cm⁻¹. Transmission coefficients range from 0.6662 to 0.9952. $R(F) = 0.0309$; $R_w(F) = 0.0389$. An empirical correction based on Psi scans was applied to the unique data set. Data were collected with an Enraf-Nonius CAD4 diffractometer and were processed with the programs provided by them. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

racemic pairs describable as *meso*- $\Lambda(\delta\lambda)[\text{Co}\{\textit{trans}-(R,S)\textit{N-Me-en}\}_2(\text{C}_2\text{O}_4)]\text{Pb}_2\text{Cl}_5\cdot 2\text{H}_2\text{O}$ and *meso*- $\Delta(\lambda\delta)[\text{Co}\{\textit{trans}-(S,R)\textit{N-Me-en}\}_2(\text{C}_2\text{O}_4)]\text{Pb}_2\text{Cl}_5\cdot 2\text{H}_2\text{O}$, where *meso* refers to the fact that the two chiral NH(Me) centres are an (*R,S*) pair, located *trans* to each other, and occupying the axial positions about the Co coordination sphere. The basal plane is defined by two oxalato oxygens and the two NH₂ moieties of the *N-Me-en* ligands (see Fig. 1). Interestingly, ¹H and ¹³C NMR data show that D₂O solutions prepared with single crystals of **1** contain exclusively the *meso* cations, whereas D₂O solutions of the solid obtained by stripping the reaction medium show a second species (ratio 40:60). Thus, the Pb₂Cl₅⁻ derivative constitutes a rather remarkable case of ion pair specificity.

Now, for a description of Pb₂Cl₅⁻ anion present in crystalline **1**. The packing diagram shown in Fig. 1 is needed for a description of this remarkable species since it is a polymer consisting of Cl₂Pb(μ_3 -Cl₃)PbCl₂ units which are interlinked into an infinite, three-dimensional lattice. The two Pb cations are linked to one another by three μ -Cl⁻ ligands. Each Pb has two additional Cl⁻ ligands, giving each cation a coordination number of five, and a geometry that can be described as a distorted octahedron with one open position. One of the oxalato oxygens, which do not coordinate to the Co^{III} cation, is oriented in the direction of the open site, the Pb...O distance being about 0.5 Å longer than normal Pb-O bonds. The Pb-Cl-Pb bridges, with $\angle\text{Pb-Cl-Pb} = 180^\circ$, clearly shown on the fragments outside the unit cell (see Fig. 1) are due to Cl⁻ ligands lying at inversion centres. Finally, this is a polymeric ribbon which coils into large cavities composed of eight Pb₂Cl₅⁻ units, each containing the cations and waters of crystallization. Fig. 1 shows only one cation and one water, per cage, in order to avoid cluttering.

Inspection of the literature on haloplumbate anions suggests they have a tendency to form condensed species with large cations having the approximate volume of ours. For example, Mauersberger *et al.*² determined the structure of

[Co(NH₃)₆][Pb₄Cl₁₁] and Haupt and Huber³ determined that of [Co(en)₃][Pb₂Cl₉]Cl·3H₂O, both of which contain condensed haloplumbate anions with geometries totally different from ours, but forming cavities within which the cations and/or waters of crystallization are to be found as well. Thus, the evidence available suggests a high flexibility for the composition and stereochemistry of these anions, the exact details of which may be controlled by the counter-cations used.

We find it fascinating that such a seemingly small change in the amine ligand results in such major change in the compounds eventually isolated since: (a) in reaction (1), using en as a ligand, the oxalato cation is isolated as the chloride; (b) crystallization of a hot solution of (1:2) {[Co(en)₂(C₂O₄)]Cl·4H₂O + PbCl₂} with various amounts of Cl⁻ produce only crystals of the starting materials; (c) the haloplumbate anion, (Pb₂Cl₅⁻)_n, precipitates only as *meso*- $\Lambda(\delta\lambda)[\text{Co}\{\textit{trans}-(R,S)\textit{N-Me-en}\}_2(\text{C}_2\text{O}_4)]\text{Pb}_2\text{Cl}_5\cdot 2\text{H}_2\text{O}$ and its enantiomer; (d) finally, we have recently found that the anionic specificity is not limited to the Pb₂Cl₅⁻ anion, inasmuch as the geometrical isomer with a methyl in the axial and in the equatorial positions can selectively be precipitated as the iodide.

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