A Novel Chain Structure in the $[Pb_2Cl_9]_n^{5n-}$ Anion; Crystal and Molecular Structure of $[Co(NH_2CH_2CH_2NH_2)_3]_2[Pb_2Cl_9]Cl.3H_2O$

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Summary Reaction of chloroplumbic acid and trisethylendiaminecobalt(III) chloride gives orange-yellow crystals of composition $Co(en)_3PbCl_5.1{\cdot}5H_2O$; an *X*-ray crystallographic investigation has shown the presence of a novel type of chain $[Pb_2Cl_9]^{5n-}$, formed from $PbCl_6$ octahedra by alternate sharing of vertices and edges.

STUDIES of the structures of complex chlorides have shown that in addition to those containing mononuclear finite complexes there are examples of polynuclear complexes or of infinite ionic structures.[1] Among finite polynuclear complexes the simplest which have been proved to exist in crystalline form are $[M_2^{III}Cl_9]^{3-}$ ions,[2] consisting of two MX_6 octahedra sharing a face; polymeric ions of the same stoicheiometry are formed when the octahedra share three vertices with three other octahedra, giving rise to corrugated layers.[2] Infinite chains of composition MCl_4 result if octahedral MCl_6 groups share opposite edges, and more complex chains, or bands, of composition MCl_3 result if two sets of octahedra are joined laterally.[1]

We found a novel type of chain of composition $[Pb_2Cl_9]^{5n-}$ in $[Co(en)_3]_2[Pb_2Cl_9]Cl.3H_2O$ (en = ethylenediamine); the chain (Figure) is in the form of a two-fold screw axis and results from alternate sharing of vertices and edges of $PbCl_6$ octahedra.

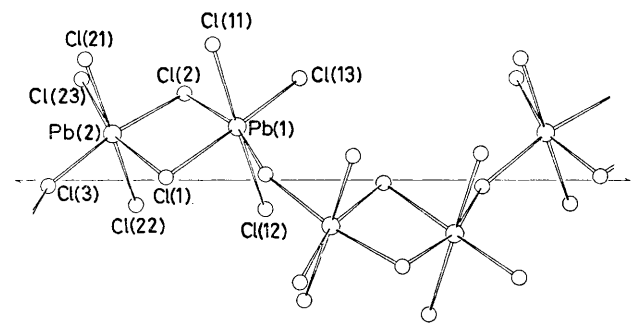

FIGURE. The folding of the polynuclear $[Pb_2Cl_9]_n^{5n-}$ anion about the two-fold screw axis.

$[Co(en)_3]_2[Pb_2Cl_9]Cl.3H_2O$ was obtained in an attempt to prepare the mixed valency compound $Co(en)_3PbCl_6$; to this end equimolar amounts of H_2PbCl_6 and trisethylenediaminecobalt(III) chloride solutions were mixed at *ca.* 80 °C; orange-yellow crystals precipitated on cooling while a gas was evolved. In different preparations crystals elongated along either *a* or *b* axes were obtained. The formula, $Co(en)_3PbCl_5.1{\cdot}5H_2O$, determined by standard analytical methods, clearly indicates the presence of an unusual

structure, and we have therefore carried out a single-crystal *X*-ray diffraction analysis.

Crystal data: $Co(en)_3PbCl_5.1{\cdot}5H_2O$, monoclinic, space group $P2_1$; $Z = 4$; $a = 11{\cdot}60(2)$; $b = 14{\cdot}74(3)$; $c = 11{\cdot}29(2)$ Å; $\beta = 91{\cdot}0(0{\cdot}3)°$. The structure was solved by Patterson and Fourier methods employing 2344 independent reflections measured with Cu-K_α radiations on a Siemens AED diffractometer. The present conventional R is 0·095.†

In the structure the polymeric $[Pb_2Cl_9]^{5n-}$ ions are folded around the screw axis at 0,0 and are surrounded by $[Co(en)_3]^{3+}$ cations; hydrated chloride anions fill the channels along the screw axis at $1/2a$, $1/2c$. Pb–Cl bond distances fall in a rather wide range (2·78—3·04 Å) around the value found in $PbCl_2$ (2·86 Å);[3] the two lead atoms are displaced by *ca.* 0·3 Å from the basal least-squares plane towards apical Cl(12) and Cl(21), which define the longest Pb–Cl distances.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] A. F. Wells, 'Structural Inorganic Chemistry,' Oxford University Press, 3rd edn., 1962, pp. 358—363.
[2] F. Lazarini, *Acta Cryst.*, 1977, **B33**, 2961, and references quoted therein.
[3] H. Braukken, *Z. Krist.*, 1932, **83**, 222.