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# Hexachloroplumbate(IV) Salts

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*Nineteen compounds of the type $M_2PbCl_6$, where M represents an aliphatic or aromatic amine type cation, have been prepared by a modification of a previous method. Some characteristic properties of the compounds have been observed.*

## Introduction

Few compounds of the type $M_2PbCl_6$ have been prepared. The $PbCl_6^{2-}$ anion is relatively large and forms insoluble products with large cations, but most simple metal ions are small and the corresponding salts are quite soluble and unstable. Sakellarios[4] and Chattaway, *et al.*,[2] prepared some diazonium salts of this type. The compounds were crystalline solids which decomposed explosively at a temperature below their melting point. Heal and May[3] prepared $Cs_2PbCl_6$ and studied the stability of the $PbCl_6^{2-}$ ion in hydrochloric acid solutions. The preceding experimenters all used the method shown in the following equation:

$$PbCl_2 + 2HCl + Cl_2 \rightarrow H_2PbCl_6.$$

The chloroplumbic acid solution was then added to a solution containing the large cation. Walton[5] gives a procedure for the preparation of $(NH_4)_2PbCl_6$ which involves the addition of both HCl and $Cl_2$ to a suspension of $PbO_2$.

## Experimental Section

*Preparative method.* Eighteen compounds of the type $M_2PbCl_6$, in which M represents an aliphatic or aromatic amine type cation, and $K_2PbCl_6$ were prepared by a modification of Walton's[5] method. The products were isolated by filtration through a sintered glass crucible of medium porosity. They were rinsed with small volumes of cold concentrated hydrochloric acid and dried by drawing air through the crucibles. The compounds were then further dried in a vacuum desiccator containing both NaOH and $P_2O_5$.

*Analytical procedures.* Duplicate analyses were made for the chloride and lead content of the compounds. The samples used for the determination of lead were reduced with an excess of sodium oxalate, buffered to pH 10, and titrated with a standard solution of EDTA using Eriochrome Black T as an indicator. The chloride content was found by decomposing the samples in water into the amine salts, hydrochloric acid, and solid lead dioxide. The chloride was then determined by potentiometric titration with a standard solution of silver nitrate using a mercury-mercurous sulfate reference electrode and a silver indicating electrode. A summary of the analytical data is given in Table I.

*Properties of the compounds.* The compounds are finely divided yellow solids. They dissolve in water with decomposition in the following manner:

$$M_2PbCl_6 + 2H_2O \rightarrow PbO_2 + 2MCl + 4HCl.$$

They are slightly soluble in methanol, but decompose to form lead chloride, amine hydrochloride salts, and chlorine. Attempts to determine the rate of this reaction by spectral methods were unsucessful. The compounds are insoluble in solvents of low dielectric constant such as benzene, carbon tetrachloride and chloroform.

The compounds are all unstable when heated. Attempts to oven dry them at 105°C, always resulted in the formation of a product having a chloride content lower than theoretical. A differential gravimetric analysis of the compounds $K_2PbCl_6$, $[(C_2H_5)_3NH]_2PbCl_6$ and $[(CH_3)_4N]_2PbCl_6$ was made with 100 mg. samples at a heating rate of 10°C, per minute in air. A mole of chlorine gas per mole of complex salt was gradually evolved in the 100-160°C, range. The resulting amine hydrochloride salts were unstable as the temperature was increased, but no clearly defined mechanism could be formulated from the additional loss in weight. The decomposition of the amine salts continued through a temperature range of about 100°C, and apparently involved several simultaneous processes. The final product was $PbCl_2$ in the case of the complex amine salts while stoichiometric amounts of KCl and $PbCl_2$ were formed from $K_2PbCl_6$. There was no further loss in weight until these compounds began to vaporize.

The absorption spectra of $[(CH_3)_4N]_2PbCl_6$, $[(C_2H_5)_3NH]_2PbCl_6$ and $PbCl_6$ were measured in varying concentrations of hydrochloric acid. The absorption spectra of the complex salts were identical within the limits of experimental error. Three of the absorption maxima of the $PbCl_2$ solutions corresponded to the

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(1) A. I. Biggs, H. N. Parton and R. A. Robinson, *J. Am. Chem. Soc.*, *77*, 5844 (1955).
(2) F. D. Chattaway, F. L. Garton and G. D. Parkes, *J. Chem. Soc.*, *125*, 1980 (1924).
(3) H. G. Heal and J. May, *J. Am. Chem. Soc.*, *80*, 2374 (1958).
(4) E. Sakellarios, *Chem. Ber.*, *56B*, 2536 (1923).
(5) H. F. Walton, «Inorganic Preparations», Prentice Hall, Englewood Cliffs, N. J., pp. 83-84.

**Table I.**

| | Chlorine (%) | | Lead (%) | |
|---|---|---|---|---|
| | Calcd. | Found | Calcd. | Found |
| $(CH_3NH_3)_2PbCl_6$ | 43.95 | 44.0±0.2 | 42.80 | 42.7±0.1 |
| $[(CH_3)_2NH_2]_2PbCl_6$ | 41.54 | 40.9±0.3 | 40.47 | 40.6±0.2 |
| $[(CH_3)_3NH]_2PbCl_6$ | 39.38 | 37.6±0.3 | 38.36 | 37.9±0.1 |
| $[(CH_3)_4N]_2PbCl_6$ | 37.44 | 38.1±0.1 | 36.46 | 35.4±0.1 |
| $(C_2H_5NH_3)_2PbCl_6$ | 41.54 | 41.0±0.2 | 40.47 | 40.6±0.1 |
| $[(C_2H_5)_2NH_2]_2PbCl_6$ | 37.44 | 37.7±0.2 | 36.46 | 36.4±0.1 |
| $[(C_2H_5)_3NH]_2PbCl_6$ | 34.07 | 33.9±0.1 | 33.19 | 33.2±0.1 |
| $(iso\text{-}C_3H_7NH_3)_2PbCl_6$ | 39.38 | 38.7±0.1 | 38.36 | 38.5±0.1 |
| $[(iso\text{-}C_3H_7)_2NH_2]_2PbCl_6$ | 34.07 | 34.1±0.1 | 33.19 | 32.9±0.1 |
| $(CH_2NH_3)_2PbCl_6$ | 44.13 | 43.9±0.3 | 42.98 | 42.9±0.3 |
| $[(2\text{-}HOC_2H_4)(C_2H_5)_2NH]_2PbCl_6$ | 32.41 | 32.3±0.1 | 31.57 | 31.7±0.2 |
| $[H_3CCH(CH_3)CH_2CH(CH_3)NH_3]_2PbCl_6$ | 34.07 | 33.5±0.1 | 33.19 | 33.5±0.2 |
| $(C_5H_5NH)_2PbCl_6$ | 36.67 | 36.6±0.1 | 35.71 | 35.6±0.1 |
| $(C_6H_5CH_2NH_3)_2PbCl_6$ | 33.43 | 32.9±0.2 | 32.56 | 32.6±0.1 |
| $(3\text{-}CH_3.C_5H_4NH)_2PbCl_6$ [a] | 34.98 | 34.8±0.2 | 34.08 | 33.9±0.1 |
| $(4\text{-}CH_3.C_5H_4NH)_2PbCl_6$ [b] | 34.98 | 35.3±0.1 | 34.08 | 34.0±0.1 |
| $(2,4\text{-}CH_3.C_5H_3NH)_2PbCl_6$ [c] | 33.43 | 33.2±0.1 | 32.56 | 32.6±0.1 |
| $(C_9H_7NH)_2PbCl_6$ | 3.127 | 31.4 | 30.46 | 31.0±0.1 |
| $K_2PbCl_6$ | 42.71 | 42.6±0.2 | 41.60 | 41.7±0.1 |

[a] 3-methyl pyridinium. [b] 4-methyl pyridinium. [c] 2,4-dimethyl pyridinium.

maxima of the complex salts. The absorption spectrum of $PbCl_2$ in 1.0 *M* HCl showed maxima at 207 and 234 mμ. These have been assigned by Biggs, Parton and Robinson[1] to transitions involving the $Pb^{2+}$ and $PbCl^+$ ions, respectively. The absorption spectra of $PbCl_2$ in HCl solutions more concentrated than 6 M/l showed a maximum at 270 mμ perhaps due to a more highly complexed species such as $PbCl_3^-$ or $PbCl_4^{2-}$. The absorption spectra of the complex salts in 1.0 *M* HCl changed rapidly with time. In freshly prepared solutions, an absorption maximum was observed at 305 mμ which faded rapidly. This peak has been attributed to $PbCl_5^-$ by Heal and May.[3] The absorption spectra of the complex salts in concentrated HCl solutions show the same absorption maxima but the stability of the form producing the 305 mμ maximum is increased at higher concentrations of HCl. However, this species is not stable even in 12 *M* HCl and the absorption at 305 and 270 mμ change with time.