

Preliminary communication

Complexes of plumbous chloride and dimethyllead dichloride with methylaluminium dichloride

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The results of our earlier investigations of the syntheses of organolead compounds from organoaluminium compounds and lead salts^{1,2} indicated that as in other reactions of organoaluminium compounds, the first stage of these syntheses involved formation of a donor-acceptor complex.

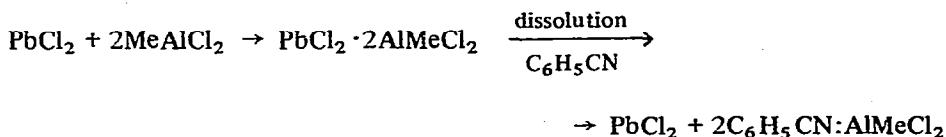
The formation of complexes $\text{GeCl}_4 \cdot \text{AlR}_3$ and $\text{R}_2\text{GeCl}_2 \cdot \text{AlRCl}_2$ accompanying the synthesis of organogermanium compounds has been reported in the literature³ together with the formation of analogous complexes with tin, $\text{R}_3\text{SnCl}_3 \cdot \text{AlCl}_3$ ⁴. However, the formation of similar complexes involving organolead and organoaluminium compounds has not been hitherto reported.

The present study deals with complexes of methylaluminium dichloride with plumbous chloride and dimethyllead dichloride.

On synthesizing these complexes it was found that plumbous chloride dissolves in a solution of methylaluminium dichloride until a mole ratio of Pb/Al 1/2 is attained, the solution being accompanied by a considerable evolution of heat. Evaporation of the solvent yielded the complex as colourless homogeneous crystals containing 39.8% Pb and 10.52% Al which corresponds to a mole ratio Pb/Al 1/2 (theoretical Pb value of 41.1% and an Al value of 10.7%).

The formation of the complex of dimethyllead dichloride with methylaluminium dichloride occurred in a similar manner yielding crystals containing 39.14% Pb and 9.94% Al (theoretical Pb value of 38.8% and Al value of 10.1%).

When methylaluminium dichloride was used in considerable excess, a complex of the well-defined mole ratio Pb/Al 1/2 was obtained (e.g. reactant mole ratio, $\text{PbCl}_2/\text{MeAlCl}_2$ 1/4; found: Al, 11.5; Pb, 40.83%; calcd.: Al, 10.7; Pb, 41.1%). On treatment with a strong Lewis base, solid white lead compounds were precipitated from solutions of these complexes, a reaction which can be represented by the following equation:



The molecular weight of the Pb/Al 1/2 complex formed in the dimethyllead dichloride–methylaluminium dichloride system was determined cryoscopically (Fig.1). Extrapolation of the curve to infinite dilution gives a molecular weight value of 530–540 the theoretical value for the complex $\text{Me}_2\text{PbCl}_2 \cdot 2\text{AlMeCl}_2$ being 530. For solutions of higher concentrations, however the curve in Fig.1 indicates that appreciable association or even polymerization of the complex occurs in solution. Thus, for a concentration of 7.3% complex in solution the presence of a trimer of mol.wt. 1550 is indicated.

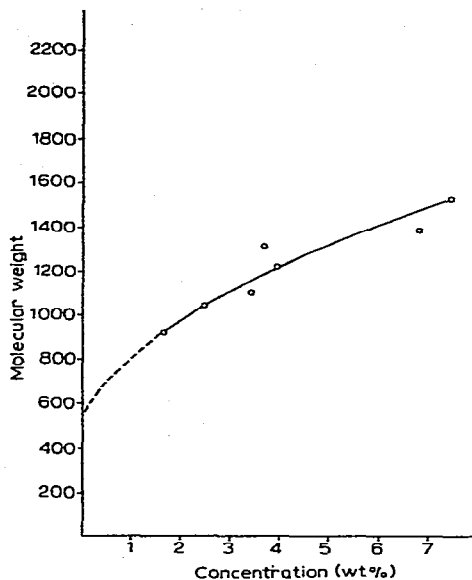


Fig.1. The molecular weight of the complex $\text{Me}_2\text{PbCl}_2 \cdot 2\text{MeAlCl}_2$ in relation to its concentration in benzene as solvent.

NMR spectral studies of the complexes were also undertaken. Changes in the chemical shift of methyl group attached to the aluminium atom in relation to the type of lead compound used and to the Pb/Al mole ratio in the resulting complex are presented in Fig.2.

At a Pb/Al ratio of 1/2 the chemical shift makes a characteristic band suggesting the presence of complexes of the following compositions: $\text{PbCl}_2 \cdot 2\text{Al}(\text{CH}_3)\text{Cl}_2$ and $(\text{CH}_3)_2\text{PbCl}_2 \cdot 2\text{Al}(\text{CH}_3)\text{Cl}_2$.

The chemical shifts of the methyl group attached to the aluminium atom, e.g. in the complex $\text{PbCl}_2 \cdot 2\text{Al}(\text{CH}_3)\text{Cl}_2$, is equal to 14 cps with respect to that for pure methylaluminium dichloride, and is comparable to the shift of the methyl group in the complex $\text{C}_6\text{H}_5\text{CN}:\text{Al}(\text{CH}_3)\text{Cl}_2$.

Studies in progress are directed towards the determination of the structures of the above complexes and to the isolation and definition of the complexes of dialkylaluminium chloride and trialkylaluminium with plumbous chloride and organolead chloride derivatives.

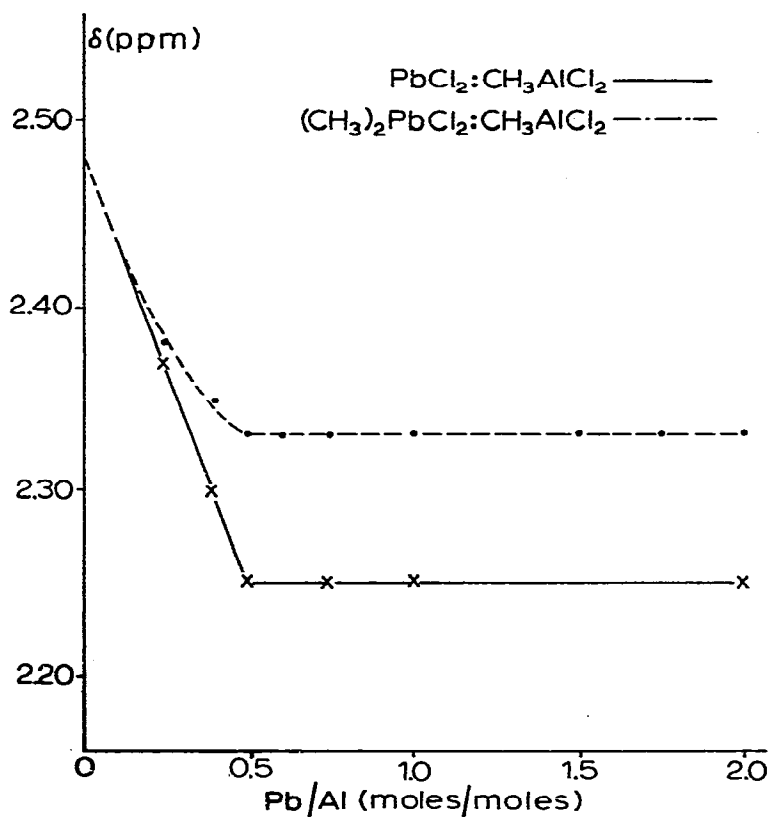


Fig.2. The NMR chemical shift of the CH_3Al group in relation to the Pb/Al mole ratio.

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