[CONTRIBUTION FROM THE FUEL SECTION, GENERAL MOTORS RESEARCH CORPORATION, AND THE RESEARCH LABORATORY OF APPLIED CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# A NEW METALLO-ORGANIC COMPOUND: DIPLUMBIC HEXA-ETHYL[1]

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## Introduction

Two ethyl lead compounds are reported in the literature.

Tetra-ethyl lead was prepared by P. Pfeiffer by the action of lead chloride on ethyl-magnesium iodide,[2] according to the equation: $4C_2H_5MgI + 2PbCl_2 \longrightarrow Pb + Pb(C_2H_5)_4 + 2MgI_2 + 2MgCl_2$. Löwig reported the preparation of "hexa-ethyl lead" by interaction of sodium-lead alloys and ethyl iodide.[3] However, the formulas given by Löwig are antiquated, as they refer to water as HO. Löwig also considered lead as having an atomic weight of 103, and it is impossible to ascertain whether he assumed the formula for his compound to be $PbEt_3$ or $Pb_2Et_6$. At any rate, his statement is not confirmed either by a molecular-weight determination or by an analysis for lead. Moreover, a more recent experimenter[4] duplicated Löwig's work, and showed that the product obtained by Löwig was actually impure tetra-ethyl lead, the same as had been obtained in the meanwhile by Buckton[5] by interaction of lead chloride and zinc ethyl, according to the equation, $2PbCl_2 + 2ZnEt_2 = Pb + PbEt_4 + 2ZnCl_2$. To quote Ghira, "I think it is not too much to presume that at the present time no lead compounds of the type $PbX_3$ or $Pb_2X_6$ have ever been reported, studied or isolated."

An exhaustive study of organic compounds of tetravalent lead has been made during the past few years by E. Krause and his co-workers. Krause prepared all his lead alkyls by Pfeiffer's method, and reported[6] the following constants for $Pb(C_2H_5)_4$: b. p., 83° (14 mm.); $d^{18}$, 1.6591.

The method used by Krause, namely, the decomposition of an alkyl or aryl magnesium halide by lead chloride, always yields a tetra-alkyl lead compound when an alkyl halide is used. However, using aryl halides and an insufficient amount of lead chloride, Krause was able to prepare a series of compounds of the type, $PbX_3$ or $Pb_2X_6$, which he considers as corresponding to trivalent lead.[7]

## Experimental Part

In the work done by the authors of this paper, 65 g. of triethyl lead chloride, covered with 100 cc. of distilled water, was stirred with 40 cc. of 5 *N* sodium hydroxide solution until all had dissolved. The triethyl lead hydroxide formed was precipitated from this solution by the addition of 200 cc. of 5 *N* sodium hydroxide solution, and was separated; 60 g. of this hydroxide was dissolved in 200 cc. of 95% ethyl alcohol and electrolyzed with lead electrodes, using a current density of 0.01 amperes per sq.

[1] Read at the New Haven Meeting of the American Chemical Society, April, 1923.

[2] Pfeiffer, *Ber.*, **37**, 1126 (1904).

[3] Löwig, *J. prakt. Chem.*, **60**, 304 (1853).

[4] Ghira, *Gazz. chim. ital.*, **24**, 1, 42 (1894).

[5] Buckton, *Ann.*, **109**, 222 (1859).

[6] Krause, *Ber.*, **49**, 1415 (1916).

[7] Krause, *ibid.*, **55**, 888 (1922).

cm. An oil was formed at the cathode, and much gas evolved at the anode. This oil was heavy and insoluble in alcohol, so that it collected at the bottom of the cell. The reaction is expressed by the following equations: $Pb(C_2H_5)_3OH = Pb(C_2H_5)_3^+ + (OH)^-$; $2Pb(C_2H_5)_3^+ + 2\ominus = Pb_2(C_2H_5)_6$.

**Properties of the Oil.**—The oil so obtained is yellowish and easily decomposed by air, giving a yellowish powder that darkens rapidly; d., 1.94. It distilled with steam without decomposition, but very slowly, in the ratio of 1 cc. of diplumbic hexa-ethyl, $Pb_2(C_2H_5)_6$, to 25–30 cc. of water. It could not be distilled directly without decomposition, but under 2mm. pressure it boiled at about 100°. It did not freeze at —80°.

*Analysis.*—A sample of the oil was analyzed for lead by the method of Krause.[8]

Subs., 0.235: $PbBr_2$, 0.291. Calc. for $C_{12}H_{30}Pb_2$: Pb, 70.4; calc. for $C_8H_{20}Pb$: Pb, 64.1. Found: 69.8.

The molecular weight was determined by the freezing-point lowering of benzene, using 5.10° as the cryoscopic constant for benzene, this being the value used by Krause for all lead compounds.

Subs., 0.6285, 0.0482, 0.0212, 0.0182: benzene, 9.184, 13.35, 11.48, 14.44; $\Delta t$, 0.600, 0.040, 0.032, 0.022. Calc. for $Pb_2(C_2H_5)_6$: mol. wt., 588; calc. for $Pb(C_2H_5)_3$; 294. Found: 582, 460, 294, 292.

Thus, diplumbic hexa-ethyl, like the corresponding aryl compounds[7] is dissociated in 2 $PbX_3$ groups in dilute solutions, but exists as $Pb_2X_6$ at higher concentrations.

This shows one more similarity between organic lead and tin compounds, as it was usually considered that the last one only is able to give organic compounds containing a chain of 2 atoms of the metal. However, the easy dissociation shown by these compounds is very different from what is observed with carbon chains, and leaves but little hope as to the possibility of preparing longer chains of lead atoms.

An attempt was made to prepare the chlorine derivative of this compound. Since tetra-ethyl lead reacts with hydrochloric acid to form ethane and triethyl lead chloride, it was hoped that the hexa-ethyl compound might react similarly to give a substance, $Pb_2(C_2H_5)_5Cl$. Such is not the case; instead, the Pb-Pb linkage is apparently broken, giving as the main products of the reaction lead triethyl chloride $Pb(C_2H_5)_3Cl$, and lead chloride, while gas is given off. The reaction may probably be written as follows: $Pb_2(C_2H_5)_6 + 3HCl = Pb(C_2H_5)_3Cl + PbCl_2 + 3C_2H_6$.

## Summary

Inasmuch as all organic lead compounds of the type $PbX_4$ are able to yield derivatives of the general formulas $PbX_3Cl$ and $PbX_3OH$, a method has been developed by which the corresponding $Pb_2X_6$ compounds can be obtained readily.

[8] Krause, *Ber.*, **49**, 1130 (1916).

It has been shown that such compounds are represented by the formula $Pb_2X_6$ in pure state or in concentrated solutions, and by $PbX_3$ in very dilute benzene solutions.

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# THE SUGAR CONTAINED IN TUBERCULINIC ACID, THE NUCLEIC ACID OF TUBERCLE BACILLI

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In previous papers by the authors[2] a description has been given of the method used for separating tuberculinic acid from tubercle bacilli, and also the nature of the pyrimidines which function in this acid. On the basis of new data obtained in our research we concluded that tuberculinic acid containing the pyrimidines, thymine and cytosine, but no uracil, resembles in its chemical characteristics a nucleic acid of animal origin, thereby establishing the natural group to which the tubercle bacillus is to be assigned. It is also known that the carbohydrates contained in plant and animal nucleic acids are characteristic of each group and differ in the two acids, hexose occurring in the acid of animal origin and pentose in the plant variety. Hence, an accurate knowledge of the sugar contained in tuberculinic acid would serve as a check on the above classification of the tubercle bacillus which is based on the results of a pyrimidine analysis.

The literature of the chemistry of tubercle bacillus reveals the fact that the carbohydrate phase of the work has received little attention at the hands of previous investigators, notwithstanding the fact that one of the first of them, Hammerschlag[3] recognized its importance. He was able to detect a reducing sugar in defatted bacilli, but thought he was dealing with cellulose. De Schweinitz and Dorset[4] were of the same opinion in regard to the nature of the carbohydrate contained in this material. Levene[5] isolated a carbohydrate of a glycogen-like nature as an impurity of the nucleic acid from tubercle bacilli, but did not further investigate it beyond the point of ascertaining that it formed a soluble copper salt which permitted its separation from the insoluble copper nucleate.

Bendix[6] was the first investigator to report the finding of a sugar complex in the nucleoprotein obtained from the tubercle bacillus. He characterized his product as a pentose, but gave no details as to the method employed in its isolation, nor any characteristic chemical tests in support of his conclusion. The only other investigator, so far

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[2] Brown and Johnson, *J. Biol. Chem.*, **54**, 721; 731 (1922).

[3] Hammerschlag, *Monatsh.*, **10**, 9 (1892).

[4] De Schweinitz and Dorset, THIS JOURNAL, **17**, 605 (1895).

[5] Levene, *J. Exp. Med.*, **6**, 135 (1901).

[6] Bendix, *Deut. med. Wochschr.*, **1901**, 16.