

fades as the residual ammonia is withdrawn, and the dry, cream-colored salt formed is stable at room temperature.

**Preparation of Triphenylethyllead.**—Since the properties of triphenylethyllead had been established previously,<sup>12</sup> its preparation was undertaken to demonstrate the existence of the triphenylplumbide ion in the ammonia solution of the sodium salt. An excess of ethyl bromide was admitted to the reaction vessel and white crystals of triphenylethyllead were precipitated. A pure product was obtained by dissolving the crude material in a small quantity of ethyl ether, adding about twice the quantity of methyl alcohol and evaporating the solution *in vacuo* at room temperature. The material precipitated in white curds, which when dried *in vacuo* formed a fine white powder. The melting point was 39° and molecular weight determinations and analyses for lead identified it as triphenylethyllead. It is very soluble in ether, acetone, carbon tetrachloride and petroleum ether, less soluble in methyl alcohol and only very slightly soluble in ammonia.

**Ammonium Triphenylplumbide.**—When an ammonium salt,<sup>13</sup> in equivalent amount, is added to a liquid ammonia solution of sodium triphenylplumbide, no reaction is observed. If a small excess is added, no change in appearance of the solution is apparent, but in the presence of great excess, complete destruction of the triphenylplumbide radical results, accompanied by the separation of metallic lead in large, heavy, black curds and the production of benzene.

When the solution containing sodium and ammonium triphenylplumbides is evaporated at low temperatures under reduced pressure, crystals do not appear until it has become very concentrated and no indication of reaction between the ammonium ion and the triphenylplumbide ion is detectable. If ethyl bromide is added to the

(12) Krause and Schmitz, *Ber.*, **52**, 2150 (1919); Krause and Schlöttig, *ibid.*, **58**, 430 (1925).

(13) Compressed tablets (5 grain) of ammonium bromide, supplied by Burroughs, Wellcome and Co., New York, serve as a very satisfactory source of ammonium ions.

dilute solution, a white precipitate of triphenylethyllead separates, indicating that the triphenylplumbide ion remains unchanged. Ammonium triphenylplumbide appears to be stable and very soluble in liquid ammonia at -33.4°.

**Reaction of Sodium Triphenylplumbide with Methylene Chloride.**—Sodium triphenylplumbide, freed of ammonia at -33.4°, was allowed to react with an excess of dry methylene chloride. The salt dissolved at first to form a yellow solution, but the color gradually faded, due presumably to reaction. A soft, waxy solid of indefinite melting point and soluble in petroleum ether was isolated from the product. A single molecular weight determination gave a value of 640, suggesting that the product might contain two triphenyllead radicals, comparable to the product of the reaction of sodium triphenylgermanide with methylene chloride.<sup>14</sup> No similar product was detected, however, when the reaction was carried out in liquid ammonia solution. Since no pure, well characterized product could be obtained, this reaction was not investigated further.

### Summary

1. Methods for the preparation of tetraphenyllead, triphenyllead iodide, hexaphenyldilead, sodium triphenylplumbide and triphenylethyllead are described and some of the reactions and properties of these compounds are recorded.

2. Use is made of tetrasodium nonaplumbide, Na<sub>4</sub>Pb<sub>9</sub>, as a mild reducing agent in liquid ammonia solutions.

3. The existence of ammonium triphenylplumbide as a fairly stable and soluble salt in liquid ammonia has been indicated, but triphenylplumbane does not appear to be formed.

(14) Kraus and Nutting, *THIS JOURNAL*, **54**, 1622 (1932).

PROVIDENCE, R. I.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

## Ammino Compounds of Triphenyllead Chloride

BY LAURENCE S. FOSTER, IRVING J. GRUNTFEST AND LINTON A. FLUCK

When ammonia is condensed upon crystalline triphenyllead chloride at the boiling point of liquid ammonia, the volume of the solid increases greatly, indicating that a reaction occurs. It has been shown that a series of ammino compounds exists, none of which is stable at room temperature. Two methods have been employed in an attempt to establish the composition of the solid phases: in the first, method I, which was entirely volumetric, the amount of ammonia which was added or withdrawn from the reaction chamber was measured by means of a gas buret; and in the second, method II, the gas buret was used to

make small, definite adjustments in the amount of ammonia in the system, but the composition of the phase under investigation was determined by decomposing it and absorbing and weighing the ammonia evolved. Method I was found to be useful for a preliminary exploration of the system, but since the errors in the volume measurements were cumulative, it did not prove to be entirely satisfactory. Method II was used in determining the composition of the highest ammino compound only, and had the advantage that it was much more rapid.

Using the volumetric method (I), two runs

were carried out, each taking about three months, due to the slowness with which equilibrium is established between the solid phases. The results were not in very good agreement, and from the data it was not possible to determine the ratio of the number of moles of ammonia per mole of triphenyllead chloride with an error of less than 10%. The results are shown graphically in Fig. 1, where the equilibrium pressures are plotted against the number of moles of ammonia per mole of triphenyllead chloride present in the condensed phase. There are indications of the existence of at least four ammino compounds which have the following approximate compositions

Vapor pressure, mm.	400	160	100	50
Moles NH <sub>3</sub>	9.65	2.7	1.8	1.3

The vertical line in the graph, corresponding to 9.72 moles of ammonia, was drawn from the data obtained using method II. The existence of a metastable compound with a vapor pressure of 415 mm. is suggested, but its composition was not established.

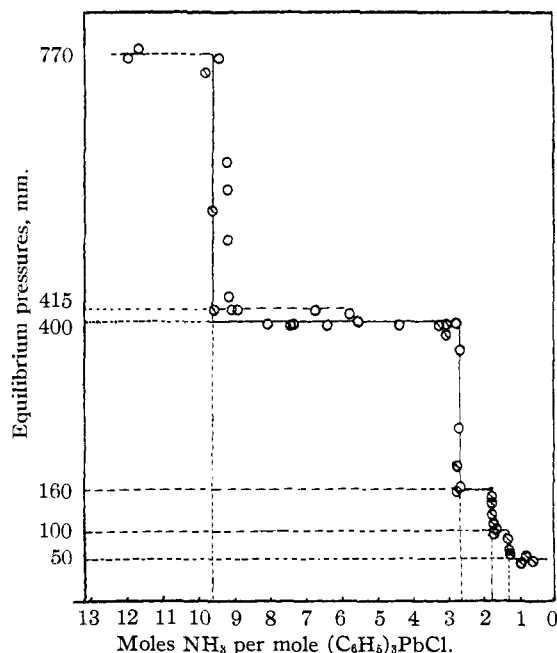


Fig. 1.—Pressure-composition diagram for the system  $(C_6H_5)_3PbCl-NH_3$  at  $-33.4^\circ$ .

Due to the uncertainties of the results, it was decided to repeat part of the work, focusing the attention upon the compound containing the largest amount of ammonia, since it could be prepared readily in equilibrium with the saturated

solution and analyzed conveniently by the use of method II. The experiments were performed independently by two operators who used different equipment and different preparations of triphenyllead chloride. The results of eight experiments gave an average composition of 9.72 moles of ammonia per mole of triphenyllead chloride, and the deviations of the individual results from the mean were less than 1%. The composition for this single compound is in fair agreement, thus, with that obtained through the use of the first method.

While it is not usual for the numbers of molecules in complex ammino compounds to be so far from a ratio of small whole numbers, it appears that the tentative conclusion must be drawn that with triphenyllead chloride the ratio of the number of moles of ammonia per mole of chloride, in the highest complex, has a value of about 29 to 3 or 68 to 7. Additional information concerning the structure will be needed before a formula can be assigned. The experimental data for the other ammino compounds are so inaccurate that no statement concerning their compositions is justified at this time.

Few studies have been made of the compounds formed between organo-metallic substances and neutral molecules, like those described here. In the index of the treatise by Krause and von Grosse,<sup>1</sup> out of the 6000 organo-metallic compounds listed only two dozen ammino or similar complex derivatives are catalogued, and none of them show any irregularities. It may be noted, however, that Biltz and Fischer<sup>2</sup> found that several ammino compounds are formed by the lead dihalides, the compositions of some of which do not correspond to ratios of small whole numbers; *e. g.*,  $4PbCl_2 \cdot 13NH_3$  and  $2PbCl_2 \cdot 11NH_3$ . They postulated that these compounds consist of mixtures of simpler amines, but until structure determinations have been made the question as to their formulas also remains unanswered.

### Experimental

**Preparation of Triphenyllead Chloride.**—The starting material was tetraphenyllead and it was converted to triphenyllead chloride by the method of Gilman and Robinson.<sup>3</sup> The samples used were shown to be pure by the melting point,  $206^\circ$ , and by analysis for chlorine. The material is stable toward ammonia; the weights and melt-

(1) Krause and von Grosse, "Die Chemie der metall-organischen Verbindungen," Berlin, 1937.

(2) Biltz and Fischer, *Z. anorg. allgem. Chem.*, **124**, 230 (1922).

(3) Gilman and Robinson, *This Journal*, **51**, 3112 (1929).

ing points of the samples remained unaltered, even though the outward appearance was considerably changed during the formation and decomposition of the complexes. Triphenyllead chloride is stable toward air and atmospheric moisture.

**Apparatus and Procedure.**—The sample of triphenyllead chloride was sealed in a "Pyrex" glass bulb (vol., 17 ml.) attached to a long stem of capillary tubing, a stopcock and one part of a ground joint. The reaction bulb thus could be removed from the system and weighed. It was cooled to  $-33.4^\circ$  in a bath of liquid ammonia. In addition to connections to the source of purified and redistilled ammonia and to a "Hyvac" vacuum pump, the remaining apparatus consisted of a mercury manometer; a removable bulb, similar to the reaction bulb, holding anhydrous calcium chloride for absorbing and weighing the ammonia evolved upon decomposition of the compounds; and a jacketed gas-measuring buret<sup>4</sup> equipped with a Pettersson compensator set for 760 mm. and  $0^\circ$ ,<sup>5</sup> so that the number of moles of gaseous ammonia added or withdrawn from the reaction vessel could be determined without laborious calculations. The volumes of the connecting tubes were determined so that it was possible to compute at any time, from the total amount of ammonia in the system, the amount of ammonia held in the condensed phase.

Since the vapor pressures of the solid compounds were found not to vary appreciably with small temperature fluctuations, no attempt was made to maintain the boiling point of the bath ammonia at a strictly constant temperature. The vapor pressure of the saturated solution of triphenyllead chloride, on the other hand, did vary considerably with temperature, and it seemed advisable, prior to recording significant vapor pressure values, to replace the ammonia in the bath with a fresh supply and to allow it to evaporate against a definite pressure, to ensure that the temperature was  $-33.4^\circ$ .

Sufficient ammonia was condensed in the reaction tube to form a saturated solution of triphenyllead chloride in equilibrium with the highest ammino complex. After the crystals had been allowed to remain in contact with the solution for several days, ammonia was withdrawn, either in measured quantities by means of the gas buret (method I) or more rapidly by means of the vacuum pump (method II). In either case, when the sample was nearly dry the remaining excess ammonia was taken off slowly by means of the buret, and when it was established that the dry salt was in equilibrium with the vapor, the pressure was recorded and the composition of the complex compound was determined.

Using method I, additional ammonia was removed in known decrements and the system was allowed to return to equilibrium after each removal. In this way the equilibrium pressure-composition diagram, shown in Fig. 1, was arrived at.

In method II, once the ammino compound was formed, in the manner just described, it was decomposed by allowing it to warm to room temperature and the ammonia evolved was absorbed in the weighing tube containing cal-

cium chloride, cooled to  $-33.4^\circ$ . By subtracting the amount of ammonia computed to be in the gas phase in the reaction bulb, at  $-33.4^\circ$ , the amount of ammonia held in the solid phase was obtained. The data are given in Table I, expressed in moles of reactants.

TABLE I  
COMPOSITION OF THE HIGHEST AMMINO COMPOUND OF TRIPHENYLLEAD CHLORIDE FORMED AT  $-33.4^\circ$  (BY METHOD II)

Moles of $(C_6H_5)_3PbCl$	Moles of $NH_3$	Ratio of moles $NH_3$ to moles $(C_6H_5)_3PbCl$
0.003163	0.03107	9.82
	.03064	9.69
	.03063	9.68
.002558	.02495	9.75
.002079	.02030	9.76
	.02021	9.72
	.02021	9.72
	.02017	9.70
	Av.	9.72

TABLE II  
EQUILIBRIUM PRESSURES OF THE AMMINO COMPOUNDS OF TRIPHENYLLEAD CHLORIDE

Compound	Vapor pressure, mm. At start	At equilib.	Time elapsed
400 mm. compound	410	401.5	18 hrs.
	379	399.8	4 days
	386.5	397.5	2 days
	394	399	1 day
	396	400	1 day
	418	408	3 days
	Accepted pressure	400	
160 mm. compound	154	158.5	1 day
	236	161	1 day
		Accepted pressure	160
100 mm. compound	202	96.5	1 day
	91.3	98	1 day
	149.5	101.5	1 day
		Accepted pressure	100
50 mm. compound	93	55.5	1 day
	74	50.5	1 day
	119	65.2	1 day
	104	57.5	1 day
		Accepted pressure	50
Metastable	755	416	1 day
415 mm. compound	411.5	417.5	12 hrs.
	375	415.2	17 hrs.
	442	413	1 day
	403.5	417	20 hrs.
	357	415	1 day
	462	417	1 day
	Accepted pressure	415	
Possible 38 mm. compound	80	38	1 day
	18.5	37	1 day
	Accepted pressure	38	

(4) The apparatus was somewhat similar to that described by Friedrichs, *Z. anorg. allgem. Chem.*, **116**, 141 (1921).

(5) Pettersson, *Z. anal. Chem.*, **25**, 467 (1886); cf. Dennis, "Gas Analysis." The Macmillan Co., New York, N. Y., 1929, page 95.

In Table II the data are given from which the values of the equilibrium pressures were estimated. It will be noted that in most cases it was possible to approach the equilibrium from both sides.

### Summary

The compounds formed between ammonia and

triphenyllead chloride have been investigated and their vapor pressures measured at  $-33.4^{\circ}$ . Several compounds were detected, but the composition of only one was determined accurately. In this compound the number of moles of ammonia per mole of triphenyllead chloride cannot be expressed as the ratio of small whole numbers.

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## The Standardization of Strong Oxidizing Agents with Potassium Iodide by the Acetone Method

BY I. M. KOLTHOFF AND H. A. LAITINEN

Lewis<sup>1</sup> attributes the low results obtained by us<sup>2</sup> in the standardization of potassium permanganate with pure potassium iodide by the acetone method of Berg<sup>3</sup> to the use of too low an acidity. The acidity used in our work was 0.9 *N*, while Berg used 2.0–2.5 *N* with potassium iodate as the oxidant. According to his comments the most suitable acidity seems to vary with the oxidant which is being standardized. In order to determine whether our low results were caused by too low an acidity, we have extended our experiments over a range of varying concentrations of acid. The same sample of pure potassium iodide as described previously<sup>2</sup> was used. An accurately weighed amount of the pure iodide was dissolved in water, 50 ml. of acetone, water and varying amounts of 9 *M* sulfuric acid were added to make a volume of 200 ml. One tenth normal potassium permanganate, standardized by the accurate method previously described, was added from a weight buret to within about 1% of the end-point (40 to 50 ml.) and the titration was then finished with 0.01 *N* permanganate which was added from an ordinary buret. The results were found to be independent of the acidity when the initial sulfuric acid concentration lay between 0.5 and 4 *N*. The results were always low, but depended upon the speed with which the 0.01 *N* permanganate was added in the immediate vicinity of the end-point. When it was added at a rate of about ten seconds per drop the results were 1.0%, low; on the other hand, if the permanganate was added

rapidly until the color change persisted for thirty seconds, the results were 0.2% low. The speed of addition of the permanganate up to 0.5% before the equivalence point did not affect the results. Apparently, the low results have to be attributed to the fact that part of the 0.01 *N* permanganate added in the immediate vicinity of the end-point reacts with the acetone and the iodoacetone and is withdrawn from reaction with iodide. If the titration was carried out and finished with 0.1 *N* permanganate, which was added either from a weight or a volume buret, the results were found to be close to the theoretical value but always slightly low. This is evident from the experiments reported in Table I which were carried out at varying acidity. In all these experiments 25 ml. of acetone was used in an initial volume of 100 ml.

TABLE I  
STANDARDIZATION OF 0.1 *N* PERMANGANATE WITH POTASSIUM IODIDE BY BERG'S METHOD. THEORETICAL VOLUME OF PERMANGANATE 47.70 ML.

Initial normality of H <sub>2</sub> SO <sub>4</sub>	0.25	0.5	1.0	2.0	3.0	4.0
0.1 <i>N</i> permanganate used	<sup>a</sup>	47.69 <sup>b</sup>	47.68 <sup>b</sup>	47.67	47.62	47.63
Error, %		-0.02	-0.04	-0.06	-0.16	-0.14

<sup>a</sup> Reaction velocity too small to allow titration.

<sup>b</sup> Average of two to three titrations.

Under the specified conditions the titration yields excellent results, particularly when the initial acidity is between 0.5 and 2 *N* and the titration is carried out with 0.1 *N* permanganate. It was found that the amount of acetone in the initial volume of 100 ml. could be changed between 10 and 50 ml. without changing the results

(1) D. Lewis, *THIS JOURNAL*, **59**, 1401 (1937).

(2) I. M. Kolthoff, H. A. Laitinen and J. J. Lingane, *ibid.*, **59**, 429 (1937).

(3) R. Berg, *Z. anal. Chem.*, **69**, 369 (1926).