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I. DERIVATIVES OF THE TETRACHLORIDES OF ZIRCONIUM, THORIUM, AND LEAD.[1]

BY J. MERRITT MATTHEWS.

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1. INTRODUCTION.

THE tetrachlorides of several of the members of Group IV have been studied in their deportment with certain organic nitriles and amines, and the results seem to indicate that there is a general tendency toward reactions between these tetrachlorides and the latter-named reagents, giving rise to definitely constituted compounds. That is to say, the tetrachlorides of Group IV appear to possess an acidic character in their ability to combine with certain organic bases to form neutral salts. This behavior has already been studied with reference to the tetrachlorides of carbon, silicon, titanium, and tin; and although the data at our command are neither as connected nor as complete as might be desired, nevertheless, they may be regarded as sufficient to establish a characteristic group reaction. In these reactions, however, there appear to be several unaccountable fluctuations and divergences among the different members of the group. It would be natural to expect a difference in the behavior of the metallic subgroup including germanium, tin, and lead, from the more non-metallic subgroup including titanium, zirconium, and thorium. But such a conclusion does not

[1] From author's thesis for the Degree of Doctor of Philosophy.

appear to receive the necessary strength from the actual facts observed in order to give it a sure foundation; for titanium seems to exhibit a greater analogy in its reactions to those of tin than to any other. The number of reactions studied, however, have been so few that it would be presumptuous to formulate a comprehensive law regarding the general reactions of the two subgroups in question, and in consequence of there being no such law established, it would be illogical to argue that apparently diverging reactions pointed necessarily to inconsistencies in the behavior of the two subgroups.

The tetrachlorides of silicon, titanium, and tin have been rather comprehensively studied in their behavior toward nitriles and amines. Titanium tetrachloride has been found to be reactive with formonitrile, acetonitrile, benzonitrile, toluonitrile, succinonitrile, chlorcyanogen, sulphur monochloride, phosphorus pentachloride, and the vapors of aqua regia. The tetrachloride of tin also exhibits analogous reactions with every one of the above-mentioned reagents; silicon tetrachloride, however, shows no evidence of reacting with these compounds.

All three of these tetrachlorides give derivatives with ammonia and aromatic amines, as does also carbon tetrachloride. With the fatty amines, however, only the chlorides of silicon and tin have been found to be reactive.

2. PREPARATION OF THE TETRACHLORIDES OF ZIRCONIUM, THORIUM, AND LEAD.

A. ZIRCONIUM TETRACHLORIDE.

The zirconium tetrachloride used in this research was prepared in the following manner: Carefully selected crystals of zircon were finely powdered and fused with acid potassium sulphate; the fusion was lixiviated with water, and filtered; the residue was dried and fused with potassium hydroxide in a nickel dish. This fusion, after being digested with water, and filtered, left a white amorphous residue of zirconium dioxide. The oxide was mixed with pulverized starch and molasses to a thick batter, which was then rolled into small pellets about one centimeter in diameter. These were slowly dried in an air oven until all moisture was expelled, when they were transferred to a covered silver crucible and charred until no more vapors were evolved. These pellets, containing zirconium dioxide intimately mixed with pure charcoal, were placed in a long glass combustion tube, and strongly heated in a current of dry chlorine gas. Zirconium tetrachloride was formed by this procedure, and collected in the cooler part of the tube in the form of a white powder or minute crystals. The salt thus obtained was dissolved in ether which had been carefully dehydrated by repeated distillation over sodium, until thin slices of the metal remained untarnished on being in contact with the ether for several days. The zirconium tetrachloride in the form of this ethereal solution was used in all the experiments, as it gave a convenient and uniform method for testing the reactions.

B. THORIUM TETRACHLORIDE.

This salt was prepared in a manner precisely analogous to that given for zirconium. The dioxide, ThO_2, was obtained from a quantity of the nitrate which was available for the purpose, by precipitation with ammonium hydroxide and subsequent ignition. The tetrachloride was dissolved in dehydrated ether, as in the case of the zirconium salt, and this solution was used in all of the reactions.

C. LEAD TETRACHLORIDE.

This compound was prepared by the method of Friedrich.[1] One part of lead chloride was suspended in twenty parts of concentrated hydrochloric acid, and a current of chlorine gas was conducted through the liquid until nearly all of the lead dichloride had gone into solution, which required about twenty hours. The temperature of the liquid during the entire process was kept at about 4° C. by means of a freezing-mixture. The yellow-colored liquid which resulted from this treatment consisted of a solution of lead tetrachloride in concentrated hydrochloric acid. Two parts of ammonium chloride dissolved in ten parts of water were then added, and a bright lemon-yellow crystalline precipitate was produced, consisting of the ammonium double salt of lead tetrachloride, which, according to Friedrich, has the formula $PbCl_4.2NH_4Cl$. Classen and Zahorski,[2] however, apparently obtain the same salt—by practically the same

1 *Ber. d. chem. Ges.*, **26**, 1434.
2 *Ztschr. anal. Chem.*, 4, 100.

method—and they ascribe to it the formula $2PbCl_4.5NH_4Cl$. The ammonium double salt was filtered off and washed free from hydrochloric acid and chlorine with absolute alcohol and ether. A portion of this salt was placed in a separatory funnel and digested with fuming sulphuric acid of specific gravity 1.879. A brisk reaction took place and yellow oily drops of lead tetrachloride soon separated out; these were washed by decantation several times with fuming sulphuric acid, and finally dissolved in chloroform which had been carefully dehydrated over fuming sulphuric acid. This chloroform solution of the lead tetrachloride was used for all the reactions; but fresh portions and solutions had to be made for each experiment, as the tetrachloride decomposed into the lower chloride in a few hours. It was found impossible to work with the liquid tetrachloride itself, as it was immediately decomposed on coming in contact with the air, and even decomposed in about twelve hours when kept under fuming sulphuric acid. The strength of the acid used for the decomposition of the ammonium double salt is an important factor in this preparation, as an acid of less strength than that used above will fail to give the lead tetrachloride in any appreciable quantity.

3. THE ACTION OF NITRILES, ETC., ON THE TETRACHLORIDES.

As zirconium occupies the next position to titanium in the same subgroup, it was natural to suppose that its tetrachloride would exhibit reactions with the nitriles somewhat analogous to those of the latter element, and that the analogy might also be followed into the fatty and aromatic amines. Contemporary with this present work there was carried to completion in this same laboratory a study of the reactions of silicon tetrachloride; and as both tin and titanium have been studied in this same connection, it was considered that a research into the possible derivatives of the allied members of this group might lead to results which would be useful in establishing analogies and comparisons between the different members of Group IV, as viewed from their respective behavior with the reagents used in this study. By this means it was thought probable that a definite law might be formulated for the group with regard to these reactions, and that the heterogeneous data, heretofore lying dissociated and useless, might be brought together and systematically understood.

a. Vapors of Aqua Regia.—The dry vapors of aqua regia conducted into the solution of zirconium tetrachloride gave no reaction, the solution only becoming discolored by the gases, which were again liberated on raising the temperature. Portions of the dry zirconium salt were also placed in a porcelain boat, and heated in a current of the dry vapors of aqua regia; but the salt appeared to volatilize unchanged, and no compound was formed. In this behavior zirconium shows a deviation from that of titanium, as the tetrachloride of the latter reacts readily with the vapors of aqua regia, giving a compound corresponding to the formula $3TiCl_4.2NO_2Cl$, Hampe.[1] An analogous compound with tin tetrachloride has been prepared by the same investigator. Baeyer[2] also records the compound $SnCl_4.2NOCl$.

The solutions of the tetrachlorides of thorium and lead behaved similarly to that of zirconium, and gave no derivatives.

b. Nitrogen Dioxide.—This gas, obtained by heating lead nitrate, on being conducted into the solutions of the tetrachlorides, gave no reaction beyond a simple solution of the gas. The dry salts of zirconium and thorium, heated in a current of the gas, volatilized unchanged and gave no compound.

c. Sulphur Monochloride.—On mixing this substance with the solutions of the tetrachlorides, no reaction was observed.

d. Chlorides of Phosphorus.—The action of both the tri- and pentachlorides of phosphorus was tried on the solutions of the tetrachlorides, but no combination resulted.

e. Dicyanogen.—On conducting this gas into the solutions of the tetrachlorides, no reaction took place; nor does it seem to have formed any compounds with the corresponding salts of titanium or tin.

f. Formonitrile.—Though both titanium and tin tetrachlorides give derivatives with hydrocyanic acid, yet no product was obtained by allowing this compound to act on the three tetrachlorides here investigated.

g. Cyanogen Chloride.—It was prepared by the action of chlo-

[1] *Ann. Chem.* (Liebig), 126, 43.
[2] *Ber. d. chem. Ges.*, 7, 1639.

rine on mercuric cyanide, but it gave no reactions with the solutions of the tetrachlorides.

h. Acetonitrile.—The vapors of this nitrile passed into the solutions of the tetrachlorides yielded no compounds, although derivatives have been obtained with the titanium and tin salts.

i. Benzonitrile.—Like acetonitrile, this aromatic body yielded no derivatives with the tetrachlorides.

SUMMARY.

From these experiments it is to be observed that the nitriles and the other reagents here used, which for the most part gave additive compounds with the tetrachlorides of titanium and tin, are without action on the corresponding salts of zirconium, thorium, and lead.

4. ACTION OF FATTY AND AROMATIC AMINES.

It was in this field that positive results were at last encountered. Silicon, titanium, and tin tetrachlorides all give compounds with the amines, and analogy would lead us to expect that the chlorides here used would behave in a similar manner, as indeed was the case. These derivatives with the amine bases, including ammonia, are apparently peculiar additive products, showing that these tetrachlorides, in common with the other chlorides of this group, possess an acid character.

The compounds herein described were obtained by the simple addition of the pure anhydrous reagents to the solutions of the respective tetrachlorides. The zirconium and thorium derivatives, for the most part, were white flocculent precipitates; the lead salts, however, gave compounds of various colors.

The analysis of these derivatives was carried out in the following manner: With the zirconium and thorium compound a weighed quantity was placed in a small beaker-glass and covered with nitric acid containing a solution of silver nitrate, and gently warmed. This sufficed to decompose the substance, the chlorine present being precipitated as silver chloride. The liquid was diluted with water, the chloride filtered off, and from its weight the chlorine was estimated. Excess of ammonia water was added to the filtrate, and the resulting precipitate of zirconium or thorium hydroxide was filtered off and ignited to the corresponding dioxide, from the weight of which the zirconium or thorium was estimated. The nitrogen present in the ammonia derivatives was determined by heating a portion with a strong solution of sodium hydroxide, and passing the evolved ammonia into a standardized solution of hydrochloric acid, and either titrating the excess of acid with standard alkali, or precipitating the ammonia in the usual manner with a solution of platinic chloride, and from the weight of the platinum left after ignition calculating the quantity of nitrogen. With the amine derivatives the Kjeldahl method was employed; and the Will and Varrentrap method was used for the quinoline and pyridine compounds. The lead compounds were decomposed with warm nitric acid, and the lead determined as sulphate by evaporation with sulphuric acid in the usual manner, the chlorine being determined by heating the compound with sulphuric acid in a distilling flask, passing the evolved hydrochloric acid gas into a solution of silver nitrate, and weighing the silver chloride as usual. The nitrogen present was estimated as with the zirconium and thorium derivatives.

A. AMMONIA.

Paykull[1] obtained a compound of zirconium tetrachloride with ammonia by heating the former with NH_4Cl, and to this compound he ascribes the formula $ZrCl_4.4NH_3$. Besson[2] has also obtained an ammonia derivative with silicon tetrachloride, giving it the formula $SiCl_4.6NH_3$. With tin tetrachloride Rose[3] obtained the compound $SnCl_4.4NH_3$, though Persoz[4] claims to have made $SnCl_4.6NH_3$. With titanium tetrachloride Rose[3] obtained the compound $TiCl_4.4NH_3$, though Persoz[5] gives the formula as $TiCl_4.6NH_3$.

a. Zirconium Tetrachloride, $ZrCl_4.8NH_3$. — On passing dry ammonia gas into the solution of zirconium tetrachloride, a white flocculent precipitate was immediately produced, with considerable evolution of heat. This compound on drying appeared to be stable in the air, though on gently heating it

1 *Ber. d. chem. Ges.*, 6, 1467.
2 *Compt. rend.*, 110, 240.
3 Pogg. *Ann.*, 20, 147.
4 *Ann. chim. phys.*, 46, 305.
5 *Vide supra.*

gave off fumes of ammonium chloride. Its analysis showed the presence of eight molecules of ammonia.

I. 0.5625 gram material gave:

0.8729 gram silver chloride = 0.2161 gram chlorine = 38.42 per cent. chlorine.

0.1860 gram zirconium dioxide = 0.1374 gram zirconium = 24.44 per cent. zirconium.

II. 0.1862 gram material gave:

0.2881 gram silver chloride = 0.0713 gram chlorine = 38.30 per cent. chlorine.

0.0623 gram zirconium dioxide = 0.0460 gram zirconium = 24.71 per cent. zirconium.

0.0624 gram material gave 0.0228 gram ammonia = 36.60 per cent. ammonia.

0.5625 gram material gave 0.2084 gram ammonia = 37.05 per cent. ammonia.

	Calculated for $ZrCl_4.8NH_3$.	Found. I.	II.
Chlorine	38.52	38.42	38.30
Zirconium	23.58	24.44	24.71
Ammonia	36.90	36.60	37.05

$ZrCl_4.2NH_3$.—On passing dry ammonia gas over the solid zirconium tetrachloride contained in a porcelain boat, a considerable evolution of heat was observed, evidently showing that combination resulted. The compound thus obtained was white in color, fumed in the air, and rapidly took up moisture, rendering it difficult to analyze with accuracy.

0.5304 gram zirconium tetrachloride, after being treated with ammonia gas for two hours, on reweighing gave 0.6247 gram.

This on analysis gave:

1.3778 gram silver chloride = 0.3163 gram chlorine = 50.67 per cent. chlorine.

0.2927 gram zirconium dioxide = 0.2163 gram zirconium = 34.62 per cent. zirconium.

	Calculated for $ZrCl_4.2NH_3$.	Found.
Chlorine	51.81	50.67
Zirconium	33.21	34.26
	Gram.	Gram.
Increase in weight	0.0917	0.0943

$ZrCl_4.4NH_3$.—On heating zirconium tetrachloride in a current of dry ammonia gas, a compound was obtained which was white in color, and unstable on exposure to the air.

0.4713 gram zirconium tetrachloride being gently heated (to about 100° C.) in ammonia gas, on reweighing gave 0.6123 gram. This on analysis gave:

1.1397 gram silver chloride = 0.2821 gram chlorine = 46.07 per cent. chlorine.

0.2588 gram zirconium dioxide = 0.1912 gram zirconium = 31.23 per cent. zirconium.

	Calculated for $ZrCl_4.4NH_3$.	Found.
Chlorine	47.24	46.07
Zirconium	30.14	31.23
	Gram.	Gram.
Increase in weight	0.1378	0.1410

These results seem to indicate that zirconium tetrachloride may be combined with ammonia in three proportions, depending upon the conditions under which the combination is brought about. When in ethereal solution it takes up eight molecules of ammonia, giving $ZrCl_4.8NH_3$; the dry salt unaided by heat gives $ZrCl_4.2NH_3$; and with the aid of heat the latter also gives the compound $ZrCl_4.4NH_3$. All of these bodies are white in color, the first one only being stable in the air. The last of the above derivatives seems to be identical with the one obtained by Paykull.

b. Thorium Tetrachloride.—As the field of thorium derivatives has not been investigated in any very exhaustive manner, one would not be likely to encounter any preceding research in the rather remote class of compounds herein dealt with. Chydenius,[1] however, has prepared a derivative of thorium tetrachloride with ammonium chloride, to which he has given the formula $ThCl_4.8NH_4Cl$. It is of interest to note that the compound prepared in this present research also contains the same molecular proportions of ammonia to thorium.

$ThCl_4.8NH_3$.—Dry ammonia gas passed into the solution of thorium tetrachloride produced a white flocculent precipitate, which, on drying, continued stable in the air. On heating, it

[1] *Jsb. Chem.*, *1863*, 194.

decomposed with the evolution of fumes of ammonium chloride.

I. 0.5870 gram material gave:

0.6526 gram silver chloride = 0.1616 gram chlorine = 27.52 per cent. chlorine.

0.3054 gram thorium dioxide = 0.2684 gram thorium = 45.73 per cent. thorium.

II. 0.6212 gram material gave:

0.5928 gram silver chloride = 0.1715 gram chlorine = 27.61 per cent. chlorine.

0.3212 gram thorium dioxide = 0.2824 gram thorium = 45.46 per cent. thorium.

0.5172 gram material gave 0.1366 gram ammonia = 26.41 per cent. ammonia.

	Calculated for $ThCl_4.8NH_3$.	Found. I.	Found. II.
Chlorine	27.80	27.52	27.61
Thorium	45.55	45.73	45.46
Ammonia	26.64	26.41	....

$ThCl_4.6NH_3$.—On allowing dry ammonia gas to pass over a portion of thorium tetrachloride placed in a porcelain boat, a considerable evolution of heat was observed, the ammonia evidently reacting with the salt. The resulting compound was white in color, and fumed in moist air, though it appeared to be more stable than the corresponding zirconium derivative obtained under the same conditions.

0.4217 gram material, on being treated with ammonia gas for two hours, on reweighing gave 0.5352 gram. This on analysis gave:

0.6274 gram silver chloride = 0.1553 gram chlorine = 29.01 per cent. chlorine.

0.3021 gram thorium dioxide = 0.2656 gram thorium = 49.62 per cent. thorium.

	Calculated for $ThCl_4.6NH_3$.	Found.
Chlorine	29.79	29.01
Thorium	48.80	49.62
	Gram.	Gram.
Increase in weight	0.1148	0.1135

On gently heating thorium tetrachloride to about 100° C. in a current of ammonia gas, a compound was obtained identical with the one just described above; it possessed the same appearance and analyzed for the same formula. At a higher temperature decomposition seemed to take place and copious fumes of ammonium chloride were formed.

c. Lead Tetrachloride, $PbCl_4.4NH_3$.—On treating the chloroform solution of lead tetrachloride with dry ammonia gas, an orange-yellow precipitate was at first produced, which rapidly became white in color as more ammonia was absorbed. A great amount of heat was evolved in the reaction, and the compound continued stable in the air.

I. 0.3600 gram material gave:

0.2597 gram lead sulphate = 0.1774 gram lead = 49.30 per cent. lead.

0.2614 gram material gave:

0.3205 gram silver chloride = 0.0816 gram chlorine = 33.76 per cent. chlorine.

II. 0.2582 gram material gave:

0.1874 gram lead sulphate = 0.1281 gram lead = 49.62 per cent. lead.

0.2075 gram material gave:

0.2844 gram silver chloride = 0.0704 gram chlorine = 33.92 per cent. chlorine.

0.4201 gram material gave:

0.3817 gram platinum = 0.0664 gram ammonia = 15.81 per cent. ammonia.

	Calculated for $PbCl_4.4NH_3$.	Found. I.	II.
Lead	49.88	49.30	49.62
Chlorine	34.05	33.76	33.92
Ammonia	16.07	15.81	....

$PbCl_4.2NH_3$.—By using a more concentrated solution of lead tetrachloride, and interrupting the treatment with ammonia gas before all of the lead salt was neutralized, an orange-yellow precipitate was obtained. This fumed in the air and decomposed on standing. Its analysis indicated the above formula.

0.3017 gram material gave:

0.2375 gram lead sulphate = 0.1622 gram lead = 53.75 per cent. lead.

0.2332 gram material gave:

0.3525 gram silver chloride = 0.0873 gram chlorine = 37.42 per cent. chlorine.

0.2716 gram material gave:

0.1430 gram platinum = 0.0249 gram ammonia = 9.16 per cent. ammonia.

	Calculated for $PbCl_4.2NH_3$.	Found.
Lead	54.16	53.75
Chlorine	37.00	37.42
Ammonia	8.85	9.16

B. METHYLAMINE.

a. Zirconium Tetrachloride, $ZrCl_4.4CH_3NH_2$.—On conducting the vapors of methylamine into the solution of zirconium tetrachloride, a white flocculent precipitate was formed. Analysis showed that it followed the same general type as the other derivatives.

I. 0.2417 gram material gave:

0.3833 gram silver chloride = 0.0949 gram chlorine = 39.26 per cent. chlorine.

0.0838 gram zirconium dioxide = 0.0619 gram zirconium = 25.62 per cent. zirconium.

II. 0.5432 gram material gave:

0.8674 gram silver chloride = 0.2147 gram chlorine = 39.53 per cent. chlorine.

0.1786 gram zirconium dioxide = 0.1339 gram zirconium = 25.65 per cent. zirconium.

0.6021 gram material gave:

0.1165 gram ammonia = 0.0969 gram nitrogen = 15.95 per cent. nitrogen.

	Calculated for $ZrCl_4.4CH_3NH_2$.	Found. I.	Found. II.
Chlorine	39.82	39.36	39.53
Zirconium	25.41	25.62	25.65
Nitrogen	16.18	15.95	....

b. Thorium Tetrachloride, $ThCl_4.4CH_3NH_2$.—The compound obtained with thorium tetrachloride showed the presence of four molecules of the base. Indeed this seems to be the general type after which all these derivatives are modeled.

0.6513 gram material gave:

0.7451 gram silver chloride = 0.1802 gram chlorine = 28.32 per cent. chlorine.

0.3461 gram thorium dioxide = 0.3040 gram thorium = 46.71 per cent. thorium.

0.5318 gram material gave:

0.0712 gram ammonia = 0.0587 gram nitrogen = 11.03 per cent. nitrogen.

	Calculated for $ThCl_4.4CH_3NH_2$.	Found.
Chlorine....................	28.48	28.32
Thorium....................	46.65	46.71
Nitrogen	11.24	11.03

c. Lead Tetrachloride, $PbCl_4.4CH_3NH_2$.—The compound obtained with lead tetrachloride was also white in color, and stable in the air. Analysis proved it to be analogous to the preceding derivatives.

0.2506 gram material gave:

0.2969 gram silver chloride = 0.0735 gram chlorine = 29.32 per cent. chlorine.

0.2716 gram material gave:

0.1757 gram lead sulphate = 0.1200 gram lead = 44.17 per cent. lead.

0.2517 gram material gave:

0.2005 gram platinum = 0.0289 gram nitrogen = 11.42 per cent. nitrogen.

	Calculated for $PbCl_4.4CH_3NH_2$.	Found.
Chlorine....................	30.02	29.32
Lead	43.76	44.17
Nitrogen	11.84	11.42

C. ETHYLAMINE.

a. Zirconium Tetrachloride, $ZrCl_4.4C_2H_5NH_2$.—As would be expected from its behavior with the preceding amine, zirconium tetrachloride was found to yield a derivative with ethylamine.

0.5418 gram material gave:

0.7478 gram silver chloride = 0.1856 gram chlorine = 34.26 per cent. chlorine.

0.1619 gram zirconium dioxide = 0.1196 gram zirconium = 22.08 per cent. zirconium.

0.6516 gram material gave:

0.0861 gram ammonia = 0.0709 gram nitrogen = 10.89 per cent. nitrogen.

	Calculated for $ZrCl_4.4C_2H_5NH_2$.	Found.
Chlorine	34.42	34.26
Zirconium	21.96	22.08
Nitrogen	10.79	10.89

b. Thorium Tetrachloride, $ThCl_4.4C_2H_5NH_2$. — Ethylamine gave a white compound with thorium tetrachloride.

0.2102 gram material gave :

0.2137 gram silver chloride = 0.0528 gram chlorine = 25.12 per cent. chlorine.

0.0995 gram thorium dioxide = 0.0874 gram thorium = 41.58 per cent. thorium.

0.5912 gram material gave :

0.0712 gram ammonia = 0.0587 gram nitrogen = 9.92 per cent. nitrogen.

	Calculated for $ThCl_4.4C_2H_5NH_2$.	Found.
Chlorine	25.60	25.12
Thorium	41.94	41.58
Nitrogen	10.10	9.92

c. Lead Tetrachloride, $PbCl_4.4C_2H_5NH_2$.—Ethylamine gave at first a yellow precipitate with the solution of lead tetrachloride, which went over to a white compound on the addition of more ethylamine.

0.2072 gram material gave :

0.2220 gram silver chloride = 0.0550 gram chlorine = 25.52 per cent. chlorine.

0.2506 gram material gave :

0.1459 gram lead sulphate = 0.0996 gram lead = 39.76 per cent. lead.

0.3817 gram material gave :

0.2746 gram platinum = 0.0394 gram nitrogen = 10.32 per cent. nitrogen.

	Calculated for $PbCl_4.4C_2H_5NH_2$.	Found.
Chlorine	26.84	26.52
Lead	39.13	39.76
Nitrogen	10.59	10.32

D. PROPYLAMINE.

a. Zirconium Tetrachloride, $ZrCl_4.4C_3H_7NH_2$.—With propylamine, zirconium tetrachloride gave a white compound similar in appearance to the foregoing derivatives.

0.3390 gram material gave :

0.4112 gram silver chloride = 0.1020 gram chlorine = 30.10 per cent. chlorine.

0.0897 gram zirconium dioxide = 0.0663 gram zirconium = 19.55 per cent. zirconium.

0.6229 gram material gave :

0.0892 gram ammonia = 0.0736 gram nitrogen = 11.80 per cent. nitrogen.

	Calculated for $ZrCl_4.4C_3H_7NH_2$.	Found.
Chlorine	30.30	30.10
Zirconium	19.33	19.55
Nitrogen	11.96	11.80

b. Thorium Tetrachloride, $ThCl_4.4C_3H_7NH_2$. — Propylamine gave a white compound with thorium tetrachloride.

0.2682 gram material gave:

0.2537 gram silver chloride = 0.0628 gram chlorine = 23.40 per cent. chlorine.

0.1167 gram thorium dioxide = 0.1026 gram thorium = 38.22 per cent. thorium.

0.4213 gram material gave :

0.0460 gram ammonia = 0.0379 gram nitrogen = 9.01 per cent. nitrogen.

	Calculated for $ThCl_4.4C_3H_7NH_2$.	Found.
Chlorine	23.25	23.40
Thorium	38.09	38.22
Nitrogen	9.18	9.01

c. Lead Tetrachloride, $PbCl_4.4C_3H_7NH_2$.—Propylamine at first gave a dark reddish brown precipitate with lead tetrachloride soon becoming almost white in color, having a faint yellow tinge.

0.2507 gram material gave :

0.2065 gram silver chloride = 0.0511 gram chlorine = 20.39 per cent. chlorine.

0.2672 gram material gave :

0.1195 gram lead sulphate = 0.0817 gram lead = 30.56 per cent. lead.

0.2817 gram material gave:

0.1513 gram platinum = 0.0217 gram nitrogen = 7.82 per cent. nitrogen.

	Calculated for $PbCl_4.4C_8H_7NH_2$.	Found.
Chlorine	20.73	20.39
Lead	30.22	30.56
Nitrogen	8.28	7.82

E. ANILINE.

Schiff[1] has obtained a compound of tin tetrachloride with aniline, to which he has given the formula $SnCl_4.4C_6H_5NH_2$, while with titanium tetrachloride Leeds[2] describes a derivative having the formula $TiCl_4.4C_6H_5NH_2$.

In all of these derivatives the aniline appears to be merely additive. With silicon tetrachloride, however, aniline seems to form a substitution product corresponding to the formula $SiCl_2.(C_6H_5NH)_2$; Harden,[3] Reynolds,[4] and Harold.[5]

a. Zirconium Tetrachloride, $ZrCl_4.4C_6H_5NH_2$.—On the addition of aniline to the solution of zirconium tetrachloride a grayish flocculent precipitate was produced. This was carefully washed with anhydrous ether until all traces of aniline were removed. It appeared to be stable on drying, and its analysis showed the presence of four molecules of aniline.

I. 0.5382 gram material gave:

0.5053 gram silver chloride = 0.1251 gram chlorine = 23.25 per cent. chlorine.

0.1080 gram zirconium dioxide = 0.0798 gram zirconium = 14.83 per cent. zirconium.

II. 04817 gram material gave:

0.4538 gram silver chloride = 0.1123 gram chlorine = 23.32 per cent. chlorine.

0.0982 gram zirconium dioxide = 0.0726 gram zirconium = 15.06 per cent. zirconium.

I. 0.5382 gram material gave:

1 *Jsb. Chem.*, *1863*, 412.

2 This Journal, 3, 145.

3 *J. Chem. Soc.*, 51, 40.

4 *Ibid.*, 55, 474.

5 *Thesis*, Univ. of Pennsylvania, *1897*.

0.0600 gram ammonia = 0.0494 gram nitrogen = 9.19 per cent. nitrogen.

II. 0.6108 gram material gave :

0.0678 gram ammonia = 0.0559 gram nitrogen = 9.15 per cent. nitrogen.

	Calculated for $ZrCl_4.4C_6H_5NH_2$.	Found. I.	II.
Chlorine	23.49	23.25	23.32
Zirconium	14.98	14.83	15.06
Nitrogen	9.27	9.19	9.15

Since analysis would show no difference in the composition of $ZrCl_4.4C_6H_5NH_2$ and a mixture of $ZrCl_2(C_6H_5NH)_2+2C_6H_5NH_2.HCl$, the following method was resorted to in order to prove that it was the first and not the second compound which was formed. The substance, after having been completely freed from aniline, was treated with chloroform, in which it proved to be easily and completely soluble, whereas aniline hydrochloride is insoluble in the same reagent, and hence was not present in the compound. Also no substituted chloraniline, $C_6H_4ClNH_2$, could have been formed, as this is soluble in ether, and the existence of no such substance was indicated in the ethereal filtrate. This conclusively proves that the compound is purely additive in nature, and has the formula $ZrCl_4.4C_6H_5NH_2$. This same proof may be used as an argument for the additive character of all the zirconium and thorium derivatives described in this research.

b. Thorium Tetrachloride, $ThCl_4.4C_6H_5NH_2$. — Aniline produced a precipitate slightly gray in color, and soluble in chloroform. Its analysis indicated a formula in correspondence with that of the zirconium derivative.

0.2536 gram material gave :

0.1940 gram silver chloride = 0.0479 gram chlorine = 18.89 per cent. chlorine.

0.0906 gram thorium dioxide = 0.0796 gram thorium = 31.39 per cent. thorium.

0.5536 gram material gave :

0.0488 gram ammonia = 0.0402 gram nitrogen = 7.41 per cent. nitrogen.

	Calculated for $ThCl_4.4C_6H_5NH_2$.	Found.
Chlorine	19.02	18.89
Thorium	31.15	31.39
Nitrogen	7.61	7.41

c. Lead Tetrachloride, $PbCl_4.3C_6H_5NH_2$.—Aniline gave a dark green, stable compound with lead tetrachloride in dilute solution. A more concentrated solution of the lead salt reacts very violently with aniline, probably giving rise to the same chlorinated products as tin tetrachloride, such as violaniline, mauvaniline, rosaniline, and triphenylendiamine blue—Girard and Pabst.[1] The dark green compound analyzed for three molecules of aniline.

0.2104 gram material gave:

0.1950 gram silver chloride = 0.0483 gram chlorine = 22.94 per cent. chlorine.

0.2042 gram material gave:

0.0963 gram lead sulphate = 0.0658 gram lead = 32.22 per cent. lead.

0.4012 gram material gave:

0.1929 gram platinum = 0.0277 gram nitrogen = 6.90 per cent. nitrogen.

	Calculated for $PbCl_4.3C_6H_5NH_2$.	Found.
Chlorine	22.61	22.94
Lead	32.96	32.22
Nitrogen	6.69	6.90

F. TOLUIDINE.

a. Zirconium Tetrachloride, $ZrCl_4.4C_6H_4CH_3NH_2$.—As aniline gave a derivative with zirconium tetrachloride, toluidine was also tried with like result. Analysis indicated that this compound contained four molecules of toluidine, showing it to be analogous to the aniline derivative.

0.3772 gram material gave:

0.3240 gram silver chloride = 0.0802 gram chlorine = 21.26 per cent. chlorine.

0.0694 gram zirconium dioxide = 0.0512 gram zirconium = 13,60 per cent. zirconium.

0.4296 gram material gave:

0.0456 gram ammonia = 0.0376 gram nitrogen = 8.74 per cent. nitrogen.

1 *Bull. Soc. Chim.*, 34, 33.

	Calculated for $ZrCl_4.4C_6H_4CH_3NH_2$.	Found.
Chlorine	21.50	21.26
Zirconium	13.72	13.60
Nitrogen	8.48	8.74

b. Thorium Tetrachloride, $ThCl_4.3C_6H_4CH_3NH_2$.—This was a greenish white precipitate and showed a departure from the other derivatives and from its analogous zirconium compound in that it only contained three molecules of the base.

0.5012 gram material gave:

0.4074 gram silver chloride = 0.1008 gram chlorine = 20.12 per cent. chlorine.

0.1940 gram thorium dioxide = 0.1705 gram thorium = 34.01 per cent. thorium.

0.7500 gram material gave:

0.0526 gram ammonia = 0.0433 gram nitrogen = 5.78 per cent. nitrogen.

	Calculated for $ThCl_4.3C_6H_4CH_3NH_2$.	Found.
Chlorine	20.41	20.12
Thorium	33.44	34.01
Nitrogen	6.04	5.78

c. Lead Tetrachloride.—With toluidine no additive product could be obtained, even by using quite dilute solutions of lead tetrachloride, as the amine was decomposed, giving a deep purple solution. Hence lead tetrachloride evidently has about the same action on toluidine as bleaching lime or tin tetrachloride.

G. PYRIDINE.

As pyridine and quinoline are strong bases, and as they may be considered tertiary amines, it was thought probable that these reagents would form derivatives with the tetrachlorides in a manner similar to aniline and toluidine. Experiment proved this surmise to be a correct one, as a compound was formed in both instances. It may be stated that Classen and Zahorski[1] have obtained compounds of lead tetrachloride with the hydrochlorides of pyridine and quinoline, and they are described as additive products. Goebbles[2] has also obtained compounds of lead tetrachloride with the salts of such complex organic bases as picoline, lutidine and collidine.

[1] *Ztschr. anorg. Chem.*, **4**, 100.

[2] *Ber. d. chem. Ges.*, **28**, 792.

The compounds of zirconium and thorium tetrachlorides with pyridine and quinoline are light gray to brown flocculent precipitates. Unlike the derivatives with the preceding amines, they appeared to be rather unstable in moist air, in consequence of which considerable difficulty was experienced in obtaining suitable portions for analysis, as the compounds had to be preserved under anhydrous ether.

a. Zirconium Tetrachloride, $ZrCl_4.2C_5H_5N$.—The best analysis that could be obtained for the pyridine derivative approximated to a formula containing two molecules of the base.

0.5420 gram material gave:

0.7805 gram silver chloride = 0.1932 gram chlorine = 35.64 per cent. chlorine.

0.1758 gram zirconium dioxide = 0.1299 gram zirconium = 23.97 per cent. zirconium.

0.6118 gram material gave:

0.0506 gram ammonia = 0.0417 gram nitrogen = 6.83 per cent. nitrogen.

	Calculated for $ZrCl_4.2C_5H_5N$.	Found.
Chlorine	36.35	35.64
Zirconium	23.19	23.97
Nitrogen	7.18	6.83

b. Thorium Tetrachloride, $ThCl_4.C_5H_5N$.—0.5002 gram material gave:

0.6270 gram silver chloride = 0.1552 gram chlorine = 31.02 per cent. chlorine.

0.2939 gram thorium dioxide = 0.2583 gram thorium = 51.64 per cent. thorium.

0.4107 gram material gave:

0.0126 gram ammonia = 0.0104 gram nitrogen = 2.53 per cent. nitrogen.

	Calculated for $ThCl_4.C_5H_5N$.	Found.
Chlorine	31.30	31.02
Thorium	51.28	51.64
Nitrogen	3.09	2.53

c. Lead Tetrachloride, $PbCl_4.2C_5H_5N$.—Pyridine gave a pale yellow precipitate with lead tetrachloride of much greater stability than the foregoing compounds.

0.2506 gram material gave:

0.2780 gram silver chloride = 0.0688 gram chlorine = 27.46 per cent. chlorine.

0.3125 gram material gave:

0.1842 gram lead sulphate = 0.1258 gram lead = 40.26 per cent. lead.

0.3062 gram material gave:

0.1112 gram platinum = 0.0161 gram nitrogen = 5.21 per cent. nitrogen.

	Calculated for $PbCl_4.2C_5H_5N$.	Found.
Chlorine	28.01	27.46
Lead	40.83	40.26
Nitrogen	5.52	5.21

H. QUINOLINE.

a. Zirconium Tetrachloride, $ZrCl_4.2C_9H_7N$. — 0.6140 gram material gave:

0.6977 gram silver chloride = 0.1727 gram chlorine = 28.12 per cent. chlorine.

0.1592 gram zirconium dioxide = 0.1177 gram zirconium = 19.17 per cent. zirconium.

0.7226 gram material gave:

0.0478 gram ammonia = 0.0394 gram nitrogen = 5.45 per cent. nitrogen.

	Calculated for $ZrCl_4.2C_9H_7N$.	Found.
Chlorine	28.94	28.12
Zirconium	18.47	19.17
Nitrogen	5.72	5.45

b. Thorium Tetrachloride, $ThCl_4.C_9H_7N$.—0.4110 gram material gave:

0.4634 gram silver chloride = 0.1147 gram chlorine = 27.91 per cent. chlorine.

0.2175 gram thorium dioxide = 0.1911 gram thorium = 46.50 per cent. thorium.

0.4212 gram material gave:

0.0129 gram ammonia = 0.0106 gram nitrogen = 2.52 per cent. nitrogen.

	Calculated for $ThCl_4.C_9H_7N$.	Found.
Chlorine	28.19	27.91
Thorium	46.18	46.50
Nitrogen	2.78	2.52

c. Lead Tetrachloride, $PbCl_4.2C_9H_7N$.—Quinoline reacted very energetically with lead tetrachloride, yielding a lemon-yellow precipitate which proved to be quite stable.

0.3012 gram material gave:

0.2806 gram silver chloride = 0.0695 gram chlorine = 23.06 per cent. chlorine.

0.2298 gram material gave:

0.1140 gram lead sulphate = 0.0779 gram lead = 33.90 per cent. lead.

0.2792 gram material gave:

0.0845 gram platinum = 0.0121 gram nitrogen = 4.34 per cent. nitrogen.

	Calculated for $PbCl_4.2C_9H_7N$.	Found.
Chlorine	23.39	23.06
Lead	34.10	33 90
Nitrogen	4.61	4.34

I. β-NAPHTHYLAMINE.

a. Zirconium Tetrachloride, $ZrCl_4.2C_{10}H_7NH_2$.—On adding a solution of naphthylamine in anhydrous ether to a solution of zirconium tetrachloride a grayish brown precipitate was produced, the analysis of which approximated to the formula given above.

0.5736 gram material gave:

0.6419 gram silver chloride = 0.1589 gram chlorine = 27.70 per cent. chlorine.

0.1397 gram zirconium dioxide = 0.1032 gram zirconium = 18.00 per cent. zirconium.

0.7012 gram material gave:

0.0426 gram ammonia = 0.0351 gram nitrogen = 5.01 per cent. nitrogen.

	Calculated for $ZrCl_4.2C_{10}H_7NH_2$.	Found.
Chlorine	27.38	27.70
Zirconium	17.47	18.00
Nitrogen	5.41	5.01

b. Thorium Tetrachloride, $ThCl_4.C_{10}H_7NH_2$.—This derivative was grayish white in color and comparatively stable in the air.

0.2582 gram material gave:

0.2844 gram silver chloride = 0.0704 gram chlorine = 27.27 per cent. chlorine.

0.1329 gram thorium dioxide = 0.1168 gram thorium = 45.25 per cent. thorium.

0.6045 gram material gave :

0.0166 gram ammonia = 0.0137 gram nitrogen = 2.27 per cent. nitrogen.

	Calculated for $ThCl_4.C_{10}H_7NH_2$.	Found.
Chlorine	27.43	27.27
Thorium	44.94	44.25
Nitrogen	2.70	2.27

c. Lead Tetrachloride, $PbCl_4.C_{10}H_7NH_2$.—Naphthylamine gave a dark green precipitate with lead tetrachloride in a dilute solution ; in more concentrated solutions the naphthylamine was apparently decomposed.

0.2276 gram material gave :

0.2604 gram silver chloride = 0.0645 gram chlorine = 28.32 per cent. chlorine.

0.3006 gram material gave :

0.1914 gram lead sulphate = 0.1307 gram lead = 43.47 per cent. lead.

0.2416 gram material gave :

0.0544 gram platinum = 0.0079 gram nitrogen = 3.24 per cent. nitrogen.

	Calculated for $PbCl_4.C_{10}H_7NH_2$.	Found.
Chlorine	28.86	28.32
Lead	42.07	43.47
Nitrogen	2.84	3.24

J. ACID AMIDES.

The action of acetamide and benzamide was tried on the solutions of the tetrachlorides, but no compound resulted in any case, the acid amides evidently not being sufficiently basic to form derivatives like the amines.

Diphenylamine was also tried, but it gave no reaction with either the zirconium or thorium salt. The lead salt gave a deep blue solution and lead chloride separated out, showing that the lead tetrachloride in this case acted like bleaching lime on diphenylamine.

5. GENERAL REMARKS.

On comparing the derivatives of the three tetrachlorides here used, many similarities will at once be evident. In order to facilitate with such a comparison, it will not be superfluous to present a tabular résumé of the various derivatives herein prepared and described.

	With $ZrCl_4$ mols. amine.	With $ThCl_4$ mols. amine.	With $PbCl_4$ mols. amine.
Ammonia (from solution)	8	8	4, 2
Ammonia (without heat)	2	6	.
Ammonia (with heat)	4	6	.
Methylamine	4	4	4
Ethylamine	4	4	4
Propylamine	4	4	4
Aniline	4	4	3
Toluidine	4	3	decomp.
Pyridine	2	1	2
Quinoline	2	1	2
Naphthylamine	2	1	1
Diphenylamine	no reaction	no reaction	decomp.
Acid amides	no reaction	no reaction	no reaction

Nearly all these derivatives are stable in the air, the only noticeable exceptions being the pyridine, quinoline, and the lower ammonia compounds of zirconium and thorium. None of them show any tendency toward a crystalline structure, but come down as amorphous precipitates resembling hydroxides.

On heating these compounds in the air they readily split up into the amine hydrochloride and the dioxides ; with lead, however, lead dichloride is left on ignition. They are also decomposed when treated with water, and the fixed alkalies precipitate the hydroxides of the three metals.

It will also be noticed that the majority of these derivatives seem to obey the law of Remsen in its application to molecular compounds ; and the tendency is apparently toward an even number of molecules, though several of the thorium and lead derivatives deviate from this general law in having an odd number of additive molecules.

Two of the chlorine atoms in lead tetrachloride are very loosely combined, splitting off at the slightest disturbance to the chemical equilibrium of the compound ; and yet it is of interest to note that the amines seem to fix these two atoms of chlorine into a more stable form, doubtless due to some peculiar internal linking in the compound. That these two atoms of chlorine are exceedingly active is seen by the behavior of lead tetrachloride with toluidine, where no additive compound could be obtained, as the amine was decomposed even with dilute solutions, giving rise no doubt to complex chlorinated and condensed products. In fact, concentrated solutions of lead tetrachloride will decompose any of the aromatic amines, with the production of blue, purple, and green-colored solutions and resinous products. In this great activity of two of its atoms of chlorine, lead tetrachloride differs widely from the corresponding salts of zirconium and thorium, as these latter show no tendency to break down to lower chlorides.

UNIVERSITY OF PENNSYLVANIA.

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II. DERIVATIVES OF THE TETRABROMIDES OF ZIRCONIUM AND THORIUM.

BY J. MERRITT MATTHEWS.

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1. INTRODUCTION.

THIS investigation was taken up as an adjunct to the preceding research on the derivatives of the tetrachlorides. Only derivatives with the four most typical amines—ammonia, ethylamine, aniline and pyridine—were prepared, as it was considered needless to extend the investigation further, when the aim was only to prove a general reaction between the amine bases and the tetrahalides of the fourth group.

The anhydrous tetrabromides of zirconium and thorium were prepared in a manner exactly similar to their tetrachlorides, dry bromine vapors in a current of carbon dioxide gas, being substituted for chlorine. Mellis[1] and Troost and Ouvrard.[2]

Owing to the slight solubility of the tetrabromides in any of the usual organic solvents, the reagents in all cases were added to the dry salts, any excess being removed by washing the product so formed with ether.

1 *Ztschr. Chem.* (2), 6, 296.
2 *Ann. chim. phys.* (6), 17, 229.