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.

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[1] *Ztschr. Chem.* (2), 6, 296.

[2] *Ann. chim. phys.* (6), 17, 229.

Several attempts were made to prepare the tetrabromide of lead, proceeding in a manner analogous to that used in the preparation of the tetrachloride, but without success.

2. THE AMINE DERIVATIVES.

A. AMMONIA.

a. Zirconium Tetrabromide, $ZrBr_4.4NH_3$.—On passing dry ammonia gas over zirconium tetrabromide at a slightly elevated temperature, a white compound was formed.

0.5186 gram zirconium tetrabromide increased in weight to 0.6035 gram.

0.2246 gram of this compound, on analysis, gave :

0.3511 gram silver bromide = 0.1494 gram bromine = 66.50 per cent. bromine.

0.0584 gram zirconium dioxide = 0.0432 gram zirconium = 19.22 per cent. zirconium.

0.3024 gram material gave :

0.2426 gram platinum = 0.0422 gram ammonia = 13.96 per cent. ammonia.

	Calculated for $ZrBr_4 4NH_3$.	Found.
Bromine	66.80	66.50
Zirconium	18.96	19.22
Ammonia	14.23	13.96
	Gram.	Gram.
Increase in weight	0.0861	0.0849

b. Thorium Tetrabromide, $ThBr_4.3NH_3$.—This was prepared in the same manner as the zirconium compound, and was white in color.

0.4712 gram thorium tetrabromide, increased in weight to 0.5119 gram which, on analysis, gave :

0.6491 gram silver bromide = 0.2762 gram bromine = 53.96 per cent. bromine.

0.2273 gram thorium dioxide = 0.1997 gram thorium = 39.01 per cent. thorium.

	Calculated for $ThBr_4.3NH_3$.	Found.
Bromine	53.07	53.96
Thorium	38.47	39.01
	Gram.	Gram.
Increase in weight	0.0435	0.0407

B. ETHYLAMINE.

a. Zirconium Tetrabromide, $ZrBr_4.4C_2H_5NH_2$. — 0.2506 gram zirconium tetrabromide, treated with ethylamine, gave 0.3572 gram of a white compound which, on analysis, yielded:

0.4597 gram silver bromide = 0.1956 gram bromine = 54.75 per cent. bromine.

0.0769 gram zirconium dioxide = 0.0569 gram zirconium = 15.92 per cent. zirconium.

	Calculated for $ZrBr_4.4C_2H_5NH_2$.	Found.
Bromine	54.12	54.75
Zirconium	15.36	15.92
	Gram.	Gram.
Increase in weight	0.1098	0.1066

b. Thorium Tetrabromide, $ThBr_4.4C_2H_5NH_2$. — 0.3121 gram thorium tetrabromide, treated with ethylamine, gave 0.4098 gram of a white compound which, on analysis, yielded:

0.4246 gram silver bromide = 0.1807 gram bromine = 44.09 per cent. bromine.

0.1502 gram thorium dioxide = 0.1320 gram thorium = 32.21 per cent. thorium.

	Calculated for $ThBr_4.4C_2H_5NH_2$.	Found.
Bromine	43.71	44.09
Thorium	31.69	32.21
	Gram.	Gram.
Increase in weight	0.1018	0.0977

C. ANILINE.

a. Zirconium Tetrabromide, $ZrBr_4.4C_6H_5NH_2$.—0.2075 gram zirconium tetrabromide, treated with aniline, gave 0.4117 gram of a brownish colored compound which, on analysis, yielded:

0.3821 gram silver bromide = 0.1626 gram bromine = 40.47 per cent. bromine.

0.0631 gram zirconium dioxide = 0.0467 gram zirconium = 11.62 per cent. zirconium.

	Calculated for $ZrBr_4.4C_6H_5NH_2$.	Found.
Bromine	40.83	40.47
Zirconium	11.46	11.62
	Gram.	Gram.
Increase in weight	0.1911	0.1932

b. Thorium Tetrabromide, $ThBr_4.4C_6H_5NH_2$. — 0.2214 gram thorium tetrabromide, treated with aniline, gave 0.3675 gram of a brown-colored compound which, on analysis, yielded :

0.3032 gram silver bromide = 0.1290 gram bromine = 35.10 per cent. bromine.

0.1069 gram thorium dioxide = 0.0939 gram thorium = 25.56 per cent. thorium.

	Calculated for $ThBr_4.4C_6H_5NH_2$.	Found.
Bromine	34.63	35.10
Thorium	25.11	25.56
	Gram.	Gram.
Increase in weight	0.1492	0.1461

D. PYRIDINE.

a. Zirconium Tetrabromide, $ZrBr_4.2C_5H_5N$.—0.3551 gram zirconium tetrabromide, treated with pyridine, gave 0.3718 gram of a brown compound which, on analysis, yielded :

0.4876 gram silver bromide = 0.2075 gram bromine = 55.82 per cent. bromine.

0.0802 gram zirconium dioxide = 0.0604 gram zirconium = 16.24 per cent. zirconium.

	Calculated for $ZrBr_4.2C_5H_5N$.	Found.
Bromine	56.22	55.82
Zirconium	15.95	16.24
	Gram.	Gram.
Increase in weight	0.1357	0.1325

b. Thorium Tetrabromide, $ThBr_4.C_5H_5N$.—0.2817 gram thorium tetrabromide, treated with pyridine, gave 0.3343 gram of a brownish compound which, on analysis, yielded :

0.3960 gram silver bromide = 0.1685 gram bromine = 50.42 per cent. bromine.

0.1412 gram thorium dioxide = 0.1241 gram thorium = 37.11 per cent. thorium.

	Calculated for $ThBr_4.C_5H_5N$.	Found.
Bromine	50.71	50.42
Thorium	36.77	37.11
	Gram.	Gram.
Increase in weight	0.0403	0.0426

It will be noticed that these derivatives of the tetrabromides correspond very closely to those of the tetrachlorides of these same elements in the number of molecules of the amine in combination with one molecule of the halogen salt.

It may be remarked that Classen and Zahorski[1] have obtained additive compounds of lead tetrabromide and lead tetraiodide with the hydrobromic and hydriodic acid salts of several of the organic amines, by decomposing the corresponding chlorine compounds with cooled solutions of potassium bromide or potassium iodide. Thus $PbCl_4.2(C_9H_7N.HCl)$ with potassium bromide gave $PbBr_4.2(C_9H_7N.HBr)$, and with potassium iodide, $PbI_4.2(C_9H_7N.HI)$.

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III. THE PREPARATION OF ZIRCONIUM NITRIDES.

BY J. MERRITT MATTHEWS.

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THE ammonia derivative of titanium tetrachloride, $TiCl_4.4NH_3$, when heated in a current of ammonia gas, yields a nitride of titanium; Rose,[2] Persoz.[3] This nitride has been given the formula Ti_3N_4, and has been thoroughly investigated. From this knowledge it was of interest to ascertain if a zirconium nitride could be prepared from its ammonia derivative. The attempt was made and a corresponding zirconium nitride was obtained.

A portion of the zirconium tetrachloride derivative with ammonia, $ZrCl_4.8NH_3$, obtained by passing dry ammonia gas into an ethereal solution of the zirconium salt,[4] was placed in a porcelain boat and gradually heated to redness in a current of nitrogen in a glass combustion tube. Abundant fumes of ammonium chloride were given off and condensed in the cooler part of the tube; the residue left in the boat was pearl-gray in color and in the form of a light powder. On heating this residue in a current of hydrogen, ammonia was evolved, which was conducted into a standardized solution of hydrochloric acid, and thus determined.

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

[2] Pogg. *Ann.*, 16, 57.

[3] *Ann. chim. phys.*, 44, 321.

[4] This Journal, 20, 821.