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.

Received September 2, 1898.

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.

When this compound was heated in the air it lost weight, and became pure white in color, passing over into the dioxide, ZrO_2, and the zirconium was estimated in this form.

ANALYSES.

I. 0.2416 gram material gave :

0.0836 gram ammonia = 0.0688 gram nitrogen = 28.47 per cent. nitrogen.

0.0654 gram material gave :

0.0629 gram zirconium dioxide = 0.0465 gram zirconium = 71.10 per cent. zirconium.

II. 0.2006 gram material gave :

0.0691 gram ammonia = 0.0569 gram nitrogen = 28.36 per cent. nitrogen.

0.2572 gram material gave :

0.2469 gram zirconium dioxide = 0.1827 gram zirconium = 71.05 per cent. zirconium.

These analyses show a close approximation to the formula Zr_3N_8.

	Calculated for Zr_3N_8.	Found.	
		I.	II.
Zirconium	70.82	71.10	71.04
Nitrogen	29.18	28.47	28.36

The residue left after heating this nitride in a current of hydrogen, was lead-gray in color and amorphous; it was soluble in hydrofluoric acid, but proved to be insoluble in the other mineral acids. This appearance and behavior leave little doubt but that this residue consists of metallic zirconium, the action of hydrogen being to reduce the nitride to the metal with the formation of ammonia.

In the preparation of the pure nitride care must be exercised in excluding all air from the apparatus, otherwise a mixture of the oxide and nitride will be obtained. In the preparation of the sample used for the above analyses, all the air was first driven out by means of a vigorous current of carbon dioxide gas, after which a current of nitrogen was allowed to pass through the apparatus for two hours before the compound was heated.

Zr_2N_3.—This second nitride was prepared by a procedure differing somewhat from that used in the first. Zirconium tetrachloride was placed in a porcelain boat and gradually heated to redness in a current of dry ammonia gas. By this method the ammonia derivative, $ZrCl_4.4NH_3$, was at first formed.[1] This by the action of heat was broken down into a nitride of zirconium together with the formation of ammonium chloride, which was given off in dense fumes and condensed in the cooler part of the tube, leaving the nitride in the boat in the form of a gray amorphous powder. It was somewhat darker in color than the preceding compound, but resembled it exactly in its behâvior. The nitrogen was estimated by heating the compound in a current of hydrogen, and collecting the ammonia evolved in a standardized solution of hydrochloric acid. By heating another portion in the air it became pure white in color, increasing in weight, leaving the dioxide, ZrO_2, from the weight of which the zirconium was estimated.

ANALYSES.

I. 0.2537 gram material gave :

0.0478 gram ammonia = 0.0402 gram nitrogen = 19.23 per cent. nitrogen.

0.2462 gram material gave :

0.2707 gram zirconium dioxide = 0.2001 gram zirconium = 81.27 per cent. zirconium.

II. 0.2217 gram material gave :

0.0523 gram ammonia = 0.0431 gram nitrogen = 19.42 per cent. nitrogen.

0.2546 gram material gave :

0.2792 gram zirconium dioxide = 0.2064 gram zirconium = 81.05 per cent. zirconium.

	Calculated for Zr_3N_4.	Found. I.	II.
Zirconium	81.18	81.27	81.05
Nitrogen	18.82	19.23	19.42

Mallet[2] obtained a nitride of zirconium by heating the metal in ammonia gas ; it is described as a dark gray amorphous powder. A similar product, and one identical, in every way, with that obtained in this present research, was also prepared by Mallet, by heating anhydrous zirconium tetrachloride in ammonia gas. This procedure is exactly similar to that described

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[1] This Journal, 20, 823.

[2] *Jsb. Chem.*, *185* 145.

above; but Mallet made no investigation into the constitution of the compound which he prepared in this manner.

A nitride of thorium has been prepared by Chydenius[1] by a procedure identical with that used in the preparation of the first zirconium nitride above described. This nitride of thorium is spoken of as a white amorphous powder, and behaves in a manner very similar to the zirconium compound. Thus the analogy existing between these two elements is once more strikingly manifested.

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IV. ON THE SEPARATION OF IRON FROM ZIRCONIUM AND CERTAIN OTHER ALLIED METALS.

BY J. MERRITT MATTHEWS.

Received September 2, 1898.

THOUGH there have been several methods proposed in the past for the separation of iron from zirconium, still chemists have not considered that this problem has, as yet, been satisfactorily solved. All methods which have been recommended for the quantitative separation of these two metals have proved, in some particular, to be untrustworthy, for in all of them traces of iron appear to remain with the zirconium with great pertinacity.

As it may be of interest in connection with the present subject, a brief résumê will here be given of the principal methods which have hitherto been proposed for the separation of iron from zirconium.

Bailey,[2] by the use of a moderately concentrated solution of hydrogen peroxide precipitates Zr_2O_5, whereas neither iron, aluminum, nor titanium salts are precipitated by this reagent. No accurate results, however, have been worked out by this method.

Berlin[3] observes that if zirconium dioxide, contaminated with iron, is fused with sodium carbonate to a white heat, and the fusion treated with hydrochloric acid, the iron salt dissolves,

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

[2] *J. Chem. Soc.*, 49, 481.

[3] *J. prakt. Chem.*, 58, 147.