[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KENTUCKY]

SOME DOUBLE FLUORIDES OF ZIRCONIUM[1]

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Schaeffer[2] prepared 13 double fluorides of titanium with certain alkaloids, with the idea that a better method might be devised for the separation of titanium from columbium and tantalum. Similar double fluorides of zirconium with some of the same alkaloids have now been prepared here, in the hope that one might be found which could be used in a more convenient method of separating zirconium and titanium.

These salts were prepared by dissolving zirconium dioxide in hydrofluoric acid and adding an alcoholic solution containing an equivalent quantity of the base. From the resulting solution they were obtained either by crystallization (Method A) or precipitation brought about by the addition of acetone (Method B). They were white and when dry were transparent. All were easily soluble in alcohol and in hot and cold water except the strychnine salt which dissolved slowly in cold water.

The zirconia used in these preparations was obtained from the natural silicate, zircon. This was converted to the dioxide by the method used by Hornberger.[3]

The composition of these salts was determined by estimating the content of fluorine, zirconium, base or nitrogen, and water of crystallization. The amount of fluorine present was obtained by titrating a water solution of the salt at the boiling point with 0.1 *N* sodium hydroxide solution, using phenolphthalein as the indicator. The zirconium hydroxide that was formed at the same time was dissolved with 6 *N* sulfuric acid, reprecipitated with ammonium hydroxide, ignited and weighed as the dioxide. In this way one sample served for the determination of both fluorine and zirconium. Water of crystallization was determined by heating a sample of the air-dried material in a toluene-xylene bath at 105° for one-hour periods until constant weight was obtained. At first, the amount of alkaloid present was calculated from the percentage of nitrogen as determined by the Kjeldahl method. It was often impossible to get results to check by this method, so we made direct determinations of the alkaloid by measur-

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[2] Schaeffer, THIS JOURNAL, **30**, 1862 (1908).

[3] Hornberger, *Ann.*, **181**, 232 (1876). By this procedure zircon is fused with KHF_2, the K_2ZrF_6 that is formed separated by crystallization and converted to the double sulfate by fusion with concd. H_2SO_4, the zirconium precipitated as the hydroxide with NH_4OH and ignited to the dioxide.

ing the optical rotation of a solution of the salt. For this purpose readings were made on both a solution of the salt and on a standard solution containing a known quantity of the free alkaloid. This method was much more rapid and gave more concordant results than that first used.

Table I contains the data obtained from the analysis of the six salts together with the formula corresponding most closely, the method of formation, and the general appearance of each.

TABLE I

DOUBLE FLUORIDES OF ZIRCONIUM

		Aniline[a]	Brucine	Cinchonine	Quinine	Quinidine[b]	Strychnine
Method		A	A	B	B	B	A
Formula[c]		$(An)_2H_2ZrF_6.H_2O$	$B_2H_2ZrF_6.7H_2O$	$(C)H_2ZrF_6.2H_2O$	$Q(ZrF_4)_2.$	$Q(HZrF_5).ZrF_4.4H_2O$	$(S)_3(HZrF_5)_2.2H_2O$
F	Calcd.	27.87	10.78	21.23	23.10	22.80	13.48
	Found	26.88	9.48	20.15	23.26	22.35	13.56
Zr	Calcd.	22.25	8.61	16.93	27.66	24.26	12.91
	Found	23.34	8.35	17.76	27.58	24.58	12.83
N	Calcd.	6.84	...	5.22	...	...	...
	Found	6.91	...	4.28	...	...	...
Base	Calcd.	...	68.49	...	49.24	...	...
	Found	...	72.6	...	50.2	...	...
H_2O	Calcd.	...	11.92	...	...	9.59	2.55
	Found	...	11.43	...	...	9.63	2.47
Appearance		cubes	slender needles	microscopic cubes	microscopic cubes	microscopic cubes	long, flat plates

[a] During the preparation of this salt, a number of red crystals were noted distributed among the white ones. These were much less soluble than the white ones, so the two were separated by fractional crystallization. It was later noticed that the white salt left after being heated for a water determination turned the same red color when moistened with a little water. Therefore, the red salt must have been the double fluoride of some oxidation product of aniline. Its fluorine and zirconium contents were considerably higher than those of the white salt as indicated by the following analytical data. White salt: F, 26.88; Zr, 23.34. Red salt: F, 29.87; Zr, 32.68. The crystalline forms of the two were different, the red salt existing as comparatively large transparent rhombohedra.

[b] The solutions of this salt were bluish and opalescent.

[c] The formulas proposed are those that correspond most closely to the experimental data, although in the cases of aniline, brucine and cinchonine the calculated and observed values are not in the closest accord and in the case of the other three salts the formulas are irregular compared with those given by Schaeffer for the corresponding titanium salts. Since fluorine is generally low, it is probable that some of it was lost either through partial hydrolysis of the solution or slight decomposition on exposure to the air.

Attempts were made to prepare a double fluoride with cinchonidine but it could not be made to crystallize by any of the methods used with the other salts. Aqueous and alcoholic solutions yielded a stiff, brown jelly when evaporated almost to dryness. The addition of acetone caused a milky precipitate to form but this soon disappeared and the original jelly was deposited again in the bottom of the dish. After long standing the jelly solidified, but the product was colored brown by oxidation products and was too impure to be analyzed.

Summary

Six new double fluorides of zirconium with the organic bases, aniline, brucine, cinchonine, quinine, quinidine and strychnine, have been prepared, their probable formulas proposed, and some of their properties noted.

No definite solubility determinations were made and, therefore, the idea of a new procedure for the separation of zirconium and titanium could not be fully investigated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE CONDUCTANCE OF SOLUTIONS OF ALKALI METALS IN LIQUID AMMONIA AND IN METHYLAMINE

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The absorption spectra of the blue solutions of the alkali metals have been investigated by Gibson and Argo.[1] They showed that their observations could be accounted for by the following hypotheses.

The color of the solution is due in all cases to electrons combined with the solvent. In ammonia the dissociation of the metal into electrons is nearly complete, and the concentration of electrons uncombined with solvent is negligible compared with that of the solvated electrons. In other words, the solvation of the electrons is nearly complete. In methylamine, on the other hand, the concentration of un-ionized metal is no longer negligible and is responsible for the increased absorption at the shorter wave lengths. The solvation of the electrons in methylamine is incomplete and diminishes as the temperature is increased.

In order to throw further light on these questions, the conductances and the temperature coefficient of conductance of the blue solutions were investigated and form the subject of the present paper.

Since liquid ammonia was more available than methylamine, it was used as solvent in all earlier experiments, and later, when the manipulation was well established, solutions in methylamine were studied. While the investigation was in progress, the comprehensive study by Kraus[2] of conductances in liquid ammonia was published, and his results are confirmed at many points by our own.

Apparatus and Manipulation

The apparatus shown diagrammatically in Fig. 1 is constructed entirely of Pyrex glass.

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[1] Gibson and Argo, THIS JOURNAL, **40**, 1327 (1918).

[2] Kraus, *ibid.*, **43**, 749 (1921).