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REACTIONS OF HAFNIUM TETRAMANDELATE

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Introduction

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Since hafnium is similar to zirconium in many of its properties, this study was undertaken to find if there were any similarities (or differences) in the reactions of the mandelates of zirconium and hafnium.

Experimental

A stock solution of pure hafnium oxychloride in hydrochloric acid solution was prepared. It was then standardized against cupferron and mandelic acid according to usual procedures. The weights were determined as HfO_2 after ignition to constant weight. The results are tabulated below:

<u>Volume of HfOCl_2 solution used</u>	<u>Reagent used</u>	<u>Wt of HfO_2 found</u>	
		<u>Exp I</u>	<u>Exp II</u>
20 ml	cupferron	0.4876	0.4876
20 ml	mandelic acid	0.4874	0.4875
Average 0.4875 gm per 20 ml			

Preparation of hafnium tetramandellate

After preliminary experiments, a larger quantity was prepared as follows: 100 ml of the stock solution was mixed with 100 ml of concentrated hydrochloric acid. To this was added dropwise with good stirring 500 ml. of 16% mandelic acid solution. The temperature was then slowly raised to 85°C and kept there for 25 minutes. The resulting white precipitate was allowed to settle, then filtered, and the precipitate on the filter was washed with a hot solution composed of 2% hydrochloric

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acid and 5% mandelic acid. The precipitate was dried under suction, washed twice with acetone, finally with ether and dried in the vacuum desiccator.

Purity of the hafnium tetramandelate

This was determined by igniting known weights to constant weight of HfO_2 , and by microcombustion values.

<u>Wt. of Hafnium mandelate</u>	<u>Wt. of HfO_2 obtained</u>	<u>% purity of $\text{Hf}(\text{C}_6\text{H}_5\text{CHOHCOO})_4$ $\text{Hf}(\text{Mandelate})_4$ on formula basis</u>
0.4704	0.1267	99.96
0.2051	0.0538	99.97

The ignition of hafnium mandelate had to be carefully done in platinum crucibles by slowly raising the temperature in the course of several hours, up to 1000°C . The hafnium mandelate on analysis gave the following results:

C - 49.31%
H - 3.75%
 HfO_2 - 27.21%

$\text{Hf}(\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COO})_4$ requires: C - 49.1%

H - 3.9%

HfO_2 - 26.9%

Reaction of hafnium tetramandelate with ammonium hydroxide

This reaction was studied in the following ways:

A. Potentiometric titration.

Definite weights of hafnium mandelate were taken in clean beakers. Excess of ammonium hydroxide of known strength were added and the beakers were kept aside for some hours after

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covering with watch glasses. They were stirred until the hafnium mandelate was completely dissolved. The excess of ammonium hydroxide was then determined by potentiometric titration against standard hydrochloric acid using a glass electrode. By plotting pH against ml, the volume of hydrochloric acid used for equivalence point as well as the volume of excess ammonium hydroxide were calculated. From the volume of standard ammonium hydroxide used to react with a known weight of hafnium mandelate, it was found that four molecules of ammonium hydroxide were required for every molecule of hafnium mandelate.

B. From the pH values derived from the above titration, it was found that direct titration, against standard hydrochloric acid, of the excess of ammonium hydroxide could be carried out using methyl red as indicator.

The results of A and B are given in the following table:

<u>Wt. of hafnium mandelate</u>	<u>Vol. of NH_4OH used by $\text{Hf}(\text{Ma})_4$</u>	<u>No. of molecules of NH_4OH reacting with $\text{Hf}(\text{Ma})_4$ molecule</u>
A 0.3128 gm	13.6	3.97 (4)
0.3131 gm	13.65	3.98 (4)
B 0.2954	12.25	3.94 (4)
0.1480	16.1	3.95 (4)

C. Incomplete dissolution of hafnium mandelate

A definite weight of hafnium mandelate was taken. Insufficient ammonium hydroxide of known strength was added so that a portion of the hafnium mandelate was not dissolved. Sufficient time and stirring were allowed to dissolve as much of hafnium mandelate as possible. Then the undissolved hafnium

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mandelate was removed by careful filtration through a weighed Selas crucible, dried in the air oven at 110°C and weighed. From the weight of hafnium mandelate that dissolved in the standard ammonium hydroxide, the number of hydrogen atoms in a molecule of hafnium mandelate reacting with ammonium hydroxide could be found.

<u>Wt. of hafnium mandelate</u>	<u>Volume of NH_4OH added</u>	<u>Normality of NH_4OH</u>	<u>Wt. of $\text{Hf}(\text{Ma})_4$ dissolved</u>	<u>Mole ratio of NH_4OH to $\text{Hf}(\text{Ma})_4$</u>
0.3354 gm	10 ml	0.1164	0.2422	3.91 (4)
0.3378 gm	10 ml	0.1164	0.2439	3.89 (4)

Reaction with Sodium Bicarbonate

A. The same procedure as C above was adopted using instead of ammonium hydroxide, a weighed amount of sodium bicarbonate which was insufficient to react with the whole hafnium mandelate. The reaction was carried out in freshly distilled water (30 ml).

<u>Wt. of hafnium mandelate</u>	<u>Wt. of NaHCO_3 used</u>	<u>Wt. of $\text{Hf}(\text{Ma})_4$ left</u>	<u>Wt. of $\text{Hf}(\text{Ma})_4$ dissolved (reacted)</u>	<u>Molar ratio of NaHCO_3 to $\text{Hf}(\text{Ma})_4$</u>
0.4872	0.1706	0.0904	0.3968	3.98 (4)
0.3248	0.1138	0.0603	0.2645	3.97 (4)

B. Excess of sodium bicarbonate solution containing a known weight of sodium bicarbonate was added to a definite weight of hafnium mandelate. A slow current of nitrogen was bubbled through the solution to expel the carbon dioxide formed. After complete dissolution of precipitate of hafnium mandelate. A slow current of nitrogen was bubbled through the solution to expel the carbon dioxide formed. After complete dissolution of precipitate of

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hafnium mandelate and removal of carbon dioxide formed, the excess of sodium bicarbonate was estimated against standard acid. The current of nitrogen was kept up during titration. From the weight of sodium bicarbonate used up by the known quantity of hafnium mandelate the number of reactive hydrogen atoms in the latter was again found to be 4.

Reaction with ethylene diamine

As with ammonium hydroxide, a known excess of standard ethylene diamine solution was added to a weighed amount of hafnium mandelate. The excess of ethylene diamine remaining after complete dissolution of hafnium mandelate was estimated both potentiometrically and by titration against standard hydrochloric acid. Methyl red served as indicator for the titration. The number of equivalents of ethylene diamine and hence number of reactive hydrogen atoms in hafnium tetramandelate were again found to be four within slight experimental errors. Results are tabulated.

Reaction with diethylamine

The same experiments were repeated with diethylamine and the results were in very good agreement.

<u>Wt. of hafnium mandelate</u>	<u>Reagent</u>	<u>Initial Volume of reagent added (exc)</u>	<u>Volume of reagent used by Hf (Ma)₄</u>	<u>Normality of Reagent</u>	<u>Number of equivalents of amine used</u>
0.2481	ethylene diamine	30 ml	11.7	0.1161	4.02 (4)
0.3724	"	40 ml	17.5	0.1161	4.03 (4)
0.3042	diethyl amine	40 ml	18.15	0.0837	4.09 (4)
0.2848	"	40 ml	17.0	0.0837	4.08 (4)

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Discussion

The reactions of hafnium tetramandelates with ammonium hydroxide, ethylene diamine, diethylamine and sodium bicarbonate, clearly shows that it contains four equivalents of replacable hydrogen. These hydrogen atoms must be from the (OH) groups present in the inner complex salt. An enhanced acidity of the weakly acidic alcoholic (OH) group of mandelic acid is possible through co-ordination of hafnium with the oxygen atom of the (OH) group which renders the hydrogen atom more mobile and thus more acidic. Hence, the inner complex salt shows the character of an acid towards an alkali. This substantiates the formula proposed by Feigl.

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