

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, WAYNE STATE UNIVERSITY]

Studies of Hafnium Tetramandelate

BY RICHARD B. HAHN AND P. T. JOSEPH

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Hafnium ions react with mandelic acid solutions to form a white, insoluble compound. This compound was found to be hafnium tetramandelate, $\text{Hf}(\text{C}_8\text{H}_7\text{O}_3)_4$. Hafnium tetramandelate exhibits acidic properties and reacts with weak bases to form salt-like compounds. These properties indicate hafnium tetramandelate is probably a chelate-type compound rather than a simple salt. Data are presented to show that four hydrogen ions per molecule are involved in these reactions.

Zirconium tetramandelate, its properties and its uses in analytical chemistry have been the topics of several investigations.¹⁻⁴ Because hafnium resembles zirconium in many respects, this study was undertaken to compare similarities and differences in the properties and reactions of hafnium and zirconium tetramandelates.

Experimental

Reagents.—Hafnium chloride, $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$ (99.92% pure) was obtained from the Oak Ridge National Laboratory. A solution was prepared by dissolving the salt in 1 *M* hydrochloric acid.

d,l-Mandelic acid was from Eastman Kodak Co. no. 722. A 1 *M* aqueous solution (about 15%) was used.

Standardization of Hafnium Chloride Solution.—A 20-ml. aliquot of the solution was used for standardization. Two methods were employed. Precipitations were made from 3.6 *N* sulfuric acid solutions using cupferron⁵ and from 1 *N* hydrochloric acid solutions using mandelic acid.⁴ The precipitates were filtered, washed, then ignited to the oxide at 1000°. The results given in Table I show that hafnium is precipitated quantitatively by mandelic acid.

Preparation and Composition of Hafnium Tetramandelate.—Preliminary experiments showed that precipitates of constant composition could be obtained only in strongly acid solution (1 *M* or more in HCl). In weakly acid solution basic salts are precipitated. In this respect hafnium behaves similarly to zirconium.² The following procedure was used to prepare the hafnium tetramandelate.

One hundred ml. of a solution of hafnium chloride was mixed with 100 ml. of concd. (12 *M*) hydrochloric acid and heated to 80–90°. Two hundred ml. of 1 *M* mandelic acid solution was added dropwise with stirring. A fine, white, crystalline precipitate of hafnium tetramandelate formed slowly as the mandelic acid was added. After the addition of mandelic acid was complete, the mixture was digested for about 30 minutes at 80–90°. The precipitate was allowed to settle and then was filtered through a sintered glass crucible using suction. The precipitate was washed first with a hot solution composed of 2% of hydrochloric acid and 5% mandelic acid, then two times with acetone, and finally with ethyl ether. The precipitate was dried in a vacuum desiccator.

Analysis of the compound for carbon, hydrogen, and hafnium dioxide gave the following:

Anal. Calcd. for $\text{Hf}(\text{C}_8\text{H}_7\text{O}_3)_4$: C, 49.07; H, 3.58; HfO_2 , 26.91. Found: C, 49.20; H, 3.62; HfO_2 , 26.94.

These data show that the compound is hafnium tetramandelate, $\text{Hf}(\text{C}_8\text{H}_7\text{O}_3)_4$. This pure compound was used in the following experiments.

Reactions of Hafnium Tetramandelate with Aqueous Ammonia. (a) **With Excess Ammonia.**—A known weight of hafnium tetramandelate was dissolved in excess standard ammonia solution. After complete dissolution, the excess ammonia was determined by titration against standard hydrochloric acid using a glass electrode as indicator (Beck-

man pH meter, model H-2). The results are given in Table II.

(b) **With Excess Hafnium Tetramandelate.**—Weighed samples of hafnium tetramandelate were kept suspended in 25 ml. each of water contained in erlenmeyer flasks. Into each flask was added a measured quantity of standard ammonia insufficient to dissolve all of the hafnium tetramandelate. The flasks were stoppered and agitated in a mechanical shaker for two hours to assure that equilibrium was attained. The undissolved hafnium tetramandelate then was filtered off, dried and weighed. Analysis showed no change in the composition of the undissolved precipitate. The difference between the weight of the undissolved hafnium tetramandelate and the weight of the original sample gave the weight of hafnium tetramandelate reacting with the ammonia.

The solution remaining was acidified with hydrochloric acid and mandelic acid was added to reprecipitate the hafnium tetramandelate. This was filtered off, dried and weighed. Its weight agreed exactly with the amount dissolved by ammonia. The molar relationship of the hafnium tetramandelate to the ammonia was found to be 1:4. These data are contained in Table III.

(c) **Preparation and Composition of Ammonium Hafnium Tetramandelate.**—The ammonium salt of hafnium tetramandelate was prepared by adding the calculated amount of standard ammonia solution to a known weight of hafnium tetramandelate so as to form a mole ratio of 4:1. The resulting solution was slowly evaporated under partial vacuum at room temperature. A gummy, hygroscopic solid was obtained. This was crystallized twice from benzene, taking care not to expose to moist air. Analysis of a highly purified and thoroughly dried sample gave the following results.

Anal. Calcd. for $(\text{NH}_4)_4\text{Hf}(\text{C}_8\text{H}_7\text{O}_3)_4$: C, 44.91; H, 5.14; HfO_2 , 24.68. Found: C, 44.75; H, 5.19; HfO_2 , 24.60.

TABLE I
STANDARDIZATION OF HAFNYL CHLORIDE SOLUTION

Reagent	Wt. of HfO_2 (g.)	
	Exp. I	Exp. II
Cupferron	0.4876	0.4876
Mandelic acid	0.4874	0.4875

TABLE II

DISSOLUTION OF HAFNIUM TETRAMANDELATE IN AMMONIA

Hafnium tetramandelate (g.)	0.1164 <i>N</i> NH_4OH added, ml.	Vol. NH_4OH found to be excess, ml.	Vol. NH_4OH used by $\text{Hf}(\text{C}_8\text{H}_7\text{O}_3)_4$, ml.	Molar ratio $\frac{\text{NH}_4\text{OH}}{\text{Hf}(\text{C}_8\text{H}_7\text{O}_3)_4}$
0.3128	25.00	11.40	13.60	3.97
.3131	25.00	11.35	13.65	3.98
.2954	25.00	12.75	12.25	3.94
.1480	10.00	3.90	6.10	3.95

TABLE III

PARTIAL DISSOLUTION OF HAFNIUM TETRAMANDELATE IN AMMONIA

Hafnium tetramandelate (g.)	0.1164 <i>N</i> NH_4OH added, ml.	Wt. of residue (g.)	Wt. $\text{Hf}(\text{C}_8\text{H}_7\text{O}_3)_4$ dissolved (g.)	Molar ratio $\frac{\text{NH}_4\text{OH}}{\text{Hf}(\text{C}_8\text{H}_7\text{O}_3)_4}$
0.3354	10.00	0.0932	0.2422	3.91
0.3378	10.00	0.0939	0.2439	3.89

(1) R. Belcher, A. Sykes and J. C. Tatlow, *Anal. Chim. Acta*, **10**, 34 (1954).

(2) R. B. Hahn and E. S. Baginski, *Anal. Chim. Acta*, **14**, 45 (1956).

(3) R. B. Hahn and Leon Weber, *This Journal*, **77**, 4777 (1955).

(4) C. A. Kumins, *Anal. Chem.*, **19**, 376 (1947).

(5) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis," John Wiley and Sons, New York, N. Y., 1953.

Reactions of Hafnium Tetramandelate with Sodium Bicarbonate.—A solution of sodium bicarbonate containing a known weight of the salt in excess was agitated with a definite weight of hafnium tetramandelate. A slow current of pure nitrogen was bubbled through the solution to expel the carbon dioxide. After complete dissolution of the hafnium tetramandelate and removal of the carbon dioxide, the excess of sodium bicarbonate was determined by titration with standard hydrochloric acid. From the weight of sodium bicarbonate required to dissolve a known quantity of hafnium tetramandelate, the number of reactive hydrogen atoms in a molecule of the latter was again found to be four (Table IV).

TABLE IV

PARTIAL DISSOLUTION OF HAFNIUM TETRAMANDELATE IN SODIUM BICARBONATE

Hafnium tetramandelate (g.)	Wt. NaHCO ₃ added as soln. (g.)	Wt. residual Hf(C ₈ H ₇ O ₃) ₄ (g.)	Wt. of Hf(C ₈ H ₇ O ₃) ₄ dissolved (g.)	Molar ratio NaHCO ₃ /Hf(C ₈ H ₇ O ₃) ₄
0.4872	0.1706	0.0904	0.3968	3.98
0.3248	0.1138	0.0603	0.2645	3.97

(b).—Incomplete dissolution of hafnium tetramandelate by use of an insufficient amount of sodium bicarbonate solution and the determination of the dissolved, as well as undissolved amounts of hafnium tetramandelate, were carried out exactly as described under the ammonia procedure. The results given in Table V indicate the same molar relationship for sodium bicarbonate also.

TABLE V

DISSOLUTION OF HAFNIUM TETRAMANDELATE IN SODIUM BICARBONATE

Hafnium tetramandelate (g.)	0.1122 N NaHCO ₃ added, total ml.	Vol. of NaHCO ₃ found in excess, ml.	Vol. of NaHCO ₃ used by Hf(C ₈ H ₇ O ₃) ₄ , ml.	Molar ratio NaHCO ₃ /Hf(C ₈ H ₇ O ₃) ₄
0.3126	25	11.0	14.00	3.96
0.3284	25	10.30	14.70	3.97

The sodium salt of hafnium tetramandelate was prepared as white crystals by gentle evaporation under vacuum of a solution made by dissolving hafnium tetramandelate in the requisite volume of sodium bicarbonate solution.

Reaction of Hafnium Tetramandelate with Sodium Carbonate.—When solid hafnium tetramandelate was agitated with a solution of sodium carbonate the former slowly dissolved and carbon dioxide gas was evolved. Though a clear solution resulted, it gradually became turbid due to the formation of hydrous hafnia. Addition of excess mandelate ions tended to keep the solution clear. Though the formation of carbon dioxide gas was a clear indication of the acidic properties of hafnium tetramandelate, the results obtained by reaction between hafnium tetramandelate and sodium carbonate were erratic due possibly to the tendency to form hydrous hafnia by hydrolysis.

Other Solvents for Hafnium Tetramandelate.—Hafnium tetramandelate was found to be soluble in many weakly basic solvents such as ethylenediamine, diethylamine as well as many primary and secondary amines. All of these

substances seemed to act as bases which reacted with the weakly acidic (OH) groups of hafnium tetramandelate to form soluble complexes. The results are given in Table VI for the reactions with ethylenediamine and diethylamine.

TABLE VI

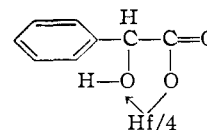
DISSOLUTION OF HAFNIUM TETRAMANDELATE IN BASES

Sample (g.)	Reagent used	Normality of reagent	Total vol. of reagent added, ml.	Vol. of excess reagent, ml.	Vol. of reagent used by Hf(C ₈ H ₇ O ₃) ₄ , ml.	No. of equiv. of base per mole of Hf(C ₈ H ₇ O ₃) ₄
0.2481	Ethylenediamine	0.1161	30	18.30	11.70	4.02
.3724	Ethylenediamine	.1161	40	22.50	17.50	4.03
.3042	Diethylamine	.0837	40	21.85	18.15	4.09
.2848	Diethylamine	.0837	40	22.95	17.05	4.08

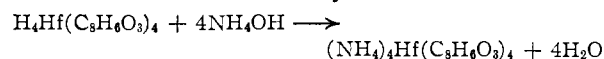
X-Ray Diffraction Studies.—X-Ray diffraction patterns were made on hafnium tetramandelate, ammonium hafnium mandelate, sodium hafnium mandelate, sodium mandelate and *d,l*-mandelic acid by the powder method. Separate and distinct patterns were obtained in all cases. This indicates that ammonium hafnium mandelate and sodium hafnium mandelate are distinct compounds and not mixtures of hafnium tetramandelate with sodium or ammonium mandelate.

Conclusion

The above studies suggest that hafnium tetramandelate is probably a chelate type compound having a structure similar to the one proposed by Feigl⁶ for zirconium tetramandelate.



The reaction between ammonium hydroxide and hafnium tetramandelate may be formulated.



Several other weak bases also react with the weakly acidic hydroxyl groups of hafnium tetramandelate (indicated by the above structure) to form inner salts. Addition of strong bases such as sodium hydroxide, however, leads to hydrolysis and final precipitation of hydrous hafnia.

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(6) F. Feigl, "Chemistry of Specific, Sensitive and Selective Reactions," Academic Press Inc., New York, N. Y., 1949.