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STUDIES OF ZIRCONIUM TETRAMANDELATE

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In studying the reactions of various organic acids with the zirconyl ion, Kumins (3) observed that a precipitate was formed in the reaction of zirconyl ions with *dl*-mandelic acid. The precipitate was shown to be zirconium tetramandelate, $\text{Zr}(\text{C}_8\text{H}_7\text{O}_3)_4$. Using mandelic acid as a reagent, Kumins developed an analytical method for the determination of zirconium in the presence of various other ions. Hahn (2) found that quantitative precipitation of zirconium tetramandelate occurs even in strongly acid solution and that hafnium was also precipitated by mandelic acid.

Kumins considered the zirconium tetramandelate precipitate as a simple salt $\text{Zr}(\text{C}_8\text{H}_7\text{O}_3)_4$ whereas Feigl (1) postulated a chelate type structure:

When zirconium tetramandelate is treated with ammonium hydroxide it dissolves, forming a clear solution. Strong bases, however, react to form a gelatinous precipitate of zirconium hydroxide. Kumins regarded the reaction with ammonium hydroxide as being the formation of a complex ion with ammonia, but no experiments were cited to verify this. If Feigl's structure were correct, however, the reaction could be interpreted as an acid-base reaction resulting in the formation of a soluble salt. Because of these conflicting theories this investigation was made in order to clarify the structure and reactions of zirconium tetramandelate.

EXPERIMENTAL

Reagents:

Chemically pure zirconyl chloride $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, Fisher Scientific Co., was used in all experiments. This was checked spectrographically and found to be free of impurities except for a small amount of hafnium.

d,l-Mandelic acid Eastman Kodak Co. #722 melting point $119^\circ - 121^\circ$ was used. A saturated aqueous solution (about 15%) was used in all experiments.

Sodium mandelate (Mallenkrodt) was purified by several recrystallizations from 95% ethyl alcohol (4). The final salt was assumed to be $\text{NaC}_8\text{H}_7\text{O}_3$.

Reaction of zirconyl ions with d,l-mandelic acid.

When a solution containing zirconyl ions is treated with mandelic acid a precipitate does not form immediately. A clear solution is obtained which persists for a moment or two even when a large excess of mandelic acid is present. If the mandelic acid is added dropwise, a precipitate does not form until almost equivalent amounts are mixed. It was considered that an intermediate soluble complex is first formed which then reacts with more mandelic acid to form a precipitate. In order to test this hypothesis a conductometric titration was carried out. Standard solutions of zirconyl chloride and sodium mandelate were prepared. The zirconyl chloride was titrated with the standard sodium mandelate solution using the apparatus described by Willard, Merritt and Dean (5). The results are shown in Fig. I. 50.0 ml of 0.0163M zirconyl chloride were found to react with 1.9 ml of 1M sodium mandelate.

This indicates that approximately 2.3 moles of sodium mandelate react with 1 mole of zirconyl ion to form a soluble complex. The reaction might be formulated as follows:

When an excess of mandelate ion is added a precipitate of zirconium tetramandelate results:

The first reaction takes place rapidly whereas the second reaction proceeds slowly. This is indicated by the fact that no break in the conductometric titration curve is obtained when precipitation takes place.

It was thought that zirconyl ions might preferentially react with either the d or l isomer of mandelic acid. In order to test this a solution of d,l-mandelic acid was treated with a quantity of zirconyl chloride insufficient to react with all of the mandelic acid. The precipitate of zirconium tetramandelate was removed and the solution was examined in a polarimeter. No optical rotation was observed, consequently it appears that there is no preference as to which optical form of mandelic acid zirconium may react.

Preparation of zirconium tetramandelate.

Chemically pure zirconyl chloride was dissolved in a solution containing three parts by volume of water and one part by volume of concentrated hydrochloric acid. The resulting solution was heated to 50°C. and a 15% solution of d,l-mandelic acid was added dropwise until precipitation was complete. The precipitate was filtered and washed three times with

acetone and several times with ether and finally dried at 110°C . Analysis of the precipitate was as follows:

Observed: C, 55.28; H, 4.15; ZrO_2 , 17.80.

Theoretical: C, 55.24; H, 4.06; ZrO_2 , 17.71.

Reaction of zirconium tetramandelate with ammonia.

Varying amounts of zirconium tetramandelate were suspended in about 25 ml. of water in glass stoppered flasks. Assuming that one mole of zirconium tetramandelate reacts with four moles of ammonium hydroxide, a sufficient amount of standard ammonium hydroxide was pipetted into each flask to dissolve about one-half of the zirconium tetramandelate present. The flasks were stoppered then shaken in a mechanical shaker for two hours.

After reaching equilibrium, the undissolved zirconium tetramandelate precipitate was dried and weighed. The remaining solution was acidified with hydrochloric acid. Mandelic acid was then added which caused the reprecipitation of zirconium tetramandelate. The amount of zirconium tetramandelate recovered agreed exactly with the amount dissolved by the ammonia. The molar relationship of the zirconium tetramandelate to the ammonium hydroxide was 1 to 3 (one mole of zirconium tetramandelate reacts with three moles of ammonium hydroxide). These data are shown in Table 1.

Table 1

Partial Dissolution of zirconium tetramandelate in ammonium hydroxide.

wt. sample	wt. residue as ZrO_2	ml of .1157N NH_4OH added	Molar ratio $\frac{\text{NH}_4\text{OH}}{\text{Zr}(\text{C}_8\text{H}_7\text{O}_3)_4}$
0.4789	0.0374	10.00	3.01
0.6216	0.0384	15.00	2.98
0.8629	0.0574	20.00	2.99
1.0393	0.0644	25.00	2.98

To further determine the ratio of ammonium hydroxide to zirconium tetramandelate a potentiometric titration was performed.

A weighed amount of zirconium tetramandelate was dissolved in excess standard ammonium hydroxide. The excess ammonia was titrated with standard hydrochloric acid using a glass electrode as indicator (Bechman pH meter model H²). The results shown in Table 2 indicate that about 3.5 moles of ammonium hydroxide reacted with one mole of zirconium tetramandelate. Ethylene diamine was substituted for ammonia and the above experiment repeated. The results are given in Table 3, which shows same relationship holds for ethylene diamine also. A typical titration curve is given in Fig. 2.

Table 2

Back Titration of Excess NH_4OH
used to dissolve $\text{Zr}(\text{C}_8\text{H}_7\text{O}_3)_4$

wt. sample	ml of .1157N NH_4OH added	ml of .1509N HCl required	molar ratio $\frac{\text{NH}_4\text{OH}}{\text{Zr}(\text{C}_8\text{H}_7\text{O}_3)_4}$
0.4051	50.00	25.02	3.45
0.3676	50.00	26.15	3.48

Table 3

Back Titration of Excess Ethylene Diamine
used to dissolve $\text{Zr}(\text{C}_8\text{H}_7\text{O}_3)_4$

wt. sample	ml of .1106 Ethylene- Diamine added	ml of .1509N HCl required	molar ratio $\frac{\text{En}}{\text{Zr}(\text{C}_8\text{H}_7\text{O}_3)_4}$
0.3237	50.00	25.6	1.76

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Preparation of other Complexes.

It was found that other basic solutions such as sodium bicarbonate, sodium carbonate, various primary and secondary amines would also dissolve zirconium tetramandelate. Attempts were made to isolate the sodium and ammonium salts.

The sodium derivative of zirconium tetramandelate was prepared by treating an excess amount of zirconium tetramandelate with a sodium bicarbonate solution and boiling to expel the carbon dioxide formed in the reaction. This solution was evaporated in an oven at 110°C. leaving a white residue. This solid dissolved in water and formed a precipitate of zirconium tetramandelate when acidified.

The ammonium compound proved to be more difficult to prepare. Zirconium tetramandelate was dissolved in ammonium hydroxide and the solution concentrated by evaporating off the water and excess ammonia. This gave a thick syrup which upon further heating produced a gummy solid. Upon evaporation in vacuum, a white hygroscopic solid was obtained. A water solution of this solid gave a precipitate of zirconium tetramandelate upon being acidified.

X-ray Diffraction Studies.

X-ray diffraction pattern (powder method) were made on zirconium tetramandelate, ammonium mandelate, ammonium zirconium mandelate, sodium zirconium mandelate and sodium mandelate. In each case a separate distinct pattern was obtained. This indicates that in the reaction of zirconium tetramandelate with ammonia and sodium bicarbonate, no extensive hydrolysis takes place but a new salt-like compound is formed.

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Conclusion

These studies show that zirconium tetramandelate must be a chelate type compound as postulated by Feigl. The reaction of ammonia with an excess of zirconium tetramandelate can be formulated:

When an excess of ammonia is added, the tetrabasic salt $(\text{NH}_4)_4\text{Zr}(\text{C}_8\text{H}_7\text{O}_3)_4$ is also formed. The reaction however is not stoichiometric as indicated by the molar ratio 1:3.5 of zirconium tetramandelate to ammonia. With other weak bases and basic salts like sodium carbonate corresponding reactions take place. With strong bases, however, hydrolysis takes place and zirconium hydroxide is precipitated. Because of the lack of stoichiometry the above reactions are not suitable as analytical methods.

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Bibliography

- (1) Feigl, F. "Chemistry of Specific, Sensitive, and Selective Reactions" Academic Press. New York 1949.
- (2) Hahn, R. B. Anal Chem 21 1579 (1949).
- (3) Kumins, C. A. Anal Chem 19 376-377 (1947).
- (4) Ross, J. D. M. and Morrison, R. J., J. Chem. Soc. 1016 (1933).
- (5) Willard, H. H., Merritt, L. L., and Dean, J.A.: "Instrumental Methods of Analysis" D. VanNostrand Co. New York (1951) p. 224.

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