

Studies on Coordination Compounds of Cobalt Nitrate with Mandelic Acid

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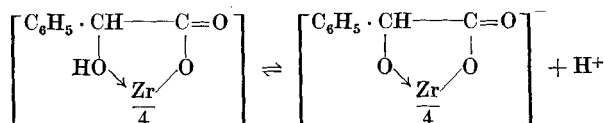
With 4 Figures

Summary

Conductometric and pH studies of the mixed solutions of Cobalt nitrate and sodium mandelate reveal the existence of three complexes in the ratios of (1:1), (1:2) and (1:3). Two compounds having ratios (1:2) and (1:3) were isolated in pure state and their constitutions established by estimation of Cobalt and mandelic acid contents. pH titration of isolated compound (1:3) with alkali consumes four equivalents of alkali which indicates that an anionic type of compound is formed.

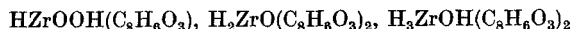
In 1947 KUMINS¹⁾ discovered that mandelic acid quantitatively and selectively precipitated Zirconium from solutions of Zirconyl chloride in concentrated hydrochloric acid. He considered the precipitate to be a simple salt, Zirconium tetramandelate i. e. $Zr(C_8H_7O_3)_4$.

FEIGEL²⁾ however postulated the formation of a chelate type structure



to explain the solubility of the tetramandelate in aqueous ammonia. Experiments by HAHN and WEBER³⁾ substantiated this view.

HAHN and BAGINSKI⁴⁾ were able to prepare pure Zirconium tetramandelate at high acid concentration only and to account for this they postulated the existence of basic salts formulated by BHIMENTHAL⁵⁾ as



¹⁾ C. A. KUMINS, *Analyt. Chem.* **19**, 326 (1947).

²⁾ F. FEIGEL, *Chemistry of Specific, Selective and Sensitive Reactions* (Academic Press, New York), 1949, 213-15.

³⁾ R. B. HAHN and L. WEBER, *J. Amer. Chem. Soc.* **77**, 4777 (1955).

⁴⁾ R. B. HAHN and E. S. BAGINSKI, *Anal. Chem. Acta* **14**, 45 (1956).

⁵⁾ W. BHIMENTHAL, "The Chemical Behaviour of Zirconium". VAN NOSTRAND, New York (1958).

Hahn and Joseph⁶⁾ prepared Hafnium tetramandellate soluble in aqueous Ammonia.

The chelate nature of mandelic acid was further proved by Klingenberg and Theis⁷⁾. They used α -Methoxy phenyl acetic acid in place of mandelic acid for precipitation of Zirconium from Zirconyl chloride in hydrochloric acid and no insoluble compound with Zirconium was obtained.

Recently Aluminium and Uranium chelates were studied by Srivastava and Manohar⁸⁾ and Pande and Misra⁹⁾ respectively, but studies on chelate compounds of Cobalt with mandelic acid are lacking. Physicochemical studies of the Cobalt and mandelic acid complexes have been carried out and the nature of complexes formed have also been studied in the present work. Evidence has been found for the formation of three complexes at 1:1, 1:2 and 1:3 molecular ratios of cobalt and mandelic acid.

Experimental

M/10 solutions of cobalt nitrate hexahydrate (BDH/extra pure) and sodium mandelate were prepared. The solutions having the molar ratios of (1:1) and (1:2) of cobalt nitrate and sodium mandelate were prepared by mixing the two solutions in the respective stoichiometric ratios and diluted to constant volume.

Conductometric Titrations

An electrical magic eye apparatus (Type GM 4249/Phillips) was used to determine the resistance of the solutions during the titration. A pyrex glass conductivity cell with platinum electrodes was used for such measurements. The cell was rinsed several times with the solution and at least three readings were taken for each solution. Conductometric titrations were carried out in the cell which was kept in electrically heated thermostat at 35 ± 0.1 °C.

Table I

No.	Equivalent Alkali added ml	Reading for Resistance $\times 10^3$	
		(1:1) Mixture Soln.	(1:2) Mixture Soln.
1.	0.00	0.240	0.250
2.	0.30	0.270	0.270
3.	0.65	0.290	0.280
4.	1.00	0.310	0.305
5.	1.30	0.300	0.270
6.	1.65	0.280	0.250
7.	2.00	0.250	0.235
8.	2.30	0.235	0.230
9.	2.65	0.230	0.220
10.	3.00	0.220	0.210

⁶⁾ R. B. Hahn and D. T. Joseph, *J. Am. Chem. Soc.* **79** 1298-9 (1957).

⁷⁾ J. J. Klingenberg and R. J. Theis, *Ohio. J. Sci.*, **61**, 186-9 (1961).

⁸⁾ S. N. Srivastava and Manohar, *Ind. Chemical Soci. Vol.* **37**, No. 5, 299-302 (1960).

⁹⁾ C. S. Pande and S. K. Misra, *J. prakt. Chem.*, **17**, 5 (1962).

30 ml of each of the mixed solution of Cobalt nitrate and sodium mandelate in the ratios of (1:1) and (1:2) was taken in the conductivity cell and the cell was kept for 15 minutes in the thermostat to attain the temperature of the bath. It was titrated with 1M NaOH solution noting the resistance of the solution each time after adding 0.1 ml alkali solution. The solution was left for 5 minutes after each 0.1 ml alkali addition in order to attain the temperature of the bath. In both the cases it was observed that at about 2 equivalents of-alkali a ppt. is formed. The observations are given in Table I page 238.

Electrometric Titrations

Electrometric titrations were carried out by adding alkali from a micro-pipette to the mixed solutions having molar ratios (1:1) and (1:2) of cobalt nitrate and sodium mandelate. pH measurements were made by using a LEEDS and NORTHRUTH pH meter (No. 7663—AI Assembly). The instrument was standardized with a 0.05 M solution of potassium hydrogen phthalate (pH 4.005 at 25°).

30 ml of the mixed solution was taken in a beaker and the electrodes of the pH-meter were dipped in the solution. The pH-was noted after stirring the solution for 2 minutes. The titration was performed by adding 0.1 ml of 1M NaOH solution each time from a micropipette. The observations are recorded in the table II below

Table II

No.	Equivalent alkali ml	pH Readings		
		1:0 mixture	1:1 mixture	1:2 mixture
1.	0.0	2.30	2.40	3.00
2.	0.25	3.50	2.70	3.25
3.	0.50	7.00	3.10	3.55
4.	0.75	8.30	3.65	3.90
5.	0.85	8.80	3.95	4.25
6.	1.00		4.40	4.75
7.	1.10		5.30	7.90
8.	1.25		7.75	8.10
9.	1.50		8.15	8.45
10.	1.75		8.50	8.75

In all the titrations a precipitate begins to appear at pH 8.00 and the extent of precipitate increases with the rise in pH of the solution.

Reaction Between M/20 Cobalt nitrate and M/2 Sodium mandelate

Thirty-five ml of 0.05 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was titrated with 0.5 M sodium mandelate solution using a glass electrode. After each addition of sodium mandelate, the mixture was stirred well for 2 minutes and pH was recorded. The results of the titration are shown in Figure 1.

Isolation of the Compounds

After ascertaining the evidence for the formation of complexes by physicochemical methods attempts were made to isolate these compounds. Solutions of cobalt nitrate with excess of mandelic acid were mixed and the mixed solution was concentrated on water bath. After concentration a precipitate (compound I) was obtained which was filtered, washed, and dried. The compound was light pink in appearance and slightly soluble in water.

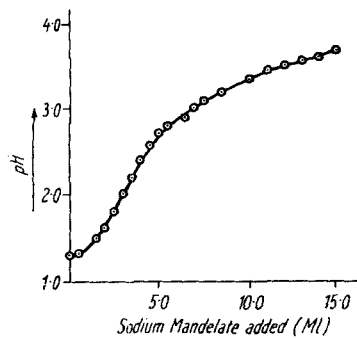


Fig. 1. Electrometric titration curve of M/20 Cobalt Nitrate against M/2 Sodium Mandelate Solution

The filtrate obtained after removal of above precipitate was again concentrated on water bath. On cooling a second crop of crystals was obtained. The crystals (Compound 2) were filtered and washed with small quantity of alcohol and then dried when shining and light pink crystals were obtained.

When cobalt nitrate and sodium mandelate solutions were mixed in stoichiometric ratios of 1:3 and 1:4 and kept for some time, a precipitate separated out which on analysis was found to be similar to compound I.

Compounds 1 and 2 prepared above were then analysed by the following methods to derive their possible formulae.

Estimation of Cobalt

Cobalt content was estimated in the compounds by complexometric titrations¹⁰ and the percentage of Cobalt thus found was compared with the theoretical values calculated on the basis of (1:2) and (1:3) ratios.

Table III

No.	Percentage of Cobalt					
	Compound (1:2) Co (C ₈ H ₆ O ₃) ₂			(1:3) Compound Co(C ₈ H ₆ O ₃) ₃		
	Estimated	Theoretical	Difference	Estimated	Theoretical	Difference
1.	16.92		0.52	11.15		43
2.	17.00	16.40	0.60	10.94	11.58	64
3.	16.84		0.44	11.05		53
4.	17.05		0.65	11.21		37

¹⁰) G. SCHWARZENBACH, *Complexometric Titrations* 78–79 (1957).

Estimation of Mandelic Acid

The mandelic acid content in the compounds was estimated by ceric sulphate method¹¹). The results obtained are given in the Table IV below.

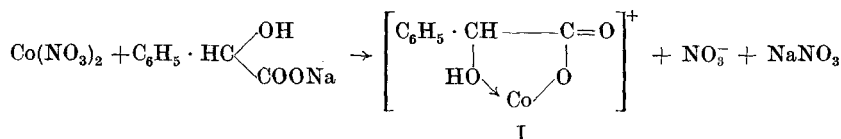
Table IV

No.	Percentage of Mandelic Acid					
	(1:2) Compound $\text{Co}(\text{C}_8\text{H}_6\text{O}_3)_2$			(1:3) Compound $\text{Co}(\text{C}_8\text{H}_6\text{O}_3)_3$		
	Estimated	Theoretical	Difference	Estimated	Theoretical	Difference
1.	82.80		0.80	87.50		0.92
2.	83.00	83.60	0.60	89.30	88.42	0.88
3.	82.71		0.89	88.98		0.56
4.	83.10		0.50	89.15		0.73

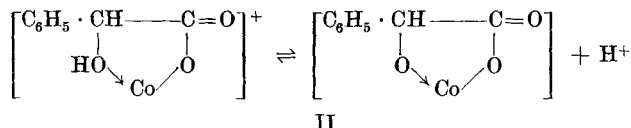
Discussion

Compound (1:1)

The electrometric titration of cobalt nitrate with sodium mandelate (curve I) indicates a chelation of the type I.



This chelation by the donation of a lone pair of electrons from the hydroxyl oxygen atom makes the hydrogen atom more "labile" and acidic and thus the extent of lowering in the pH is a direct measure of the above type of chelation. Thus the equilibrium of the type II may be supposed to exist.



The formation of this (1:1) chelate compound is further suggested by the electrometric titration (Figure 2) of $\text{Co}(\text{NO}_3)_2$ and sodium mandelate with equivalent NaOH which indicates a slow rise in pH of the solution initially but when one equivalent of alkali has been added there is a sudden rise in the pH.

Fig. 3 represents the conductometric titration values of cobalt nitrate and sodium mandelate against equivalent alkali. The addition of an alkali solution to a solution of cobalt nitrate and sodium mandelate in the molar

¹¹) M. A. VERMA and S. D. PAUL, J. Sci. Industr. Res. **13** B, 347 (1954).

ratio of 1:1 increases the resistance of the latter. The continued addition of alkali results in the progressive rise in the resistance which reaches a maximum when one equivalent of alkali has been added, with any further addition of the alkali the resistance decreases. The increase in the resistance

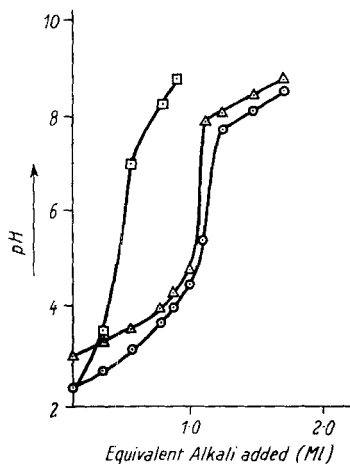


Fig. 2. Electrometric titration curve of (1:1) and (1:2) mixtures of Cobalt Nitrate and Sodium Mandelate Solutions against equivalent alkali

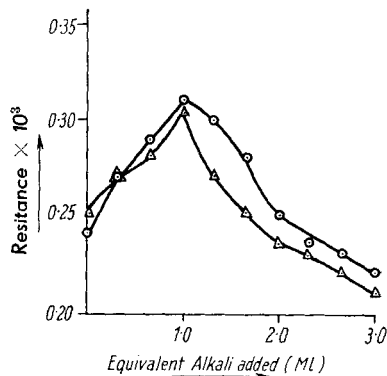


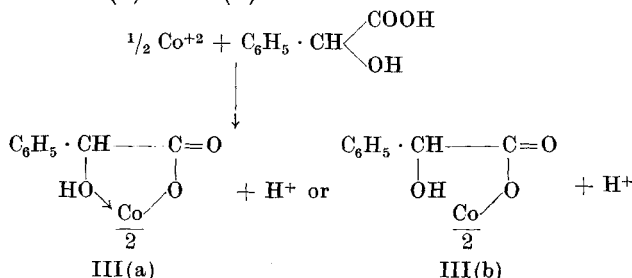
Fig. 3. Conductometric titration of (1:1) and (1:2) mixtures of Cobalt nitrate and Sodium Mandelate against equivalent alkali

or decrease in conductance is due to the removal of H^+ ions and when all the hydrogen ions have been removed the resistance decreases due to the excess of sodium hydroxide. The break in the graph at one equivalent of alkali may be attributed to the formation of (1:1) complex in the solution.

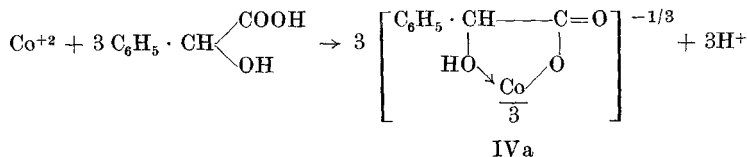
The attempts to separate this compound were unsuccessful.

Compounds of Ratios (1:2) and (1:3)

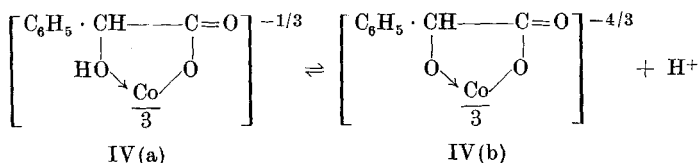
When cobalt nitrate and excess of mandelic acid were taken, two compounds were obtained having ratios (1:2) and (1:3). First compound (1:2) was found to be $Co(C_8H_6O_3)_2$ on detailed analysis. The compound was insoluble in water. This compound may be supposed to possess any one of the following structures III(a) or III(b)



The second compound (1:3) was found to be $\text{Co}(\text{C}_8\text{H}_6\text{O}_3)_3$, which is soluble in water. This compound appears to have the structure IVa as shown below



As this compound is soluble in alkali, it may have a structure of the type given below



The above type of equilibrium is substantiated by titrating a solution, containing a known quantity of the second compound $\text{H} \cdot \text{Co}(\text{C}_8\text{H}_7\text{O}_3)_3$, in water electrometrically with sodium hydroxide and ammonium hydroxide and break occurs when four moles of alkali have been consumed (Fig. 4).

When the second compound is dissolved in water and heated, it is converted into $\text{Co}(\text{C}_8\text{H}_6\text{O}_3)_2$ which is probably due to its hydrolysis.

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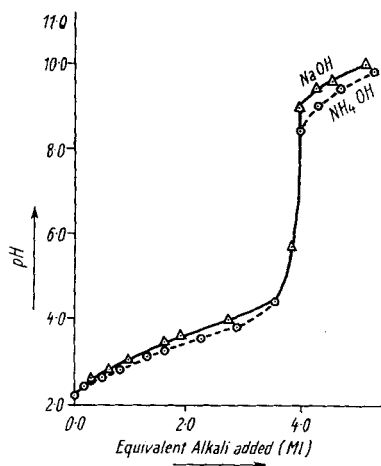


Fig. 4. pH-titration curve of (1:3) compound against equivalent alkali