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Infrared Evidence for the Structure of Cobalt (II) Tartrate Trihydrate

by

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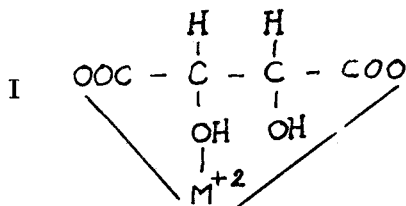
Cobalt (II) Tartrate Trihydrate was obtained as a paramagnetic pinkish violet solid. The infrared spectral evidence shows that the compound is octahedral, isostructural with that of Cu (II). [1]

INTRODUCTION

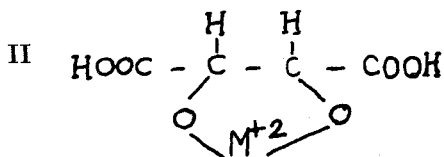
The stereochemistry of the d^7 -ion, Co^{2+} , has proved much more difficult to interpret than that of the d^6 -ion, Co^{3+} . It is only during the last few years that a deeper understanding of magnetic properties and absorption spectra has made it possible to make reliable assignments of stereochemistry to cobalt (II) compounds without X-ray analysis [2].

Five different structures of divalent metal tartrate complexes M^{2+} , (where $\text{M} = \text{Co}$ and Cu) in the solid state are proposed. Only one of these proposed structures agrees with the infrared studies of the Co (II) and Cu (II) tartarates trihydrate. A different structure is shown for the Ni (II) compound. The structure of the first row transition metals tartrate has been the subject of interest for many years [3-7]. There has been a difference of opinion [8, 5] as to the way of bonding of the tartrate anion to that of the transition metal cation. Several methods have been used in the study of such compounds in order to verify their structure, namely conductometric, spectrophotometric, potentiometric, and

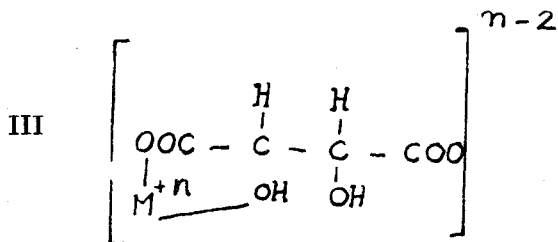
polarographic methods [5], as well as polarimetric and crystallization procedure [7]. There are six principal proposed structures which describe the bonding of the tartrate ion in metal tartrate complexes. The first proposed structure [9 & 2] that a metal ion can be coordinated to the tartrate anion through the oxygens of the two carboxylate groups.



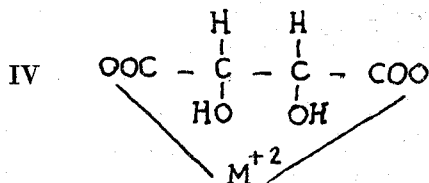
A second proposal implies coordination through the hydroxyl oxygens rather than carboxyl oxygens



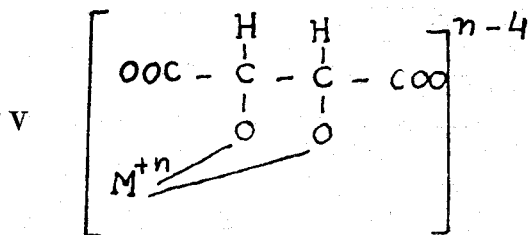
A third proposal [9, 10] involves that one hydroxyl oxygen and one carboxylate oxygen of the tartrate anion coordinate to a metal ion.



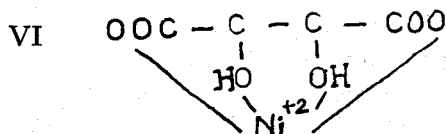
A fourth proposal suggests that tartrate may be coordinated through a hydroxyl group and two of the carboxylate groups.



A fifth proposal states that one of the carboxylate oxygens and two of the hydroxyl oxygens of the tartrate can be involved in the coordination to Co (II) giving the bridge structure (V)



The only proposed structure for Ni (II) tartrate dihydrate is



DISCUSSION

Cobalt (II) tartrate is very slightly soluble in water, but it dissolves readily in sodium hydroxide solutions to give blue solu-

tion. This fact creates much speculation about the role of the alcoholic hydroxyl groups in Co (II)-tartrate complex. A comparative study of the infrared spectra of Co (II)-tartrate trihydrate and of tartaric acid is discussed. The infrared spectrum of d-tartaric acid shows a sharp peak at 1750 cm^{-1} which indicates free carboxyl groups [12 & 13]. Both such groups are alike in the acid. The spectrum of Co (II) tartrate-trihydrate, shows a single sharp peak at 1600 cm^{-1} . The shift of such peak to lower frequency is a good indication of coordinated carboxylate group [13, 14]. The sharp peak indicates that both coordinated carboxylate groups are alike and therefore structures II, III and V are excluded for Co (II) tartrate trihydrate in the solid state.

The spectrum of d-tartaric acid shows also a peak at 1097 cm^{-1} corresponding for a secondary alcohol group, C-O stretching [15]. This peak is shifted to lower frequencies and split into doublet (1055 and 1090 cm^{-1}) in the spectrum of Co (II) tartrate trihydrate. A third characteristic peak is found at 1450 cm^{-1} (the O-H bonding) in the spectrum of tartaric acid. This peak undergoes no change in the spectrum of Co (II) complex. This is a good indication that the alcoholic hydroxyl groups both remain as OH groups without any loss of the protons. The conversion of a single peak into a double one and the shift [14] to lower frequencies indicates that the alcoholic hydroxyl groups are different in the Co (II) compound. The C-O stretching frequency is expected to be reduced through coordinate of an oxygen to the metal ion. The fact that both peaks are shifted to lower frequency than the corresponding single peak in tartaric acid indicates that there is an attraction between the Co (II) ion and the hydroxyl groups. But, the splitting of the peak indicates a stronger attraction for one hydroxyl group by the Co^{+2} ion than for the second. Thus structure I, is ruled out since it shows no coordination of a hydroxyl group to the metal. The elimination of this structure is expected [2], since coordination number 5 for Co^{+2} is very rare and the formation of seven membered rings is not common.

The spectrum of Co (II) tartrate trihydrate shows extra bands in the region $810\text{--}770\text{ cm}^{-1}$ which are characteristic for coordinated H_2O [16]. No corresponding bands are found in the spectrum of tartaric acid.

As far as the bonding of tartrate to Co^{+2} is concerned structure IV fits quite well based on the infrared spectral results. The structure of Co (II) tartrate trihydrate in the hydrated solid state is presumably as given in Fig. (1).

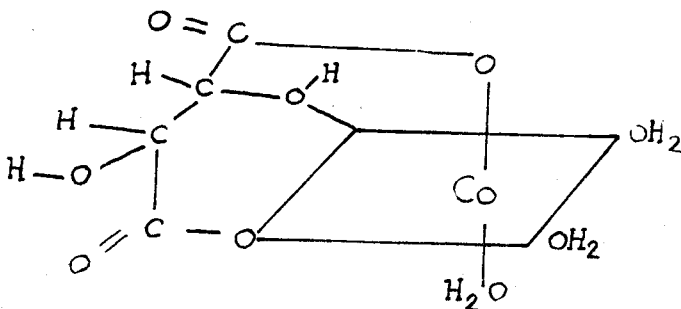


Fig. 1.

The spectrum of Cu (II) tartrate was also measured for comparison. The spectrum shows a single sharp peak at 1620 cm^{-1} for the coordinated carboxylate groups, and a doublet at 1080 and 1060 cm^{-1} for the secondary alcohol groups (C-O stretching). Thus Co (II) tartrate trihydrate is isostructural with that of the Cu (II) complex.

The spectrum of Ni (II) tartarate dihydrate was found to be different. The C-O stretching band shifts to lower frequency (1075 cm^{-1}), but without splitting. The shift to lower frequency indicates that the two alcoholic hydroxyl groups are alike in the Ni (II) compound. The spectrum also shows a single peak characteristic for coordinated carboxylate groups at 1610 cm^{-1} .

Structure VI agrees well with the infrared evidence for Ni (II) compound. The Ni (II) tartrate dihydrate is presumably tetrahedrally coordinated as there are no bands in its spectrum corresponding to coordinated water molecules. Broad band in the region $3500\text{--}3400\text{ cm}^{-1}$ is clear. The two water molecules in the Ni (II) tartrate dihydrate are held as lattice water. The structure of Ni (II) tartrate dihydrate may be as given in Fig. (2).

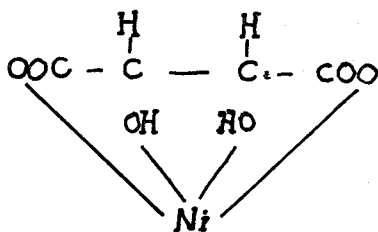


Fig. 2.

EXPERIMENTAL

Infrared spectra were recorded on a Unicam SP. 200 G infrared spectrophotometer. The samples were mulled with nujol. Similar spectra were also obtained on using anhydrous potassium bromide discs [11]. The spectral measurements were made on fresh samples, and also after about six months to study the effects of any structure changes in the compounds on standing but no difference was observed.

Analytical data were determined in the microanalytical unit, Cairo University. Melting points were measured using an ordinary tube melting point apparatus.

Starting materials:

Hydrated solid Co (II) sulphate, prolabo, m.p. decomp. at 140°C, Ni (II) sulphate hexahydrates Apolda grade, m. p. no change up to 200°C, and Cu (II) sulphate pentahydrate of the same grade were used without any further purification.

d-Tartaric acid, BDH grade m.p. 170–172°C was found to be the only suitable form of the acid for the preparation of the tartarate compounds.

Compounds:

Reactions of stoichiometric quantities of d-tartaric acid with Ni (II) sulphate were carried out in aqueous solutions *Ca.* 1 M. Three factors are found effective in preparing the tartrate com-

pounds. The first one is the pH value of the reaction medium which was kept in the vicinity of 7 throughout the reaction by adding sodium hydroxide solutions. The second factor was the concentration of the starting solutions which was 1 M for the Co (II) and Cu (II) compounds. When dilute solutions were used (0.1 - 0.5 M), hydrolysed products were obtained.

In case of the preparation of Ni (II) tartrate dihydrate 0.1 M solutions were found suitable. From the experimental data it is found that Ni (II) tartrate dihydrate is less susceptible to hydrolysis than either Co (II) or Cu (II) tartrates.

The third factor is the addition of few ml. of ethyl alcohol to the reaction mixture, this facilitates the precipitation of the compounds.

Co (II) tartrate trihydrate was obtained as a pinkish violet solid (yield, 83 %) m. p., no change up to 200°C.

(Found : C, 18.4 : H, 3.6 . $C_4 H_{10} O_9 Co$

requires : C, 18.3 : H, 3.8 %).

Ni (II) tartrate dihydrate was obtained as green solid which was filtered off and washed with water several times then dried (yield 86 %), m. p. no change up to 200°C.

(Found : C, 19.7 : H, 3.7 . $C_4 H_8 O_6 Ni$

requires : C, 19.7 : H, 3.3 %).

Cu (II) tartrate trihydrate prepared by the same method gave an authentic sample like the one prepared by using potassium tartrate.

All the compounds were insoluble in most of the solvents tried and thus no physical measurements were carried out.

The magnetic moment of Co (II) tartrate trihydrate was found to be 4.9 B. This value established the octahedral Co - coordination of Co^{2+} in this compound [2].

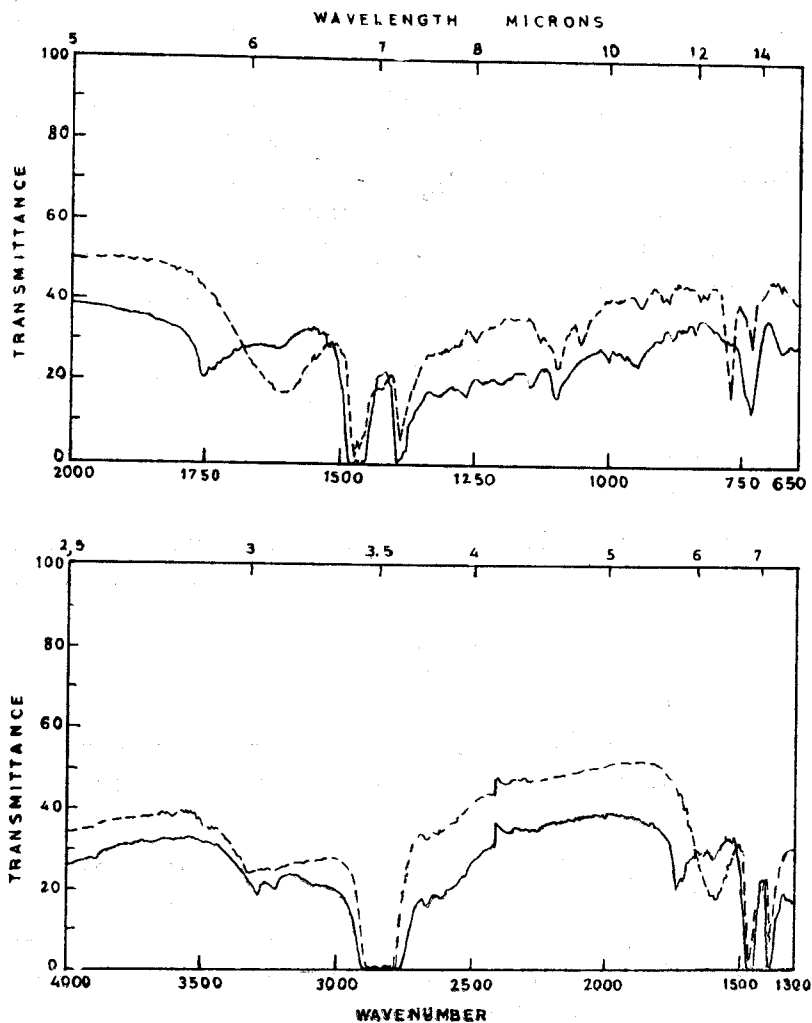


Fig 1. Infrared spectra of d- Tartaric acid and Co (II) tartrate trihydrate. (dotted line).

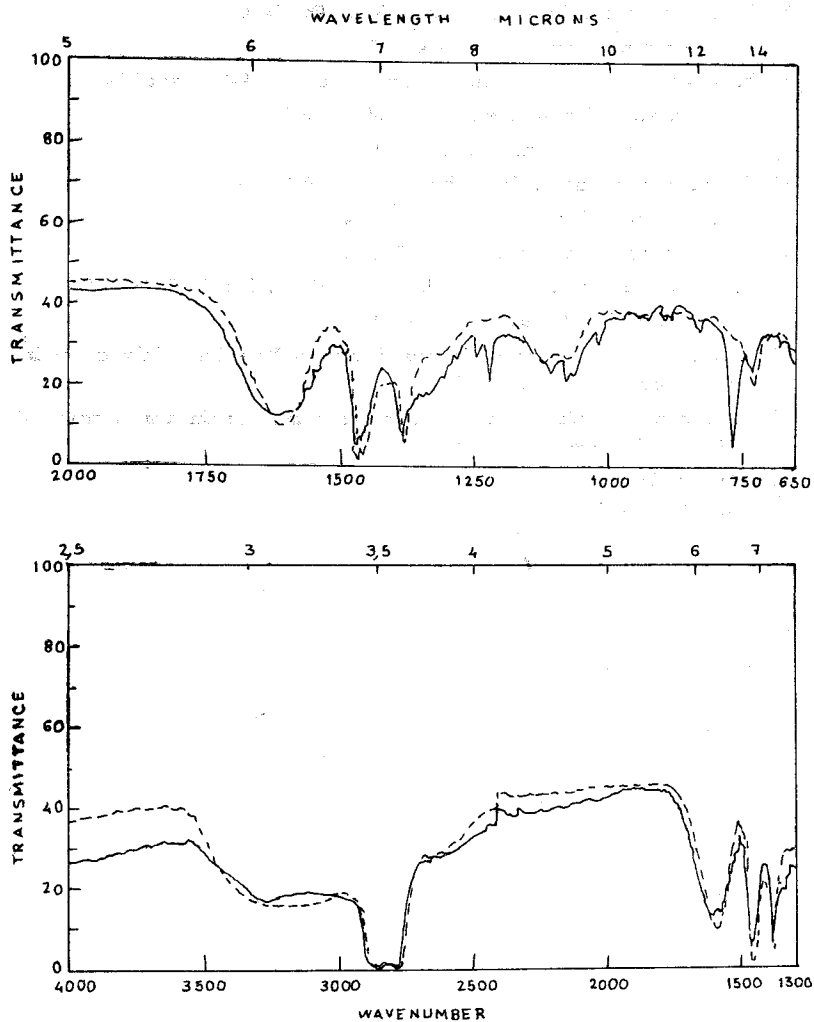


Fig. 2. Infrared spectra of Ni (II) tartrate dihydrate and Cu (II) tartrate trihydrate (Solid line).

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