The Preparation and Tentative Structural Assignment of the Geometrical Isomers of Bis-(L-histidinato)cobalt(III) Ion

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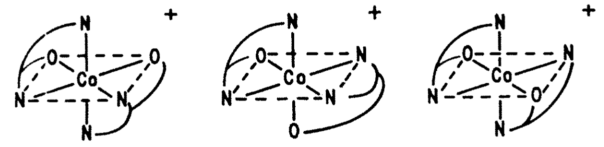
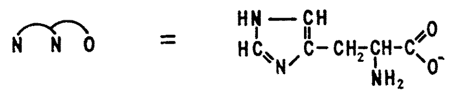
Summary The three geometrical isomers of bis-(L-histidinato)cobalt(III) ion have been isolated; one isomer has been identified and the configuration of the remaining isomers tentatively assigned by means of their electronic absorption spectra.

THE recent publication by Freeman and Liu[1] prompts us to report our preliminary findings concerning the isolation and some of the properties of the three geometrical isomers of bis-(L-histidinato)cobalt(III) ion, CoL_2^+ (illustrated below).



(I) *trans*-imidazole (II) *trans*-amine (III) *trans*-carboxylate



Aqueous solutions containing 2 : 1 molar ratios of L-histidine and hexa-amminecobalt(III) salts (pH 7) were heated on the steam bath for several hours in the presence of activated carbon.[2] When the resulting red solutions were eluted from Dowex 50W-X4 cation-exchange resin with mineral acid, distinct bands of violet, red, and orange appeared.[3] Solids obtained from the coloured fractions were consistent with the presence of CoL_2^+. I.r. spectra of the solids were nearly identical, ν_{asym} CO_2^- appears at 1650 cm.$^{-1}$ [ν_{asym} CO_2^- in bis(histidino)cobalt(II) has been reported[4] at 1582 cm.$^{-1}$]. The electronic absorption spectra of the fractions are shown in the Figure.

Red crystals of composition $[CoL_2]X,nH_2O$ ($X = Cl^-$, $n = 1$; $X = NO_3^-$, $n = 2{\cdot}5$; $X = ClO_4^-$, $n = 1$) were isolated by slow evaporation of the original reaction products. All evidence indicated that these crystals contain the same isomers as the red fraction referred to above.

The spectrum of the violet fraction is similar to spectra obtained with complexes containing four nitrogen and two oxygen donor atoms arranged in D_{4h} symmetry about a cobalt(III) ion.[1,5,6] The spectra of complexes with this configuration are also consistent with crystal-field calculations.[7,8] Therefore, the violet fraction has been assigned the *trans*-carboxylate configuration (III).

Freeman and Liu[1] assigned the structures of three geometrical isomers of bis-(L-2,3-diaminopropionato)-cobalt(III) ion, Co dap_2^+, by means of circular dichroism spectropolarimetry. The ligand dap differs from histidine only in that it contains a methylamino-group in the position occupied by the imidazole group in histidine. The electronic absorption spectra reported for the isomers of Co dap_2^+ which correspond to the *trans*-imidazole (I) and *trans*-amine (II) configurations of the CoL_2^+ isomers are similar to the spectra obtained from the red and orange fractions, respectively. Although intensities vary somewhat, band positions are nearly identical. Charge-transfer bands which tail into the visible region in the spectra of the CoL_2^+ complexes are absent in the Co dap_2^+ complexes A π-electron interaction between the imidazole group and the metal ion seems likely.

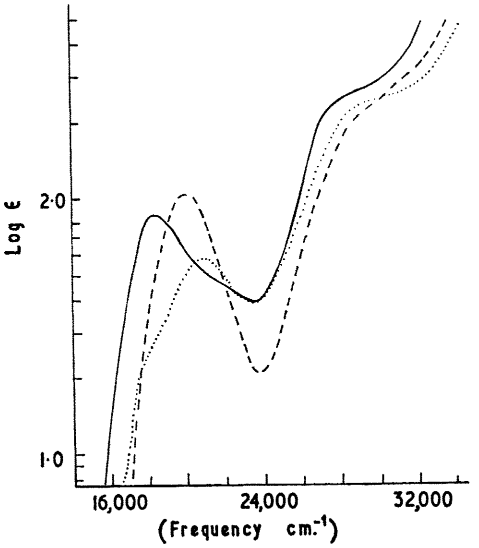


FIGURE. *The absorption spectra of the three fractions: violet* (*full line*); *red* (*broken line*); *orange* (*dotted line*).

From previous spectroscopic studies,[9] it would appear that imidazole and ammonia occupy almost identical positions in the spectrochemical series. Co-ordination of the β-imidazole and δ-amino-groups in CoL_2^+ and Co dap_2^+ respectively, might be expected to result in essentially equivalent absorption spectra. Therefore, the red material is tentatively assigned as the *trans*-imidazole isomer and the orange material, the *trans*-amine isomer.

Conclusive structural assignment will depend upon *X*-ray studies now being made with the red crystals.

(*Received, April* 16*th*, 1969; *Com.* 523.)

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[2] Several methods were used to prepare mixtures of the isomers, but the procedure described was found most convenient.
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