

## On the Properties of a Tricenter Iron(II)dicobalt(III) Coordination Compound

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In a previous study<sup>1</sup> a novel tricenter compound,  $K_2\{[Co(L-his)_2]_2Fe(CN)_6\} \cdot nH_2O$  ( $n=0-10$ ), was isolated. It was synthesized in aqueous solution from bis(histidinato)cobalt(II) and hexacyanoiron(III).

The available evidence<sup>1</sup> from IR and <sup>13</sup>C NMR data indicates a structure as shown in Fig. 1. Two carboxylate groups are uncoordinated and the three metal centers are connected through cyano bridges.

For a more complete structural characterization an X-ray structure determination is desirable.

Several attempts by use of standard techniques<sup>2</sup> have been made to grow large crystals for this purpose. However, the crystals tend to grow in sheet-like colonies of parallel thin needles and it has not been possible to obtain a satisfactory single crystal.

The ion  $[(L-his)_2Co.NC.Fe(CN)_6.CN.Co(L-his)_2]^{2-}$  formally has the metal ion sequence Co(III), Fe(II), Co(III) and is abbreviated  $[III,II,III]^{2-}$  in the following.

The possible existence of the corresponding oxidation states  $[III,III,III]^{1-}$ ,  $[II,II,III]^{3-}$ , and  $[II,II,II]^{4-}$  has been investigated.

For this purpose a spectro-electrochemical thin-layer cell with an optically transparent electrode<sup>3,4</sup> was applied. A micromesh gold net operates as the working electrode in a three-electrode voltammetric circuit. The cell allows controlled potential electrolysis experiments to be performed in the sample compartment of a Cary 11 spectrophotometer with simultaneous recording of absorption spectra.

When an aqueous solution of  $[III,II,III]^{2-}$  is oxidized at potentials between 750 and 950 mV (*vs.* N.H.E.) spectrum b in Fig. 2 is obtained. A subsequent reduction at -50 mV

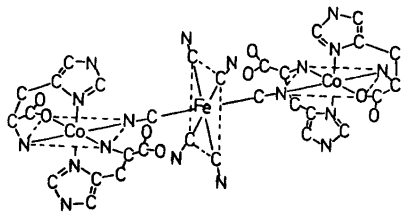


Fig. 1. Hypothetical structure of the iron-dicobalt complex based upon the available evidence. (Hydrogen atoms omitted.)

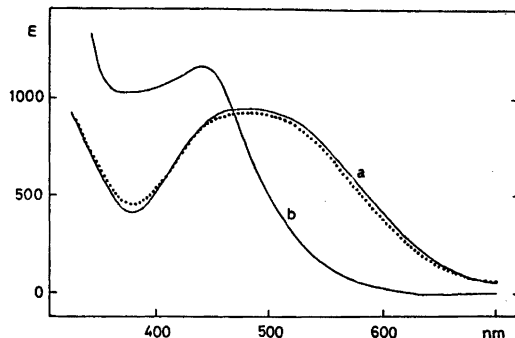


Fig. 2. *a.* Spectrum of  $[III,II,III]^{2-}$ ; original (full drawn) and regenerated (dotted). *b.* Spectrum of oxidized  $[III,II,III]^{2-}$ . The concentration is  $10^{-3}$  M in aqueous 0.5 M sodium perchlorate.  $t=25.0^\circ C$ . Path length 0.019 cm.  $\epsilon$  is given in  $dm^3 mol^{-1} cm^{-1}$ .

(*vs.* N.H.E.) regenerates the spectrum of  $[III,II,III]^{2-}$ . An analysis of the current *vs.* time curves shows that one-electron reactions take place. The spectrum *b* of  $[III,III,III]^{1-}$  is stable at least for several minutes, which means that this oxidation state is relatively robust.

After reduction of  $[III,II,III]^{2-}$  it is not possible to regenerate the original spectrum by oxidation. This is in accordance with the expected lability of  $[II,II,III]^{3-}$  and  $[II,II,II]^{4-}$ . Rapid dissociation takes place after their formation.

A potentiometric semimicro titration with cerium(IV) of an air-dried sample of  $K_2\{[Co(L-his)_2]_2Fe(CN)_6\} \cdot nH_2O$  in acid solution yielded an equivalent weight of 1182 (average of 1178, 1166, 1177, and 1207). This corresponds to  $n=10$ . It has been observed that the crystals can lose and take up water of crystallisation without deteriorating.

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