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

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In a previous study, a novel tricenter compound, $K_{n}[\text{Co(T-his)}_4\text{Fe(CN)}_4\text{.nH}_2\text{O} \ (n = 0 - 10)$, was isolated. It was synthesized in aqueous solution from bis(histidinate)cobalt(II) and hexacyanoiron(III).

The available evidence from IR and $^1$H 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 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 $[(\text{L-his})_4\text{Co.NC.Fe(CN)}_4\text{.CN.Co(L-his)}_4]^\text{2-}$ 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]$^{3-}$, [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 was applied. A micromesh gold net operates as the working electrode in a three-electrode voltametric 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]$^{3-}$ is oxidized at potentials between 750 and 850 mV (vs. N.H.E.) spectrum b in Fig. 2 is obtained. A subsequent reduction at $-50 \text{ mV}$ (vs. N.H.E.) regenerates the spectrum of [III, II, III]$^{3-}$. An analysis of the current vs. time curves shows that one-electron reactions take place. The spectrum b of [III,III,III]$^{2-}$ is stable at least for several minutes, which means that this oxidation state is relatively robust.

After reduction of [III,II,III]$^{3-}$ it is not possible to regenerate the original spectrum by oxidation. This is in accordance with the expected lability of [II,III,II]$^{3-}$ 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 $K_{n}[\text{Co(T-his)}_4\text{Fe(CN)}_4\text{.nH}_2\text{O} \text{ acid solution}$ 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 crystallization without deteriorating.


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