

Formation of μ -Cyano Species in Reactions between Bis(histidinato)cobalt and Hexacyanoferrate Complexes

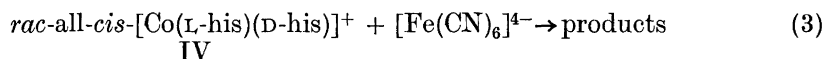
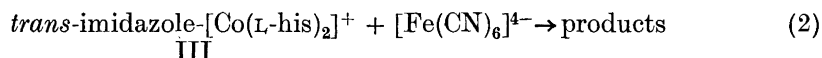
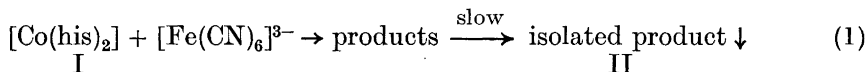
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Evidence for the formation of stable, diamagnetic di- and tri-nuclear μ -cyano species in aqueous systems of bis(histidinato)cobalt(II) plus hexacyanoferrate(III) and of bis(histidinato)cobalt(III) plus hexacyanoferrate(II) is presented.

An intense, red-purple colour is rapidly generated by mixing aqueous solutions of bis(histidinato)cobalt(II) and hexacyanoferrate(III). A similar colour slowly develops when bis(histidinato)cobalt(III) and hexacyanoferrate(II) are allowed to react in solution. In both cases the colour persists for weeks. The chemistry underlying these phenomena is the subject of this paper.

The reactions studied may be represented by (1), (2), and (3):



where his stands for histidinate (Fig. 1); I is a mixture of labile cobalt(II) isomers prepared with either L- or *rac*-histidine and III and IV are single isomers of cobalt(III) complexes. The isomerism of bis(histidinato) chelates was treated in a previous paper.¹

EXPERIMENTAL RESULTS

The absorption spectra before and immediately after mixing the reactants of (1) are shown in Fig. 2a. The spectral changes were almost identical using either L- or *rac*-histidine. The spectra before and 25 h after mixing the reactants

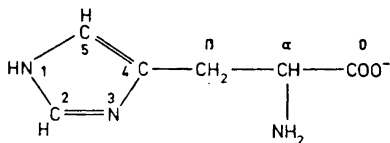


Fig. 1. Histidinate with the numbering system used.

of the slow processes (2) and (3) are shown in Figs. 3a and 3b. The time course was followed at 500 nm (Fig. 4).

To obtain information on the stoichiometry of reactions (1), (2), and (3), Job's method of continuous variation² was applied. The results are shown in

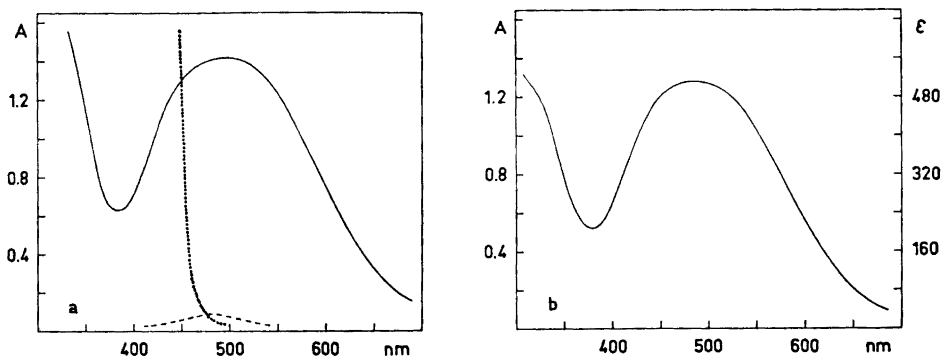


Fig. 2. Absorption spectra of reactants and products of reaction (1). a: --- 5.0 mM $[\text{Co}(\text{L-his})_2]$; ... 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-}$; — 2.5 mM $[\text{Co}(\text{L-his})_2] + 2.5$ mM $[\text{Fe}(\text{CN})_6]^{3-}$, immediately after mixing. b: 1.25 mM product II, ϵ given with respect to the total cobalt concentration (2.5 mM). Path-lengths 1 cm.

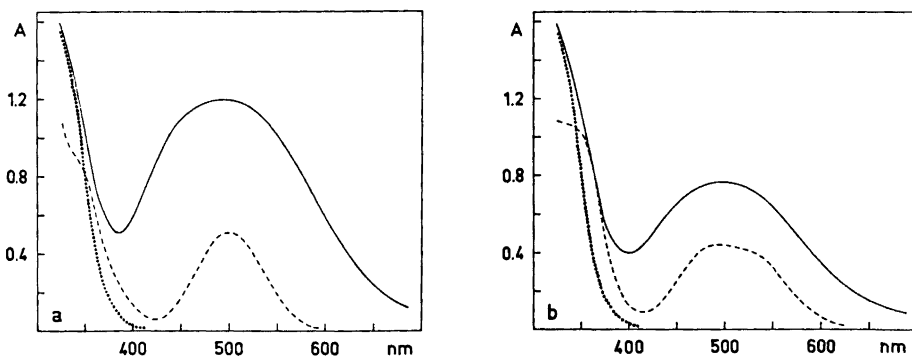


Fig. 3. Absorption spectra of reactants and products of reactions (2) and (3). a: --- 5.0 mM *trans*-imidazole- $[\text{Co}(\text{L-his})_2]^+$; ... 5.0 mM $[\text{Fe}(\text{CN})_6]^{4-}$; — 2.5 mM $[\text{Co}(\text{L-his})_2]^+ + 2.5$ mM $[\text{Fe}(\text{CN})_6]^{4-}$, 25 h after mixing. b: --- 5.0 mM *rac-all-cis*- $[\text{Co}(\text{D-his})(\text{L-his})]^+$; ... 5.0 mM $[\text{Fe}(\text{CN})_6]^{4-}$; — 2.5 mM $[\text{Co}(\text{D-his})(\text{L-his})]^+ + 2.5$ mM $[\text{Fe}(\text{CN})_6]^{4-}$, 25 h after mixing. Path-lengths 1 cm.

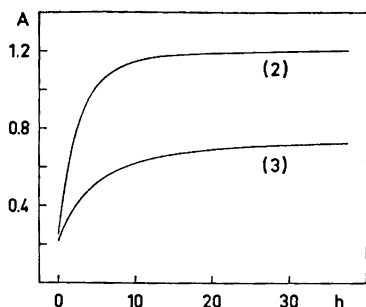


Fig. 4. Change of absorbance at 500 nm with time for reactions (2) and (3). (2): 2.5 mM $[\text{Co}(\text{L-his})_2]^+$ + 2.5 mM $[\text{Fe}(\text{CN})_6]^{4-}$. (3): 2.5 mM $[\text{Co}(\text{D-his})(\text{L-his})]^+$ + 2.5 mM $[\text{Fe}(\text{CN})_6]^{4-}$. Path-lengths 1 cm.

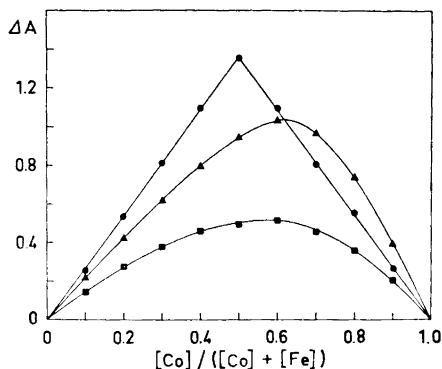


Fig. 5. Job plots at 500 nm for reactions (1), (2), and (3). (\bullet) $[\text{Co}(\text{L-his})_2]$ plus $[\text{Fe}(\text{CN})_6]^{3-}$. (\blacktriangle) *trans*-imidazole- $[\text{Co}(\text{L-his})_2]^+$ plus $[\text{Fe}(\text{CN})_6]^{4-}$. (\blacksquare) *rac*-all-*cis*- $[\text{Co}(\text{D-his})(\text{L-his})]^+$ plus $[\text{Fe}(\text{CN})_6]^{4-}$. Path-lengths 1 cm.

Fig. 5, where ΔA , the difference between the measured absorbance and the absorbance calculated assuming no reaction, is plotted against composition. Again the data for reaction (1) were collected immediately after, and those for (2) and (3) 25 h after mixing.

When reaction (1) is performed with concentrated solutions of $[\text{Co}(\text{L-his})_2]$ and $[\text{Fe}(\text{CN})_6]^{3-}$ in ethanol/water solvent a precipitate is *slowly* formed. (When *rac*-histidinate was used in identical experiments, no precipitate formed.) The isolated material, II, was found to contain Co and Fe in the ratio 2:1, and the analysis was consistent with the formula $\text{K}_2\{[\text{Co}(\text{L-his})_2]_2\text{Fe}(\text{CN})_6\} \cdot 2\text{H}_2\text{O}$. The absorption spectrum of a fresh solution of II is shown in Fig. 2b.

Cationic cobalt complexes in fresh solutions of II or in the immediate products of reaction (1) could not be detected by ion exchange experiments.

Some infrared spectra of aqueous solutions, covering pertinent regions, are given in Fig. 6; the cyanide stretching bands of reaction (1) products and of the isolated complex II are compared to that of $[\text{Fe}(\text{CN})_6]^{4-}$, and the carboxylate antisymmetric stretching bands of the same materials are compared to that of $[\text{Co}(\text{his})_2]^+$.

Data from proton-decoupled natural abundance ^{13}C -NMR spectra are summarized in Table 1. Chelated histidine in all cases exhibited sharp lines and the δ -values were approximately the same as in the corresponding spectrum of free histidine; this indicates that all the materials are diamagnetic.

The assignment of the ^{13}C resonances for free histidine was checked by an off-resonance experiment (two lines are assigned erroneously in Ref. 3).

Circular dichroism spectra of the optically active complexes were measured, and the data are given in Fig. 7.

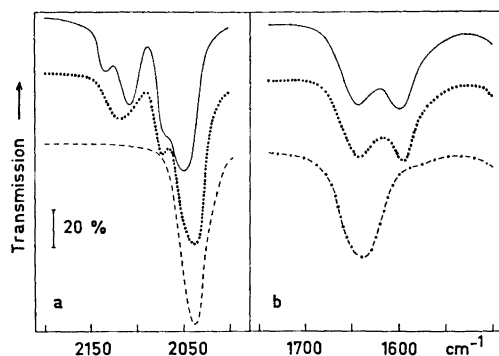


Fig. 6. Infrared spectra in aqueous solution. Path-lengths 36 μm : a: — isolated product II; \cdots $[\text{Co}(\text{L-his})_2] + [\text{Fe}(\text{CN})_6]^{3-}$; - - - $[\text{Fe}(\text{CN})_6]^{4-}$. $[\text{Fe}] = 0.1 \text{ M}$ in all cases, solvent H_2O . b: — isolated product II; \cdots $[\text{Co}(\text{L-his})_2] + [\text{Fe}(\text{CN})_6]^{3-}$; - . - . - *trans*-imidazole- $[\text{Co}(\text{L-his})_2]^+$. $[\text{Co}] = 0.1 \text{ M}$ in all cases, solvent D_2O .

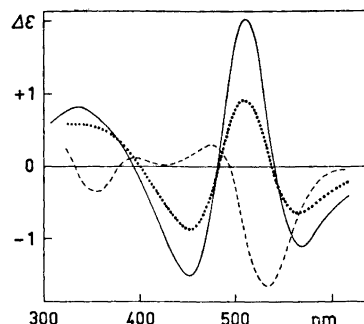


Fig. 7. Circular dichroism; $\Delta\epsilon$ calculated with respect to the total cobalt concentration. — $[\text{Co}(\text{L-his})_2] + [\text{Fe}(\text{CN})_6]^{3-}$ and isolated product II (these two curves were the same, within experimental error); \cdots *trans*-imidazole- $[\text{Co}(\text{L-his})_2]^+ + [\text{Fe}(\text{CN})_6]^{4-}$, 25 h after mixing; - - - *trans*-imidazole- $[\text{Co}(\text{L-his})_2]^+$.

Table 1. Experimental ^{13}C chemical shifts.

	Assignment							Uncertain
	C(0)	C(2)	C(4)	C(5)	C(α)	Terminal C(β)	CN	
Histidine.HCl	173.2	134.9	128.0	118.6	54.5	26.7	—	—
$[\text{Co}(\text{L-his})_2]^+$	184.7	137.2	132.7	117.6	56.4	27.1	—	—
$[\text{Co}(\text{L-his})_2]^+ + [\text{Fe}(\text{CN})_6]^{4-}$	186.5	138.6	132.8	117.5	55.6	27.6	176.8	136.9 ^a
	175.0	140.9	135.0	116.6	53.7	26.6	—	—
Product II	185.5	138.5	132.8	117.5	55.6	28.1	176.8	173.4 ^b
	—	140.4	134.9	116.5	53.7	27.3	—	172.7 ^c
$[\text{Fe}(\text{CN})_6]^{4-}$	—	—	—	—	—	—	176.8	—

^a Weak resonance. ^b and ^c C(0) and possibly bridged CN.

Apparatus. Electronic absorption spectra were measured with a Cary 11 spectrophotometer and CD spectra with a Roussel-Jouan Dichrographe II.

Proton-decoupled 22.63 MHz ^{13}C -NMR spectra were obtained with a Bruker WH 90 spectrometer using the Fourier transform technique; the solvent was D_2O and the spectra were run at ambient temperature. δ -Values are reported relative to TMS; dioxane ($\delta = 67.40$) served as an internal reference.

IR spectra were measured with a Beckman IR 20 spectrometer using solution cells with CaF_2 windows.

Materials. L- and DL-Histidine (*puriss.*, chromatographic purity) were obtained from Fluka. All other chemicals were analytical grade.

Cobalt(III) complexes. *rac*-all-*cis*- $[\text{Co}(\text{L-his})(\text{D-his})]\text{Br}$ was prepared as in Ref. 1.

trans-Imidazole- $[\text{Co}(\text{L-his})_2]\text{ClO}_4$ was prepared as follows: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (3.57 g, 15 mmol) and L-histidine (5.13 g, 33 mmol) were dissolved in 50 ml water and 0.5 g activated charcoal was added. Air was bubbled through the solution while the temperature was

maintained at 75°C. After 90 min the solution was cooled, the charcoal filtered off and 60 ml water containing 8 g NaClO₄ was added. After standing overnight the pink needle crystals were filtered off and washed with cold water and ethanol. The product was then recrystallized from warm water and air dried. Yield 2.7 g (37 % of total Co). (Found: C 29.18; H 3.72; N 17.08; Cl 6.88. Calc. for [Co(C₆H₈N₃O₂)₂]ClO₄·1.5H₂O: C 29.19; H 3.87; N 17.10; Cl 7.18.) Samples of this perchlorate salt were washed with water through an anion exchange column (Dowex I X-8) in the bromide form; evaporation of the eluent yielded the bromide salt which was used in the NMR experiments. The absorption, CD and PMR spectra of *trans*-imidazole-[Co(L-his)₂]⁺ prepared in this way were in complete agreement with those reported¹ for the chromatographically purified isomer.

Job experiments. Reaction (1): Solutions of [Co(his)₂], pH 9 (5.0 mM, made from CoCl₂·6H₂O, L- or DL-histidine and NaOH) and of K₃[Fe(CN)₆] (5.0 mM) were mixed in volume ratios 10:0.9:1, . . . , 0:10. The absorption spectra of the resulting solutions were measured immediately. All operations were carried out under strict O₂-free conditions at room temperature.

Reactions (2) and (3): Solutions of [Co(his)₂]⁺ and K₄[Fe(CN)₆] (both 5.0 mM) were mixed in the same way and the spectra were recorded repeatedly until no further change was observed. O₂ was excluded and the temperature was maintained at 20°C throughout.

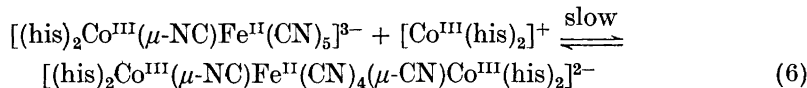
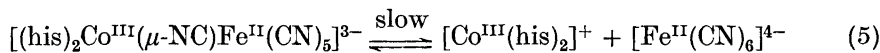
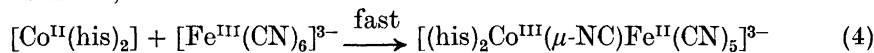
Isolation and analysis of product II. A concentrated solution of [Co(L-his)₂] was prepared by adding CoCl₂·6H₂O (1.00 g, 4.20 mmol) to L-histidine (1.38 g, 8.58 mmol) dissolved in 15 ml 0.59 M NaOH. This was cooled in an ice-bath and protected from the atmosphere with a stream of nitrogen. A solution of K₃[Fe(CN)₆] (1.38 g, 4.20 mmol) in 15 ml H₂O was run in with stirring. 14 ml of ethanol was added dropwise and the mixture kept in a refrigerator overnight. The bulky precipitate which formed was filtered off, washed with ice-cold water/ethanol (2:1) and ethanol and air dried. Subsequent drying over H₂SO₄ *in vacuo* resulted in a weight loss of ca. 15 %. Yield 1.2 g. Red-purple powder, dissolves readily in water to give neutral solutions. (Found: Fe 5.3; Co 11.1; H 3.8; C 32.5; N 23.2. Calc. for K₂{[Co(his)₂]₂Fe(CN)₆}·2H₂O: Fe 5.3; Co 11.2; H 3.4; C 34.1; N 23.9.)

For the Fe and Co determinations, the complex was destroyed by refluxing with 72 % perchloric acid for 24 h. The resulting clear solution was diluted and Fe determined gravimetrically by the standard cupferron method. The combined filtrates from the Fe determination were reconcentrated to fumes of perchloric acid and Co determined electrolytically after neutralisation with aqueous ammonia. (Test analyses on samples made by combining known amounts of [Co(L-his)₂] and K₃[Fe(CN)₆] gave results within 2 % of the expected.)

C, H, and N analyses were carried out by the Microanalytical Department, Chemistry Laboratory II, University of Copenhagen.

DISCUSSION

Our interpretation of the experimental results is based upon the following reaction scheme,



where (4) is orders of magnitude faster than (5) and (6). Thus the observed colour changes result from formation of di- and trinuclear species.

A related, but transient, dinuclear species has been observed⁴ as an intermediate in the reaction of [Co^{II}(edta)]²⁻ with [Fe(CN)₆]³⁻.

The proposed reaction scheme predicts that the reaction between $[\text{Co}^{\text{II}}(\text{his})_2]$ and $[\text{Fe}(\text{CN})_6]^{3-}$ would be characterized by a Job plot with a sharp extremum where the concentrations of the two components are equal. This is consistent with Fig. 5. The initial dinuclear products have not been isolated. The substance precipitated from the $[\text{Co}(\text{I-his})_2]$ system is a trinuclear complex formed by the subsequent slow, reversible reactions.

The reaction between $[\text{Co}^{\text{III}}(\text{his})_2]^+$ and $[\text{Fe}(\text{CN})_6]^{4-}$ is described by (5) and (6). When equilibrium has been established, then mono-, di-, and also trinuclear species will be present. This will result in a curved Job plot with an extremum where the Co:Fe ratio is > 1 , in agreement with the experiments (Fig. 5).

The formation of μ -cyano bridges in reactions (5) and (6) must involve bond breaking between low-spin Co(III) and histidinate, and therefore these reactions are expected to be slow.

Bridging cyano groups have previously been shown to exhibit a $25-100 \text{ cm}^{-1}$ higher cyanide stretching frequency than terminal cyano groups.^{5,6} Accordingly the higher frequency bands in Fig. 6a are taken to prove the occurrence of cyano bridges. The IR spectrum of the solid isolated trinuclear complex in KBr pellets was very similar to the solution spectrum, indicating no change in the cyano groups on dissolution.

It should be noted that the trinuclear species may exist with the bridged cyano groups in either *cis*- or *trans*-positions in the octahedral Fe(II) coordination sphere. Molecular models do not indicate substantial steric crowding in the statistically favoured *cis*-structure.

In both $[\text{Co}(\text{his})_2]$ and $[\text{Co}(\text{his})_2]^+$ each histidinate is coordinated *via* the imidazole nitrogen number 3, the amino nitrogen, and a carboxylate oxygen. However, in the cyano bridged complexes only five coordination sites on each cobalt are occupied by histidinate. Thus bridge formation must be associated with displacement of one ligating histidinate group, and therefore two types of histidinate, bidentate and tridentate, must result.

If the displaced histidinate group is carboxylate then two IR absorptions, due to the antisymmetric stretching of free and coordinated carboxylate, should be observable, just as in the related case of $[(\text{his})_2\text{Co}.\text{O}_2.\text{Co}(\text{his})_2]$.⁷ As is shown in Fig. 6b, two bands are observed both with the products of reaction (1) and with the trinuclear complex II. The higher frequency component is assigned to carboxylate bound to Co(III) and the lower frequency component to uncoordinated carboxylate.

Since two types of histidinate ligands occur, two sets of histidinate resonances arise in the proton-decoupled ^{13}C spectra of the complexes containing cyano bridges (Table 1). Unfortunately, the small differences between the ^{13}C chemical shifts of CN and COO makes an unambiguous assignment of these difficult in the μ -cyano compounds. The ^{13}C resonance of free COO is seen to be shifted *ca.* 11 ppm downfield on coordination to Co(III).

The visible absorption spectrum of a freshly prepared solution of the isolated trinuclear complex II resembles that of the dinuclear product of reaction (4) if the extinction coefficients are calculated with respect to cobalt (see Fig. 2). The high intensities suggest that the visible absorption is dominated by an

Fe(II)→Co(III) charge transfer; apparently this transition is twice as probable in the trinuclear as in the dinuclear complex.

The circular dichroism spectra, when $\Delta\epsilon$ is calculated with respect to cobalt, are the same for the mono- and dibridged species as is seen in Fig. 7. This is reasonable as the cobalt coordination sphere is supposed to be the same in the two cases.

The CD and absorption spectra of the equilibrated mixtures of $[\text{Co}(\text{his})_2]^+$ and $[\text{Fe}(\text{CN})_6]^{4-}$ and the corresponding Job plots show that the equilibria (5) and (6) are displaced further in favour of mononuclear complexes with racemic histidinate than with L-histidinate.

In conclusion, $[\text{Co}^{\text{II}}(\text{his})_2]$ is quantitatively oxidized by $[\text{Fe}(\text{CN})_6]^{3-}$ in a one-electron inner-sphere reaction. Both metal ions achieve low-spin d^6 electron configuration and a rather stable cyano bridged reaction product results. The same kind of μ -cyano species are formed in simple substitution reactions when isomers of $[\text{Co}^{\text{III}}(\text{his})_2]^+$ are equilibrated with $[\text{Fe}(\text{CN})_6]^{4-}$.

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