

Tricenter Iron(II)dicobalt(III) Complexes with Two Cyanide Bridges

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Owing to the ambidentate nature of cyanide it is in some cases possible to link metallic coordination centers together through cyano bridges. This represents a way of utilizing known metal complexes as units for building compounds with new properties.

Recently it was reported that strongly coloured species of notable stability containing the Co(III)–NC–Fe(II)–CN–Co(III) chain are formed in reactions between isomers of bis(histidinato)cobalt(III) and hexacyanoiron(II).¹ The aim of this work was to examine whether bis(histidinato)cobalt(III) generally combines with low-spin iron(II) complexes having two or more cyano ligands to give tricenter μ -cyano species.

Experimental. $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$ was obtained from B.D.H. ("Analar" purity). The compounds $[\text{Fe}(\text{CN})_2(\text{bpy})_2] \cdot 3\text{H}_2\text{O}$, $\text{K}_2[\text{Fe}(\text{CN})_4(\text{bpy})] \cdot 3\text{H}_2\text{O}$, $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{py})] \cdot 1\frac{1}{2}\text{H}_2\text{O}$, $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{NH}_3)] \cdot 3\text{H}_2\text{O}$, $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$, and $\text{Na}_4[\text{Fe}(\text{CN})_5(\text{NO}_2)] \cdot 10\text{H}_2\text{O}$ were prepared according to procedures given in Refs. 2, 3, 4, 5, 6, and 7, respectively. *trans*-Imidazole- $[\text{Co}(\text{I-his})_2]\text{ClO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ and racemic all-*cis*- $[\text{Co}(\text{I-his})(\text{D-his})]\text{Br}$ were prepared as previously.¹ (py = pyridine, bpy = 2,2'-bipyridine, his = histidinato).

All the spectrophotometric measurements were carried out under O_2 -free conditions at 20.0 °C.

Results. Information obtained from the visible absorption spectra before and after mixing aqueous solutions of bis(histidinato)cobalt(III)

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Table 1. Results from mixing experiments.

	[Co(his) ₂] ⁺ -isomer ^a	
	<i>trans</i> -imidazole	all- <i>cis</i>
$[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$	—	—
$[\text{Fe}(\text{CN})_2(\text{bpy})_2]$	—	—
$[\text{Fe}(\text{CN})_4(\text{bpy})]^{2-}$	—	—
$[\text{Fe}(\text{CN})_5(\text{py})]^{2-}$	+	+
$[\text{Fe}(\text{CN})_5(\text{NH}_3)]^{3-}$	+	+

^a A plus sign means that an additional broad band appeared in the spectrum of the mixed solution. A minus sign means that no evidence of interaction was found.

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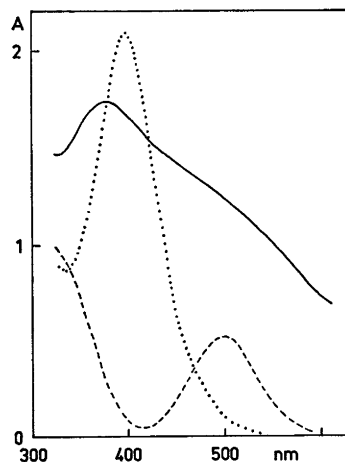


Fig. 1. Absorption spectra in aqueous solution (1 cm cells). ---, 5.0 mM *trans*-imidazole- $[\text{Co}(\text{his})_2]^+$; ···, 5.0 mM $[\text{Fe}(\text{CN})_5(\text{NH}_3)]^{2-}$; and —, the 1:1 mixture of these two solutions after 3 h.

isomers and cyanoiron(II) complexes is summarized in Table 1. In the four combinations of reactants with a plus sign in Table 1 a broad charge-transfer absorption band developed in the spectra of the mixtures, and a constant spectrum was reached after some hours. For illustration of the phenomenon the spectra from one of the experiments are shown in Fig. 1.

In order to elucidate the stoichiometry of the four established reactions, Job's method of continuous variations was applied in the same way as previously.¹

Job plots at three wavelengths for one of the reactions are shown in Fig. 2. All four reactions

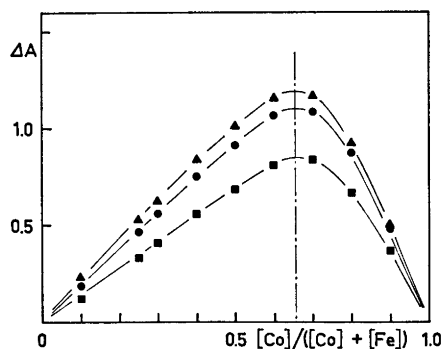


Fig. 2. Job plots for the *trans*-imidazole- $[\text{Co}(\text{his})_2]^+ / [\text{Fe}(\text{CN})_5(\text{NH}_3)]^{2-}$ system with experimental points indicated. \blacktriangle , at 468 nm; \bullet , at 500 nm; \blacksquare , at 600 nm. The concentration of the two solutions used was 5.0 mM.

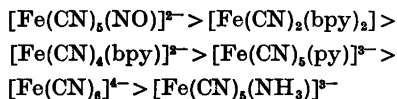
were found to show the same pattern with a maximum in the Job plot at a Co:Fe ratio of about 2:1.

Each of the complexes in Table 1 were found to follow Beer's law at concentrations used in the Job experiments. $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3+}$ and $[\text{Fe}(\text{CN})_5(\text{NO}_2)]^{4-}$ also react with the two $[\text{Co}(\text{his})_2]^+$ isomers to give brown species, but the behaviour of these two iron(II) complexes is more complicated since their solutions do not comply with Beer's law.

Conclusions. The experimental results suggest that two of the cyanoiron(II) complexes, $[\text{Fe}(\text{CN})_5(\text{py})]^{3-}$ and $[\text{Fe}(\text{CN})_5(\text{NH}_3)]^{3-}$, form tricenter μ -cyano-iron(II)dicobalt(III) species with each of the two $[\text{Co}(\text{his})_2]^+$ isomers. This is in analogy with the mode of reaction found for $[\text{Fe}(\text{CN})_6]^{4-}$, which has been studied in more detail.¹

Of the factors controlling the formation of a stable Co-NC-Fe-CN-Co chain the redox properties of the iron center and the charge of the iron(II) complex are likely to be important.

The standard redox potentials for the Fe(II)/Fe(III) couples⁸⁻¹⁰ presumably decrease in the order



Our experiments have shown that only the three more reducing of these iron(II) complexes form μ -cyano species. The same three complexes are also the more favoured with regard to coulombic interaction with the positively charged cobalt(III) complexes.

The electrochemistry of the new tricenter compounds appears to be interesting. The Co(III)-NC-Fe(II)-CN-Co(III) moiety may undergo a one-electron oxidation as well as a two-electron reduction.

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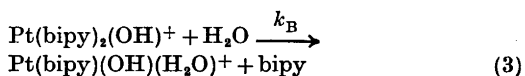
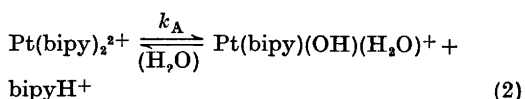
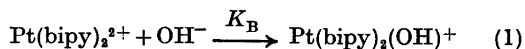
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The Base Hydrolysis of Bis(2,2'-bipyridyl)platinum(II) Perchlorate

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The cation $[\text{Pt}(\text{bipy})_2]^{2+}$ of the title compound reacts with aqueous acid and base as follows:



These reactions are followed by fast proton equilibration of the products of the slow steps 2 and 3 and by the very slow dissociation of the second (bipy) ligand.

Equilibrium 1 is fast as is evidenced by the pH dependence of the compositions of the solutions, resulting in the changes of ultraviolet absorption which were reported by Gillard *et al.*¹⁻³ These authors envisage attachment of OH to a carbon atom of the ligand with no increase in the coordination number of the metal ion. Although we have, ourselves, shown^{4,5} that the oxidation of OH⁻ by $\text{Fe}(\text{bipy})_3^{3+}$ and related oxidising complexes occurs through "a highly reactive precursor complex $[\text{Fe}(\text{bipy})_2\text{R}\cdot\text{OH}]^{2+}$ where R·OH is probably the pseudo-base of a radical formed by addition of an electron to a ligand which approaches the structure of a quaternary cation" we consider it likely that $\text{Pt}(\text{bipy})_2^{2+}$ in solution contains coordinated water. Such water would be acid and equilibrium 1 thus involve addition of OH⁻ to the metal ion. The fact that neither $\text{Pt}(\text{py})_4^{2+}$ (py = pyridine) nor $\text{Pt}(\text{bipy})(\text{py})_2^{2+}$ show pH dependent spectral behaviour similar to that of $\text{Pt}(\text{bipy})_2^{2+}$ suggests to us that distorted square planar coordination is necessary for equilibria such as (1) and that this is a consequence of the steric, not of the chemical properties of the coordinated ligands. Two molecules of bipy, or of 1,10-phenanthroline, cannot form unstrained square planar complexes because of steric interaction between the H atoms at the 6,6' and 2,9 positions, respectively. This strain may be relieved by distortion - as may easily be seen from models.