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Characterization of a Mixed Valence Cyano-bridged Cobalt(III)iron(II) Complex

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The mixed valence ion $[(en)_2(NH_3)Co\cdot NC\cdot Fe(CN)_5]^-$ has been isolated. Its optical and electrochemical properties have been studied. A comparison with the analogous cobalt(III)ruthenium(II) complex has been made.

The mixed valence complexes $[(NH_3)_5Co\cdot NC\cdot Ru(CN)_5]^-$ and $[(en)_2(NH_3)Co\cdot NC\cdot Ru(CN)_5]^-$, both of which contain the central unit {Co(III)·NC·Ru(II)}, have been described in the literature.[1,2] It would be of interest to compare these two ions with analogous iron complexes of composition $[(NH_3)_5Co\cdot NC\cdot Fe(CN)_5]^-$ and $[(en)_2(NH_3)Co\cdot NC\cdot Fe(CN)_5]^-$.

However, it has been reported that attempts to prepare $[(NH_3)_5Co\cdot NC\cdot Fe(CN)_5]^-$ were unsuccessful. We have confirmed the finding that $[Co(NH_3)_5(H_2O)]^{3+}$ reacts with $[Fe(CN)_6]^{4-}$ in aqueous solution to form a *greenish precipitate,* presumably consisting of cobalt(II)hexacyanoferrate(III) and cobalt(II)hexacyanoferrate(II).[1,3]

If *trans*-$[Co(en)_2(NH_3)(H_2O)]^{3+}$ is used instead of $[Co(NH_3)_5(H_2O)]^{3+}$ in a similar experiment, we observe a strikingly different behaviour. The reaction with $[Fe(CN)_6]^{4-}$ yields a *clear, intensely brown-red solution.* The appearance of this solution is stable for weeks on standing at room temperature. This observation encouraged us to search for the complex $[(en)_2(NH_3)Co\cdot NC\cdot Fe(CN)_5]^-$.

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Notation and Terminology

In this paper *1* stands for $[(en)_2(NH_3)Co\cdot NC\cdot Fe(CN)_5]^-$; en is the abbreviation for 1,2-ethanediamine (ethylenediamine).

For the molar absorption coefficient, ε, the traditional dimension M^{-1} cm^{-1} is used.

The characteristic strong colour of many mixed valence complexes arises from a charge-transfer transition which occurs between orbitals centered on different metal atoms.[4] This is called an IT-transition, IT being the abbreviation for intervalence transfer.

EXPERIMENTAL

An aqueous solution containing equimolar concentrations of *trans*-$[Co(en)_2(NH_3)(H_2O)]^{3+}$ and $[Fe(CN)_6]^{4-}$ develops a strong, brown-red colour within some hours. The colour is due to a broad absorption in the visible region, and after about 24 h the spectrum is virtually constant.

Ion-exchange chromatography of the brown-red solution shows that at least five strongly coloured, quite robust, anionic species are present. By column chromatography with the anion exchanger QAE-Sephadex as packing material and aqueous NaCl solution as eluent, five distinct zones are developed with relative R_f-values 127, 36, 9, 3 and 1.

During the chromatographic work it was discovered that the slow zones appeared somewhat sharper if O_2 was removed from the eluent.

All conditions being the same, it was found that the fastest moving component – in this paper named *1* – travels through the column at the same rate as $[(en)_2(NH_3)Co\cdot NC\cdot Ru(CN)_5]^-$.[2]

All five chromatographic zones contain cobalt and iron and were analyzed by atomic absorption

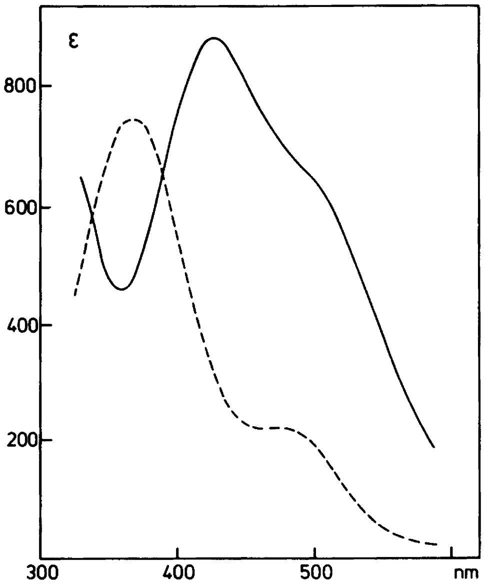

Fig. 1. Absorption spectra of solutions. ——, *1*; – – –, $[(en)_2(NH_3)Co{\cdot}NC{\cdot}Ru(CN)_5]^-$. The IT-transitions occur at 369 and 428 nm, respectively.

spectrometry.

The molar Co:Fe ratio of an eluted sample of *1* was found to be 1.

The remaining four zones were not eluted from the column before analysis, but after development all the content of the column was extruded and samples absorbed on Sephadex were obtained. The analysis showed Co:Fe molar ratios significantly lower than 1. Probably these four slow-moving species are cyano-bridged complexes with more than two metal centers, and they are not considered further in this paper.

The yield of chromatographically pure *1* is only *ca.* 10 %, relative to the complexes used for preparation of the initial raw solution.

An absorption spectrum and a single sweep triangular wave voltammogram of *1* are given in Figs. 1 and 2.

Like $[(en)_2(NH_3)Co{\cdot}NC{\cdot}Ru(CN)_5]^-$, *1* is photo-sensitive. A solution rapidly becomes cloudy when exposed to strong daylight.

1 is not so stable as its ruthenium analogue on standing at room temperature. In a day-old preparation changes are seen in the absorption spectrum and an extra wave has developed in the cyclic voltammogram.

Attempts to obtain IR- and NMR-spectra were hampered by partial decomposition of *1* during the procedure of preparing sufficiently concentrated samples. We have not succeeded in preparing a crystalline salt of *1*.

Experimental Details

General. Solutions of *1* were handled in subdued light and measurements were carried out on freshly chromatographed samples.

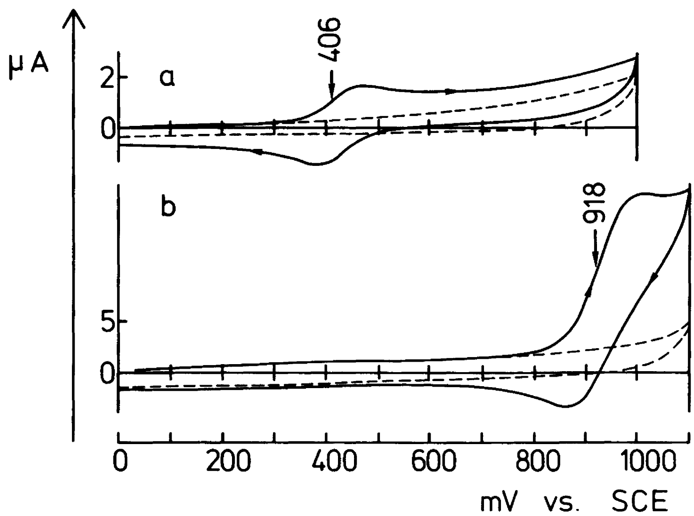

Fig. 2. Single-sweep triangular wave voltammograms. a, freshly eluted solution of *1;* b, $[(en)_2(NH_3)Co{\cdot}NC{\cdot}Ru(CN)_5]^-$. $E_{p/2}$-values for the anodic waves are indicated. Sweep rate: 100 mV s^{-1}. Supporting electrolyte: saturated NaCl. The dashed curves show the residual current. ($E_{p/2}$ for $[Fe(CN)_6]^{4-}$ and $[Ru(CN)_6]^{4-}$ are 287 mV and 904 mV, respectively, under the same conditions.[2])

Materials. *trans*-$[Co(en)_2(NH_3)(H_2O)](NO_3)_3$ was prepared according to a published procedure.[5] The anion exchanger used was QAE-Sephadex A-25 from Pharmacia (Sweden).

Synthesis and isolation of 1. An aqueous raw solution containing *1* was typically prepared as follows. Two solutions, 0.100 g *trans*-$[Co(en)_2(NH_3)(H_2O)](NO_3)_3$ (0.250 mmol) in 15 ml H_2O and 0.116 g $K_4[Fe(CN)_6].3H_2O$ (0.275 mmol) in 10 ml H_2O, were mixed in an Erlenmeyer flask. With these relatively concentrated solutions a yellow precipitate, probably $[Co(en)_2(NH_3)(H_2O)]_4[Fe(CN)_6]_3$, initially formed. After standing at room temperature in the dark for 24 h the precipitate had disappeared and an optically clear, strongly brown-red solution resulted. This solution was chromatographed.

For a preparative experiment a glass column of 50 mm internal diameter was packed with Sephadex ion exchanger to a height of about 40 mm. 25 ml of the solution described above was applied to the column. During this operation it was observed that some unreacted $[Co(en)_2(NH_3)(H_2O)]^{3+}$ passed through the Sephadex. After elution with about 350 ml 0.25 M aqueous NaCl solution a brown-red zone of *1* had separated from a dark-coloured band at the top of the column. As a precaution the eluent was deaerated by bubbling with N_2 before entering the column. The yield from an experiment like this was typically 0.02 mol *1* in 0.25 M NaCl.

Analyses. Solutions of *1* were analyzed for Co and Fe by atomic absorption spectrometry. A Perkin-Elmer model 305A spectrometer was used. Samples for analysis were prepared by evaporation, fuming with conc. HNO_3 and $HClO_4$, and finally appropriate dilution with H_2O.

The experimental Co:Fe molar ratio for *1* was 0.99.

Cyclic voltammetry. The method and the electrochemical apparatus of three-electrode design with a vitreous carbon indicator electrode was the same as described previously.[2] The supporting electrolyte was saturated NaCl in order to allow direct comparison with earlier results.[2]

DISCUSSION

On the basis of the available evidence *1* is formulated $[(en)_2(NH_3)Co{\cdot}NC{\cdot}Fe(CN)_5]^-$.

The absorption band at 428 nm with ε=883, which has no counterpart in either of the separate species $[Co(en)_2(NH_3)(H_2O)]^{3+}$ and $[Fe(CN)_6]^{4-}$, is assigned to an Fe(II)→Co(III) IT-transition

Table 1. Data on IT-transitions of {Co(III)·NC·Fe(II)} species.

	IT-band	Ref.
$[(edta)Co{\cdot}NC{\cdot}Fe(CN)_5]^{5-}$ [a]	λ=565 nm ε=*ca.* 800	6
$[(cydta)Co{\cdot}NC{\cdot}Fe(CN)_5]^{5-}$ [b]	λ=540 nm ε=690	7
$[(NC)_5Co{\cdot}NC{\cdot}Fe(CN)_5]^{6-}$	λ=395 nm ε=700	6
1	λ=428 nm ε=883	This work

[a] edta=ethylenediaminetetraacetate. [b] cydta=*trans*-1,2-cyclohexanediaminetetraacetate.

mediated by the CN-bridge. The *d–d* transitions in Co(III) appear as a shoulder at about 500 nm.

In Table 1 the ε-value of the IT-absorption of *1* is compared with literature values for related {Co(III)·NC·Fe(II)} species.

$[(edta)Co{\cdot}NC{\cdot}Fe(CN)_5]^{5-}$ and $[(cydta)Co{\cdot}NC{\cdot}Fe(CN)_5]^{5-}$ have been detected as short-lived intermediates in electron transfer reactions between cobalt(II) complexes and hexacyanoferrate(III).

In the present study the reactants are a cobalt(III) complex and hexacyanoferrate(II). *1* is probably formed by a substitution reaction in which $[Fe(CN)_6]^{4-}$ displaces H_2O in $[Co(en)_2(NH_3)(H_2O)]^{3+}$.

Fig. 1 shows that in $[(en)_2(NH_3)Co{\cdot}NC{\cdot}Ru(CN)_5]^-$ the IT-band occurs at higher energy than in $[(en)_2(NH_3)Co{\cdot}NC{\cdot}Fe(CN)_5]^-$. This is in accordance with expectation, since $[Fe(CN)_6]^{4-}$ is more easily reduced than $[Ru(CN)_6]^{4-}$.

The redox reaction reflected in the waves of the cyclic voltammograms in Fig. 2 is

$$\{Co(III) \cdot NC \cdot M(II)\} \rightleftarrows \{Co(III) \cdot NC \cdot M(III)\} + e$$

In the voltammogram of *1* a simple behaviour is observed. The heights of the oxidation wave (outward scan) and the reduction wave (homeward scan) are the same. This was found to be the case even at much lower sweep rates.

In the case of $[(en)_2(NH_3)Co{\cdot}NC{\cdot}Ru(CN)_5]^-$ the reduction wave is almost absent; it becomes more pronounced with faster sweeps. This indicates that the simple redox reaction is complicated by fast side-reactions of the {Co(III)·NC·Ru(III)} species.

$[(NH_3)_5Co{\cdot}NC{\cdot}Fe(CN)_5]^-$ does not exist as a stable species at room temperature because a spontaneous, intramolecular, thermal electron transfer would result in a labile Co(II) complex and hexacyanoferrate(III).[1] We have shown that *1* is moderately stable.

As deduced from the relative positions of the IT-bands of $[(en)_2(NH_3)Co{\cdot}NC{\cdot}Ru(CN)_5]^-$ and $[(NH_3)_5Co{\cdot}NC{\cdot}Ru(CN)_5]^-$ the group $(en)_2$-$(NH_3)Co-$ is less liable to reduction than $(NH_3)_5Co-$.[2] This rationalizes that the tendency for $[(en)_2(NH_3)Co{\cdot}NC{\cdot}Fe(CN)_5]^-$ to disintegrate as a consequence of intramolecular electron transfer is less pronounced than for $[(NH_3)_5Co{\cdot}NC{\cdot}Fe(CN)_5]^-$.

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