

Photochemical Formation of a Mixed Valence Compound Containing Cobalt(III) and Ruthenium(II)

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An aqueous solution containing hexacyanoruthenate(II) and an isomer of bis(histidinato)cobalt(III) develops a strong red-orange colour when exposed to visible light. The chemistry behind this observation has been investigated. Evidence is presented that a mixed valence compound is formed where cobalt(III) and ruthenium(II) are linked by a cyano bridge.

In previous work¹⁻⁴ it has been shown how the coordination entity bis(histidinato)cobalt can be coupled to different metal centers to form ligand-bridged polynuclear complexes. In the following, a new, photogenerated compound of this type is described. The two mononuclear complexes used as building blocks are hexacyanoruthenate(II) and the *trans*-imidazole isomer of bis(histidinato)cobalt-(III) shown in Fig. 1.

Notation and Terminology

In the discussion of ligand-bridged complexes the term *central unit* is used. It is defined as the aggregate of metal ions and bridging ligand(s), e.g. the central unit of $[(L)M \cdot L \cdot M'(L')]^z$ is $\{M \cdot L \cdot M'\}$. (Cf. *central atom* for mononuclear complexes.)

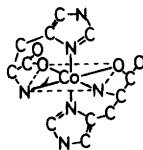


Fig. 1. The structure of *trans*-*i*-[Co(L-his)₂]⁺ (hydrogen atoms omitted).

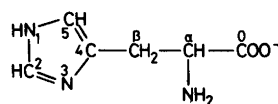


Fig. 2. Histidinate.

The numbering system for histidinate, applied in Table 1, is given in Fig. 2.

The abbreviations *his*⁻ and *trans*-*i* are used for histidinate and *trans*-imidazole in formulae.

EXPERIMENTAL RESULTS

The change in the visible absorption spectrum as a result of irradiation with visible light of a solution containing [Ru(CN)₆]⁴⁻ and *trans*-*i*-[Co-

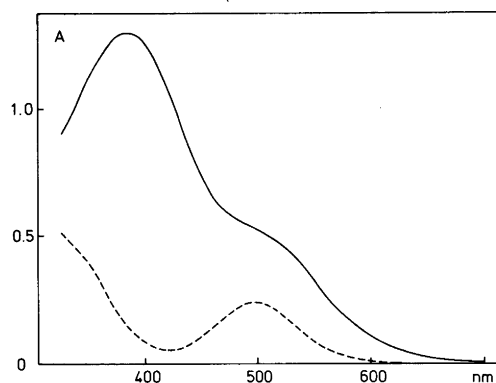


Fig. 3. Spectral change caused by visible light: --- before irradiation; — after 20 h of irradiation. 2.5 mM *trans*-*i*-[Co(L-his)₂]⁺ and 2.5 mM [Ru(CN)₆]⁴⁻. 1 cm cell.

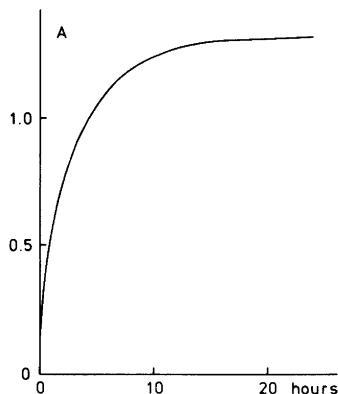


Fig. 4. The absorbance at 385 nm vs. irradiation time. (Cf. Fig. 3).

$(\text{L-his})_2^+$ is shown in Fig. 3. A strong new band is seen to appear at 385 nm.

Fig. 4 shows the time course of the spectral change.

In this experiment the irradiation was carried out using a small 15 W, 6 V filament lamp as light source, and the sample solution was contained in a 1 cm quartz spectrophotometric cell, thermostatted at 25 °C.

The solution remained optically clear during irradiation and no precipitation took place. No spectral changes could be detected if the solution was kept in the dark for several days.

An aqueous solution of the cobalt complex alone is inert to visible light.

The spectrum before irradiation shown in Fig. 3 is in fact the spectrum of $\text{trans-i-}[\text{Co}(\text{L-his})_2]^+$ because $[\text{Ru}(\text{CN})_6]^{4-}$ does not absorb above 300 nm. The photochemical reaction is consequently caused by an excitation of the cobalt complex.

This was confirmed in an experiment where an argon laser was used for irradiation. Apart from the light source the conditions were the same as above. The wavelength 514.5 nm was used with a power of 200 mW. After 30 min of irradiation the spectral change was the same as shown in Fig. 3. This proves that the photoreaction is induced by irradiating exclusively in the ligand-field region of $[\text{Co}(\text{his})_2]^+$.

Qualitatively it seems that the photosensitivity is higher than usually observed for cobalt(III) complexes exposed to visible light, but quantum yields have not been determined.

An irradiated solution was chromatographed using a Sephadex anion exchanger column. The developed column showed an intensely red-orange coloured main zone separated from several weaker zones. The product, *1*, forming the main zone was

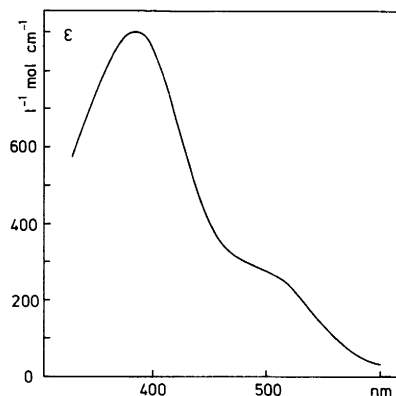


Fig. 5. Absorption spectrum of *1* in solution.

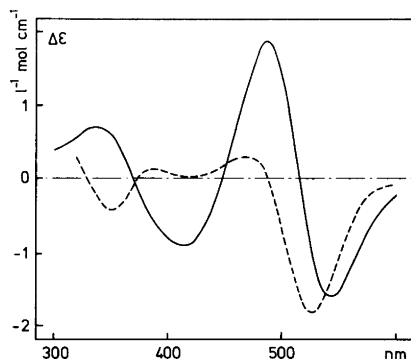


Fig. 6. CD spectra of *1* (—) and $\text{trans-i-}[\text{Co}(\text{L-his})_2]^+$ (---).

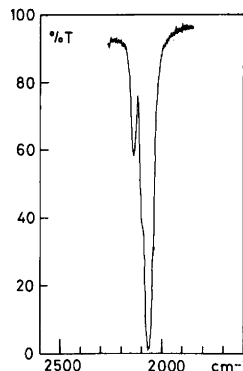


Fig. 7. IR spectrum in the CN-stretching region of *1*.

Table 1. Experimental ^{13}C chemical shifts and their assignment.

	C(0)	C(2)	C(4)	C(5)	C(α)	C(β)	CN
L-Histidine	174.7	137.2	133.1	117.6	55.6	29.1	—
$[\text{Ru}(\text{CN})_6]^{4-}$	—	—	—	—	—	—	162.4
<i>trans-i</i> - $[\text{Co}(\text{l-his})_2]^+$	185.2	137.5	133.0	117.8	56.3	26.9	—
Compound 1	185.8	140.9	135.0	117.8	55.6	28.1	160.8
	177.3	139.0	132.9	116.8	53.7	27.2	

obtained chromatographically pure in 1 M aqueous NaCl.

In the following, evidence is presented which identifies 1 as $[(\text{l-his})_2\text{Co} \cdot \text{NC} \cdot \text{Ru}(\text{CN})_5]^{3-}$.

Attempts to crystallize 1 have not been successful, but it could be quantitatively precipitated by Zn^{2+} . A small amount of this insoluble zinc salt was isolated and analysed. Found: Co 7.24; C 28.37; H 2.98; N 21.50. Calc. for $\text{Zn}_3[(\text{C}_6\text{H}_8\text{O}_2)_2\text{Co} \cdot \text{NC} \cdot \text{Ru}(\text{CN})_5]_2 \cdot 7\text{H}_2\text{O}$: Co 7.50; C 27.52; H 2.95; N 21.40.

To characterize 1 the visible absorption and circular dichroism spectra, the ^{13}C NMR spectrum, and the IR-spectrum in the CN-stretching region were measured. These spectral data are presented in Figs. 5–7 and in Table 1.

Experimental Details

Materials. *Trans-i*- $[\text{Co}(\text{l-his})_2]\text{ClO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ was prepared as previously described.⁵ $\text{K}_4[\text{Ru}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ was purchased from Alfa. The anion exchanger used was QAE-Sephadex A-25 from Pharmacia.

Analyses. Cobalt was determined colorimetrically using the nitroso-R-salt method⁶ following decomposition of the complex by fuming with concentrated perchloric acid; by this procedure ruthenium is removed as RuO_4 . Carbon, hydrogen, and nitrogen analyses were carried out by the Microanalytical Department, Chemistry Laboratory II, University of Copenhagen.

Spectra. The electronic spectra were measured with a Cary 11 spectrophotometer and a Roussel-Jouan dichrograph, and IR spectra with a Perkin-Elmer model 337 instrument.

The IR spectrum in Fig. 7 was obtained by the KBr technique using an evaporated sample of the chromatographed compound. The additional high-energy peak was also observed in a solution spectrum before the chromatographical separation.

The proton-decoupled 22.63 MHz ^{13}C NMR spectra reported in Table 1 were obtained by means of 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 given relative to TMS; dioxane ($\delta = 67.40$) was used as an internal standard.

Laser irradiation. A continuous wave argon laser from Coherent Radiation was used. The internal wavelength selection was set at 514.5 nm, and furthermore the light beam passed an interference filter with peak wavelength 514.5 nm and bandwidth 3.0 nm in order to exclude any background radiation.

Chromatography. For the preparative experiments a column of internal diameter 5 cm was packed with the Sephadex ion exchanger to a height of 6 cm. 225 ml of an irradiated solution, 2.5 mM with respect to both $[\text{Co}(\text{his})_2]^+$ and $[\text{Ru}(\text{CN})_6]^{4-}$, was applied to the column. After elution with ca. 20 l of 0.15 M NaCl the packing material was extruded from the column and the red-orange main zone was isolated.

It was established that under the conditions used $[\text{Co}(\text{his})_2]^+$ passed straight through the column, and that $[\text{Ru}(\text{CN})_6]^{4-}$ stayed at the top.

The solution for the preparative chromatography was irradiated with visible light from a normal 100 W, 220 V light bulb placed at a distance of ca. 5 cm from the glass flask containing the sample. The flask, provided with a stirrer, was submerged in a water bath thermostatted at 25 °C. The duration of irradiation was a couple of days.

DISCUSSION

The experimental data presented for the photo-generated product 1 are consistent with the formula $[(\text{l-his})_2\text{Co}(\text{III}) \cdot \text{NC} \cdot \text{Ru}(\text{II})(\text{CN})_5]^{3-}$ and with the structure shown in Fig. 8.

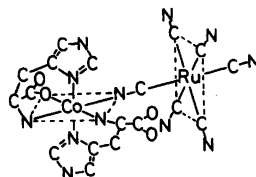


Fig. 8. The structure of 1 (hydrogen atoms omitted)

The central unit of *1*, {Co(III)·NC·Ru(II)}, is of the mixed valence type since it contains an oxidized and a reduced metal ion coupled together. A complex, [(H₃N)₅Co·NC·Ru(CN)₅]⁻, having the same central unit as *1* has been studied,⁷ and in accordance with the mixed valence character its absorption spectrum was found to exhibit a strong intervalence transfer band at 375 nm. By analogy the band at 385 nm in the spectrum of *1*, not seen in either [Co(L-his)₂]⁺ or [Ru(CN)₆]⁴⁻, is assigned to a charge transfer from Ru(II) to Co(III).

A good diagnostic sign of bridging cyanide is the appearance of an additional IR peak on the high energy side of the usual band for terminal cyanide.^{7,8} Accordingly the IR spectrum in Fig. 7 indicates the presence of a cyanide bridge in *1*.

The occurrence of two types of histidinate ligands in the structure of *1* (see Fig. 8) is reflected in the ¹³C NMR spectrum which is seen (Table 1) to exhibit two histidinate patterns. The resonances with chemical shifts 177.3 and 185.8 are assigned to free and bound carboxylate, respectively.

The NMR spectrum indicates that *1* is diamagnetic, which is consistent with a *t*_{2g}⁶ configuration for both metal ions in the central unit.

It has been established that the substitution-type reaction by which [Co(his)₂]⁺ is coupled to [Ru(CN)₆]⁴⁻ is associated with a stimulation of the *d-d* band in the cobalt complex.

It is noted that [Fe(CN)₆]⁴⁻ reacts with [Co(his)₂]⁺ in a thermal process at room temperature² whereas [Ru(CN)₆]⁴⁻ does not. No dark reaction could be detected for the ruthenium complex.

It has been observed that the isomers *trans*-amine-[Co(L-his)₂]⁺ and all-*cis*-[Co(L-his)(D-his)]⁺ follow the same reaction pattern as described here for the *trans*-imidazole isomer.

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