

Preparation and Characterization of a Mixed Valence Cyanobridged Cobalt(III)ruthenium(II) Complex

SVEN BAGGER and PER STOLTZE

Chemistry Department A, Building 207, The Technical University of Denmark, DK-2800 Lyngby, Denmark

The ion $[(en)_2(NH_3)Co \cdot NC \cdot Ru(CN)_5]^-$ has been prepared from $trans-[Co(en)_2(NH_3)(H_2O)]^{3+}$ and $[Ru(CN)_6]^{4-}$. The experimental methods which have been applied to characterize this new ligand-bridged cobalt(III)ruthenium(II) complex include chromatography, electronic absorption spectrometry, IR spectrometry, ^{13}C NMR and cyclic voltammetry. A comparison with a known, analogous complex, $[(NH_3)_5Co \cdot NC \cdot Ru(CN)_5]^-$, has been utilized in establishing the identity of the new complex.

The chemical literature from recent years shows an increasing interest in the study of coordination compounds having *central units* of the form $\{M \cdot L \cdot M'\}$, where L is a bridging ligand.

This interest partly originates in the circumstance that the active sites of a considerable number of proteins and enzymes involve ligandbridged metal ions.¹

The designation *mixed valence* is used if the central unit includes an "oxidize-able" as well as a "reduce-able" metal ion. Such complexes attract attention because their properties often differ markedly from the simple sum of properties of the component mononuclear complexes. Mixed valence chemistry was brought into focus in two pioneering reviews.^{2,3}

The mixed valence central unit $\{Co(III) \cdot NC \cdot Ru(II)\}$ under study in the present work is already known from the complexes $[(NH_3)_5Co \cdot NC \cdot Ru(CN)_5]^-$,⁴ $[(CN)_5Co \cdot NC \cdot Ru(CN)_5]^{6-}$,⁵ and $[(histidinate)_2Co \cdot NC \cdot Ru(CN)_5]^{3-}$.⁶

Notation

For the sake of brevity the complex $[(en)_2(NH_3)Co \cdot NC \cdot Ru(CN)_5]^-$ is denoted *I*.

en is the abbreviation for 1,2-diaminoethane (ethylenediamine).

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

In the voltammograms an anodic current is defined positive and a cathodic current negative. The half-peak potential, $E_{p/2}$, is the potential of the indicator electrode at which the difference between the total current and the residual current is equal to one-half of the peak current.

EXPERIMENTAL AND RESULTS

In analogy with $[(NH_3)_5Co \cdot NC \cdot Ru(CN)_5]^-$ the complex *I* was prepared in a thermal solid phase reaction by coupling $trans-[Co(en)_2(NH_3)(H_2O)]^{3+}$ with $[Ru(CN)_6]^{4-}$.

I was isolated and purified by column chromatography using a Sephadex anion exchanger with aqueous NaCl as eluent.

In spite of many attempts it was not possible to prepare a pure, crystalline salt of *I*. This circumstance, quite common with ligandbridged complexes, obviously created some problems in the experimental work.

A quantitative precipitation of chromatographed *I* in an NaCl solution was possible by addition on Zn^{2+} . The very insoluble, flocculent precipitate became gelatinous after washing by repeated sequences of centrifuging – decantation – addition of water, and apparently it was not possible to remove co-precipitated ions. Nevertheless, an analysis for C and N of the dried precipitate could be used for determination of the concentration of *I*. The mol ratio C:N found by chemical analysis was .93; the theoretical value for $[(en)_2(NH_3)Co \cdot NC \cdot Ru(CN)_5]^-$ is .91.

All solutions of *I* used for the experimental inves-

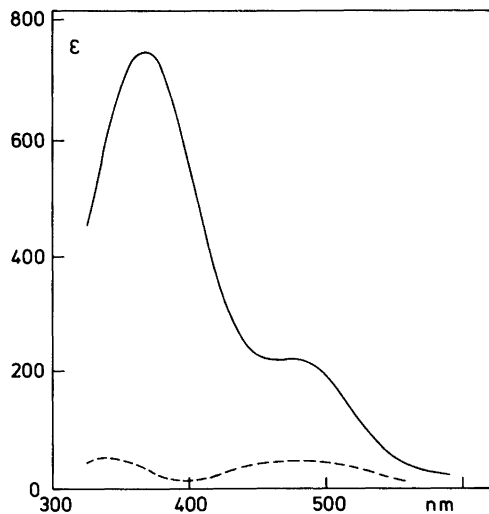


Fig. 1. Electronic absorption spectra in solution. —, *1*; ---, $[\text{Co}(\text{en})_2(\text{NH}_3)(\text{H}_2\text{O})]^{3+}$. $[\text{Ru}(\text{CN})_6]^{4-}$ does not absorb in the region shown.

tigations described in the following contained NaCl from the chromatographic procedure.

The visible spectrum of *1* is shown in Fig. 1. Its most striking feature is an intense absorption at 369 nm ($\epsilon = 752 \text{ M}^{-1} \text{ cm}^{-1}$), not present in any of the two component mononuclear complexes. The spectrum of *1* is very similar to that of $[(\text{NH}_3)_5\text{Co} \cdot \text{NC} \cdot \text{Ru}(\text{CN})_5]^-$, which has a maximum at 375 nm ($\epsilon = 690 \text{ M}^{-1} \text{ cm}^{-1}$).⁴

For IR spectrometry a solid dispersion of *1* in NaCl was prepared by evaporation of a chromatographed solution. Special attention was paid to the CN-stretching region in the IR spectrum. The same pattern as has been observed previously^{4,6} for $[(\text{NH}_3)_5\text{Co} \cdot \text{NC} \cdot \text{Ru}(\text{CN})_5]^-$ and $[(\text{histidinate})_2\text{Co} \cdot \text{NC} \cdot \text{Ru}(\text{CN})_5]^{3-}$ was found, i.e. in addition to a strong peak (2068 cm^{-1}), characteristic for complexes containing only terminal CN, a separate weak peak was found at a higher wavenumber (2102 cm^{-1}). This pattern indicates cyanide bridging.⁷

The proton-decoupled ^{13}C NMR spectrum of *1* exhibited only a single resonance with a chemical shift of 45.7 ppm. This signal is assigned to the carbon atoms in the ethylenediamine ligands.

In accordance with a ^{13}C NMR study of *trans*- and *cis*-isomers of ethylenediaminecobalt(III) complexes⁸ it was found that the spectrum of *trans*- $[\text{Co}(\text{en})_2(\text{NH}_3)(\text{H}_2\text{O})]^{3+}$ only shows one resonance (at 45.2 ppm), whereas the spectrum of *cis*- $[\text{Co}(\text{en})_2(\text{NH}_3)(\text{H}_2\text{O})]^{3+}$ is more complex with three resonances (at 46.4, 45.7 and 44.3 ppm). Consequently,

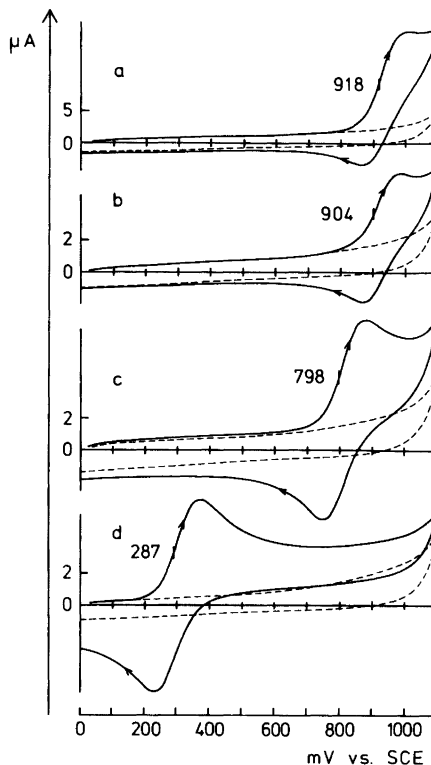


Fig. 2. Single-sweep triangular wave voltammograms. a, *1*; b, $[(\text{NH}_3)_5\text{Co} \cdot \text{NC} \cdot \text{Ru}(\text{CN})_5]^-$; c, $[\text{Ru}(\text{CN})_6]^{4-}$; d, $[\text{Fe}(\text{CN})_6]^{4-}$. Potential sweep: 0 mV–1100 mV–0 mV. Sweep rate: 100 mV s^{-1} . The affixed numbers give values of $E_{p/2}$ for the anodic wave in mV vs. SCE. Dashed curves show the residual current. In all four cases the supporting electrolyte was saturated NaCl.

the single line pattern of *1* indicates that the *trans*-configuration around cobalt is retained in the dinuclear complex. No resonance from cyanide could be detected under the routine conditions used. The reason is possibly slow relaxation.⁹

The redox behaviour of *1* has been examined by simple triangular wave voltammetry¹⁰ using a vitreous carbon indicator electrode. The single-sweep voltammogram for *1* in saturated aqueous NaCl is shown in Fig. 2. For comparison the results for $[(\text{NH}_3)_5\text{Co} \cdot \text{NC} \cdot \text{Ru}(\text{CN})_5]^-$, $[\text{Ru}(\text{CN})_6]^{4-}$, and $[\text{Fe}(\text{CN})_6]^{4-}$ under the same conditions are also shown. A feature common to the voltammograms of the two dinuclear complexes is the weakness of the cathodic wave which follows the initial anodic wave.

Experimental Details

General. All experiments were performed in subdued light owing to the photosensitivity of *1*. An aqueous solution quickly becomes cloudy when exposed to full daylight.

Materials. $K_4[Ru(CN)_6] \cdot 3H_2O$ was purchased from Alfa (USA).

The anion exchanger used was QAE-Sephadex A-25 from Pharmacia (Sweden).

trans- $[Co(en)_2(NH_3)(H_2O)](NO_3)_3$ was prepared according to a published procedure.¹¹

$[(NH_3)_5Co \cdot NC \cdot Ru(CN)_5]^-$ was prepared using $[Co(NH_3)_5(H_2O)](ClO_4)_3$ and $K_4[Ru(CN)_6] \cdot 3H_2O$ as starting materials.⁴ First the yellow, insoluble salt $[Co(NH_3)_5(H_2O)]_4[Ru(CN)_6]_3 \cdot 5H_2O$ was prepared.⁴ This salt was heated in an electric oven for 8 days at 60°C. Extraction of the product with water gave a solution containing $[(NH_3)_5Co \cdot NC \cdot Ru(CN)_5]^-$. This solution was chromatographed in the same way as described below for *1*. $[(NH_3)_5Co \cdot NC \cdot Ru(CN)_5]^-$ and *1* had equal R_f -values.

An aqueous solution of *1* was prepared by a procedure analogous to that described above for $[(NH_3)_5Co \cdot NC \cdot Ru(CN)_5]^-$. A typical synthesis was started from 0.1000 g $[Co(en)_2(NH_3)(H_2O)](NO_3)_3$ (0.25 mmol) and 0.0877 g $K_4[Ru(CN)_6] \cdot 3H_2O$ (0.19 mmol) and this yielded ca. 70 ml orange coloured solution containing *1*. This amount was appropriate for one preparative chromatographic experiment as described below.

Chromatographic Purification of 1. Some initial investigations to optimize the conditions were carried out using small columns of 9 mm internal diameter.

For a preparative experiment a glass column of 50 mm internal diameter was packed with the Sephadex ion exchanger to a height of ca. 50 mm. 70 ml of a solution containing *1*, prepared as described above, was applied to the column. After elution with ca. 3.0 l of 0.05 M NaCl one distinct orange coloured zone had developed. The zone was ca. 11 mm broad and the front had moved ca. 25 mm. Subsequently the packing material was extruded from the column and the orange coloured section was mechanically isolated, transferred to a column, and finally eluted with ca. 60 ml 0.5 M NaCl. The yield was typically 0.04 mmol of chromatographically pure *1*.

Analyses. By addition of Zn^{2+} ($ZnSO_4 \cdot 7H_2O$ was used) in slight excess *1* was quantitatively precipitated. The completeness of this reaction was checked spectrophotometrically. C and N analyses of this precipitate were performed by the Microanalytical Department, Chemistry Laboratory II, University of Copenhagen.

Spectra. The electronic spectra were measured with a Cary 11 spectrophotometer and the IR

spectra with a Perkin Elmer model 337 instrument.

IR samples were prepared by the mull technique using Fluorolube perfluorohydrocarbon as the mulling agent.

Proton-decoupled 22.63 MHz ¹³C NMR spectra were obtained with a Bruker WH 90 spectrometer using the Fourier transform technique. The solvent was D₂O, and the spectra were run at ambient temperature with dioxane ($\delta = 67.40$) as internal standard.

Cyclic Voltammetry. The electrochemical apparatus of conventional three-electrode design, including a triangular wave generator, was built by C. E. Foverskov of our laboratory. The recording device was either a Hewlett-Packard XY-recorder type 7004B or a Tektronix storage oscilloscope type 5103N/D11.

The indicator electrode was a cylindrical rod of vitreous carbon (Grade V10 from Le Carbone-Lorraine, France) sealed into the end of a glass tubing. The rod was ground flush with the glass and carefully polished. An area of 6.1 mm² was in contact with the test solution. A saturated calomel electrode (Radiometer, type K 401) and a platinum foil electrode (Radiometer, type P131) were used as reference and counter electrodes, respectively.

It was found that use of a platinum indicator electrode gave irreproducible results, apparently due to the presence of chloride.¹²

As described above, NaCl was always present in the chromatographed samples of *1* and therefore saturated NaCl was chosen as the supporting electrolyte.

Concentrations of electroactive species in the samples were 0.5–1 mM.

The measurements were performed at room temperature. A blank curve on saturated NaCl was always run in immediate connection with each voltammogram.

DISCUSSION AND CONCLUSIONS

On the basis of the experimental evidence presented, *1* is formulated $[(en)_2(NH_3)Co \cdot NC \cdot Ru(CN)_5]^-$. Ammonia is bound to cobalt in *trans*-position to the cyanide bridge.

In the absence of light, *1* is very stable and robust in aqueous solution. This is in accordance with a low-spin d^6 ground-state configuration for both cobalt(III) and ruthenium(II).

The mixed valence character of the $\{Co(III) \cdot NC \cdot Ru(II)\}$ unit is displayed in the electronic spectrum by the presence of the intense band at 369 nm. This absorption is assigned to an $Ru(II) \rightarrow Co(III)$ charge transfer,^{4,6} exemplifying the phenomenon called *intervalence transfer*.³

Aminocobalt(III) complexes have been found to be more easily reduced than ethylenediaminecobalt(III) complexes, *e.g.* the standard potential for $[\text{Co}(\text{NH}_3)_6]^{3+}/[\text{Co}(\text{NH}_3)_6]^{2+}$ is higher than for $[(\text{Co}(\text{en})_3)]^{3+}/[(\text{Co}(\text{en})_3)]^{2+}$.¹³ This rationalizes the fact that the intervalence transfer occurs at a higher energy in $[(\text{en})_2(\text{NH}_3)\text{Co} \cdot \text{NC} \cdot \text{Ru}(\text{CN})_5]^-$ than in $[(\text{NH}_3)_5\text{Co} \cdot \text{NC} \cdot \text{Ru}(\text{CN})_5]^-$.

The anodic wave in the voltammogram of *1* is ascribed to a $\{\text{Co}(\text{III}) \cdot \text{NC} \cdot \text{Ru}(\text{II})\} \rightarrow \{\text{Co}(\text{III}) \cdot \text{NC} \cdot \text{Ru}(\text{III})\}$ oxidation. A comparison of the voltammograms in Fig. 2 for the two dinuclear complexes indicates that this oxidation requires the higher potential in *1*.

The weakness of the reduction wave for both *1* and $[(\text{NH}_3)_5\text{Co} \cdot \text{NC} \cdot \text{Ru}(\text{CN})_5]^-$ is possibly due to a chemical reaction which removes the $\{\text{Co}(\text{III}) \cdot \text{NC} \cdot \text{Ru}(\text{III})\}$ species in competition with the cathodic reaction. Further studies are needed to clarify this point.

Acknowledgements. The authors wish to acknowledge experimental contributions by Erik Christensen and Henning Mikkelsen, who took part in the present study as undergraduate students. The NMR spectrometer was placed at our disposal by the Danish Natural Science Research Council.

REFERENCES

1. Cohen, I. A. *Struct. Bonding Berlin* 40 (1980) 1.
2. Robin, M. B. and Day, P. *Adv. Inorg. Chem. Radiochem.* 10 (1967) 247.
3. Allen, G. C. and Hush, N. S. *Prog. Inorg. Chem.* 8 (1967) 357.
4. Vogler, A. and Kunkely, H. *Ber. Bunsenges. Phys. Chem.* 79 (1975) 83.
5. Vogler, A. and Kunkely, H. *Ber. Bunsenges. Phys. Chem.* 79 (1975) 301.
6. Bagger, S. *Acta Chem. Scand. A* 34 (1980) 63.
7. Dows, D. A., Haim, A. and Wilmarth, W. K. *J. Inorg. Nucl. Chem.* 21 (1961) 33.
8. House, D. A. and Blunt, J. W. *Inorg. Nucl. Chem. Lett.* 11 (1975) 219.
9. Narayanan, B. A. and Manoharan, P. T. *J. Inorg. Nucl. Chem.* 40 (1978) 1993.
10. Headridge, J. B. *Electrochemical Techniques for Inorganic Chemists*, Academic, London 1969.
11. Tobe, M. L. and Martin, D. F. *Inorg. Synth.* 8 (1966) 198.
12. Peters, D. G. and Lingane, J. J. *J. Electroanal. Chem.* 4 (1962) 193.
13. Bjerrum, J. *Metal Ammine Formation in Aqueous Solution*, P. Haase and Son, Copenhagen 1941.

Received December 19, 1980.