Short Communication

Photoredox reaction of a trinuclear Co(III), Co(III), Ru(II) complex induced by metal-to-metal charge transfer excitation and a subsequent charge shift

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Abstract

The trinuclear complex $(NH_3)_5Co^{III}(\mu\text{-}NC)Co^{III}(CN)_4(\mu\text{-}CN)Ru^{II}(CN)_5^{3-}$ shows a long wavelength absorption near 370 nm which is assigned to a metal-to-metal charge transfer (MMCT) transition from Ru(II) to the central Co(III) ion. Light absorption by this bands leads to a redox decomposition: $(NH_3)_5Co^{III}(\mu\text{-}NC)Co^{III}(CN)_4(\mu\text{-}CN)Ru^{II}(CN)_5^{3-} \rightarrow 5NH_3 + Co^{2+} + Co^{III}(CN)_6^{3-} + Ru^{III}(CN)_5H_2O^{2-}$. It is suggested that the initial MMCT transition is followed by a charge shift from the central Co(II) to the cobalt(III) ammine moiety which subsequently undergoes a rapid irreversible decay.

Introduction

Photoinduced charge separation as it takes place in natural and artificial photosynthesis has been studied extensively for many years [1]. The charge separation is facilitated by a charge shift which follows the primary electron transfer. The charge shift may increase the distance between electron and hole. Suitable systems are supramolecular species (e.g. 'triads') which contain a primary electron donor/acceptor pair and a further redox active site. The primary electron transfer can be initiated by excited state electron transfer or by a direct optical charge transfer excitation. Appropriate supramolecular species include organic molecules as well as transition metal complexes [1]. Here we describe the photochemistry of a trinuclear metal complex which undergoes a primary electron transfer by metal-to-metal charge transfer (MMCT) excitation and a subsequent charge shift. Generally, such processes are reversible

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and studied by time-resolved spectroscopy. In our system the secondary electron acceptor is reduced irreversibly and thus indicates the occurence of a charge shift. Our choice of $(NH_3)_5Co^{III}(\mu\text{-}NC)Co^{III}(CN)_4(\mu\text{-}CN)Ru^{II}(CN)_5^{3-}$ as a suitable trinuclear complex was based on our experience with photoredox processes of binuclear complexes [2].

Experimental

Materials

$K_4[Ru(CN)_6]3H_2O$ was purchased from Heraeus. $[(NH_3)_5Co(\mu\text{-}NC)Co(CN)_5]$ was synthesized according to a published procedure [3]. Solutions of $K_3[Ru(CN)_5H_2O]$ were prepared *in situ* [4] in the presence of $[(NH_3)_5Co(\mu\text{-}NC)Co(CN)_5]$ or $K_3[Co(CN)_6]$.

Synthesis of $K_3[(NH_3)_5Co(\mu\text{-}NC)Co(CN)_4(\mu\text{-}CN)Ru(CN)_5]6H_2O$

To a solution of 1.2 g (0.003 mol) $K_4[Ru(CN)_6]3H_2O$ and 1.08 g (0.003 mol) $[(NH_3)_5Co(\mu\text{-}NC)Co(CN)_5]$ in 75 ml of water was added slowly under stirring a solution of 1.19 g (0.01 mol) KBr and 0.16 ml (0.003 mol) of Br_2 in 100 ml of water. After this mixture was stirred for 1 h the solution was filtered. Upon addition of a mixture of 250 ml of methanol and 200 ml of ether a crude product precipitated. It was allowed to stand for 1 h, collected by filtration, washed with methanol, and dried under vacuum. The crude product (1.3 g) was recrystallized three times by dissolution in 20 ml of water, filtration, and reprecipitation upon addition of 60 ml of a mixture of methanol and ether (1:1) and then 80 ml of ether. The yellowish product was collected by filtration, washed with methanol, then with ether, and dried under vacuum; yield 0.5 g ($\approx 20\%$). *Anal.* Calc. for $C_{11}N_{16}H_{15}Co_2K_3Ru6H_2O$: C, 16.20; N, 27.47; H, 3.33. Found: C, 16.25; N, 27.15; H, 3.38%.

Photolysis

The light source was a Hanovia Xe/Hg 977 B-1 (1000 W) lamp. Monochromatic light ($\lambda_{irr} = 254$, 313 and 366 nm) was obtained by means of a Schoeffel GM 250-1 high-intensity monochromator. The photolyses were carried out at room temperature in 1-cm spectrophotometer cells. For quantum yield determinations the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light inten-

sities were determined by a Polytec pyroelectric radiometer, which was calibrated and equipped with a RkP-345 detector.

Instrumentation

Progress of the photolysis was monitored by UV–Vis spectrophotometry, using a 8452A Hewlett Packard diode array spectrophotometer and a Shimadzu UV-2100 spectrometer.

Results

The trinuclear complex $(NH_3)_5Co^{III}(\mu\text{-}NC)Co^{III}(CN)_4(\mu\text{-}CN)Ru^{II}(CN)_5^{3-}$ (A) was prepared by the reaction of $(NH_3)_5Co^{III}(\mu\text{-}CN)Co^{III}(CN)_5$ with $Ru^{II}(CN)_5H_2O^{3-}$ which contains a kinetically labile water ligand [4–9]. IR measurements of A in the region of the cyanide stretching frequencies provide evidence for the presence of terminal and bridging CN^- ligands. The terminal cyanides absorb at 2050 cm^{-1} (Ru^{II}–CN) [10, 11] and 2140 cm^{-1} (Co^{III}–CN) [3, 11–13] while a split band at higher frequencies (2200 and 2180 cm^{-1}) is consistent with the occurence of cyanide bridges [3, 10–14] which originate from the central $Co(CN)_6^{3-}$ unit of A.

The electronic absorption spectrum of A in water (Fig. 1) displays bands at $\lambda_{max} = 475$ nm ($\epsilon = 220$) and 280 nm (shoulder, $\epsilon = 6800$). In 1 M H_2SO_4 additional features are visible. A maximum appears at approximately 390 nm and a further shoulder shows up at about 310 nm.

For the purpose of comparison a solution of $(NC)_5Co^{III}(\mu\text{-}CN)Ru^{II}(CN)_5^{6-}$ was prepared by the reaction of $Co^{III}(CN)_6^{3-}$ with $Ru^{II}(CN)_5H_2O^{3-}$. The binuclear complex is characterized by an absorption maximum at $\lambda_{max} = 312$ nm ($\epsilon = 1300$) and a pronounced shoulder at $\lambda_{max} = 370$ nm ($\epsilon = 140$).

The photolysis of aqueous A ($\lambda_{irr} = 366$ nm) was associated with the formation of Co^{2+} which was identified as a blue thiocyanate complex ($\lambda_{max} = 625$ nm)
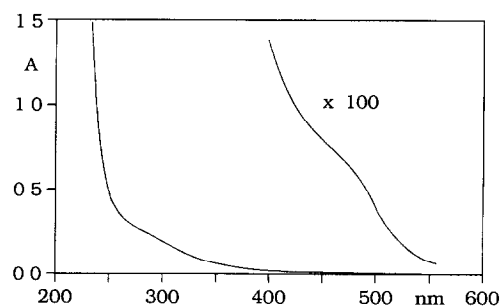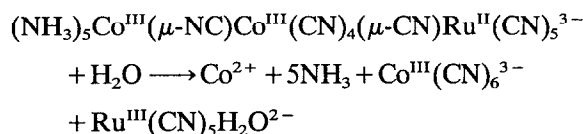

Fig. 1. Electronic absorption spectrum of aqueous 3.18×10^{-5} M $(NH_3)_5Co^{III}(\mu\text{-}NC)Co^{III}(CN)_4(\mu\text{-}CN)Ru^{II}(CN)_5^{3-}$ at room temperature, 1 cm cell.

[15]. In addition, the irradiation was accompanied by an increase of pH and by spectral variations which indicated the formation of $Ru^{III}(CN)_5H_2O^{2-}$ ($\lambda_{max} = 400$ nm, $\epsilon = 1500$) [16]. The presence of this complex was confirmed. Upon addition of N-methylpyrazinium iodide and dithionite as a reductant $Ru^{III}(CN)_5H_2O^{3-}$ was converted to $Ru^{II}(CN)_5$-N-methylpyrazinium^{2-} which was detected by its intense long wavelength absorption at $\lambda_{max} = 522$ nm ($\epsilon = 6850$) [5, 7]. These observations are consistent with a photoredox decomposition of A:

$$(NH_3)_5Co^{III}(\mu\text{-}NC)Co^{III}(CN)_4(\mu\text{-}CN)Ru^{II}(CN)_5^{3-}$$
$$+ H_2O \longrightarrow Co^{2+} + 5NH_3 + Co^{III}(CN)_6^{3-}$$
$$+ Ru^{III}(CN)_5H_2O^{2-}$$

The concentration of $Ru(CN)_5H_2O^{2-}$ was determined by measuring the change of optical density at 400 nm. At $\lambda_{irr} = 366$ nm $Ru(CN)_5H_2O^{2-}$ was formed with $\theta = 0.05$. The quantum yield remained nearly constant upon shorter wavelength irradiation ($\theta = 0.07$ at $\lambda_{irr} = 313$ nm and 0.06 at 254 nm).

Discussion

In analogy to other cyanide-bridged binuclear complexes [1c, 2, 17] the electronic coupling of the mononuclear components of A is apparently rather weak, since they preserve largely their identity in the trinuclear complex. The assumption that the metals occur in their regular oxidation states is supported by IR and UV–Vis spectral measurements. In the cyanide stretching region the frequencies of the terminal cyanides are an indication for the presence of cyanide complexes of Co(III) ($\nu = 2140$ cm^{-1}) and Ru(II) ($\nu = 2050$ cm^{-1}) [10, 11].

The electronic spectrum of A displays a band at $\lambda_{max} = 475$ nm and a shoulder at 280 nm. The 475 nm absorption is assigned to the first ligand field (LF) transition of the $Co(III)(NH_3)_5NC^{2+}$ moiety [10]. The first LF absorption of $Co(NH_3)_6^{3+}$ appears at nearly the same wavelength ($\lambda_{max} = 476$ nm) since the LF strength of ammonia corresponds to that of N-coordinating cyanide [3, 10, 13]. The 280 nm band of A is assigned to the first LF transition of the $Ru^{II}(CN)_5NC^{4-}$ component of the trinuclear complex. This assumption is supported by the observation that $Ru^{II}(CN)_5NH_3^{3-}$ displays its first LF band at comparable energies ($\lambda_{max} = 285$ nm, $\epsilon = 4600$) [9]. $Co(CN)_6^{3-}$ as the central unit of A does not show up in the absorption spectrum. The first LF band of $Co(CN)_6^{3-}$ ($\lambda_{max} = 312$ nm; $\epsilon = 196$) [3, 13] is apparently obscured by other absorptions of the trinuclear complex.
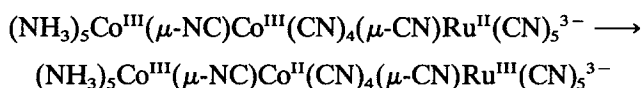
A comparison of the electronic spectrum of A with those of its binuclear components is also rather instructive. The complex $(NH_3)_5Co^{III}(\mu\text{-}NC)Co^{III}(CN)_5$

displays two absorptions at $\lambda_{max} = 313$ and 474 nm [3, 13, 18] which consist of the superimposed LF bands of the mononuclear constituents $Co(NH_3)_5NC^{2+}$ and $Co(CN)_6^{3-}$. The binuclear complex is also characterized by a clear minimum at 390 nm. Only the longest wavelength LF band of the binuclear complex at $\lambda_{max} = 474$ nm can be identified in the spectrum of A.

The other binuclear component of A, $(NC)_5Co^{III}(\mu\text{-}CN)Ru^{II}(CN)_5^{6-}$, shows the first LF band of $Co(CN)_6^{3-}$ at $\lambda_{max} = 312$ nm and a pronounced long wavelength shoulder at 370 nm. We assign this shoulder to the Ru(II) to Co(III) MMCT transition. This MMCT band should also appear in the spectrum of A. Although it does not show up as a clear feature (Fig. 1), it is assumed that its appearance is responsible for the absence of a minimum near 390 nm which occurs in the spectrum of $(NH_3)_5Co^{III}(\mu\text{-}NC)Co^{III}(CN)_5$ [18].

The presence of a Ru(II) to Co(III) MMCT band near 370 nm is also supported by further observations. Other binuclear complexes which contain Co(III) and Ru(II) display MMCT absorptions in the same wavelength region [10, 11]. Moreover, it is well known that the protonation of the cyanide ligand of Ru(II) complexes leads to an increase of the energy of MLCT transitions with Ru(II) as the donor [19–21]. The protonation of A is indeed associated with the appearance of the minimum at 390 nm. The MMCT band is apparently shifted to shorter wavelength where it is obscured by absorptions of higher intensity.

The photolysis of A can now be understood on the basis of our spectral assignments. Light absorption by the MMCT band ($\lambda_{irr} = 366$ nm) leads to the formation of a redox isomer.

$$(NH_3)_5Co^{III}(\mu\text{-}NC)Co^{III}(CN)_4(\mu\text{-}CN)Ru^{II}(CN)_5^{3-} \longrightarrow$$

$$(NH_3)_5Co^{III}(\mu\text{-}NC)Co^{II}(CN)_4(\mu\text{-}CN)Ru^{III}(CN)_5^{3-}$$

The central Co(II) cyano complex is a strong reductant [12, 22] which transfers an electron back to Ru(III) or to the oxidizing $Co^{III}(NH_3)_5$ moiety. The Co(II) ammine complex undergoes then the well-known irreversible decomposition [23]. The other photolysis product $(NC)_5Co^{III}(\mu\text{-}CN)Ru^{III}(CN)_5^{5-}$ is apparently also not stable but aquates with the formation of $Ru^{III}(CN)_5H_2O^{3-}$. The kinetic lability is a general feature of Ru(III) cyano complexes [16]. Finally, it is important to emphasize that the photolysis of A cannot be caused by an electronic excitation within the binuclear $(NH_3)_5Co^{III}(\mu\text{-}NC)Co^{III}(CN)_5$ component which is rather photoinert upon irradiation with long wavelength light ($\lambda_{irr} > 300$ nm) [18].

References

1 (a) M. A. Fox and M. Chanon (eds.), *Photoinduced Electron Transfer*, Parts A–D, Elsevier, Amsterdam, 1988; (b) J. Mattay (ed.), *Photoinduced Electron Transfer I (Top. Curr. Chem., 156* (1990), *II (Top. Curr. Chem., 159* (1991)), *IV (Top. Curr. Chem., 163* (1992))); (c) V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, UK, 1991.

2 (a) A. Vogler, A. H. Osman and H. Kunkely, *Coord. Chem. Rev., 64* (1985) 159; (b) A. Vogler, in M. A. Fox and M. Chanon (eds.), *Photoinduced Electron Transfer*, Part D, Elsevier, Amsterdam, 1988, p. 179.

3 R. A. de Castello, C. Piriz Mac-Coll, N. B. Egen and A. Haim, *Inorg. Chem., 8* (1969) 699.

4 C. R. Johnson and R. E. Shepherd, *Inorg. Chem., 22* (1983) 1117.

5 C. R. Johnson and R. E. Shepherd, *Inorg. Chem., 22* (1983) 2439.

6 S. Siddiqui, W. W. Henderson and R. E. Shepherd, *Inorg. Chem., 26* (1987) 3101.

7 J. M. A. Hoddenbugh and D. H. Macartney, *Inorg. Chem., 25* (1986) 380.

8 L. A. Gentil, H. O. Zerga and J. A. Olabe, *J. Chem. Soc., Dalton Trans.,* (1986) 2731.

9 J. A. Olabe, H. O. Zerga and L. A. Gentil, *J. Chem. Soc., Dalton Trans.,* (1987) 1267.

10 A. Vogler and H. Kunkely, *Ber. Bunsenges. Phys. Chem., 79* (1975) 93.

11 A. Vogler and H. Kunkely, *Ber. Bunsenges. Phys. Chem., 79* (1975) 301.

12 A. Haim and W. K. Wilmarth, *J. Am Chem. Soc., 83* (1961) 509.

13 R. A. de Castello, C. Piriz Mac-Coll and A. Haim, *Inorg. Chem., 10* (1971) 203.

14 D. A. Dows, A. Haim and W. K. Wilmarth, *J. Inorg. Nucl. Chem., 21* (1961) 33.

15 R. E. Kitson, *Anal. Chem., 22* (1950) 664.

16 F. M. Crean and K. Schug, *Inorg. Chem., 23* (1984) 853.

17 F. Scandola, M. T. Indelli, C. Chiorboli and C. A. Bignozzi, *Top. Curr. Chem., 158* (1990) 73.

18 M. Nishizawa and P. C. Ford, *Inorg. Chem., 20* (1981) 2016.

19 S. H. Peteron and J. N. Demas, *J. Am. Chem. Soc., 101* (1979) 6571.

20 M. T. Indelli, C. A. Bignozzi, A. Marconi and F. Scandola, in H. Yersin and A. Vogler (eds.), *Photochemistry and Photophysics of Coordination Compounds*, Springer, Berlin, 1987, p. 159.

21 V. Balzani, N. Sabbatini and F. Scandola, *Chem. Rev., 86* (1986) 319.

22 A. G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals*, Academic Press, London, 1976.

23 M. Simic and J. Lilie, *J. Am. Chem. Soc., 96* (1974) 291.