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Note

Photoredox behavior of a trinuclear Ru(III),Ru(II),Co(III) complex induced by metal-to-metal charge transfer excitations

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Abstract

The trinuclear complex $[(NH_3)_5Ru(III)(\mu\text{-}NC)Ru(II)(CN)_4(\mu\text{-}CN)Co(III)(NH_3)_5]Cl_2 \cdot 2H_2O$ was prepared and characterized by IR and UV–Vis spectroscopy. The aqueous complex shows two long-wavelength absorptions at $\lambda_{max} = 647$ and 372 nm which are assigned to Ru(II) to Ru(III) and Ru(II) to Co(III) MMCT transitions, respectively. Photolysis of the aqueous solution led to a redox decomposition. Co^{2+} was formed with $\phi = 2 \times 10^{-4}$ at $\lambda_{irr} = 577$ and 0.18 at 366 nm. The electronic spectrum as well as the photoreactivity of the trinuclear complex are discussed on the basis of a Hush diagram which accommodates three redox-active metal centers.

Keywords: Photoredox reactions; Ruthenium complexes; Cobalt complexes; Charge transfer excitation

1. Introduction

Photoredox reactions of binuclear ligand-bridged metal complexes induced by metal-to-metal charge transfer (MMCT) excitation have been studied extensively for nearly two decades [1,2]. These investigations are facilitated if the light-induced electron transfer processes take place in complexes which provide a redox asymmetry of both metal centers. Symmetrical mixed-valence compounds are thus less suitable for this purpose.

In 1975, we reported the first observation of a photoredox reaction initiated by an MMCT transition. Ru(II) to Co(III) CT excitation of aqueous $[(NH_3)_5Co(III)(\mu\text{-}NC)Ru(II)(CN)_5]^-$ led to the formation of Co^{2+} and $[Ru(III)(CN)_6]^{3-}$ [3]. The irreversible product formation is based on the rapid decay of the Co(II) ammine complex fragment [4] which is generated by light absorption.

In 1982 we prepared the complex $[(NH_3)_5Ru(III)(\mu\text{-}NC)Ru(II)(CN)_5]^-$ and characterized this compound with regard to the Ru(II)/Ru(III) CT interaction [5]. Owing to the different ligand environments at both metals this complex is also quite redox asymmetrical. Ru(II) to Ru(III) MMCT excitation does, however, not yield permanent photoproducts. Nevertheless, various spectroscopic techniques have provided a detailed picture of the electronic coupling of both metals and the dynamics of back electron transfer which follows the initial optical MMCT [6–14]. These studies were quite beneficial to the development of electron transfer theories. Moreover, $[(NH_3)_5Ru(\mu\text{-}NC)Ru(CN)_5]^-$ may be also utilized for other purposes. Owing to its CT interaction it shows promising non-linear optical properties [15].

In the present work the components of both binuclear complexes mentioned above were combined in the trinuclear ion $[(NH_3)_5Ru(III)(\mu\text{-}NC)Ru(II)(CN)_4(\mu\text{-}CN)Co(III)(NH_3)_5]^{2+}$. The aim of this study was to find out how different optical MMCT transitions, Ru(II) to Ru(III) and Ru(II) to Co(III), would affect the photoreactivity. The Co(III) ammine moiety has a dual function. It serves as one of the acceptors for optical MMCT and provides a suitable site for an irreversible reaction which is required for the detection of an electron transfer process by conventional techniques [1,2]. This strategy was also used in our recent work on $[(NH_3)_5Co(III)(\mu\text{-}NC)Co(III)(CN)_4(\mu\text{-}CN)Ru(II)(CN)_5]^{3-}$ which undergoes a photoredox decomposition

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induced by Ru(II) to Co(III) MMCT excitation and a subsequent charge shift [16].

2. Experimental

2.1. Materials

$[Ru(NH_3)_5Cl]Cl_2$ was commercially available (Alfa) and $Na[(NC)_5Ru(\mu\text{-}CN)Co(NH_3)_5]\cdot 3H_2O$ [3] was prepared according to a published procedure. The water used in the photochemical experiments was triply distilled.

2.2. Synthesis of $[(NH_3)_5Ru(\mu\text{-}NC)Ru(CN)_4(\mu\text{-}CN)Co(NH_3)_5]Cl_2\cdot 2H_2O$

To a solution of 0.53 g (1.1×10^{-3} mol) $Na[(NC)_5Ru(\mu\text{-}CN)Co(NH_3)_5]\cdot 3H_2O$ in 50 ml of water was added a solution of 0.29 g (1×10^{-3} mol) $[Ru(NH_3)_5Cl]Cl_2$ in 60 ml of water. The combined solution was heated to 50 °C and stirred for 5 h in the dark. The dark blue solution was filtered and purified by anion exchange chromatography. The solution was run through a column filled with DEAE Sephadex A-25 and eluted with water. The first fraction was discarded. The eluted solution was concentrated by vacuum evaporation to 20 ml. Upon addition of 100 ml of methanol, a dark blue powder precipitated. It was collected by filtration, washed with methanol, acetone and finally with ether, and dried under vacuum; yield 0.038 g (5.5%). *Anal.* Calc. for $C_6H_{30}N_{16}Cl_2CoRu_2\cdot 2H_2O$: C, 10.37; N, 32.27; H, 4.94. Found: C, 10.29; N, 31.96; H, 5.08%.

2.3. Photolysis

The light source was an Osram HBO 100 W/2 lamp. The mercury lines at 366 and 577 nm were selected by use of Schott PIL/IL interference filters. 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 intensities were determined by a Polytec pyroelectric radiometer, which was calibrated and equipped with an RkP-345 detector.

Co^{2+} was determined by forming the complex ion $[Co(NCS)_4]^{2-}$ in water–acetone solution and measuring the absorbance ($\epsilon = 1.7\times10^3$ at 625 nm), according to a literature procedure [17]. Under the conditions of this measurement (acidic solution) the absorption maximum of the trinuclear complex shifted to 530 nm.

2.4. Instrumentation

Electronic absorption spectra were measured using an 8452A Hewlett Packard diode array spectrometer. IR spectra were measured with a Perkin-Elmer 325 IR spectrophotometer.

3. Results and discussion

The trinuclear complex $[(NH_3)_5Ru(III)(\mu\text{-}NC)\text{-}Ru(II)(CN)_4(\mu\text{-}CN)Co(III)(NH_3)_5]^{2+}$ was synthesized according to the equation

$$[Ru(NH_3)_5Cl]^{2+} + [(NC)_5Ru(\mu\text{-}CN)Co(NH_3)_5]^- \longrightarrow$$

$$[(NH_3)_5Ru(\mu\text{-}NC)Ru(II)(CN)_4(\mu\text{-}CN)Co(NH_3)_5]^{2+} + Cl^-$$

The preparation was carried out in analogy to the synthesis of $[(NH_3)_5Ru(\mu\text{-}NC)Ru(CN)_5]^-$ [5]. Since side reactions led to the formation of large amounts of insoluble polymeric materials, the yield of the trinuclear complex was rather low. IR and UV–Vis spectral measurements confirmed the presence of the metals in their regular oxidation states. The IR spectrum measured in nujol displays absorptions at 2060, 2095 and 2140 cm^{-1}. The lower-frequency bands are an indication for the occurrence of terminal cyanide ligands coordinated to Ru(II) [3,6,16,18], while the higher-frequency band at 2140 cm^{-1} is consistent with the presence of cyanide bridges [3,16,18,19]. In the case of $[(NH_3)_5Ru(\mu\text{-}NC)Ru(CN)_5]^-$ and $[(NH_3)_5Co(\mu\text{-}NC)Ru(CN)_5]^-$ the bridging cyanides absorb at 2130 and 2135 cm^{-1} [3], respectively.

The electronic absorption spectrum of the trinuclear complex in water (Fig. 1) displays bands at $\lambda_{max} = 647$ ($\epsilon = 3400\ M^{-1}\ cm^{-1}$), 372 (720) and 290 (2500) nm. The long-wavelength absorption at 647 nm which causes the blue color of the trinuclear cation is assigned to the Ru(II) to Ru(III) MMCT transition which appears at $\lambda_{max} = 680$ nm in the spectrum of $[(NH_3)_5Ru(\mu\text{-}NC)Ru(CN)_5]^-$ [5,20]. The second band of the trinuclear complex at 372 nm is attributed to the Ru(II)

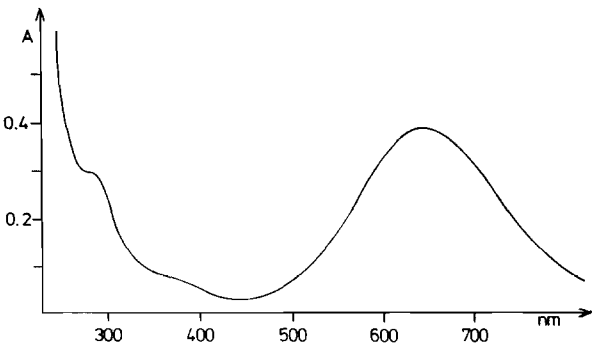

Fig. 1. Electronic absorption spectrum of aqueous 1.15×10^{-5} M $[(NH_3)_5Ru(III)(\mu\text{-}NC)Ru(II)(CN)_4(\mu\text{-}CN)Co(III)(NH_3)_5]^{2+}$ at room temperature; 1 cm cell.

to Co(III) MMCT transition. The binuclear complex $[(NC)_5Ru(\mu\text{-}CN)Co(NH_3)_5]^-$ exhibits this MMCT absorption at $\lambda_{max}=375$ nm [3]. The third band of the trinuclear complex at 290 nm is of uncertain origin. It corresponds to an absorption of $[(NH_3)_5Ru(\mu\text{-}NC)Ru(CN)_5]^-$ at $\lambda_{max}=292$ nm.

The CT interaction of the metal centers in the trinuclear complex can be described by the Hush model [21] which is extended to three redox-active metal centers. The diagram (Fig. 2) is based on several assumptions and approximations which are certainly not fully valid, but may be used for a qualitative description. The relative energies of thc ground and lowest-energy MMCT states are obtained from the differences of the redox potentials of the mononuclear complexes which constitute the trinuclear cation. These potentials are $E°=+0.05$ V for $[Ru(NH_3)_6]^{3+/2+}$ [22], +0.86 V for $[Ru(CN)_6]^{3-/4-}$ [6] and 0.06 V for $[Co(NH_3)_6]^{3+/2+}$ [23]. This latter potential may not be quite correct [24], but a modest deviation should not affect our qualitative picture. In addition, the application of those potentials requires that the mononuclear components do not change their redox potentials upon incorporation in the trinuclear complex. Moreover, the representation of the mononuclear components $[Ru(NH_3)_5NC]^{2+}$ and $[Co(NH_3)_5CN]^{2+}$ by the corresponding hexaammine complexes is based on the observation that ammonia and cyanide coordinated via nitrogen have almost the same ligand field strength [3,19a,c]. For $[Co(NH_3)_6]^{2+}$ an additional low-energy excited state with the low-spin configuration $t_{2g}^6e_g^1$ has been included (Fig. 2, dashed line). This state is estimated to lie 6000 cm^{-1} above the high-spin ($t_{2g}^5e_g^2$) ground state [25a–c] which cannot be reached by a spin-allowed MMCT transition terminating at Co(III)(t_{2g}^6). Finally, the central pair of the potential curves (Fig. 2) implies a sufficient interaction of both terminal metals in the MMCT states. This is a reasonable assumption in view of increasing evidence of remote CT interaction in polynuclear complexes [26,27].

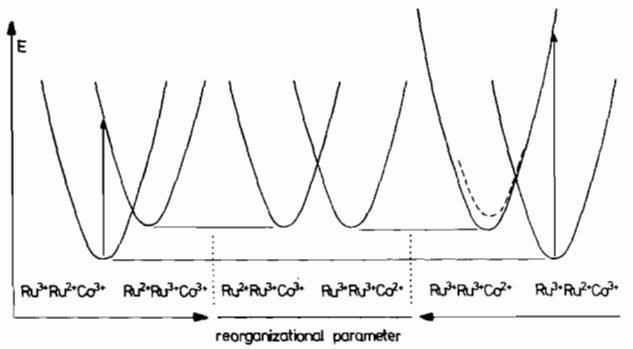

Fig. 2. Potential energy diagram of $[(NH_3)_5Ru(III)(\mu\text{-}NC)\text{-}Ru(II)(CN)_4(\mu\text{-}CN)Co(III)(NH_3)_5]^{2+}$ including optical MMCT transitions.

The horizontal displacements of the potential curves in the pairs (Fig. 2) reflect qualitatively the structural reorganization which is associated with the reduction or oxidation of the metals. This change is relatively small for $Ru^{2+/3+}$ since only the t_{2g} orbitals are affected while the reduction of Co^{3+} leads to the population of σ-antibonding e_g orbitals. This effect is somewhat larger in the high-spin ground state of $[Co(NH_3)_6]^{2+}$ which has to accommodate two electrons in the e_g orbitals [25a–c]. As a result of the larger reorganization energy for the $Co^{3+/2+}$ couple the Ru(II) to Co(III) band appears at much shorter wavelengths than the Ru(II) to Ru(III) MMCT absorption. The Ru(II) to Co(III) MMCT transition could yield Co(II) in the high- or low-spin configuration (Fig. 2). Both transitions are expected to occur at comparable energies ($\Delta E \sim 2000$ cm^{-1}) [25a–c] since the higher energy of the low-spin state is compensated by its smaller reorganization energy. However, in agreement with the reasonably high intensity ($\epsilon=720$) of the absorption at $\lambda_{max}=372$ nm, the MMCT transition from Ru(II) to Co(III) is certainly spin-allowed and yields low-spin Co(II) which finally relaxes to the substitutionally labile high-spin ground state.

Irrespective of the irradiating wavelength the aqueous trinuclear complex underwent only a photoredox decomposition with the formation of Co^{2+} and an unidentified Ru(III) ammine complex. $[Ru(CN)_6]^{3-}$ ($\lambda_{max}=422$ nm, $\epsilon=1050$) [3,28] was not detected in the photolyzed solution. However, the quantum yield of Co^{2+} formation was very small ($\phi=2\times10^{-4}$ at $\lambda_{irr}=577$ nm) when the light was absorbed by the Ru(II) to Ru(III) MMCT band, but rather large ($\phi=0.18$ at $\lambda_{irr}=366$ nm) upon irradiation of the Ru(II) to Co(III) MMCT absorption.

In view of the general photoredox behavior of Co(III) ammine complexes [29] and, in particular, the redox photolysis of $[(NC)_5Ru(\mu\text{-}NC)Co(NH_3)_5]^-$ [3] it is certainly not surprising that direct Ru(II) to Co(III) excitation of the trinuclear complex leads to an efficient decomposition with the formation of Co^{2+}. Ru(II) to Ru(III) MMCT excitation of the trinuclear ion might not be expected to initiate any photoreaction since the binuclear complex $[(NH_3)_5Ru(\mu\text{-}NC)Ru(CN)_5]^-$ is not light sensitive [5]. Contrary to this expectation light absorption by the Ru(II) to Ru(III) MMCT band of the trinuclear complex produces some Co^{2+}. The small quantum yield of this photolysis reflects the competition of electron transfer from the terminal Ru(II) to the central Ru(III) (back to the ground state, left side of Fig. 2) and to Co(III) (generation of the Ru(II) to Co(III) MMCT state, central part of Fig. 2). The latter process requires a much larger activation energy and is thus rather inefficient. In this context it is quite interesting that Co(III) ammine complexes undergo a facile reduction by $[Ru(NH_3)_6]^{2+}$ in the ground state

[30]. As an alternative the small quantum yield of Co(II) formation upon irradiation at 577 nm could be also caused by direct MMCT excitation if the Ru(II) to Co(III) CT band at $\lambda_{max}=372$ nm had a residual extinction at the irradiating wavelength.

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