

Photochemical Redox Decomposition of μ -Cyano-pentacyanoruthenium (II)pentaamminecobalt(III) Ion

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In the complex ion $[(\text{NH}_3)_5\text{Co(III)NCRu(II)(CN)}_5]^-$ both metals are linked by a cyanide bridge. The electronic spectrum of this compound exhibits a new absorption band which does not occur in the spectra of the two isolated Co(III) and Ru(II) complexes which constitute the binuclear complex. This new band is assigned to an intervalence transfer (IT) transition from Ru(II) to Co(III). Upon irradiation into this band the aqueous binuclear complex underwent a redox reaction under formation of Ru(CN)_6^{3-} and Co^{2+} with a quantum yield $\phi = 0.46$.

The mechanism of this photochemical reaction and its relationship to similar thermal redox reactions is discussed.

Im Komplexion $[(\text{NH}_3)_5\text{Co(III)NCRu(II)(CN)}_5]^-$ sind beide Metalle durch eine Cyanidbrücke verbunden. Das Elektronenspektrum dieser Verbindung enthält eine neue Absorptionsbande, die nicht in den Spektren der beiden isolierten Co(III)- und Ru(II)-Komplexe, die den zweikernigen Komplex bilden, auftritt. Diese neue Bande wird einem intervalence transfer (IT)-Übergang vom Ru(II) zum Co(III) zugeordnet. Der in Wasser gelöste Komplex unterliegt einer Redoxreaktion unter Bildung von Ru(CN)_6^{3-} und Co^{2+} mit der Quantenausbeute $\phi = 0,46$, wenn Licht in diese IT-Bande eingestrahlt wird. Der Mechanismus dieser photochemischen Reaktion und ähnlicher thermischer Redoxreaktionen wird diskutiert.

Introduction

Thermal electron transfer reactions between coordination compounds have been extensively investigated [1]. An electron exchange between two metal centers may not only be achieved by thermal activation but also by an optical charge transfer transition from one metal to another [2, 3, 4]. This phenomenon is well known as intervalence transfer (IT) [2, 3]. However, it has not yet been observed to our knowledge that light-induced intervalence transfer does lead to a permanent and detectable change in the valency of the participating transition metals. Apparently fast radiationless transitions restore the thermodynamically stable oxidation states which existed prior to IT excitation. But under favorable conditions it should be possible to observe a photochemical redox reaction initiated by IT excitation of a complex containing two transition metal centers.

We have explored this possibility and have found that the irradiation of aqueous $[(\text{NH}_3)_5\text{Co(III)NCRu(II)(CN)}_5]^-$ leads to a redox reaction under formation of Co^{2+} and Ru(CN)_6^{3-} . We believe that this photochemical redox reaction is initiated by a direct optical electron transfer from Ru(II) to Co(III). If Ru(II) is replaced by Fe(II) the redox reaction occurs as a thermal process [5, 6]. In our opinion these photochemical and thermal redox reactions are closely related processes which

find a common explanation on the basis of a theory advanced by N. S. Hush [3, 7].

Experimental Section

Materials. $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ [8], $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ [9], and $\text{K}_4\text{Ru(CN)}_6$ [10] were prepared according to the literature.

$\text{K}_3\text{Ru(CN)}_6$, $\text{K}_3\text{Ru(CN)}_6$ could not be isolated. A solution of $\text{K}_3\text{Ru(CN)}_6$ was prepared by oxidation of an acidic solution of $\text{K}_4\text{Ru(CN)}_6$ with H_2O_2 . The spectrum of this solution shows all the characteristic absorption bands of $\text{K}_3\text{Ru(CN)}_6$ [11].

$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]_4[\text{Ru(CN)}_6]_3 \cdot 5\text{H}_2\text{O}$. Equal volumes of diluted solutions of $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ and $\text{K}_4\text{Ru(CN)}_6$ were mixed, whereby slow precipitation of insoluble, yellow crystals of $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]_4[\text{Ru(CN)}_6]_3 \cdot 5\text{H}_2\text{O}$ took place. The crystals were filtered out, washed with water, ethanol, ether, and dried under reduced pressure at room temperature. The yield was essentially quantitative. Anal. Calcd. for $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]_4[\text{Ru(CN)}_6]_3 \cdot 5\text{H}_2\text{O}$: C, 14.30; N, 34.90; H, 5.15; Co, 15.63. Found: C, 14.40; N, 34.67; H, 5.20; Co, 15.59.

$\text{Na}[(\text{NH}_3)_5\text{CoNCRu(CN)}_5] \cdot 3\text{H}_2\text{O}$. $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]_4[\text{Ru(CN)}_6]_3 \cdot 5\text{H}_2\text{O}$ was heated at 60° for several days, whereby its color changed from yellow to dark brown. The brown product was taken up with water. An insoluble residue was filtered out and discarded. The clear solution was percolated through a cation-exchange column. The orange solution which passed the cation-exchange column was then percolated through an anion-exchange column where it was absorbed. Upon elution with a solution of sodium chloride the orange solution was recovered and evaporated under reduced pressure until orange crystals separated. This material was collected

by filtration and dissolved in water. Addition of ethanol yielded an orange product which was filtered out, washed with ethanol and ether. Anal. Calcd. for $\text{Na}[(\text{NH}_3)_5\text{CoNCRu}(\text{CN})_5] \cdot 3\text{H}_2\text{O}$: C, 15.0; N, 32.12; H, 4.42. Found: C, 14.91; N, 32.08; H, 5.30.

Photolysis Procedure

The light source used was a 100 W Osram high-pressure mercury lamp. A Schott interference filter 366 limited the ultraviolet radiation emitted to the wavelength of the mercury line at 366 nm. Alternatively, the filter combination of the interference filters Balzer K 3 plus Balzer K 4 transmitted light between 520 and 560 nm.

The photolysis were carried out at room temperature in a 5-cm cylindrical spectrophotometer cell, using concentrations of complex such as to have essentially complete light absorption (about $3 \cdot 10^{-3}$ M for irradiations in the uv region and 10^{-2} M for those in the visible region). An aliquot of the solution to be analysed was kept in the dark, at the same temperature, so that any thermal reaction could be noted and allowed for. However, the rate constant for the thermal reaction is very small, and since irradiation times did not exceed 40 minutes, correction for the thermal reaction was negligible. The total amount of photolysis was limited to about 10% to avoid possible secondary photochemical reactions. Absorbed light intensities were determined by Ferrioxalate actinometry [12] or by Reineckate actinometry [13] in the visible region.

Analytical Procedure

Cobaltous ion was determined by forming the blue complex ion, $\text{Co}(\text{NCS})_4^{2-}$ in a water-acetone solution and measuring the absorbance ($\epsilon = 1.7 \cdot 10^3$ at 625 nm), according to a procedure taken from the literature [14].

Measurements

Infrared spectra were measured with a Perkin Elmer 325 IR spectrophotometer. Samples were bromide pellets. Visible and ultraviolet spectra were measured in 1-cm cells with a Cary 14 recording spectrophotometer and a Zeiss PMQ II spectrophotometer for measurements at selected wavelengths.

Results and Discussion

The complex ion $[(\text{NH}_3)_5\text{Co}(\text{III})\text{NCRu}(\text{II})(\text{CN})_5]^-$ was prepared in analogy to the synthesis of $[(\text{NH}_3)_5\text{Co}(\text{III})\text{NC} \cdot \text{Co}(\text{III})(\text{CN})_5]$ [15]. The existence of a CoNCRu bridge was confirmed by IR spectroscopy. The compound $[\text{Co}(\text{NH}_3)_5 \cdot \text{H}_2\text{O}]_4[\text{Ru}(\text{CN})_6]_3 \cdot 5\text{H}_2\text{O}$, which was obtained in the first step of the synthesis, shows essentially the same absorption spectrum as $\text{K}_4[\text{Ru}(\text{CN})_6]$ in the region of the cyanide stretching vibrations. The absorption maximum of both compounds, which shows some structure, appears at 2050 cm^{-1} . However, the final product $\text{Na}[(\text{NH}_3)_5\text{CoNCRu}(\text{CN})_5] \cdot 3\text{H}_2\text{O}$ exhibits a well separated additional band (2135 cm^{-1}) at higher wavenumbers which is characteristic of bridging cyanide [16].

The electronic structure of a binuclear complex is influenced by the interaction of both metal centers [3, 4]. If the interaction is weak the electronic structure can be described as the sum of the electronic structures of two mononuclear complexes which constitute the binuclear complex. For example, the absorption spectrum of $[(\text{NH}_3)_5\text{Co}(\text{III})\text{NC} \cdot \text{Co}(\text{III})(\text{CN})_5]$ [15] consists of the superimposed spectra of $\text{Co}(\text{NH}_3)_6^{3+}$ (the ligand field strength of cyanide coordinated via nitrogen is about the same as that of ammonia) [15, 17, 18] and $\text{Co}(\text{CN})_6^{3-}$. Similarly, the spectrum of $[(\text{NH}_3)_5\text{Co}(\text{III}) \cdot \text{CNC}(\text{III})(\text{CN})_5]$ [17], which is a linkage isomer of $[(\text{NH}_3)_5 \cdot$

$\text{CoNCCo}(\text{CN})_5]$, has been shown to be a superimposition of the spectra of $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ and $\text{Co}(\text{CN})_5\text{NH}_3^{2-}$. The IR spectra of these binuclear complexes are also largely identical with those of the mononuclear components with the exception of the additional bands caused by the bridging cyanide. However, an important consequence of the weak interaction of both metal centers is the possibility of the occurrence of electronic transitions between both metals which give rise to additional absorption bands in the electronic spectrum [2, 3, 4]. Since such a transition leads to the reduction of one metal and oxidation of the other one this charge transfer has been termed intervalence transfer (IT) [2, 3]. In the case of the binuclear complexes mentioned above an IT band does not occur in the experimentally accessible region probably because the energy of any of the possible transitions from $\text{Co}(\text{III})/\text{Co}(\text{III})$ to $\text{Co}(\text{II})/\text{Co}(\text{IV})$ is very high. However, the complex ions $[(\text{NH}_3)_5\text{Ru}(\text{II})\text{pyrazine Ru}(\text{III}) \cdot (\text{NH}_3)_5]^{5+}$ [19] and $[(\text{NC})_5\text{Fe}(\text{II})\text{CNFe}(\text{III})(\text{CN})_5]^{6-}$ [20] exhibit IT bands even in the near infrared since the electron exchange does not require much energy. In analogy to these examples the ion $[(\text{NH}_3)_5\text{Co}(\text{III})\text{NCRu}(\text{II})(\text{CN})_5]^-$ may also be expected to contain weakly interacting metal centers. This assumption is supported by the IR spectrum of the binuclear complex which is essentially identical with those of the constituting mononuclear complexes, again with the exception of the additional band caused by the bridging cyanide. Since also the electronic spectrum should be composed of the spectra of both components the binuclear complex should exhibit only the ligand field bands of $\text{Co}(\text{NH}_3)_6^{3+}$ above 300 nm (Fig. 1) because $\text{Ru}(\text{CN})_6^{4-}$ does not absorb above 300 nm [11, 21]. However, only the first ligand field band of $\text{Co}(\text{NH}_3)_6^{3+}$ at 475 nm is clearly identified in the spectrum of the binuclear complex (Fig. 1). The second ligand field band of $\text{Co}(\text{NH}_3)_6^{3+}$ at 340 nm is hidden under another more intense band at 375 nm. In our opinion this new absorption, which does not have a counterpart in both mononuclear complexes, belongs to an IT transition from $\text{Ru}(\text{II})$ to $\text{Co}(\text{III})$ which is the energetically most probable redox process between $\text{Ru}(\text{II})$ and $\text{Co}(\text{III})$. This assignment is also supported by the photochemical redox reaction of $[(\text{NH}_3)_5\text{Co}(\text{III})\text{NCRu}(\text{II})(\text{CN})_5]^-$ which will be discussed below. Only recently an absorption band in the spectrum of $[(\text{histidinato})_2\text{Co}(\text{III})\text{NCF}(\text{II}) \cdot (\text{CN})_5]^{3-}$ near 500 nm was assigned to an IT $[\text{Fe}(\text{II})$ to $\text{Co}(\text{III})]$ transition [22].

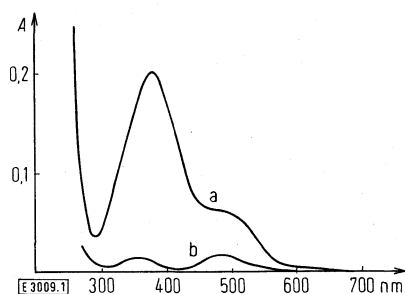


Fig. 1
Electronic absorption spectra
a $3 \cdot 10^{-4}$ M $\text{Na}[(\text{NH}_3)_5\text{CoNCRu}(\text{CN})_5]$
b $3 \cdot 10^{-4}$ M $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

expected to be rather slow because it is initiated by a spin forbidden transition. However, it has been shown recently that radiationless transitions even if they are strongly spin forbidden can be very fast compared to the rates of chemical redox reactions [35].

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