luminescence we assign to delayed fluorescence was not observed in the three cases in which the energy barrier is largest, for which return to the quartet either would not occur at all or would occur so rarely that any delayed fluorescence would be below the limit of detectability. The observation of delayed fluorescence tempts one to think of rapid equilibration between the excited quartet and the phosphorescent doublet. As discussed further below, we do not have any evidence that there is a thermally equilibrated excited quartet, so we do not speak of an electronically equilibrated quartet either. We do not know the ratio of intersystem crossing rates to decay rates for the excited quartet.

As a corollary, the applicability of the FAS model itself is supported. Agreement for the octahedral complexes is better than for complexes that are distorted from octahedral. Even the latter fall generally within the range expected. Furthermore, the discrepancies that exist in those cases are considerably reduced from what appears in Table I, if one introduces approximate corrections for the deviations from octahedral symmetry. These were worked out in another place.[22] Additional detail is becoming available for a wider variety of complexes about the states existing in ambient solutions. For example, it has been reported that the ordering of the doublet states in quadrate Cr(III) complexes changes with solvent.[23] One of our systems, *trans*-$[Cr(py)_4F_2]^+$ has the atypical, inverted ordering. The FAS model does not address such details.

The present work agrees with an earlier study,[16] based on a quite different approach, in concluding that the lifetime of the lowest doublet state varies inversely with the energy separation between the lowest doublet and the excited quartet for energy gaps up to some limit.

As a further test of whether there is a common decay mechanism for doublets in all Cr(III) compounds, consider the Barclay–Butler plot of Figure 3. It is evident that the correlation noted previously[11] for the long-lived species is destroyed when the short-lived complexes are included in the analysis. One must conclude that there are at least two important decay mechanisms, one of which dominates for the long-lived species and the other for the short-lived species. The former exhibits an activation energy that is never too far from 40 kJ mol^{-1} while the latter shows an activation energy that correlates reasonably well with estimates for the barrier to RISC.

What is the significance of the limiting value of 35–40 kJ mol^{-1} for the activation energy of the lifetime-limiting process in the lowest doublet? It might conceivably mean that there is some direction in the multidimensional coordinate space in which a barrier between doublet and excited quartet has a constant value of that magnitude, despite the fact that the spectroscopic energy separation has no such limit. More likely, however, is the common suggestion that there is some process in the doublet itself which sets that limit, as has been assumed throughout this paper. This process may be taken to be photochemistry, although that term would need some elucidation. It may be better to think of a more generalized curve crossing.

Although we have considered "a limit" to the measured activation energy from the point of view of RISC losing out to a competitive process, we must now stress that the "limit" is not a unique value. Rather, the range of activation energies attributed to the "photochemical" process extends over a factor of 2.[9-11] While still quite small, that may be large enough to support correlations with some parameter governing such processes, as has been discussed in those reports.

We also point out that the very strong ligand field instances ($Cr(CN)_6^{3-}$ and the polypyridyl complexes) have always been considered to be unlikely candidates for control of doublet lifetime by RISC. If the regime of domination by "chemical reaction" is reached already with the compounds treated in this paper, one would expect that those very strong field cases would fall also within that class. Since we are aware of no serious dispute in that area, we have not reviewed the substantial and convincing literature.

Finally, we would remark that RISC itself is also somewhat ill-defined if, as now seems possible, a thermally relaxed quartet does not exist.[24] It may be well to think in terms of a multidimensional potential surface having saddlepoint barriers in several directions. Then the terms "reverse intersystem crossing" and "photochemical reaction" are attempts to label particular saddlepoints in ways that are useful for correlating patterns of behavior observed in different molecules over a range of conditions, but the terms should not automatically carry all the connotations they have in other branches of photophysics.

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Registry No. $[Cr(urea)_6]^{3+}$, 15276-06-9; $[Cr(ox)_3]^{3-}$, 15054-01-0; $[Cr(NCS)_6]^{3-}$, 15276-09-2; *trans*-$[Cr(NH_3)_2(NCS)_4]^-$, 16248-93-4; *trans*-$[Cr(en)_2(NCS)_2]^+$, 29845-02-1; $[Cr(en)_3]^{3+}$, 15276-13-8; *trans*-$[Cr(py)_4F_2]^+$, 47514-84-1.

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Contribution from the Institut für Anorganische Chemie der Universität Regensburg, D-8400 Regensburg, Federal Republic of Germany

Heterobinuclear Transition-Metal Complexes. Synthesis and Optical Metal to Metal Electron Transfer

A. Vogler,* A. H. Osman, and H. Kunkely

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Binuclear mixed-valence transition-metal complexes have been investigated extensively during the last 15 years.[1-6] Usually these mixed-valence compounds contain one metal in two different oxidation states connected by a bridging ligand. Such homobinuclear complexes are characterized by low-energy metal to metal charge-transfer (MMCT) absorption bands that are assigned to an electronic transition from the reducing to the oxidizing metal. Most investigations were carried out with Ru(II)/Ru(III) complexes.[1-5]

In a more general sense the concept of mixed-valence compounds can be extended to heterobinuclear complexes that contain different metals as reducing and oxidizing centers.[7] Due to the redox asymmetry of such systems MMCT bands are shifted to higher energies and occur frequently in the visible region. In many cases bridging ligands such as pyrazine were used to facilitate the inner-sphere metal–metal interaction.[1-5] These ligands are not well suited to observe MMCT absorptions in the visible region because CT transitions from the reducing metal to the bridging ligand (MLCT) occur in the same energy range. Intense MLCT bands may then hide or obscure MMCT absorptions. Cyanide as bridging ligand avoids these complications since MLCT transitions involving this ligand do not occur at low energies.[8]

In 1975 we started to investigate cyanide-bridged heterobinuclear mixed-valence compounds with particular reference to their

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photochemical properties.[9,10] The present work is an extension of these studies. We selected Fe(II), Ru(II), and Os(II) as reducing and Os(III), Co(III), and Cr(III) as oxidizing metals.[11]

Experimental Section

Materials. $K_4[Ru(CN)_6]$ was purchased from Heraeus. $[Os(NH_3)_5N_2]Cl_2$,[12] $[Os(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$,[13] $K_4[Os(CN)_6]$,[14] and $[Cr(NH_3)_5H_2O](NO_3)_3$[15] were prepared according to published procedures.

Syntheses. $Na[(NH_3)_5Os^{III}(\mu\text{-}NC)Fe^{II}(CN)_5]$. To a solution of 1.24 g of $[Os(NH_3)_5N_2]Cl_2$ in 50 mL of 0.2 M HCl was added a solution of 0.99 g of $K_3[Fe(CN)_6]$ in 20 mL of water. The solution turned dark blue to violet. After the solution was stirred for 1 h at room temperature it was heated to boiling for a few seconds. The solution was then filtered and run through a cation-exchange resin (Dowex 50W-X8, 20–50 mesh) in the Na^+ form. The binuclear complex was eluted with water. The eluted solution was concentrated by evaporation to 10 mL. After slow addition of 20 mL of methanol, dark blue crystals separated. After the mixture was allowed to stand for 10 min, the desired compound was collected by filtration and washed with methanol/H_2O (2:1) several times and then with methanol, acetone, and finally ether. It was dried under vacuum; yield 0.75 g (≈50%). Anal. Calcd for $C_6H_{15}N_{11}FeNaOs$: C, 14.12; H, 2.96; N, 30.19. Found: C, 14.12; H, 3.38; N, 29.98.

$Na[(NH_3)_5Os(\mu\text{-}NC)Ru(CN)_5]$. A solution of 0.8 g of $K_4[Ru(CN)_6]$ in 20 mL of water was saturated with argon. To this solution were added 0.1 mL CF_3SO_3H and, under stirring, 1.7 g of $[Os(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ in small portions. The next portion was added only after the previous one was completely dissolved. After the mixture was allowed to stand for 10 min, it was acidified slightly by addition of $HClO_4$ and passed through a cation-exchange resin (Dowex 50W-X8, 20–50 mesh) in the Na^+ form. The eluted dark red solution was concentrated by evaporation to 10 mL. Upon addition of 10 mL of methanol, a red powder precipitated. It was recrystallized twice by dissolution in water and reprecipitation upon addition of methanol. The red powder was collected by filtration, washed with methanol, acetone, and finally with ether, and dried under vacuum; yield 0.35 g (31%). Anal. Calcd for $C_6H_{15}N_{11}NaOsRu$: C, 12.97; H, 2.7; N, 27.73. Found: C, 13.12; H, 2.9; N, 27.76.

$Na[(NH_3)_5Os(\mu\text{-}NC)Os(CN)_5]\cdot 5H_2O$. The preparation was achieved by the same procedure that was used for the synthesis of $Na[(NH_3)_5Os(\mu\text{-}NC)Ru(CN)_5]$. The 0.8-g sample of $K_4[Ru(CN)_6]$ was replaced by 1 g of $K_4[Os(CN)_6]$. The pure compound was obtained as red-violet crystals; yield 0.3 g (23%). Anal. Calcd for $C_6H_{25}N_{11}O_5NaOs_2$: C, 9.81; H, 3.4; N, 20.97. Found: C, 9.85; H, 3.1; N, 21.03.

$K_6[(NC)_5Co(\mu\text{-}NC)Os(CN)_5]\cdot 12H_2O$. A solution of 1.5 g of $K_4[Os(CN)_6]$ in 10 mL of water was cooled in an ice bath. A 0.5-g sample of PbO_2 was added. Under stirring, 1 mL of 0.1 M H_2SO_4 was slowly added. An excess of acid should be avoided since $K_3[Os(CN)_6]$, which is formed in this reaction, is not very stable in acidic solution. Unreacted PbO_2 was removed by filtration. The gold-yellow solution was saturated with nitrogen and added to a solution of 0.83 g of $K_3[Co(CN)_5]$[16] in 15 mL of water saturated with nitrogen. The combined solution was stirred for 10 min. Exclusion of air was then no longer necessary. Upon addition of 80 mL of methanol, a red oil and a yellow powder precipitated. The oil and the powder were collected by decantation and filtration. The crude product was purified by several recrystallizations from water/methanol. After the product was dried under vacuum, a slightly yellow powder was obtained; yield 0.96 g (36%). Anal. Calcd for $C_{11}H_{24}N_{11}O_{12}CoK_6Os$: C, 13.40; H, 2.45; N, 15.62. Found: C, 13.17; H, 1.52; N, 15.16.

$Na[(NH_3)_5Cr(\mu\text{-}NC)Fe(CN)_5]\cdot 2H_2O$. To a solution of 3.4 g of $[Cr(NH_3)_5H_2O](NO_3)_3$ in 40 mL of water was slowly added a solution of 2.1 g of $K_4[Fe(CN)_6]\cdot 3H_2O$ in 20 mL of water. After the mixture was stirred in the dark for 10 min, the precipitate was collected by filtration, washed with water, ethanol, acetone, and ether, and dried under vacuum. The yellow material was heated at 60 °C for 3 h. The solid turned dark orange. It was treated with 100 mL of 0.1 M $HClO_4$. A dark red oil separated and was discarded. The clear red solution was passed through a cation-exchange resin (see above) in the Na^+ form. The product was eluted with 100 mL of water. Upon addition of 100 mL of methanol an orange powder precipitated. It was collected by filtration, washed with methanol and ether, and dried under vacuum; yield 0.52 g (23%). Anal. Calcd for $C_6H_{19}N_{11}O_2FeNa$: C, 17.65; H, 4.69; N, 37.75. Found: C, 17.45; H, 5.14; N, 37.54.

Photolysis. The light source was an Osram HBO 100 W/2 lamp. A Schott PIL 366 interference filter was used for the selection of the mercury line at 366 nm. Photolyses were carried out in aqueous solution in 1-cm spectrophotometer cells at room temperature. For quantum-yield determinations the complex concentrations (≈10^{-3} M) 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 photoproducts. Absorbed light intensities were determined by a Polytec pyroelectric radiometer, which was calibrated and equipped with a RkP-345 detector. At 366 nm the light intensity was approximately 10^{-8} einstein s^{-1}.

Progress of the photolyses was monitored by UV–visible spectrophotometry. The extent of photolysis of $[(NC)_5CoNCOs(CN)_5]^{6-}$ in acidic solution was determined by measuring the increase of extinction at 412 nm. At this wavelength the photoproduct $[Os(CN)_6]^{3-}$ has an extinction coefficient of ϵ = 1500 M^{-1} cm^{-1}.[17] The amount of photolysis of $[(NH_3)_5CrNCFe(CN)_5]^-$ was determined by measuring the decrease of extinction at the absorption maximum of the starting complex (λ_{max} = 376 nm, ϵ = 2400 M^{-1} cm^{-1}). The products of the photolysis have an extinction coefficient of about ϵ = 1200 M^{-1} cm^{-1} at this wavelength.

Instrumentation. Electronic absorption spectra were obtained on a Varian-Techtron Super Scan 3 recording spectrophotometer or a Kontron Uvikon 810 spectrophometer.

Results and Discussion

Synthesis. The formation of the binuclear complex ions $[(NH_3)_5Os^{III}NCM^{II}(CN)_5]^-$ with M = Fe, Ru, and Os by the photochemical reaction of the ion pairs $[Os(NH_3)_5Cl]^{2+}[M(CN)_6]^{4-}$ was shortly mentioned before.[7] However, pure compounds were not obtained by this procedure.[11] The following methods yielded analytically pure materials. The salt $Na[(NH_3)_5Os^{III}NCFe^{II}(CN)_5]$ was prepared in aqueous solution according to the stoichiometric equation

$$[Os^{II}(NH_3)_5N_2]^{2+} + [Fe^{III}(CN)_6]^{3-} \rightarrow [(NH_3)_5Os^{III}NCFe^{II}(CN)_5]^- + N_2$$

Since $[Os(NH_3)_5N_2]^{2+}$ is rather substitution inert,[18] the first step of the reaction is certainly an outer-sphere oxidation of Os(II) by Fe(III). The N_2 ligand of the oxidized complex $[Os(NH_3)_5N_2]^{3+}$ is known to be very labile.[18] It is apparently substituted by $[Fe(CN)_6]^{4-}$, yielding the binuclear complex. The sodium salt is obtained as a dark blue crystalline material.

For the preparation of the corresponding compounds $Na[(NH_3)_5Os^{III}NCM(CN)_5]$ with M = Ru and Os another procedure was chosen since the oxidized cyano complexes $[M(CN)_6]^{3-}$ are not very stable and difficult to prepare as pure substances.[17,19] A simple substitution reaction proved to be successful:

$$[Os^{III}(NH_3)_5(CF_3SO_3)]^{2+} + [M^{II}(CN)_6]^{4-} \rightarrow [(NH_3)_5Os^{III}NCM(CN)_5]^- + CF_3SO_3^-$$

$CF_3SO_3^-$ is known to be a weakly coordinating ligand that is easily substituted by better coordinating anions,[13] in our case $M(CN)_6^{4-}$. The binuclear Os/Ru complex was obtained as a red powder that was difficult to crystallize. The Os/Os compound was isolated as a red-violet crystalline material.

The salt $K_6[(NC)_5Co^{III}NCOs^{II}(CN)_5]$ was prepared in analogy to the corresponding anions $[(NC)_5Co^{III}NCM^{II}(CN)_5]^{6-}$ with M = Fe[16] and Ru.[10] The oxidation of $[Os(CN)_6]^{4-}$ by PbO_2 in dilute sulfuric acid yielded a solution of $[Os(CN)_6]^{3-}$ which reacted with $[Co(CN)_5]^{3-}$ according to

$$[Co^{II}(CN)_5]^{3-} + [Os^{III}(CN)_6]^{3-} \rightarrow [(NC)_5Co^{III}NCOs^{II}(CN)_5]^{6-}$$

This reaction proceeds probably by an inner-sphere electron-

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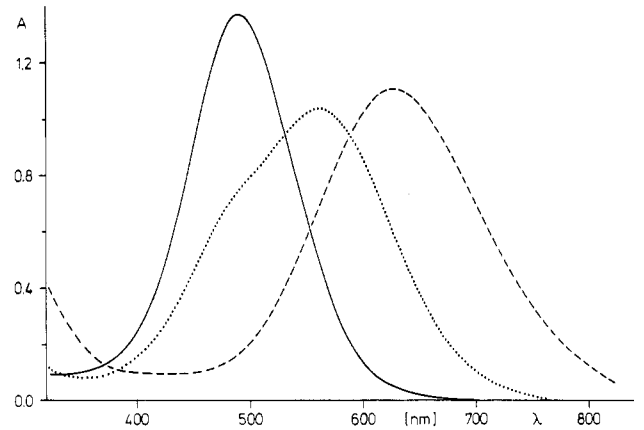

Figure 1. Absorption spectra of aqueous $Na[(NH_3)_5Os^{III}NCM^{II}(CN)_5]$ with M = Fe (6.75×10^{-4} M; --), Ru (7.40×10^{-4} M; —), and Os (4.97×10^{-4} M; ···) at room temperature, 1-cm cell.

Table I. Spectral Data for MMCT Bands of Binuclear Complexes

complex	$\bar{\nu}_{max}$,[a] cm^{-1}	ϵ,[b] M^{-1} cm^{-1}	$\bar{\nu}_{1/2}$,[c] cm^{-1}
$[(NH_3)_5Os^{III}NCFe^{II}(CN)_5]^-$	15920	1640	4320
$[(NH_3)_5Os^{III}NCRu^{II}(CN)_5]^-$	20410	1840	4520
$[(NH_3)_5Os^{III}NCOs^{II}(CN)_5]^-$	17890	2090	6130
$[(NH_3)_5Cr^{III}NCFe^{II}(CN)_5]^-$	26600	2400	6310
$[(CN)_5Co^{III}NCOs^{II}(CN)_5]^{6-}$	27780	730	

[a] Energy of absorption maximum. [b] Molar extinction coefficient. [c] Bandwidth at half-maximum.

transfer mechanism leading directly to the stable bridged complex.

The binuclear anion $[(NH_3)_5Cr^{III}NCFe^{II}(CN)_5]^-$ was synthesized before but obtained as an impure material.[7,11] According to the elemental analysis it was described with the composition $[(NH_3)_4(H_2O)CrNCFe(CN)_5]^-$.[7] The pure salt $Na[(NH_3)_5CrNCFe(CN)_5]\cdot 2H_2O$ was prepared by a solid-state reaction that was also used to prepare numerous other cyanide-bridged binuclear complexes.[9,20] Generally, a salt consisting of a cyano complex and a complex of opposite charge containing a volatile ligand such as H_2O is heated. The solid-state reaction is a substitution. The volatile ligand is replaced by the cyano complex. It our case, when aqueous solutions of $[Cr(NH_3)_5H_2O]^{3+}$ and $Fe(CN)_6^{4-}$ were mixed, the salt $[Cr(NH_3)_5H_2O]_4[Fe(CN)_3]_3$ precipitated. Heating of the salt led to the substitution. After purification the binuclear Cr/Fe complex was obtained as an orange powder.

Optical Metal to Metal Electron Transfer. Metal to Metal Charge-Transfer (CTTM) Absorption Bands. The electronic spectra of the binuclear complexes $[(NH_3)_5Os^{III}NCM^{II}(CN)_5]^-$, with M = Fe, Ru, and Os, $[(NH_3)_5Cr^{III}NCFe^{II}(CN)_5]^-$, and $[(NC)_5Co^{III}NCOs^{II}(CN)_5]^-$ are characterized by a fairly intense absorption band (Figures 1–3, Table I) in the visible or near-UV region. This band is assigned to a MMCT transition from the reducing metals Fe(II), Ru(II), and Os(II) to the oxidizing metals Os(III), Co(III), and Cr(III). This assignment requires a weak interaction between both metals in the binuclear complexes.[1-6] Consequently, in addition to the MMCT bands the electronic spectra of the binuclear complexes should consist of the spectra of their mononuclear components.

These components are the hexacyano complexes $[M(CN)_6]^{4-}$, $[Os(NH_3)_5NC]^{2+}$, $[Cr(NH_3)NC]^{2+}$, and $[Co(CN)_5NC]^{3-}$. The latter three complexes do not exist since cyanide, which coordinates as terminal ligand via nitrogen, does not form stable complexes. However, it has been shown that the ligand field strength of a bridging cyanide coordinated via nitrogen compares well with that of ammonia.[9-10] It follows that the binuclear complexes should show spectral features of the mononuclear components $[M(CN)_6]^{4-}$,[17,21] $[Os(NH_3)_6]^{3+}$,[12] $[Cr(NH_3)_6]^{3+}$,[22] and $[Co(CN)_5NH_3]^{2-}$[23] in addition to the MMCT bands.

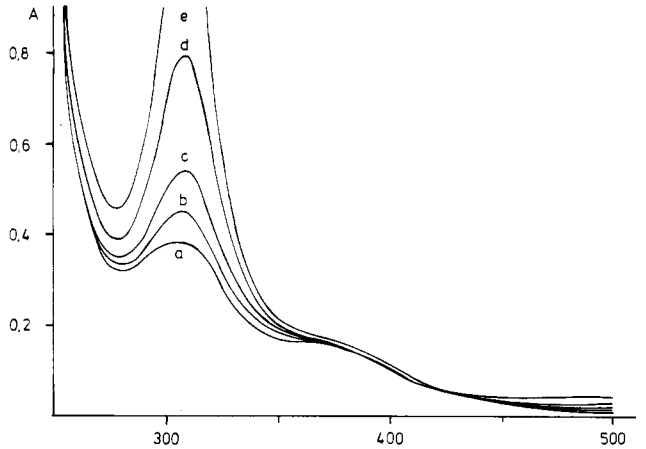

Figure 2. Spectral changes during the photolysis of 2.18×10^{-4} M $K_6[(NC)_5Co^{III}NCOs^{II}(CN)_5]\cdot 12H_2O$ in 1 M KOH saturated with oxygen at (a) 0 and (e) 160 s irradiation time, with λ_{irr} = 366 nm and a 1-cm cell.

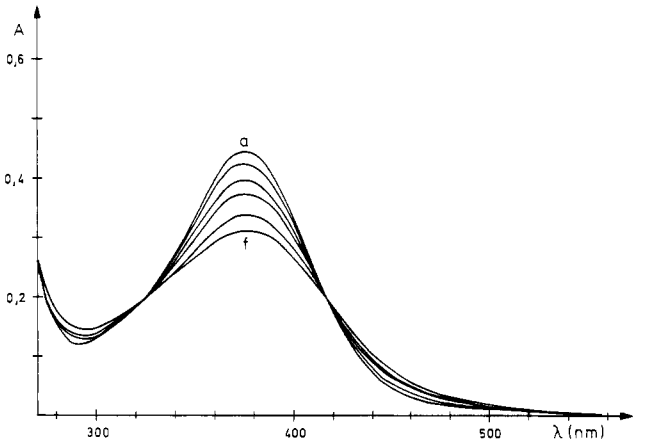

Figure 3. Spectral changes during the photolysis of aqueous 1.87×10^{-4} M $Na[(NH_3)_5Cr^{III}NCFe^{II}(CN)_5]\cdot 2H_2O$ at (a) 0 and (f) 15 min irradiation time, with λ_{irr} = 366 nm and a 1-cm cell.

The complex $[Os(NH_3)_6]^{3+}$ absorbs only weakly at λ_{max} = 229 (ϵ = 759 M^{-1} cm^{-1}) and 221 nm (ϵ = 760 M^{-1} cm^{-1}),[12] while $[M(CN)_6]^{4-}$ shows very intense MLCT bands in the UV region (M = Fe, λ_{max} = 218 nm, ϵ = 24200 M^{-1} cm^{-1}; M = Ru, λ_{max} = 206 mm; M = Os, λ_{max} = 212 nm, ϵ = 47400 M^{-1} cm^{-1}).[17,21] The UV spectra of $[(NH_3)_5Os^{III}NCM^{II}(CN)_5]^-$ are indeed dominated by the intense MLCT bands of $[M(CN)_6]^{4-}$. In the case of $[(NH_3)_5OsNCOs(CN)_5]^-$ an alternate description as the redox isomer $[(NH_3)_5Os^{II}NCOs^{III}(CN)_5]^-$ is feasible but not consistent with these observations. The intense long-wavelength bands of $[Os^{III}(CN)_6]^{3-}$ do not appear in the spectrum of the binuclear complex.[17] The increase of the energy of the MMCT band (Table I) from M = Fe to Os and Ru is also in qualitative agreement with the variation of the redox potentials of $[M(CN)_6]^{3-/4-}$ (M = Fe, $E_{1/2}$ = +0.19 V vs. SCE; M = Os, $E_{1/2}$ = +0.40 V; M = Ru, $E_{1/2}$ = +0.70 V).[24]

The complex $Cr(NH_3)_6^{3+}$ shows weak ligand field (LF) bands in the visible and an increasing absorption with decreasing wavelength in the UV region.[22] In addition to the MMCT band the electronic spectrum of $[(NH_3)_5Cr^{III}NCFe^{II}(CN)_5]^-$ displays only the MLCT band of $[Fe(CN)_6]^{4-}$ as a prominent feature. In the binuclear complex this absorption is slightly shifted (λ_{max} = 210 nm). The LF bands of $[Cr(NH_3)_6]^{3+}$ do not appear in the spectrum of the binuclear complex. They are certainly obscured by the more intense MMCT band. The absorption spectrum of

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$[(NC)_5Co^{III}NCOs^{II}(CN)_5]^{6-}$ is less instructive since it is rather featureless at short wavelength in the UV region. However, the MMCT assignment of the band at λ_{max} = 359 nm (Table I) is supported by the spectra of the analogous complexes $[(NC)_5Co^{III}NCM^{II}(CN)_5]^{6-}$ with M = Fe and Ru. Within the series M = Fe (λ_{max} = 385 nm),[10] Os, and Ru (λ_{max} = 312 nm)[10] the MMCT bands move to higher energies since the reducing power of $M(CN)_6^{4-}$ decreases in this direction.

Photochemistry. The binuclear complexes $[(NH_3)_5Os^{III}NCM^{II}(CN)_5]^-$ with M = Fe, Ru, and Os are not light-sensitive upon MMCT excitation. The redox isomers $[(NH_3)_5Os^{II}NCM^{III}(CN)_5]^-$, which are formed upon CT excitation, are certainly not very labile toward substitution. A rapid back electron transfer regenerates apparently the starting Os^{III}/M^{II} complexes.

Upon MMCT excitation (λ_{irr} = 366 nm) the complex $[(NC)_5Co^{III}NCOs^{II}(CN)_6]^{6-}$ underwent a photolysis in aqueous solution in analogy to the related ions $[(NC)_5Co^{III}NCM^{II}(CN)_5]^{6-}$ with M = Fe and Ru.[10] When the photolysis was carried out in basic solution (1 M KOH) and in the presence of oxygen, the spectral changes during the photolysis (Figure 2) indicated the formation of the superoxo complex $[Co_2(CN)_{10}O_2]^{5-}$ (λ_{max} = 310 nm, ϵ = 24 800 M^{-1} cm^{-1}).[25] The absorption of this complex is so intense that it obscures bands of other photoproducts. In acidic solution (10^{-4} M HCl) the superoxo complex is not formed. The spectral variations during the photolysis were consistent with the formation of $[Os(CN)_6]^{3-}$, which shows absorption maxima at 412, 332, 307, and 280 nm.[17]

The quantum yield for the formation of $[Os(CN)_6]^{3-}$ in acidic solution was Φ = 0.32 at λ_{irr} = 366 nm. According to these observations and in agreement with previous results that were obtained with $[(NC)_5Co^{III}NCM^{II}(CN)_5]^{6-}$ (M = Fe and Ru), the photolysis should proceed by the following mechanism:

$$[(NC)_5Co^{III}NCOs^{II}(CN)_5]^{6-} \xrightarrow{h\nu} [(NC)_5Co^{II}NCOs^{III}(CN)_5]^{6-}$$

$$[(NC)_5Co^{II}NCOs^{III}(CN)_5]^{6-} \rightarrow [Co^{II}(CN)_5]^{3-} + [Os^{III}(CN)_6]^{3-}$$

$$2[Co(CN)_5]^{3-} + O_2 \rightarrow [Co_2(CN)_{10}O_2]^{6-}$$

The redox isomer Co^{II}/Os^{III} produced in the primary photochemical step is certainly strongly distorted at Co^{II}.[10] This distortion and the electrostatic repulsion of both anionic components of the redox isomer apparently facilitates the dissociation into the mononuclear complexes. The dissociation then competes successfully with back electron transfer within the redox isomer.

The anion $[Co(CN)_5]^{3-}$ generated in the dissociation of the redox isomer is intercepted by oxygen. The peroxo complex that is formed in this reaction is known to decompose in acidic solution:

$$[Co^{III}(CN)_{10}O_2]^{6-} + 2H^+ + 2H_2O \rightarrow 2[Co^{III}(CN)_5H_2O]^{2-} + H_2O_2$$

Since $[Co(CN)_5H_2O]^{2-}$ has only rather weak absorption bands at long wavelengths,[10] the spectrum of the photolyzed solution is dominated by $[Os(CN)_6]^{3-}$. In basic solution the peroxo complex does not hydrolyze but is oxidized by $[Os(CN)_6]^{3-}$ to yield the superoxo complex:

$$[Co_2(CN)_{10}O_2]^{6-} + [Os(CN)_6]^{3-} \rightarrow [Co_2(CN)_{10}O_2]^{5-} + [Os(CN)_6]^{4-}$$

The complex $[(NH_3)_5Cr^{III}NCFe(CN)_5]^-$ underwent also an efficient photolysis in aqueous solution upon MMCT excitation (λ_{irr} = 366 nm). The accompanying spectral changes (Figure 3) are consistent with the formation of $[Fe^{III}(CN)_6]^{3-}$ (λ_{max} = 420 nm, ϵ = 1050 M^{-1} cm^{-1}).[17] At this wavelength a shoulder develops. When the irradation is continued, a secondary photolysis or thermal side reactions take place as indicated by the disappearance of the isosbestic points. However, the spectral features of $[Fe(CN)_6]^{3-}$ can then be recognized much better. The fate of the chromium complex is not known. The disappearance quantum yield of the starting complex was approximately Φ = 0.1.

It is suggested that the photolysis proceeds according to

$$[(NH_3)_5Cr^{III}NCFe^{II}(CN)_5]^- \xrightarrow{h\nu} [(NH_3)_5Cr^{II}NCFe^{III}(CN)_5]^-$$

$$[(NH_3)_5Cr^{II}NCFe^{III}(CN)_5]^- \rightarrow Cr^{2+} + 5NH_3 + [Fe^{III}(CN)_6]^{3-}$$

The redox isomer Cr^{II}/Fe^{III} generated by MMCT excitation is expected to decompose since ammine complexes of Cr(II) are well-known to be kinetically very labile.[26] The ligand displacement at the Cr(II) center of the Cr(II)/Fe(III) redox isomer is apparently fast enough to compete successfully with the back electron transfer. Finally, Cr(II) is oxidized by oxygen.

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Contribution from the Department of Chemistry, Furman University, Greenville, South Carolina 29613

Electrogenerated Chemiluminescence of Hexacyanochromate(III) and Tris(2,2'-bipyridine)chromium(III) in Aprotic Solvents

Noel A. P. Kane-Maguire,* Jeffrey A. Guckert, and Patrick J. O'Neill

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The number of examples of chemiluminescence involving reactions of transition-metal (TM) complex species is still relatively small. Of increasing interest in recent years[1-12] is the identification of chemiluminescent TM systems other than the well-documented case of $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine).[13-15] Literature examples of Cr(III) chemiluminescence appear to date back to only

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