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Intramolecular energy transfer in Cr(III)-Cr(III) and Ru(II)-Cr(III)-Cr(III) polynuclear complexes

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Abstract

The binuclear NC-*trans*-Cr(cyclam)-CN-Cr(CN)$_5^-$ complex has been synthesized and characterized. Efficient energy transfer from the NC-*trans*-Cr(cyclam)-CN$^+$ to the -CN-Cr(CN)$_5^{3-}$ component was observed to occur.

The reaction of *cis*-Ru(bpy)$_2$[NC-*trans*-Cr(cyclam)-CN]$_2^{4+}$ with Cr(CN)$_5$(DMF)$^{2-}$ in DMF was studied. In the pentanuclear product *cis*-Ru(bpy)$_2$[-NC-*trans*-Cr(cyclam)-CN-Cr(CN)$_5$]$_2$, which was detected in the reacting solution but not isolated, stepwise energy transfer occurs along the Ru(II)-Cr(III)-Cr(III) cyano bridged chain.

1. INTRODUCTION

In the recent development of supramolecular photochemistry,[1] a relevant role has been played by supramolecular systems made up of covalently linked molecular components (dyads, triads etc).[2,3] These systems are particularly suited for the study of fundamental aspects of light-induced electron and energy transfer processes [4-11] and for the design of artificial biomimetic systems for light energy conversion [12-14] and photochemical molecular devices.[15-18] Polynuclear complexes are a particular class of covalently linked supramolecular systems in which metal-containing fragments are connected via bridging ligands.

Polynuclear complexes featuring intercomponent energy transfer have been studied in some detail,[3,19,20] with particular regard to the possibility to obtain light-induced functions such as spectral sensitization and antenna effects.[18,21-23] In particular, the *cis*-Ru(bpy)$_2$[NC-*trans*-Cr(cyclam)-CN]$_2^{4+}$ chromophore-luminophore complex (bpy = 2,2'-bipyridine, cyclam = 1,4,8,11-tetra-aza-cyclotetradecane) was found to exhibit intense emission from the Cr(cyclam)(CN)$_2^+$ luminophoric unit following light absorption by the -Ru(bpy)$_2$-$^{2+}$ chromophore, as a consequence of efficient chromophore →luminophore energy transfer.[24]

The occurrence of facile energy transfer processes between cyano-bridged metal centers suggests the interesting possibility to achieve stepwise energy transduction along cyano-bridged metal chains in complexes of higher nuclearity. As a first step in this direction, we have synthesized and characterized the binuclear complex

$$\text{NC-}trans\text{-Cr(cyclam)-CN-Cr(CN)}_5^-,$$

to check the feasibility of energy transfer between two Cr(III) centers. Then, we have attempted the synthesis of the pentanuclear complex

$(CN)_5$Cr-NC-*trans*-Cr(cyclam)-CN-*cis*-Ru(bpy)$_2$-NC-*trans*-Cr(cyclam)-CN-Cr$(CN)_5^-$

which could feature stepwise energy transfer along a three-center system. We describe here the results obtained.

2. EXPERIMENTAL

2.1. Preparation of Na[NC-*trans*-Cr(cyclam)-CN-Cr(CN)$_5$]

0.1 g (2.4x10^{-4} mol) of [Cr(cyclam)(CN)$_2$]Cl were added to 50 mL of a freshly prepared methanolic solution containing 0.1 g (1.4x10^{-4} mol) of [Cr(CN)$_5$(DMF)](TBA)$_2$ (prepared by photolysis of DMF solutions of $Cr(CN)_6^{3-}$ followed by purification on Sephadex LH20). The reaction mixture was kept under continuous stirring at room temperature in the dark for 48 h. The solution was then rotary evaporated to dryness and the product was purified by gel filtration chromatography in two steps. First the solid was dissolved in water and loaded onto a 2x30 cm column of CM Sephadex C25 cationic resin (Na form) in order to eliminate the excess of $Cr(cyclam)(CN)_2^+$. Elution with water gave a yellow solution that was rotary evaporated to dryness, dissolved in a minimum volume of CH_3OH, and loaded on 2x30 cm column of Sephadex LH20. Elution with CH_3OH gave a main yellow band. The main band was preceded by a pale yellow band containing unreacted $Cr(CN)_5(DMF)^{2-}$, and was followed by a small yellow band containing unidentified products. The solution containing the main yellow band was rotary evaporated to dryness and converted to tetrabutylammonium salt by ion exchange chromatography.

2.2. Apparatus and procedures

The instrumentation for recordering UV-vis and fluorescence spectra, and the apparatus and procedures for time resolved emission experiments were described elsewere[25].

3. RESULTS

3.1 Properties of [NC-*trans*-Cr(cyclam)-CN-Cr(CN)$_5$]$^-$.

DMF solutions of the TBA[NC-*trans*-Cr(cyclam)-CN-Cr(CN)$_5$] complex are indefinitely stable in the dark. While some decomposition (presumably heterolytic bridge cleavage) is observed under photochemical conditions, the solutions are appreciably stable under room light in the time scale of the experiments performed.

The absorption spectrum of NC-*trans*-Cr(cyclam)-CN-$Cr(CN)_5^-$ in DMF is shown in Fig. 1. The complex gives rise to an emission with maximum at 781 nm (Fig. 1), quantum yield 5.9x10^{-4}, and lifetime 81 μs. The excitation spectrum of this emission is shown in Fig 1. The lifetimes and excitation spectra measured at various wavelengths in the 750-830-nm range are constant, indicating that a single emission is present in this system. In pulsed experiments, the risetime of the emission signal is indistinguishable from that of the exciting laser pulse, setting an upper limit of ≤10 ns for any intrinsic delay between excitation and emission.

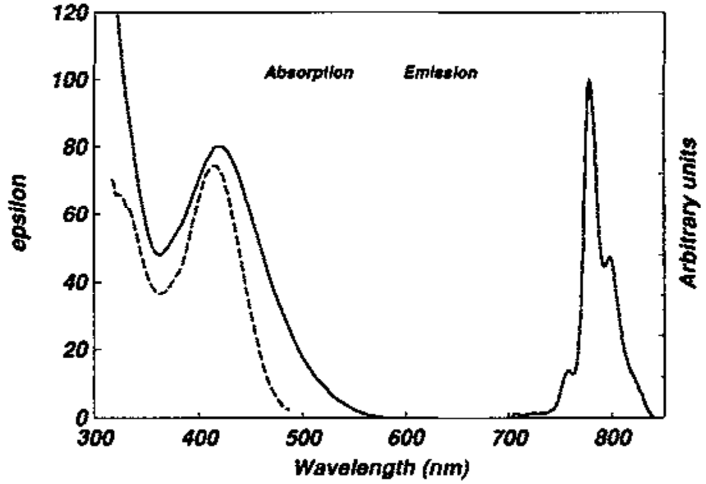

Figure 1. Absorption and emission spectra of NC-*trans*-Cr(cyclam)-CN-Cr$(CN)_5^-$. The broken line represents the excitation spectrum of the emission.

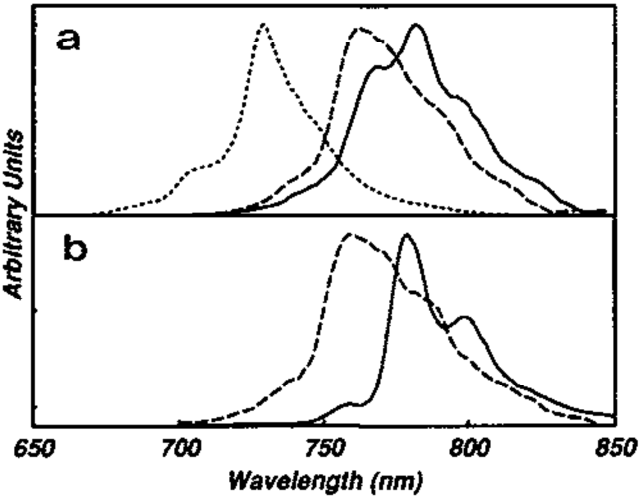

Figure 2. (a) Emission spectral changes during reaction (see text). (dotted line) DMF solution of *cis*-Ru$(bpy)_2$[NC-*trans*-Cr(cyclam)-CN]$_2^{4+}$; (broken line) upon addition of an excess of Cr$(CN)_5(DMF)^{2-}$; (full line) after staying at room temperature for 48 h.
(b) Emission spectra of Cr$(CN)_5(DMF)^{2-}$ (broken line) and NC-*trans*-Cr(cyclam)-CN-Cr$(CN)_5^-$ (full line)

3.2. Reaction of *cis*-Ru(bpy)$_2$[NC-*trans*-Cr(cyclam)-CN]$_2^{4+}$ with Cr(CN)$_5$(DMF)$^{2-}$

The emission spectrum of a DMF solution ($3.0\text{x}10^{-4}$ M) of *cis*-Ru(bpy)$_2$[NC-*trans*-Cr(cyclam)-CN]$_2^{4+}$ is shown in Fig 2a, (dotted line). When $3.0\text{x}10^{-3}$ M Cr(CN)$_5$(DMF)$^{2-}$ is added to this solution, the emission changes instantaneously to that shown in Fig. 2a, (broken line). When the solution containing both reactants is kept at room temperature a new emission with λ_{max} = 778 nm develops. The limiting spectrum observed after 48 h is also reported (Fig. 2a, full line). All the attempts to isolate the reaction product from the reaction mixture were unsuccessful, apparently for reasons of thermodynamic instability. As a matter of fact, rapid fading of 778-nm emission occurred when the excess Cr(CN)$_5$(DMF)$^{2-}$ was removed from the reacted solution by ion exchange on anionic DEAE Sephadex A25 resin.

4. DISCUSSION

4.1. Energy transfer in the NC-*trans*-Cr(cyclam)-CN-Cr(CN)$_5^-$ binuclear complex

The absorption spectrum of NC-*trans*-Cr(cyclam)-CN-Cr(CN)$_5^-$ (Fig. 1) consists of a broad band centered at 420 nm. While the intensity of this band is in the typical range for metal-centered ligand field transitions, its width is clearly too large, suggesting that the band arises from the superposition of various transitions belonging to the two Cr(III) centers. To a first approximation, it may be assumed that the NC-*trans*-Cr(cyclam)-CN-$^+$ subunit of the binuclear complex has the same spectrum as free NC-*trans*-Cr(cyclam)-CN$^+$. Within the limits of this assumption, the spectrum of the -CN-Cr(CN)$_5^{3-}$ subunit (for which no reliable mononuclear model is available) can be obtained by difference (Fig. 3).

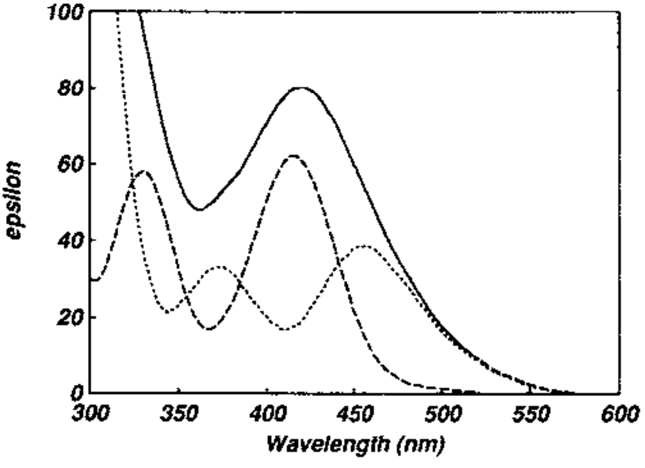

Figure 3. Absorption spectra of NC-*trans*-Cr(cyclam)-CN-Cr(CN)$_5^-$ (full line) of NC-Cr(cyclam)-CN$^+$ (broken line) and difference spectrum (dotted line).

The resulting spectrum shows two ligand field bands, and looks reasonable, in terms of bandwidths, intensities, and energy separation, for a Cr(III) chromophore. The relatively low energy of these bands indicates that the N-bonding bridging cyanide performs as a week field ligand in this complex (compare, e.g., $\lambda_{max} = 460$ nm for -CN-$Cr(CN)_5^{3-}$ with $\lambda_{max} = 391$ nm for $Cr(CN)_6^{3-}$,[26] $\lambda_{max} = 406$ nm for $Cr(CN)_5(NH_3)^{2-}$,[27] and $\lambda_{max} = 444$ nm for $Cr(CN)_5(DMF)^{2-}$).

The nature of the emission of the binuclear complex can be discussed by comparing the properties of this emission ($\lambda_{max} = 778$ nm and $\tau = 81$ µs in DMF, complete quenching in H_2O) with those of some model compounds. This emission is definitely different from the known emissions of free NC-*trans*-Cr(cyclam)-CN^+ ($\lambda_{max} = 714$ nm and $\tau = 335$ µs in DMSO, practically solvent independent) and *cis*-$Ru(bpy)_2$[NC-*trans*-Cr(cyclam)-$CN]_2^{4+}$ ($\lambda_{max} = 730$ and $\tau = 300$ µs in DMF, almost solvent independent). On the other hand, the emission resembles those of $Cr(CN)_5(NH_3)^{2-}$ ($\lambda_{max} = 777$ nm and $\tau = 32$ µs in DMSO, complete quenching in H_2O)[27] and $Cr(CN)_5(DMF)^{2-}$ ($\lambda_{max} = 760$ nm, $\tau = 38$ µs in DMF, complete quenching in water). Based on these comparisons, the observed emission can be confidently assigned to the -CN-$Cr(CN)_5^{3-}$ subunit.

According to the above analysis of the absorption spectrum, visible light absorption by NC-*trans*-Cr(cyclam)-CN-$Cr(CN)_5^-$ corresponds to simultaneous excitation (in a wavelength-dependent ratio) of both Cr(III) centers. The absence of any emission from the NC-Cr(cyclam)-CN^{-+} subunit (expected at higher energy) and the ubiquitous presence of emission from the -CN-$Cr(CN)_5^{3-}$ subunit clearly indicate the occurrence of highly efficient intramolecular energy transfer from the former to the latter Cr(III) center. Given the extremely short lifetime of the quartet excited states of Cr(III) complexes, the energy transfer process is believed to be of the doublet-doublet type (Fig. 4). The energy transfer process is fast ($k \geq 10^8\ s^{-1}$), presumably as a consequence of the strong exchange interaction between the metal centers mediated by the cyanide bridge. Some bimolecular energy transfer processes between doublet states of Cr(III) complexes have been observed.[27,28]

The excitation spectrum of (Fig. 1) is similar but not identical to the absorption spectrum of the complex (Fig. 1): the maxima are almost coincident but the band is definitely much narrower in excitation than in absorption. This indicates that the efficiency of conversion from the absorbing states to the emitting state is not constant throughout the absorption spectrum. The fact that the excitation spectrum resembles quite closely the absorption spectrum of the NC-Cr(cyclam)-CN^{-+} subunit (Fig. 3) indicates that the efficiency of the $Cr_a(Q_1) \rightarrow Cr_b(D_1)$ conversion via intersystem crossing and energy transfer (Fig. 4) is much higher than that of the $Cr_b(Q_1) \rightarrow Cr_b(D_1)$ intersystem crossing. The efficiency of the former conversion is presumably unitary, given the unitary intersystem crossing efficiency of NC-*trans*-Cr(cyclam)-CN^+ [24] and the complete quenching of the emission of this fragment. The efficiency of intersystem crossing within the -CN-$Cr(CN)_5^{3-}$ fragment is not easily predictable, although it is known to be ca. 0.5 in the free linkage isomer $Cr(CN)_6^{3-}$.[26] The excitation spectrum obtained can be reasonably fitted (taking into consideration the approximations involved in the spectral analysis of Fig. 3) assuming an intersystem crossing efficiency of the -CN-$Cr(CN)_5^{3-}$ fragment in the range 0.1-0.2.

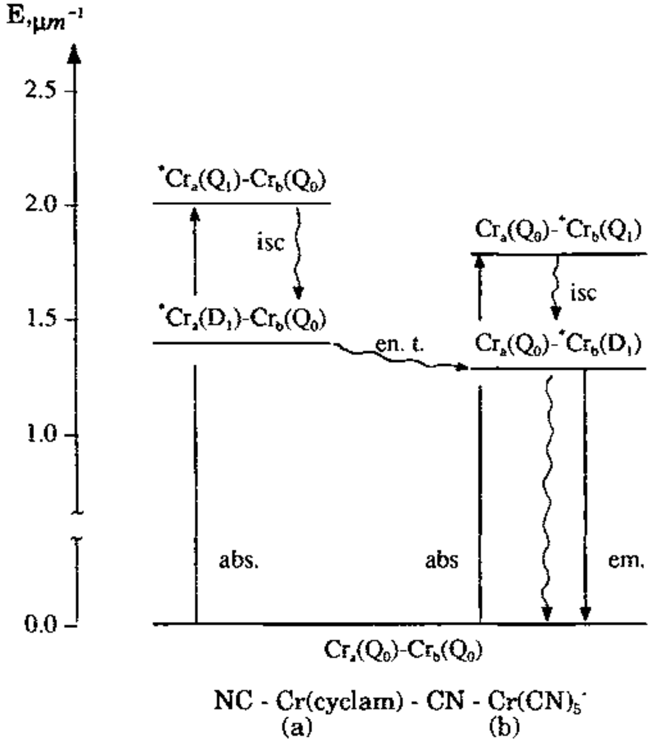

Figure 4. Jablonsky diagram for the binuclear NC-*trans*-Cr(cyclam)-CN-Cr(CN)$_5^-$ complex

4.2. Stepwise energy transfer in the *cis*-Ru(bpy)$_2$[-NC-*trans*-Cr(cyclam)-CN-Cr(CN)$_5$]$_2$ reaction product

In previous work, efficient energy transfer was demonstrated to occur in the trinuclear complex *cis*-Ru(bpy)$_2$[NC-*trans*-Cr(cyclam)-CN]$_2^{4+}$ (Ru(II)-Cr(III)$_a$) from the lowest excited state of the chromophoric unit -Ru(bpy)$_2$-$^{2+}$ to the doublet state of the -NC-Cr(cyclam)-CN$^+$ units.[24] The observation of efficient energy transfer in the binuclear NC-*trans*-Cr(cyclam)-CN-Cr(CN)$_5^-$ complex (Cr(III)$_a$-Cr(III)$_b$) suggests that interesting processes could be obtained in more extended systems based on the same molecular components. In particular, systems containing the sequence -Ru(bpy)-NC-Cr(cyclam)-CN-Cr(CN)$_5^+$ should give rise to efficient two-step energy transfer from the -Ru(bpy)$_2$-$^{2+}$ chromophoric unit to the terminal -CN-Cr(CN)$_5^{3-}$ unit. The synthesis of such systems has been attempted by reacting *cis*-Ru(bpy)$_2$[NC-*trans*-Cr(cyclam)-CN]$_2^{4+}$ with excess Cr(CN)$_5$(DMF)$^{2-}$.

The emission of the *cis*-$Ru(bpy)_2[NC$-*trans*-$Cr(cyclam)$-$CN]_2^{4+}$ is instantaneously quenched upon addition of excess $Cr(CN)_5(DMF)^{2-}$ in DMF, and is replaced by a new emission at 760 nm which closely matches that of $Cr(CN)_5(DMF)^{2-}$ (Fig. 2b). The sensitization of the $Cr(CN)_5(DMF)^{2-}$ emission (note that under the experimental conditions used direct light absorption by this species is negligible) and the quenching of the *cis*-$Ru(bpy)_2[NC$-*trans*-$Cr(cyclam)$-$CN]_2^{4+}$ emission arise from efficient energy transfer between the two species, which in the experimental conditions used are likely to be extensively ion paired (eq 1). On

$$\text{-Ru(bpy)}_2\text{-NC-}^*\text{Cr(cyclam)-CN}^{3+}\cdot\text{Cr(CN)}_5\text{(DMF)}^{2-} \rightarrow \qquad (1)$$

$$\text{-Ru(bpy)}_2\text{-NC-Cr(cyclam)-CN}^{3+}\cdot{}^*\text{Cr(CN)}_5\text{(DMF)}^{2-}$$

a much longer time scale, then, a new emission at 778 nm develops, which matches closely that of the $-CN-Cr(CN)_5^{3-}$ subunit of the NC-*trans*-$Cr(cyclam)$-CN-$Cr(CN)_5^{-}$ complex. This is indicative of a thermal substitution reaction (eq. 2) in which *cis*-$Ru(bpy)_2[NC$-*trans*-$Cr(cyclam)$-$CN]_2^{4+}$ acts as an entering ligand (through the terminal cyanides) on $Cr(CN)_5(DMF)^{2-}$.

$$\text{-Ru(bpy)}_2\text{-NC-Cr(cyclam)-CN}^{3+} + \text{Cr(CN)}_5\text{(DMF)}^{2-} \rightarrow \qquad (2)$$

$$\text{-Ru(bpy)}_2\text{-NC-Cr(cyclam)-CN-Cr(CN)}_5^{-}$$

In view of the excess of $Cr(CN)_5(DMF)^{2-}$ present, and of the non-anionic nature of the product, the product is most likely the pentanuclear species *cis*-$Ru(bpy)_2[$-NC-*trans*-$Cr(cyclam)$-CN-$Cr(CN)_5]_2$. It is important to notice that in this system light absorption by the $-Ru(bpy)_2-^{2+}$ chromophoric component is followed by emission from the remote $-CN-Cr(CN)_5^{3-}$ component. In view of what is known to occur in the two *cis*-$Ru(bpy)_2[NC$-*trans*-$Cr(cyclam)$-$CN]_2^{4+}$ and NC-*trans*-$Cr(cyclam)$-CN-$Cr(CN)_5^{-}$ model compounds, this most likely involves a two-step energy transfer through the intervening $-NC-Cr(cyclam)-CN^{+}$ molecular component (eq 3).

$$\ldots\text{-}^*\text{Ru(bpy)}_2\text{-NC-Cr(cyclam)-CN-Cr(CN)}_5^{-} \rightarrow \qquad (3)$$

$$\ldots\text{-Ru(bpy)}_2\text{-NC-}^*\text{Cr(cyclam)-CN-Cr(CN)}_5^{-} \rightarrow$$

$$\ldots\text{-Ru(bpy)}_2\text{-NC-Cr(cyclam)-CN-}^*\text{Cr(CN)}_5^{-}$$

Unfortunately, the pentanuclear species that forms under the reaction conditions used is not stable enough as to be isolated as a pure compound. Evidently, the equilibrium constant of eq. 2 is relatively small, and the product re-dissociates upon removal of the excess $Cr(CN)_5(DMF)_2^{-}$. The instability of the Cr-CN-Cr bridge in the reaction product is somewhat surprising, given the stability of the same bridge in NC-*trans*-$Cr(cyclam)$-CN-$Cr(CN)_5^{-}$. This contrasting behavior suggests that strong *trans* effects may operate through the -NC-*trans*-$Cr(cyclam)$-CN^{+} component.

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