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Bis(2,2′-bipyridine)ruthenium(II)–Hexacyanochromate(III) Chromophore–Luminophore Complexes. Intramolecular Energy Transfer, Excited-State Intervalence Transfer, and Doublet–Doublet Annihilation

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Abstract: The binuclear $[NC\text{–}Ru(bpy)_2\text{–}NC\text{–}Cr(CN)_5]^{2-}$ and trinuclear $[(CN)_5Cr\text{–}CN\text{–}Ru(bpy)_2\text{–}NC\text{–}Cr(CN)_5]^{4-}$ bimetallic complexes have been synthesized and their photophysical behavior has been studied. Visible light absorption by the $Ru(bpy)_2^{2+}$ chromophore leads to phosphorescence from the $Cr(CN)_6^{3-}$ luminophore. The results demonstrate the occurrence of a fast ($\tau < 10$ ns), efficient ($\eta = 1$) intramolecular exchange energy transfer process from the MLCT triplet of the Ru(II) fragment to the doublet state of the $Cr(CN)_6^{3-}$ fragment. Distinctive features of these chromophore–luminophore complexes with respect to the behavior of the isolated luminophore are as follows: (i) large light-harvesting efficiency (antenna effect); (ii) response to visible light (spectral sensitization); (iii) 100% efficient population of the emitting state; (iv) photostability. The excited-state absorption (ESA) spectrum of both bimetallic complexes exhibits a peculiar visible band not shown by free $Cr(CN)_6^{3-}$. This band corresponds to intervalence-transfer transitions from Ru(II) to excited Cr(III). Contrary to the behavior of free $Cr(CN)_6^{3-}$, the bimetallic complexes also undergo a distinct bimolecular doublet–doublet annihilation process (rate constants k of the order of 10^7–10^8 M^{-1} s^{-1}). The mechanism is thought to involve oxidation of Ru(II) and reduction of Cr(III). Intramolecular processes of the same type are probably responsible for the failure to observe doubly excited species upon two-photon excitation of the trinuclear complex.

There has been considerable interest recently in the study of intramolecular electron-[1-7] and energy[8-14]-transfer processes taking place in large organic molecules made up of covalently linked donor and acceptor fragments. Several reasons have contributed to the rapid growth of this field of research. From a fundamental standpoint, the study of intramolecular processes occurring at fixed geometry is more convenient than that of analogous bimolecular processes in order to disentangle the various factors that determine the rate of the transfer process. On the other hand, energy and electron transfer in synthetic polychromophoric systems can be used to model analogous processes taking place in biological systems. Finally, the ability to control intramolecular energy- and electron-transfer rates is likely to be the key to the development of successful artificial photochemical molecular devices.[15]

Recent work in this and other laboratories has focused on the synthesis and photophysical characterization of polynuclear transition-metal complexes in which an electron-transfer photosensitizer and various electron donor and acceptor complex moieties are bound together by appropriate bridging ligands.[16-21] These systems were suitable for studying optical and/or photoinduced intramolecular electron transfer. Polynuclear complexes in which an energy-transfer sensitizer and energy acceptor complex moieties are covalently bound have also been developed by a number of laboratories.[22-27] Such systems are in principle capable of undergoing *intramolecular energy transfer*. Although for most of these polynuclear complexes the conditions for detecting the intramolecular energy-transfer process were not ideal, in two cases[22,25] definite evidence for the occurrence of this process has been reached.

We have now designed and synthesized the bi- and trinuclear complexes

$$[NC\text{–}Ru(bpy)_2\text{–}NC\text{–}Cr(CN)_5]^{2-}$$

and

$$[(CN)_5Cr\text{–}CN\text{–}Ru(bpy)_2\text{–}NC\text{–}Cr(CN)_5]^{4-}$$

The idea was that of coupling together two molecular fragments such that (i) selective excitation of the fragments could be easily achieved and (ii) the excited states of both fragments could be easily detected and clearly distinguished from each other. We report here the results of a thorough photophysical study of these

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systems.[28-31] Besides providing clear-cut evidence for the occurrence of efficient intramolecular energy transfer between the fragments, this study reveals a number of intriguing new excited-state properties characteristic of the bimetallic systems.

Experimental Section

Materials. $Cr(OOCCH_3)\cdot H_2O$ (Alfa), $RuCl_3\cdot 3H_2O$ (Aldrich), tetrabutylammonium chloride, and tetrabutylammonium tetrafluoroborate (Fluka) were commercial products of reagent grade. $K_3[Cr(CN)_6]$,[32] $Ru(bpy)_2Cl_2$,[33] and $[Ru(bpy)_2(NO)(CN)](PF_6)_2$[26] were prepared according to literature methods. Reagent-grade methanol, spectrograde DMF, and triply distilled water were used as solvents. When necessary, methanol was dried over molecular sieves.

Sephadex G15 and Sephadex LH20 resins (Pharmacia) were used in gel filtration chromatography. The resins were allowed to swell for at least 3 h in the appropriate solvent before packing the columns.

$[Ru(bpy)_2(CN)(CH_3OH)]PF_6$. Solutions of this complex were prepared by slow addition of a stoichiometric amount of NaN_3 to a suspension of $[Ru(bpy)_2(NO)(CN)](PF_6)_2$ in anhydrous methanol. After 2 h at room temperature the reaction was complete. Solid $NaPF_6$ was filtered off and the red-brown solution was ready for use.

$K_2[NC-Ru(bpy)_2-NC-Cr(CN)_5]$. The synthesis was carried out in red light, due to the photosensitivity of $Cr(CN)_6^{3-}$. A 30-mL aliquot of a freshly prepared methanolic solution of $[Ru(bpy)_2(CN)(CH_3OH)]PF_6$ (4.29×10^{-4} mol) was slowly added dropwise (0.1 mL/min) to 30 mL of an aqueous solution containing 2.8 g of $K_3[Cr(CN)_6]$ (8.6×10^{-3} mol), under continuous stirring at 30 °C. This procedure was devised to minimize the precipitation of insoluble salts and the formation of polynuclear complexes of higher Ru:Cr ratio. After 24 h, the reaction mixture was filtered to remove insoluble (probably polymeric) material, and the solution was rotary evaporated to dryness. The solid was extracted at room temperature with three 20-mL portions of methanol, leaving unreacted $K_3[Cr(CN)_6]$ as the main residue. The red-orange solution was rotary evaporated to dryness and the product was purified by gel filtration chromatography in two steps. First, the solid was dissolved in the minimum amount of water and loaded onto a 2 × 80 cm column of Sephadex G15. Elution with water gave a main red-orange band. The main band was preceded by a yellow-orange band containing unidentified (probably polymeric) products and then by an almost colorless band containing some unreacted $Cr(CN)_6^{3-}$ and was followed by a small yellow band containing $Ru(bpy)_2(CN)_2$. The red-orange fraction was evaporated to dryness, dissolved in a small volume of methanol, and loaded onto a 2 × 80 cm column of Sephadex LH20. Elution with methanol gave a main red-orange fraction, preceded by a small yellow-orange band that was discarded. The red-orange solution was rotary evaporated and the resulting brown solid was dried. Anal. Calcd for $K_2[NC-Ru(bpy)_2-NC-Cr(CN)_5]\cdot 3H_2O$: C, 41.50; N, 19.75; H, 2.84. Found: C, 41.23; N, 19.72; H, 2.58. The product was converted into the tetrabutylammonium salt by ion exchange on cationic CM Sephadex C-25 resin in aqueous solution, followed by evaporation to dryness.

$K_4[(CN)_5Cr-CN-Ru(bpy)_2-NC-Cr(CN)_5]$. The synthesis was carried out in red light. A 0.3-g aliquot of $Ru(bpy)_2Cl_2$ (5.84×10^{-4} mol) was dissolved in 30 mL of boiling water. After being cooled to room temperature, the solution was slowly added dropwise (0.1 mL/min) to 60 mL of an aqueous solution containing 9.5 g of $K_3[Cr(CN)_6]$ (2.92×10^{-2} mol), under continuous stirring at 30 °C. The reaction time and the purification procedures were the same as those used in the previous synthetic procedure. The product obtained was a red solid. Anal. Calcd for $K_4[(CN)_5Cr-CN-Ru(bpy)_2-NC-Cr(CN)_5]\cdot 6H_2O$: C, 35.13; N, 20.48; H, 2.58. Found: C, 35.48; N, 20.27; H, 2.41. The product was converted into the tetrabutylammonium salt by ion exchange on cationic CM Sephadex C-25 resin in aqueous solution, followed by evaporation to dryness.

Apparatus and Procedures. UV-vis spectra were recorded with a Perkin-Elmer 323 spectrophotometer. Infrared spectra were recorded with a Perkin-Elmer 283 spectrophotometer.

Emission spectra were taken with a Perkin-Elmer spectrofluorometer equipped with a R928 Hamamatsu tube. The emission spectra were corrected by calibrating the instrumental response with respect to a NBS standard quartz tungsten-halogen lamp. Emission quantum yield values were obtained by using $Ru(bpy)_3^{2+}$ in water ($\Phi = 0.042$)[34] as a reference emitter, with appropriate correction[35] for the difference in refractive index.

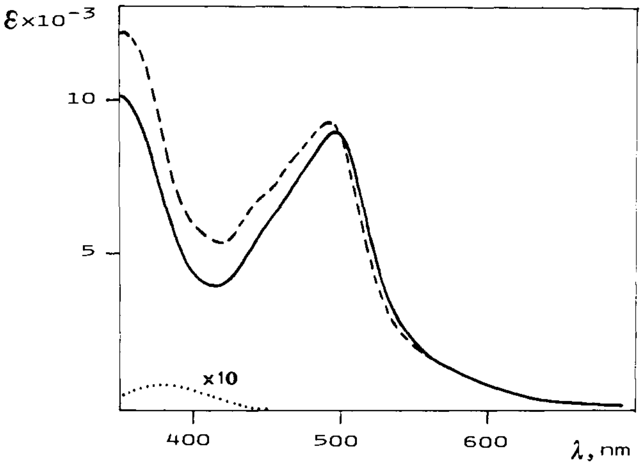

Figure 1. Absorption spectra of $[NC-Ru(bpy)_2-NC-Cr(CN)_5]^{2-}$ (continuous line), $[(CN)_5Cr-CN-Ru(bpy)_2-NC-Cr(CN)_5]^{4-}$ (broken line), and $Cr(CN)_6^{3-}$ (dotted line, ×10 expansion) in DMF.

Time-resolved emission experiments were performed using 347-nm pulses (halfwidth, 20 ns) from a J&K System 2000 frequency-doubled ruby laser. Emission decays were recorded on a Tektronix 7834 storage oscilloscope, digitized manually, and computer analyzed.

Excited-state absorption (ESA) spectra were measured with a laser flash photolysis apparatus (Applied Photophysics detection system, J&K System 2000 frequency-doubled ruby laser).

Laser actinometry was performed using the benzophenone triplet as standard, following previously described procedures.[36,37]

For the determination of the saturation curves of the emission intensity, the laser pulse intensity was measured by deflecting a small fraction of the laser beam into a photodiode whose output was calibrated against benzophenone triplet absorption.

Deaeration of the solutions was achieved with five consecutive freeze-pump-thaw cycles at 10^{-6} Torr.

Results

Solutions of $[NC-Ru(bpy)_2-NC-Cr(CN)_5]^{2-}$ and $[(CN)_5Cr-CN-Ru(bpy)_2-NC-Cr(CN)_5]^{4-}$ (as tetrabutylammonium salts) in DMF were indefinitely stable in the dark at room temperature. These solutions were also appreciably stable to light in the visible and near-ultraviolet range. Based on the constancy of the absorption spectra and emission intensity (vide infra) during irradiation, an upper limit of 10^{-3} could be estimated for the photoreaction quantum yield in these systems.

The visible absorption spectra of the two complexes in DMF are shown in Figure 1, together with that of $Cr(CN)_6^{3-}$. The prominent MLCT band of the $Ru(bpy)_2^{2+}$ chromophore shifts in going to aqueous solution [λ_{max} = 496 nm (DMF), 440 nm (H_2O) for $[NC-Ru(bpy)_2-NC-Cr(CN)_5]^{2-}$; λ_{max} = 490 nm (DMF), 454 nm (H_2O) for $[(CN)_5Cr-CN-Ru(bpy)_2-NC-Cr(CN)_5]^{4-}$]. The blue shift is larger for the dinuclear complex, which has the possibility of undergoing second-sphere donor-acceptor interactions[30,38] with the solvent at the nonbridging cyanide.

Infrared spectra of the two complexes in the CN stretching region are consistent with the formulation given and, in particular, indicate that the cyanide-bonding mode implied by the synthetic procedure used (bridging cyanides C-bonded to Cr and N-bonded to Ru) is maintained in the complexes.[39,40]

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(28) Preliminary results on these systems have been reported elsewhere.[29-31]

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(40) This is presumably not the thermodynamically stable mode. Indeed, prolonged heating of solid samples of the complexes in KBr pellets induced infrared spectral changes that suggest linkage isomerization of the bridging cyanides.[39]

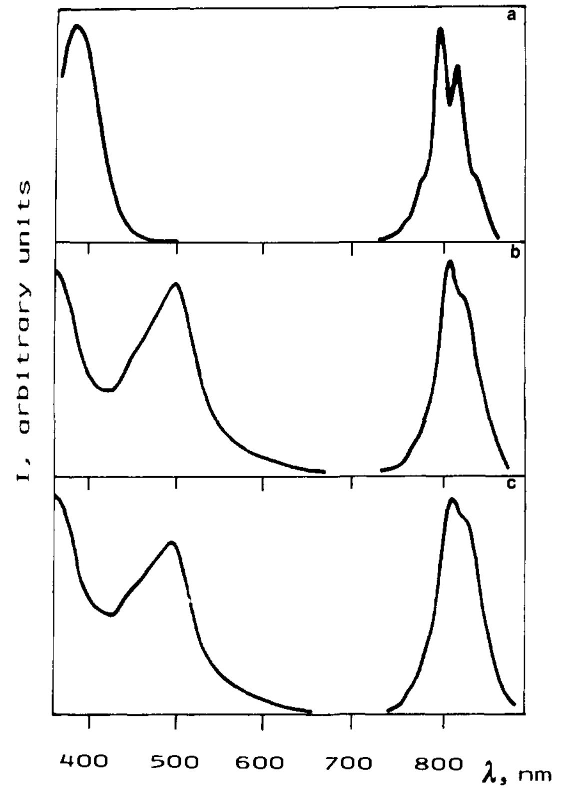

Figure 2. Excitation (left) and emission (right) spectra of $Cr(CN)_6^{3-}$ (a), $[NC-Ru(bpy)_2-NC-Cr(CN)_5]^{2-}$ (b), and $[(CN)_5Cr-CN-Ru(bpy)_2-NC-Cr(CN)_5]^{4-}$ (c). DMF, 25 °C.

Table I. Emission Quantum Yields and Lifetimes[a]

complex	Φ	τ, ms
$Cr(CN)_6^{3-}$	1.7×10^{-3}	6.4
$[NC-Ru(bpy)_2-NC-Cr(CN)_5]^{2-}$	8.5×10^{-4}	1.1
$[(CN)_5Cr-CN-Ru(bpy)_2-NC-Cr(CN)_5]^{4-}$	9.2×10^{-4}	1.3

[a] DMF, 25 °C, deaerated solution.

Cyclic voltammetry of the complexes in DMF in the 0.0–1.5 V range exhibited a single reversible wave that can be assigned to the oxidation of Ru(II) to Ru(III) by analogy with the behavior of related systems.[26] The $E_{1/2}$ values are +0.89 V (vs SCE) for $[NC-Ru(bpy)_2-NC-Cr(CN)_5]^{2-}$ and +0.84 V (vs SCE) for $[(CN)_5Cr-CN-Ru(bpy)_2-NC-Cr(CN)_5]^{4-}$. Cyclic voltammetry in the negative potential range gave, besides the usual bpy-centered reduction waves,[37] only a small irreversible wave at ca. −1.4 V (vs SCE). This most probably corresponds to reduction of Cr(III) to Cr(II), as inferred from the known behavior of the free $Cr(CN)_6^{3-}$ moiety.[41,42] The complexes were observed to emit at room temperature in deaerated DMF solution. Emission and excitation spectra are shown in Figure 2 together with corresponding data for $Cr(CN)_6^{3-}$. The emission was partially quenched by oxygen (k_q of the order of 10^6 M^{-1} s^{-1}). Emission quantum yields in deaerated DMF solutions are given in Table I. As with $Cr(CN)_6^{3-}$,[43] no emission could be detected with the bimetallic complexes in water or in other polar organic solvents. Emission at 77 K in absolute ethanol or 9:1 DMF/CH_2Cl_2 glasses was quite similar to the room-temperature emission in DMF, except for a sharpening of the vibrational structure.

Time-resolved experiments (pulsed 347-nm laser excitation, 5×10^{-4} M deaerated DMF solutions) showed that the emission intensity reached its maximum value within the laser pulse, indicating that the emitting state is formed in a time scale shorter than a few nanoseconds. The emission then decayed in a much longer time scale. In aerated solutions, first-order decays were observed for both $[NC-Ru(bpy)_2-NC-Cr(CN)_5]^{2-}$ and $[(CN)_5Cr-CN-Ru(bpy)_2-NC-Cr(CN)_5]^{4-}$, with lifetimes of 195 and 140 μs, respectively.

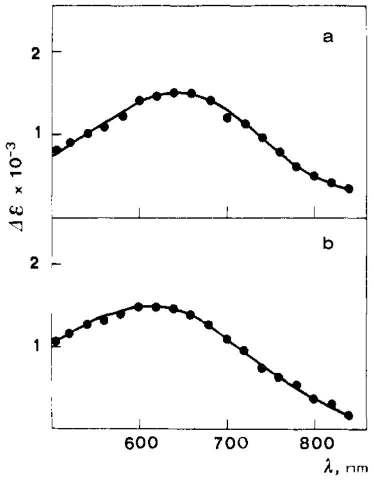

Figure 3. ESA spectra of $[NC-Ru(bpy)_2-NC-Cr(CN)_5]^{2-}$ (a) and $[(CN)_5Cr-CN-Ru(bpy)_2-NC-Cr(CN)_5]^{4-}$ (b).

In deaerated solutions, however, the decay kinetics exhibited a strong sensitivity to experimental conditions such as the power of the exciting laser pulse and the presence of added electrolytes. In fact, good monoexponential decays could only be obtained working at low absorbed laser intensity (e.g., 1×10^{-6} einstein·L^{-1}/pulse) and in solutions of low ionic strength (e.g., $\mu = 5 \times 10^{-3}$ M). Lifetimes obtained in these conditions are reported in Table I. Increasing the laser power and/or the concentration of added electrolyte, on the other hand, gave rise to faster and clearly nonexponential decays. In these conditions, the decays of the emission intensity were found to obey a mixed first-order, second-order rate law (eq 1). The reciprocal of the first-order

$$-d[I]/dt = k_1[I] + k_2[I]^2 \qquad (1)$$

constant always coincided with the lifetime obtained at low laser power. The experimental second-order constants were converted into true bimolecular rate constants by means of laser actinometry,[36,37] giving a reasonably intensity-independent value at each ionic strength (e.g., at $\mu = 0.5$ M, 5.3×10^8 M^{-1} s^{-1} for $[NC-Ru(bpy)_2-NC-Cr(CN)_5]^{2-}$ and 9.3×10^7 M^{-1} s^{-1} for $[(CN)_5Cr-CN-Ru(bpy)_2-NC-Cr(CN)_5]^{4-}$). Control experiments performed with free $Cr(CN)_6^{3-}$ always gave good single-exponential decays, under any condition of laser power and ionic strength.

Laser flash photolysis experiments in DMF solution showed transient absorbance changes (maximum absorbance changes of the order of 0.14) in the visible that decayed with the same kinetics as the emission and can thus be assigned to an excited-state absorption (ESA). The visible ESA spectra of $[NC-Ru(bpy)_2-NC-Cr(CN)_5]^{2-}$ and $[(CN)_5Cr-CN-Ru(bpy)_2-NC-Cr(CN)_5]^{4-}$ are shown in Figure 3. Analogous experiments showed that the ESA spectrum of $Cr(CN)_6^{3-}$ only features weak ultraviolet absorption, being completely transparent in the visible.

Experiments aimed at detecting possible differences in the saturation characteristics of the emission of $[NC-Ru(bpy)_2-NC-Cr(CN)_5]^{2-}$ and $[(CN)_5Cr-CN-Ru(bpy)_2-NC-Cr(CN)_5]^{4-}$ (vide infra) were performed on 2×10^{-5} M solutions by monitoring the initial emission intensity (50 ns after flash) as a function of the pulse intensity. The results are shown in Figure 4.

Discussion

Energy Levels of the Polynuclear Complexes. The visible absorption spectra of $[NC-Ru(bpy)_2-NC-Cr(CN)_5]^{2-}$ and $[(CN)_5Cr-CN-Ru(bpy)_2-NC-Cr(CN)_5]^{4-}$ (Figure 1) are quite

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(41) A half-wave potential of −1.385 V vs SCE has been observed by Kolthoff[42] in the polarography of $Cr(CN)_6^{3-}$ in 1 M NaCN aqueous solutions. Some differences in reduction potential are expected to occur between $Cr(CN)_6^{3-}$ and the polynuclear complexes, due to the presence of the coordinated Ru(II) center in the latter species. The poorly reversible behavior of the reduction processes, however, precludes any detailed analysis of this aspect.

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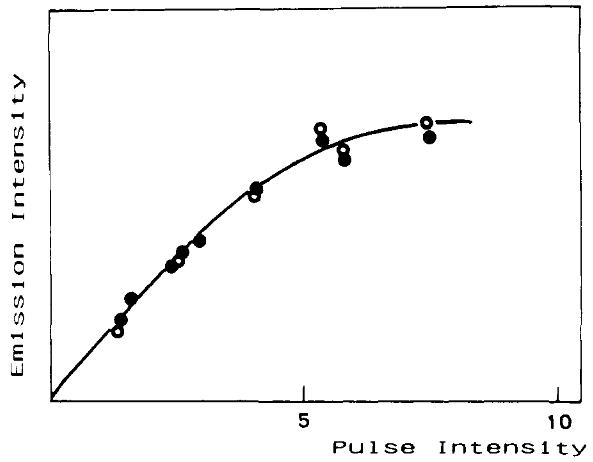

Figure 4. Dependence of the initial (t = 50 ns) emission intensity on the intensity of the exciting laser pulse. $[NC–Ru(bpy)_2–NC–Cr(CN)_5]^{2-}$ (●); $[(CN)_5Cr–CN–Ru(bpy)_2–NC–Cr(CN)_5]^{4-}$ (○). Units of pulse intensity correspond to concentrations of absorbed photons in einstein·L^{-1} × 10^{-5}. Complex concentration: 2 × 10^{-5} M.

straightforward. They are dominated by the metal-to-ligand charge-transfer (MLCT) band of the $Ru(bpy)_2^{2+}$ unit, as shown by their close similarity in shape, energy, and intensity to the spectrum of $Ru(bpy)_2(CN)_2$ in DMF.[37,44] No appreciable contribution of the $Cr(CN)_6^{3-}$ fragment to the visible absorption of the bimetallic complexes is expected on the basis of the properties of the isolated molecule (Figure 1).[43] No new band characteristic of the polynuclear species is observed at low energy in these systems.

The above considerations suggest that the photophysical behavior of $[NC–Ru(bpy)_2–NC–Cr(CN)_5]^{2-}$ and $[(CN)_5Cr–CN–Ru(bpy)_2–NC–Cr(CN)_5]^{4-}$ can be described in terms of an energy level diagram that is simply made by superimposing the low-lying excited states of the $Cr(CN)_6^{3-}$ and $Ru(bpy)_2^{2+}$ units. The conventional Jablonski diagram for an octahedral Cr(III) complex involves the $^4A_{2g}$ ground state (thereafter referred to as Q_0) and ^2E_g and $^4T_{2g}$ excited states of ligand field character (thereafter referred to as D_1 and Q_1, respectively). For $Cr(CN)_6^{3-}$, the 0–0 energies of these excited states are 1.25 μm^{-1} (directly measured from phosphorescent emission[43]) and between 1.8 and 2.4 μm^{-1} (estimated from sensitization experiments[45]), respectively. These energies, and in particular that of the D_1 state, are not likely to be appreciably altered by bridging of one cyanide ligand to ruthenium. The relevant states of the $Ru(bpy)_2^{2+}$ fragment, on the other hand, are the singlet ground state (S_0) and singlet (S_1) and triplet (T_1) excited states of MLCT character. In the polynuclear complexes, the 0–0 energy of S_1 should be around 1.6 μm^{-1} (considering the onset of the intense MLCT band). Plausible energy values for the triplet state of the $Ru(bpy)_2^{2+}$ fragment in $[NC–Ru(bpy)_2–NC–Cr(CN)_5]^{2-}$ and $[(CN)_5Cr–CN–Ru(bpy)_2–NC–Cr(CN)_5]^{4-}$ can be deduced from the emission of suitable model compounds[46] or extrapolated from the energy of the MLCT absorption band.[47,48] The energy level diagram deduced from the above considerations for $[NC–Ru(bpy)_2–NC–Cr(CN)_5]^{2-}$ is depicted in Figure 5. Except for minor energy differences, the same diagram can be used for discussing the behavior of the trinuclear species.

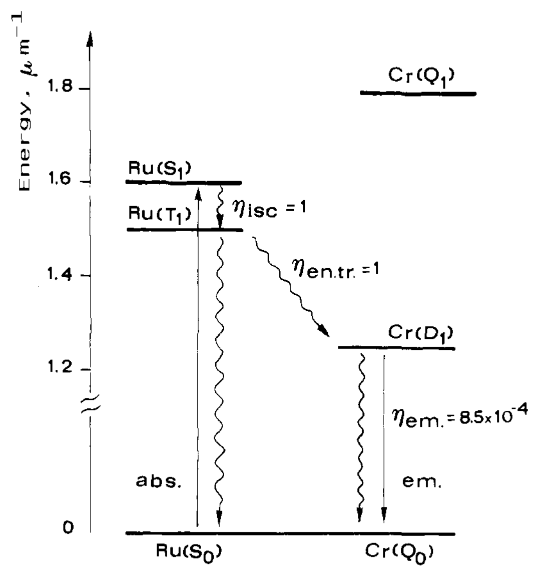

Figure 5. Energy level diagram and photophysical processes of $[NC–Ru(bpy)_2–NC–Cr(CN)_5]^{2-}$ (see text).

Intramolecular Energy Transfer. As a basis for the discussion the photophysical and photochemical behavior of the polynuclear complexes, let us first summarize the behavior expected from the individual subunits.

The photochemistry and photophysics of $Cr(CN)_6^{3-}$ in DMF at room temperature are well understood.[43,45,49,50] Excitation of $Cr(CN)_6^{3-}$ initially populates the Q_1 state. The quartet state undergoes an efficient solvation reaction (quantum yield, 0.08) in competition with intersystem crossing to the D_1 state. The intersystem crossing efficiency is ca. 0.5. In DMF, the doublet state gives rise to a typical, narrow emission in the far red (Figure 2) with lifetime in the millisecond range (Table I). The emission is completely quenched in water, presumably due to the coupling with high-frequency solvent acceptor modes.

As is the rule for Ruthenium(II) bipyridine complexes,[51] excitation of the $Ru(bpy)_2^{2+}$ fragment to the MLCT singlet state is expected to be followed by prompt, 100% efficient intersystem crossing to the triplet. The behavior of the T_1 state is known to depend heavily on the nature of the ligands occupying the two additional coordination sites at the metal (ancillary ligands).[52] When strong-field ancillary ligands (e.g., C-bonded cyanide) are present, the characteristic broad MLCT phosphorescence is observed, with lifetimes of the order of 10^{-7} s at room temperature. With weak-field ancillary ligands (e.g., ammonia) the emission is usually quenched at room temperature due to efficient radiationless deactivation via low-lying d–d states. It is difficult to decide a priori which type of behavior will be induced by the ancillary ligands of the binuclear (one C-bonded, one N-bonded cyanide) and trinuclear (two N-bonded cyanides) complexes. The behavior of suitable model compounds,[46] however, indicates that MLCT emission with lifetime in the 10^{-8} s range is to be expected as an intrinsic property of the $Ru(bpy)_2^{2+}$ fragment in these complexes.

Experimentally, visible excitation of the bimetallic complexes is found to give an emission (Figure 2) that, based on energy, band shape, and lifetime (Table I), must be clearly assigned to phosphorescence from the $Cr(CN)_6^{3-}$ fragment. Important observa-

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(44) The comparable MLCT energy of these mono-, bi-, and trinuclear systems presumably comes from compensation between the bathochromic effect of changing from C-bonded to N-bonded cyanide[26] and the hypsochromic effect of metalation.[16,17,30,37,38]

(45) Sabbatini, N.; Scandola, M. A.; Carassiti, V. *J. Phys. Chem.* **1973**, *77*, 1307.

(46) The previously studied $[NC–Ru(bpy)_2–NC–Ru(bpy)_2–CN]^+$ and $[NC–Ru(bpy)_2–CN–Ru(bpy)_2–NC–Ru(bpy)_2–CN]^{2+}$ complexes[26] are known to have the lowest excited state localized on the N-bonded chromophoric unit and can thus be taken as reasonably good models for the $Ru(bpy)_2^{2+}$ chromophore in the bi- and trinuclear complexes of this work. The room-temperature emission properties of the two model compounds are, respectively, as follows: ν_{max} = 1.40 μm^{-1}, τ = 90 ns; ν_{max} = 1.36 μm^{-1}, τ = 50 ns. At 77 K, ν_{max} = 1.59 and 1.46 μm^{-1}, respectively.

(47) A good correlation has been observed between MLCT absorption and emission energies for bis(bpy)Ru(II) complexes.[48] Application of this correlation to the polynuclear complexes studied in this work gives estimates of the triplet energy comparable to those based on the model compounds.

(48) (a) Fung, E. Y.; Chua, A. C. M.; Curtis, J. C. *Inorg. Chem.* **1988**, *27*, 1294. (b) Bignozzi, C. A., unpublished results.

(49) Sabbatini, N.; Scandola, M. A.; Balzani, V. *J. Phys. Chem.* **1974**, *78*, 541.

(50) Bolletta, F.; Maestri, M.; Balzani, V. *J. Phys. Chem.* **1976**, *80*, 2499.

(51) Watts, R. J. *J. Chem. Educ.* **1983**, *60*, 834.

(52) Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 2444.

tions are as follows: (i) the $Cr(CN)_6^{3-}$ fragment is totally transparent in the visible; (ii) the excitation spectrum closely corresponds to the MLCT absorption of the $Ru(bpy)_2^{2+}$ fragment; (iii) no appreciable MLCT emission is observed. These results constitute clear, direct evidence for the occurrence of intramolecular energy transfer from the $Ru(bpy)_2^{2+}$ light-absorbing fragment to the $Cr(CN)_6^{3-}$ light-emitting fragment in these polynuclear complexes. After ruling out processes originating from $Ru(S_1)$ (due to its intrinsically very short lifetime) and processes leading to $Cr(Q_1)$ (that are energetically forbidden) the only plausible energy-transfer process in these systems is that leading from $Ru(T_1)$ to $Cr(D_1)$ (Figure 5).

Given the spin-forbidden character of both of the coupled transitions (T_1–S_0 and Q_0–D_1) involved in the energy-transfer process and the negligible absorptivity of the acceptor unit in the spectral range of the donor emission, there is little doubt that the mechanism of the intramolecular energy-transfer process is in this case of the exchange (Dexter) type.[53] The energy-transfer step occurs within the time resolution of the laser flash, implying a rate constant greater than 10^8 s^{-1}. This result is not unexpected. In fact, the rates of related bimolecular quenching processes [e.g., excited $Ru(bpy)_2(CN)_2$[54] or $Ru(bpy)_3^{2+}$[55] quenched by $Cr(CN)_6^{3-}$] correspond to unimolecular rate constants within the encounter pair in the 10^8 s^{-1} range. Binding the two centers with a cyanide bridge is expected to induce a substantial increase in the electronic matrix element[56] (and thus in the rate) of the energy-transfer process. In a recent study, Closs[12] investigated the dependence of the rate of intramolecular exchange energy transfer on the length of the bridge connecting an organic donor to an organic acceptor. The shortest saturated bridging groups involved in those systems gave rate constants in the nanosecond time scale. As these bridges certainly provide much smaller exchange interactions than cyanide, it is quite likely that intramolecular energy transfer in the polynuclear complexes occurs in the subnanosecond time domain.

The efficiency of the energy-transfer step can be obtained by comparing the emission quantum yields of the bimetallic complexes with that of the free $Cr(CN)_6^{3-}$ fragment. The emission quantum yield is given by

$$\Phi = \eta k_r \tau \tag{2}$$

where η is the efficiency of population, k_r is the radiative rate constant, and τ is the lifetime of the $Cr(D_1)$ state. If k_r is assumed to be unaffected by bridging to ruthenium,

$$\frac{\Phi(\text{bimetallic complex}) \times \tau(Cr(CN)_6^{3-})}{\Phi(Cr(CN)_6^{3-}) \times \tau(\text{bimetallic complex})} = \frac{\eta(\text{bimetallic complex})}{\eta(Cr(CN)_6^{3-})} \tag{3}$$

The data in Table I yield ratios of 2.9 and 2.7 for $[NC-Ru(bpy)_2-NC-Cr(CN)_5]^{2-}$ and $[(CN)_5Cr-CN-Ru(bpy)_2-NC-Cr(CN)_5]^{4-}$, respectively. Since $\eta(Cr(CN)_6^{3-})$ is known to be ca. 0.5,[49] these numbers indicate that the efficiency of population of the $Cr(D_1)$ emitting state following light absorption by the ruthenium-centered chromophore is essentially unitary for both complexes.[57] The emission quantum yield thus essentially represents the efficiency of emission from the $Cr(D_1)$ state in the polynuclear complex (Figure 5).[58]

The unitary efficiency of population of the emitting state in the bimetallic complexes (as compared with the relatively inefficient $Q_1 \rightarrow D_1$ intersystem crossing of the free chromium complex) further confirms the conclusion that the intramolecular energy-transfer step leads directly from the T_1 state of the $Ru(bpy)_2^{2+}$ fragment to the emitting D_1 state of the $Cr(CN)_6^{3-}$ moiety, bypassing the $Cr(Q_1)$ state. Since the quartet state is the reactive state in the direct photolysis of $Cr(CN)_6^{3-}$,[43,45] it is to be anticipated that the bimetallic complexes should be much less photosensitive than the bare chromium complex. This expectation is borne out by the results showing that the bimetallic complexes are indeed appreciably photostable.

Photochemical molecular devices have been defined as appropriate assemblies of molecular components capable of performing light-induced functions.[15] From this point of view, the bimetallic complexes studied here can be seen as very simple devices made up of a light-absorbing component (chromophore) and one or two light-emitting units (luminophores). The performance of the luminophoric unit is controlled (and upgraded) by the presence of the attached chromophoric component in several ways. First, the presence of the $Ru(bpy)_2^{2+}$ chromophore greatly enhances the light-harvesting efficiency of the luminophore, providing high absorptivity and spectral sensitization in the visible region. In other words, the $Ru(bpy)_2^{2+}$ chromophore may be considered as an efficient "antenna" component of the molecular device. The device is superior to the bare luminophore not only in harvesting the incident light but also in funneling the absorbed energy to the emitting state, due to the avoidance of the inefficient intersystem crossing process of the luminophore. Finally, the bimetallic device is appreciably photostable, whereas the isolated luminophore is so photosensitive as to be hardly of any practical use. From this viewpoint, the antenna component behaves also as an efficient inner filter protecting the luminophore against its own photoreactivity.

Excited-State Absorption Spectra. In the long-lived excited state of $[NC-Ru(bpy)_2-NC-Cr(CN)_5]^{2-}$, the $Ru(bpy)_2^{2+}$ fragment is in its electronically ground state while the $Cr(CN)_6^{3-}$ fragment is in its doublet excited state. Therefore, to a first approximation, the ESA spectrum of the bimetallic complex is expected to be the sum of the ground-state absorption spectrum of the $Ru(bpy)_2^{2+}$ fragment (that coincides with that of the complex) and the ESA of the $Cr(CN)_6^{3-}$ ion. Since this latter spectrum is constituted by relatively weak absorption below 400 nm, the ESA of the bimetallic complex should practically coincide with the ground-state spectrum. The same conclusion holds for $[(CN)_5Cr-CN-Ru(bpy)_2-NC-Cr(CN)_5]^{4-}$. On simple grounds, therefore, no significant transient absorbance changes would be expected following pulsed excitation of these species. Both of the ESA difference spectra shown in Figure 3, however, clearly contain a broad, moderately intense (ϵ_{max}, 1500) visible band (λ_{max}, 620 and 640 nm). This new band must clearly arise from electronic transitions *between* the fragments, i.e., from intramolecular charge-transfer transitions.

A clue to the assignment of this transition is given by the spectra of some previously studied complexes. The ground-state absorption spectra of $[NC-Ru(bpy)_2-CN-Ru(NH_3)_5]^{3+}$ and $[(NH_3)_5Ru-NC-Ru(bpy)_2-CN-Ru(NH_3)_5]^{6+}$ exhibit intense visible bands (ϵ_{max}, 3500 and 5600; λ_{max}, 695 and 660 nm, respectively) that

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(53) Lamola, A. A. In *Energy Transfer and Organic Photochemistry*; Lamola, A. A., Turro, N. J., Eds.; Interscience: New York, 1969; p 17.

(54) Demas, J. N.; Addington, J. W.; Peterson, S. H.; Harris, E. W. *J. Phys. Chem.* **1977**, *81*, 1039.

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(56) Studies of optical electron transfer in related systems[16,17] show that cyanide bridges provide relatively strong electronic coupling between metal centers. Although the electronic matrix elements for electron and exchange energy transfer are somewhat different in nature,[12] bridging cyanides are also expected to provide good electronic coupling in the energy-transfer case.

(57) The actual values coming out from the calculation would be somewhat higher than unity (1.4 and 1.3). Although this could well be accommodated within the error limits of the measurements involved, it might also be taken as an indication of a small increase in the radiative rate constant of the chromium doublet because of the heavy-atom effect of ruthenium.

(58) It can be noticed that the lifetimes of the $Cr(D_1)$ excited state in the polynuclear complexes are definitely shorter than that of free $Cr(CN)_6^{3-}$ (Table I). As the doublet state of $Cr(CN)_6^{3-}$ is known to be very sensitive to environmental factors (e.g., solvent),[43] this effect could be easily ascribed to changes in the $Cr(D_1) \rightarrow Cr(Q_0)$ intersystem crossing upon bridge formation at cyanide. On the other hand, thermally activated repopulation of the $Ru(T_1)$ state should not be discarded as a possible source of this effect. In fact, with preexponential factors larger than 10^9 s^{-1}, the $Cr(D_1) \rightarrow Ru(T_1)$ process would take place in the submillisecond range, thus successfully competing with the lifetime of the $Cr(D_1)$ state. In such a case, a convenient kinetic scheme would be that of an equilibrium between the intrinsically long-lived, highly populated $Cr(D_1)$ state and the intrinsically short-lived, scarcely populated $Ru(T_1)$ state. Temperature-dependent experiments should, in principle, help to assess this point (Indelli, M. T., work in progress).

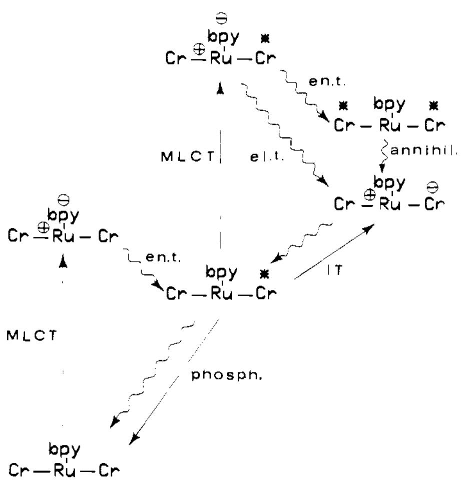

Figure 6. Schematic representation of the radiative and radiationless processes that can occur upon one- and two-photon excitation of $[(CN)_5Cr–CN–Ru(bpy)_2–NC–Cr(CN)_5]^{4-}$ (see text). Spin labels are omitted. Charge-transfer states [including MLCT states of the $Ru(bpy)_2{}^{2+}$ unit and excited-state IT] are indicated as electron-hole pairs, while the metal-centered excited states of the $Cr(CN)_6{}^{3-}$ unit are denoted with an asterisk.

correspond to Ru(II) → Ru(III) intervalence-transfer (IT) transitions.[16,17] It should be pointed out that, from the redox point of view, the *excited* $Cr(CN)_6{}^{3-}$ fragment is not very different from the Ru(III) pentammine unit (reduction potential, ca. −0.1 V vs SCE)[16] of the above mentioned complexes. In fact, the reduction potential of excited $Cr(CN)_6{}^{3-}$, as estimated from the excited-state energy and the ground-state potential, is about +0.1 V vs SCE. Therefore, a Ru(II) → *Cr(III) IT transition is expected to occur in the ESA spectra of these systems in the same spectral range[59,60] as the Ru(II) → Ru(III) IT transitions of the above compounds. We assign the new band in the ESA spectra of $[NC–Ru(bpy)_2–NC–Cr(CN)_5]^{2-}$ and $[(CN)_5Cr–CN–Ru(bpy)_2–NC–Cr(CN)_5]^{4-}$ to such types of transitions.[61,62] The lower intensity of the IT band in the Ru(II)–*Cr(III) systems with respect to the Ru(II)–Ru(III) case is likely due to the smaller spatial extension of the chromium orbitals, reflecting in a smaller electronic coupling between the metal centers.

This appears to be the first report of an intervalence-transfer transition involving an electronically excited metal center. This finding adds a new, intriguing facet to the electronic spectroscopy of polynuclear metal complexes.

Two-Photon Excitation. For both bimetallic complexes, the extinction coefficients of the excited state at the laser wavelength are practically the same as those of the ground state. Therefore, working with dilute solutions and relatively intense laser pulses, it is easy to induce absorption of a second photon by the long-lived excited state of $[NC–Ru(bpy)_2–NC–Cr(CN)_5]^{2-}$ or $[(CN)_5Cr–CN–Ru(bpy)_2–NC–Cr(CN)_5]^{4-}$. As the laser light is absorbed by the $Ru(bpy)_2{}^{2+}$ chromophore, this second absorption step must initially give a doubly excited state in which both the $Ru(bpy)_2{}^{2+}$ chromophore and a $Cr(CN)_6{}^{3-}$ group are excited, as depicted schematically in Figure 6 for the trinuclear case. Considering the efficiency and promptness of the intramolecular energy-transfer process observed upon one-photon excitation, an intriguing possibility can be envisioned for $[(CN)_5Cr–CN–Ru(bpy)_2–NC–Cr(CN)_5]^{4-}$ upon two-photon excitation. It is in fact conceivable that an intramolecular energy-transfer step may follow each of the absorption process, producing a complex in which *two* $Cr(CN)_6{}^{3-}$ fragments are simultaneously excited (Figure 6). A long-lived doubly excited state of this kind would be expected to have many of the experimental properties (e.g., emission spectrum and lifetime) in common with the singly excited state. Nevertheless, such a state could be of considerable interest from a number of more subtle points of view such as, e.g., simultaneous pair emission and light energy upconversion.[63]

The most sensible way to look for such a doubly excited state is to examine the dependence of emission intensities on the laser power: as such state can be formed in the trinuclear complex but not in the binuclear one, saturation of the emission intensity could be expected to occur at lower laser powers for $[NC–Ru(bpy)_2–NC–Cr(CN)_5]^{2-}$ than for $[(CN)_5Cr–CN–Ru(bpy)_2–NC–Cr(CN)_5]^{4-}$. The experimental results (Figure 4) give coincident saturation curves for both complexes, indicating that the doubly excited state of the trinuclear complex either is not formed at all or is intrinsically very short-lived. Both of these possibilities appear indeed quite likely in the light of the new IT band observed in the ESA spectra of Figure 3. The relaxed IT state is expected to lie at lower energy than the doubly excited state, thus providing an efficient channel for radiationless deactivation of the state initially populated by two-photon absorption (intramolecular electron-transfer quenching) or of the doubly excited state reached following intramolecular energy transfer (intramolecular electron-transfer doublet–doublet annihilation, Figure 6).

Bimolecular Doublet–Doublet Annihilation. The nonexponential decays observed in relatively concentrated solutions with high-intensity laser pulses can be ascribed to a bimolecular doublet–doublet annihilation processes, as shown schematically in eq 4 for

$$2[NC–Ru(bpy)_2–NC–Cr^*(CN)_5]^{2-} \rightarrow \text{products} \qquad (4)$$

the case of the binuclear species. This conclusion is based on the following evidence. The decays can always be analyzed in terms of a competition between first-order and second-order kinetics, with the weight of the second-order component increasing with laser power. The first- and second-order components give appreciably constant rate constant values. The second-order process is faster for the binuclear than for the trinuclear species and is enhanced by increasing the ionic strength, as expected on the basis of the ionic charges.

There is precedent in the literature for bimolecular doublet–doublet annihilation processes of mononuclear Cr(III) complexes,[36] which, in principle, may occur either by an energy- or an electron-transfer process. The surprising result here is that the bimolecular annihilation is exhibited both by the $[NC–Ru(bpy)_2–NC–Cr(CN)_5]^{2-}$ and the $[(CN)_5Cr–CN–Ru(bpy)_2–NC–Cr(CN)_5]^{4-}$ complexes but *not* by $Cr(CN)_6{}^{3-}$. No simple reasons for these difference in behavior are apparent, as the lifetimes of the three species are comparable and the electric charge of $Cr(CN)_6{}^{3-}$ is intermediate between those of the dinuclear and trinuclear species. Thus, one is left with the conclusion that, although the excitation is localized on the Cr(III) fragments, Ru(II) must play an active role in the annihilation process.[64] In other words,

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(59) An actual estimate of the expected energy is difficult. According to the Hush model,[60] the energy of an intervalence band depends on (increases with) (i) the difference between the potentials for oxidation and reduction of the two metal centers and (ii) the reorganizational energy associated with the electron transfer. For Ru(II) → *Cr IT, the first factor is smaller than for the Ru(II) → Ru(III) case.[16] The reorganizational energy, on the other hand, is likely to be larger for the poorly reversible chromium(III)/(II) couple than for the reversible Ru(III)/(II) couple. Presumably because of compensation between the two terms, the IT bands have very similar energies in the two cases.

(60) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

(61) The IT bands in the ESA spectra of $[NC–Ru(bpy)_2–NC–Cr(CN)_5]^{2-}$ and $[(CN)_5Cr–CN–Ru(bpy)_2NC–Cr(CN)_5]^{4-}$ should occur at comparable energies on the basis of the electrochemical potentials for oxidation of Ru(II) (see Results), provided that the reorganizational energies are comparable in the two systems. It has been pointed out by Sutin[21] that, because of their larger size (excluded volume), trinuclear complexes may have larger solvent reorganization energies than similar binuclear ones. As in the case of previously studied related systems,[16,17] the excluded-volume effect seems to be here quite a minor one.

(62) According to this assignment, an analogous intervalence transfer band (involving the ground-state $Cr(CN)_6{}^{3-}$ fragment) should be found in the ground-state absorption spectrum, blue-shifted with respect to the ESA by an amount corresponding to the excited-state energy. It is quite possible that the increase in the near-UV absorption observed in going from $Ru(bpy)_2(CN)_2$[37] to $[NC–Ru(bpy)_2–NC–Cr(CN)_5]^{2-}$ and $[(CN)_5Cr–CN–Ru(bpy)_2–NC–Cr(CN)_5]^{4-}$ (Figure 1) is, at least in part, due to the presence of this type of band.

(63) Endicott, J. F. *Acc. Chem. Res.* **1988**, *21*, 59.

the bimolecular annihilation must be of the electron-transfer type, leading to reduction of one of the initially excited chromium centers and to oxidation of a ruthenium center (e.g., eq 5 or 6). Whether the oxidized and reduced centers lie on the same (eq 5)

$$\text{products} = [\text{NC–Ru}^{+}(\text{bpy})_2\text{–NC–Cr}^{-}(\text{CN})_5]^{2-} + [\text{NC–Ru}(\text{bpy})_2\text{–NC–Cr}(\text{CN})_5]^{2-} \quad (5)$$

$$\text{products} = [\text{NC–Ru}^{+}(\text{bpy})_2\text{–NC–Cr}(\text{CN})_5]^{2-} + [\text{NC–Ru}(\text{bpy})_2\text{–NC–Cr}^{-}(\text{CN})_5]^{2-} \quad (6)$$

or on different (eq 6) molecules, it is difficult to tell on experimental grounds. It should be noticed that the annihilation mechanism emerging from this analysis is the bimolecular counterpart of the intramolecular annihilation process envisioned following two-photon excitation of $[(\text{CN})_5\text{Cr–CN–Ru}(\text{bpy})_2\text{–NC–Cr}(\text{CN})_5]^{4-}$.

Conclusion

The Ru(II)–Cr(III) bimetallic complexes synthesized and studied in this work provide clear-cut examples for the occurrence of intramolecular exchange energy transfer processes. These systems also constitute examples of how covalent coupling to a photosensitizer (chromophore) can improve in several ways (antenna effect, spectral sensitization, reduction of energy losses, protection against photoreactivity) the performance of a light emitter (luminophore). The behavior of the chromium-localized excited state of these Ru(II)–Cr(III) systems is peculiar in several respects, when compared with that of the isolated Cr(III) luminophore. The presence of intervalence-transfer transitions in the ESA and the occurrence of electron-transfer doublet–doublet annihilation are different but interlocked aspects of this peculiarity.

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(64) A reviewer has made the interesting suggestion that local dipole–dipole interactions between polynuclear complex ions may occur, and that this may differentiate the behavior of these complexes in the annihilation process from that of Cr(CN)_6^{3-}. We tend to maintain, however, the idea that the presence of Ru(II) is *chemically* important, as it seems unlikely that at high ionic strength dipolar interactions alone can make the sharp difference between Cr(CN)_6^{3-} and its bi- and trinuclear derivatives. These interactions could be important at a quantitative level, however, as they may contribute to the stability of the encounter pairs and thus to relatively high values observed for the bimolecular rate constants.

Spectroscopic Studies of the Charge Transfer and Vibrational Features of Binuclear Copper(II) Azide Complexes: Comparison to the Coupled Binuclear Copper Active Site in Met Azide Hemocyanin and Tyrosinase

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Abstract: Spectroscopic studies have been performed on a series of copper(II) azide compounds to determine the effects of ligand bridging on their charge-transfer bands. Structurally characterized copper(II) azide model complexes in three limiting geometries (terminal, μ-1,3, and μ-1,1) have been examined using absorption, resonance Raman, and infrared spectroscopies to identify the spectral features of the bound azide. The charge-transfer spectrum of azide bound in a terminal geometry consists of a single intense $\Pi^{\text{nb}}{}_{\sigma}$ band ($\epsilon = 2000\ \text{M}^{-1}\ \text{cm}^{-1}$) at approximately 400 nm. This feature splits into two bands at 365 ($\epsilon = 2100\ \text{M}^{-1}\ \text{cm}^{-1}$) and 420 nm ($\epsilon = 1000\ \text{M}^{-1}\ \text{cm}^{-1}$) in the μ-1,3 dimer. The effects of bridging on the azide-to-copper(II) charge-transfer spectra have been interpreted by using a transition dipole vector coupling model which has been evaluated experimentally with use of structurally defined complexes. The asymmetric intraazide stretch is observed to undergo resonance enhancement in each of the three azide geometries. The Raman excitation profiles have been interpreted by using A-term and B-term formalisms for the μ-1,1 and μ-1,3 complexes, respectively. Mixed isotope ($^{14}\text{N}^{14}\text{N}^{15}\text{N}$) data of the asymmetric intraazide stretch have also been obtained for this series of complexes, and the mixed isotope splitting is found to correlate with the coordination geometry of the azide. A normal coordinate analysis of this data has provided further insight into the origin of the observed mixed isotope splitting and has been used to determine electronic polarization within the azide. These results have been used to further interpret the spectroscopic data from met azide derivatives of mollusc (Busycon) and arthropod (Limulus) hemocyanins and tyrosinase to probe for variations in the active structure among these coupled binuclear copper proteins.

The properties of the coupled binuclear copper active site in hemocyanin, tyrosinase, and the multicopper oxidases have been studied in some detail.[1] In all of these metalloproteins, the active site is involved in interaction with dioxygen. Both hemocyanin and tyrosinase, when in the deoxy $[\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}]$ form, react with dioxygen to produce stable oxygenated species which exhibit similar spectroscopic features. Resonance Raman spectroscopy has demonstrated that in both systems, the bound dioxygen has been formally reduced to peroxide with an intraligand stretching frequency of $\sim 750\ \text{cm}^{-1}$.[2] X-ray absorption edge studies[3] have

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(1) (a) Solomon, E. I. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; ACS Symposium Series No. 372; American Chemical Society: Washington, DC, 1988; pp 116–150. (b) Solomon, E. I. In *Oxidases and Related Redox Systems*; A. Liss: New York, 1988; pp 309–329. (c) Solomon, E. I.; Pate, J. E.; Westmoreland, T. D.; Kau, L. S.; Allendorf, M. D.; Spira-Solomon, D. J. *Organic and Inorganic Low-Dimensional Crystalline Materials*; Delhaes, P., Drillon, M., Eds.; Plenum Publishing Corp.: 1987; pp 243–269. (d) Solomon, E. I. *Pure Appl. Chem.* **1983**, *55*, 1069–1088. (e) Solomon, E. I.; Penfield, K. W.; Wilcox, D. E. *Structure Bonding* **1983**, *53*, 1–57.

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