is followed by a rapid cleavage of one of the Mo-Hg bonds, producing a mercury-centered radical and a 16-electron molybdenum-containing cation. This cation coordinates solvent, the anion of the oxidant, or any other available ligand. The radical will abstract a chlorine atom from CCl_4 if it is present. If no easily abstractable atoms are available, the radical is proposed to dimerize to a tetrametallic species, which reacts with half of the available 16-electron cation to produce an observable pentametallic intermediate **7**. Compound **7** may decompose to **1** and a 16-electron cation, or it may undergo further oxidation, leading to a mercury-containing cation. This cation will coordinate triphenylphosphine to form a stable product **6**. Other ligands, such as CH_3CN or BF_4^-, form unstable adducts which extrude mercury to yield a second mole of the 16-electron Mo-containing cation.

In the absence of species which intercept reactive intermediates, the overall oxidation is a two-electron process, as confirmed by electrochemical measurements. The resulting tetrafluoroborate complex is a useful intermediate in the synthesis of substituted complexes. This work has demonstrated an alternate route to complexes of the type $CpMo(CO)_2(PR_3)L$, including the synthesis of the previously unreported CH_3CN complex (**3**). The unique mercury-phosphine complex $[CpMo(CO)_2(PPh_3)HgPPh_3]^+$ (**6**) has been discovered. And finally, the mechanism for this oxidative metal-metal bond cleavage reaction has been elucidated in detail.

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Intramolecular Energy Transfer in Ruthenium(II)-Chromium(III) Chromophore-Luminophore Complexes. $Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$

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A new trinuclear Ru(II)-Cr(III) chromophore-luminophore complex, $Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$, has been synthesized and characterized. Visible light absorption by the $Ru(bpy)_2^{2+}$ chromophore leads to emission from the $Cr(cyclam)(CN)_2^+$ luminophore, as a consequence of very efficient ($\geq 99\%$) and fast (subnanosecond time scale) chromophore-luminophore exchange energy-transfer process. The emission is intense ($\Phi = 5.3 \times 10^{-3}$ in H_2O) and long-lived ($\tau = 260$ μs in H_2O). The photophysical properties of the luminophore are slightly perturbed by interaction with the chromophore, resulting in a sharper emission band shape and shorter radiative and radiationless lifetimes. The presence of a Ru(II) → Cr(III) intervalence transfer state, hardly detectable in the ground-state spectrum, is clearly revealed by the excited-state absorption spectrum of the chromophore-luminophore complex.

Introduction

In the recent development of supramolecular photochemistry,[1] a relevant role has been played by studies on covalently linked multicomponent systems.[2,3] The field has seen a progressive evolution from the study of simple donor-acceptor systems ("dyads") toward that of more and more complex supramolecular species ("triads", "tetrads", and "pentads").[2-16] The main purpose of such studies has been the understanding of fundamental aspects of light-induced intercomponent electron and energy-transfer processes[4-11] and its application to the design of artificial biomimetic systems for light energy conversion[12-14,17] and photochemical molecular devices.[18-21] In this context, an interesting class of covalently linked systems is that of *chromophore-luminophore* complexes, i.e., systems in which the light energy is efficiently absorbed by appropriate molecular components (chromophores) and is then conveyed, by means of intercomponent energy-transfer processes, to a specific molecular component, which gives back the energy in the form of light emission (luminophore).[15,22,23] An interesting aspect of the behavior of such chromophore-luminophore complexes is the mimicry of the "antenna effect" of natural systems.[21,24,25] From a more practical standpoint, their peculiarity lies in the possibility to achieve separate optimization of the absorption and emission properties. From this viewpoint, chromophore-luminophore complexes are likely to be useful wherever

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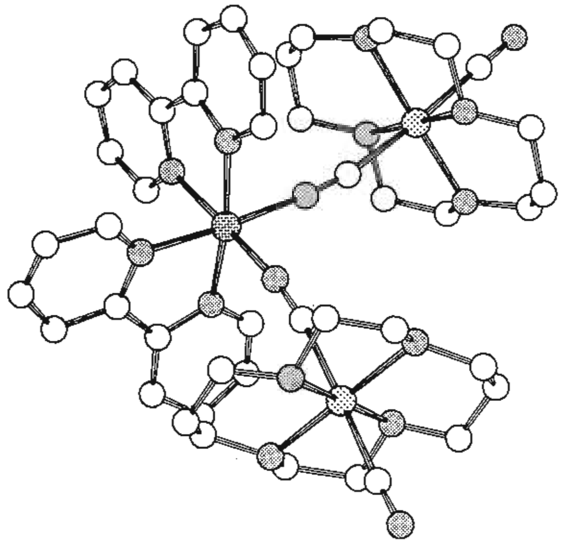

Figure 1. Structure of the $Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$ complex ion (adapted from ref 31).

very specific light absorption and light emission characteristics are required (e.g., in the design of luminescent labels for biochemical applications).[26]

Recently, some chromophore–luminophore complexes have been developed which couple the strong visible metal-to-ligand charge-transfer (MLCT) absorption of ruthenium(II) polypyridine complexes with the very sharp and typical doublet emission of Cr(III) complexes.[27,28] The best characterized systems are those based on the $Ru(bpy)_2^{2+}$ (bpy = 2,2′-bipyridine) chromophoric unit and $Cr(CN)_6^{3-}$ luminophoric units, linked via cyanide bridges.[27] In room-temperature DMF solution, efficient phosphorescence from the colorless Cr(III) unit is obtained upon visible absorption by the Ru(II)-based chromophore.[27]

We report now on the synthesis and photophysical characterization of a new Ru(II)–Cr(III) chromophore–luminophore, namely

$$Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$$

(cyclam = 1,4,8,11-tetraazacyclotetradecane). The *trans*-$Cr(cyclam)_2(CN)_2^{+}$ unit has been chosen as an ideal Cr(III) luminophore based on a number of unique properties, among which are high chemical and photochemical stability, emission in most solvents including water, and a relatively temperature-independent lifetime.[29] Moreover, the trans structure of the fragment, with two potentially bridging cyanide ligands, is particularly suited for future extension to complexes of higher nuclearity.[30] This chromophore–luminophore complex is one of the very few trinuclear metal complexes for which a crystal structure (Figure 1) is available.[31]

Experimental Section

Materials. $RuCl_3 \cdot 3H_2O$ (Aldrich), $CrCl_3 \cdot 3THF$ (Alfa), 1,4,8,11-tetraazacyclotetradecane (Aldrich), and tetraethylammonium tetrafluoroborate [TEA]TFB (Fluka) were commercial products of reagent grade. $Ru(bpy)_2Cl_2$,[32] $K_2Ru(bpy)(CN)_4$,[33] and *trans*-$[Cr(cyclam)(CN)_2]Cl$[34] were prepared according to literature procedures or available from previous studies. Sephadex CM-C25 (Pharmacia) was used in ion exchange chromatography.

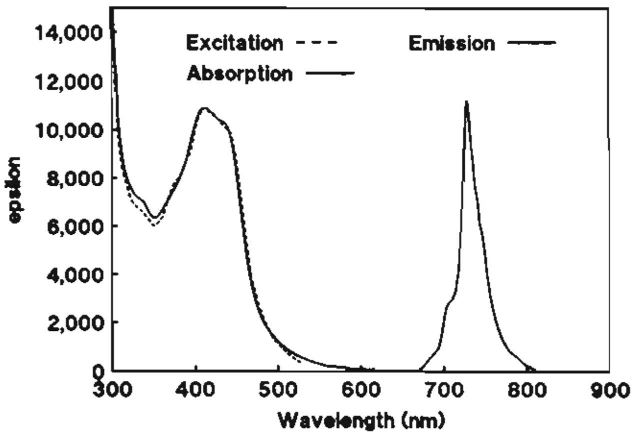

Figure 2. Absorption, emission, and excitation spectra of $Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$ in aqueous solution.

$\{Ru(bpy)_2[Cr(cyclam)(CN)_2]_2\}(PF_6)_4$. A 0.125-g amount of $Ru(bpy)_2Cl_2 \cdot H_2O$ (4.9×10^{-4} mol) was dissolved in 30 mL of boiling water, under an argon atmosphere. The solution was filtered and cooled at 60 °C, and a 1.7-g amount of $[Cr(cyclam)(CN)_2]Cl$ (5×10^{-3} mol) was added. Heating at 60 °C was continued for 60 h, maintaining the solution under Ar and in the dark. After cooling, the solution was loaded on a 2 × 20 cm Sephadex CM-C25 column. Elution was first performed with 0.04 M NaCl to collect the unreacted $[Cr(cyclam)(CN)_2]Cl$, 0.1 M NaCl to remove a small orange fraction, which was discarded, and 0.16 M NaCl to collect a main (red-orange) fraction, which was observed to contain the trinuclear complex. The 0.16 M NaCl fraction was concentrated to 20 mL and the product precipitated by addition of NH_4PF_6 and air-dried. Anal. Calcd for $\{Ru(bpy)_2[Cr(cyclam)(CN)_2]_2\}(PF_6)_4 \cdot 2H_2O$: C, 33.71; H, 4.11; N, 14.28; Ru, 6.45; Cr, 6.63. Found: C, 34.13; H, 4.07; N, 14.06; Ru, 7.10; Cr, 6.52.

Apparatus and Procedures. UV–vis spectra were recorded with a Kontron Uvikon 860 spectrophotometer. Infrared spectra were recorded on KBr pellets with a IFS88 Bruker FTIR spectrophotometer.

Emission spectra were taken with a Perkin-Elmer spectrofluorimeter 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 ($\Phi = 0.042$) as a reference emitter.

Laser flash photolysis experiments were carried out using an Applied Photophysics detection system coupled with a J&K System 2000 frequency-doubled ruby laser source, delivering 25-ns (half-width) pulses of 347-nm radiation. The excited-state absorption (ESA) spectrum was taken 50 ns after the start of the laser pulse. The absorbance changes were converted into molar absorptivity changes by standardization against absorbance-matched solutions of benzophenone in benzene (molar absorptivity of benzophenone triplet at 532 nm, 7630 M^{-1} cm^{-1}).[35] In this procedure, complex concentrations higher than the concentration of absorbed photons (ca. 10^{-4} M) were always used, in order to avoid bleaching artifacts.

Cyclic voltammetry measurements were carried out on Ar-purged DMSO and water solutions containing 0.1 M [TEA]TFB using a previously described apparatus.[36]

The FAB mass spectrometric measurements were performed on a double-focusing, reverse-geometry VG ZAB2F instrument. The bombarding Xe atom beam had a translational energy of 8 keV. Glycerol was used as the matrix.

Results

The trinuclear complex was characterized, besides by elemental analysis (see Experimental Section) and X-ray diffraction (Figure 1),[31] also by FAB mass spectrometry. In the FAB spectrum, the peak of highest m/z ratio was found at 1457. This corresponds to the value expected for a species originating from the salt examined by loss of one counterion (i.e., $\{Ru(bpy)_2[Cr(cyclam)$-

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Table I. Redox Potentials of the Trinuclear Complex and Some Model Compounds[a]

complex	redox process Ru(III)/Ru(II)	 bpy/bpy$^-$(1)	 bpy/bpy$^-$(2)	 Cr(III)/Cr(II)
$Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$	+1.35[b]	−1.44[c]	−1.58[c]	−1.82[d]
$Ru(bpy)_2(CN)_2$	+0.85[c,e,f]	−1.54[c,e,f]	−1.80[c,e,f]	
$Ru(bpy)_2(CH_3CN)_2^{2+}$	+1.44[c,g,h]			
$Cr(cyclam)(CN)_2^+$				−1.81[d]

[a] Data from cyclic voltammetry vs SCE; in DMSO, unless otherwise noted. [b] Irreversible process, anodic peak potential. [c] Reversible process, halfway potential. [d] Irreversible process, cathodic peak potential. [e] In DMF. [f] Reference 42. [g] In CH_3CN. [h] Reference 43.

$(CN)_2]_2{\cdot}(PF_6)_3\}^+$), a feature common to other cyano-bridged polynuclear complex salts.[37] Infrared spectra were also measured, to help in establishing the coordination mode of the bridging cyanides (which is left undetermined by the crystallographic data). The weakness of the bands in the CN stretching region (2133, 2062 cm^{-1}) is consistent with the fact that the bridging cyanides are C-bonded to Cr(III) and N-bonded to Ru(II).[38–40]

Solutions of the hexafluorophosphate salt of $Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$ in water and in polar organic solvents were appreciably stable both in the dark and under room light.[41] The absorption spectrum of the trinuclear complex in aqueous solution is shown in Figure 2. The lowest MLCT transition appears as a pronounced shoulder at 440 nm. This transition occurs at the same wavelength in acetonitrile but shifts to 455 nm in DMF.

The electrochemical behavior of the $Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$ complex was studied by cyclic voltammetry in DMSO solution (0.1 M [TEA]TFB supporting electrolyte, glassy-carbon working electrode, SCE reference electrode, sweep rate 200 mV/s). The cyclic voltammograms were characterized in the anodic region by an irreversible wave attributable to oxidation of the Ru(II) center. In the cathodic region, two reversible waves corresponding to reduction of the two bpy ligands and an irreversible wave assignable to the reduction of the Cr(III) centers were observed. In Table I, the redox potentials of the trinuclear complex are compared with those of the $Cr(cyclam)(CN)_2^+$ molecular component and those of possible models for the bis(bipyridine)ruthenium(II) unit.[42,43] In water (0.1 M [TEA]TFB supporting electrolyte, platinum or mercury working electrode, SCE reference, sweep rate 200 mV/s), the cyclic voltammetry was qualitatively similar to that in DMSO, although the results are less clear-cut because of (i) the superposition of the Cr(III) reduction with the first bpy reduction at ca. −1.4 V and (ii) the superposition of the oxidation of Ru(II) (shoulder at +1.20 V) with the onset of the solvent discharge. When one changes the solvent from DMSO to water, a substantial shift in the cathodic peak potential for Cr(III) reduction was also observed with free $Cr(cyclam)(CN)_2^+$ (DMSO, −1.81 V; H_2O, −1.34 V; vs SCE).

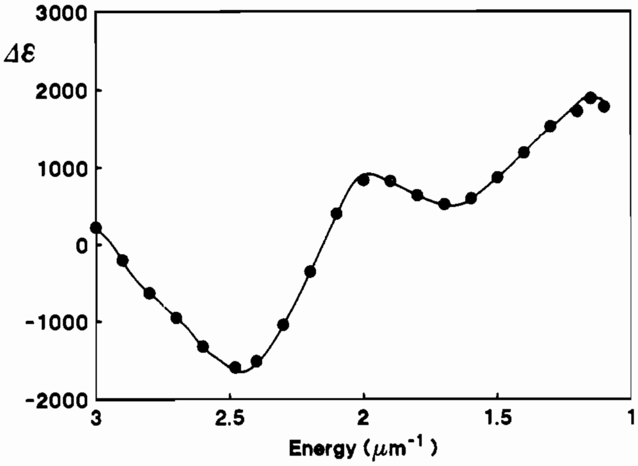

Figure 3. Transient difference spectrum obtained in the laser flash photolysis of $Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$ in aqueous solution.

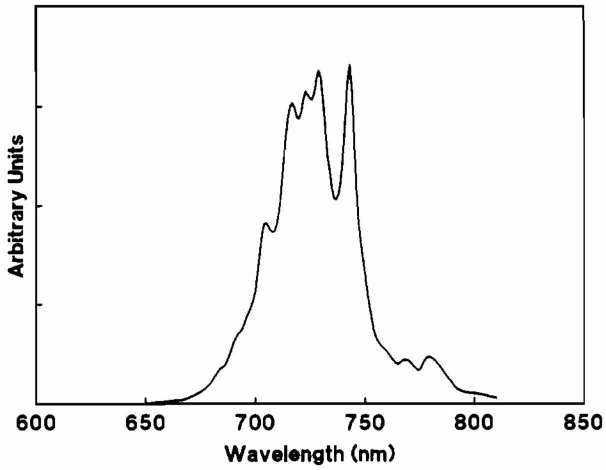

Figure 4. Emission spectrum of $Cr(cyclam)(CN)_2^+$ in aqueous solution.

The $Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$ complex was found to emit in room-temperature aqueous solution.[44] The emission spectrum consists of a very sharp band at 727 nm (Figure 2). A quantum yield $\Phi = 5.3 \times 10^{-3}$ was measured for this emission in aqueous aerated solutions. No appreciable ($\Phi \geq 10^{-6}$) emission was present in the 600–700-nm region. The excitation spectrum of the 727-nm emission is also shown in Figure 2. The rise time of the emission was experimentally indistinguishable from that of the exciting laser pulse. At low laser power (concentration of excited species in the irradiated pathway $\leq 10^{-5}$ M) the decay was monoexponential, with lifetime τ = 260 μs in aerated aqueous solution. No appreciable change was observed upon deaeration of the aqueous solutions. Relatively small changes in lifetime were observed by changing the solvent to DMF (τ = 300 μs). At higher laser powers, nonexponential decays were observed, due to the occurrence of bimolecular excited-state annihilation processes.[45]

In laser flash photolysis, aqueous solutions of $Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$ exhibited the transient spectral changes shown in Figure 3. The decay of the transient absorbance change always occurred with the same lifetime as that of the 727-nm emission, identifying the transient as excited-state absorption (ESA).

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(38) The infrared spectra of ruthenium(II) cyanide complexes are characterized by intense bands in the cyanide stretching region, whereas for chromium(III) cyanide complexes much weaker features are generally observed. This is a consequence of the different back-bonding ability of the two metal ions.[39]

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(40) Prolonged heating in the solid state (KBr pellets at 150 °C) is required to observe some isomerization of the bridging cyanides, as shown by a pronounced intensification of the bridging cyanide bands (2060, 2091 cm^{-1}).[39]

(41) Irradiation with photochemical light sources or repeated laser flashes caused some photodecomposition (presumably, release of $Cr(cyclam)(CN)_2^+$), with estimated $\Phi \approx 10^{-3}$.

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(44) Because of facile quenching by bases of the doublet state of the luminophore,[29] all the experiments were performed in solutions containing 1.0×10^{-3} M $HClO_4$.

(45) As for related Ru(II)–Cr(III) complexes,[27] the occurrence of bimolecular excited-state annihilation was proven by studying the dependence of the kinetics of excited-state decay on laser intensity and ionic strength.

For purposes of comparison, some experimental data were also obtained for the free luminophore, Cr(cyclam)(CN)$_2$$^+$.[44] The emission spectrum of the complex in aqueous solution is shown in Figure 4. In agreement with previous findings,[29] the emission lifetime and quantum yield were 310 μs and 3.3×10^{-3}, respectively, in aqueous solution. Aside from direct excitation, the emission could be observed in sensitization experiments[46,47] using Ru(bpy)(CN)$_4$$^{2-}$ as energy donor in aqueous solution.[33] The spectral profile and the lifetime of the sensitized emission were indistinguishable from those of the direct one. The sensitization technique was used to estimate the efficiency of the quartet–doublet intersystem crossing in the Cr(III) complex.[48] The comparison between the direct and sensitized emission intensities (absorbance-matched solutions, sensitized emission extrapolated to total quenching) gave a value for the intersystem crossing efficiency of 1.0 ± 0.1. In the laser flash photolysis of Cr(cyclam)(CN)$_2$$^+$, no appreciable spectral changes were observed in the visible region.

Discussion

Properties of Molecular Components. The proof that a given polynuclear complex is indeed a supramolecular species lies in the fact that the molecular components have recognizable, albeit perhaps mutually perturbed, individual properties.[49] Aside from those related to the excited-state behavior (see subsequent sections), relevant intrinsic properties of the components are spectroscopic energies and redox potentials.

The energies of the MLCT bands in a –Ru(bpy)$_2$$^{2+}$– chromophore depend strongly on the electron-donating properties of the groups that occupy the two remaining coordination sites at the metal (ancillary ligands).[50] In Ru(bpy)$_2$[Cr(cyclam)(CN)$_2$]$_2$$^{4+}$ (λ_{max} = 455 nm in DMF), the "ancillary ligands" of the –Ru(bpy)$_2$$^{2+}$– chromophore are the Cr(cyclam)(CN)$_2$$^+$ fragments, which coordinate through the N end of one cyanide. Such fragments can be formally regarded as pseudonitrile ligands. The MLCT energy can be compared with that of a few other trinuclear species with similar pseudonitrile fragments: Ru(bpy)$_2$[Ru(bpy)$_2$(CN)$_2$]$_2$$^{2+}$ (λ_{max} = 480 nm in CH$_3$CN)[36] and Ru(bpy)$_2$[Cr(CN)$_6$]$_2$$^{4-}$ (λ_{max} = 490 nm in DMF).[27] This comparison shows that not only the type of metal but also the composition of its coordination sphere influence the electron-donating properties of the pseudonitrile fragments. The solvent effect on the MLCT band of Ru(bpy)$_2$[Cr(cyclam)(CN)$_2$]$_2$$^{4+}$ is relatively small, consistent with the fact that the chromophore in the trinuclear complex is shielded from second-sphere donor–acceptor interactions.[51-54] For the Cr(III)-containing components, no spectroscopic considerations can be made because of the low intensity of the ligand field bands, which are completely hidden below the intense MLCT bands of the Ru(II)-containing component.

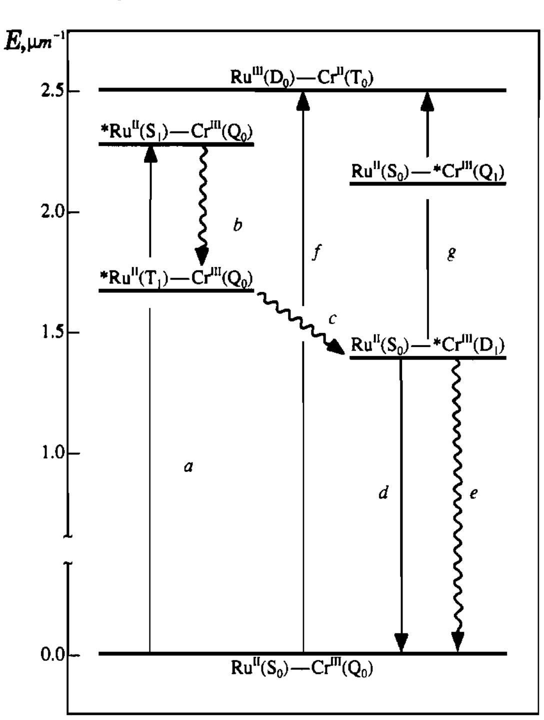

Figure 5. Energy level diagram for the Ru(bpy)$_2$[Cr(cyclam)(CN)$_2$]$_2$$^{4+}$ chromophore–luminophore complex. The photophysical pathway leading from chromophore absorption to luminophore emission is represented by processes a–e. Processes f and g correspond to the intervalence transfer transitions detected from the ESA spectrum.

The redox properties of the molecular components in the trinuclear complex can be straightforwardly analyzed (Table I). The reduction of Cr(III) takes place at the same potential and with the same (irreversible) wave form as in the isolated Cr(cyclam)(CN)$_2$$^+$ complex, indicating that bridge formation does not substantially alter the electron density at Cr(III). For the oxidation of the Ru(II) center, a difficulty is represented by the unavailability of the component (the N-bonded isomer of Ru(bpy)$_2$(CN)$_2$) as an individual species. If a comparison is made with the potentials (Table I) of the C-bonded cyanide complex and of the N-bonded bis(acetonitrile) complex, it is seen that, beyond the formal similarity, the NC–Cr(cyclam)–CN$^+$ fragment behaves indeed as a pseudonitrile ligand toward Ru(II). The relatively high potential for Ru(II) oxidation (e.g., with respect to Ru(bpy)$_2$(CN)$_2$) indicates that this pseudonitrile ligand is a relatively poor electron donor.[55] The reduction of the bipyridine ligands occurs in a typical potential range for this type of processes. The samll shift toward less negative values with respect to Ru(bpy)$_2$(CN)$_2$ is an indirect consequence of the decreased electron density at the metal.

On the whole, the spectroscopic and electrochemical results are fully consistent with the description of the trinuclear complex as a supramolecular species, i.e., an electronically localized multicomponent system in which the molecular components have well-defined individual properties, perturbed in a relatively small and reasonably understandable way by intercomponent interactions.

Nature of the Emission. The emission of the Ru(II)–Cr(III) chromophore–luminophore complex undoubtedly originates from the Cr(III) luminophoric unit. Its energy and lifetime (ν_{max} = 1.37 μm^{-1}, τ = 260 μs) are similar to those of Cr(cyclam)(CN)$_2$$^+$

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(46) The bimolecular quenching constant, as obtained from Ru(bpy)(CN)$_4$$^{2-}$ lifetime measurements, is 2.7×10^9 M^{-1} s^{-1} (μ = 2.7×10^{-3} M). In addition to this dynamic quenching process, some static quenching[47] also takes place in this system, as shown by intensity quenching measurements, due to the occurrence of ion pairing.

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(52) While being smaller, the solvent effect for Ru(bpy)$_2$[Cr(cyclam)(CN)$_2$]$_2$$^{4+}$ (MLCT energies in the order DMF < H$_2$O ≈ CH$_3$CN) is also qualitatively different from that for systems in which the solvatochromism is regulated by acceptor (e.g. Ru(bpy)$_2$(CN)$_2$, MLCT energy DMF ≈ CH$_3$CN < H$_2$O)[53] or donor (e.g., Ru(bpy)$_2$(NH$_3$)$_2$$^{2+}$, MLCT energy DMF < CH$_3$CN)[54] second-sphere interactions. Tentative explanations could be based on any of the following solvatochromic mechanisms for the trinuclear complex: (i) third-sphere donor–acceptor effects with competition between donor interactions (at the aza positions of cyclam) and acceptor interactions (at the free cyanides); (ii) a solvent repolarization mechanism, in which the $(1/n^2) - (1/D_s)$ function (with n = refractive index and D_s = static dielectric constant) is the relevant solvent parameter.

(53) Kitamura, N.; Sato, M.; Kim, H.-B.; Obata, R.; Tazuke, S. *Inorg. Chem.* **1988**, *27*, 651.

(54) Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224.

(55) This conclusion should not be generalized to all the metal–cyano fragments as ligands. For example, in previous work[36] it was concluded that Ru(bpy)$_2$(CN)$_2$ behaves as a rather good electron donor toward the same Ru(II) center as considered here. It is clear that the nature, oxidation state, and coordination environment of the metal carrying the cyanide function is of paramount importance in determining the donor properties of the donor N atom.

(ν_{max} = 1.40 μm^{-1}, τ = 310 μs). On the other hand, any plausible emission from the $Ru(bpy)_2^{2+}$ chromophore would be expected at a higher energy (ca. 1.65 μm^{-1}; see next section) and with a much shorter lifetime (typically,[50] $\tau \leq 1$ μs). Aside from a moderate decrease in lifetime and increase in quantum yield (see below for a discussion of this point), the main difference between the emission of the Ru(II)–Cr(III) complex and that of the free $Cr(cyclam)(CN)_2^+$ unit lies in the sharp band shape of the chromophore–luminophore complex (Figure 2), as contrasted with the wider and highly structured profile of the free chromophore emission (Figure 4). In Cr(III) emission spectroscopy, prominent structure (very weak 0–0 band, intense vibronic side bands) is typical of centrosymmetric coordination (O_h, D_{4h}), whereas sharp bands are often observed in noncentrosymmetric environments (i.e., C_{4v}, C_{2v}, D_{3d}).[56] The sharpening of the emission obtained when the luminophore $Cr(cyclam)(CN)_2^+$ is incorporated into the chromophore–luminophore complex is most probably due to the lowering in symmetry of the Cr(III) coordination environment upon bridge formation (Figure 1).

Energy Levels. The energy level diagram of the $Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$ trinuclear complex is depicted in Figure 5.

The energy of the singlet MLCT state of the $-Ru(bpy)_2^{2+}-$ chromophore ($Ru(S_1)$) can be directly obtained from the lowest energy shoulder in the absorption spectrum (2.27 μm^{-1}). That of the corresponding triplet state ($Ru(T_1)$) can be estimated as ca. 1.65 μm^{-1} from a correlation between absorption energy and emission energy for complexes containing the bis(bipyridine)ruthenium(II) chromophore.[57-59]

The energy of the Cr(III)-centered doublet state ($Cr(D_1)$) is directly measured from the emission spectrum of the complex (1.37 μm^{-1}). For that of the Cr(III)-centered lowest quartet excited state ($Cr(Q_1)$), a value of ca. 2.1 μm^{-1} can be estimated from the lowest ligand field band in the absorption spectrum of $Cr(cyclam)(CN)_2^+$ using the 5% intensity empirical criterion.[60]

The electrochemistry of the trinuclear complex (Table I) shows that it is relatively easy to oxidize the Ru(II) center and to reduce the Cr(III). This implies the presence of a Ru(II) → Cr(III) charge-transfer (or intervalence-transfer, IT) state, with a zero–zero energy approximately[61-63] equal to the difference in redox potentials for these two processes (ca. 2.5 eV in aqueous solution). According to Hush theory,[62] the spectroscopic energy of an IT state, E_{op}, is related to the zero–zero energy, E^{0-0}, by $E_{op} = E^{0-0} + \lambda$, where λ is the reorganizational energy of the electron-transfer process. A plausible value for the reorganizational energy in this system, 0.48 μm^{-1}, can be taken from the IT spectra of related cyano-bridged complexes in water.[64,65] Using such a value, a spectroscopic energy of ca. 2.5 μm^{-1} can be estimated for the Ru(II) → Cr(III) IT state. The corresponding spectral transition, which is expected to be moderately intense ($\epsilon_{max} \leq 3000$),[66] is likely to be completely hidden by the very intense MLCT bands of the $Ru(bpy)_2^{2+}$ chromophore, which lie in the same spectral region (Figure 2).

Intercomponent Energy Transfer. Following excitation of the $-Ru(bpy)_2^{2+}-$ chromophore (process a in Figure 5), electronic energy is very efficiently transferred to the $Cr(cyclam)(CN)_2^+$ luminophore. This is demonstrated by the absence of any broad-band emission from the chromophore (expected at ca. 605 nm, see previous section) and by the efficient sensitization (Figure 2) of the luminophore phosphorescence (process d in Figure 5). On the basis of the extent of chromophore emission quenching (which, by comparison with common free chromophores of the same type, is >99%), the energy-transfer efficiency is unity. Assuming that, as usual for Ru(II) polypyridine complexes,[67] $Ru(S_1) \rightarrow Ru(T_1)$ intersystem crossing in the chromophore (process b in Figure 5) takes place in the picosecond time scale and precedes any other process, the only energetically allowed energy-transfer process is $Ru(T_1) \rightarrow Cr(D_1)$ (process c in Figure 5). As to the rate of this process, both the lack of a measurable rise time for the luminophore emission and the extent of chromophore emission quenching indicate that this process takes place in the subnanosecond time scale. The energy-transfer process, involving spin-forbidden excited states on both components, must definitely occur by an exchange mechanism.[68] The fast rate of the energy-transfer process is a further proof of the already noticed[36,65] ability of bridging cyanides to provide electronic coupling between metal centers.[69] It should be noted that many $Ru(bpy)_2X_2$ species (X = ancillary ligand) give rise to efficient photodissociation of the ancillary ligands, with the nitrile complexes being particularly photoreactive in this regard (Φ = 0.3–0.4 for X = CH_3CN).[70] The fact that the chromophore–luminophore complex is only slightly photoreactive is consistent with efficient intramolecular quenching of the Ru(II)-based excited state.

The quantitative comparison between the emissions of the chromophore–luminophore complex and of the free luminophore deserve some discussion. The ratio between quantum yield and lifetime is proportional to the product, ηk_r, of the efficiency of population of the doublet state and the radiative rate constant of the doublet emission. The results indicate that ηk_r for the chromophore–luminophore complex is approximately twice that for the free luminophore. By analogy with what is commonly made in analyzing data from bimolecular sensitization,[47,48] it would be tempting to attribute the variations in ηk_r to changes in η for the two pathways ($Ru(S_1) \rightarrow Ru(T_1) \rightarrow Cr(D_1)$ vs $Cr(Q_1) \rightarrow Cr(D_1)$), assuming a constant k_r value for free and complexed luminophore.[71] This cannot be true in the present case, however, as η is already close to unity in the free luminophore. Thus, the observed increase in ηk_r must be attributed to an increase in k_r. As a matter of fact, the radiative rate constants of Cr(III) are known to be sensitive to the environment.[56,72] Aside from other possible effects (associated with lowering of effective coordination symmetry[56] or small changes in the $Cr(Q_1)$–$Cr(D_1)$ energy gap[72])

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(56) Foster, L. S. *Chem. Rev.* **1990**, *90*, 331.

(57) A triplet energy value of 1.65 μm^{-1} can be estimated by comparison with a series of bi- and trinuclear complexes containing the bis(bipyridine)ruthenium(II) chromophore,[28,58] for which the absorption and room-temperature emission energies correlate in an appreciably linear fashion. Using the correlation observed between absorption and emission for $Ru(bpy)_2(CN)_2$ in solvents of various acceptor character,[59] a similar value (1.60 μm^{-1}) would have been obtained.

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(59) Fung, E. Y.; Chua, A. C. M.; Curtis, J. C. *Inorg. Chem.* **1988**, *27*, 1294.

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(61) Besides the usual approximations involved in the estimation of zero–zero energies from differences in electrochemical potentials,[62] the irreversible nature of the electrochemical processes observed should also contribute to the uncertainty in this estimate.

(62) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(63) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107.

(64) The model systems are of the type $Ru(bpy)_2[(CN)M^{III}]_2$ (M^{III} = $Ru(NH_3)_5^{3+}$ or $Ru(NH_3)_4py^{3+}$).[65] Given the practical identity of geometry and metal–metal distance, the outer part of the reorganization energy can be safely considered to be the same as in the present case. The inner part, which is known to be very small when M(III) = $Ru(NH_3)_5^{3+}$, is likely to give a small contribution in the present case as well, due to the steric constraint imposed by the cyclam macrocycle on the Cr(III) coordination sphere.

(65) Bignozzi, C. A.; Paradisi, C.; Roffia, S.; Scandola, F. *Inorg. Chem.* **1988**, *27*, 408.

(66) This estimate, based on complexes of the $Ru(bpy)_2[(CN)M^{III}]_2$ type (M^{III} = $Ru(NH_3)_5^{3+}$),[65] should be considered as an upper limit, due to the smaller radial extension of the Cr(III) relative to Ru(III) orbitals.

(67) Kirk, A. D.; Hoggard, P. E.; Porter, G. B.; Rockley, M. G.; Windsor, M. W. *Chem. Phys. Lett.* **1976**, *37*, 199.

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

(69) The energy transfer process in the chromophore–luminophore complex ($k \geq 10^9$ s^{-1}) is definitely faster than expected on the basis of similar bimolecular processes. For example, the bimolecular rate constant for energy transfer between $Ru(bpy)_3^{2+}$ and $Cr(cyclam)(CN)_2^+$ in water at μ = 0.01 M is 2.0 × 10^7 M^{-1} s^{-1} (M. T. Indelli, unpublished results), implying a unimolecular rate constant within the encounter complex of ca. 1.0 × 10^7 s^{-1}.

(70) Pinnick, D. V.; Durham, B. *Inorg. Chem.* **1984**, *23*, 1440.

(71) The assumption of constant k_r was made in a previous paper on related Ru(II)–Cr(III) complexes, in which, however, η of the free luminophore was known to be lower than unity.[27]

(72) Endicott, J. F.; Lessard, R. B.; Lynch, D.; Perkovic, M. W.; Ryu, C. K. *Coord. Chem. Rev.* **1990**, *97*, 65.

some increase in k_r is likely to be expected in the chromophore–luminophore complex because of the additional spin–orbit coupling provided by the presence of the heavier Ru(II) metal ion in the second coordination sphere of Cr(III).[73]

Excited-State Absorption Spectrum. The long-lived excited state of the chromophore–luminophore complex is definitely localized on the luminophoric component. This notwithstanding, the ESA spectrum of the chromophore–luminophore complex is quite different from that of the free luminophore. In fact, while $Cr(cyclam)(CN)_2^+$ does not give rise to appreciable absorbance changes in the whole visible region upon excitation,[74] the ESA difference spectrum of $Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$ (Figure 3) exhibits a bleaching at 2.45 μm^{-1} and a prominent absorption which appears to peak at 1.10 μm^{-1}, both with comparable molar absorptivity changes. The assignment of these spectral features becomes straightforward upon consideration of the energy level diagram of the chromophore–luminophore complex (Figure 5), where a Ru(II) → Cr(III) IT state is expected to occur at ca. 2.5 μm^{-1}. Upon excitation of the Cr(III) center, the transition to the IT state (process f in Figure 5) is expected to be bleached and replaced by a new absorption (process g in Figure 5), red-shifted with respect to the ground-state band by an amount corresponding to the doublet energy. The energy of the bleaching compares well with the expected energy of the IT state (given the approximations involved in the estimate, see above). The shift between bleaching and absorption closely matches the doublet energy (1.37 μm^{-1}). The half-widths of the bleaching and absorption in the ESA spectrum (0.5 ± 0.1 μm^{-1}), which are related to the reorganizational energies upon ground- and excited-state electron transfer,[62] are of the same magnitude as for mixed-valence cyano-bridged polynuclear complexes.[36,65,75] The intensities of the ground- and excited-state IT bands (ϵ_{max}, ca. 1500), which reflect the degree of metal–metal electronic coupling,[62] are similar to those of IT bands of other Ru(II)–Cr(III) cyano-bridged complexes.[27,75–77] The observation of ground- and excited-state intervalence-transfer spectra, with reasonable energies, intensities, and half-widths, gives further support to the picture of these Ru(II)–Cr(III) chromophore–luminophore complexes as electronically localized species, from the standpoint of both metal oxidation states and excitation energy.

Conclusions. The electronic interaction between the molecular components in the $Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$ trinuclear complex is sufficiently weak as to allow a localized description. Nevertheless, coupling to the chromophore induces some perturbation in the luminophoric units, resulting in a narrowing of the emission band shape and an increase in radiative and radiationless rate constants. The $Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$ complex is a chromophore–luminophore complex with a number of interesting properties, among which are (i) strong visible absorption, (ii) very sharp, long-lived, and intense (for a Cr(III) system) phosphorescence, and (iii) behavior relatively independent of environment (solvent, temperature, oxygen), including good performance in water.

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Registry No. $\{Ru(bpy)_2[Cr(cyclam)(CN)_2]_2\}(PF_6)_4$, 137467-25-5; $Ru(bpy)_2Cl_2$, 15746-57-3; *trans*-$[Cr(cyclam)(CN)_2]Cl$, 85245-74-5.

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[73] Most probably, the same type of effect acts on radiationless deactivation as well (process e in Figure 5), being responsible for the shorter lifetime observed (both here and the previously studied case[27]) for the Ru(II)–Cr(III) chromophore–luminophore complex relative to the free luminophore.

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[77] The IT intensities of the cyano-bridged Ru(II)–Cr(III) complexes are definitely smaller than those of analogous Ru(II)–Ru(III) complexes.[36,65] This may be ascribed to the smaller radial extension of Cr(III) orbitals relative to Ru(III) orbitals.

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^{13}C CP-MAS, ^{13}C, and ^1H NMR Spectroscopic Study of Mixed-Valence 1,1″-Biruthenocenium Salts

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1,1″-Biruthenocene (**1**) reacts with FeX_3 salts in $HX-NH_4PF_6$ (X = Br, Cl) solution and with I_2, giving diamagnetic $[RcRcX]^+PF_6^-$ (**2**, X = Br; **3**, X = Cl) and $[RcRcI]^+I_3^-$ (**4**) salts, respectively. These salts are formulated as mixed-valence biruthenocenium salts $[Ru^{II}Cp(C_5H_4)(C_5H_4)CpRu^{IV}X]^+Y^-$ (X = Cl, Br, I; Y = PF_6, I_3) in the solid state on the basis of ^{13}C CP-MAS NMR spectroscopy. A rapid intramolecular electron transfer between Ru^{II} and Ru^{IV} has been observed accompanied with exchange of the X atom in organic solvent at room temperature: $[Ru^{II}Cp(C_5H_4)(C_5H_4)CpRu^{IV}X]^+ \rightleftharpoons [XRu^{IV}Cp(C_5H_4)(C_5H_4)CpRu^{II}]^+$. The electron-transfer rate increases in the order of **4** < **2** < **3** on the basis of ^{13}C and ^1H NMR spectroscopies. Upon decrease of temperature, the rate decreases, and finally, the salts contain trapped-valence states: $[Ru^{II}Cp(C_5H_4)(C_5H_4)CpRu^{IV}X]^+Y^-$.

Introduction

Trapped- and averaged-valence states have been observed for a large number of mixed-valence binuclear ferrocene derivatives.[2–4] The results of ^{57}Fe Mössbauer spectroscopy and other physicochemical measurements of the salts show that some of the monocationic salts are in either an averaged- or a trapped-valence state independent of temperature, while others are in a temperature-dependent trapped- to averaged-valence state in a pertinent temperature range. Few studies of the chemistry of 1,1″-biruthenocene and related species, however, have been reported, probably because of the low yield of biruthenocene $[RuCp(C_5H_4)(C_5H_4)CpRu]$ (abbreviated as RcRc, **1**) (Chart I).[5,6] We prepared **1** in high yield by a radical coupling of ruthenocene (RcH) in concentrated sulfuric acid at 80 °C. Mixed-valence 1,1″-biruthenocenium

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