

Second sphere donor acceptor interactions in excited states of coordination compounds. Ruthenium(II) bipyridine cyano complexes

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Abstract. Donor-acceptor interactions at the periphery of a coordination compound can have important consequences on its photochemical and photophysical behavior. Effects of this type have been explored using Ru(II) bipyridine complexes containing cyanide ligands. The cyanide ligands of these complexes behave as electron donors in interactions with acceptor solvents, protonation, methylation, and bridging to other metals with formation of polynuclear complexes. A variety of effects have been observed, ranging from (i) weak perturbations of the properties of the original complex, to (ii) major changes in the photophysical behavior of the complex via changes in redox potentials and excited state energy ordering, to (iii) induction of completely new properties characteristic of the complex-acceptor "supermolecule". Examples of such effects are discussed in some detail. The use of second-sphere donor-acceptor interactions to tune excited-state properties is stressed.

INTRODUCTION

The composite ("complex") nature of transition metal compounds was recognized since the early times of coordination chemistry. Contrary to what happens for most organic and simple inorganic molecules, Werner-type complexes can be split into (or obtained from) component subunits, the metal ion and the ligands, that are capable of separate existence. From a practical point of view, this gives to coordination chemistry its typical combinatory flavor. On the theoretical side, it justifies the widespread use of models such as ligand-field theory, in which energy levels are seen to arise as the consequence of perturbations of one type of subunit (the ligands) on the other (the metal ion). Even when using intrinsically delocalized MO descriptions, the MOs are usually classified according to their predominant metal or ligand parentage. Thus, in discussing the photochemistry and photophysics of coordination compounds (refs. 1-4), it is customary to label the excited states as metal-centered (MC, or d-d), ligand-centered (LC, or $\pi-\pi^*$), metal-to-ligand charge transfer (MLCT, or $d-\pi^*$), and ligand-to-metal charge transfer (LMCT).

Werner-type complexes are usually considered to be coordinatively saturated when no coordination site at the metal is vacant, i.e., when the "first coordination sphere" is complete. In these conditions, the complex is expected to show negligible chemical affinity towards external species (except for the obvious possibility of electrostatic ion-pairing interactions). This metal-based viewpoint, however, should not be taken too literally, since there are cases in which "coordinatively saturated" complexes are able to establish additional interactions with surrounding molecules through the ligands (Fig. 1). A wide variety of such interactions are known, ranging from specific solvation, through hydrogen bonding and proton transfer, to the formation of stable chemical bonds with other molecular fragments. All of these interactions are of the donor-acceptor type in the wide sense used by Gutmann

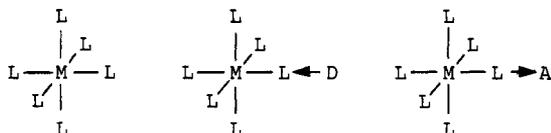


Fig. 1. Schematic representation of a coordinatively saturated complex (left) and of its SSDA interactions with electron donors (center) and acceptors (right)

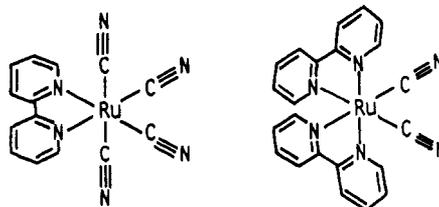


Fig. 2. Schematic structures of the $\text{Ru}(\text{bpy})_2(\text{CN})_2$ and $\text{Ru}(\text{bpy})(\text{CN})_4^{2-}$ complexes.

(ref. 5). As they occur outside the first coordination sphere, they may be called second-sphere donor-acceptor interactions (SSDA). Depending on their strength and on the position of the interaction site, these interactions may have important consequences on several properties of the complex.

The photochemistry and photophysics of simple Werner-type complexes have been actively investigated during the last two decades, and are now reasonably well understood (refs. 1-4). The study of how the excited-state behavior of these species is affected by selected SSDA interactions appears to be an interesting extension of the field. In particular, the possibility that SSDA interactions may be used to tune or modify in a predictable way the photophysical or photochemical properties of a complex (ref. 6) seems worth of attention.

In principle, SSDA interactions with both electron donors and acceptors can affect the excited-state behavior of a coordination compound. Classical ligands usually do not possess true electron-pair Lewis acid sites, but frequently do have (e.g., ammonia and amines) peripheral electrophilic hydrogens that may establish SSDA interactions with solvents of appreciable donor character. In this regard, an interesting study of the correlation between solvent effects on some Ru(II) ammine complexes and the Gutmann solvent donicity has been performed (ref. 7). Much more common is the case, however, in which the coordinated ligands possess free Lewis basic sites, in addition to those already involved in the coordination to the metal. A number of simple ambidentate ligands such as cyanide (refs. 8-11), and more complex bifunctional ligands such as aza- (refs. 12-15) or carboxy- (refs. 16-18) substituted polypyridines form stable complexes with interesting photophysical and photochemical behavior. In these systems, the effects of SSDA interactions with electron acceptors on the excited-state behavior can be studied in detail.

In this article, a number of recent studies on complexes of Ru(II) containing 2,2'-bipyridine (bpy) and cyanide ligands are discussed. With these molecules, SSDA interactions between the cyanides and a variety of electron acceptors have been probed. The results provide examples of a wide range of effects that go from (i) simple quantitative perturbation of the photophysical properties of the complex, to (ii) major changes in the photophysical behavior via changes in the excited-state energy ordering, to (iii) induction of completely new properties characteristic of the complex-acceptor "supermolecule".

RUTHENIUM(II) BIPYRIDINE COMPLEXES WITH CYANIDE LIGANDS

The photophysics of $\text{Ru}(\text{bpy})_2(\text{CN})_2$ (refs. 8-10,19) and $\text{Ru}(\text{bpy})(\text{CN})_4^{2-}$ (ref. 11) (Fig. 2) has been studied in some detail. Unlike most other Ru(II) mixed ligand complexes containing bipyridine and other ancillary ligands, these complexes resemble the parent $\text{Ru}(\text{bpy})_3^{2+}$ (ref. 20,21) in that they exhibit a long-lived, emitting MLCT ($d_{\text{Ru}} \rightarrow \pi^*_{\text{bpy}}$) excited state. This is due to the

Table 1. Properties of Ru(II) bipyridine/cyanide mixed ligand complexes (Data from refs. 11,19,21 unless otherwise noted)

	Ru(bpy) ₃ ²⁺		Ru(bpy) ₂ (CN) ₂		Ru(bpy)(CN) ₄ ²⁻	
	DMF	H ₂ O	DMF	H ₂ O	DMF	H ₂ O
$\nu_{\text{abs}}, \mu\text{m}^{-1}$	2.21	2.21	2.17	2.40	1.78	2.50
$\nu_{\text{em}}, \mu\text{m}^{-1}$	1.64	1.65	1.47	1.61	1.23	1.64
τ, ns	930	670	205	250	4	100
E^{00}, eV^a	2.10	2.13 ^b	2.05	2.20	2.03	2.38
E^{ox}, V	+1.27	+1.24	+0.73	+0.90 ^b	+0.20	+0.78
E^{red}, V	-1.25		-1.68		-1.95	
* E^{ox}, V	-0.83	-0.89	-1.32	-1.30	-1.83	-1.60
* E^{red}, V	+0.85		+0.37		+0.08	

a) 77 K, 9:1 DMF/CH₂Cl₂ ("DMF") or 9 M aqueous LiCl ("H₂O") glasses; b) ref 23.

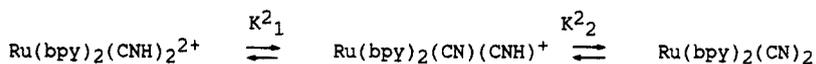
fact that, contrary to most other ancillary ligands, cyanide provides a strong enough ligand field to keep the MC (d-d) states at higher energy than the emitting MLCT state. When energetically accessible, in fact, the highly distorted MC states constitute a very efficient radiationless deactivation channel in this class of compounds (refs. 4,22). Some of the relevant properties of these complexes are summarized in Table 1.

The most evident feature emerging from the data in Table 1 is the solvent-dependent behavior of the cyano-substituted complexes, as contrasted with the essentially solvent-independent behavior of Ru(bpy)₃²⁺. The solvent dependence of absorption spectra, emission spectra, and redox potentials is larger for the tetracyano complex than for the bis-cyano species. These observations can be consistently accommodated by a model in which the solvent is acting as an acceptor in SSDA interactions at the nitrogen end of the cyanides. Due to such interactions, good acceptor solvents (e.g. water) will increase the π -acceptor character and perhaps decrease the σ -donor ability of the cyanide ligands towards Ru, thus resulting in a withdrawal of electronic charge from the metal. This explains the blue shifts in MLCT absorption and emission, for which good correlations with the Gutmann solvent acceptor number are observed over an extended series of solvents (refs. 10,23). This also accounts for the remarkable anodic shifts in the potentials for Ru(II)/Ru(III) oxidation in going from DMF to water.

The interpretation of the solvent dependence of the MLCT excited-state lifetime is less trivial, as it requires a detailed picture of the energy shifts of various types of states (at least MLCT and MC) following SSDA interaction. Moreover, it should be noticed that a simple picture of the potential energy surfaces of these states as a function of one, generic M-L stretching coordinate (such as that usually adopted for discussing Ru(bpy)₃²⁺) (refs. 4,21) is probably inadequate here. In fact, in these complexes different degrees of distortion are expected to occur along Ru-bpy, Ru-CN, and internal C-N coordinates for the various types of state, and all these distortions are likely to play a role in determining the effective radiationless decay path. Although a number of interpretations for the observed solvent effect could be devised along these lines, it is difficult to find a simple one that is consistent with all the lifetime data obtained for these and other SSDA interactions (vide infra) of the same complexes. Thus, discussion of SSDA interaction effects on lifetimes will not be pursued further in this article.

PROTON TRANSFER PROCESSES

The cyano bipyridine complexes of Ru(II) protonate in acidic aqueous solution according to the equilibria (H^+ ions omitted for clarity):



and



The following pK values are known: $pK^2_1 = -0.07$, $pK^2_2 = 0.13$ (refs. 8,9); $pK^4_3 \sim -1$, $pK^4_4 = 1.8$ (ref. 24). Thus, work in quite acidic solutions is required to study these systems. In concentrated sulfuric acid the fully protonated forms are presumably obtained. For both complexes, protonation is found to induce large blue shifts in the MLCT absorption (refs. 8,9,24), in agreement with the expected effect of SSDA interactions at the cyanides.

It has been known since the pioneering work of Demas (ref. 8,9) that acidic aqueous solutions of the bis-bpy complex in which $Ru(bpy)_2(CN)(CNH)^+$ is the dominant form give the same emission as neutral $Ru(bpy)_2(CN)_2$ solutions, indicating that the MLCT excited states are more acidic than the ground state and deprotonate prior to emission. This is in keeping with the Ru(III)-bpy⁻ electron distribution of the MLCT excited state that, due to decreased Ru→CN back bonding with respect to the ground state, makes the cyanides less prone to SSDA interactions. The $Ru(bpy)_2(CN)_2$ ground- and excited-state protonation has recently been studied (ref. 25) in acetonitrile/water solvent mixtures using $HClO_4$ as proton source. The use of this solvent system has the following advantages over aqueous solution: (i) protonation can be achieved using much lower acid concentrations and the successive steps are better separated, (ii) emission from excited $*Ru(bpy)_2(CN)(CNH)^+$ can be easily detected, and (iii) excited-state $*pK^2_2$ values can be obtained. The $*Ru(bpy)_2(CN)(CNH)^+$ emission is blue-shifted with respect to that of the unprotonated form, and the excited-state pK is shifted towards negative values with respect to the ground-state pK as expected on the basis of Forster cycle considerations. In this mixed-solvent system, the study of the behavior of $Ru(bpy)_2(CN)_2$ as a function of the water content is interesting, as it shows the transition between distinct kinetic regimes of excited-state proton transfer (ref. 25): at low water concentrations excited-state deprotonation, though thermodynamically favoured, is kinetically inefficient with respect to excited-state deactivation (no difference between ground- and excited-state acid-base behavior shows up), whereas at higher water concentrations the proton transfer steps are fast and the new excited-state equilibrium regime is fully established. At intermediate water concentrations, interesting hybrid regimes are found. The excited-state equilibrium constants depend on high powers of the water concentration, giving some information on the average size of the water clusters solvating the proton.

The excited-state proton transfer equilibria of $Ru(bpy)(CN)_4^{2-}$ in sulfuric acid aqueous solutions have also been recently investigated (ref. 24). Here again excited-state protonation starts at considerably higher acidities than ground state-protonation, consistent with the predicted acidity changes. Emission spectra obtained at various acid concentrations are shown in Figure 3, exhibiting again the blue shift in the energy of the MLCT state upon protonation. The four protonation steps, however, are not separable in this system and no definite emission spectra for the various protonated forms can be obtained. The interesting observation about the emission spectra of Figure 3 is that in concentrated sulfuric acid, where $Ru(bpy)(CNH)_4^{2+}$ is presumably the dominant species, the emission is clearly different from those obtained in less acidic conditions. The structured emission is typical of a LC $\pi-\pi^*$ bipyridine phosphorescence. This suggests that the upward shift of the MLCT state caused by protonation ultimately leads to an inversion in the nature of the lowest excited state of the complex.

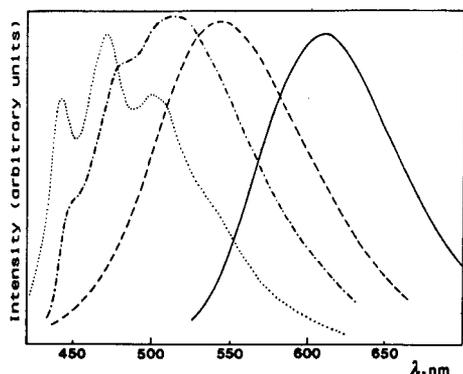


Fig. 3. Emission spectra of $\text{Ru}(\text{bpy})(\text{CN})_4^{2-}$ in aqueous sulfuric acid solutions.

(—) water;
 (---) 12 N H_2SO_4 ;
 (-·-·-) 15 N H_2SO_4 ;
 (····) concentrated H_2SO_4

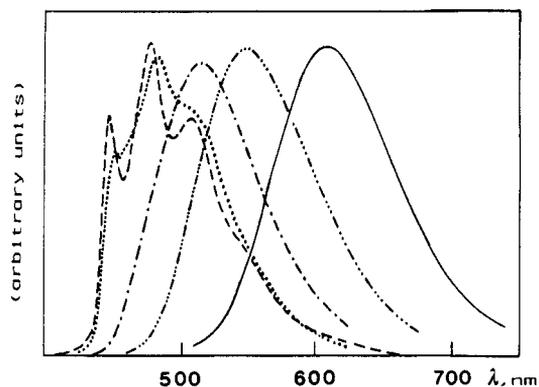


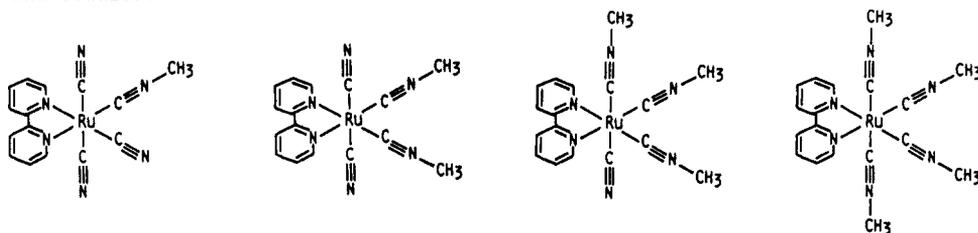
Fig. 4. Emission spectra in aqueous solution of

$\text{Ru}(\text{bpy})(\text{CN})_4^{2-}$ (—),
 $\text{Ru}(\text{bpy})(\text{CN})_3(\text{CNCH}_3)^-$ (---),
 $\text{Ru}(\text{bpy})(\text{CN})_2(\text{CNCH}_3)_2$ (-·-·-),
 $\text{Ru}(\text{bpy})(\text{CN})(\text{CNCH}_3)_3^+$ (····),
 $\text{Ru}(\text{bpy})(\text{CNCH}_3)_4^{2+}$ (- - -)

Aside from their intrinsic interest, the studies on the excited-state acid-base behavior of $\text{Ru}(\text{bpy})_2(\text{CN})_2$ and $\text{Ru}(\text{bpy})(\text{CN})_4^{2-}$ have shown that protonation is a type of SSDA interaction that can be used to alter in a substantial and predictable way the energy levels of this class of complexes. Judging from the parallel behavior observed for MLCT energies and redox potentials in solvent effects, it is to be anticipated that the $\text{Ru}(\text{II})/\text{Ru}(\text{III})$ oxidation potentials should also undergo pronounced anodic shifts upon protonation. This could lead to quite different excited-state redox properties for fully protonated complexes with respect to the common unprotonated forms. Unfortunately, concentrated sulfuric acid media are not the best environment to test these expected unusual excited-state redox properties.

RUTHENIUM(II) BIPYRIDINE COMPLEXES WITH METHYL ISOCYANIDE LIGANDS

A way to mimic the effects of protonation without resorting to the extremely acidic conditions described in the previous paragraph could be that of looking at methylated analogs of the protonated cyano complexes, i.e., methyl isocyanide complexes. The study of well-defined molecular species in mild experimental conditions, without the problem of fast equilibria interconverting various species, could in principle yield detailed information on the effects of strong SSDA interactions at the cyanides. This possibility has been explored by looking at a series of bis-bpy and mono-bpy isocyanide complexes obtained by methylation of $\text{Ru}(\text{bpy})_2(\text{CN})_2$ and $\text{Ru}(\text{bpy})(\text{CN})_4^{2-}$ (ref. 26). For the mono-bpy series, the following complexes have been synthesized and studied:



As expected, the trends observed with increasing degree of methylation parallel qualitatively those obtained upon protonation. The emission spectra are shown in Figure 4. It is seen very clearly that $\text{Ru}(\text{bpy})(\text{CN})_4^{2-}$, $\text{Ru}(\text{bpy})(\text{CN})_3(\text{CNCH}_3)^-$, and $\text{Ru}(\text{bpy})(\text{CN})_2(\text{CNCH}_3)_2$ have a MLCT emission whereas $\text{Ru}(\text{bpy})(\text{CNCH}_3)_4^{2+}$ gives a LC (bpy-centered) phosphorescence. The $\text{Ru}(\text{bpy})(\text{CN})(\text{CNCH}_3)_3^+$ complex exhibits a dual emission, indicating excited-state equilibrium between nearby MLCT and LC states. The energy shifts responsible for the observed change in the nature of the emitting state are

schematized in Figure 5. The position of the MC states along this series is not known. In view of the long lifetimes obtained, however, the experimental indication is that these states probably increase in energy upon methylation so as to remain at substantially higher energy than the emitting states.

The excited-state equilibrium in $\text{Ru}(\text{bpy})(\text{CN})(\text{CNCH}_3)_3^+$ is interesting and can be studied as a function of temperature to obtain the energy gap between the two emitting states. It is noteworthy that in this complex the equilibrium composition depends on the solvent, with the proportion of MLCT emission decreasing as the solvent acceptor power increases. This is the consequence of tuning of the MLCT state energy by SEDA interactions between the free cyanide and the solvent. In this series of complexes, therefore, in addition to the coarse tuning provided by methylation we have the possibility of achieving fine tuning with the solvent.

In going from $\text{Ru}(\text{bpy})(\text{CN})_4^{2-}$ to $\text{Ru}(\text{bpy})(\text{CNCH}_3)_4^{2+}$, the potential for oxidation of Ru undergoes a dramatic anodic shift from +0.27 to +2.3 V (in acetonitrile vs SCE), with stepwise increases of about 0.5 V for each methylation step. As a consequence, the excited-state redox properties of the cyanide and methyl isocyanide complexes are extremely different: $\text{Ru}(\text{bpy})(\text{CN})_4^{2-}$ is a very strong excited-state reductant ($E^{\text{OX}} = -1.83$ V vs SCE in DMF) but $\text{Ru}(\text{bpy})(\text{CNCH}_3)_4^{2+}$ is a strong excited-state oxidant ($E^{\text{red}} = +1.42$ V vs SCE in acetonitrile). For the intermediate species, the excited-state redox properties change within these limits in a regular way. This series of redox photosensitizers is a remarkable example of how SEDA interactions can be used to control useful excited-state properties in coordination compounds.

POLYNUCLEAR COMPLEXES

Second-sphere donor-acceptor interactions can also be explored by using cyanide complexes of the above-mentioned type and other transition-metal containing moieties as the Lewis acid partners. In this case bi- or polynuclear complexes are formed, e.g.,

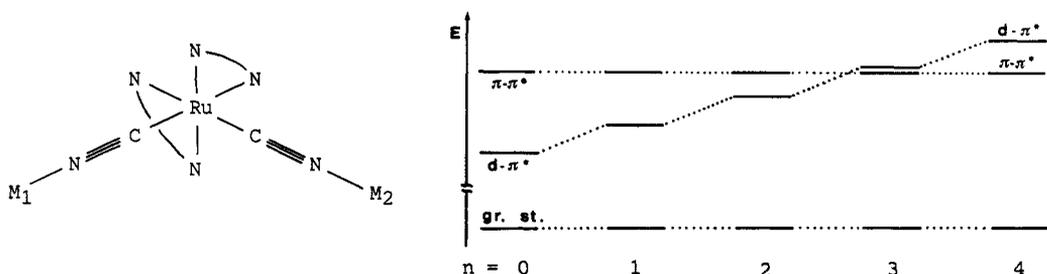


Fig. 5. Schematic representation of the effect of methylation on the energy of MLCT and LC states in the series of complexes $\text{Ru}(\text{bpy})(\text{CN})_{4-n}(\text{CNCH}_3)_n^{n-2}$ ($n = 0-4$)

A number of such systems using Cr, Ru, and Pt complex moieties as M_1 and M_2 have been recently synthesized and studied (refs. 6,19,27,28). In analyzing the excited-state behavior of these polynuclear complexes, the approach followed until now (i.e., to look at the SEDA interaction as a perturbation of the $\text{Ru}(\text{bpy})_2(\text{CN})_2$ chromophoric unit) can still be used provided that the M_1, M_2 units do not have either low-energy redox sites or low energy excited states on their own. This is the case, e.g., of bi- and trinuclear complexes containing $\text{Pt}(\text{dien})^{2+}$ as M_1 and/or M_2 (ref. 19). In this case, effects similar to those observed upon SEDA interaction with acceptor solvents and protons (e.g., blue shifts in MLCT energies and anodic shifts in oxidation potentials) are observed.

Much more complex are the situations in which M_1 and M_2 constitute low-energy redox sites of the polynuclear complex. In this case, new excited states of charge transfer character, not shown by any of the component subunits, are present in the polynuclear complex. This is the case, e.g., of

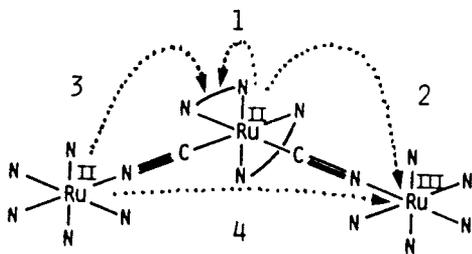


Fig. 6. Schematic representation of the optical electron transfer transitions observed in $\text{Ru}(\text{bpy})_2(\text{CN})_2[\text{Ru}(\text{NH}_3)_5]_2^{5+}$

- 1) MLCT;
- 2) intervalence transfer;
- 3) remote MLCT;
- 4) remote intervalence transfer.

bi- and trinuclear complexes containing Ru(II) and Ru(III) ammine complexes as M_1 and M_2 (refs. 27,28). The types of new excited states formed are shown schematically in Figure 6 for the trinuclear $\text{Ru}(\text{bpy})_2(\text{CN})_2[\text{Ru}(\text{NH}_3)_5]_2^{5+}$ complex. The presence of these excited states is established by the observation of the corresponding transitions in the absorption spectrum. The new excited states are all lower in energy than the MLCT state and are responsible for the fast radiationless deactivation of the excited $\text{Ru}(\text{bpy})_2(\text{CN})_2$ chromophore. The pathways for deactivation of the MLCT state through these lower states can be viewed as series of intramolecular electron transfer processes (ref. 29). The study of these systems is therefore of some interest in connection with long-range electron transfer mechanisms and photoinduced charge separation.

Interesting types of behavior are also observed in cases in which the M_1 , M_2 moieties possess local excited states lower in energy than that of the $\text{Ru}(\text{bpy})_2(\text{CN})_2$ unit. In these cases, the MLCT state may deactivate *via* intramolecular energy transfer to M_1 and M_2 . The process can be easily detected if the excited states of the attached subunits are luminescent.

This is the case, e.g., of trinuclear complexes containing Cr(III) complex moieties as M_1 , M_2 . One example (ref. 29) is shown schematically in Figure 7. In this case, visible light absorption by the $\text{Ru}(\text{bpy})_3^{2+}$ chromophoric unit leads to efficient (estimated energy transfer efficiency, nearly 1) emission from the $\text{Cr}(\text{CN})_6^{3-}$ doublet state. The photosubstitution reaction characteristic of direct Cr(III) excitation is not observed, showing that the photoreactive quartet is bypassed in the energy transfer step (ref. 30). In this case, the bound $\text{Ru}(\text{bpy})_2^{2+}$ chromophoric fragment acts both as an efficient *antenna* and as a protective group towards the $\text{Cr}(\text{CN})_6^{3-}$ luminophore. In systems of this type having free (i.e., non-bridging) cyanides in the Ru(II)-based chromophore, there is the additional interesting possibility to switch on/off the sensitized Cr(III) emission by tuning the energy of the MLCT state *via* SSSA interactions (e.g., solvent changes) at the free cyanides.

Clearly, with polynuclear or polymetallic systems of this kind, the study of SSSA interactions of simple coordination compounds begins to exceed its original limits, pointing towards the new fascinating fields of supramolecular photochemistry and molecular photochemical devices (ref. 31).

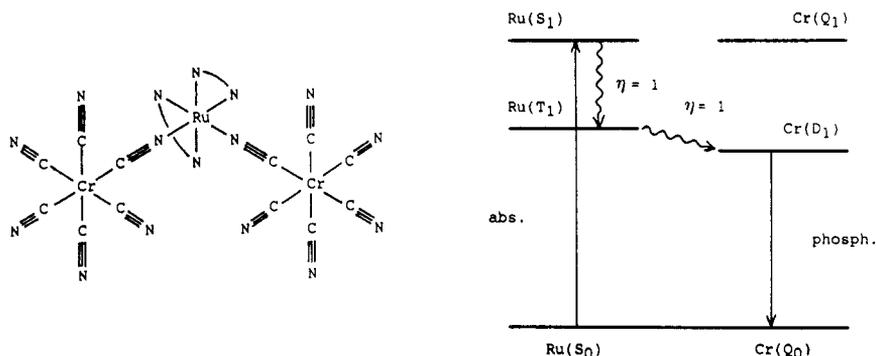


Fig. 7. Schematic representation of the structure of $\text{Ru}(\text{bpy})_2[\text{Cr}(\text{CN})_6]_2^{4-}$ and of the intramolecular energy transfer occurring in this trinuclear complex following visible light absorption.

CONCLUSIONS

The study of SSDA interactions and their effects on excited-state behavior constitutes an interesting extension in the field of photochemistry of transition metal complexes. On one side, these studies suggest useful ways to control and tune the photophysical and photochemical properties of a complex through physical interactions or chemical modifications at the ligands. On the other hand, SSDA interactions can be viewed as ways for assembling transition-metal complex molecular subunits into supramolecular species capable of performing light-induced intramolecular energy or electron transfer processes.

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