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“Second-Sphere” Photochemistry and Photophysics of Coordination Compounds

VINCENZO BALZANI* and NANDA SABBATINI

Istituto Chimico "G. Ciamician" dell'Università and Istituto FRAE-CNR, Bologna, Italy

FRANCO SCANDOLA

Istituto Chimico dell'Università and Centro di Fotochimica del CNR, Ferrara, Italy

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I. Introduction

A. Scope and Limitations

In several fields of chemistry the knowledge at a molecular level has made a substantial progress in the last two decades. A natural consequence is the trend of today's chemistry to study more complex systems. A representative example of this trend is the rapid development of the host–guest chemistry.[1-10] The photochemical and photophysical properties of simple coordination compounds have been extensively studied in recent years, and the results obtained have given important information on the behavior of the various types of electronically excited states.[11-14] While further investigations on the excited-state behavior of simple coordination compounds are required to arrive at a complete understanding of their properties, there is now the need to study more complex species to extend our knowledge of basic photochemical and photophysical processes and to find systems that might be useful for practical applications. As first shown by Werner, coordination compounds, being made by metal ions and ligands which are capable of separate existence, are already complex systems. However, they are at the same time well-characterized molecular species which can interact with other molecules. Such interactions may range from so weak to perturb slightly the molecular properties to so strong to give rise to new chemical species.

In this review we will illustrate and discuss the results of experiments dealing with the effects of perturbations on the photochemical and photophysical properties of Werner-type transition-metal complexes in homogeneous solutions. The effects of ligand replacements in the first coordination sphere are well-known[11,12,15-20] and will not be reviewed here. We will only examine perturbations taking place outside the first coordination sphere. Selected examples will be discussed in an attempt to underline the peculiar aspects of the various types of perturbations and to lay out an approach for a rational understanding of these phenomena.

B. Types of Excited States in Coordination Compounds

Photochemical and photophysical processes originate from electronically excited states and reflect the electronic distribution of the excited molecules. In simple, isolated coordination compounds, which may be exemplified by M–L, one can distinguish the following types of excited states on the basis of a localized molecular orbital approach:[11-14] *metal-centered* (MC) excited states, which derive from electronic transitions between orbitals that are mainly localized on the metal; *ligand-centered* (LC) excited states, which derive from electronic transitions between orbitals that are mainly

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Vincenzo Balzani was born in 1936 and received his "laurea" in Chemistry at the University of Bologna in 1960. He is now Professor of Chemistry at the University of Bologna and Director of the Photochemistry and Radiation Chemistry Institute (FRAE) of the Italian National Research Council. His research interests include photochemistry, luminescence, chemiluminescence, and photochemical conversion of solar energy, with particular emphasis on reactions involving coordination compounds.

Nanda Sabbatini was born in Bologna in 1939 and received her "laurea" in Chemistry at the University of Bologna in 1963. She is Associate Professor of Chemistry at the University of Bologna. Her research interests are in the field of photochemistry and photophysics of transition-metal and lanthanide complexes.

Franco Scandola was born in 1942 and received his "laurea" in Chemistry in 1964 at the University of Bologna. He is Professor of Chemistry at the University of Ferrara. His research interests include photophysics of coordination compounds and thermal and photoinduced electron-transfer reactions.

localized on the ligands; *charge-transfer* (CT) excited states, which derive from electronic transitions between orbitals of different localization (*ligand-to-metal charge-transfer* (LMCT) or *metal-to-ligand charge-transfer* (MLCT) excited states). For complexes containing different types of metals (e.g., M(a)–L–M(b)), *metal-to-metal charge-transfer* (MMCT) excited states, sometimes called intervalence transfer (IT) excited states, may also appear.[21,22] Analogously, for complexes containing different types of ligands (e.g., L(a)–M–L(b)), *ligand-to-ligand charge-transfer* (LLCT) excited states may appear.[23,24]

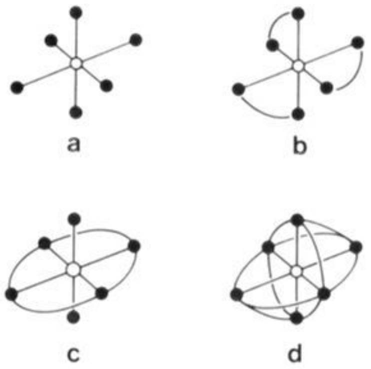

Figure 1. Schematic representation of complexes containing (a) monodentate, (b) chelate, (c) macrocyclic, and (d) cage ligands.

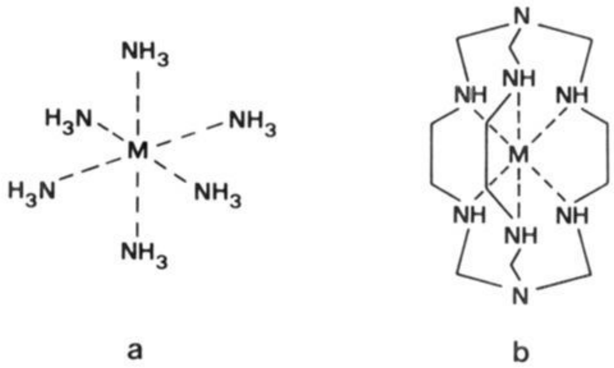

Figure 2. Schematic representation of (a) hexaamine and (b) sepulchrate complexes.

When coordination compounds interact with solvent molecules or with other species belonging to the second coordination sphere, *second-sphere charge-transfer* (SSCT) (also called *outer-sphere charge-transfer* (OSCT)) excited states may occur. Excited states of this type are those involving charge transfer to the solvent (CTTS)[25] and charge transfer within ion pairs (IPCT).[22,26]

II. Complexes with Constrained Coordination Sphere

A. Cage-Type Ligands

A particular type of perturbation is that introduced by linking together the ligands of a coordination compound by single covalent bonds. Since the presence of the bridging groups does not substantially modify the composition and symmetry of the first coordination sphere, which is constituted by the ligand atoms surrounding the metal ion, such a perturbation may be considered a pseudo-second-sphere one (Figure 1). In the simplest case, *n*-unidentate ligands are replaced by an *n*-dentate ligand (chelate effect).[27] A further step in this direction is the replacement of *n*-unidentate ligands with an *n*-dentate macrocyclic ligand (macrocyclic effect).[27,28] The ultimate step is to encapsulate the metal ion into a cage-type ligand (cage effect).[28,29] This type of second-sphere perturbation has long been known to affect the thermodynamic and kinetic properties of coordination compounds,[27-29] while it leaves almost unchanged the absorption spectra because light absorption is a Franck–Condon-type process which is only sensitive to the symmetry and composition of the first coordination sphere. Photochemical reactions and radiationless deactivation processes, however, do involve nuclear displacements and thus they depend on the location of the minima and on the shape of the potential energy surfaces rather than on the vertical spectroscopic levels. The presence of chelate, macrocyclic, and especially cage-type ligands may profoundly affect the nuclear motions (particularly in their asymptotic regions) and may thus cause tremendous changes in the photochemical and photophysical behavior.

As a paradigmatic example of the effects of this type of perturbation we will compare the behavior of $M(NH_3)_6^{3+}$ and $M(sep)^{3+}$ complexes (M = Co or Cr,[30] sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane, Figure 2). Other extremely interesting cage-type structures have recently been reported by Sauvage et al.[31] (catenands of macrocyclic phenanthroline derivatives), by Lehn et al.[32] (cryptands containing bipyridine and phenanthroline groups), and by Cram et al.[8] (the so-called carcerands); it is easy to predict that there will be soon a great expansion on the studies of the photochemical and photophysical properties of cage-type compounds.

1. $Co(NH_3)_6^{3+}$ vs. $Co(sep)^{3+}$

It is well-known that the Co(III) complexes are kinetically inert while the Co(II) complexes are very labile because of the presence of electrons in the $\sigma^*(e_g)$ antibonding orbitals.[33] As a consequence, reduction of the central metal ion of $Co(NH_3)_6^{3+}$ in aqueous solution causes the decomposition of the complex. Such a reduction may be carried out by the following: (i) pulse radiolysis,[34]

$$[Co^{III}(NH_3)_6]^{3+} + e_{aq}^- \rightarrow [Co^{II}(NH_3)_6]^{2+} \quad (1)$$

$$[Co^{II}(NH_3)_6]^{2+} \xrightarrow[k > 1 \times 10^3\ s^{-1}]{H^+} Co_{aq}^{2+} + 6NH_4^+ \quad (2)$$

(ii) ion pair charge-transfer (IPCT) photoexcitation ($\Phi = 0.2$),[35]

$$[Co^{III}(NH_3)_6]^{3+} \cdot I^- \xrightarrow[IPCT]{h\nu} [Co^{II}(NH_3)_6]^{2+} \cdot I \quad (3)$$

$$[Co^{II}(NH_3)_6]^{2+} \cdot I \rightarrow [Co^{III}(NH_3)_6]^{3+} \cdot I^- \quad (4)$$

$$[Co^{II}(NH_3)_6]^{2+} \cdot I \xrightarrow{H^+} Co_{aq}^{2+} + 6NH_4^+ + {}^1/_2 I_2 \quad (5)$$

or (iii) intramolecular ligand-to-metal charge-transfer (LMCT) photoexcitation ($\Phi = 0.16$)[36]

$$[Co^{III}(NH_3)_6]^{3+} \xrightarrow[LMCT]{h\nu} [Co^{II}(NH_3)_5(NH_3^+)]^{3+} \quad (6)$$

$$[Co^{II}(NH_3)_5(NH_3^+)]^{3+} \rightarrow [Co^{III}(NH_3)_6]^{3+} \quad (7)$$

$$[Co^{II}(NH_3)_5(NH_3^+)]^{3+} \xrightarrow{H^+} Co_{aq}^{2+} + 5NH_4^+ + \text{products} \quad (8)$$

Simple chelation does not substantially change the situation because $Co(en)_3^{3+}$ (en = ethylenediamine) after pulse radiolysis reduction loses its ligands with $k \geqslant 25\ s^{-1}$,[34] and upon LMCT excitation undergoes redox decomposition with $\Phi = 0.13$.[36]

TABLE I. Comparison between Some Spectroscopic, Photochemical, and Photophysical Properties of $M(NH_3)_6^{3+}$ and $M(sep)^{3+}$ Complexes[a]

	$Co(NH_3)_6^{3+}$ [b]	$Co(sep)^{3+}$ [c]	$Cr(NH_3)_6^{3+}$ [d]	$Cr(sep)^{3+}$ [d]
absorption				
λ_{max}, nm	339; 472	340; 472	351; 459	345; 460
ϵ_{max}	46; 56	116; 109	38; 45	102; 100
emission				
λ_{max}, nm			658	667
lifetime, μs			17	10
phot quant yields				
LMCT exc	0.16	$<10^{-6}$ [e]		
IPCT exc (I^- ion)	0.2[f]	$<10^{-6}$ [e]		
MC exc			0.45	<0.03

[a] Data in aqueous solution at room temperature. [b] Reference 36, except otherwise noted. [c] Reference 37, except otherwise noted. [d] Reference 48. [e] Reference 39. [f] Reference 35.

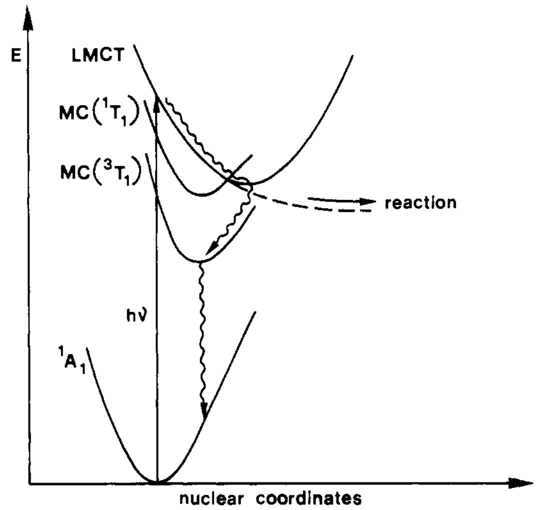

Figure 3. Schematic representation of the difference at long metal–ligand bond distances between the lowest LMCT excited states of $Co(sep)^{3+}$ (—) and $Co(NH_3)_6^{3+}$ (- -).

When the six NH_3 ligands are replaced by the cage ligand sep (Figure 2), the first coordination sphere of Co^{3+} remains unchanged. As one can see from Table I, the two complexes exhibit quite similar absorption spectra. Since the sep ligand is a cage, the Co(II) complex obtained upon reduction of the corresponding Co(III) complex cannot undergo ligand dissociation. In fact, there is no simple ligand to eject, but a single polydentate cage ligand structure whose atoms are all kept together by covalent bonds. Thus the following obtain: (i) one-electron reduction leads to a product that is fairly inert,[37,38]

$$[Co^{III}(sep)]^{3+} + e_{aq}^- \rightarrow [Co^{II}(sep)]^{2+} \quad (9)$$

$$[Co^{II}(sep)]^{2+} \underset{k < 10^{-6}\ s^{-1}}{\nrightarrow} Co_{aq}^{2+} + \text{products} \quad (10)$$

(ii) ion pair photoexcitation does not lead to appreciable product formation ($\Phi < 10^{-6}$; see, however, section III.A),[39]

$$[Co^{III}(sep)]^{3+} \cdot I^- \xrightarrow[IPCT]{h\nu} [Co^{II}(sep)]^{2+} \cdot I \quad (11)$$

$$[Co^{II}(sep)]^{2+} \cdot I \rightarrow [Co^{III}(sep)]^{3+} \cdot I^- \quad (12)$$

$$[Co^{II}(sep)]^{2+} \cdot I \nrightarrow Co_{aq}^{2+} + \text{products} \quad (13)$$

and (iii) intramolecular LMCT excitation does not cause appreciable photodecomposition ($\Phi < 10^{-6}$)[39]

$$[Co^{III}(sep)]^{3+} \xrightarrow[LMCT]{h\nu} [Co^{II}(sep^+)]^{3+} \quad (14)$$

$$[Co^{II}(sep^+)]^{3+} \rightarrow [Co^{III}(sep)]^{3+} \quad (15)$$

$$[Co^{II}(sep^+)]^{3+} \nrightarrow Co_{aq}^{2+} + \text{products} \quad (16)$$

Figure 3 tries to show, on the basis of potential energy curves, which is the reason of the different photochemical behavior of $Co(NH_3)_6^{3+}$ and $Co(sep)^{3+}$. For the hexaammine complex, LMCT excitation is presumably followed[40] by ligand detachment which competes with radiationless deactivation to the ground state. In $Co(sep)^{3+}$, a nuclear perturbation is introduced (covalent bonding between the single ligands) which prevents ligand detachment. Thus, radiationless transitions remain the only processes through which deactivation can occur.

Because of the inertness of its one-electron reduction product, $Co(sep)^{3+}$ can be used as a relay[41-43] and as a photosensitizer[44] for hydrogen generation from water, as it will be discussed in section III.A.

2. *$Cr(NH_3)_6^{3+}$ vs. $Cr(sep)^{3+}$*

As one can see from Table I, also in this case the absorption bands are only slightly affected by "sepulchration". Cr(III) complexes are known to undergo ligand substitution and luminescence emission when excited in the $^4T_2$ and $^4T_1$ MC bands.[11,12,14] While emission originates from the lowest lying ^2E level, there is controversy regarding the pathway which leads to the ligand substitution reaction.[45-47] The ^2E level belongs to the same electronic configuration as the ground state and thus it has nearly the same nuclear coordinates and vibrational frequencies as the ground state. In other words, there is no nuclear reorganization in passing from the $^4A_2$ ground state to the ^2E excited state. By contrast, the $^4T_2$ and $^4T_1$ excited states are expected to be strongly distorted with respect to the ground-state geometry because of the presence of a σ^* antibonding electron.

Sepulchration is not expected to affect the properties of the thermally equilibrated ^2E level. This is in agreement with the quite similar values of emission energy and excited-state lifetime (at room temperature) in the two complexes[48] (Table I). Nuclear reorganization, however, must be heavily involved in the ligand photosubstitution reaction. Thus, no matter whether the reaction takes place directly from the distorted $^4T_2$ excited state or from vibrationally activated ^2E (via surface crossing to $^4T_2$ or directly to a chemical intermediate), it is expected and found[48] (Table I) that the quantum yield is strongly affected by such a nuclear perturbation (Figure 4). More recently photochemical and photophysical data reported by Sargeson et al.[49] for other Cr(III) complexes of the $Cr(sep)^{3+}$ family confirm the above expectations but show that the ^2E lifetime at room temperature actually decreases on sepulchration.[50]

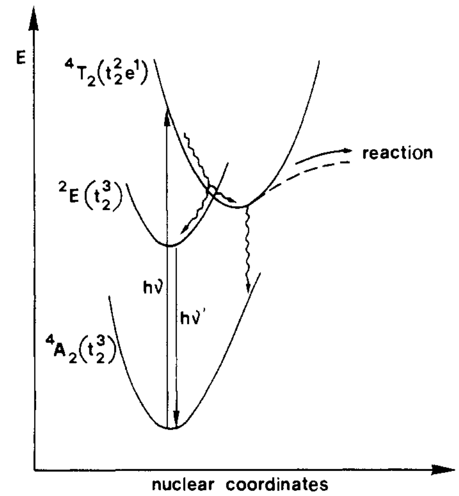

Figure 4. Schematic representation of the potential energy curves along a metal–ligand stretching coordinate of the ground state and the lowest metal-centered excited states of chromium sepulchrate. The curves for chromium hexamine are expected to be identical except for the behavior at long metal–ligand bond distances (– –).

The strong effects caused on the photochemical and photophysical behavior of Cr(III) complexes by the presence of the macrocyclic tetradentate amine ligand cyclam (1,4,8,11-tetraazacyclotetradecane) have been discussed by several authors.[51] Regardless of the detailed reaction mechanism, which is still the object of much debate,[51] the trans Cr(III) mixed ligand complexes are known to undergo efficient photosubstitution with formation of cis products.[46] By contrast, the *trans*-$Cr(cyclam)_2X_2^{z+}$ complexes are almost photoinert, giving at most small yields of the trans aquo product.[46,47] Clearly, stereochemical change, which seems to be a key step in the mechanism of Cr(III) photoreactivity,[46] is prevented by the steric constraints of the macrocyclic ligand. It is worth noting that the presence of the macrocyclic ligand in the equatorial positions indirectly protects the molecule against labilization of the axial ligands.

B. Supercomplexes

A perturbation quite similar to that observed by linking together unidentate ligands of a simple coordination compound is that occurring when a Werner-type complex is coordinated to (or, in the limiting case, enclosed into) an appropriate receptor. The supramolecular structures so obtained may be considered as complexes of complexes, i.e., supercomplexes.[3,4,7,52-54] They represent one of the aspects of the so-called *concave chemistry*.[55]

1. *$Co(CN)_6^{3-}$ with Polyammonium Macrocyclic Receptors*

As far as photochemistry is concerned, a clear example of perturbation via formation of supercomplexes has been recently described. The cyanide complexes are among the best studied Werner-type complexes from a photochemical point of view,[11,12] and the photochemical behavior of $Co(CN)_6^{3-}$ is particularly simple and reasonably well understood.[56] Excitation with light corresponding to the $^1A_{1g} \rightarrow {}^1T_{1g}$ (312 nm) and $^1A_{1g} \rightarrow {}^1T_{2g}$ (260 nm) metal-centered bands leads to a clean aquation reaction (eq 17) with quantum yield 0.30 ± 0.02. The reactive excited state is thought to be the

$$Co(CN)_6^{3-} + H_2O \xrightarrow{h\nu\ (MC)} Co(CN)_5H_2O^{2-} + CN^- \qquad (17)$$

lowest triplet $^3T_{1g}$. The quantum yield of population of the reactive $^3T_{1g}$ excited state has been estimated to be ~0.4 from photosensitization studies[57] and ~0.9 from direct irradiation experiments in the $^3T_{1g}$ region.[58] Since the quantum yield of the photoreaction remains the same in a variety of solvents,[59,60] it has been suggested that it reflects an intrinsic "molecular" characteristic, only weakly (if at all) affected by any solvent parameter.[60] The simplest explanation of this behavior is that the primary photochemical process is, in all

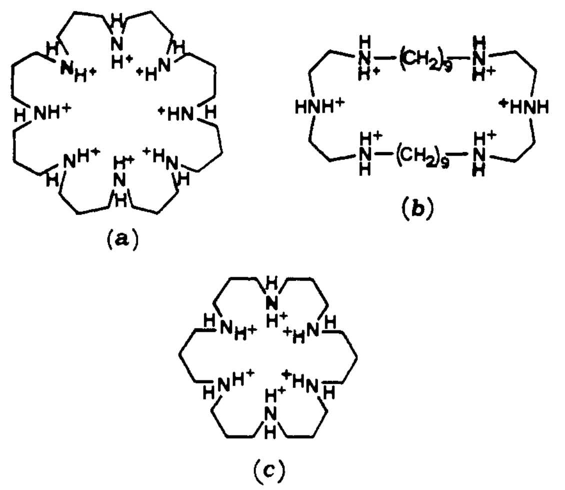

Figure 5. Structures of the macrocyclic polyammonium ions (a) 32-$N_8H_8^{8+}$, (b) 32-C_9-$N_6H_6^{6+}$, and (c) 24-$N_6H_6^{6+}$.

cases, a CN^- photodissociation originating from the $^3T_{1g}$ level (eq 18). The lower than unity quantum yield can

$$(^3T_{1g})Co(CN)_6^{3-} \rightarrow Co(CN)_5^{2-} + CN^- \quad (18)$$

be due to a lower than unity efficiency of population of $^3T_{1g}$[57] and/or an efficient radiationless deactivation of $^3T_{1g}$ to $^1A_{1g}$.[58] A simple dissociative initial step without any significant concerted rearrangement of the five-coordinated fragment has also been taken as a basis for a general interpretation of the ligand field photochemistry of d^6 coordination compounds.[61-63] In high viscosity media, evidence for cage recombination effects in the photochemistry of $Co(CN)_6^{3-}$ has also been reported.[64]

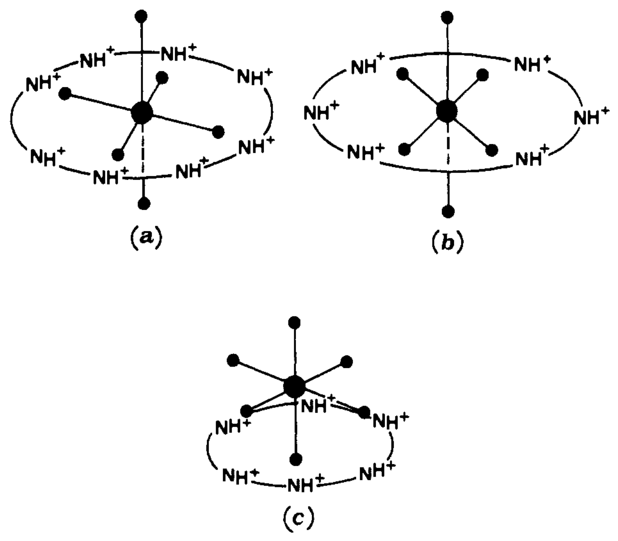

Figure 6. Possible supramolecular structures for the adducts between $Co(CN)_6^{3-}$ and (a) 32-$N_8H_8^{8+}$, (b) 32-C_9-$N_6H_6^{6+}$, or (c) 24-$N_6H_6^{6+}$.

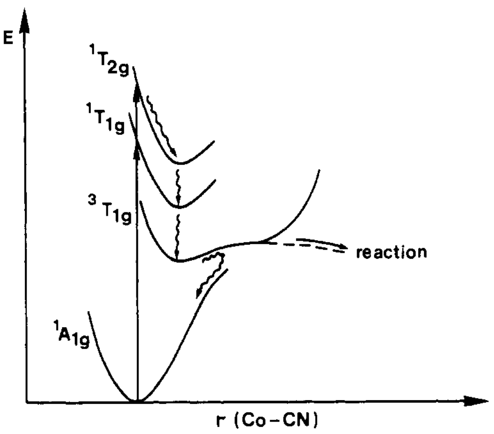

Figure 7. Schematic representation of the behavior at long metal–ligand bond distances of the potential energy curves for the $^3T_{1g}$ excited state of $Co(CN)_6[32\text{-}N_8H_8]^{5+}$ (Figure 6a) along equatorial (—) and axial (--) Co–CN stretching coordinates.

When $Co(CN)_6^{3-}$ gives rise to adducts[65] with the polyammonium macrocycles 32-$N_8H_8^{8+}$, 32-C_9-$N_6H_6^{6+}$, and 24-$N_6H_6^{6+}$ shown in Figure 5, the absorption spectrum above 265 nm is essentially the same as that of the "free" $Co(CN)_6^{3-}$,[66] as expected for ion pairs between partners which cannot give rise to low-energy charge-transfer transitions. The relative high values of the association constants ($K_s = 10^3$–10^6) must reflect an ionic-type interaction, probably with a large contribution from hydrogen bonds between the peripherical nitrogen atoms of the complex anion and the hydrogen atoms of the polyammonium cations. When solutions containing the adducts are excited in the $^1A_{1g} \rightarrow {}^1T_{1g}$ band of $Co(CN)_6^{3-}$, the observed spectral changes are qualitatively identical with those obtained on irradiation of $Co(CN)_6^{3-}$ alone.[66] In other words, the adducts undergo the same photoaquation reaction exhibited by $Co(CN)_6^{3-}$. For example, see eq 19. The quantum yield

$$Co(CN)_6[32\text{-}N_8H_8]^{5+} + H_2O \xrightarrow{h\nu\ (MC)} Co(CN)_5(H_2O)[32\text{-}N_8H_8]^{6+} + CN^- \quad (19)$$

of the photoreaction, however, is noticeably smaller than that found (0.30) for "free" $Co(CN)_6^{3-}$, decreasing to 0.10, 0.11, and 0.16 for the ion pairs with 32-$N_8H_8^{8+}$, 32-C_9-$N_6H_6^{6+}$, and 24-$N_6H_6^{6+}$, respectively. Since adduct formation does not introduce new low energy levels and does not cause any appreciable spectral change in the low-energy metal-centered levels of $Co(CN)_6^{3-}$, it seems fair to assume that the reactive excited state of the adducts is the same as that of free $Co(CN)_6^{3-}$.[67] This implies that each one of the six CN^- ligands of $Co(CN)_6^{3-}$ involved in the adducts has still the same probability to undergo photodissociation. Nevertheless, the reaction quantum yields of the adducts are considerably smaller than that of "free" $Co(CN)_6^{3-}$. A striking result is that adduct formation reduces the quantum yield to values substantially equal to a multiple of $^1/_6$, which suggests that in the adduct only a discrete number of the six CN^- groups are allowed to undergo photodissociation. This suggestion finds support from examination of space-filling models which show that a well-defined number of CN^- ligands may be prevented to dissociate because they are forced into their coordination position by the structure of the adduct (Figure 6). In terms of potential energy curves, the situation along the Co–CN stretching coordinates may be represented as in Figure 7. Thus, this is a case in which an outer sphere molecular perturbation of nuclear nature does not affect the spectroscopic levels (at least those at low energy) but modifies the photochemical properties preventing, in their asymptotic region, those nuclear motions (i.e., metal–ligand stretching) which are responsible for the chemical change. Such a perturbation may be used for practical purposes, such as to protect a complex toward photodissociation and, in mixed ligand complexes, to orient photosubstitution reactions toward specific products.

The photophysical behavior of the supercomplexes obtained upon association of Ru(II)–diimine complexes with β-cyclodextrin has recently been investigated.[68] With phenyl-substituted ligands, association takes place via inclusion of the phenyl groups into the cyclodextrin cavity. Multiple binding occurs, leading to complex effects on the excited-state lifetime. The binding interaction shields the complex from the oxygen quenching. Since the effect exceeds just a simple geometric shielding of the excited molecule, a localized excitation in the MLCT excited state is supported.[68]

As limiting cases of supercomplex effect one could also consider the changes caused on the Ru(II)–diimine photophysical properties by incorporation into micelles or other organized media.[69,70]

III. Ion Pairs

Coordination compounds are usually charged species which can give rise to ion-association phenomena. If the complexes involved in an ion pair maintain their chemical identity (i.e., when their coordination spheres remain intact), the system is called an *outer-sphere* ion pair and the interaction is generally weak.

When in an outer-sphere ion pair system the interaction between the two ions is extremely weak, each partner maintains its spectroscopic, photochemical, and photophysical properties. When the interaction, though weak, is not negligible, *second-sphere charge-transfer* (SSCT)[71] transitions between the two ions can occur, and the spectroscopic, photochemical, and photophysical properties of the two isolated partners can be profoundly modified. The three limiting cases of interest are the following.

(i) The SSCT levels lie at very high energy (Figure 8a). In such a case, the absorption spectrum of the ion pair is essentially the summation of the spectra of the two isolated ions, and no SSCT photochemical reaction takes place. However, the weak interaction may induce radiationless transitions between levels centered on the different ions. This may cause a cascade nonradiative deactivation to the lowest excited state of the system, with quenching of the excited-state manifestations (photochemical reactions and/or luminescence) of one of the two partners and sensitization of those of the other one.

(ii) The SSCT levels lie in the energy range of the spectroscopic levels of the two isolated partners (Figure 8b). In such a case the ion pair shows, in some spectral region, a somewhat stronger absorption than that corresponding to the summation of the absorption spectra of the two isolated ions. Excitation of the ion pair in the SSCT band or in higher energy bands may cause either a photoreaction of SSCT origin or radiationless deactivation to the lowest excited state of the system. Excitation below the SSCT levels may be followed by radiationless deactivation to the lowest energy excited state, which is essentially localized on one of the two ions. From this level luminescence and/or reaction can take place as in case i.

(iii) An SSCT level is the lowest excited state of the system (Figure 8c). In such a case, a new, broad absorption band may appear at low energy. Radiationless deactivation to the lowest excited state can take place, with complete quenching of the photochemical and luminescence properties of the two partners. New photochemical properties[72] resulting from the lowest SSCT excited state may or may not appear depending on the stability of the primary electron transfer products (vide infra).

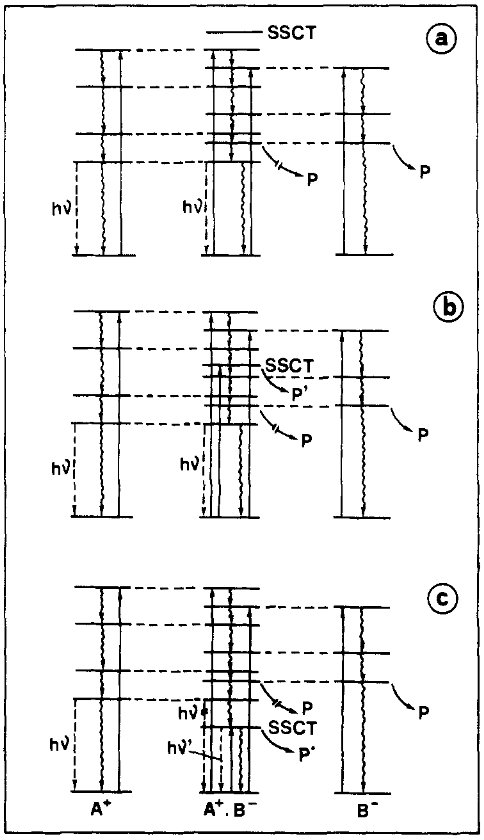

Figure 8. Schematic representation of three limiting cases of outer-sphere ion pair interaction. The cationic and anionic species are assumed to exhibit luminescence emission and photochemical reaction, respectively, when they are separated. (a) The SSCT levels lie at very high energy and are not involved in the excitation processes. The cascade radiationless deactivation within the ion pair may cause the quenching of the photoreaction of B^- and the sensitization of the emission of A^+. (b) The SSCT levels lie at intermediate energies. Excitation in the SSCT bands or in higher energy bands may cause a SSCT photochemical reaction. Excitation below the SSCT levels leads to the same results as in a. (c) An SSCT level is the lowest excited state of the ion pair. Complete quenching of the luminescence and photochemical properties of the two separated ions may occur and a SSCT photochemical reaction may take place.

In terms of potential energy surfaces, a SSCT transition can be represented as in Figure 9. Light excitation in the SSCT band leads to A·B, an electronic isomer of the starting $A^+·B^-$ species. Excitation is generally followed by rapid back electron transfer to the $A^+·B^-$ species, as shown in Figure 9a (in photophysical terms, the back electron transfer reaction is described as a radiationless deactivation). Dissociation and reassociation of the two partners of the A·B species (which in some cases is still an ion pair) can also occur. Irreversible formation of stable photoproducts can only take place when A and/or B undergo a fast irreversible reaction such as ligand dissociation (Figure 9b) or reaction with a scavenger.

We will now illustrate some typical examples of effects caused by SSCT perturbations on the photochemical and photophysical behavior of coordination compounds. The theoretical and spectroscopic aspects of ion association have been reviewed by several authors.[22,73-77]

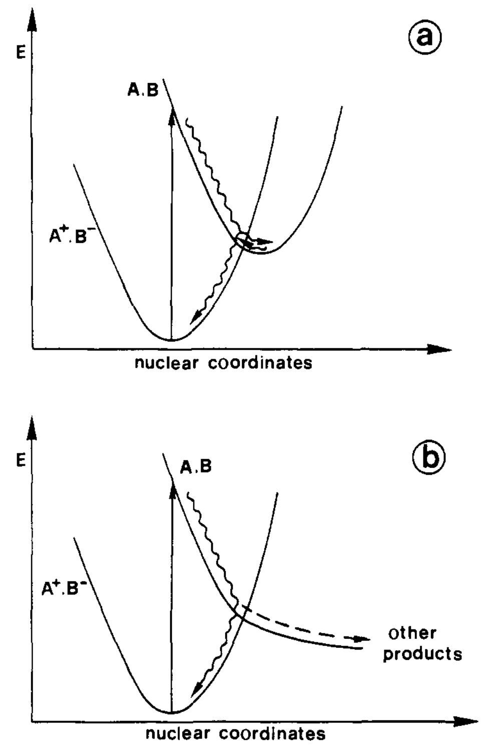

Figure 9. Schematic representation of the potential energy curves for an $A^+{\cdot}B^-$ outer-sphere ion pair. (a) A and B are stable species so that back electron transfer leads to the starting $A^+{\cdot}B^-$ pair. (b) A and/or B are either unstable or may be scavenged, in competition with the back electron transfer. A more complete picture should also consider the possibility of dissociation and reassociation of the A·B pair before the formation of the final products.

A. Induced Photochemical Reactions

1. *Ion Pairs Involving Co(III) Amine Complexes*

Co(III) complexes with 3+ electric charge are known to give ion pairs with most anions.[78,79] When the anion is a reducing species, SSCT bands appear in the near-UV or visible spectral region. Light excitation into such SSCT bands causes the promotion of an electron from the anion in the second coordination sphere to the Co(III) center which is reduced to Co(II).[35,80] Since Co(II) complexes are usually labile,[27] light excitation into the SSCT bands eventually leads to a redox decomposition reaction (Figure 9b). For example, in the $[Co(NH_3)_6]^{3+}{\cdot}I^-$ system in aqueous solution[35,80] SSCT excitation (λ_{max} 300 nm, case ii, Figure 8b) leads to redox decomposition ($\Phi = 0.2$) (eq 20–22).

$$[Co^{III}(NH_3)_6]^{3+}{\cdot}I^- \xrightarrow{h\nu\ (SSCT)} [Co^{II}(NH_3)_6]^{2+}{\cdot}I \qquad (20)$$

$$[Co^{II}(NH_3)_6]^{2+}{\cdot}I \rightarrow [Co^{III}(NH_3)_6]^{3+}{\cdot}I^- \qquad (21)$$

$$[Co^{II}(NH_3)_6]^{2+}{\cdot}I \rightarrow Co_{aq}{}^{II} + 6\ NH_3 + {}^1/_2I_2 \qquad (22)$$

A similar reaction takes place for the $[Co^{III}(NH_3)_6]^{3+}{\cdot}[Ru^{II}(CN)_6]^{4-}$ ion pairs.[81] The lower value of the quantum yield ($\Phi = 0.034$ in Me_2SO) is likely due to the more difficult cage escape of the two reaction partners after the electron transfer.

An interesting photochemical reaction of ion pairs involving Co(III) amines has been reported by Nakashima and Kida.[82] In the presence of bis(2-hydroxymethyl)dithiocarbamate (htc⁻), Co(III) amines give rise to ion pairs which undergo a photochemical reaction leading to Co(II) complexes and htc· radicals. Since the Co(II) complexes are labile, the amine ligands are released and Co(II) complexes containing the htc⁻ ligand (which is present in a large concentration) are formed. Since such complexes are able to reduce the Co(III) amine thermally, a dark catalytic ligand substitution reaction follows light excitation, as is shown in Figure 10. Reactions of this type may be interesting for applications in the field of unconventional photographic materials.[83]

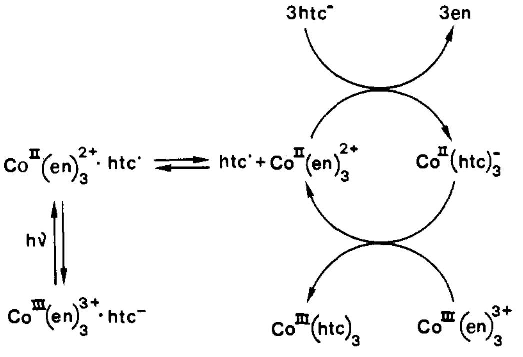

Figure 10. Photocatalytic ligand substitution induced by ion pair photochemistry.[82]

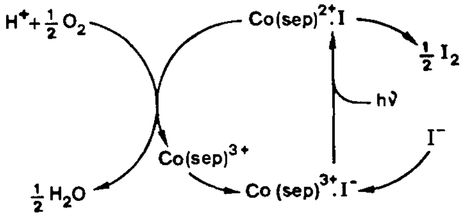

Figure 11. Photosensitized oxidation of I^- by O_2 via ion pairing with $Co(sep)^{3+}$.[39]

As we have seen in section II.A.1, $Co(sep)^{3+}$ is quite similar to $Co(NH_3)_6{}^{3+}$ as far as the spectroscopic properties are concerned. Because of the cage-type ligand; however, $Co(sep)^{3+}$ does not undergo ligand replacement upon one-electron reduction. Thus, excitation of $[Co(sep)]^{3+}{\cdot}I^-$ ion pairs does not lead to any net reaction[39,84] (Figure 9a) (eq 23–25). Equation 24 stands for any type of back electron transfer reaction, including the bulk processes involving I_2 and related species.[39]

$$[Co^{III}(sep)]^{3+}{\cdot}I^- \xrightarrow{h\nu\ (SSCT)} [Co^{II}(sep)]^{2+}{\cdot}I \qquad (23)$$

$$[Co^{II}(sep)]^{2+}{\cdot}I \rightarrow [Co^{III}(sep)]^{3+}{\cdot}I^- \qquad (24)$$

$$[Co^{II}(sep)]^{2+}{\cdot}I \not\rightarrow Co_{aq}{}^{2+} + \text{products} \qquad (25)$$

However, when aerated aqueous solutions of the $[Co(sep)]^{3+}{\cdot}I^-$ ion pair are irradiated in the presence of methyl isobutyl ketone (which is a good solvent for I_2 and does not mix with water) the net photoreaction (eq 26) is observed with $\Phi = 10^{-3}$–10^{-2}, depending on the experimental conditions.[39] As is better shown in Figure 11, in this system $Co(sep)^{3+}$ plays the role of an electron-transfer photosensitizer.

$$4I^- + O_2 + 4H^+ \xrightarrow[{[Co^{III}(sep)]^{3+}}]{h\nu} 2I_2 + 2H_2O \qquad (26)$$

A similar but perhaps more interesting case is that of the $[Co^{III}(sep)]^{3+}{\cdot}C_2O_4H^-$ ion pairs,[44] which exhibit an SSCT band with maximum at 275 nm. Excitation of these ion pairs in the SSCT spectral region in deoxygenated solutions causes the reduction of $[Co^{III}(sep)]^{3+}$ to $[Co^{II}(sep)]^{2+}$ and the oxidation of oxalate ions

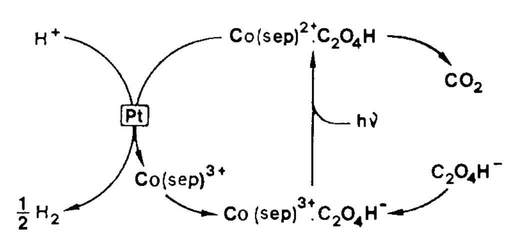

Figure 12. Photosensitized evolution of dihydrogen from water based on the excitation of $Co(sep)^{3+}\cdot C_2O_4H^-$ ion pairs.[44]

(Φ = 0.1–0.3). This is due to the fast decomposition of the primary oxidation product of $C_2O_4H^-$, which competes with the back electron transfer reaction (Figure 9b). When colloidal platinum is present in the solution, no net reduction of $Co(sep)^{3+}$ takes place, and, besides carbon dioxide, dihydrogen also evolves from the solution (eq 27). The $Co(sep)^{3+}$ complex plays again the role of an electron-transfer photosensitizer (Figure 12), with turnover number higher than 700.[44]

$$C_2O_4H^- + H^+ \xrightarrow[Co(sep)^{3+}]{h\nu} 2CO_2 + H_2 \qquad (27)$$

The above discussed examples show that second-sphere perturbation may be used to improve the performance of a photochemical system. The photochemistry of Co(III) complexes has been extensively investigated in the last 20 years,[11,12,63] and the main feature that emerged from such studies has been the strong tendency of these complexes to undergo redox decomposition upon irradiation in ligand-to-metal charge transfer or ion pair charge-transfer bands. Such photodecomposition reactions are interesting but useless. When the importance of photosensitized electron transfer reactions was realized[86-89] and the search for relays and photosensitizers became a popular research field, Co(III) complexes were discarded because they did not meet the main requirements needed, which are (i) reversible redox behavior for a relay and (ii) reversible redox behavior and long excited-state lifetime for a photosensitizer. The synthesis by Sargeson et al.[29,37] of Co(III) complexes having cage-type ligands has allowed one to overcome the problem of redox reversibility and to use Co(III) complexes as relays in photosensitization cycles.[41-43] The ion pair approach described in this section allows one to use Co(III) complexes as photosensitizers. Useful photochemistry can thus be obtained even from Co(III) complexes by means of appropriate nuclear and electronic perturbations.

2. *Ion Pairs Involving Ru(III) Amine Complexes*

With suitable ligands, ion pairs involving complexes of the same metal ion in two different oxidation states can be obtained which exhibit SSCT bands.[77,85,90,91] The $[Ru^{III}(NH_3)_5Cl]^{2+}\cdot[Ru^{II}(CN)_6]^{4-}$ ion pair shows an SSCT band with λ_{max} = 510 nm in aqueous solution (case iii, Figure 8c).[91] Upon light absorption in this band, the ion pair is converted to the binuclear complex $[(NH_3)_5Ru^{III}NCRu^{II}(CN)_5]^-$ with $\Phi = 2 \times 10^{-3}$. The reaction is thought to proceed via the rapid aquation (in competition with back electron transfer, Figure 9b) of the $[Ru^{II}(NH_3)_5Cl]^+$ primary product of the SSCT process, with successive replacement of the labile H_2O ligand by $[Ru^{II}(CN)_6]^{4-}$; the $[(NH_3)_5Ru^{II}NCRu^{II}(CN)_5]^{2-}$ product obtained in this way is then oxidized by $[Ru^{III}(CN)_6]^{3-}$ (eq 28–32).

$$[Ru^{III}(NH_3)_5Cl]^{2+}\cdot[Ru^{II}(CN)_6]^{4-} \xrightarrow{h\nu} [Ru^{II}(NH_3)_5Cl]^{+}\cdot[Ru^{III}(CN)_6]^{3-} \qquad (28)$$

$$[Ru^{II}(NH_3)_5Cl]^{+}\cdot[Ru^{III}(CN)_6]^{3-} \rightarrow [Ru^{II}(NH_3)_5Cl]^{+} + [Ru^{III}(CN)_6]^{3-} \qquad (29)$$

$$[Ru^{II}(NH_3)_5Cl]^{+} + H_2O \rightarrow [Ru^{II}(NH_3)_5H_2O]^{2+} + Cl^- \qquad (30)$$

$$[Ru^{II}(NH_3)_5H_2O]^{2+} + [Ru^{II}(CN)_6]^{4-} \rightarrow [(NH_3)_5Ru^{II}NCRu^{II}(CN)_5]^{2-} \qquad (31)$$

$$[(NH_3)_5Ru^{II}NCRu^{II}(CN)_5]^{2-} + [Ru^{III}(CN)_6]^{3-} \rightarrow [(NH_3)_5Ru^{III}NCRu^{II}(CN)_5]^{-} + [Ru^{II}(CN)_6]^{4-} \qquad (32)$$

The photochemical behavior of the ion pairs formed by $[Ru^{III}(NH_3)_5py]^{3+}$ with halide ions or $C_2O_4^{2-}$ has been studied by Ford and co-workers using continuous and flash photolysis excitation in the SSCT bands.[92] Under flash photolysis conditions, the transients $[Ru^{II}(NH_3)_5py]^{2+}$ and I_3^- are formed, followed by the back electron transfer reaction which leads to the starting materials. However, when the counterion is an irreversible reductant like $C_2O_4^{2-}$ (Figure 9b), photolysis in the SSCT bands can lead to substantial net photoreduction of the metal center under continuous photolysis. Similar results have been obtained with the $[Os^{III}(NH_3)_5Cl]^{2+}\cdot[M^{II}(CN)_6]^{4-}$ (M = Fe, Ru, Os) ion pairs.[85]

3. *Ion Pairs Involving $Mo(CN)_8^{4-}$*

Systems that are borderline between the ion pairs discussed in this section and the coordinatively bound couples described in section IV have been studied by Hennig et al.[83] $[Mo^{IV}(CN)_8]^{4-}$, as well as other cyanide complexes, gives rise to ion pairs (or more likely to cyano-bridged compounds) with a variety of Cu^{2+} species and other cations like Fe^{3+} and UO_2^{2+}. The SSCT bands extend to the visible and, in some cases, to the near-infrared. Photochemical investigation of the $[Mo^{IV}(CN)_8]^{4-}\cdot Cu^{2+}$ systems has shown that irradiation in the SSCT bands leads to formation of free cyanide, as expected because of the known kinetic lability (Figure 9b) of $[Mo^{V}(CN)_8]^{3-}$. The relevance of these studies for practical applications has been emphasized.[83]

B. Luminescence Quenching

1. *$[Eu\subset 2.2.1]^{3+}\cdot[M(CN)_6]^{4-}$ Ion Pairs*

Encapsulation of Eu^{3+} into the 4,7,13,16,21-pentaoxo-1,10-diazabicyclo[8.8.5]tricosane ligand (Lehn's[2,3] [2.2.1] cryptand) yields a stable cryptate complex, $[Eu^{III}\subset 2.2.1]^{3+}$, which exhibits intense luminescence emission in aqueous solution (λ_{max} = 615 nm; τ = 215 μs).[93] This luminescence emission is quenched by $[M^{II}(CN)_6]^{4-}$ (M = Fe, Ru, Os) complexes.[94] At low quencher concentration the quenching process is *dynamic* in nature and is due to a bimolecular electron-transfer mechanism (eq 33). When relatively concentrated aqueous solutions of $[Eu^{III}\subset 2.2.1]^{3+}$ and $[M^{II}(CN)_6]^{4-}$ are used, formation of ion pairs clearly occurs, as is shown by the appearance of a new, low-energy broad absorption band in the visible region (case iii,

$$^*[Eu^{III}\subset 2.2.1]^{3+} + [M^{II}(CN)_6]^{4-} \rightarrow [Eu^{II}\subset 2.2.1]^{2+} + [M^{III}(CN)_6]^{3-} \qquad (33)$$

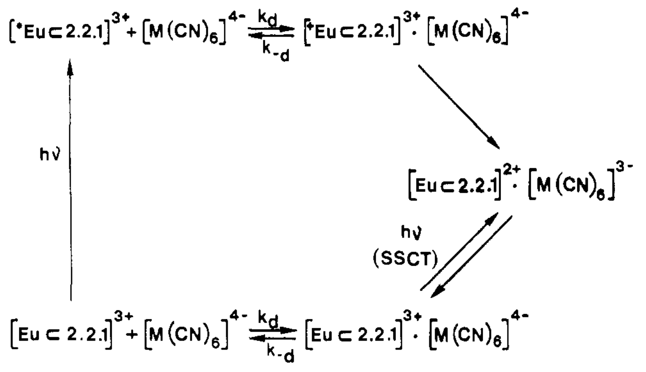

Figure 13. Scheme of the light-induced and thermal reactions occurring in the $[Eu\subset 2.2.1]^{3+}\cdot[M(CN)_6]^{4-}$ systems (M = Fe, Ru, or Os).[94]

Figure 8c). The position of the absorption maximum moves to higher energies in the series Fe < Os < Ru, which parallels the oxidation potential of the cyanide complexes, as is expected for an SSCT transition[94] (eq 34). Since no net chemical effect is observed upon

$$[Eu^{III}\subset 2.2.1]^{3+}\cdot[M^{II}(CN)_6]^{4-} \xrightarrow[SSCT]{h\nu} [Eu^{II}\subset 2.2.1]^{2+}\cdot[M^{III}(CN)_6]^{3-} \quad (34)$$

excitation in the SSCT band, the photoinduced SSCT reaction must be followed by a fast back electron transfer process which leads the system to its original situation (Figure 9a).

An interesting feature of this system is that (Figure 13) the excited state obtained upon SSCT excitation of the ground-state ion pair is the same species as the successor complex obtained upon quenching of $*[Eu^{III}\subset 2.2.1]^{3+}$ via a dynamic mechanism. The relationships between the thermal and the two light-induced electron-transfer reactions that take place in these systems are quite interesting,[94] but they are outside the scope of this review.

2. *$[Ru(bpy)_3]^{2+}\cdot[CoSiW_{11}O_{39}H_2O]^{6-}$ Ion Pairs*

Quenching of the $[Ru(bpy)_3]^{2+}$ luminescence by $[CoSiW_{11}O_{39}H_2O]^{6-}$ via static and dynamic electron-transfer quenching has been observed.[95] The interesting point of this system is that in flash experiments the luminescence emission decreases with time according to two distinct decays. This happens because (see Figure 14) k_{el} is sufficiently larger than $1/\tau^\circ + k_d[Q^{6-}]$ and $1/k_{el}$ is sufficiently longer than the time resolution of the apparatus used (2 ns). Under such conditions, the $[Ru(bpy)_3]^{2+}$ ions excited when they are involved in ion pairs with $[CoSiW_{11}O_{39}H_2O]^{6-}$ decay faster than the free $[Ru(bpy)_3]^{2+}$ ions but still slowly enough to have a chance to emit and to remain within the time resolution of the equipment. The quenching of the preformed excited ion pairs is then followed by the slower dynamic quenching of the free $*[Ru(bpy)_3]^{2+}$ ions. The results obtained have shown that the lifetime of $*[Ru(bpy)_3]^{2+}$ reduces from 400 to ~10 ns upon second sphere interaction with $[CoSiW_{11}O_{39}H_2O]^{6-}$. The decrease in the lifetime is caused by the availability of a relatively low-lying SSCT excited state ($A^{3+}\cdot Q^{7-}$ in Figure 14).

A similar behavior (but without the observation of the two distinct emission decays) has been reported to occur for the $[Os(5\text{-}Clphen)_3]^{2+}\cdot[Fe(CN)_6]^{4-}$[96] and the $[Ru(bpy)_3{}^{2+}]\cdot[S_2O_8]^{2-}$[97] ion pairs.

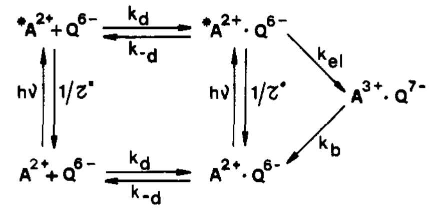

Figure 14. Kinetic scheme for the dynamic and static quenching of the luminescence of $Ru(bpy)_3{}^{2+}$, A^{2+}, by $[CoSiW_{11}O_{39}H_2O]^{6-}$, Q^{6-}.[95]

C. Tuning of Excited State Energies and Lifetimes

1. *Ion Pairs Involving $Os(phen)_3{}^{2+}$*

The properties of the metal-to-ligand charge-transfer (MLCT) excited states of polypyridine metal complexes are affected by the environment. The polar, uncharged $M(LL)_2X_2$ complexes (M = Ru or Os; LL = polypyridine type ligands; X = Cl or CN) are strongly influenced by the nature of the solvent;[98-101] the charged $M(LL)_3{}^{2+}$ species are influenced both by the solvent[102] and by ion pair formation.[103]

Meyer et al.[103] have recently studied the luminescence properties of $Os(phen)_3X_2$ and $Os(4,4'\text{-}Ph_2phen)_3X_2$ (phen is 1,10-phenanthroline; 4,7-Ph_2phen is 4,7-diphenyl-1,10-phenanthroline; X is $PF_6{}^-$, $ClO_4{}^-$, Cl^-, Br^-, or SCN^-) in CH_2Cl_2, a solvent of very low dielectric constant (D_s = 9). Both the emission energies and the emission lifetimes were found to vary on changing the anion. The microscopic origin of the anion effect is essentially electrostatic, and it is related to the localization of the excited electron into a single polypyridine ligand, which provides a basis for positioning of the anions near the other two ligands. As the emission energy increases the emission lifetime (which is essentially controlled by the nonradiative rate constant) also increases, as expected according to the energy gap law.[103] This ion pair effect may be useful to produce a fine tuning on the excited-state properties.

IV. *Donor–Acceptor Interactions*

Werner-type complexes are usually considered to be "coordinatively saturated" provided that no coordination site *at the metal* is vacant (or may become available through fast ligand labilization). In several cases, however, this statement may not be really accurate, in that additional positions available for donor–acceptor interactions with other species may still remain *on the ligands.* The donor–acceptor interactions by which a "coordinatively saturated" complex binds other chemical species via the ligands can be conveniently termed *second-sphere donor–acceptor* (SSDA) interactions.

By far, the most common SSDA interactions are those in which the complex acts as a Lewis base. Examples of this type of situation are frequent in complexes containing ligands such as cyanide,[83,98,104-117] and aza-[22,118-120] or carboxyl-substituted[121-123] pyridyl ligands. Less frequent is the case in which the SSDA interactions involve the complex as a Lewis acid. Notably, weak SSDA interactions of the latter type have been invoked to account for solvent effects on some ammine complexes.[124]

The SSDA interactions can modify to a more or less pronounced extent several properties of the parent

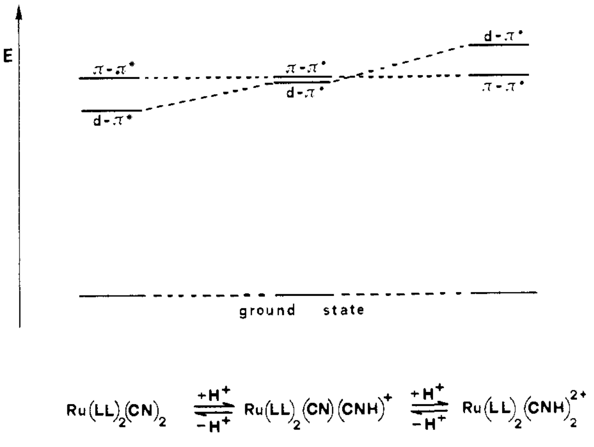

Figure 15. Change in the orbital nature of the lowest excited state upon protonation of $Ru(LL)_2(CN)_2$.[108]

complex. In this section, we will discuss a number of selected examples in which SSDA interactions affect significantly the photophysical or photochemical behavior of a complex. The knowledge of the factors governing SSDA effects appears to be interesting, in view of the possibility to use such effects to tune in the desidered direction photochemical (and related) properties of a complex (e.g., absorption and emission spectra, excited-state energies and lifetimes, photoreactivity, redox potentials, primary product yields).

A. Proton-Transfer Equilibria

The literature on proton transfer equilibria involving excited states of coordination compounds is not as rich as that pertaining to organic systems.[125] Nevertheless, there are a number of well-documented cases in which SSDA interactions with protons are found to substantially modify the photochemical (or related) properties of a coordination compound. Some relevant examples of this behavior are discussed in the following subsections.

1. $Ru(bpy)_2(CN)_2$ and Related Complexes

It has long been known that complexes of the *cis*-$M(LL)_2(CN)_2$ type (where LL represents a bipyridine-type ligand and M = Fe(II), Ru(II), Os(II)) protonate in acidic media.[126,127] The effect of protonation on the photophysics of the Ru(II) complexes of this type (LL = bpy, phen) has been thoroughly investigated in the last decade, particularly by Peterson and Demas.[107,108]

Given the equilibrium constants for the two proton-transfer steps in eq 35 and 36 substantial amounts of the mono- and diprotonated forms are present in acidic (e.g., pH 0) aqueous solutions of the bpy and phen complexes. In keeping with the Ru → LL d-π* character of the lowest electronic transition, definite blue shifts are observed upon protonation in the absorption spectra.

$$Ru(LL)_2(CNH)_2^{2+} \xrightarrow{K_1} Ru(LL)_2(CNH)(CN)^+ + H^+ \qquad pK_1 = -0.07 \quad (35)$$

$$Ru(LL)_2(CNH)(CN)^+ \xrightarrow{K_2} Ru(LL)_2(CN)_2 + H^+ \qquad pK_2 = 0.13 \quad (36)$$

Interestingly, no parallel shifts in the emission spectra were observed by Peterson and Demas[107,108] over the same pH range, indicating that the excited states of these molecules are remarkably more acidic than the ground states so that fast deprotonation of the excited states precedes the emission. The direction of the shift in the pK_a values in going from the ground state to the excited state (ground state, 0.13; excited state, <-1.0) emphasizes the fact that the d-π* transition leads to a *decrease* in charge density at the protonation site. The magnitude of the shift is as expected on the basis of energy considerations (Forster cycles).[108]

An important observation made by Peterson and Demas[108] was that in concentrated sulfuric acid at 77 K, where substantial amounts of excited protonated forms are expected to be present, a qualitatively different emission takes over. Based on structure, lifetime, and similarity with the free ligand emission, this emission was assigned as a ligand-centered π-π* phosphorescence. This finding has been interpreted in terms of the shifts in excited-state energies depicted in Figure 15. It is seen that the SSDA interaction with protons acts so as to alter the energy spacing of the d-π* and π-π* levels. This may lead to a substantial admixture (via configuration interaction) of π-π* character into the lowest d-π* state, or even to a change in the nature of the lowest excited state.

Similar observations have been made in one of our laboratories on other $Ru(LL)_2(CN)_2$ complexes.[101] In particular for LL = 2,2′-biisoquinoline, the π-π* state is already sufficiently low in energy as to be substantially mixed with the d-π* state. Upon protonation, the π-π* state clearly becomes the lowest one, giving rise to a long-lived, pure π-π* phosphorescence.

2. $Ru(bpy)_2(4,4'\text{-}(COO)_2bpy)$

This complex, which was studied several years ago by Wrighton and co-workers[121] and has been very recently reinvestigated independently by Lay et al.[122] and Shimidzu et al.,[123] gives an example of the opposite shift in acid-base properties between ground and excited state.

The two-proton-transfer equilibria of this species are depicted in Figure 16. Red shifts in the low-energy absorption features of this complex are observed in going from neutral to acidic solutions, indicating that the lowest excited state is of the Ru → (4,4′-(COO)$_2$bpy) d-π* type. Based on these spectral variations, a pK_2 value of 2.7 ± 0.1 was obtained by all authors for the first protonation step. Although the pK_1 value could

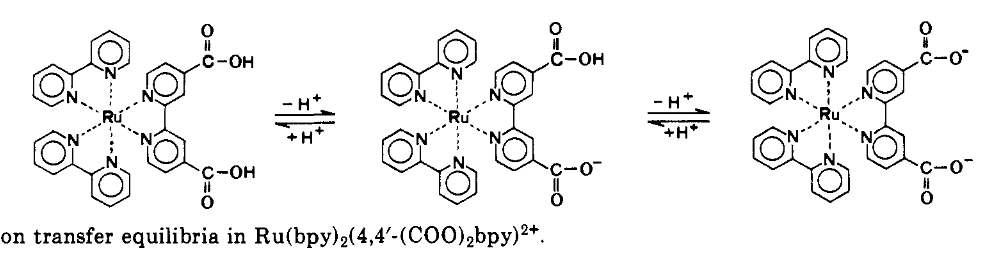

Figure 16. Proton transfer equilibria in $Ru(bpy)_2(4,4'\text{-}(COO)_2bpy)^{2+}$.

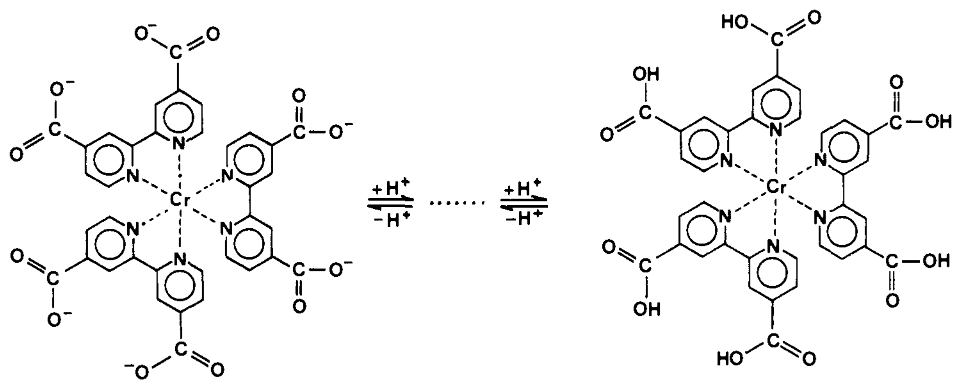

Figure 17. Proton transfer equilibria in $Cr(4,4'-(COO)_2bpy)_3^{3-}$.

not be detected by Wrighton et al.,[121] more recent work by Lay et al.[122] and Shimidzu et al.[123] indicates that this value is in the 0.5–1.7 range.

Red shift and lifetime shortening were also observed for emission in acidic solutions. Spectrofluorimetric and lifetime titrations, however, indicated a pK_2^* value for the excited state of 4.3 ± 0.2.[121–123] Lay et al.[122] were also able to estimate a pK_1^* value of 3.7. Thus, the lowest excited state of this complex is significantly less acidic than the ground state, and at appropriate pH (e.g., pH 3.5) the excited dicarboxylate species protonates prior to deactivation. The magnitude of the pK_a shift is as expected on the basis of Forster cycle calculations.[123] The direction of the shift underlines the fact that in this case the d–π* transition leads to an *increase* in electron density at the protonation site.

3. $Cr(4,4'-(COO)_2bpy)_3^{3-}$

This complex, recently studied in one of our laboratories,[128] gives an example of proton-transfer equilibria which do not differ appreciably in the ground and lowest excited state.

At neutral pH, the complex is present as the fully deprotonated anionic form. Six consecutive protonation steps can be envisioned for this complex, leading to the fully protonated cationic species (Figure 17) in sufficiently acidic solutions. A spectrophotometric titration indicates that protonation starts at pH 4, proceeds in several closely spaced steps, and is not yet completed at pH 0. As far as the emission is concerned, no spectral shift was observed to occur in the 0–10 pH range. However, the emission lifetime changed from 25 μs at pH 7 to 8 μs at pH 0. A titration based on lifetime indicates that protonation of the excited state begins at the same pH value and extends over the same pH range as for the ground state. These results are consistent with the nature of the lowest excited state of this complex. This state is a metal-centered, intraconfigurational (t_{2g}^3) ^2E_g state, in which the electron density at the protonation sites is expected to be virtually identical with that of the ground state. The lifetime shortening obtained upon protonation is as expected for a weak coupling limiting case,[129] following introduction of high-energy intramolecular accepting modes and enhanced coupling with solvent modes (see, for comparison, analogous effects on intraconfigurational emission in Eu^{3+} systems, section V.A).

In this example, SSDA interactions with protons do not appreciably modify the spectroscopic properties of the complex. Nevertheless, it can be pointed out that in this case protonation can be used to tune a molecular property which is quite relevant to bimolecular photochemical processes, namely, the electric charge of the complex. This aspect has been probed by studying a number of electron-transfer quenching processes of the type shown in Figure 18. For most practical purposes, a very important parameter of such processes is the efficiency of primary products escaping the solvent cage before undergoing prompt back electron transfer.[130–132] Evidence has been accumulating in recent years that for inorganic complexes cage-escape yields depend strongly on product charges, being usually negligible for oppositely charged products. Cage-escape yields have been measured[128] by laser photolysis using $Cr^{III}(4,4'-(COO)_2bpy)_3^{3-}$ or its protonated species as photosensitizers ($Cr^{III}(LL)_3$ in Figure 18) and Fe_{aq}^{2+} or $Fe(CN)_6^{4-}$ as quenchers (Red in Figure 18). The results show a striking pH effect: in conditions of complete excited-state quenching, Fe_{aq}^{2+} gives high cage-escape yields (~0.3) at pH 0 but undetectable yields at pH 5; on the contrary, $Fe(CN)_6^{4-}$ gives negligible yields at pH 0 and high yields (~0.6) at pH 5. These results are quite clearly attributable to the change in electric charge of the photosensitizer with pH which, depending on the quencher, switches the charge product of the $Cr^{II}(LL)_3{\cdot}Ox$ pair from positive to negative or vice versa.

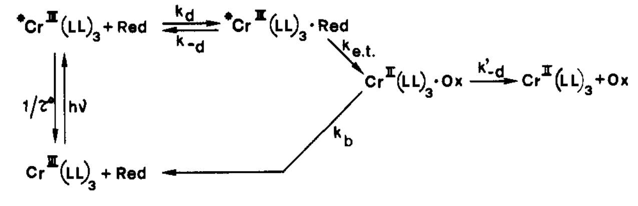

Figure 18. Kinetic scheme used to discuss the relevance of the electric charge on the yield of cage escape. (For details, see text.)

B. Metalation

1. The $Ru(bpy)_2(CN)_2$ Unit

When Lewis basic sites are available on the ligands of a complex, metalation is another important type of SSDA interaction. The resulting adducts are bi- or polynuclear metal complexes which can exhibit interesting photochemical and photophysical properties of their own. Rather than attempting a comprehensive review of the photochemical and photophysical behavior of binuclear and polynuclear complexes, we will only focus our attention on the perturbations caused by metalation on the excited state properties of the original

TABLE II. Photophysical Data for Adducts of Ru(bpy)$_2$(CN)$_2$ with Metal-Containing Moieties (M)[a]

M	absorption λ_{max}(d–π^*), nm	emission λ_{max}, nm	τ,[b] ns	lowest excited state	ref
c	428	620	250	d–π^*	115
c,d	505	680	205	d–π^*	115
Zn^{2+} [e,f]	415	615	520	d–π^*	133
Cu^{+} [e,g]	430	620	500	d–π^*	133
Ag^{+} [e,f]	430	650	600	d–π^*	111
Co^{2+} [h]	*i*	*j*	*j*	d–d	98
Ni^{2+} [h]	*i*	*j*	*j*	d–d	98
Cu^{2+} [h]	*i*	*j*	*j*	d–d	98
Fe^{3+} [e]	395	*j*	*j*	IT	133
cis-$PtCl_2(C_2H_4)py$ [d,h]	460	620	670	d–π^*	113
trans-$PtCl_2(C_2H_4)py$ [d,h]	456	620	700	d–π^*	113
cis-$PtCl_2(DMS)py$ [d,h]	420	620	620	d–π^*	113
trans-$PtCl_2(DMS)py$ [d,h]	470	620	650	d–π^*	113
$PtCl_3(C_2H_4)^{-}$ [d,g]	450	620	640	d–π^*	113
$Pt(dien)^{2+}$ [d,f]	460	630	630	d–π^*	115
$Fe(CN)_5{}^{2-}$ [f]	420	*j*	*j*	IT	133
$Ru(NH_3)_5{}^{2+}$ [f]	413	*j*	*j*	d–π^*	117
$Ru(NH_3)_5{}^{3+}$ [f]	403	*j*	*j*	IT	117
$Ru(NH_3)_4py^{2+}$ [f]	416	*j*	*j*	d–π^*	134
$Ru(NH_3)_4py^{3+}$ [f]	400	*j*	*j*	IT	134
$Ru(bpy)_2CN^{+}$	446	655	60	d–π^*	134

[a] Data in aqueous solution, unless otherwise noted. [b] Deaerated solutions. [c] Data for the parent Ru(bpy)$_2$(CN)$_2$. [d] DMF solution. [e] CH_3CN solution. [f] 1:1 adduct. [g] 1:2 adduct. [h] Unresolved mixture of 1:1 and 1:2 adducts. [i] Data not given in the original paper. [j] Nonemitting species.

complex. In the last few years, a considerable number of adducts between the Ru(bpy)$_2$(CN)$_2$ chromophore and solvated metal ions or transition-metal complexes have been described.[98,111,113-115,117,133-135] Although in some of the original papers alternative approaches have been used (e.g., polynuclear complex chemistry, mixed-valence behavior, etc.), all these systems can be viewed as examples of strong SSDA perturbations on the Ru(bpy)$_2$(CN)$_2$ chromophore. We will use this family of compounds to exemplify and discuss various types of this second sphere perturbation effect.

Some of these systems and their photophysical properties are reported in Table II. Since Ru(bpy)$_2$(CN)$_2$ has two cyanides as potential bridging sites, both 1:1 and 1:2 adducts can be expected as the result of SSDA interactions with metal-containing moieties. Actually, in some cases 1:1 and 1:2 species have been isolated and characterized, while in other cases only equilibrium mixtures in solution have been investigated. Depending on the system, either 1:1 or 1:2 species or typical equilibrium mixtures are considered in Table II. As one can see, except for one case (Ru(bpy)$_2$(CN)$^+$ as bound group), SSDA interaction via cyanide bridge with other metals produces a blue shift of the dominant d–π^* Ru → bpy absorption band. This shift is reminiscent of that observed upon protonation of the same chromophore (section IV.A.1) and can be accounted for[115] on the basis of the electron-withdrawing (or t_{2g} orbital stabilizing) effect of the bound metal-containing moiety.

Again with the exception of the Ru(bpy)$_2$(CN)$^+$ group, emission is only observed with bound units consisting of nontransition (d^{10}) metals or Pt(II) complex moieties. With these groups, no low-lying excited states are introduced since (i) d–d states of the bound group are either absent or at very high energy and (ii) the redox properties of the bound metal do not allow the occurrence of low-energy metal-to-metal intervalence transfer transitions. Thus, in these systems metalation only brings about a blue shift in emission parallel to that observed in absorption (Table II). The general increase in lifetimes obtained upon metalation can be tentatively interpreted in terms of reduced d–π^* to π–π^* energy gap and increased configuration interaction mixing of these two states, although alternative explanations cannot be ruled out.[115]

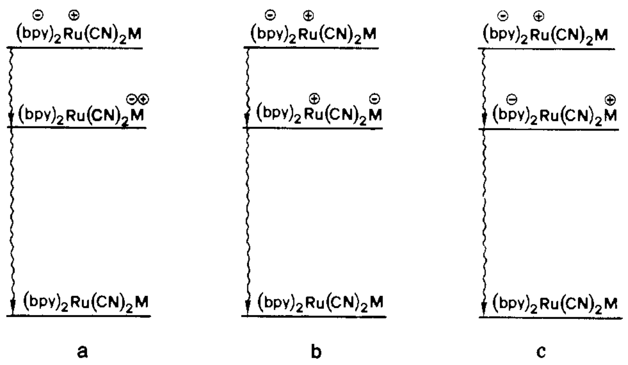

Figure 19. Different pathways for metalation-induced deactivation of the lowest LMCT excited state of Ru(bpy)$_2$(CN)$_2$. A simple electron-hole pair formalism is used. (a) Quenching by energy transfer; (b) oxidative quenching; (c) reductive quenching. (For details concerning absorption processes, see text.)

One point is worth mentioning in comparing the effects of metalation and protonation of the Ru(bpy)$_2$(CN)$_2$ chromophore. For the same reasons that make the protonated form of the chromophore more acidic in the excited state than in the ground state, the metalated chromophore should have some tendency to lose the attached groups upon excitation. The fact that no photochemical demetalation is observed in these systems (absorption and emission shifts are always parallel) is very likely due to kinetic factors (demetalation much slower than deprotonation).

The adducts with Co$_{aq}$(II), Ni$_{aq}$(II), and Cu$_{aq}$(II) do not emit.[98] Most probably this is due to an efficient decay path provided by low-lying ligand field states localized on the attached metal. This pathway, which may be viewed as an intramolecular energy-transfer sequence, is depicted in Figure 19a, in which a schematic electron-hole pair formalism is used to designate the excited states. The alternative possibility of an intramolecular electron-transfer pathway seems to be unlikely in view of the absence of observable intervalence transfer transitions in these systems (vide infra).

With Fe(III)$_{aq}$, $Fe(CN)_5{}^{2-}$, $Ru(NH_3)_5{}^{3+}$, and $Ru(NH_3)_4py^{3+}$, the lack of emission is easily justified by the presence of prominent intervalence transfer (IT) bands at low energy in the spectra of the adducts.[117,133,134] The wide and important topic of IT in mixed-valence polynuclear complexes is covered in a number of recent reviews.[21,22,136] In the present context, we shall only remark that the presence of these IT states provides a very efficient radiationless deactivation path to the adducts. This pathway, which may be viewed as a two-step intramolecular electron transfer process, is depicted in Figure 19b.

The adducts of $Ru(NH_3)_5{}^{2+}$ and $Ru(NH_3)_4py^{2+}$ do not emit,[117,134] in spite of the absence of IT states and probably also of low-lying d–d states. The reason lies in a peculiar, and to some extent unexpected, consequence of this type of metalation: a new, low-energy band is observed in the spectrum which corresponds to a d-π^* transition from the attached metal to the bpy ligands on the main chromophore.[117] This "long range" charge transfer introduces a new deactivation pathway, consisting of two consecutive intramolecular electron-transfer steps, as depicted in Figure 19c.

The case in which the $Ru(bpy)_2(CN)^+$ unit is attached to the "main" $Ru(bpy)_2(CN)_2$ chromophore is a rather exceptional one. In this case, both absorption and emission are *red*-shifted with respect to $Ru(bpy)_2(CN)_2$.[134] This is no doubt due to the fact that in the $(NC)(bpy)_2Ru$–CN–$Ru(bpy)_2(CN)^+$ adduct the lowest d-π^* transition involves the $Ru(bpy)_2$ unit containing N-bonded bridging cyanide. In this case, the straight picture of a binuclear, quasisymmetrical complex is clearly more appropriate than that of a SSDA perturbation of the "main" $Ru(bpy)_2(CN)_2$ chromophore.

As a class of compounds, the cyano-bridged adducts of $Ru(bpy)_2(CN)_2$ with various metal-containing moieties usefully exemplify the variety of ways in which SSDA interactions can affect the photophysics of the parent complex. Depending on the energy and type of new electronic states introduced by the metalation, situations ranging from a slightly perturbed original chromophore to completely new, bimetallic chromophoric systems may be encountered.

V. "Second-Sphere" Perturbation of Lanthanide Ions

A d-block transition-metal ion in solution has a well-defined first coordination sphere, which is surrounded by other species that may be viewed as constituting a second coordination sphere.[27] The most important properties of such a system are determined by the type of metal ion and the nature and symmetry of the first coordination sphere. In these cases it is appropriate to consider the metal and its first coordination sphere as a single molecular species called complex, while the second coordination sphere is best considered as a perturbing environment of the complex. For f-block ions, the situation is quite different: the first coordination sphere is most often ill-defined,[24,137,138] and several important properties of the system (e.g., the spectroscopic levels) depend only slightly on the metal ion environment. This is due to the fact that the valence electrons occupy inner f orbitals that are strongly shielded by outer s and p electrons.[137,139,140] For f-block ions, therefore, it may be more appropriate to consider the first coordination sphere as a perturbing environment of the "bare" metal ion. Thus, the first coordination sphere of a f-metal ion plays a role similar to that played by the second coordination sphere of d-block metal complexes. For example, the intensity of the ligand (first coordination sphere)-to-metal charge transfer bands for f-block ions[139,141,142] is as weak as that of the ligand (second coordination sphere)-to-metal charge transfer bands of d-block metal complexes.[26]

Following this approach, one could discuss the excited-state behavior of lanthanide ions in various environments in terms of a second sphere perturbation of the f-electrons. Since the photochemistry of the f-block elements is poor, we will only deal with their photophysical properties, which are quite interesting and easy to study. As a paradigmatic example we will discuss the Eu^{3+} ion. The same approach could be used for other lanthanide ions for which, however, fewer experimental data are available.

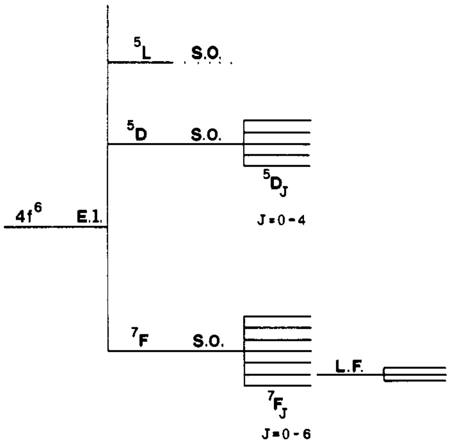

Figure 20. Splitting of the $4f^6$ electronic configuration of Eu^{3+} ion owing to electrostatic interaction, spin-orbit coupling, and ligand field.

A. The Eu^{3+} Ion

1. General Spectroscopic and Photophysical Concepts

The basic principles related to the excited-state properties of the lanthanide ions have been extensively described in many monographs.[137,140,143-147] We will illustrate here only those general concepts concerning the Eu^{3+} ion spectroscopy and photophysics that are essential to discuss the luminescence properties of the systems dealt with in the following section.

The $4f^6$ electronic configuration of Eu^{3+} ions gives rise to several terms, whose energies are determined by combination of interelectronic repulsion, spin-orbit coupling, and, in a coordination environment, ligand field (Figure 20). The electrostatic interaction yields terms with separations of the order of 10^4 cm^{-1}. The spin-orbit interaction then splits these terms into J states, with typical splitting of 10^3 cm^{-1}. Finally, the J degeneracy of the free ion states is partially or fully removed in the coordination compounds by the ligand field, the splitting being of the order of 10^2 cm^{-1}. It is important to note that the relative importance of spin-orbit and ligand field effects is reversed with respect to the situation in d-block transition-metal complexes.

The intensities of the f → f absorption spectra can be interpreted in detail by the Judd-Ofelt theory.[148] Electric dipole transitions between 4f levels, involving no change in parity, are forbidden by the Laporte rule. They may become allowed as "forced" electric dipole transitions by mixing into the $4f^n$ configuration an excited configuration having opposite parity. Such mixing may be accomplished by the odd parity terms of the expansion of the ligand field. If the ion is located in a center of symmetry, the odd ligand field terms are absent, and the parity prohibition cannot be lifted. Besides the static ligand field potential, another mechanism whereby configurations of opposite parity may be mixed into the $4f^n$ configuration is the potential produced by non-totally symmetric vibrations. Magnetic dipole transitions are parity allowed between states of f^n configuration. They are in general at least an order of magnitude less intense than electric dipole transitions. The spin selection rules are strongly relaxed

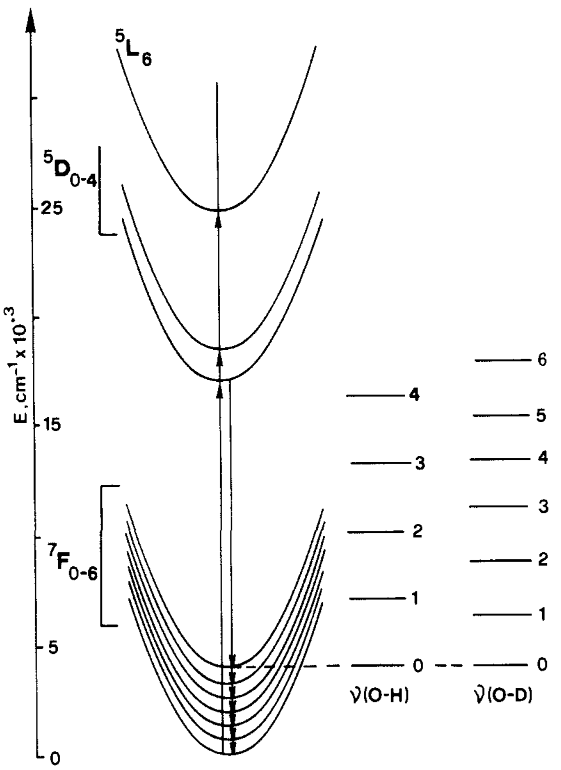

Figure 21. Schematic representation of the energy levels involved in the spectroscopy and photophysics of Eu^{3+} ion. The energy scale shown is appropriate for Eu_{aq}^{3+}. The energy levels of the OH and OD acceptor vibrational modes are also shown.

in lanthanide complexes because of the high spin–orbit coupling, which allows mixing of states having different multiplicities.

The exceedingly weak absorption bands (extinction coefficient of the order of 1) and the very long radiative lifetime of the excited states (millisecond range) indicate how strictly forbidden the f–f transitions are.

The emission of the Eu^{3+} ion consists of transitions from the ^5D manifold (mainly from the $^5D_0$ level) to the ^7F manifold (Figure 21). If we consider the $^5D_0 \rightarrow {}^7F$ emission, the selection rules for forced electric dipole transitions allow the $^5D_0 \rightarrow {}^7F_{2,4,6}$ transitions and those for magnetic dipole transitions the $^5D_0 \rightarrow {}^7F_1$ one. The $^5D_0 \rightarrow {}^7F_{0,3,5}$ transitions are strictly forbidden. They occur with extremely low intensity in some compounds and this is usually explained as due to "J-mixing". The electric dipole transitions dominate in compounds without an inversion symmetry, i.e., the $^5D_0 \rightarrow {}^7F_{2,4,6}$ transitions are more intense than the $^5D_0 \rightarrow {}^7F_1$ one, while they are very weak in compounds with a center of symmetry. This indicates that the vibronic intensity is very weak compared to the static one.

The ground and excited states have the same equilibrium geometry (Figure 21), because excitation only involves rearrangement of the electrons within f orbitals which are screened by the outer electron shells. Therefore, the observed bands are always very sharp.

The changes in the emission spectra on changing the first coordination sphere, although very small compared to those observed for d-transition-metal ions, are very specific, especially as far as the relative intensities and the splitting patterns of the bands are concerned. The transitions from the $^5D_0$ level to the ^7F_J manifold are particularly useful in determining the composition, structure, and symmetry of the metal ion environment.[137,146,149,150] In fact, the nondegenerate $^5D_0$ level cannot be split in any symmetry and so the number of emission bands observed under high-resolution conditions reflects the splitting of the ^7F_J levels in a ligand field. The application of the symmetry selection rules allows a prediction of the number of allowed transitions for a given symmetry and J value. Since both the $^5D_0$ and $^7F_0$ levels cannot be split by ligand field effects, the number of components in the $^5D_0 \rightarrow {}^7F_0$ region indicates the minimum number of differently coordinated Eu species present in the system. Analogous information can be got from excitation spectra obtained by tunable laser excitation of the $^7F_0 \rightarrow {}^5D_0$ transition.[149] Very recently Horrocks and Albin[151] were able to correlate the energy of the $^7F_0 \rightarrow {}^5D_0$ transition to the total charge on the ligands bound to Eu^{3+}, using luminescence excitation spectroscopy. The shift of the $^7F_0 \rightarrow {}^5D_0$ transition to lower energy as the environment about the europium ion becomes more negative has been attributed to a nephelauxetic effect on the parameters of interelectronic repulsion.

The generally low emission quantum yields[152] and the fact that the measured decay times are usually one or two orders of magnitude lower than the estimated radiative lifetimes[148] indicate that the decay of the $^5D_0$ level is mainly governed by nonradiative transitions. According to the theory of nonradiative transitions in lanthanide complexes,[140,143,153] the nonradiative relaxation between various J states may occur by interaction of the electronic levels of the rare earth with suitable vibrational modes. The efficiency of these processes is governed by the energy gap and the vibrational energy of the oscillators.[129,140,143]

Owing to the pronounced hard character of Eu^{3+}, the most frequent neighbor atom to europium ion is oxygen.[138,139] Therefore, water molecules are commonly coordinated to europium ions simultaneously with other ligands. An efficient nonradiative deexcitation of the emitting $^5D_0$ level of the Eu(III) ions takes place via a weak vibronic coupling with the vibrational states of the high frequency OH oscillators.[152,154] If the O–H oscillators are replaced by the low frequency O–D ones the vibronic deexcitation pathway becomes much less efficient.[152,154] This fact enables one to determine the number of OH oscillators in the first coordination sphere by carrying out separate experiments in H_2O and D_2O solutions. Horrocks and Sudnick[149,155] have shown that for Eu^{3+} complexes the number of coordinated water molecules, q, is given, within an estimated uncertainty of 0.5, by eq 37, where k_{H_2O} and k_{D_2O} are the

$$q = 1.05(k_{H_2O} - k_{D_2O}) \qquad (37)$$

reciprocal (in ms^{-1}) of the experimental excited-state lifetimes in H_2O and D_2O solutions. Other interesting studies on the effect of the vibronic coupling with high frequencies solvent modes have been reported.[156]

2. *Selected Examples*

We discuss here a few selected examples where the perturbations produced by the environment on the Eu^{3+} ions can be studied on the basis of a detailed analysis of high-resolution emission and excitation spectra and lifetime values. The examples deal with compounds where the Eu^{3+} ions are complexed with polydentate ligands. These compounds, in fact, because of their

TABLE III. Luminescence Properties of Eu^{3+} Ions in Various Environments and Inferred Structures of the Coordination Spheres[a]

compd	phys state	$^5D_0 \rightarrow {}^7F_0$,[b] cm^{-1}	$^5D_0 \rightarrow {}^7F_1$,[b] cm^{-1}	$^5D_0 \rightarrow {}^7F_2$,[b] cm^{-1}	$^5D_0 \rightarrow {}^7F_4$,[b] cm^{-1}	coordin symmetry	τ_{H_2O}, ms	τ_{D_2O}, ms	nH_2O[c]	ref
$[Eu(ODODA)_2](BF_4)_3$	solid	17 273[d]	16 750	16 080	14 220	D_{2h}[e]				165
			16 890	16 190	14 350					
			17 060	16 330	14 420					
					14 570					
	solut[f]	17 273[d]				[g]	1.40	0.54	1	
$Na[EuDOTMA].5H_2O$	solid	17 283	16 992			C_{2v}				166
			16 818							
			16 784							
	solut[h]	17 283[i]	16 992			[l]	0.405	0.690	1	
			16 923							
			16 806							
$Na_9[EuW_{10}O_{36}].18H_2O$	solid	17 237	16 811	16 101		D_{4d}[m]	2.9	3.1[n]	0	168
			16 968	16 289						
				16 446						
	solut[o]	17 254[p]	16 844			C_{4v}	0.24	3.7	4	
			16 961							
$[Eu\subset 2.2.1]Cl_3.2H_2O$	solid						0.310	[q]	2	170
	solut[h]	17 240	16 807	16 103	14 164	C_{2v}	0.215	0.640	3	
			16 863	16 155	14 184					
			16 920	16 234	14 245					
				16 287	14 388					
					14 451					
					14 493					
					14 535					

[a] Data at room temperature. [b] Emission maxima of the observed components of the transition. [c] Number of coordinated H_2O molecules. [d] From the excitation spectrum. [e] Or lower symmetry (see text). [f] Acetone–water solution. [g] Symmetry only slightly altered compared to the solid state (see text). [h] Aqueous solution. [i] Broader than in the solid state. [l] No symmetry is given, since at least two nonequivalent Eu^{3+} species are present (see text). [m] Slightly distorted (see text). [n] Crystallized from D_2O. [o] The values refer to diluted aqueous solutions in the absence of added neutral salts (see text). [p] Another small peak (less than 10% of the overall area of the $^5D_0 \rightarrow {}^7F_0$ transition) is observed at 17 233 cm^{-1} (see text). [q] Assumed equal to the lifetime in D_2O solution.

higher stability and symmetry compared to complexes with monodentate ligands, seem to be particularly suitable for studying the coordination environment under different conditions. Extremely broad literature is available on more general aspects of luminescence of the lanthanide ions in coordination compounds.[137,140,157–160] Very recently this subject has been extensively reviewed by Horrocks and Albin,[161] with particular emphasis on the use of lanthanides as probes in biomolecular structures. The properties and the applications of the complexes between the lanthanide ions and macrocyclic ligands like crown ethers, heterosubstituted crown ethers, and cryptands have been extensively examined by Bünzli and Wessner in a recent review article.[162] The luminescence properties in aqueous solution of a variety of complexes of Eu^{3+} ions with macrocyclic ligands has been carried out by Bryden and Relley,[163] with the aim to study their properties as NMR shift reagents. A detailed analysis of excitation and emission spectra of Eu^{3+} in coordination environments of octahedral, near-octahedral, and trigonal symmetry in microcrystalline samples has been performed by Richardson et al.[164]

The data pertaining to the examples selected for our purposes are summarized in Table III. The structures of the ligands coordinating Eu^{3+} are shown in Figure 22.

Luminescence spectroscopy of $[Eu(ODODA)_2](BF_4)_3$, where ODODA stands for 4,5-dimethyl-*N,N,N′,N′*-tetrapropyl-3,6–dioxaoctanediamide (Figure 22a), in the solid state and solution has been studied by Horrocks et al.[165] X-ray crystallography of an analogous calcium compound shows that the metal ion coordinates two ligand molecules through two ether and two carbonyl oxygen atoms for each ligand. In the solid state the laser excitation spectrum shows a single peak for the $^7F_0 \rightarrow {}^5D_0$ transition, indicating the presence of a single species. The $^7F_0 \rightarrow {}^5D_1$ transition in the excitation spectrum and the $^5D_1 \rightarrow {}^7F_3$ transition in the emission spectrum each consist of three peaks, suggesting that the Eu^{3+} site symmetry must be less than tetragonal, i.e., D_{2h} or lower symmetry. In anhydrous acetone solution the spectrum is identical with that of the solid. When water is added, changes in the $^7F_0 \rightarrow {}^5D_1$, $^5D_2$ excitation spectra are observed while the $^7F_0 \rightarrow {}^5D_0$ transition does not change. Excited-state lifetime measurements in these conditions indicate that one water molecule is coordinated to the Eu^{3+} ion in the complex. It is concluded that in going from the solid

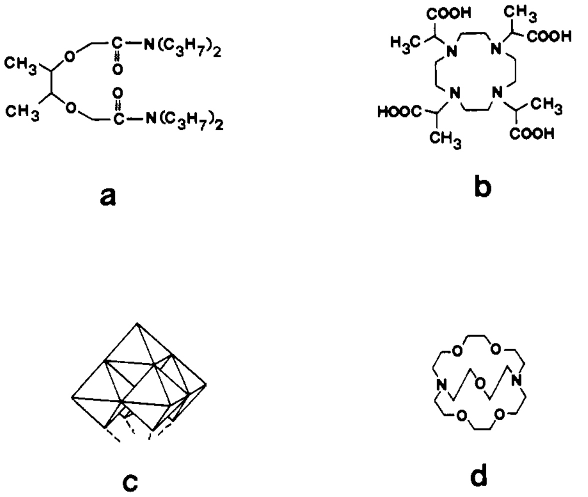

Figure 22. Schematic representation of the ligands of the Eu(III) complexes discussed in the text. (a) ODODA; (b) DOTMA; (c) $W_5O_{18}^{6-}$; (d) 2.2.1.

state to aqueous acetone solution the coordination sphere has not drastically altered but that the coordination number is simply increased by one to accommodate the water molecule.

High-resolution luminescence spectra of Na[EuDOTMA]$\cdot 5H_2O$, where DOTMA stands for [1*R*-(1*R**,4*R**,7*R**,10*R**)]-$\alpha,\alpha',\alpha'',\alpha'''$-tetramethyl-1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (Figure 22b), as a microcrystalline powder and in aqueous solution at room temperature have been examined by Brittain et al.[166] The structure of the analogous Na[EuDOTA$\cdot H_2O$]$\cdot 4H_2O$ complex, determined from X-ray diffraction,[167] shows that the coordination polyhedron of the europium ion is a distorted capped square antiprism, where the ion is coordinated to four nitrogen atoms and four carboxyl oxygen atoms of the ligand, and one water oxygen atom. In the crystalline solid, only one emitting Eu(III) species exists, as shown by the presence of only one peak in the $^5D_0 \rightarrow {}^7F_0$ transition. Moreover, the splitting of the $^5D_0 \rightarrow {}^7F_1$ transition in three peaks indicates that the metal ion site symmetry cannot be higher than C_{2v}. This conclusion is supported by the number of peaks that appear in the $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions. The emission spectrum is strongly modified when the complex is dissolved in water. The $^5D_0 \rightarrow {}^7F_0$ band becomes broader, new bands appear within the $^5D_0 \rightarrow {}^7F_1$ band system, and a difference in intensity and position of the $^5D_0 \rightarrow {}^7F_1$ bands which appeared in the solid sample is observed. All these facts indicate that the solid and solution phases have different structures and suggest that at least two nonequivalent Eu(III) species exist in aqueous solution. The emission lifetimes in H_2O and D_2O show that, on an average, a single water molecule is coordinated by the metal ion in the Eu(III) species present in solution.

The photophysical properties of $Na_9[EuW_{10}O_{36}]\cdot 18H_2O$ under a variety of experimental conditions have been reported.[168] X-ray diffraction diagrams and IR spectra have been shown that in this complex the Eu^{3+} ion is coordinated to two $W_5O_{18}{}^{6-}$ fragments (Figure 22c) through four oxygen atoms for each fragment.[169] In the solid state no splitting of the $^5D_0 \rightarrow {}^7F_0$ transition is observed, which indicates that there is only one type of $EuW_{10}O_{36}{}^{9-}$ anion and that these anions occupy substantially equivalent symmetry sites. The splitting of the $^5D_0 \rightarrow {}^7F_1$ transition into two components and the presence of two peaks in the $^5D_0 \rightarrow {}^7F_4$ transition are in agreement with a D_{4d} symmetry. However, since the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition, which is forbidden in the D_{4d} symmetry, is observed with quite a high intensity, the D_{4d} symmetry must be slightly distorted. The lifetime values indicate that no water molecule is coordinated to the Eu^{3+} ion in the solid sample. In diluted solutions at low ionic strength the $^5D_0 \rightarrow {}^7F_0$ transition shows two components whose relative intensities depend on the pH of the solution. This indicates that two species related by an acid–base equilibrium are present (9:1 ratio at natural pH). The emission spectrum of the predominant species in solution shows an enhanced $^5D_0 \rightarrow {}^7F_0$ peak, two peaks within the $^5D_0 \rightarrow {}^7F_1$ transition, two peaks within the $^5D_0 \rightarrow {}^7F_2$ transitions (the intensity of this transition increases strongly in passing from the solid state to solution), and four peaks within the $^5D_0 \rightarrow {}^7F_4$ transition and is therefore fully consistent with a C_{4v} symmetry. The emission lifetimes in H_2O and D_2O solution show that in diluted solutions the europium ion of $EuW_{10}O_{36}{}^{9-}$ is coordinated to four water molecules. Coordination of four water molecules lowers in fact the D_{4d} symmetry of the solid sample to the C_{4v} symmetry. Increasing ionic strength causes the appearance of a higher number of species, as shown by the four components of the $^5D_0 \rightarrow {}^7F_0$ transition, containing fewer coordinated H_2O molecules.

The composition and structure of the coordination environment of the cryptate $[Eu\subset 2.2.1]^{3+}$, where 2.2.1 is the 4,7,13,16,21-pentaoxa-1,10-diazabicyclo-8,8,5-tricosane cryptand (Figure 22d), has been studied by using photophysical techniques.[170] The presence in the emission spectrum of only one component in the $^5D_0 \rightarrow {}^7F_0$ transition under high-resolution conditions suggests that only one Eu^{3+}-containing species is present in the cryptate solution. The relatively high intensity of the $^5D_0 \rightarrow {}^7F_0$ transition, the splitting of the $^5D_0 \rightarrow {}^7F_1$ transition into three components, the splitting of the $^5D_0 \rightarrow {}^7F_2$ transitions into four components, and the splitting of the $^5D_0 \rightarrow {}^7F_4$ transition into seven components are compatible with a C_{2v} coordination symmetry, which is that expected for the cryptate on the basis of space-filling models. Lifetime measurements indicate that encapsulation of Eu^{3+} in the cryptand cage does not completely shield the metal ion from interaction with H_2O, since three water molecules in solution and two in the solid state are still coordinated to Eu^{3+} through the cryptand holes.

The above reported examples stress that the very peculiar spectral and decay characteristics of the luminescence emission of Eu^{3+} can be profitably used to highlight subtle modifications produced in Eu^{3+} compounds by changes in environment conditions. More specifically, it is possible to know the variations produced in coordination symmetry, number of present species, number of coordinated water molecules in passing from solid state to solution and changing concentration, pH, and ionic strength. To know whether a compound maintains its integrity or not in different conditions seems to be fundamental in view of the very diffuse tendency nowadays to study Eu^{3+} complexes having new coordination environments for applicative purposes.[150,161-163,168,171]

VI. Closing Remarks

The examples discussed above show that second-sphere interaction may have different effects on the spectroscopic, photochemical, and photophysical behavior of coordination compounds. In an attempt to present a unifying view of this topic, we will make reference to Figure 23, where the excited state behavior of a "free" complex is schematically represented.

From a spectroscopic point of view (Franck–Condon radiative transitions originating from the minima of the reactant potential energy surfaces) we may distinguish two qualitatively different effects of second-sphere interaction:[172] (i) introduction of new types of excited levels (Figure 24) and (ii) perturbation of the spectroscopic levels of the original chromophore (Figure 25). In the first case, the perturbation may have different effects depending on the position of the new level(s) relative to those of the original chromophore (Figure

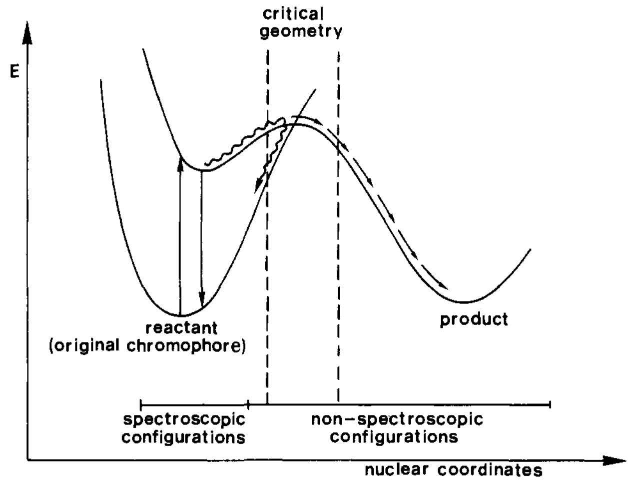

Figure 23. Schematic representation of the excited-state behavior of a complex in terms of spectroscopic and nonspectroscopic nuclear configurations.

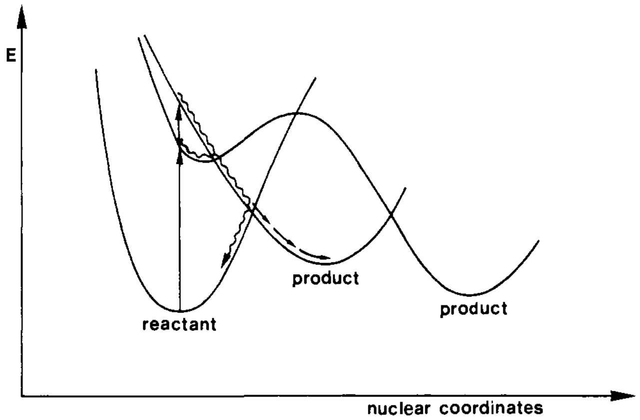

Figure 24. Schematic representation of second-sphere interaction effects: introduction of a new type of excited level (cf. Figure 23).

8, section III). In the second case, the degree of perturbation can range from so strong (Figure 25) to cause spectral shifts in the absorption and emission bands (section IV) to so weak to affect mainly the transition probabilities (extinction coefficients and radiative lifetimes, section V).

From a more general point of view, it must be pointed out that in some cases second-sphere interaction may leave almost unchanged the energy-level diagram near the equilibrium nuclear configurations of the reactant and, nevertheless, cause dramatic changes in the photochemical and photophysical properties of a coordination compound. This may happen when second-sphere interaction affects the shapes of the potential energy surfaces only at nonspectroscopic molecular configurations (i.e., far from the minima of the reactant potential energy surfaces, Figure 26). It is well-known, in fact, that radiationless deactivations and photochemical reactions often take place at "critical"[173] molecular configurations where crossing or touching of potential energy surfaces occur. Typical examples of such a situation are discussed in section II.

From a practical point of view, the second-sphere perturbations on excited-state properties described in this review can be used for interesting applications. On one side, perturbations can provide a means to control and orient the photochemical and photophysical behavior of a complex, which may be useful to design new photosensitizers and new luminescent materials. On the other hand, an accurate and detailed analysis of the perturbation effects may offer the possibility to obtain important information on the compositon and structure of supramolecular species.

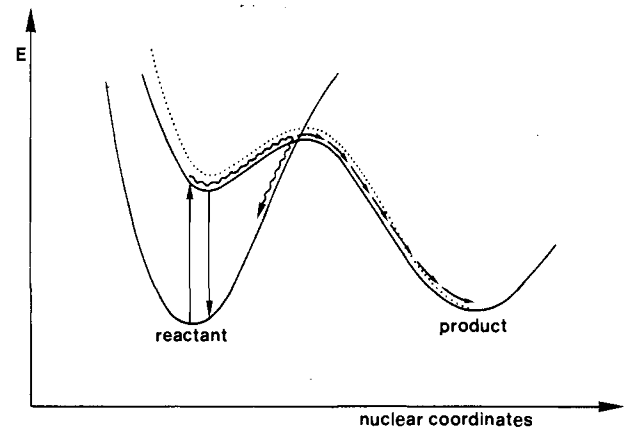

Figure 25. Schematic representation of second-sphere interaction: perturbation of the spectroscopic levels of the original chromophore. The dotted line represents the excited state potential energy curve of the original chromophore (cf. Figure 23).

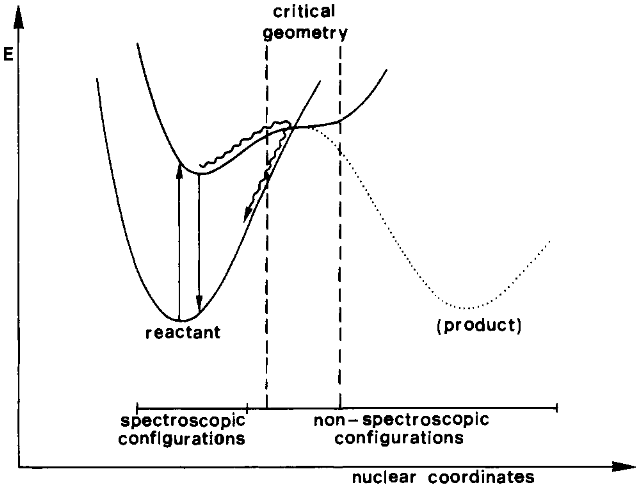

Figure 26. Schematic representation of second-sphere interaction: nonspectroscopic perturbation of the potential energy surfaces of the original chromophore. The dotted line represents the excited-state potential energy curve of the original chromophore for nonspectroscopic nuclear configurations (cf. Figure 23).

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(173) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.