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Transition metal complex exciplexes

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Abstract

The photophysical and photochemical properties of exciplexes are summarized considering the electronic structure and role of energetics and kinetics in the formation and stabilization of these molecular entities. Exciplexes involving transition metal complexes, are known as transition metal complex exciplexes (TMCEs) and are classified on the basis of the reactive site of the excited metal complex and the properties of the ground state reactant. There are two main groups; ligand-centered exciplexes and metal-centered exciplexes. A survey of the

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literature of TMCEs is presented. Common features of exciplexes classified into different groups are revealed. A strategy for searching for new TMCEs is suggested.

Keywords: Transition metal complexes; Exciplexes; Photophysical properties; Photochemical properties; Reactive sites; Electronic structure

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1. Introduction

An electronically excited species generally has a different chemical nature from the ground state species from which it is formed. Hence it may have the ability to undergo a strong interaction with another ground state species even though an interaction between the two species in their ground states may be very weak or completely absent. The complexes formed between excited and ground state species are termed exciplexes. Exciplexes are usually characterized by a strong binding energy (20–80 kJ mol^{-1}), a charge transfer nature [1], a relatively long lifetime and moderate stability. The appearance of a broad structureless emission band is often considered to be an indicator of exciplex formation, although absorption properties and chemical reactivity may also be used for the assignment of exciplexes. Exciplex formation is a common phenomenon in organic photochemical systems; however, there have been only a few reports of such exciplexes involving excited transition metal complexes. Thus the goals of this paper are (1) to present a survey of the literature of exciplexes possessing an excited coordination compound constituent, (2) to consider the general properties of exciplexes, such as electronic structure, energetics and kinetics, (3) to develop a classification scheme for the transition metal complex exciplexes (TMCEs) and (4) to suggest a strategy for searching for new exciplexes belonging to this category.

2. General considerations: electronic structure, energetics and kinetics of exciplexes

2.1. Electronic structure

The electronic interaction in an exciplex formed by an encounter between two neutral species can be expressed by a linear combination of wavefunctions of the possible states [2]:

$$\Psi = c_1\Psi({}^*\mathrm{DA}) + c_2\Psi(\mathrm{DA}^*) + c_3\Psi({}^{\cdot}\mathrm{D}^{+\cdot}\mathrm{A}^{-}) + c_4\Psi({}^{\cdot}\mathrm{D}^{-\cdot}\mathrm{A}^{+}) + c_5\Psi(\mathrm{DA}) \qquad (1)$$

where the first and second terms describe the energy transfer states, the third and fourth terms represent the charge transfer states and the final term gives the ground state interactions, with the coefficients representing the relative contributions of the states. If the ground state interactions can be neglected and A is exclusively an electron acceptor, the exciplex wavefunction simplifies to

$$\Psi = c_1\Psi({}^*\mathrm{DA}) + c_2\Psi(\mathrm{DA}^*) + c_3\Psi({}^{\cdot}\mathrm{D}^{+\cdot}\mathrm{A}^{-}) \qquad (2)$$

If c_2 is smaller than the other two coefficients, the charge transfer character of the exciplex is rather large and therefore it tends to dissociate into a radical ion pair, especially in polar solvents. For exciplexes involving an excited transition metal complex, the two constituents frequently have either the same or different electric charge so that the role of the polar solvent can be rather different in the two cases. As we shall see below, the solvent polarity can assist the creation of an inorganic exciplex consisting of two species with the same sign of electric charge.

Emission from exciplexes proceeds by a vertical Franck–Condon allowed transition from a minimum on an excited state potential surface to a low-lying repulsive ground state surface. If the transition to the ground state is accompanied by a significant change in molecular geometry, then luminescence may not be observed; rather, other processes, such as dissociation into a solvent-separated radical ion-pair or a chemical reaction, may occur.

If $c_3 \ll c_2$ the exciplex can be an emitting species, or its separation can occur via the formation of an excited acceptor and the ground state of the donor.

2.2. Energetics of exciplexes

Stabilization in exciplexes originates from the overlap between either the highest bonding orbitals or the lowest antibonding orbitals [3]. Mixing between the bonding or antibonding orbitals of the locally excited state and the radical ion pair stabilizes the exciplex E_{stab}, while the interaction of the singlet charge-transfer state with the ground state, involving the mixing of antibonding with bonding orbitals, results in a loss of energy E_{dest}. The net energy change ΔE_{EX} of these interactions is given by their difference:

$$\Delta E_{\text{EX}} = E_{\text{stab}} - E_{\text{dest}} \tag{3}$$

The free-energy change of exciplex formation involves this orbital stabilization term, the ionization energy E_{I} of the electron donor species, the electron affinity E_{EA} of an acceptor [4], the excitation energy E^*, the Coulombic interaction between the excited species and the ground state molecule ($E_{\text{CEX}} = z_{\text{D}} z_{\text{A}} e^2/d_{\text{EX}}$) and the energy of exciplex solvation ($E_{\text{EXsolv}} = \mu^2(\varepsilon - 1)/[\rho^3(2\varepsilon + 1)]$) [4–6]:

$$\Delta G_{\text{EX}} = E_{\text{I}} - E_{\text{AA}} - E^* - \Delta E_{\text{EX}} - E_{\text{EXsolv}} + E_{\text{CEX}} \tag{4}$$

where d_{EX} is the distance between the exciplex constituents, z_{D} and z_{A} are the unit charges of donor and acceptor respectively, μ is the dipole moment of the exciplex, ρ is its radius and ε is the permitivity of the solvent.

An exciplex can dissociate into a solvent-separated ion pair ($D^+ \ldots A^-$) that can be stabilized by interaction with solvent molecules, or it can form a contact ion pair D^+A^- as a result of electron transfer between the constituents of the exciplex when the orbital interaction is not strong enough to favor the exciplex structure [5,7]. The free-energy terms for these species (ΔG_{SSIP} and ΔG_{CIP} where SSIP denotes solvent-separated ion pair, and CIP denotes contact ion pair) involve the coulombic and solvation energies [5]:

$$\Delta G_{\text{SSIP}} = E_{\text{I}} - E_{\text{EA}} - E^* + E_{\text{SSIPsolv}} + E_{\text{CSSIP}} \tag{5}$$

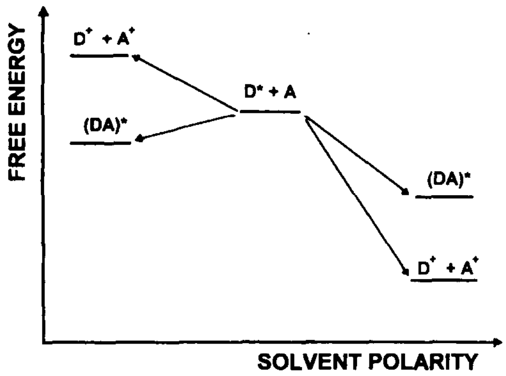

Fig. 1. The effect of solvent polarity on the energy and electron transfer. (Reproduced with permission from Ref. [6].)

$$\Delta G_{\mathrm{CIP}} = E_{\mathrm{I}} - E_{\mathrm{EA}} - E^{*} - E_{\mathrm{CIPsolv}} + E_{\mathrm{CCIP}} \qquad (6)$$

where $E_{\mathrm{SSIPsolv}} = z_{\mathrm{D}} z_{\mathrm{A}} e^2 [(1/r_{\mathrm{D}} + 1/r_{\mathrm{A}})(1 - 1/\varepsilon)]/2$, $E_{\mathrm{CSSIP}} = z_{\mathrm{D}} z_{\mathrm{A}} e^2/\varepsilon d_{\mathrm{SSIP}}$, $E_{\mathrm{CIPsolv}} = \mu^2(\varepsilon - 1)/[\rho^3(2\varepsilon + 1)]$ and $E_{\mathrm{CCIP}} = z_{\mathrm{D}} z_{\mathrm{A}} e^2/d_{\mathrm{CIP}}$. When the two constituents of the exciplex or ion pair have electric charges of opposite sign, the coulombic and solvation energy terms for SSIP are negative. In polar solvents, where $(E_{\mathrm{SSIPsolv}} + E_{\mathrm{CSSIP}}) < (-\Delta E_{\mathrm{EX}} - E_{\mathrm{EXsolv}} + E_{\mathrm{CEX}})$, the exciplex dissociates into a solvent-separated ion pair. Similarly, contact ion pair formation is favored when $(-E_{\mathrm{CIPsolv}} + E_{\mathrm{CCIP}}) < (-\Delta E_{\mathrm{EX}} - E_{\mathrm{EXsolv}} + E_{\mathrm{CEX}})$ (Fig. 1). However, for an encounter pair in which the two species have the same charge sign, $(E_{\mathrm{SSIPsolv}} + E_{\mathrm{CSSIP}})$, E_{CCIP} and E_{CEX} are all positive; hence, if the exciplex stabilization energy ΔE_{EX} is sufficiently large, exciplex formation is more probable than creation of either a solvent-separated or a contact ion pair, and exciplex emission can be observed. This simplified description clearly indicates that the dynamic interconversion between encounter pairs such as the exciplex and contact or solvent-separated ion-pairs is strongly influenced by interactions with the solvent molecules.

2.3. Kinetics of exciplex formation and decay

In a simple mechanism involving exciplex formation and its decay via back-reaction or radiative and non-radiative processes, and assuming that the interaction between the two ground-state molecules can be excluded, the following kinetic scheme applies to the system [8]:

$$\begin{array}{ccccc} {}^{*}\mathrm{A} & + & \mathrm{B} & \underset{k_{\mathrm{E}^{-}}}{\overset{k_{\mathrm{E}}}{\rightleftharpoons}} & {}^{*}(\mathrm{A}\ldots\mathrm{B}) \\ k_{\mathrm{Anr}}\downarrow \quad k_{\mathrm{Ar}}\downarrow & & & & k_{\mathrm{Enr}}\downarrow \quad k_{\mathrm{Er}}\downarrow \end{array} \qquad (\mathrm{I})$$

However, it has been suggested recently that even if there is a ground state reaction, as long as the excited state equilibrium constant is larger than that of the corresponding ground state process we can still regard the excited state reaction as exciplex formation [9,10]:

$$\begin{array}{ccc} {}^*\mathrm{A} + \mathrm{B} & \underset{k_{\mathrm{E}}^{-}}{\overset{k_{\mathrm{E}}}{\rightleftharpoons}} & {}^*(\mathrm{A...B}) \\ \uparrow h\nu \;\; \downarrow k_{\mathrm{Anr}} \;\; \downarrow k_{\mathrm{Ar}} & & \uparrow h\nu \;\; \downarrow k_{\mathrm{Enr}} \;\; \downarrow k_{\mathrm{Er}} \\ \mathrm{A} + \mathrm{B} & \rightleftharpoons & (\mathrm{A...B}) \end{array} \qquad \mathrm{(II)}$$

If we assume that the exciplex precursor *A and the exciplex *(A ... B) are formed by excitation in a time interval described by a Dirac delta function, the decay rates of the two excited species are given by

$$\mathrm{d}[{}^*\mathrm{A}]/\mathrm{d}t = -(k_{\mathrm{Anr}} + k_{\mathrm{Ar}} + k_{\mathrm{E}}[B])[{}^*\mathrm{A}] + k_{\mathrm{E}}^{-}[{}^*(\mathrm{A} \ldots \mathrm{B})] \qquad (7)$$

$$\mathrm{d}[{}^*(\mathrm{A} \ldots \mathrm{B})]/\mathrm{d}t = k_{\mathrm{E}}[\mathrm{B}][{}^*\mathrm{A}] - (k_{\mathrm{E}}^{-} + k_{\mathrm{Enr}} + k_{\mathrm{Er}})[{}^*(\mathrm{A} \ldots \mathrm{B})] \qquad (8)$$

The general solution of these equations is well known [8,11] and can be applied to this mechanism by considering that, under general conditions $[{}^*\mathrm{A}]_{t=0} = A_1$ and $[{}^*(\mathrm{A} \ldots \mathrm{B})]_{t=0} = A_2$, the time dependences of the concentration of the excited species are given by

$$[{}^*\mathrm{A}] = b_{11}\exp(\lambda_1 t) + b_{12}\exp(\lambda_2 t) \qquad (9)$$

$$[{}^*(\mathrm{A} \ldots \mathrm{B})] = b_{21}\exp(\lambda_1 t) + b_{22}\exp(\lambda_2 t) \qquad (10)$$

where

$$b_{11} = [A_1(x + \lambda_2) - A_2 k_{\mathrm{E}}^{-}]/(\lambda_2 - \lambda_1) \qquad (11)$$

$$b_{12} = [A_2 k_{\mathrm{E}}^{-} - A_1(x + \lambda_1)]/(\lambda_2 - \lambda_1) \qquad (12)$$

$$b_{21} = [A_2(y + \lambda_2) - A_1 k_{\mathrm{E}}[\mathrm{B}]]/(\lambda_2 - \lambda_1) \qquad (13)$$

$$b_{22} = [A_1 k_{\mathrm{E}}[\mathrm{B}] - A_2(y + \lambda_1)]/(\lambda_2 - \lambda_1) \qquad (14)$$

where

$$x = k_{\mathrm{Anr}} + k_{\mathrm{Ar}} + k_{\mathrm{E}}[\mathrm{B}] \qquad y = k_{\mathrm{Enr}} + k_{\mathrm{Er}} + k_{\mathrm{E}}^{-} \qquad (15)$$

$$\lambda_{1,2} = -[(x + y) \pm [(x - y)^2 + 4k_{\mathrm{E}}k_{\mathrm{E}}^{-}[\mathrm{B}]]^{1/2}]/2 \qquad (16)$$

Simpler expressions are derived if either the equilibrium limit [12–14] or the steady state approximation is satisfied. In the equilibrium limit where $k_{\mathrm{E}}[\mathrm{B}] \gg k_{\mathrm{Anr}} + k_{\mathrm{Ar}}$ and $k_{\mathrm{E}}^{-} \gg E_{\mathrm{Enr}} + k_{\mathrm{Er}}$, the ratio of populations of *A and *(A ... B) is described by the equilibrium constant $K_{\mathrm{E}} = k_{\mathrm{E}}[\mathrm{B}]/k_{\mathrm{E}}^{-}$. Since the lifetimes of *A and *(A ... B) are $\tau_{\mathrm{A}} = 1/(k_{\mathrm{Anr}} + k_{\mathrm{Ar}})$ and $\tau_{(\mathrm{A} \ldots \mathrm{B})} = 1/(k_{\mathrm{Enr}} + k_{\mathrm{Er}})$, the observed lifetime τ_{obs} for the exciplex is given by

$$1/\tau_{obs} = f_A/\tau_A + f_{(A...B)}/\tau_{(A...B)} \tag{17}$$

where $f_A = 1/(1+K_E[B])$ and $f_{(A...B)} = K_E[B]/(1+K_E[B])$. In the steady state approximation, where $[{}^*A] \ll [{}^*(A...B)]$ is valid, the following expression can easily be derived:

$$1/\tau_{obs} = \frac{1/\tau_A(k_E^- + 1/\tau_{(A...B)}) + k_E[B]/\tau_{(A...B)}}{1/\tau_A + k_E[B]} \tag{18}$$

As mentioned in Section 2.2, exciplex formation can be followed by an electron transfer process resulting in an ion pair. The efficiency of this reaction is strongly dependent on the nature of the solvent and of the encounter species. In this case deactivation of the excited states is described by the scheme [15,16]

$$\begin{array}{lcl} {}^*A + B \underset{k_E^-}{\overset{k_E}{\rightleftharpoons}} {}^*(A...B) & \underset{k_{bet}}{\overset{k_{et}}{\rightleftharpoons}} & (A^+, B^-) \xrightarrow{k_p} \text{product} \\ k_d\downarrow & & \quad k_{di}\downarrow \end{array} \tag{III}$$

where k_d and k_{di} are the rate constants of the exciplex precursor and the ion pair respectively, k_{et} is the forward electron transfer rate, k_{bet} is the back electron transfer rate and k_p represents the rate constant for the ion pair dissociation and/or formation of products etc. By applying the steady-state approximation to the various intermediates and assuming that $k_{et} \gg k_{bet}$, we can obtain the rate constant for quenching:

$$k_q = k_{et}k_E/(k_{et} + k_E^-) \tag{19}$$

Two limiting forms of Eq. (19) exist, and they depend on the relative magnitudes of k_{et} and k_E^-. When $k_E^- \gg k_{et}$ and $k_q \approx k_{et}k_E/k_E^-$, the activation enthalpy for quenching is the sum of the activation enthalpies of the three steps, and it can have a negative value. However in the case where $k_E^- \ll k_{et}$ and $k_q \approx k_E$, a non-negative enthalpy should be observed. Hence the temperature dependence of the reaction kinetics may be a useful tool for revealing the excited state equilibrium in the luminescence quenching mechanism.

3. Classification of TMCEs

Transition metal complex exciplexes can be grouped into ligand-centered exciplexes, i.e. those which are formed from coordinatively saturated complexes and another species, and metal-centered exciplexes, i.e. those which are formed from coordinatively unsaturated metal ecomplexes and another species. The implication is that the source of the interaction forming the exciplex is the ligand in the former case and the metal in the latter case. Further subclassifications result from the nature of the other species involved in the exciplex.

3.1. Ligand-centered exciplexes

3.1.1. Ligand–molecule exciplexes

Interaction between the excited ($\lambda_{exc} = 405$ nm) Re(4,7-diphenyl-1,10-phenanthroline) $(CO)_3Cl$ and an aromatic amine was observed in non-polar solvent [17], and is an example of a lingand-centered exciplex between a ligand and a neutral molecule. At the exciting wavelength light was absorbed only by the complex. The orange emission of Re(4,7-diphenyl-1,10-phenanthroline) $(CO)_3Cl$ ($\lambda_{max} = 575$ nm) dissolved in acetonitrile was quenched by *N*,*N*-dimethylaniline (DMA), obeying simple Stern–Volmer kinetics, and the luminescence was not detectable above a DMA concentration of 8×10^{-3} M. However, upon addition of DMA to a solution of the complex in decaline or isooctane, the emission band shifted to longer wavelengths and its intensity decreased (Fig. 2). This conversion was found to be almost complete at 8×10^{-3} M DMA, and further increases in the DMA concentration did not affect the red emission. The absorption spectrum of the rhenium complex was not changed at DMA concentrations below 10^{-2} M in decaline and isooctane. These results strongly suggest that the new emission that peaks at 600 nm in alkanes in the presence of DMA originates from an exciplex. It was found that the emission intensity of the exciplex decreased with temperature, while that of the triplet excited complex increased. From the temperature dependence of the emission spectra the enthalpy of exciplex formation has been determined to be $\Delta H = -5.7$ kcal mol^{-1}. In addition to DMA, other amines were found to form emitting exciplexes with Re(4,7-dimethyl-1,10-phenanthroline) $(CO)_3Cl$. However, in the presence of electron acceptors such as quinones and 1,4-dicyanobenzene, exciplex luminescence was not observed.

A thermodynamic study of the electron transfer reactions between photoexcited

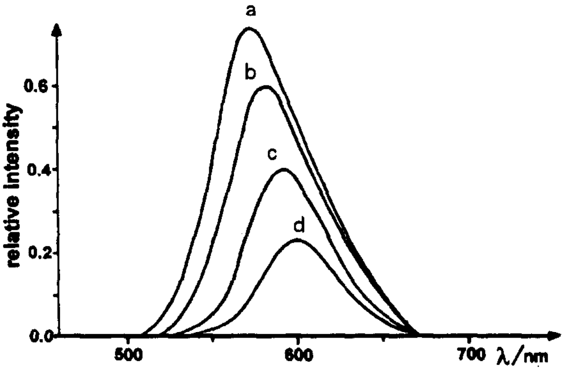

Fig. 2. Emission spectra of 1.5×10^{-4} M Re(4,7-diphenyl-1,10-phenanthroline) $(CO)_3Cl$ in decaline in the presence of (a) 0 M, (b) 8×10^{-4} M, (c) 2×10^{-3} M and (d) 8×10^{-3} M *N*,*N*-dimethylaniline. (Reproduced with permission from Ref. [17].)

$Ru(bpy)_3^{2+}$ and an organic electron donor or acceptor in acetonitrile was reported by Kitamura et al. [18]. Significant differences between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ between oxidizing and reducing quenchers were observed. In particular, the donor quenchers always had positive activation enthalpies and small negative activation entropies, while negative temperature dependences of k_q yielded $-2\ \mathrm{kcal\ mol^{-1}} < \Delta H^{\ddagger} < -5\ \mathrm{kcal\ mol^{-1}}$ for oxidative quenching by electron acceptor molecules such as methyl-*m*-nitrobenzoate (MmNBzo), 4,4′-dinitrobiphenyl (DNbPh) and duraquinone (DQ). These negative $\Delta H^{\ddagger}$ values are overcompensated by the large negative $\Delta S^{\ddagger}$, which suggests that the electron transfer reaction is strongly entropy controlled, implying a mechanism containing the formation of a rigid "exciplex-like" intermediate:

$$^{*}Ru(bpy)_3^{2+} + Q \rightleftharpoons ({}^{*}Ru(bpy)_3^{3+} \ldots Q^{-}) \rightarrow \text{product} \tag{20}$$

An interesting study by Ayala et al. [12] showed that an excited state complex forms between $^{*}Ir(phen)_3^{3+}$ and $^{*}Ir(terp)_2^{3+}$ in the presence of $HgCl_2$. The lifetimes and intensities of the luminescence are increased by about an order of magnitude on adding $HgCl_2$ to the solution of the iridium complex in a non-protic solvent (Figs. 3 and 4). Solvent changes as well as the addition of different inert anions (ClO_4^-, Cl^-) can radically alter the observed interactions. An increase in the concentration of $HgCl_2$ decreases the lifetime and emission quantum yield in MeOH. In the presence of a large amount of ClO_4^-, $HgCl_2$ has a very small effect on the excited state lifetimes in different solutions. If an amount of Cl^- is added which exceeds the concentration of $HgCl_2$, a decrease in the lifetime occurs without any change in the emission bandshape. It has been suggested that the interaction between the excited Ir(III)-α-diimine complex and $HgCl_2$ has its origins in the well-known interaction of $HgCl_2$ with extended π systems. The effect of the ClO_4^- anion was interpreted in terms of the formation of $IrL_n^{3+}(ClO_4^-)$, $IrL_n^{3+}(ClO_4^-)_2$, and $IrL_n^{3+}(ClO_4^-)_3$ ion pairs, while the weak influence of the chloride ion on exciplex formation was attributed to the coordination of chloride ligand to the unsaturated central atom of $HgCl_2$, resulting in tri- and tetrachloro complexes of Hg(II).

Quenching of triplet states of metalloporphyrins such as zinc and magnesium etioporphyrin I by low concentrations of nitro aromatics and organic chloro compounds has been investigated in non-polar solvents [19–21]. An increase in quencher concentration caused a decrease in the lifetime of the porphyrin triplet. For zinc etioporphyrin I with *p*-nitrotoluene (PNT), low concentrations of PNT quenched the triplet porphyrin with a rate constant of $k_q = 3 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$. However, new transients were detected at high concentrations of some quenchers, and an increase in transient lifetime with PNT concentration was also observed. These species had absorption spectra similar to, but not identical with, the metal porphyrin triplet. In addition, the absorption spectra of intermediates did not resemble the oxidized metalloporphyrin or the reduced quencher whose spectra were reported earlier. Hence the transient species were assigned as exciplex intermediates of the light-induced processes.

To elucidate the nature of the transients, a correlation between the triplet quenching

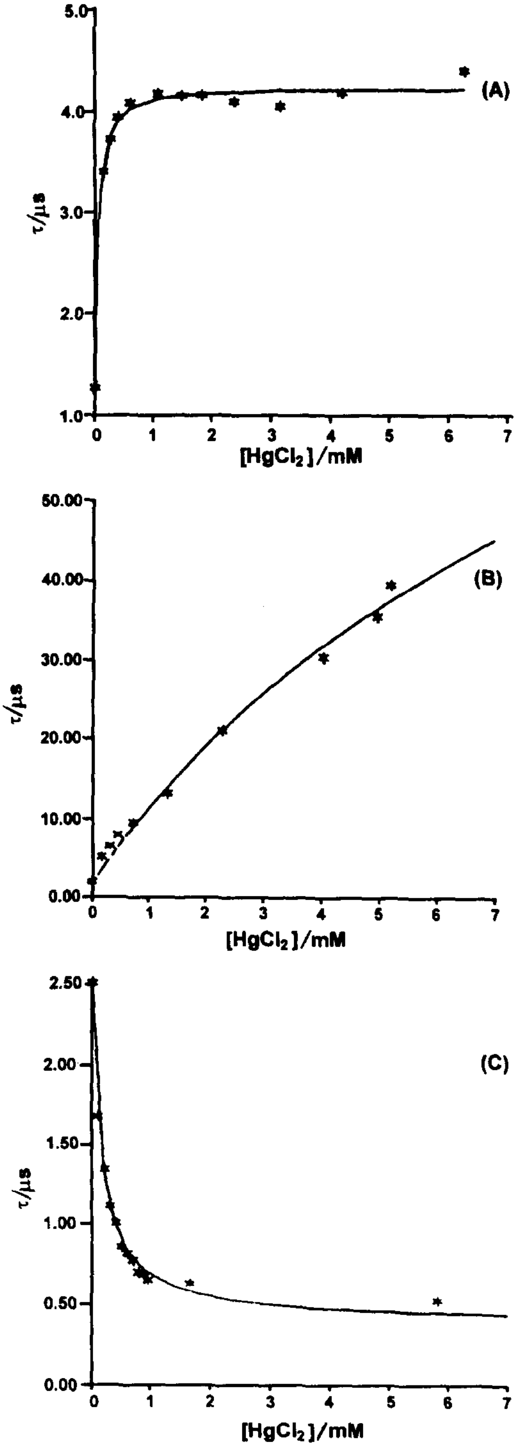

Fig. 3. Lifetime titration of Ir(phen)$_3^{3+}$ with $HgCl_2$ in (A) DMF, (B) MeCN and (C) MeOH. (Reproduced with permission from Ref. [12].)

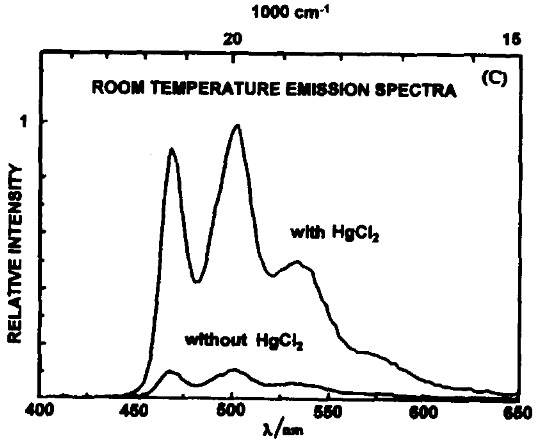

Fig. 4. Influence of $HgCl_2$ on room temperature emission spectrum of $[Ir(terp)_2]$ $(CF_3CO_2)_3$ in MeCN. (Reproduced with permission from Ref. [12].)

rates and the reduction potentials of different electron acceptor quenchers was investigated. Although k_q varied linearly with reduction potential for nitro aromatics and for the chloro compounds, a distinctly different pattern of reactivity between the two groups was observed. Comparison of these results with those obtained for anthracene triplet quenching [20] and 1,4-dimethoxybenzene fluorescence quenching led to the conclusion that the Stern–Volmer quenching rate constant for the metal porphyrin studied must depend on other factors in addition to simple electron transfer parameters. More compelling evidence that exciplexes were observed in these systems derived from energetic considerations. On the basis of experimental results obtained at different temperatures, activation parameters such as activation energy E_a and activation entropy ΔS were calculated. The activation energies for the reaction of zinc etioporphyrin triplet with nitro aromatics were found to be very small, and the differences in reactivity appeared to be determined primarily from the variation of activation entropy. These results were rationalized in terms of a model in which the quencher molecule associates adiabatically with the excited triplet metalloporphyrin by a slight overlap of molecular orbitals with some degree of charge transfer character. These exciplexes were considered as being molecular entities similar to weak ground state charge transfer complexes.

The nature of triplet metalloporphyrin exciplexes formed from the metals Mg, Al, Ga and In, and the porphyrins tetraphenylporphyrin (TPhP) and tetra-4-tri-t-butylphthalocyanine (Pc) was studied by Kapinus and coworkers [22–24]. Flash photolysis experiments revealed two exponential decay curves on a time-scale of several hundred microseconds. Kinetic curves of similar shape were obtained for triplet quenching by quinones and aromatic nitro compounds. Analysis of the results was based on the following scheme:

$$^{*}P + Q \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^{*}(PQ) \xrightarrow{k_2} P + Q \qquad (21)$$

$$^{*}\mathrm{P} \xrightarrow{k_3} \mathrm{P} \tag{22}$$

$$^{*}\mathrm{P} + \mathrm{Q} \xrightarrow{k_4} \mathrm{P} + \mathrm{Q} \tag{23}$$

The rate constants k_1 and k_4, and the limiting value λ_{lim} of the reciprocal triplet lifetime at a high concentration of quencher were estimated in order to characterize the quencher-induced deactivation of triplet molecules. Thus λ_{lim} values were plotted against $\Delta G'$, which is related to the change in electron transfer free energy:

$$\Delta G' = E_{1/2}^{\mathrm{ox}} - E_{1/2}^{\mathrm{red}} - E_{\mathrm{T}} - e^2/\varepsilon r \tag{24}$$

where $E_{1/2}^{\mathrm{ox}}$ and $E_{1/2}^{\mathrm{red}}$ are the oxidation potential of the porphyrin and the reduction potential of the quencher respectively, E_{T} is the energy of triplet porphyrin and $e^2/\varepsilon r$ represents the electrostatic interaction between the triplet porphyrin and the quencher. Since the last term of the expression proved to be slightly dependent on the nature of the systems under investigation, the experimental data were analyzed using $\Delta G'$ ($\Delta G' = E_{1/2}^{\mathrm{ox}} - E_{1/2}^{\mathrm{red}} - E_{\mathrm{T}}$). Plots of λ_{lim} vs. $\Delta G'$ indicated rather different behavior for TPhPMgPy and TPhPGaOH complexes for $\Delta G' < 10\ \mathrm{kJ\ mol^{-1}}$, whereas in the range where $\Delta G' > 10\ \mathrm{kJ\ mol^{-1}}$ similar trends but slightly different values were obtained for these compounds. The nature of the PcAlCl triplet was found to be rather similar to that of TPhPGaOH. It was also found that, for the majority of systems studied, the rate constants of triplet exciplex formation were smaller than those of diffusiion-controlled processes. The features of the plot of k_1 vs. $\Delta G'$ for TPhPMgPy suggested an electron transfer reaction step as the rate-determining process. These observations were interpreted by a multistage mechanism for exciplex formation involving electron transfer processes:

$$\begin{tikzcd}
{}^{3}\mathrm{P} + \mathrm{Q} \arrow[r, shift left, "k_{12}"] & ({}^{3}\mathrm{P} \ldots \mathrm{Q}) \arrow[l, shift left, "k_{21}"] \arrow[r, shift left, "k_{23}"] & ({}^{3\cdot}\mathrm{P}^{+} \ldots {}^{\cdot}\mathrm{Q}^{-}) \arrow[l, shift left, "k_{32}"] \arrow[r, shift left, "k_{34}"] \arrow[d] & {}^{3}(\mathrm{PQ}) \arrow[l, shift left, "k_{43}"] \arrow[r, "k_{40}"] & \mathrm{P} + \mathrm{Q} \\
 & & \mathrm{P} + \mathrm{Q} & &
\end{tikzcd} \tag{25}$$

Investigations of the photochemistry of Pt(II) and Pd(II) porphyrins demonstrated that these complexes show very weak fluorescence and prominent phosphorescence in fluid media at ambient temperature [23]. Since the palladium porphyrins have particularly long triplet lifetimes, these complexes permitted the observation of relatively slow and energetically uphill excited state reactions. Irradiation of palladium α,β,γ,δ-mesotetraphenylporphyrin (PdTPP) in degassed solutions of various solvents (benzene, pyridine, acetone 2-propanol, isobutylnitrile) in the presence of 0.5–5 M DMA, with light absorbed only by the metal complex, lead to the formation of reductive adducts [24]. In addition to the photoreactions, changes in both the lifetime and the intensity of the PdTPP luminescence were observed. Initial quenching of phosphorescence was detected at low DMA concentration, while a leveling off was measured at moderate value of [DMA] and no further quenching was obtained at concentrations over 1 M DMA (Fig. 5). Phosphorescence lifetime data showed similar results. The fluorescence, consisting of a prompt and a delayed component,

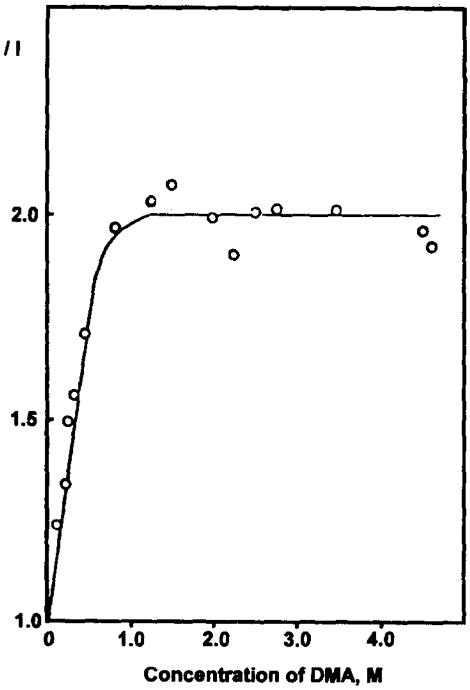

Fig. 5. Stern–Volmer plot of phosphorescence quenching of PdTPP by DMA in pyridine. (Reproduced with permission from Ref. [26].)

was slightly influenced by the DMA, and was interpreted by quenching of the delayed component. The luminescence and transient absorption spectra of PdTPP in the presence and absence of large amounts of DMA were identical within experimental error. Since the absorption spectrum of PdTPP was not affected by addition of DMA, little or no complex formation was assumed in the ground state. The results strongly suggested a reaction of the excited triplet PdTPP with DMA to form a luminescent exciplex:

$$\mathrm{PdTPP} \xrightarrow{h\nu} {}^{*1}\mathrm{PdTPP} \rightleftharpoons {}^{*3}\mathrm{PdTPP} \tag{26}$$

$$ {}^{*3}\mathrm{PdTPP} \xrightarrow{k_p} \mathrm{PdTPP} + h\nu \tag{27}$$

$$ {}^{*3}\mathrm{PdTPP} \xrightarrow{k_d} \mathrm{PdTPP} \tag{28}$$

$$ {}^{*3}\mathrm{PdTPP} + \mathrm{DMA} \underset{k_e^-}{\overset{k_e}{\rightleftharpoons}} {}^{*3}\mathrm{PdTPP} \ldots \mathrm{DMA} \tag{29}$$

$$ {}^{*3}\mathrm{PdTPP} \ldots \mathrm{DMA} \xrightarrow{k_p'} \mathrm{PdTPP} + \mathrm{DMA} + h\nu \tag{30}$$

$$*^3\text{PdTPP} \ldots \text{DMA} \xrightarrow{k_d'} \text{PdTPP} + \text{DMA} \quad (31)$$

The formation constant and the quenching rate constant were estimated by fitting the parameters of the "modified Stern–Volmer" equation to the experimental data. This procedure resulted in a relatively small exciplex formation constant ($K \approx 10\ \text{M}^{-1}$). Considering the value of K and the redox potentials of the exciplex constituents, it was suggested that formation of $*^3$PdTPPDMA must result in a "non-polar exciplex" in which the energy minimum may originate from weak charge transfer interactions but the excitation remains largely localized on the metalloporphyrin. These results confirmed that exciplexes should occur for a variety of metal complexes having long excited state lifetimes.

3.1.2. Ligand–metal cation exciplexes

Laser flash photolysis studies were carried out for chloroindium(III) tetraphenylporphyrin (ClInTPP) in methanol solutions containing methylviologen (MV^{2+}) and triethanolamine (TEA) [27]. It was pointed out that in the ground state the $InTPP^+$ cation forms $InTPP^+(TEA)$ and $InTPP^+(TEA)_2$ complexes with formation constants of $K_1 = (1.0 \pm 0.1) \times 10^2\ \text{M}^{-1}$ and $K_2 = 7 \pm 2\ \text{M}^{-1}$ respectively.

The TEA molecules in $InTPP^+(TEA)$ and $InTPP^+(TEA)_2$ were assumed to occupy the axial positions. Excitation of the metalloporphyrin with a 532 nm laser pulse initiated a transient absorption with a peak at 460 nm, which is characteristic of triplet–triplet transitions in metalloporphyrins with diamagnetic central atoms. The decay of this intermediate obeyed first-order kinetics with a rate constant of $(1.8 \pm 0.1) \times 10^4\ \text{s}^{-1}$ in a deaerated solution. In the presence of oxygen the lifetime decreased. These observations confirmed the triplet nature of the excited In(III) porphyrin. Addition of TEA to a methanol solution of $InTPP^+$ resulted in very little change in either the transient absorption spectrum or the triplet lifetime. Therefore the interaction between the triplet $InTPP^+$ and TEA in the ground state was considered to be very weak. The decay rate of the triplet $InTPP^+$ increased on addition of MV^{2+}. However, a leveling off was observed at a higher concentration of electron acceptor (Fig. 6). This feature of the triplet quenching kinetics suggested a mechanism involving an excited state equilibrium reaction. The authors suggested three excited equilibria as a cause of the leveling-off: (a) a reversible energy transfer, (b) electron transfer resulting in an ion pair consisting of two species of positive charge and (c) triplet exciplex formation. The former two cases were excluded since the transient absorption spectrum for $InTPP^+$ in methanol containing MV^{2+} was found to be very similar to the triplet–triplet absorption of $^{3*}InTPP^+$. Moreover the intensity of this absorption was invariant in the MV^{2+} concentration range from zero to 1×10^{-2} M. The mechanism proposed is rather similar to that suggested for other metalloporphyrin exciplexes [19–21,25,26]:

$$^{3*}\text{InTPP}^+ + \text{MV}^{2+} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} {}^{3*}\text{InTPP}^+ \ldots \text{MV}^{2+} \quad (32)$$

$$^{3*}\text{InTPP}^+ \xrightarrow{k_1} \text{InTPP}^+ \quad (33)$$

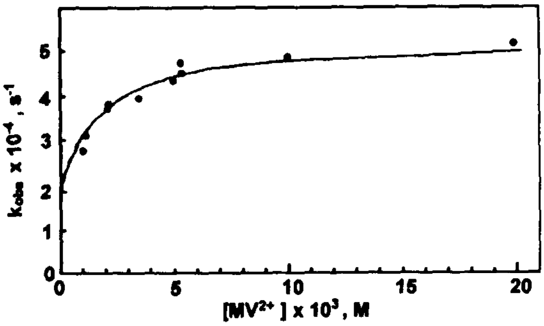

Fig. 6. The first-order decay constants k_{obsd} of ^{3}InTPP$^+$ measured at 460 nm as function of MV^{2+} concentration. (Reproduced with permission from Ref. [27].)

$$^{3*}\text{InTPP}^+ + \text{MV}^{2+} \xrightarrow{k_q} \text{InTPP}^+ + \text{MV}^{2+} \qquad (34)$$

$$^{3*}\text{InTPP}^+ \ldots \text{MV}^{2+} \longrightarrow \begin{cases} \text{InTPP}^+ + \text{MV}^{2+} \\ {}^{\cdot}\text{InTPP}^{2+} + {}^{\cdot}\text{MV}^+ \end{cases} \qquad (35)$$

Analogously to the ground state complexes of metalloporphyrins with electron acceptor molecules, MV^{2+} was assumed to interact with the porphyrin ring in the triplet state. Further investigations revealed that the triplet exciplex reacts with a TEA molecule to form ^{3*}InTPP$^+$(TEA)(MV^{2+}) without undergoing electron transfer. The triplet InTPP$^+$(TEA)$_2$ effectively transfers an electron to MV^{2+} resulting in $^{\cdot}$InTPP$^+$(TEA)$_2^+$ and $^{\cdot}$MV$^+$. The back electron transfer reaction between $^{\cdot}$InTPP^{2+} and $^{\cdot}$MV^{2+} regenerates InTPP$^+$ and MV^{2+}, while the $^{\cdot}$TPP$^+$ moiety in $^{\cdot}$InTPP$^+$(TEA)$^+$ or $^{\cdot}$InTPP$^+$(TEA)$_2^+$ is reduced by one-way intramolecular electron transfer from TEA. The triplet In(III) porphyrin exciplex was the first example of inorganic exciplex formation between two species of positive charge in a polar solvent.

The luminescence behavior of the Ru(bpy)$_3^{2+}$–Ag$^+$ system was studied by Whitten and coworkers in the early 1980s [28,29]. They interpreted the apparent quenching by invoking an electron transfer mechanism in which Ru(III) and Ag(0) were formed in the primary step. However, the quenching rate constants were very low, and positive deviations from Stern–Volmer kinetics were observed at high Ag$^+$.

A detailed investigation of Ag$^+$ ion quenching was carried out by Ayala et al. [30,31] and Tsobomura et al. [32]. They found that the lowest energy metal-to-ligand charge transfer (MLCT) absorption band of Ru(bpy)$_3^{2+}$ in aqueous solution at 3 M ionic strength exhibits a small red shift (3–5 nm) in the presence of Ag$^+$ ions at a concentration of 1.5 M. The luminescence studies revealed a dramatic red shift (60 nm) and a decrease in the peak emission intensity with increasing Ag(I) ion concentration up to 3 M (Fig. 7). Stern–Volmer plots of luminescence lifetime and integrated emission intensity exhibited strong negative deviations from linear behavior (Fig. 8), which is contrary to the observations of Whitten and coworkers [28,29]. Although the apparent oxygen Stern–Volmer quenching constants were found to be

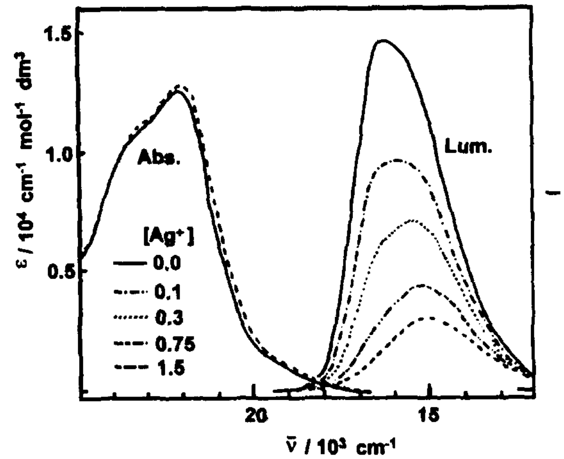

Fig. 7. Absorption and luminescence spectra of $[Ru(bpy)_3]^{2+}$ vs. $[Ag^+]$. (Reproduced with permission from Ref. [32].)

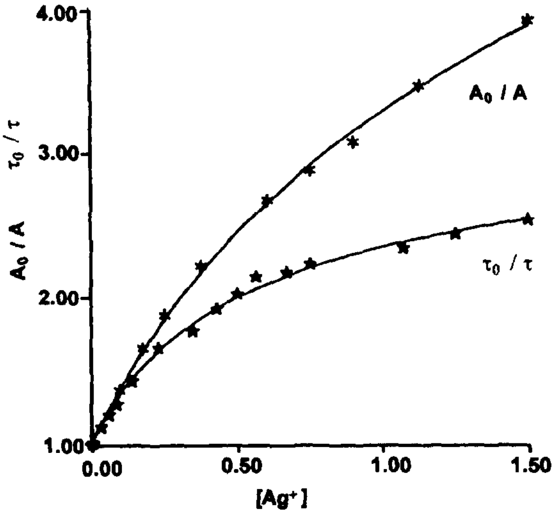

Fig. 8. Luminescence intensity (*) and lifetime (★) Stern–Volmer quenching plots for the $Ru(bpy)_3^{2+}$–Ag^+ system at an ionic strength of 3 M. (Reproduced with permission from Ref. [29].)

dependent on Ag^+ concentration, the oxygen bimolecular quenching constant was only slightly changed within experimental error. Similar results were obtained for $Ru(Me_2phen)_3^{2+}$. The Ru(III) species was not detected by a flash photolysis experiment. The slow production of metallic silver was observed with the addition of 0.01 M triethylamine in the presence or absence of light ($\lambda > 400$ nm). The authors considered and rejected a number of simple models, such as only bimolecular or static quenching, because of their inability to fit one or more experimentally detected features of the system. The large shift in the emission spectrum suggested that there is at least one new excited luminescent species. Finally, they proposed a model involving *Ru(II)Ag$^+$ and *Ru(II)Ag$_2^{2+}$ exciplexes, which is consistent with all the experimental observations. Ru(bpy)$_3^{2+}$(Ag$^+$)$_x$ and Ru(Me$_2$phen)$_3^{2+}$(Ag$^+$)$_x$ exciplexes ($x = 1, 2$) were characterized by stepwise formation constants at different temperatures, and other thermodynamic parameters ($\Delta H, \Delta S$) were also calculated for the formation of *Ru(bpy)$_3^{2+}$Ag$^+$ and *Ru(bpy)$_3^{2+}$Ag$_2^{2+}$ exciplexes. It is interesting to note that emission from the monomeric Ag$^+$ exciplex at increased concentration of MeCN in water + MeCN mixtures is more efficient than that from the parent complex.

Tsobomura et al. [32] confirmed the formation of *Ru(bpy)$_3^{2+}$Ag$^+$ and *Ru(bpy)$_3^{2+}$Ag$_2^{2+}$ exciplexes by circularly polarized luminescence spectroscopy. Exciplex formation in the [Ru(phen)$_3$]$^{2+}$ + Ag$^+$ system was also studied in addition to that of the bpy complex. In aqueous solutions containing 0–1.5 M Ag$^+$ almost the same red shift was observed as in the case of the bpy derivative, but the luminescence intensity did not decrease simply in proportion to the concentration of Ag$^+$. The emission intensity of the solution containing 0.1 M Ag$^+$ was larger than that of [Ru(phen)$_3$]$^{2+}$ alone. Addition of more Ag$^+$ led to a decrease in the intensity, which was regarded as a further indication of the formation of bimolecular and termolecular exciplexes.

The lowest excited MLCT state of the [Ru(bpz)$_3$]$^{2+}$ was also shown to react with Ag$^+$ ions in aqueous or acetonitrile solution to form exciplexes with up to six Ag$^+$ ions per excited complex [33]. The excited state reduction potential of the exciplex is about 100 mV more positive than that of *[Ru(bpz)$_3$]$^{2+}$. The data are not good enough to delineate any special dependence on the number of Ag$^+$ ions associated with the excited complex.

3.2. Metal-centered exciplexes

3.2.1. Metal–electron donor exciplexes

The luminescence behavior of Cu(I) complexes with phenanthroline ligands has been intensively studied for about two decades [34]. The detailed studies revealed that Lewis bases and coordinating anions quench the metal-to-ligand charge transfer (MLCT) excited state and the quenching is ascribed to exciplex formation [35–37]. The emission from *Cu(dmp)$_2$ (dmp = 2,9-dimethyl-1,10-phenanthroline) was not detected in strong electron donor solvents such as water, acetonitrile and acetone at ambient temperature. Whatever the nature of quenching, it is not as effective in a rigid medium. Low temperature measurements revealed that *Cu(dmp)$_2^+$ is luminescent in a 4:1 ethanol + methanol solvent below 100 K [35] (Fig. 9). At ambient temperature, emission can be observed in weakly basic solvents like CH$_2$Cl$_2$. The luminescence lifetime in CH$_2$Cl$_2$ at 25°C strongly depends on the nature of the diimine ligand: 20 ns for tmbp (tmbp = 4,4′6,6′-tetramethyl-2,2′-bipyridine), 90 ns for dmp and 250 ns for dpp (dpp = 2,9-diphenyl-1,10-phenanthroline). Addition of Lewis bases to the CH$_2$Cl$_2$ solution quenches the emission.

The importance of steric effects on luminescence quenching was clearly demonstrated

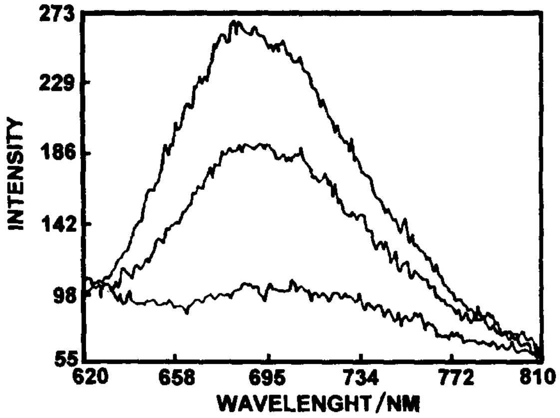

Fig. 9. Uncorrected emission spectra of $^{*}\mathrm{Cu(dmp)}_2^+$ in 4:1 ethanol + methanol. In order of decreasing emission intensity, the sample temperature was 90 K, 100 K and 110 K. (Reproduced with permission from Ref. [35].)

using pyridine and 2,6-dimethyl-pyridine as electron donor species. Pyridine was found to be an excellent quencher of $^{*}\mathrm{Cu(dmp)}_2^+$ ($k_q = 1 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$), but 2,6-dimethyl-pyridine, which possesses a higher $\mathrm{p}K_a$ (6.8) than pyridine ($\mathrm{p}K_a = 5.2$), does not efficiently quench the excited species ($k_q = 10^6\ \mathrm{M^{-1}\,s^{-1}}$). However, when the phenanthroline ligand has bulky groups in the 2 and 9 positions, coordination by a donor molecule to the metal center is hindered; hence even pyridine does not quench the luminescence (e.g. for $^{*}\mathrm{Cu(dpp)}_2^+$).

In the MLCT excited state the electron configuration of the copper center is d^9 so that it has the ability to increase the coordination number. This tends to lead to luminescence quenching by Lewis bases via coordination to the metal, resulting in an exciplex. The mechanism of exciplex formation is interpreted by a simplified potential energy surface diagram in which the ground state surface is assumed to be repulsive but the excited state prefers formation of a five-coordinate species (Fig. 10). A simplified kinetic scheme was given by the following:

$$^{*}\mathrm{Cu(dmp)}_2^+ + \mathrm{Q} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} {}^{*}\mathrm{Cu(dmp)}_2^+ \ldots \mathrm{Q} \tag{36}$$

$$^{*}\mathrm{Cu(dmp)}_2^+ \ldots \mathrm{Q} \overset{k_Q}{\rightleftharpoons} \mathrm{Cu(dmp)}_2^+ + \mathrm{Q} \tag{37}$$

where Q denotes the quencher. This mechanism requires that the observed k_q cannot be regarded as an elementary rate constant, but must be a composite quantity. The existence of the k_{-a} step is supported by the negative apparent activation enthalpy, which has often been interpreted as an indication of exciplex quenching. Negative activation enthalpies were observed for a series of electron donor quenchers. The activation enthalpy values show a complicated change with the Guttman donor number of the Lewis bases (Fig. 11). For weaker donors $\Delta H^{\ddagger}$ becomes more negative with increasing base strength, whereas for bases stronger than ethyl acetate $\Delta H^{\ddagger}$

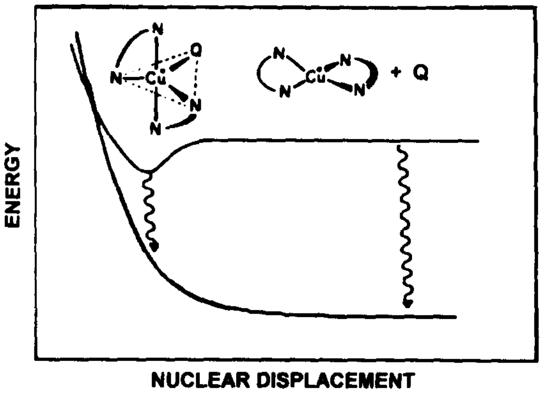

Fig. 10. Schematic energy surfaces for exciplex quenching. From right to left the interaction distance between the quencher Q and the copper complex decreases. The lower curve pertains to the ground state while the upper curve represents the excited state. The arrows show that the energy gap is smaller in the exciplex configuration. (Reproduced with permission from Ref. [36].)

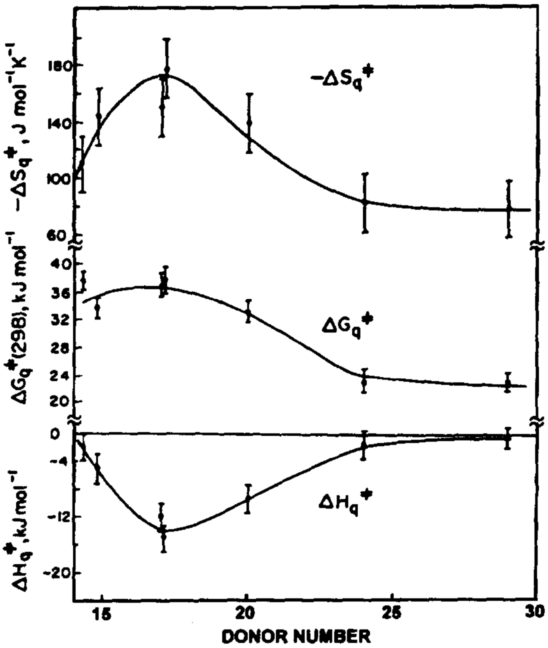

Fig. 11. Activation parameters as a function of donor number in methylene chloride. The curved lines draw through the $\Delta H_q^{\ddagger}$, $\Delta S_q^{\ddagger}$, and $\Delta G_q^{\ddagger}$ (298 K) data are simply visual aids. (Reproduced with permission from Ref. [37].)

shifts to smaller negative values. The kinetic studies also revealed that the changes in activation enthalpy are compensated by the activation entropy values resulting in positive $\Delta G^{\ddagger}$ values for all electron donor quenchers investigated. These results clearly demonstrated that coordinatively unsaturated excited states such as $^*Cu(dmp)_2^+$ are excellent candidates for exciplex formation via coordination to the metal center.

The study of pressure effects on excited state dynamics of $Cu(dmp)_2^+$ and $Cu(dpp)_2^+$ yielded different activation volumes $\Delta V^{\ddagger}$ for luminescence decay in CH_2Cl_2: $\Delta V^{\ddagger} = -3.4 \pm 0.2\ cm^3\ mol^{-1}$ for the dmp derivative, whereas $\Delta V^{\ddagger} = -1.6 \pm 0.2\ cm^3\ mol^{-1}$ for the dpp complex [38]. Values of $\Delta V^{\ddagger}$ for non-radiative decay ($\Delta V_n^{\ddagger}$) and quenching ($\Delta V_q^{\ddagger}$) were also determined for the quenching of $Cu(dmp)_2^+$ by CH_3CN and CH_3OH respectively. The results ($\Delta V_q^{\ddagger} = -6.2 \pm 0.5\ cm^3\ mol^{-1}$; $\Delta V_q^{\ddagger} = -5.4 \pm 0.5\ cm^3\ mol^{-1}$) clearly indicated that the quenching constants k_q are considerably more pressure sensitive than are the values of k_n ($\Delta V_n^{\ddagger} = -3.4\ cm^3\ mol^{-1}$). In contrast, the values of $\Delta V_q^{\ddagger}$ for $^{3*}Cu(dpp)_2^+$ in neat CH_2Cl_2, in 0.3 M CH_3CN in CH_2Cl_2 and in neat CH_3CN are identical within experimental uncertainty. The magnitude of the negative $\Delta V_n^{\ddagger}$ for $^{3*}Cu(dmp)_2^+$ in CH_2Cl_2, as well as the even more negative values of $\Delta V_q^{\ddagger}$, confirm the associative nature of the major contributions to the non-radiative deactivation mechanism from the MLCT excited state of the $Cu(dmp)_2^+$ complex. Correspondingly, the small medium-insensitive $\Delta V_n^{\ddagger}$ for $Cu(dpp)_2^+$ confirmed the steric effect of the 2,9-diphenylphenanthroline ligand, which prevents the copper center from attack by Lewis bases.

Exciplex formation was confirmed for the tetranuclear cluster $Cu_4I_4py_4$ (py = pyridine) in benzene [38]. This Cu(I) complex displays emission from two uncoupled states, *MLCT ($\lambda_{max} = 490$ nm, $\tau = 450$ ns) and a lower-energy cluster-centered state (*MCC) $\lambda_{max} = 690$ nm, $\tau = 10.7$ μs). Addition of pyridine to a $Cu_4I_4py_4$ solution in dry deaerated benzene at ambient temperature results in a decrease in the *MLCT luminescence lifetime, while the *MCC lifetime is found to be invariant within experimental error. The bimolecular quenching constant $k_q = 5.9 \times 10^9\ M^{-1}\ s^{-1}$ was obtained from a linear Stern–Volmer plot. In view of the quenching mechanism, energy transfer from the *MLCT excited state of the tetranuclear complex to the free pyridine molecule can be excluded since the lowest-lying triplet state of pyridine ($29\,650\ cm^{-1}$) is energetically too high. The exciplex mechanism is supported by the effects of pyridine substituents in the sterically significant *ortho* position. Increase of the substituent steric bulk leads to a decrease in quenching constant: $9.5 \times 10^8\ M^{-1}\ s^{-1}$ and less than $10^6\ M^{-1}\ s^{-1}$ for 2,6-dimethylpyridine and 2,6-di-tert-butylpyridine respectively.

3.2.2. Metal–anion exciplexes

Evidence has recently been presented that coordinatively unsaturated $^*Cu(CN)_2^-$ formed upon UV irradiation in aqueous solutions of dicyanocuprate(I) associates with halide ions in the ground state to create a longer-lived luminescent exciplex [9,40–42]. The halide-ion-dependent luminescence quantum yield first increases and then decreases at increasing halide ion concentration, reaching a maximum value at about 2.5 M, 2.0 M and 0.1 M chloride ion, bromide ion and iodide ion respectively (Fig. 12). Similar behavior was observed for luminescence lifetime vs. halide concentration data measured by laser flash photolysis on the nanosecond time-scale (Fig. 13). Since association was also observed in the ground state, the luminescence characteristics were interpreted by a mechanism involving both ground and excited state equilibrium reactions (Scheme III, where P is the precursor of luminescent species, E is the exciplex, D is non-radiative decay, L is luminescent decay and products represents species formed by bimolecular reaction of the exciplex with

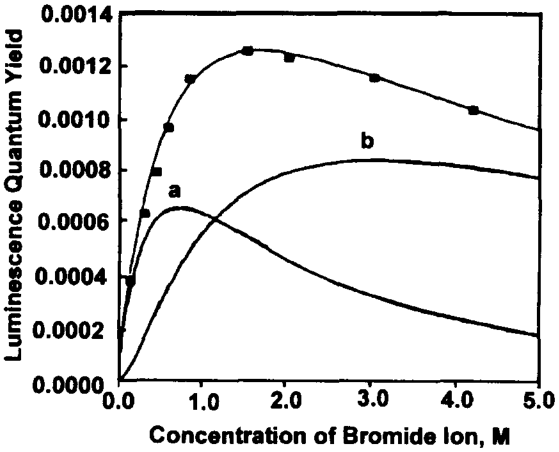

Fig. 12. Dependence of luminescence quantum yield on bromide ion concentration at 5 M ionic strength (■ measured; —— calculated): (a) "partial" quantum yield derived from excitation of dicyanocuprate(I); (b) "partial" quantum yield derived from excitation of dicyanobromocuprate(I). (Reproduced with permission from Ref. [9].)

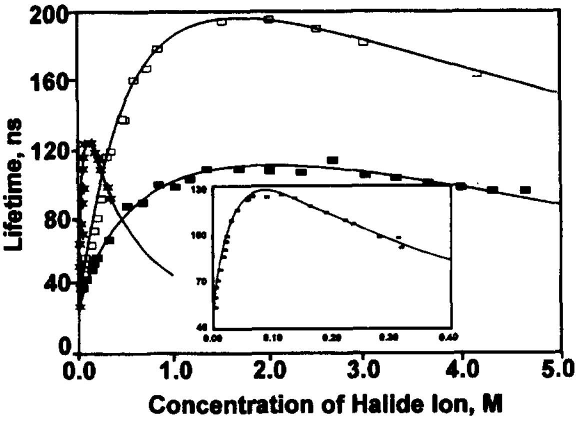

Fig. 13. Dependence of the luminescence lifetime on the concentration of halide ion in aqueous solutions of $Cu(CN)_2^- + X^-$ at 5 M ionic strength: ■ X = Cl; □ X = Br, ★ X = I. (Reproduced with permission from Ref. [40].)

excess halide ion). The general solution of the kinetic equation gives the expression for the luminescence lifetime:

$$\tau = 2/\{(x+y) - [(x-y)^2 + 4k_E k_{E^-}[X^-]]^{1/2}\} \tag{38}$$

where $x = k_{PD} + k_E[X^-]$ and $y = k_{E^-} + k_{EL} + k_{ED} + {}_{ER}[X^-]$. The rate constants involved in the mechanism were estimated by fitting Eq. (38) to the lifetime vs. halide concentration data using a procedure given elsewhere [40,41].

The luminescence decay rates of these systems have been observed to be very sensitive to temperature, which permitted a reasonable estimation of the activation parameters in the exciplex model. These investigations revealed a very small but negative activation enthalpy for exciplex formation. This is rather similar to what was observed in reactions between excited Cu(I) bis-phenanthroline complexes [28] and Lewis bases in the ground state, and between the triplet excited $Ru(bpy)_3^{2+}$ and organic electron donors [18]; hence this was regarded as further evidence of the exciplex formation. The formation of the exciplex was found to be both kinetically and thermodynamically favored by halide ions of higher polarizability such as bromide and iodide. Hence it was concluded that, because of the overlap between the "diffuse" orbitals of the excited metal complex and the halide ion in the ground state, the covalent part of the exciplex interaction is more effective than the electrostatic attraction between the halide ion and the metal center considered to be very similar to the Cu(II) after the charge transfer excitation.

Time-resolved absorption measurements indicated that the 266 nm laser pulse initiates the formation of at least three different species absorbing in the 300–900 nm range.

(1) The transient absorption band peaking at 700 nm was identified as the spectrum of the solvated electron. This species is ejected by the excited state of higher energy possessing charge transfer to solvent (CTTS) character directly achieved by the photon absorption.

(2) A short-lived absorption between 300 and 400 nm, with the same lifetime as the luminescence, was assigned as the absorption of the exciplex [41].

(3) A longer-lived intermediate with absorption bands peaking at 360 nm (strong) and at 700 nm (weak) was assigned as the $^{\cdot}Br_2^-$ radical anion [41,42]. The creation of this species is initiated by the reaction characterized by k_{ER}.

3.2.3. Metal–metal exciplexes

A systematic study of pressure effects on bimolecular reductive quenching of the Pt(II) dimer $Pt_2(\mu\text{-}\eta^2\text{-}H_2P_2O_5)_4^{4-}$ by an organic substrate provided valuable insight into the intimate mechanism of dehydrogenation photocatalytic cycles [43]. Quenching of the lowest-energy long-lived triplet excited state of the dimeric platinum complex at increasing pressures indicated relatively large negative volumes of activation for benzyl alcohol ($\Delta V^{\ddagger} = -5.4 \pm 0.6$ cm^3 mol^{-1}) and benzyl methyl ether ($\Delta V^{\ddagger} = -4.1 \pm 0.7$ cm^3 mol^{-1}). These negative $\Delta V^{\ddagger}$ values were interpreted by an associative interaction between the excited state dimer and the hydrogen atom donor molecule.

Luminescent exciplex formation involving $Pt_2(\mu\text{-}\eta^2\text{-}H_2P_2O_5)_4^{4-}$ and Tl(I) ion in aqueous solution was verified recently [44]. It was observed that, upon addition of $TlNO_3$ to the aqueous solution of the dimeric Pt complex, the absorption of Pt_2 was only slightly affected by the addition of up to 10^{-3} M Tl(I) (from Tl_2SO_4, $TlNO_3$ or TlBr). Fluorescence, produced only by 368 nm excitation with emission at 405 nm, was not influenced by Tl^+ in this concentration range. However, addition of Tl(I) ions to the solution which was irradiated at either 368 or 453 nm led to a considerable shift in the green phosphorescence of $^{3*}Pt_2$ ($\lambda_{max} = 514$ nm) and resulted in a yellow-green emission peaking at 565 nm (Fig. 14). Both the measured lifetime (10.2 ± 0.2 μs) and quantum yield (0.53 ± 0.03) of the 565 nm phosphorescence are the same, within experimental error, as those for the 514 nm emission of the excited dimeric Pt complex in the absence of Tl^+. Considering these similarities and the single exponential decay of the luminescence, provide strong evidence that the two species have almost the same radiative and non-radiative decay rates.

The 565 nm luminescence was assigned to the $*Pt_2Tl^+$ exciplex, and a value of $(2.0 \pm 0.3) \times 10^4$ at 25°C was determined for the formation constant. The luminescence intensity ratio of the 565–514 nm bands was reduced by HNO_3 (0.1 M), KNO_3 (0.1 M) and O_2 (air-saturated solutions). The effects of the first two solutes were attributed to ion-pairing, whereas an efficient competitive quenching of $*Pt_2$ by O_2 was suggested. Decreasing the temperature of a 2:1 1,2-ethanediol + water solution to 190 K gave a frozen solution in which the 565 nm luminescence disappeared as the 514 nm phosphorescence reappeared, indicating the importance of the diffusional process for exciplex formation.

The tendency for exciplex formation between the ground state Tl^+ ion and the triplet excited dimeric Pt complex was interpreted in terms of a simple molecular orbital picture. The interaction of the half-filled σ^* ($5d_z2$) and σ ($6p_z$) orbitals of $*Pt_2$ with the filled 6s and empty $6p_z$ orbitals of Tl^+ in the axial direction was expected. This interaction yields a net two-electron stabilization, a covalent

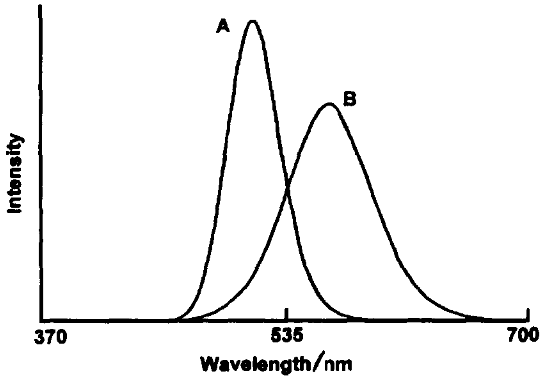

Fig. 14. Corrected emission spectra of (A) 10^{-5} M $Pt_2(P_2O_5H_2)_4^{4-}$ and (B) 10^{-5} M $Pt_2(P_2O_5H_2)_4^{4-}$ and 10^{-3} M $TlNO_3$, both in deoxygenated water at room temperature. (Reproduced with permission from Ref. [44].)

interaction which differs from the charge transfer behavior of more common singlet organic exciplexes.

Further studies of this system clearly demonstrated that at higher Tl^+ concentrations $^{3*}Pt_2(Tl^+)_2$ and even $^{1*}Pt_2(Tl^+)$ are formed at ambient temperature [10]. The termolecular exciplex shows luminescence at 588 nm with the same lifetime and luminescence quantum yield as does the $^{3*}Pt_2Tl^+$ exciplex ($\tau = 10$ µs, $\phi_{1\,\mu m} = 0.5$). The singlet exciplex ($\lambda_{em} = 431$ nm, $\phi_{1\,\mu m} < 1 \times 10^{-3}$) is formed at higher Tl^+ concentrations ($1 \times 10^{-3} < [Tl^+] < 0.1$ M) in a range where some ground state equilibrium reaction was also detected by a noticeable red shift in the spin-allowed absorption band ($\lambda = 368$ nm) of Pt_2.

Photoacoustic calorimetry measurements were also performed on this system [45]. It was found that the photoexcitation of the Pt_2 complex, which populates the long-lived $^3A_{2u}$ triplet state via a highly efficient intersystem crossing from the initially formed $^1A_{2u}$ singlet state, results in a very small positive volume change. However, in the presence of Tl^+ ion (0.01 M), a significant negative change in volume was observed (Fig. 15). The temperature-independent change in reaction volume and the reaction enthalpy were calculated from the experimental data. The reaction enthalpy for formation of $*Pt_2$ (54.5 kcal mol^{-1}) as well as that of $*Pt_2Tl^+$ (46 kcal mol^{-1}) are in reasonable agreement with the spectroscopically determined values (58 kcal mol^{-1} and 49 kcal mol^{-1} respectively).

The negligible reaction volume change for excitation of Pt_2 to $*Pt_2$ suggested that the partial molar volume of the $^1A_{1g}$ ground state and $^3A_{2u}$ triplet state are approximately equal. However, resonance Raman spectroscopic studies indicated that photoexcitation of Pt_2 to the $^3A_{2u}$ triplet state results in a significant change in the Pt—Pt bond length (21 pm). Hence the small observed reaction volume change can be explained by the following: (a) the bond-length reduction is anisotropic, which leads to a small change in volume; (b) compensating increases in other bond lengths in

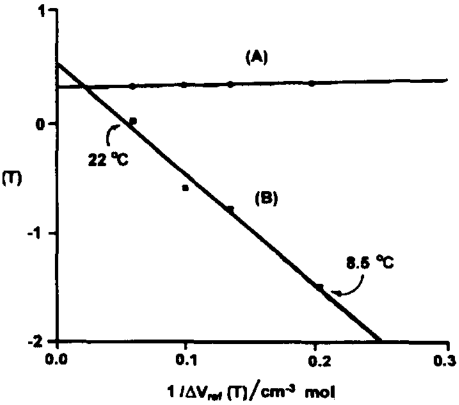

Fig. 15. Plot of the total volume changes observed upon excitation of $Pt_2(P_2O_5H_2)_4^{4-}$ in water vs. the volume change of a calibration compound $FeCl_3$ at various temperatures (8.5°C, 11.1°C, 13.5°C, 22.0°C): (A) 0 M $TlNO_3$; (B) 0.01 M $TlNO_3$. (Reproduced with permission from Ref. [45].)

the excited state occur, so that the ground and excited state volumes are rather similar; (c) the surrounding water molecules do not fill the empty space created by shortening of the Pt—Pt bond length.

In contrast, the large decrease in reaction volume ($-10.6\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$) observed upon excitation of Pt_2 in the presence of Tl^+ ions clearly indicated exciplex formation. A 260 pm Pt—Tl bond length estimated from the data confirmed the appreciable interaction between the $^*Pt_2$ and Tl^+.

4. Conclusions

A survey of the literature dealing with exciplex formation and characterization in systems involving excited transition metal complexes has revealed that, although few examples of these molecular entities have been reported, this phenomenon should be more common than previously thought. In addition, the "colorful world" of transition metal complexes and organometallic compounds provides a deepening of our knowledge of the nature of exciplexes and a better understanding of their role in the mechanisms of light-induced chemical processes. Theoretical considerations based on extensive experimental results make it possible to design optimal routes in photochemical reactions. By changing the medium and the coordination sphere we can enhance the processes by involving an exciplex if this leads to formation of the final product with high efficiency, or we can avoid exciplex formation if necessary. The primary significance of this possibility is that we can fine tune the potential barriers, either by solvent media or by the structure of the transition metal constituent.

We classified the transition metal exciplexes by considering the properties of the two constituents of the exciplex interaction. Although this is a simple and formal method, we obtained well-characterized classifications with different unique behavior. However, if we consider only the nature of the orbital overlap, we can distinguish only two types of exciplex interaction.

In the first type, molecules possessing extended delocalized π electron systems tend to create exciplexes with properties very similar to those of organic exciplexes. Formation of this type of transition metal exciplex is favored in non-polar solvents with aromatic reaction partners. Prominent members of this group are the excited Re(4,7-dimethyl-1,10-phenanthroline)$(CO)_3Cl$ with *N,N'*-dimethylaniline and the triplet-excited metalloporphyrins with nitro aromatic compounds.

In the second type of exciplex interaction, the exciplexes are characterized by the fact that metal orbitals play a dominant role in the interaction. The transition metal constituent in the exciplex can be either an excited molecule such as bis-2,9-dimethylphenanthroline-Cu(I) in the exciplex $^*Cu(dmp)_2^+ \ldots MeCN$, or dicyanocuprate(I) in the exciplex $^*Cu(CN)_2^- \ldots X^-$ (where X = Cl, Br, I), or it can be a ground state species such as Ag^+ in $^*Ru(LL)_3^{2+} \ldots (Ag^+)_n$ (where $n = 1, 2$ for bipyridine and phenanthroline derivatives and $n = 1, 2, \ldots, 6$ for the bipyrazine complex). A remarkable feature of this group is that most of the metal centers, both in the excited species and in the metal ions of the ground state involved in the exciplex interaction, have an $(n-1)d^{10}$ electron configuration in the ground state (Cu(I), Ag(I), Hg(II)). The excitation of these central atoms results in the population of the diffuse *n*s orbital providing an efficient overlap with an appropriate orbital of the molecular entity of the ground state, which accompanies the stabilization of the exciplex. However, the empty *n*s orbital of the ground state $(n-1)d^{10}$ ion (e.g. Ag^+) can strongly overlap with a "diffuse orbital" populated by the excitation in the other constituent of the exciplex. Similar behavior is expected for the excited metal complex of a coordinatively unsaturated d^8 central atom and ground state metal ions with ns^2 configuration, as is observed in the exciplex $^*Pt_2(\mu\text{-}\eta^2\text{-}H_2P_2O_5)_4^{4-} \ldots (Tl^+)_{1,2}$. The interaction between the metal center of the d^8 configuration and Tl^+ possessing a ns^2 configuration results in an electronic structure very similar to that which emerges in the overlapping of the excited metal center originating from an $(n-1)d^{10}$ ground state and the ns^0 orbitals of the other constituent.

It has been demonstrated that non-polar solvents are favorable for organic exciplexes formed by neutral molecules. A simple energetic consideration clearly indicates that ion pair formation via electron transfer becomes a dominant reaction step instead of exciplex formation when the solvent polarity increases. However, for inorganic exciplexes, in which the constituents have like electric charges, an increase in solvent polarity results in a considerable decrease in solvation energy when the exciplex is created instead of an ion pair.

Solvent polarity as well as ionic strength are also very important factors in the kinetics of inorganic exciplex formation. The increase in shielding of a charged species owing to an increase in either the solvent polarity or the ionic strength can lead to a considerable change in the rate constant for exciplex formation. Higher solvent polarity and ionic strength are favorable for particles of the same sign of electric charge.

This work clearly indicates the following.

(1) Exciplex formation in inorganic systems is probably a more common phenomenon that has been expected.

(2) Fertile ground for the discovery of new transition metal exciplexes will be provided by investigating compounds possessing $(n-1)d^{10}$ electron configurations.

(3) Transition metal exciplex formation is favored in polar solvents, for energetic reasons, and at high ionic strength, from a kinetic point of view, particularly for exciplexes originating from particles of similar electric charge.

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