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Ligand- and metal-centered inorganic exciplexes generated by excited transition metal complexes

Attila Horváth

Department of General and Inorganic Chemistry, University of Veszprém, PO Box 158, Veszprém H-8201, Hungary

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Contents

Abstract

The photophysical and photochemical properties of two prominent groups of exciplexes generated by the excited transition metal complexes are discussed. The strong interaction between the excited tris-(α-diimine) ruthenium(II) complex and the ground state silver ion results in both bimolecular and termolecular exciplexes. Since the stabilization originates from the overlap between the low-lying π^* level of a coordinated ligand and the empty 5s orbital of the silver ion, these exciplexes are called ligand-centered exciplexes (LCEs). In contrast, coordinatively unsaturated dicyanocuprate(I) in the excited state associates with halide ions to create longer-lived, more highly luminescent metal-centered exciplexes (MCEs). The stepwise formation constants of exciplexes and the thermodynamic parameters of the excited state equilibrium determined by temperature-dependent measurements have been compared and discussed. The kinetics and energetics of LCEs and MCEs strongly depend on the ionic strength and the solvent properties. Although the exciplex constituents of the two groups and their interaction have a rather different nature, some common behavior of these transition metal complex exciplexes have been elucidated. © 1997 Elsevier Science S.A.

Keywords: Excited transition metal complexes; MCE; LCE; Exiplex

1. Introduction

An electronically excited molecule may form a reasonably stable complex with another ground-state molecular entity even though they do not interact significantly

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in their ground state, since the excited species is considerably different in chemical nature than the ground-state molecule from which it is generated. The complexes created by such an interaction are called exciplexes [1]. Luminescent exciplexes are generally characterized by a new, red shifted emission band, which is usually structureless, because the radiation 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. Solvent effects on the emission spectrum and correlation of both spectrum and enthalpy of formation with the redox properties of exciplex constituents are indicative of the nature of exciplex. Time-resolved experiments performed by nanosecond or subnanosecond time resolution show double exponential luminescence transients; a double exponential decay at the wavelength of the precursor emission and a development followed by the decay at the wavelength of exciplex emission. The rate of the exciplex formation, as well as the stability constant of the exciplex, can be determined by these experiments. Difficulties with the direct observation of the non-emitting exciplexes should be emphasized. In this case the investigation of transient absorption spectra and chemical reactivity can provide the identification of the exciplex.

The electronic structure can be characterized by the wave function of an exciplex, which is expressed as a linear combination of wave functions of the possible states [2]:

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

where the first and second terms describe the energy transfer states, the third and fourth are the charge transfer states, and the last term gives the ground state interactions, with the coefficients representing the relative contributions of the states. If the ground-state interactions can be neglected the wave function simplifies to

$$\Psi = c_1\Psi({}^{*}\mathrm{DA}) + c_2\Psi(\mathrm{DA}^{*}) + c_3\Psi({}^{\cdot}\mathrm{D}^{+}\,{}^{\cdot}\mathrm{A}^{-}) + c_4\Psi({}^{\cdot}\mathrm{D}^{-}\,{}^{\cdot}\mathrm{A}^{+}) \tag{2}$$

Depending on the values of the coefficients c_1–c_4, exciplexes may be classified into two basic groups: non-polar (covalent) exciplexes (c_3, $c_4 < c_1$ or c_2) and charge-transfer exciplexes (c_1, $c_2 < c_3$ or c_4).

In principle, exciplex stabilization originates from the overlap between the highest bonding orbitals or between the lowest antibonding orbitals [3]. However, the interaction of bonding with antibonding orbitals results in a destabilization. The net energy change of the interactions ΔE_{EX} is given by the difference of the stabilization and destabilization energy ($\Delta E_{\mathrm{EX}} = E_{\mathrm{stab}} - E_{\mathrm{dest}}$). The free energy change of the exciplex formation involves this orbital stabilization term, the ionization energy of the electron donor species E_{I}, the electron affinity of an acceptor E_{EA} [4], the excitation energy E^{*}, the Coulombic interaction between the excited species and the ground state molecule E_{EXC}, and the energy of exciplex solvation E_{EXsolv} [4–6].

$$\Delta G_{\mathrm{EX}} = E_{\mathrm{I}} - E_{\mathrm{EA}} - E^{*} - \Delta E_{\mathrm{EX}} - E_{\mathrm{EXsolv}} + E_{\mathrm{EXC}} \tag{3}$$

Exciplexes are common intermediates in organic photochemical systems. In the coordination chemistry literature, however, only a few exciplexes possessing excited transition metal complex and inorganic ground-state constituents have been reported so far [7–17]. Recently, we compiled a survey of the literature of exciplexes formed by excited transition metal complexes [18]. In this review we developed a classification scheme for the transition metal complex exciplexes (TMCEs) and suggested a strategy for searching for new TMCEs. The classification is based on the structure of the coordination sphere of excited transition metal complex and the nature of another species. TMCEs originated from coordinatively saturated complexes are termed ligand-centered exciplexes (LCEs) and those which are formed from coordinatively unsaturated metal complexes are called metal-centered exciplexes (MCEs). The implication is that the interaction forming the exciplex is localized on the ligands in the former case, and the metal in the latter case. The further sub-classifications results from the nature of the other constituent of the exciplex.

The goals of the present study are to compare the photophysical and photochemical properties of two prominent groups of TMCEs: (1) LCEs formed by excited tris-(α-diimine) ruthenium(II) complexes and silver ion; (2) MCEs generated by excited dicyanocuprate(I), in which the halide ions coordinate to the excited metal center. Although these two groups of TMCEs are different in the nature of the exciplex interaction, their other properties are very similar: (1) both constituents of the exciplexes are ionic species; (2) they have the same sign of electric charge; (3) the ground state constituents are mononuclear ions.

2. Exciplexes of tris(α-diimine)ruthenium(II) complexes

Although $[Ru(bpy)_3]^{2+}$ has been studied extensively since the discovery of its excellent photophysical and photochemical properties, the bimolecular and termolecular exciplexes formed by $*[Ru(bpy)_3]^{2+}$ and silver ion were identified only in the late 1980s [7,8]. Exciplex formation of related diimine complexes, such as $*[Ru(phen)_3]^{2+}$, $*[Ru(dmphen)_3]^{2+}$ and $*[Ru(bpz)_3]^{2+}$, with silver(I) ion have also been reported [7,8,10,11].

The luminescence behavior of the $[Ru(bpy)_3]^{2+}$–Ag^+ system was investigated by Whitten and co-workers in the early 1980s [19,20]. Upon irradiation by visible or near-UV light of aqueous or acetonitrile solutions containing $[Ru(bpy)_3]^{2+}$ and $AgNO_3$, $AgClO_4$ or $[Ag(bpy)_2]^+$ quenching of the luminescence but no permanent chemistry was observed. Addition of low concentrations of strong electron donor species such as triethylamine, however, resulted in the formation of colloidal silver in acetonitrile. They interpreted the apparent quenching by an electron-transfer mechanism in which ruthenium(III) and silver atoms are formed in the primary step. It is followed by conversion of Ag^0 to Ag_2^+, and then the back-electron transfer reaction regenerates the ruthenium(II) complex and the silver ion in the absence of electron donor molecule.

However, the quenching rate constants were very low, and positive deviations from the Stern–Volmer kinetics were observed at high Ag^+ concentration. In addition to the luminescence quenching, a slow ligand substitution was also detected in acetonitrile [20]. A mechanism involving a ligand-labilized intermediate, which is intercepted by Ag^+ in a process assisting the substitution by removal of a bpy ligand, was proposed.

Thorough steady state and time-resolved investigations of silver ion quenching carried out by Ayala et al. [7,8] and Tsubomura et al. [11] revealed the exciplex formation. They found a very small red shift (3–5 nm) in the lowest energy metal-to-ligand charge-transfer (MLCT) absorption band of $Ru(bpy)_3^{2+}$ in aqueous solution at 3 M ionic strength in the presence of Ag^+ ion at 1.5 M concentration. In contrast, a considerable red shift (60 nm) in the corrected luminescence spectrum and a decrease in the emission intensity with increasing silver(I) ion concentration up to 1.5 M were detected (Fig. 1). Stern–Volmer plots of integrated emission intensity and luminescence lifetime indicated a deviation from linear behavior and the dependence of luminescence intensity/lifetime ratio on the silver ion concentration. These results strongly suggest that at least one equilibrium reaction of the excited species plays an important role in the luminescence dynamics. Exciplex formation in the $[Ru(phen)_3]^{2+}$–Ag^+ system was also studied using absorption, emission and circularly polarized luminescence spectroscopy [11]. In aqueous solutions of 0–1.5 M Ag^+, nearly the same red shift was observed in the emission spectra as in the case of the bpy derivative, but the luminescence intensity did not decrease simply in proportion to the concentration of Ag^+ (Fig. 2). The emission was found to be stronger in the solution containing 0.1 M Ag^+ than that of $[Ru(phen)_3]^{2+}$ alone. However, addition of more Ag^+ led to a decrease in the intensity. These phenomena were regarded as experimental evidence for the formation of bimolecu-

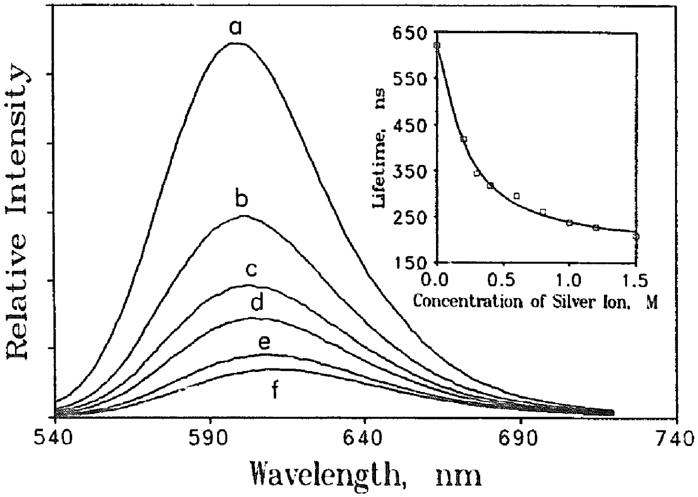


Fig. 1. Change in the uncorrected emission spectrum and the luminescence lifetime (inset) with silver ion concentration in aqueous solution of $[Ru(bpy)_3]^{2+}$ at 3 M ionic strength and ambient temperature: $[Ag^+]=0$ M (a); 0.2 M (b); 0.4 M (c); 0.6 M (d); 1.0 M (e); 1.5 M (f); $\lambda_{exc}=450$ nm for measurement of luminescence spectrum and $\lambda_{exc}=355$ nm for lifetime measurements.

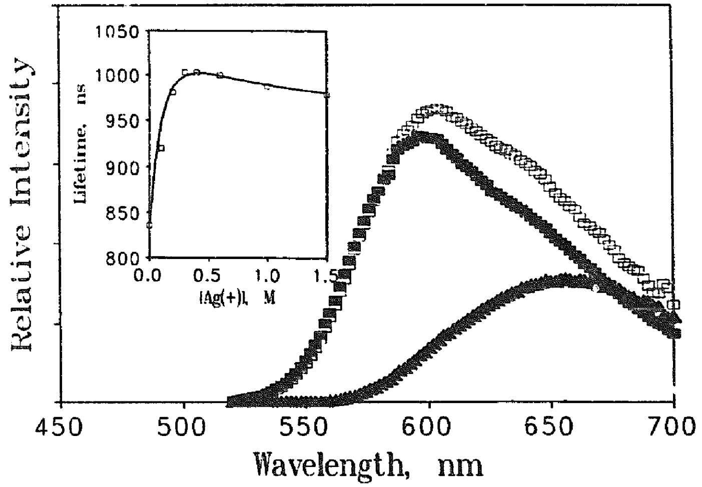


Fig. 2. The calculated luminescence spectra of $^*[Ru(phen)_3]Ag_n^{(n+2)+}$ species; (■) $n=0$, (□) $n=1$ and (▲) $n=2$. The inset shows the change in luminescence lifetime with silver ion concentration in aqueous solution of $[Ru(phen)_3]^{2+}$ at 3 M ionic strength and ambient temperature; measured (□) and calculated values (———).

lar, $[Ru(phen)_3]Ag^{3+}$, and termolecular, $[Ru(phen)_3]Ag_2^{4+}$, exciplexes, and as confirmation of the mechanism proposed by Ayala et al. [7,8], who considered a number of simple models, such as only bimolecular or static quenching for describing the nature of luminescence. They proved that luminescence quenching of the lowest energy MLCT by silver(I) ion in aqueous solutions proceeds not by an oxidative electron transfer mechanism, as previously believed, but predominantly by formation of luminescent bimolecular and termolecular exciplexes.

$$^*[Ru(L)_3]^{2+} + Ag^+ \rightleftarrows {}^*[Ru(L)_3]Ag^{3+} \qquad (4)$$

$$^*[Ru(L)_3]Ag^{3+} + Ag^+ \rightleftarrows {}^*[Ru(L)_3]Ag_2^{4+} \qquad (5)$$

According to the model, all luminescent species decay via radiative and non-radiative processes:

$$^*[Ru(L)_3]^{2+} = [Ru(bpy)_3]^+ + h\nu \text{ or } \Delta \qquad (6)$$

$$^*[Ru(L)_3]Ag^{3+} = [Ru(bpy)_3]^{2+} + Ag^+ + h\nu \text{ or } \Delta \qquad (7)$$

$$^*[Ru(L)_3]Ag^{3+} = [Ru(bpy)_3]^{3+} + Ag^0 \qquad (8)$$

$$^*[Ru(L)_3]Ag_2^{4+} = [Ru(bpy)_3]^{2+} + 2Ag^+ + h\nu \text{ or } \Delta \qquad (9)$$

$$^*[Ru(L)_3]Ag_2^{4+} = [Ru(bpy)_3]^{2+} + Ag^+ + Ag^0 \qquad (10)$$

$Ru(bpy)_3^{2+}(Ag^+)_n$ and $Ru(Me_2phen)_3^{2+}(Ag^+)_n$ exciplexes ($n=1,2$) were characterized by lifetime, rate constants of radiative and non-radiative decays at room temperature, and stepwise formation constants at two different temperatures using the fitting procedure based on the following equations:

$$I_{\mathrm{em}}(\lambda)=\sum f_i I_i(\lambda) \text{ and } 1/\tau_{\mathrm{obs}}=\sum f_i(1/\tau_i) \tag{11}$$

$$f_i=\beta_i[\mathrm{Ag}^+]^i/\sum\beta_i[\mathrm{Ag}^+]^i \text{ and } \beta_i=\prod K_i \tag{12}$$

where $I_{\mathrm{em}}(\lambda)$ is the corrected luminescence spectrum, $I_i(\lambda)$ represent the spectra of the excited ruthenium complex ($i=0$) the bimolecular exciplex ($i=1$) and the termolecular exciplex ($i=2$), f_i are the mole fractions of the luminescent molecular entities, β_i are the overall formation constants ($\beta_0=1$), K_i are the stepwise formation constants, τ_{obs} is the observed lifetime and τ_i represents the lifetime of the different luminescent species.

In addition to the stepwise formation constants, other thermodynamic parameters (ΔH, ΔS) were also estimated for $^*\mathrm{Ru(bpy)}_3^{2+}\mathrm{Ag}^+$ and $^*\mathrm{Ru(bpy)}_3^{2+}\mathrm{Ag}_2^{2+}$ exciplexes using data from measurements carried out at two different temperatures. Recently, luminescence lifetime measurements ranging between 0 and 70 °C were thoroughly performed for $[\mathrm{Ru(bpy)_3}]^{2+}$–$\mathrm{Ag}^+$ and $[\mathrm{Ru(phen)_3}]^{2+}$–$\mathrm{Ag}^+$ systems in aqueous solutions of 3 M ionic strength at various silver ion concentration [21,22]. These experiments provided reliable thermodynamic parameters for the formation of bimolecular and termolecular exciplexes. A summary of these quantities is given in Table 1. The stabilities of these exciplexes largely result from their enthalpy values. The negative entropy values are consistent with the associative mechanism. The negative entropy values of termolecular exciplex formation are higher than those of bimolecular exciplexes, which can be interpreted as the creation of a compact solvent layer organized by the relatively large charge density of the termolecular exciplex.

Different features have been obtained for temperature-dependent luminescence lifetimes of $^*[\mathrm{Ru(bpy)_3}]\mathrm{Ag}_n^{(2+n)+}$ and $^*[\mathrm{Ru(phen)_3}]\mathrm{Ag}_n^{(2+n)+}$ complexes in aqueous solution at 3 M ionic strength [21,22]. The lifetime decreases monotonously in the case of the $^*[\mathrm{Ru(bpy)_3}]^{2+}$–$\mathrm{Ag}^+$ system (inset in Fig. 1), while a maximum is observed in the τ–$[\mathrm{Ag}^+]$ curve for the $^*[\mathrm{Ru(phen)_3}]^{2+}$–$\mathrm{Ag}^+$ system at room temperature (inset in Fig. 2). A dramatic difference in luminescence lifetime is detected near 0 °C for bpy derivatives. The lifetime of the MLCT excited complex is about 700 ns, but

Table 1
Thermodynamic parameters for $[\mathrm{Ru(L)_3}]\mathrm{Ag}_n^{(n+2)+}$ exciplexes

Ligand	n	K_n (M^{-1})	β_n (M^{-n})	ΔH ($\mathrm{kJ\,mol^{-1}}$)	ΔS ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	ΔG ($\mathrm{kJ\,mol^{-1}}$)
bpy	1	4.7 ± 0.5	8.9 ± 1.0	-6.0 ± 0.5	-7 ± 1	-3.8 ± 0.8
	2	1.9 ± 0.5		-6.2 ± 0.6	-15 ± 2	-1.6 ± 0.4
phen	1	7.9 ± 0.6	21.3 ± 1.3	-7.0 ± 0.8	-7 ± 1	-5.0 ± 0.9
	2	2.7 ± 0.7		-8.0 ± 0.8	-19 ± 3	-2.4 ± 0.5
DMphen	1	12 ± 1[a]				-6.0 ± 1[a]
	2	1 ± 0.7[a]	12 ± 1.7[a]			0 ± 1[a]

[a] Data from Ref. [7].

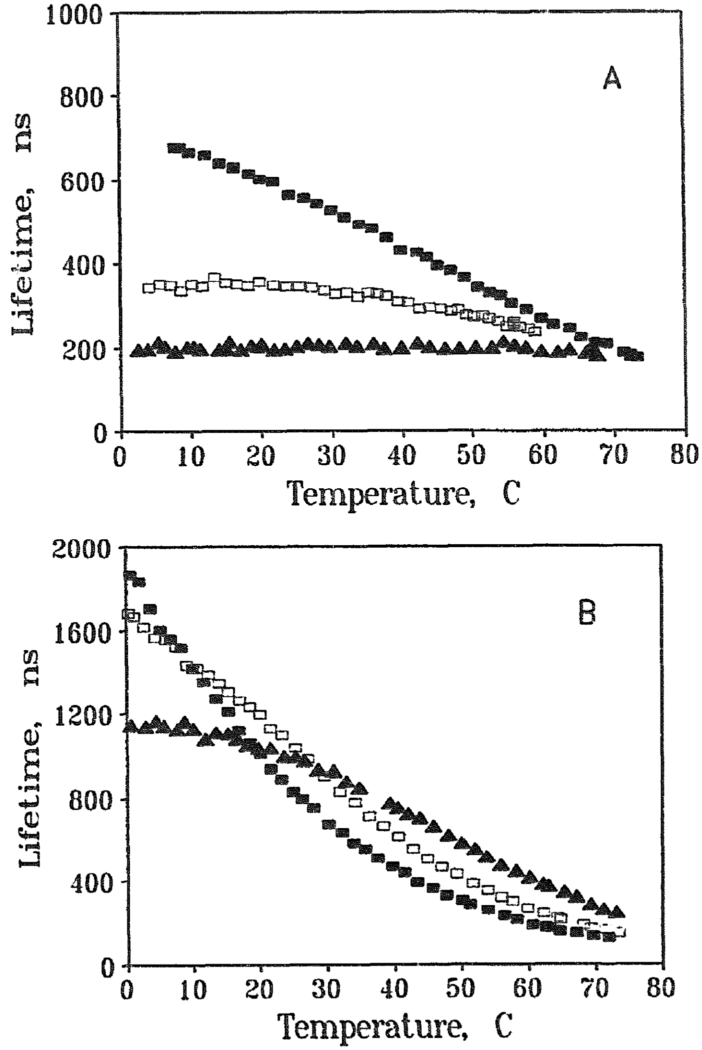


Fig. 3. Temperature dependence of luminescence lifetime in aqueous solution of $[Ru(L)_3]^{2+}$–Ag^+ systems at ambient temperature: L = bpy (a) and L = phen (b); $[Ag^+] = 0$ M (■), $[Ag^+] = 0.3$ M (□) and $[Ag^+] = 1.5$ M (▲).

decreases to 200 ns at 1.5 M silver concentration. The luminescence lifetime of this system is constant ($\tau = 200$ ns) between 3 and 50 °C (Fig. 3(A)). The τ–T curves obtained for $[Ru(phen)_3]^{2+}$ solutions at various silver concentrations cross each other; the lifetimes of exciplexes are smaller than that of $*[Ru(phen)_3]^{2+}$ at low temperature, while at higher temperature these molecular entities have longer lifetimes than the excited ruthenium(II) complex (Fig. 3(B)).

The analysis of the temperature-dependent lifetime data revealed a difference in the photophysics of *[Ru(bpy)$_3$]$^{2+}$, *[Ru(phen)$_3$]$^{2+}$ and their bimolecular and termolecular exciplexes. The luminescence lifetime can be expressed by an equation involving two exponential terms for the bpy derivative, while a reasonable fitting can be obtained by an expression possessing only one exponential term for the phenanthroline compound. The results are consistent with the electronic structure of the charge transfer (CT) excited state reported earlier [23,24]. The fourth CT state of *Ru(bpy)$_3^{2+}$ is 725 cm^{-1} (ΔE_2) over the three low-lying ^{3}CT states with a spacing of several tens of wavenumbers. Another energy gap of 3670 cm^{-1}, has been attributed to the activation barrier for the MLCT to dd state conversion. The temperature-dependent term of luminescence lifetime for the phenanthroline derivative, however, involves only the second type of activation ($\Delta E_1 = 3420$ cm^{-1}, which is in good agreement with the literature data [25]). A considerable increase in ΔE_1 was obtained for bimolecular and termolecular exciplexes of *[Ru(bpy)$_3$]$^{2+}$ and *[Ru(phen)$_3$]$^{2+}$, which accompanied a decrease in ΔE_2 for bpy exciplexes and the appearance of $\Delta E_2 = 320$ cm^{-1} for the molecular phenanthroline exciplex. Interpretation of these effects postulates an overlap between the low-lying π^* level of one bpy or phen ligand, to which the electron is promoted, and the empty 5s orbital of the silver ion. Owing to this interaction, the MLCT excited state is stabilized. However, the formation of bimolecular and termolecular exciplexes from *[Ru(bpy)$_3$]$^{2+}$ also leads to a considerable decrease in the energy gap between the three lower-lying ^{3}MLCT state and the fourth MLCT state possessing strong singlet nature. This results in an increase in the rate of the non-radiative deactivation processes. In contrast to the *[Ru(bpy)$_3$]Ag^{3+}, only the MLCT states are stabilized for the bimolecular phenanthroline exciplex, hence the luminescence lifetime of *[Ru(phen)$_3$]Ag^{3+} is longer than that of the parent complex. The 'appearance' of the ΔE_2 value for the termolecular exciplex of *[Ru(phen)$_3$]$^{2+}$ suggests that the MLCT stabilization accompanies the 'opening' of a new channel for the photophysical deactivation, which is probably a transition to the fourth higher-lying MLCT.

It is interesting to note that the emission spectra of the exciplexes in water–acetonitrile solvent mixture are much less red-shifted with increasing [MeCN] relative to their spectra in water, which indicate a higher energy of exciplex in MeCN media than observed in pure water [7,8]. This remarkable effect may be attributed to the change of the solvent polarity resulting in a decrease in the solvation energy. Moreover, it can be regarded as experimental evidence that the exciplex stabilization by solvent polarity has an opposite tendency for the exciplex created by neutral molecules and the exciplex formed by two ionic species of similar sign of electric charge.

3. Exciplexes of dicyanocuprate(I) complex

It has been demonstrated recently, that the coordinatively unsaturated *Cu(CN)$_2^-$ formed upon UV irradiation in aqueous solutions of dicyanocuprate(I) associates with halide ions to create a longer-lived luminescent exciplex [14–17].

Steady-state luminescence studies indicate that as the halide ion concentration is increased, the very weak emission of the UV-excited dicyanocuprate peaking below 400 nm disappears, while a new, structureless emission emerges between 400 and 600 nm. The characteristic change in the intensity of this emission and in the luminescence lifetime with increasing halide ion concentration was found to be dependent on the nature of the halide ions. The 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 for chloride, bromide and iodide ion respectively (Fig. 4(a)). A similar feature was observed for luminescence lifetime vs. halide concentration data obtained by laser flash photolysis of nanosecond time-resolution (Fig. 4(b)). The features of these plots are reminiscent of those shown

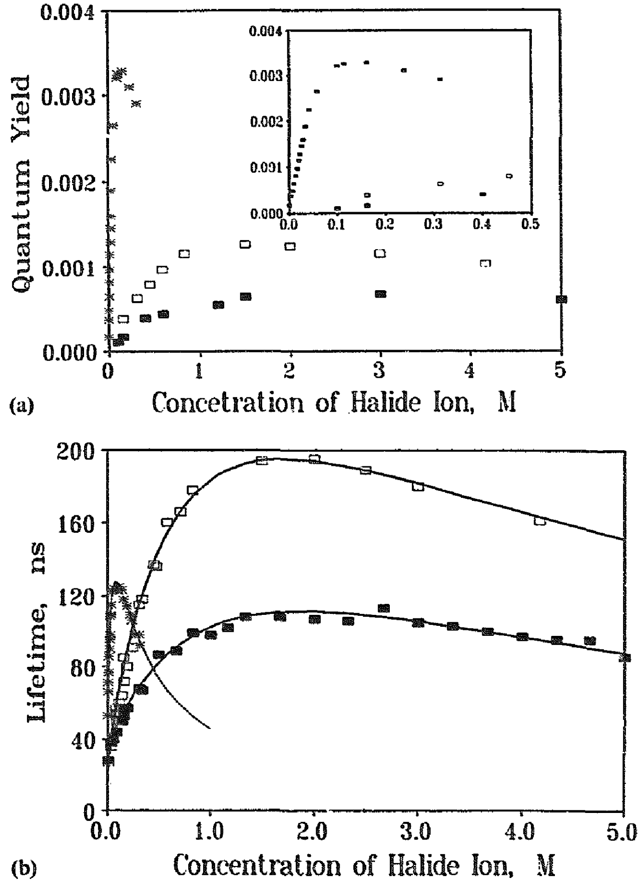
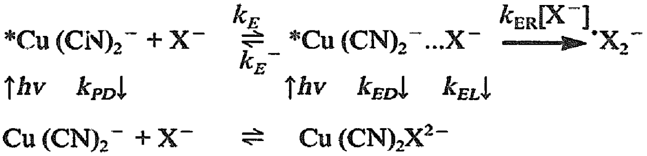


Fig. 4. Dependence of luminescence quantum yield (a) and lifetime (b) on halide ion concentration in aqueous solution of $[Cu(CN)_2]^-$–X^- systems at 5 M ionic strength and room temperature: X=Cl (■); X=Br (□); X=I (*) [15].

for the $[Ru(phen)_3]^{2+}$–Ag^+ system at different silver ion concentrations. However, in the dicyanocuprate(I)–halide ion systems, there is also association in the ground state. The stepwise formation constant for the ground state reaction is about one order of magnitude smaller than that of the excited state reaction. Hence the luminescence characteristics have been interpreted by a mechanism involving both ground and excited state equilibrium reactions (Scheme 1, where P = precursor of luminescent species, E = exciplex, D = non-radiative decay, L = luminescent decay, and R = reactive decay).



$$\begin{tikzcd}
{}^*Cu(CN)_2^- + X^- \arrow[r, shift left, "k_E"] \arrow[d, shift left, "k_{PD}"] & {}^*Cu(CN)_2^-...X^- \arrow[l, shift left, "k_{E^-}"] \arrow[r, "k_{ER}[X^-]"] \arrow[d, shift left, "k_{ED}"] \arrow[d, shift left=3, "k_{EL}"] & {}^{\bullet}X_2^- \\
Cu(CN)_2^- + X^- \arrow[u, shift left, "h\nu"] \arrow[r, shift left] & Cu(CN)_2X^{2-} \arrow[l, shift left] \arrow[u, shift left, "h\nu"] &
\end{tikzcd}$$

The general solution of such a coupled system gives a double-exponential function for the time dependence of the luminescent species. It has been proven that the exciplex forms in several nanoseconds or subnanoseconds, and the decay of exciplex, which is a slower process than the exciplex formation, obeys first-order kinetics with a lifetime depending on the halide ion concentration:

$$\tau = 2/\left\{(x+y) - [(x-y)^2 + 4k_E k_{E^-}[X^-]]^{1/2}\right\} \tag{13}$$

where $x = k_{PD} + k_E[X^-]$ and $y = k_{E^-} + k_{EL} + k_{ED} + k_{ER}[X^-]$. The rate constants involved in the mechanism were estimated by a procedure given elsewhere [15–17]. The results, summarized in Table 2, indicate that the values of k_E and k_{ER}, which are the rate constants for processes resulting in an increase of the coordination number of the excited metal center, vary significantly when changing the halo ion. The increasing value of k_E and K_{EX} with the polarizability of the ligand is especially pronounced in the case of iodide ions.

The exciplex luminescence lifetime is very sensitive to temperature. This behavior

Table 2
Rate constants and the formation constant of exciplex calculated from the τ vs. $[X^-]$ data measured at ambient temperature [15]

Rate constant	X = Cl	X = Br	X = I
$k_{PD} \times 10^{-7}$ (s^{-1})	6.6±0.4	6.3±0.8	7.2±1.1
$k_E \times 10^{-8}$ ($M^{-1}\,s^{-1}$)	2.6±0.2	14±1	78±4
$k_E^- \times 10^{-7}$ (s^{-1})	2.4±0.2	5.2±0.2	1.8±0.1
$k_{ED} \times 10^{-6}$ (s^{-1})	4.7±0.8	2.7±0.1	4.5±0.3
$k_{ESD} \times 10^{-6}$ (s^{-1})	1.1±0.2	0.7±0.1	17±1
K (M^{-1})	0.7±0.12	2.5±0.6	16±4
$K_{EX} = k_E/k^-_E$ (M^{-1})	11±3	27±4	430±40

permitted a reasonable estimation of the activation parameters of the rate constants involved in the exciplex model. The systematic measurement of exciplex emission lifetimes at varying halide ion concentrations and temperatures between 10 and 50 °C at 5 M ionic strength revealed a very small but negative activation enthalpy for exciplex formation (Table 3). This was regarded as further evidence of exciplex formation, since rather similar values were observed for other reactions resulting in an exciplex, e.g. the reactions between excited copper(I) bis-phenanthroline complexes [26] and Lewis bases in the ground state, and between the triplet excited $Ru(bpy)_3^{2+}$ and organic electron donor molecules [27]. The formation of the exciplex was favored by halide ions of higher polarizability (Table 3). Hence, it was concluded that the covalent part of the exciplex interaction is more effective than the electrostatic attraction between the halide ion and the metal center which is considered to be very similar to the Cu(II) after the CT excitation.

Transient spectroscopy and quenching studies confirmed the triplet nature of the luminescent species, $^*Cu(CN)_2X^{2-}$ [16]. The reaction of this triplet excited molecule with halide ion results in the formation of $^{\cdot}X_2^-$. In principle, the reaction can proceed by two different mechanisms: (1) the second halide ion can coordinate to the metal center and an electron transfers to the d^9 orbital of the copper atom, which is followed by the formation of $^{\cdot}X_2^-$ within the coordination sphere; (2) the second halide ion directly attacks the halide ligand coordinated to the copper atom. Irrespective of whether the first or the second mechanism is valid, the short lived $^*Cu(CN)_2X_2^{3-}$ can be regarded as a termolecular exciplex.

The quenching experiments also illustrated that $^*Cu(CN)_2X^{2-}$ can act both as an electron donor, when methylviologen is used as quencher, and as an electron acceptor, in a reaction with halide ion at high concentration [16]. It can also transfer energy to another molecule.

The sensitivity of exciplex luminescence to the solvent nature [17] and the large Stokes shift [15] strongly suggest that the geometric relaxation of the excited state can be a very important factor in influencing the lifetime.

The ionic strength effect on the luminescence dynamics is demonstrated by Fig. 5. The shape of the τ vs. iodide ion concentration curves shows the characteristic

Table 3
Thermodynamic parameters of exciplex formation in $Cu(CN)_2^-$–X^- systems in aqueous solutions at 298 K

X	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
Cl	-7^a	-20^a	-44^a
Br	-8^a	-23^a	-52^a
I	-15^a -11^b -7^c	-34^a	-61^a

Estimated errors; ±6 kJ mol^{-1} for ΔH and ±15 J mol^{-1} K^{-1}: [a] measured at 5 M ionic strength; [b]measured at 2.5 M ionic strength; [c] measured at 0.5 M ionic strength.

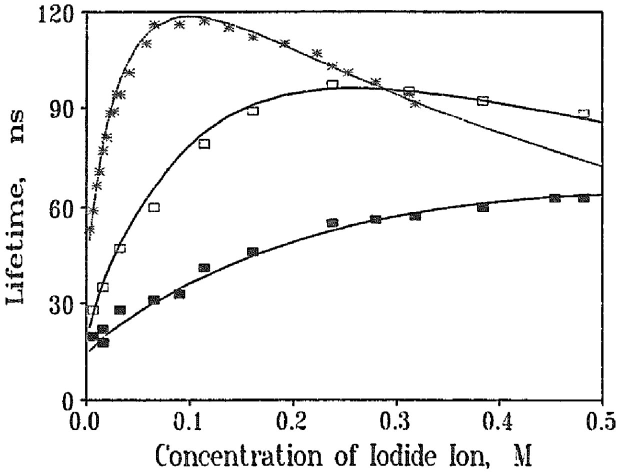


Fig. 5. Influence of ionic strength on luminescence lifetime vs. iodide ion concentration in aqueous solution of dicyanocuprate at ambient temperature, $\lambda_{exc}=266$ nm: $\mu=0.5$ M (■); $\mu=2.5$ M (□); $\mu=5.0$ M (*) [17].

behavior of the system. The maximum value and the initial slope of the curves dramatically increase with ionic strength, which is consistent with a shift of the peak to the lower concentrations of iodide ion. The free energy of exciplex formation, which was estimated through the stepwise formation constant by the procedure described above, confirms the important role of the solvent medium. Owing to the strongly organized solvent structure at high ionic strength, the decrease in entropy caused by coordination of the iodide ion to the metal center of the excited dicyanocuprate can be comparable with the increase of the entropy originating from the increase in the disorder of the medium.

4. Conclusions

This study, which summarizes and compares the most important properties of the recently discovered two prominent groups of TMCEs, has elucidated some common behavior of the TMCEs, although the exciplex constituents of the two groups and their interaction have a rather different nature.

The excited transition metal complex, which can be attacked either on the ligand possessing the electron promoted by the MLCT excitation to the antibonding ligand orbital, such as $^*[Ru(L)_3]^{2+}$ complexes, or on the excited metal center, as in the case of $^*[Cu(CN)_2]^-$, can form bimolecular and termolecular exciplexes with mononuclear ground state ions.

The exciplex stabilization originates from the overlap of the diffuse orbitals of the exciplex constituents: π^* ligand orbital and the empty s orbital of the silver ion overlap in ruthenium(II) exciplexes, and it is reasonable to suppose an interaction between the $4s^1$ orbital of the excited copper complex and the empty d orbital of the halide ion. It should be noted that the coordination of the halide ion to $^*Cu(CN)_2^-$ is also forced by the interaction between the unfilled d orbital of the central copper atom and the σ donor orbital of the halide ion.

The ionic strength and the solvent polarity are very important factors in the kinetics and energetics of the exciplex formation. The increase in shielding of a charged species due to an increase either in the ionic strength or in the solvent polarity can lead to a considerable change in the rate constant for exciplex formation. The excitation of a molecule in a strongly organized media, such as an aqueous solution of high ionic strength, results in an increase of disordering in the environment of the excited molecule. Hence the entropy of exciplex formation can be increased by ionic strength.

The experiences of this study strongly suggest that exciplexes having constituents of similar electric charge can play very important roles in biochemical and biological systems.

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