ELSEVIER

The effect of H/D-bond solute–solvent interaction on deactivation channels of MLCT excited state of $[Ru(bpy)(CN)_4]^{2-}$

Margit Kovács, Attila Horváth*

Department of General and Inorganic Chemistry, University of Veszprém, P.O.B. 158, Veszprém H-8201, Hungary

Abstract

Photophysics of $[Ru(bpy)(CN)_4]^{2-}$ (bpy = 2,2′-bipyridine) in CH_3OH, CH_3OD, CD_3OD, and CH_3OH/C_2H_5OH and CH_3OD/C_2H_5OD solvent mixtures has been investigated by steady state and time-resolved techniques at various temperatures. The Franck–Condon analysis of the emission spectra observed between 80 and 165 K indicates similar and significant decrease in energy of the luminescent excited state (E_{0-0}) and a small difference in the increasing solvent reorganizational energies for solvent mixtures of CH_3OH/C_2H_5OH and CH_3OD/C_2H_5OD, respectively. The rate of non-radiative (k_{nr}) and radiative decay (k_{phos}) to the ground state and the parameters of thermally activated deactivation pathways (A_{4th}, ΔE_{4th} and A_{dd}, ΔE_{dd}) have been determined between 250 and 330 K in CH_3OH, CH_3OD and CD_3OD. The rate of phosphorescence and apparent activation energy of temperature dependent deactivations are not sensitive to the replacement of H to D, while the k_{nr} and the pre-exponential factor of thermally activated decay through the 4th MLCT state decreases with the replacement of H to D in the OH group of the solvent. The deuteriation of the methyl group in the solvent results in a small change of k_{nr}. The results provide further experimental evidence of the hydrogen-bond determined specific solvent–solute interaction playing important role in the decay of the lowest energy MLCT excited state of $[Ru(LL)(CN)_4]^{2-}$ complexes.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Ruthenium(II) complex; MLCT excited state; Photophysics; Specific solute–solvent interaction

1. Introduction

The photophysics of polypyridyl complexes of d^6 metal centers continue to be of great interest due to their applicability in the design and construct of supramolecular systems for conversion of solar energy to chemical energy and for constructing molecular-scale electronic devices [1–8]. Their spectroscopic properties are dominated by low energy metal-to-ligand charge transfer (MLCT) tunable by changing σ-donor and π-acceptor characteristics of the polypyridil ligands [6]. These complexes are very useful probes for revealing various solvent effects [9]. A consecutive replacement of one diimine ligand (LL) of the $[Ru(LL)_3]^{2+}$ complexes with two simple inorganic ligands such as CN^- yields a series of complexes $[Ru(LL)_3]^{2+}$, $[Ru(LL)_2(CN)_2]$ and $[Ru(LL)(CN)_4]^{2-}$ [10,11]. The more cyanide ions are coordinated to the Ru(II) the shorter is the lifetime of the excited complex and the smaller is their luminescence quantum yield, that predicts an increase in the rate of the non-radiative decay channels by replacement of one bpy to two CN^-. A

considerable blue shift in both absorption and emission spectra of this series is also observed [10,12]. The shift is more pronounced in the absorption than in the emission spectra. The MLCT excitation induces a significant change in electronic distribution inside the complex resulting in the reorganization of the surrounding solvent molecules. The energetic and dynamics of this motion is usually treated by the dielectric continuum model of Marcus. According to this model, the energy of an electronic transition is solvent dependent because of the solvation energies are different in the ground and in the excited states. The mixed ligand cyano complexes are very sensitive for donor–acceptor properties of solvents [12]. The position of the low-lying MLCT absorption band of $[Ru(LL)(CN)_4]^{2-}$ complexes in the visible range is strongly depends on the acceptor number (AN) of the solvent, which is attributed to the second sphere donor–acceptor interaction between the amphidentate cyanide ligand and the solvent molecule. If the solvent is participating in such a specific solvent–solute interaction breaking down of the dielectric continuum model is expected [9].

In our previous paper, the effects of diimine ligand and the replacement of water with D_2O on the photophysics of some $[Ru(LL)(CN)_4]^{2-}$ complexes have been demonstrated [13]. Analysis of steady state and time resolved emission

* Corresponding author. Tel.: +36-88-422022/4341;
fax: +36-88-427915.
E-mail address: attila@vegic.sol.vein.hu (A. Horváth).

spectra and the decay kinetics has revealed that the interaction between the complex and the solvent molecule through H or D bond is an important factor that strongly influences the rate of the non-radiative deactivation pathways. The experiments presented and discussed in this contribution extend these studies using CH_3OH, CH_3OD and CD_3OD as solvents in liquid phase and $CH_3OH–C_2H_5OH$ and $CH_3OD–C_2H_5OD$ solvent mixtures in glass and fluid state, respectively. The results provide further evidence for $O–H \cdots NC–Ru$ or $O–D \cdots NC–Ru$ induced perturbation of electronic excited state decay processes.

2. Experimental

2.1. Materials

High purity CH_3OH, CH_3OD, CD_3OD and D_2O were purchased from Aldrich and were used without further purification. The double distilled water was purified by a Millipore Super-Q system.

$K_2[Ru(bpy)(CN)_4]\cdot2H_2O$ (bpy = 2,2′-bipyridine) was synthesized by the method published by Jiwan et al. [14]. The complex was checked by H NMR, IR and UV-Vis spectroscopy and the results of these experiments match those reported in the literature [15,16].

2.2. Apparatus and measurements

The absorption spectra were measured on a Specord S100 diode array UV-Vis spectrophotometer. Luminescence excitation and emission spectra were recorded on a Perkin-Elmer LS50B spectrofluorimeter and were corrected for the detector sensitivity. For low temperature measurements, a luminescence accessory of Perkin-Elmer (L2250136) was applied. The temperature of the sample was measured by Cole Palmer Digi Sense thermocouple thermometer. Steady state luminescence measurements for the samples of liquid phase were carried out in optical thin solution and $Ru(bpy)_3^{2+}$ ($\Phi = 0.042$ in water [17] and $\Phi = 0.376$ in methanol–ethanol mixture (1/4) at 77 K [18]) was used as reference emitter. The quantum yields were determined by using the following equation [19]:

$$\Phi_s = \Phi_{ref} \frac{I_s}{I_{ref}} \frac{F_{ref}}{F_s} \left(\frac{n_s}{n_{ref}}\right)^2 \qquad (1)$$

Where Φ_s is the radiative quantum yield of the sample, Φ_{ref} is the radiative quantum yield of the reference emitter, I_s and I_{ref} are the integrated emission intensities of the sample and the standard, respectively, F_s and F_{ref} are the absorbed light fraction of the sample and the standard, respectively at the excitation wavelength and n_s and n_{ref} are the refraction indices of the sample and the standard solution. The luminescence lifetimes were measured by a laser flash photolysis system described elsewhere [20]. All photophys-

ical measurements (Φ, τ) were carried out on deoxygenated samples.

2.3. Fitting procedures

A single mode Franck–Condon analysis were performed on emission spectra measured at low temperature using the theoretical equation [21–24] that calculates the emission spectrum as a sum of individual Gaussians corresponding to vertical transitions between the excited state and the vibrational levels of the ground state:

$$I(\nu) = \sum_{\nu_M=0}^{N} \left(\frac{E_{0–0} - \nu_M \hbar \omega_M}{E_{0–0}}\right)^3 \frac{S_M^{\nu_M}}{\nu_M!}$$

$$\times \exp\left[-4(\ln 2)\left(\frac{\nu - E_{0–0} + \nu_M \hbar \omega_M}{\Delta \bar{\nu}_{1/2}}\right)^2\right] \qquad (2)$$

In the above equation, $E_{0–0}$ is the energy difference between the $\nu_M^* = 0$ level of the excited and the $\nu_M = 0$ level of the ground state, where ν_M^* and ν_M are the vibrational quantum numbers of the excited and the ground state respectively, $\hbar \varpi_M$ is the vibrational spacing between the medium frequency promoting modes, which can be assigned as the aromatic ring stretching modes for Ru(II) diimine complexes [25]. S_M is the electron-vibrational coupling constant or Huang–Rhys factor for the combined modes and $\Delta \bar{\nu}_{1/2}$ is the half width of the individual transitions and and $\hbar = h/2\pi$ where h is the Planck constant.

The procedure involving Marquard method for multiparameter minimization gave reasonable fitting. The parameter sets obtained are considered as independent values according to the correlation matrix of the fit and the solutions are the global minimum of the problem.

The lifetimes measured for luminescent species at various conditions were estimated by a single exponential fitting.

3. Results and discussion

3.1. Absorption and emission spectra detected in water and in MeOH

UV-Vis absorption and emission spectra of [Ru(bpy)(CN)_4]^{2-} in water and in MeOH are shown in Fig. 1. Spectra and spectral assignments for the complex in various solvents have been reported [11–13,26]. The visible absorption spectra dominated by $t_{2g} \rightarrow \pi^*$ MLCT transitions with a $\lambda_{max} = 400$ nm in water. This band shifts to 445 nm in MeOH. The maximum of the higher energy MLCT band appears at 325 nm in MeOH which is observed as a shoulder of the intense intraligand $\pi \rightarrow \pi^*$ transition in the UV range (300 nm) in water.

The figure clearly demonstrates that the solvent dependence is quite large for MLCT absorption bands. It is smaller for the emission band ($^3\pi^* \rightarrow t_{2g}$) and rather small

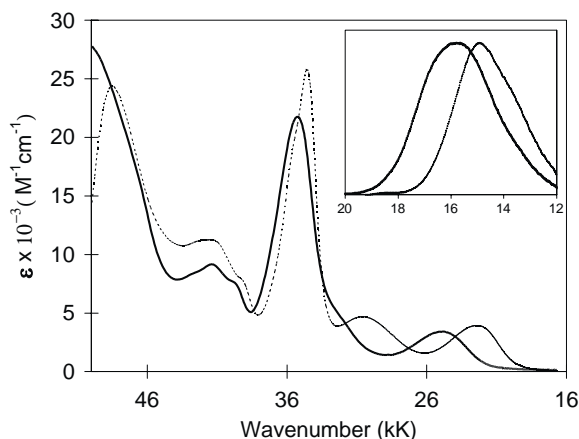Fig. 1. Absorption and emission spectra (inset) of $[Ru(bpy)(CN)_4]^{2-}$ in water (solid line) and MeOH (dashed line) at ambient temperature.

for intraligand transition ($\pi \rightarrow \pi^*$). As it has been pointed out [12], there is a strong correlation between the acceptor number of the solvent and the energy of the transitions (both $t_{2g} \rightarrow {}^1\pi$ and ${}^3\pi^* \rightarrow t_{2g}$), with a more pronounced dependence of the absorption bands than the emission band. It is considered as an indication of the difference in basicity of the complex in the ground and in the excited state, respectively [27,28]. Because of the $[Ru(bpy)(CN)_4]^{2-}$ complex is a stronger base than ${}^{3*}[Ru(bpy)(CN)_4]^{2-}$, the excitation leads to the decrease in the interaction between the nitrogen atom of the coordinated cyanide ligands and the solvent molecules via hydrogen bond [27].

The transient absorption spectra obtained by excitation at 450 nm in MeOH (Fig. 2) is quite similar to that was reported for aqueous solution of this complex [11] and for $Ru(bpy)_3^{2+}$ [28–32]. A very strong absorption band peaks at 370 nm and possesses a shoulder at 350 nm.

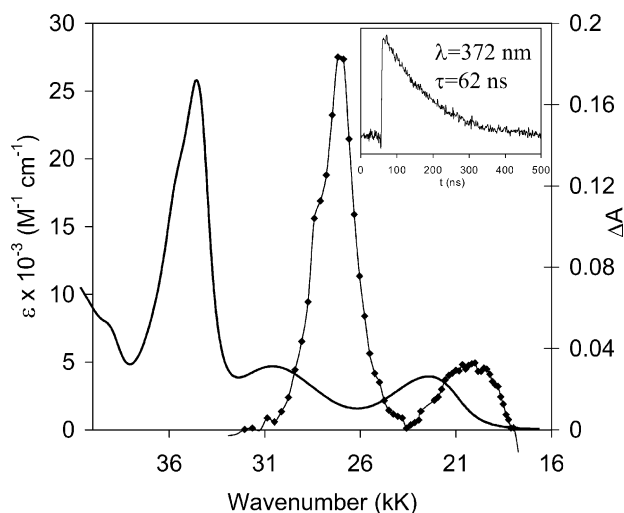Fig. 2. The absorption spectra of $[Ru(bpy)(CN)_4]^{2-}$ and the transient absorption spectra of the complex (●) in MeOD detected by the excitation of a laser pulse ($\lambda_{exc} = 450$ nm, 10 mJ and 5 ns halfwidth), with a 75 ns delay and a transient decay (inset).

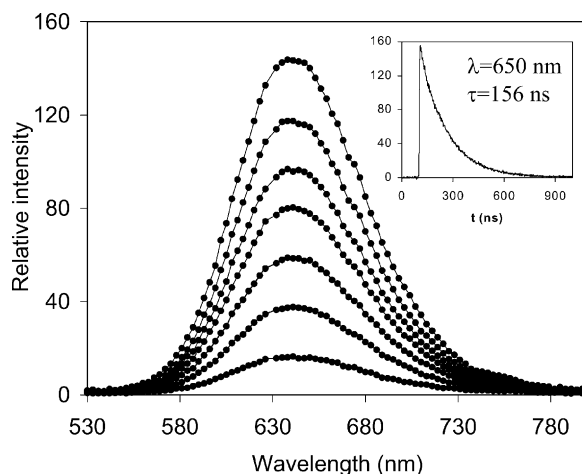Fig. 3. Time-resolved emission spectra of ${}^{3*}[Ru(bpy)(CN)_4]^{2-}$ detected in MEOD at 254 K. The inset shows a decay curve detected at 650 nm.

The shape of this absorption is like that of having absorption maximum at 285 nm for the ground state complex and assigned as $\pi \rightarrow \pi^*$ transition localized on diimine ligand. Hence this transient absorption is considered as a result of $\pi \rightarrow \pi^*$ transition within the ^{3}MLCT excited state. Another absorption appears between 430 and 550 nm. This relatively broad band is more intense in MeOH than in water and it has smaller molar absorbance than the higher energy absorption band of the triplet excited state. A transient decay observed is depicted in the inset of Fig. 2. The fitting procedure using a single exponential decay to all transient curves resulted in a lifetime of 62 ± 4 ns for the excited species which is identical to the data obtained by luminescence measurements.

Fig. 3 demonstrates the time resolved emission spectra detected at 254 K in MeOD. The inset shows a luminescence decay curve detected at the maximum of the emission spectrum. The lifetime determined using all transient signals obtained between 600 and 700 nm is 156 ± 8 ns, which is rather long compared to the lifetime measured at room temperature in MeOH.

3.2. Characteristics of emission spectra detected in glass and fluid state of MeOH/EtOH and MeOD/EtOD

Significant enhancement of the emission spectra is detected when the MeOH/EtOH ($\Phi = 0.200$) solvent is replaced by MeOD/EtOD mixture ($\Phi = 0.254$) at 77 K. The single mode Franck–Condon analysis of the spectra of $[Ru(bpy)(CN)_4]^{2-}$ detected in both solvent mixtures for temperatures ranged from 77 to 165 K has been performed and the results have been compared to that was obtained for $Ru(bpy)_3^{2+}$ measured in MeOH/EtOH solvent [33]. Fig. 4 shows the temperature dependence of E_{0-0} in the range of 80–165 K. The data indicate a drastic red shift of the emission maximum occurring between 90 and 130 K in both solvent mixtures, which is in accordance with the results of Hirota et al. obtained in MeOH/EtOH and it was attributed
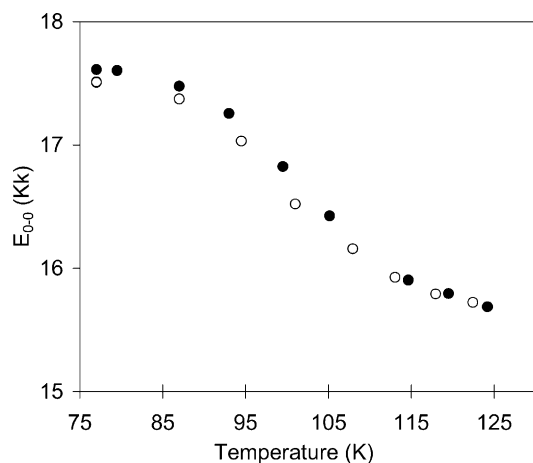
Fig. 4. Plots of the E_{0-0} vs. temperature for $[Ru(L)(CN)_4]^{2-}$ in CH_3OH/C_2H_5OH (○) and CH_3OD/C_2H_5OD (●) mixtures.

Fig. 5. Temperature dependence of the lifetime of the luminescent species generated by the MLCT excitation of $[Ru(L)(CN)_4]^{2-}$ in various solvents: CH_3OH (■), CH_3OD (△) and CD_3OD (○).

to the transition from the glass to the fluid state [26]. In these conditions, the change in the energy for $[Ru(bpy)_3]^{2+}$ is smaller than that of for $[Ru(bpy)(CN)_4]^{2-}$. On the other hand, there is a very small difference in data for tetracyano complex determined in normal and deuteriated alcohol mixtures confirming that the energy gap is not influenced by the deuteriation of the solvent.

In the same temperature range, the bandwidth ($\Delta \nu_{1/2}$) of the emission spectra increases and its fine structure continuously disappears when transition from a glassy to a fluid state occurs. The change in $\Delta \nu_{1/2}$ is somewhat smaller in deuteriated solvent that suggest a little difference in the increasing of the solvent reorganizational energy through the glass to fluid transition for normal and deuteriated solvent mixtures, respectively.

3.3. Decay parameters measured in CH_3OH, CH_3OD and CD_3OD in liquid phase

The temperature-dependent lifetime measurements are consistent with the earlier results revealed for this and other Ru(II) complexes. The lowest-lying MLCT excited state is actually manifold of three closely spaced states of common $d\pi-\pi^*(pp)$ MLCT orbital parentage possessing largely triplet in character. These states are in rapid Boltzmann equilibrium and can decay to the ground state by non-radiative process, by phosphorescence and by thermally activated processes through the 4^{th}MLCT state contaminated by some singlet character or through the metal centered ^3d-d state. Hence the lifetimes measured at various temperatures (250–310 K) can be estimated by the following equation:

$$\tau = \frac{1 + \exp(-\Delta E_{4th}/k_B T) + \exp(-\Delta E_{dd}/k_B T)}{k_d + A_{4th} \exp(-\Delta E_{4th}/k_B T) + A_{dd} \exp(-\Delta E_{dd}/k_B T)} \tag{3}$$

where τ is the lifetime of the luminescent species, $k_d = k_{nr} + k_{phos}$ where k_{nr} is the rate constant for the non-radiative
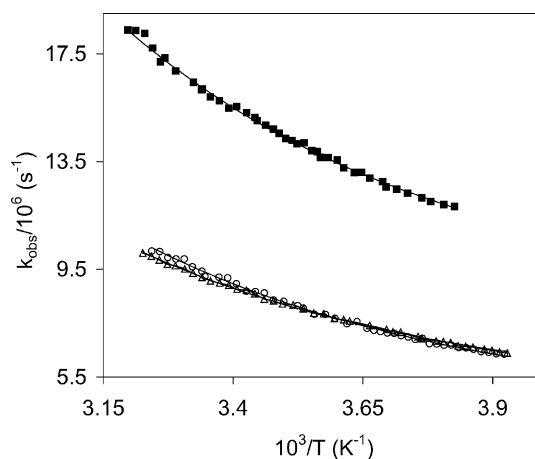
decay and k_{phos} is the rate constants for the phosphorescence determined by the ratio of luminescence quantum yield and lifetime $k_{phos} = \Phi_{ph}/\tau$, k_B is the Boltzmann constant, T is the temperature, A_{4th} and ΔE_{4th} are the parameters of the temperature dependent deactivation through the 4^{th}MLCT state and A_{dd} and ΔE_d are the parameters of the temperature dependent deactivation through dd state. The rate of radiative decay is smaller in MeOH than in water, which is in accordance with the expectation of Einstein law for spontaneous emission. The temperature dependence of lifetimes measured at various solvents is depicted in Fig. 5.

The fitting procedure using Eq. (3) resulted in parameters of relatively high uncertainties. Therefore, first we estimated only one potential barrier instead of two:

$$\tau = \frac{1 + \exp(-\Delta E/k_B T)}{k_d + A \exp(-\Delta E/k_B T)} \tag{4}$$

Using this equation the values of k_d, ΔE and A were obtained by the fitting procedure. The rate of radiative decay was calculated by the ratio of luminescence quantum yield and the lifetime of the luminescent species determined by independent measurements performed at 25 °C. The results are given in Table 1 in which data obtained for aqueous solution and D_2O solution are also presented. To compare the deuteriation effect some relevant data of $[Ru(bpy)_3]^{2-}$ are also demonstrated.

The potential barriers are $1150 \pm 50\,cm^{-1}$ suggesting that ΔE does not depend on the nature of protic solvent and its deuteriation. On the other hand, the preexponential factor is sensitive for solvent deuteriation $(18.2–11.0) \times 10^8\,s^{-1}$ and for the replacement of solvent from methanol to water $(18.2–6.4) \times 10^8\,s^{-1}$. In addition, the rate of nonradiative decay is also influenced by solvent deuteriation $(78.9–41.9) \times 10^5$ and by the exchange of methanol to water $(78.9–42.0) \times 10^5$. The energy gap law predicts the latter observation. The ΔE and A parameters are intermediate between those characteristic for two pathways

Table 1
Photophysical parameters for $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)(CN)_4]$ determined in various solvents at 25 °C

Complex	Solvent	Φ_{ph}	$k_{ph} \times 10^{-4}$ (s^{-1})	$k_{nr} \times 10^{-5}$ (s^{-1})	$A \times 10^{-8}$ (s^{-1})	ΔE (cm^{-1})
$[Ru(bpy)(CN)_4]^{2-}$	H_2O	0.0076	6.3 ± 0.5	42 ± 3	6.4 ± 1.0	1010 ± 50
	D_2O	0.028	7.6 ± 0.5	9.9 ± 0.7	4.2 ± 0.6	1150 ± 40
	CH_3OH	0.0022	3.6 ± 0.3	78.9	18.2 ± 2.8	1120 ± 50
	CH_3OD	0.0040	3.6 ± 0.3	46.9	11.1 ± 1.2	1150 ± 40
	CD_3OD	0.0040	3.7 ± 0.4	41.9	11.1 ± 1.4	1120 ± 45
$[Ru(bpy)_3]^{2+a}$	H_2O	0.042	6.94	12.22	10^5	3559
	D_2O	0.07	6.80	5.67	10^5	3568

[a] Data from [17].

involved into Eq. (3) and determined by various authors for different ruthenium(II) complexes. It has been pointed out by Meyer et al. that the ^{3}MLCT-^{3}dd energy gap derived from temperature-dependent lifetimes of Ruthenium(II) diimine complexes fall in the ranges 2100–4000 cm^{-1} with pre-exponential factors of 10^{12}–10^{14} s^{-1} [21,34–36]. On the other hand, study of Ru(bpy)$_3^{2+}$ incorporated into a dry rigid cellulose acetate film revealed a temperature-dependent deactivation channel characterized by 810 ± 120 cm^{-1} energy gap and 1.7×10^7 s^{-1} frequency [37]. In addition, there is direct spectroscopic evidence for an additional MLCT state of $[Ru(bpy)_3]^{2+}$ appearing at 650 ± 130 cm^{-1} above the low lying three MLCT states [38]. Sykora et al. investigated the temperature dependence of the lifetime for a series of ruthenium(II) complexes containing bipyrazine and substituted bipyridine ligands in propylene carbonate [39]. Using Eq. (4), they estimated 1400 cm^1 $< \Delta E < 1860$ cm^{-1} with pre-exponential factors of 1.9×10^8–1.3×10^9 s^{-1} for three different complexes. By extending the temperature range, very good fitting was obtained using equation consists of two thermally independent (k_{ph} and k_{nr}) and two thermally activated deactivation channels. The rate of the latter two pathways are determined by the pre-exponential factor and activation energy. This procedure resulted in $A_{4th} = 8 \times 10^6$ s^{-1} with $\Delta E_{4th} = 706$–736 cm^{-1} and $A_{dd} = 9 \times 10^{13}$–$1.4 \times 10^{14}$ s^{-1} with $\Delta E_{dd} = 4632$–4720 cm^{-1}. Our data derived by fitting of Eq. (4) to temperature dependent lifetimes are very similar to that was obtained by Sykora et al. for Ru(bpz)$_2$(dmb)$^{2+}$, Ru(bpz)$_2$(dmb)$^{2+}$ and Ru(bpz)$_2$(bpy)$^{2+}$ complexes (bpz = 2,2'-bipyrazine, dmb = 4,4'-dimethyl-2,2'-bipyridine). Hence it is reasonable to assume two different temperature dependent deactivation channels for $[Ru(bpy)(CN)_4]^{2-}$ complex, which can be predicted by other experimental data.

Regarding the first temperature dependent decay, the low temperature measurements of Hirota et al. [26] pointed out that the luminescent state of $[Ru(bpy)(CN)_4]^{2-}$ actually consists of a manifold of three closely spaced states ($\Delta E_{2-1} = 8$ cm^{-1} and $\Delta E_{3-1} = 53$ cm^{-1}) similarly to that was revealed for $[Ru(bpy)_3]^{2+}$ by Crosby and co-workers [40,41] ($\Delta E_{2-1} = 11$ cm^{-1} and $\Delta E_{3-1} = 61.2$ cm^{-1}) and by Hirota et al. ($\Delta E_{2-1} = 11$ cm^{-1} and $\Delta E_{3-1} = 59$ cm^{-1}). Considering the similarities in the electronic structure of $[Ru(bpy)(CN)_4]^{2-}$ and $[Ru(bpy)_3]^{2+}$ complexes, the nearly same differences between their three low lying triplet MLCT states and the energy barrier between the ^{3}MLCT and 4thMLCT of $[Ru(bpy)_3]^{2+}$ a $\Delta E_{4th} = 610$–850 cm^{-1} can be predicted for tetracyano complex.

On the other hand, for the second temperature dependent decay, as the cyanide ligand has stronger field than bpy an increase in ligand field splitting between t$_{2g}$ and e$_g^*$ is expected by the replacement of two bpy with four cyanides. For the energy barrier between the ^{3}MLCT and ^{3}dd 3560 cm^{-1} [21] and 3665 cm^{-1} [42] were found in aqueous solution at room temperature, hence it is reasonable to assume a $\Delta E_{dd} > 3700$ cm^{-1} for $[Ru(bpy)(CN)_4]^{2-}$.

Although the temperature range is limited for methanol as solvent we have made an estimation for k_d, A_{4th}, ΔE_{4th} and ΔE_{dd} by fitting Eq. (3) to temperature dependent lifetime data and by keeping A_{dd} as constant (1.5×10^{14}). The data (Table 2) resulted in by this procedure confirm the sensitivity of k_d and A_{4th} to deuteriation of solvent OH group. The efficiency of the deactivation by thermally independent channels decreases from 0.54 to 0.33 between 255 and 310 K while the efficiency of the process through 4thMLCT increases from 0.45 to 0.61. It means that the second thermally dependent decay pathway has very small efficiency (~ 0.01) at 255 K, and it reaches only 0.04–0.09 value at 310 K as it

Table 2
Photophysical parameters estimated by fitting Eq. (3) to temperature dependent lifetime data and using quantum yield data measured at various temperature

Solvent	$k_{ph} \times 10^{-4}$ (s^{-1})	$k_{nr} \times 10^{-6}$ (s^{-1})	$A_{4th} \times 10^{-8}$ (s^{-1})	ΔE_{4th} (cm^{-1})	$A_{dd} \times 10^{-14}$ (s^{-1})	ΔE_{dd} (cm^{-1})
CH_3OH	3.8 ± 0.3	6.04	4.85	790	1.5	4100
CH_3OD	4.2 ± 0.3	3.50	2.50	788	1.5	4260
CD_3OD	4.3 ± 0.4	3.54	2.55	791	1.5	4060

has been predicted by the reasonable good fitting obtained by the Eq. (4).

It is important to note that those two deactivation channels are found to be sensitive to the solvent deuteration, which involve states coupled weakly with the ^{3}MLCT excited state. For nonradiative decay, the excess energy of the excited state is channeled into the acceptor modes of complex and solvent. The dominance of medium frequency acceptor mode (or average mode) in this process is generally accepted for ruthenium(II) diimine complexes and the rate constant k_{nr} for $\hbar\omega = \hbar\omega'$ and for $\hbar\omega \gg k_B T$ is given by Eq. (5) [9] in which the solvent is treated classically.

$$k_{nr} = \frac{2\pi}{\hbar} \frac{V_k}{(4\pi\lambda_0 RT)^{1/2}} \sum_{v'} \exp(-S_M) \frac{S_M^{v'}}{v'!}$$
$$\times \exp\left[-\frac{(|\Delta G^0| - v\hbar\omega - \lambda_0)^2}{4\lambda_0 RT}\right] \quad (5)$$

In this equation, V_k is the vibrationally induced electronic coupling matrix element, λ_0 is the solvent reorganizational energy and ΔG^0 is the free energy change of the process. The energy gap law from Eq. (5) with $E_0 = (\Delta G^0 - \lambda_0) \gg S\hbar\omega$ and $\hbar\omega \gg k_B T$ is given by

$$k_{nr} = \frac{\pi\omega_k C_k^2}{(2\pi\hbar\omega E_0)^{1/2}} \exp\left[-S - \frac{\gamma E_0}{\hbar\omega} + \left(\frac{\gamma+1}{\hbar\varpi}\right)^2 \lambda_0 k_B T\right]$$
$$(6)$$

where $C_k = V_k(2/\hbar\omega_k)^{1/2}$ and $\gamma = \ln(E_0/S\hbar\omega) - 1$. The Franck–Condon analysis of the emission spectra indicate that the deuteration of the solvent OH group does not lead to significant change either in the energy gap and in the electron vibration coupling constant or in the solvent reorganizational energy. Hence a considerable decrease in electronic coupling term C_k due to the solvent deuteration is concluded. For Ru(II) diimine complexes a quite large spin-orbit coupling has been proved. Thus, the electronic states have substantial contributions from both singlet and triplet components and all states should interconvert quite rapidly without significant problems in intersystem crossing. The influence of solvent deuteration on this coupling can be excluded. On the other hand, the effect on the vibrationally induced electronic coupling matrix element (V_k) is expected. A reasonable mechanism for the coupling of solvent modes to excited decay has been suggested by Claude et al. for fac-[Re(bpy)(4-Etpy)(CO)$_3$] complex (4-Etpy = 4-ethylpyridine) [33]. Such a mechanism can be adapted for [Ru(bpy)(CN)$_4$]$^{2-}$. The solvent molecules are hydrogen bounded to the nitrogen atom of the coordinated cyanide ligands. This specific solvent–solute interaction provides a mechanism for coupling the quantum modes of the complex with the stretching and banding modes of the solvent. The stretching modes of CN$^-$ is coupled with the vibration modes of the bpy through the back bonding of the dπ(t$_{2g}$) orbitals of the metal center, because of these metal orbital overlap with π^* orbitals of both the diimine and the
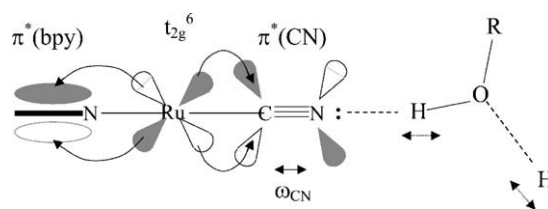
Scheme 1.

cyanide ligands (Scheme 1). In the ground state, there is a strong back bonding to the cyanide ligand resulting in a decrease in the ν_{CN} and the increase in the donor strength of the nitrogen atom related to that of the free CN$^-$. On the other hand, the formation of the hydrogen bond between the solvent and the coordinated cyanide ligand results in an increase of ν_{CN} which influences the vibration modes of bpy via interaction of dπ(t$_{2g}$) with π^* orbitals of both bpy and CN$^-$. In the MLCT excited state, Ru^{III}(bpy$^{\bullet-}$) leads to an increase of the dσ character of the Ru–CN bond and its polarization to the metal center. Due to the hole in dπ(Ru) created by the excitation the dπ–π^*(CN) back bonding decreases resulting in an increase of the ν_{CN}.

4. Conclusions

The results presented in this contribution provide further experimental evidence of the hydrogen-bond determined specific solvent–solute interaction controlling the decay of the lowest energy MLCT excited state of [Ru(LL)(CN)$_4$]$^{2-}$ complexes. Scheme 1 illustrates a reasonable mechanism for coupling the solvent modes with the quantum modes of the complex. The vibration modes of the solvent molecules coupled through the hydrogen bond between the nitrogen atom of the coordinated cyanide ligand and the solvent molecule leads to a perturbation on the electronic coupling matrix element.

References

[1] D.J. Stufkens, A. Vlcek Jr., Coord. Chem. Rev. 177 (1998) 127.
[2] K. Kalyanasundaram, Photochemistry of Polypyridine and Porphyrin Complexes, Academic Press, New York, 1992.
[3] A. Juris, P. Belser, A. von Zelewsky, F. Barigeletti, V. Balzani, Coord. Chem. Rev. 84 (1988) 85.
[4] E.M. Kober, B.P. Sullivan, W.J. Dressick, J.V. Caspar, T.J. Meyer, J. Am. Chem. Soc. 102 (1980) 7385.
[5] K. Kalyanasundaram, M. Graetzel, Coord. Chem. Rev. 177 (1998) 347.

[6] V. Balzani, A. Juris, Coord. Chem. Rev. 211 (2001) 97.

[7] R. Amadelli, R. Argazzi, C.A. Bignozzi, F. Scandola, V. Balzani, J. Am. Chem. Soc. 121 (1999) 4207.

[8] V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, Acc. Chem. Res. 31 (1998) 26.

[9] P. Chen, T.J. Meyer, Chem. Rev. 98 (1998) 1439.

[10] J.N. Demas, J.W. Addington, S.H. Peterson, E.W. Harris, J. Phys. Chem. 81 (1977) 1039.

[11] C.A. Bignozzi, C. Chiorboli, M.T. Indelli, M.A. Rampi Scandola, G. Varani, F. Scandola, J. Am. Chem. Soc. 108 (1986) 7872.

[12] C.J. Timpson, C.A. Bignozzi, B.P. Sullivan, E.M. Kober, T.J. Meyer, J. Phys. Chem. 100 (1996) 2915.

[13] M. Kovács, A. Horváth, Inorg. Chim. Acta 335 (2002) 69.

[14] J.H. Jiwan, B. Wegenijs, M.T. Indelli, F. Scandola, S.E. Braslavsky, Recl. Trav. Chim. Pays-Bas 114 (1995) 542.

[15] M.A. Rampi, M.T. Indelli, F. Scandola, F. Pina, A.J. Parola, Inorg. Chem. 35 (1996) 3355.

[16] C.J. Timpson, C.A. Bignozzi, B.P. Sullivan, E.M. Kober, T.J. Meyer, J. Phys. Chem. 100 (1996) 2915.

[17] J. Van Houten, R.J. Watts, J. Am. Chem. Soc. 98 (1976) 4853.

[18] J.N. Demas, G.A. Crosby, J. Am. Chem. Soc. 93 (1971) 2841.

[19] J.N. Demas, G.A. Crosby, J. Phys. Chem. 75 (1971) 991.

[20] A. Horvath, Z. Uzonyi, Inorg. Chim. Acta 170 (1990) 1.

[21] J.V. Caspar, T.J. Meyer, Inorg. Chem. 22 (1983) 2444.

[22] J.V. Caspar, T.J. Meyer, J. Am. Chem. Soc. 105 (1983) 5583.

[23] E.M. Kober, J.V. Caspar, R.S. Lumpkin, T.J. Meyer, J. Phys. Chem. 90 (1986) 3722.

[24] J.P. Claude, T.J. Meyer, J. Phys. Chem. 99 (1995) 51.

[25] E. Krausz, J. Ferguson, in: S.J. Lippard (Ed.), Progress in Inorganic Chemistry, vol. 37, Wiley, New York, 1989, p. 293.

[26] M. Kato, S. Yamauchi, N. Hirota, J. Phys. Chem. 93 (1989) 3422.

[27] F. Scandola, M.T. Indelli, Pure Appl. Chem. 60 (1988) 973.

[28] M.T. Indelli, C.A. Bignozzi, A.M. Marconi, F. Scandola, in: H. Yersin, A. Vogler (Eds.), Photochemistry and Photophysics of Coordination Compounds, Springer, Berlin, 1987, p. 169.

[29] R. Bensasson, C. Salet, V. Balzani, J. Am. Chem. Soc. 98 (1976) 3772.

[30] U. Lachish, P.P. Infelta, M. Grätzel, Chem. Phys. Lett. 62 (1979) 317.

[31] C. Creutz, M. Chou, T.L. Netzel, M. Okumura, N. Sutin, J. Am. Chem. Soc. 102 (1980) 1309.

[32] P.S. Braterman, A. Harriman, G.A. Heath, L.J. Yellowlees, J. Chem. Soc. Dalton Trans. (1983) 1801.

[33] J.D. Kestell, Z.L. Williams, L. K Stultz, J.P. Claude, J. Phys. Chem. A 106 (2002) 5768.

[34] G.H. Allen, R.P. White, D.P. Rillema, T.J. Meyer, J. Am. Chem. Soc. 106 (1984) 2613.

[35] K.R. Barqawi, A. Llobet, T.J. Meyer, J. Am. Chem. Soc. 110 (1988) 7751.

[36] R.S. Limpkin, E.M. Kober, L.A. Worl, Z. Murtaza, T.J. Meyer, J. Phys. Chem. 94 (1990) 239.

[37] S.R. Allsopp, A. Cox, T.J. Kemp, W.J. Reed, J. Chem. Soc., Faraday Trans. 1 (74) (1978) 1275.

[38] H. Yersin, E. Gallhuber, A. Vogler, H. Kunkely, J. Am. Chem. Soc. 105 (1983) 5583.

[39] M. Sykora, J.R. Kincaid, Inorg. Chem. 34 (1995) 5852.

[40] G.D. Hager, G.A. Crosby, J. Am. Chem. Soc. 97 (1975) 7031.

[41] G.D. Hager, R.J. Watts, G.A. Crosby, J. Am. Chem. Soc. 97 (1975) 7037.

[42] L. Fodor, A. Horváth, J. Photochem. Photobiol. A: Chem. 112 (1998) 213.