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Photochemistry of bridged symmetrical polypyridyl ruthenium(II) complexes

Nickolai I. Veletsky, Ilia A. Dementiev, Aleksei Yu. Ershov *, Aleksei B. Nikol'skii

Institute of Chemistry of St. Petersburg State University, St. Petersburg 198904, Russia

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Abstract

The photochemical behaviour of $[RuL_2(BL)X]^+$ (**1**) and $[L_2XRu(BL)RuXL_2]^{2+}$ (**2**) (L ≡ 2,2′-bipyridyl (bpy), 1,10-phenanthroline (phen); BL ≡ 4,4′-bipyridyl (4,4′-bpy), pyrazine (pyz) and *trans*-1,2-bis(diphenylphosphino)ethylene (dppene); X ≡ Cl, NO_2) in acetonitrile and methanol solutions during steady state irradiation at $\lambda = 450$ nm was studied. Compounds **1** and **2** (L ≡ bpy, X ≡ Cl) with both bridging and terminal dppene ligands were found to be photochemically inert. The irradiation of compounds **1** and **2** with BL ≡ pyz and 4,4′-bpy resulted in the formation of solvate complexes $[RuL_2(Solv)X]^+$ (**3**) in both acetonitrile and methanol; however, the photolysis of **2** proceeded via a mixture (1 : 1) of **1** and **3** in the first step. The quantum yields of the processes under study are discussed in terms of the excited states.

Keywords: Polypyridyl ruthenium(II) complexes; Irradiation; Excited states

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1. Introduction

Polypyridyl ruthenium(II) complexes are of great interest in the study of excited state redox and sensitization processes due to the low-lying, metal-to-ligand charge transfer (MLCT) excited states [1]. From the viewpoint of the development of supramolecular photochemistry, these complexes are of interest as building sites for the design of photochemical molecular devices (PMDs). Although the chemistry of polynuclear complexes containing ruthenium(II) sites with different bridging ligands (BLs) has been actively studied as the subject of mixed-valence chemistry [2–10] and electron transfer processes [11–19], the stability towards photochemical decomposition of these complexes, one of the important properties for the design of PMDs, has received less attention.

To determine the potential of bridged polynuclear ruthenium(II) complexes for the design of PMDs, we have studied the general rules of their photochemical behaviour. As a first step towards this, the photochemical stability of mononuclear complexes $[RuL_2(BL)X]^+$ (**1**) and symmetrical dimers $[L_2XRu(BL)RuXL_2]^{2+}$ (**2**) (where L ≡ 2,2′-bipyridyl (bpy), 1,10-phenanthroline (phen); BL ≡ 4,4′-bipyridyl (4,4′-bpy), pyrazine (pyz) and *trans*-1,2-bis(diphenylphosphino)ethylene (dppene); X ≡ Cl, NO_2) (Fig. 1, Table 1) is considered in this work. These compounds were chosen to estimate the effect of the nature of the ligands (L, BL, X) and solvents (acetonitrile, methanol) on the photochemical

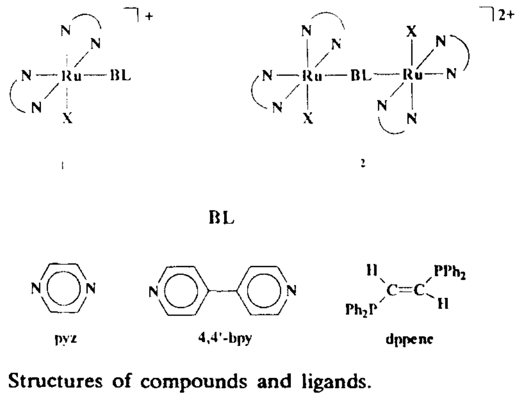

Fig. 1. Structures of compounds and ligands.

Table 1
Ligands in compounds **1a**–**1e** and **2a**–**2e**

L	BL	X	1	2
bpy	pyz	Cl	**1a**	**2a**
bpy	4,4′-bpy	Cl	**1b**	**2b**
phen	4,4′-bpy	Cl	**1c**	**2c**
bpy	dppene	Cl	**1d**	**2d**
bpy	4,4′-bpy	NO_2	**1e**	**2e**

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* Corresponding author.

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behaviour of ruthenium(II) binuclear polypyridyl complexes.

2. Experimental details

2.1. Materials

Acetonitrile and methanol, freshly distilled and stored over molecular sieves, were used as solvents in all measurements. Ruthenium(II) complexes were synthesized and purified as described elsewhere [4,17–20]. The complexes were isolated as their tetrafluoroborate salts and were identified by C, H, N analysis, UV–visible spectra and cyclic voltammetry (CV).

2.2. Measurements

UV–visible spectra were recorded on a KSVU-12 spectrophotometer. CV was carried out using a PI-50-1 potentiostat coupled to a PR-8 programmer. The CV measurements were performed using a cell with two Pt (wire) electrodes and an Ag/AgCl reference electrode. Tetra-*n*-butylammonium perchlorate (0.1 M) was used as the supporting electrolyte. The values of $E_{1/2}$ were taken as midpoints between anodic and cathodic peaks. All measurements were carried out at 20±2 °C. X-Ray photoelectron spectra were obtained using an HP-5952A electron spectroscopy for chemical analysis (ESCA) spectrometer with Al Kα monochromatic radiation ($E=1486.6$ eV) excitation. All energies for the ESCA measurements were referenced to $E_{\mathrm{C1s}}=284.6$ eV and $E_{\mathrm{Au4f}}=84.08$ eV.

2.3. Photochemical measurements

The photolysis was carried out under steady state irradiation. The photochemical device included a halogen lamp with a stabilized power supply, a collimator, a water filter and a glass filter (with a transmission maximum at 450 nm and a halfwidth of 20 nm). The cell compartment enabled solutions of complexes to be stirred and controlled thermostatically during irradiation. Solutions were degassed using argon, and then irradiated in 1 cm fluorescence cells capped with septa. The concentrations of the solutions were chosen to achieve total absorption of the incident light, and the light intensity was measured by Reinecke salt actinometry [21] in the same cells under identical conditions.

The effective quantum yields of the photoprocesses were calculated according to the equation $\phi=(c_o-c_t)V/It$ (c_o and c_t are the initial and current molar concentrations of the complex, V is the solution volume (dm^3), I is the radiation intensity (einstein s^{-1}) and t is the irradiation time in seconds). The experiments were carried out at times representing less than 10% conversion to products. The real quantum yields were determined as intercepts from plots of the effective quantum yields vs. the irradiation time. These plots were linear with standard deviations of the quantum yields of less than 10%. The accuracy of the quantum yield measurements was limited by the extinction coefficients and the sensitivity of the following equations to errors in the extinction coefficients.

When the dimers **2** were photolysed, there were three coloured species in solution, consisting of the starting dimer **2** and two products of its photodissociation. The last two are the mononuclear complex **1** with the terminal BL and the solvate $[\mathrm{RuL_2(Solv)X}]^+$ (**3**). The current concentration of the dimer c_t was calculated according to the equation $c_t=[D_t-(\epsilon_m+\epsilon_s)c_o]/(\epsilon_d-\epsilon_m-\epsilon_s)$, where D_t is the optical density of the solution at the wavelength of maximum absorption of **2** and ϵ_d, ϵ_m and ϵ_s are the extinction coefficients of the dimer, monomer and solvate complexes respectively at the wavelength of maximum absorption of **2**.

Mononuclear compounds of type **1** were independently synthesized to determine the quantum yields of the photosubstitution of the terminal BL. The current concentration of the mononuclear complexes was calculated using the equation $c_t=(c_o\epsilon_m-D_t)/(\epsilon_m-\epsilon_s)$. The experimental error in the measurement of the quantum yields did not exceed 20%.

3. Results and discussion

It was estimated in special experiments [20] that complexes **2** are relatively stable in deaerated solutions in the absence of light. The spectral characteristics of these complexes ($c=10^{-4}$ M) did not change for at least 3 days. At the same time, the irradiation of the complexes bridged by pyz or 4,4′-bpy using visible light resulted in essential changes in their spectral and electrochemical characteristics. The changes in the UV–visible spectrum of **2b** in acetonitrile are shown in Fig. 2. Both the visible spectrum of the final product ($\lambda_{max}=480$ nm, $\epsilon=7800$ M^{-1} cm^{-1}) and its cyclic voltammogram ($E_{1/2}=0.86$ V) are identical with the solvate $[\mathrm{Ru(bpy)_2(CH_3CN)Cl}]^+$ (**3a**), which was synthesized independently [22]. The first step of photolysis is characterized by the isosbestic point at 372 nm (Fig. 2). The isosbestic point disappears on further irradiation. The second point at 344 nm accompanies the second step of photolysis. Thus the following mechanism of photolysis can be proposed

$$[\mathrm{(bpy)_2ClRu(4,4'\text{-}bpy)RuCl(bpy)_2}]^{2+}+\mathrm{CH_3CN}\xrightarrow{h\nu}[\mathrm{Ru(bpy)_2(4,4'\text{-}bpy)Cl}]^{+}+[\mathrm{Ru(bpy)_2(CH_3CN)Cl}]^{+} \qquad (1)$$

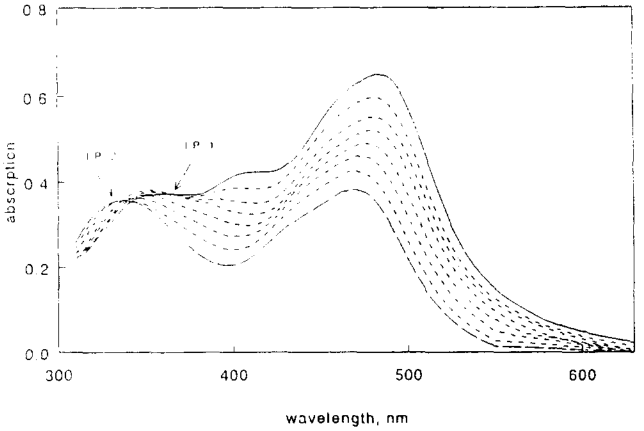

Fig. 2. Spectral changes observed in acetonitrile solutions of **2b** (2×10^{-5} M) on prolonged irradiation at $\lambda = 450$ nm: full line, initial complex; --, reaction mixture; ––, final product.

$$[Ru(bpy)_2(4,4'\text{-bpy})Cl]^+ + CH_3CN \xrightarrow{h\nu} [Ru(bpy)_2(CH_3CN)Cl]^+ + 4,4'\text{-bpy} \quad (2)$$

To confirm the possibility of reaction (2), we investigated the photochemical behaviour of complexes **-1e**. The spectral and electrochemical properties of the product formed on photolysis of **1b** in acetonitrile correspond to those observed for **3a**. There is only one isosbestic point at 344 nm, which indicates that the photolysis occurs via Eq. (2).

Similar data were obtained for other ruthenium(II) complexes in which 4,4′-bpy and pyz were ligated in both bridging and terminal fashion. The difference in the photochemical behaviour of these complexes is outlined below.

The rate of photodissociation of **2b**, **2c** and **2e** (reaction (3)) and the rate of photosolvation of 4,4′-bpy in **1b**, **1c** and **1e** (reaction (4)) are similar. In the case of **2a** and **1a** (BL ≡ pyz), the rate of photodissociation is less than the rate of photosolvation.

$$[L_2XRu(BL)RuXL_2]^{2+} + Solv \xrightarrow{h\nu} [RuL_2(BL)X]^+ + [RuL_2(Solv)X]^+ \quad (3)$$

$$[RuL_2(BL)X]^+ + Solv \xrightarrow{h\nu} [RuL_2(Solv)X]^+ + BL \quad (4)$$

In contrast with the complexes with nitrogen-containing BLs, the species **2d** and **1d** are photochemically inactive. Prolonged irradiation ($I = 3.85 \times 10^{-9}$ einstein s^{-1}, $t = 5$ h) of **1d** and **2d** does not change the spectra of their solutions in acetonitrile.

We have shown that complexes **1** and **3** ($c \approx 10^{-4}$ M) do not associate in the absence of light at 20 °C in acetonitrile and methanol to form the dimer **2**. There is also no interaction between **3** and free pyz or 4,4′-bpy which could provide **1** under the same conditions. Hence the reverse processes for reactions (3) and (4) are negligible. The formation of dimers takes place at higher concentrations of reagents ($c > 10^{-2}$ M) and temperatures higher than 50 °C.

The quantum yields observed for reactions (3) and (4) in acetonitrile and methanol are shown in Table 2, together with the spectral and electrochemical characteristics of complexes **1** and **2**. The energies of the N $1s_{1/2}$ electrons of the coordinated nitrogen atoms of the pyz and 4,4′-bpy ligands for these complexes are also presented in Table 2. The following conclusions are suggested by the data.

(1) The complexes with nitrogen BLs are highly photoactive, whereas the phosphine species display high photostability.
(2) The relative photostability of the pyz-bridged dimer **2a** when compared with **1a** clarifies the effect of the bonding of the second metal centre to BL. The quantum yield of the photodissociation of the Ru–N bond in **1a** is ten times higher than that in **2a**.
(3) The replacement of the chloride ligand in **1b** and **2b** by the stronger π-acceptor nitro group in the inner sphere of **1e** and **2e** leads to an increase in the photoactivity.
(4) Acetonitrile solutions show an increase in the quantum yield for all the reactions studied compared with methanol solutions. Reaction (3) probably proceeds via a dissociative mechanism and the solvent molecules do not participate in the rate-limiting step; therefore a twofold decrease in the quantum yields (on going from acetonitrile to methanol) can be rationalized by cage effects. In the case of the stronger coordinating acetonitrile molecule, the probability of BL and **3** recombination in the solvent cage is higher.
(5) The nature of similar bidentate polypyridyl ligands (bpy, phen), as expected, has no significant effect on the photochemistry of dinuclear complexes.

The variation of the ligands showed no clear relation to the quantum yields obtained for the compounds under study; however, the values of the quantum yields for these reactions can be interpreted using an excited state scheme [23]. During irradiation by visible light, polypyridyl ruthenium(II) complexes are transformed into the short-lived singlet state ^{1}CT. This state then rearranges into the corresponding triplet state ^{3}CT with a probability of near unity [23]. The triplet state undergoes deactivation or thermal occupation of the ligand field state (^{3}LF). Occupation of the ^{3}LF state is necessary for ligand loss photochemistry to occur [24].

The efficiency of the population of the ^{3}LF state from the lowest ^{3}CT state is determined by the energy of the long-wave MLCT band and the Ru(II)/Ru(III) redox potential [25]. The lower the value of λ_{max} and the higher the value of $E_{1/2}$, the higher the probability of ^{3}LF state occupation. These are the criteria which determine the photochemical reactivity of $[Ru(bpy)_2XY]^{n+}$ complexes [26].

Table 2
Spectral, electrochemical and quantum yield data for polypyridyl ruthenium(II) complexes

Number	Complex	λ_{max} (ϵ) [a]	$E_{1/2}$ [b]	E(N(1s)) [c]	ϕ_{MeCN} [d]	ϕ_{MeOH} [d]
1a	$[Ru(bpy)_2(pyz)Cl]^+$	355 (6.27) 384 (6.42) 482 (8.34)	0.93	399.6	0.260	0.161
2a	$[\{Ru(bpy)_2Cl\}_2pyz]^{2+}$	338 (11.3) 510 (22.0)	0.97 1.06	399.0	0.026	0.013
1b	$[Ru(bpy)_2(4,4'\text{-}bpy)Cl]^+$	374 (10.8) 490 (11.4)	0.79	399.3	0.025	0.015
2b	$[\{Ru(bpy)_2Cl\}_2 4,4'\text{-}bpy]^{2+}$	370 (16.0) 410 (18.0) 490 (27.5)	0.93	399.2	0.043	0.017
1c	$[Ru(phen)_2(4,4'\text{-}bpy)Cl]^+$	456 (14.5)	0.84	399.5	0.064	0.052
2c	$[\{Ru(phen)_2Cl\}_2 4,4'\text{-}bpy]^{2+}$	466 (31.4)	0.87	399.2	0.038	0.018
1d	$[Ru(bpy)_2(dppene)Cl]^+$	460 (5.79)	1.16	–	$<10^{-4}$	$<10^{-4}$
2d	$[\{Ru(bpy)_2Cl\}_2dppene]^{2+}$	450 (14.4)	1.07 1.17	–	$<10^{-4}$	$<10^{-4}$
1e	$[Ru(bpy)_2(4,4'\text{-}bpy)NO_2]^+$	380 (9.4) 432 (10.1)	1.16	399.5	0.068	0.052
2e	$[\{Ru(bpy)_2NO_2\}_2 4,4'\text{-}bpy]^{2+}$	445 (31.0)	1.26	399.4	0.053	0.028

[a] Units: nm (10^{-3} M^{-1} cm^{-1}) in acetonitrile.
[b] Units: V, in acetonitrile.
[c] Units: eV.
[d] Units: mol einstein^{-1}.

Pyz is the weakest σ donor of the BLs studied ($pK_a = 0.60$ in comparison with $pK_a = 5.23$ for pyridine). This is probably the reason why the quantum yield for **1a** is much higher than that for the corresponding monomeric complex with 4,4′-bpy (**1b**). The coordination of the second ruthenium atom to pyz causes a significant red shift (from 482 to 510 nm) of the long-wave band. The energy of the N $1s_{1/2}$ band is decreased by 0.6 eV, and therefore the Ru–N bond (pyz) is strengthened [26]. The result is a greater stabilization of complex **2a** in comparison with **1a** ($\phi_{1a} = 0.26$, $\phi_{2a} = 0.026$).

For complexes **2b**, **2c** and **2e**, which are bridged with the 4,4′-bpy ligand, the observed λ_{max} and $E_{1/2}$ values are similar to the related monomeric compounds (**1b**, **1c** and **1e**). Likewise, the quantum yields are similar to those observed for the photosubstitution of pyridine (py) in $[Ru(bpy)_2(py)Cl]^+$ ($\phi = 0.04$) [27].

Replacement of the coordinated chloride ion by the π-acceptor nitro ligand leads to a decrease in the electron density at the metal centre. The long-wave bands for the nitro complexes were observed to shift to the blue region and the nitrogen line in the ESCA spectra moved to higher energy. Thus the quantum yields for the nitro complexes **2e** and **1e** are higher than for the respective chloro complexes **2b** and **1b**.

We cannot provide a clear explanation for the high photostability of the phosphine-bridged complexes **1d** and **2d**. It can be suggested that the Ru–BL bond becomes stronger on moving from pyridyl to phosphine ligands. On the other hand, the ligand field state of **1d** and **2d** could lie above the MLCT state. Photophysical measurements are in progress to clarify the mechanism of reactions (3) and (4).

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References

[1] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, *84* (1988) 85.
[2] C. Creutz and H. Taube, *J. Am. Chem. Soc.*, *95* (1973) 1086.
[3] D.E. Richardson and H. Taube, *Coord. Chem. Rev.*, *60* (1984) 107.
[4] R.W. Callahan, G.M. Brown and T.J. Meyer, *Inorg. Chem.*, *14* (1975) 1443.
[5] M.J. Powers, R.W. Callahan, D.J. Salmon and T.J. Meyer, *Inorg. Chem.*, *15* (1976) 1457.
[6] J.P. Chang, E.Y. Fung and J.C. Curtis, *Inorg. Chem.*, *25* (1986) 4233.

[7] J.C. Curtis, R.L. Blackbourn, K.S. Ennix, S. Hu, J.A. Roberts and J.T. Hupp, *Inorg. Chem., 28* (1989) 3791.
[8] J.T. Hupp, *J. Am. Chem. Soc., 112* (1990) 1563.
[9] M.S. Ram and A. Haim, *Inorg. Chem., 30* (1991) 1319.
[10] M.H. Chon, C. Creutz and N. Sutin, *Inorg. Chem., 31* (1992) 2318.
[11] T.J. Meyer, *Acc. Chem. Res., 11* (1978) 94.
[12] M.J. Powers, D.J. Salmon, R.W. Callahan and T.J. Meyer, *J. Am. Chem. Soc., 98* (1976) 6731.
[13] R.W. Callahan, F.R. Keene, T.J. Meyer and D.J. Salmon, *J. Am. Chem. Soc., 99* (1977) 1064.
[14] M.J. Powers and T.J. Meyer, *Inorg. Chem., 17* (1978) 1785.
[15] J.C. Curtis, J.S. Bernstein and T.J. Meyer, *Inorg. Chem., 24* (1985) 385.
[16] K.S. Ennix, P.T. McMahon, R. Rosa and J.C. Curtis, *Inorg. Chem., 26* (1987) 2660.
[17] S.A. Adeyemi, E.C. Johnson, F.J. Miller and T.J. Meyer, *Inorg. Chem., 12* (1973) 2371.
[18] M.J. Powers and T.J. Meyer, *Inorg. Chem., 17* (1978) 2955.
[19] M.J. Powers and T.J. Meyer, *J. Am. Chem. Soc., 102* (1980) 1289.
[20] A.Yu. Ershov, N.I. Veletsky, A.M. Popov, I.A. Dementiev, N.I. Sokolova and A.B. Nikol'skii, *Zh. Obch. Khim., 64* (1994) 1223.
[21] E.E. Wegner and A.W. Adamson, *J. Am. Chem. Soc., 88* (1966) 394.
[22] B. Durham, J.V. Caspar, J.R. Nagle and T.J. Meyer, *J. Am. Chem. Soc., 104* (1981) 4803.
[23] J.N. Demas and D.J. Taylor, *Inorg. Chem., 18* (1979) 3177.
[24] J. van-Houten and R.J. Watts, *Inorg. Chem., 17* (1978) 3381.
[25] A. Juris, S. Campagna, V. Balzani, G. Gremaud and A. von Zelewsky, *Inorg. Chem., 20* (1988) 3652.
[26] E.M. Shustorovitch, *The Chemical Bond in Coordination Compounds*, Znanie, Moscow, 1975, p. 107.
[27] D.V. Pinnick and B. Durham, *Inorg. Chem., 23* (1984) 1440.