Thesis of the PhD dissertation

Characterization of exciplexes generated by excited tris-diimine-ruthenium(II) complexes and silver(I) ion of ground state

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I. Introduction and aim of the work

Diimine-ruthenium(II) complexes have emerged as one of the most studied inorganic compounds in the past decades and it is the most efficient sensitizer for solar cells even nowadays. These complexes have also been applied for example as photocatalyst or luminescent pH- and oxigen-sensers. However exciplexes of these compounds have rarely been investigated, although their study would be important because exciplexes are formed as intermediers in several photochemical reactions. By the help of exciplexes the efficiency of photochemical reactions can be increased, while the yield of unwished byproducts can be decreased. Their study might also enable us to get an insight into the reaction mechanism.

So the main aim of this research work was to identify and the characterize exciplexes formed as a result of the interaction of $*Ru(LL)_3^{2+}$ (LL: bpy = 2,2'-bipiridil, phen = 1,10-fenantrolin) complexes and Ag^+ ion of ground state. It was also aimed to determine the characteristic parameters of deactivation pathways of exciplexes and the thermodynamic parameters of the equilibration between excited species and to reveal the effect of the exciplex formation to the electron transfer processes of the excited complex.

II. Experimental methods

Room-temperature absorption spectra were obtained using a Specord M40 (Zeiss) or a Specord S100 spectrophotometer connected to IBM compatible PC. Luminescence emission and excitation spectra were recorded on a Perkin-Elmer LS50B fluorimeter. Time resolved measurements were performed by an Applied Photophysics laser flash photolysis system containing a Nd:YAG laser source. The computer controlling of this equipment was solved by a software written in Visual Basic programming language. Bruker B-E 15 electromagnet was used for kinetic measurements made at external magnetic field. MS Excel program based on least squares method was used for the fitting of luminescence lifetime and emission spectra.

III. Scientific achievements

1. It is proved by the analysis of absorption, luminescence emission and excitation spectra that excited $[Ru(LL)_3]^{2+}$ complexes (LL = bpy, phen) form exciplexes with silver ions of ground state.

2. On the basis of time resolved phosphorescence measurements it is verified that luminescence decays follow a single exponential curve. The luminescence lifetime (τ) depends on temperature and the concentration of silver ion however it is independent of the wavelength of luminescence.
   (a) Therefore it has been concluded that the equilibration in the excited state is much faster than the decay paths to the ground state.
   (b) The characteristics of the τ-$[Ag^+]$ curves at constant temperatures are explained by the formation of both bi- and termolecular exciplexes.

3. Considering these observations a model containing three luminescent species being in fast equilibrium has been proposed that provides correct interpretation of all data.
   (a) Solving the differential equation system according to paragraph II. it is proved that the equation proposed by Ayala et al. is improper for the deconvulation of luminescence emission spectra recorded by continuous irradiation. Thus an equation is proposed, which shows formal accordance with the formula given by Scandola et al. for describing of the luminescence intensity in the case of the protonation of $^3Ru(bpy)_2(CN)_2$ complex.
   (b) Parameter fitting procedure for luminescence spectra and luminescence lifetime values determined at different concentrations of silver ion and different temperatures has confirmed that the model – in which the perturbation effect of the formation of exciplex on the radiative and nonradiative decay process of the excited species is considered – properly describes of all data.

4. The rate constants of deactivation processes of the excited $Ru(LL)_3|Ag_n^{(2+n)+}$ (n=0, 1, 2) species, namely the rate constant of the decay from the low-lying ^{3}MLCT state (k_0), the energy gap between the ^{3}MLCT and ^{3}d-d excited states (ΔE_1) and the frequency factor characterizing the decay process from the ^{3}d-d state (k_1) have been determined.
    (a) k_0, k_1 and ΔE_1 parameters resulted in from the fitting procedure for $Ru(LL)_3^{2+}$ complexes are in good agreement with literature data.
    (b) It has been revealed that the formation of exciplexes causes an increase in k_0 and ΔE_1 while k_1 does not change.
    (c) Therefore it has been concluded that
        i. the bimolecular exciplexes are formed as a result of the overlapping of the π* orbital of the diimine ligand and the empty 5s orbital of Ag^+,
        ii. when the termolecular exciplex is formed silver ions bond to one diimine ligand as Ag_2^+ species.

5. The thermodynamic parameters of the formation of bi- and termolecular exciplexes have been determined. The small negative enthalpies indicate the charge transfer character of the interaction between the excited complex and silver ion, and the small negative entropies confirm the associative process.

6. Using absorption and luminescence spectra and luminescence lifetime data measured at various silver ion concentrations ($c_{Ag+} = 0–1.5$ M) and temperatures (T = 0 – 80 °C) in water, in deuterated water and in propylene carbonate a considerable solvent effect on the rate of the direct deactivation process of the ^{3}MLCT state is demonstrated.

7. By the investigation of electron transfer reactions it has been concluded that
    (a) the quenching rate constants for the reaction of $^*Ru(LL)_3|Ag_n^{(2+n)+}$ (n=0, 1, 2) species with methylviologen (MV^{2+}) and the escape efficiencies of the $\cdot MV^+$ radical as a product of the reaction are decreased by the number of silver ion (n),

(b) k_q increases and η_{ce} decreases for $[Ru(bpy)_n(CN)_{6-2n}]^{(2n-4)+}$ (n=1, 2, 3) complexes as the bpy ligand is replaced by two cyanides in water, deuterium oxide and methanol,

(c) the increase of ionic strength in the $[Ru(bpy)_3]^{2+}$ – MV^{2+} system results in the increase of k_q and the decrease of η_{ce}.

8. The rate constant of backward electron transfer (k_{bet}) and the rate coefficient of cage escape (k_{ce}) from the radical pair (RP) formed in the oxidative quenching reaction and the spin-relaxation time (τ_s) of the RP were determined by kinetic measurements made at external magnetic fields (0-3.3 T), and it has been pointed out that

   (a) k_{bet} and τ_s are smaller while k_{ce} is larger at 1.5 M than at 0 M silver ion concentration for the $[Ru(bpy)_3]^{2+}$ – Ag^+ – MV^{2+} system,

   (b) both k_{ce}, k_{bet} as well as τ_s parameters decrease by the replacement of one bpy ligand with two cyanides for the $[Ru(bpy)_n(CN)_{6-2n}]^{(2n-4)+}$ – MV^{2+} (n=1, 2, 3) systems in water, deuterium oxide and methanol,

   (c) the increase of ionic strength leads to the decrease of k_{bet} and k_{ce} and results in a small increase in τ_s parameter.

   (d) In addition, the results of magneto kinetic studies confirm the exciplex formation in the $[Ru(bpy)_3]^{2+}$ – Ag^+ system.

IV. Development of laser flash photolysis system

1. A program running under MS Windows to control a laser kinetic spectrophotometer equipment has been developed. This program controls

   (a) a QUANTEL laser light source via serial port,

   (b) a SPECTRON laser light source, a monochromator stepping motor, a Xe-lamp pulsing unit and two shutter control units through an LKS control unit via parallel port,

   (c) a Hamamatshu power supply and two oscilloscopes (Philips, Tektronix) through IEEE 488.2 cable where reading and converting of data are also possible.

2. By the help of AX5216 (4 MHz) counter/timer board the time-tuning of the Xe-lamp pulsing unit with the other devices and the control of timing by PC has been also performed.

3. The program supports the use of macros, which help users to execute frequently used commands easily and by taking advantage of automation it decreases the possibility of user's errors during serial measurements of large number.

V. Scientific publications and presentations related to the thesis

Publications

1. L. Fodor, A. Horváth, "Characterization of Exciplexes Generated by Excited Tris-Diimine-Ruthenium(II) Complexes and Silver(I) Ion of Ground State" *J. Photochem. Photobiol. Chem. A*. **112** (1998) 213-23.

2. L. Fodor, A. Horváth, K. A. Hötzer, S. Walbert, U. E. Steiner, "Enhancement of magnetic field effect in $Ru(bpy)_3^{2+}$ - MV^{2+} system by $Ru(bpy)_3^{2+}$ - Ag^+ exciplex formation" *Chem. Phys. Lett.* **316** (2000) 411-418.

3. Fodor L., Horváth A.: „Characterization of exciplexes formed by excited $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ complexes with silver(I) ion of ground state in propilene-carbonate" *Acta Pharmaceut. Hung.* **70** (2000) 103.

4. L. Fodor, A. Ülveczky, A. Horváth, U. E. Steiner, "Ligand dependence of magnetic spin effects on photooxidation of $[Ru(bpy)_{3-n}(CN)_{2n}]^{-2-2n}$ type complexes" *Inorg. Chim. Acta* **338** (2002) 133-141.

Presentations

1. Fodor L., Horváth A., 11th International Symposium on the Photochemistry and Photophysics of Coordination Compounds, Kraków, Poland, July 9-13th 1995 (Poster)
2. Horváth A., Fodor L., 211th Am. Chem. Soc. National Meeting, New Orleans, LA, March 24-28th 1996 (Oral)
3. Horváth A**.,** Fodor L., Horváth O., Stevenson K. L., “Identification of Short-lived Species in Photochemical System Generating Inorganic Exciplexes” Fast Reactrions in Solutions, The Royal Society of Chemistry, Graz, Austria, September 4-7th 1996 (Oral)
4. Horváth A**.,** Horváth O., Fodor L., Stevenson K. L., “Photochemistry and Photophysics of Polynuclear Species and Exciplexes of Some Ru(II) and Cu(I) Complexes” XVII IUPAC Symposium on Photochemistry, Barcellona, Spain, July 19-24th 1998 (Oral)
5. L. Fodor, K. A. Hötzer, S. Walbert, “Solvent and Magnetic Field Effects on Electron Transfer Reaction from $\{RuL_3..Ag_n\}^{(n+2)+}$ (n = 1,2) Exciplexes” EPA Graduate Student Symposium in Photochemistry, Fribourg, Switzerland, February 23-26th 2000 (Poster)
6. Fodor L., Horváth A., 14th International Symposium on the Photochemistry and Photophysics of Coordination Compounds, Veszprém, Hungary, July 7-12th 2001 (Poster)
7. Fodor L., MTA Szervetlen és Fémorganikus Kémiai Munkabizottság ülése, Veszprém, 1995. április 27-28. (Előadás)
8. Fodor L., Horváth A., XXX. Komplexkémiai Kollokvium, Mátraháza, 1995. június 6-8. (Előadás)
9. Fodor L., Horváth A., XXXI. Komplexkémiai Kollokvium, Tata, 1996. június 5-7. (Előadás)

10. Fodor L., MTA Reakciókinetikai és Fotokémiai Munkabizottság ülése, Gyöngyöstarján, 1998. november 26-27. (Előadás)
11. Fodor L., “Fotoindukált elektronátadási reakciók ‘hangolása’ külső mágneses térrel” MTA Fizikai Kémiai és Szervetlen Kémiai Bizottság – Reakciókinetikai és Fotokémiai Munkabizottság ülése, Balatonalmádi, 2000. április 27-28. (Előadás)

VI. Other presentations

1. A. Horváth., L. Fodor., K. L. Stevenson., ”Short-lived species in photochemical systems generating transition metal complex exciplexes”, Proceedings of COST Chemistry Action D6 Workshop on Chemical Processes and Reactions under Extreme or Non-Classic Conditions, Chambery, France, November 29-December 1st, 1996
2. Kardos A., Horváth A., Fodor L., Országos Lumineszcencia-Spektroszkópia Iskola, Pécs, 1999. október 19-21.