Theses of PhD Dissertation

PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES OF $[Ru(LL)(CN)_4]^{2-}$ COMPLEXES

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1. Introduction, Aims

It has been already realised in the XIX. century that there is a great possibility in the utilization of solar energy. Nowadays, due to the damaging consequence of the continuously increasing consumption of fossil fuels and the decrease of their reserves there is a considerable pressure on mankind to search for renewable and environmentally friendly alternatives. In the light of these facts, it is not surprising that the molecules with promising photophysical and photochemical properties are in the focus of chemical research. The study of photoactive complexes is not only important for developing solar energy conversion systems but also for application of them in various fields such as photocatalysis, medical therapy, luminescencence and electroluminescence sensors which stimulates new scientific efforts. Within photoactive molecules, coordination compounds especially the different ruthenium(II) complexes play important role in inorganic photochemical systems.

From the very beginning, great interest has been dedicated to the different cyano complexes of transition metal ions due to their solvent dependent absorption spectra and the ability to act as a bridge in polynuclear systems. The tetracyano-monodiimine-ruthenate(II) complexes can be considered as ideal molecules because their diimine ligand ensures the advantageous properties typical for *tris*-diimine-ruthenium(II) complexes while the possibilities offering by cyano complexes are also included. The latter means that the photophysical properties are highly solvent dependent and they can be built up in more complex supramolecular system. During the last three decades considerable amount of data was collected about *tris*-diimine ruthenium(II) complexes. The influences of different diimine ligands on the level of the lowest energy luminescent excited state and on the rate of photophysical deactivation processes from this state were investigated

systematically. To know these characteristics is fundamental for designing efficient light driven molecular level devices.

Although a series of tetracyano-monodiimine-ruthenate(II) complexes of different diimin ligands have been already synthesised and they have been also used in various supramolecular systems, their detailed photophysical characterisation has not been performed so far. Therefore the main goal of this PhD work was to reveal the feature of photophysical processes of the excited complexes in detail and to understand the influence of the nature of diimine ligand on those characteristics. Considering the solvent dependence of complexes it was expected that the solvent deuteration can modify the decay rates of excited state and so the investigation of this effect has been also carried out.

Our long term project is related to continue the study of this complex family. Although the tetracyano complexes can be implied easily to polynuclear systems with the cyanide side of the molecule, their variability can be increased by using diimine ligand possessing extra donor site available to coordinate further metal ions. Two complexes with this possibility have been also prepared and characterised in order to build up more complex systems with definite function (e.g. single redox centre antenna type system).

2. Applied experimental methods

All complexes investigated in the frame of this research were prepared in our lab, and they were synthesised by literature method or by its modified version. The absorption spectra were recorded on a double beam Specord M40 and a diode array Specord S100 spectrophotometers. Luminescence spectra were measured on Perkin-Elmer LS50B spectrofluorimeter and they were corrected to the detector sensitivity. The time-resolved luminescence measurement was carried out with laser-flash photolysis system equipped

with a Quantel Brillant type Nd:YAG laser as a light source. The low temperature (77 K) luminescence spectra were fitted according to single-mode Franck-Condon analysis with the minimalization algorithm of Marquard. The NMR spectra (^{1}H, ^{2}D, ^{13}C és ^{13}C-HSQC) required for the characterization of complexes and for the investigation of acid-base equilibria were measured on Varian Unity 300 and Bruker Avance 400 NMR spectrometer.

3. Theses

I. $[Ru(LL)(CN)_4]^{2-}$ complexes with 18 different diimine ligands (LL=1,10-phenanthroline, 2,2'-bipyridine and their substituted and deuteriated derivatives) have been prepared and characterised. Among these complexes 14 are considered as new compounds.

II. The absorption and emission spectra show that the methyl substitution results in a blue shift while the phenyl substitution gives red shift in the MLCT band energy for $[Ru(LL)(CN)_4]^{2-}$ complexes.

III. On the basis of single mode Franck-Condon analysis of the luminescence spectra measured at 77 K, it can be concluded that:

   (i) The phenathroline derivatives due to their more rigid structure than that of bipyridine complexes have smaller excited state distortion compared to those of bipyridine analogues.

   (ii) The phenyl groups reduce, while methyl groups increase the excited state distortion. The former can be explained by the extended delocalization of the electron promoted to the $*\pi$ orbital of diimine ligand.

IV. The rate constant of temperature independent deactivations (k_{ph} and k_{nr}) and the parameters of temperature dependent deactivation processes (*A*

and ΔE) have been determined by luminescence lifetime and quantum yield measured at various temperature in water as solvent.

(i) It is demonstrated that the rate of the temperature independent radiative decay (k_{ph}) and that of nonradiative deactivation process (k_{nr}) depend significantly on the skeleton and substituents of diimine ligand.

(ii) The phenyl groups give rise to reduction of k_{nr}, which can be attributed to a moderate excited state distortion.

(iii) Values of the parameters A and ΔE show that for the investigated $[Ru(LL)(CN)_4]^{2-}$ complexes the important temperature dependent deactivation channel leads through the ^{4th}MLCT state while the efficiency of the other process crossing through the ^{3}dd state is small.

(iv) The deuteriation of diimine ligands results in a small decrease of k_{nr} and A.

(v) The photophysical parameters of complexes with partially deuteriated dpphen ligand reveal that the 5,6 position of phen skeleton has minor influence on decay processes, while 2,9 position have important role in the nonradiative deactivations.

V. The significant role of the secondary coordination sphere on the nonradiative decay process has been revealed by temperature dependent lifetime measurements performed on $[Ru(LL)(CN)_4]^{2-}$ dissolved in deuterium-oxide and in different deuteriated forms of methanol.

(i) The solvent deuteriation reduces the values of k_{nr} and A in higher extent than the ligand deuteriation.

(ii) The sensitivity of A parameter to solvent and to ligand deuteriation confirms that the temperature dependent deactivation mainly takes place through the ^{4th}MLCT state.

(iii) The obtained photophysical data in different deuteriated forms of methanol show that the OH group of solvent molecules strongly influences the rate of nonradiative decay.

(iv) Evaluation of the experimental curves measured in different deuteriated forms of methanol shed light on the fact that the efficiency of deactivation through ^{3}dd is small.

VI. The investigation of acid-base equilibria of two $[Ru(LL)(CN)_4]^{2-}$ complexes possessing electron donating sites on the diimine ligand shows that:

(i) The energy of MLCT state for the $[Ru(bppz)(CN)_4]^{2-}$ complex does not change under the first protonation step, while the protonation of the $[Ru(dcb)(CN)_4]^{4-}$ complex on the diimine ligand is accompanied by a considerable red shift.

(ii) The electron withdrawing effect of diimine ligand results in a smaller pK_s for the protonation of cyanides in both complexes compared to that of the bpy analogue.

(iii) The pH dependence of ^{13}C-NMR spectra confirms that the first protonation of $[Ru(bppz)(CN)_4]^{2-}$ occurs on the nitrogen of free pyridine ring.

(iv) There is a strong electronic coupling between the diimine and cyanide side in the $[Ru(dcb)(CN)_4]^{4-}$ complex, while such a coupling is rather weak in the case of bppz complex.

(v) On the basis of luminescence spectra and laser flash photolysis it is demonstrated that the basicity of protonation site on the diimine ligand is enhanced in the excited state.

(vi) The formation of monoprotonated form leads to considerable decrease in the luminescence lifetime of both complexes.

4. SCIENTIFIC PUBLICATIONS AND PRESENTATIONS

Publications closely related to the dissertation

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Presentations

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