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Ground and excited state dynamics of new dinuclear ruthenium complexes: NMR, UV–Vis, IR, electrochemical, photophysical characterization, and theoretical study of $Ru(bpy)_2(\mu\text{-}dpp)Ru(CN\text{–}X)_4{}^{n+}$ complexes

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ABSTRACT

Two novel binuclear complexes of ruthenium(II) have been synthesized and characterized by various spectroscopic (NMR, IR, UV–Vis absorption and emission) and electrochemical methods. Extensive and detailed NMR studies of $[(bpy)_2Ru(\mu\text{-}dpp)Ru(CN)_4]$ **1** and $[(bpy)_2Ru(\mu\text{-}dpp)Ru(CNCH_3)_4]^{4+}$ **2** complexes have revealed a dynamic equilibrium between the stereo isomers of the ground-state complexes. Small energy difference between the two isomers of **1** has been estimated using NMR data (2.7 kJ mol^{-1}) and by quantum chemistry calculations (4.7 kJ mol^{-1}). The relatively broad lowest energy absorption band appearing in the visible range is assigned as overlapping metal-to-ligand charge-transfer (MLCT) $d\pi(Ru)_A \rightarrow \pi^*(\mu\text{-dpp})$ ($MLCT_{1A}$) and $d\pi(Ru)_B \rightarrow \pi^*(\mu\text{-dpp})$ ($MLCT_{1B}$) transitions. The MLCT bands of complex **1** are solvatochromic (e.g. the lowest energy $MLCT_1$ band shifts from 506 to 540 nm upon changing the solvent from water to MeOH), while the same band of the complex **2** is not sensitive to the solvent nature. The luminescence properties of the excited **1** and **2** complexes are significantly different: (i) a rather small blue shift of the emission band (623 cm^{-1}) is observed when the luminescence of complex **1** is detected at 77 K in rigid matrix instead of at ambient temperature in liquid phase. This blue shift is considerably larger (1923 cm^{-1}) in the case of complex **2**. (ii) Time resolved luminescence studies have revealed that the $^3MLCT_{1A}$ and $^3MLCT_{1B}$ excited states of complex **1** decay independently. On the other hand a dynamic equilibration occurs between two triplet excited states of complex **2**. A slight interaction between the metal centers of complex **1** has been assumed by considering the electrochemical data, while a stronger coupling of the ruthenium atoms in complex **2** has been concluded by comparison of the oxidation potentials of the complex **2** with that of other binuclear ruthenium complexes of the metal centers possessing different chemical environment.

1. Introduction

Dinuclear and polynuclear ruthenium(II) complexes bridged by various ligands of bis bidentate and tridentate nature have attracted much interest as antennas and intramolecular energy- and/or electron-transfer units for light energy harvesting and converting artificial systems, photoluminescent sensors, light driven molecular switches and machines, etc. [1–6]. The tetradentate 2,3-bis(pyridyl)pyrazine (dpp) ligand has been successfully utilized to build up homo- and hetero-multinuclear diimine-based systems with several transition metal ions like ruthenium(II), osmium(II), nickel(II) or copper(II) [7–10]. The direction of the intramolecular energy and electron transfer within a polynuclear dendrimer having ruthenium(II/III) and osmium(II/III) central atoms can be tuned by the central atoms (position of ruthenium and osmium atoms and their oxidation state) and by the nature of bridging and terminal diimine ligands. Introducing mononuclear complexes as ligands to construct multinuclear species has provided a further possibility for controlling the intramolecular energy and electron transfer processes.

The main characteristic of the $[Ru(LL)(CN)_4]^{2-}$ complexes as the simplest members of the Ru(II) diimine complex family is that the energy of their lowest level triplet state is widely tuneable using various tools, such as modifying the framework of the diimine ligand, substituting the hydrogen atom(s) of the diimine ligand with electron donating and/or withdrawing groups, varying the positions of these groups. In addition, one can exploit the specific solute-solvent interaction that strongly depends on the acceptor character of the solvent molecule due to the electron donating nature of the nitrogen atom of the coordinated cyanide ligands

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[11,12]. Moreover, the cyanide ligands can be used as bridging units to form polynuclear species. The latter has been utilized to synthesise a great variety of coordination networks involving various lantanoide(III) ions and $[Ru(LL)(CN)_4]^{2-}$ or $[Os(LL)(CN)_4]^{2-}$ complexes [13–16].

The aim of our recent research is to synthesize and characterize bi- and polynuclear complexes consisting of ruthenium(II) central atom(s), terminal diimine and bridging polyimine ligands and terminal cyanide ligands. The advantage of the inclusion of cyano ligands in the coordination sphere is that, in principle, besides the above-mentioned ones, they can provide an additional tool for controlling the energy transfer processes in the excited polynuclear dendrimer species. Namely, one can also exploit the specific solute–solvent interactions that arise due to the presence of an ancillary ligand like cyanide that is able to form a secondary coordination sphere by the lone pair of its nitrogen atom. We chose the dpp ligand as bridging unit, because we expected that in identifying the nature of bridging we can utilize the knowledge we accumulated in our earlier studies concerning the photophysical characteristics of the $[Ru(dpp)(CN)_4]^{2-}$ complex and their variation due to the stepwise protonation of the complex [17]. As a first step the new dinuclear moiety, $Ru(bpy)_2(\mu\text{-dpp})Ru(CN)_4$ and its methylated derivative $Ru(bpy)_2(\mu\text{-dpp})Ru(CN{-}CH_3)_4{}^{4+}$ have been synthesized. In the present article, we describe the synthesis and the characterization of these complexes using various spectroscopic (UV–Vis absorption and emission, IR, NMR) procedures and time-resolved techniques. The assignment of two isomers of complex **1** by comparison of the results obtained by NMR, IR spectroscopy and theoretical calculations will also be demonstrated.

2. Experimental

2.1. Materials

The starting material $RuCl_3{\cdot}xH_2O$, $K_4[Ru(CN)_6]$, 2,2′-bipyridine and 2,3-(bis(2-pyridyl)pyrazine were purchased from Aldrich and used without further purification. $Ru(bpy)_2Cl_2$ [18] $[Ru(bpy)_2(dpp)]Cl_2$ and $[\{Ru(bpy)_2\}_2(dpp)](PF_6)_4$ [19] were synthesised according to literature procedures. All solvents employed in the synthesis were reagent grade or better, for photophysical measurements HPLC grade solvents were used.

2.2. Syntheses

2.2.1. $Ru(bpy)_2(\mu\text{-dpp})Ru(CN)_4$ (**1**)

100 mg of $[Ru(bpy)_2(dpp)]Cl_2$ (0.154 mmol) and 64 mg of $K_4[Ru(CN)_6]$ (0.154 mmol) in 10 cm^3 water was stirred at 80 °C for 3 days. The pH of the reaction mixture was kept at 3. At the end of reaction the mixture was neutralized by KOH and concentrated. NH_4PF_6 was added to precipitate the unchanged starting material in the form of $[Ru(bpy)_2(dpp)](PF_6)_2$ and the mixture was filtered off. The filtrate was concentrated to 1 cm^3 and 40 cm^3 of acetone was added and the precipitate was filtered. It was dissolved again in methanol and the unreacted $K_4[Ru(CN)_6]$ was removed by filtration. The crude product was purified by gel-filtration on Sephadex G-15 column with water as eluent. Yield 45%. IR, ν(CN): 2040 (sh), 2054, 2073 (sh), 2094. ^{1}H NMR (D_2O, 400 MHz): see Table 1. ^{13}C NMR (D_2O) from ^{1}H–^{13}HSQC: see in supplementary information Table S1.

2.2.2. $[Ru(bpy)_2(\mu\text{-dpp})Ru(CN{-}CH_3)_4](PF_6)_4$ (**2**)

The method for the preparation of $[Ru(bpy)(CN{-}CH_3)_4](PF_6)_2$ was applied [20]. 38 mg of **1** was refluxed in 2 ml of dimethyl sulfate till the UV–Vis spectrum of the reaction mixture did not show any change (7 h). The reaction mixture was extracted with portions of 2 cm^3 water three times. The product was precipitated with NH_4PF_6, filtered and dried under vacuum. Yield 71%, IR ν(CN) 2230, 2266 cm^{-1}, ^{1}H NMR (ACN, 400 MHz): see Table 1. ^{13}C NMR (ACN) from ^{1}H–^{13}HSQC: see in supplementary information Table S1.

2.3. Apparatus and methods

NMR spectra were recorded on a Bruker Avance II 400 NMR spectrometer equipped with a 5 mm broadband Z-gradient probe. Infrared spectra were measured on a Bio-Rad FTS-60A spectrometer. UV–Vis absorption spectra were obtained by a Perkin-Elmer Lambda 25 UV–Vis spectrophotometer. The emission spectra were measured on a Horiba Fluoromax-4 fluorimeter. The spectra detected at room temperature and at 77 K were corrected to the detector sensitivity. Time resolved luminescence measurements were performed by a Horiba Fluoromax-4 equipped with Time Correlated Single-Photon Counting (TCSPC) apparatus using as a light source for excitation a nano-LED emitting at 452 nm with pulse duration of 1.2 ns. Oxidation and reduction potentials were measured by cyclic voltammetry in deoxygenated solution. As electrolyte 0.1 M KNO_3 in water and 0.1 M tetrabutylammonium tetrafluoro borate in acetonitrile were used. The electrochemical apparatus was equipped with a glassy carbon working, platinum counter- and tungsten reference electrode. As potentiostate a Uniscan PG580 equipment was applied and sweep rate of 100 mV/s was chosen. The oxidation potentials for ferrocene and potassium hexacyanoferrate(II) were also measured in acetonitrile and water, respectively and the potentials measured against tungsten reference electrode have been converted to values related to saturated calomel electrode according to literature data [21,22].

2.4. Electronic structure calculations

The density functional theory methods used in our earlier studies [23] were used. Briefly, molecular geometries were determined using the B3LYP [24–26] combination of functionals as well as the M05 [27] functional in combination with the LANL2DZ [28–30] basis set. Vibrational frequency analysis confirmed that the structures found are genuine minima.

3. Results and discussion

3.1. Synthesis and NMR spectroscopy of new complexes

The complexes of $(bpy)_2Ru(\mu\text{-dpp})Ru(CN{-}X)_4{}^{n+}$ (where: X = nil and $n = 0$ or $X = CH_3$ and $n = 4$, respectively) prepared, together with the notation of the central atoms (a and b) and the aromatic rings (A–G) of the complexes are given in Scheme 1.

The synthesis of both compounds have been started from $RuCl_3$ and in the first step $Ru(bpy)_2Cl_2$ was obtained. In the second step two chloride ligands were exchanged for a dpp ligand according to a literature procedure [7]. Finally the dinuclear compound **1** was gained by adding potassium hexacyanoruthenate(II) in acidic media and the product was purified on Sephadex G-15. Methylation of compound **1** was achieved in dimethyl sulfate at 95 °C.

Detailed NMR investigations have been carried out to identify the structure of the complexes and to get a deeper insight in their stereochemistry. Tris chelate complexes, e.g. $[(bpy)_2Ru(\mu\text{-dpp})Ru(CN)_4]$, having a helical chirality axis consist of an enantiomeric pair indistinguishable by NMR or IR spectroscopy. However, the ^{1}H NMR spectra of both **1** and **2** show broad peaks at room temperature indicating dynamic behavior of the molecule with an exchange process of intermediate speed. Heating the samples