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ORIGINAL ARTICLE

Synthesis, characterization and molecular modeling of new ruthenium(II) complexes with nitrogen and nitrogen/oxygen donor ligands

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KEYWORDS

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Spectroscopy;
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Abstract Ru(II) complexes with some dinitrogen ligands; 3,4-diamino benzoic acid (DABA), 2-hydazinopyridine (hzpy), 2,2′-bipyridyl (bipy) and anthranilic acid (anth) have been synthesized and characterized by using IR, mass, and UV–Vis spectrometry and thermal analysis. The thermodynamic parameters (ΔE, ΔH, ΔS and ΔG) have been calculated by using Coats–Redfern and Horowitz–Metzger methods. The electrochemical properties of these complexes have been studied by using cyclic voltammetry. The evaluated energies of the HOMO and LUMO are in the range of −4.94 to −4.85 eV and −2.86 to −2.68 eV, respectively. The complexes have been proven to have an octahedral geometry with DABA, hzpy and bipy as N2 donor ligands and NSC as monodentate ligand. The structure of the Ru(II) complexes has been geometrically optimized by using parameterized PM3 semiempirical method.

1. Introduction

Metal complexes containing nitrogen chelating ligands have interesting physicochemical properties and important biological activities (Ali and Livingstone, 1974; Campbell, 1975; Crichton, 2012; Padhye and Kauffman, 1985). The transition metal ruthenium has a rich chemistry (McCleverty and Meyer, 2004; O'Regan and Grätzel, 1991). This allows the utilization of its complexes, such as ruthenium(II) polypyridyl complexes, in dye sensitized solar cells (DSSCs) (Kalyanasundaram and Grätzel, 1998; Gratzel, 2004;

Abbreviations: Hzpy, 2-hydrazinopyridine hydrochloride; DABA, 3,4-diaminobenzoic acid; Bipy, 2,2′-bipyridine; DSSC, dye sensitized solar cell; MLCT, metal-ligand charge transfer

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Nazeeruddin et al., 1993; O'Regan and Grätzel, 1991; Sahin et al., 2010a,b), molecular electronic devices (Robertson and McGowan, 2003), organic light emitting diodes (Oner et al., 2012), DNA structural probes and new antitumor agents (Dos Santos et al., 2013; Metcalfe and Thomas, 2003). Recently, depending on massive data on ruthenium polypyridyl complexes, the replacement of 2,2′-bipyridine (bipy) by other ligands with nitrogen-containing heterocyclic compounds, has received attention as this causes changes in their photophysical and electrochemical properties (Balzani et al., 1996; Chao and LN, 2005; De Cola and Belser, 1998; Juris et al., 1988; Kaes et al., 2000; Vos and Kelly, 2006). These properties actually represent the most important factors on their performances in relative application areas. In this study, we prepared five new ruthenium complexes by using anthranilic acid (anth), 3,4-diaminobenzoic acid (DABA), 2-hydrazinopyridine (hzpy) and 2,2′-bipyridyl (bipy) as the ligands and investigated their structural, thermodynamic, optical and electrochemical properties.

2. Experimental

2.1. Materials

All chemicals used in this study were of the highest purity available. 3,4-diaminobenzoic acid was purchased from Arcos Organics, ruthenium trichloride hydrate was purchased from Merck while, 2,2′-bipyridine, 2-hydrazino pyridine, anthranilic acid, dichloro(p-cymene)ruthenium(II) dimer, ethanol, *N*,*N*-dimethylformamide (DMF), tetrabutyl ammonium hexafluorophosphate ($TBAPF_6$) and methanol were purchased from Sigma–Aldrich. The structural formulas of the investigated ligands are given in Scheme 1.

2.2. Measurements

Infrared measurements of the complexes were taken by using Jasco FT-IR – 460 plus (range 400–4000 cm^{-1}). Mass spectra were taken with a Jeol JMS-AX500 mass spectrometer. Thermal analysis of the complexes was carried out by using a Shimadzu thermo-gravimetric analyzer TGA-50H; under a nitrogen atmosphere with a heating rate of 10 °C/min over a temperature range from room temperature up to 1000 °C. UV–Vis and fluorescence spectra were recorded in a 1 cm path length quartz cell by using an Analytic Jena S 600 UV diode array spectrophotometer and Edinburgh FLS920P fluorescence spectrometers, respectively. Electrochemical data were obtained using a CH Instrument 660 B Model Electrochemical Workstation. Cyclic voltammograms were measured in a cell containing a glassy carbon working electrode, silver wire reference electrode, platinum wire counter electrode and supporting electrolyte consisting of 0.1 M $TBAPF_6$ in DMF (scan rate 100 mV s^{-1}).

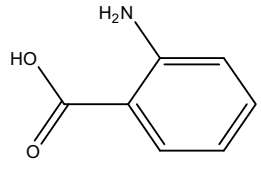
2.3. Synthesis of complexes

2.3.1. [Ru(II)(bipy)(DABA)$(NCS)_2$] (*I*)

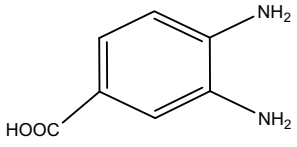
0.1 g (0.16 mmol) of $[RuCl_2(p\text{-cymene})]_2$ was dissolved in 100 ml of methanol and a few drops of DMF mixture, and then 0.049 g (0.32 mmol) of bipy and 0.097 g (0.64 mmol) of DABA were added to this solution and heated under argon atmosphere at 65 °C for 4 h with constant stirring. This reaction resulted in the formation of a violet precipitate. The precipitated complex was filtered and dried under vacuum and kept in a vacuum desiccator (0.12 g; yield: 71.4%). ^1H NMR (DMSO-d_6) δ ppm: 9.39 (d, J = 5.2 Hz, 2H), 8.75 (d, J = 8.4 Hz, 2H), 8.35 (d, J = 4.4 Hz, 1H), 8.29 (t, J = 8.0 Hz, 2H), 7.79 (t, J = 6.4 Hz, 2H), 6.30 (d, J = 6.0 Hz, 2H), 6.05 (d, J = 6.8 Hz, 2H).

2.3.2. [Ru(II)(DABA)(hzpy)$(NCS)_2$] (*II*)

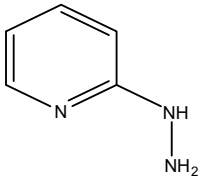
0.2 g (0.32 mmol) of $[RuCl_2(p\text{-cymene})]_2$ was dissolved in 100 ml of methanol and a few drops of DMF mixture, and then 0.0972 g (0.64 mmol) of DABA and 0.116 g (0.64 mmol) of hzpy were added to this solution and heated under argon atmosphere at 65 °C for 4 h with constant stirring. This reaction resulted in the formation of a black precipitate. The precipitated complex was dried under vacuum and kept in a vacuum desiccator (0.110 g; yield: 35.9%). ^1H NMR (DMSO-d_6) δ ppm: 8.30 (s, 1H), 7.93 (s, 1H) 7.26 (s, broad, 2H), 6.95–7.17 (m, 5H), 2.65 (s, 1H), 2.31 (s, 1H).



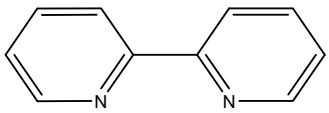
Anthranilic acid (anth)



3,4-Diaminobenzoica cid (DABA)



2-Hydrazinopyridine (hzpy)



2,2'-bipyridyl (bipy)

Scheme 1 Structural formulas of the investigated ligands.