Inorganica Chimica Acta 365 (2011) 439–446

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Unsymmetric diruthenium complexes

Nicholas Prokopuk [a,*], Andrew Chafin [a], Richard Gilardi [b], Jeffrey R. Deschamps [b]

[a] Research Department, Navair, China Lake, CA, United States
[b] The Naval Research Laboratory, Washington, DC, United States

ARTICLE INFO

Article history:
Received 19 August 2010
Received in revised form 29 September 2010
Accepted 30 September 2010
Available online 15 October 2010

Keywords:
Charge transfer
Electronic coupling
Ruthenium
Cyclic voltammetry
DFT calculations

ABSTRACT

The new diruthenium complexes *trans*-$[(NH_3)_5Ru(L–L)Ru(NH_3)_4(bpy\text{-}Me)](PF_6)_5$ (L–L are the bridging ligands pyrazine, **2a**; 4,4′dipyridyl, **2b**; and *trans*-1,2-bis(4-pyridyl)-ethylene, **2c**; bpy-Me is *N*-methyl-pyridyl-pyridinium) are generated from the new complexes $(L–L)Ru(NH_3)_4(bpy\text{-}Me)](PF_6)_3$ (**1a–c**) and $[(NH_3)_5Ru(H_2O)](PF_6)_2$. Cyclic voltammetry on the new compounds in acetonitrile electrolyte reveals two quasi-reversible oxidation steps corresponding to the two $Ru^{II/III}$ couples in **2b** and **2c** and a single oxidations for **1a–c**. In addition, two reduction waves are observed for the bpy-Me ligands of **1a–c** and **2a–c**. All of the new compounds exhibit multiple metal-to-ligand charge transfer (MLCT) bands in the visible region of the spectrum. For compounds **1a**–**c** the most intense absorption in the visible region decreases in energy as the length of the aromatic bridging ligands increases. By contrast the strongest absorption band of **2a** is lower in energy than the most intense bands of both 2**b** and **2c**. Single crystal X-ray analysis of **2a** reveals that the bridging pyridine is coplanar with the pyridyl ring of the bpy-Me ligand that is attached to the Ru center. DFT calculations on **2a** indicate that the HOMO is localized predominately on the $\{(NH_3)_5Ru\text{-}pyz\text{-}Ru(NH_3)_4\}$ portion of the complex and the LUMO has slightly more contribution from the bpy-Me ligand.

Published by Elsevier B.V.

1. Introduction

Nonlinear optical (NLO) materials derived from molecular chromophores provide a versatile approach to developing optoelectronic and photonic technologies, as the optical properties of the material can be tailored by tuning the chemical composition and structure of the chromophore [1–7]. Several organic chromophores that exhibit large first hyperpolarizabilities, β, have been developed for second-order NLO applications. A significant portion of the molecular work centers on one-dimensional donor–acceptor systems, D-π-A, in which an electron-donor is separated from an electron-acceptor by a π-conjugated bridge. For example, the NLO chromophore dimethylaminonitrostilbene contains a conjugated network with a strong donor (dimethylamino group) and strong acceptor (nitro group) [8]. The first hyperpolarizabilities in these compounds are associated with intense, low-energy charge-transfer absorptions. Controlling the redistribution of electron density upon excitation provides a mechanism for tuning the quadratic NLO behavior of the chromophore. The relatively simple two-state model of Oudar and Chemla allows for meaningful predictions of a molecule's static hyperpolarizability β_0 from its intramolecular charge transfer properties by considering only the differences in the ground and first excited state [9]. However, as the electronic structure of the chromophore becomes more complex and multiple or overlapping absorptions contribute to the NLO properties, the analysis becomes more difficult and the two-state model is no longer accurate.

Recently, transition metals have been integrated into the NLO chromophores with the metal center serving as either the electron donor, electron acceptor, or both [10–12]. Incorporating transition metals into the chromophore offers the possibility of combining the NLO behavior of the chromophore with the magnetic or electrochemical properties of the metal centers. In these complexes, the intramolecular charge-transfer process occurs between the ligands and the metal centers (metal-to-ligand charge transfer or ligand-to-metal charge transfer) or between two metal centers. Coe et al. have prepared a series of *trans*-$\{L^DRu^{II}(NH_3)_4L^A\}^{n+}$ (L^D = electron donor ligand; L^A = electron acceptor ligand) chromophores with a variety of pyridinium groups as the electron acceptor [13–22]. The NLO properties of these complexes are associated with a MLCT process and, upon oxidation of the ruthenium centers, the hyperpolarizability is significantly attenuated [23]. The one-dimensional nature of the charge transfer process provides a geometry that can be easily tuned by varying the coordinating environment about the metal center and the nature of the donor and acceptor ligands [24,25]. Electroabsorption (Stark) spectroscopy has been extremely useful in correlating the structure and composition of the inorganic chromophores with their charge-transfer and NLO properties [17,18,20,21,26–28]. Push-pull chromophores were synthesized from metalloporphyrins and Schiff bases [29–32]. In both of these

---

[*] Corresponding author.
E-mail address: nicholas.prokopuk@navy.mil (N. Prokopuk).

0020-1693/$ - see front matter Published by Elsevier B.V.
doi:10.1016/j.ica.2010.09.059

cases, the transition metal enhances the nonlinearity response by increasing the planarity and conjugation of the macrocycle rather than serving as a highly polarizable bridge between the donor and acceptor. In this paper we describe the synthesis and characterization of a series of unsymmetrical diruthenium complexes afixed with a strong electron accepting ligand on one end and an oxidizable metal center on the distal end. The central ruthenium atom separates the donor and acceptor ends of these chromophore.

2. Experimental

2.1. Materials and procedures

Solvent manipulations during the synthesis of the metal complexes were performed under Ar using standard Schlenk and syringe techniques. The solvents acetone and deionized water used for synthesis of the ruthenium complexes were degassed with argon prior to use. Acetone, methylene chloride, and triethyl amine employed for recrystallization, were used as received from Aldrich. Acetonitrile for electrochemical measurements was distilled from CaH$_2$ over N$_2$. The solvents dimethyl sulfoxide (Burdick and Jackson Laboratories), acetonitrile (Aldrich), acetone (Aldrich), propylene carbonate (Burdick and Jackson Laboratories), and *N*, *N*-dimethylformamide (Aldrich) utilized for electronic spectroscopy were used as received by Aldrich. The chemicals 4,4′-bipyridyl (bpy), pyrazine (pyz), *trans*-1,2-bis(4-pyridyl)-ethylene (bpe), ammonium hexafluorophosphate, and tetrabuthylammonium chloride were obtained from Aldrich and used as received. Tetrabutylammonium hexafluorophosphate was obtained from Aldrich and recrystallized from acetonitrile and diethyl ether. *N*-methyl-4,4′-bipyridinium iodide was synthesized via the alkylation of 4,4′-bipyridyl by methyl iodide [14]. The complexes [(NH$_3$)$_5$Ru(H$_2$O)](PF$_6$)$_2$ and [(NH$_3$)$_5$Ru(bpy-Me)](PF$_6$)$_3$ (**4**) were synthesized by the method of Curtis et al. [33]. *trans*-[(SO$_4$)Ru(NH$_3$)$_4$(bpy-Me)]Cl$_2$ was prepared from a 100 mg sample of *trans*-[(SO$_2$)Ru(NH$_3$)$_4$Cl]Cl as an oil or sticky solid as described by Coe et al. [14]. Yields from reactions of *trans*-[(SO$_4$)Ru(NH$_3$)$_4$(bpy-Me)]Cl are reported with respect to the starting material *trans*-[(SO$_2$)Ru(NH$_3$)$_4$Cl]Cl. The compounds [(NH$_3$)$_5$Ru(L–L)](PF$_6$)$_2$ (L–L = pyz (**3a**), bpy (**3b**), and bpe (**3c**)) were prepared by the method of Callahan et al. [39].

2.1.1. Synthesis of trans-[(pyz)Ru(NH$_3$)$_4$(bpy-Me)](PF$_6$)$_3$ (**1a**)

A solution of *trans*-[(SO$_4$)Ru(NH$_3$)$_4$(bpy-Me)]Cl (prepared from 100 mg of *trans*-[(SO$_2$)Ru(NH$_3$)$_4$Cl]Cl, approximately 0.33 mmol) in Ar-degassed water (6 mL) was reduced over zinc amalgam with a few drops of concentrated sulfuric acid with argon agitation for 30 min. The resulting blue solution was filtered and transferred to a flask containing pyrazine (250 mg, 3.13 mmol) in 4 mL of Ar-degassed water under an argon atmosphere. After stirring for 12 h under Ar in the dark, sodium carbonate (0.5 g) was added and the mixture was allowed to stir until the solids dissolved (approximately 5 min). Ammonium hexafluorophosphate (0.5 g) was then added to induce precipitation. The mixture was cooled to 5 °C and the resulting solid was isolated by vacuum filtration in air. The product was recrystallized from acetone/ether to yield a magenta powder: yield 120 mg (43% based on *trans*-[(SO$_2$)Ru(NH$_3$)$_4$Cl]Cl). δ_H(d_6-acetone) 9.19 (4H, m), 9.02 (2H, d, *J* 4.6), 8.72 (2H, d, *J* 7.0), 8.56 (2H, d, *J* 4.4), 8.16 (2H, d, *J* 6.9), 4.65 (3H, s), 2.79 (12H, s). *Anal.* Calc. for C$_{15}$H$_{27}$N$_8$RuP$_3$F$_{18}$: C, 21.06; H, 3.18; N, 13.10. Found: C, 21.01; H, 3.07; N, 12.75%.

2.1.2. Synthesis of trans-[(bpy)Ru(NH$_3$)$_4$(bpy-Me)](PF$_6$)$_3$ (**1b**)

A solution of *trans*-[(SO$_4$)Ru(NH$_3$)$_4$(bpy-Me)]Cl (prepared from 100 mg of *trans*-[(SO$_2$)Ru(NH$_3$)$_4$Cl]Cl, approximately 0.33 mmol) in Ar-degassed water was reduced over zinc amalgam with a few drops of concentrated sulfuric acid with argon agitation for 30 min. This solution was transferred via syringe to a Schlenk flask containing bpy (500 mg, 3.21 mmol) dissolved in Ar-degassed acetone. After stirring in the dark for 12 h, the reaction mixture was concentrated to approximately 5 mL and filtered in air. The solid (unreacted bpy) was washed two times with 5 mL portions of deionized water. The filtrate and washings were combined and ammonium hexafluorophosphate (1 g) was added. The mixture was cooled to 5 °C to complete the precipitation. The resulting solid was isolated by filtration and recrystallized twice from acetone/methylene chloride/triethylamine to remove protonated bpy. A third recrystallization from acetone/ether produced pure material: yield 80 mg (26% based on *trans*-[(SO$_2$)Ru(NH$_3$)$_4$Cl]Cl). δ_H(d_6-acetone) 9.21 (4H, m), 9.07 (2H, d, *J* 6.7), 8.75 (4H, m), 8.13 (2H, d, *J* 6.9), 8.00 (2H, d, *J* 5.3), 7.85 (2H, d, *J* 4.5), 4.63 (3H, s), 2.77 (12H, s). *Anal.* Calc. for C$_{21}$H$_{31}$N$_8$RuP$_3$F$_{18}$ + 1 acetone: C, 29.13; H, 3.77; N, 11.32. Found: C, 28.48; H, 3.64; N, 11.54%.

2.1.3. Synthesis of trans-[(bpe)Ru(NH$_3$)$_4$(bpy-Me)](PF$_6$)$_3$ (**1c**)

This compound was prepared in a manner similar to **1b** using bpe (500 mg, 2.8 mmol) in place of bpy. After two recrystallizations from acetone/methylene chloride/triethylamine, the product was further purified by recrystallization from acetone/ether to yield a dark magenta solid: yield 180 mg (57% based on *trans*-[(SO$_2$)Ru(NH$_3$)$_4$Cl]Cl). δ_H(d_6-acetone) 9.17 (4H, m), 8.91 (2H, d, *J* 6.8), 8.72 (2H, d, *J* 7.0), 8.61 (2H, d, *J* 4.5), 8.10 (2H, d, *J* 6.2), 7.79 (2H, d, *J* 6.7), 7.67 (2H, d, *J* 2.0), 7.60 (2H, d, *J* 4.5), 4.63 (3H, s), 2.85 (12H, s). *Anal.* Calc. for C$_{23}$H$_{33}$N$_8$RuP$_3$F$_{18}$: C, 28.85; H, 3.47; N, 11.70. Found: C, 28.69; H, 3.51; N, 11.13%.

2.1.4. Synthesis of trans-[(NH$_3$)$_5$Ru(pyz)Ru(NH$_3$)$_4$(bpy-Me)](PF$_6$)$_5$ (**2a**)

A Schlenk flask was charged with [(NH$_3$)$_5$Ru(H$_2$O)](PF$_6$)$_2$ (100 mg, 0.2 mmol), *trans*-[(pyz)Ru(NH$_3$)$_4$(bpy-Me)](PF$_6$)$_3$ **1a** (80 mg, 0.09 mmol), and a stir bar. The flask was cycled between vacuum and an argon purge three times. Acetone (7 mL) was added and the solution was allowed to stir for 12 h. Ether (10 mL) was added to precipitate the product as a blue powder. The solid was isolated by filtration under an argon atmosphere, washed with ether, and dried under vacuum. Recrystallization from acetone/ether yielded analytically pure material: yield 75 mg (62% based on *trans*-[(pyz)Ru(NH$_3$)$_4$(bpy-Me)](PF$_6$)$_3$). δ_H(d_6-acetone) 9.17 (4H, m), 8.87 (2H, d, *J* 5.1), 8.73 (2H, d, *J* 6.8), 8.43 (2H, d, *J* 4.2), 8.16 (2H, d, *J* 4.8), 4.64 (3H, s), 3.72 (3H, s), 2.72 (12H, s), 2.58 (12H, s). *Anal.* Calc. for C$_{15}$H$_{42}$N$_{13}$Ru$_2$P$_5$F$_{30}$: C, 13.53; H, 3.18; N, 13.67. Found: C, 13.51; H, 3.68; N, 13.18%.

A large excess of [(NH$_3$)$_5$Ru(H$_2$O)](PF$_6$)$_2$ is required due to the inherent impuity of the aqua complex. If less than a 30% excess of [(NH$_3$)$_5$Ru(H$_2$O)](PF$_6$)$_2$ is used a mixture of **1a** and **2a** is obtained. This mixture can be converted to the desired diruthenium complex by adding more [(NH$_3$)$_5$Ru(H$_2$O)](PF$_6$)$_2$ under the anaerobic conditions described above.

2.1.5. Synthesis of trans-[(NH$_3$)$_5$Ru(bpy)Ru(NH$_3$)$_4$(bpy-Me)](PF$_6$)$_5$ (**2b**)

This compound was prepared similarly to **2a** using **1b** (84 mg, 0.09 mmol) in place of **1a** and 64 mg (0.13 mmol) of [Ru(NH$_3$)$_4$(H$_2$O)](PF$_6$)$_2$. Recrystallization from acetone/ether forded a magenta solid: yield 120 mg (90% based **2A**). δ_H(d_6-acetone) 9.19 (4H, m), 8.98 (4H, m), 8.76 (2H, d, *J* 7.4), 8.11, (2H, d, *J* 6.2), 8.02 (2H, d, *J* 6.2), 7.82 (2H, d, *J* 6.4), 4.63 (3H, s), 3.29 (3H, s), 2.84 (12H, s), 2.63 (12H, s). *Anal.* Calc. for C$_{21}$H$_{46}$N$_{13}$Ru$_2$P$_5$F$_{30}$: C, 17.91; H, 3.29; N, 12.94. Found: C, 17.90; H, 3.63; N, 12.03%.

2.1.6. Synthesis of trans-[(NH$_3$)$_5$Ru(bpe)Ru(NH$_3$)$_4$(bpy-Me)](PF$_6$)$_5$ (**3b**)

This compound was prepared similarly to **2a** using **1c** (98 mg, 0.10 mmol) in place of **1a** and 76 mg (0.15 mmol) of [Ru(NH$_3$)$_4$(H$_2$O)](PF$_6$)$_2$. After recrystallization from acetone/ether a magenta solid was isolated: yield 133 mg (93% based on **3A**). δ_H(d_6-acetone)