Inorg. Chem. **1993,** *32,* 4982–4984

Spectroscopic and Electrochemical Characterization of the Asymmetric Bimetallic Ruthenium(II) Complex $[(bpy)_2Ru^{II}(bpym)Ru^{II}(NH_3)_4](PF_6)_4 \cdot 3H_2O$

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Received June 3, 1993

Introduction

A number of recent reports have appeared which deal with asymmetric bimetallic complexes in which one end of the molecule is particularly solvent sensitive.[1] The solvent-sensitive portion of these complexes typically consists of ammine ligands, while the solvent-insensitive portion contains polypyridyl ligands. One key feature of these bimetallic species is that, through specific solvation effects, the relative reduction potentials of the two metal centers can be varied systematically by simply varying the solvent.

As part of a larger project involving the synthesis of tri- and tetrametallic ammine complexes, we recently prepared the asymmetric bimetallic Ru(II)/Ru(II) species $[(bpy)_2Ru^{II}(bpym)Ru^{II}(NH_3)_4](PF_6)_4 \cdot 3H_2O$ (I), where bpy = 2,2′-bipyridine and bpym = 2,2′-bipyrimidine. This note involves a description of the preparation and the spectroscopic and electrochemical investigation of this complex.

Experimental Section

Materials. Trifluoromethanesulfonic acid (triflic acid, HTFMS), hexaammineruthenium(III) chloride ($[Ru(NH_3)_6Cl_3]$, 95%), ammonium hexafluorophosphate (NH_4PF_6, 99.99%), and silver trifluoromethanesulfonate (AgTFMS, 99+%) were purchased from Aldrich Chemical Co. and used as received.[2] 2,2′-Bipyrimidine (98+%) was purchased from Lancaster Synthesis, Inc.

$[Ru(NH_3)_5TFMS](TFMS)_2$ and $Ru(bpy)_2Cl_2 \cdot 2H_2O$ were prepared by literature procedures.[3,4] $[(bpy)_2Ru^{II}(bpym)](PF_6)_2 \cdot H_2O$ was prepared by the method reported by Rillema et al.[5] Acetonitrile used for electrochemical measurements was purchased from either Burdick & Jackson or Aldrich Chemical Co. (HPLC grade) and stored over activated Molecular Sieves (4A). Absolute ethanol (Midwest Grain Products) was used as received. House-deionized water was purified using a Millipore Milli-Q system.

$[(NH_3)_4Ru^{II}(bpym)](PF_6)_2$. This complex was synthesized by using a modification of the preparation of the perchlorate salt originally reported by Ruminski et al.[6] $[Ru(NH_3)_5TFMS](TFMS)_2$ (0.1008 g, 0.159 mmol) and 2,2′-bipyrimidine (0.2502 g, 1.58 mmol) were dissolved in absolute ethanol (15 and 10 mL, respectively) in separate three-necked flasks connected by a cannula. (The absolute ethanol had previously been deoxygenated by bubbling Ar through the system for 15 min.) Both flasks were deoxygenated with Ar for an additional 20 min. Zn amalgam[7] was quickly introduced into the flask containing $[Ru(NH_3)_5(TFMS)](TFMS)_2$, and the stirring solution turned lime green. After 7 min, the ruthenium solution was forced through the cannula (under Ar) into the stirring solution of 2,2′-bipyrimidine, forming a dark red solution. Diethyl ether (50 mL) was quickly introduced, forming a red precipitate which slowly turned dark green. The mixture was filtered through a fine glass frit, and the solid obtained was washed with 5 mL of chloroform and then with excess ether. The green-black solid was then dissolved in 25 mL of water, and the solution was filtered. An aqueous solution of NH_4PF_6 (77 mg in 1 mL) was added to the filtrate, and the solution was refrigerated for 3 days. No precipitate formed from this procedure. Over the course of 3 days more, a total of 130 mg of solid NH_4PF_6 was added to promote crystallization.[8] The dark microcrystalline solid obtained was filtered off, washed with absolute ethanol and ether, and then vacuum-dried. Yield: 32 mg (32.6%). Purity was checked by UV–vis and cyclic voltammetry (see Tables I and II).

Table I. Electrochemical Data[a,b]

complex	solvent	$E_{1/2}$, V (ΔE_p, mV)
$[(bpy)_2Ru^{II}(bpym)]^{2+}$	CH_3CN/0.1 M TBAH	+1.41 (66)
$[(NH_3)_4Ru^{II}(bpym)]^{2+}$	CH_3CN/0.1 M TBAH	+0.66 (58)
	H_2O/0.1 M KCl	+0.49 (77)
	H_2O/0.1 M KCl	+0.51[c]
$[(bpy)_2Ru^{II}(bpym)Ru^{II}(NH_3)_4]^{4+}$	CH_3CN/0.1 M TBAH	+0.89 (70)
		+1.57 (110)

[a] All complexes are PF_6^- salts unless otherwise noted. [b] Cyclic voltammograms were taken at a scan rate of 100 mV/s on either a Pt (for acetonitrile) or a glassy carbon (for water) electrode. The auxiliary electrode was Pt, and all potentials were referenced to the saturated sodium chloride calomel electrode (SSCE). TBAH = tetrabutylammonium hexafluorophosphate. [c] ClO_4^- salt; ref 6 (obtained by subtracting 0.248 V from the reported value vs NHE).

Table II. Spectral Data[a]

complex	solvent	λ_{max}, nm ($10^{-3}\epsilon$, $M^{-1}\,cm^{-1}$)
$[(bpy)_2Ru^{II}(bpym)]^{2+}$	CH_3CN	241 (36.4), 285 (47.4), 399 (sh), 423 (9.67), 472 (sh)
$[(NH_3)_4Ru^{II}(bpym)]^{2+}$	CH_3CN	243 (22.1), 258 (sh), 399 (10.3), 564 (2.74)
$[(bpy)_2Ru^{II}(bpym)Ru^{II}(NH_3)_4]^{4+}$	CH_3CN	257 (30.2), 283 (55.7), 427 (19.5), 505 (sh), 704 (3.2)
$[(bpy)_2Ru^{II}(bpym)Ru^{III}(NH_3)_4]^{5+}$	CH_3CN/0.1 M TEAP[b]	251 (37.0), 281 (59.7), 411 (17.8), 577 (3.7)
$[(NH_3)_4Ru^{II}(bpym)Ru^{II}(NH_3)_4]^{4+}$	H_2O[c]	424 (18), 697 (4.0)
$[(bpy)_2Ru^{II}(bpym)Ru^{II}(bpy)_2]^{4+}$	CH_3CN[d]	243 (sh), 280 (75), 411 (24), 545 (sh), 594 (8.2)

[a] All complexes are PF_6^- salts unless otherwise stated. Absorption coefficients for all spectra reported for this work were determined using a single solution concentration. [b] TEAP = tetraethylammonium perchlorate. [c] ClO_4^- salt; ref 6. [d] ClO_4^- salt; ref 12.

$[(bpy)_2Ru^{II}(bpym)Ru^{II}(NH_3)_4](PF_6)_4 \cdot 3H_2O$ (I). $Ru(bpy)_2Cl_2 \cdot 2H_2O$ (0.062 g, 0.119 mmol) and AgTFMS (0.061 mg, 0.237 mmol) were added to 20 mL of acetone (previously deoxygenated for 30 min) under Ar. The mixture was stirred under Ar for 2 h under reduced light. After filtration of the mixture on a fine glass frit, the filtrate was quickly put back under Ar and $[(NH_3)_4Ru^{II}(bpym)](PF_6)_2$ (0.073 g, 0.118 mmol) was added. The mixture was warmed to 35–40°C and stirred under Ar for 5.5 h. (During this time a total of 30 mL of deoxygenated acetone was introduced to replace solvent lost by evaporation.) The dark green mixture was then poured into a beaker, 5 mL of water was added, and the mixture was left to evaporate overnight.

The solid present in the beaker after evaporation was dissolved in a minimum volume of water (~50 mL), and the solution was filtered on a fine glass frit. The filtrate was chilled in an ice bath, and solid NH_4PF_6 was added to precipitate the product. When precipitation appeared complete (the supernatant was a pale color), the suspension was filtered. The solid obtained was washed with several drops of cold absolute ethanol and then with excess ether and vacuum-dried. Yield: 0.100 g (61.1%)

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(1) (a) Chang, J. P.; Fung, E. Y.; Curtis, J. C. *Inorg. Chem.* **1986,** *25,* 4233. (b) Curtis, J. C.; Roberts, J. A.; Blackbourn, R. L.; Dong, Y.; Massum, M.; Johnson, C. S.; Hupp, J. T. *Inorg. Chem.* **1991,** *30,* 3856. (c) Roberts, J. A.; Bebel, J. C.; Absi, M. L.; Hupp, J. T. *J. Am. Chem. Soc.* **1992,** *114,* 7957.

(2) Some difficulties with low yields and impure products which we experienced in the preparation of several of our compounds seemed to have been traced back to variations in the composition of $[Ru(NH_3)_6Cl_3]$. We had good success with a sample of $[Ru(NH_3)_6Cl_3]$ with a lot analysis of 35.8% Ru and 34.1% Cl.

(3) Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; Taube, H. In *Inorganic Synthesis;* Shreeve, J. M., Ed.; John Wiley & Sons: New York, 1986; Vol. 24, pp 258–259.

(4) (a) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978,** *17,* 3334. (b) Sprintschnik, G.; Sprintschnik, H. W.; Kirsch, P. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1977,** *99,* 4947.

(5) Rillema, D. P.; Mack, K. B. *Inorg. Chem.* **1982,** *21,* 3849.

(6) Ruminski, R. R.; Petersen, J. D. *Inorg. Chem.* **1982,** *21,* 3706.

(7) *Handbook of Preparative Inorganic Chemistry,* 2nd ed.; Brauer, G., Ed.; Academic Press: New York, 1965; Vol. 2, pp 1806–1807.

(8) This laborious procedure was used in an attempt to crystallize pure $[(NH_3)_4Ru^{II}(bpym)](PF_6)_2$ without contamination by bimetallic $[(NH_3)_4Ru^{II}(bpym)Ru^{II}(NH_3)_4](PF_6)_4$.

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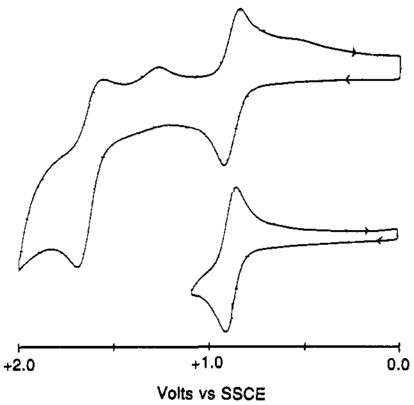

Figure 1. Cyclic voltammograms (Pt electrode) of $[(bpy)_2Ru^{II}(bpym)Ru^{II}(NH_3)_4]^{4+}$ in CH_3CN/0.1 M TBAH. Scan rate = 100 mV/s.

Anal. Calcd for $[(bpy)_2Ru^{II}(bpym)Ru^{II}(NH_3)_4](PF_6)_4 \cdot 3H_2O$: C, 24.46; H, 2.93; N, 12.23. Found: C, 24.58; H, 2.86; N, 12.06.[9]

Methods. UV-vis-near-IR spectra were taken on a Shimadzu UV-3100 spectrophotometer. Electrochemical measurements were carried out using a PAR 173 potentiostat/galvanostat contolled by a PAR 175 universal programmer. Cyclic voltammograms were obtained in a single glass cup (~2-mL samples) using either a platinum or a glassy carbon working electrode (Bioanalytical Systems), a platinum auxiliary electrode, and a saturated sodium chloride calomel (SSCE) reference electrode (Bioanalytical Systems). Spectroelectrochemical results were obtained using a quartz cell fused to a three-compartment electrochemical cell (University of North Carolina at Chapel Hill—Chemistry Department Glass Shop). Elemental analyses were carried out by Galbraith Laboratories, Inc.

Results and Discussion

Electrochemistry. The cyclic voltammogram of I (in acetonitrile) is shown in Figure 1. A scan out to +1.10 V showed a fairly reversible wave (ΔE_p = 70 mV) centered at $E_{1/2}$ = +0.89 V. We have assigned this wave as a one-electron (metal-centered) oxidation of the $(bpym)Ru^{II}(NH_3)_4{}^{2+}$ portion of space I. This compares with an $E_{1/2}$ = +0.66 V (ΔE_p = 58 mV) for $[(bpym)Ru^{II}(NH_3)_4](PF_6)_2$ in the same solvent (see Table I). The +0.23-V shift in $E_{1/2}$ for I is thus due to the effect of coordination of a second Ru^{II} center on the 2,2′-bipyrimidine.

A second oxidation was observed for I at $E_{1/2}$ = +1.57 V (ΔE_p = 110 mV). We have assigned this as a one-electron (metal-centered) oxidation of the $(bpy)_2Ru^{II}(bpym)^{2+}$ portion of the complex adjacent to $-[Ru^{III}(NH_3)_4]^{2+}$. As expected, this oxidation was shifted in a positive direction from that measured for *monometallic* $[(bpy)_2Ru^{II}(bpym)]^{2+}$ in the same solvent ($E_{1/2}$ = +1.41 V).[10] Figure 1 also shows that the Ru(III)/Ru(III) species generated was unstable even on the CV time scale, as decomposition peaks emerged in the reverse scan at +1.27 V and around +0.58 V. These may correspond to reduction of monometallic decomposition products.

UV-Vis Spectra. The absorption spectra (in acetonitrile) of I (the Ru(II)/Ru(II) form) is shown in Figure 2, and the results are tabulated and compared with those for the corresponding mono- and bimetallic complexes in Table II. We have assigned the low-energy band at 704 nm to a $[a_4Ru^{II}]$ ($d\pi$) → [bpym] (π^*) MLCT transition.[11] The absorption envelope centered at 427 nm has been assigned as a sum of a second $[a_4Ru^{II}]$ ($d\pi$) → [bpym] (π^*) MLCT transition and a $[b_2Ru^{II}]$ ($d\pi$) → [bpy] (π^*) MLCT band. Moreover, the shoulder at ~505 nm in I is most likely a $[b_2Ru^{II}]$ ($d\pi$) → [bpym] (π^*) MLCT transition, which is red-shifted from the corresponding transition in $[(bpy)_2Ru^{II}(bpym)]^{2+}$(472 nm). These assignments have been made on the bases of the data in Table II and comparisons with band assignments made by Ruminski et al.[6] and Sahai et al.[12] for the symmetrical bimetallic complexes $[(NH_3)_4Ru^{II}(bpym)Ru^{II}(NH_3)_4]^{4+}$ and $[(bpy)_2Ru^{II}(bpym)Ru^{II}(bpy)_2]^{4+}$, respectively.

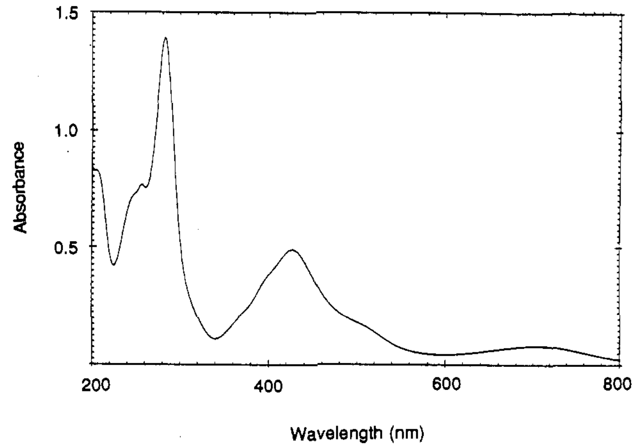

Figure 2. UV–vis spectrum of $[(bpy)_2Ru^{II}(bpym)Ru^{II}(NH_3)_4]^{4+}$ in CH_3CN.

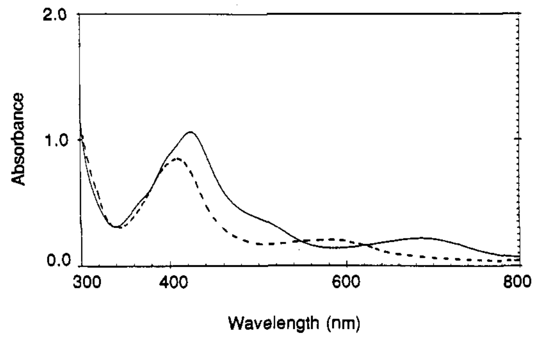

Figure 3. UV–vis spectra of $[(bpy)_2Ru^{II}(bpym)Ru^{II}(NH_3)_4]^{4+}$ (—) and $[(bpy)_2Ru^{II}(bpym)Ru^{III}(NH_3)_4]^{5+}$ (- - -) in CH_3CN/0.1 M TEAP (uncorrected for background).

Figure 3 compares the UV–vis spectrum of the Ru(II)/Ru(II) form of I with its mixed-valence Ru(II)/Ru(III) form. The mixed-valence species was produced by exhaustive oxidation of I in acetonitrile at a Pt mesh electrode at +1.2 V vs SSCE.[13] The spectrum of the mixed-valence complex was characterized by loss of the $[a_4Ru^{II}]$ ($d\pi$) → [bpym] (π^*) MLCT band at 704 nm and red-shifting of the $[b_2Ru^{II}]$ ($d\pi$) → [bpym] (π^*) MLCT transition to 577 nm (Table II). In addition, the original band centered at 427 nm for I shows a loss of intensity (and an apparent blue shift) due to the loss of the second $[a_4Ru^{II}]$ ($d\pi$) → [bpym] (π^*) MLCT band.

Scans out to ~1500 nm revealed no conclusive evidence for a metal-to-metal charge-transfer (MMCT) transition for the mixed-valence form of I in acetonitrile. Due to the large difference in redox potentials between the two metal sites ($\Delta E_{1/2}$ = 0.68 V), we expected that any MMCT band observed might be on the edge of the visible spectrum (600–800 nm) and have an extremely low absorption coefficient. Using data for the asymmetric mixed-valence species $[(bpy)_2ClRu^{II}\text{–pyrazine–}Ru^{III}(NH_3)_5]^{5+}$ reported by Meyer et al.,[14] we have estimated that the MMCT band for the mixed-valence form of complex I should be

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[9] C,H,N values represent the average of two runs on the same sample.

[10] (a) Dose et al.[10b] reported +1.29 V for this complex in CH_3CN/0.1 M $NaClO_4$, although ref 12 reported this result as +1.36 V. (b) Dose, E. V.; Wilson, L. *Inorg. Chem.* **1978**, *17*, 2660.

[11] We will use the notation $[a_4Ru^{II}]$ and $[b_2Ru^{II}]$ to denote the two different Ru^{II} centers coordinated by NH_3 and bpy, respectively.

[12] Sahai, R.; Morgan, L.; Rillema, D. P. *Inorg. Chem.* **1988**, *27*, 3495.

[13] Re-reduction at 0.0 V vs SSCE resulted in ≥81% recovery of I, based on absorption measurements.

[14] Callahan, R.; Brown, G. M.; Meyer, T. J. *Inorg. Chem.* **1975**, *14*, 1443.

observed around 780 nm.[15] As stated earlier, we saw no conclusive evidence for the existence of this MMCT band.[16]

Preliminary data show that the ammine portion of I is indeed solvent sensitive. In DMF (Gutmann donor number, DN = 26.6),[17] the [a_4Ru^{II}] ($d\pi$) → [bpym] (π^*) MLCT is red-shifted to 725 nm and $E_{1/2}(1) = +0.70$ V. Conversely, in nitromethane (DN = 2.7), the MLCT band blue-shifts to 673 nm and $E_{1/2}(1) = +0.93$ V. However, as in acetonitrile, no evidence was found for a MMCT band in the mixed-valence form of I in these solvents.[18]

In an effort to reduce the measured $\Delta E_{1/2}$ value in these asymmetric bimetallic species, we are currently synthesizing mixed-metal analogs of I.

Acknowledgment. This work was supported by a grant from the Petroleum Research Fund (Type B), administered by the American Chemical Society.

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(15) The energy of the MMCT band (E_{op}) for an asymmetric mixed-valence species can be estimated as $E_{op} = E_0 + E_{FC}$, where E_0 = the difference in internal energy between the thermally equilibrated [$b_2Ru^{II}/Ru^{III}a_4$] and [$b_2Ru^{III}/Ru^{II}a_4$] forms of I and E_{FC} = Franck–Condon energy.[14] $E_0 = E_{1/2}[b_2Ru^{III}/Ru^{II}a_4 \rightarrow b_2Ru^{II}/Ru^{II}a_4] - E_{1/2}[b_2Ru^{II}/Ru^{III}a_4 \rightarrow b_2Ru^{II}/Ru^{II}a_4]$, or more concisely, $E_0 = E_1 - E_2$. $E_2 = +0.89$ V (Table I), and E_1 can be estimated from $E_{1/2}$ of the symmetrical species $[(bpy)_2Ru^{II}\text{–}bpym\text{–}Ru^{II}(bpy)_2]^{4+}$; $E_1 = +1.49$ V (average of values reported in refs 10b and 12). Thus, $E_0 = 0.60$ V. E_{FC} can be estimated from the measured MMCT spectra (in acetonitrile) reported by Meyer et al.[14] for $[(bpy)_2ClRu^{II}\text{–}pyrazine\text{–}Ru^{III}(NH_3)_5]^{5+}$; $E_{FC} = 8000$ cm^{-1}. Therefore $E_{op} = 1.28 \times 10^4$ cm^{-1} (~780 nm).

(16) An extremely low intensity MMCT could be hidden (in the 600–800-nm range) by the long-wavelength tail of the 577-nm band in Figure 3 or could be indistinguishable from residual absorption of unoxidized I around 700 nm.

(17) Gutmann donor number values taken from ref 1a.

(18) We expected that using nitromethane as solvent would decrease the measured $\Delta E_{1/2}$ for I by increasing $E_{1/2}(1)$ (for the more solvent-sensitive ammine portion) and not $E_{1/2}(2)$. However, the presence of a more electron-deficient [a_4Ru^{III}] shifted the [b_2Ru^{II}] $E_{1/2}(2)$ as well (to about +1.60 V), leaving $\Delta E_{1/2}$ at nearly the same value as in acetonitrile.