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Photoisomerization in an analogous set of ruthenium sulfoxide complexes

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ABSTRACT

Complexes of the type $[Ru(bpy)_2(OSOBnR)](PF_6)$ where bpy is 2,2′-bipyridine and OSOBnR is a 4-substituted benzylsulfinylbenzoate with R = NO_2, F, Cl, H, CH_3, CF_3 and OCH_3, have been prepared and investigated by ^{1}H NMR spectroscopy, cyclic voltammetry and UV–vis spectroscopy. Despite the distance of the R group from ruthenium, the $Ru^{3+/2+}$ reduction potential and charge transfer absorption maximum vary predictably with the electron withdrawing nature of the group.

1. Introduction

Electron transfer induced conformational changes are central to the operation of molecular machines and other types of molecular bistability [1–3]. A number of studies have revealed that reduction or oxidation of interlocked rotaxanes results in translocation of a molecular unit from one site to another [4–6]. However, certain transition metal complexes exhibit bistability through isomerization of bound ambidentate ligands [7–12]. For example, pentaammine ruthenium complexes of dimethylsulfoxide (DMSO) undergo intramolecular linkage isomerization (S vs. O) following oxidation and reduction of ruthenium [13–16]. We have developed a class of simultaneously photochromic and electrochromic polypyridine ruthenium sulfoxide complexes based on S → O and O → S isomerization [17–26]. In our study of these complexes, we have found that changes to a substituent R group affects the S-bonded $Ru^{3+/2+}$ reduction potential, the S-bonded charge-transfer absorption maximum and the S → O isomerization quantum yield. Interestingly, the corresponding O-bonded properties show no correlation with the identity of the R group.

2. Experimental

2.1. Materials

The reagents $RuCl_3{\cdot}xH_2O$ and silver hexafluorophosphate ($AgPF_6$) were purchased from Strem. The reagents 2,2′-bipyridine (bpy), thiosalicylic acid, *m*-chloroperoxybenzoic acid, triethylamine, 4-trifluoromethylbenzyl bromide, 4-fluorobenzyl bromide, benzyl bromide, 4-methylbenzyl bromide, 4-chlorobenzyl bromide, 4-methoxybenzyl bromide, and 4-nitrobenzyl bromide were purchased from Aldrich and used as received. The compounds *cis*-$[Ru(bpy)_2Cl_2]{\cdot}2H_2O$ and $[Ru(bpy)_2(OSO\text{-}Bn)](PF_6)$ were synthesized according to published methods [27,28]. The solvents acetone, methanol, ethanol, diethyl ether, and dichloromethane were purchased from VWR and used without further purification. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was purchased from Aldrich and recrystallized three times from ethanol. Acetonitrile for electrochemical experiments was HPLC grade and purchased from Burdick and Jackson and used without further purification. The synthesis and isolation of all ruthenium sulfoxide complexes were carried out in the dark or under red light conditions.

2.2. Instrumentation

Electronic absorption spectra were collected on an Agilent 8453 spectrophotometer. Bulk photolysis experiments were conducted using a 75 W Xenon-arc lamp (Oriel) fitted with a Canon standard camera UV filter. Proton nuclear magnetic resonance (^{1}H

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NMR) spectra were collected in deuterated acetone (d^6-acetone) on either a 300 MHz Bruker spectrometer or a 500 MHz Varian INOVA500 spectrometer. Cyclic voltammetry was performed on a CH Instruments CHI 730A Electrochemical Analyzer. This workstation contains a digital simulation package as part of the software package to operate the workstation (CHI version 2.06). The working electrode was a Pt disk (Cypress Systems) electrode (1 mm). The counter and reference electrodes were Pt wire and Ag/Ag^+, respectively. Electrochemical measurements were performed in acetonitrile solutions containing 0.1 M $TBAPF_6$ electrolyte in a one compartment cell.

2.3. Quantum yield measurements

Quantum yield of isomerization measurements were determined by irradiating solutions of the complexes $[Ru(bpy)_2(OSO\text{-}BnR)]^+$ in methanol at room temperature. Photolysis was achieved using a PTI C-60 fluorimeter at the lower energy isosbestic point between S-bonded and O-bonded isomers. Incident radiation intensity, I_o, was determined using potassium ferrioxalate actinometry. Quantum yields of isomerization were calculated according to Eq. (1) [29] in which $d[O]/dt$ is the slope of the O-bonded concentration, [O] as a function of time for less than 10% converted to O-bonded, A_λ is the absorbance at the isosbestic point (λ) and V is the volume of irradiated solution (3 mL). The concentration of O-bonded isomer was determined using multi-linear regression:

$$\Phi_{s\to o} = \frac{(d[O]/dt)}{(I_o/V)(1-10^{-A\lambda})} \quad (1)$$

2.4. Crystallography

Crystals suitable for structural determination were obtained by slow evaporation of a concentrated methanol solution. Single crystal X-ray diffraction data were collected at 100 K (Bruker KRYOFLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.71073 Å). The detector was placed at a distance of 5.009 cm from the crystal. Crystals were placed in paratone oil upon removal from the mother liquor and mounted on a plastic loop in the oil. Integration and refinement of crystal data were done using Bruker SAINT software package and Bruker SHELXTL (version 6.1) software package, respectively [30]. Absorption correction was completed by using the SADABS program.

2.5. Synthesis of ruthenium complexes

2-(4-Methyl-benzylsulfanyl)-benzoic acid, $OSBnCH_3$ (1). The compound thiosalicylic acid (598 mg, 3.88 mmol) was dissolved in 75 mL of methanol. Sodium hydroxide (330 mg, 8.25 mmol) was added in excess to the solution. The solution was stirred at 25 °C for 30 min. The solvent was removed by rotary evaporation. The remaining white precipitate was dissolved in 75 mL acetone. The compound 4-methylbenzyl bromide (800 mg, 4.32 mmol) was added to the solution. The solution was refluxed for approximately 4 h. The white precipitate was isolated by vacuum filtration and rinsed with diethyl ether. The precipitate was air dried for 1 h. The precipitate was dissolved in 35 mL of methanol. Concentrated HCl was added dropwise (approximately 20 mL) until the product precipitated as a white solid. The solid was isolated by vacuum filtration and rinsed with water and air dried. Yield: 903 mg (91%). ^{1}H NMR (d^6-acetone, 300 MHz) δ: 8.00 (d, 1 H), 7.49 (m, 2 H), 7.35 d, 2 H), 7.22 (t, 1 H), 7.15 (d, 2 H), 4.18 (s, 2 H), 2.29 (s, 3 H).

2-(4-Methyl-benzylsulfinyl)-benzoic acid, $OSOBnCH_3$ (2). The ligand $OS\text{-}BnCH_3$ (397 mg, 1.55 mmol) was dissolved in 60 mL of acetone. In another 20 mL of acetone 1 equivalent of *m*-chloroperoxybenzoic acid (453 mg 60% peroxo reagent by ^{1}H NMR, 1.58 mmol) was dissolved. The solution of *m*-chloroperoxybenzoic acid was added dropwise to the solution of $OS\text{-}BnCH_3$ over a period of 5 min. The solution was stirred at 25 °C for approximately 15 min. The acetone was removed by rotary evaporation. A minimum amount of diethyl ether was added to the residue and a white precipitate was isolated via vacuum filtration and air dried. Yield: 333 mg (79%). ^{1}H NMR (d^6-acetone, 300 MHz) δ: 8.19 (d, 1 H), 7.91 (d, 1 H), 7.74 (t, 1 H), 7.63 (t, 1 H), 7.10 (m, 4 H), 4.43 (d, 1 H), 3.75 (d, 1 H), 2.30 (s, 3 H).

$[Ru(bpy)_2(OSOBnCH_3)](PF_6)\cdot 1.8H_2O$ (3). This procedure and purification are done in the dark or under red light. The dark purple complex $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (212 mg, 0.408 mmol) was dissolved in 50 mL of ethanol with $OSO\text{-}BnCH_3$ (124 mg, 0.455 mmol), 2 equivalents of silver hexafluorophosphate ($AgPF_6$) (219 mg, 0.852 mmol) and excess triethylamine (150 μL). The solution was brought to reflux under nitrogen gas for approximately 4 h. The solution was cooled to −30 °C overnight to allow maximum precipitation of the AgCl. The AgCl was isolated by vacuum filtration and rinsed with ethanol and dichloromethane until filtrate was colorless. The solvent was removed by rotary evaporation. In order to remove the byproduct NEt_3HPF_6, the oily residue was dissolved in dichloromethane and extracted with an aqueous solution of $LiOH\cdot H_2O$ (~25 mg in 10 mL). The dichloromethane layer was dried with anhydrous magnesium sulfate and the solvent was removed by rotary evaporation. A minimal amount of methanol was added to the resulting residue. Approximately 5 mL of diethyl ether was added to the concentrated solution to precipitate the product. The solution was cooled to −30 °C for 15 min for complete precipitation. The product was isolated by vacuum filtration and air dried. Yield: 277 mg (82%). UV–vis (MeOH) $\lambda_{max}(\varepsilon)$ = 399 nm (7400) S-bonded, 349 nm (9400) and 496 nm (9400) O-bonded. $E^{\circ\prime}$ $Ru^{3+/2+}$ vs. Ag/Ag^+ = 0.89 V S-bonded, 0.52 V O-bonded. ^{1}H NMR (d^6-acetone, 500 MHz) δ: 9.50 (d, 1 H), 9.05 (d, 1 H), 8.90 (d, 1 H), 8.69 (m, 3 H), 8.52 (t, 1 H), 8.21 (t, 1 H), 8.10 (m, 3 H), 8.05 (t, 1 H), 7.90 (d, 1 H), 7.60 (m, 2 H), 7.45 (m, 5 H), 6.90 (d, 2 H), 6.60 (d, 2 H) 4.25 (d, 1 H), 3.94 (d, 1 H), 2.22 (s, 3 H). Elemental Analysis: Calculated for $[Ru(C_{10}H_8N_2)_2(C_{15}H_{13}O_3S)]PF_6\cdot 1.8H_2O$: Calculated: C: 48.64%, H: 3.81%, N: 6.48%. Found: C: 48.27%, H: 3.41%, N: 6.76%.

2.6. Synthesis of $[Ru(bpy_2)(OSO\text{-}BnCF_3)](PF_6)\cdot 1.3H_2O$

2-(4-Trifluoromethyl-benzylsulfanyl)-benzoic acid, $OSBnCF_3$ (4). 4 was prepared following the procedure as described above for complex 1 using 300 mg thiosalicylic acid and 520 mg of 4-trifluoromethylbenzyl bromide. Yield: 220 mg (54%). ^{1}H NMR (d^6-acetone, 300 MHz) δ: 8.02 (d, 1 H), 7.70 (dd, 4 H), 7.51 (m, 2 H), 7.25 (t, 1 H), 4.35 (s, 2 H).

2-(4-Trifluoromethyl-benzylsulfinyl)-benzoic acid, $OSOBnCF_3$ (5). 5 was prepared following the procedure as described above for complex 2 starting with 184 mg of 4. Yield: 147 mg (76%). ^{1}H NMR (d^6-acetone, 300 MHz) δ: 8.18 (d, 1 H), 7.80 (d, 1 H), 7.59–7.74 (m, 4 H), 7.37 (d, 2 H), 4.55 (d, 1 H), 4.02 (d, 1 H).

$[Ru(bpy_2)(OSOBnCF_3)](PF_6)\cdot 1.3H_2O$ (6). 6 was prepared following the procedure as described above for complex 3 starting with 76 mg $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ and 64 mg of 5. Yield: 102 mg (77%). UV–vis (MeOH) $\lambda_{max}(\varepsilon)$ = 392 nm (7100) S-bonded, 350 nm (9200) and 496 nm (9300) O-bonded. $E^{\circ\prime}$ $Ru^{3+/2+}$ vs. Ag/Ag^+ = 0.93 V S-bonded, 0.53 V O-bonded. ^{1}H NMR (d^6-acetone, 500 MHz) δ: 9.54 (d, 1 H), 8.99 (d, 1 H), 8.87 (d, 1 H), 8.68 (m, 3 H), 8.53 (t, 1 H), 8.26 (t, 1 H), 8.16 (m, 3 H), 8.10 (t, 1 H), 7.93 (d, 1 H), 7.58 (m, 2 H), 7.52 (t, 2 H), 7.46 (t, 1 H), 7.38 (m, 3 H), 7.29 (d, 1 H), 6.88 (d, 2 H), 4.46 (d, 1 H), 4.18 (d, 1 H). Elemental Analysis: Calculated for $[Ru(C_{10}H_8N_2)_2(C_{15}H_{10}O_3F_3S)]PF_6\cdot 1.3H_2O$: Calculated: C: 46.23%, H: 3.18%, O: 7.57%, N: 6.16%, S: 3.53%. Found: C: 45.92%, H: 3.13%, O: 7.59%, N: 6.44%, S: 3.30%.