Inorganic Chemistry

Communication

Phototriggered S → O Isomerization of a Ruthenium-Bound Chelating Sulfoxide
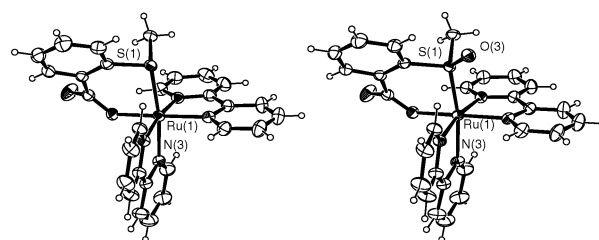
Dennis P. Butcher, Jr.,† Aaron A. Rachford,† Jeffrey L. Petersen,‡ and Jeffrey J. Rack*,†

Clippinger Laboratories, Department of Chemistry and Biochemistry, Ohio University, Athens, Ohio 45701, and C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045

We have prepared and characterized $[Ru(bpy)_2(OS)]^+$ (bpy = 2,2′-bipyridine; OS = 2-methylthiobenzoate) and the chelating sulfoxide S-$[Ru(bpy)_2(OSO)]^+$ (OSO = methylsulfonylbenzoate) by ^{1}H NMR (1-D and 2-D COSY), IR, UV–visible spectroscopy, electrochemistry, and X-ray crystallography. Many of the metrical and crystal parameters are nearly identical between the two structures. The sulfoxide is produced from *m*-cpba oxidation of the thioether. Photolysis of S-$[Ru(bpy)_2(OSO)]^+$ results in a dramatic shift in the metal-to-ligand charge-transfer (^{3}MLCT) transition from 396 to 496 nm, with a new higher-energy ^{3}MLCT transition appearing at 355 nm. Concomitant with this change, the $Ru^{3+/2+}$ reduction potential shifts from 1.25 V vs Ag/AgCl to 0.9 V vs Ag/AgCl. These changes are ascribed to phototriggered excited-state isomerization of the sulfoxide from S- to O-bonded. Examination of the ^{1}H NMR spectra in a CD_3OD solvent before, during, and after irradiation shows the presence of two O-bonded complexes that revert to the structurally characterized S-bonded ground state. This represents the first report of isomerization of a chelating sulfoxide in a photochromic Ru complex.

Photochromic compounds are molecular devices that employ photonic energy for bond construction. Bond rupture and formation are achieved through population of electronic excited states in these chromophores. Our approach has been to access the stored potential energy within metal-to-ligand charge-transfer (^{3}MLCT) excited states of d^6 transition-metal polypyridine complexes for these reactions.[1-7] Specifically, we have examined ruthenium and osmium polypyridine

* To whom correspondence should be addressed. E-mail: rackj@ohio.edu.
† Ohio University.
‡ West Virginia University.

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Figure 1. Molecular structures of $[Ru(bpy)_2(OS)]^+$ (left) and $[Ru(bpy)_2(OSO)]^+$ (right). Ellipsoids are scaled to enclose 30% probability.

complexes containing dimethyl sulfoxide that undergo S → O isomerization when irradiated. Isomerization quantum yields ($\Phi_{S\rightarrow O}$) of up to 0.8 have been observed, indicative of an electronic structure that proficiently accesses this stored potential energy.[3] A deficiency of these photochromic complexes is their incompatibility with traditional organic solvents, due to ligand substitution following isomerization. One strategy to address this shortcoming is the incorporation of a photoisomerizable sulfoxide moiety within a chelating ligand. In a related report, it has been demonstrated that a sulfoxide tethered to a phenanthroline unit may be utilized for the formation of bistable complexes, though no photoisomerization of the sulfoxide is presented.[8] Herein we report our results of phototriggered isomerization of a chelating sulfoxide in a photochromic Ru complex.

Shown in Figure 1 are the structures of the Ru complexes containing the parent chelating thioether, $[Ru(bpy)_2(OS)]^+$, and the chelating sulfoxide, S-$[Ru(bpy)_2(OSO)]^+$, produced from *m*-cpba oxidation (bpy = 2,2′-bipyridine; OS = 2-methylthiobenzoate; OSO = methylsulfonylbenzoate). The chelating thioether is bound to the $[Ru(bpy)_2]^{2+}$ moiety and features a slight twist of the phenyl ring relative to the carboxylate group. This torsion persists in the S-$[Ru(bpy)_2(OSO)]^+$ structure. Metrical parameters associated with the thioether show the expected changes upon oxidation. The Ru−S(1) and Ru−N(3) distances [trans to S(1)] are 2.333-

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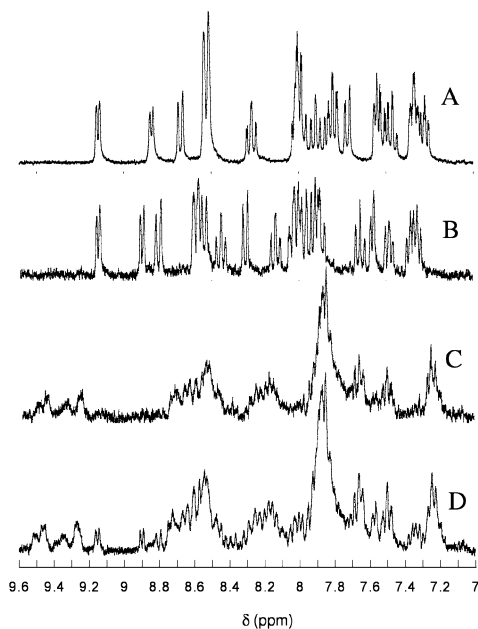
Figure 2. ^{1}H NMR spectra of [Ru(bpy)$_2$(OS)]$^+$ (A), S-[Ru(bpy)$_2$(OSO)]$^+$ (B), O-[Ru(bpy)$_2$(OSO)]$^+$ (C), and O-[Ru(bpy)$_2$(OSO)]$^+$ after 1 h of relaxation (D). Irradiation details: 100-W Xe arc lamp; 3 h in a standard 5-mm NMR tube.

(9) and 2.066(2) Å, respectively, which change to 2.213(1) and 2.098(1) Å for Ru$-$S(1) and Ru$-$N(3), respectively, in the sulfoxide. This change in the bonding distances is consistent with the dπ t$_{2g}$ stabilization typically observed in bonding of sulfoxide ligands to Ru^{2+}.[9] The S(1)$-$O(3) bond distance in the sulfoxide is 1.479(2) Å. These distances are in accord with standard Ru$-$N$_{bpy}$, Ru$-$S$_{thioether}$, Ru$-$S$_{sulfoxide}$ and S$-$O bond distances.[9-12] Comparison of the IR spectra of the two complexes reveals a unique peak at 1091 cm^{-1} for the sulfoxide complex, which is ascribed to ν(S=O) and is in the expected range for S-bonded sulfoxides.[9,10] Further structural characterization comes from 1-D and 2-D (COSY) ^{1}H NMR spectroscopy (CD$_3$OD solvent). The methyl resonance of [Ru(bpy)$_2$(OS)]$^+$ shifts downfield from δ 1.86 ppm to δ 2.76 ppm upon oxidation. In addition, two doublets and two triplets representing four protons located on the benzoate ring shift downfield in response to this oxidation (Figure 2A,B). The doublets at δ 7.78 and 7.72 ppm move to δ 8.33 and 7.96 ppm, respectively, while the triplets at δ 7.47 and 7.53 ppm move to δ 7.92 and 7.67 ppm, respectively.

Electronic spectra of [Ru(bpy)$_2$(OS)]$^+$ show two moderately intense MLCT transitions at 346 and 467 nm in the visible region. The S-bonded sulfoxide ruthenium complex features one MLCT transition in the visible at 396 nm ($\epsilon \sim$ 6000 M^{-1} cm^{-1}), with the other higher-energy MLCT transition in the UV region. The low-energy tail of the 396-nm transition exhibits considerable intensity, a characteristic of other Ru complexes with large isomerization quantum yields.[3] Consistent with the absorption spectra, cyclic vol-
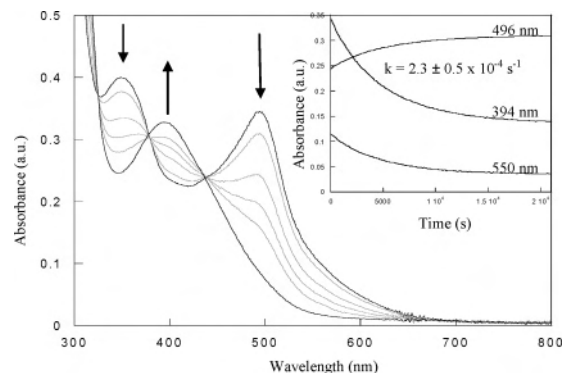
Figure 3. Absorption spectra showing thermal reversion of O-bonded [Ru-(bpy)$_2$(OSO)]$^+$ to S-[Ru(bpy)$_2$(OSO)]$^+$ in MeOH.

tammetry reveals Ru$^{3+/2+}$ $E^{\circ\prime}$ = 0.9 V vs Ag/AgCl for [Ru-(bpy)$_2$(OS)]$^+$, which shifts to 1.25 V vs Ag/AgCl for S-[Ru(bpy)$_2$(OSO)]$^+$. Reversible ligand reductions are observed at -1.56 V in both complexes and are ascribed to reduction of the bipyridine.

Charge-transfer excitation of S-[Ru(bpy)$_2$(OSO)]$^+$ in MeOH results in dramatic changes both in the electronic spectrum and in the cyclic voltammogram. In the absorption spectrum, two new MLCT maxima appear at 355 and 496 nm while the peak at 396 nm diminishes in intensity (Figure 3). This new complex is ascribed to O-bonded [Ru(bpy)$_2$(OSO)]$^+$, O-[Ru(bpy)$_2$(OSO)]$^+$. The isomerization quantum yield ($\Phi_{S\rightarrow O} = 0.45$) is quite large, indicating that isomerization occurs from the S-bonded ^{3}MLCT excited state.[4,13] These new maxima are in accord with other spectra containing the [Ru(bpy)$_2$]$^{2+}$ fragment with two O-bonded ligands. For example, both [Ru(bpy)$_2$(OH$_2$)$_2$]$^{2+}$ (λ_{max} = 355 and 498 nm; aqueous solution) and the bis-O-bonded [Ru(bpy)$_2$(dmso)$_2$]$^{2+}$ (λ_{max} = 347 and 496 nm; DMSO solution) complexes show comparable absorption maxima.[5,14-16] However, irradiation of [Ru(bpy)$_2$(dmso)$_2$]$^{2+}$ in a MeOH solution will eventually lead to the bis(methanol) adduct via ground-state ligand substitution of O-bonded dmso. In contrast, O-[Ru(bpy)$_2$-(OSO)]$^+$ reverts to S-[Ru(bpy)$_2$(OSO)]$^+$ in MeOH. The kinetics show predictable first-order behavior for Ru, and the apparent intramolecular O $\rightarrow$ S isomerization rate constant is $(2.3 \pm 0.5) \times 10^{-4}$ s^{-1}. This is an order of magnitude slower than what is typically observed in related systems.[2] Irradiation of electrochemical solutions containing 0.1 M TBAH converts $\sim$0.1 mM S-[Ru(bpy)$_2$(OSO)]$^+$ to O-[Ru(bpy)$_2$(OSO)]$^+$. The subsequent voltammogram shows no evidence of the S-bonded isomer and only reveals a new couple at 0.90 V vs Ag/AgCl, ascribed to O-[Ru(bpy)$_2$-(OSO)]$^+$. Absorption spectra confirm the presence of O-[Ru(bpy)$_2$(OSO)]$^+$ in the electrochemical solution.

Additional changes are seen in the ^{1}H NMR spectrum in a CD$_3$OD solvent before and after irradiation (Figure 2). In Figure 2B, the ^{1}H NMR spectrum of S-[Ru(bpy)$_2$(OSO)]$^+$

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is shown before irradiation. The spectrum in panel C is that obtained after irradiation of the NMR tube for 3.5 h with a 150-W Xe lamp equipped with a Canon UV filter. It is notably different from the spectrum in panel B. The doublets at δ 9.15, 8.90, and 8.81 ppm are no longer apparent and have been replaced with four broad resonances downfield of their initial positions. Further substantial changes are observed upfield where many of the multiplets overlap, such as the intense multiplet near δ 7.85 ppm. We ascribe this spectrum to that of O-[Ru(bpy)$_2$(OSO)]$^+$. A more informative spectrum is found in panel D, which is obtained after 1 h of relaxation of the sample in the dark. Features indicative of both S-[Ru(bpy)$_2$(OSO)]$^+$ and O-[Ru(bpy)$_2$(OSO)]$^+$ are evident as the doublets at δ 9.15, 8.90, and 8.81 ppm, and the unresolved multiplet at δ 7.85 ppm is present. Examination of the spectra in panels C and D suggests the presence of two distinct O-[Ru(bpy)$_2$(OSO)]$^+$ complexes. The aliphatic region (not shown) features two methyl singlets at δ 2.11 and 1.86 ppm. In the aromatic region, two multiplets of similar intensity are observed at δ 9.27 and 9.45 ppm and two multiplets of differing intensity from the first set are observed at δ 9.52 and 9.36 ppm. These unresolved multiplets likely correspond to two of the three well-resolved doublets observed in S-[Ru(bpy)$_2$(OSO)]$^+$. Further relaxation of the sample shown in panel D leads to the well-resolved spectrum shown in panel B. The photochemical process is quite robust because the spectra shown in Figure 2 are those obtained after five irradiation−relaxation cycles.

It is interesting to compare the spectral resolution in panels B−D. Panel B shows a well-resolved spectrum that upon irradiation yields the poorly resolved spectrum in panel C. Indeed, identification of discrete doublets and triplets is difficult. Panel D shows well-resolved peaks attributed to S-[Ru(bpy)$_2$(OSO)]$^+$, while the two sets of poorly resolved peaks are assigned to O-[Ru(bpy)$_2$(OSO)]$^+$. A reasonable suggestion is that upon irradiation of S-[Ru(bpy)$_2$(OSO)]$^+$

two O-[Ru(bpy)$_2$(OSO)]$^+$ complexes, perhaps diastereomers (both S and Ru are chiral), are formed that are in equilibrium with one another. The rapid equilibrium (relative to the NMR time scale) broadens the resonances associated with O-[Ru(bpy)$_2$(OSO)]$^+$. The identity of the two isomers at present is unknown, but they both must yield the structurally characterized S-[Ru(bpy)$_2$(OSO)]$^+$ upon relaxation (panel B). Formulating one of these products as a solvated complex seems unlikely from the kinetic analysis; one expects a separate rate constant for the formation of S-[Ru(bpy)$_2$-(OSO)]$^+$ from the solvate relative to O-[Ru(bpy)$_2$(OSO)]$^+$. Furthermore, the ^{1}H NMR spectrum in CD$_3$OD of the photoproduct from bulk photolysis in CH$_3$OH shows no evidence of unbound CH$_3$OH following reversion. One expects the appearance of unbound CH$_3$OH in this spectrum if the photoproduct comprises the solvate.

We have demonstrated that efficient S → O isomerization may be observed in a chelating sulfoxide and have evidence for two O-bonded isomers. This work will expand the types of solvents compatible with phototriggered ruthenium sulfoxide complexes. Future work will include direct observation of the isomerization as well as the synthesis of other complexes employing chelating sulfoxides.

Supporting Information Available: X-ray crystallographic data (CIF), ^{1}H COSY NMR spectra, cyclic voltammagrams, and synthetic and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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