Inorg. Chem. **2006**, *45*, 8–10

Inorganic Chemistry
Communication

Subnanosecond Isomerization in an Osmium–Dimethyl Sulfoxide Complex

Nicholas V. Mockus,[†] Jeffrey L. Petersen,[‡] and Jeffrey J. Rack*,[†]

Department of Chemistry and Biochemistry, Ohio University, Athens, Ohio 45701,
and C. Eugene Bennett Department of Chemistry, West Virginia University,
Morgantown, West Virginia 26505-6045

Received October 5, 2005

We report the structure, spectroscopy, and electrochemistry of *cis*-$[Os(bpy)_2(DMSO)_2](OTf)_2$, where bpy is 2,2′-bipyridine, DMSO is dimethyl sulfoxide, and OTf is trifluoromethanesulfonate. Electrochemical measurements are consistent with S-to-O isomerization following the oxidation of Os^{2+} (1.8 V vs Ag/AgCl). Visible irradiation of the metal-to-ligand charge-transfer transition (355 nm) of $[Os(bpy)_2(DMSO)_2]^{2+}$ in the solid state and solution yields an emissive S-bonded excited state and S-to-O excited-state isomerization on a subnanosecond time scale. These results and a comparison to the nonphotoactive $[Os(bpy)_2Cl(DMSO)]^+$ are discussed.

The development of photochemical molecular devices requires strict control of the electronic structure of molecular units. As a result, synthetic strategies that minimize nonproductive excited-state deactivation pathways while enhancing desirable features are valued. For example, ligand-field deactivation of charge-transfer excited states in ruthenium polypyridine complexes is a predominant relaxation pathway that sometimes limits their effectiveness in photochemical molecular devices.[1] To combat this effect, osmium is often favored over ruthenium because of the larger ligand-field energy gap exhibited by osmium. In an effort to examine the role of ligand-field states in ruthenium−dimethyl sulfoxide (DMSO) photochromic complexes,[2−5] we have chosen to examine phototriggered excited-state isomerization in osmium−polypyridyl complexes containing DMSO.

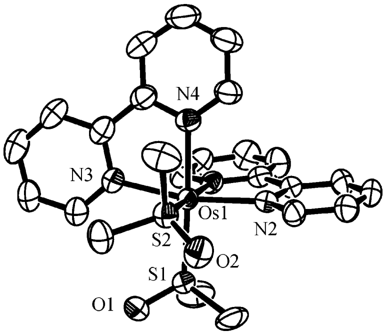

Figure 1. Molecular structure of $[Os(bpy)_2(DMSO)_2]^{2+}$. Ellipsoids are displayed at 50% probability. All hydrogen atoms have been removed for clarity. The N1 atom label has been omitted for clarity.

Few osmium complexes feature photoisomerizable ligands.[6] The best studied examples are $[Os(CN)_5(NO)]^{2-}$ and $[Os(NH_3)_5(N_2)]^{2+}$.[7,8] In the former example, infrared spectra show evidence for isonitrosyl (O-bonded) and η^2-NO bonding modes following irradiation of the crystalline complex at low temperature. In the latter example, Coppens et al. showed the first crystallographic evidence for side-on bonding of N_2 in $[Os(NH_3)_5(N_2)]^{2+}$ formed from irradiation of the solid at low temperature.[8] These examples provide precedence for phototriggered linkage isomerization in osmium complexes. Herein, we report the spectroscopic and electrochemical data for photochromic action in a simple osmium−DMSO coordination complex.

The molecular structure of $[Os(bpy)_2(DMSO)_2]^{2+}$ features two S-bonded DMSO ligands in a cis geometry (Figure 1).[9] There are two unique molecules in the unit cell (triclinic; $P\bar{1}$), which show only subtle differences between the two structures. Only one molecule is depicted in Figure 1. The Os−S bond distances of 2.279(1), 2.281(1) and 2.268(1),

---

* To whom correspondence should be addressed. E-mail: rack@helios.phy.ohiou.edu.

[†] Ohio University.

[‡] West Virginia University.

(1) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 88−277.

(2) Rachford, A. A.; Petersen, J. L.; Rack, J. J. *Inorg. Chem.* **2005**, *44*, 8065−8075.

(3) Rack, J. J.; Rachford, A. A.; Shelker, A. M. *Inorg. Chem.* **2003**, *42*, 7357−7359.

(4) Rack, J. J.; Mockus, N. V. *Inorg. Chem.* **2003**, *42*, 5792−5794.

(5) Rack, J. J.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **2001**, *123*, 2432−2433.

(6) Coppens, P.; Novozhilova, I.; Kovalevsky, A. *Chem. Rev.* **2002**, *102*, 861−883.

(7) Guida, J. A.; Piro, O. E.; Aymonino, P. J. *Inorg. Chem.* **1995**, *34*, 4113−4116.

(8) Fomitchev, D. V.; Bagley, K. A.; Coppens, P. *J. Am. Chem. Soc.* **2000**, *122*, 532−533.

(9) Kober, E. M.; Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4587−4598.

10.1021/ic051720f CCC: $33.50

2.276(1) Å and S−O bond distances of 1.474(2), 1.470(2) and 1.477(3), 1.471(1) Å are in accord with that observed for other $\mathrm{Os^{II}}$−DMSO complexes.[10,11] For example, in *cis*-$[\mathrm{OsCl_2(DMSO)_4}]$, the four Os−S bond distances range from 2.275(1) to 2.355(1) Å, while the S−O bond distances range from 1.467(4) to 1.483(3) Å.[10] The Os−N bond distances are typical [2.092(3)−2.101(3) Å] and show characteristic asymmetric metal−N bond distances for coordinated bipyridine. The complexes also feature large torsion angles that are represented as a rotation of DMSO about the Os−S bond. The angles are 34° for O1−S1−Os1−N3 and 37° for O2−S2−Os1−N2. The corresponding angles in the second molecule are both 44°. Large torsion angles are typical of photochromic ruthenium−DMSO compounds.[2]

Cyclic voltammograms of $[\mathrm{Os(bpy)_2(DMSO)_2}]^{2+}$ are consistent with S → O isomerization following oxidation of Os^{2+} (Supporting Information). The S-bonded $\mathrm{Os}^{3+/2+}$ couple occurs at 1.8 V vs Ag/AgCl. Similar to $[\mathrm{Ru(bpy)_2(DMSO)_2}]^{2+}$, voltammograms indicate that isomerization rates are on the order of 50−100 s^{-1}.[4,12] A new $\mathrm{Os}^{3+/2+}$ couple is observed at 1.0 V vs Ag/AgCl and is consistent with an O-bonded DMSO. There is no evidence for room-temperature O → S isomerization following reduction of Os^{3+}. The bis-O-bonded couple in the ruthenium analogue is observed at 0.8 V vs Ag/AgCl. The more positive osmium couple is not suggestive of a bis-O-bonded structure but rather a mixed S- and O-bonded structure. Interestingly, voltammograms of $[\mathrm{Os(bpy)_2(DMSO)Cl}]^{+}$ do not show evidence of isomerization following oxidation of Os^{2+} or Os^{3+} (Supporting Information). Indeed, two reversible one-electron couples are observed in the voltammogram of this complex. The first couple is assigned to $\mathrm{Os}^{3+/2+}$ (0.1 V vs Ag/AgCl), while the second couple is assigned to $\mathrm{Os}^{4+/3+}$ (1.5 V vs Ag/AgCl). The presence of the chloride has a dramatic effect on the electronic structure of the complex.

The electronic spectra of $[\mathrm{Os(bpy)_2(DMSO)_2}]^{2+}$ are shown in Figure 2. The high-energy absorption band at 355 nm is assigned to a metal-to-ligand charge-transfer (MLCT) transition. A similar band appears at 348 nm in the corresponding ruthenium complex.[4,12] The related osmium complex, $[\mathrm{Os(bpy)_2(DMSO)Cl}]^{+}$, exhibits a high-energy band at 408 nm. Given the spectral similarities of Cl^- and O-bonded DMSO, isomerization of just one DMSO should yield a similar maximum in the electronic spectrum.

Irradiation of bis-S-bonded $[\mathrm{Os(bpy)_2(DMSO)_2}]^{2+}$ in organic solvents (e.g., propylene carbonate, acetonitrile, and dichloromethane) causes substantial changes in the absorption spectrum (Figure 2). The absorption maximum at 355 nm decreases, and a new peak at 403 nm appears. The isomerization quantum yield ($\Phi_{\mathrm{S\rightarrow O}}$) was determined to be 0.042 ± 0.002, utilizing ferrioxalate actinometry (Supporting Information).[2] The absorption maximum and shape are similar to those of $[\mathrm{Os(bpy)_2(DMSO)Cl}]^{+}$, yet they are in stark contrast to those of the bis-O-bonded $[\mathrm{Ru(bpy)_2(DMSO)_2}]^{2+}$, which features two absorption maxima at 347 and 496 nm.[4,12] Furthermore, while $[\mathrm{Ru(bpy)_2(DMSO)_2}]^{2+}$ features two separate O → S isomerization rates ($\sim 10^{-3}$ and $\sim 10^{-4}$ s^{-1}) at room temperature, thermal reversion to *S*,*S*-$[\mathrm{Os(bpy)_2(DMSO)_2}]^{2+}$ is monophasic but only at higher temperatures ($T > 50$ °C). The absorption and electrochemical data strongly support an assignment of one S-bonded DMSO and one O-bonded DMSO in the metastable state of $[\mathrm{Os(bpy)_2(DMSO)_2}]^{2+}$ formed following irradiation and electrochemical oxidation.

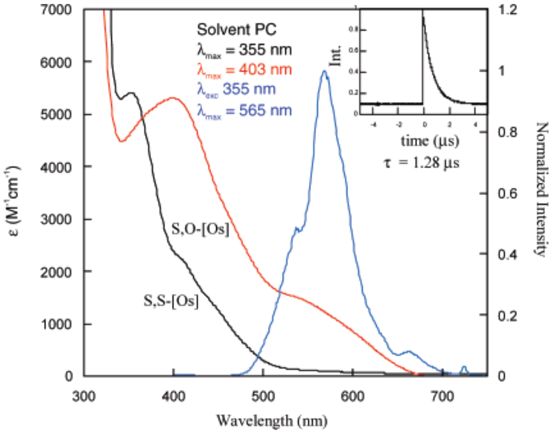

Figure 2. Absorption spectra (left abscissa) of *S*,*S*-$[\mathrm{Os(bpy)_2(DMSO)_2}]^{2+}$ (black) and *S*,*O*-$[\mathrm{Os(bpy)_2(DMSO)_2}]^{2+}$ (red) complexes. The emission spectrum (right abscissa) and lifetime decay (inset) correspond to those of *S*,*S*-$[\mathrm{Os(bpy)_2(DMSO)_2}]^{2+}$.

Emission studies of photochromic $[\mathrm{Os(bpy)_2(DMSO)_2}]^{2+}$ reveal a room-temperature excited-state lifetime of 1.28 μs in acetonitrile. The steady-state spectrum is shown in Figure 2. The inset shows the single-wavelength decay kinetics at 565 nm, the emission maximum. The decay is well fit by a simple monoexponential equation. There were no other observable emissive features at lower energy. Irradiation of the S,O-bonded $[\mathrm{Os(bpy)_2(DMSO)_2}]^{2+}$ formed from photoconversion shows that this complex is nonemissive. As a result, the complex giving rise to the emission at 565 nm is assigned to the bis-S-bonded $[\mathrm{Os(bpy)_2(DMSO)_2}]^{2+}$. The emission quantum yield (Φ_{em}) was found to be 0.23 ± 0.02, utilizing $[\mathrm{Ru(bpy)_3}]^{2+}$ as an actinometer.

Nanosecond transient absorption spectroscopy was performed to correlate ground-state formation with excited-state deactivation. Monitoring at the isosbestic point (375 nm) of the S,S- and S,O-bonded $[\mathrm{Os(bpy)_2(DMSO)_2}]^{2+}$, 355-nm excitation shows the formation of an absorption within the laser pulse and its decay (Figure 3). The lifetime of this signal is 1.33 μs and matches well the emission lifetime of *S*,*S*-$[\mathrm{Os(bpy)_2(DMSO)_2}]^{2+*}$. The correspondence of the emission lifetime with the 375-nm decay lifetime indicates that this signal is due to the reduced bipyridine ligand of the ^{3}MLCT excited state.[13,14] The 500-ns transient absorption spectrum shows a narrow peak at 375 nm and a less intense broad

---

(10) McDonagh, A. M.; Humphrey, M. G.; Hockless, D. C. R. *Aust. J. Chem.* **1998**, *51*, 807−811.

(11) Alessio, E.; Serli, B.; Zangrando, E.; Calligaris, M.; Panina, N. S. *Eur. J. Inorg. Chem.* **2003**, 3160−3166.

(12) Smith, M. K.; Gibson, J. A.; Young, C. G.; Broomhead, J. A.; Junk, P. C.; Keene, F. R. *Eur. J. Inorg. Chem.* **2000**, 1365−1370.

(13) Damrauer, N. H.; Cerullo, G.; Yeh, A.; Boussie, T. R.; Shank, C. V.; McCusker, J. K. *Science* **1997**, *275*, 54−87.

(14) Yeh, A. T.; Shank, C. V.; McCusker, J. K. *Science* **2000**, *289*, 935−938.

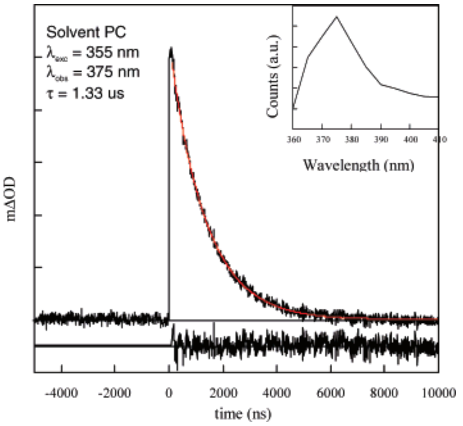

Figure 3. Single-wavelength transient absorption decay kinetics observed at 375 nm following 355-nm excitation. The initial absorption is due to the reduced bipyridine ligand. The inset shows the spectrum of reduced bipyridine at 500 ns after the laser pulse. The decay corresponds to the bleaching of the MLCT excited state. The residuals from the monoexponential fit (red) are shown at the bottom.

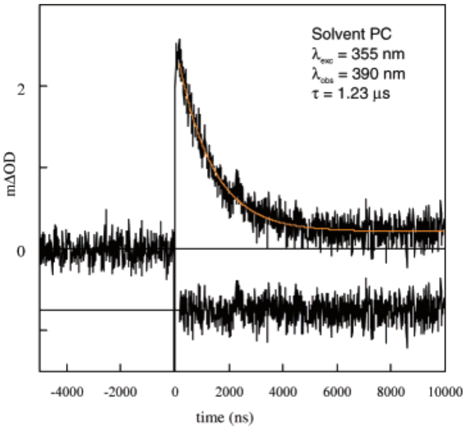

Figure 4. Single-wavelength transient absorption decay kinetics observed at 390 nm following 355-nm excitation. The initial absorption is due to the reduced bipyridine ligand. The decay corresponds to ground-state recovery of *S*,*S*-$[Os(bpy)_2(DMSO)_2]^{2+}$. The long-lived absorption corresponds to the formation of *S*,*O*-$[Os(bpy)_2(DMSO)_2]^{2+}$. The residuals from the monoexponential fit are shown at the bottom.

shoulder between 390 and 410 nm. The 375-nm peak corresponds well with that observed for a reduced bipyridine ligand, while the lower energy shoulder is likely due to the *S*,*O*-$[Os(bpy)_2(DMSO)_2]^{2+}$ photoproduct.[13,14] This indicates that the S,O ground state has formed while the S,S excited state has yet to decay.

The kinetic trace at 390 nm, which corresponds to the wavelength of greatest absorption difference between *S*,*S*- and *S*,*O*-$[Os(bpy)_2(DMSO)_2]^{2+}$ (Figure 4; 355-nm excitation), shows the rapid formation of an absorption and its decay. The decay lifetime of this monoexponential signal is 1.23 μs, which is in accord with the 375-nm kinetic signal and the emission measurements (565 nm) and as such is due to decay of the ^{3}MLCT of *S*,*S*-$[Os(bpy)_2(DMSO)_2]^{2+}$. The presence of a nonzero signal in this trace indicates the formation of a photoproduct prior to the ^{3}MLCT *S*,*S*-$[Os(bpy)_2(DMSO)_2]^{2+}$ decay. Isomerization is expected to be relatively slow ($\sim$30 μs) if it occurs from an emissive ^{3}MLCT *S*,*S*-$[Os(bpy)_2(DMSO)_2]^{2+}$ state. This slow kinetic phase is not observed at any wavelength. In independent experiments, excitation of photoconverted *S*,*O*-$[Os(bpy)_2(DMSO)_2]^{2+}$ suggests an excited-state lifetime of less than 3.5 ns (the response time of our instrument).

Our interpretation of these data is subnanosecond excited-state isomerization of DMSO on osmium. The $\Phi_{S\rightarrow O} = 0.042$ value represents the branching ratio from an initial excited state, which yields distinct ^{3}MLCT *S*,*S*-$[Os(bpy)_2(DMSO)_2]^{2+}$ and *S*,*O*-$[Os(bpy)_2(DMSO)_2]^{2+}$ excited states on different surfaces (see the synopsis figure). From the respective ^{3}MLCT states, ground-state formation of the S,S complex is relatively slow ($\sim$1.3 μs), whereas ground-state formation of the S,O complex is rapid ($<$3.5 ns). The metastable S,O complex reverts to ground-state *S*,*S*-$[Os(bpy)_2(DMSO)_2]^{2+}$ only at elevated temperatures. That DMSO isomerization occurs on osmium strongly suggests that this reaction does not require intervention of photoreactive ligand-field states. Future efforts will focus on the direct measurement of S-to-O isomerization rates and the development of other osmium–DMSO photochromic complexes. In addition to picosecond intramolecular ligand substitution reactions in organometallic complexes,[15,16] this study provides further evidence that dramatic molecular rearrangements can occur on a fast time scale in transition-metal complexes.

Acknowledgment. We thank Aaron A. Rachford and Beth McClure for experimental assistance as well as P. Greg van Patten and Michael P. Jensen for helpful discussions. PRF (Grant 38071-G3), Ohio University (1804 Fund), and the Condensed Matter Surface Science Program are acknowledged for financial support.

Supporting Information Available: Synthetic and experimental procedures, cyclic voltammograms of $[Os(bpy)_2(DMSO)_2]^{2+}$ and $[Os(bpy)_2Cl(DMSO)]^{+}$, and the CIF file for $[Os(bpy)_2(DMSO)_2](SO_3CF_3)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051720F

---

(15) To, T. T.; Barnes, C. E.; Burkey, T. J. *Organometallics* **2004**, *23*, 2708–2714.

(16) Yeston, J. S.; To, T. T.; Burkey, T. J.; Heilweil, E. J. *J. Phys. Chem. B* **2004**, *108*, 4582–4585.