

Phototriggered Ru(II)–Dimethylsulfoxide Linkage Isomerization in Crystals and Films

Jeffrey J. Rack,[†] Jay R. Winkler,* and Harry B. Gray*

Beckman Institute, California Institute of Technology
Pasadena, California 91125

Received January 18, 2000

Revised Manuscript Received December 6, 2000

Photochromic materials are of interest because of their potential applications in optical information storage devices.^{1–4} Measurements on photochromic sodium nitroprusside (Na₂[Fe(CN)₅(NO)]) indicate that two metastable states are formed by irradiations of the crystalline solid: the first is an isonitrosyl (O-bonded NO); the second is an η^2 -NO (side-on) complex.^{4,5} Phototriggered linkage isomerizations also occur in dimethylsulfoxide (dmsO) complexes: notably, both photochemical Ru–S \rightarrow Ru–O and thermal Ru–O \rightarrow Ru–S reactions are observed in dmsO solutions of [Ru(bpy)₂(dmsO)₂]²⁺ (bpy = 2,2'-bipyridine);⁶ and, as reported here, we find photochromism attributable to Ru–S \rightarrow Ru–O rearrangement upon visible excitation of [Ru(tpy)(bpy)(dmsO)]²⁺ (tpy = 2,2':6',2''-terpyridine) in single crystals and films as well as in solution.⁷

Crystal structure analysis⁸ of [Ru(tpy)(bpy)(dmsO)](SO₃CF₃)₂ gives Ru–S and S–O distances of 2.282(1) and 1.467(3) Å, respectively (vs 1.492(2) Å S–O distance for free dmsO).⁹ An increase in the S=O bond strength inferred from IR data (ν (SO) = 1102 cm⁻¹;¹⁰ uncomplexed dmsO: ν (SO) = 1055 cm⁻¹)¹¹ is typical of S-bonded Ru–dmsO complexes.¹² Despite the short S=O distance and the relatively high stretching frequency, the blue-shifted MLCT band (CH₃CN: 412 nm, 24 390 cm⁻¹; ϵ = 8080 M⁻¹ cm⁻¹) relative to that of [Ru(tpy)(bpy)(CH₃CN)]²⁺ (CH₃CN: 454 nm, 22 030 cm⁻¹; ϵ = 10 900 M⁻¹ cm⁻¹)¹³ indicates that Ru(II) is stabilized by $d\pi \rightarrow$ dmsO back-bonding.

Cyclic voltammograms of [Ru(tpy)(bpy)(dmsO)]²⁺ reveal two irreversible electron-transfer processes.¹⁰ Analysis based on an ECEC mechanism indicates that the Ru(III/II) reduction potential

in the S-bonded complex is 1.6 V (vs Ag/AgCl in CH₃CN).¹⁴ This potential is more positive than that of [Ru(bpy)₃]^{3+/2+} (E° = 1.25 V),¹⁵ in accord with Ru(II) stabilization by dmsO. A lower-potential couple, only observed following oxidation at 1.6 V, is at 1.1 V (vs Ag/AgCl in CH₃CN); it is likely that Ru–S \rightarrow Ru–O isomerization¹⁶ accompanies oxidation of [Ru(tpy)(bpy)(dmsO)]²⁺. Simulations of the voltammograms suggest that the S \rightarrow O rate constant is 100 s⁻¹ in the Ru(III) complex; Ru–O \rightarrow Ru–S isomerization in the Ru(II) ion is much slower (0.01 s⁻¹).

Upon irradiation at 441.6 nm, crystalline [Ru(tpy)(bpy)(dmsO)](SO₃CF₃)₂ undergoes an *immediate* color change from yellow to red; the original color returns after several minutes. In solution (acetone, tetrahydrofuran, dmsO) and poly(methyl methacrylate) (pmma) films, 430–450 nm irradiation of [Ru(tpy)(bpy)(dmsO)]²⁺ produces a new species with an absorption maximum at 490 nm.¹⁷ The wavelength of this absorption maximum is close to that reported for the product formed in the reaction of (CH₃)₂S with [(tpy)(bpy)Ru(O)]²⁺ (486 nm)¹⁸ and is consistent with O-bonded Ru–dmsO.

Crystals and pmma films containing [Ru(tpy)(bpy)(dmsO)]²⁺ are luminescent at room and low temperatures (Figure 1).¹⁹ At room temperature, 441.6-nm excitation produces a weak luminescence band at 720 nm. Upon cooling the sample to 170 K, the 720-nm luminescence intensity increases, and a new feature appears at 625 nm.²⁰ The far-red luminescence must arise from a photoproduct, and O-bonded Ru–dmsO is the most likely candidate. At low temperatures, both the 625 and 720-nm luminescence profiles display vibrational structure with peak spacings of lower energy (\sim 900 cm⁻¹) than those typically observed in Ru–polypyridine complexes (\sim 1300 cm⁻¹).²¹ Single-crystal luminescence decay kinetics (135 K) reveal that the two emitting states have different lifetimes: τ_1 = 550 ns at 720 nm; τ_2 = 100 ns at 625 nm.¹⁹

The 625-nm luminescence band in [Ru(tpy)(bpy)(dmsO)]²⁺ is shifted farther to the red than would be expected on the basis of

[†] Chemistry Division, MS J514, Los Alamos National Laboratory, Los Alamos, NM 87545.

(1) Imlau, M.; Woike, T.; Schieder, R.; Rupp, R. A. *Phys. Rev. Lett.* **1999**, *82*, 2860–2863.

(2) Imlau, M.; Haussühl, S.; Woike, T.; Schieder, R.; Angelov, V.; Rupp, R. A.; Schwarz, K. *Appl. Phys. B* **1999**, *68*, 877–885.

(3) Woike, T.; Haussühl, S.; Sugg, B.; Rupp, R. A.; Beckers, J.; Imlau, M.; Schieder, R. *Appl. Phys. B* **1996**, *63*, 243–248.

(4) Carducci, M. D.; Pressprich, M. R.; Coppens, P. *J. Am. Chem. Soc.* **1997**, *119*, 2669–2678.

(5) Fomitchev, D. V.; Coppens, P. *Comments Inorg. Chem.* **1999**, *21*, 131–148.

(6) 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.

(7) Orange-yellow [Ru(tpy)(bpy)(dmsO)](SO₃CF₃)₂ was prepared from [Ru(tpy)(bpy)(H₂O)](SO₃CF₃)₂ (0.191 g, 0.24 mmol; Takeuchi, K. J.; Thompson, M. S.; Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 1845–1851) and dimethylsulfoxide (Burdick and Jackson, 500 μ L, 7 mmol) in 6 mL of absolute ethanol. The reaction mixture was allowed to stir overnight at room temperature in air. The orange product was filtered and washed with cold ethanol (2 \times 15 mL) and diethyl ether (2 \times 15 mL). Isolated yield: 62%.

(8) Red-orange crystals of [Ru(tpy)(bpy)(dmsO)](SO₃CF₃)₂ were grown from acetonitrile/diethyl ether solutions. X-ray data were collected at 293 K on a Bruker Smart 1000 diffractometer. The structure was solved by direct methods. In the final least squares refinement cycle on F^2 , R = 5.03%, R_w = 8.88% and GOF = 2.060 on 7976 reflections with 560 parameters. Crystal data: a = 25.7825(17) Å, b = 11.0774(7) Å, c = 23.6971(16) Å, β = 96.8620(10)°, V = 6719.5(8) Å³, space group $C2/c$, Z = 8, MW = 866.8 and ρ (calcd) = 1.714 g/cm³.

(9) March, F. C.; Ferguson, G. *Can. J. Chem.* **1971**, *49*, 3590–3595.

(10) Root, M. J.; Deutsch, E. *Inorg. Chem.* **1985**, *24*, 1464–1471.

(11) Senoff, C. V.; Maslowsky, E., Jr.; Goel, R. G. *Can. J. Chem.* **1971**, *49*, 3585–3589.

(12) Calligaris, M.; Carugo, O. *Coord. Chem. Rev.* **1996**, *153*, 83–154.

(13) Hecker, C. R.; Fanwick, P. E.; McMillin, D. R. *Inorg. Chem.* **1991**, *30*, 659–666.

(14) E = electron transfer; C = chemical reaction: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods. Fundamentals and Applications*; John Wiley and Sons: New York, 1980. Cyclic voltammograms were collected in a traditional two-compartment cell using a polished and sonicated 3 mm-diameter glassy carbon working electrode (BAS), Pt wire auxiliary electrode, and Ag/AgCl reference electrode. Measurements were conducted at room temperature with a CH instruments 660 electrochemical workstation. Electrochemical measurements were performed in acetonitrile, acetone, dichloromethane, and tetrahydrofuran solutions, deaerated with argon, containing 0.1 M *n*-tetrabutylammonium hexafluorophosphate (SACHEM). Cathodic waves corresponding to the anodic wave of the high potential couple were only observed for scan rates > 10 V/s. Scan rates from 100 V/s to 0.005 V/s were employed.

(15) Juris, A.; Balzani, V.; Barigelli, F.; Campagna, S.; Belser, P.; Zelewsky, A. V. *Coord. Chem. Rev.* **1988**, *84*, 85–277.

(16) Tomita, A.; Sano, M. *Inorg. Chem.* **2000**, *39*, 200–205. Yeh, A.; Scott, N.; Taube, H. *Inorg. Chem.* **1982**, *21*, 2542–2545.

(17) Steady-state UV–vis spectra (HP-8452) of irradiated solutions (HeCd laser, 441.6 nm) reveal two isosbestic points (365 and 432 nm) during formation of the photoproduct (λ_{max} 490 nm). Reversion to the starting material is only observed in dmsO ($\tau_{1/2} \approx 8$ min). Photodissociation occurs in acetonitrile. Spectra in pmma (poly(methyl methacrylate), Scientific Polymer Products) films reveal the 490-nm feature following irradiation. The photoproduct is stable for hours (solution) to days (pmma films).

(18) Roecker, L.; Dobson, J. C.; Vining, W. J.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 779–781.

(19) Solid samples were prepared in pmma films deposited on glass cover slips from CH₂Cl₂ solutions. Luminescence (441.6 nm excitation, \sim 28 mW, HeCd, Liconix) was collected and dispersed using an Acton Research SpectraPro-275 spectrograph. Intensities were monitored using a Princeton Instruments dual diode array (model DPDA-1024). Measurements of emission decay kinetics employed an instrument described elsewhere (Low, D. W.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1996**, *118*, 117–120) using 430-nm excitation from a Nd:YAG pumped OPO (Spectra Physics).

(20) Crystals or films of [Ru(tpy)(bpy)(dmsO)]²⁺ that had no prior exposure to blue light ($\lambda < 450$ nm) were not luminescent when excited at 488.7 nm. Following exposure to 441.6 nm radiation, however, samples exhibited 720-nm luminescence upon 488.7-nm excitation.

(21) Hager, G. D.; Watts, R. J.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7037–7042.

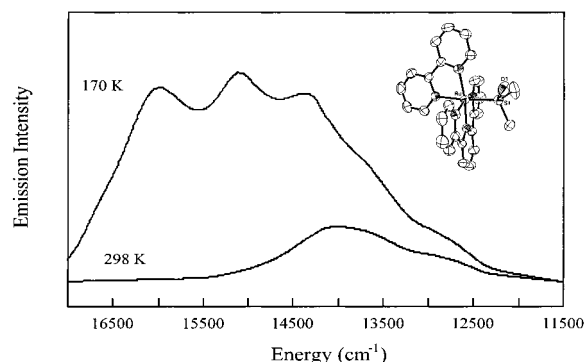


Figure 1. Emission spectra of $[\text{Ru}(\text{tpy})(\text{bpy})(\text{dmsO})](\text{SO}_3\text{CF}_3)_2$ in a pmma film at 298 and 170 K (uncorrected for instrument response). Inset: structure of the Ru(II) cation.

its absorption spectrum. The high Ru(III/II) reduction potential ($E^\circ = 1.84$ V) leads to an MLCT absorption maximum for the S-bonded complex (412 nm) that is substantially higher in energy than that of $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\lambda_{\text{max}}(\text{abs}) = 450$ nm) or $[\text{Ru}(\text{tpy})_2]^{2+}$ ($E^\circ = 1.26$ V, $\lambda_{\text{max}}(\text{abs}) = 470$ nm).¹⁵ Interestingly, luminescence from $[\text{Ru}(\text{tpy})(\text{bpy})(\text{dmsO})]^{2+}$ (625 nm) is not similarly blue-shifted ($[\text{Ru}(\text{bpy})_3]^{2+}$, $\lambda_{\text{max}}(\text{em}) = 620$ nm; $[\text{Ru}(\text{tpy})_2]^{2+}$, $\lambda_{\text{max}}(\text{em}) = 628$ nm), and the vibronic structure that appears in the low-temperature spectrum has a reduced peak spacing. These observations suggest that the 625-nm luminescence arises from a structurally distorted form of $[\text{Ru}(\text{tpy})(\text{bpy})(\text{dmsO})]^{2+}$. One intriguing possibility is that the reduced electron density at the Ru center in the MLCT excited state induces a ligand slip, producing an η^2 coordination geometry for the dmsO ligand.

The photochromism observed in films and single crystals of $[\text{Ru}(\text{tpy})(\text{bpy})(\text{dmsO})]^{2+}$ can arise only from intramolecular Ru-S \rightarrow Ru-O isomerization of the dmsO ligand (Figure 2). Since the lifetime of the $^3\text{MLCT}$ state in the Ru-S isomer is ≤ 100 ns, the rate constant for the excited-state isomerization process must be at least 10^5 s $^{-1}$.²² This rate is 10^3 times higher than thermal Ru-S \rightarrow Ru-O rearrangement in $[\text{Ru}(\text{tpy})(\text{bpy})(\text{dmsO})]^{3+}$ (100 s $^{-1}$), and $> 10^8$ times that of the corresponding Ru(II) ground-state reaction.²³ If the $^3\text{MLCT}$ excited state is highly distorted along a Ru-S \rightarrow Ru-O reaction coordinate (e.g., η^2 -dmsO), then the barrier to formation of O-bonded dmsO could be substantially reduced (Figure 2).²⁴ Alternatively, the impetus for such a reaction could be provided by a $^3\text{MLCT}$ nonradiative decay channel that populates a ligand-field (LF) excited state. Weakening of the Ru-dmsO bond in a $d\sigma^*$ LF state undoubtedly would promote rapid isomerization to the O-bonded form.

Intramolecular photochemical linkage isomerizations are uncommon transformations; most of the known examples involve metal nitrosyls.^{4,5,25,26} Our finding that irradiation of $[\text{Ru}(\text{tpy})(\text{bpy})(\text{dmsO})]^{2+}$ induces Ru-S to Ru-O rearrangement in crystals and films opens new avenues for the development of photochromic

(22) The isomerization rate constant is proportional to the quantum yield; this estimate is based on an assumed quantum yield of 10^{-2} .

(23) This limit derives from the assumption that the equilibrium constant for Ru-S \rightleftharpoons Ru-O isomerization in $[\text{Ru}(\text{tpy})(\text{bpy})(\text{dmsO})]^{2+}$ is ≤ 0.1 .

(24) Nonradiative deactivation of the distorted Ru-S excited state would produce a species on the ground-state potential surface; this species could rearrange to a Ru-O isomer or revert to the nondistorted Ru-S ground state.

(25) Kim, C.; Novozhilova, I.; Goodman, M. S.; Bagley, K. A.; Coppens, P. *Inorg. Chem.* **2000**, *39*, 5791–5795.

(26) Smith et al.⁶ suggest that photoinduced Ru-S to Ru-O isomerization in $[\text{Ru}(\text{bpy})_2(\text{dmsO})]^{2+}$ is a bimolecular process.

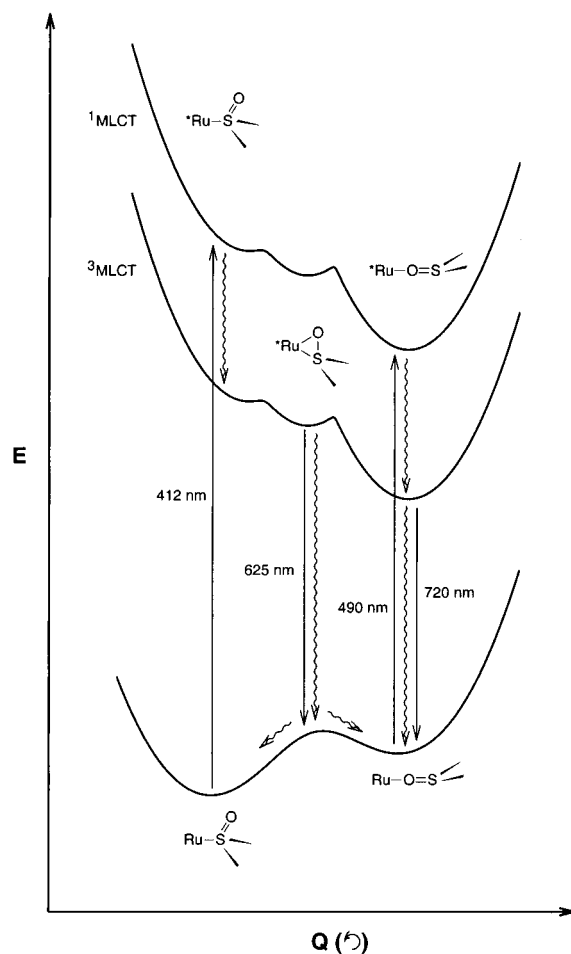


Figure 2. Excitation of the Ru-S isomer of $[\text{Ru}(\text{tpy})(\text{bpy})(\text{dmsO})]^{2+}$ produces a $^1\text{MLCT}$ state, which decays rapidly (< 10 ns) to form emissive species on the $^3\text{MLCT}$ potential surface. The distorted (η^2 -dmsO) state on this surface can decay directly to the Ru-S ground state (radiatively, 625 nm), or it can rearrange to produce an electronically excited Ru-O isomer that luminesces at 720 nm.

materials. The substituents on the sulfur of the S=O unit can be varied widely to modulate barrier heights of isomerizations. In addition, the ancillary imine ligands in complexes such as $[\text{Ru}(\text{tpy})(\text{bpy})(\text{dmsO})]^{2+}$ can be modified both sterically and electronically. Exploiting these chemical modifications could lead to photoactive materials with variable wavelength responses as well as selectively tunable dynamics properties.

Acknowledgment. We thank Will Wehbi, Larry Henling, Mike Day, and Brian Crane for experimental assistance and helpful discussions. This work was supported by ARO (DAAH04-95-1-0125), NSF, and NIST (ATP) Award 70NANB5H1031.

Supporting Information Available: Complete tables of crystal data, atomic coordinates, and bond distances and angles for $[\text{Ru}(\text{tpy})(\text{bpy})(\text{dmsO})](\text{SO}_3\text{CF}_3)_2$ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA000179D