Photoinduced Ligand Isomerization in Dimethyl Sulfoxide Complexes of Ruthenium(II)

Matthew K. Smith,[a] John A. Gibson,[b] Charles G. Young,[b][+] John A. Broomhead,[b][++] Peter C. Junk,[a] and F. Richard Keene*[a]

Keywords: Dimethyl sulfoxide / Isomerizations / Photochemistry / Ruthenium

Upon exposure to sunlight or UV irradiation, a DMSO solution of $[Ru(bpy)_2(DMSO)_2]^{2+}$ **(1)** (bpy = 2,2′-bipyridine; DMSO = dimethyl sulfoxide) turns rapidly from yellow to red, but subsequently slowly reverts to yellow in the dark. The photochemical sequence is explained in terms of a photopromoted linkage isomerization of the DMSO ligands from *S*- to *O*-bound, with a relaxation back to the thermodynamically stable yellow *S*-bound form in the dark by an intermolecular mechanism. The "dark" reaction has been studied by UV/Vis spectrophotometry, NMR and IR spectroscopy. The *S*-bound ligation of DMSO in the yellow cation was established by X-ray crystallographic studies of *cis*-$[Ru(bpy)_2(DMSO)_2](CF_3SO_3)_2$.

Introduction

Polypyridyl complexes of ruthenium(II) and their photochemistry have been widely studied, particularly with regard to potential application to storage of light energy and light-activated switches.[1,2] In the latter context, the development of systems which undergo reversible photoactivated chemical or structural changes are of particular interest.[3]

The complex $[Ru(bpy)_2(DMSO)_2](PF_6)_2$ {bpy = 2,2'-bipyridine, DMSO = dimethyl sulfoxide} undergoes an interesting reaction of this type. A yellow solution of the complex in DMSO rapidly turns red upon exposure to sunlight; in the dark, the solution subsequently slowly reverts to the yellow form. This process appears completely reversible as it can be performed many times on the same solution with no apparent degradation of the complex. The phenomenon appears to arise from linkage isomerization: photoactivated linkage isomerizations are known but uncommon in ruthenium chemistry,[4−6] and the present study was undertaken to elucidate aspects of the process.

[a] School of Biomedical and Molecular Sciences, James Cook University,
Townsville, Queensland 4811, Australia
Fax: (internat.) + 61-74/781-4600
E-mail: Richard.Keene@jcu.edu.au
[b] Department of Chemistry (Faculties), Australian National University,
Canberra, A.C.T. 0200, Australia
[+] Present address: School of Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia.
[++] Present address: School of Chemistry, Australian Defence Force
Academy, University College (UNSW),
Canberra, A.C.T. 2600, Australia.

Results and Discussion

Synthesis and Characterization

Reactions of blue $[Ru(bpy)_2(CO_3)]$ or $[Ru(Me_2bpy)(CO_3)]$ with non-coordinating acids HX {$X^- = PF_6^-$, $CF_3SO_3^-$} in DMSO resulted in the formation of the yellow bis(dimethyl sulfoxide) complexes, $[Ru(bpy)_2(DMSO)_2]^{2+}$ and $[Ru(Me_2bpy)_2(DMSO)_2]^{2+}$, which were precipitated as the X^- salts by addition of ethanol/hexane. Microanalytical and spectroscopic data for the dimethyl sulfoxide complexes were consistent with the proposed formulations, and IR, NMR and X-ray diffraction data (vide infra) indicate the dimethyl sulfoxide ligands are *S*-bound. In DMSO solution, the complexes undergo a reversible colour change to red upon irradiation with intense sunlight (ca. 5 min) or UV radiation [0.5 h; 100 W medium-pressure Hg lamp (354 nm)].

X-ray Crystallographic Studies

The structure of $[Ru(bpy)_2(DMSO)_2](CF_3SO_3)_2$ was determined by X-ray crystallography. The Ru centre shows a distorted octahedral environment; the DMSO ligands are *S*-bound and exhibit a *cis* relationship.

Two different conformations were observed in the asymmetric unit (Figure 1); in one form the O-atom of each of the DMSO ligands was orientated towards the opposite DMSO molecule (Figure 1a), and in the other form the oxygen atoms were orientated towards the aromatic ligands (Figure 1b). The origin of this anomaly may be steric. Selected bond lengths and angles are given in Table 1. The Ru−S bond lengths [2.292−2.293 Å] are slightly longer than those observed in other DMSO-containing ruthenium species, such as $[Ru(NH_3)_5(DMSO)]^{2+}$ [2.188 Å],[7] and *cis*-

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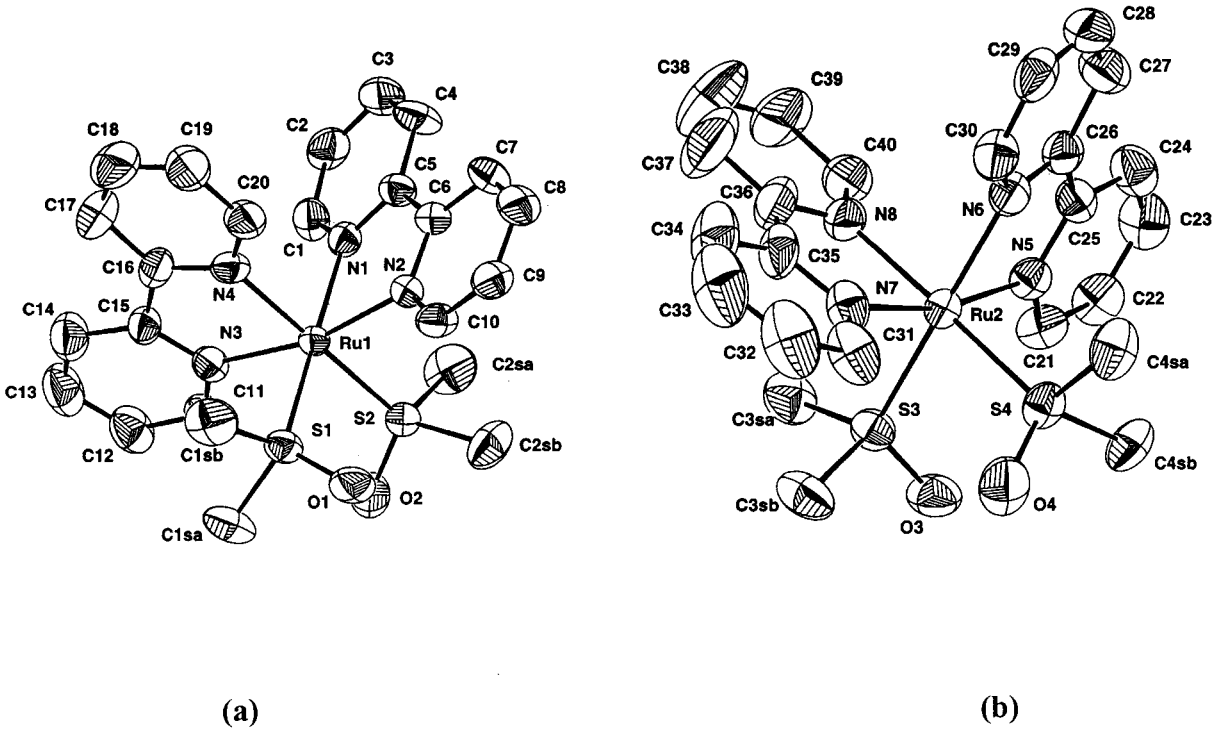

(a) (b)

Figure 1. The two conformations (a) and (b) observed in the crystal structure of *cis*-$Ru(bpy)_2(DMSO)_2](CF_3SO_3)_2$ (thermal ellipsoids at 50% probability)

Table 1. Selected bond lengths and angles in the structure of *cis*-$[Ru(bpy)_2(DMSO)_2](CF_3SO_3)_2$

Bond	Bond length (Å)	Bonds	Angle
Ru(1)−S(1)	2.293(2)	S(1)−Ru(1)−S(2)	89.42(5)°
Ru(1)−S(2)	2.292(1)	Ru(1)−S(1)−O(1)	115.6(2)°
Ru(1)−N(1)	2.096(4)	S(3)−Ru(2)−S(4)	88.78(5)°
Ru(1)−N(2)	2.094(4)	Ru(2)−S(3)−O(3)	115.7(2)°
Ru(1)−N(3)	2.094(4)	O(1)−S(1)−C(1sa)	105.9(3)°
Ru(1)−N(4)	2.086(4)	O(1)−S(1)−C(1sb)	107.5(3)°
S(1)−O(1)	1.473(4)	O(2)−S(2)−C(2sa)	106.7(4)°
S(2)−O(2)	1.476(5)	O(2)−S(2)−C(2sb)	106.7(3)°
S(3)−O(3)	1.480(4)		
S(4)−O(4)	1.479(4)		

$[RuCl_2(DMSO)_4]$ [2.276−2.277 Å; *trans* to Cl^-].[8] This observation possibly results from competition for π-backbonding electron density exerted by the *trans* bipyridine ligands: precedence for this may be seen in the structures of complexes *cis*(Cl)-$[RuCl_2(PzH)(DMSO)_3]$ [2.281−2.286 Å, *trans* to Cl^-; 2.310Å *trans* to pyrazole (which is π-backbonding)],[9] and *trans*-$[RuCl_2(DMSO)_4]$ [2.352 Å; *trans* to DMSO ligands (which are π-backbonding)].[10] Steric interactions between the *cis*-disposed DMSO ligands may also contribute to the bond lengthening. The S−Ru−S bond angle was slightly less than 90° [89.45° and 88.93° in the two conformers].

It is noted that on the basis of steric interactions alone, O-ligation would be preferred. Accordingly, electronic and bonding factors seem to be critical in the determination of the binding mode.

Electronic Spectroscopy and Kinetic Studies

The UV/Visible absorption spectra for the yellow solution in DMSO of the freshly synthesized complex $[Ru(bpy)_2(DMSO)_2](PF_6)_2$ and the irradiated (red) solution are

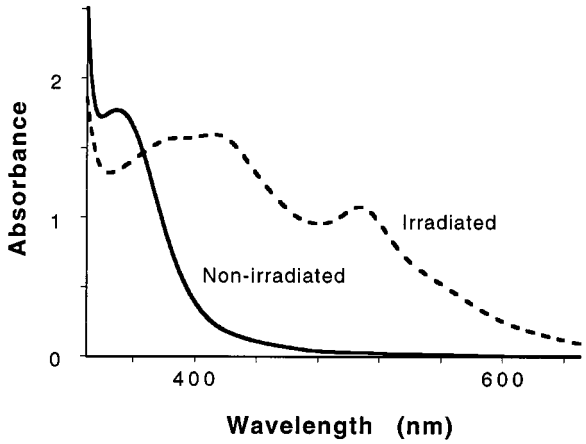

Figure 2. Absorbance spectra of $[Ru(bpy)_2(DMSO)_2](PF_6)_2$ (DMSO solution) before and after irradiation

shown in Figure 2 [λ_{max} = 348 nm, ε = 5760 $M^{-1}cm^{-1}$; λ_{max} = 507 nm, ε = 3500 $M^{-1}cm^{-1}$ and λ_{max} = 412 nm, ε = 5530 $M^{-1}cm^{-1}$, respectively]. The bathochromic shift on irradiation is consistent with a change from the "soft" *S*-bound (high field) to the "hard" *O*-bound (low field) ligands.

In DMSO solution, the red solution formed on irradiation reverted slowly in the dark to the original yellow spe-

cies. The initial light-induced reaction only occurred in DMSO, or non-coordinating solvents which contained DMSO. In other solvents the reaction proceeded not at all or to a minor extent (e.g. nitromethane, acetonitrile, dichloromethane, methanol, 1-methyl-2-pyrrolidinone), or there was an irreversible change due to the formation of a solvated species (e.g. water, *N*,*N*-dimethylformamide).[11]

The sequence observed for the "dark reaction" in DMSO solution is shown in the two segments of scan cycles (Figure 3), which illustrate a rapid initial reaction and a slower subsequent process. For the first reaction, continuous scans of the spectrum in the wavelength range 320−700 nm showed isosbestic points at λ = 440 nm and 390 nm (Figure 3a). The rate of the reaction was measured by following the time-dependence of the decay of the absorbance at 507 nm of the red complex ($t_{1/2}$ = 2.91 min. at 25 °C). The subsequent slower decay ($t_{1/2}$ = 111 min. at 25 °C) showed a different isosbestic point at 370 nm, which remained for the duration of the reaction (Figure 3b). Accordingly, the reaction proceeds via a two-step process from the red (irradiated) solution to the original yellow compound via an intermediate species.

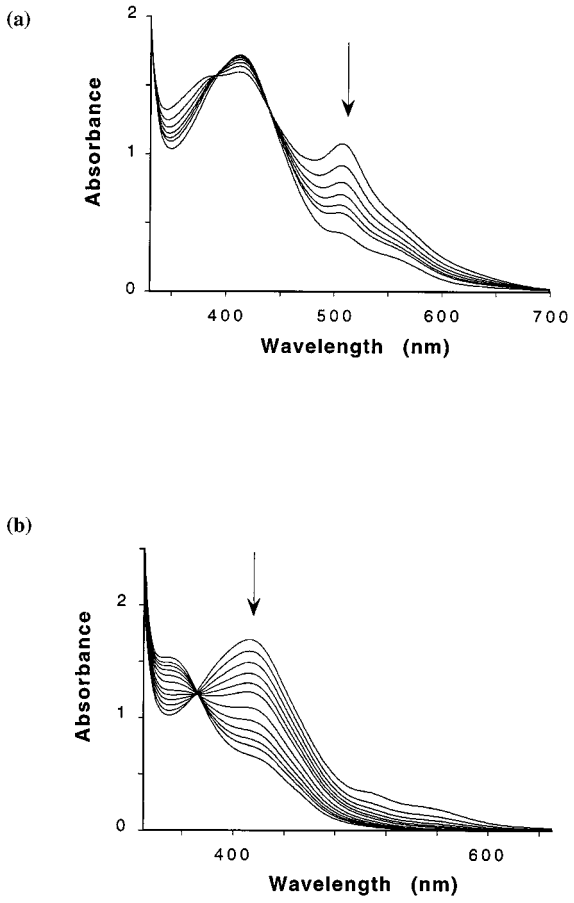

Figure 3. Absorbance spectra of $[Ru(bpy)_2(DMSO)_2](PF_6)_2$ (DMSO solution) after irradiation: (a) first 10 minute period (scan every 1 min), and (b) subsequent 285 minute period (15 min cycles)

The kinetics of the "dark" reactions which occurred after irradiation were followed using UV/Visible absorption spectral techniques over a range of temperatures. The two reactions observed were found to be pseudo-first order [plots of $\ln(A - A_{inf})$ vs. t were linear for > 3 $t_{1/2}$ in the two time domains]. The reaction rates were found to be unaffected by sample concentration, as expected.

Rate constants for the two reactions in DMSO solution at various temperatures are given in Table 2. The activation parameters for these two reactions were calculated: for the initial fast Red→Intermediate [**R**→**I**] reaction, $\Delta H^{\ddagger}$ = 58 (± 5) kJ mol^{-1} and $\Delta S^{\ddagger}$ = 83 (± 6) J mol^{-1}K^{-1}; for the slower Intermediate→Yellow [**I**→**Y**] reaction, $\Delta H^{\ddagger}$ = 92 (± 4) kJ mol^{-1} and $\Delta S^{\ddagger}$ = 162 (± 14) J mol^{-1}K^{-1}.

Table 2. Reaction rates for "dark" reactions [**I**→**Y**] for $[Ru(bpy)_2(DMSO)_2]^{2+}$ [complex concentration ca. 3−6 × 10^{-4} M]

Temp (K)	Solvent	k (s^{-1})[a] Slow Reaction	k (s^{-1})[a] Fast Reaction
25 °C (298 K)	DMSO	1.1 × 10^{-4}	4.0 × 10^{-3}
30 °C (303 K)	DMSO	2.1 × 10^{-4}	6.4 × 10^{-3}
35 °C (308 K)	DMSO	3.9 × 10^{-4}	8.7 × 10^{-3}
40 °C (313 K)	DMSO	6.9 × 10^{-4}	1.4 × 10^{-2}
45 °C (318 K)	DMSO	1.2 × 10^{-3}	1.8 × 10^{-2}
25 °C (298 K)	DMSO (50%) Nitromethane (50%)	9.1 × 10^{-5}	4.1 × 10^{-3}
25 °C (298 K)	DMSO (75%) Nitromethane (25%)	1.0 × 10^{-4}	4.2 × 10^{-3}

[a] Average of triplicate runs: estimated error ±5%.

From the structural studies reported above, the yellow form contains two *S*-bound DMSO ligands and it is highly probable that the red species formed immediately after irradiation contains two *O*-bound DMSO ligands. This may be rationalized in terms of the nature of the metal centre before and on irradiation: before irradiation, the Ru^{II} metal centre has a preference for ligands which possess the ability to backbond via ligand π-electron donation (i.e. "soft" ligands). After irradiation, however, the metal will have Ru^{III}-like character in the MLCT excited state and consequently will prefer ligands with strong σ-donating properties (i.e. "hard" ligands). Since DMSO has both "soft" (sulfur) and "hard" (oxygen) donor atoms, it is believed the DMSO switches its mode of bonding to the *O*-bound form to suit the nature of the metal. There is some precedence for this assertion: in Ru^{II} complexes involving strongly backbonding carbonyl (CO)[12] and nitrosyl (NO^+)[13] ligands, and in complexes involving Ru^{III} centres,[14,15] there is a significantly greater occurrence of *O*-bound DMSO than in the body of Ru^{II} species. In one case, Taube and coworkers have studied the kinetics of S→O isomerization on oxidation of $[Ru(NH_3)_5(DMSO)]^{2+}$.[16] More recently, an electrochemical study by Rack and Gray[17] of the system *mer*-$[RuCl_3(DMSO)(tmen)]$ {tmen = *N*,*N*,*N*',*N*'-tetramethylethylenediamine} demonstrated *S*-DMSO⇄*O*-DMSO isomerizations associated with Ru^{II}⇄Ru^{III} changes. It is probable therefore that the intermediate species observed in the "dark" reaction contains one *S*-bound and one *O*-bound DMSO ligand. This proposal is consistent with the IR analysis (see later), and is consistent with the UV/Visible spectral changes observed (Figure 3).

In principle, there are two possible mechanistic paths for the linkage isomerization reactions of *O*- to *S*-bound

DMSO; *viz.* an intermolecular substitution process in which the original DMSO ligands are replaced by solvent molecules, or an intramolecular switching mechanism involving a seven-coordinate species. There have been several investigations of linkage isomerization reactions involving the calculation of volumes of activation ($\Delta V^{\ddagger}$) which have also investigated the activation parameters $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$.[18,19] In these mechanistic studies, for those reactions which were assigned as intramolecular in nature from the $\Delta V^{\ddagger}$ data, the corresponding $\Delta S^{\ddagger}$ values were found to be near-zero or negative, whereas a positive value indicated an intermolecular mechanism. This distinction is rationalized in terms of the increase in the number of individual molecules in going from the reactants to the transition state because of the dissociation of the ligands involved in an intermolecular process, thereby increasing the entropy of the system and resulting in a positive $\Delta S^{\ddagger}$ value. In the present system, the $\Delta S^{\ddagger}$ values for the **R→I** and **I→Y** reactions are positive, indicating that the reactions are intermolecular; i.e. the original DMSO ligands are replaced by DMSO solvent molecules during the isomerization process.

Photo-induced intramolecular linkage isomerization reactions involving tumbling mechanisms have been observed in thiocyanate-isothiocyanate, nitro-nitrito and cyanide-isocyanide conversions.[20] The reported cases of linkage isomerization involving DMSO ligands have been intermolecular[10,21,22] including Ru-DMSO systems, and it is possible that some steric or electronic factor prevents the intramolecular mechanistic path.

The rate constants of the **R→I** and **I→Y** reactions in nitromethane solutions containing 50% DMSO and 75% DMSO were comparable to those of pure DMSO solutions at 25 °C (see Table 2).

Infrared Analysis

The IR spectra of complexes containing DMSO ligands provide a means of differentiating between the *S*- and *O*-bound attachment. In ruthenium complexes, an *S*-bound DMSO exhibited a distinctive $\nu_{S=O}$ peak between 1080 and 1150 cm^{-1}, depending on the electronic nature of the other ligands in the coordination sphere. An *O*-bound form had a signal of slightly lower energy between 900 and 1000 cm^{-1}. In addition, a ν_{Ru-S} vibration occurred between 410−430 cm^{-1}, while the Ru−O signal occurred at slightly higher energy (460 to 490 cm^{-1}).[12]

The IR spectrum of yellow $[Ru(bpy)_2(DMSO)_2](PF_6)_2$ using KBr discs showed two distinct peaks which confirmed the *S*-DMSO ligation: $\nu_{S=O}$ = 1096 cm^{-1}, and ν_{Ru-S} = 425 cm^{-1}. Solid-state investigations of the red form were not possible, since a solid sample could not be isolated. Accordingly, solution IR studies were undertaken to enable assignment of the red form. A solution of the yellow complex in DMSO exhibited a peak at 1098 cm^{-1} ($\nu_{S=O}$), confirming the *S*-bound configuration remained after dissolution. Due to absorption by the DMSO solvent, the ν_{Ru-S} peak at ca. 425 cm^{-1} was obscured.

Upon irradiation of the solution and immediate measurement of its spectrum, the peak at 1098 cm^{-1} disappeared and a new absorption at 997 cm^{-1} was observed, consistent with *O*-bound DMSO. A second scan recorded ten minutes later showed this latter peak had decreased significantly, while the peak at 1098 cm^{-1} had increased slightly. A final scan five hours later showed the peak at 1098 cm^{-1} had reverted to its original intensity. This evidence indicates that, upon irradiation, the yellow solution containing the *S*-bound form converted into the *O*-bound red form. As the red species returned to the yellow form, the $\nu_{S=O}$ absorption corresponding to *O*-DMSO decreased in intensity, suggesting the DMSO ligands were reverting to the *S*-bound configuration. This decrease in intensity of this peak occurred rapidly in the first ten minutes, but slowed markedly as time progressed: this is consistent with the observations from UV/Visible spectroscopy, where the "dark" reaction of the irradiated red complex to the yellow form occurred in two stages, interpreted as a rapid conversion of the *O*-bound form rapidly to an *S*-bound/*O*-bound intermediate, which in turn slowly reverted to the fully *S*-bound form.

^{1}H NMR Spectroscopic Studies

^{1}H NMR spectral studies were also used to probe the nature of bonding changes in the DMSO ligands upon irradiation. For *S*-bound DMSO, the methyl proton resonance(s) shift downfield by up to 1 ppm from free DMSO, whereas for *O*-bound DMSO there is little shift.[21]

The aliphatic region of the spectrum of yellow $[Ru(bpy)_2(DMSO)_2](PF_6)_2$ in [D_6]dimethyl sulfoxide is shown in Figure 4a. Two peaks were observed at δ = 2.81 and 2.69, assigned as the CH_3 resonances from the *S*-bound DMSO ligands.

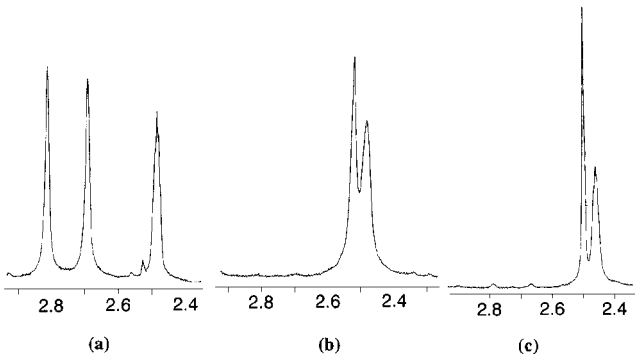

Figure 4. The 300 MHz ^{1}H NMR spectrum ([D_6]dimethyl sulfoxide solution) of the complex $[Ru(bpy)_2(DMSO)_2](PF_6)_2$: (a) before irradiation; (b) the same solution immediately after irradiation, and (c) the same solution after 5 h in the dark; ratio of integration of peaks at δ = 2.52 and 2.49 is identical in (b) and (c)

On irradiation by direct sunlight, the solution turned red and the ^{1}H NMR spectrum recorded immediately revealed the two CH_3 resonances observed in the original yellow solution had disappeared. A new resonance had developed at δ = 2.52, on the lowfield side of the solvent resonance centred at δ = 2.49 (Figure 4b), and consistent with either *O*-bound or free DMSO. When the irradiated solution was placed in the dark for five hours and the ^{1}H NMR spectrum re-measured, it was unchanged from that observed immediately after irradiation, even though the solution had

reverted completely back to the yellow form (Figure 4c). Repeating this irradiation procedure did not alter the spectrum. The loss of the peaks assigned to the *S*-bound form was established to be a consequence of the irradiation and not due to simple solvent exchange, as a freshly-prepared non-irradiated solution of the yellow complex in DMSO retained these two *S*-bound peaks for several days.

The data provide a number of insights into the photochemical sequence. The disappearance of the two resonances at $\delta = 2.81$ and 2.69 on irradiation and development of the new peak at $\delta = 2.52$ are consistent with the photoisomerization of *S*-bound form to the *O*-bound form, although the new peak is consistent with either *O*-bound or free DMSO. Following the subsequent reversion to the yellow form in the "dark" reaction, no change was observed within the aliphatic region of the spectrum: since the conversion of the *O*-bound to the *S*-bound form is known to be intermolecular (see above), the implication is that the photo-induced S→O linkage isomerization is also intermolecular. On the basis that the solvent [D_6]dimethyl sulfoxide would then be attached to the metal, no change would be expected in NMR spectra if the sequence was repeated, as was observed. This conclusion is in contrast to an earlier assessment on the system $[Ru(NH_3)_5(DMSO)]^{2+}$, where oxidation-induced S→O isomerization was thought to occur via a seven-coordinate intermediate i.e. via an intramolecular process.[16] The conclusion is also consistent with the observation that the photoreaction does not occur in the absence of DMSO and is not reversible in coordinating solvents which do not contain DMSO.

Other Systems

An attempt was made to obtain a further insight into the reaction by variation of the ligands not directly involved in the isomerization; for example, by replacement of the bpy ligands with 4,4'-dimethyl-2,2'-bipyridine (Me_2bpy), in which the substituent methyl groups are electron donating. The same general chemistry was observed, but the rate at which the photo-promoted red form reverted back to the yellow form was seen to increase relative to that of the non-methylated complex; this increase was marginal for the faster reaction (4.4×10^{-3} *cf.* 4.04×10^{-3} s^{-1}; 25 °C) but nearly double for the slower process (2.0×10^{-4} *cf.* 1.1×10^{-4} s^{-1}; 25 °C). It is not known at this stage whether the reasons for the difference are steric or electronic.

We have also observed similar photo-promoted linkage isomerizations for other ligands {such as SCN^- in the complex $[Ru(tpy)(bpy)(SCN)]^+$; tpy = 2,2':6',2''-terpyridine}[23,24] and we will report on these studies in due course.

Conclusions

The photo-induced linkage isomerization of *cis*-$[Ru(bpy)_2(DMSO)_2](PF_6)_2$ was investigated in DMSO solution. The complex contained two *S*-bound DMSO ligands (established in the solid state by X-ray crystallography) and underwent a colour change from yellow to red when irradiated with sunlight or UV light. On the basis of NMR, electronic and IR spectral studies, this was attributed to linkage isomerization from *S*- to *O*-bound DMSO. The complex subsequently slowly reverted to the yellow form in the dark in a two-step process. Kinetic studies, in association with NMR and IR spectral observations, show that these two "dark" reactions are intermolecular and involve an intermediate which is the $[Ru(bpy)_2(S\text{-DMSO})(O\text{-DMSO})]^{2+}$ species.

Experimental Section

Materials: 2,2'-Bipyridine (bpy; Aldrich), 4,4'-dimethyl-2,2'-bipyridine (Me_2bpy; Aldrich) hexafluorophosphoric acid (Aldrich), and dimethyl sulfoxide (DMSO; Aldrich, HPLC grade) were used as received. Nitromethane (BDH) was distilled over anhydrous calcium chloride before use. Trifluoromethanesulfonic acid (3 M) was distilled under vacuum and used in the short term.

Measurements: ^{1}H NMR spectra were recorded on a Varian Unity Inova-300 spectrometer in [D_6]dimethyl sulfoxide solutions at room temperature. Electronic absorption spectra were obtained using a Varian Cary 5E UV/Vis-NIR spectrophotometer in DMSO solution using 1 cm quartz cells. A Varian temperature control system was used to thermostat the kinetic studies. Infrared measurements were carried out on a Perkin−Elmer 1600 series FTIR spectrophotometer using solid KBr pressed plates, or a Presslok solution cell (32 mm diameter), comprising KBr plates and a 0.1 mm Teflon spacer. Elemental microanalyses were performed within the School of Biomedical and Molecular Sciences at James Cook University.

Syntheses: $[Ru(bpy)_2CO_3]\cdot 2H_2O$ and $[Ru(Me_2bpy)_2CO_3]$ were prepared using the literature method.[25]

$[Ru(bpy)_2(DMSO)_2](PF_6)_2$: $[Ru(bpy)_2(CO_3)]\cdot 2H_2O$ (0.05 g, 0.098 mmol) was dissolved in DMSO (0.4 mL) and HPF_6 (6 drops) added to the dark blue solution, which turned yellow. The mixture was stirred for 2 mins. to ensure the reaction went to completion. Ethanol (40 mL) and hexane (20 mL) were then sequentially added to the solution, producing a yellow precipitate. After stirring for twenty mins., the suspension was refrigerated overnight. The bright yellow crystals were collected by vacuum filtration. Yield: 0.066 g, 78%. $C_{26}H_{28}F_{12}N_4O_2P_2RuS_2$ (883.67): calcd. C 33.5, H 3.3, N 6.5, S 7.5; found C 33.7, H 3.1, N 6.3, S 6.9.

$[Ru(bpy)_2(DMSO)_2](CF_3SO_3)_2$: This complex was synthesized as described above except trifluoromethanesulfonic acid was substituted for hexafluorophosphoric acid. Yield: 0.067 g, 79%. $C_{28}H_{28}F_6N_4O_8RuS_4$ (891.86): calcd. C 36.1, H 3.23, N 6.5, S 14.7; found C 36.0, H 3.57, N 6.4, S 14.9.

$[Ru(Me_2bpy)_2(DMSO)_2](PF_6)_2\cdot[(C_2H_5)_2O]$: This compound was synthesized as for the bpy analogue, except $[Ru(Me_2bpy)_2CO_3]$ was used as the precursor. The complex was recrystallized from acetone/diethyl ether. Yield: 0.0606 g, 71%. $C_{32}H_{46}F_{12}N_4O_3P_2RuS_2$ (989.88): calcd. C 38.8, H 4.68, N 5.7; found C 39.0, H 4.71, N 6.1.

X-Ray Cystallographic Structure Determination of $[Ru(bpy)_2(DMSO)_2](CF_3SO_3)_2$: Crystals of $[Ru(bpy)_2(DMSO)_2](CF_3SO_3)_2$ were grown by slow evaporation of an ethanol/hexane solution of the complex. A unique room temperature diffractometer data set (Enraf−Nonius CAD-4 diffractometer; $T \approx 295$ K; monochromatic Mo-K_α radiation, $\lambda = 0.7107_3$Å; $2\theta/\theta$ scan mode) was measured, yielding 12314 independent reflections, 8800 with $I > 3\sigma(I)$

being considered "observed" and used in the large-block least-squares refinements. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and were not refined. Conventional residuals R, R_w on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Neutral atom complex scattering factors were employed, and computation was by the XTAL 3.4 program system, implemented by Hall et al.[26] For crystal and refinement details see Table 3.

Table 3. Crystallographic data for *cis*-[Ru(bpy)$_2$(*S*-DMSO)$_2$]/(CF$_3$SO$_3$)$_2$

Formula	$C_{26}H_{28}F_6N_4O_8RuS_4$
Mol. wt.	867.84
$F(000)$	1752
a (Å)	13.405(2)
b (Å)	13.730(2)
c (Å)	18.636(5)
α (deg)	86.12(2)
β (deg)	88.09(2)
γ (deg)	78.48(1)
V (Å^3)	3352(1)
Molecules/unit cell, Z	4 (2 molecules in asymmetric unit)
Space group	Triclinic, $P\bar{1}$ (# 2)
Diffractometer	CAD4
Radiation: λ (Å)	Mo-K_α (0.71073)
2θ range, deg	2 − 50
Sigma cutoff	3σ
D_c, g cm^{-3}	1.719
μ, cm^{-1}	26.4
A* min,max	1.365, 1.800
Crystal dimensions, mm	0.74 × 0.42 × 0.84
Weighting scheme	4 × 10^{-4}
No. of reflections collected	12314
No. of observed reflections	8800
No. of parameters varied	884
T (K)	296
R	0.057
R_W	0.066

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Centre as supplementary publication no. CCDC-134337. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Kinetic Studies: Temperature-dependent kinetic studies were carried out using UV/Vis spectroscopy. Individual spectra of the yellow and red forms were obtained by measurement of a fresh solution of [Ru(bpy)$_2$(DMSO)$_2$](PF$_6$)$_2$ in DMSO (0.0066 g in 25 ml; $c = 3.07 \times 10^{-4}$ M) before and after irradiation for 10 min by sunlight. For the kinetic studies, the above solution of [Ru(bpy)$_2$(DMSO)$_2$](PF$_6$)$_2$ in DMSO was irradiated and the absorption spectra between 700 nm and 350 nm recorded in scan mode at 1 min intervals for 12 min, followed immediately by a cycle period of 15 min intervals for up to 6 h, depending on the temperature. The A_{inf} for both the **R**→**I** [Red→Intermediate] and **I**→**Y** [Intermediate→Yellow] reactions were estimated using a correlation program within Microsoft Excel software, and refined iteratively. The reactions were performed in triplicate, and agreement between the three replicates was high (within 5%).

The same procedure was repeated for [Ru(Me$_2$bpy)$_2$(DMSO)$_2$](PF$_6$)$_2$ at 25 °C.

IR Analysis: Solid state IR analyses were measured using pressed KBr discs (3 mg complex and 60 mg anhydrous KBr). Solution IR spectra (in DMSO) were obtained using a 32 mm Presslok solution cell with a 0.1 mm teflon spacer and KBr windows in absorbance mode, and the DMSO background subtracted. The spectra were recorded before and immediately after irradiation (10 mins. in sunlight). In the latter case, a second spectrum of the solution was recorded 10 mins. later, and a third after an interval of 5 h.

^{1}H NMR Spectoscopic Analysis: The ^{1}H NMR spectra of [Ru(bpy)$_2$(DMSO)$_2$](PF$_6$)$_2$ in [D$_6$]dimethyl sulfoxide solution were recorded on a fresh solution, then immediately after irradiation in sunlight (10 minutes with shaking in the NMR tube), and 5 h after irradiation.

Acknowledgments

The research was funded by the Australian Research Council.

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Received November 12, 1999
[I99404]