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Unusual Photooxidation of S-Bonded Mercaptopyridine in a Mixed Ligand Ruthenium(II) Complex with Terpyridine and Bipyridine Ligands

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S Supporting Information

ABSTRACT: An unusual photooxidation of a coordinated 4mercaptopyridine (SpyH) ligand in the $[Ru(Hmctpy)(dmbpy)(\kappa S-$ SpyH)]²⁺complex (Hmctpy = 4'-carboxy-2,2';6',2"-terpyridine, dmbpy = 4,4'-dimethyl-2,2'-bipyridine) takes place under visible and UV irradiation, in aerated acetonitrile. The [Ru(mctpy)(dmbpy)(KS-SO₂py)] sulfinato product has been characterized by a variety of methods, including X-ray diffraction which supports the presence of the Ru-KS-SpyH isomer in the starting complex. The photooxidation of the 4-mercaptopyridine ligand enhances the back-bonding interactions in the complex by means of the strongly acceptor 4-pyridinesulfinato-SO₂py species, increasing the redox potential of the Ru(III)/Ru(II)



couple significantly from 1.23 to 1.62 V. It also led to pronounced changes in the electronic and NMR spectra of the complexes, corroborated by DFT and ZINDO-S calculations. A possible mechanism based on referenced data of photooxidation has been proposed, which involves the formation of a reactive oxygen species and intermediate endoperoxide species, yielding a very stable Ru-sulfinato product. This novel species exhibits stronger luminescence ($\Phi_f = 0.004$) than the starting complex under UV excitation.

INTRODUCTION

Ruthenium polypyridine complexes exhibit remarkable photochemical and photophysical properties, supporting applications in photosensor devices, catalysis, photodynamic therapy, and energy conversion.¹⁻⁵ In particular, carboxyterpyridine ruthenium complexes are being currently employed in high performance dye sensitized solar cells (DSSC),⁶ because of their ability to interact with the TiO₂ semiconducting surface, promoting light harvesting and efficient photoelectron transfer in the excited state. In addition, they also provide interesting systems for exploring vectorial photoelectron transfer⁷ based on a suitable design encompassing the use of appropriate donoracceptor ancillary ligands. Along this line, a new mixed ligand complex [Ru^{II}(Hmctpy)(dmbpy)(SpyH)]²⁺ has been synthesized in this work, by employing 4,4'-dimethyl-2,2'-bipyridine (dmbpy) and 4-mercaptopyridine (SpyH, when protonated on nitrogen) as vectorial electron donor species in relation to the (2,2';6',2"-terpyridine)-4'-carboxylic acid (Hmctpy) acceptor ligand. However, the investigation of this particular complex proved more challenging than expected, revealing an unusual photochemical behavior in the presence of dioxygen. This unexpected reactivity raised fundamental questions regarding the binding modes of the 4-mercaptopyridine ligand in the complex, and its involvement in the selective photooxidation by singlet oxygen. For this reason, the chemistry and photochemistry of the mixed complexes were here investigated in detail, before exploring their use as a dye sensitizing agent in DSSC.

It should be noted that in ruthenium polypyridine complexes the photoexcitation primarily leads to the singlet excited state and then to the long-lived triplet state by intersystem crossing, where they can interact with other molecules by electron transfer or energy transfer.^{8,9} The interaction of the triplet excited ruthenium complexes with the triplet oxygen species $({}^{3}O_{2})$ generates very reactive oxygen singlet species $({}^{1}O_{2})^{10,11}$ which can easily react with other molecules in solution forming photooxidized products. In this sense, photooxidation reactions of sulfur compounds have been reported by Schenck and Krauch since 1962, and several papers focusing on thioanisoles and thiophene derivatives, including aliphatic organosulfur compounds, have also been publisheed.^{12,13} However, most of them refer to the oxidation mediated by hydrogen peroxide^{13,14} or by irradiation of an air saturated solution with a sensitizer, in order to generate singlet oxygen to oxidize the sulfur compound.¹⁵ Oxidation of coordinated sulfur ligands has also been reported in the literature; for instance, Buonomo et al. reported on the oxidation of Ni-thiolates by H_2O_2 and singlet

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Figure 1. (A) Spectral changes of a solution of the $[Ru^{II}(Hmctpy)(dmbpy)(SpyH)]^{2+}$ complex in acetonitrile $(1.3 \times 10^{-5} \text{ mol/L})$ under irradiation with blue light (456 nm); (B) under N₂.

oxygen, showing the retention of the metal-S bound to give mono-oxygenated sulfenato and or bioxygenated sulfinato metal complexes.¹⁶ Addition of a sensitizer to promote the formation of singlet oxygen species in solution has also been performed,¹⁷ but in some cases, such as the platinum sulfur complex described by Connik and Gray,¹⁸ the complex itself seems to sensitize the production of singlet oxygen, followed by oxidization of its ligand.

In general, it is accepted that photooxidation starts with the generation of singlet oxygen by the sensitizer, followed by a step where the target molecule reacts with such reactive species forming a sulfonate product.¹⁹ Alternatively, the oxidation can initially form a mono-oxygenated product, followed by its reaction with another oxygen species to give the dioxygenated product. The solvent can also play a very important role in the reaction, since protic and aprotic solvents give different proportions of mono- and dioxygenated products.²⁰

In order to understand the photoreactivity of the $[Ru^{II}(Hmctpy)(dmbpy)(\kappa S-SpyH)]^{2+}$ complex, its absorption and emission properties have been examined, including its photochemical behavior in the presence of dioxygen. As a matter of fact, pronounced changes in the electrochemical and spectroscopic properties have been observed after the irradiation process, raising many questions concerning the donor–acceptor abilities of the ligand derived from the photooxidation reaction at the sulfur atom. Fortunately, during the course of the investigation, the X-ray crystal structure of the product has been obtained, which supports the discussion of the chemistry and photochemistry involved in this interesting system.

EXPERIMENTAL SECTION

Materials. (2,2':6',2''-Terpyridine)-4'-carboxylic acid methyl ester,²¹ [Ru(Hmctpy)Cl₃],²² and [Ru(Hmctpy)(dmbpy)(H₂O)]-(PF₆)₂⁵ starting materials were synthesized as previously described.

Synthesis of $[Ru(Hmctpy)(dmbpy)(\kappa S-SpyH)](PF_6)_2$ or Complex 1. To a solution of 50 mg $(5.65 \times 10^{-5} \text{ mol})$ of the complex $[Ru(Hmctpy)(dmbpy)(H_2O)](PF_6)_2$ in 50 mL of methanol/water 5:1, 6.5 mg $(5.65 \times 10^{-5} \text{ mol})$ of 4-mercaptopyridine, previously dissolved in 5 mL of methanol, was added. The reaction mixture was refluxed for 24 h in the dark under a N₂ atmosphere. The brown-red product was purified by column chromatography (SiO_2) with 5:1 methanol/aqueous KNO₃ as eluent. The main fraction was collected, and the solvent was removed under reduced pressure, giving a solid residue that was dissolved in water and then reprecipitated with an aqueous solution of KPF₆. Hydrolysis of the ester groups occurred in basic medium with triethylamine in a 2:1 methanol/water mixture, kept in the dark under reflux for 24 h. The solvent was removed, and the complex was purified on a silica column with 10:1 methanol/aqueous KNO₃ and precipitated with HPF₆ to give 0.035 g (3.67×10^{-5} mol) of a brown solid. Elemental analysis: Calculated for C₃₃H₂₈F₁₂N₆O₂P₂RuS: C, 41.13; H, 2.93; N, 8.72; S, 3.33. Experimental: C, 41.15; H, 3.28; N, 9.47; S, 3.97. [Ru(Hmctpy)-(dmbpy)(κ S-SpyH)](PF₆)₂: ¹H NMR (CD₃CN, 400 MHz): δ ppm: 9.65 (1H,d, *J* = 5.7 Hz, H8); 8.95 (2H, s, H1 and H1'); 8.51 (3H, m, H2, H2' and H10); 8.25 (1H, s, H11); 7.94 (2H, t, *J* = 8.1 Hz, H3 and H3'); 7.83 (2H, d, *J* = 5.1 Hz, H5 and 5'); 7.73 (1H, d, *J* = 5.7 Hz, H9); 7.47 (2H, d, *J* = 6.4 Hz, H7 and H7'); 7.36 (2H, t, *J* = 6.6 Hz, H4 and H4'); 6.94 (1H, d, *J* = 5.7 Hz, H12); 2.75 (3H, s, H14); 2.36 (3H, s, H15).

Nuclear magnetic resonance (NMR) spectra (400 MHz) were recorded in CD₃CN at room temperature (rt), on a Bruker AV400 spectrometer. Chemical shifts are reported in part per million (ppm) relative to residual solvent protons (1.94 ppm for acetonitrile-d₃). Absorption spectra and emission spectra were measured in deaerated acetonitrile or acetone at room temperature, on a Cary 5000 UV–vis– NIR Spectrophotometer and PerkinElmer LS55 Fluorescence Spectrophotometer, respectively. For the luminescence lifetimes, an Edinburgh OB 900 single-photon-counting spectrometer was used, employing a Hamamatsu PLP2 laser diode as pulse (wavelength output, 408 nm; pulse width, 59 ps). The fluorescence quantum yield (Φ_f) of complex **2** was determined in degassed acetonitrile by using $[Ru(bpy)_3]^{2+}$ dye as the standard.²³

Electrochemical measurements were carried out in nitrogen-purged acetonitrile at room temperature with a BAS CV50W multipurpose potentiostat. The working electrode was a glassy carbon electrode, the counter electrode a Pt wire, and the pseudoreference electrode a silver wire. The reference was set using an internal ferrocene sample (400 mV vs SCE in acetonitrile). The concentration of the compounds was about 1 mM. Tetrabutylammonium hexafluorophosphate (TBAP) was used as the supporting electrolyte, and its concentration was 0.10 M.

UV–vis Photooxidation Reaction. Freshly prepared solutions of complex 1 [Ru(Hmctpy)(dmbpy)(κ S-SpyH)](PF₆)₂ in acetonitrile were irradiated with blue light (10 W LED centered at 456 nm) or white light (LED 10 W), and the spectral changes were monitored by UV–vis spectroscopy. The reaction products were analyzed by ¹H NMR and ESI-MS. In general, irradiation with white light yielded the same photoproduct obtained with blue light. The only source of dioxygen came from the air-saturated solvent.

Theoretical Calculations. All theoretical calculation were made in the Gaussian09 package²⁴ with basis function $6-31G(d,p)^{25-29}$ for light atoms and SDD pseudopotentials and its associated double- ζ functions³⁰ for the Ru atom. In order to consider the solvent effect (acetonitrile) the SMD³¹ continuum model was employed. Optimizations were done with the ω B97XD functional,³² and optimized

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structures were confirmed as minimum by frequency calculations. TD-DFT^{33,34} calculations were used to simulate the electronic spectrum using the M06³⁵ functional, as suggested by literature, ^{36,37} for the 50 lowest spin-allowed transitions (singlet–singlet). Both compounds were analyzed by Electron Density Difference Map using the GaussSUM 3.0 package.^{38,39}

RESULTS AND DISCUSSION

The $[Ru^{II}(Hmctpy)(dmbpy)(SpyH)]^{2+}$ complex has two possible linkage isomers, corresponding to the Ru- $\kappa N(HSpy)$



Figure 2. X-ray structure of complex 2 (ellipsoids at 50% probability, hydrogens omitted for clarity).

and Ru- $\kappa S(SpyH)$ species. In this work, an important clue for the specific binding mode was provided by the photochemical behavior of the complex in the presence of molecular oxygen. Irradiation with blue light led to pronounced spectral changes (Figure 1A), with the decay of the MLCT bands at 423 and 514 nm, forming a product absorbing at 467 nm. The photoreaction proceeds according to two well-defined, simultaneous isosbestic points, confirming the transformation into a single product. It should be noted that when the irradiation was performed under a N₂ atmosphere, the spectral changes were practically

Table 1. Theoretical and X-ray Bond Lengths (Å) for the $[Ru(Hmctpy)(dmbpy)(\kappa S-SpyH)]^{2+}$ and $[Ru(mctpy)(dmbpy)(\kappa S-SO_3py)]$ Complexes

[Ru(Hmctpy)(dmbpy)(κS-S	pyH)] ²⁺ I	OFT/ωB97XD	X-ray
Ru-S		2.476	not available
Ru–N(bipy)		2.084, 2.130	not available
Ru–N(tpy)		2.090; 1.962	not available
[Ru(mctpy)(dmbpy)(<i>kS</i> - SO ₂ py)] ^a	DFT/@B9	97XD	X-ray
S-O	1.496	1.474(1)	
Ru-S	2.327	2.284(1)	
Ru–N(dmbpy)	2.138; 2.12	1 2.106(1)	; 2.099(1)
Ru–N(tpy)	2.104; 2.09 1.984	8; 2.081(1) 1.957(; 2.084(1); 1)

 $^a\mathrm{Charge}$ zero when deprotonated carboxylate and nitrogen from $\mathrm{SO}_2\mathrm{py}.$

negligible in the first 60 s (Figure 1B), indicating that dioxygen is an essential reagent in the photooxidation process.

After the photolysis, needle-shaped, orange crystals, suitable for X-ray analyses, could be isolated from the slow evaporation of the acetonitrile solution containing the photo-oxidized product. However, the crystal decomposed quickly and the data set obtained was incomplete and heavily disordered. We were nevertheless able to obtain a preliminary model, which, to our surprise, supported the formation of S-bound sulfinato product $[Ru(mctpy)(dmbpy)(\kappa S-SO_2py)]$ or complex **2**. We also grew a new batch of crystals from an irradiated basic solution of triethylamine/acetonitrile and obtained the neutral complex as red blocks with the same structure of the first analysis, as shown in Figure 2 (X-ray details in the Supporting Information), confirming that both cases (neutral or basic) are compatible with a deprotonated carboxylic acid group in the product.

Although suitable single crystals of the starting [Ru-(Hmctpy)(dmbpy)(κ S-SpyH)]²⁺ complex have not been obtained yet, the presence of the S-bound sulfinato complex clearly pointed to a chemical reaction occurring at the coordinated S-atom, involving reactive oxygen species



Figure 3. (A) Theoretical structure obtained by DFT. (B) Electronic spectrum of the starting complex 1 in acetonitrile solution $(1.3 \times 10^{-5} \text{ mol/L})$, showing the theoretical bands generated TD-DFT calculations. (C) Electron Density Difference Maps of the vertical singlet transitions, where the blue surface shows decreased electronic density and the red surface shows increased electronic density.



Figure 4. (A) Theoretical structure of complex 2 (deprotonated) obtained by DFT. (B) Electronic spectrum of the starting complex 1 in acetonitrile solution $(1.3 \times 10^{-5} \text{ mol/L})$, showing the theoretical bands generated TD-DFT calculations. (C) Electron Density Difference Maps of the vertical singlet transitions where the blue surface shows decreased electronic density and the red surface shows increased electronic density.



Figure 5. (A) Proton NMR spectra of complex 1 in acetonitrile at t = 0 (dark line), after 24 h of irradiation with white light (red line) in CD₃CN (blue line). (B) ESI-MS spectra of complex 1 before (dark line) and after irradiation with white light (red line) in acetonitrile.

generated photochemically. The results were thus indicative of the Ru- $\kappa S(SpyH)$ isomer in the starting complex. Alternatively, the Ru- $\kappa N(pySH)$ isomer would undergo preferential oxidation of the terminal SH groups, leading to -S-S- bonds and keeping the inert Ru-N bond, with little chances of isomerizing to the Ru- κ S form. No such disulfide adduct could be observed during our MS analysis (vide infra). We optimized both isomers in wb97xd/(6-31G(d,p)) (light atoms)/SDD(Ru) with its respective pseudopotential level of theory, and the complex with the 4-mercaptopyridine ligand coordinated by the S atom is 5.6 kcal·mol⁻¹ more stable than when the ligand is coordinated by nitrogen. We also performed the TD-DFT calculations with an implicit solvent model (acetonitrile) for both complexes and compared with the experimental UV-vis in acetonitrile. As shown in Figure S3 the simulated spectra fit better when the ligand 4-mercaptopyridine is bounded by sulfur (Figure 3B).

The structures and electronic spectra of the [Ru(Hmctpy)-(dmbpy)(κ S-SpyH)]²⁺ and [Ru(mctpy)(dmbpy)(κ S-SO₂py)] complexes have been simulated by means of DFT and TD-DFT calculations, as well as by semiempirical calculations using the classical ZINDO-S method. The molecular geometry parameters obtained by iterative MM⁺/ZINDO-S calculations, and by the DFT method, can be compared in Table S3. Bond distances of complex **2** obtained by X-ray are in good agreement with calculated data by DFT/ ω B97XD as shown in Table 1.

The UV-visible absorption spectrum in acetonitrile was compared with TD-DFT results, and vertical transitions were analyzed by EDDM and are summarized in Figure 3. Complex 1 exhibits intense bands at 281 and 322 nm, which are mostly of $\pi \rightarrow \pi^*$ bands of the bipyridine and terpyridine ligands and the 4-mercaptopyridine ligand. In addition, contributions of the $\sigma(\text{Ru}-\text{S})$ bond to the π^* of the aromatic ligands are present in the transitions as well (Figure 3C). The lowest energy bands in the visible region were observed at 423 and 514 nm and are consistent with the metal-ligand charge transfer (MLCT) transitions expected for this type of polypyridine complex and also ligand-metal charge transfer (LMCT) of the sulfur atom to ruthenium, respectively.

The electronic spectrum of the complex **2** can be seen in Figure 4, with the corresponding theoretical TD-DFT

Scheme 1. Proposed Mechanism for the Photochemical Formation of the Sulfone Complex in Acetonitrile Solutions^a



^aComplex 2 is presented in its deprotonated form.



Figure 6. Cyclic voltammograms of the complex 1 in acetonitrile (0.1 M Bu_4NPF_6 ; 100 mV/s) with carbon electrode vs NHE before irradiation (black line) and after irradiation (red line).

simulations, which were done using the deprotonated carboxylate species to fit better the experimental and the X-ray data whose crystals were obtained from a basic solution. Accordingly, the main bands in the visible region are associated with Ru orbitals and nonbonding 2p orbitals from oxygens in SO₂ to dmbpy and mctpy charge-transfer transitions. In comparison with complex 1, these bands reflect hypsochromic shifts indicative of the stabilization of the ruthenium d π orbitals by back-bonding interactions with the κ S-SO₂py ligand which was stabilized due to S–O bond formation.

The ¹H NMR spectrum of the complex 1 in CD_3CN displayed four signals corresponding to the terpyridyl protons, with two magnetically equivalent peripheral rings (Figure 5A),



Figure 7. Cyclic voltammograms of complex 1 in acetonitrile (0.1 M Bu_4NPF_6 ; 100 mV/s) with carbon electrode vs NHE before irradiation (black line) and after irradiation (red line) larger window.

and because of the low symmetry⁵ all six aromatic protons of the 4,4'-dimethyl-2,2'-bipyridyl ligand appeared as distinct signals in the aromatic region for both complexes. A labeled structure is shown in Scheme 1. In the aliphatic region there are two singlet signals in δ 2.75 and δ 2.36 ppm. The doublets centered at δ 7.47 and δ 6.89 ppm with J = 6.5 Hz were assigned to the magnetically equivalent protons 7, 7' and 6, 6', respectively, of the 4-mercaptopyridine ligand. After irradiation, the position of the protons 7, 7' and 6, 6' of the 4mercaptopyridine ligand shifted to a low field region (8.31 and 6.96 ppm, respectively, with J = 6.7 Hz), corroborating the electron-withdrawing effect of the two oxygen atoms bonded to



Figure 8. (A) Emission spectra of complex 1 (red line) and complex 2 (blue line) in acetonitrile. (B) Lifetime decay for complex 1 (red line) and complex 2 (blue line).

the sulfur atom. Likewise, proton 8 from the dmbpy ligand, found at δ 9.65 (J = 5.7) before irradiation, was significantly deshielded after photooxidation, to δ 10.66 (J = 5.7) because of the proximity with the oxygen atoms of the oxidized 4mercaptopyridine ligand.⁴⁰ Based on the ¹H NMR spectrum of the 4-mercaptopyridine ligand in Figure S7, it is possible to exclude any possibility of ligand photosubstitution by acetonitrile.⁴⁰ The irradiated solutions were also analyzed by mass spectrometry (ESI-MS), and the spectra are shown in Figure 5A. Before irradiation (black line), the main peak in m/z673.06 refers to complex **1**, and after irradiation (red line), it is possible to see the main peak with m/z = 705.08 related to the oxidized product (complex **2**).

The cyclic voltammogram of complex 1 in acetonitrile with a glassy carbon electrode (Figures 6 and 7) showed a reversible wave at $E_{1/2}$ = 1.23 V (vs SHE), which was assigned to the Ru(III)/Ru(II) redox couple. At 1.78 V there is another reversible electrochemical process which can be assigned to the Ru(IV)/Ru(III) couple. The alternative assignment involving ligand exchange by acetonitrile⁴¹ in the Ru(III) complex is not plausible in our case, since the two waves are preserved in the reverse, cathodic scan, excluding the possibility of successive chemical reactions occurring. After irradiation, the sulfur ligand photooxidation shifted the Ru(III)/Ru(II) waves from 1.23 to 1.62 V, corroborating the influence of the back-bonding interactions with the κ S-SO₂py ligand. By similar reasoning, the Ru(IV)/Ru(III) wave in this complex should be located above 2.20 V and cannot be detected in the electrochemical window.

By extending the electrochemical window in the -1.60 to 2.50 V range, in acetonitrile, it is possible to detect a third, irreversible oxidation wave at 2.26 V for complex 1 (Figure 7), presumably associated with electrocatalytic reactions of the solvent promoted by the oxidized complex at the limit of the electrochemical window.

In the cathodic region of the voltammogram for complex 1, it is possible to observe overlapped successive reduction waves of the coordinated mctpy ligand at -0.72 and -1.05 V and the dmbpy ligand at -1.28 V. After photoirradiation, the reduction wave of the mctpy and dmbpy ligands shifted to -0.77 V and -1.01 V, respectively, while a new signal was observed at -1.48 V, possibly related to the reduction of the 4-pyridysulphinate ligand (Figure 7).

Photochemical Behavior in Acetonitrile. The emission spectra of complexes 1 and 2 in acetonitrile, obtained under similar anaerobic conditions, are superimposed on Figure 8 for comparison purposes. As one can see, the complex 2 exhibits a strong emission with maximal intensity at 766 nm and $\Phi_f = 0.004$, upon excitation at 424 nm, decaying according to monoexponential emission with a lifetime of 98 ns. In contrast, complex 1 has a very poor photoemission, and its decay proceeds relatively fast according to a biexponential kinetics, corresponding to lifetimes of t1 = 6.7 ns (44%) and t2 = 86 ns. The second lifetime is indeed very close to that observed for complex 2 and may arise from the presence of traces of the oxidized product in the sample.

Finally, as we have shown, the photochemical formation of the S-bound sulfinate product in acetonitrile solutions requires the presence of dioxygen, as reported by the literature.^{42,43} Accordingly, it is plausible that the photooxidation process starts with a self-sensitized production of singlet oxygen by complex 1, which can lead to the terminal peroxide (I1) or endoperoxide (I2) intermediates shown in Scheme 1^{17,44,19} and then to the sulfinato complex product. Considerable differences are observed in the UV-vis spectra when the irradiation process takes place in water and methanol solution (Figure S2) instead of acetonitrile. When an aqueous solution of the complex is irradiated, the band at 495 nm decreases while a band at 433 nm starts to grow in. The same behavior is observed in methanol but with lower intensity. One of the reasons for this is that protic solvents such as water and methanol could react with the intermediate (I1 or I2) competitively by inhibiting the formation of the sulfonated compound by means of hydrogen-bonding interactions.^{20,19} In addition, it is also important to consider that studies conducted on the effects of solvents on deactivation of ¹O₂ indicate that the lifetime of ¹O₂ in solvents such as water and methanol is very low compared to solvents such as acetone and acetonitrile.45 Also, it is mentioned in the literature that in aprotic solvents, such as acetonitrile and DMF, the photooxidation of sulfides by singlet oxygen preferentially generates sulfinato compounds compared with protic solvents in which

the major products formed are sulfenato.²⁰ In our results we could not see by ESI-MS the formation of a sulfenate complex.

CONCLUSION

The $[Ru(Hmctpy)(dmbpy)(\kappa S-SpyH)]^{2+}$ complex can be photochemically converted, in the presence of dioxygen, into the unusual [Ru(mctpy)(dmbpy)(κ S-SO₂py)] product which has been isolated and characterized, including by X-ray diffraction analysis. Before oxidation, the complex [Ru- $(Hmctpy)(dmbpy)(\kappa S-SpyH)]^{2+}$ exhibits poor luminescence under UV excitation, in contrast to the [Ru(mctpy)(dmbpy)- $(\kappa S-SO_2 py)$ product with $\Phi_f = 0.004$. The oxidation of the 4mercaptopyridine ligand enhances the back-bonding interactions in the complex by the formation of the strongly acceptor 4-pyridysulphinate species, increasing the redox potentials of the Ru(III)/Ru(II) couple from 1.23 to 1.62 V. The pronounced changes in the electronic and electrochemical properties were consistent with the observed shifts in the electronic and NMR spectra of the complexes, as corroborated by DFT calculations. The proposed mechanism for the photooxidation reaction involves the formation of a reactive oxygen species starting from ¹O₂, proceeding through the conversion into the stable sulfinato species.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02965.

Synthetic details, additional spectroscopic data, X-ray diffraction study data (PDF)

Accession Codes

CCDC 1582382 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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