Photocatalyzed Oxidation of SO_3^{2-} by Co(dimethylglyoximato)$(SO_3)_2^{3-}$ and Its {Co(dimethylglyoximato)$(SO_3)_2^{3-}$, Cu(2,6-Me_2pyo[14]-1,4,6-triene-1,4,7,11,N_4)$^{2+}$} Adduct

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Introduction

The oxidation of aqueous S(IV) has been a subject of continued interest.[1−5] Some questions about the mechanism of the uncatalyzed reaction with oxygen, eq 1, have been addressed

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-} \qquad (1)$$

in recent literature reports. Interest in the mechanism of the catalyzed and uncatalyzed reactions stems not only from the standpoint of basic science but also from the reaction being at the center of a number of long-recognized technical problems, i.e., gas desulfurization, pollution, health problems, etc.[6−8] In addressing some of the practical motives of the S(IV) oxidations, the reactions

$$SO_2{\cdot}xH_2O \rightleftarrows H_2 + SO_4^{2-} + 2H^+,\ \Delta G° \approx 16.4\ \text{kJ/mol} \qquad (2)$$

$$SO_3^{2-} + H_2O \rightleftarrows H_2 + SO_4^{2-},\ \Delta G° \approx -10.6\ \text{kJ/mol} \qquad (3)$$

can be considered interesting propositions when is desired to combine the desulfurization process and the production of a convenient fuel.[9] Present knowledge of the S(IV) aqueous chemistry suggests that, apart from the free energy issue, these reactions may require a catalyst to proceed with appropriate rates. Moreover, when medium conditions make the oxidation of S(IV) endoergonic, eq 2, the catalyst must be designed in a manner that it absorbs photochemically supplied energy and, in addition, increases the overall rate of the process. Competition among various absorbing species for the incident UV light dictates that the catalyst should be photoactive for irradiation above 350 nm. It has been shown that Co(II) complexes are photoactive, i.e., the dimethylglyoximato complex is photoreduced to Co(I) products without oxidation of the pseudomacrocyclic ligand.[10−12] Moreover, $Co(DMG)_2(H_2O)_2^+$ and $Co(DMG)_2(SO_3)H_2O^-$ complexes undergo fast anation reactions with sulfite and bisulfite to regenerate $Co(DMG)_2(SO_3)_2^{3-}$.[13−15] These properties suggest that Co(III) complexes of the DMG or other macrocyclic ligand may fulfill the requirements considered above for a catalyst or photocatalyst in oxidations of aqueous S(IV). Little is known, however, about the photochemistry of sulfito complexes of Co(III).[16,17] The large stability of $Co(DMG)_2(SO_3)_2^{3-}$ frees it of the hydrolytic reactions of the pentaammine complex and makes it an interesting substrate for photochemical studies.[18] We have recently investigated the photochemistry of several Co(III) macrocyclic sulfito complexes. In this report we communicate our observations about the photoinduced reduction of $Co(DMG)_2(SO_3)_2^{3-}$ and its adduct with $Cu(CR)^{2+}$, {$Co(DMG)_2(SO_3)_2^{3-}$,$Cu(CR)^{2+}$}.[19]

Experimental Section

Photochemical Procedures. Steady-state photolyses were carried out with light from an Oriel, 500 W, XeHg lamp. Light from the lamp was focused with appropriate fused-silica optics into a Bausch and Lomb monochromator for the isolation of the 365 nm spectral band. An electrically operated shutter after the monochromator's exit slit allowed us to time the irradiations with errors smaller than ±0.1 s. Absolute values of the light intensity were determined with Parker's actinometer.[20] Stability of the 365 nm output was controlled at various moments of the experiment with a photocell-millivoltmeter apparatus. Solutions of $Co(DMG)_2(SO_3)_2^{3-}$ were prepared by adding appropriate weights of the solid salt to previously deaerated $HClO_4$ solutions. In photolyses of the adduct {$Co(DMG)_2(SO_3)_2^{3-}$, $Cu(CR)^{2+}$}, appropriate weights of $Co(DMG)_2(SO_3)_2^{3-}$ were added to deaerated solutions of $Cu(CR)^{2+}$ in $HClO_4$. A literature procedure was followed for the preparation of $Co(DMG)_2$ solutions.[21]

Liquids were deaerated with streams of O_2-free N_2. Apparatuses used for 354 nm flash photolysis experiments in a pico- to millisecond time domain have been described in the literature reports.[22,23] A Quanta Ray Nd:YAG laser and a Quantel mode-locked Nd:YAG laser were used for time-resolved spectroscopy and reaction kinetics times lasting longer than 10 ns and shorter than 1 ns, respectively.

Analytical Procedures. ESR spectra were recorded with a Bruker ER 080 instrument fitted with a $TE10_2$ wave bridge. Optical UV−vis spectra were recorded with a computer-interfaced Cary-219 spectrophotometer. Multicomponent analysis of spectral changes induced by steady-state photolyses was used for the determination of $Co(DMG)_2$ and $Co(DMG)_2(SO_3)H_2O^-$ concentrations.

Materials. Published procedures were followed for the preparation and purification of $[Co(DMG)_2(SO_3)_2]Na_3{\cdot}12H_2O$ and $[Cu(CR)](ClO_4)_2$.[13,24,25] The purity of the compounds was established by means of their elemental analysis and frequently verified by comparing their

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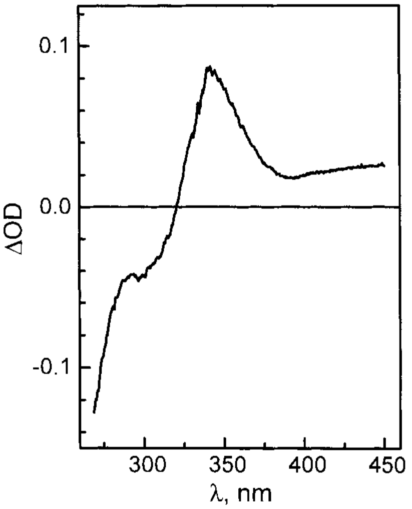

Figure 1. Difference optical spectrum of a mixed solution having 3.5 × 10^{-5} M $Co(DMG)_2(SO_3)_2^{3-}$ and 2.0 × 10^{-4} M $Cu(CR)^{2+}$ in 1.0 × 10^{-5} M $HClO_4$. Spectrum recorded against a reference having solutions of the Co and Cu compounds with analogous concentrations but separately placed in a double-compartment cell.

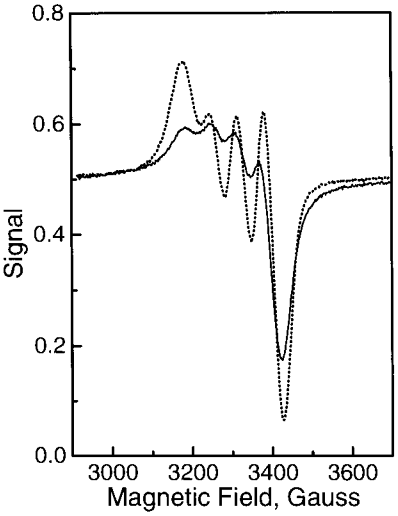

Figure 2. Typical ESR spectra in methanol of (a) $Cu(CR)^{2+}$ (dotted line) and (b) $Co(DMG)_2(SO_3)_2^{3-}$ and $Cu(CR)^{2+}$ (solid line) in a 1:1 molar relationship. Solutions were prepared with concentrations ranging from 10^{-4} to 10^{-2} M.

UV−vis spectra with those in the literature reports. Other materials were reagent grade and used without further purification.

Results

Thermal Redox Stability. The $Co(DMG)_2(SO_3)_2^{3-}$ and $Co(DMG)_2(SO_3)H_2O^-$ complexes were stable with regard to thermal redox decomposition in aerated and deaerated aqueous solutions. Also, $Co(DMG)_2(SO_3)_2^{3-}$, 10^{-4} to 10^{-5} M, was stable in deaerated solutions having between 10^{-3} and 10^{-2} M excess SO_3^{2-}. While these experimental observations were in agreement with literature reports,[13−15] the oxidation of sulfite to sulfate and the consumption of O_2 were observed with aerated solutions of $Co(DMG)_2(SO_3)_2^{3-}$, 10^{-4} to 10^{-5} M, and excess SO_3^{2-}, 10^{-3} to 10^{-2} M. In addition to the formation of SO_4^{2-}, spectral changes, e.g., the disappearance of the 325 nm absorption band in the spectrum of $Co(DMG)_2(SO_3)_2^{3-}$, are in accordance with the formation of $Co(DMG)_2(H_2O)_2^+$. The thermal oxidation of sulfite ions by $Co(DMG)_2(SO_3)_2^{3-}$ is probably initiated by a direct reaction, eq 4

$$CO(DMG)_2(SO_3)_2^{3-} + HSO_3^- + H^+ \rightleftarrows CO(DMG)_2 + 2HSO_3^- + SO_3^{\bullet -} \quad (4)$$

whose equilibrium constant, $K \approx 10^{-5}$ M^2, and experimental conditions of this work displace it considerably toward the products' side. Irreversible reactions of $Co(DMG)_2$ and $SO_3^{\bullet -}$ with O_2 already investigated in the literature reports will lead to the detected products, $Co(DMG)_2(H_2O)_2^-$ and SO_4^{2-}.[1− 5,21]

Adduct of $Co(DMG)_2(SO_3)_2^{3-}$ with $Cu(CR)^{2+}$. The $Co(DMG)_2(SO_3)_2^{3-}$ complex was also stable with respect to redox decay in 10^{-4} M $HClO_4$ containing $Cu(CR)^{2+}$ in concentrations between 10^{-4} and 10^{-2} M. The UV−vis spectrum of such solutions exhibited absorptions different of those present in the spectra of the individual Co(III) and Cu(II) constituents, Figure 1. Evidence of the formation of an adduct, i.e., ion pair or binuclear complex, between $Co(DMG)_2(SO_3)_2^{3-}$ and $Cu(CR)^{2+}$ was also provided by differences between the ESR spectra of the $Cu(CR)^{2+}$ alone and in the presence of the Co(III) complex, Figure 2. The ESR of $Cu(CR)^{2+}$ alone was characterized by $g = 2.13$ and by an hyperfine splitting, $A_{hfs} =$ 70 G, in agreement with those observed in similar macrocyclic complexes.[25,26] In aqueous or methanol solutions, the spectrum of the adduct is less intense and displaced with respect to the spectrum of $Cu(CR)^{2+}$ alone. It is possible to interpret such spectral dissimilarities by assuming that electron donation in the axial positions of free $Cu(CR)^{2+}$ and $Cu(CR)^{2+}$ in the adduct are different. Such a difference in axial donation must determine distinct interactions of the copper electronic density with nitrogen atoms of the macrocycle. Since stable pentacoordinate complexes of $Cu(CR)^{2+}$ with halides and pseudohalides have been isolated,[24] the association with a $Co(DMG)_2(SO_3)_2^{3-}$ moiety, more negatively charged than the halides or pseudohalides constitutes no exception. It can be argued, therefore, that the S-coordination of SO_3^{2-} to Co(III) leaves only a sulfito oxygen free to interact with the Cu(II) center. This adduct, either a pentacoordinate Cu(II) or an ion pair, is identified as $\{Co(DMG)_2(SO_3)_2^{3-}, Cu(CR)^{2+}\}$ in the rest of the paper.[27]

Steady-State Photolysis of $Co(DMG)_2(SO_3)_2^{3-}$ and $Co(DMG)_2$. Solutions of $Co(DMG)_2(SO_3)_2^{3-}$, concentrations between 1.5 × 10^{-4} and 7.0 × 10^{-4} M, in deaerated $HClO_4$, concentrations between 2.5 × 10^{-5} and 2.5 × 10^{-6} M, were irradiated at 365 nm, $I_0 = (6.8 \pm 0.1) \times 10^{-6}$ Einstein dm^3 s^{-1}. These concentrations ensured that 99.9% of the incident light was absorbed by $Co(DMG)_2(SO_3)_2^{3-}$ when less than 10% of its concentration was converted to products. In addition to SO_4^{2-}, UV−vis spectral changes reveal that $Co(DMG)_2(SO_3)H_2O^-$ and $Co(DMG)_2$ are the main photolysis products. Their concentrations, Figure 3, exhibit a nonlinear dependence on the length of the irradiation. The dependencies on photolyte concentration and irradiation time suggest that the departure from linearity is caused by the $Co(DMG)_2$ secondary photolysis. Indeed, $Co(DMG)_2$ exhibited considerable photoreactivity under experimental conditions similar to those described above for the 365 nm photolysis of $Co(DMG)_2(SO_3)_2^{3-}$. These irradiations produced $Co(DMG)_2(H_2O)_2^+$ with less than a 1:1 stoi-

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(27) Present experimental evidence allows no distinction between a structure with SO_3^{2-} functioning as a bridge between Co and Cu, i.e., a binuclear complex or as an ion pair. Indeed, our rough estimate of the association constant, $10^4 > K > 10^3$ M^{-1}, of $Co(DMG)_2(SO_3)_2^{3-}$ to $Cu(CR)^{2+}$ is accommodated by either structural proposition. This limiting considerations should be associated with our representation, $\{Co(DMG)_2(SO_3)_2^{3-}, Cu(CR)^{2+}\}$, of the species in solution.

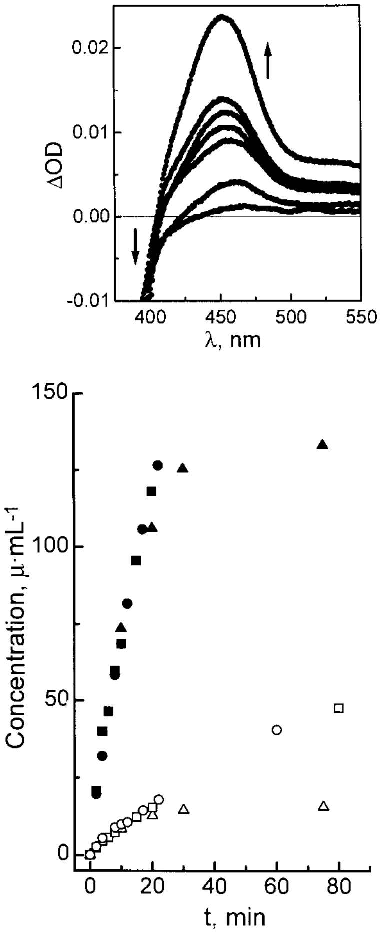

Figure 3. Concentrations of $Co(DMG)_2$, open, and $Co(DMG)_2(SO_3)(H_2O)^-$, solid, in 365 nm photolyses, $I_0 = (6.8 \pm 0.1) \times 10^{-6}$ Einstein dm^3 s^{-1}, of $Co(DMG)_2(SO_3)_2^{3-}$ in deaerated solutions. The concentrations of photolyte are as follows: ▲, 1.0×10^{-4} M; ■, 4.5×10^{-4} M; and ●, 6.9×10^{-4} M, with similar values for open symbols. The inset shows the spectral changes accompanying the 365 nm photolysis of 6.9×10^{-4} M $Co(DMG)_2(SO_3)_2^{3-}$.

chiometry expected from the consumption of $Co(DMG)_2$. The quantum yield measured for the disappearance of the Co(II) complex, $7 \times 10^{-3} \leq \phi \leq 3 \times 10^{-2}$, was dependent on the presence of some electrolytes, i.e., $CH_3CO_2^-$, $S_2O_6^{2-}$, and NO_3^- in concentrations between 10^{-2} and 10^{-3} M.[28] Thermal reactions of the primary photoproduct, $Co(DMG)_2(SO_3)H_2O^-$ with SO_3^{2-} and/or HSO_3^- decreased the rate of the aquo product formation. Quantum yields, Table 1, for the coproducts were calculated, therefore, by using their instantaneous rates

$$\lim_{t \to 0} \left[\frac{\partial \text{ concentration}}{\partial t} \right] \qquad (5)$$

extrapolated to the start of the irradiation. The same products indicated above were detected in 365 nm photolyses of a deaerated solution containing, 7.0×10^{-4} M $Co(DMG)_2(SO_3)_2^{3-}$ and 10^{-2} M $Cu(CR)^{2+}$ in 2.5×10^{-5} M $HClO_4$. Although the concentration of $Cu(CR)^{2+}$ remained unchanged through the irradiation, different quantum yields were measured for the photogeneration of $Co(DMG)_2(SO_3)H_2O^-$ and $Co(DMG)_2$, Table 1.[6]

Flash Photolysis of $Co(DMG)_2(SO_3)_2^{3-}$. Flash irradiations ($\lambda_{exc} = 354$ nm) of deaerated $Co(DMG)_2(SO_3)_2^{3-}$ (10^{-5} to 10^{-4} M) in 10^{-5} to 10^{-6} M $HClO_4$ produced a prompt growth of the $Co(DMG)_2$ spectrum ($\lambda_{max} = 460$ nm). A simultaneous bleach of the optical density between 370 and 425 nm was in agreement with a photoinduced decrease of the $Co(DMG)_2(SO_3)_2^{3-}$ concentration. Slower spectral changes detected within a period of 200 ms in solutions with a pH 5, showed the partial disappearance of $Co(DMG)_2$. No change in the rate of this process was observed in flash photochemical experiments with acidic solutions, pH 5, of $Co(DMG)_2(SO_3)_2^{3-}$ containing 10^{-3} M $S_2O_6^{2-}$.[28] No transient or stable spectral changes related to the photogeneration of O-bonded sulfito complexes were observed in a time scale, $t \geq 10$ ns.

Flash Photolysis of $\{Co(DMG)_2(SO_3)_2^{3-}, Cu(CR)^{2+}\}$. The spectrum of $Cu(CR)^+$ was recorded when 10^{-4} M $Co(DMG)_2(SO_3)_2^{3-}$ and 10^{-2} M $Cu(CR)^{2+}$ in deaerated 10^{-5} M $HClO_4$ were flash irradiated at 354 nm, Figure 4. Although the growth of the Cu(I) absorptions and the 10 ns laser pulse exhibited a partial overlap and were too slow for flash photolysis in the pico- to nanosecond time domain, the combined experimental observations show that the product must be generated with a $1 \leq \tau \leq 10$ ns lifetime. The spectrum of the $Cu(CR)^+$ decayed and shifted toward the red over several hundred ns, Figure 4. A lifetime, $\tau = 50$ ns, was measured at 650 nm for the spectral transformation. By contrast, no Cu(I) was photogenerated in the 354 nm irradiation of blanks prepared without $Co(DMG)_2(SO_3)_2^{3-}$. This is a expected result because of the small 350–360 nm extinction coefficients of $Cu(CR)^{2+}$ and small literature-reported quantum yields for irradiation at 354 or 365 nm.[29]

Discussion

The products of the 354 nm photolysis of $Co(DMG)_2(SO_3)_2^{3-}$, i.e., $Co(DMG)_2$ and SO_4^{2-}, suggest that the photoaquation of SO_3^{2-}, eq 6

$$Co(DMG)_2(SO_3)_2^{3-} + H_2O + h\nu \xrightarrow{\phi_2} Co(DMG)_2(SO_3)(H_2O)^- + HSO_3^- \qquad (6)$$

and photoreduction of the complex, eq 7

$$Co(DMG)_2(SO_3)_2^{3-} + H^- + h\nu \xrightarrow{\phi_2} Co(DMG)_2 + HSO_3^- + SO_3^{\bullet -} \qquad (7)$$

are the dominant photoprocesses.

The oxidation of $Co(DMG)_2$ by photogenerated $SO_3^{\bullet -}$ and $S_2O_6^{2-}$, eqs 8 and 9[30–33]

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[28] A half-life, $t_{1/2} > 60$ min, was estimated for the oxidation of 10^{-3} M $Co(DMG)_2$ by 10^{-3} M $S_2O_6^{2-}$ at $5 \leq pH \leq 6$. Therefore, this reaction can only have some marginal effect on the rate of product formation at the longer irradiations in our steady-state photolyses and cannot be observed in flash photolysis.

(29) Granifo, J.; Ferraudi, G.; Rillema, D. P. *J. Photochem.* **1983**, *23*, 51.

(30) The photogeneration of $SO_3^{\bullet -}$ radicals in 354 nm photolyses of several sulfite complexes, including $Co(DMG)_2(SO_3)_2^{3-}$, was confirmed by means of the ESR spectra of glassy solutions. S. C. Gibney and G. Ferraudi, work in progress.

(31) The disproportionation and dimerization reactions of $SO_3^{\bullet -}$ radicals have pH dependent rates.[32,33] The fraction of the rate of $SO_3^{\bullet -}$ decay corresponding to the dimerization has been indicated by α. A literature report established that a value, $\alpha \approx 0.3$ and $2k_1 \sim 10^9$ M^{-1} s^{-1}, must be used in our experimental conditions.[32]

(32) Eriksen, T. E. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 208

(33) Huie, R. E.; Neta, P. *J. Phys. Chem.* **1985**, *89*, 3918.

Table 1. Kinetic Data for the 365 nm Photolysis of $Co(DMG)_2(SO_3)_2^{3-}$ and $\{Co(DMG)_2(SO_3)_2^{3-}, Cu(CR)^{2+}\}$

	initial rates of		quantum yield[c]	
photolyte concentrations[a] ($M/10^{-4}$)	SO_3^{2-} aquation[b] ($M\ s^{-1}/10^{-7}$)	CO reduction[b] ($M\ s^{-1}/10^{-7}$)	ϕ_{aq}	$\phi_{Co(II)}$
$[Co(DMG)_2(SO_3)_2^{3-}] = 1.6$	0.98	0.12	0.014	0.0017
$[Co(DMG)_2(SO_3)_2^{3-}] = 4.5$	1.0	0.14	0.014	0.0020
$[Co(DMG)_2(SO_3)_2^{3-}] = 6.9$	1.1	0.14	0.15	0.0021
$[\{Co(DMG)_2(SO_3)_2^{3-}, Cu(CR)^{2+}\}] = 5.5$	1.1	0.62	0.016	0.0089

[a] All these measurements were carried out with deaerated acidic (3.0×10^{-6} M $HClO_4$) solutions. [b] Rates of $Co(DMG)_2(SO_3)(H_2O)^-$ and $Co(DMG)_2$ photoproduction under 365 nm photolysis, $I_0 = (6.8 \pm 0.1) \times 10^{-6}$ Einstein $dm^3\ s^{-1}$. [c] Quantum yield resulting from the initial rates of $Co(DMG)_2(SO_3)(H_2O)^-$ and $Co(DMG)_2$ photoproduction. Errors are equal to or less than 10%.

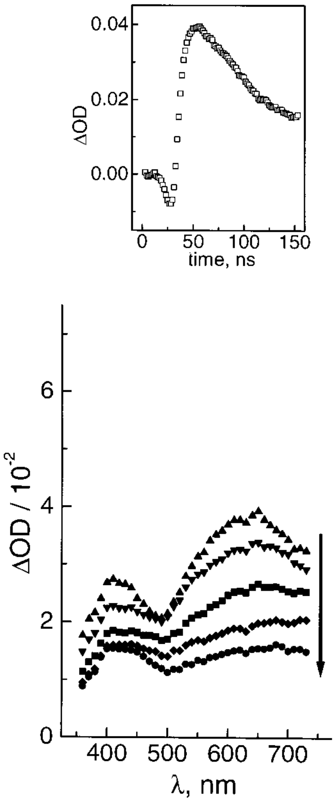

Figure 4. Transient spectra recorded in 354 nm photolysis of the $\{Co(DMG)_2(SO_3)_2^{3-}, Cu(CR)^{2+}\}$ adduct. Deaerated solutions of 1.5×10^{-4} M $Co(DMG)_2(SO_3)_2^{3-}$ and 1.0×10^{-2} M $Cu(CR)^{2+}$ in 1.0×10^{-4} M $HClO_4$ were used for these irradiations. Spectra recorded with 39, 70, 95, 130, and 175 ns delays from the 10 ns laser flash. The inset shows a typical trace for the growth and decay of the 640 nm optical density associated with $Cu(CR)^+$.

$$2SO_3^{\bullet -} \xrightarrow{k_1\alpha} S_2O_6^{2-}, \alpha \approx 0.3 \tag{8}$$

$$2SO_3^{\bullet -} + H_2O \xrightarrow{k_1(1-\alpha)} HSO_3^- + H^+ + SO_4^{2-} \tag{9}$$

can be ignored. Indeed the reaction with to $SO_3^{\bullet -}$, not observed in our flash photolysis experiments, must be too slow to compete with the disproportionation and dimerization of the radical, eqs 8 and 9. The oxidation of $Co(DMG)_2$ by $S_2O_6^{2-}$ can only make a negligible contribution to the rate of Co(II) photogeneration at the longer times of our steady-state photolyses, $t \geq 60$ min in Figure 3.

To rationalize the experimental observations, the 365 and 354 nm photolysis mechanism must also incorporate eq 10

$$Co(DMG)_2SO_3(H_2O)^- + HSO_3^- \xrightarrow{k_3} Co(DMG)_2(SO_3)_2^{3-} + H^+ \tag{10}$$

in addition to the reactions already discussed, eqs 6−9. The mechanism of the $Co(DMG)_2(SO_3)(H_2O)^-$ anation by HSO_3^-, eq 10, and by other ligands has been reported elsewhere in the literature.[13−15] The rate constants for such a process result in anation lifetimes of 7.5×10^2 s under the conditions of our photochemical experiments. Therefore, the anation of $Co(DMG)_2(SO_3)(H_2O)^-$ by photogenerated SO_3^{2-} will depress the rate of this Co(III) product formation when 365 nm steady-state photolyses span times longer than 10 min. To obtain kinetic information from the experimental results, rate law equations were written for all the species in the mechanism, eqs 6−10. The assumption of a stationary concentration in steady-state photolysis was applied to $SO_3^{\bullet -}$. On this basis, the ratio of the rates for the formation of $Co(DMG)_2(SO_3)(H_2O)^-$ and $Co(DMG)_2$ is

$$\frac{\partial[Co(DMG)_2(SO_3)(H_2O)^-]/\partial t}{\partial[Co(DMG)_2]/\partial t} = \{(\phi_1 + 0.54\phi_2)(1 - 0.56[\phi_1 + 1.23\phi_2]t^2 I_{ab})\}/0.26\phi_2 \tag{11}$$

Equation 11 accounts for the dependence of $\{\partial[Co(DMG)_2(SO_3)(H_2O)^-]/\partial t\}/\{\partial[Co(DMG)_2]/\partial t\}$ on the irradiation time and the intensity of absorbed light, I_{ab}. For short irradiation times, the rates relationship becomes independent of I_{ab} and t. A ratio $\phi_1/\phi_2 = 3.0 \pm 0.1$ was calculated from eq 11 and the limiting rates, eq 5 and Table 1. Also, a quantum yield, $\phi_2 = (2.6 \pm 0.1) \times 10^{-3}$ for the photoredox process, eq 11, was calculated from the limiting rate of $Co(DMG)_2$, eq 12.

$$\lim_{t \to 0}\left[\frac{\partial[Co(DMG)_2]}{\partial t}\right] = 2\phi_2 \frac{(1-\alpha)}{(2-\alpha)} I_{ab} \tag{12}$$

The quantum yield for the photoaquation process, $\phi_1 \approx 7.8 \times 10^{-3}$, is comparable to those reported for various Co(III) complexes.[34,35] Moreover, differences between ϕ_1 and those reported for the aquation process in Table 1 suggests an efficient secondary photolysis of $Co(DMG)_2$.

The photochemical behavior of $Co(DMG)_2(SO_3)_2^{3-}$ can now be compared with that of the adduct between $Cu(CR)^{2+}$ and $Co(DMG)_2(SO_3)_2^{3-}$. Flash photolysis ($\lambda_{exc} = 354$ nm) of $\{Co(DMG)_2(SO_3)_2^{3-}, Cu(CR)^{2+}\}$ generates $Cu(CR)^+$ with a lifetime $1 \leq \tau \leq 10$ ns. The formation of the Cu(I) product is, therefore, too slow to be adscribed to a primary photochemical process of the $Cu(CR)^{2+}$ in the adduct. Also, the formation of $Cu(CR)^+$ is too fast for a bimolecular reaction between $SO_3^{\bullet -}$ and $Cu(CR)^{2+}$ with a diffusion-controlled rate. It is possible that the radical remains either coordinated or ion-paired after the primary photoreduction of $Co(DMG)_2(SO_3)_2^{3-}$, eq 13

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(34) Ferraudi, G. In *Elements of Inorganic Photochemistry*; Wiley-Interscience: New York, 1987; Chapter 5.

(35) Horváth, O.; Stevenson, K. L. In *Charge Transfer Photochemistry of Coordination Compounds*; VCH: New York, 1993; Chapter 12.

$$\{Co(DMG)_2(SO_3)_2{}^{3-}, Cu(CR)^{2+}\} + H^+ + h\nu \xrightarrow{\phi_3} Co(DMG)_2 + HSO_3{}^- + \{SO_3{}^{\bullet -}, Cu(CR)^{2+}\} \quad (13)$$

in the same manner that $Cu(CR)^{2+}$ is known to associate with halides.[25] In this proposition, the appearance of the Cu(I) product with a lifetime $1 \leq \tau \leq 10$ ns can be related to the reduction of $Cu(CR)^{2+}$ in an ion pair or pentacoordinated species, eq 14.

$$\{SO_3{}^{\bullet -}, Cu(CR)^{2+}\} \xrightarrow{t \leq 10\ \mathrm{ns}} \{SO_4{}^{2-}, Cu(CR)^+\} \quad (14)$$

The correlation of the spectral changes with a 50 ns lifetime in Figure 4 and eqs 15 and 16

$$\{SO_4{}^{2-}, Cu(CR)^+\} \rightleftarrows SO_4{}^{2-} + Cu(CR)^+ \quad (15)$$

$$\{Co(DMG)_2(SO_3)_2{}^{3-}, Cu(CR)^{2+}\} + 2H^+ + Cu(CR)^+ \rightarrow Co(DMG)_2 + 2HSO_3{}^- + 2Cu(CR)^{2+} \quad (16)$$

is consistent with equilibrium constants of ion pairs in literature reports. Indeed, if one assumes that the association of $SO_4{}^{2-}$ and $Cu(CR)^+$ has a diffusion-controlled rate, the relaxation of the equilibrium, eq 15, will occur with a lifetime of several tens of nanoseconds. A similar process, previously observed when perchlorate ions dissociate from $\{Cu(TIM)^+, ClO_4{}^-\}$, can be regarded as a precedent for this experimental observation. Moreover, self-exchange rate constants and redox potentials of the Co(III/II) and Cu(II/I) couples in eq 16 suggest that it must also proceed with a near diffusion-controlled rate, i.e., $k_{16} \approx 10^9$ M^{-1} s^{-1}, and be difficult to differentiate kinetically from the equilibrium relaxation, eq 15. These final considerations lead to the conclusion that the observed increase in the quantum yield for the photogeneration of $Co(DMG)_2$ in the adduct may have two sources, a quantum yield ϕ_3, eq 13, larger than ϕ_2, eq 7, and to reactions, eqs 15 and 16, which make the quantum yield of $Co(DMG)_2$ twice the value of the primary quantum yield ϕ_3. In addition, absorptions at 350 nm in the spectrum of the adduct, Figure 1, can be assigned to charge transfer excited states involving Cu(II). Such excited states must be photochemically inactive and their conversion to Co(III) charge transfer excited states must be faster than their dissociation into redox products. Otherwise, the formation of Cu(I) products will be much faster than that observed in our experiments.

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