

Ultraviolet Photochemistry of $\text{Co}^{\text{III}}\text{L}(\text{H}_2\text{O})\text{SO}_3^+$ [$\text{L} = \text{Me}_6[14]\text{dieneN}_4, [14]\text{aneN}_4$] Complexes. Quandaries about the Linkage Isomerization to O-Bonded Sulfite and the Photogeneration of Cobalt(I) in Sequential Biphotonic Photolysis

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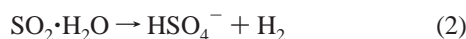
Two new macrocyclic complexes with S-bonded sulfite, $\text{Co}(\text{Me}_6[14]\text{diene N}_4)(\text{H}_2\text{O})\text{SO}_3^+$ and $\text{Co}([14]\text{ane N}_4)(\text{H}_2\text{O})\text{SO}_3^+$, were prepared. The type of the SO_3^{2-} linkage in $[\text{Co}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})\text{SO}_3]\text{ClO}_4$ was established by means of the X-ray structure (crystal system, orthorhombic; space group, $P2_12_12_1$ (No. 19); $a = 7.0342(8)$ Å, $b = 14.696(2)$ Å, $c = 23.302(5)$ Å). In a study of the photochemical properties, transient spectra revealed the photoredox formation of Co(II) macrocycles and the photoisomerization to O-bonded sulfite. Precursors of these products were also observed and tentatively identified as an ion pair ($\tau = 60$ and 140 ns, respectively) and an adduct of the $\text{SO}_3^{\cdot-}$ radical and the unsaturated macrocycle $\text{Me}_6[14]\text{diene N}_4$ ($\tau = 2.5$ μs). The photogeneration of $\text{SO}_3^{\cdot-}$ was verified by means of the radical's ESR spectrum. High power laser irradiations resulted in the secondary photolysis of the intermediates and the formation of Co(I) products. The mechanism of the primary and secondary photolysis is discussed.

Introduction

The catalyzed and uncatalyzed oxidation of sulfite, eq 1,



have been a matter of continued interest.^{1–6} Attention to these processes has a basic science motive as well as the need to resolve a number of long-recognized technical problems, i.e., gas desulfurization, pollution, and health problems.^{7–9} In addressing some of the practical motives of the S(IV) oxidation, it is possible to combine the desulfurization process with the production of a convenient fuel.^{1,10} The reactions



illustrate some endoenergetic processes where the catalyst must

be capable of absorbing photochemically supplied energy in addition to increase the overall reaction rate. The sulfite complexes of Co(III) may be interesting materials from the standpoint of their applications to the thermal and photochemical oxidation of sulfite. If solar light is required for the sulfite photooxidation, these catalysts must be photoactive at longer wavelengths than 350 nm. Fast anation of the corresponding aquo Co(III) complexes with SO_3^{2-} and HSO_3^- to regenerate the catalyst will be an important requirement. Moreover, some Co(II) macrocyclic complexes are photoactive, e.g., the dimethylglyoximate, DMG^- , complex, and yield Co(I) products while the integrity of the macrocyclic or pseudomacrocyclic ligand is preserved.^{11–13} It must be noted that such Co(I) macrocycles have been used as catalysts for the reduction of CO_2 and in the production of H_2 .^{14,15} These properties suggest that Co(III) complexes of various macrocyclic ligands may fulfill the requirements for a catalyst or photocatalyst in the oxidations of aqueous S(IV). Despite the considerable progress made on our knowledge of the photochemistry of Co(III) complexes,^{16,17} little is known about the photochemical details of the Co(III) sulfite complexes.^{18–20} Linkage photoisomerization to O-bonded sulfite was observed in the photolysis of $\text{Co}(\text{en})_2(\text{SO}_2\text{CH}_2\text{CH}_2-$

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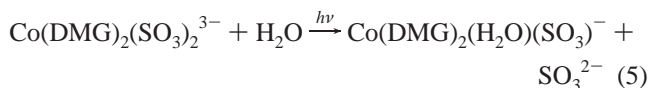
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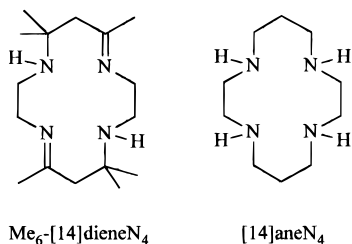
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$\text{NH}_2)^{2+}$ and considered a process initiated in the $\text{S}(\sigma) \rightarrow \text{Co}(\sigma^*)$ charge transfer state, i.e., $\text{LMCT}_{\text{S}(\sigma) \rightarrow \text{Co}(\sigma^*)}$. By contrast, sulfite hydrolysis and oxidation, eqs 4 and 5,¹ were observed in the charge-transfer photochemistry of $\text{Co}(\text{DMG})_2(\text{SO}_3)_2^{3-}$, $\text{DMG}^- = \text{dimethylglyoximate}$.



We have recently investigated the photochemistry of several $\text{Co}(\text{III})$ macrocyclic sulfite complexes. In this report we communicate our observations about the photoinduced reduction and linkage isomerization of $\text{CoL}(\text{H}_2\text{O})(\text{SO}_3)^+$ ($\text{L} = \text{Me}_6[14]\text{dieneN}_4$, $[14]\text{aneN}_4$).



Experimental Section

Materials. Published procedures were followed for the preparation and purification of $\text{CoSO}_3 \cdot 5\text{H}_2\text{O}$,²¹ $[\text{Co}^{\text{II}}(\text{Me}_6[14]\text{dieneN}_4)](\text{ClO}_4)_2$,²² $\text{Me}_6[14]\text{dieneN}_4 \cdot 2\text{HClO}_4$, and $[14]\text{aneN}_4 \cdot 4\text{HClO}_4$.²³ (**Warning!** *The perchlorate salts used in this study are explosive and potentially hazardous.*)

$[\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})(\text{SO}_3)]\text{ClO}_4$. The compound was prepared by an adaptation of the synthesis of $\text{Na}_3[\text{Co}(\text{dimethylglyoximate})_2(\text{SO}_3)_2] \cdot 12\text{H}_2\text{O}$.^{1,24,25} A suspension of 27.09 g (0.0562 mol) of $\text{Me}_6[14]\text{dieneN}_4 \cdot 2\text{HClO}_4$ in 400 cm^3 of a 1:1 (by volume) solution of methanol in water was deaerated for 25 min with Ar in a 500 cm^3 Erlenmeyer flask. This mixture was heated on a steam bath ($\sim 65^\circ\text{C}$) while $\text{CoSO}_3 \cdot 5\text{H}_2\text{O}$ (9.27 g, 0.05 mol) was added to it. The pink suspension, kept overnight at 65°C and under Ar, turned green, and a yellow solid formed in the bottom of the flask. Addition of 14.9 g (0.115 mol) of Na_2SO_3 and bubbling O_2 , instead of Ar, through the mixture caused the liquid to turn orange and the transitory formation of a green solid. The green precipitate dissolved after 2 h and the solution turned red-orange. Any remaining solid was filtered out by suction over a glass frit after the solution reached room temperature. An orange solid was precipitated by reducing the volume of liquid on a rotary evaporator at 35°C . Dark brown needle-shaped crystals about 2–3 mm long were obtained when, instead of the rotary evaporator, the solvent was slowly evaporated at room temperature. The compound was purified by recrystallization from hot methanol. Yield 7.3 g (27%). Anal. Calcd for $[\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})(\text{SO}_3)]\text{ClO}_4$: C, 35.78; H, 6.39; N, 10.44; S, 5.97. Found: C, 35.80; H, 6.42; N, 10.32; S, 6.04.

$[\text{Co}^{\text{III}}([14]\text{aneN}_4)(\text{H}_2\text{O})(\text{SO}_3)]\text{ClO}_4$. A solution containing 4.65 g (7.77×10^{-3} mol) of $[14]\text{aneN}_4 \cdot 4\text{HClO}_4$ in 100 cm^3 of a 1:1 (by volume) methanol–water mixture was deaerated for about 30 min with a stream of Ar while it was heated on a steam bath ($\sim 65^\circ\text{C}$). The

addition of 1.44 g (7.77×10^{-3} mol) of freshly prepared $\text{CoSO}_3 \cdot 5\text{H}_2\text{O}$ under a blanket of Ar resulted in a solution that turned red over an 18 h period. Evaporation caused a nearly 50% reduction of the volume but no precipitation was observed at this point of the preparation. Additions of 2.25 g (0.0179 mol) of Na_2SO_3 and 1:1 methanol–water until a total volume of 180 cm^3 were made before bubbling O_2 during 1 h. The liquid phase was transferred to a 500 cm^3 Erlenmeyer flask while the solid phase was partially dissolved in 150 cm^3 of water, filtered and any remaining solid discarded. The two liquid fractions were mixed together, placed on a steam bath, and bubbled with O_2 for an additional 2 h. Vacuum evaporation of the solvent in a rotary evaporator at 50°C leads to a brown crystalline product. This solid was filtrated and dissolved in the minimum amount of hot 2:1 methanol–water, and any remaining solid was filtered off. A pure compound was obtained by reducing the volume in a rotary evaporator at 35°C until precipitation of a solid. The filtered solid was dried under vacuum. Yield 0.65 g (18%). Anal. Calcd for $[\text{Co}^{\text{III}}([14]\text{aneN}_4)(\text{H}_2\text{O})(\text{SO}_3)]\text{ClO}_4$: C, 26.29; H, 5.75; N, 12.27; S, 7.02. Found: C, 26.33; H, 5.78; N, 12.18; S, 7.08.

Other materials used were of reagent grade and required no further purification.

Determination of the Crystal Structure. Crystals of $[\text{Co}(\text{Me}_6[14]\text{dieneN}_4)(\text{SO}_3)(\text{OH}_2)](\text{ClO}_4) \cdot \text{H}_2\text{O}$ were grown by the liquid diffusion method A saturated aqueous solution of the complex was placed in a test tube and layered with *tert*-butyl alcohol. The test tube was sealed with a cork and placed in a dark cupboard for approximately one week. The orange platelike crystal used had approximate dimensions of $0.48 \times 0.22 \times 0.05$ mm and was mounted on a glass fiber in a random orientation. Measurements, structure solution and data refinement were carried out at the Notre Dame X-ray Crystallographic Facility. Crystallographic parameters are shown in Table 1.

Structure Solution and Refinement. Structure solution and refinement were performed on a PC by using the SHELXTL package.^{26,27} Most of the nonhydrogen atoms were found in succeeding difference Fourier synthesis. Least-squares refinement was carried out on F^2 for all reflections. After all nonhydrogen atoms were refined anisotropically, except for the two hydrogen atoms of the solvent water molecule, difference Fourier synthesis located all hydrogen atoms. In the final refinement, alkyl hydrogen atoms were refined with riding models, while those of the amine and water ligands were refined isotropically with bond restraints. All reflections, including those with negative intensities, were included in the refinement and the $I > 2\sigma(I)$ criterion was used only for calculating R1. The refinement converged to a final value of $R1 = 0.0410$ and $wR2 = 0.1007$ for observed unique reflections ($I > 2\sigma(I)$) and $R1 = 0.0496$ and $wR2 = 0.1134$ for all unique reflections including those with negative intensities. The weighted R factors, wR , are based on F^2 and conventional R factors, R , on F , with F set to zero for negative intensities. The maximum and minimum residual electron densities on the final differences Fourier map were 0.436 and $-0.397 \text{ e}/\text{\AA}^3$, respectively, and the first 9 peaks were all around the metal atoms. The full covariance matrix was used for all esd's. The cell esd's were included in the estimation of bond distances and angles.

The correctness of the chirality of this structure was confirmed by a near zero Flack absolute structure parameter, 0.09(2).²⁸ Refinement on its enantiomorph yielded a detrimentally high value of 0.90(3) for the Flack parameter and higher values of 0.0498, 0.1251, 0.0587, and 0.1363 for the above four corresponding convergence factors.

Photochemical and Radiolytic Procedures. Continuous photolyses were carried out with light from a 500 W Oriol Xe–Hg lamp. Light from the lamp was focused with appropriate fused-silica optics into a Bausch & Lomb monochromator for the isolation of appropriate spectral

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Table 1. Crystal Data and Structure Refinement of $[\text{Co}(\text{Me}_6[14]\text{dieneN}_4)(\text{SO}_3)(\text{OH}_2)](\text{ClO}_4) \cdot \text{H}_2\text{O}$

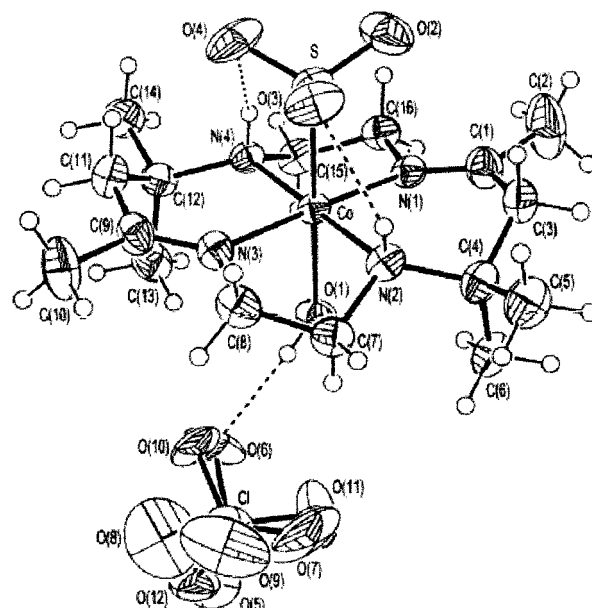
empirical formula	$\text{C}_{16}\text{H}_{36}\text{ClCoN}_4\text{O}_9\text{S}$
fw	554.93
cryst syst	orthorhombic
space group	$P2_12_12_1$ (No. 19)
unit cell dimensions	$a = 7.0342(8) \text{ \AA}$ $b = 14.696(2) \text{ \AA}$ $c = 23.302(3) \text{ \AA}$
volume	$2408.8(5) \text{ \AA}^3$
Z	4
density (calculated)	1.530 Mg/m^3
$F(000)$	1168
wavelength	0.71073 \AA
absorption coefficient	0.963 mm^{-1}
cryst size	$0.48 \times 0.22 \times 0.05 \text{ mm}$
temperature	$293(2) \text{ K}$
diffractometer	Enraf-Nonius CAD4
θ range for data collection	2.23 to 24.99°
index ranges	$0 \leq h \leq 8, 0 \leq k \leq 17, -27 \leq l \leq 27$
scan method	$\omega/2\theta$
scan rate	1.27 – $8.24^\circ/\text{min}$ (in ω)
scan width	$0.70^\circ + 0.35^\circ \tan \theta$ (in ω)
total data collected	4774
unique data	4239 [$R(\text{int}) = 0.0253$]
unique observed data [$I > 2\sigma(I)$]	3817
absorption correction	semi-empirical from ψ scans ²⁶
max and min transmission	1.0000 and 0.9295
refinement method	full-matrix on F^2 (SHELXL-93)
weighting scheme	sigma weight
data/restraints/parameters	4236/25/345
goodness-of-fit on F^2	1.126
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0410^a$ $wR2 = 0.1007^b$
R indices (all data)	$R1 = 0.0496$ $wR2 = 0.1134$
absolute structure parameter	$0.09(2)$
largest diff. peak and hole	0.436 and $-0.397 \text{ e \AA}^{-3}$

^a $R1 = \sum |F_o - F_c| / \sum F_o$. ^b $R2 = (\sum w(F_o - F_c)^2 / \sum wF_o^2)^{1/2}$, $w = 1/\sigma^2(F_o)$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (0.02)^2 F_o^2] / \text{Lp}^2$, where S = scan rate, C = total integrated peak count, B = total background, and Lp = Lorentz-polarization factor.

lines. Also various Rayonet lamps were used as sources of 254, 300, or 350 nm light was. An electrically activated shutter, placed before the reaction cell, allowed us to time the irradiations with errors smaller than ± 0.1 s. Absolute values of the light intensity were determined with Parker's actinometer²⁹ or $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$.³⁰ The intensity of the light was investigated at various moments of the experiment with a photocell-millivoltmeter apparatus.

An apparatus used for 351 and 248 nm flash photolysis experiments in a ns to ms time domain has been described in the literature reports.^{31,32} An excimer laser, Lambda Physik LPX 200, was used for time-resolved spectroscopy and reaction kinetics longer than 10 ns. In double flash irradiations, a Continuum Powerlite Nd:YAG laser was synchronized to the firing of the excimer laser. A fixed delay of the 355 nm flash from the YAG laser with respect to the 248 nm flash of the excimer laser was preadjusted to values equal to or longer than $1 \mu\text{s}$. The flash intensity was measured by an actinometric procedure described elsewhere.^{30,32} In this procedure, acid solutions of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ in 10^{-2} M Br^- are irradiated at wavelengths shorter than 380 nm and the photogenerated concentrations of Br_2^- are used for the calculation of the light intensity.

The apparatus used for pulse radiolysis and the procedures followed for the anaerobic handling of the solutions have been described elsewhere.³²

**Figure 1.** Molecular structure of $[\text{Co}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})\text{SO}_3]\text{ClO}_4$ showing the atom number scheme. Thermal ellipsoids are drawn at a 50% probability level.

Solutions of Co(III) complexes for the photochemical and pulse radiochemical experiments were prepared by adding appropriate weights of the solid salt to previously deaerated solutions of HClO_4 . Liquids were deaerated with streams of O_2 -free N_2 .

Analytical Procedures. ESR spectra were recorded with a Bruker ER 080 spectrometer fitted with a TE102 waveguide. UV-vis spectra were recorded with a computer-interfaced Cary-219 spectrophotometer. Multicomponent analysis of spectral changes induced by continuous photolyses was used for the determination of $\text{Co}^{\text{II}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{2+}$ and $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{3+}$ concentrations. The extinction coefficients used in these work were measured with the prepared compounds under the medium conditions of the experiments. The modified Kitson procedure was used for the investigation of $\text{Co}(\text{H}_2\text{O})_6^{2+}$.³³ IR spectra were recorded with a Bio-Rad FTS 175 spectrometer.

Results

Characterization and Properties of the Macrocyclic Complexes. The Co(III) sulfite complexes of [14]ane N_4 and $\text{Me}_6[14]\text{dieneN}_4$ were assigned as monosulfite complexes on the basis of their respective elemental analyses. In addition, the X-ray crystallographic structure of the $\text{Me}_6[14]\text{dieneN}_4$ complex showed that the sulfite was coordinated through the sulfur atom to Co(III), Figure 1 and Tables 1–3. It was also evident from this structure that two oxygen atoms of the sulfite were hydrogen-bonded to protons located in the amino groups of the macrocycle. A splitting of the S–O stretching mode at 1010 cm^{-1} was observed in the IR spectra of the complexes. While a splitting of the S–O stretching is commonly associated with an O-bonded sulfite,^{25,33} it must be related here to these intrinsic interactions of the sulfite oxygens with surrounding atoms.

In deaerated or aerated acidic solutions, i.e., in solutions with 10^{-5} to 10^{-1} M HClO_4 , these Co(III) complexes were inert. Less than 10% conversion to $\text{Co}^{\text{III}}\text{L}(\text{H}_2\text{O})_2^{3+}$ ($\text{L} = \text{cyclam}$, $\text{Me}_6[14]\text{dieneN}_4$) was observed over 24 h.³⁴ Such inertness with regard to hydrolysis in acid media is in accordance with S-bonded complexes.^{35–37}

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Table 2. Bond Lengths (Å) for $[\text{Co}(\text{Me}_6[14]\text{dieneN}_4)(\text{OH}_2)(\text{SO}_3)]-(\text{ClO}_4)(\text{H}_2\text{O})$

Co-N(1)	1.921(3)	C(5)-H(5c)	0.96
Co-N(3)	1.936(4)	C(6)-H(6A)	0.96
Co-N(4)	1.976(4)	C(6)-H(6B)	0.96
Co-N(2)	1.9.84(4)	C(6)-H(6C)	0.96
Co-O(1)	2.044(3)	C(7)-C(8)	1.500(7)
Co-S	2.2305(11)	C(7)-H(7A)	0.97
O(1)-H(01)	0.85(4)	C(7)-H(7B)	0.97
O(1)-H(02)	0.87(5)	C(8)-H(8A)	0.97
S-O(3)	1.449(4)	C(8)-H(8B)	0.97
S-O(2)	1.454(4)	C(9)-C(10)	1.495(7)
S-O(4)	1.461(4)	C(9)-C(11)	1.506(7)
N(1)-C(1)	1.266(6)	C(10)-H(10A)	0.96
N(1)-C(16)	1.475(5)	C(10)-H(10B)	0.96
N(2)-C(7)	1.485(6)	C(10)-H(10C)	0.96
N(2)-C(4)	1.496(6)	C(11)-C(12)	1.523(7)
N(2)-H(2)	0.79(4)	C(11)-H(11A)	0.97
N(3)-C(9)	1.279(6)	C(11)-H(11B)	0.97
N(3)-C(8)	1.483(6)	C(12)-C(13)	1.525(7)
N(4)-C(15)	1.473(5)	C(12)-C(14)	1.529(6)
N(4)-C(12)	1.506(6)	C(13)-H(13A)	0.96
N(4)-H(4)	0.75(4)	C(13)-H(13B)	0.96
C(1)-C(2)	1.492(8)	C(13)-H(13C)	0.96
C(1)-C(3)	1.505(7)	C(14)-H(14A)	0.96
C(2)-H(2A)	0.96	C(14)-H(14B)	0.96
C(2)-H(2B)	0.96	C(14)-H(14C)	0.96
C(2)-H(2C)	0.96	C(15)-C(16)	1.492(6)
C(3)-C(4)	1.526(7)	C(15)-H(15A)	0.97
C(3)-H(3A)	0.97	C(15)-H(15B)	0.97
C(3)-H(3B)	0.97	C(16)-H(16A)	0.97
C(4)-C(6)	1.518(7)	C(16)-H(16B)	0.97
C(4)-C(5)	1.530(6)	Cl-O(7)	1.300(13)
C(5)-H(5A)	0.96	Cl-O(10)	1.368(12)
C(5)-H(5B)	0.96	Cl-O(12)	1.370(12)
Cl-O(8)	1.40(2)	Cl-O(5)	1.424(14)
Cl-O(9)	1.402(14)	Cl-O(11)	1.450
Cl-O(6)	1.405(11)		

Time-Resolved Spectroscopy and Kinetics of Photo-reactions. Flash photolysis, λ_{exc} 248 or 350 nm, of $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})\text{SO}_3^+$ in acidic, pH 1.03 or 5.62, de-aerated solutions increased the optical density between 300 and 500 nm within the 20 ns irradiation, Figure 2. The transient spectra was dependent on the solutions pH as it is shown in the top and bottom parts of Figure 2. Further spectral changes were observed following the irradiation. Two successive processes causing a partial decrease of the photochemically generated 340 nm optical density were observed, i.e., one with a lifetime $\tau = 60$ ns and the other with a lifetime $\tau = 2.5 \mu\text{s}$. The rate of these two processes exhibited little if any dependences on transient species and acid concentrations between pH 5 and 1. By contrast, the lifetime for decay of the long-lived component of the optical density near 420 nm varied from tens of μs to ms as a function of the pH, Figure 3 and inset, but was independent of the concentration of the photogenerated species. Least-squares curve fitting of exponential decays to the oscillographic traces recorded at 420 nm confirmed that the rate law was first order in transient concentration. In addition, the plot of the rate constant on acid concentration, measured between pH 5 and 1, resembles a titration curve, inset to Figure 3. The dependence

Table 3. Bond Angles (deg) for $[\text{Co}(\text{Me}_6[14]\text{dieneN}_4)(\text{OH}_2)(\text{SO}_3)]-(\text{ClO}_4)(\text{H}_2\text{O})$

N(1)-Co-N(3)	178.4(2)	C(9)-N(3)-C(8)	118.2(4)
N(1)-Co-N(4)	86.2(2)	C(9)-N(3)-Co	128.9(3)
N(3)-Co-N(4)	94.18(14)	C(8)-N(3)-Co	112.7(3)
N(1)-Co-N(2)	94.3(2)	C(15)-N(4)-C(12)	115.2(3)
N(3)-Co-N(2)	85.4(2)	C(15)-N(4)-Co	106.9(3)
N(4)-Co-N(2)	179.2(2)	C(12)-N(4)-Cl	122.0(3)
N(1)-Co-O(1)	88.82(14)	C(15)-N(4)-H(4)	102(3)
N(3)-Co-O(1)	89.64(14)	C(12)-N(4)-H(4)	107(3)
N(4)-Co-O(1)	89.60(14)	Co-N(4)-H(4)	101(3)
N(2)-Co-O(1)	91.0(2)	N(1)-C(1)-C(2)	123.0(5)
N(1)-Co-S	90.41(11)	N(1)-C(1)-C(3)	122.2(4)
N(3)-Co-S	91.13(11)	C(2)-C(1)-C(3)	114.7(5)
N(4)-Co-S	89.50(11)	C(1)-C(2)-H(2A)	109.5(3)
N(2)-Co-S	89.89(12)	C(1)-C(2)-H(2B)	109.5(4)
O(1)-Co-S	178.85(10)	H(2A)-C(2)-H(2B)	109.5
Co-O(1)-H(01)	120(3)	C(1)-C(2)-H(2C)	109.5(4)
Co-O(1)-H(02)	128(4)	H(2A)-C(2)-H(2C)	109.5
H(01)-O(1)-H(02)	110(4)	H(2B)-C(2)-H(2C)	109.5
O(3)-S-O(2)	111.1(3)	C(1)-C(3)-C(4)	119.0(4)
O(3)-S-O(4)	112.7(2)	C(1)-C(3)-H(3A)	107.6(3)
O(2)-S-O(4)	108.6(3)	C(4)-C(3)-H(3A)	107.6(3)
O(3)-S-Co	106.7(2)	C(1)-C(3)-H(3B)	107.6(3)
O(2)-S-Co	110.3(2)	C(4)-C(3)-H(3B)	107.6(2)
O(4)-S-Co	107.4(2)	H(3A)-C(3)-H(3B)	107.0
C(1)-N(1)-C(16)	119.0(4)	N(2)-C(4)-C(6)	112.8(4)
C(1)-N(1)-Co	128.6(3)	N(2)-C(4)-C(3)	107.6(4)
C(16)-N(1)-Co	111.5(3)	C(6)-C(4)-C(3)	110.5(4)
C(7)-N(2)-C(4)	115.4(4)	N(2)-C(4)-C(5)	108.3(4)
C(7)-N(2)-Co	105.4(3)	C(6)-C(4)-C(5)	109.7(4)
C(4)-N(2)-Co	121.6(3)	C(3)-C(4)-C(5)	107.7(4)
C(7)-N(2)-H(2)	105(4)	C(4)-C(5)-H(5A)	109.5(3)
C(4)-N(2)-H(2)	105(3)	C(4)-C(5)-H(5B)	109.5(3)
Co-N(2)-H(2)	102(3)	H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5(3)	C(9)-C(11)-H(11B)	107.6(3)
H(5A)-C(5)-H(5C)	109.5	C(12)-C(11)-H(11B)	107.6(2)
H(5B)-C(5)-H(5C)	109.5	H(11A)-C(11)-H(11B)	107.0
C(4)-C(6)-H(6A)	109.5(3)	N(4)-C(12)-C(11)	108.2(4)
C(4)-C(6)-H(6B)	109.5(3)	N(4)-C(12)-C(13)	112.6(4)
H(6A)-C(6)-H(6B)	109.5	C(11)-C(12)-C(13)	110.3(4)
C(4)-C(6)-H(6C)	109.5(2)	N(4)-C(12)-C(14)	109.1(4)
H(6A)-C(6)-H(6C)	109.5	C(11)-C(12)-C(14)	107.4(4)
H(6B)-C(6)-H(6C)	109.5	C(13)-C(12)-C(14)	109.0(4)
N(2)-C(7)-C(8)	109.0(4)	C(12)-C(13)-H(13A)	109.5(3)
N(2)-C(7)-H(7A)	109.9(2)	C(12)-C(13)-H(13B)	109.5(3)
C(8)-C(7)-H(7A)	109.9(2)	C(13A)-C(13)-H(13B)	109.5
N(2)-C(7)-H(7B)	109.9(2)	C(12)-C(13)-H(13C)	109.5(2)
C(8)-C(7)-H(7B)	109.9(3)	H(13A)-C(13)-H(13C)	109.5
H(7A)-C(7)-H(7B)	108.3	H(13B)-C(13)-H(13C)	109.5
N(3)-C(8)-C(7)	108.1(4)	C(12)-C(14)-H(14A)	109.5(3)
N(3)-C(8)-H(8A)	110.1(2)	C(12)-C(14)-H(14B)	109.5(3)
C(7)-C(8)-H(8A)	110.1(2)	H(14A)-C(14)-H(14B)	109.5
N(3)-C(8)-H(8B)	110.1(2)	C(12)-C(14)-H(14C)	109.5(3)
C(7)-C(8)-H(8B)	110.1(3)	H(14A)-C(14)-H(14C)	109.5
H(8A)-C(8)-H(8B)	108.4	H(14B)-C(14)-H(14C)	109.5
N(3)-C(9)-C(10)	123.1(5)	N(4)-C(15)-C(16)	108.6(3)
N(3)-C(9)-C(11)	122.0(4)	N(4)-C(15)-H(15A)	110.0(2)
C(10)-C(9)-C(11)	114.8(4)	C(16)-C(15)-H(15A)	110.0(2)
C(9)-C(10)-H(10A)	109.5(3)	N(4)-C(15)-H(15B)	110.0(2)
C(9)-C(10)-H(10B)	109.5(3)	C(16)-C(15)-H(15B)	110.0(3)
H(10A)-C(10)-H(10B)	109.5	H(15A)-C(15)-H(15B)	108.4
C(9)-C(10)-H(10C)	109.5(4)	N(1)-C(16)-C(15)	110.6(3)
H(10A)-C(10)-H(10C)	109.5	N(1)-C(16)-H(16A)	109.5(2)
H(10B)-C(10)-H(10C)	109.5	C(15)-C(16)-H(16A)	109.5(2)
C(9)-C(11)-C(12)	118.8(4)	N(1)-C(16)-H(16B)	109.5(2)
C(9)-C(11)-C(11A)	107.6(3)	C(15)-C(16)-H(16B)	109.5(2)
C(12)-C(11)-H(11A)	107.6(3)	H(16A)-C(16)-H(16B)	108.1
O(10)-Cl-O(12)	114.9(11)	O(7)-Cl-O(5)	12.3(12)
O(7)-Cl-O(8)	115.0(13)	O(8)-Cl-O(5)	104.9(10)
O(10)-Cl-O(9)	112.7(13)	O(6)-Cl-O(5)	105.4(11)
O(12)-Cl-O(9)	112.5(11)	O(10)-Cl-O(11)	102.7(11)
O(7)-Cl-O(6)	113.0(12)	O(12)-Cl-O(11)	111.1(12)
O(8)-Cl-O(6)	105.4(11)	O(9)-Cl-O(11)	101.8(12)

(34) The reverse processes, anation of the $\text{CoL}(\text{H}_2\text{O})_2^{3+}$ complexes by sulfite, were not exhaustively investigated in this work. It was observed, however, that a large fraction of millimolar $\text{CoL}(\text{H}_2\text{O})_2^{3+}$ was converted to $\text{CoL}(\text{H}_2\text{O})\text{SO}_3^+$ within tens of minutes of mixed with 10^{-3} to 10^{-4} M SO_3^{2-} . It must be noted that this is the time scale of continuous photolysis.

(35) van Eldik, R.; Harris, G. M. *Inorg. Chem.* **1980**, *19*, 880.

(36) El-Awady, A. A.; Harris, G. M. *Inorg. Chem.* **1986**, *25*, 1323.

(37) Kraft, J.; van Eldik, R. *Inorg. Chem.* **1985**, *24*, 3391.

of the reaction rate on pH looks like those in the literature for the hydrolysis of O-bonded sulfite $\text{Co}(\text{III})$ complexes. In this regard the unstable product absorbing near 420 nm can be

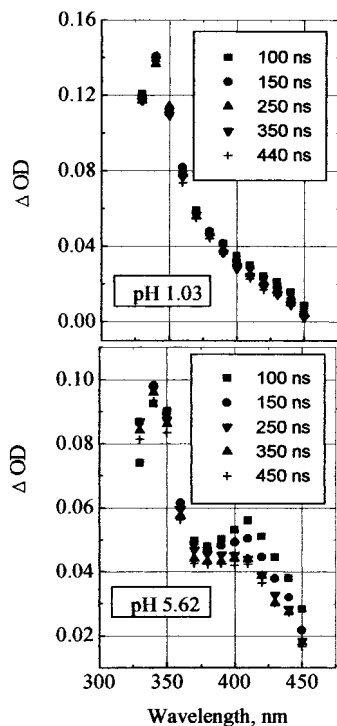


Figure 2. Transient spectra recorded with 248 nm flash irradiations of $\text{Co}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})\text{SO}_3^+$ in deaerated pH 1.03 and 5.62 solutions.

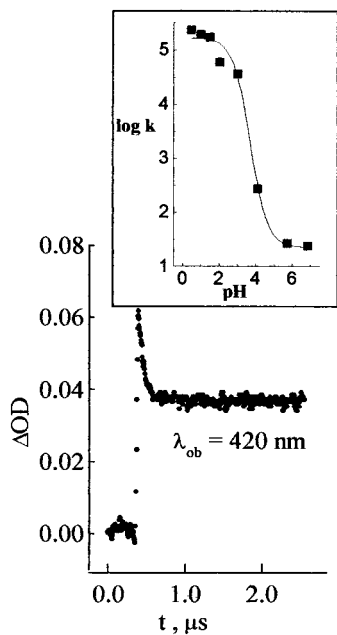


Figure 3. Typical biphasic decay of the flash-generated 420 nm optical density, ΔOD , in 248 nm irradiations of $\text{Co}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})\text{SO}_3^+$ in deaerated pH 5.62 solutions. The acid dependence of the rate constant for the hydrolysis of the O-bonded sulfite complex, $\text{Co}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})\text{OSO}_2^+$, is shown in the inset.

identified as $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})(\text{OSO}_2)^+$, i.e., an O-bonded sulfite complex. Displacements of the equilibrium between $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})(\text{OSO}_2)^+$ and $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})(\text{OSO}_2\text{H})^{2+}$ account for the pH dependency of the transient spectra between 390 and 500 nm, top and bottom of Figure 2. Since the rate of disappearance of O-bonded species was fast enough between pH 1 and 3, flash photolysis of solutions with such acid concentrations allowed the characterization of the second product with λ_{max} 340 nm as

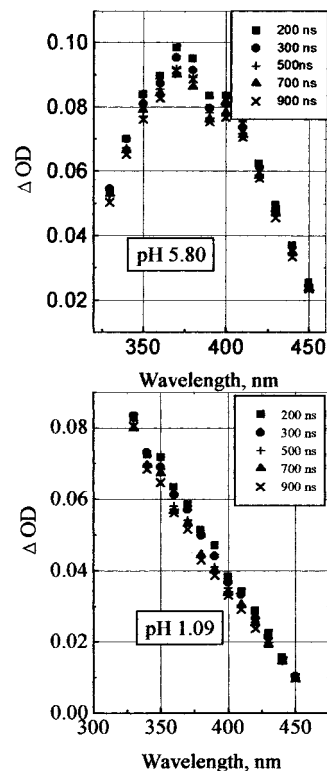


Figure 4. Transient spectra recorded with 248 nm flash irradiations of $\text{Co}([14]\text{aneN}_4)(\text{H}_2\text{O})\text{SO}_3^+$ in deaerated pH 5.80 and 1.09 solutions.

$\text{Co}^{\text{II}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{2+}$. The ratio of flash photochemically generated O-bonded sulfite complex to $\text{Co}^{\text{II}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{2+}$ changed when solutions were made in methanol–water mixed solvent with a 3:1 molar relationship. A larger optical density at 440 nm than at 340 nm revealed that photolysis in those methanolic solutions produced O-bonded sulfite complexes with a larger yield than in aqueous solutions.

In terms of the formation of Co(II) and O-bonded sulfite Co(III) complexes, the photochemistry of $\text{Co}^{\text{III}}([14]\text{aneN}_4)(\text{H}_2\text{O})\text{SO}_3^+$ was similar to the one described above for $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})\text{SO}_3^+$ for irradiations, λ_{exc} 248 or 350 nm, in deaerated acidic solutions. However, only one short-lived transient, $\tau = 140$ ns, was observed at 360 nm instead of the two observed with $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})\text{SO}_3^+$, Figure 4.

Photogeneration of Co(I) Products. The photochemical experiments described above were carried out with low photonic densities and laser powers to prevent a secondary photolysis of any product. The spectrum of $\text{Co}^{\text{I}}(\text{H}_2\text{O})_2^+$, λ_{max} 700 nm for $\text{L} = \text{Me}_6[14]\text{dieneN}_4$, was detected after the 20 ns flash irradiations with larger laser powers. In Figure 5, the flash-generated optical density changes at 700 nm, ΔOD_{700}^0 , and at 340 nm, ΔOD_{340}^0 , are plotted as a function of photonic density per unit time.³⁸ A comparison of these optical changes reveal that the Co(I) product concentration increases at the expense of the photoproducts absorbing at 340 nm, i.e., $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})(\text{OSO}_2)^+$ and $\text{Co}^{\text{II}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{2+}$. Also, the quadratic dependence of ΔOD_{700}^0 on the laser flash intensity shows that one of such products, or a precursor of them, must be photolyzed for

(38) The photonic density per unit time was calculated on the basis of the Br_2^- concentration generated by the 25 ns laser flash photolysis of the actinometer.³⁰ This quantity increased linearly with the number of photons in the laser pulse while the later quantity, measured as total thermal energy, was determined with a Scientek Energy/Power meter.

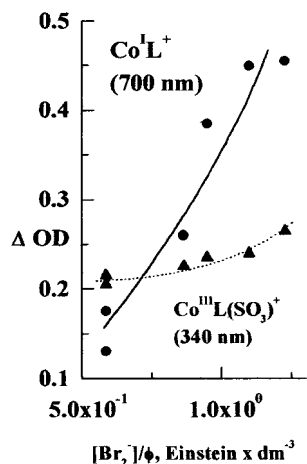


Figure 5. Dependence of the flash generated optical absorptions of Co(I), λ_{ob} 700 nm, and Co(II), λ_{ob} 700 nm, on the laser intensity.

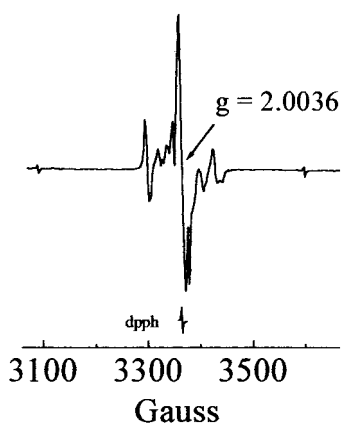


Figure 6. ESR spectrum of the $\text{SO}_3^{\bullet-}$ radical generated in 254 nm photolyses of $\text{Co}(\text{[14]aneN}_4)(\text{H}_2\text{O})\text{SO}_3^+$ in a 4:1 ethanol/methanol glass at 77 K.

the formation of Co(I). To investigate the photochemical source of Co(I), deaerated acidic solutions of $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})\text{SO}_3^+$ were subjected to sequential dual laser irradiations. Each 248 nm flash from the excimer laser was followed, after a preselected delay, by a 355 nm flash from the synchronized YAG laser. The photogeneration of Co(I) was only observed with delays equal to or shorter than 2 μs . No Co(I) could be observed when solutions of the Co(III) complex were irradiated with only one of the lasers and with that laser delivering the same light powers that it had during the two-laser photolysis. Since $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})(\text{OSO}_2)^+$ and $\text{Co}^{\text{II}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{2+}$ have lifetimes longer than 2 μs in flash photochemical experiments, the photogeneration of Co(I) must be ascribed to the photolysis of a precursor of the products considered above.

ESR Spectrum of a Reaction Intermediate. Glassy solutions of $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})\text{SO}_3^+$ or $\text{Co}^{\text{III}}(\text{[14]aneN}_4)(\text{H}_2\text{O})\text{SO}_3^+$ in MeOH/EtOH at 77 K were irradiated at 254 or 300 nm for various intervals. The literature ESR spectrum of the $\text{SO}_3^{\bullet-}$ radical anion³⁹ was observed in all the irradiated samples with a signal intensity that increased with the duration of the photolysis, Figure 6. Changes in the shape of the ESR spectrum and/or the appearance of new signals were not detected when the irradiation was gradually extended from 10 to 60 s.

Reaction of $\text{SO}_3^{\bullet-}$ Radicals with $\text{Co}^{\text{II}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{2+}$. Since $\text{SO}_3^{\bullet-}$ radicals can in principle function as oxidants and reductants, their reaction with $\text{Co}^{\text{II}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{2+}$ was investigated via pulse radiolysis. In these experiments with N_2O saturated solutions having a pH 5, the pulse radiochemically generated $\bullet\text{OH}$ radicals were scavenged with 10^{-2} M HSO_3^- to generate $\text{SO}_3^{\bullet-}$. The diffusion-controlled reaction of the Co(II) complex with $\bullet\text{OH}$ was avoided by scavenging $\text{SO}_3^{\bullet-}$ with $\text{Co}^{\text{II}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{2+}$ in concentrations equal to or less than 8×10^{-4} M. Spectral changes, a bleach of the Co(II) absorption band at 335 nm and the growth of absorptions below 250 nm, indicated the nearly quantitative formation of $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{3+}$. No spectral evidence was observed that supported the formation of the Co(I), $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})\text{SO}_3^+$ or $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})(\text{OSO}_2)^+$ products. A rate constant, $k = 6.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, was calculated from the time-resolved recovery of the bleaching of the Co(II) absorption at 340 nm.

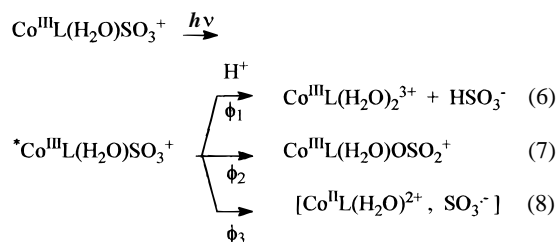
Continuous Photolysis. Monochromatic irradiations, $\lambda_{\text{exc}} = 254, 300, \text{ or } 350 \text{ nm}$, of $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})\text{SO}_3^+$ in acidic deaerated solutions, $5 \geq \text{pH} \geq 1$, led to the formation of SO_4^{2-} . A small concentration of $\text{Co}(\text{H}_2\text{O})_6^{2+}$, if any at all, was found in solutions irradiated for very short times, i.e., $\phi \leq 10^{-4}$. Since the hydrolysis of O-bonded sulfite complexes detected in flash photolysis is fast at $\text{pH} < 3$, $\text{Co}^{\text{II}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{2+}$ and $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{3+}$ were the only products spectrophotometrically detected in 254 nm continuous photolyses when conversions to such products remained below 5%. Although the $\text{Co}^{\text{II}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{2+}$ concentration increased linearly with irradiation time, a diminishing rate of $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{3+}$ was measured within this range of conversions. The departure from linearity in a plot of the $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{3+}$ concentration vs the irradiation time is partly related to the anation of this product by photogenerated SO_3^{2-} over longer periods.³⁴ The oxidation of $\text{Co}^{\text{II}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{2+}$ by sulfite radicals observed in pulse radiolysis influences also the rate of the photolysis. However, concentrations of the Co(II) photoproduct had to be larger than those reached with a 5% conversion in order to observe the effect of this reaction. A quantum yield of $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{3+}$, $\phi_{\text{Co(III)}} = (2.0 \pm 0.2) \times 10^{-2}$, and a quantum yield of $\text{Co}^{\text{II}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{2+}$, $\phi_{\text{Co(II)}} = (0.40 \pm 0.02) \times 10^{-2}$, were calculated, therefore, by extrapolation of the product formation rates to the beginning of the photolysis.

Discussion

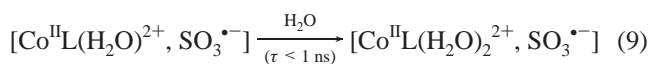
Irradiation of the macrocycle, [14]aneN₄ and Me₆[14]dieneN₄, Co(III) sulfite complexes in their charge-transfer bands produce $\text{SO}_3^{\bullet-}$ radicals and the corresponding Co(II) complexes, linkage isomerization to the O-bonded sulfite product and possibly photoaquation. Since the same product, $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{3+}$, is produced by the photoaquation and the rapid hydrolysis of the O-bonded sulfite complex, the experimental techniques used in this work provided no information about the relative weights of the two reaction paths. Time-resolved spectral changes indicate that the Co(III) photoproducts must be formed in excited-state processes initiated and completed within the irradiation of the laser. In accordance with this experimental evidence and the known photochemistry of Co(III) complexes,^{16–20} it is proposed, that ligand field and/or sulfite-to-cobalt(III) charge-transfer excited states, $^*\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})\text{SO}_3^+$, undergo conversions to the indicated Co(III) products, eqs 6 and 7, and to a radical-ion pair, $[\text{Co}^{\text{II}}$

(39) Chantry, G. W.; Horsfield, A.; Morton, J. R.; Rowlands, J. R.; Whiffen, D. H. *Mol. Phys.* **1962**, *5*, 233.

(Me₆[14]dieneN₄)²⁺, SO₃^{•-}, eq 8.



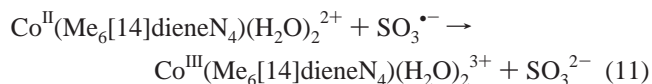
Such radical-ion pairs are known to undergo recombination or separation in aqueous solutions within a nanosecond.⁴⁰ The presence of reaction intermediates longer lived than radical-ion pairs is signaled by the photogeneration of Co(I) products in secondary photolyses and by the spectral changes with lifetimes 60 ns and 2.5 or 140 μs in the respective photolyses of Me₆[14]dieneN₄ and [14]aneN₄ complexes. In a time scale $t \leq 10^2$ ns, the metal center can restore an octahedral coordination by trapping water without a concomitant oxidation of the metal center (eqs 9 and 10).



Indeed, these reactions can be regarded as a possible source of spectral changes with lifetimes shorter than a microsecond in Figures 2 and 4.^{41,42} The spectral changes agree with expectations for charge-transfer transitions in a [Co^{II}L(H₂O)₂²⁺, SO₃^{•-}] ion pair. Calculations of these optical energies were based on methods, values of the redox potentials and reorganization energies for the Co(III/II) couples and SO₃^{•-} radicals in the literature reports.^{10,17,30} They placed the ion-pair charge-transfer transitions at wavelengths longer than 360 nm.¹⁷

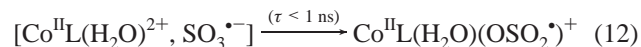
It can be argued that the relaxation time of the equilibrium, eq 10, and the lifetime of the associated spectral changes may reach a value of several hundred ns if K , the association constant in eq 10, is large enough, i.e., $10^2 \geq K \geq 10^1 \text{ M}^{-1}$. The back electron-transfer in the pair must also be slow with respect to the dissociation of the pair to prevent reoxidation of the Co(II) complex. One must inspect the behavior of sulfite radicals and Co^{II}L(H₂O)₂²⁺ (L = Me₆[14]dieneN₄ or [14]aneN₄) in electron-transfer reactions to find a possible rationale for the longevity of [Co^{II}L(H₂O)₂²⁺, SO₃^{•-}] with regard to the back-electron transfer. A rate constant, $k_{\text{xchg}} = 6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, for the SO₃^{•-}/SO₃²⁻ self-exchange, was reported in the literature on the basis that some SO₃^{•-} electron-transfer reactions obey the Marcus theory.^{43,44} This value of the self-exchange rate constant and those calculated in these work by using other reactions, e.g. the oxidation of SO₃²⁻ by Cl₂⁻, were in good agreement, i.e., $k_{\text{xchg}} = (4 \pm 3) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.^{45,46} The macrocycles Co^{II}L(H₂O)₂²⁺, (L = Me₆[14]dieneN₄ or [14]aneN₄) are poor reduc-

tants that undergo very slow self-exchange electron transfer, $k_{\text{xchg}} = 4.5 \times 10^{-5}$ and $8 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ respectively.⁴⁷ A rate constant, $k = 8.0 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$, was calculated for the oxidation of Co^{II}(Me₆[14]dieneN₄)(H₂O)₂²⁺, eq 11, using rate constants given above and literature redox potentials.^{10,48}



The discrepancy between experimental ($k = 6.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) and calculated ($k = 8.0 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$) values of the rate constant suggests that eq 11 proceeds by an inner-sphere mechanism that provides a 10⁶ enhancement over the rate of the outer-sphere path. A possible association of the radical to the unsaturated macrocycle Me₆[14]dieneN₄ could mediate in this reaction. Some evidence about this intermediate will be considered below in relation to the optical transient with a $\tau = 2.5 \mu\text{s}$ lifetime. It must be also noted that eq 11, a second-order reoxidation of Co(II) with $k = 6.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, cannot compete with the disproportionation and dimerization of the SO₃^{•-} radicals unless the photolysis of the Co(III) macrocycles produces a very high concentration of the Co(II) product.

A radical-ion pair process which could also lead to the formation of the O-bonded sulfite complex, eqs 12 and 13, in addition to the previously considered eq 7 is too slow.



In eq 12, the Co(II) recovers an octahedral coordination by complexation to SO₃^{•-} radicals in the ion-pair. The intramolecular electron transfer, reorganization energies from the Co(III)/Co(II) and SO₃^{•-}/SO₃²⁻ self-exchange reactions show that the effective nuclear vibration, $\nu_n \approx 10^{13} \text{ s}^{-1}$, will be diminished by a nuclear factor, $\kappa_n \approx 3 \times 10^{-17}$,^{44,49,50} a value that is mainly determined by the small exchange rate constant of the macrocyclic couple, $k_{\text{exch}} = 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$, and small Gibbs energy of the reaction, $\Delta G^\circ \approx -24 \text{ kJ mol}^{-1}$. Therefore, if a Co(II) ligand-radical species is formed in the solvent cage, it would undergo processes such as hydrolysis, eq 14, instead of a back electron transfer, eq 13. The larger yield of O-bonded sulfite complex in methanolic solutions respect to the yield in aqueous solution appears to reflect more a medium-dependent photophysics, i.e., a medium dependence of the quantum yields

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(41) This proposition is based on the literature structures of various Co(II) macrocyclic complexes.⁴²

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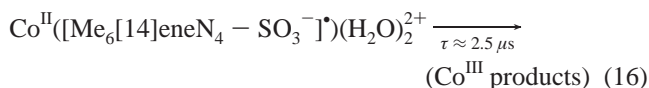
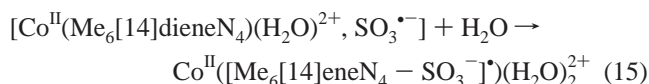
(48) The rate constant, k_{12} , for the cross reaction was calculated with the equation, $k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12}$, where $\ln f_{12} = \{[(w_{12} - w_{21})/RT + \ln K_{12}^2]/\{4[(w_{11} + w_{22})/RT + \ln(10^{-24}k_{11}k_{22})]\}$ and $W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT]$ account for the various work terms, w_{ij} .⁴¹ Values for the self-exchange rate constants, k_{11} and k_{22} , are given in the text. The equilibrium constant K_{12} was calculated with the redox potentials of the corresponding couples.

(49) The reaction was considered an intramolecular electron transfer with a rate constant, $k = \nu_n \kappa_{\text{el}} \kappa_n$.⁴¹ In this equation, $\nu_n \approx 10^{13}$ is the effective nuclear frequency, $\kappa_{\text{el}} \approx 1$ is the electronic transmission coefficient, and $\kappa_n = \exp\{-[(\lambda_o + \lambda_i + \Delta G^\circ)^2]/\{4(\lambda_o + \lambda_i)\}\}$ is a nuclear factor containing the outer and inner sphere reorganization energies, λ_o and λ_i , and the reaction's standard free energy, ΔG° . The last factor was calculated in this work with the values of the corresponding self-exchange rate constants of the radical and the Co(III)/Co(II) couple.⁵⁰

(50) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

in eqs 6–8, than a change in the rate of the ion-radical pair reactions, eqs 9 and 12.

Lifetimes of several μs have been communicated for the hydrolyses of halides coordinated to related $\text{Co}(\text{II})$ macrocycles.⁴² The hydrolysis in eq 14 could be occurring in a similar time scale but without spectral changes that are detectable by our flash photolysis technique. The observed optical changes with a 2.5 μs lifetime and the secondary photolysis to form $\text{Co}(\text{I})$ products must be related, therefore, to other transient species. The known sulfonation reactions of $\text{SO}_3^{\bullet-}$ radicals,^{43,51–53} suggest that addition of the radical to the $\text{Me}_6[14]\text{dieneN}_4$ macrocycle, eqs 15 and 16, can be the source of these experimental observations.



Since [14]ane N_4 is a fully saturated macrocycle, no sulfonation is possible and only the 140 ns transient related to eqs 9 and 10 is observed in flash photolysis experiments.

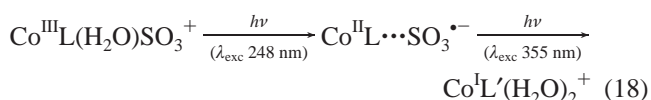
In continuous photolysis, the absence of the $\text{Co}(\text{H}_2\text{O})_6^{2+}$ product implies that the intramolecular electron-transfer, eq 16, occurs without opening the macrocyclic ligand. The concentrations of $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{3+}$ measured in these experiments suggest that the bis aquo $\text{Co}(\text{III})$ complex could be the major product of eq 16. Reoxidation of $\text{Co}(\text{II})$ must take place with the detachment of sulfite, i.e., ($\text{Co}(\text{III})$ products) is $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{3+} + \text{SO}_3^{2-}$. Results of the continuous photolysis can now be interpreted in terms of eqs 6–16. Since flash photolysis shows that the acid-catalyzed hydrolysis of $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})\text{OSO}_2^+$ is fast in acidic solutions, the O-bonded sulfite complex can be regarded as a reaction intermediate in the time scale of continuous photolysis. A constant ratio between the product yields of $\text{Co}^{\text{II}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{2+}$, $\phi_{\text{Co}(\text{II})} = 1.4 \times 10^{-2}$, and $\text{Co}^{\text{III}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{3+}$, $\phi_{\text{Co}(\text{III})} = 7 \times 10^{-2}$, results, eq 17, when reaction intermediates in eq 6–16 have steady-state concentrations during very short irradiations, i.e., less than 5% conversion to products.

$$\frac{\phi_{\text{Co}(\text{III})}}{\phi_{\text{Co}(\text{II})}} = \frac{(\phi_1 + \phi_2)(k_9 + k_{12} + k_{15}) + \phi_3 k_{15}}{\phi_3(k_9 + k_{12})} = 5 \quad (17)$$

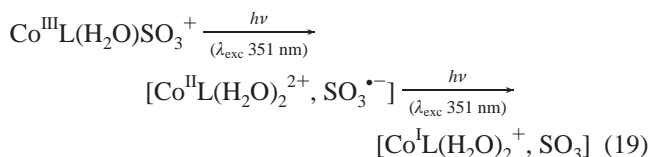
In eq 17, ϕ_i , $i = 1, 2, 3$, represent quantum yields of the various processes, eqs 6–8, and k_i , $i = 9, 12, 15$, are the rate constants for the decay of the radical-ion pair, eqs 9, 12, and 15. If the rate constants k_i are assumed to be of the same order of

magnitude, i.e., close to the collapse of the solvent cage, is $(\phi_1 + \phi_2)/\phi_3 \approx 3$. In this rather drastic assumption, it must be concluded that the photoredox quantum yield is of the same magnitude of the quantum yield for the photogeneration of $\text{Co}(\text{III})$ products.

Some of the $\text{Co}(\text{II})$ species in eq 8–16 can now be appraised as sources for the photogeneration of $\text{Co}(\text{I})$ in secondary photolyses. Since a literature report has shown that 254 nm irradiations of $\text{Co}^{\text{II}}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{2+}$ photoinduces the hydrolysis of the macrocyclic ligand, this product cannot be considered the photochemical source of $\text{Co}(\text{I})$. Other $\text{Co}(\text{II})$ complexes are photoreduced to $\text{Co}(\text{I})$ in processes where solvent molecules or counterions function as reductants.^{11–13} The observed photogeneration of $\text{Co}(\text{I})$ in double-flash, two-wavelength, irradiations must be ascribed, therefore, to photo-reactions of $\text{Co}^{\text{II}}\text{L}(\text{OSO}_2^{\bullet})^+$, eq 12, or $\text{Co}^{\text{II}}([\text{Me}_6[14]\text{eneN}_4 - \text{SO}_3^-](\text{H}_2\text{O})_2^{2+}$, eq 15. In eq 18 these species are represented by $\text{Co}^{\text{II}}\text{L}\cdots\text{SO}_3^{\bullet-}$ and L' is an open or close ring macrocycle.



In the high intensity 351 nm single flash irradiations, photolysis of the ion pair, eq 19, may also contribute to the photogeneration of $\text{Co}(\text{I})$.



It can be concluded that the photochemical behavior of various sulfite complexes when irradiated at wavelengths of the charge transfer bands is more complex than has been previously assumed. This type of photochemistry, associated with the first intense charge transfer band, is most likely related to LM-CT $_{\text{S}(\sigma) \rightarrow \text{Co}(\sigma^*)}$ excited states. Linkage photoisomerization has been previously ascribed to a recombination within ion-radical pairs.^{18–20} However, the experimental evidence in the literature and the one in this work cannot unequivocally rule out the unimolecular processes initiated in an excited state, eqs 6 and 7. The photoredox products signal, however, that radical-ion pairs must have a definitive participation in the mechanism.

Supporting Information Available: Crystal structure listings of crystal and refinement data, bond distances, angles and thermal parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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