HEBA or HMBA, the interception is more effective, yielding greater percentage of Co(II) whereas the ligands, HEBA and HMBA, probably react more slowly with Cr(IV) than does V(IV).[14]

As the Co(III) center is separated from the hydroxyl group by a saturated fragment, Cr(IV) oxidation necessarily occurs first at the hydroxyl center, generating a radical that should collapse with C–C fission and one-electron transfer to Co(III), occurring synchronously or very nearly so, resulting in the formation of Co(II) (Scheme I).[15,16]

Acknowledgment. The author wishes to thank Professor E. S. Gould, Kent State University, for the award of the postdoctoral fellowship, during 1979–1981, when part of this work was done.

Registry No. Cr, 7440-47-3; $[(H_3N)_5Co^{III}(lactato)]^{2+}$, 34464-03-4; $[(H_3N)_5Co^{III}(mandelato)]^{2+}$, 73543-61-0; $[(H_3N)_5Co^{III}(benzilato)]^{2+}$, 47253-58-7; $[(H_3N)_5Co^{III}(HEBA)]^{2+}$, 83174-77-0; $[(H_3N)_5Co^{III}(HMBA)]^{2+}$, 83174-78-1.

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(14) Under the reaction conditions either Cr(VI) or V(V) oxidizes the Co^{III}–mandelato complex but not the Co^{III}–HEBA or Co^{III}–HMBA complex at any considerable rate. Also, either Cr(VI) or V(V) oxidizes mandelic acid at a faster rate than either HEBA or HMBA. Hence, a similar order of reactivity is assumed for Cr(IV) also.

(15) Though no kinetic evidence for complex formation has been obtained, the mechanism proposed is similar to that proposed for the Ce(IV) oxidation of the same compounds.[3]

(16) Similar Fe(III)-induced electron transfer on C-bound Cr(III)–α-hydroxy acid complexes leads to the formation of Fe^{2+} and Cr^{2+}: Espenson, J. H.; Bakac, A. *J. Am. Chem. Soc.* **1980**, *102*, 2488.

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Photooxidation of Bis(maleonitriledithiolate) Complexes, $[M(S_2C_2(CN)_2)_2]^{2-}$ (M = Ni, Pd, Pt, Co, Cu)[1]

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Although transition-metal dithiolene complexes have been extensively investigated,[2] the photochemistry of these complexes has received little attention. The presence of intense UV–visible absorption bands and the accessibility of two or more oxidation states suggests that dithiolene complexes should display interesting redox photochemistry. Several recent reports substantiate this expectation.[3-6] Photooxidation of dithiolene complexes[3] and mixed diimine–dithiolene complexes[4,5] has been observed. Additionally, several bis(dithiolene) complexes were shown to catalyze photochemical H_2 production in H_2O/tetrahydrofuran mixtures.[6] This latter result suggests that transition-metal dithiolenes may ultimately prove useful in solar energy conversion. Some progress has been reported in identifying the reactive excited states. Vogler and Kunkely suggested that reaction occurs from a charge-transfer-to-solvent (CTTS) state in the photooxidation of the 1,2-dithiolene complexes $M(S_2C_2R_2)^Z$ (M = Ni, Pd, Pt, R = CN, Z = 2–; M = Ni, R = C_6H_5, Z = 1–) in chloroform.[3] We have also investigated the photochemistry of maleonitriledithiolate (mnt) complexes in chlorocarbon solutions under somewhat different conditions. One-electron oxidation was observed for each complex, with strongly wavelength-dependent quantum yields, but our results differ significantly from those of Vogler and Kunkely and indicate that additional excited states are reactive.

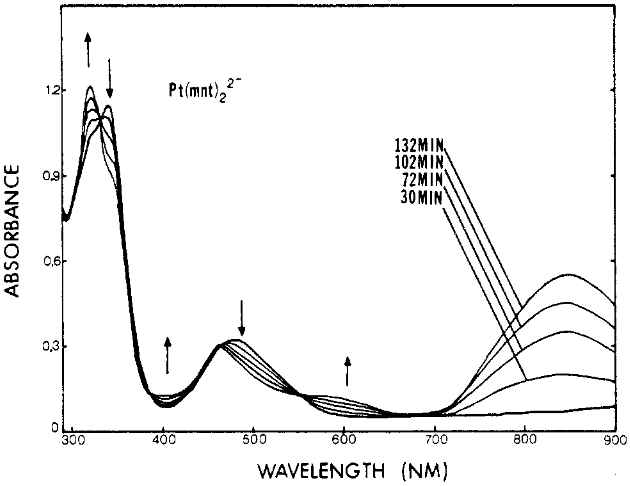

Figure 1. Electronic absorption spectral changes during 254-nm photolysis of $Pt(mnt)_2^{2-}$ in $CHCl_3/CH_3CN$ (24:1 v/v) at 23 °C. Isosbestic points appear at 540, 435, 395, and 315 nm.

Table I. Quantum Yields in 24:1 $CHCl_3/CH_3CN$[a]

	wavelength[d]				
complex	405	365	300	254	$E_{1/2}$[b]
$Ni(mnt)_2^{2-}$	7.3×10^{-4}	5.9×10^{-3}	0.096	0.71	+0.23
$Pd(mnt)_2^{2-}$	5.6×10^{-4}	3.3×10^{-3}	0.071	0.49	+0.46
$Pt(mnt)_2^{2-}$		0.046[c]	0.065	0.52	+0.21
$Co(mnt)_2^{2-}$	1.6×10^{-3}	7.5×10^{-3}	0.11	0.58	+0.05
$Cu(mnt)_2^{2-}$		4.0×10^{-3}		1.0	+0.34

[a] Quantum yields were reproducible within ±10%. [b] In volts vs. SCE in CH_3CN.[2a] [c] Measured at 335 nm. [d] All wavelengths are given in nm.

Experimental Section

Reagent grade chemicals were used without further purification. $PdCl_2$ and $PtCl_2$ were obtained from Alfa and used as received. All other metal salts were from J. T. Baker. Sodium maleonitriledithiolate was purchased from Strem Chemical and used as received or synthesized by literature methods.[7] All photochemical experiments were carried out in spectrophotometric grade solvents from Aldrich. Tetrabutylammonium salts of $Co(mnt)_2^{2-}$, $Cu(mnt)_2^{2-}$, $Pd(mnt)_2^{2-}$, and $Pt(mnt)_2^{2-}$ and the tetraethylammonium salt of $Ni(mnt)_2^{2-}$ were synthesized as previously described.[7] Satisfactory melting points, elemental analyses (Galbraith Laboratories), and UV–visibile absorption spectra were obtained for all the complexes.

Quantum Yields. Irradiations were performed at room temperature with an Ealing Stabilarc 250 system equipped with a 200-W Osram medium-pressure mercury-arc lamp. Wavelength selection was made with appropriate interference filters (Oriel) or with an Oriel 7240 monochromator set for a 10-nm band-pass. Lamp intensities were determined with use of ferrioxalate actionmetry for $\lambda < 440$ nm[8] and Reinecke's salt actinometry for longer wavelengths.[9] Reactions were monitored with a Cary 219 spectrophotometer. Quantum yields were calculated by using extinction coefficients for the intense near-IR band of the product monoanions[2] except for $Pd(mnt)_2^-$ and $Cu(mnt)_2^-$. For these complexes $\Delta\epsilon$ at 440 and 460 nm, respectively, was measured and used to calculate quantum yields. The fraction of incident light absorbed was generally ~1, but corrections were applied as necessary.

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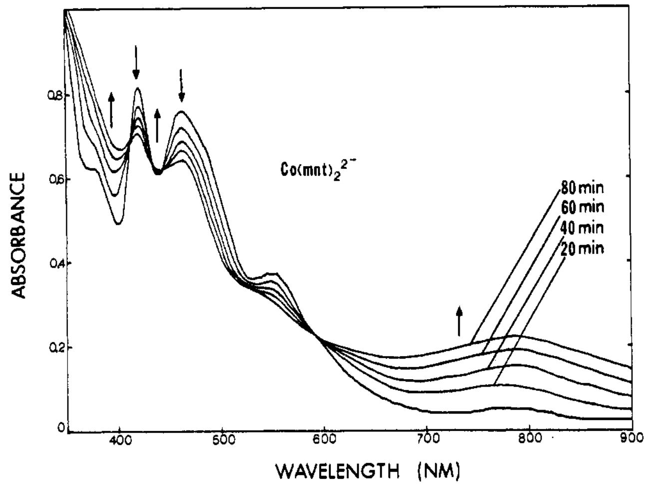

Figure 2. Electronic absorption spectral changes during 365-nm photolysis of $Co(mnt)_2^{2-}$ in $CHCl_3/CH_3CN$ (24:1 v/v) at 23 °C. Isosbestic points appear at 590, 445, 435, and 410 nm.

For the minimization of inner filter effects, quantum yields were determined at several irradiation times up to 10–15% maximum conversion.

Results and Discussion

Irradiation at a variety of wavelengths of $M(mnt)_2^{2-}$ (M = Ni, Pd, Pt, Co, Cu) in $CHCl_3/CH_3CN$ solutions (24:1 v/v) led to formation of the monoanions, which were identified by their characteristic absorption spectra. Spectral changes during photolysis of $Pt(mnt)_2^{2-}$ and $Co(mnt)_2^{2-}$ are shown in Figures 1 and 2, respectively. Several good isosbestic points were observed during the photolysis of all the complexes. Depending on the complex, 50–80% of the dianion could be converted to the monanion before secondary photoreactions, leading to products we have not yet identified, were evident. Quantum yield data are displayed in Table I. It is evident that nonzero quantum yields are obtained at widely separated irradiation energies. In 24:1 (v/v) CH_2Cl_2/CH_3CN the quantum yields at 254 nm were 0.35 ± 0.03 for $Ni(mnt)_2^{2-}$, 0.18 ± 0.006 for $Pd(mnt)_2^{2-}$, and 0.24 ± 0.01 for $Pt(mnt)_2^{2-}$. Quantum yields at 254 nm cannot be measured in CCl_4 solutions; however, quantum yields at 300 nm in CCl_4/CH_3CN were 0.43 ± 0.02 for $Ni(mnt)_2^{2-}$ and 0.60 ± 0.03 for $Pt(mnt)_2^{2-}$. This reactivity order parallels the relative redox potentials of CH_2Cl_2, $CHCl_3$, and CCl_4.[10]

A plausible mechanism is bimolecular excited-state electron transfer to a chlorocarbon acceptor,[4,11] e.g.

$$M(mnt)_2^{2-} \underset{k_d}{\overset{h\nu}{\rightleftharpoons}} (M(mnt)_2^{2-})^*$$

$$(M(mnt)_2^{2-})^* + CHCl_3 \xrightarrow{k_r} [M(mnt)_2^{-}\cdots CHCl_3^{-}]$$

$$[M(mnt)_2^{-}\cdots CHCl_3^{-}] \xrightarrow{k_p} M(mnt)_2^{-} + \cdot CHCl_2 + Cl^-$$

$$[M(mnt)_2^{-}\cdots CHCl_3^{-}] \xrightarrow{k_b} M(mnt)_2^{2-} + CHCl_3$$

Steady-state treatment of this scheme yields

$$\frac{1}{\phi} = \frac{k_p + k_b}{k_p}\,\frac{k_d}{k_r}\left(\frac{1}{[CHCl_3]} + 1\right)$$

The linear double-reciprocal plot (Figure 3) for $Ni(mnt)_2^{2-}$ oxidation at low concentrations of $CHCl_3$ is consistent with this mechanism. $Pt(mnt)_2^{2-}$ oxidation in $CHCl_3/CH_3CN$ solutions also gives a linear double-reciprocal plot. At concentrations of $CHCl_3$ greater than ~0.12 M the quantum yields increase dramatically. That is, the limiting quantum yield obtained from the intercept in Figure 3 is 0.19, as compared to the experimental value 0.71 (Table I). Such large differences between extrapolated and measured quantum yields at high $CHCl_3$ concentrations can be attributed to a changeover from diffusive bimolecular electron-transfer reactions to a situation where excited-state electron transfer occurs within the initial solvent cage.

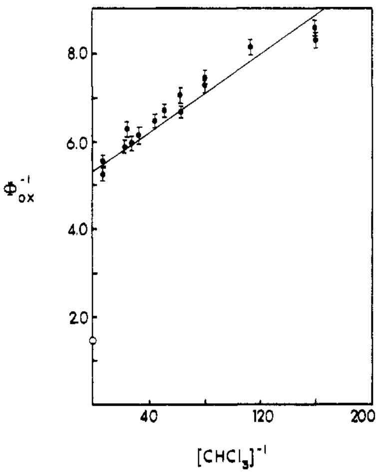

Figure 3. Stern–Volmer plot for the photooxidation (λ = 254 nm) of $Ni(mnt)_2^{2-}$ in dilute CH_3CN solutions of $CHCl_3$ at 23 °C. ○ = measured quantum yield in 24:1 (v/v) $CHCl_3/CH_3CN$.

The electronic absorption spectra of $M(mnt)_2^{2-}$ complexes have been assigned on the basis of approximate MO calculations,[12,13] but substantial experimental evidence is available only for the lowest energy bands for M = Ni, Pd, Pt.[14] Resonance Raman and low-temperature absorption spectroscopy established that the lowest energy intense bands in $Ni(mnt)_2^{2-}$ and $Pt(mnt)_2^{2-}$ correspond to metal-to-ligand charge-transfer (MLCT) states and that the lowest energy band in $Pd(mnt)_2^{2-}$ arises from overlapping MLCT and ligand-to-metal charge-transfer (LMCT) states.[14,15] Similar assignments are reasonable for the lowest energy transitions of $Co(mnt)_2^{2-}$ and $Cu(mnt)_2^{2-}$. Remarkably, the complexes were completely unreactive upon excitation of these transitions at 546 (M = Co, Cu, Ni), 470 (M = Pt), and 440 nm (M = Pd). Additional MLCT, LMCT, and intraligand $L \rightarrow L^*$ states are all expected at higher energies. Gray's assignment of the band centered around 320 nm in these complexes to a $L \rightarrow L^*$ transition is likely correct since the band is present in bis(methylthio)maleonitrile and its energy is nearly independent of metal identity.[13] Interestingly, this state is considerably more reactive than states populated by longer wavelength excitation. Similar reactivity has been observed in the photooxidation of *o*-semiquinone diimine Ni(II) and Pt(II) complexes.[16] Several transitions are possible in the UV region, and band assignments are uncertain. Therefore, associating the photochemistry at 254 nm with a particular

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(15) Owing to the highly covalent nature of these complexes such descriptions are, at best, approximate. In this context charge transfer denotes a decrease in electron density on the metal (or ligand) and a corresponding increase in electron density on the ligand (or metal).

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excited state would be premature, although we note that a LMCT transition from ligand σ orbitals is calculated to occur in this region.[13]

Vogler and Kunkely proposed that photooxidation of M(mnt)$_2^{2-}$ complexes occurs via a CTTS state.[3] However, it is likely that additional excited states are reactive for the following reasons: (1) $E_{1/2}$ values do not correlate with the quantum yields (Table I); (2) quantum yields in 24:1 (v/v) CHCl$_3$/CH$_3$CN are significantly lower than in CHCl$_3$ (compare our values to those in ref 3), whereas the redox potentials of these solvents should be almost identical. Decreased quantum yields in the presence of coordinating solvents has previously been observed in the charge-transfer photochemistry of dithiocarbamate complexes in chlorocarbons and attributed to quenching of either the excited state or a reactive intermediate.[11,17] Both LMCT and CTTS states are thought to be involved in the chlorine-abstraction reactions of dithiocarbamate complexes in chlorocarbon solutions.[11] In view of the fact that redox reactions in M(mnt)$_2^{2-/-}$ complexes are primarily ligand localized, we suggest that excited states with *decreased* bonding electron density on the ligands (relative to the ground state) are potentially reactive, although other factors (e.g., energy, lifetime, etc.) clearly must influence the reactivity as well. We are currently carrying out both spectroscopic and photochemical experiments designed to identify the reactive excited states and to explore further aspects of the redox photochemistry of dithiolene complexes.

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Registry No. Ni(mnt)$_2^{2-}$, 14876-79-0; Pd(mnt)$_2^{2-}$, 37562-15-5; Pt(mnt)$_2^{2-}$, 15152-99-5; Co(mnt)$_2^{2-}$, 40706-01-2; Cu(mnt)$_2^{2-}$, 19562-26-6; CHCl$_3$, 67-66-3; CH$_3$CN, 75-05-8; CCl$_4$, 56-23-5.

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Magnetic Susceptibility of Dimers with Anisotropic Exchange Interactions

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As was demonstrated by a typical example of hydrated copper acetate,[1] there have been reported many dimeric compounds with antiferromagnetic Heisenberg exchange interactions between pairing spins of $S = {}^1/_2$. Most of their magnetic properties such as the susceptibility and specific heat have been explained by assuming an isotropic or Heisenberg Hamiltonian:

$$H' = -2J\mathbf{S}_1\cdot\mathbf{S}_2 \qquad (1)$$

Then, the so-called Bleaney–Bowers formula, namely, the magnetic susceptibility per mole of dimers, is calculated as

$$\chi = \frac{2Ng^2\mu_B^2}{3kT}[1 + {}^1/_3 \exp(-2J/kT)]^{-1} \qquad (2)$$

where N is Avogadro's number, μ_B is the Bohr magneton, g is the g factor, and k is the Boltzmann constant. If the g factor has been settled, for instance, by ESR experiment, the only adjustable parameter is the separation $2J$ between the ground singlet and the excited triplet. Usually, the J value has been assumed to be constant, and the experimental behavior of the susceptibility vs. temperature in most of the dimeric copper

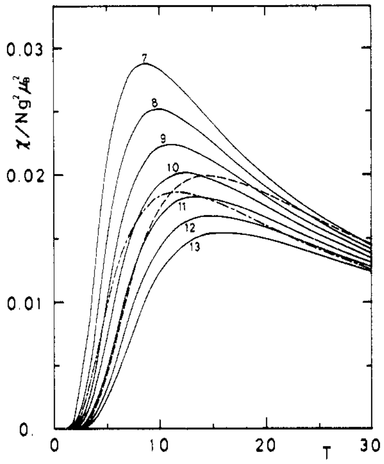

Figure 1. Magnetic susceptibility of dimers of spin $^1/_2$ ions coupled antiferromagnetically in the Heisenberg (—), XY (- - -), and Ising (–·–·) approximations. The values of $|J|/k$ are shown for each curve of the Heisenberg case. For the XY and the Ising cases, the curves have been calculated for $|J|/k = 22.5$ K and $|J|/k = 15$ K, respectively.

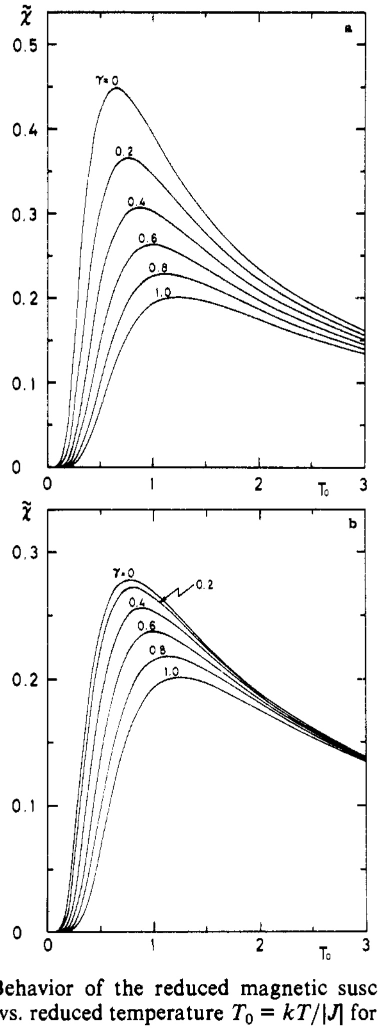

Figure 2. Behavior of the reduced magnetic susceptibility $\tilde{\chi} = \chi|J|/Ng^2\mu_B^2$ vs. reduced temperature $T_0 = kT/|J|$ for various values of the anisotropy parameter γ: (a) the XY-Heisenberg case; (b) the Ising-Heisenberg case.

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