four alkali metal acetates in anhydrous acetic acid have been reported.[14] Although these values are for acetates, and not trifluoroacetates, it would appear likely that the basicity of acetate ion toward strong acid ($HClO_4$) in acetic acid would be influenced by metal cations in a way highly similar as TFA^- is influenced as a hydrogen acceptor in hydrogen bond formation with HTFA, and consequently as it influences the chemical shift of the resulting $H(TFA)_2^-$. Figure 4 shows this to be true as it exhibits an excellent linear relationship for the chemical shifts used in Figure 3 when plotted against the pK_b values of the corresponding alkali metal acetates when in anhydrous acetic acid. The pK_b value for cesium acetate was not reported in the set of data used in Figure 4. The excellent correlation from the figure permits the estimation of this value, $pK_b = 5.94$, from the chemical shift of $CsH(TFA)_2$ reported herein.

On the basis of the above considerations it may be concluded that the presence of a cation near the $H(TFA)_2^-$ anion causes the downfield chemical shift of that anion to be smaller. The effectiveness of the cation in bringing about this effect depends largely upon the nearness of approach of the two ions. If this conclusion is valid, it would be anticipated that sodium hydrogen maleate and potassium hydrogen maleate would exhibit different chemical shifts for their intramolecular hydrogen-bonded acidic hydrogen. As is seen in Table III, this is true; the smaller cation produced an upfield shift in the pertinent absorption relative to the larger cation's effect. In this case there is a difference of only 0.37 ppm in the chemical shifts, while the analogous hydrogens of the hydrogen bonds of $NaH(TFA)_2$ and $KH(TFA)_2$ absorb 2.23 ppm differently. It must be noted, however, that the data for the maleates (III and IV) were obtained in DMSO, which is particularly effective at cationic solvation, and thereby at reducing association of cations with accompanying anions.

In order to examine the generality of the large downfield chemical shifts (decreased shielding) of hydrogen bonds formed between anions and their conjugate acids, we have extended this work in a preliminary way to the acetic and methanesulfonic acid systems. The results indicate a similar magnitude for the hydrogen-bond shift in these cases. We plan to continue the examination of the generality of this phenomenon in other liquid acids and to examine the effects of still other cations.

Acknowledgment. The authors are grateful to Professors C. L. Liotta, D. J. Royer, H. M. Neumann, and W. G. Trawick for valuable discussions during the course of this work. The expert technical assistance rendered by Miss Joyce M. Wilkins at Georgia State University in many of the experimental aspects of the work is also appreciated.

Photochemical Behavior of Ethylenediaminetetraacetate Complexes of Cobalt(III). Sensitization and Excited-State Reaction Pathways[1]

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Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received July 27, 1972*

Abstract: The direct and $Ru(bipy)_3^{2+}$ sensitized photodecompositions of $Co(HEDTA)X^-$ (X = Cl, Br, NO_2) have been examined. Products of redox decomposition were Co^{2+} and CO_2 in each case; ligand field excitation produced aquation of the ligand X and/or linkage isomerization (X = NO_2). Product yields and product ratios were strongly wavelength dependent. It is inferred that the reactive excited states have triplet spin multiplicity and that the carboxylate to cobalt charge-transfer excited state has a lower dissociation energy than the X^- to cobalt excited states.

The photochemical behavior found for most cobalt(III) complexes is reasonable photosensitivity (ϕ_{redox} is commonly about 0.2) on irradiation of their charge transfer to metal (CTTM) absorption bands but relatively little reaction following irradiation of their ligand field absorption bands ($\phi < 0.01$).[2–5] The most notable exceptions to this pattern may occur among the pentacyanocobaltate(III) complexes where irradiation of the ligand field bands appears to produce relatively large product yields.[2,6–9a] The photochemistry of cobalt(III) complexes thus presents some unique and challenging problems.

The classical problem of the photochemistry of cobalt(III) complexes has been to identify and characterize the photochemically significant intermediates.

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This problem has been more difficult than might have been expected, at least partly due to the experimental difficulties which have been encountered in identifying all the primary photoproducts and determining their yields.[2,10–13] Relatively recently there have been suggestive,[2,14–17] if ambiguous,[9b,15] studies using triplet donors to photosensitized the redox decomposition of cobalt(III) complexes. Most of the quantitative information available from these studies is consistent with reaction products being produced from a charge transfer excited state of triplet spin multiplicity;[5,14–17] however, in several cases[9b,16,17] an additional problem is posed in that the sensitized product yield exceeded the product yield obtained from direct excitation, and that the sensitized redox yield was found to be very high (nearly unity) despite the fact that there are potential acceptor states (the ligand field states) of lower energy than the apparent energy[9b,15,18] of the CTTM acceptor state. Additionally, these observations suggest that charge-transfer triplet states may undergo reaction at a more rapid rate than they relax to either the lower energy ligand field triplet states or to the ground singlet state. However, considerable mechanistic complexity of the energy transfer process is indicated by the recent report of Gafney and Adamson[15] on the quinoline sensitized redox decomposition of $Co(NH_3)_6^{3+}$.

Some recent studies of the photochemical behavior of rhodium(III) pentaammine complexes provide instructive comparisons with the cobalt analogs.[19–21] In particular, it has been found that relaxation of charge-transfer excited states, generated in the rhodium complexes, directly to the ground state is more efficient than relaxation to low energy ligand field excited states;[19,21] furthermore, the ligand field excited states of triplet spin multiplicity are very reactive in these complexes.[20] The former observation has implications consistent with the Scandolas' biphenyl sensitization study,[9b] provided the singlet CTTM excited states relax efficiently to the ground state in the case of each of the d^6 metals.

We have undertaken the photochemical study of ethylenediaminetetraacetate (EDTA) complexes of cobalt(III) in the hope of resolving some of the problems raised above. The choice of the cobalt(III) substrate has been dictated by two considerations. By analogy with the case of $Co(NH_3)_5O_2CCH_3^{2+}$,[22] we expected that the photoredox reactions of the EDTA complexes would be irreversible, and we wished to make use of the very convenient cationic triplet sensitizer $Ru(bipy)_3^{2+}$.[23,24] Since our preliminary report of the $Ru(bipy)_3^{2+}$ photosensitization of $Co(HEDTA)X^-$ complexes,[17a] Adamson[25] has suggested that the sensitization mechanism might involve electron transfer rather than energy transfer. A detailed report of our investigation of the mechanism of the $Ru(bipy)_3^{2+}$ sensitization reaction will be published separately;[17b] these studies rule out electron transfer from $Ru(bipy)_3^{2+}$ triplet states as a predominant reaction mode for the systems described in the present report.

Experimental Section

The complexes were prepared by literature procedure.[26–28] Continuous irradiations were carried out using a Model 720 spectral irradiator (Xenon Corp., Medord, Mass.)[19,20] or with a low-pressure Ultraviolet Products Inc., immersion lamp[10] and a high-intensity, low-pressure mercury lamp.[5] The latter source was mainly used for the experiments in which carbon dioxide analysis was done quantitatively. Irradiations at 214 nm were carried out with a Philips zinc lamp;[19b] a Philips cadmium lamp was used for irradiations at 229 nm. Incident light intensity was measured using ferrioxalate actinometry or uranyl oxalate actinometry.[29,30] Constancy of the light beam was checked frequently before and after irradiations using a thermopile and microvoltmeter.[19,20]

Solutions of $Ru(bipy)_3^{3+}$ were prepared by means of the PbO_2 oxidation of $Ru(bipy)_3^{2+}$ in 1 M H_2SO_4.

Photolyses were carried out while bubbling Cr^{2+} scrubbed nitrogen gas to deaerate the solution. For quantum yield measurements the concentration of the irradiated solution was adjusted so that more than 99% of the incident light was absorbed.

Quantitative determination of carbon dioxide was made using a F and M Model 720 dual column programmed gas chromatograph. Known amounts of carbon dioxide were used to calibrate the instrument and a Toepler pump was used to collect the gas sample from the sealed and evacuated irradiation cell.

Flash photolysis was performed using a Xenon Corp. apparatus.[11,19] A 250-J pulse with a half-life of 30 μsec was used. Transients were monitored using a Tektronix storage oscilloscope.[11,19]

For the sensitization experiments the concentration of the sensitizer was so adjusted that it absorbed >95% of the light. After we had completed the major portion of the work reported here, we discovered that there is some nearly reversible photochemistry ($\phi \sim 10^{-3}$) associated with $Ru(bipy)_3^{2+}$ which might in principle affect the sensitized product yields.[31] In examining these systems more closely we have also found that $Ru(bipy)_3^{2+}$ is very susceptible to oxidation by various radicals and that the resulting $Ru(bipy)_3^{3+}$ is a metastable species under the prevailing conditions of our photolyte solutions.[17b] Thus, the apparent constancy of sensitizer absorptivity at the excitation wavelength (λ 450 nm; ϵ 1.4×10^4 M^{-1} cm^{-1}) is not a sufficient criterion for determining that there

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(18) Although with $Co(NH_3)_6^{3+}$ there are grounds to believe that the lowest energy CT triplet is appreciably higher in energy than the lowest energy ligand field triplet state ($\gtrsim$21 kK compared to ~12 kK; these estimates will be described in detail elsewhere), this may not be the case for complexes containing more easily oxidized ligands; for example, these lowest energy triplets may be of comparable energy in $Co(NH_3)_5Br^{2+}$. Also note that proper accounting for the contribution of radical reactions would probably make the limiting yield in ref 9b about 0.4.

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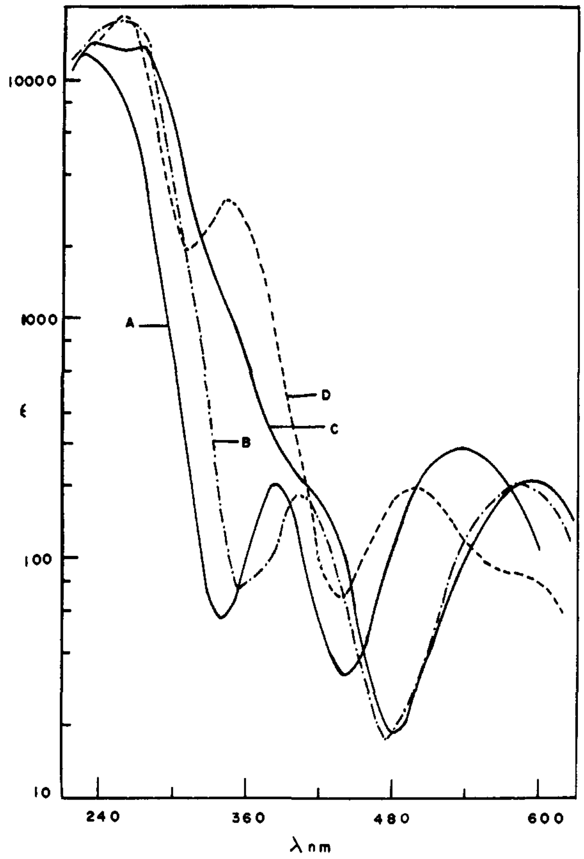


Figure 1. Absorption spectra of Co(HEDTA)X$^-$ complexes: (A) Co(EDTA)$^-$; (B) Co(HEDTA)Cl$^-$; (C) Co(HEDTA)Br$^-$; (D), Co(HEDTA)NO$_2$$^-$.

are no chemical complications in the sensitization studies. Detailed studies of the sensitization mechanism and many aspects of the associated radical reactions will be published separately.[17b] In the present report we describe the sensitization products and yields.

Photosensitization experiments were carried out in 0.1 *M* HClO$_4$, 0.1 *M* H$_2$SO$_4$, and 1.0 *M* H$_2$SO$_4$. Since [Ru(bipy)$_3$](ClO$_4$)$_2$ is not very soluble in 0.1 *M* HClO$_4$, but precipitates slowly (on standing a few hours), freshly prepared solutions (often prepared from Ru(bipy)$_3$Cl$_2$) could be used with convenience. The Ru(bipy)$_3$$^{2+}$ emission was stimulated and recorded using an Aminco-Bowman fluorimeter, and the solutions for emission experiments were thoroughly deaerated by purified N$_2$ through rubber stopper sealed cells.

Attempts to separate photoaquation products (Co(EDTA)$^-$ and X$^-$) using anion exchange resins were unsuccessful as the resins were found to catalyze aquation of Co(HEDTA)X$^-$. Since the absorption spectra (Figure 1) of Co(HEDTA)X$^-$ complexes differ significantly from the spectra of Co(HEDTA)OH$_2$ (Figure 2) and Co(EDTA)$^-$, we have used spectral changes to determine the extent of aquation. Since irradiations were performed at pH $\simeq$ 1.0, the immediate aquation product is presumed to be Co(HEDTA)OH$_2$; the aquo complex eventually converts to Co(EDTA)$^-$ on standing in acidic aqueous solution. For comparison purposes Co(HEDTA)OH$_2$ has been prepared from Co(HEDTA)Br$^-$ by means of the stoichiometric precipitation of AgBr in acidic solutions. Solutions of Co(HEDTA)OH$_2$ and Co(EDTA)$^-$ have very similar absorption spectra (Figures 1 and 2) in 0.1 *M* HClO$_4$.

Since the complex ion Co(HEDTA)ONO$^-$ is unknown, quantum yield determinations for linkage isomerization had to be indirect. The initial spectral changes (Figure 2) observed on irradiating ligand field bands did not result from Co^{2+} or correspond to the presence of Co(EDTA)$^-$ or Co(HEDTA)OH$_2$; the only other process possible would yield the linkage isomer, as in the case of Co(NH$_3$)$_5$NO$_2$$^{2+}$.[32] The initial spectral changes which we have observed on irradiating Co(HEDTA)NO$_2$$^-$ are analogous to those reported for Co(NH$_3$)$_5$NO$_2$$^{2+}$, and the yields of Co(HEDTA)ONO$^-$ have been estimated by assuming the same ratio of extinction coefficients and relative band maxima for the EDTA complexes as previously found for the ammines.

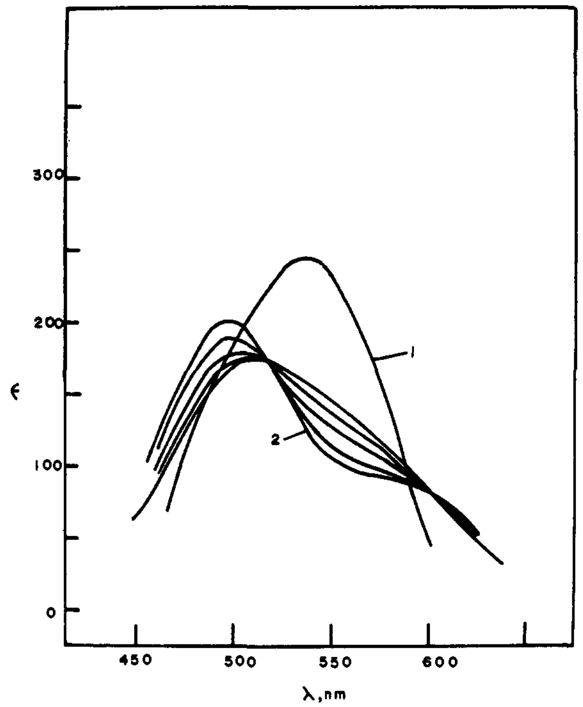


Figure 2. Visible spectrum of Co(HEDTA)OH$_2$ (1) and spectral changes which occur upon ligand field irradiation of Co(HEDTA)NO$_2$$^-$ (2). Irradiations of 10 min duration at 400 nm. On standing, the product spectrum eventually changes to the Co(HEDTA)OH$_2$ spectrum. Approximate isosbestic points at 518 and 600 nm.

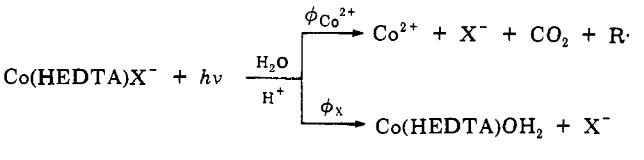
Cobalt(II) was analyzed by the ammonium thiocyanate method.[11,33] In the photosensitization experiments it was necessary to remove the Ru(bipy)$_3$$^{2+}$ from solution in order to determine the extent of aquation spectrophotometrically. The separation was accomplished using a cation exchange resin (Bio-Rad Ag 50W-X2 or X4, 200–400 mesh; Na$^+$ form). After a correction was made for the amount of Co^{2+} formed in the sensitization, the extent of aquation was determined from the absorbance differences between the cation exchanged photolyte and a blank solution of Co(HEDTA)X$^-$ treated by the identical procedure.

Results

A. Direct Photolysis. Product Yields in Aqueous Solution. The only thermal reaction observed for the Co(HEDTA)X$^-$ complexes is aquation of the acido group.[28,34]

$$\mathrm{Co(HEDTA)X^- + H_2O \longrightarrow Co(HEDTA)OH_2 + X^-}$$

No thermal linkage isomerization has been reported for Co(HEDTA)NO$_2$$^-$. Irradiation of these complexes in acidic aqueous solution results in both oxidation–reduction reactions and labilization of the acido ligands (including linkage isomerization in the case that X = NO$_2$).[35]



$$\mathrm{Co(HEDTA)X^- + h\nu \xrightarrow[H^+]{H_2O} \begin{cases} \xrightarrow{\phi_{Co^{2+}}} Co^{2+} + X^- + CO_2 + R\cdot \\ \xrightarrow{\phi_X} Co(HEDTA)OH_2 + X^- \end{cases}}$$

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(35) The radicals formed in photoredox decomposition of Co(HEDTA)X$^-$ complexes generally appear to be *N*-methyleneethylenediaminetriacetate radicals. In the immediate reaction products this radical must be coordinated to cobalt(II) (see below).

Table I. Product Yields from Irradiation of Co(HEDTA)X^- Complexes

X	Absorption band irradiated[a]	Irradiation wavelength,[b] nm	$10^5 \times I_a$, einstein l.$^{-1}$ min^{-1}	$\phi_{Co^{2+}}$ [c]	ϕ_X[c]
NO_2	LF	450	15	4×10^{-3}	4×10^{-3} 0.01[d]
	LF[e]	400	16	4×10^{-3}	4×10^{-3} 0.01[d]
	CTTM	300	1.7	0.069	
	CTTM	254	1.8	0.17	$\leq 10^{-3}$ 0.01[d]
	CTTM	229	0.62	0.25	$\leq 10^{-3}$
	CTTM	214	6.0	0.43	$\leq 10^{-3}$
Cl	LF	450	15	0.025	0.01
	LF	400	16	0.030	0.01
	CTTM	300	1.7	0.080	0.04
	CTTM	254	1.8	0.18	0.05
	CTTM	229	0.62	0.27	0.05
	CTTM	214	6.0	0.28	0.05
Br	LF	450	15	0.009	0.03
	LF[e]	350	3.5	0.035	0.09
	CTTM	300	1.7	0.056	0.03
	CTTM	254	1.8	0.14	0.04
	CTTM	214	6.0	0.45	0.03

[a] LF = ligand field; CTTM = charge transfer to metal. The free ligand also absorbs in the deep uv regions (200–230 nm), and there may be appreciable ligand-centered absorption in these regions. [b] Band half-width = ±20 nm except at 254, 229, and 214 nm where irradiation band half-widths are about 2 nm. [c] Average of 2 to 4 determinations, except as indicated. Average deviations are less than or equal to 10% of the value quoted except for instances where only one significant figure is cited. These are yields as determined experimentally. The primary quantum yield of Co^{2+} is probably $\simeq 1/2\phi_{Co^{2+}}$ as given here (see text and ref 17b). [d] Estimated yield for linkage isomerization. [e] Overlaps with low energy CTTM band.

The net product yields obtained at various wavelengths are summarized in Table I. In the case of Co(HEDTA)Cl^- and Co(HEDTA)Br^- we found $\phi_{Co^{2+}}$ to be the same at 25 and 45°.

Identification of Primary Radical Products. Photoredox processes, with either direct or sensitized (section B below) excitation, in Co(HEDTA)X^- complexes resulted in the net formation of Co^{2+} and CO_2 independent of X (Table II). The observed yields of CO_2 and Co^{2+} were in a ratio of about 1:1 in each case (ranging from 0.72 ± 0.07 to 1.0 ± 0.1). In the case of Co(HEDTA)Br^-, flash photolysis produced observable Br_2^- [36] in an amount approximately 25% of the concentration of substrate decomposed. However, the yield of Br_2^- increased markedly with [Br^-], becoming approximately stoichiometric with Co^{2+} in 0.1 *M* Br^-. It was not possible to ascertain from these studies how much of the Br_2^- resulted from the primary photochemical step since the flash photolysis of $Co(NH_3)_5Br^{2+}$, Co(HEDTA)Br^-, and Co(EDTA)$^-$ in 0.1 *M* Br^- each produced comparable amounts of Br_2^-. A critical examination of the reactions between Br^- and radicals from oxidation of EDTA will be presented in ref 17b. An additional radical reaction was found to be characteristic of all the Co(HEDTA)X^- and Co(EDTA)$^-$ complexes: the primary radical oxidation of $Ru(bipy)_3^{2+}$ to $Ru(bipy)_3^{3+}$ and a competitive but slower secondary radical reduction of $Ru(bipy)_3^{3+}$ to $Ru(bipy)_3^{2+}$. Oscilloscope traces showing the characteristic very rapid loss of $Ru(bipy)_3^{2+}$ absorbance at 480 nm, followed by a slower partial (or in the case that $X^- = NO_2^-$, a total recovery occurring in two stages) recovery of this absorbance, are presented in Figure 3. The radical reactions responsible for these reactions are discussed in detail in ref 17b.

Table II. Photoredox Product Yields from Excitation of Co(HEDTA)X^- Complexes[a]

X	10^3[Co(HEDTA)X^-], *M*	Product yields, mol × 10^6		$\phi_{CO_2}/\phi_{Co^{2+}}$
		CO_2	Co^{2+}	
NO_2	3.0	1.6	1.7	0.94
	2.0	3.5	3.2	1.1
	2.0[b]	0.20	0.22	0.92
Cl	3.0	6.0	5.8	1.03
	2.5[c]	1.3	2.5	0.55
	2.0[d]	0.15	0.22	0.68
	2.0[d]	0.17	0.24	0.74
	2.5[e]	0.12	0.46	0.27
	2.5[e]	0.27	0.72	0.38
	2.0[b]	0.45	0.54	0.83
Br	2.0	3.2	4.2	0.76
	3.0	0.9	1.43	0.63
	2.0	3.45	4.4	0.78
	5.0[f]	1.85	2.6	0.71
	1.0[d]	0.7	0.54	1.3
	2.0[d]	0.85	1.02	0.83
	2.0[d]	0.77	0.76	1.0
	2.0[b]	0.95	1.43	0.66
	2.0[b]	0.28	0.42	0.67

[a] Complexes irradiated at 254 nm with $I_a \simeq 3 \times 10^{-3}$ einstein l.$^{-1}$ min^{-1}, 25°, and 0.1 *M* $HClO_4$, except as indicated. [b] Irradiated at 214 nm; $I_a \simeq 6 \times 10^{-5}$ einstein l.$^{-1}$ min^{-1}. [c] Solutions containing 50% 2-propanol. [d] $Ru(bipy)_3^{2+}$ sensitization. Sensitizer irradiated at 450 nm, $I_a = 1.4 \times 10^{-4}$ einstein l.$^{-1}$ min^{-1}, in 0.1 *M* H_2SO_4. [e] $Ru(bipy)_3^{2+}$ sensitization. Sensitizer irradiated at 450 nm, $I_a \simeq 1.4 \times 10^{-4}$ einstein l.$^{-1}$ min^{-1} in 50% 2-propanol solutions 0.1 *M* in H_2SO_4. [f] Solutions containing 0.1 *M* NaBr.

Finally we have some evidence[37] that *N*-methylethylenediaminetriacetate can be isolated from the photoredox decomposition of Co(EDTA)$^-$ in the presence of alcohols. Thus, the primary radical resulting from photooxidation of EDTA can react with Br^-, $Ru(bipy)_3^{2+}$, or an alcohol. These radical reactions and

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Table III. Photoproducts from $Ru(bipy)_3^{2+}$ Sensitized Decomposition of $Co(HEDTA)X^-$

X	$\phi_{Co^{2+}}{}^{lim}$	$\phi_{X^-}{}^{lim}$	$k_q \times 10^9$,[a] M^{-1} sec^{-1}	$k_{q,Co(II)} \times 10^9$,[b] M^{-1} sec^{-1}	$k_{q,X} \times 10^9$,[c] M^{-1} sec^{-1}	χ_X[d]	Dq(X),[e] cm^{-1}
NO_2	0.71 ± 0.09	[f]	1.3	≥ 1[g]	≤ 0.3[g]	2.89	3120
Br	0.80 ± 0.03	0.10 ± 0.02	3.0	2.7	0.3	2.8[h]	1366
Cl	0.24 ± 0.01	0.40 ± 0.06	0.8	0.3	0.5	3.0[h]	1559
O_2CR[i]	0.10	[j]	0.3	≥ 0.03[g]	≤ 0.30[g]	3.16	2021

[a] From emission quenching assuming a triplet lifetime of 0.6×10^{-6} sec for $Ru(bipy)_3^{2+}$ (ref 25). [b] Rate constant for quenching by CTTM acceptor state, assuming $k_{q,Co} = k_q/(1 + \phi_{X^-}{}^{lim}/\phi_{Co^{2+}}{}^{lim})$. [c] Rate constant for quenching by ligand field acceptor state, assuming $k_{q,X} = k_q - k_{q,Co}$. [d] Optical electronegativity, ref 40. Estimated from $Co(HEDTA)X^-$ relative to $Co(HEDTA)Cl^-$. [e] Crystal field splitting parameters from ref 44. [f] Quantitative estimates of linkage isomerization were not possible. [g] Limiting rate constant estimated assuming $\phi_{Co^{2+}}{}^{lim} + \phi_{X^-}{}^{lim} \simeq 1$. [h] Pauling electronegativity: L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960. [i] $Co(EDTA)^-$. [j] Estimate of aquation not possible.

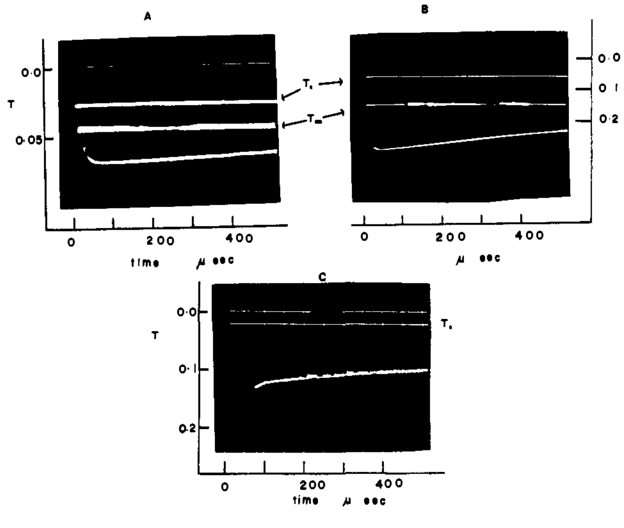

Figure 3. Transient changes in $Ru(bipy)_3^{2+}$ absorbance (480 nm) following a 40-μsec, 250-J flash pulse in 1 M H_2SO_4 solutions containing $Co(HEDTA)Cl^-$ (A), $Co(HEDTA)Br^-$ (B), or $Co(HEDTA)NO_2^-$ (C).

the different reactions of X· radicals are useful in distinguishing among possible oxidations of coordinated ligands.

Product yields for labilization reactions were determined from changes in absorption spectrum (allowing for Co^{2+} formation). The differences in spectra of $Co(HEDTA)OH_2$ and $Co(EDTA)^-$ are not large enough that we could make meaningful determinations for these complexes. For $Co(HEDTA)NO_2^-$, the changes in spectrum were appreciable and exhibited well-defined isosbestic points at 518 and 600 nm (Figure 2). The product formed in this case underwent further changes of spectrum over a period of several hours corresponding to the eventual formation of $Co(HEDTA)$-OH_2 in 0.1 M $HClO_4$. The most reasonable explanation of those observations is a photoinduced linkage isomerization, followed by acid hydrolysis of the Co-O-N-O product, analogous to the case of $Co(NH_3)_5NO_2^{2+}$.[32]

B. Photosensitization Experiments. The 450-nm light stimulated emission of $Ru(bipy)_3^{2+}$ ion was efficiently quenched by all of the acido EDTA complexes. The intensity of the emission was measured as a function of the quencher concentration. Assuming the intensity of the emission to be proportional to the quantum yield of the emission, plots of I_0^D/I^D *vs.* [quencher], where I_0^D and I^D are the emission intensities in the absence and in the presence of the quencher, were linear with unit intercept. Knowing the mean lifetime (0.6×10^{-6} sec) of the donor,[24] the bimolecular quenching constant was calculated to be ($1.3 \pm 0.1) \times 10^9$, ($0.8 \pm 0.1) \times 10^9$, and ($3.0 \pm 0.3) \times 10^9$ M^{-1} sec^{-1} for X = NO_2, Cl, and Br, respectively.

Quantum yields for photosensitized reactions were determined by using various [$Co(HEDTA)X^-$] and graphically determining the intercepts of plots of $1/\phi_{obsd}$ *vs.* $1/[Co(HEDTA)X^-]$. In order to accurately define ϕ^{lim}, two series of 3 to 6 determinations (with different [Co(III)]) were made for each acceptor substrate; first a series of sensitized yields was determined for solutions purged with Cr^{2+} scrubbed N_2, then a series of sensitized yields was determined for solutions through which air was passed. In each case the sets of data were found to be consistent with the Stern–Volmer relation,[38] $1/\phi_{obsd} = 1/\phi^{lim} + 1/K_s[Co(HEDTA)X^-]$. The value of ϕ^{lim} was taken as the common intercept of plots of $1/\phi_{obsd}$ *vs.* $1/[Co(HEDTA)X^-]$ for the aerated and deaerated series of studies. As noted in a previous study[20b] our deaeration procedures were necessarily far better in the emission quenching studies than in the sensitization studies; for this reason values of K_s tended to be of the same magnitude as $k_q\tau_D$ (τ_D = donor lifetime) but most often smaller than $k_q\tau_D$ in numerical value. In the case of $Co(HEDTA)Br^-$, K_s and $k_q\tau_s$ agree to within the stated error limits. Limiting photoredox and photoaquation yields are presented in Table III. Similar data for $Co(EDTA)^-$ [37] are included in Table III for convenient reference.

Discussion

In the present study we have obtained information which contributes both some remarkable reaction modes and a set of model systems, thus providing new insights into some of the problems and controversies in the photochemistry of cobalt(III) complexes.[2–5] On the other hand aspects of the present work[17a] have already generated some new controversies.[25] In order to deal adequately with the large number of issues, we have presented in a separate report[17b] most of those studies dealing specifically with the mechanism of the $Ru(bipy)_3^{2+}$ sensitization reactions and many aspects of the reactions of oxidized ligand radicals. The present report has as its primary focus the photochemical reaction modes of the cobalt(III) complexes and the mechanistic inferences which may be based on the sensitization studies.

A. Photoredox Processes and Stoichiometries. We

(38) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, N. Y., 1970, Chapter 11.

have found that the radicals generated from $Co(EDTA)^-$ and from the $Co(HEDTA)X^-$ complexes all have the following properties: (1) Co^{2+}, CO_2, and radicals R· are primary photolysis products, apparently generated in a 1:1:1 ratio;[17b] (2) the radicals R· or their successors appear to react further with $Co(EDTA)^-$ or $Co(HEDTA)X^-$ to produce additional Co^{2+} and CO_2 in a 1:1 ratio[17b] (additional products of this step may be CH_2O and one or more amino acids);[39] (3) the radicals R· oxidize Br^- and $Ru(bipy)_3{}^{2+}$ with rate constants near to the diffusion limit; (4) the R· oxidation of Br^- can be quenched by 2-propanol;[17b] and (5) a secondary species, which also may be a radical, and which can reduce $Ru(bipy)_3{}^{3+}$, is produced from R· either in an intramolecular reaction or in a very fast reaction of R· with the cobalt(III) substrate.[17b] By way of contrast, the X· radicals (X = Cl, Br, NO_2): (1) would not be formed in a primary step which also resulted in the evolution of CO_2; (2) can in principle produce secondary reducing species ($Cl_2{}^-$, $Br_2{}^-$, or $NO_2{}^-$), but these often react relatively slowly, are formed slowly in the case of NO_2, and would act as electron transfer reagents rather than generating CO_2; (3) NO_2 is not strong enough an oxidant[40] to oxidize Br^- or $Ru(bipy)_3{}^{2+}$; and (4) the formation of $Br_2{}^-$ from Br· is not quenched in 2-propanol.[17b] We conclude that in each case the EDTA ligand, rather than X^- (X = Cl, Br, NO_2), is photooxidized.

Examination of the charge-transfer absorption spectra of the $Co(HEDTA)X^-$ complexes (Figure 1) reveals that they exhibit many of the features of the charge-transfer spectra of $Co^{III}(NH_3)_5X$ complexes.[41] More specifically, the lowest energy CTTM absorption maxima decrease in energy in the order $Co(EDTA)^-$ > $Co(HEDTA)Cl^-$ > $Co(HEDTA)Br^-$ > $Co(HEDTA)NO_2{}^-$. Thus, it would appear reasonable to assume a relatively high optical electronegativity for EDTA (the optical electronegativity, based on the 230-nm absorption maximum, is of course lower than that of NH_3) and to assign the lowest energy transitions in the respective cases as EDTA → Co(III), Cl^- → Co(III), Br^- → Co(III), and $NO_2{}^-$ → Co(III), by analogy with the pentaammine complexes. It is therefore quite surprising that in each case irradiation of the low energy CTTM bands leads predominately to EDTA oxidation.

It is to be noted that the variations in the energies of their CTTM absorption maxima of the EDTA complexes might not reflect the order of variation of the ease of oxidizing the various ligands. For example, we find that irradiation ($I_a \sim 3 \times 10^{-3}$ einstein $l.^{-1}$ min^{-1}) of $Co(NH_3)_5Br^{2+}$ (10^{-3} *M*), in the presence of 2×10^{-3} *M* Na_2H_2EDTA, resulted in $\phi_{Co^{2+}}/\phi_{CO_2} \simeq 1.8$, indicating that reaction 1 occurs to some extent even though $k_2 \simeq 10^9$ M^{-1} sec^{-1}.[36] If we set $2[Br\cdot] \sim$

$$(Br\cdot \text{ or } Br_2{}^-) + H_2EDTA^{2-} \longrightarrow 2Br^- + CO_2 + R\cdot \quad (1)$$

$$2Br_2{}^- \longrightarrow Br_2 + 2Br^- \text{ or } 2Br\cdot \longrightarrow Br_2 \quad (2)$$

$(\phi I_a/k_2)^{1/2}$ and $k_1[H_2EDTA^{2-}]/k_2[Br\cdot] \sim 0.8$, then $k_1 \sim 3 \times 10^4$ M^{-1} sec^{-1}. However, since (1) is irreversible in acidic solution, due to evolution of CO_2, the fact that it occurs does not provide information about the relative oxidizing potentials of the radicals involved. In fact we have reported evidence elsewhere[17b] which indicates that R· in this case is probably a stronger oxidant than Br·. Nevertheless, our inference that the optical electronegativity of EDTA is greater than the optical electronegativity of X^- (X = Br or Cl) must be regarded as somewhat tentative.

Despite possible reservations with regard to the relative optical electronegativities of the halogens and EDTA, carboxylate oxidation is observed when $Co(HEDTA)NO_2{}^-$ is irradiated, and there can be little doubt about the relative energetics in this case; NO_2 is a relatively very poor oxidant.[40]

At the present time we believe that the most self-consistent, as well as the simplest, analysis of these observations is that the lowest energy spectroscopic CTTM excited states (all of singlet electronic spin multiplicity) decrease in energy in the order $Co(EDTA)^-$ > $Co(HEDTA)Cl^-$ > $Co(HEDTA)Br^-$ > $Co(HEDTA)NO_2{}^-$, and that the photochemical products are determined by factors other than the nature of the state initially populated by absorption of radiation. Of course, optical electronegativities do not provide direct information about the relative dissociation energies of the various excited state electronic manifolds; it is evident that the energy of (Co^{2+} + X· + EDTA) must be greater than the energy of (Co^{2+} + X^- + CO_2 + radical–EDTA) for X = Cl and Br.

It should be observed that while values obtained for $\phi_{Co^{2+}}$ in the cases of $Co(EDTA)^-$[17b] and $Co(HEDTA)Cl^-$ approach a maximum value with increasing irradiation energy, values of $\phi_{Co^{2+}}$ obtained for $Co(HEDTA)Br^-$ and $Co(HEDTA)NO_2{}^-$ may not. Since the kind of photoredox product was the same at all wavelengths, we infer that communication between the various CTTM excited states is reasonably good, but that the intersystem crossing yields vary with the electronic and possibly even the vibrational state reached by excitation.

Some of the features of the CTTM photochemistry of cobalt(III) do seem reasonably clear. The reactive states appear to have triplet spin multiplicity[17] and very high intrinsic yields (Table III) for redox product formation.[42] Direct excitation of the $Co(HEDTA)X^-$ complexes can produce aquation (or linkage isomerization) reactions, but with characteristically low quantum yields (Table I), while the $Ru(bipy)_3{}^{2+}$ sensitized aquation yields for $Co(HEDTA)Cl^-$ and $Co(HEDTA)Br^-$ are relatively higher (Table III). It is instructive to compare ϕ_X to $\phi_{Co^{2+}}$ for the several types of excitation of these two complexes. Thus, in the former case $\phi_X/\phi_{Co^{2+}}$ was found to be about 0.4 on ligand field excitation, to reach a limit of 0.18 on CTTM excitation, and to be 1.7 on $Ru(bipy)_3{}^{2+}$ sensitization; the respective values of $\phi_X/\phi_{Co^{2+}}$ for $Co(HEDTA)Br^-$ were found to be 2.6, 0.07, and 0.12. Such a wide variation of product yields with the energy of excitation and with the manner of excitation suggests a very complex situation. A relatively simple model which is capable of accounting for these observations is: (1) that the products are in each case produced

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(39) C. H. Langford, private communication.

(40) W. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952.

(41) (a) C. K. Jørgenson, *Mol. Phys.*, 2, 309 (1959); (b) *ibid.*, 5, 271 (1962); (c) "Orbitals in Atoms and Molecules," Academic Press, New York, N. Y., 1962.

(42) This statement is consistent with quinoline sensitized[16] as well as the biphenyl sensitized[9] photoreduction of $Co(NH_3)_6{}^{3+}$ if the quenching of the triplet donor in the former case can occur by means of a path competitive with the population of the triplet CTTM state.

from excited states of triplet spin multiplicity; (2) population of a ligand field state results in the aquation reactions and population of a charge-transfer state results in redox reactions; (3) the ligand field and charge-transfer states do not communicate efficiently; and (4) the efficiency of populating the reactive ligand field and charge-transfer triplet states varies with the nature of the vibronic state reached on direct excitation or on the nature of the triplet sensitizer. A lack of communication between CTTM and ligand field excited states has been noted among pentaamminerhodium(III) complexes[20] and may be a general characteristic of excited states of nd^6 metals. The high intrinsic product yields from states of triplet spin multiplicity suggests that these states are shallow compared to RT (at 25°, see similar comments on ligand field excited states of rhodium(III) in ref 20b); thus, these states may have very short lifetimes which may account for their experimentally observed lack of communication.

The higher sensitized than direct excitation yields are suggestive of very efficient relaxation of the singlet excited states. The model proposed for relaxation of the CTTM excited states of $Rh(NH_3)_5I^{2+}$ [20b] directly to the ground state may be applicable in part here.

B. Photoaquation Processes. This study demonstrates that ligand field excited states of triplet spin multiplicity can be very reactive in cobalt(III) complexes. The apparent insensitivity[43] to direct excitation of the ligand field bands of cobalt(III) complexes may arise from a very small ligand field singlet → ligand field triplet intersystem crossing yield.[17a]

In the case of $Co(HEDTA)Br^-$, the yield of Br^- aquation goes through a maximum when the complex is irradiated at about 350 nm (Table I). This unusual behavior may also be a feature of the photochemistry of $Co(NH_3)_5Br^{2+}$ (compare the yields reported for irradiation in the near ultraviolet[3,4] to those reported at 254 nm[5]). The $Co(HEDTA)Br^-$ transition excited at 350 nm appears to be largely CTTM in character, although there is strong overlap with a ligand field band (Figure 1). If the CTTM singlet excited states undergo electronic relaxation more rapidly than vibrational relaxation, then this behavior could be characteristic of population of low energy vibrational levels in a CTTM singlet electronic excited state manifold. The behavior itself indicates that the state reached has a relatively high yield for intersystem crossing into a reactive ligand field state. This interesting behavior would certainly bear closer and more careful study.

C. Linkage Isomerization of $Co(HEDTA)NO_2^-$. It appears that $Co(HEDTA)NO_2^-$, like $Co(NH_3)_5NO_2^{2+}$,[32] undergoes linkage isomerization when its absorption bands are irradiated. The present case is free of some of the ambiguities which made interpretation of the photochemistry of $Co(NH_3)_5NO_2^{2+}$ difficult. In the present case linkage isomerization is the predominant reaction resulting from irradiation of the ligand field absorption bands. The relatively small redox yields resulting from these excitations indicate that linkage isomerization is independent of the formation of NO_2. Unfortunately, the source of the isomerization reaction is further complicated by the existence of low energy ligand centered electronic excited states.[44,45]

Owing to sensitizer absorptivity and difficulties separating reaction products, we have been unable to determine whether linkage isomerization in $Co(HEDTA)NO_2^-$ can be sensitized by $Ru(bipy)_3^{2+}$.

D. Triplet-to-Triplet Quenching Kinetics with $Co(HEDTA)X^-$ Substrates. The quenching constants, k_q, deduced from the $Co(HEDTA)X^-$ quenching of $Ru(bipy)_3^{2+}$ phosphorescence are relatively insensitive to errors from oxygen and other impurities and so can be used as a relative measure of the variations in the efficiency of the triplet-to-triplet quenching efficiency with changes in the ligands X. Superficially we observe about a tenfold variation of k_q, with values of k_q increasing as $\phi_{Co^{2+}}{}^{lim}$ increases (Table III). Since the two observed reaction modes, redox and aquation, seem to occur for all excitations, but with product yields (and ratios of product yields) varying with the energy and manner (*i.e.*, whether direct or sensitized) of excitation, we infer that these two processes are largely uncoupled (as proposed in the model introduced above). Since both of these processes occur in the sensitized reactions, it seems reasonable to propose that CTTM and ligand field triplet states are competitively populated in the $Ru(bipy)_3^{2+}$ sensitizations (eq 3 and 4). In three of the four cases listed in Table III ($\phi_{Co^{2+}}{}^{lim} + \phi_{X^-}{}^{lim}$) approaches 1. It should be approximately true that $k_{q,X}/k_{q,Co} = \phi_X{}^{lim}/\phi_{Co^{2+}}{}^{lim}$, where $k_q = k_{q,X} + k_{q,Co}$. Values of the quenching rate constants so estimated have been included in Table III. In the case of $Co(EDTA)^-$ it has proved to be experimentally infeasible to detect aquation under our experimental conditions. For this case and for $Co(HEDTA)NO_2^-$ we have listed limiting values of $k_{q,X}$ and $k_{q,Co}$ based on the assumption that for these complexes ($\phi_X{}^{lim} + \phi_{Co^{2+}}{}^{lim}$) ~ 1.0.

$$Ru(bipy)_3{}^{2+}(T_1) + Co(HEDTA)X^-({}^1A_1) \xrightarrow{k_{q,X}} Ru(bipy)_3{}^{2+}(S_0) + Co(HEDTA)X^-(T_{LF}) \quad (3)$$

$$Ru(bipy)_3{}^{2+}(T_1) + Co(HEDTA)X^-({}^1A_1) \xrightarrow{k_{q,Co}} Ru(bipy)_3{}^{2+}(S_0) + Co(HEDTA)X^-(T_{CT}) \quad (4)$$

There are two remarkable features of the relative rate constants deduced for reactions 3 and 4. Finally, the values of $k_{q,X}$ are all about the same, $10^8\ M^{-1}\ sec^{-1}$. On the basis of variations in crystal field strengths of ligand X[46] (and by analogy to $Rh(NH_3)_5X^{2+}$ [45,47]) we would estimate that lowest energy ligand field triplet states in the $Co(HEDTA)X^-$ complexes vary in their energies over a range of 2 kK which would result in about a 10^4-fold variation in $k_{q,X}$ if it is not diffusion

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[43] The values of ϕ_X in Table I are in many cases larger than aquation yields of the corresponding pentaammine complexes; furthermore, recent work in this laboratory (G. Ferraudi and J. F. Endicott, unpublished observations) indicates a high yield for ammonia aquation (ϕ_{NH_3} ~ 0.3) on ligand field excitation of $Co(NH_3)_5N_3^{2+}$.

[44] H. J. Maria, A. T. Armstrong, and S. P. McGlynn, *J. Chem. Phys.*, **48**, 4694 (1968).

[45] T. R. Thomas and G. A. Crosby, *J. Mol. Spectrosc.*, **38**, 118 (1971).

[46] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

[47] If the triplet state of $Rh(NH_3)_5I^{2+}$ is about 19 kK (based on the high energy with about 1% of the emission intensity of the phosphorescence maximum[45]) above the ${}^1A_1$ ground state, then in $Co(HEDTA)X^-$ the analogous triplet states (assuming crystal field splittings are in the ratio of 36:24 for rhodium(III) and cobalt(III) and values of Dq as tabulated in ref 46) are at 15, 13.8, 13.3, and 13.1 kK respectively for $Co(HEDTA)NO_2^-$, $Co(EDTA)^-$, $Co(HEDTA)Cl^-$, and $Co(HEDTA)Br^-$.

limited, and if it depends only on the energy difference[13,40,48] between donor and acceptor.[38] Both the relative constancy of $k_{q,X}$ and the relatively small magnitude of these constants argue that the magnitude of the gap between the energies of donor and acceptor states is not the sole nor always the most important factor determining the rate of triplet-to-triplet energy transfer.

The rates of Ru(bipy)$_3^{2+}$ sensitized excitation of CTTM states in Co(HEDTA)X$^-$ complexes vary by about 10^2 as the ligand X is changed from Br to O$_2$CR (*i.e.*, for Co(EDTA)$^-$); the variation is about tenfold on changing X from Br to Cl. This sensitivity of $k_{q,Co}$ to X is about the magnitude expected if the CTTM triplet acceptor states vary in their energies in about the same way as do the CTTM spectroscopic (X$^-$ → Co(III); see section A above) states through the series of four compounds. Yet in each instance, the products of sensitized CTTM excitation correspond to oxidation of carboxylate ligands, not X$^-$. The sensitivity to X of $k_{q,Co}$ for a process yielding carboxylate oxidation can be reconciled if the electronic manifolds for the X$^-$ → Co(III) and the RCO$_2^-$ → Co(III) CTTM triplet states are strongly interacting and, in a limiting case, if the latter state has a lower dissociation energy than the former as illustrated in Figure 4.

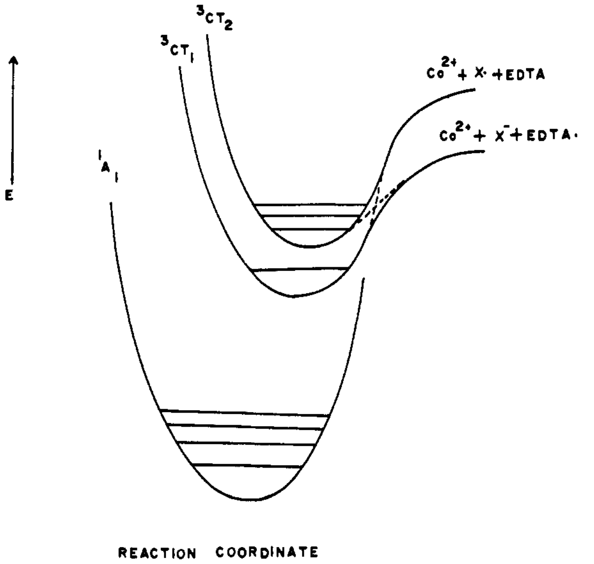

Figure 4. Hypothetical potential energy surfaces for CTTM excited states of triplet spin multiplicity. Charge transfer to metal triplet excited states correspond to X$^-$ → Co^{III}(^{3}CT$_1$) and RCO$_2^-$ → Co^{III}(^{3}CT$_2$).

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[48] D. A. Buckingham and A. M. Sargeson, "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, Chapter 6.

Mass Spectrometric Study of Polydentate Schiff Base Coordination Compounds. I. Cobalt(II), Nickel(II), and Copper(II) Complexes of Salen[1] and Oaben[2]

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Abstract: Positive and negative ion mass spectra have been measured for the cobalt(II), nickel(II), and copper(II) neutral complexes with Salen and Oaben. Parent ion clusters are detected in both the positive and negative ion mass spectra. Polymeric positive ions containing two metal ions and a single ligand are detected in low abundance for all compounds. Ionization potentials of the compounds have been measured. Fragmentation patterns for the metal-containing ions are presented and discussed. The fragmentation patterns suggested are supported by metastable transitions.

Metal coordination compounds play an important role in biological energy transfer systems.[3] Schiff base metal complexes may show some utility as model compounds for describing energy transfer for certain of these biological molecules. Ionization data and appearance potential information may be of importance to an understanding of the energy levels in these complexes and the application of theoretical models to describe the levels. A systematic study of neutral coordination compounds of polydentate Schiff base ligands with the first-row transition metals has been initiated.

The mass spectra of metal chelates including β-diketones as ligands have been investigated.[4-12] In

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[1] Salen = bis(salicylidene)ethylenediamine.

[2] Oaben = bis(*o*-aminobenzylidene)ethylenediamine.

[3] "Bioinorganic Chemistry," *Advan. Chem. Ser.*, No. **100** (1972).

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