discussions and their contributions relating to spectroscopic studies of the system described.

Note Added in Proof. An EXAFS study of **2** and related relevant compounds reveals that the Cu···Cu distance in this dioxygen complex is 3.31 Å.[41] This finding precludes a μ-1,1-type of peroxo coordination to the dicopper(II) center. The resonance Raman investigation shows that the peroxo ligand is bound in an asymmetric fashion, suggesting either a terminal coordination to a single Cu(II) atom or a μ-1,2 peroxo binding to inequivalent coppers.[28]

Supplementary Material Available: ORTEP diagram of the complete cation of **3b** and listings of bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors for **1** (Tables VII-X) and **3b** (Tables XII-XV) (21 pages); listings of structure factors (33 pages). Ordering information is given on any current masthead page.

Effect of a Dipole Moment on the Ionic Strength Dependence of Electron-Transfer Reactions of Cytochrome *c*

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Abstract: The ionic strength dependence of electron-transfer reactions between metal ion complexes of varying overall charge, $Fe^{II}edta^{2-}$, $Fe^{II}cydta^{2-}$, $Fe^{II}dtpa^{3-}$, $Co(oxalate)_3^{3-}$, and $Ru(NH_3)_6^{2+}$, and horse-heart ferri- and ferrocytochrome *c* was measured. Cytochrome *c* has a large dipole moment (~300 D) which intersects the protein surface near the presumed site of electron transfer close to the solvent accessible haem edge. The equation derived by Van Leeuwen et al. [*Biochim. Biophys. Acta* **1981**, *635*, 434], which, in addition to net charges, takes into account the dipole moment of a protein, fits the experimental ionic strength dependences very well. The following known parameters were inserted in the equation: net charges of $+7e$ and $+6e$ for ferri- and ferrocytochrome *c*, respectively, an angle of 30° between the dipole vector and the haem plane, and dipole moments of 312 and 300 D for ferri- and ferrocytochrome *c*, respectively.

Studies of reactions of singly modified horse heart cytochromes *c* with small redox agents showed that electron transfer takes place at the solvent accessibile haem edge,[1-4] which forms only 0.6% of the total surface area[5] of the molecule. The distribution of charges on the surface of cytochrome *c* is asymmetric.[6] It guides negatively charged redox agents to a location near the haem edge and increases thereby the number of productive encounters. One would expect the dipole moment to have an effect on the ionic strength dependence of the simple reactions of cytochrome *c* with small, charged, molecules. Currently, there are only two theories which take into account the effect of a dipole moment on the kinetic ionic strength effect. While these theories are in agreement with each other as far as the effect of net charges on the ionic strength dependence is concerned, the equation derived by Koppenol[7] indicates a contribution from the dipole moment to the ionic strength dependence which is approximately twice as large as that predicted by the theory of Van Leeuwen et al.[8] Both theories could be used to estimate the site of electron transfer relative to the dipole axis of a protein molecule if the location of this site were unknown. Neither theory has been applied to kinetic data obtained over a wide range of ionic strengths. We report here on the ionic strength dependences of the reactions of a protein molecule with a known site of interaction, cytochrome *c*, with a variety of small redox agents. Equations which take into account only the net charge of the reactants do not adequately describe the reactions, while the equation derived by Van Leeuwen et al.[8] fits the observed dependences quite well.

Experimental Section

Kinetic experiments were performed either with a Beckmann DU-6 HS spectrophotometer or a Kinetic Instruments, Inc. stopped-flow apparatus equipped with an OLIS optical system and data acquisition system (OLIS 3920). All experiments requiring anaerobic conditions were performed with the stopped-flow apparatus. Ionic strength was maintained with NaCl. The contribution to ionic strength from the buffer (Na,K-phosphate, pH 7.0 ± 0.2) was included. At low salt concentrations (0.1 mM ≤ ionic strength ≤ 5 mM) the buffer contributed up to 15% to the ionic strength and ca. 5% at higher ionic strengths. pH's were checked at the stopped-flow exhaust port when small buffer concentrations were employed. Experiments were carried out at 25 °C.

Reactions were studied at 550 nm under pseudo-first-order conditions in mediator concentrations. Rate constants were the mean of three runs (generally reproducible to within 5%), and bimolecular rate constants were calculated from three runs over a four-to-eight-fold range of mediator concentrations.

Solutions of horse heart ferricytochrome *c*, Type VI (Sigma), were freshly prepared and degassed with N_2 (99.99%) for a minimum period to prevent denaturation. Ferrocytochrome *c* was prepared by reaction with sodium ascorbate, followed by gel filtration (Sephadex G-15) and elution with deaerated (N_2) 0.2 M phosphate buffer.

Stock solutions of the ferrous edta, dtpa, and cydta complexes were prepared by dissolving $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in a deaerated (N_2) solution containing 30% excess of ligand. The purity of the synthesized ruthenium(II) hexammine chloride[9] was determined to be 98±% by comparison of its absorption spectrum with literature values[10] [$\lambda_{max}(\epsilon)$ = 275 nm (640 M^{-1} cm^{-1}), 385 nm (40 M^{-1} cm^{-1})]. Solutions of this compound are reported to react slowly with dissolved N_2. Therefore, small amounts of solution were prepared and used within 10 min. Potassium (trisoxalato)cobaltate(III) was prepared by oxidizing a $CoCl_2$-$K_2C_2O_4$ (1:3) solution with lead dioxide and precipitating the green

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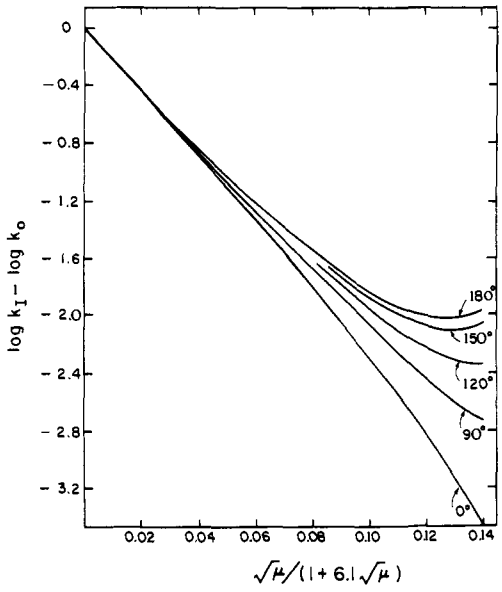

Figure 1. Simulation of the ionic strength dependences of the reaction of $Fe^{II}dtpa^{3-}$ with ferricytochrome *c* as a function of the site of electron transfer. The angles given refer to the angles between the dipole vector and the vector from the center of mass to the site of electron transfer.

product crystals with ethanol. Final concentrations of stock solutions were determined by the absorption spectrum of the $Co(C_2O_4)_3^{3-}$ ion [$\lambda(\epsilon)$ = 425 nm (230 M^{-1} cm^{-1}), 605 nm (175 M^{-1} cm^{-1})].[11] The chemicals used directly were of reagent grade. Water was doubly distilled or purified by reverse osmosis (Osmonics) followed by deionization and filtration (Mar Cor Services, Inc.).

Results

Equations 1[8] and 2[12] were used for the evaluation of kinetic ionic strength data.

$$\ln k = \ln k_0 + \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0\epsilon k_B T R}\left[1 - \frac{e^{-\kappa R_2}}{1+\kappa R_1}\right] + \frac{Z_2 e P_1 \cos\theta}{4\pi\epsilon_0\epsilon k_B T R^2}\left[1 - \frac{1+\kappa R}{1+\kappa R_1}e^{-\kappa R_2}\right] \quad (1)$$

$$\ln k = \ln k_\infty - \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0\epsilon k_B T R}\left(\frac{1}{2}\left[\frac{e^{-\kappa R_2}}{1+\kappa R_1} + \frac{e^{-\kappa R_1}}{1+\kappa R_2}\right]\right) \quad (2)$$

Their derivations are based upon the electrostatic energy of a small ion in the field of a much larger protein molecule. Equation 1 differs in that a term for the protein dipole is included. Abbreviations used in eq 1, 2, and 3 are given in footnote 13.

Both equations reduce to the Brønsted–Debye–Hückel equation at low ionic strength.

$$\log k \simeq \log k_0 + \frac{2Z_1 Z_2 A\mu^{1/2}}{1 + 6.1\mu^{1/2}} \quad (3)$$

Simulations for the reaction of $[Fe^{II}dtpa]^{3-}$ with ferricytochrome *c* are depicted in Figure 1. As shown, eq 1 predicts that the kinetic ionic strength effect depends on the location of the electron transfer site relative to the dipole axis. A nearly straight line is obtained if the site of electron transfer is equatorial to the dipole axis. Such a dependence is also predicted by eq 2 and 3. For a reaction close to the haem edge one would expect an ionic strength dependence between that shown for an equatorial (90°) reaction site and a site at the positive end of the dipole vector (0°).

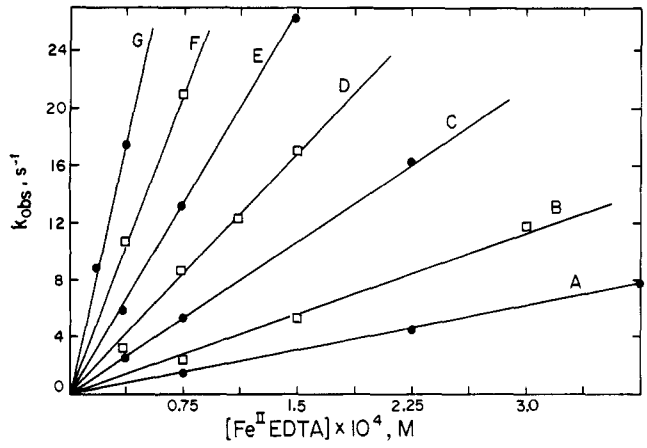

Figure 2. Kinetic data for reaction of $Fe^{II}edta^{2-}$ with ferricytochrome *c* at *t* = 25 °C and various ionic strengths. *I* = 0.10 M (A), 0.050 M (B), 0.025 M (C), 0.0125 M (D), 0.0063 M (E), 0.0025 M (F), and 0.00125 M (G).

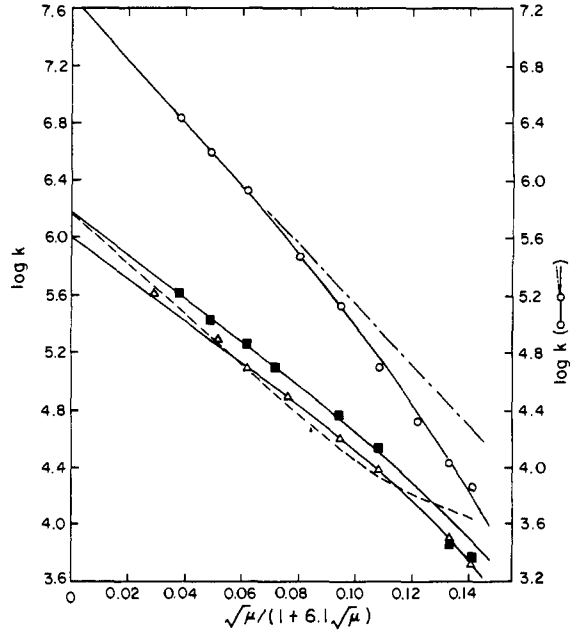

Figure 3. Ionic strength dependence of the reduction of ferricytochrome *c* by ferrous $edta^{2-}$ (Δ), $dtpa^{3-}$ (○), and $cydta^{2-}$ (■). NaCl was used as an inert electrolyte. The continuous curves are obtained with eq 1 for a net charge of +7, a dipole moment of 310 D, and an angle θ of 30°. The dashed line is a dependence predicted by eq 2 ($k_\infty = 1 \times 10^4$ M^{-1} s^{-1}). A net charge of +8 gives qualitatively the best fit. The dot-dashed line follows from eq 3.

Second-order rate constants for reactions 4–8 were determined as a function of the ionic strength. The above reactions were

$$Fe^{II}edta^{2-} + Fe^{III}\,c \rightarrow Fe^{III}edta^{-} + Fe^{II}\,c \quad (4)$$

$$Fe^{II}dtpa^{3-} + Fe^{III}\,c \rightarrow Fe^{III}dtpa^{2-} + Fe^{II}\,c \quad (5)$$

$$Fe^{II}cydta^{2-} + Fe^{III}\,c \rightarrow Fe^{III}cydta^{-} + Fe^{II}\,c \quad (6)$$

$$Co(C_2O_4)_3^{3-} + Fe^{II}\,c \rightarrow Co^{II} + Fe^{III}\,c + 3C_2O_4^{2-} \quad (7)$$

$$Ru(NH_3)_6^{2+} + Fe^{III}\,c \rightarrow Ru(NH_3)_6^{3+} + Fe^{II}\,c \quad (8)$$

well-behaved, i.e., the second-order rate constants were smooth functions of the ionic strength over most of the range studied. All were first order in redox agent concentration, as shown for reaction 4 in Figure 2. Below μ = 0.01 M, reaction 8 appeared to become independent of ionic strength for uncertain reasons, and measurements below 0.005 M were not continued.

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(13) Abbreviations used: *e*, elementary charge in coulombs; k_B, Boltzmann's constant; k_0, rate constant at zero ionic strength; k_∞, *idem* at infinitely high ionic strength; $2A$ = 1.02; P_1, dipole moment in coulomb·meter; *T*, temperature in K; R_1, "hydrated" radius; R_1 is the radius of cytochrome *c*, 17 Å plus that of a water molecule, 1.5 Å; R_2 is the radius of the inorganc redox agent; $R = R_1 + R_2$; Z_i, net charge is units of *e*; ϵ_0, permittivity constant; ϵ, static dielectric constant; θ, angle between dipole vector and vector from center of mass to site of electron transfer; $\kappa = 0.33^{1/2}\mu$ (unit, $Å^{-1}$); μ, ionic strength.

Table I. Parameters for Equation 1

mediator	radius,[a] Å	k_0, M^{-1} s^{-1}	Z(protein)
$Fe^{II}edta^{2-}$	4	1.0×10^6 M[c]	+7[c]
$Fe^{II}dtpa^{3-}$	4	1.16×10^7 [c]	+7[c]
$Fe^{II}cydta^{2-}$	4	1.45×10^6 [c]	+7[c]
$Co^{III}(C_2O_4)^{3-}$	3[b]	1750[c]	+6[c]
$Ru(NH_3)_6^{2+}$	3.3	1050	+7

[a] The data were calculated from van der Waals radii. [b] Approximate radii. [c] These parameters were also measured with eq 3 from low ionic strength data and are within ±5% of the parameters that fit eq 1.

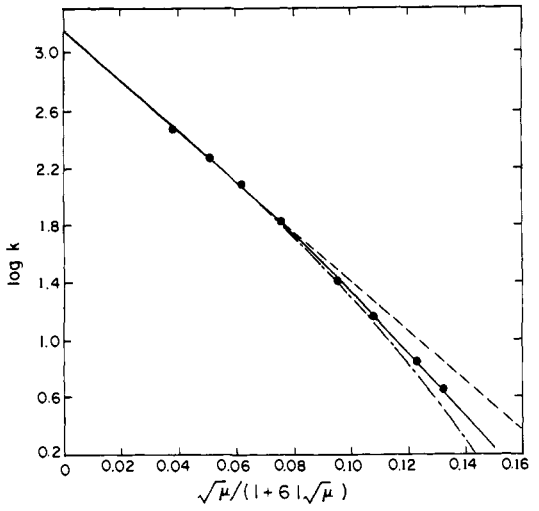

Figure 4. Ionic strength dependence of the oxidation of ferrocytochrome *c* by (trisoxalato)cobaltate(III). The continuous line is a fit according to eq 1 ($Z_1 = +6$, $\theta = 40°$, $P = 300$ D) with the dot-dashed line one for $\theta = 30°$, and the dashed line follows from eq 3.

The ionic strength dependences of reactions 4–6 are shown in Figure 3. Plotted against the function $\mu^{1/2}/(1 + 6.1\ \mu^{1/2})$ of eq 3, the data at $\mu < 0.01$ M become nearly linear for all three reactions. When divided by the charge of the small ion the slopes yield a charge $Z_1 = +7.0$ (± 0.2) for ferricytochrome *c*. Equation 1 reproduces the experimental data over the entire ionic strength range when an integral value of $Z_1 = +7$ and values of k_0 obtained by extrapolation of the Brønsted–Debye–Hückel slope were used. The parameters used to obtain the solid curves in Figure 3 are listed in Table I. The radius of the iron(II) complexes was taken as 4 Å. However, eq 1 is not very sensitive to small variations in this parameter.

The ionic strength data for the reactions 7 and 8 are shown graphically in Figures 4 and 5, respectively. The Brønsted–Debye–Hückel limiting slope for reaction 8 yields a charge of 6.1 ± 0.1 for ferrocytochrome *c*. The best fit to the data is given by eq 1 in which the interaction angle is 40° with respect to the dipole moment vector. However, there is no independent justification for increasing this angle, and alternatively, some ion-pairing of Na^+ with $Co(C_2O_4)_3^{3-}$ may reduce the average charge of the reactant species at higher ionic strength. The data for $Ru(NH_3)_6^{2+}$ are shown in Figure 5. Since low ionic strength data were not useable, the protein charge was postulated to be +7 and k_0 was adjusted to obtain the best fit of eq 1 to the data at $\mu > 0.005$ M. A qualitative fit using eq 2 predicts a tendency toward ionic strength independence at higher ionic strength which is not observed.

To study the effect, if any, of binding of the phosphate anion (HPO_4^{2-}) to cytochrome *c*, the reduction by ferrous edta was repeated at two ionic strengths, 25 and 100 mM, in the presence of 2.5 and 10 mM sodium cacodylate, respectively. The cacodylate anion reportedly does not bind to cytochrome *c*. The rate constants obtained, 8.3×10^4 and 2.5×10^4 M^{-1} s^{-1}, are 10% higher than those obtained in the presence of phosphate, 7.3×10^4 and 2.25×10^4 M^{-1} s^{-1}, respectively.

An estimated error of 5% in the rate constants (see Experimental Section) yields an absolute error of ±0.02 in log *k*. Error bars would have a length of 0.04, slightly larger than the symbols, and are not shown.

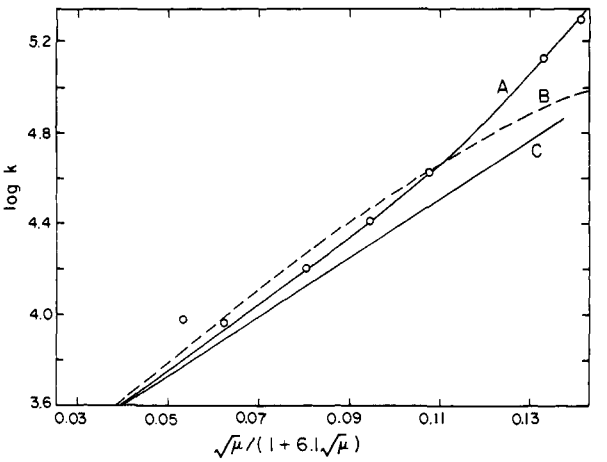

Figure 5. Ionic strength dependence of the reduction of ferricytochrome *c* by hexammine ruthenium(II). The solid line, A, is calculated from eq 1. The dashed line, B, is calculated from eq 2 ($k_\infty = 1 \times 10^5$ M^{-1} s^{-1}, $Z_1 = +8$), and line C is from eq 3, where $k_0 = 1050$ M^{-1} s^{-1} and $Z_1 = +7$.

Individual rate constants are compiled in Table II, available as Supplementary Material.

Discussion

In Table I, the parameter Z_1 for the protein net charge requires a charge of +7 on ferricytochrome *c* and +6 for ferrocytochrome *c*. For reactions 4–7 in which this parameter followed directly from the Brønsted–Debye–Hückel equation at low ionic strength, the uncertainties appear to be less than 5%, and for reaction 9 other integral values are not compatible with eq 1. The overall charge calculated for ferricytochrome *c* is +7 at pH 7 based upon charged amino acid residues, the haem charge, and two propionic side chains (23 positive minus 16 negative charges). The propionic acid groups of horse heart cytochrome *c* have been found not to ionize over the pH range 4.5–9.[14] However, it has been suggested that one or more of these groups have pK_a values below 4.5.[15,16] The inclusion of two additional propionate negative charges reduces the previously calculated dipole moment by ~4% (325 to about 310 D) for ferricytochrome *c*, and the angle of the dipole vector relative to the haem plane is virtually unchanged.[17]

Phosphate is known to bind to cytochrome *c* in two locations, a high affinity site near lysine 87 and a low affinity site close to residues 25–27.[18-20] Chloride has also been reported to bind to cytochrome *c*,[21,22] presumably near residues 13 and 60.[20,23,24] However, binding constants reported in the literature for either anion differ by many orders of magnitude as discussed by Osheroff et al.[19] Binding of anions and negatively charged reaction partners would reduce the net charge and change the dipole moment of cytochrome *c*. Thus, in cacodylate, a nonbinding buffer,[21] one would expect a stronger ionic strength dependence than in phosphate. However, the rate constants obtained at two different ionic strengths were 10% higher than those in phosphate, showing the same dependence on ionic strength. We do not consider the 10% difference significant. In addition, if binding with the reactants occurred, one would not observe consistently net charges

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of +7 and +6 for ferri- and ferrocytochrome *c*, respectively. We conclude that except possibly for high chloride concentrations binding phenomena do not interfere with our experiments.

The extent to which a dipole moment can influence a diffusion-controlled reaction with a negatively charged reactant has recently been calculated in a Brownian dynamics simulation study. When the active site is small compared to the total surface area of the protein, as is the case with cytochrome *c*, a line dipole (346 D) enhances the rate when the dipole vector pointed toward the active site, and this effect was also found at physiological ionic strength.[25] This study appears to be in qualitative agreement with the results reported here, although the reactions we studied are not diffusion-controlled.

It is remarkable that eq 1 fits the experimentally determined rate constants up to the highest ionic strength employed, while the Debye-Hückel theory breaks down above 0.1 M. We currently have no explanation for this phenomenon.

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Conclusions

The data presented in this study suggest that the dipole moment of cytochrome *c* contributes to its reactivity at biologically significant ionic strength. The magnitude of this effect depends strongly on the charge of the mediator. Equation 1, proposed by Van Leeuwen et al.,[8] accounts quantitatively for this effect. Significantly, this equation requires substantial structural information about cytochrome *c* to predict the direction and magnitude of the ionic strength dependence. It seems possible that the kinetic ionic strength effect may be useful in elucidating the interaction sites of proteins about which less is known than cytochrome *c*.

Acknowledgment. Supported by Grant GM 33883 from the National Institutes of Health.

Supplementary Material Available: Table of rate constants for the reactions studied (3 pages). Ordering information is given on any current masthead page.

Wavelength Dependence in the Ligand Field Photochemistry of Cobalt(III) Amines

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Abstract: The low quantum yield ligand field excitation photosubstitution reactions of Co(III) amine complexes are shown to be plausibly interpretable as the superposition of two component reactions. The first is an excitation wavelength-independent process which is associated with the ligand field triplet which has figured strongly in discussion of photosubstitution of the analogous Rh(III) complexes. The second is a wavelength-dependent reaction which is associated with direct reaction from the ligand field singlet. This interpretation of wavelength dependence in conjunction with recent interpretations of the picosecond transient absorption spectra suggests a unified model of the photochemistry of d^6 complexes.

Adamson's introduction of the use of lasers to allow accurate evaluation of the quantum yields of inefficient photoreactions[1] initiated an era of precise evaluation of the low-yield photosubstitution pathways exhibited by Co(III) amine complexes irradiated in their ligand field bands. The results supported an earlier impression, that the large differences in quantum yield might imply a significant mechanistic difference between Co(III) amines and the other d^6 complexes such as Rh(III) or Cr, Mo, and W(0) systems where photosubstitution yields are relatively large. Recently, we have reported subnanosecond flash studies of selected Co(III) complexes which might lead us to an alternate view.[2] In these studies we found a transient absorbance which could be associated with a ligand field triplet with a short lifetime. A consistent kinetic scheme implies that the reactivity of the ligand field triplet of a Co(III) complex may be quite similar to that of a Rh(III) complex[3] and that the difference between the two is mainly in the increased (by about 2 orders of magnitude) rate of radiationless decay of the triplet. The existence of a closely spaced quintet[4] provides a mechanism for this enhanced radiationless decay, as Adamson has observed.

In contrast, some years ago it was established that the reactivity of certain Co(III) amines is lower when the triplet region of the spectrum is directly irradiated,[5] and we have recently shown that this is not an abrupt change of reactivity between the singlet and triplet regions but rather reflects a progressive decrease of the mode of reactivity which characterizes irradiation near the singlet maximum as one scans across the low-energy side of the singlet absorption band. The present report expands these observations to include several Co(III) complexes and proposes, for *future evaluation*, a model which might unify the "differing" patterns of photochemistry of d^6 systems. It is based on a wavelength-independent pattern of reactions arising from vibrationally equilibrated triplets and a wavelength-dependent reaction arising in the singlet which occurs on time scales close to vibrational and/or solvent relaxations.

Experimental Section

Materials. All starting materials were reagent grade commercial products used without further purification. Water was deionized and doubly distilled. Other solvents were spectrograde.

$[Co(NH_3)_5Cl](NO_3)_2$ was prepared following ref 6. It was characterized by the visible spectrum.[7] *trans*-$[Co(en)_2Cl_2]NO_3$ was prepared by Krishnamurthy's method.[8] The corresponding *cis*-dichloro isomer

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