Picosecond Excited-State Dynamics in Octahedral Cobalt(III) Complexes: Intersystem Crossing versus Internal Conversion

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The results of transient absorption experiments are reported for aqueous solutions of the low-spin d^6 complexes $[Co(en)_3](ClO_4)_3$, $[Co(tpen)](ClO_4)_3$, and $[Co(tppn)](ClO_4)_3$, where en is ethylenediamine, tpen is tetrakis(2-pyridylmethyl)ethylenediamine and tppn is tetrakis(2-pyridylmethyl)-1,2-propylenediamine. Following excitation at 314 nm with a ~500-fs pulse, all three complexes exhibit biphasic relaxation kinetics. In the case of $[Co(tpen)]^{3+}$ excited-state decay is biphasic with relaxation time constants of $\tau_1 = 4 \pm 2$ ps and $\tau_2 = 44 \pm 5$ ps. The data for $[Co(tppn)]^{3+}$ give the similar values $\tau_1 = 3 \pm 1$ ps and $\tau_2 = 51 \pm 3$, whereas the data for $[Co(en)_3]^{3+}$ give $\tau_1 = 2 \pm 1$ ps and $\tau_2 = 450 \pm 100$ ps. On the basis of these results and the fact that no emission was observed for any of these complexes in the 350–900-nm range with a time-correlated single-photon-counting detection system, it is proposed that the lowest-energy excited state in these three Co^{III} complexes is the $^5T_2$ ligand-field state. Transient absorption spectra for the Co^{III} complexes indicate that the slower process (τ_2) is very likely a decay of the $^5T_2$ ligand-field state back to the $^1A_1$ ground state. Corresponding $^5T_2 \rightarrow {}^1A_1$ relaxation times for Fe^{II} complexes have been reported to be in the ~1–120-ns range. The faster process (τ_1) for each of the Co^{III} complexes is tentatively assigned as excited-state decay from the lowest-energy singlet state, the $^1T_1$ excited state. The results suggest that the ^1LMCT state in both $[Co(tpen)](ClO_4)_3$ and $[Co(tppn)](ClO_4)_3$ has a lifetime of <1 ps.

Introduction

Six-coordinate complexes of Co^{III} are among the oldest known and most widely studied transition metal complexes.[1] The stability of the Co^{III} oxidation state and its inertness to thermal ligand loss make these complexes relatively easy to prepare and analyze in solution. Octahedral Co^{III} complexes are isoelectronic with low-spin Fe^{II} complexes; thus Co^{III} analogs have often been used to help interpret the electronic spectra of Fe^{II} complexes. This is the context in which we first began examining the photophysics of Co^{III} complexes. The stronger effective ligand-field strength and change in the nature of the charge-transfer absorption induced by Co^{III} relative to Fe^{II} result in a blue shift of the charge-transfer band, allowing direct observation of ligand-field transitions which are obscured in the analogous Fe^{II} complex.

A review of the literature shows that little is known about the photo*physical* characteristics of six-coordinate Co^{III} complexes despite the large variety of molecules which have been prepared. There is considerable literature concerning the photo*chemistry* of Co^{III}, in particular complexes of the general form $[Co(L)_5X]^{n+}$ where L is usually NH_3 or CN^- and X is a monodentate ligand such as a halide (or X = L). In general, Co^{III} complexes can undergo two types of photochemical reactions: photoredox and ligand substitution. The photochemical quantum yields for substitution are low for complexes in the $[Co(NH_3)_5X]^{n+}$ subgroup; typical values reported[2] range from 10^{-2} to 10^{-4}. The photosubstitution yields for these complexes tend to be strongly wavelength dependent. For example, excitation of $[Co(NH_3)_6]^{3+}$ in the $^1T_{1g} \leftarrow {}^1A_{1g}$ absorption band results in photoaquation with a yield of 3.1×10^{-4}, whereas $^1T_{2g} \leftarrow {}^1A_{1g}$ excitation gives $\Phi = 5.4 \times 10^{-3}$.[2b,3a] In contrast, $[Co(CN)_5X]^{n-}$ complexes have photosubstitution quantum yields as large as 0.3 and do not exhibit a marked wavelength dependence.[3] These observations suggest that the low-lying excited electronic structures in these two types of complexes may be different.

While photosubstitution dominates upon ligand-field excitation of Co^{III} complexes, photoredox reactions have been observed following charge-transfer excitation of Co^{III} systems. The charge-transfer transitions in Co^{III} complexes are generally LMCT in nature, so the photoexcited state is formally Co^{II}. Since Co^{II} is much more coordinatively-labile than Co^{III}, it is no surprise that decomposition can accompany short-wavelength excitation. Photoinduced redox decomposition of $[Co(NH_3)_6]^{3+}$ following $^1LMCT \leftarrow {}^1A_{1g}$ excitation occurs with $\Phi = 0.16$.[4] Simple chelation does not inhibit the decomposition reaction, as $\Phi = 0.13$ for LMCT excitation of $[Co(en)_3]^{3+}$.[4,5] An extreme example of a chelation effect, however, is provided by $[Co(sep)]^{3+}$, where the complex has the form
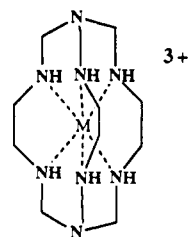
In this case, the lability of the Co^{II} excited state is much reduced; $\Phi < 10^{-6}$ was reported[6] for the quantum yield for photodegradation. The details of the photoredox and photosubstitution chemistry for octahedral Co^{III} complexes have been discussed by Endicott[7a] and Langford,[7b] respectively.

The only Co^{III} complex reported to exhibit emission is $[Co(CN)_6]^{3-}$. Several groups have reported[8] low-temperature

(1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988.

(2) (a) Adamson, A. W. *Discuss. Faraday Soc.* 1960, *29*, 163. (b) Poribush, R. A.; Pook, C. K.; Bruce, C. M.; Adamson, A. W. *J. Am. Chem. Soc.* 1974, *96*, 3027. (c) Endicott, J. F.; Ferraudi, G. *J. Phys. Chem.* 1976, *80*, 949.

(3) (a) Moggi, L.; Bolletta, F.; Balzani, V.; Scandola, F. *J. Inorg. Nucl. Chem.* 1966, *28*, 2589. (b) Ferraudi, G.; Endicott, J. F. *J. Chem. Soc., Chem. Commun.* 1973, 674. (c) Adamson, A. W.; Sporer, A. H. *J. Am. Chem. Soc.* 1958, *80*, 3865.

(4) Manfrin, M. F.; Varani, G.; Moggi, L.; Balzani, V. *Mol. Photochem.* 1969, *1*, 387.

(5) For a review of some of these reactions, see: Balzani, V.; Sabbatini, N.; Scandola, F. *Chem. Rev.* 1986, *86*, 319.

(6) Pina, F.; Ciano, M.; Moggi, L.; Balzani, V. *Inorg. Chem.* 1985, *24*, 844.

(7) (a) Endicott, J. F. In *Concepts in Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P., Eds.; Wiley: New York, 1975. (b) Langford, C. H. *Acc. Chem. Res.* 1984, *17*, 96.

luminescence of K$_3$[Co(CN)$_6$], with Solomon and co-workers[8b] describing as well the single-crystal electronic absorption spectrum of the complex. Emission at $\lambda \approx 715$ nm has been attributed to a $^1A_{1g} \leftarrow {}^3T_{1g}$ transition, with the corresponding absorption band centered at approximately $\lambda = 385$ nm. The large Stokes shift, which is to be expected for excited singlet and triplet ligand-field states in the d^6 configuration, was interpreted[8b] in terms of a tetragonally-distorted excited-state geometry involving both a$_{1g}$ and e$_g$ Co–C stretching vibrations. The only transient absorption spectroscopy which has been done on Co^{III} complexes was reported by Langford et al.[9] These workers performed excited-state kinetic measurements on [Co(NH$_3$)$_5$Cl]$^{2+}$, *cis*- and *trans*-[Co(en)$_2$Cl$_2$]$^+$, *trans*-[Co(en)$_2$(NO$_2$)$_2$]$^+$, and *cis*-[Co(en)$_2$(NCS)Cl]$^+$ following excitation at 355 nm with a $\sim$30-ps pulse from a mode-locked Nd:YAG laser. Data on the cis isothiocyanato complex show an excited-state absorption in the near-UV which rapidly decays (pulse width-limited) in favor of an absorption at $\lambda = 605$ nm; this latter transient had a measured lifetime of $\tau = 40 \pm 20$ ps. The dinitro complex was reported to exhibit similar transient absorption characteristics with a long-lived low-energy absorption band having $\tau_{obs} = 150 \pm 30$ ps. The transient absorption bands were tentatively assigned as $\pi^* \leftarrow {}^3T_{2g}$ by the authors. To our knowledge no follow-up to this communication has appeared.

In this study we present sub-picosecond time-resolved kinetic data on three six-coordinate, low-spin Co^{III} complexes. These data in conjunction with published data on the photochemistry of Co^{III} complexes allow us to construct a preliminary picture of the excited-state dynamics of Co^{III} complexes which is quite distinct from the picture developed for isoelectronic Fe^{II} complexes.

Experimental Section

All chemicals were purchased from either Aldrich or Fisher and used as received unless otherwise indicated. Optical spectra were recorded using a Hewlett-Packard HP8452A diode array spectrophotometer at ambient temperature. The ligands tpen and tppn were prepared as previously described.[10a]

Compound Preparation. The syntheses for [Co(tpen)](ClO$_4$)$_3$ and [Co(tppn)](ClO$_4$)$_3$ have been reported elsewhere.[10] The ligand was dissolved in a minimum amount of MeOH, and the mixture was added to an aqueous solution of CoCl$_2$·6H$_2$O (ca. 20 mL/mmol), resulting in a clear, pink solution. A small amount of activated charcoal (ca. 0.2 g for a 1-mmol reaction) was added to the reaction mixture, and air was drawn through the solution by vacuum for a period of approximately 12 h. The catalyst was filtered off, yielding a clear, deep-orange solution. An aqueous solution of NaClO$_4$ (e.g., 3 mmol in ca. 5 mL of H$_2$O) was added, and the reaction mixture was heated gently to remove the solvent. A powdered solid formed after evaporation of most of the solvent. The compound was recrystallized twice from hot H$_2$O, yielding a micro-crystalline solid following slow evaporation. The optical spectra of the compounds were identical to those reported in the literature.[10b]

[Co(en)$_3$](ClO$_4$)$_3$ was prepared analogously by following well-known synthetic procedures.[10d] The crude product was recrystallized twice from H$_2$O. The optical spectrum of the sample was identical to the known spectrum of the compound.

Sub-Picosecond Transient Absorption Spectroscopy. Kinetic measurements on the sub-picosecond time scale were performed on aqueous solutions of the Co^{III} complexes using a colliding-pulse mode-locked ring dye laser amplified at 10 Hz by a Q-switched Nd:YAG. The details of this apparatus are described in the literature.[11] Sample concentrations
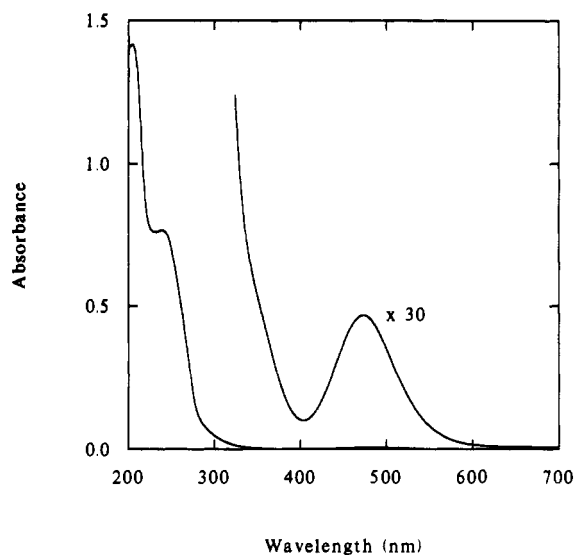
were on the order of 5 $\times$ 10^{-3} M for [Co(tpen)](ClO$_4$)$_3$ and [Co(tppn)]-(ClO$_4$)$_3$ and approximately 0.2 M for [Co(en)$_3$](ClO$_4$)$_3$.

Picosecond Time-Resolved Emission Spectroscopy. The apparatus used to search for emission from the Co^{III} complexes has been described in detail elsewhere.[12] The excitation beam was directed toward the sample, on occasion through a second harmonic generator to effect excitation in the UV. The sample was either placed in a 1-cm optical cuvette for room-temperature solution measurements or pressed between two optical plates for solid-state measurements at 77 K. Low-temperature measurements were achieved using an Air Products dewar. Light was collected at an angle of 90° to the excitation beam and focused onto the entrance slit of a Spex Model 1870 0.5-m monochromater. Single-photon detection was done using a Hamamatsu 1564U-01 microchannel plate (MCP) photomultiplier operated at –20 °C. This configuration resulted in dark current of less than 10 counts/s.

Results and Discussion

Transient Kinetics of [Co(tpen)](ClO$_4$)$_3$ and [Co(tppn)](ClO$_4$)$_3$. Two low-spin d^6 Co^{III} complexes with hexadentate ligands were studied: [Co(tpen)]$^{3+}$ and [Co(tppn)]$^{3+}$. The hexadentate ligands tpen and tppn have the following structures:
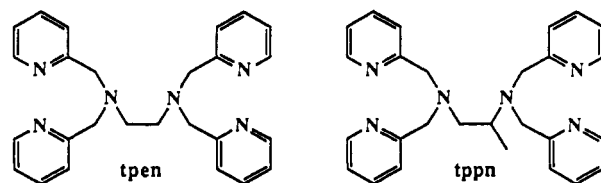
The ground-state electronic absorption spectrum of [Co(tpen)]-(ClO$_4$)$_3$ in H$_2$O—identical to that of [Co(tppn)](ClO$_4$)$_3$—is shown in Figure 1. It can be seen that there are several features in the region from 200 to 600 nm. The absorption band centered at $\lambda = 474$ nm is assigned as the lowest-energy spin-allowed ligand-field transition, $^1T_1 \leftarrow {}^1A_1$ ($\epsilon = 308$ M^{-1} cm^{-1}; see Table I). The $^1T_2 \leftarrow {}^1A_1$ transition appears as a shoulder at $\sim$350 nm. This second ligand-field band is largely obscured by a more intense absorption at shorter wavelength, assigned as a ^{1}LMCT $\leftarrow {}^1A_1$ transition. The much more intense bands present at $\lambda < 275$ nm are likely ligand-localized, $\pi^* \leftarrow \pi$ transitions. Absorptions corresponding to spin-forbidden transitions (e.g., $^3T_2 \leftarrow {}^1A_1$) were not observed in solution; these bands are expected to be extremely weak and would be very difficult to detect, except in single-crystal absorption spectra.

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(9) Langford, C. H.; Malkhasian, A. Y. S.; Sharma, D. K. *J. Am. Chem. Soc.* **1984**, *106*, 2727.

(10) (a) Toftlund, H.; Yde-Andersen, S. *Acta Chem. Scand., Ser. A* **1981**, *35*, 575. (b) Mandel, J. B.; Maricondi, C.; Douglas, B. E. *Inorg. Chem.* **1988**, *27*, 2990. (c) Mandel, J. B.; Douglas, B. E. *Inorg. Chim. Acta* **1989**, *155*, 55. (d) Broomhead, J. A.; Dwyer, F. P.; Hogarth, J. W. *Inorg. Synth.* **1960**, *6*, 183.

(11) Jongeward, K. A.; Magde, D.; Taube, D. J.; Marsters, J. C.; Traylor, T. G.; Sharma, V. S. *J. Am. Chem. Soc.* **1988**, *110*, 380.

(12) Magde, D.; Campbell, B. F. *SPIE—Fluorescence Detection III* **1989**, *1054*, 61.

Figure 1. Room-temperature electronic absorption spectrum of [Co-(tpen)](ClO$_4$)$_3$ in H$_2$O.

Table I. Molar Absorptivities for the Electronic Spectrum of [Co(tpen)](ClO$_4$)$_3$ in H$_2$O

λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})
205	2.8 × 10^4	~350 (sh)	~3.0 × 10^2
240	1.5 × 10^4	474	3.08 × 10^2
~280 (sh)	~2.5 × 10^3		

For the sub-picosecond transient absorption experiment, excitation was carried out at 314 nm. Although there is some $^1T_2 \leftarrow {}^1A_1$ contribution at this wavelength, the dominant absorption is due to the charge-transfer transition.[13] The kinetics following ^{1}LMCT $\leftarrow {}^1A_1$ excitation of [Co(tpen)](ClO$_4$)$_3$ in aqueous solution are illustrated in Figure 2 as a plot of change in absorbance as a function of time; the corresponding data for [Co(tppn)](ClO$_4$)$_3$ are shown in a figure in the supplementary material, as is a figure which shows the excited-state minus ground state transient difference spectrum of [Co(tppn)](ClO$_4$)$_3$. A very weak transient absorption is observed at $\lambda = 385$ nm with a long tail extending into the mid-visible region of the spectrum.

Both the transient spectrum and the kinetics following charge-transfer excitation of the Co^{III} complex are significantly different from what was observed for [Fe(tpen)](ClO$_4$)$_2$.[14] One obvious difference is that the Co^{III} complexes show an excited-state absorption, whereas the Fe^{II} complexes exhibit transient bleaching in the near-UV and visible regions of the spectrum. This is not very significant since it depends on the relative absorption characteristics of ground and excited states, which can change from molecule to molecule (or between different spectral regions of the same molecule) without impacting on the nature of the excited electronic states involved.

The more important difference between Co^{III} and Fe^{II} involves the details of the decay kinetics. In contrast to the decay occurring in Co^{III} on the picosecond time scale, the difference spectrum persists unchanged for some nanoseconds in the corresponding Fe^{II} complexes. Secondly, the excited-state decay kinetics of the Co^{III} systems are not well-represented by a simple single-exponential decay but require a biphasic decay process of the form given in eq 1 (see Figure 2). With the exception of the

$$k = A \exp(-k_1 t) + B \exp(-k_2 t) \qquad (1)$$

biphasic $^5T_2 \rightarrow {}^1A_1$ relaxation observed at nanosecond times for [Fe(t-tpchxn)](ClO$_4$)$_2$,[15] all of the analogous Fe^{II} complexes show monophasic excited-state decay. In the case of [Co(tpen)](ClO$_4$)$_3$, excited-state decay occurs with time constants of $\tau_1 = 4 \pm 2$ ps and $\tau_2 = 44 \pm 5$ ps. These correspond to rates of $k_1 = (2.5 \pm 1.25) \times 10^{11}$ s^{-1} and $k_2 = (2.3 \pm 0.26) \times 10^{10}$ s^{-1}. An analysis of the data for [Co(tppn)](ClO$_4$)$_3$ yields similar results, with $\tau_1 = 3 \pm 1$ ps and $\tau_2 = 51 \pm 3$ ps. Other regions of the spectrum were checked for additional transient features; none were found out to 620 nm, which was the limit of our equipment. It should be noted that the excited-state absorption features for these compounds are extremely weak. However, the above results are very reproducible from sample to sample and we are convinced that these signals *do not* arise from impurities.[16]

Excited-State Assignments for Co^{III} Complexes. Two species, either chemically unique complexes or two electronic states of the same complex, are needed in order to account for the kinetics observed for [Co(tpen)](ClO$_4$)$_3$ and [Co(tppn)](ClO$_4$)$_3$. There

(13) The estimated absorbance ratio of ^{1}LMCT $\leftarrow {}^1A_1$ to $^1T_2 \leftarrow {}^1A_1$ at $\lambda = 314$ nm is greater than 10:1.

(14) (a) McCusker, J. K.; Walda, K. N.; Dunn, R. C.; Simon, J. D.; Magde, D.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1992**, *114*, 6919. (b) McCusker, J. K.; Walda, K. N.; Dunn, R. C.; Simon, J. D.; Magde, D.; Hendrickson, D. N. *J. Am. Chem. Soc.*, in press.

(15) McCusker, J. K.; Toftlund, H.; Rheingold, A. L.; Hendrickson, D. N. *J. Am. Chem. Soc.*, in press.

(16) Very weak emission ($\Phi \approx 10^{-5}$) was observed for these complexes; however, this emission was traced to an impurity from the ligand starting materials that was present in trace amounts in the recrystallized Co^{III} complexes.
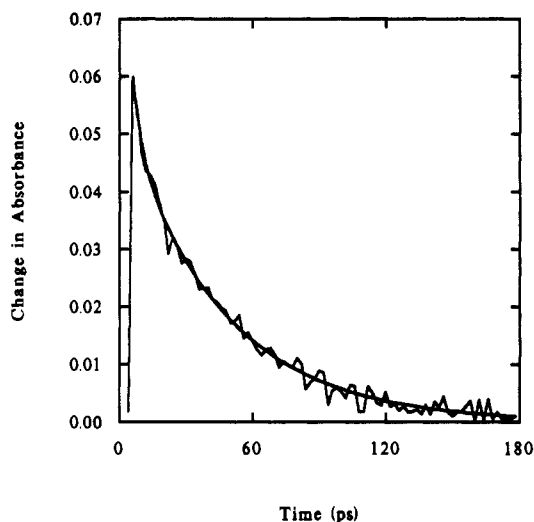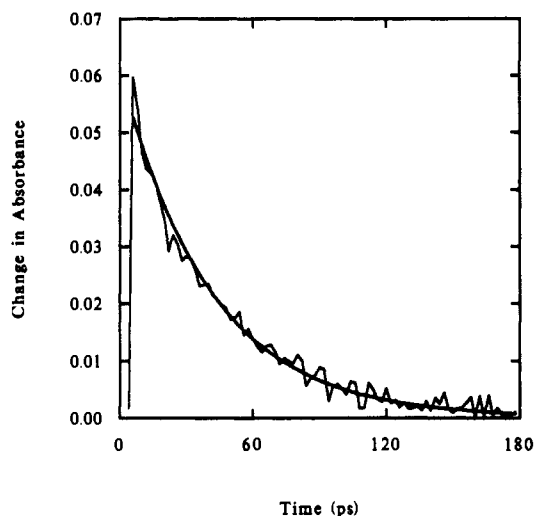
Figure 2. Plots of the change in absorbance versus time for an aqueous solution of [Co(tpen)](ClO$_4$)$_3$ following excitation at $\lambda = 314$ nm with a ~500-fs laser pulse, monitored at $\lambda = 390$ nm: upper panel, single-exponential decay ($\tau = 40$ ps); lower panel, biexponential decay. The smooth solid line in each panel represents the best fit to the kinetic model indicated. See text for details.

are numerous possibilities. It has been mentioned that Co^{III}–amine complexes are susceptible to photoredox decomposition upon LMCT excitation. Part of the decay might involve redox chemistry. This is not likely for the following reasons: (1) both tpen and tppn are hexadentate ligands, albeit not as rigid as the sep ligand, and their large formation constant would tend to preclude dissociation; (2) the optical spectra of the compounds are identical both before and after photolysis, implying that any chemistry occurring is completely reversible; and (3) the recovery of the kinetic traces back to Δ(OD) = 0 is characteristic of a relaxation process, not a chemical reaction such as photodegradation. Reversible electron transfer (e.g., self-exchange) is a remote possibility in light of the relatively high sample concentrations required in these experiments (vide supra). However, it is unlikely that bimolecular self-exchange would occur at a rate of ~10^{10} s^{-1}. We therefore proceed from the assumption that ^{1}LMCT $\leftarrow {}^1A_1$ excitation in [Co(tpen)]$^{3+}$ and [Co(tppn)]$^{3+}$ *does not* involve photoredox chemistry to any significant extent.

Several possibilities remain for assignment of the biphasic decay in these compounds. The initially formed state, i.e., the Franck–Condon state, is formally low-spin Co^{II}. This electronic structure is not likely to be stable since a Co^{II}N$_6$ system will preferentially be high-spin.[1] Thus, one possibility for excited-state decay is a spin-state change; this corresponds to an $S = \frac{1}{2} \rightarrow S = \frac{3}{2}$
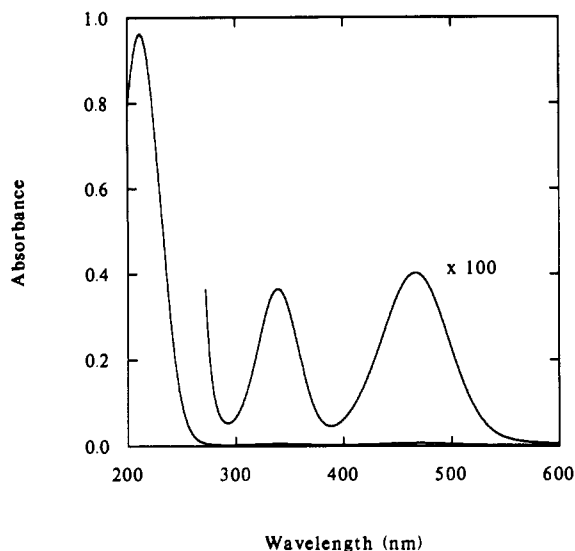
Figure 3. Ground-state absorption spectrum of an aqueous solution of [Co(en)$_3$](ClO$_4$)$_3$, showing both the ligand-field and LMCT bands.

Figure 4. Plot of the change in absorbance versus time of an aqueous solution of [Co(en)$_3$](ClO$_4$)$_3$ following $^1T_2 \leftarrow {}^1A_1$ excitation at $\lambda = 314$ nm. The smooth solid line indicates a fit to a baseline-offset single-exponential decay with $\tau = 2 \pm 1$ ps. See text for details.

conversion at the metal site and an overall state transformation for the complex of ^{1}LMCT $\rightarrow$ ^{3}LMCT. The biphasic decay could therefore be attributed to a low-spin $\rightarrow$ high-spin conversion of Co^{II} (fast component), followed by decay of the ^{3}LMCT state to excited ligand-field states of Co^{III} and/or the ground state. A second scenario involves the same overall conversion but within the framework of an $S = {}^1/_2$ metal by intersystem crossing in the charge-transfer manifold, analogous to what occurs upon ^{1}MLCT $\leftarrow$ $^1A_1$ excitation in [Ru(bpy)$_3$]$^{2+}$. The biphasic decay would be assigned as in the first mechanism, the only difference being in the specific origin of the ^{3}LMCT state. These two mechanisms attribute both kinetic components to decay from the charge-transfer manifold. Other possible decay schemes involve excited ligand-field configurations of the parent Co^{III} complex. The simplest of these assigns the fast component as decay from the charge-transfer manifold to excited ligand-field states, while the slow component is ligand-field decay to the ground state. Finally, both components could be wholly attributed to metal-centered ligand-field states of Co^{III}, implying that the ^{1}LMCT state is so short-lived so as to be unobserved on this time scale. Obviously, given only the data in Figures 2 and 3, it is difficult to establish a mechanism for the excited-state decay in these two compounds. Since the absorption spectra of the excited electronic states mentioned are unknown, one cannot even use the transient absorption spectrum (see supplementary material) as a guide.

In an effort to secure additional data, these Co^{III} complexes were examined to see if they exhibit emission either in solution or in the solid state. Excitation at various wavelengths both in the ^{1}LMCT $\leftarrow$ $^1A_1$ band and in the $^1T_1 \leftarrow {}^1A_1$ band at room temperature and at 77 K did not *in any case* result in emission in the 350–900-nm range from either compound.[16] On the basis of the sensitivity of the apparatus, we place an upper limit on the radiative quantum yield for these complexes of $\Phi \leq 10^{-5}$–10^{-6}. With these data we can be reasonably certain that radiative decay from charge-transfer states does not occur in these complexes. Since even a 1-ps-duration CT state should exhibit a luminescence yield in that range, this is one argument that neither of the states is a CT state. Unfortunately, the lack of *detectable* luminescence reveals little about LF assignments, since LF emission is expected to have lower oscillator strength and to be red-shifted beyond our detector response.

Excited-State Kinetics of [Co(en)$_3$](ClO$_4$)$_3$. Some of the complexity inherent in assigning the excited-state decay in [Co(tpen)]$^{3+}$ and [Co(tppn)]$^{3+}$ may be eliminated if we remove the charge-transfer manifold from consideration altogether and study the excited-state kinetics of [Co(en)$_3$]$^{3+}$. Although the

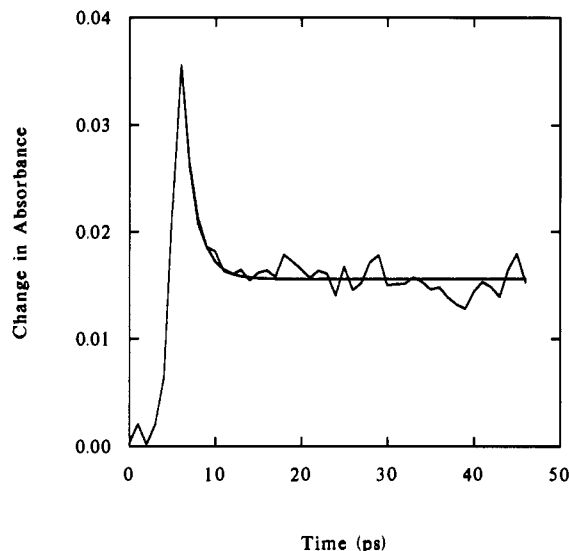spectrum of this compound is well-known, it is given in Figure 3 for convenience. Three absorption bands are observed in the region from 200 to 600 nm. The two ligand-field transitions are found at 466 nm ($^1T_1 \leftarrow {}^1A_1$, $\epsilon = 105$ M^{-1} cm^{-1}) and 340 nm ($^1T_2 \leftarrow {}^1A_1$, $\epsilon = 94.8$ M^{-1} cm^{-1}). The third band at 212 nm ($\epsilon = 2.50 \times 10^4$ M^{-1} cm^{-1}) is likely LMCT in nature. Sub-picosecond excitation at $\lambda = 314$ nm corresponds to excitation on the high-energy shoulder of the $^1T_2 \leftarrow {}^1A_1$ transition. Therefore, all of the dynamics observed will be in the context of Co^{III} LF excited states, since charge-transfer to the ligand is achieved. By comparing the results obtained on this system with those obtained for the polypyridyl complexes, one may observe some correlations that help in the assignment of the biphasic kinetics in those systems.

The observed excited-state kinetics from 0 to 50 ps for [Co(en)$_3$]$^{3+}$ in aqueous solution following $^1T_2 \leftarrow {}^1A_1$ excitation are illustrated in Figure 4. The biphasic nature of the transient absorption for this compound is clearly evident from this figure. The fast component has a lifetime of 2 ± 1 ps, corresponding to a rate of $k_1 = (5 \pm 2.5) \times 10^{11}$ s^{-1}. The slow component is essentially time-independent on this time scale, implying a relatively long lifetime. Given the extremely weak signal, it was difficult to follow this component to longer delay times; the best plot of change in absorbance versus time for [Co(en)$_3$]$^{3+}$ in H$_2$O is shown in a figure in the supplementary material. The lifetime for this long-lived component is $\tau_2 = 450 \pm 100$ ps. The transient absorption spectrum associated with the biphasic decay is given in Figure 5. It can be seen that there is a band in the excited-state spectrum at $\lambda = 390$ nm which tails into the visible; we were unable to detect any transient in any other region of the spectrum out to 620 nm. One curious feature of the transient absorption spectrum is that the same decay kinetics are observed at all wavelengths, i.e., both the 2- and 450-ps components have roughly the same absorption spectrum in this spectral region.[17]

In assigning the transient excited states in [Co(en)$_3$]$^{3+}$, we do not have the advantage present in the spin-crossover Fe^{II} complexes, in which one may thermally populate the lowest electronic excited state. In these cases, there is direct spectral evidence that the lowest excited state is $^5T_2$.[14] The Co^{III} complexes do have the advantage that ligand-field transitions are directly observable. However, even if *accurate* ligand-field parameters could be obtained,[18] the values of $10Dq$ and the Racah B and C

parameters when inserted into the ligand-field equations[19] yield Franck–Condon energy differences, appropriate only for vertical transitions from the $^1A_1$ state. Since the potential surfaces of the electronic excited states of the d^6 configuration are displaced relative to the $^1A_1$ ground state, these Franck–Condon energies *do not* accurately reflect differences in the zero-point energies of the excited states. To obtain zero-point energies in the absence of excited-state emission, one would have to make assumptions regarding the energetics of nuclear reorganization and vibrational relaxation in the excited state. The conclusions drawn from this kind of an analysis would be tenuous at best since so little is known about excited-state vibrational relaxation in transition metal complexes. It is possible, however, to obtain some information about the ordering of various excited states in low-spin Co^{III} complexes by considering the photochemistry. It has already been mentioned above in the Introduction that a dramatic contrast exists between the photochemical properties of $[Co(NH_3)_5X]^{n+}$ complexes and $[Co(CN)_5X]^{n-}$ complexes following ligand-field excitation. Specifically, the amine complexes are photoinert, while the cyano complexes show appreciable photosubstitution quantum yields. This has been interpreted by some authors as being indicative of different lowest-lying excited states for these two classes of compounds. The emission observed for $[Co(CN)_6]^{3-}$ at $\lambda = 715$ nm strongly suggests that the lowest-lying excited state in this complex is the $^3T_{1g}$ state. Then the "different lowest excited state" for the other Co^{III} complexes is presumably the $^5T_2$ state. Proving this conjecture is difficult, despite its plausibility. However, Langford[7b] has presented some interesting insights into the wavelength dependence of the photosubstitution quantum yield for $[Co(NH_3)_5X]^{n+}$ which may help. The wavelength dependence of ligand substitution for Co^{III}–amine complexes has been studied by several workers.[2b,20] It has been found that the photosubstitution quantum yields for $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_5Cl]^{2+}$ are smaller upon excitation at 647 nm than at 488 or 514 nm. A more complete study[20b] of the wavelength dependence in the region 560–620 nm showed a decrease in the quantum yield on tuning to longer wavelengths, leading to the suggestion by Langford[7b] that intersystem crossing processes may compete with vibrational relaxation in the singlet state. However, the fact that at longer wavelengths the quantum yield *decreases* suggests that conversion to the triplet state is not the final stage of intersystem crossing in these complexes. This conclusion is reached on the basis of the fact that excitation at ca. 650 nm corresponds to the region of the spectrum where the triplet state is expected to absorb.[19] If the triplet were responsible for photosubstitution, as implied for the cyano complexes, then the quantum yield should *increase* upon direct excitation into the triplet manifold. A likely cause for quenching of photosubstitution quantum yields is therefore intersystem crossing to the $^5T_2$ state. This state, when thermally relaxed, would be sufficiently low in energy such that the energetic threshold for ligand substitution would probably not be satisfied. Wilson and Solomon[21] provide further evidence supporting the notion that the $^5T_2$ state is the
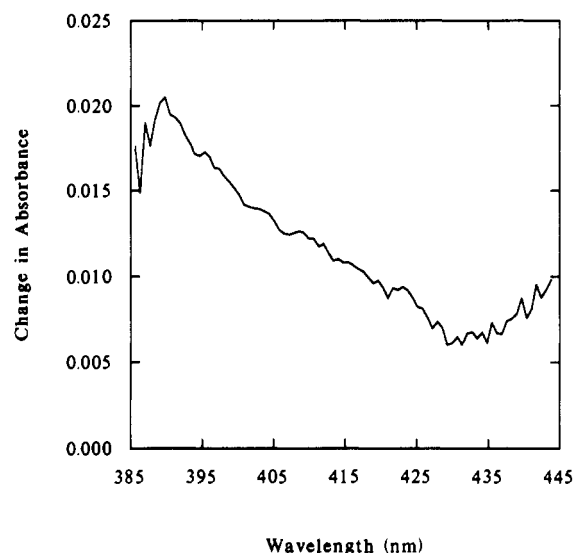

Figure 5. Transient absorption spectrum of an aqueous solution of $[Co(en)_3](ClO_4)_3$ following $^1T_2 \leftarrow {}^1A_1$ excitation at $\lambda = 314$ nm. The maximum of the excited-state absorption occurs at $\lambda \approx 390$ nm.

lowest-energy excited state in Co^{III}–amine complexes. They present detailed single-crystal absorption spectra and vibrational fine structue analyses to construct an experimental potential-surface diagram for the ligand-field states of $[Co(NH_3)_6]^{3+}$ and conclude that the $^5T_{2g}$ surface crosses the $^3T_{1g}$ surface near the minimum of the latter, providing a very efficient nonradiative decay pathway via intersystem crossing. They point out that their results are nicely consistent with the low photoaquation quantum yield observed for $[Co(NH_3)_6]^{3+}$ as mentioned above. The work by Langford et al.[7b] and Wilson and Solomon[21] make us reasonably confident in assigning the $\tau = 450 \pm 100$ ps component of the biphasic decay in $[Co(en)_3]^{3+}$ as decay of the $^5T_2$ ligand-field state back to the $^1A_1$ ground state.

The short-lived component in $[Co(en)_3]^{3+}$ can be examined in terms of both its lifetime and the transient absorption spectrum presented in Figure 5. Excitation of $[Co(en)_3]^{3+}$ at $\lambda = 314$ nm places this complex initially in a high-lying vibrational excited state of the $^1T_2$ state. In pseudooctahedral symmetry there are only a few electronic states which lie below $^1T_2$, so presumably the 2 ± 1 ps component in $[Co(en)_3]^{3+}$ is due to the $^1T_1$, $^3T_2$, or $^3T_1$ states. Alternatively, the decay could correspond to depopulation of the $^1T_2$ state. It is interesting that the $\lambda_{max} = 390$ nm in the transient absorption spectrum of $[Co(en)_3]^{3+}$ corresponds exactly to the difference in energy between the $^1T_1 \leftarrow {}^1A_1$ and $^1LMCT \leftarrow {}^1A_1$ absorptions of the ground state. From this standpoint it would be tempting to assign the short-lived feature as $^1LMCT \leftarrow {}^1T_1$ absorption. Even if the zero-point energies of the states differ from the Franck–Condon vertical energy differences, coincidence of the ground-state absorption features and the proposed $^1LMCT \leftarrow {}^1T_1$ excited-state transition could still match better than expected if the lifetime of the $^1T_1$ state is shorter than the rate of vibrational cooling in the excited state.[22] Given the short lifetime of the fast component and Langford's suggestion that other excited-state dynamical processes may compete with nuclear reorganization, this is a reasonable possibility. However, it should be stressed that the assignment of the 2 ± 1 ps component in the excited-state decay of $[Co(en)_3]^{3+}$ as relaxation from the $^1T_1$ state is tentative.

Since biphasic decay occurs even in the absence of the charge-transfer manifold in $[Co(en)_3]^{3+}$, we have a second argument (lack of luminescence being the first) suggesting that neither of

(17) The excited-state features for this compound were also examined by singular-valued decomposition (SVD). This matrix method of processing data generates a basis set of trial spectra, temporal profiles, and eigenvalues (weighting factors) to reconstruct kinetic data. It is useful in identifying hidden spectral features which may be overlooked in doing the more conventional, single-wavelength kinetic trace. SVD analysis showed that all of the temporal characteristics of the transient decay, i.e., the biphasic nature of the decay, is accounted for by the single absorption spectrum. For more on SVD, see: Walda, K. Ph.D. Dissertation, University of California, San Diego, 1992.

(18) Accurate values of $10Dq$, B, and C would require observation of all four ligand-field transitions, namely $^1T_2 \leftarrow {}^1A_1$, $^1T_1 \leftarrow {}^1A_1$, $^3T_2 \leftarrow {}^1A_1$, and $^3T_1 \leftarrow {}^1A_1$, since the commonly employed assumption that $C = 4B$ is not very accurate. See: Hauser, A. *J. Chem. Phys.* **1991**, *94*, 2741.

(19) Griffith, J. S. *The Theory of Transition Metal Ions*.

(20) (a) Langford, C. H.; Vuik, C. P. *J. Am. Chem. Soc.* **1976**, *98*, 5409. (b) Langford, C. H.; Malkhasian, A. Y. S. *J. Chem. Soc., Chem. Commun.* **1982**, 1210.

(21) Wilson, R. B.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 4085.

(22) The condition on the relative rates of vibrational cooling versus excited-state decay could be relaxed by suitable arrangement of the ^1LMCT and $^1T_1$ potential surfaces relative to the ground state. However, such an arrangement would be highly fortuitous.
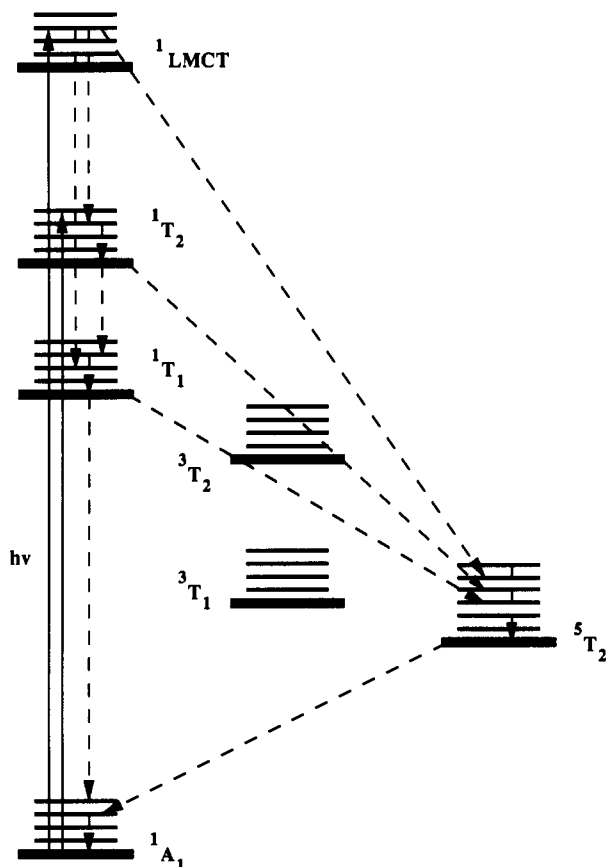
Figure 6. Jablonski diagram showing possible mechanisms for excited-state decay in octahedral Co^{III} complexes for which the $^5T_2$ state is lowest in energy. Decays following both ligand-field and charge-transfer excitation are shown. The dashed lines indicate nonradiative processes.

the kinetic components observed in [Co(tpen)]$^{3+}$ or [Co(tppn)]$^{3+}$ involves dynamics in charge-transfer states, despite the fact that the initial excitation is to a ^{1}LMCT state. For all three complexes, we assign the short component as decay of the $^1T_1$ state and the longer-lived component as $^5T_2 \rightarrow {}^1A_1$ relaxation. Since the absorption spectrum does not change noticeably between the assigned $^1T_1$ and $^5T_2$ states, the observation of a kinetic distinction implies either that a significant portion of the $^1T_1$ population decays to some other state bypassing the $^5T_2$ state (most likely the ground state) or that the molar absorptivity of complexes in the $^1T_1$ state is significantly greater despite the spectral similarity.

The $^1T_1$ lifetimes in all three compounds are similar; we do not attach much significance to the 1- or 2-ps differences in lifetimes. The reason for the much shorter lifetime of $\tau \approx 50$ ps in the polypyridyl complexes relative to [Co(en)$_3$]$^{3+}$ is difficult to know for certain but may simply reflect the stronger ligand field presented by the polypyridyl ligand as compared to ethylenediamine. This would then result in a higher-energy $^5T_2$ state and subsequently a shorter lifetime, in accord with the energy gap law as applied to strongly coupled systems.[23] Presumably such

a ligand-field effect would also impact on the $^1T_1$ lifetime. However, the slightly *longer* $^1T_1$ lifetime in the polypyridyl complexes may reflect a smaller difference in the relative $^1T_1/{}^5T_2$ energy separation due to the fact that the energy of the $^5T_2$ state changes as $20Dq$, whereas that of the $^1T_1$ state changes as $10Dq$. This would then result in an increase in the $^1T_1$ lifetime relative to that observed for [Co(en)$_3$]$^{3+}$, provided that $^1T_1 \rightarrow {}^1A_1$ decay is not kinetically competitive with intersystem crossing.

Concluding Comments

The transient kinetic data for aqueous solutions of [Co(tpen)](ClO$_4$)$_3$, [Co(tppn)](ClO$_4$)$_3$, and particularly [Co(en)$_3$](ClO$_4$)$_3$ allow us to piece together a preliminary, general schematic of the excited-state dynamics of six-coordinate Co^{III} complexes; this is given in Figure 6. This diagram is specific for Co^{III} complexes having the $^5T_2$ state as the lowest-energy excited ligand-field state. Since no kinetic evidence exists to suggest the involvement of a third state, e.g., a ^3T state, we have chosen to depict intersystem crossing from the singlet ligand-field manifold in terms of direct conversion to the $^5T_2$ state. It would be helpful if we could measure quantum yields of formation for transient species. However, the lack of detectable emission and the weak transient absorption signals for all of these complexes preclude the determination of quantum yields in these types of complexes at the present time.

As far as a comparison with the data[14] for the isoelectronic Fe^{II} compounds is concerned, there are similarities and differences. In both cases, we assign the longest-lived transient to a $^5T_2$ state. In the Fe^{II} complexes, that is the only transient we are able to detect on any time scale (down to ~ 700 fs). Consequently, we concluded that intersystem crossing was the fastest of the three excited-state processes (intersystem crossing, internal conversion, and vibrational relaxation). This might be somewhat counter-intuitive on the basis of spin–orbit coupling-type arguments, since the larger value of spin–orbit coupling for Co^{III} as compared to Fe^{II} complexes would be expected to increase the propensity for intersystem crossing for the Co^{III} complexes; however the traditional arguments were developed for weak coupling situations that are not directly applicable. In the Co^{III} complexes, another shorter-lived transient is detectable and is assigned to higher LF states, probably predominantly $^1T_1$. In both Co^{III} and Fe^{II} complexes, it appears that the charge-transfer states are extremely short-lived (≤ 700 fs). This contrasts with what is observed for second- and third-row metals. The difference is very likely due to the fact that the ^{3}MLCT states are the lowest-energy excited states for second- and third-row systems, whereas the smaller ligand-field splitting induced by first-row metals leaves several ligand-field states below the charge-transfer states in energy. These ligand-field states provide efficient decay pathways for the nonradiative dissipation of energy and explains why no charge-transfer-based emission is generally observed for first-row metals.

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