Photophysical and Photochemical Properties of Cobalt(III) Phosphite Complexes

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Emission from the $^3T_{1g}$ ligand field state of $[Co(P)_6](ClO_4)_3$ (P = $P(OCH_2)_3CCH_3$)) (λ_{max} = 700 nm) and from the new complex $[Co(pom\text{-}pom)_3](ClO_4)_3$ (pom-pom = $(CH_3O)_2PCH_2CH_2P(OCH_3)_2$) ($\lambda_{max}$ = 620 nm) is reported. The latter complex shows emission in 50% aqueous LiCl glass at 78 K (τ = 650 ± 50 μs, ϕ = 0.06 ± 0.01) as well as in the crystalline state (τ = 320 ± 30 μs at 78 K, 1.1 ± 0.2 μs at 300 K); a detailed study of the temperature dependence yielded activation parameters of ΔE = 2120 cm^{-1} and A = 3.1 × 10^{12} s^{-1}, and simultaneous studies of emission lifetimes and quantum yields indicated the activated process to be nonradiative. Photolysis of $Co(pom\text{-}pom)_3^{3+}$ in aqueous solution at 300 K results in photoaquation with ϕ = 0.26 ± 0.05 at both 254 nm (charge-transfer absorption) and 313 nm (lowest energy ligand field absorption) with negligible photoredox chemistry. The photoproduct (λ_{max} = 370 nm) is assigned as a monoaquated species. Laser flash photolysis at 265 nm reveals prompt formation both of permanent photoproduct and of a prompt transient (λ_{max} = 450 nm) that decays to starting material with strongly pH-dependent first-order kinetics. The behavior of $Co(pom\text{-}pom)_3^{3+}$ is discussed with respect to the well-studied emissive complex $K_3[Co(CN)_6]$ and to Rh(III) complexes.

Introduction

The $^3T_{1g}$ ligand field excited state of d^6 octahedral metal complexes has been well characterized by electronic emission for many second- and third-row metal ion examples.[1-3] For Rh(III) complexes,[1] low-temperature emission lifetimes for the crystal or for glassy solutions are in the microsecond to millisecond range; in fluid solution, lifetimes are of the order of nanoseconds, with photosubstitution becoming a dominant decay pathway.[1a]

In contrast, observations of electronic emission for complexes of the first-row d^6 transition-metal ion Co(III) are limited to the $Co(CN)_6^{3-}$ ion[4] and a few substituted cyanocobaltates.[5] Except for the cyanocobaltates,[6] fluid solution photosubstitution quantum yields for Co(III) complexes are also very low.[6a,7]

The anomalous photophysical behavior of Co(III) complexes has been attributed[8] to a crossing of the $^3T_{1g}$ and $^5T_{2g}$ excited states. For relatively small values of 10Dq, the $^5T_{2g}$ is the lowest excited state. Only at large ligand field strength is the energy of the vibrationally relaxed $^5T_{2g}$ transition (whose vertical transition energy is dependent upon 20Dq, rather than the 10Dq of $^3T_{1g}$) high enough to allow $^3T_{1g}$, the emissive state of $Co(CN)_6^{3-}$,[4] to be the lowest excited state. In second- and third-row metal complexes, 10Dq due to given ligands is generally larger, and many ligands are capable of creating the strong ligand field necessary to make $^3T_{1g}$ the lowest excited state. But among common ligands, only CN^- provides a strong enough ligand field in the case of Co(III).

Verkade[9] found that Co(III) complexes of trialkyl phosphites had electronic spectra indicating a ligand field strength similar to that of CN^-, and we therefore surmised that such complexes might be emissive. This proved to be the case. Of greatest interest was the Co(III) complex of the chelating diphosphite ligand 1,2-bis(dimethoxyphosphino)ethane, $(CH_3O)_2PCH_2CH_2P(OCH_3)_2$ (which we abbreviate as pom-pom), which has properties rather different from those of the other Co(III) complexes, and we report detailed studies of this complex.

Experimental Section

The ligand pom-pom was prepared by the method of King and Rhee.[10] The complex $[Co(P)_6](ClO_4)_3$, where P is the "melon" phosphite 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, P-$(OCH_2)_3CCH_3$, was prepared by the method of Verkade and Piper.[9a]

$[Co(pom\text{-}pom)_3](ClO_4)_3$ was prepared as follows. To $Co(ClO_4)_2\cdot6H_2O$ (2 g) dissolved in 20 mL of ethanol under N_2 was added

5 mL of pom-pom dropwise with stirring, and a precipitate formed. After addition was complete, air was introduced, and the stirred suspension became white. The filtered precipitate, after being washed with ethanol and air-dried, was dissolved in boiling water, and precipitation was induced by dropwise addition of saturated aqueous $NaClO_4$. The white powder may be recrystallized from hot water or CH_3CN to yield small colorless diamond-shaped plates. Anal. Calcd for $CoC_{18}H_{48}O_{24}P_6Cl_3$: C, 21.62; H, 4.84; P, 18.6. Found: C, 21.59; H, 4.85; P, 19.1. The air-oxidation step can be replaced by oxidation with Fe^{3+} or H_2O_2. It is worth noting that $[Co(pom\text{-}pom)_3](ClO_4)_3$ is *much* more thermally stable than $[Co(P)_6](ClO_4)_3$ both as the solid and in aqueous solution. *Caution!* Small solid samples were observed to *detonate* when strongly heated or, on one occasion, when subjected to intense 353-nm Nd/YAG laser excitation at room temperature. While we have not observed any shock sensitivity, ("hammer test"), extreme caution is nonetheless recommended in handling this material.

Absorption spectra were recorded on Cary 17 or 219 instruments, while emission spectra were recorded on an Hitachi Perkin-Elmer MPF-3 and were then corrected.[11] Emission quantum yield determinations employed aqueous $Ru(bpy)_3^{2+}$ as a standard and took account of the temperature dependence of $Co(pom\text{-}pom)_3^{3+}$ absorption, as determined in a separate experiment.

Flash photolysis experiments employed the 353-nm (frequency-tripled) or 265-nm (frequency-quadrupled) lines of a Nd/YAG laser system described elsewhere[12] or a microsecond flash photolysis system also described elsewhere.[13] Low-temperature experiments employed

(1) (a) Bergkamp, M. A.; Brannon, J.; Magde, D.; Watts, R. J.; Ford, P. C. *J. Am. Chem. Soc.* **1980**, *102*, 2627. (b) Bergkamp, M. A.; Watts, R. J.; Ford, P. C. *J. Phys. Chem.* **1981**, *85*, 684. (c) Thomas, T. R.; Crosby, G. A. *J. Mol. Spectrosc.* **1971**, *38*, 118. (d) Huang, W. L.; Segers, D. P.; DeArmond, M. K. *J. Phys. Chem.* **1981**, *85*, 2080.

(2) Douglas, I. N.; Nicholas, J. V.; Wybourne, B. G. *J. Chem. Phys.* **1968**, *48*, 1415.

(3) Wrighton, M. S.; Morse, D. L.; Gray, H. B.; Ottesen, D. K. *J. Am. Chem. Soc.* **1976**, *98*, 1111.

(4) (a) Miskowski, V. M.; Gray, H. B.; Wilson, R. B.; Solomon, E. I. *Inorg. Chem.* **1979**, *18*, 1410. (b) Hipps, K. W.; Crosby, G. A. *Inorg. Chem.* **1974**, *13*, 1543. (c) Wolpl, A.; Oelkrug, D. *Ber. Bunsenges. Phys. Chem.* **1975**, *79*, 394. (d) Conti, C.; Castelli, F.; Forster, L. S. *J. Phys. Chem.* **1979**, *83*, 2371. (e) Mazur, U.; Hipps, K. W. *J. Phys. Chem.* **1979**, *83*, 1884.

(5) Loeb, B.; Zuloaga, F. *J. Phys. Chem.* **1977**, *81*, 59.

(6) (a) Balzani, V.; Carasitti, V. "Photochemistry of Coordination Compounds"; Academic Press: New York, 1970. (b) Nakamura, K.; Jin, K.; Tazawa, A.; Kanno, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3486. (c) Nishazawa, M.; Ford, P. C. *Inorg. Chem.* **1981**, *20*, 294. (d) Adamson, A. W.; Chiang, A.; Zinato, E. *J. Am. Chem. Soc.* **1969**, *91*, 5467.

(7) Zinato, E. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975.

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

(9) (a) Verkade, J. G.; Piper, T. S. *Inorg. Chem.* **1963**, *2*, 944. (b) Verkade, J. G. *Coord. Chem. Rev.* **1972**, *9*, 1.

(10) King, R. B.; Rhee, W. M. *Inorg. Chem.* **1978**, *17*, 2961.

(11) Parker, C. A.; Rees, W. T. *Analyst (London)* **1960**, *85*, 587.

(12) Nocera, D. G.; Winkler, J. R.; Yocum, K. M.; Bordignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 5145.

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Table I. Absorption (Room Temperature) and Emission (77 K) Data for Co(III) Complexes in Aqueous Solution

	λ, nm (ϵ)			
compd	CT	$^1A_{1g} \rightarrow {}^1T_{2g}$	$^1A_{1g} \rightarrow {}^1T_{1g}$	$^3T_{1g} \rightarrow {}^1A_{1g}$
$K_3[Co(CN)_6]$	198 (35 400)^a	260 (180)^a	312 (243)^a	710^b
$[CoP_6](ClO_4)_3$	224 (35 000)^c	280 (2000, sh)^c	320 (340, sh)^c	700^d
$[Co(pom\text{-}pom)_3](ClO_4)_3$	248 (33 100)	280 (9000, sh)	310 (1500, sh)	620^e

^{a} Alexander, J. J.; Gray, H. B. *J. Am. Chem. Soc.* 1968, *90*, 4260. ^{b} Crystal; ref 4a. ^{c} Reference 9a. ^{d} Crystal; this work. ^{e} Crystal emission is at the same wavelength.
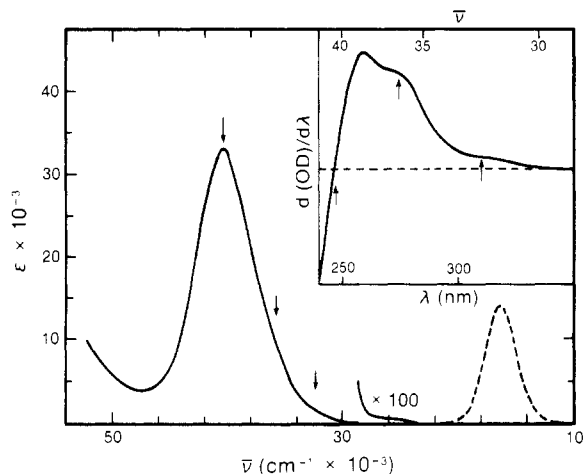

Figure 1. Electronic absorption spectrum in aqueous solution at 300 K and emission spectrum (dashed line) in 50% saturated aqueous LiCl glass at 77 K of Co(pom-pom)$_3$$^{3+}$. Emission intensity is in arbitrary units. The inset shows the derivative mode absorption spectrum in aqueous solution at 300 K.

either an Air Products DE-202 Displex closed-cycle refrigeration system or immersion in liquid N$_2$.

Static photolysis experiments employed either a 1000 W Hanovia mercury lamp, appropriately filtered, or a 450-W Oriel Xe lamp passed through a Bausch & Lomb 0.25-m monochromator. Either a YSI-Kettering Model 65A radiometer or, at 313 nm, photolysis[6] of an aqueous solution of K$_3$Co(CN)$_6$ was used to estimate photon flux. We analyzed for Co(II) product by the method of ref 14.

Results

Electronic Absorption and Emission. The electronic absorption and emission spectra of Co(CN)$_6$$^{3-}$, Co(pom-pom)$_3$$^{3+}$, and Co(P)$_6$$^{3+}$ are summarized in Table I. The absorption spectra of the phosphite complexes are dominated by an intense charge-transfer band (see Figure 2). In all probability, this is the σ(P) $\rightarrow$ dσ*(Co) ligand-to-metal charge-transfer (LMCT) transition. It occurs at much higher energy than the analogous LMCT transition of (arylphosphine)cobalt(III) complexes,[15] which is, no doubt, in some way connected with the much higher[9,15] ligand field strength of the phosphite complexes.

For the P and pom-pom complexes, ligand field (LF) transitions are observed[16] as poorly defined shoulders; those of the pom-pom complex are more clearly defined in the derivative mode spectrum included in the inset to Figure 1. It is clear from Table I that these three complexes have very

(13) Milder, S. J.; Goldbeck, R. A.; Kliger, D. S.; Gray, H. B. *J. Am. Chem. Soc.* 1980, *102*, 6761.
(14) Houlding, V. H.; Mäcke, H.; Adamson, A. W. *Inorg. Chem.* 1981, *20*, 4279.
(15) Miskowski, V. M.; Robbins, J. L.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* 1976, *98*, 2477. Following arguments in this reference (strong stabilization of P(σ) levels in metal complexes), we consider the assignment of these bands as "ligand-localized" transitions to be unlikely.
(16) There is very little improvement in resolution for low-temperature absorption spectra of glassy solutions, even at 20 K. While the LMCT band sharply narrows at low temperature, there is a compensatory loss of intensity for the LF transitions; the latter effect is consistent with the expected vibronic intensity mechanism for these transitions.

Table II. Lifetime Data (μs, Except As Indicated) for $^3T_{1g}$ of Co(III) Complexes

	[Co(pom-pom)$_3$](ClO$_4$)$_3$		$K_3[Co(CN)_6]$	
T, K	cryst	aq^d	cryst	aq
300	1.1 ± 0.2	<20 ns	8^a	2.6 ns^b
77	320 ± 30	650 ± 50	680^a	c

^{a} Reference 4c. ^{b} Reference 4d. ^{c} No data available. ^{d} 50% saturated aqueous LiCl.
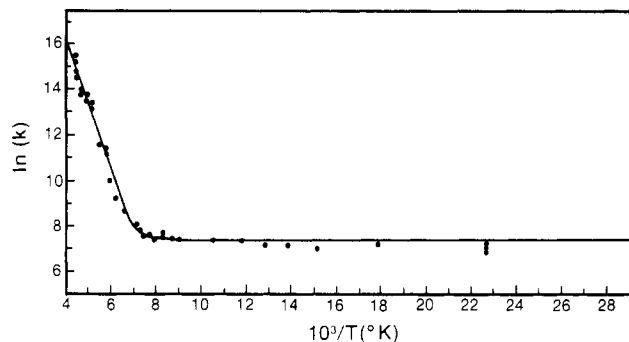

Figure 2. Temperature dependence of the emission decay rate k (s^{-1}) of Co(pom-pom)$_3$$^{3+}$ in 50% saturated aqueous LiCl glass. Excitation was at 353 nm. The solid line is a theoretical fit; see text.

similar LF absorption maxima.

[Co(P)$_6$](ClO$_4$)$_3$ shows red emission from the solid at 77 K, very near the K$_3$[Co(CN)$_6$] emission under the same conditions. Thus, the emission is assigned[4] to $^3T_{1g} \rightarrow {}^1A_{1g}$. The P complex did not show measurable emission in an aqueous glass at 77 K up to 800 nm, which is, however, analogous[4a] to Co(CN)$_6$$^{3-}$.

[Co(pom-pom)$_3$](ClO$_4$)$_3$ was exceptional. Both the solid and 50% saturated aqueous LiCl glasses at 77 K showed strong *orange* emission; the emisson maximum is shifted ~2000 cm^{-1} to higher energy relative to the other two complexes. Some emission lifetime data are summarized in Table II. The difference in lifetime for Co(pom-pom)$_3$$^{3+}$ emission between the crystal and glasses argues against the glass emission being assigned to "microcrystallites". Furthermore, we saw no evidence for scattering of the laser beam from the glasses.

We performed a detailed study of the temperature dependence of the emission lifetime of Co(pom-pom)$_3$$^{3+}$ in aqueous glass, and data[17] are shown in Figure 2. The solid line is a

(17) Most of our emission lifetime data were obtained for 353-nm excitation, but consistent data were obtained for 265-nm excitation. Reliable lifetimes could not be obtained with our instrumentation above ~220 K ($\tau \sim$ 300 ns). Most of our decay curves gave greatly improved fits if biexponential decay was assumed; in addition to the dominant decay component characterized by the data in Figure 2, there was a fster decay component accounting for, on the average over all our data, ~20% of the total light received by the phototube. However, the contribution of the fast component varied wildly over various experiments (in some data, it is not evident at all), and we consider it to be an artifact. Whether it is of instrumental origin, or results from inhomogeneity or impurities in the samples (possibly photochemically produced) is unclear at this time. At low temperature, computer fit of the data indicated that the fast-decay component had a lifetime about four times shorter than the slow component. The disparity in the two lifetimes decreased rapidly above 140 K.

fit to Arrhenius temperature dependence, $k_{obsd} = k_0 + A \exp(-\Delta E/kT)$, and our best fit values were $k_0 = 1.41 \times 10^3$ s^{-1} ($\tau_0 = 710$ μs), $\Delta E = 2120$ cm^{-1} (6.1 kcal/mol), and $A = 3.1 \times 10^{12}$ s^{-1}. The extrapolated lifetime at room temperature is 8.5 ns, very consistent with measured values[1,4] for isoelectronic systems.

At the lowest temperatures, the lifetime is actually not completely temperature independent, as implied by this fit. We found that τ underwent a further small increase from ~700 μs at 77 K to ~1100 μs at 34 K. The temperature dependence over the range 34–110 K could be fit to an equilibrium among two thermally populated spin–orbit states of $^3T_{1g}$ (see ref 4e) with a splitting of the order of 100 cm^{-1}. Both the scatter in our data and uncertainty as to degeneracies of the levels involved preclude more definitive characterization. However, we emphasize that this low-temperature τ variation has essentially no effect upon fits (Figure 2) to the much stronger high-temperature variation. The temperature range and magnitude of the spin–orbit lifetime variation is similar to that reported for salts[4e] of the Co(CN)$_6^{3-}$ ion but differs in that these last show decreasing lifetimes at the lowest temperatures.

Attempts to perform analogous temperature studies for crystalline [Co(pom-pom)$_3$](ClO$_4$)$_3$ were discontinued after the detonation noted in the Experimental Section. But, it should be clear from the room-temperature lifetime in Table II that the temperature dependence is very different from that of glasses.

The emission quantum yield of Co(pom-pom)$_3^{3+}$ in glassy solution at 77 K was determined to be 0.06 ± 0.01 for 313-nm excitation; this is very similar to a value of 0.05 reported[4c] for crystalline K$_3$Co(CN)$_6$ at 77 K. It is of interest that the corrected emission excitation spectrum tracked the CT band through the UV region. Thus, excitation of this charge-transfer state evidently leads to predominant population of the lowest energy LF excited state, at least, at 77 K. The temperature dependence of the quantum yield was studied over the limited range 77–150 K (emission was too weak to measure accurately at higher temperatures), and within experimental error it accurately tracked the lifetime data, with the same activation energy. This indicates[3] that k_{nr} is responsible for the temperature sensitivity, with k_r at least roughly temperature independent in this range. Thus, assuming unit efficiency for $^3T_{1g}$ population, k_r could be calculated to be 92 s^{-1}, corresponding to a "natural" radiative lifetime of ~11 ms. The data of ref 4c indicate this lifetime to be ~14 ms for crystalline K$_3$Co(CN)$_6$ at 77 K; this is, of course, a thermal average over a number of spin–orbit levels in both cases.[4e] Note that unit efficiency for $^3T_{1g}$ population has been established[6c] for Co(CN)$_6^{3-}$.

Photochemistry in Fluid Solution. Electronic emission from fluid solutions was too weak to measure on a conventional spectrometer. Repeated attempts to measure lifetimes at room temperature resulted in the conclusion that the emission lifetime of Co(pom-pom)$_3^{3+}$ must be less than our laser pulse width, or ≤20 ns. This result is consistent with a reported[4d] lifetime for aqueous Co(CN)$_6^{3-}$ of 2.6 ns at room temperature and with our extrapolated value of 8.5 ns in 50% saturated aqueous LiCl solution.

Steady-state photolysis of aqueous solutions of Co(pom-pom)$_3^{3+}$ resulted in photochemistry. Figure 2 shows the spectral changes ensuing upon 265-nm photolysis. Identical spectral changes, with the same isosbestic points (230 and 290 nm) occurred upon 313-nm photolysis. Unfortunately, the isosbestic points were lost upon extended photolysis, due to secondary photolysis and/or thermal product degradation (the latter definitely observed upon storage of photolyzed solutions).
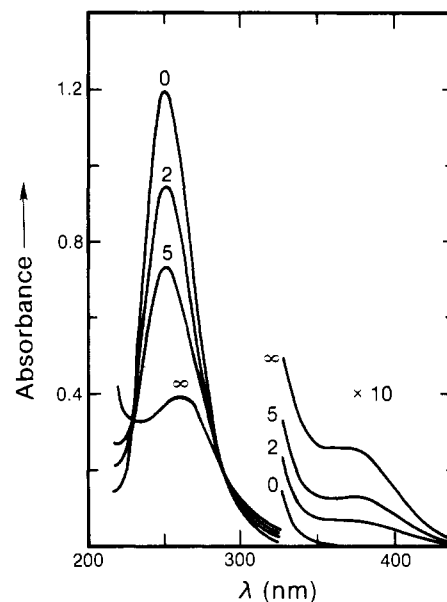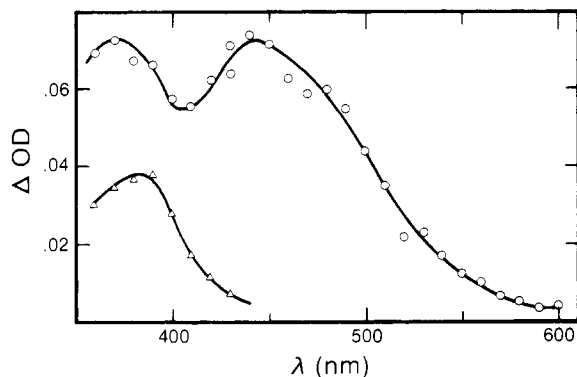

Figure 3. Photolysis at 265 nm of Co(pom-pom)$_3^{3+}$ in degassed aqueous solution. Photolysis times are in minutes, and the ∞-time spectrum is calculated (see text).

We calculated a quantum yield for 265-nm photolysis data (dilute solutions), in the range where the isosbestic points were maintained, by assuming that the quantum yield is constant, real yields decreasing as a function of photolysis time because of both decreased starting material absorbance *and* "inner filter" absorbance by product.[18] An iterative procedure yielded a $\Delta\epsilon$ (ϵ(Co(pom-pom)$_3^{3+}$) – ϵ(product)) of 22 500 at 265 nm and a quantum yield of 0.27. The ∞ time product spectrum could then be calculated and is also shown in Figure 3; it has a broad peak at 260 nm (ϵ 10 800) and a shoulder at 370 nm (ϵ 700). Very similar spectra, but with somewhat lower apparent ϵ's, were observed for extensively photolyzed (partially decomposed) solutions.

With $\Delta\epsilon$ known, ϕ could also be calculated for 313-nm photolysis (determined for both dilute and very concentrated solutions), and the derived value was 0.25. Probable uncertainties for our quantum yields are ±20%. That they are essentially identical at 265 and 313 nm is more certain, however, as this conclusion is independent of the assumed product ϵ's. Thus, in agreement with emission results, we conclude that the CT state decays efficiently to the lowest energy LF excited state.

Little or no Co(II) (≤5% of total product) could be detected in photolyzed solutions that had not undergone secondary degradation. The product absorption at 370 nm is of reasonable intensity for assignment to a Co(III) LF transition, and the similarity to the lowest LF band of[6b] Co(CN)$_5$OH$_2^{2-}$ at 382 nm (ϵ 294) suggests that our product is an aquation product. In agreement with this interpretation, incubation of product solutions with concentrated Cl$^-$ led to a shift of the band to 390 nm (now a definite maximum) while photolysis of Co(pom-pom)$_3^{3+}$ in CH$_3$CN resulted in a shoulder at 350 nm (isosbestic points in this solvent at 225 and 265 nm). These

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(18) A critical assumption here is that light absorption by the product does not regenerate starting material to a significant extent; if it did, our calculated product ϵ would be high and ϕ too low. So, it is worth noting that we could photolyze solutions to loss of about half of the 248-nm absorption without loss of isosbestic points. Taking ϵ (248) of the product to be just half that of starting material gives a lower limit to the real $\Delta\epsilon$, and resulting calculated ϕ's of ~0.35 are upper limits to ϕ. A lower limit for ϕ results from the assumption that the products have no absorption at 248 nm; hence, $\phi \sim 0.17$. We feel that the uncertainties that should be placed on the ϕ's in the text are considerably smaller than that of about ±35% established by these limits.

Figure 4. Transient difference spectra obtained for flash photolysis at 265 nm of Co(pom-pom)$_3^{3+}$ in aqueous solution at natural pH: O, 500 ns after the laser pulse; △, 200 μs after the laser pulse.

Table III. Transient (450-nm Absorption) Decay Lifetimes for Aqueous Co(pom-pom)$_3^{3+}$ at Indicated pH's (Room Temperature)

pH (buffer)	τ, μs
9.1 (borate)	320 (30)
7.9 (phosphate)	25 (5)
6.2 (phosphate)	1.3 (2)

values are closely comparable to LF maxima of Co(CN)$_5$Cl^{3-} at 392 nm[19] and Co(CN)$_5$NCCH$_3^{2-}$ at 353 nm.[6b]

The suggested assignment of the product is then to a complex in which one end of one pom-pom ligand has dissociated. An analogous photoproduct is well established for Cr(en)$_3^{3+}$ photolysis in aqueous solution.[20] We do not observe any thermal regeneration of starting material; however, hydrolysis[9] of the "dangling" phosphite may suppress this reaction. Modest air sensitivity of the product solutions may also represent[10] reaction of the dissociated P(III) ligand.

Flash photolysis of aqueous solutions resulted in absorption signals shown in Figure 4. Their risetime was ≲20 ns. Two maxima are present immediately after the laser pulse, at ∼380 and ∼450 nm. The latter undergoes first-order decay, with a (somewhat variable) lifetime of ∼20 μs at "natural" pH. Decay data obtained in a series of buffered solutions are summarized in Table III. The solutions were degassed, but aeration had no effect. The decay rate appears to be roughly proportional to hydrogen ion concentration.

The decay of the 450-nm absorption leaves the 380-nm absorption essentially unchanged; the observed decrease in 380-nm ΔOD (Figure 4) can be accounted for solely by decay of the broad, overlapping 450-nm band. Indeed, the 380-nm absorption undergoes no further decay for at least 10 s, according to microsecond flash experiments, and it must therefore be due to permanent (aquation) photoproduct.

It is clear that the 450-nm transient does not give rise to any substantial amount of aquation product, since 380-nm absorption does not increase during 450-nm decay; the final (380-nm) product is, instead, prompt and evidently arises directly from the $^3T_{1g}$ LF excited state of Co(pom-pom)$_3^{3+}$. Exactly what the 450-nm transient is, is less clear. In order to obtain large absorption of the laser pulse to give large signals in short-time scale transient absorption experiments, we were forced by solubility considerations to excite at 265 nm, into the CT state. While all of our data indicate that this should result in predominant $^3T_{1g}$ population, it is nonetheless possible that the 450-nm transient could be some intensely absorbing species formed in low yield from the CT state.

Alternatively, and perhaps more interestingly, the 450-nm transient might be the linkage isomer:
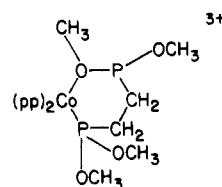
Rapid first-order decay of such a complex to starting material would be understandable as the phosphite O atom should be an exceptionally weak donor. But we emphasize that this is a purely speculative proposal, and other possibilities are definitely not excluded. Our major pont is that the 450-nm transient is irrelevant to the net photochemistry observed.

Discussion

The complex Co(pom-pom)$_3^{3+}$ turns out to have photophysical behavior remarkably similar to that of second-transition series analogues such as [Rh(NH$_3$)$_6$](ClO$_4$)$_3$. The important feature is that in a glassy or fluid medium,[21] a nonradiative decay process of large activation energy ($\gtrsim 10^3$ cm^{-1}) but very large frequency factor ($A \sim 10^{12}$–10^{13} s^{-1}) dominates excited-state decay. The much less drastic temperature dependence of the emission lifetime in crystals has been shown to have very different activation parameters for Rh(III) complexes.[1b] A common feature of all of these complexes is high quantum yield photochemistry in fluid solution, and particularly in view of recent work indicating solvent independence of photophysical parameters for the Co(CN)$_6^{3-}$ ion,[22] it seems clear that this deactivation pathway is closely connected to photosubstitution, most likely via a dissociative pathway.[22] Our present observation of high quantum yield photochemistry in room-temperature fluid solution is consistent with this interpretation.

A subject of interest is the apparent uniqueness of Co(pom-pom)$_3^{3+}$ among Co(III) complexes. We noted a blue-shift of ∼2000 cm^{-1} for its emission maximum relative to [Co(P)$_6$](ClO$_4$)$_3$ and K$_3$[Co(CN)$_6$]. We suspect that this shift is related to the trigonal constraint imposed upon the $^3T_{1g}$ state by the chelating ligands. The absence of large effects upon LF absorption maxima indicates that ground-state trigonal distortion is insignificant. However, such a large tetragonal distortion as estimated by Wilson and Solomon[8] for the $^3T_{1g}$ state of K$_3$[Co(CN)$_6$] must certainly be affected by the chelate constraint. It is noteworthy that studies[23] of ethylenediamine complexes of Co(III) have indicated strong vibronic involvement of "chelate-ring deformation" modes in ligand field absorption. Large cation effects on the emission maxima of Co(CN)$_6^{3-}$ salts have been noted,[4e] which supports the importance of "local environment" effects.

We attribute the smaller Stokes shift for Co(pom-pom)$_3^{3+}$ vs. Co(P)$_6^{3+}$ or Co(CN)$_6^{3-}$ to restricted excited-state distortion, resulting in a smaller effective Huang-Rhys (Franck-Condon) factor. While the data in hand do not define[8] the nature of the excited-state distortion, we postulate that a strong trigonal (rather than tetragonal) distortion might be reasonable, as a trigonal distortion will also remove Jahn-Teller instability, and

(19) Miskowski, V. M.; Gray, H. B. *Inorg. Chem.* **1975**, *14*, 401.
(20) Cimolino, M. C.; Linck, R. G. *Inorg. Chem.* **1981**, *20*, 3499.

(21) The glass transition temperature of 9 M LiCl(aq) has been estimated to be 143 K: Angell, C. A.; Sore, E. J. *J. Chem. Phys.* **1970**, *52*, 1058. This is very close to the onset of strong temperature dependence of τ in our system, and it is therefore unclear whether the high-temperature decay process would be observed in a rigid, noncrystalline medium. We visually observed evidence for "fluidity" (in particular, annealing of cracks) of our glasses at temperatures above ∼135 K.
(22) Milder, S. J.; Gray, H. B.; Miskowski, V. M. *J. Am. Chem. Soc.* **1984**, *106*, 3764.
(23) Hakamata, K.; Urushiyama, A.; Degen, J.; Kupka, H.; Schmidtke, H. H. *Inorg. Chem.* **1983**, *22*, 3519 and references cited therein.

would be favored by the steric constraint. Note that the steric constraint does *not* prevent efficient photosubstitution chemistry in fluid solution. Since the source of the activation energy of this process is not yet understood, the significance of this is unclear.

A final interesting point is that chelate constraints appear to have much smaller effects upon emission maxima for Rh-(III) complexes; e.g., $Rh(NH_3)_6^{3+}$ and $Rh(en)_3^{3+}$ emission maxima[1c,24] differ by only ~700 cm^{-1}. Conceivably, unrestricted equilibrium excited-state distortions are larger for the first-row transition series species, hence more subject to ligand

or lattice perturbation. But excited-state distortions appear to be exceptionally large for[8] $Co(CN)_6^{3-}$, relative to Co-$(NH_3)_6^{3+}$, so the comparison may not be fair.

(24) DeArmond, M. K.; Hillis, J. E. *J. Chem. Phys.* **1971**, *54*, 2247.

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The Transition Metal–Carbon Monoxide Bond

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The concept of absolute electronegativity is used to show that the transition metal acts as a Lewis base and that carbon monoxide is a Lewis acid in the neutral metal carbonyls. This means that π-bonding dominates, though some σ-bonding will be induced. The values of χ, the absolute electronegativity, and η, the absolute hardness, are calculated for a number of metal atoms in their low-spin valence states. From these values the amount of electron density transferred from the metal to each CO is calculated. The resulting values are shown to be approximately proportional to $\bar{D}_o$, the mean bond strength, as predicted.

Recent work has developed the concepts of absolute electronegativity, χ,[1] and absolute hardness, η.[2] The definitions are

$$\chi_S = -(\partial E / \partial N)_Z = -\mu_S \qquad \eta_S = \frac{1}{2}(\partial^2 E / \partial N^2)_Z \qquad (1)$$

where E is the electronic energy of a molecule S, N is the number of electrons, and Z is a fixed set of nuclear charges. The absolute electronegativity is also equal to the electronic chemical potential, μ, with change in sign. The operational (and approximate) definitions are

$$\chi_S = \frac{1}{2}(I_S + A_S) \qquad \eta_S = \frac{1}{2}(I_S - A_S) \qquad (2)$$

where I_S is the ionization potential of S and A_S is the electron affinity. The absolute electronegativity is the same as the Mulliken value.

We assume that, for small changes in N, we can write

$$\mu_S = \mu^0_S + 2\eta_S(\Delta N_S) \qquad (3)$$

If we have two chemical species, A and B, that are allowed to react, there will be a shift of electrons from the less electronegative molecule, B, to the more electronegative molecule, A. The condition of equilibrium is that the chemical potentials, μ_A and μ_B, become equal.[2] This leads to a shift in charge, ΔN, from B to A

$$\Delta N = (\chi^0_A - \chi^0_B) / 2(\eta_A + \eta_B) \qquad (4)$$

Equation 4 is only an approximation, since it is based on (3), which ignores terms in $(\Delta N)^2$ and so on. This means that the hardness, η, is considered as a constant. This is not quite valid, especially for anions, where η changes rapidly as charge

is transferred. The chemical potential is also a function of external fields, so that if A (or B) is charged, this will affect μ_B (or μ_A) as a function of the distance.[3] Also, covalent bonding can also lower the energy even when $\Delta N = 0$, as for the reaction of two identical atoms.[4]

In spite of these shortcomings, (4), or some elaboration of it, has often been used to estimate the ionic character of chemical bonds.[5] It has the great virtue (and weakness) of containing a minimum number of parameters to characterize the chemical behavior of a molecule. Values of I_S are becoming available for more and more molecules. Values of A_S are still few in number. In fact for most molecules, the electron affinity cannot be detected. In such cases, A_S is set equal to zero, meaning that E is a minimum when the extra electron is at infinity.

The chemical potential and the absolute electronegativity are molecular properties and not orbital properties. However, in considering the transfer of electrons from B to A, it becomes necessary to consider the electrons as coming from definite occupied orbitals in B and going into definite empty orbitals in A. This defines the relative orientations of A and B to give the greatest possible overlap between these frontier orbitals.[6] Also, μ_S and χ_S are state functions, and while ground states are most often considered, sometimes it is useful to consider valence states or excited states, particularly for the reactions of atoms.

Electron transfer leads to an energy lowering, given by[2]

(1) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801. See also: Iczkowski, R. P.; Margrave, J. L. *J. Am. Chem. Soc.* **1961**, *83*, 3547.

(2) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.

(3) Nalewajski, R. F. *J. Am. Chem. Soc.* **1984**, *106*, 944.

(4) Pritchard, H. O. *J. Am. Chem. Soc.* **1963**, *85*, 1876.

(5) Hinze, J.; Whitehead, M. A.; Jaffe, H. H. *J. Am. Chem. Soc.* **1963**, *85*, 148. Iczkowski, R. P. *J. Am. Chem. Soc.* **1964**, *86*, 2329. Huheey, J. E. *J. Phys. Chem.* **1965**, *69*, 3284. Jolly, W. L.; Perry, W. B. *J. Am. Chem. Soc.* **1973**, *95*, 5442.

(6) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049.