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Registry No. $Ru(4,4'\text{-}(CH_3)_2bpy)_3^{2+}$, 32881-03-1; $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(4,7\text{-}(CH_3)_2phen)_3^{2+}$, 24414-00-4; $Ru(phen)_3^{2+}$, 22873-66-1; $Ru(5\text{-}Cl\text{-}phen)_3^{2+}$, 47860-47-9; $Ru(4,4'\text{-}(CH_3)_2bpy)_3^{3+}$, 65605-26-7; $Ru(bpy)_3^{3+}$, 56977-24-3; $Ru(4,7\text{-}(CH_3)_2phen)_3^{3+}$, 65545-47-3; $Ru(phen)_3^{3+}$, 65545-46-2; $Ru(5\text{-}Cl\text{-}phen)_3^{3+}$, 65545-45-1; Eu(II), 16910-54-6; Eu(III), 22541-18-0.

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Photoreaction Quantum Yields for the Cobalt(III) Complexes $Co(NH_3)_5(PhCN)^{3+}$ and $Co(NH_3)_5(CH_3CN)^{3+}$ [1]

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The nature and quantum yield of the photoreactions which take place on irradiation of aqueous $Co(NH_3)_5(CH_3CN)^{3+}$ and $Co(NH_3)_5(PhCN)^{3+}$ have been examined. Excitation at 254 nm corresponds to direct charge-transfer to metal excitation of $Co(NH_3)_5acn^{3+}$ (acn = acetonitrile) and to intraligand (IL) π–π^* excitation of $Co(NH_3)_5bzn^{3+}$ (bzn = benzonitrile). In both cases photoreduction to Co^{2+} is the predominant reaction but the former complex is the considerably more active. Thus, it is argued that the IL $\pi\pi^*$ state can undergo internal conversion to give a redox-active CTTM state but also may have independent pathways for deactivation perhaps including internal conversion to the lower energy ligand field states. At 313-nm excitation the relative redox activity is reversed, suggesting that the IL $\pi\pi^*$ states of $Co(NH_3)_5bzn^{3+}$ provide a more facile channel for populating the CTTM states than do the LF states of $Co(NH_3)_5acn^{3+}$ produced at this wavelength. Lastly 365- and 460-nm photolyses which correspond to LF excitation in both cases lead principally to aquation of the coordinated organonitriles despite the higher position on the spectrochemical series of these ligands compared to NH_3. At 460 nm the quantum yields for RCN aquation (0.010 mol/einstein) greatly exceed those for ammonia aquation from the same complex (<0.001 mol/einstein) or from $Co(NH_3)_6^{3+}$ (0.0005 mol/einstein). In this context, the patterns for ligand photoaquation from various $M(NH_3)_5L^{3+}$ and $M(NH_3)_5X^{2+}$ (M = Co(III), Rh(III), Ir(III); L = RCN, H_2O; X = Cl^-, Br^-, I^-) are compared and discussed qualitatively in terms of metal–ligand bonding in ligand field excited states.

Introduction

Previous studies[3-6] in this laboratory have been concerned with the quantitative photochemistry of various heavier group 8 metal ammine complexes of the general formula $M(NH_3)_5L^{n+}$. Ligands L which have proved especially interesting have been π-unsaturated, nitrogen-donor organic ligands such as the organonitriles (RCN) and the aromatic nitrogen heterocycles (e.g., pyridine). The use of substituents at positions on L remote from the coordination site allows one to examine series of complexes displaying wide variations in the ligand properties (i.e., σ-donor ability, π-acceptor/π-donor character, etc.) yet having the same stereochemical environment at the coordination site. Such perturbations of ligand properties not only may lead to systematic variations of metal–ligand bonding in the ground and excited states but also in some cases can be used to tune excited-state energies.[3a,d] Another advantage is that these organic ligands generally carry no ionic charge, thus minimizing this contribution to the complexity of comparing the relative ligand photosubstitution pathways of L and of NH_3.

The organonitriles display some unusual aspects as ligands. Despite the poor σ-donor ability suggested by its low Brønsted basicity, acetonitrile forms a wide variety of complexes.[7,8] In addition, spectroscopic series based on the positions of ligand field (LF) bands in the absorption spectra of various d^6 complexes[8,9] show acetonitrile to have a ligand field strength comparable to or greater than that of ammonia. It has been argued that the strength of the metal–acetonitrile interactions must include significant π-bonding contributions. For example, π back-bonding to acetonitrile is clearly evident in lower valent metal complexes such as those of ruthenium(II)[10] and can be invoked[4a] to explain the relatively strong-field spectroscopic behavior of rhodium(III) pentaammine complexes $Rh(NH_3)_5RCN^{3+}$. Similar rationalizations have been introduced[11] to explain the observation that while gas-phase binding energies between saturated ligands and the cyclopentadienylnickel cation ($CpNi^+$) display a linear correlation with the gas-phase proton affinities, acetonitrile displays a much higher metal binding energy than would be predicted according to its proton affinity.

In the present work, we have studied the pentaamminecobalt(III) complexes of acetonitrile and benzonitrile with the goal of examining the generality of the photochemical properties of analogous organonitrile complexes for different

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Table I. Spectral Properties of Pentaammine(organonitrile) Complexes $Co(NH_3)_5RCN^{3+}$ in Aqueous Solution[a]

Complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	Assign
$Co(NH_3)_5(PhCN)^{3+}$	469	79	$^1E,^1A_2 \leftarrow {}^1A_1$
	332	82	$^1E,^1B_2 \leftarrow {}^1A_1$
	272	2.36×10^3	$\pi^* \leftarrow \pi$
	254	3.15×10^3	$\pi^* \leftarrow \pi$
	233	2.12×10^4	$\pi^* \leftarrow \pi$
$Co(NH_3)_5(CH_3CN)^{3+}$	467	63	$^1E,^1A_2 \leftarrow {}^1A_1$
	333	56	$^1E,^1B_2 \leftarrow {}^1A_1$
PhCN[b]	278	0.88×10^3	$\pi^* \leftarrow \pi$
	271	0.94×10^3	$\pi^* \leftarrow \pi$
	265 sh	0.67×10^3	$\pi^* \leftarrow \pi$
	231 sh	1.04×10^4	$\pi^* \leftarrow \pi$
	223	1.27×10^4	$\pi^* \leftarrow \pi$

[a] Measured in acidic aqueous solution at 25 °C. [b] Transparent in visible region, $\epsilon < 3$ M^{-1} cm^{-1} at $\lambda > 290$.

metal systems. Notably, previous studies[12-14] of $Co(NH_3)_5L^{3+}$ have included few cases where L is an uncharged ligand, a feature which may play some importance at least with the photosubstitution pathways resulting from ligand field excitation. In addition, the benzonitrile complex displays a ligand-centered chromophoric site owing to the intraligand (IL) $\pi\pi^*$ transitions. Thus, it is of interest to examine whether direct excitation of such IL transitions is followed by internal conversion to give states involving more intimately the metal centers[6,15,16] or by independent pathways for deactivation[17] or reaction.[18,19]

Also reported is a brief study of LF excitation of the bromide complex $Co(NH_3)_5Br^{2+}$ to reexamine[14b] whether NH_3 photoaquation is an important reaction pathway for this system.

Experimental Section

Materials. The known cobalt(III) acetonitrile complex[20] was synthesized by the procedure similar to that reported by Piriz-MacColl[21] for the preparation of various $[Co(NH_3)_5L](ClO_4)_3$. A solution containing 1.0 g of the dimethyl sulfoxide complex $[Co(NH_3)_5(Me_2SO)](ClO_4)_3$, ~1.5 mL of Me_2SO, and 16 mL of acetonitrile was heated at reflux for ~25 min. This was cooled in an ice bath and 15 mL of 6 M $HClO_4$ was added dropwise. After overnight refrigeration, the solution was filtered to give an orange powder. This was recrystallized by dissolving in 60 °C 0.5 M $HClO_4$ and then adding 60% $HClO_4$ (~5 mL) until a precipitate began to appear. Gentle heating reestablished solution homogeneity, and slow cooling resulted in the formation of golden platelets of the acetonitrile complex salt. This material was recrystallized in a similar manner twice more to give an overall yield of 0.40 g of the gold crystals. Spectral properties agreed with literature values.[20]

The known benzonitrile complex $[Co(NH_3)_5bzn](ClO_4)_3$ was prepared in a similar manner with the modifications that the dimethyl sulfoxide complex was heated with Me_2SO (1 mL) and benzonitrile (10 mL) for 4.5 h at 85 °C and that recrystallization was carried out at ~40 °C owing to the lesser stability of the benzonitrile complex. The spectral properties of the material prepared in this manner agreed with the literature values[22] and with another sample prepared independently by Jordan's procedure.[22]

The bromide complex $[Co(NH_3)_5Br][ClO_4]_2$ was prepared from $[Co(NH_3)_5Br]Br_2$ by dissolving in hot water and then precipitating from solution by adding concentrated perchloric acid. The complex when recrystallized from perchloric acid solution and then vacuum-dried displayed electronic spectra in agreement with the literature values.[23]

Photolysis Procedures. Photolyses were carried out in dilute, acidic aqueous solution, thermostated at 25.0 °C with photolysis apparatus described previously.[3d,24] In order to minimize complications potentially arising from ion-pairing in solution, supporting-electrolyte concentrations were kept at a minimum, typically 0.0001–0.01 M HCl or $HClO_4$. Initial concentrations of the cobalt complexes typically were in the range 10^{-3} M to 2×10^{-2} M, depending upon the analysis procedures used. No significant spectral or quantum-yield differences between the dilute $HClO_4$ or HCl solutions or for different Co(III) concentration were seen. Most photolyses at 254 nm were carried out on an apparatus utilizing an Oriel Corp. low-pressure mercury–argon pen lamp with an Oriel "short-wave" filter. This source supplies an irradiation intensity of $\sim 7 \times 10^{-7}$ einstein/(L s) (more than 95% at 254 nm) to a 1-cm path length thermostated cell.

Photoreactions of the complexes were followed by periodic recording of the solution spectra during the photolyses. Quantum yields based on these spectral data (Φ_{spec}) were calculated from known or estimated changes in the optical densities between reactants and products (see Results). A Cary 14 or a Cary 118C spectrophotometer was used for these spectral measurements. When possible, these values were extrapolated to zero time to correct for secondary photolyses, and all quantum yields were corrected for dark reactions under analogous conditions. Quantum yields for the consumption of acid (Φ_{H^+}) were evaluated from pH changes between the initial and final solutions measured to an accuracy of ±0.01 pH unit on a Sargent Model NX pH meter. Yields for the formation of Co(II) resulting from photoreduction of the Co(III) complexes ($\Phi_{Co^{2+}}$) were determined by the standard thiocyanate analysis procedure[25] at the conclusion of irradiation. Yields for benzonitrile release from coordination (Φ_L) were determined by spectral analysis (at 223 nm) of aliquots from chromatography of the reaction solutions from Bio-Rad AG 50W-X4 (200–400 mark) ion-exchange resin. Benzonitrile elution and pH measurements were also carried out for control solutions and all reported quantum yields are corrected for the minor dark reactions. Cobalt-containing products from the 254-nm irradiations were characterized by their elution behavior from Bio-Rex 70 (100–200 mesh, Na^+ form).

Results

The spectra of aqueous $Co(NH_3)_5(CH_3CN)^{3+}$ and $Co(NH_3)_5(PhCN)^{3+}$ are summarized in Table I while photochemical quantum yields at various wavelengths are summarized in Table II.

Photolysis at 460 nm corresponds to excitation of the lowest energy spin-allowed LF band ($^1E,^1A_2 \leftarrow {}^1A_1$) for each of these complexes. In agreement with previous studies of cobalt(III)–ammine complexes, photoreduction to cobalt(II) is not

Table II. Quantum Yields (mol/einstein) for Photolyses of Cobalt(III) Complexes[a]

Complex	λ_{irr}, nm	Assign	$\Phi_{Co^{2+}}$[b]	Φ_{spec}[c]	Φ_{H^+}[d]	Φ_L[e]	Φ_{aquo}[f]
$Co(NH_3)_5bzn^{3+}$	460	LF	$<2 \times 10^{-4}$	0.011 ± 0.002	$<1 \times 10^{-3}$	0.010 ± 0.002	0.010
	365	LF	$<5 \times 10^{-4}$	0.014 ± 0.002	0.0016 ± 0.0005	0.013 ± 0.002	0.013
	313	LF, CT, IL	0.017 ± 0.001			0.032 ± 0.003	0.015
	254	IL, CT	0.05 ± 0.01	0.04 ± 0.01	0.21 ± 0.03	0.046 ± 0.008	~0.01
$Co(NH_3)_5acn^{3+}$	460	LF	$<10^{-4}$	0.010 ± 0.001	$\leq 1 \times 10^{-4}$		0.010
	365	LF	$<4 \times 10^{-4}$	0.041 ± 0.003	$<4 \times 10^{-4}$		0.041
	313	LF, CT	0.004 ± 0.001	0.109 ± 0.001			0.10
	254	CT	0.19 ± 0.01	0.22 ± 0.03	0.93		0.005

[a] Quantum yields and average deviations measured in acidic aqueous solution at 25 °C and corrected for dark reactions. [b] Based on chemical analysis for Co(II) in solution. [c] Spectral quantum yield based on the assumed reactions at the following wavelengths: at λ_{irr} 254 nm, photoreduction to Co^{2+} only; at λ_{irr} 313 (acn complex), 365, and 460 nm, aquation of unique ligand, acn or bzn, only. Spectral changes measured at λ_{max} of longer wavelength LF band in each case. [d] Consumption of H^+ as determined from pH changes. [e] Φ_{bzn} determined from the direct measurement of free benzonitrile released and analyzed by chromatography. [f] Determined from ion-exchange analysis of $Co(NH_3)_5H_2O^{2+}$ for 254-nm photolyses. For 460-, 365-, or 313-nm photolyses of $Co(NH_3)_5bzn^{3+}$, Φ_{aquo} is based on Φ_{bzn} corrected for $\Phi_{Co^{2+}}$ while for these wavelengths with $Co(NH_3)_5acn^{3+}$, Φ_{aquo} is based on Φ_{spec} corrected for changes attributable to the photoredox reaction.

a significant pathway when the lower energy LF bands are irradiated. The $\Phi_{Co^{2+}}$ values listed for 460 nm represent upper limits of Co(II) formation based upon experimental uncertainties using the standard thiocyanate analysis procedure. Irradiation at these wavelengths led to very small increases in the pH of these solutions initially at 2–4. Since the major cause of pH increases would be the release of ammonia and its subsequent neutralization, the low Φ_{H^+} values indicate that ammonia aquation is at most a minor photoreaction at this wavelength. Also, since photoreduction of Co(III) to Co(II) would release up to five NH_3's per Co(II) into solution, the low quantum yields for H^+ uptake confirm the low values for $\Phi_{Co^{2+}}$.

The above experiments indicate that the spectral changes seen with the low-conversion 460-nm photolyses of $Co(NH_3)_5(CH_3CN)^{3+}$ and $Co(NH_3)_5(PhCN)^{3+}$ represent photoaquation of the nitrile ligand to give $Co(NH_3)_5H_2O^{3+}$ plus the free ligand (eq 1). For the benzonitrile complex this

$$Co(NH_3)_5RCN^{3+} + H_2O \xrightarrow{h\nu(460\ nm)} Co(NH_3)_5H_2O^{3+} + RCN \qquad (1)$$

conclusion was confirmed by chromatography. When the photolysis solution was washed through an acidic column of cation-exchange resin using only water as an eluent, the cationic complexes were trapped on the column and free benzonitrile was eluted. The resulting quantum yields for benzonitrile aquation (Φ_L) are equivalent to quantum yields (Φ_{spec}) based upon the spectral differences between the reactants and products predicted by eq 1. Notably, the analytical method based upon the benzonitrile elution is the more sensitive owing to the very large extinction coefficients of free benzonitrile in water. A similar analysis of the acetonitrile aquation is not feasible given the transparency of that ligand in the UV region.

Photolysis with 254-nm light leads to entirely different observations (Table II). For the acetonitrile complex, this wavelength corresponds to the lower energy side of the rapidly rising charge-transfer to metal (CTTM) absorption characteristic of cobalt(III)–pentaammine complexes including $Co(NH_3)_6^{3+}$, while for the benzonitrile complex this wavelength corresponds to π–π^* intraligand absorptions. Thiocyanate analyses for Co(II) indicate in each case that the principal photoreaction at 254 nm is reduction of Co(III) to Co(II) while the pH measurements and benzonitrile chromatographic analyses indicate also the release of both NH_3 and L (eq 2). The oxidation products are unknown (vide

$$Co(NH_3)_5L^{3+}(aq) \xrightarrow{h\nu(254\ nm)} Co^{2+}(aq) + NH_3 + L + ? \qquad (2)$$

infra). For both the acetonitrile and benzonitrile complexes, the various quantum yields appear independent (within experimental uncertainties) of whether the reaction solutions are air equilibrated or carefully deaerated by entraining with purified nitrogen.

The 254-nm photolysis of aqueous $Co(NH_3)_5acn^{3+}$ leads to a general decrease in both LF bands. The Φ_{spec} calculated on the assumption that Co^{2+} is the only visible absorbing product is in reasonably good agreement with $\Phi_{Co^{2+}}$. However, the small spectral differences at the monitoring wavelength (467 nm) between $Co(NH_3)_5acn^{3+}$ and $Co(NH_3)_5H_2O^{3+}$ compared to the much larger difference between Co^{2+} and the starting material could obscure substantial aquation. For this reason, ion-exchange analysis was carried out on the 254-nm photolysis products. The only products identified were Co^{2+} and a much smaller quantity of $Co(NH_3)_5H_2O^{3+}$; however, ion exchange of dark reaction products indicates that the latter material can be largely attributed to thermal aquation of acetonitrile. The Φ_{aquo} listed (Table II) is an upper limit based upon experimental uncertainties. Comparison of Φ_{H^+} to $\Phi_{Co^{2+}}$ suggests that about five ammonias are released as the consequence of each photoreduction consistent with the thermal lability of Co(II) complexes.

The 254-nm photolysis of $Co(NH_3)_5bzn^{3+}$ leads to a smaller photoreduction yield ($\Phi_{Co^{2+}}$) than for the acetonitrile analogue. The $\Phi_{Co^{2+}}$, Φ_{bzn}, and Φ_{spec} (based on the assumption that absorbance changes at 469 nm are due to eq 2 only) appear to agree within generous limits of experimental uncertainties. However, the Φ_{spec} values indeed were systematically 20–30% smaller than $\Phi_{Co^{2+}}$. The reason for this difference very likely lies in the assumption that Co^{2+} is the only visible-absorbing product. The photolysis is accompanied by substantially increased absorbance in the near-UV region extending into the visible region. This very likely results in an error in the assumed extinction coefficient differences between reactants and products and thus a low Φ_{spec} value. Ion-exchange analyses of the cobalt products indicate formation of only Co^{2+} and $Co(NH_3)_5H_2O^{3+}$. The latter ion appears in quantities exceeding the thermal reaction pathway but is at most a relatively minor product. The near-UV absorption can be largely attributed to an organic material since the chromatographic analysis for the free benzonitrile also revealed another component having a very broad absorption band at ~290 nm which eluted with benzonitrile from the cation-exchange resin. As this material is present in the analyses of 313-nm photolysis solutions but not in the analyses of 365- or 460-nm photolysis solutions, it is likely that it represents an organic oxidation product. (A secondary photolysis product of the organic ligand is excluded since $\epsilon_{313} \simeq 0$ for free benzonitrile.)

Photolyses at 313 nm revealed for both complexes photolytic behavior intermediate between those observed at 254 nm or at 460 nm. Both photoreduction of Co(II) and nitrile photoaquation were noted (Table II). Photolysis at 365 nm leads to photoaquation of the organonitrile as the major photoreaction for both complexes with photoreduction to Co(II) and the consumption of acid (photoreduction of NH_3 photoaquation) at most a minor process. The benzonitrile complex appears to have about the same quantum yield for eq 1 at 365 and at 313 nm as at 460 nm. (The approximate substitution quantum yield at 313 nm can be derived by subtracting $\Phi_{Co^{2+}}$ from Φ_{bzn} to give 0.015 mol/einstein.) However, the quantum yield for photosubstitution is much more wavelength dependent for the acetonitrile complex, increasing by roughly 1 order of magnitude from 460-nm irradiation to 313-nm irradiation. Another difference is that while the 313-nm photolysis of the acetonitrile complex shows a decrease in $\Phi_{Co^{2+}}$ by a factor of 50 from the values for 254-nm photolysis, the corresponding decrease for the benzonitrile complex is only a factor of 3. Thus, while for 254-nm irradiation $Co(NH_3)_5PhCN^{3+}$ displays a smaller $\Phi_{Co^{2+}}$ than does $Co(NH_3)_5(CH_3CN)^{3+}$, the opposite is true for 313-nm irradiation.

Photolysis of the bromide complex $Co(NH_3)_5Br^{2+}$ in aqueous perchloric acid solution (initial pH 3.40) was carried out at a wavelength (546 nm) close to the λ_{max} of the lowest energy LF absorption band. Spectral absorbance changes, assuming $Co(NH_3)_5H_2O^{2+}$ as the only product with a significantly different extinction coefficient at 550 nm, gave a quantum yield (Φ_{spec}) of $(2.6 \pm 0.4) \times 10^{-3}$ mol/einstein while pH changes gave $\Phi_{H^+} = (5 \pm 1) \times 10^{-4}$ and Co^{2+} analysis gave $\Phi_{Co^{2+}} < 2 \times 10^{-5}$. The low $\Phi_{Co^{2+}}$ indicates that Φ_{H^+} represents photoaquation of NH_3 (eq 3(a)) independent of photoreduction; however, since $Co(NH_3)_4(H_2O)Br^{2+}$ is expected to have a significant absorption at 550 nm, Φ_{spec} no doubt represents Br^- aquation as assumed (eq 3(b)). This conclusion

$$Co(NH_3)_5Br^{2+} + H_2O \xrightarrow[(550\,nm)]{h\nu} \left\{ \begin{array}{l} \xrightarrow{(a)} Co(NH_3)_4(H_2O)Br^{2+} + NH_3 \\ \xrightarrow{(b)} Co(NH_3)_5H_2O^{3+} + Br^- \end{array} \right. \qquad (3)$$

was supported by the potentiometric titration of free Br^- ion chromatographically separated from the product mixture; however, the relatively low sensitivity of this method adds a large uncertainty to the quantum yield, $\Phi_{Br^-} = (2.0 \pm 0.6) \times 10^{-3}$.

Discussion

Discussion of the photochemistry of the $Co(NH_3)_5RCN^{3+}$ complexes shall focus on three general observations: (1) Irradiation at 254 nm leads principally to redox decomposition and the acetonitrile complex is the considerably more active. (2) Photoredox and photoaquation are both noted with 313-nm irradiation, but at this wavelength, the benzonitrile complex is significantly more redox active than the acetonitrile analogue. (3) Irradiation of the lower energy LF band of either complex (λ_{irr} 460 nm) leads to RCN aquation as the only significant photoreaction and the quantum yields greatly exceed those for NH_3 aquation from the same complexes or from $Co(NH_3)_6^{3+}$.

The photoreaction pattern seen for the acetonitrile complex parallels in most respects the patterns for other cobalt(III) pentaammine complexes,[12,13] a close analogue being $Co(NH_3)_6^{3+}$.[26] Photolysis at 254 nm corresponds to exciting a low extinction coefficient ($\epsilon \sim 10^2$ M^{-1} cm^{-1}) tail of the charge-transfer to metal (CTTM) absorption for $Co(NH_3)_6^{3+}$ and for $Co(NH_3)_5acn^{3+}$ and is accompanied by redox decomposition with comparable quantum yields ($\Phi_{Co^{2+}} = 0.16$ and 0.19 mol/einstein, respectively). Increasing λ_{irr} decreases $\Phi_{Co^{2+}}$; at 460 nm, photoredox is undetectable and only ligand aquation is seen.

In contrast, 254-nm excitation of $Co(NH_3)_5bzn^{3+}$ corresponds to an IL π–π* transition. Observation of redox decomposition here suggests internal conversion from the initially populated state(s) into reactive CT state(s). Adamson and co-workers[15] have previously noted this deactivation mode for IL excited states of aqueous $Co(NH_3)_5$(*trans*-stilbenecarboxylate)$^{2+}$. However, the fact that $\Phi_{Co^{2+}}$ is much smaller for $Co(NH_3)_5bzn^{3+}$ than for $Co(NH_3)_5acn^{3+}$ indicates that the IL states initially populated may also deactivate by pathways independent of the CTTM states. Whether this involves stepwise deactivation first into the LF states cannot be unequivocally determined given the low LF state reactivities, experimental uncertainties inherent to the $\Phi_{Co^{2+}}$ and Φ_L measurements, and the λ_{irr} dependence of photosubstitution quantum yields measured for LF excitation of cobalt(III) ammines.[12,13] However, the fact that $Co(NH_3)_5bzn^{3+}$ displays measurable photoaquation at 254 nm suggests that the internal conversion IL → LF is a viable deactivation route. Notably, the photochemical behavior of the rhodium(III) analogue $Rh(NH_3)_5bzn^{3+}$ gives only photoaquation when irradiated at 254 or 313 nm and the quantum yields are essentially wavelength independent (0.29 and 0.35, respectively). At 254 nm, excitation is into an IL band while at 313 nm, it is directly into the lowest energy LF band of the Rh(III) species; thus it was concluded that internal conversion from IL to LF was occurring with high efficiency. The low value of $\Phi_{Co^{2+}}$ and observation of the $Co(NH_3)_5H_2O^{3+}$ product suggests a similar deactivation pathway for $Co(NH_3)_5bzn^{3+}$.

For 313-nm irradiation, $\Phi_{Co^{2+}}$ is far larger for $Co(NH_3)_5bzn^{3+}$ than for $Co(NH_3)_5acn^{3+}$. For the latter species, 313 nm corresponds to the short-wavelength side of the second LF band. The low extinction coefficient (ϵ_{313} 30) indicates there is very little CT character to the absorption, and the very low $\Phi_{Co^{2+}}$ value suggests that the initially populated LF state deactivates by pathways exclusive of the CT manifold. Indeed, the very modest redox decomposition seen may simply reflect some small, direct absorption into the CTTM state(s) owing to the long-wavelength tailing of the CT absorption. We have noted similar results for the 313-nm excitation of $Co(NH_3)_6^{3+}$ ($\Phi_{Co^{2+}} < 0.0012$ mol/einstein). In contrast, 313 nm corresponds to the onset of the IL bands (ϵ_{313} 66) (Figure 1) of the benzonitrile complex and one can conclude that a significant fraction of light absorption results in direct formation of IL excited states. Therefore, the much higher redox decomposition activity for this complex at 313 nm may be attributable to internal conversion from the $\pi\pi$* states into the CTTM manifold. Thus, while the results at 254 nm suggest that the benzonitrile complex IL states can deactivate by independent pathways competitive with internal conversion to a CTTM state, the 313-nm data indicate that internal conversion from IL to CTTM states of the bzn complex is considerably more efficient than LF to CTTM internal conversion in $Co(NH_3)_5acn^{3+}$.

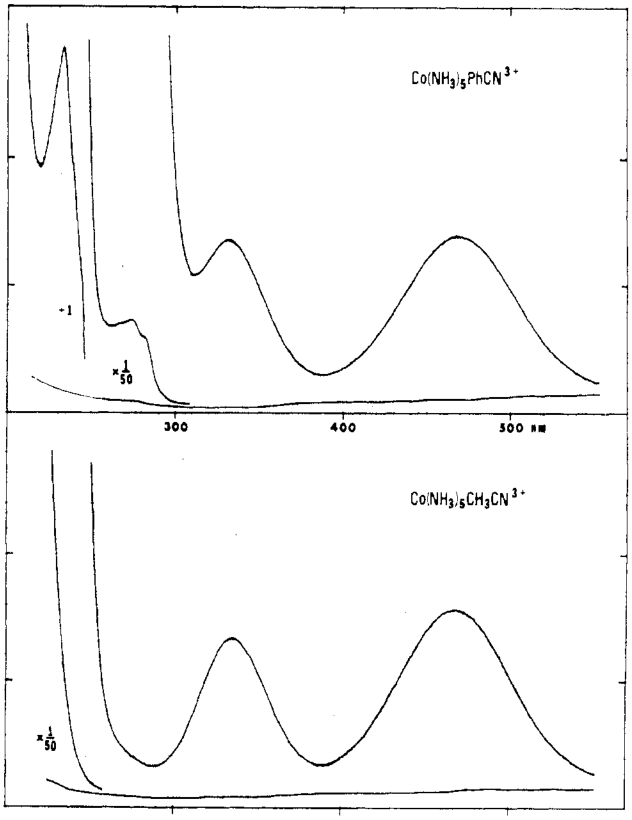

Figure 1. Spectra in dilute aqueous solutions of $Co(NH_3)_5bzn^{3+}$ (top) and of $Co(NH_3)_5acn^{3+}$ (bottom).

Irradiation at 365 and 460 nm corresponds to LF excitation of both nitrile complexes, and the wavelength dependence of the photoaquation quantum yields measured is similar to the patterns noted previously for the LF photochemistry of other cobalt(III)–amine complexes. Quantitative photochemistry has been reported for the LF excitation of various low-spin, d^6 pentaammine complexes $M(NH_3)_5L^{n+}$ (M is Ru(II), Co(III), Rh(III), or Ir(III); L is a neutral or anionic ligand)[4-6,12-14,26-28] in aqueous solution. That ligand labilization dominates when λ_{irr} corresponds to the lowest multiplicity-allowed LF band is consistent with the $t_{2g}{}^5e_g{}^1$ electronic configuration of the LF excited state(s). Among the pentaammine complexes, those of cobalt(III) usually display very low photosubstitution quantum yields when excited into their lowest energy singlet LF states. For example, ${}^1T_{1g} \leftarrow {}^1A_g$ excitation of aqueous $Co(NH_3)_6^{3+}$ leads to a Φ_{NH_3} of 5×10^{-4} mol/einstein[26] which can be compared to 0.075 and 0.09 mol/einstein for the Rh(III)[4a] and Ir(III)[6] analogues, respectively. Another difference is that the Co(III) complexes show markedly wavelength-dependent photosubstitution quantum yields while Rh(III) and Ir(III) do not. Among the organonitrile complexes, $M(NH_3)_5RCN^{n+}$, the Co(III) complexes are much less photolabile than other d^6 analogues.

Nonetheless, the patterns of photoreactivity remain consistent for the Co(III), Rh(III), and Ir(III) systems; namely, aquation of RCN is the overwhelmingly predominant photoreaction, and the quantum yield Φ_{RCN} is much larger than Φ_{NH_3} from the hexaammine of the same metal ion.

To a first approximation, the dominance of RCN photoaquation from $M(NH_3)_5RCN^{3+}$ is inconsistent with the empirical rules (the stronger field ligand of the weakest average ligand field axis will be preferentially labilized) proposed originally[29] for photoreactions of Cr(III) complexes, but said to be "mildly applicable" to Co(III) complexes.[14] The lowest energy, spin-allowed LF bands of $Co(NH_3)_5acn^{3+}$ and of $Co(NH_3)_5bzn^{3+}$ (Table I) occur at energies slightly higher than the corresponding band for $Co(NH_3)_6^{3+}$ (λ_{max} 472 nm).[30] Thus, if the absorption spectra are taken as the measure of relative ligand field strengths, benzonitrile and acetonitrile are stronger field ligands than NH_3, and aquation is occurring from the strongest field axis of the three defined by the six ligands of $Co(NH_3)_5RCN^{3+}$. However, as noted previously with the Rh(III) complexes,[4a] the organonitriles' strong-field position in a spectrochemical series very likely is a reflection of these ligands' π-acceptor properties. If the relative σ-donor abilities of the ligands are the determining factors in localizing the excitation in the relevant σ^* orbitals[4a,31] (d_{z^2} or $d_{x^2-y^2}$ in crystal field theory), then it is easily understandable why population of the lowest excited states of the weakly σ-donor organonitriles leads to ligand labilization largely confined to the unique axis.[32]

The relative labilities of the two ligands along the weak-field axis can be qualitatively rationalized in terms of differences in π and σ contributions to the metal–ligand bonding between the ground and LF excited states.[4a,33] The configurational change $t_{2g}^6 \rightarrow t_{2g}^5,e_g^1$, depletes the π-symmetry t_{2g} metal orbitals while populating a σ^* orbital (d_{z^2}) largely directed along the z axis. Thus, while the σ bonding to the metal is weakened for both axial ligands, the lessened π-donor ability of the metal additionally should result in decreased π bonding between the metal and the organonitrile. The sum of these two bonding changes may cause distortion sufficient to make RCN aquation the principal reaction channel among the excited-state deactivation mechanisms. This argument gains weight when one considers the luminescence spectroscopy of the Rh(III) complex $Rh(NH_3)_5acn^{3+}$. Although the absorption spectrum suggests acn to be comparable to NH_3 in ligand field strength, the emission spectra indicate that $Rh(NH_3)_5acn^{3+}$ has a significantly lower energy-emitting LF state than does $Rh(NH_3)_6^{3+}$. Thus, the emission spectra can also be interpreted in terms of distortion along the unique ligand bond axis owing to the decreased importance of π bonding in the excited state.[4a]

Similar considerations[33,34] suggest that a π-donor ligand would have enhanced ligand–metal π bonding compensating in part the decreased σ bonding in the excited state. This plus the ligands' negative charge provides rationalization for the LF photochemistry of $Co(NH_3)_5Cl^{2+}$ where photoaquation of NH_3 predominates over photoaquation of Cl^- (eq 4) when the

$$Co(NH_3)_5Cl^{2+} + H_2O \xrightarrow{h\nu} \begin{cases} Co(NH_3)_4(H_2O)Cl^{2+} + NH_3 \\ Co(NH_3)_5H_2O^{3+} + Cl^- \end{cases} \qquad (4)$$

lowest energy, spin-allowed LF band is irradiated.[35] Although these concepts are qualitatively useful for rationalizing the relative importance of observed photolabilization pathways from a particular complex, the quantitative predictive value is compromised by the dearth of information regarding relative metal–ligand bond strengths and the extents to which these are due to σ or π interactions with the various metal centers.[33c]

Table III. Ligands Preferentially Labilized in the LF Photolyses[a] of $M(NH_3)_5L^{n+}$ in Aqueous Solution

	Ligand aquated		
L[b]	M = Co(III)	M = Rh(III)	M = Ir(III)
acn	acn[c]	acn[d]	acn[e]
bzn	bzn[c]	bzn[d]	bzn[e]
H_2O	NH_3[f,h]	H_2O[g]	H_2O[i]
Cl^-	$NH_3 > Cl^-$ [f]	Cl^- [d]	$Cl^- > NH_3$[i]
Br^-	$Br^- > NH_3$[c,j]	$NH_3 > Br^-$ [d]	$NH_3 > Br^-$ [e,i]
I^-		NH_3[d]	NH_3[e,i]

[a] λ_{irr} in each case corresponds to irradiating the lowest energy, spin-allowed LF absorption band. [b] L's listed in order of decreasing LF strength as suggested by the position of the lowest energy, spin-allowed LF band. [c] This work. [d] Reference 5. [e] M. Talebinesab-Sarvari, A. Zanella, and P. C. Ford, unpublished data. [f] Reference 14. [g] P. C. Ford and J. D. Petersen, *Inorg. Chem.*, **14**, 1404 (1975). [h] H_2O exchange not measured. [i] Reference 6. [j] Reference 14b.

An additional problem is the lack of information of how structural perturbations affect other nonradiative deactivation pathways.[36] Lastly, the observed wavelength dependence of the cobalt(III) quantum yields[35] makes difficult comparison of the photoreaction pathways with the essentially wavelength-independent ligand field photochemistry of the Rh(III) and Ir(III) analogues.

Summarized in Table III are the photolabilization pathways for those pentaammine complexes where the photolability of the Co(III), Rh(III), and Ir(III) homologues are each known. Although the NH_3 photoaquations generally lead to trans products and the stereochemical origin of the aquated NH_3 is generally assumed to be from the trans position,[5,27] it is important to recognize the uncertainty of this conclusion given the potential photostereomobility of these systems.[37] Despite this uncertainty and the qualifications mentioned in the above paragraph, the data for each of the metals in Table III do follow reasonably parallel patterns, the patterns for Rh(III) and Ir(III) being remarkably close.[6] Qualitatively, the observation for these two metals is that the π-acceptor nitrile ligands are photoaquated preferentially over the stronger σ-donor ammonia ligands; however, as one proceeds to the π-donor halogens, NH_3 aquation becomes an important pathway when the lowest energy, spin-allowed LF bands of Co(III) are irradiated. The patterns are similar but with the differences that NH_3 aquation is measurable for L = H_2O[38] and that NH_3 aquation is predominant for the chloro complex while Br^- aquation is predominant for the bromo complex.

Interestingly, the decreasing importance of halide photoaquation vs. that of NH_3 photoaquation for the Rh(III) and Ir(III) complexes follows the decreasing thermal lability $Cl^- > Br^- > I^-$ of these $M(NH_3)_5X^{2+}$ complexes toward halide equation.[39] In the same vein, the thermal lability of $Co(NH_3)_5X^{2+}$ follows the opposite order $Br^- > Cl^-$ again consistent with the observation that Br^- photoaquation is the more facile pathway from $Co(NH_3)_5Br^{2+}$. Despite this parallel, an equally attractive rationalization of the relative photolabilities of X^- or NH_3 from these $M(NH_3)_5X^{2+}$ complexes can be drawn from the extent of M–X π bonding expected for the LF excited state. As has been pointed out previously[33c] the π bonding of Cl^- and Br^- to Co(III) should be similar, with Cl^- the slightly better π donor to Co(III). However, with the larger Rh(III) and Ir(III) ions one might expect an opposite order owing to better π overlap with the larger Br^- and I^- ions. Thus, it is possible that the photolabilization of the ammonia becomes the increasingly favored pathway as ligand-to-metal π bonding assumes an increasingly major role in determining the trajectories for excited-state deactivation.

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Registry No. $Co(NH_3)_5(PhCN)^{3+}$, 46343-53-7; $Co(NH_3)_5(CH_3CN)^{3+}$, 44819-13-8; $Co(NH_3)_5Br^{2+}$, 14970-15-1; PhCN, 100-47-0.

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Flash Kinetic Spectroscopy of $Mo_2(O_2CCF_3)_4$

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Flash photolysis of $Mo_2(O_2CCF_3)_4$ causes bleaching followed by reappearance of ground-state absorption on a microsecond time scale. In benzene solution recovery follows simple first-order kinetics with $\tau(C_6H_6) = 33\ \mu s$. In nucleophilic solvents reappearance of the original absorption is more complex and appears to be a two-step process. We believe that the principal intermediate present at the end of the 10-ns flash excitation is a triplet having the $\sigma^2\pi^4\delta^1\pi^{*1}$ configuration. We speculate that the triplet reacts with polar solvent molecules (acetonitrile, dimethylformamide, and acetone) forming short-lived adducts in which one trifluoroacetato bridge has been half opened. These intermediates have new absorption near 490 nm, relatively intense maxima in the 385-nm region, and absorption at 360 nm similar to that of the ground state of the parent compound. Half-times for formation of the intermediate adducts are $\tau(CH_3CN) = 5.5$, $\tau(\text{acetone}) = 3.9$, and $\tau(DMF) = 1.5\ \mu s$. Lifetimes for decay of the adducts to $Mo_2(O_2CCF_3)_4$ ground states are respectively 32, 16, and 13 μs. Spectral characteristics of the various transients are discussed.

We recently reported a flash kinetic study[1] of the complex ions $Re_2X_8^{2-}$ (X = Cl, Br), which contain quadrupole metal–metal bonds. The lowest excited state had a lifetime of about 100 ns in fluid solution at room temperature and was assigned the $\sigma^2\pi^4\delta^1\pi^{*1}$ configuration. In an earlier communication[2] we reported that photochemical cleavage of the complexes occurred from higher excited states with appreciable quantum yield but that irradiation in the first ab-

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