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Photochemistry of Macrocyclic Coordination Compounds. I. A Cobalt(III) Complex Containing a Tetradentate Equatorial Ligand, PnAO[1]

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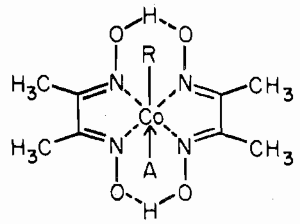
Photochemical studies are reported on the complexes $Co(PnAO)X_2$, $[Co(PnAO)(H_2O)X]^+$, and $[Co(PnAO)(H_2O)_2]^{2+}$ where X = N_3 or NO_2 and PnAO is 2,2'-(1,3-diaminopropane)bis(2-methyl-3-butanone oxime), which coordinates as a macrocyclic tetradentate equatorial ligand. Photoaquation of an axial X group is the dominant reaction for all wavelengths studied, 254, 366, and either 515 or 550 nm; quantum yields are a few thousandths at the longer wavelengths, the region of the first ligand field band, and increase to values of the order of 0.01 and then 0.1 at the shorter wavelengths, which correspond to charge-transfer absorptions. Photoredox decomposition to Co(II) also occurs, but in low yields; it is proposed that part of the time $[Co^{II}(PnAO)(H_2O)_2]^+$ results and that this species catalyzes aquation if X = N_3 but not if X = NO_2; kinetic studies on the catalyzed and noncatalyzed reactions were made and an atom-transfer type mechanism is suggested for the former. The spectra are normal relative to analogous cobalt(III)-acidoammine complexes and the photolysis mechanism is thought also to be similar, namely, heterolytic bond fission at the longer wavelengths and homolytic bond fission followed by cage reactions at the shorter wavelengths. The results are also compared to the behavior of cobaloxime complexes.

Introduction

The photochemistry of Co(III) complexes has been widely studied,[2] and for the present purpose it is useful to make three classifications of behavior. Irradiation in the wavelength region of the first charge-transfer, CT, absorption band generally leads to redox decomposition in good quantum yields; the ligand substitution (usually aquation) which may also occur has been attributed to a cage reaction following homolytic bond fission (see ref 2b). Except where intrusion of CT character seems evident from their intensity, the first and second, L_1 and L_2, absorption bands have not appeared to be sufficiently photoactive to warrant detailed study. The use of a laser–microcell technique has recently made it possible to measure low quantum yields even with complexes whose dark reaction times are of the order of minutes, and it is now evident that irradiation of the L_1 or L_2 bands of cobalt(III) ammines and acidoammines leads to stereospecific substitutional types of processes which can be accounted for by heterolytic bond fission according to rules developed for the analogous Cr(III) complexes.[3-6] The low quantum yields (relative to Cr(III) complexes) were tentatively attributed to more rapid radiationless deactivation rather than to smaller reactivity of the thermally equilibrated excited (thexi[3]) state. The term *thexi* was coined in response to the felt need to distinguish between thermally equilibrated excited states and Franck–Condon states. These last are those produced following light absorption, have the approximate geometry of the ground state, and are the states treated in conventional ligand field theory.

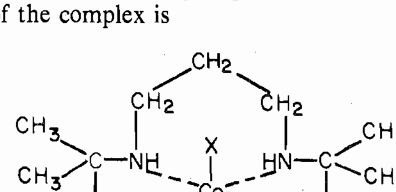
A third behavior pattern may be followed by Co(III) complexes of the glyoxime and corrin types, characterized by having a planar arrangement of four secondary or tertiary nitrogens held in a macrocyclic framework and one whose bonding may be partially delocalized. The axial coordination of these complexes typically includes one ligand making a cobalt–carbon bond. The structure for bis(dimethylglyoximato)cobalt(III) complexes is, for example



A number of variants, with R = CN, CH_3, C_2H_5, etc., and A = H_2O, pyridine, NH_3, etc., have been prepared.[7]

These complexes and also those which constitute models of vitamin B_{12} coenzyme[8] show intense absorptions throughout the visible and uv regions; irradiation in the 400–450-nm region typically leads to homolytic fission of the cobalt–carbon bond[9] in quantum yield of the order of 0.01.[7,8] The complexes may be photoinert below 500 nm,[7] although the laser–microcell technique may perhaps reveal substitutional photochemistry of the A ligand in low yields.

The present investigation was undertaken following a report of crystallographic and kinetic studies on a new type of Co(III) complex, $Co(PnAO)X_2$.[10,11] The ligand PnAO (an alternative designation is $Co(PnAO\text{-}H)_2X_2$)[10,12] is 2,2'-(1,3-diaminopropane)bis(2-methyl-3-butanone oxime);[11] when it coordinates, it looses one oxime hydrogen and the structural appearance of the complex is



In this series, the X groups are halogens, pseudohalogens, or other bases of moderately strong acids.

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The availability of these PnAO complexes made it possible to fill in the photochemistry of the series (A) *trans*-$Co(N)_4X_2^+$ [$(N)_4$ = $(en)_2$ or cyclam], (B) $Co(PnAO)X_2$, and (C) Co(dimethylglyoxime)$_2$RA. The sequence is one of increasing bridging by an –OHO– group, of increasingly unsaturated character of the coordinated nitrogens, and of increasingly intense visible and near-uv absorptions. The photochemistry of the type A complexes is one of low quantum yield aquation of the X group (around 450–550 nm and with X = Cl or Br);[2,4] in the case of *trans*-$Co(en)_2Br_2^+$, the yield rises to 0.07 at 370 nm but the photoreaction remains primarily one of aquation.[2] As noted above, for (C) the photochemistry is one of homolytic Co–C bond cleavage; the same is apparently true for methylcobalamin, although photoaquation occurs if CN^- or NH_3 is coordinated (see ref 9).

Experimental Section

Preparation of the Complexes. The PnAO ligand was prepared according to the method of Vassian and Murmann,[12] and Co(PnAO)Cl_2, through a modification of Murmann's method.[10] An aqueous solution approximately 0.1 *M* in $CoCl_2·6H_2O$ and in PnAO·2HCl was brought to pH 7.5 with aqueous NaOH. An excess of PbO_2 was added at room temperature, and the mixture was allowed to stand overnight and was then filtered. The filtrate was made 0.5 *M* in hydrochloric acid, and on warming gently, the complex precipitated as green crystals. It was found that the PbO_2 oxidation could be omitted and an air oxidation procedure employed; this modification gave good yields and was used in some of the preparations.

Co(PnAO)(N$_3$)$_2$. Co(PnAO)Cl_2 was dissolved in water containing an excess of NaN_3, and the desired complex separated out as dark green crystals after partial evaporation of the solution and then cooling. It can be recrystallized from various solvents but apparently exists in two crystallographic modifications. Violet crystals resulted on recrystallization from chloroform while if acetone was used, a mixture of mainly violet and some dark green crystals resulted. The solution in any of the above solvents, including water, was violet and gave exactly the same absorption spectra. The reflectance spectra of the two forms differed somewhat, however, and mainly in that the green form has a peak absorption at 567 nm while the violet one shows the peak at 556 nm. The X-ray powder patterns showed distinct differences, both in relative line intensities and in that lines were present in the one form which were absent in the other, and *vice versa*. Neither form contained water of crystallization, as shown by thermogravimetric analysis (using a Du Pont Model 950 instrument, a flowing nitrogen furnace atmosphere, and a heating rate of 10° min^{-1}), and by chemical analysis. This last give the following results. *Anal.* Calcd for $CoC_{13}H_{27}N_{10}O_2$: C, 37.68; H, 6.57; N, 33.80. Found for the dark green form: C, 38.09; H, 6.43; N, 32.73. Found for the violet form: C, 38.15; H, 6.52; N, 32.90.

To be isomers (cis and trans) the less stable form would have to convert to the stable one almost instantly upon dissolving. This is a rather unlikely possibility, especially since the hydrogen bond of the PnAO ligand would presumably have to be broken and it is a very stable one.[10] We conclude that we have two quite different crystal structures, but of the same molecular unit.

[Co(PnAO)(H$_2$O)N$_3$](ClO$_4$). Co(PnAO)$(N_3)_2$ was dissolved in warm water and then treated with a stoichiometric amount (1:1) of $AgClO_4$. The mixture was filtered to remove the AgN_3 formed and the filtrate was evaporated to about one-fourth of the volume. (*Warning*! dry AgN_3 is explosive.) On cooling, red-violet crystals formed, which were filtered off and air-dried. *Anal.* Calcd for $CoClC_{13}H_{29}N_7O_7$: C, 31.88; H, 5.97; N, 20.02. Found: C, 32.10; H, 6.00; N, 19.84.

Co(PnAO)(NO$_2$)$_2$. The procedure used was analogous to that for the preparation of the diazido complex. The crystal structure of the orange crystals has been determined;[10] the two nitro groups are not equivalent since the N–$(CH_2)_3$–N bridge is bent out of the equatorial plane. Our preparation was identical in its visible and uv absorption spectra with that of an authentic sample supplied by Professor Murmann.

[Co(PnAO)(H$_2$O)(NO$_2$)](ClO$_4$). The dinitro complex was dissolved in a minimum amount of warm water and then treated with a stoichiometric amount of $AgClO_4$. On cooling, red-orange crystals of product separated out and were filtered off and air-dried. Again, the absorption spectrum of our preparation was identical with that of an analyzed sample from Professor Murmann.

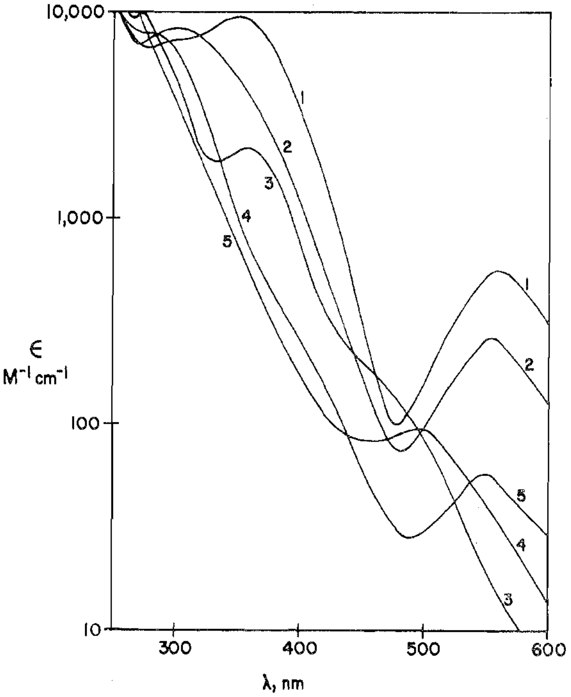


Figure 1. Absorption spectra: curves 1 and 2, Co(PnAO)$(N_3)_2$ and [Co(PnAO)$(H_2O)N_3$](ClO_4) in pH 4.75 buffer medium; curves 3 and 4, Co(PnAO)$(NO_2)_2$ and [Co(PnAO)$(H_2O)(NO_2)$](ClO_4) in pH 3.4 buffer medium; curve 5, [Co(PnAO)$(H_2O)_2$]$(ClO_4)_2$ in pH 4.75 buffer medium.

Co(PnAO)(NCS)$_2$ and [Co(PnAO)(H$_2$O)(NSC)](ClO$_4$). These compounds were prepared in a manner analogous to the other diacido and aquacido complexes, giving purple-red and pale red crystals, respectively. Both are only very slightly soluble in water and were not studied.

[Co(PnAO)(H$_2$O)$_2$](ClO$_4$)$_2$. A warm aqueous solution of the dichloro complex was treated with a stoichiometric amount (1:2) of $AgClO_4$, the mixture was then filtered, and the filtrate was evaporated to near dryness under reduced pressure, at 5°. The product which separated out was removed by filtration and recrystallized from water. The resulting brownish crystalline powder is very deliquescent and was stored in a vacuum desiccator. *Anal.* Calcd for $CoC_{13}H_{31}N_4O_{12}Cl_2$: C, 27.61; H, 5.53; N, 9.91. Found: C, 27.55; H, 5.41; N, 10.14.

The above analyses are for a preparation which had been stored under vacuum, and while they fit the calculated values well, it was observed that a freshly prepared aqueous solution underwent some reaction. The solution initially showed a peak at 520 nm, but on standing, the spectrum shifted to that shown in Figure 1. A clean isosbestic point was maintained at 305 nm; the half-life for the spectral change was about 5 min at 25°. On the other hand, a freshly prepared sample (not having been stored under vacuum) gave the spectrum of Figure 1 immediately on dissolving. A thermogravimetric analysis on a sample not stored under vacuum (using the same equipment and procedure as before) indicated some loss of loosely held water and then, at 105°, a loss of about 1.5 mol of water/mol of compound.

The molecular weight of the compound is 565 and the analyses are therefore not highly sensitive to the exact molar water content. The possibility remains that on storage under vacuum some coordinated water was lost, to give a mixture of six- and five-coordinated species. Recoordination of water then occurred on dissolving.

Elementary analyses were performed by Alfred Bernhardt, Elbach uber Engelskirchen, West Germany.

Solutions. The buffer solutions used were made up as follows. The pH 4.75 buffer was 0.1 *F* in sodium acetate and in acetic acid. The pH 3.4 buffer consisted of a solution which was 0.050 *F* in citric acid, 0.0908 *F* in sodium hydroxide, and 5.46 × 10^{-2} *F* in hydrochloric acid. All chemicals used here and in the preparations were of reagent grade.

Apparatus and Procedures. Irradiations were made at 254, 366, 515, and 550 nm. A Hg–I_2 Hytek lamp (400 W) was used for the

515-nm irradiations, in combination with 3-71 and 4-64 Corning glass filters. This combination gave maximum transmission at 515 nm and about a 20-nm bandwidth at half-maximum transmission. For the 550-nm irradiations, the same lamp was used but now with 3-69 + 3-70 + 4-97 filters; these gave the desired peak transmission wavelength with half-maximum transmission at 515 and 600 nm. This filter pack included two yellow filters to ensure that all uv light was removed. We felt the doubling of the uv filters to represent a conservative practice, although it was determined in the case of the diazido complex that no increase in redox photolysis occurred if only one was present. A General Electric AH6 lamp was used for the 366-nm irradiations, in combination with 7-51 and 4-96 filters. This filter set gave a peak transmission at 370 nm but we feel that the effective center of absorption was closer to 366 nm, since one of the output band maxima of the lamp falls at this wavelength, the width at half-maximum transmission was 40 nm. Finally, the 254-nm irradiations were carried out with the use of a low-pressure Hg lamp (Hanau NN 15/44); no filters were considered to be necessary.

Ferrioxalate actinometry[13] was used at the two shorter wavelengths, representative light intensities incident on the photolysis cell being 3×10^{-8} einstein $\sec^{-1}$ at 254 nm and 3×10^{-7} einstein $\sec^{-1}$ at 366 nm. Reineckate actinometry[14] was used for the two longer wavelength irradiations; representative incident intensities are 5×10^{-8} einstein $\sec^{-1}$ at 515 nm and 2×10^{-7} einstein $\sec^{-1}$ at 550 nm. Solutions were irradiated in 10-cm cylindrical spectrophotometer cells at 25° (unless otherwise stated) and concentrations were usually such as to give optical densities about 2 at the irradiation wavelengths. Irradiations were generally carried out to 10–20% reaction. The pH 4.75 buffer medium was used for the solutions of the diazido, aquoazido, and diaquo complexes, and the pH 3.4 medium, for the dinitro and aquonitro complexes. These are the respective pH's corresponding to the pK_a's of HN_3 and HNO_2.[15]

Visible and uv absorption spectra were obtained with the use of either a 635D Varian or a Cary Model 14 instrument. A Beckman DK 2A was used for the reflectance spectra measurements on solid samples. Measurements of pH were made by means of a Radiometer 22 instrument, and a Potentiograph E 436 (Metrolun Herisau) was used for the acid–base titrations.

Analytical Procedures. The degree of photoaquation of irradiated (and of dark) solutions was followed spectrophotometrically, using a wavelength of major change in absorbance. The values selected were 550 nm for the azido complexes, 450 nm for the dinitro one, and 480 nm for the aquonitro species. The irradiated solutions were always compared with a companion dark solution. Also, for the former, correction was made for loss of complex due to photoredox decomposition; such corrections were generally small, even for the 254-nm irradiations. Qualitative product identifications were, of course, made, by observing the changes in the complete visible and uv spectra.

As detailed in the Results, photoredox decomposition led mainly to free Co(II) but also to some $[Co^{II}(PnAO)(H_2O)_2]^+$, the latter apparently representing the fraction of events in which the ring ligand escaped oxidative destruction. Free Co(II) was estimated by two methods. The first is the colorimetric procedure due to Kitson,[16] which involves the formation of a Co(II) thiocyanato complex. A second procedure was as follows for the cases of the diazido, aquoazido, and diaquo complexes. After irradiation a moderate excess of azide ion was added (and likewise to the companion dark solutions) and complete anation to the diazido form was allowed to occur. The difference in optical density at 556 nm between the irradiated and dark solutions then gave the extent of decomposition (using 568 M^{-1} cm^{-1} as the extinction coefficient of the diazido form at this wavelength). As a matter of convenience, but also to reduce photolysis of the aquation product, catalyzed aquation was repressed in the case of the diazido complex by making the solution about 10^{-5} M in Ce(IV). As a consequence photoproduced $[Co^{II}(PnAO)(H_2O_2]^+$ was oxidized immediately and was thus not present to function as an aquation catalyst (see Results). For this system, then, the method determined only free Co(II). In the case of the dinitro and aquonitro complexes, the same general procedure was employed as for the others. After irradiation excess nitrite ion was added (and likewise to the companion dark solutions), and, after complete anation to the dinitro form had occurred, the absorbances of the irradiated and dark solutions were compared. The comparison wavelength was 450 nm and 207 M^{-1} cm^{-1} was used for the extinction coefficient of the dinitro form.

The two methods (direct colorimetric and spectrophotometric of anated species) generally agreed to within 20–30%, which was sufficiently accurate for our purposes. The procedure for the determination of $[Co^{II}(PnAO)(H_2O)_2]^+$ is described in the Results.

Acid–Base Titrations. The acid dissociation constant of $[Co(PnAO)(H_2O)N_3]^+$ was determined by potentiometric titration with aqueous sodium hydroxide. The titration curve showed a normal shape with the inflection point at pH 6.7, which value we assign to the pK_a for the reaction

$$[Co(PnAO)(H_2O)N_3]^+ = Co(PnAO)(OH)N_3 + H^+ \qquad (1)$$

This is a normal pK_a for water coordinated to Co(III).[17]

Reaction Rate Measurements. Some routine measurements were made on the aquation rates of $Co(PnAO)(N_3)_2$ and $Co(PnAO)(NO_2)_2$ by following spectral changes with time. Good linear plots were found for $f(D) = \ln [(D_0 - D_\infty)/(D_t - D_\infty)]$ *vs.* time, where D_0, D_t, and D_∞ are the optical densities at the start, at time t, and for complete reaction, respectively, measured at wavelengths of large optical density change. As an indication of the lack of complications, clean isosbestic points were found at 270 and 320 nm for the diazido case and at 495 nm for the dinitro case. Back-reaction was negligible in these experiments, as was second-stage aquation, since there was no deviation from first-order behavior for at least 2–3 half-lives; the optical density plots gave directly the respective aquation rate constants, k_1, as 3.9×10^{-5} and 1.3×10^{-4} $\sec^{-1}$ at 25°. In the case of the dinitro complex, k_1 was also determined to be 6.0×10^{-6} $\sec^{-1}$ at 4°, corresponding to an activation energy of 24 kcal mol^{-1}.

These rates were measured in the pH 4.75 buffer medium in the case of the diazido complex and in the pH 3.4 medium in the case of the dinitro complex. The former species shows a pH dependence of k_1 similar to that for *trans*-$[Co(en)_2(N_3)_2]^+$, being acid catalyzed at low pH's and base catalyzed in alkaline solution.[17] The chosen pH of 4.75 is one at which catalysis is negligible. Both k_1 values are in the range expected for a *trans*-$[Co(en)_2X_2]^+$ type of complex.[17] Qualitative observations indicated that the aquation rate of $[Co(PnAO)(H_2O)N_3]^+$ is slow enough not to have been of importance in the present study.

The second-order rate constant, k_2, was determined for the reaction

$$[Co(PnAO)(H_2O)N_3]^+ + N_3^- \rightarrow Co(PnAO)(N_3)_2 \qquad (2)$$

in the pH 4.75 buffer medium and at 25°. The procedure followed was to allow a buffered solution of the diazido complex to undergo about 30% aquation and then to add a known excess of azide ion (for example, 2.2×10^{-4} M complex and 8.34×10^{-2} N NaN_3), so that the resulting anation reaction was pseudo first order. The plot of $f(D)$ *vs.* time was linear and from its slope a value of $k_2 = 0.015$ M^{-1} $\sec^{-1}$ was calculated. In computing this value (N_3^-) was taken to be half of the total free azide concentration since the pK_a for HN_3 is 4.75. Note also that at the pH used the aquo complexes were almost entirely in the protonated form. Finally, the k_1 and k_2 values give 385 M^{-1} for the equilibrium constant for reaction (2); this is much smaller than the value of 8600 M^{-1} reported for nonacidified solutions.[11] No comparison values for k_1 or k_2 have been reported, however.

The anation rate constant for $[Co(PnAO)(H_2O)_2]^{2+}$ was similarly determined, this time by directly preparing a solution 0.01 M in the diaquo complex, 0.0674 M in NaN_3, and buffered to pH 4.75. The plot of $f(D)$ *vs.* time was accurately linear for about 30% reaction, and the slope of the plot yielded a k_2 value of 0.75 M^{-1} $\sec^{-1}$, again at 25° and taking (N_3^-) to be half of the total free azide ion concentration.

The anation rate for $[Co(PnAO)(H_2O)(NO_2)]^+$ was not determined. This complex exhibited negligible photoanation (see Results) and information about the thermal process was not necessary.

Results

Preliminary irradiations of the diacido and aquoacido complexes showed that the principal photoreaction was one of aquation, using either visible or uv light. After correction for redox decomposition, where important, the spectral changes on irradiation maintained reasonably good isosbestic points over 20–30% reaction, as illustrated in Figures 2–4. To anticipate one aspect of the results, it developed that in the case of the azido complexes, redox decomposition, although minor, produced some $[Co^{II}(PnAO)(H_2O)_2]^+$, which we will abbreviate as species B, and that this species catalyzed

Table I. Photolysis Yields for PnAO Complexes of Co(III) at 25°[a]

Complex	Wavelength, nm	Quantum yield[b]		
		Aquation product, ϕ_a	Co(II), ϕ_r	Species B,[c] ϕ(B)
Co(PnAO)$(N_3)_2$	254	0.1[d]	0.02[d]	1×10^{-4}
	366	0.02[d]	$<10^{-5}$	3×10^{-6}
	550	0.003[d]	$<10^{-5}$	1×10^{-7}
[Co(PnAO)$(H_2O)N_3]^+$	254	0.04[d]	0.005	2×10^{-4}
	366	0.01[d]	1×10^{-4}	5×10^{-6}
	550	3×10^{-4} [d]	$<10^{-5}$	1×10^{-7}
Co(PnAO)$(NO_2)_2$	254	0.2	0.003	1×10^{-4}
	366	0.05	0.002	3×10^{-5}
	515	0.004[e]	$<10^{-5}$	5×10^{-7}
[Co(PnAO)$(H_2O)(NO_2)]^+$	254	0.1	0.002*	5×10^{-5}*
	366	0.09	$<10^{-5}$	1×10^{-5}
	515	0.006	$<10^{-5}$	1×10^{-8}
[Co(PnAO)$(H_2O)_2]^{2+}$	254		0.01	0.05
	366		4×10^{-4}	2×10^{-5}
	550		$<10^{-5}$	1×10^{-6}

[a] Azido and diaquo complexes in pH 4.75 buffer; nitro complexes in pH 3.4 buffer medium. [b] Starred entries may reflect secondary photolysis (see Results). [c] Probably [Co^{II}(PnAO)$(H_2O)_2]^+$ (see Discussion). [d] Values obtained in the presence of added Ce(IV) (see Results). [e] Obtained at 4°.

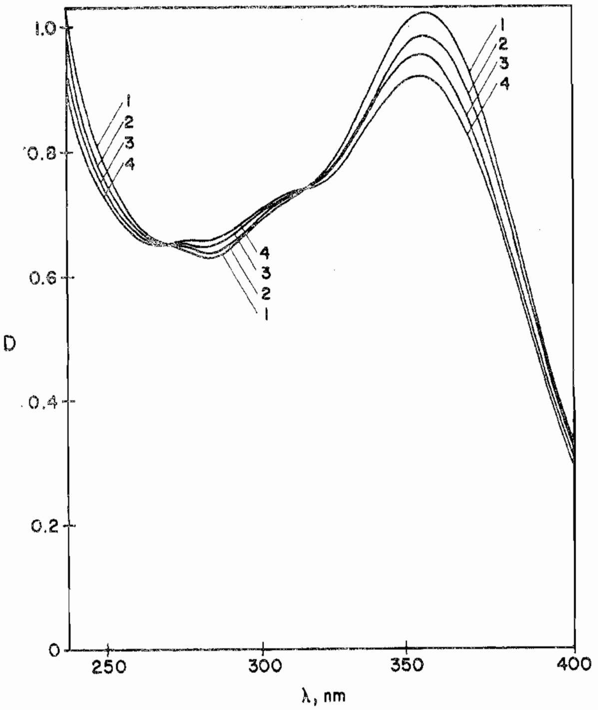


Figure 2. Photolysis of Co(PnAO)$(N_3)_2$ at 366 nm, with 1×10^{-4} *M* complex in pH 4.75 buffer containing 1×10^{-7} *M* Ce(IV): (1) initial spectrum; (2) after 30-sec irradiation; (3) after 60-sec total irradiation; (4) after 90-sec total irradiation. Irradiation conditions: 1 cm cell length, 3-cm^3 cell, incident intensity 4.5×10^{-8} einstein sec^{-1}.

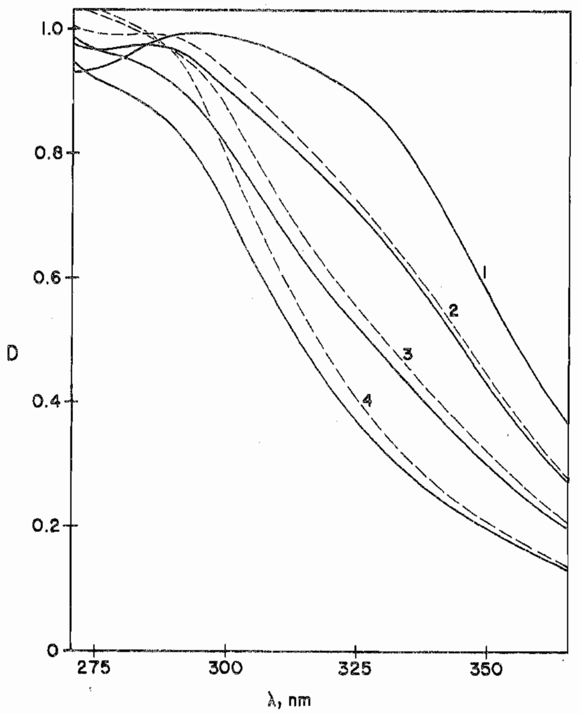


Figure 3. Photolysis of [Co(PnAO)$(N_3)(H_2O)]^+$ at 254 nm, with 1.2×10^{-5} *M* complex in pH 4.75 buffer medium (no added Ce(IV)): (1) initial spectrum; (2) after 3-min irradiation; (3) after 6-min total irradiation; (4) after 9-min total irradiation; solid curves, experimental spectra; dashed curves, spectra corrected for loss of complex by redox decomposition. Irradiation conditions: 10 cm cell length, 28-cm^3 cell, incident intensity 1.1×10^{-8} einstein sec^{-1}.

substitution reactions of the starting complexes. Table I summarizes our results for ϕ_a, the true or uncatalyzed photoaquation yields, and for the yields of free Co(II), ϕ_r, and species B, ϕ(B).

Co(PnAO)$(N_3)_2$. The above complexity first showed itself in the observation that the apparent aquation quantum yield increased with increasing time of irradiation although the small associated ϕ_r did not. Flash photolysis of a solution of Co(PnAO)$(N_3)_2$, using a bank of photographic flash bulbs, produced some aquation, which then proceeded to completion in the dark. The spectral sequence showed the same clean isosbestic points at 270 and 320 nm that are observed in the thermal aquation reaction. Plots of f(*D*) *vs.* time were not linear, however, but were of decreasing slope; the initial slope (that extrapolated to the time of the flash) was about 150 times larger than corresponding to k_1. Further, if a small portion of the irradiated solution was added to a fresh solution of the complex, a catalyzed or faster than normal aquation rate was observed.

A possibility was that Co(II) or a Co(II) complex might be the catalyzing species, and the following additional tests were therefore made. (a) Addition of a Co(II) salt only or of free PnAO ligand only to a solution of Co(PnAO)$(N_3)_2$ had no effect on the aquation rate of the latter. (b) Addition of both Co(II) and PnAO ligand strongly catalyzed the aquation. (c) If Ce(IV) (as aqueous Ce$(SO_4)_2$) was initially present, then addition of Co(II) and PnAO had no effect on the aquation rate. Also, if Ce(IV) was added to a solution of the complex which was undergoing catalyzed aquation, the aquation rate abruptly slowed down to its normal, uncatalyzed value. (d) A solution of Co(II) and PnAO lost its catalytic activity after several hours in air but retained its activity indefinitely when

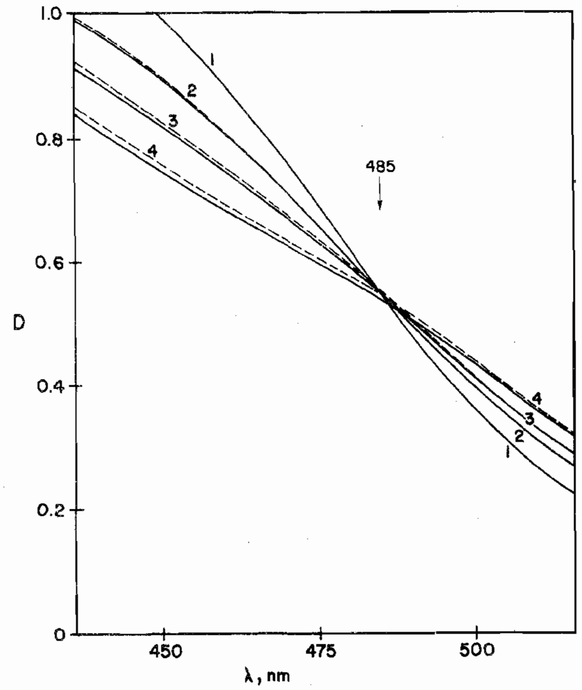


Figure 4. Photolysis of $Co(PnAO)(NO_2)_2$ at 366 nm, with 5.0×10^{-4} *M* complex in pH 3.4 buffer medium (no added Ce(IV)): (1) initial spectrum; (2) after 150-sec irradiation; (3) after 250-sec total irradiation; (4) after 350-sec total irradiation; solid curves, experimental spectra; dashed curves, spectra corrected for loss of complex by redox decomposition. Irradiation conditions: same as in Figure 3, but the intensity is 3.2×10^{-7} einstein sec^{-1}.

stored in the absence of air. (With respect to (c), Ce(IV) is reduced in the acetate buffer medium, but only at the slow rate of about 4%/hr.)

We infer that the catalytic species is a coordination complex of Co(II) and PnAO, presumably $[Co^{II}(PnAO)(H_2O)_2]^+$ (species B). Some such complex must form since the mixture (in the absence of oxygen) has a pale yellow rather than the pink color of free Co(II). Air oxidation of the solution leads to the formation of the brown $[Co(PnAO)(H_2O)_2]^{2+}$ ion, confirmed spectroscopically. Moreover, air oxidation of a solution containing Co(II), PnAO ligand, and azide ion rapidly produces green crystals of the slightly soluble $Co(PnAO)(N_3)_2$ complex. The likely mechanism for the catalyses is detailed in the Discussion.

The results of the above findings were applied in two ways. First, the presence of sufficient Ce(IV), about 10^{-5} *M*, entirely inhibits the catalysis by B, presumably through its very rapid oxidation of B to $[Co(PnAO)(H_2O)_2]^{2+}$, the system now showing a normal thermal aquation rate both in fresh and in irradiated solutions. The observation further indicates that Ce(IV) does not react rapidly with any of the other constituents of the system (the reaction with N_3^- is rapid at high concentrations, but not at those involved here). Also, while Ce(IV) is photoreducible to Ce(III),[2a] this process was not important in our situation because the large extinction coefficients of our complexes made the relative absorption of light by Ce(IV) smaller than the ratio of Ce(IV) to complex.

It was possible to make a type of titration for the amount of B produced in an irradiation. The procedure was to irradiate a series of solutions of $Co(PnAO)(N_3)_2$ containing a known amount of Ce(IV) (for instance, about 10^{-9} *M* for irradiation at 366 nm) for successively increasing lengths of time. After each irradiation a sample was tested for the thermal aquation rate of the unphotolyzed $Co(PnAO)(N_3)_2$ by following the change with time of the optical density at 550 nm. This rate remained normal so long as Ce(IV) was present to remove species B. Eventually, a further increment of irradiation produced a solution showing an enhanced thermal aquation rate and we assume that at this point the total amount of photolytically produced B equaled the amount of Ce(IV) initially added. The quantum yields $\phi(B)$ in Table I were obtained in this manner. These were usually considerably smaller than the yields for Co(II), ϕ_r, determined by the methods described in the Experimental Section, and we conclude that photoredox decomposition usually destroyed the PnAO ligand. The production of B presumably occurred only in that fraction of photolyses for which the redox decomposition led to oxidation of the azido group and thence to stable oxidation products not involving PnAO. This titration procedure probably gives a minimum value for B; also, the complexity of the procedure and the empirical degree of reproducibility indicate that the $\phi(B)$ values can be in error by ±50%.

Having estimated $\phi(B)$, it was next possible to irradiate deaerated solutions of $Co(PnAO)(N_3)_2$ to varying extents and to calculate for each case the concentrations of B present. By determining the initial rate of the subsquent dark aquation reaction for each of these experiments, which was pseudo first order up to 60–70% reaction, it was determined that the B-catalyzed aquation was first order in $Co(PnAO)(N_3)_2$ and also first order in B. The rate constant at 25°, k_3, was found to be 5.5×10^7 M^{-1} sec^{-1}. As an illustrative example, a 3×10^{-4} *M* solution of $Co(PnAO)(N_3)_2$ was deaerated and irradiated in the absence of air for 10 sec at 366 nm, giving a calculated 4.4×10^{-10} *M* concentration of B. The apparent rate constant for the subsequent dark aquation was 0.024 sec^{-1} from which the above value of k_3 was calculated. This value is, of course, subject to the same considerable error noted for $\phi(B)$.

The second application of the above findings was to obtain the true aquation quantum yield, ϕ_a. This was done by photolyzing solutions of $Co(PnAO)(N_3)_2$ containing about 10^{-7} *M* Ce(IV). As previously noted, under this circumstance the subsquent dark reaction was normal in rate. Also, the ϕ_a values were now independent of time of irradiation.

$[Co(PnAO)(H_2O)N_3]^+$. It is to be expected that if B is a catalyst for the aquation of $Co(PnAO)(N_3)_2$, it is also a catalyst for the anation of the aquoazido complex. Various initial experiments showed that B was indeed produced in the photolysis of the aquoazido complex and did act in this catalytic manner. Preliminary irradiations of 10^{-4}–10^{-5} *M* solutions of $[Co(PnAO)(H_2O)N_3]^+$ (in the pH 4.74 buffer medium) led to spectral changes which, after correction for a small amount of Co(II) production, showed a fair isosbestic point at 285 nm, as would be expected if the principal product were $[Co(PnAO)(H_2O)_2]^{2+}$. The isosbestic point held much better with the more dilute solutions than with the more concentrated ones. The spectra for these last contained features suggesting the presence of $Co(PnAO)(N_3)_2$, and this presence was confirmed by extracting an irradiated solution with Amberlite IR-120 resin (put in the sodium form by treatment with aqueous Na_2SO_4). On filtering off the resin, the filtrate absorption spectrum showed the 350-nm peak characteristic of $Co(PnAO)(N_3)_2$.

Catalyzed anation by photoproduced B was indicated by the following series of experiments. Solutions 2.48×10^{-3}, 1.25 $\times 10^{-3}$, and 2.48×10^{-4} *M* in $[Co(PnAO)(H_2O)N_3]^+$ were irradiated at 366 nm for 10 min each and the aquation yields obtained from the decrease in optical density at 550 nm were 0.004, 0.006, and 0.009, respectively. This is the expected effect; the amount of photoproduced B would be about the same in each case, but the amount of B-catalyzed anation should increase with increasing initial complex concentration. The resulting $Co(PnAO)(N_3)_2$ has a larger extinction coefficient at 550 nm and the effect of its production would be to make the apparent aquation yield of the aquoazido complex low. Extrapolation of the apparent yields to zero initial concentration gives a limiting value of about 0.01.

The presence of B was confirmed more directly. If a 10^{-3} *M* solution of $[Co(PnAO)(H_2O)N_3]^+$ containing about 10^{-6} *M* Ce(IV) was irradiated at either 366 or 254 nm, the spectral changes now showed a rather good isosbestic point at 285 nm (after correction for Co(II) formation) and were generally consistent with $[Co(PnAO)(H_2O)_2]^{2+}$ being the only product, as illustrated in Figure 3. The aquation yield was now 0.010 at 366 nm, or about the same as the extrapolated value from the preceding experiments. On the other hand, irradiation of a solution containing some Co(II) and PnAO ligand (but no Ce(IV) gave a very low apparent quantum yield for aquation. A final observation in this series was that on standing in the dark, the spectrum of irradiated solutions reverted to the original, although only very slowly in the presence of Ce(IV).

Apparent photoanation, that is, anation catalyzed by photoproduced B was directly observed. Irradiation of solutions of $[Co(PnAO)(H_2O)N_3]^+$ containing about 0.01 *M* added azide ion showed anation as the principal reaction, with apparent quantum yields of around 0.03, but the yields were dependent on the time of irradiation and to some extent on the length of postirradiation standing. Under these conditions the thermal anation is appreciable in rate and the typical experiment consisted of following the thermal process for a short period, then irradiating the solution, and again following the thermal anation. The postirradiation anation rate was faster than the initial one, and if the initial and final rate plots were extrapolated to the midirradiation time, a step increase in amount of $Co(PnAO)(N_3)_2$ was indicated. A quite analogous behavior was also observed for solutions of $[Co(PnAO)(H_2O)N_3]^+$ containing added nitrite ion, indicating that B was also able to catalyze the nitrite anation of the aquoazido complex giving $[Co(PnAO)(N_3)(NO_2)]$ (qualitative observation made based on the known $Co(PnAO)(NO_2)(N_3)$ spectrum[10]).

The same catalysis of azide anation was observed if a solution containing Co(II) and PnAO ligand were added to a thermally anating system and likewise if some irradiated $Co(PnAO)(N_3)_2$-containing solution were so added.

The yield for production of B on irradiation of the aquoazido complex was determined as follows. A deaerated solution was irradiated and small portions were added (under nitrogen atmosphere) to a solution of $Co(PnAO)(N_3)_2$ containing a known concentration of Ce(IV). At this point where the aquation rate of this last complex showed an increase it was inferred that enough photoproduced B in the irradiated solution had been added to oxidize all of the Ce(IV), so that an excess was now present.

$[Co(PnAO)(H_2O)_2]^{2+}$. As might be expected, this complex showed no photosubstitution (the likely possibility of water exchange was not examined); it was somewhat photosensitive toward redox decomposition, as noted in Table I. The decrease in the visible absorption spectrum following 254-nm irradiation was largely reversible in the dark, as air oxidation returned B to the starting material. No decrease (and no reversion) was observed if added Ce(IV) was initially present.

The yield of B was determined in a manner analogous to that employed in the case of the aquoazido complex. That is, a solution of $Co(PnAO)(N_3)_2$ containing a known amount of Ce(IV) was titrated with irradiated $[Co(PnAO)(H_2O)_2]^{2+}$ solution to the point of increase in aquation rate of the former complex.

$Co(PnAO)(NO_2)_2$ and $[Co(PnAO)(H_2O)(NO_2)]^+$. The photochemistry of the dinitro and aquonitro complexes proved to be straightforward. Photoaquation is the dominant reaction in both cases. Irradiated solutions showed fair isosbestic points, after correction for redox decomposition, and none of the complications in behavior observed for the azido complexes. Species B was neither an aquation nor an anation catalyst, although it was produced. Irradiated solutions catalyzed the aquation of $Co(PnAO)(N_3)_2$ and $\phi(B)$ was obtained by the same titration procedure as used for $[Co(PnAO)(H_2O)N_3]^+$ and $[Co(PnAO)(H_2O)_2]^{2+}$.

In the case of $Co(PnAO)(NO_2)_2$ the thermal aquation rate at 25° was fast enough that correction for it was appreciable in the case of the 515-nm irradiations. As a check, some irradiations were made at 4°, at which temperature the thermal rate was negligible. The same value for ϕ_a was obtained as that estimated from the 25° results.

A possible photoreaction is the linkage isomerization of the nitro group to the –ONO form, as has been reported for $Co(NH_3)_5NO_2^{2+}$.[18] We see no indication that this reaction occurs in our systems. The spectra of irradiated solutions were consistent with aquation as the only reaction. While the positions of –ONO and $-OH_2$ are similar in the spectrochemical series, some differences would be expected in the absorption spectra of the two types of complexes; we feel that a safe upper limit to linkage isomerization is about 10% of that of aquation. There was a postirradiation reversion to the initial spectrum, faster for irradiated $[Co(PnAO)(H_2O)(NO_2)]^+$ than for $Co(PnAO)(NO_2)_2$, which we attribute to back-anation. Irradiation of the former complex beyond 20–30% aquation led to an unexplained loss of isosbestic points; there should not have been appreciable secondary photolysis of $[Co(PnAO)(H_2O)_2]^{2+}$.

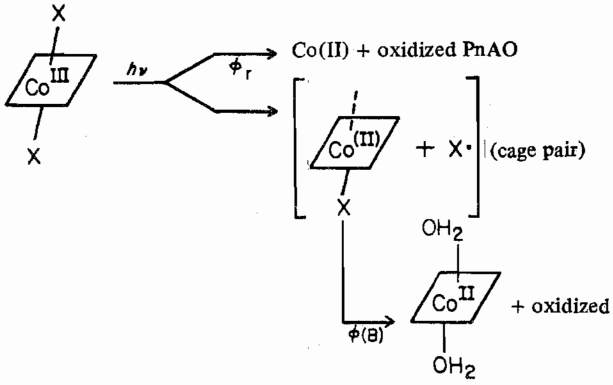
Accuracy of the Results. It should be pointed out that the results summarized in Table I are subject to two kinds of uncertainties in addition to ordinary measurement error. The values for $\phi(B)$ derive from the semiquantitative procedure of titrating Ce(IV) with photolyzed solution until the mixture showed catalytic activity. For various reasons, including the crudity of the end point searching and the possible loss of some Ce(IV) through the action of other reducing agents, these values may be in error by ±50%. More accurate measurements of $\phi(B)$ were not considered to be necessary, however, because of the minor importance of this reaction mode.

In some cases the results may reflect some secondary photolysis since irradiations were generally carried out to 10–20% reaction in order for the spectrophotometric determinations of degree of aquation to be reasonably sure. This procedure, however, did not lead to gross development of secondary aquation products since such would readily have been observed in the spectral changes. The relative hazard of secondary photolysis can be estimated from the ratio $h = \epsilon_2\phi_2/\epsilon_1\phi_1$ where 1 and 2 denote the initial complex and its first aquation product, respectively. For our degrees of reaction secondary photolysis should not be important unless h is greater than about unity. This test is met in the photoaquation of the diazido and the dinitro complexes; secondary aquation is not a problem, of course, in the cases of the aquoacido species.

On the other hand, the ϕ_r and $\phi(B)$ values may in some cases be high because of photoredox decomposition of photoproduced aquation product. These cases are starred in Table I, the most serious ones being the $\phi(B)$ values for the 254-nm irradiations of both aquoacido complexes; this is because of the high $\phi(B)$ for the diaquo species.

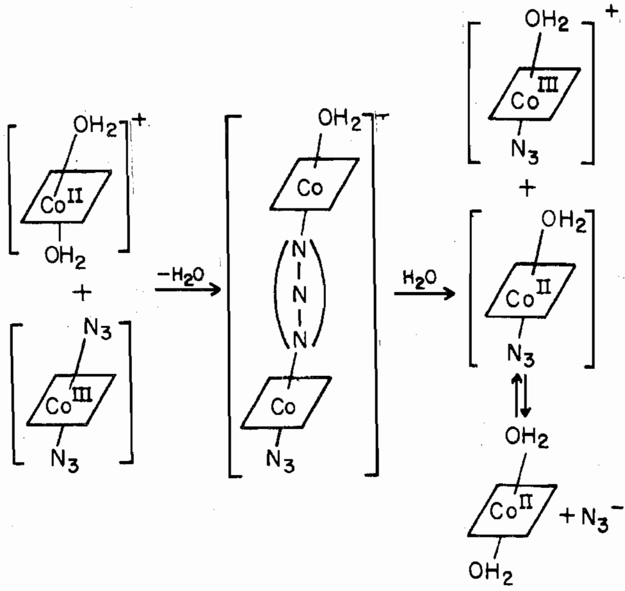
Discussion

Thermal Catalysis Effects. The major experimental preoccupation was with the catalytic effect of species B. It seems clear that this is some type of complex of Co(II) with the PnAO ligand and we take the structure to be analogous to that of $[Co(PnAO)(H_2O)_2]^{2+}$, that is, to be $[Co^{II}(PnAO)(H_2O)_2]^+$. A plausible mechanism for the formation of B and for its catalyses is that outlined in (3). The photoredox reaction may somehow lead to the destruction of the PnAO ligand, in which case free Co(II) results; otherwise coordinated Co(II) is left. In the absence of excess free X^- this last ends up as $[Co^{II}(PnAO)(H_2O)_2]^+$.



(3)

We propose a catalysis mechanism analogous to that assigned to the Pt(II) catalysis of Pt(IV) substitution reaction[17] and also to that for atom or group transfer reactions between $Co(CN)_5^{3-}$ and $Co(NH_3)_5X^{2+}$ ions (J. Halpern and coworkers as cited in ref 17). The mechanism does require our proposed structure for B and also that the axial coordination be labile so that the nature of these ligands is essentially the equilibrium one. Sequence (4), written for the diazido complex, shows the supposed association complex with B, following by the formal transfer of N_3 radical to give the aquation product.



(4)

Our second-order rate constant, k_3, is of the order of that observed for reactions between $Co(CN)_5^{3-}$ and $XCo(NH_3)_5^{2+}$ which are generally fast. This similarity suggests that complex B may be of the low-spin type, and a separate, more detailed study of this complex and of its reaction details should be of interest. Our result appears to contrast with the slow exchange reported between $Co([14]\text{-}(dienN_4)(H_2O)_2)^{2+}$ and $Co([14]\text{-}(dienN_4)(H_2O)_2)^{3+}$.[19] The ligand is different from PnAO, of course, although it also is macrocyclic and coordinates four equatorial nitrogens; the Co(II) complex, interestingly, is low spin.

The reverse of reaction 4, of course, accounts for the B-catalyzed anation of $[Co(PnAO)(H_2O)N_3]^+$. An analogous mechanism can be written for the B-catalyzed aquation of this last complex; this catalysis was not important in our studies and its investigation was reserved for possible future work.

Table II. Spectral Features for PnAO Complexes of Co(III)[a]

Complex	Absorption band, wavelength, nm (extinction coeff, M^{-1} cm^{-1})		
	L_1	L_2	CT_1
$Co(PnAO)(N_3)_2$	556 (568)		350 (9500)
$[Co(PnAO)(H_2O)N_3]^+$	554 (270)	~440 (250)	296 (8300)
$Co(PnAO)(NO_2)_2$	~450 (200)		360 (2200)
$[Co(PnAO)(H_2O)(NO_2)]^+$	485 (96)		~275 (9000)
$[Co(PnAO)(H_2O)_2]^{2+}$	548 (50)	~435 (100)	280 (7000)

[a] Values marked as approximate are estimates of band positions and intensities responsible for shoulders in the observed spectra.

An indirect confirmation of the suggested mechanism is that it appears not to be operative if X is the nitro group. This group has been noted not to function well as a bridging group in this type of mechanism (see ref 17, p 496). The reason is presumably because the initial new bonding would have to be of the less stable metal –ONO type.

Spectral Assignments. Before turning to the photochemical results some analysis of the absorption spectra should be useful. Table II summarizes the positions of band maxima and the roughly estimated positions of hidden maxima suggested by shoulders, along with respective observed or estimated extinction coefficients. The values are about as would be expected for acidoammine complexes of Co(III). The first long-wavelength feature, labeled L_1 in the table, presumably corresponds to the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition in crystal field theory for a d^6 octahedral complex. Our complexes are actually of tetragonal (C_{4v}) microsymmetry and as perhaps most recently noted by Zink,[20] the ${}^1T_{1g}$ state should be split into ${}^1E$ and ${}^1A_2$ states (dropping the "g" designation because of the lack of a center of symmetry). Our spectra do not allow resolution into such splittings and we restrict our discussion to the level of octahedral geometry. Detailed molecular orbital calculations might suggest the order to be expected for ligand field states in C_{4v} and with the PnAO ligand; such calculations have not been attempted.

To return to a more general level of discussion, the position of the L_1 band in the series $Co(NH_3)_5X^{2+}$ is at 458, 487, and 518 nm for X = NO_2, H_2O, and N_3, respectively (see ref 2b). The same ordering is seen in Table II for either the series $Co(PnAO)X_2^{n+}$ or the series $Co(PnAOH)(H_2O)X^{n+}$, X = NO_2, H_2O, or N_3, although with all maxima shifted toward longer wavelengths relative to the pentaammine series. The band intensities are similar to those in the pentaammines, increasing in the order X = H_2O, NO_2, N_3. In brief, the first absorption features appear to be normal in terms of cobalt(III)–acidoammine complexes. There is no indication that the PnAO ligand has introduced major peculiarities; it appears to be roughly equivalent spectrally to other sets of four equatorial ammine ligands. The L_1 bands seem to reflect in their positions the nature of the axial ligands; conversely, excitation at the wavelength of these bands probably produces mainly axial bonding changes. The intensity of the L_1 bands is large enough to suggest that some CT character may be present; this is particularly true for the azido complexes but also perhaps for the nitro ones.

The apparently first absorption feature in alkylcobaloximes has also been assigned to axial excitation.[7] In view of its intensity (ϵ around 1000 M^{-1} cm^{-1}) and the observed photochemistry, a high degree of charge-transfer character has been attributed to this band.

Cobalt(III) ammines show a second ligand field, L_2, band corresponding, in O_h symmetry, to the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition. Such bands are at best faintly discernible here as shoulders in the cases of $[Co(PnAO)(H_2O)_2]^{2+}$ and $[Co(PnAO)(H_2O)(H_2O)N_3]^+$. A rough estimate of their positions is included in Table II and these are about as expected from comparison with complexes such as *trans*-$Co(en)_2(H_2O)Cl^{2+}$ (see ref 2b).

The intense absorptions in the 300 nm region are readily assignable as CT processes. The positions, intensities, and progressions as water is replaced by NO_2 and N_3 are again similar to the corresponding aspects of the related cobalt(III) acidopentaammines. A possible exception is $[Co(PnAO)(H_2O)_2]^{2+}$ whose CT absorption at 285 nm is at a much lower energy than in $[Co(NH_3)_5(H_2O)]^{3+}$, for which it is at 192 nm.[2] The free ligand (in 10^{-4} *M* CH_3OH solution) shows an onset of absorption at 240 nm; conceivably its spectrum is sufficiently shifted on coordination to give the 205-nm peak. Otherwise, the energies of the CT absorption maxima are consistent with the values of the optical electronegativities of the axial ligands.[21] We therefore assign all of the first CT bands as axial ligand-to-metal charge transfer. That is, it does not appear that CT excitation directly involving the ring PnAO ligand is occurring in this wavelength region (as was similarly concluded in the case of the alkylcobaloximes[7]), with the possible exception of the 285-nm band in $[CO(PnAO)(H_2O)_2]^{2+}$. We also discount the possibility of intraligand transitions in NO_2, N_3, or PnAO as important in this region.

Finally, yet higher energy transitions are suggested by Figure 1 to be present below 240 nm. We neglect consideration of these; our lowest wavelength irradiations, at 254 nm, were mainly if not entirely in the CT_1 bands.

Photochemical Results. The general picture is one of photoaquation dominant over photoredox decomposition. The pattern is similar, for example, to that reported for *trans*-$Co(en)_2Br_2^{2+}$. In the case of the azido complexes the behavior does not, however, conform to the most recently reported photochemistry of $Co(NH_3)_5N_3^{2+}$, $Co(NH_3)_4(N_3)_2^{+}$, and $Co(NH_3)_4(H_2O)N_3^{2+}$.[22] For the first and second of these complexes it was adduced from the observation of an increasing redox quantum yield with degree of photolysis that, at 254 nm, trans ammonia photoaquation occurs in some appreciable but apparently not preponderant fraction of the time. The third complex, apparently, showed only redox decomposition at this wavelength. By contrast, we find aquation to be preferred over Co(II) formation by 50:1 in the case of the diazido complex and by 10:1 in the case of the aquoazido one.

The behavior of the dinitro and aquonitro complexes likewise contrasts with that found for $Co(NH_3)_5NO_2^{2+}$, for which redox decomposition is dominant over the wavelength range 254–442 nm.[18] The further observation that for this last complex the alternative reaction mode is one of linkage isomerization (rather than of NO_2^- aquation) and that the ratio of yields for the two modes is essentially wavelength independent rather suggests that a previously proposed cage mechanism (see ref 2) is operating, the linkage isomerization arising from a cage recapture of nascent NO_2. If this is indeed the case, the primary photoreaction for $Co(NH_3)_5NO_2^{2+}$ is entirely one of homolytic bond fission. By contrast, aquation is dominant over the entire wavelength range for our dinitro and aquonitro species. (We doubt if linkage isomerization is important—see Results.)

In summary, while the spectra of our complexes give no indication of being anomalous relative to seemingly related cobalt(III) ammines, our photochemistry differs considerably. We can seek two kinds of explanation, one spectroscopic and photophysical and the other chemical. From the first point of view, while our spectroscopic assignments seem reasonable, we do not actually know that the reacting or thexi states are. They could be triplet or quintet states, not seen spectroscopically, for example. Intra- and intersystem crossing may be occurring differently in our series relative to the comparison cobalt(III) ammines. The nearly wavelength independent yield for $Co(NH_3)_5NO_2^{2+}$ contrasts, for example, with our generally large decrease in yield with increasing wavelength. The former behavior suggests that internal conversions occur to generate the same thexi state regardless of that initially formed, while the latter behavior suggests that different reactive states are involved at different irradiation wavelengths. Note that the ratios $\phi_a/\phi(B)$ are also wavelength dependent. A chemically trivial possibility in our case is that we are observing hot ground-state reactions; absorption followed by radiationless deactivation could be producing decreasingly vibrationally hot ground-state complexes with increasing excitation wavelength.

A possible chemical explanation retains the parallel with cobalt(III) ammines. We note the low quantum yields in the wavelength region of the L_1 bands and suppose that the thexi state involved is a ligand field state obeying the usual photolysis rules[6] which specify that the weak-field axis is the one labilized and that on this axis it is the strong-field ligand which undergoes substitution. Taking the order of effective ligand field strength as given by the positions of the L_1 band maxima, $NO_2^- > H_2O > N_3^-$, we correctly predict that the yield for azide aquation should be less for $[Co(PnAO)(H_2O)N_3]^+$ than for $Co(PnAO)(N_3)_2$ but that the two nitrite aquation yields should be approximately the same. The L_1 photochemistry can thus be put in the same framework as that of other cobalt(III) ammines (see ref 4 and 5).

The 366-nm excitations are at or close to the CT_1 band maxima in the cases of the diazido and dinitro complexes and at a wavelength well up on the rise toward the CT_1 maximum in the case of the aquoazido complex. Even in the cases of the aquonitro and diaquo compounds the extinction coefficients approach 1000 M^{-1} cm^{-1} at this wavelength. Thus in all cases it appears that some CT character is present in the Franck–Condon state reached by 366-nm absorption; such character is surely present on 254-nm excitation. We therefore expect the relatively high quantum yields, 0.01–0.2, but must now account for why the reaction mode remains primarily one of axial ligand aquation and not oxidation.

A possible explanation invokes the previously proposed cage mechanism (see ref 2b). The primary excited-state reaction is taken to be one of homolytic fission of the Co–X bond, followed by (a) recombination of the primary fragments and annulment of the reaction, (b) electron transfer from the Co(II) moiety to the escaping X radical so that the net reaction is one of aquation, (c) oxidation of PnAO by the X radical so that free Co(II) results, or (d) escape of X which goes on to stable products and leaves intact $[Co^{II}(PnAO)(H_2O)_2]^+$. We account for the dominance of process (b) over processes (c) and (d) by noting that the immediate product, $[Co^{II}(PnAO)X]^{n+}$, is relatively stable toward dissociation of the ring ligand and should probably last the lifetime of the solvent cage. By contrast, in the cases of the various cobalt(III) ammines such as $Co(NH_3)_5X^{2+}$, the nascent $Co^{II}(NH_3)_5^{2+}$ should begin dissociating into Co^{2+} and free ammonia on about the same time scale as the various cage processes; reaction (b) should be reduced in efficiency relative to escape of X and perhaps also the recombination (a). We thus account for the relatively high yields at 366 and 254 nm as being characteristic of a CT excitation and for the predominance of aquation over redox decomposition in terms of a very high efficiency for process (b) in our systems.

The behavior of the cobaloximes can be explained in terms of the probable lower energy of the pair $[Co^{II}(\text{ring ligand}) + R\cdot]$ relative to $[Co^{III}(\text{ring ligand}) + R^-]$ if R is a hydrocarbon. Process (b) above should then not be favored.

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Registry No. $Co(PnAO)(N_3)_2$, 41371-80-6; $[Co(PnAO)(H_2O)N_3](ClO_4)$, 53011-16-8; $Co(PnAO)(NO_2)_2$, 41371-79-3; $[Co(PnAO)(H_2O)(NO_2)](ClO_4)$, 41371-82-8; $[Co(PnAO)(H_2O)_2](ClO_4)$, 253011-18-0.

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Temperature-Jump Study of the Rapid Complexing of Iodate with Aquometal Ions

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The reactions of pentaammineaquochromium(III) and *cis*-diaquobis(ethylenediamine)cobalt(III) with iodate have been studied at 25°, $I = 1.0\ M$ ($NaClO_4$), by the temperature-jump technique. Equilibrium formation constants for the iodato complexes have been determined spectrophotometrically and are 11.0 ± 2.2 and 2.3 ± 0.2 l. mol^{-1}, respectively. No evidence was obtained for the formation of the bis-iodato complex with *cis*-$Co(en)_2(H_2O)_2^{3+}$. The rapid rates observed suggest that substitution at the iodate is occurring rather than displacement of H_2O on the metal. Reciprocal relaxation times, τ^{-1}, give a first-order dependence on $[H^+]$, which suggests a mechanism for complex formation involving HIO_3 and not IO_3^-. Values for outer- to inner-sphere interchange rate constants k_2, involving HIO_3 and the aquo complexes, were calculated using estimates for the outer-sphere association constants. The rate constants obtained, *ca.* $5 \times 10^4\ sec^{-1}$, are similar to but greater than those for water exchange with HIO_3. Possible mechanisms for substitution at iodine(V) are considered.

Oxy anions sometimes complex rapidly with substitution-inert complexes having aquo ligands. Thus the reactions of nitrite[1] and sulfite[2] with hexaaquochromium(III) fall within this category. All oxy anions participating in such processes undergo rapid oxygen exchange with solvent water,[3] (1). A similar exchange process can also occur with a water

$$H_2O^* + OXO_x^{n-} \rightleftharpoons H_2O + O^*XO_x^{n-} \tag{1}$$

molecule already coordinated to a metal, (2). Studies on the

$$(H_2O)_5MO^*H_2^{3+} + OXO_x^{n-} \rightleftharpoons (H_2O)_5MO^*XO_x^{(3-n)+} + H_2O \tag{2}$$

rapid complexing of iodate to substitution-inert chromium(III) and cobalt(III) complexes are reported in this paper. Oxygen exchange at iodate is known to be rapid,[4,5] but no other information is available and it is not clear whether an associative or dissociative process is involved. The investigations reported therefore provide further information on substitution at iodine(V).

The reactions of iodate with $Cr(NH_3)_5OH_2^{3+}$ and *cis*-$Co(en)_2(OH_2)_2^{3+}$ have been studied in full using the temperature-jump technique. With $Co(NH_3)_5OH_2^{3+}$ complexing was not sufficiently extensive for precise measurements, and with $Cr(OH_2)_6^{3+}$ formation of a diiodato complex has been reported,[6] with possible complications because the data obtained suggest that the formation constant for addition of the second iodate is greater than the first.

Results

Spectrophotometric Determination of Formation Constants. On addition of 0.1 M iodate to $Cr(NH_3)_5OH_2^{3+}$, $[HClO_4] = 0.1\ M$, an instantaneous orange to red color change, indicative of complex formation, was observed. Scan spectra, 300–600 nm, of solutions with $[Cr(NH_3)_5OH_2^{3+}]$ constant, $[H^+] = 0.1\ M$, and $I = 1.0\ M$ ($NaClO_4$) but with varying concentrations of iodate 0.04–0.25 M gave well-defined isosbestic points at 315 (ε 5.5), 356 (ε 26.8), 423 (ε 11.8), and 486 nm (ε 30.8 l. mol^{-1} cm^{-1}). At wavelengths <300 nm the charge-transfer spectrum of iodate predominates. The formation constant $K(Cr)$ for (3) is defined in (4), where $[IO_3^-]_f$

$$Cr(NH_3)_5OH_2^{3+} + IO_3^- \rightleftharpoons Cr(NH_3)_5OIO_2^{2+} + H_2O \tag{3}$$

$$K(Cr) = \frac{[Cr(NH_3)_5OIO_2^{2+}]}{[Cr(NH_3)_5OH_2^{3+}][IO_3^-]_f} \tag{4}$$

represents the concentration of free iodate, which was calculated knowing the protonation constant for iodate (a value 1.94 l. mol^{-1} was used; see below). The free hydrogen ion