In the usual chair conformation, the value of $^3J_{3,4}$ should be large (9–10 Hz), in agreement with the trans coupling. These consideration led to the conclusion that each sugar ring in **1** and **2** is not in the usual chair conformation but adopts the β-$^3S_5$ skew-boat conformation. It is interesting that the value of $^3J_{3,4}$ is 0 Hz in **3**, which suggested that the dihedral angle between the planes of H–C3–C4 and C3–C4–H is ca. 90°. And it shows that the sugar ring in **3** takes the five-membered α-$^2T_3$ twist conformation.

From all of the results obtained coupled with the inspection of the scale models, it was concluded that the sugar unit of each tetradentate *N*-glycoside ligand facially coordinates to the cobalt atom through the N atom on C1 and through the two O atoms on C2 and C3 (Figure 1).

It is very interesting that the three-point metal bindings induce the conformational changes from the chair conformation that the free sugars usually take.[18] This coordination geometry would be generally possible for sugars containing the cis arrangement between two hydroxyl groups on C2 and C3 such as D-mannose, L-rhamnose, and D-ribose. On the other hand, it seems to be impossible for sugars containing the trans arrangement between two hydroxyl groups such as D-glucose and D-galactose. The results of this work suggest the novel aspect of selective complexation for aldoses.

Department of Synthetic Chemistry
Faculty of Engineering
The University of Tokyo
Hongo Bunkyo-ku, Tokyo 113, Japan

Katsuaki Ishida
Shigenobu Yano*
Sadao Yoshikawa*

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Articles

Contribution from the Department of Inorganic Chemistry,
Guindy Campus, University of Madras, Madras 600 025, India

Photochemical Reactions of Cobalt(III)–Amine Complexes in Nonaqueous Solvents: Mechanistic Details of the Oxygenation Reactions of Cobalt(II) Systems

P. Ramamurthy and P. Natarajan*

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Flash photolysis of a series of cobalt(III)–amine complexes dissolved in air-equilibrated neat acetonitrile and methanol produces transients due to the oxygenation of the photoproduced cobalt(II) amines. The kinetics of the oxygenation reaction has been investigated by observing the transients in a time-resolved manner at different wavelengths. The study reveals that the cobalt(II)–amine complex forms a 1:1 adduct with oxygen to give a superoxo complex that dimerizes, reacting with the starting complex to give a μ-superoxo dinuclear cobalt(III) complex. The μ-superoxo dinuclear complex is reduced to give the final product, the μ-peroxo dimer. The first step is found to depend upon the concentration of dissolved oxygen and the second step on the concentration of the cobalt(III) amine. Time-resolved absorption spectra of the transient species have been obtained, and the spectra are compared with those of well-characterized dioxygen complexes of cobalt(III). Steady photolysis studies of the cobalt(III) amines have been carried out, and the spectra for the oxygenation products have been obtained.

Introduction

The reactions of dioxygen complexes of transition metals have been of considerable interest, centered primarily on studies of cobalt–dioxygen bonding as a model for biological processes.[1-10] Cobalt(II) complexes normally form μ-peroxo-bridged complexes in aqueous solution. Whenever the chelating agent has an insufficient number of coordinating groups or is present in insufficient concentration to completely saturate the coordination sites available on the cobalt ion, a second bridge may form.[5] It was suggested that μ-peroxo-bridged complexes of cobalt are formed via an intermediate mononuclear superoxo complex.[5] It has been possible to limit the oxygenation reaction to a 1:1 (cobalt:oxygen) superoxo complex formation by using solvents of low dielectric constant or complexes in which steric hindrance prevents the bridge formation.[11] There is evidence for the formation of dinuclear μ-superoxo or μ-peroxo complexes from the mononuclear superoxo precursors.[2] A general reaction mechanism for the formation of the μ-peroxo dinuclear complex proposed by Wilkins[12] involves the reactions

$$\mathrm{CoL^{2+} + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoLO_2{}^{2+}}$$

$$\mathrm{CoLO_2{}^{2+} + CoL^{2+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{peroxo complex}}{LCo{-}O_2{-}CoL^{4+}}}$$

Earlier investigations reveal that the photochemistry of transition-metal coordination complexes has been affected significantly by the solvent medium.[13] Earlier, we have investigated[14,15] the photochemistry of *cis*-$[\mathrm{Co(en)_2(NO_2)_2}]^+$ in acetonitrile, which undergoes charge-transfer photolysis to produce the corresponding cobalt(II) complex, which in turn reacts with dissolved oxygen.

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Table I. Spectral Data of the Complexes in H_2O, CH_3CN, and CH_3OH

complexes	λ_{max}, nm (log ϵ)		
	H_2O	CH_3CN	CH_3OH
cis-$[Co(pn)_2(NO_2)_2]ClO_4$	433 (2.208)	428 (2.424)	433 (2.290)
	341 (3.459)	348 (3.630)	347 (3.584)
	250 (4.187)	253 (4.157)	253 (4.250)
trans-$[Co(pn)_2(NO_2)_2]ClO_4$	437 (2.205)	435 (2.369)	435 (2.348)
	321 (3.544)	328 (3.727)	326 (3.695)
	241 (4.319)	243 (4.321)	242 (4.340)
trans-$[Co(pn)_2Cl_2]ClO_4$		609 (1.620)	610 (1.587)
		458 (1.144)	453 (1.431)
		388 (1.722)	386 (1.694)
		305 (3.399)	305 (3.151)
trans-$[Co(tn)_2(NO_2)_2]ClO_4$	447 (2.292)	444 (2.414)	446 (2.344)
	350 (3.460)	358 (3.507)	356 (3.602)
	253 (4.322)	255 (4.111)	255 (4.335)
trans-$[Co(tn)_2NO_2Cl]ClO_4$	454 (2.151)	450 (2.152)	455 (2.122)
	348 (3.609)	355 (3.582)	355 (3.504)
	249 (4.342)	258 (4.403)	256 (4.392)
trans-$[Co(tn)_2Cl_2]ClO_4$		637 (1.602)	637 (1.600)
		480 (1.473)	475 (1.488)
		385 (1.914)	385 (1.908)
		308 (3.176)	310 (3.519)
		258 (4.479)	258 (4.807)
$[Co(dien)(NO_2)_3]$	427 (2.598)	420 (2.626)	426 (2.302)
	336 (3.817)	340 (3.914)	337 (3.593)
	252 (4.432)	255 (4.713)	253 (4.143)
$[Co(dien)(en)(NO_2)](ClO_4)_2$	431 (2.396)	420 (2.503)	432 (2.325)
	340 (3.673)	348 (3.825)	346 (3.676)
	250 (4.388)	253 (4.383)	252 (4.316)
$[Co(dien)(pn)(NO_2)](ClO_4)_2$	455 (2.297)	454 (2.163)	435 (2.217)
	325 (3.206)	350 (3.284)	330 (3.366)
	236 (4.207)	240 (4.173)	238 (4.324)

Recently, we have shown that a μ-superoxo dinuclear cobalt(III) complex is formed as an intermediate in the oxygenation reaction of the cobalt(II) complex.[16] In the present paper we discuss, in detail, the flash photolysis studies of a series of polyamine cobalt(III) complexes in methanol and acetonitrile media, which on photolysis, irradiating at the charge-transfer band, undergo oxygenation reactions.

Experimental Section

The complexes *cis*-$[Co(pn)_2(NO_2)_2]ClO_4$,[17] *trans*-$[Co(pn)_2(NO_2)_2]ClO_4$,[17] *trans*-$[Co(pn)_2Cl_2]ClO_4$,[17] *trans*-$[Co(tn)_2(NO_2)_2]ClO_4$,[18] *trans*-$[Co(tn)_2NO_2Cl]ClO_4$,[19] *trans*-$[Co(tn)_2Cl_2]ClO_4$,[20] $[Co(dien)(NO_2)_3]$,[21] $[Co(dien)(en)NO_2](ClO_4)_2$,[22] and $[Co(dien)(pn)NO_2](ClO_4)_2$[22] (pn = 1,2-propylenediamine, tn = 1,3-propylenediamine, dien = diethylenetriamine) were prepared by the procedures reported in the literature and characterized by their electronic spectra. The absorption spectral maxima and molar absorptivity at the band maximum of the complexes agreed well (±5%) with those reported in the literature. The acetonitrile solvent used was of spectral grade (Aldrich) and methanol was of AnalaR grade (BDH). The amines used as ligands were obtained from Fluka (Puriss) and were distilled before use. Electronic spectra were recorded in a Hitachi 320 UV-visible spectrophotometer. Flash photolysis experiments were carried out by using an Applied Photophysics (London, U.K.) flash system. Solutions for flash photolysis were taken in a quartz cell with 10 cm path length and flash light was used for irradiation as such without filtering. When deaerated solutions were used for the flash photolysis experiments, deaeration was carried out by the freeze–thaw method. Steady photolysis experiments were carried out by using a Varian EIMAC 300-W xenon lamp.

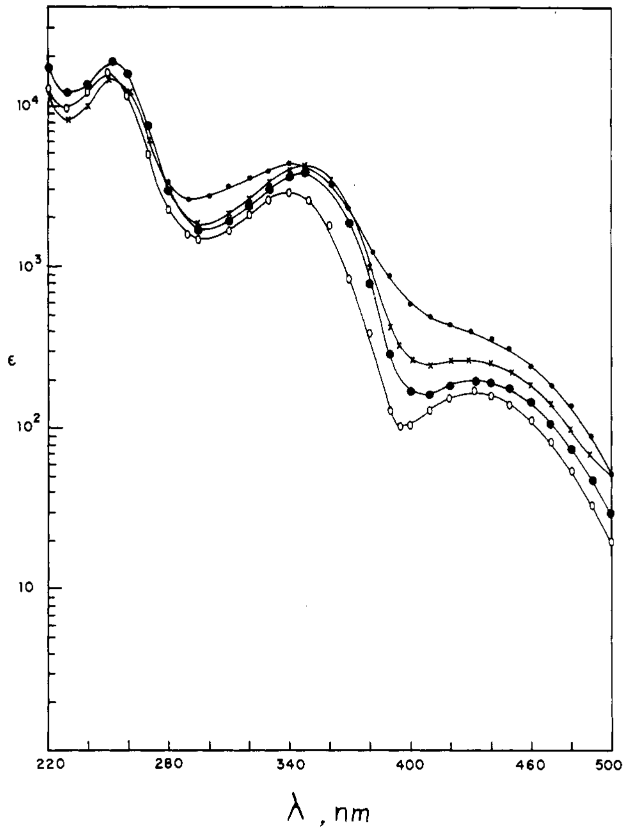

Figure 1. Absorption spectra of *cis*-$[Co(pn)_2(NO_2)_2]ClO_4$ in CH_3CN (×), CH_3OH (●), H_2O (○), and its photoproduct in CH_3CN (•).

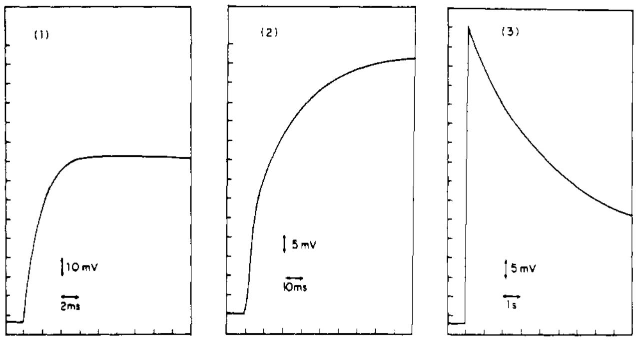

Figure 2. Transient growth at 400 (1) and 700 nm (2) and transient decay at 700 nm (3) of $[Co(dien)(en)NO_2](ClO_4)_2$ in CH_3CN.

Results

The spectral data of the complexes, dissolved in different solvent media, are collated in Table I. Spectra of a representative complex in different solvents are given in Figure 1.

Flash photolysis of the complexes in air-equilibrated or deaerated aqueous solution did not show any transient for these complexes. However, in air-equilibrated solvents (acetonitrile or methanol) a growth of absorbance at 400 nm was observed, which is followed by a slower growth of absorbance at 700 nm. The transients observed at 700 nm also decay on a slow time scale as shown in Figure 2 for a typical complex in an experiment. All three traces obeyed first-order kinetics; the plots of log $(A_\infty - A_t)$ vs. time were found to be linear (Figure 3). The first-order plots were fitted with a linear least-square program, and the correlation coefficient was >0.99. The results of the kinetics of the decay of the transient observed at 700 nm and the growth of the transient observed at 400 nm are tabulated in Table II.

The first-order rate constants determined at 400 nm depend upon the concentration of oxygen present in the medium as de-

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Table II. Flash Photolysis of Cobalt(III) Amines in CH_3CN and CH_3OH (Monitoring Wavelengths 400 and 700 nm)

	CH_3CN		CH_3OH	
complex	400-nm growth k_{obsd}, s^{-1}	700-nm decay k_3, s^{-1}	400-nm growth, k_{obsd}, s^{-1}	700-nm decay k_3, s^{-1}
cis-$[Co(pn)_2(NO_2)_2]ClO_4$	480 ± 35 595 ± 20[a] 0.5 ± 0.02[b]	2.05 ± 0.10 6.10 ± 0.30[c]	42.6 ± 5.0	0.56 ± 0.08
trans-$[Co(pn)_2(NO_2)_2]ClO_4$	300 ± 20	0.11 ± 0.01	30.1 ± 2.0	0.39 ± 0.09
trans-$[Co(pn)_2Cl_2]ClO_4$	408 ± 20	0.38 ± 0.02		
trans-$[Co(tn)_2(NO_2)_2]ClO_4$	72 ± 10	1.41 ± 0.10	8.4 ± 1.5	0.39 ± 0.10
trans-$[Co(tn)_2(NO_2)Cl]ClO_4$	146 ± 10	0.90 ± 0.12	0.3 ± 0.05	0.99 ± 0.05
trans-$[Co(tn)_2Cl_2]ClO_4$	488 ± 30	0.35 ± 0.10		
$[Co(dien)(NO_2)_3]$	50 ± 5[d,e]	0.36 ± 0.05	0.5 ± 0.1	0.98 ± 0.10
$[Co(dien)(en)NO_2](ClO_4)_2$	588 ± 10	0.15 ± 0.02	66.2 ± 8.0	0.23 ± 0.05
$[Co(dien)(pn)NO_2](ClO_4)_2$	134 ± 5	1.47 ± 0.10	289 ± 10	0.52 ± 0.08

[a] In oxygen-saturated solution. [b] In the presence of 3.26×10^{-4} M cobalt(II) perchlorate. [c] In the presence of 1×10^{-4} M sodium nitrite. [d] Wilkins[1] reported value for $[Co(dien)_2]^{2+}$: $k_1 = 1.2 \times 10^3\ M^{-1}\ s^{-1}$. [e] $k_1 = 3.1 \times 10^4\ M^{-1}\ s^{-1}$: rate constant calculated by using the dissolved oxygen concentration (1.6×10^{-3} M).[30]

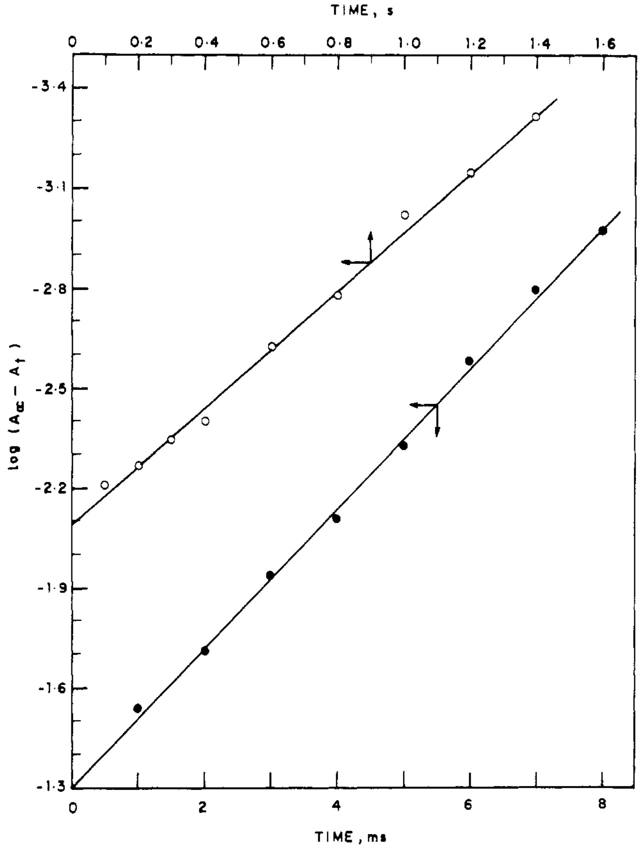

Figure 3. First-order plot of 400-nm growth (●) and 700-nm decay (○) of *trans*-$[Co(pn)_2(NO_2)_2]ClO_4$ in CH_3CN.

termined in air-saturated and oxygen-saturated solutions. However, the concentration of the starting complex does not have any effect on the rate constant. The first-order rate constants observed at 700 nm depend on the concentration of the starting complex. The data are collated in Table III. The first order plots of log $[(A_\infty - A_t)/(A_\infty - A_0)]$ vs. time for different concentrations of a representative complex at 700 nm are shown in Figure 4. A plot of k_{obsd} vs. concentration of complex for a typical case is shown in Figure 5, and from the slope, the second-order rate constant for the growth of absorbance at 700 nm is calculated; this line does not pass through the origin and an intercept was obtained.

Since the signal was very weak in the flash photolysis experiments for the complexes $[Co(dien)(NO_2)_3]$, *trans*-$[Co(tn)_2(NO_2)_2]ClO_4$, and trans-$[Co(tn)_2NO_2Cl]ClO_4$, we were not able to conduct the concentration-dependence experiments in methanol.

The absorption spectra of the transients were recorded at 700-nm absorbance growth and 400-nm absorbance growth time scales, and the data are presented in Table IV. Spectra obtained in the case of a few complexes are given in Figure 6. Transient spectra for the dichloro complexes were not recorded in methanol, since the signal for these complexes was weak, and for the same reason, the kinetic analyses of the transients for these complexes were not carried out. Flash photolysis experiments were carried out in presence of excess cobalt(II) perchlorate, which showed transient growth of absorbance only around 400 nm and did not show any transient growth of absorbance around 700 nm. The time scale for this 400-nm transient was same as that of the 700-nm transient decay in the absence of cobalt(II) perchlorate. This growth also obeyed first-order kinetics ($k \simeq 0.5\ s^{-1}$).

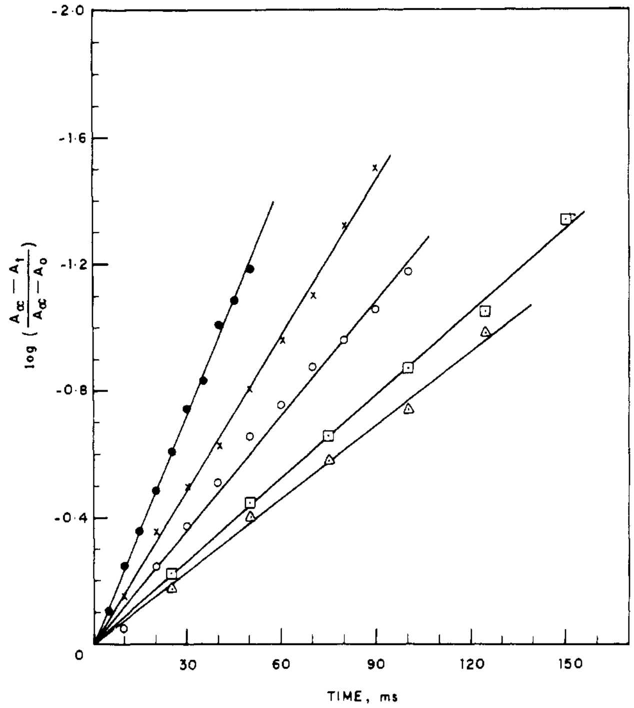

Figure 4. First-order plots of 700-nm growth of *trans*-$[Co(pn)_2(NO_2)_2]ClO_4$ in CH_3CN: (●) 2.288×10^{-3} M; (×) 1.144×10^{-3} M; (○) 4.575×10^{-4} M; (⊡) 2.287×10^{-4} M; (△) 1.144×10^{-4} M.

Steady photolysis of the complexes in nonaqueous solvents produces spectral changes in the visible region, indicating absorption bands with markedly high intensities. Well-defined isosbestic points were observed for solutions of the complexes irradiated for different periods as shown in Figure 7 for a representative system. After a certain period of irradiation, the absorption spectra of the complexes did not change any further, indicating the conversion of the initial complex to the photoproduct almost quantitatively. Spectral details of the photoproducts of the complexes on prolonged irradiation are shown in Table V.

The photoproducts of the complexes obtained in air-equilibrated solvents did not show any ESR signal. Solutions of the complexes irradiated in the ESR cavity also did not show any ESR spectrum.

Table III. Flash Photolysis of Cobalt(III) Amines in CH_3CN and CH_3OH and Effect of the Complex Concentration on the Rate Constant for the Growth of the Transient at 700 nm

	CH_3CN				CH_3OH			
complex	10^4[complex], M	k_{obsd}, s^{-1}	$10^{-4}k_2$, M^{-1} s^{-1}	k_0, s^{-1}	10^4[complex], M	k_{obsd}, s^{-1}	$10^{-4}k_2$, M^{-1} s^{-1}	k_0, s^{-1}
cis-$[Co(pn)_2(NO_2)_2]ClO_4$	2.308	60.85	4.9 ± 0.4	48 ± 3	2.867	11.40	0.34 ± 0.07	9 ± 1
	9.21	92.86			8.601	11.27		
	11.54	107.50			28.67	19.54		
trans-$[Co(pn)_2(NO_2)_2]ClO_4$	1.144	18.81			2.675	16.77		
	2.287	20.15			8.026	19.27	1.2 ± 0.2	11 ± 3
	4.575	27.82	1.7 ± 0.12	17 ± 2	26.75	45.18		
	11.44	39.80						
	22.88	55.97						
trans-$[Co(tn)_2(NO_2)_2]ClO_4$	3.08	55.84						
	12.32	119.83	7.5 ± 0.6	31 ± 6				
	15.4	150.63						
trans-$[Co(tn)_2(NO_2)Cl]ClO_4$	1.363	137.28						
	5.53	174.84	6.9 ± 0.7	131 ± 6				
	13.83	225.13						
$[Co(dien)(NO_2)_3]$	1.539	15.77						
	3.079	32.60						
	6.158	38.62	2.4 ± 0.07	24 ± 1				
	15.39	59.92						
	30.79	99.74						
$[Co(dien)(en)NO_2](ClO_4)_2$	0.719	15.23			2.196	21.49		
	1.439	19.21	1.8 ± 0.1	15 ± 1	4.518	26.73	2.1 ± 0.06	17 ± 0.4
	4.316	24.33			8.392	34.55		
	14.39	41.07						
$[Co(dien)(pn)NO2](ClO_4)_2$	3.45	15.23			1.756	154.0		
	5.171	77.35	7.9 ± 0.5	35 ± 2	5.274	277.2	9.1 ± 5.6	177 ± 60
	8.629	81.50			17.58	326.9		

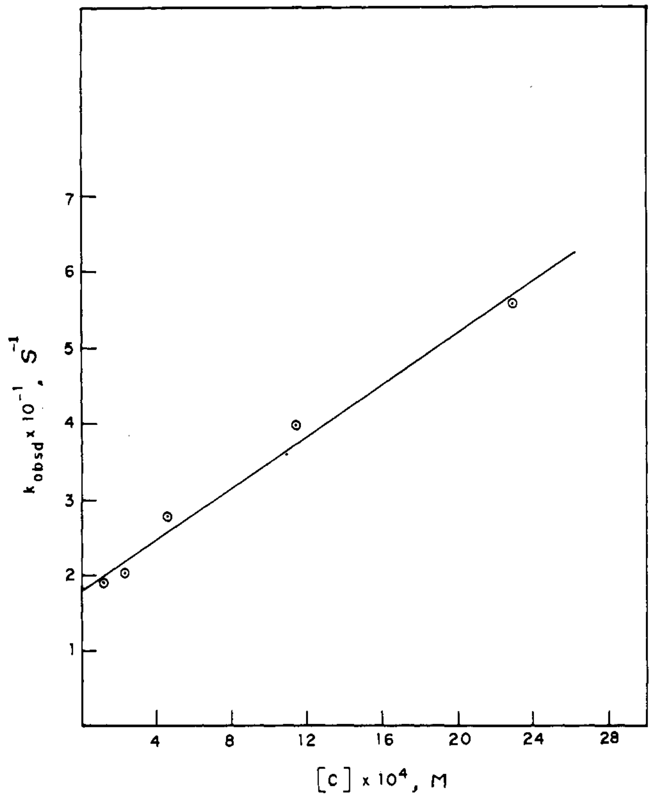

Figure 5. Plot of k_{obsd} vs. [complex] for the complex *trans*-$[Co(pn)_2(NO_2)_2]ClO_4$.

Discussion

The absorption spectra of cobalt(III)–amine complexes[23] with nitrite as one of the ligands consist of charge-transfer bands around 250 and 325 nm (the former due to Co ← amine and the latter due to Co ← NO_2) and one ligand field band ($^1A_{1g} \rightarrow {}^1T_{1g}$) around 450 nm. The second ligand field band ($^1A_{1g} \rightarrow {}^1T_{2g}$), which should lie at about 340 nm, is hidden by the intense charge-transfer transition at 325 nm. The amine complexes with chloride ligands show the second ligand field band clearly.

Cobalt(III) complexes in aqueous acidic solutions undergo three principal types of photoreactions depending on the wavelength of irradiation:[24] (1) photoredox reactions,[13,25] involving changes in oxidation number of metal and ligand(s) or counterions; (2) photosubstitution reactions,[26] involving changes in the composition of the coordination shell; (3) photoisomerization reactions,[27] involving changes in the coordination arrangement of the ligands.

In the case of irradiation cobalt(III)–amine complexes at CTTM bands in aqueous medium, owing to the high oxidation number of the central metal ions and the general reducing properties of the ligands, the reactions of the first type always consist of an electron-transfer from the ligand(s) to the metal, followed by the aquation of the labile cobalt(II) complexes so originated.

Results of steady photolysis of the cobalt(III)–amine complexes indicate that the irradiation of air-equilibrated nonaqueous solutions of the cobalt(III)–amine complexes produces dioxygen complexes by reacting with the dissolved oxygen present in the solvent. Absence of the characteristic absorption band around 700 nm in the absorption spectra and the diamagnetic nature of the photoproduct indicate that it is a dinuclear μ-peroxo complex.[28] The spectral details of dinuclear μ-peroxo dimers with the ligands used in this study are known[29] and are summarized in Table VII.

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Table IV. Spectra of Transients Observed on Flash Photolysis of Cobalt(III) Amines in CH_3CN and CH_3OH

complex	λ_{max}, nm	
	CH_3CN	CH_3OH
cis-$[Co(pn)_2(NO_2)_2]ClO_4$	400[a]	400[a]
	470	470
	705	700
	400[d]	400[b]
	470	470
trans-$[Co(pn)_2(NO_2)_2]ClO_4$	400[a]	400[a]
	480	490
	680	680
	400[b]	400[b]
	480	490
trans-$[Co(tn)_2(NO_2)_2]ClO_4$	420[c]	400
	500	520
	670	650
	420[d]	
	500	
trans-$[Co(tn)_2NO_2Cl]ClO_4$	420[c]	410
	490	600
	590	670
	690	750
	420[d]	
	490	
	590	
trans-$[Co(tn)_2Cl_2]ClO_4$	400	
	560	
	610	
	705	
$[Co(dien)(NO_2)_3]$	400	400
	480	490
	530	680
	700	
$[Co(dien)(en)NO_2](ClO_4)_2$	400[a]	400[a]
	500	480
	650	700
	730	
	400[d]	400[b]
	500	480
$[Co(dien)(pn)NO_2](ClO_4)_2$	390	390
	500	490
	660	690
trans-$[Co(pn)_2Cl_2]ClO_4$	400	
	500	
	670	
	705	

[a] Spectrum recorded after delay of 180 ms. [b] Spectrum recorded after delay of 20 ms. [c] Spectrum recorded affter delay of 90 ms. [d] Spectrum recorded after delay of 10 ms.

The close similarity of the spectra of the photoproduct with the spectra of the complexes given in Table VII indicates that the photoproduct is indeed the μ-peroxo dinuclear cobalt(III) complex. Since one of the ligands is different in some of these systems, there are minor differences in the spectral details between the known complexes and the complexes formed as photoproducts in the present study.

The oxygenation reaction seems to be quantitative with no linkage isomer and a small amount of cobaltous ion formation in the medium ($\phi < 10^{-2}$). Deaerated solutions of the complexes on irradiation in nonaqueous solvents produce low ($\phi < 10^{-2}$) amounts of cobaltous ion; no linkage isomer is observed for the complexes with nitrite as the ligand.

Absence of any transient formation on flash photolysis of these complexes in acidic aqueous solutions indicates that in aqueous solutions cobalt(II) formed is rapidly converted to the cobalt(II)-aquo complex.[36] In nonaqueous solvents, on the other hand, transients are observed in air-equilibrated solutions. In thoroughly deaerated solutions no transient is observed, indicating that the transient is due to the reaction between dioxygen and the pho-

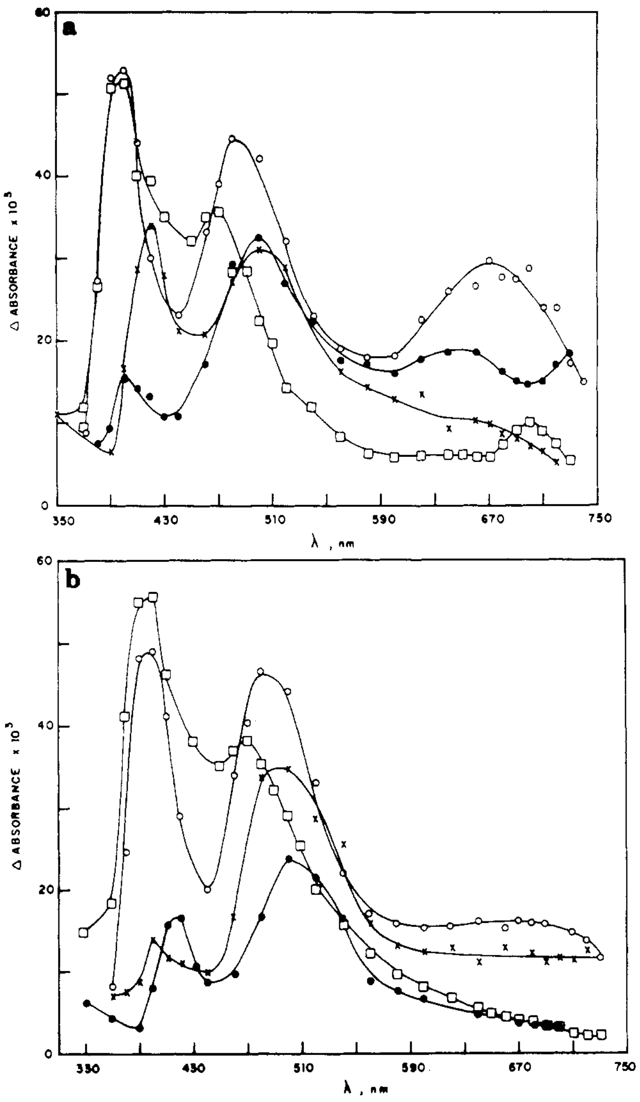

Figure 6. (A) Transient spectra of (○) *trans*-$[Co(pn)_2(NO_2)_2]ClO_4$ in CH_3CN at 180 ms, (×) *trans*-$[Co(tn)_2(NO_2)_2]ClO_4$ in CH_3CN at 90 ms, (□) *cis*-$[Co(pn)_2(NO_2)_2]ClO_4$ in CH_3CN at 180 ms, and (●) $[Co(dien)(en)NO_2](ClO_4)_2$ in CH_3CN at 90 ms. (B) Transient spectra of (○) *trans*-$[Co(pn)_2(NO_2)_2]ClO_4$ in CH_3CN at 20 ms, (●) *trans*-$[Co(tn)_2(NO_2)_2]ClO_4$ in CH_3CN at 10 ms, (□) *cis*-$[Co(pn)_2(NO_2)_2]ClO_4$ in CH_3CN at 10 ms, and (×) $[Co(dien)(en)NO_2](ClO_4)_2$ in CH_3CN at 10 ms.

Table V. Steady Photolysis of Cobalt(III) Amines in CH_3CN and CH_3OH

complex	λ_{max}, nm	
	CH_3CN	CH_3OH
cis-$[Co(pn)_2(NO_2)_2]ClO_4$	342	343
	430 sh	430 sh
trans-$[Co(pn)_2(NO_2)_2]ClO_4$	327	323
	430 sh	425 sh
trans-$[Co(pn)_2Cl_2]ClO_4$	305	305
	380 sh	390 sh
	460	460
	590	582
trans-$[Co(tn)_2(NO_2)_2]ClO_4$	352	350
	440 sh	430 sh
trans-$[Co(tn)_2NO_2Cl]ClO_4$	310	310
	385 sh	385 sh
	480	475
	630	632
$[Co(dien)(NO_2)_3]$	337	337
	430 sh	430 sh
$[Co(dien)(en)NO_2](ClO_4)_2$	340	330
	430 sh	425 sh
$[Co(dien)(pn)NO_2](ClO_4)_2$	315	324
	440 sh	450 sh

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(34) Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin: New York, 1966; p 71.

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(36) Lilie, J.; Simic, M. *J. Am. Chem. Soc.* **1974**, *96*, 291–292.

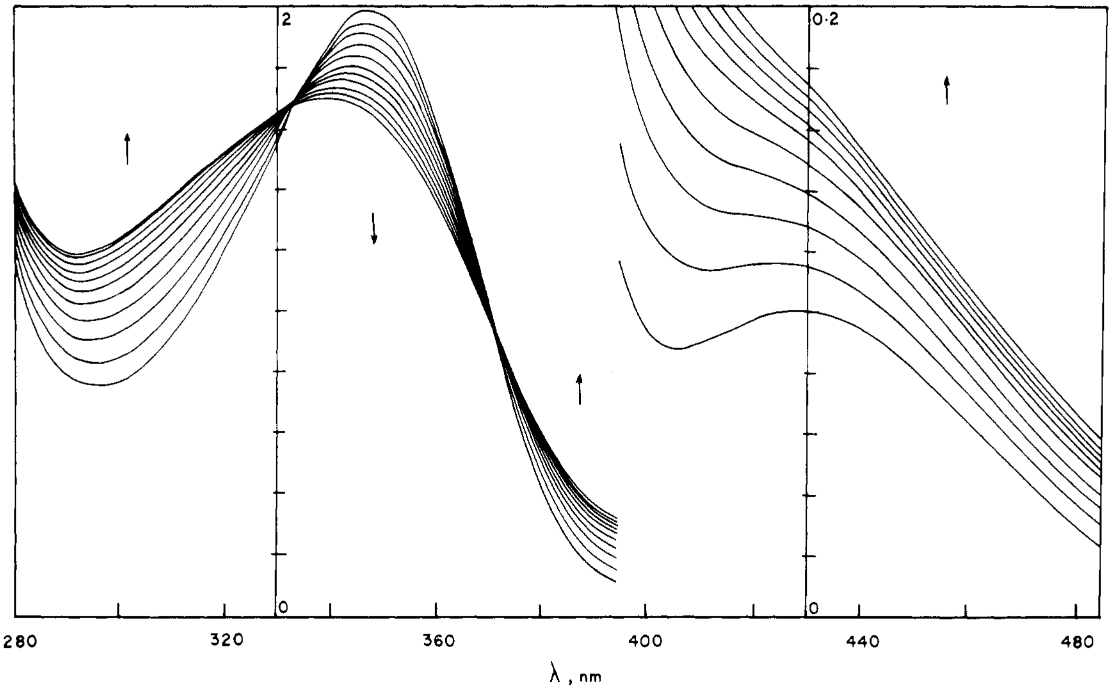


Figure 7. Steady photolysis spectrum of $[Co(dien)(en)NO_2](ClO_4)_2$ in CH_3CN.

Table VI. Electronic Spectra[11,29,35] of Superoxo–Metal Complexes

complex	λ_{max}, nm (log ϵ)			
	$\pi_h^* \rightarrow \pi_v^*$	$d\pi \rightarrow \pi_v^*$	$\pi_v^* \rightarrow d_{\sigma^*}$	$\pi_h^* \rightarrow d_{\sigma^*}$
A. Bridging Superoxo–Dimetal Complexes				
$[(NH_3)_5Co(\mu\text{-}O_2^-)Co(NH_3)_5]^{5+}$	800 (2.04)	672 (2.97)	307 (3.54)	302 (4.30)
$[(en)_2(NH_3)Co(\mu\text{-}O_2^-)Co(NH_3)(en)_2]^{5+}$		709 (3.05)	375 (3.30)	302 (4.29)
$[(trien)(NH_3)Co(\mu\text{-}O_2^-)Co(NH_3)(trien)]^{5+}$		709 (3.11)	469 (2.66)	307 (4.29)
$[(dien)(1\text{-}pn)Co(\mu\text{-}O_2^-)Co(1\text{-}pn)(dien)]^{5+}$		714 (3.19)	467 (2.79)	306 (4.36)
$[(tetren)Co(\mu\text{-}O_2^-)Co(tetren)]^{5+}$		709 (3.15)	465 (2.78)	313 (4.28)
B. Doubly Bridged Superoxo–Dimetal Complexes				
$[(en)_2Co(\mu\text{-}O_2^-,OH)Co(en)_2]^{4+}$		675 (2.72)	493 (2.67)	
$[(1\text{-}pn)_2Co(\mu\text{-}O_2^-,OH)Co(1\text{-}pn)_2]^{4+}$		671 (2.71)	483 (2.67)	
$[(en)_2Co(\mu\text{-}O_2^-,NH_2)Co(en)_2]^{4+}$		699 (2.15)	481 (2.50)	
C. 1:1 Superoxo–Metal Complexes				
$[(s\text{-}Me_2en)_2ClCoO_2]^+$		481 (2.81)		345 (3.72)
$[(s\text{-}Et_2en)_2ClCoO_2]^+$		492		371

Table VII. Spectral Data[29] for Peroxo Complexes

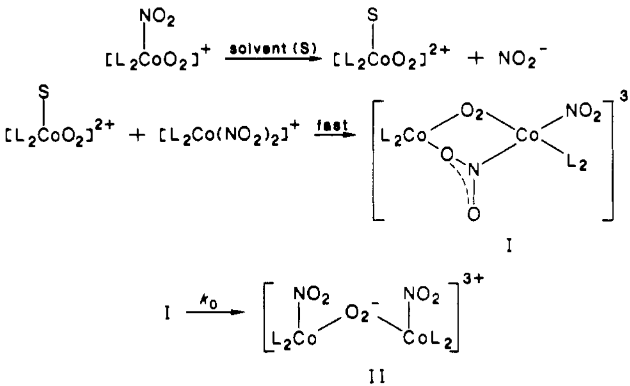
complex	λ_{max}, nm (log ϵ)	
$[(dien)(en)Co(\mu\text{-}O_2^{2-})Co(en)(dien)]^{4+}$	417 (2.78) sh	300 (3.98)
$[(dien)(1\text{-}pn)Co(\mu\text{-}O_2^{2-})Co(1\text{-}pn)(dien)]^{4+}$	417 (2.73) sh	301 (4.00)
$[(tetren)Co(\mu\text{-}O_2^{2-})Co(tetren)]^{4+}$	417 (2.87) sh	310 (4.10)
$[(en)_2Co(\mu\text{-}O_2^{2-},OH)Co(en)_2]^{3+}$	526 (2.59) sh	357 (3.69)
$[(1\text{-}pn)_2Co(\mu\text{-}O_2^{2-},OH)Co(1\text{-}pn)_2]^{3+}$	510 (2.58) sh	350 (3.76)
$[(en)_2Co(\mu\text{-}O_2^{2-},NH_2)Co(en)_2]^{3+}$	500 (2.60) sh	355 (3.59)

toproduct of the cobalt(III)–amine complex. Spectra of the transient species of the complexes show peaks around 400, 480, and 700 nm as given in Table IV. The spectra of the superoxo dioxygen complexes with 1:1 and 1:2 dioxygen to cobalt ratios reveal[11,29,35] that only dinuclear μ-superoxo complexes of cobalt(III) have a maximum around 700 nm, which is assigned as due to a charge-transfer transition from metal to ligand (Table VI). Spectral maxima observed for the transients at other wavelengths are also similar to those of monobridged μ-superoxo dinuclear complexes, which are assigned as charge-transfer transitions from ligand to metal.[35]

The transient growth of absorbance at 700 nm occurs at a slower time scale compared to transient growth at 400 nm. The transient spectrum recorded in the time scale[16] corresponding to the initial fast transient seen at 400 nm, shows maxima at 400 and 480 nm and no absorption at 700 nm, which is assigned to the 1:1 mononuclear superoxo complex.

Concentration of dissolved oxygen in acetonitrile[30] is 1.6×10^{-3} M and is very much in excess when compared to the concentration of the cobalt(II) species produced photochemically, which leads to a pseudo-first-order reaction. The rate constants observed at 400 nm also vary with the concentration of dissolved oxygen. The first-order kinetics plots for the 400-nm growth result in good straight lines as determined by the least-square fit (correlation coefficient > 0.99).

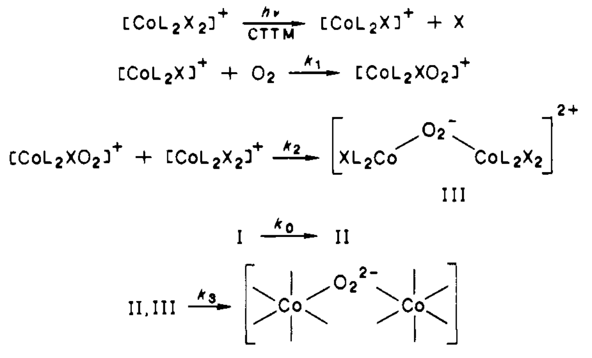
Transient growth at 700 nm also obeys first-order kinetics with k_{obsd} depending upon the concentration of the starting complex. This implies that the starting complex is also involved in the formation of μ-superoxo complex. Analysis of the kinetics of this transient at 700 nm, namely, the formation of the μ-superoxo complex, indicates a pathway dependent on the concentration of the complex and another independent of the concentration of the starting cobalt(III) complex. For the latter case we propose that the slow step is the labilization of a coordinated ligand, which is the slow step, followed by the coordination of the oxygen atom of the nitro ligand of the starting complex to give rise to the μ-superoxo complex as shown in the following scheme:



superoxo complex

L = bidentate ligand

The decay of the absorbance of the transients seen at 700 nm occurs on a slower time scale that obeys first-order kinetics. The decay of the transient is due to the formation of the final product μ-peroxo complex from the μ-superoxo intermediate. The above observations could be fitted to the following reaction scheme:



IV (peroxo complex)

L = bidentate ligand X = NO_2^- or Cl^-

The mononuclear superoxo cobalt(III) complex is not very stable and the tendency to form a dimer is high. Except in a few cases with bulky amines, the mononuclear superoxo complexes have not been isolated.[31] In the present investigation, since the different steps of the oxygenation reactions occur in a different time domain, we are able to monitor the three different steps during the course of the formation of the dinuclear μ-peroxo complex (IV). The mononuclear superoxo complex is able to react with the starting complex to form the dinuclear μ-superoxo complex (III), and the final dinuclear μ-peroxo complex results by the intramolecular reduction of the superoxo center by the coordinated nitrite ligand.[37]

Flash photolysis of complexes, in the presence of excess cobalt(II) ion, shows the growth of the transient at 400 nm, and the rate constant is much slower compared to that for the formation of mononuclear superoxo complex. Absence of any transient at 700 nm in presence of cobalt(II) ion indicates that the mononuclear superoxo complex is converted directly to the μ-peroxo complex by reacting with cobalt(II) ion.

The redox potential of the superoxo–peroxo couple is about 1.0 V, and even mild reducing agents such as NO_2^-, SO_3^-, and Fe(II) are known[32] to reduce the superoxo bridge to the peroxo form. Reduction by free NO_2^- ion present in the medium is ruled out since the decay of the 700-nm absorbance follows only first-order kinetics and not second-order kinetics. Addition of NO_2^- ion accelerates the 700-nm decay, indicating that the nitrite ion can, indeed, reduce the superoxo bridge to the peroxo form. Regarding the proposed seven-coordinate intermediate, even though the substitution at the cobalt(III) center normally proceeds through a dissociative mechanism, there was a proposal for an associative mechanism by Ingold et al.[33,34] in the substitution of $[Co(en)_2NO_2Cl]^+$ by H_2O. It was argued, in that connection, that when electron-withdrawing groups like NO_2^- are coordinated to the cobalt(III) center, the subtitution proceeds through an associative mechanism rather than a dissociative mechanism.

Analysis of the data in Table II indicates that the cis isomer is more reactive than the trans isomer in the oxygenation reaction, which implies that the reaction depends upon the basicity of the axial ligand. In the case of the cis complex the axial ligand is an amine, which is more basic than the nitro group, which is an axial group in the trans isomer.

In the case of trimethylenediamine–cobalt(III) complexes in acetonitrile, the dichloro complex is more reactive than the others. Since the nitro group is a more electron-withdrawing group when compared to chloride, the amount of electron density available at the cobalt(II) center is lower in the former case. Hence, the rate constant for the formation of the mononuclear superoxo complex is slower in the case of the nitro complex when compared to the case of the chloro complex.

Comparison of the oxygenation reactions in different solvents shows that the rate constant for the first oxygenation step is slower in methanol than that in acetonitrile, with the exception of $[Co(dien)(pn)NO_2](ClO_4)_2$.

Conclusion

The kinetics of the oxygenation of cobalt(II)–amine complexes has been investigated extensively by using the stopped-flow method.[2] In these studies cobalt(II) amines were mixed with oxygen where the μ-peroxo dinuclear complex is formed as the final product. Often, the nature of the coordination environment of the cobalt(II) complex is not well-known, the data are fitted to a mechanistic scheme, and details of the different steps involved in the reaction are not well understood. There is a large volume of literature on the thermodynamic data for the oxygenation of cobalt(II) complexes.[2]

We have developed a new approach for investigating the oxygenation reaction. The lability of cobalt(II) complexes is less in nonaqueous solvents with low dielectric constants. Photolysis of cobalt(III)–amine complexes in aqueous solutions produces a cobalt(II) complex that loses the coordinated amines before it reacts with oxygen. Since cobalt(II) aquo complexes do not react with molecular oxygen, no oxygenation reaction is observed in aqueous solution. However, photolysis of cobalt(III) amines in acetonitrile or alcohol produces a cobalt(II) complex that reacts quantitatively with dissolved oxygen. In these cases it is fairly certain that the cobalt(II) complex produced photochemically retains the coordinated ligands as in the parent complex, except for one of the ligands that was oxidized. Therefore, flash photolysis method offers a convenient way to study the oxygenation reaction in detail. Since excess cobalt(III)–amine complex is present in the medium, there is no immediate reaction to produce the μ-peroxo dinuclear cobalt(III) complex. The mononuclear superoxo complex, which is not very stable, reacts with the starting material to form the μ-superoxo dimer. Since the reactions are occurring on different time scales, it has been possible to monitor different steps in the flash photolysis investigation.

Acknowledgment. The investigations are partly supported by UGC COSIST assistance and by a DST Thrust Area Programme.

Registry No. $[Co(pn)_2(NO_2)_2]ClO_4$, 102573-37-5; $[Co(pn)_2Cl_2]ClO_4$, 36545-32-1; *trans*-$[Co(tn)_2(NO_2)_2]ClO_4$, 103639-33-4; *trans*-$[Co(tn)_2(NO_2)Cl]ClO_4$, 103639-34-5; *trans*-$[Co(tn)_2Cl_2]ClO_4$, 56295-62-6; $[Co(dien)(NO_2)_3]$, 14971-76-7; $[Co(dien)(en)NO_2](ClO_4)_2$, 49727-69-7; $[Co(dien)(pn)NO_2](ClO_4)_2$, 103639-36-7.

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(37) It is known[38] that in neutral solution the μ-superoxo complex is reduced to give the μ-peroxo complex. Even when the NO_2^- ion is not present, conversion of the μ-superoxo to the μ-peroxo complex is a relatively fast reaction.

(38) Duffy, D. L.; House, D. A.; Weil, J. A. *J. Inorg. Nucl. Chem.* **1969**, *31*, 2053–2058.