Table VII. Selected Bond Lengths (Å) for $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$

W-P(1)	2.426 (4)	W-P(2)	2.479 (4)
W-P(3)	2.494 (4)	W-P(4)	2.496 (4)
W-O	2.145 (8)	W-C(7)	2.290 (11)
O-C(1)	1.354 (14)	C(1)-C(2)	1.359 (19)
C(1)-C(6)	1.420 (18)	C(2)-C(3)	1.402 (17)
C(2)-C(7)	1.488 (16)	C(3)-C(4)	1.403 (22)
C(4)-C(5)	1.368 (26)	C(4)-C(8)	1.515 (21)
C(5)-C(6)	1.410 (22)	C(6)-C(9)	1.505 (24)

Table VIII. Selected Bond Angles (deg) for $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$

P(1)-W-P(2)	128.8 (1)	P(1)-W-P(3)	96.4 (1)
P(2)-W-P(3)	92.8 (1)	P(1)-W-P(4)	97.1 (1)
P(2)-W-P(4)	91.7 (1)	P(3)-W-P(4)	158.5 (1)
P(1)-W-O	152.1 (2)	P(2)-W-O	79.1 (2)
P(3)-W-O	79.7 (2)	P(4)-W-O	80.5 (2)
P(1)-W-C(7)	76.7 (3)	P(2)-W-C(7)	154.5 (3)
P(3)-W-C(7)	83.4 (3)	P(4)-W-C(7)	83.5 (3)
O-W-C(7)	75.4 (4)	W-P(1)-C(11)	115.8 (5)
O-C(1)-C(2)	120.4 (10)	W-O-C(1)	117.6 (8)
C(2)-C(1)-C(6)	122.1 (12)	O-C(1)-C(6)	117.5 (12)
C(1)-C(2)-C(7)	116.5 (10)	C(1)-C(2)-C(3)	119.4 (11)
W-C(7)-C(2)	109.7 (8)	C(3)-C(2)-C(7)	124.0 (12)

For $W(PMe_3)_6$, systematic absences were consistent with several space groups, of which the choice $Im\bar{3}m$ was made since (i) this produced the most successful solution and (ii) this is also the space group for the isostructural complexes $Mo(PMe_3)_6$ and $M(Me_2PCH_2CH_2PMe_2)_3$ (M = Cr, Mo, W, V, Nb, Ta).[1a,6] The methyl groups of the PMe_3 ligands are highly disordered as a result of the presence of both the 3-fold symmetry of PMe_3 and the 4-fold crystallographic symmetry. The disorder was modeled, in a similar manner to that reported for $Mo(PMe_3)_6$, by fixing two carbon atoms on two independent mirror planes that pass through P.[1a] For both $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$ and $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$, systematic absences were consistent with the space group $P2_1/n$. Hydrogen atoms on carbon were included in calculated positions (d_{C-H} = 0.96 Å; $U_{iso}(H) = 1.2U_{iso}(C)$). Selected bond lengths and angles for $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$ and $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$ are given in Tables V–VIII.

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Supplementary Material Available: Complete table of ^1H, ^{13}C, and ^{31}P NMR spectroscopic data for all new compounds (8 pages). Tables of crystal and intensity collection data, atomic coordinates, bond distances and angles, anisotropic displacement parameters, and observed and calculated structure factors and ORTEP drawings for $W(PMe_3)_6$, $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$, and $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$ are available as supplementary material to the original communications.[2] Ordering information is given on any current masthead page.

A New Approach to the Study of the Oxygenation Reactions of Transition-Metal Complexes. Formation of the μ-Superoxo Cobalt(III) Complexes in the Oxygenation Reactions of Cobalt(II) Amines

T. Dhanasekaran and P. Natarajan*

Department of Inorganic Chemistry, School of Chemistry, University of Madras, Madras 600 025, India. Received January 22, 1991

Abstract: In the reactions of molecular oxygen with cobalt(II) amines, formation of μ-superoxo complexes has been identified on photolysis of cobalt(III) amine complexes $[Co(trien)(NO_2)_2]ClO_4$ (**1**) and $[Co(tetraen)(NO_2)](ClO_4)_2$ (**2**) in oxygen-saturated aqueous solution. The kinetics of oxygenation reactions has been followed by flash photolyzing the complexes **1** and **2** in aqueous and nonaqueous solvents and the rate constants for the formation of mononuclear superoxo complex and the μ-superoxo dinuclear complex has been determined at 25 ± 1 °C. Photochemical routes for the preparation of μ-superoxo cobalt(III) complexes are suggested from this study.

Introduction

Activation of molecular oxygen by cobalt(II) amines is a classic reaction[1,2] and the subject has been extensively investigated.[3] Earlier investigations based on stopped flow kinetics have proposed two steps for the formation of the final product μ-peroxo complex. We have discovered that oxygen activation by cobalt(II) amine species photoproduced from the cobalt(III) complexes opens up possibilities to find new species during the course of the reaction and also more defined mechanistic information on the oxygenation reaction. In this paper we report on the oxygenation reactions of cobalt(II) amine systems by investigating the flash photolysis and steady photolysis of oxygenated aqueous solutions of *cis*-$[Co(trien)(NO_2)_2]ClO_4$ (**1**) and $[Co(tetraen)(NO_2)](ClO_4)_2$ (**2**). By this method the reactant is generated in situ and the coordination environment of the labile cobalt(II) amine is better characterized at the time of the reaction. The subsequent reaction with molecular oxygen could be followed on much shorter time scale compared to stopped flow time scale. In addition, cobalt(II) amine is present at much lower concentration compared to dissolved oxygen and hence the possibility of finding new types of reactions involving dioxygen has been explored.

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(1) (a) Martell, A. E.; Menif, R. *Inorg. Chem.* **1989**, *28*, 116. (b) Szpoganicz, B.; Motekaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1990**, *29*, 1467. (c) Hohenester, E.; Kratky, C.; Krautler, B. *J. Am. Chem. Soc.* **1991**, *113*, 4523.

(2) (a) Mclendon, G.; Martell, A. E. *Coord. Chem. Rev.* **1976**, *19*, 1. (b) Niderhoffer, E. C.; Timmons, J. H.; Martell, A. E. *Chem. Rev.* **1984**, *84*, 137.

(3) Lever, A. B. P.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 348.

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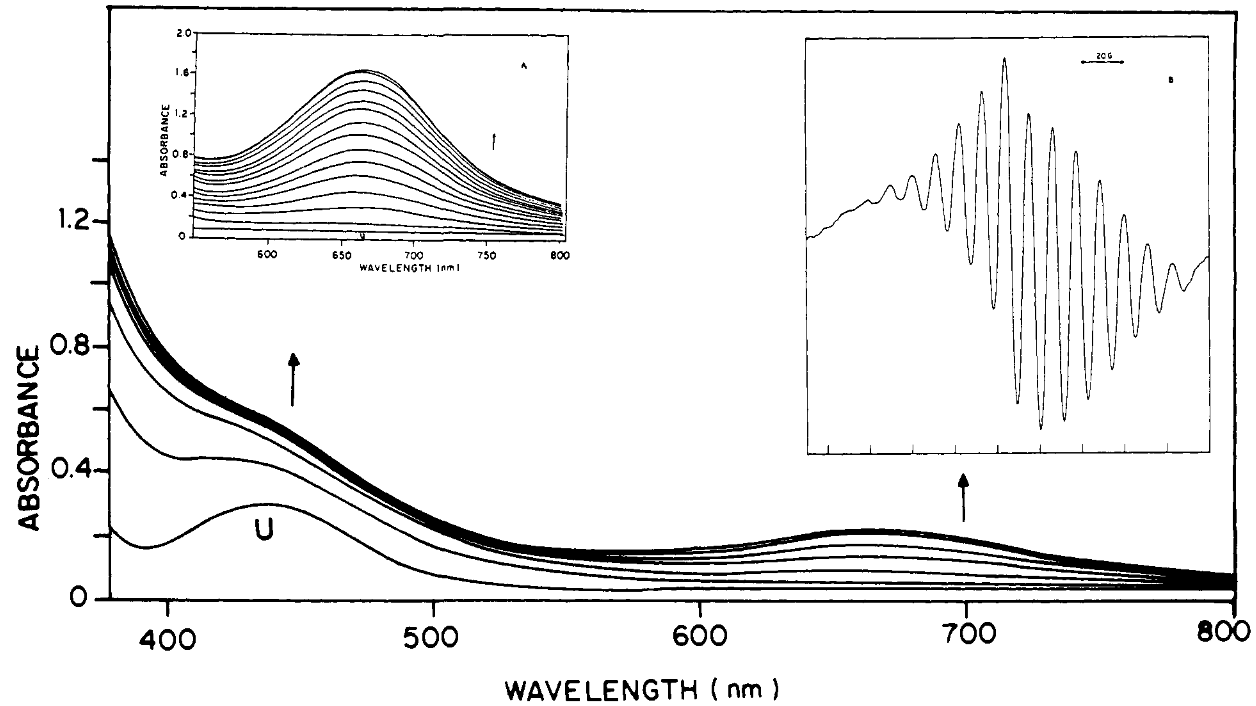

Figure 1. Steady photolysis of *cis*-$[Co(trien)(NO_2)_2]^+$ ion in oxygen-saturated aqueous solution at 4 ± 1 °C: U, unirradiated solution; increase in absorbance is due to successive irradiations; (inset A) expansion of the above region, 500–800 nm; (inset B) X-band ESR spectrum of the irradiated solution containing 50% $HClO_4$ at 0 K.

Table I

	CH₃CN			H₂O		
complex	k_1, M^{-1} s^{-1}	k_2, M^{-1} s^{-1}; k_0,[a] s^{-1}	k_3, s^{-1}	k_1, M^{-1} s^{-1}	k_2, M^{-1} s^{-1}; k_0, s^{-1}	k_3, s^{-1}
$[Co(trien)(NO_2)_2]ClO_4$	$(2.7 \pm 0.3) \times 10^5$	$(1.1 \pm 0.01) \times 10^5$; 70 ± 5.0	0.36 ± 0.02	$(3.2 \pm 0.3) \times 10^2$	$(9.0 \pm 0.5) \times 10^2$; 0.54 ± 0.05	<0.1
$[Co(tetraen)(NO_2)](ClO_4)_2$	$(6.8 \pm 0.2) \times 10^4$	$(8.6 \pm 0.4) \times 10^3$; $(1.0 \pm 0.2) \times 10^2$	0.62 ± 0.05	$(1.0 \pm 0.02) \times 10^5$	$(8.2 \pm 0.4) \times 10^4$; $(2.6 \pm 0.4) \times 10^2$	<0.1

[a] k_0 is the rate constant for the formation of **4** which is independent of the concentration of cobalt(III) amine complex.

Experimental Section

cis-$[Co(trien)(NO_2)_2]ClO_4$ (**1**) and $[Co(tetraen)(NO_2)](ClO_4)_2$ (**2**) have been prepared and characterized by well-known methods.[4] Steady photolysis experiments have been carried out using a medium-pressure Phillips HPK 125-W lamp or a low-pressure mercury vapor lamp. Flash photolysis experiments were carried out using an Applied Photophysics KN020. ESR spectra were obtained in a Bruker X-band spectrometer and the electronic absorption spectra were recorded using a HP 8452A diode array spectrophotometer.

Oxygenation reactions were studied by taking a solution of cobalt(III) complex **1** or **2** in air-equilibrated or oxygen-saturated solutions and flash photolyzing in the conventional flash photolysis apparatus. The cobalt(II) complex generated in situ reacts with dissolved oxygen and the change in absorbance of the solution is observed as a function of time. Steady photolysis experiments were carried out by taking appropriate solutions of **1** or **2** and the solution was irradiated either by a medium-pressure or low-pressure mercury vapor lamp. After irradiation the spectra of the solutions were obtained in the diode-array spectrophotometer.

Results and Discussion

Oxygenation reactions of cobalt(II) amines convert molecular oxygen to coordinated two electron reduced μ-peroxo dinuclear cobalt(III) complexes. While the mononuclear superoxo complexes have been isolated in some cases,[5] the details of the kinetics of the formation and decay of the one electron and two electron reduction products were limited by the time scale of the stopped-flow technique. The new approach described here allows the production of the labile cobalt(II) amine with a well-defined coordination environment by flash photolyzing an inert cobalt(III) complex and monitoring the reactions of oxygen on shorter time scales and at different concentration levels of the reagents.

An aqueous solution of *cis*-$[Co(trien)(NO_2)_2]ClO_4$ (0.01 M), which is orange yellow in color, on irradiation at 4–5 °C under a stream of oxygen using a medium-pressure mercury vapor lamp turns dark green and the spectral changes monitored in the diode-array spectrophotometer are shown in Figure 1. The ESR spectrum of the irradiated solution shown in Figure 1 (inset) exhibits the characteristic spectrum for the μ-superoxo dinuclear complex. The transient spectra monitored on flash photolysis of **1** and **2** show the characteristic band at ~700 nm for the μ-superoxo dinuclear complex. An identical steady photolysis behavior was shown by the complex **2**, and on warming the irradiated solution to 25 °C, the solution turns brown indicating the formation of μ-peroxo dinuclear complex. The final product of steady photolysis was confirmed to be the μ-peroxo dinuclear complex by isolating the product of photolysis of **2** and by independently preparing a sample of μ-peroxo dinuclear complex by the thermal air oxidation of cobalt(II) in presence of tetraen. The absorption spectra of the photochemically synthesized μ-peroxo dicobalt(III) tetraen complex and of the thermally prepared sample are given in Figure 2. On oxidation using potassium peroxodisulfate, both the samples are converted to the μ-superoxo complex. Flash photolysis of an aqueous solution (pH = 6.3) of **1** and **2** at 25 °C by conventional and laser flash photolysis techniques shows the formation and decay of the transients as shown in a typical experiment in Figure 3. The rate constants determined are shown in Table I and could be fit to Scheme I. The rate constant k_2 is determined by measuring the pseudo-first-order rate constants

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[4] (a) Kyuno, E.; Boucher, L. J.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 4458. (b) Selbin, J. *J. Inorg. Nucl. Chem.* **1961**, *17*, 84.

[5] (a) Gall, P. S.; Rogers, J. F.; Schaefer, W. P.; Christop, G. C. *J. Am. Chem. Soc.* **1976**, *98*, 5135. (b) Avdeef, A.; Schaefer, W. P. *J. Am. Chem. Soc.* **1976**, *98*, 5153. (c) Gall, P. S.; Schaefer, W. P. *Inorg. Chem.* **1976**, *15*, 2758.

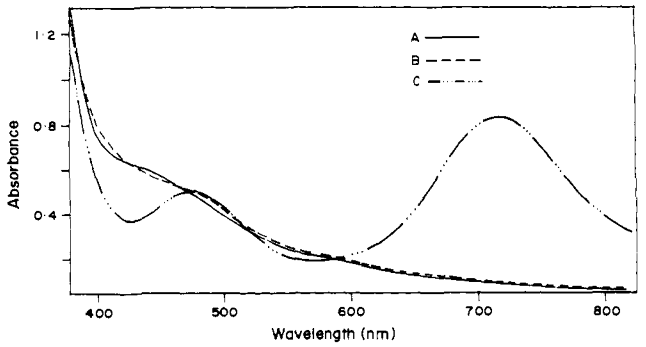
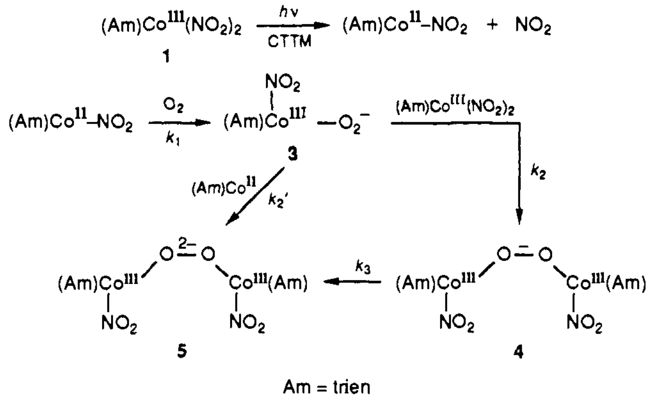


Figure 2. (A) Absorption spectrum of the brown product isolated on steady photolysis of $[Co(tetraen)(NO_2)](ClO_4)_2$ in oxygen-saturated methanol at 25 °C. (B) Absorption spectrum of $[(Co(tetraen))_2O_2](ClO_4)_4$ prepared by thermal air oxidation of Co^{II} in presence of tetraen. (C) Absorption spectrum obtained after oxidation of A or B by adding small amounts of solid potassium peroxodisulfate at ambient temperature.

Scheme I



at different concentrations of **1**. In the case of **2**, the pseudo-first-order rate constant for the first step is found to be 120 s^{-1} in air-equilibrated nonaqueous solution while the same is found to be 170 s^{-1} in oxygenated solution. The rate constant for the formation of the μ-superoxo complex in the case of **2** predominantly proceeds by a mechanism which is independent of the concentration of the cobalt(III) amine complex and the details of the mechanism are given elsewhere.[6] The μ-superoxo dinuclear cobalt(III) complexes are well-known for a good number of ligand systems with ESR and the electronic spectra are well documented.[3] With this information we have assigned the product **4** as the μ-superoxo dinuclear cobalt(III) complex and **3** as the mononuclear superoxo cobalt(II) adduct. While the mononuclear cobalt(III)–superoxo complex could not be seen in the aqueous solution on steady photolysis, a methanolic solution of **1** irradiated at −70 °C shows the characteristic absorption spectrum and the ESR spectrum as shown in Figure 4.

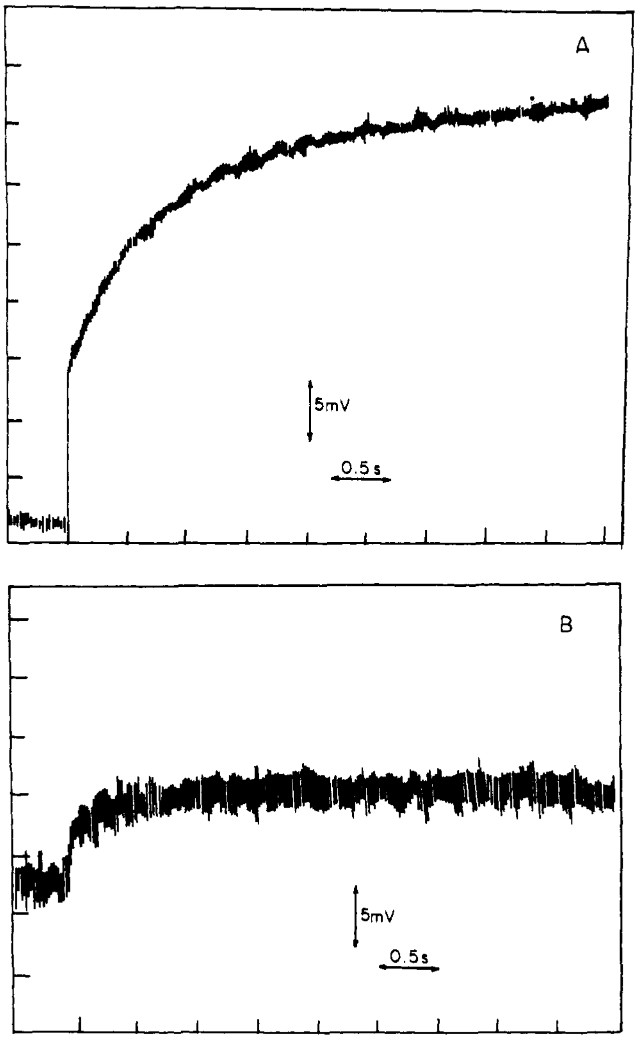


Figure 3. Flash photolysis of *cis*-$[Co(trien)(NO_2)_2]^+$ ion in oxygen-saturated water at 25 ± 1 °C: [complex] = 1×10^{-3} M; (A) monitored at 400 nm, (B) monitored at 700 nm.

The oxygenation reaction of $[Co(trien)]^{2+}$ and $[Co(tetraen)]^{2+}$ has been characterized by the studies of Wilkins et al.[7,8] It has been established that the μ-peroxo complex is formed by the reaction of Co^{II}(trien) or Co^{II}(tetraen) with the mononuclear cobalt(III) oxygen species. This is further supported by our observation that flash photolysis of **1** in the presence of added cobalt(II) decreases the amount of the μ-superoxo complex formed indicating that the direct formation of **5** occurs without the formation of the μ-superoxo intermediate whenever cobalt(II) amine is present in the medium at a certain optimum concentration. The flash photolysis experiments carried out at low concentrations of complexes **1** and **2** indicate that the reaction between the mononuclear superoxo complex and cobalt(II) species competes with the pseudo-first-order reaction (k_2) leading to the formation of μ-superoxo complex.[6,9] The absorption spectra of the transients recorded show the presence of μ-superoxo complex along with the μ-peroxo complex as shown in Figure 5. The rate constant reported in this study for the formation of **3** is 2 orders lower in magnitude than that reported from stopped flow experiments for the Co^{III}(trien) complex, **1**. In the present case we are in a position to monitor specifically the reaction of O_2 to give the mononuclear dioxygen species, whereas the time resolution of the stopped flow method does not allow this. The rate constant for the formation of **4** is found to be higher than expected for the substitution at an inert cobalt(III) center. The driving force for this reaction is the coordination of NO_2 present in the starting complex **1** with the (trien)Co–O_2 to give a six-coordinated complex which subsequently gives the μ-superoxo complex **4**. The oxidation state of the mononuclear superoxo complex is perhaps between 3 and 2 as indicated in the ESR spectra of such systems[10] and consequently the complex is less inert than the low spin cobalt(III) amine complexes.

The work reported here shows a new pathway for the reaction of the mononuclear dioxygen species **3** by way of reaction with a cobalt(III) complex to produce the μ-superoxo dinuclear complex. The kinetics of oxygenation reactions is drastically altered in nonaqueous solvents[6,9] showing the clue that in biological reactions involving oxygen, specific reactions are brought about by a change in the hydrophobicity of the environment. The rate

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(6) Ramamurthy, P.; Natarajan, P. *Inorg. Chem.* **1986**, *25*, 3554.

(7) Miller, F.; Simplico, J.; Wilkins, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 1962.

(8) Miller, F.; Wilkins, R. G. *J. Am. Chem. Soc.* **1970**, *92*, 2687.

(9) Ramamurthy, P.; Vijayaraghavan, R.; Natarajan, P. *Indian J. Chem.* **1990**, *29-A*, 1.

(10) Sykes, A. G.; Weil, J. A. *Prog. Inorg. Chem.* **1970**, *13*, 1.

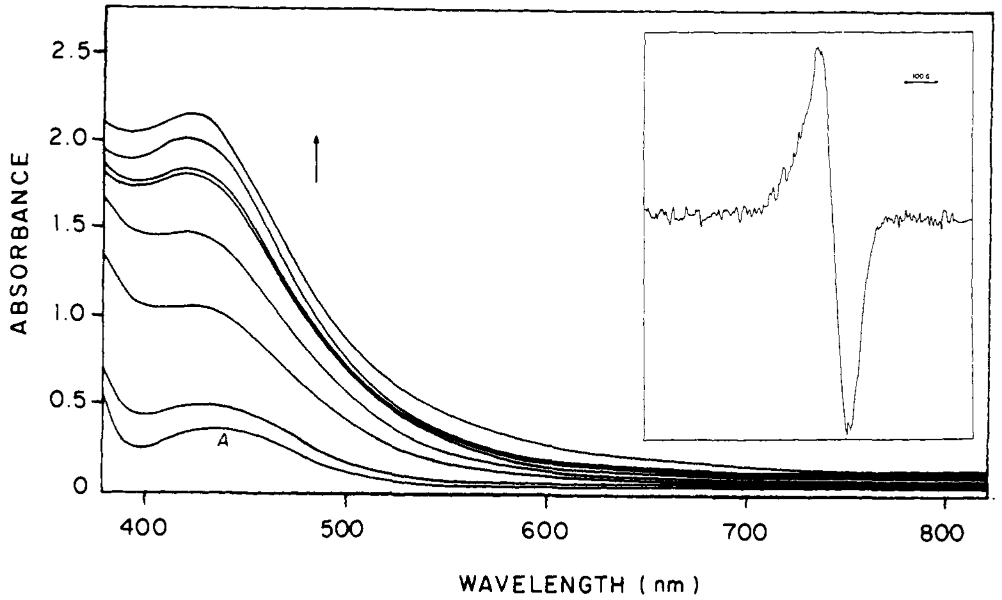

Figure 4. Steady photolysis of *cis*-$[Co(trien)(NO_2)_2]^+$ ion in oxygen-saturated methanol at −70 °C. Inset: X-band ESR spectrum of the irradiated solution at −70 °C and frozen to 77 K.

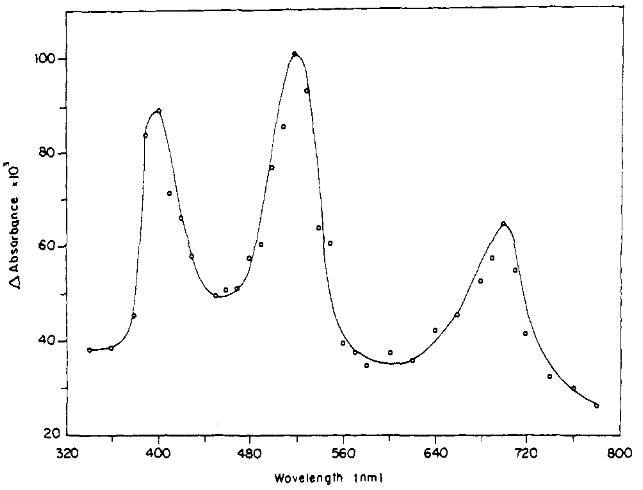

Figure 5. Absorption spectrum of the transient formed on flash photolysis of $[Co(tetraen)(NO_2)]^{2+}$ ion in oxygen-saturated aqueous solution recorded 50 ms after flash.

constant for the formation of μ-superoxo complex k_2 is much slower than the rate constant for the reaction of $Co(trien)^{2+}$, for instance with $[Co(trien)O_2]^{2+}$ to give the μ-peroxo complex. For the complexes **1** and **2** studied here the coordinated dioxygen complex **3** is able to react with a labile cobalt(II) amine or an inert cobalt(III) complex, although with a much higher rate constant with the former, and the formation of the μ-superoxo complex has been observed by flash photolysis of an aqueous or nonaqueous solution of the complex. The spontaneous conversion of the μ-superoxo complexes to μ-peroxo complexes in neutral and nonaqueous solutions is known[11] and in fact the former is stabilized only in acid solutions and the latter is synthesized in some cases by treating the μ-superoxo complex in acetone or alcohol at room temperature.[6,11] The flash photolysis results obtained for $[Co(dmg)_2(py)(NO_2)]$ again show a very similar pathway for oxygenation of the $[Co(dmg)_2(py)]$ complex.[12] The present study for the first time expands the scope to prepare μ-superoxo and μ-peroxo dioxygen complexes by the photochemical method. A photochemical method for the preparation of μ-superoxo complex can fruitfully be used in the case of macrocyclic complexes as well.[13]

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(11) Davies, R.; Mori, M.; Sykes, A. G. *Inorg. Synth.* **1971**, XII, 207.

(12) Manuscript under preparation.

(13) Ramamurthy, P. *Inorg. Chim. Acta* **1990**, *175*, 1.