

Photochemical reactions of cobalt(III)-amine complexes in non-aqueous solvents: Mechanistic details of oxygenation reaction of cobalt(II) systems-II†

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Flash photolysis and steady-state photolysis studies of a series $[\text{Co}(\text{Am})(\text{NO}_2)_2]^+$ ($\text{Am} = 2 \text{ en, trien}$) of complexes have been carried out in acetonitrile. Photolysis of the complexes in air-equilibrated acetonitrile medium produces mononuclear superoxo, dinuclear superoxo and dinuclear peroxo complexes sequentially. Transient absorptions are observed for the formation of mononuclear and dinuclear superoxo complexes at 400 and 700 nm respectively during flash photolysis. Steady state photolysis results in the dinuclear peroxo complex as the final product.

Cobalt(III)-amine complexes promote reactions similar to those promoted in biological systems by mono- and di-oxygenases¹. Photochemistry of cobalt(III)-amine complexes has been of interest during the past two decades and most of these are confined to the identification and characterization of reactive excited states²⁻⁵. Photochemistry of cobalt(III)-amine complexes is affected among others by the reaction medium⁶. Earlier we have investigated the photochemistry of a series of cobalt(III)-amine nitro complexes (amine—pn, tn & dien) in acetonitrile and methanol medium⁷. The study has been extended to another series of complexes where the amine is ethylenediamine and triethylenetetraamine.

Materials and Methods

The complexes *cis*- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{ClO}_4$ (ref. 8), *trans*- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{ClO}_4$ (ref. 9) and *cis*- $[\text{Co}(\text{trien})(\text{NO}_2)_2]\text{ClO}_4$ (ref. 10) (*en* = ethylenediamine and *trien* = triethylenetetraamine) were prepared following the literature methods. The absorption spectra and molar absorptivities of the complexes agree well those reported in literature. Acetonitrile (Fluka) was of spectral grade and the amines (Fluka, puriss) used were distilled before use. Electronic spectra were recorded on a Hitachi-320 UV-visible double-beam spectrophotometer. Flash photolysis experiments were carried out using an Applied Photophysics model KN-020 flash kinetic spectrometer. Deaeration was carried out using freeze-thaw method for experiments in deaerated solutions. Steady state photolysis experiments were carried out using a Varian EIMAC 300 W xenon lamp.

Results

Flash photolysis of the complexes in air-equilibrated acetonitrile shows a transient growth of absorbance at 400 nm, which is followed by a slower growth of absorbance at 700 nm. The transient absorption at 700 nm also decays on a slower time scale as shown in Fig. 1. Transient growth of absorbance at 400 nm obeys first order kinetics (Table 1); the plots of $\log(A_\infty - A_t)$ versus time were linear (Fig. 2). Rate constant of the transient growth of absorbance at 400 nm depends on the concentration of the oxygen present in the medium.

Transient growth of absorbance at 700 nm also obeys first order kinetics. The rate constant of the growth depends on starting [complex] (Table 2). The first order plots of $\log[(A_\infty - A_t)/(A_\infty - A_0)]$ versus time for different [complex] are shown in Fig. 3. A plot of k_{obs} versus [complex] for a typical complex is shown in Fig. 4, and from the slope the second order rate constant is calculated. Transient absorption at 700 nm also obeys first order kinetics (Table 1). The plot of $\log(A_t - A_\infty)$ versus time is shown in Fig. 2. This rate constant does not depend on [complex]. The above transients were not observed in deaerated medium. Transient absorption spectra were recorded in 400 nm growth time scale and 700 nm growth time scale (Table 3 and Fig. 5).

Table 1—Rate constants for 400 nm absorption growth and 700 nm absorption decay

Complex	$k \times 10^{-2} (\text{s}^{-1})$ (400 nm)	$k (\text{s}^{-1})$ (700 nm)
<i>cis</i> - $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{ClO}_4$	3.0 ± 0.2	0.26 ± 0.01
<i>trans</i> - $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{ClO}_4$	2.7 ± 0.4	0.64 ± 0.03
<i>cis</i> - $[\text{Co}(\text{trien})(\text{NO}_2)_2]\text{ClO}_4$	2.7 ± 0.2	0.36 ± 0.02

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Table 2—Concentration dependence of rate constants corresponding to the 700 nm transient absorption growth

Complex	[Complex] × 10 ⁴	k _{obs}	k ₂ × 10 ⁻⁴	k ₀
	(M)	(s ⁻¹)	(M ⁻¹ s ⁻¹)	(M ⁻¹ s ⁻¹)
<i>cis</i> -[Co(en) ₂ (NO ₂) ₂]ClO ₄	1.504	48.3		
	3.132	54.2	1.6 ± 3	47 ± 2
	12.530	67.3		
<i>trans</i> -[Co(en) ₂ (NO ₂) ₂]ClO ₄	2.513	84.2		
	5.032	102.1	6.3 ± 3	69 ± 2
	10.040	131.9		
<i>cis</i> -[Co(trien)(NO ₂) ₂]ClO ₄	4.067	117.3		
	8.174	162.9	11.41 ± 0.01	70 ± 1
	15.640	249.2		

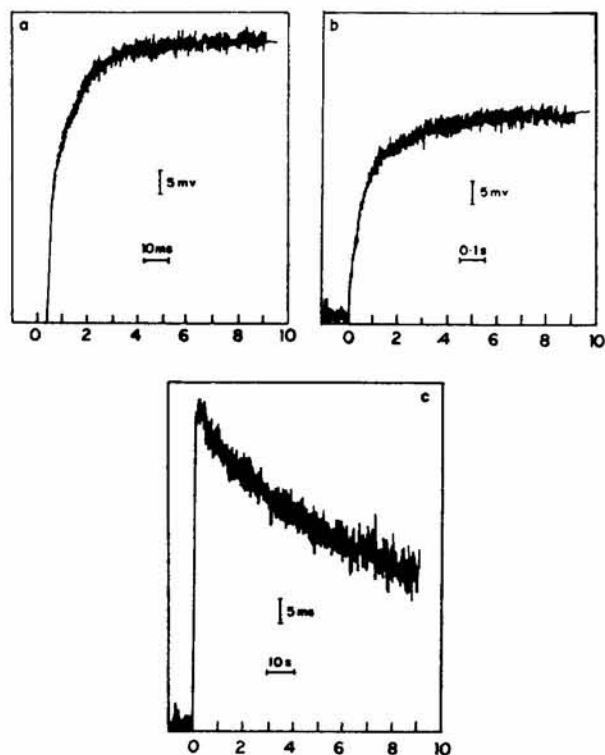


Fig. 1—Transient absorbance growth at (a) 400 nm and (b) 700 nm and transient decay at (c) 700 nm of *trans*-[Co(en)₂(NO₂)₂]⁺ in CH₃CN

Steady photolysis of the complexes in air-equilibrated acetonitrile medium shows spectral changes in the visible region, indicating absorption bands for the photoproducts with markedly high intensities. Well-defined isosbestic points are observed for solutions of the complexes irradiated for different time intervals as shown in Fig. 6. Spectral details of the products on prolonged irradiation are given in Table 4.

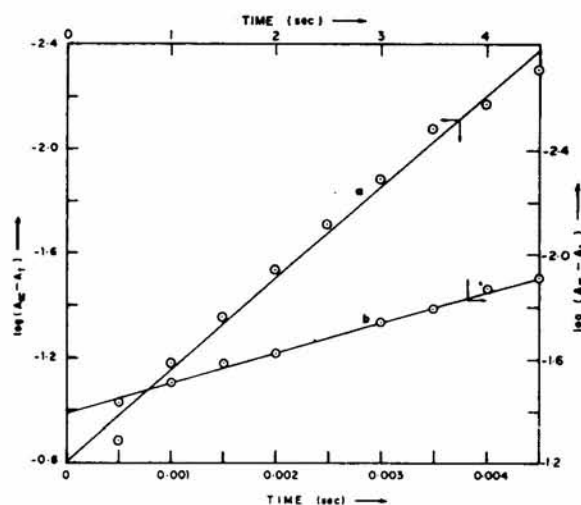


Fig. 2—First-order fit of (a) transient absorbance growth at 400 nm and (b) transient decay of 700 nm of *cis*-[Co(en)₂(NO₂)₂]⁺ in CH₃CN

Discussion

Cobalt(III) complexes in acidic aqueous medium undergo three major types of photoreactions depending on the wavelength of irradiation³; (i) photoredox reactions² to give primarily cobalt(II); (ii) photosubstitution reactions¹¹, involving changes in the composition of the coordination shell; and (iii) photoisomerisation reactions¹², involving changes in the coordination arrangement of the ligands. In the case of cobalt(III)-acido-amine complexes irradiation at charge transfer transition from ligand to metal (CTTM) band in aqueous medium, owing to the high oxidation state of the metal ion and the reducing property of the ligand, the redox reaction involving the transfer of an electron from the ligand(s) to the metal occurs followed by aquation of labile cobalt(II) complex.

Steady state photolysis of cobalt(III)-amine complexes in non-aqueous solvents generates cobalt(II)-

Table 3—Transient absorption spectra of complexes in acetonitrile

Complex	Absorption maxima (nm)
<i>cis</i> -[Co(en) ₂ (NO ₂) ₂]ClO ₄	410 ^a
	520
	410 ^b
	520
<i>trans</i> -[Co(en) ₂ (NO ₂) ₂]ClO ₄	700
	385 ^a
	460
	385 ^b
<i>cis</i> -[Co(trien)(NO ₂) ₂]ClO ₄	460
	680
	385 ^a
	460
	385 ^b
	460
	690

(a) Spectra recorded at 10 ms after flash (b) Spectra recorded at 100 ms after flash

Table 4—Spectral data of photolysis products in acetonitrile

Complex	Absorption (nm)	Maxima
<i>cis</i> -[Co(en) ₂ (NO ₂) ₂]ClO ₄	440(s)	325
<i>trans</i> -[Co(en) ₂ (NO ₂) ₂]ClO ₄	435(s)	350
<i>cis</i> -[Co(trien)(NO ₂) ₂]ClO ₄	430(s)	330

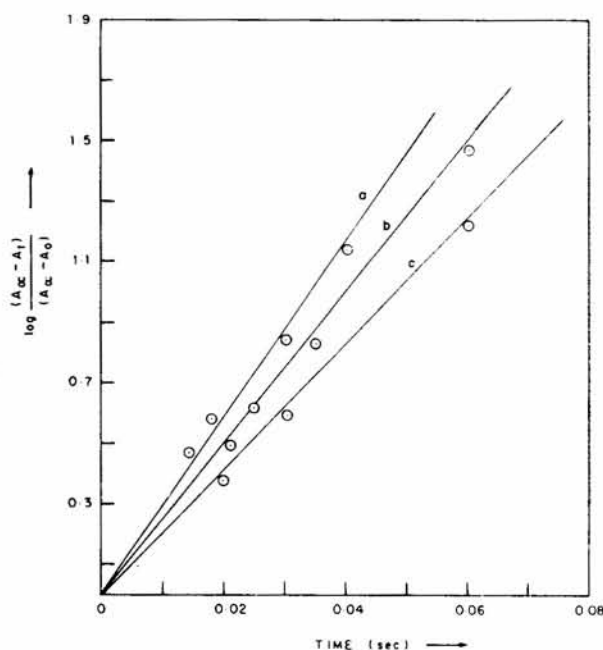


Fig. 3—First-order fit of 700 nm growth of *cis*-[Co(en)₂(NO₂)₂]⁺ in CH₃CN [(a) 1.253 × 10⁻³ M, (b) 3.132 × 10⁻⁴ M and (c) 1.504 × 10⁻⁴ M]

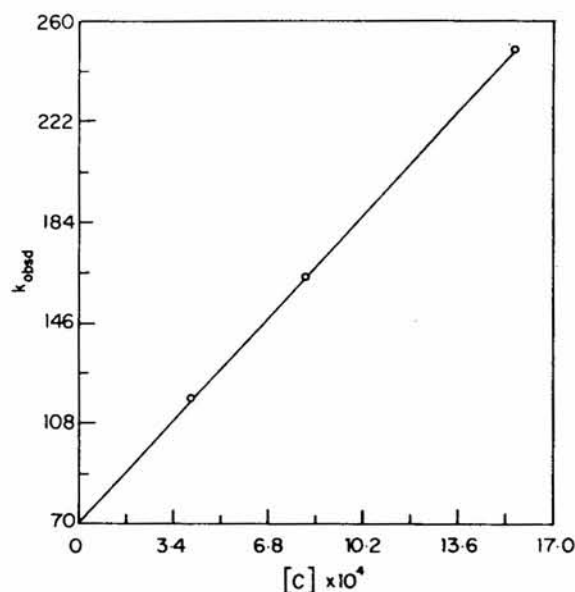


Fig. 4—Plot of k_{obs} versus [Complex] for *cis*-[Co(trien)(NO₂)₂]⁺ in CH₃CN

amine complexes, which react with the dissolved oxygen in the medium to give cobalt(III)-oxygenated complex. Absence of the absorption band around 700 nm, which is characteristic of μ -superoxo dinuclear cobalt(III) complex, and the diamagnetic nature of the photoproduct indicate that the product is a dinuclear μ -peroxo complex. Spectra of the photoproducts of the complexes are comparable with those of the dinuclear μ -peroxo complexes reported earlier¹³.

Transient absorption spectra recorded in the 700 nm growth time scale show maxima around 400, 480 and 700 nm. The spectra of 1:1 and 1:2 dinuclear superoxo complexes of cobalt(III) reveal that only dinuclear μ -superoxo complexes of cobalt(III) have a maximum around 700 nm, which is assigned for the charge transfer transition from metal to ligand^{13,14}. Spectral maxima observed at the other wavelengths are also similar to the monobridged μ -superoxo dinuclear complexes.

Transient absorption spectrum recorded in 400 nm transient growth time scale, which is occurring in shorter time scale than that in 700 nm growth time scale, is similar to the mono nuclear superoxo complex.

The rate constant of the 400 nm transient growth depends on the concentration of the oxygen, since its concentration in the medium is much larger compared to that of cobalt(II) species generated photochemically, leading to a pseudo-first order condition.

Transient growth of absorbance at 700 nm also obeys first order kinetics and k_{obs} depends on [com-

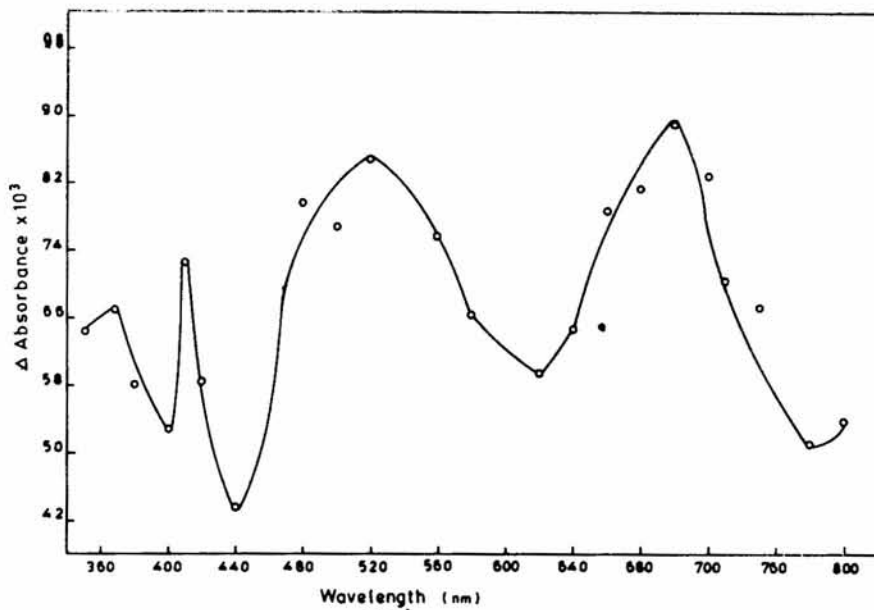
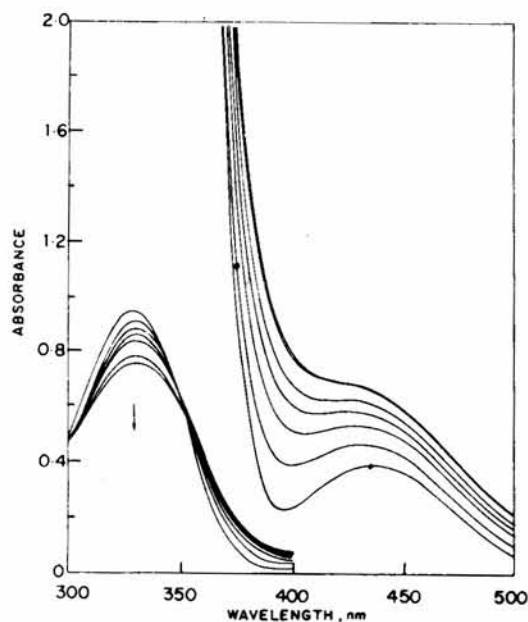
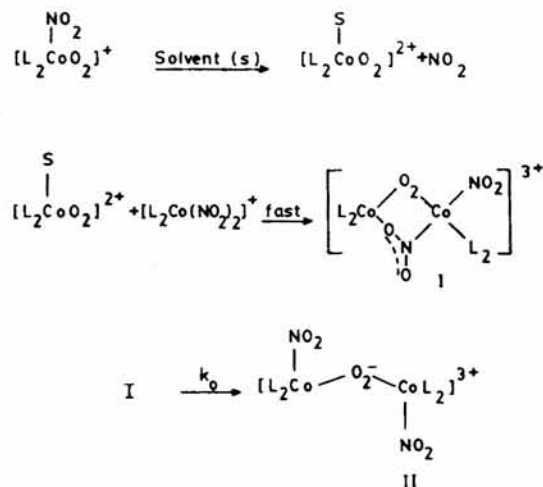


Fig. 5—Transient absorption spectrum recorded in 100 ms after flash


 Fig. 6—Steady-state photolysis of $cis\text{-}[\text{Co}(\text{trien})(\text{NO}_2)_2]^+$ in CH_3CN at different time intervals

plex]. This shows that the starting cobalt(III) complex is also involved in the formation of μ -superoxo complex. The plot of k_{obs} versus [complex] does not pass through the origin. Observed positive intercept reveals that the formation of dinuclear μ -superoxo complex goes through a pathway independent of [cobalt(III) complex] and another dependent on starting [complex]. For the former case we have pro-

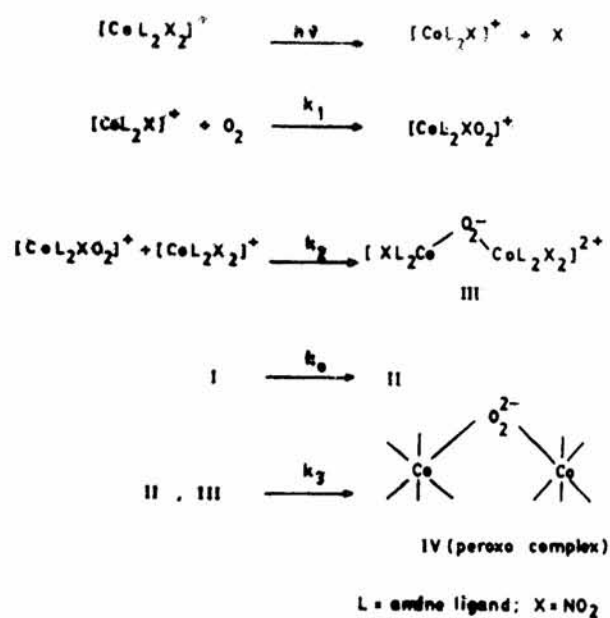
posed that the slow step is labilisation of a coordinated ligand, followed by the coordination of the oxygen atom of the nitro ligand of the starting complex to give rise to the μ -superoxo complex as shown in Scheme 1.



SCHEME 1

The decay of the transient absorption at 700 nm, which obeys first order kinetics, is due to formation of the final product, μ -peroxo complex from the μ -superoxo intermediate.

The observations of 400 nm transient growth of absorbance, 700 nm transient growth of absorbance and decay of 700 nm transient can be explained by a mechanism shown in Scheme 2.



Scheme 2

Since the different steps of oxygenation reaction take place at different time scales, it has been possible to observe the different steps independently during the course of formation of the dinuclear μ -peroxo complex. The mononuclear complex formed by the reaction between the cobalt(II) complex, generated photochemically, and oxygen present in the medium is able to react with the starting cobalt(III)-amine complex resulting in the formation of a dinuclear μ -superoxo complex which is further reduced to μ -peroxo complex by the coordinated nitrite ligand itself.

The redox couple of superoxo-peroxo cobalt(III) complex is about 1.0 V and even mild reducing agents like, nitrite, sulphite and ferrous(II) are known¹⁵ to reduce the superoxo bridge to peroxo form. Reduction by free nitrite ion present in the medium is ruled out, because the decay of the 700 nm absorbance follows only first order kinetics. Addition of nitrite ion externally accelerates the 700 nm decay, indicating that the nitrite ion can, indeed, reduce the superoxo bridge to the peroxo bridge.

It is proposed that the substitution in a cobalt(III) complex, during the formation of superoxo complex, proceeds through an associative mechanism; normally the substitution of cobalt(III) complex proceeds through a dissociative mechanism. There was a proposal for an associative mechanism by Ingold *et al.*^{16,17} in the substitution of $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$ by H_2O . It was argued, in that context, that when electron-withdrawing groups like NO_2^- are coordinated to the cobalt(III) centre, the substitution proceeds through an associative mechanism rather than a dissociative mechanism.

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