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LETTER

Photoinsertion of dioxygen in *trans*-$[Co(tet\text{-}a)(NO_2)_2]^+$ and *trans*-$[Co(tet\text{-}b)(NO_2)_2]^+$ in acetonitrile: a laser flash photolysis study

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The reversible reaction of dioxygen with solutions of cobalt complexes which results in monomeric dioxygen complexes, which serve as a model system for haemoglobin, has been of interest for some time [1–3]. Irreversible reactions of dioxygen are also important to biological systems [4]. Cobalt(II) complexes generally form 2:1 μ-peroxo bridged complexes [4]. Formation of this is preceded by formation of a 1:1 superoxo complex [4, 5]. There have been only a few reports of the reaction of $Co^{II}(N_4)$ complexes with oxygen [6–8]. Earlier, we reported the formation of mononuclear and dinuclear superoxo complexes of cobalt(III) as intermediates, during the formation of the product, peroxo complex, of a series of diacidocobalt(III)–amine complexes by conventional flash photolysis technique [5, 10, 11]. Here we report the fastest oxygenation reaction of $Co^{II}(N_4)$ complexes by laser flash photolysis technique.

Experimental

The title complexes were prepared by the literature reported [12] procedures and the purity of the complexes were ascertained by comparing the absorption maxima and molar absorptivity of the d–d and charge-transfer bands. Spectral grade acetonitrile (Fluka) was used. The complexes were photolysed at 355 nm using a Quanta Ray DCR-10 Nd-YAG laser and a Gould 4500 Biomation digital oscilloscope was used to store the signals. The signals were averaged for 4 to 16 shots and a 1 cm path length flow cell was used. A 300 W xenon lamp was used as the monitoring source. The laser and monitoring beams were arranged in a right angled geometry. The kinetic data analysis was carried out using FORTRAN software in a PDP11/23 minicomputer. The straight lines were fitted by the linear least-squares program.

Results

On photolysis at 355 nm, the title complexes show absorption growths from 350–600 nm in air-equilibrated acetonitrile with the maximum at 520 nm. The absorption growths at 500 nm obey first order kinetics and the pseudo first order rate constants are 1.02×10^4 and 1.32×10^4 s^{-1} for tet-a and tet-b complexes, respectively (Fig. 1(a)). The absorbances also decay in 10 ms full sweep and the decays also obey first order kinetics (Fig. 1(b)). The rate constants are 2.1×10^3 and 1.2×10^3 s^{-1} for tet-a and tet-b complexes, respectively. These decays are also observed with photolysis using a conventional flash photolysis spectrometer. Transient absorptions are also seen around 700 nm using a conventional flash photolysis spectrometer in 20 ms full sweep, but the signals are weak and for the same reason the signals could not be seen with a laser flash photolysis spectrometer. The transient absorption at 700 nm also obeys first order kinetics (Fig. 1(c)) and the rate constants are 3.5×10^2 and 3.1×10^2 s^{-1} for tet-a and tet-b complexes, respectively. In argon saturated medium transients are not observed confirming that the transient absorptions are due to the reaction between the photochemically generated cobalt(II) complex and dissolved oxygen.

Discussion

From the literature [13] it is observed that only mononuclear superoxo complexes absorb around 500 nm and hence the transient growth is due to the formation of a mononuclear superoxo complex. The second order rate constant for the formation of the mononuclear superoxo complex of tet-a ligand is 1.63×10^7 M^{-1} s^{-1}; it is estimated by taking the concentration of dissolved oxygen in acetonitrile [14] at 25 °C as 1.6×10^{-3} M. Due to this high reactivity it has not been possible to observe the formation of mononuclear complexes found in earlier studies [15] by other researchers. Transient absorption spectra recorded at 200 μs after flash show a maximum at 520 nm, and a broad absorption around 700 nm is due to the formation of a dinuclear superoxo complex [16] (Fig. 2).

Steady photolysis of the complexes in air-equilibrated acetonitrile results in spectral changes with a shoulder around 460 nm and a maximum at 350

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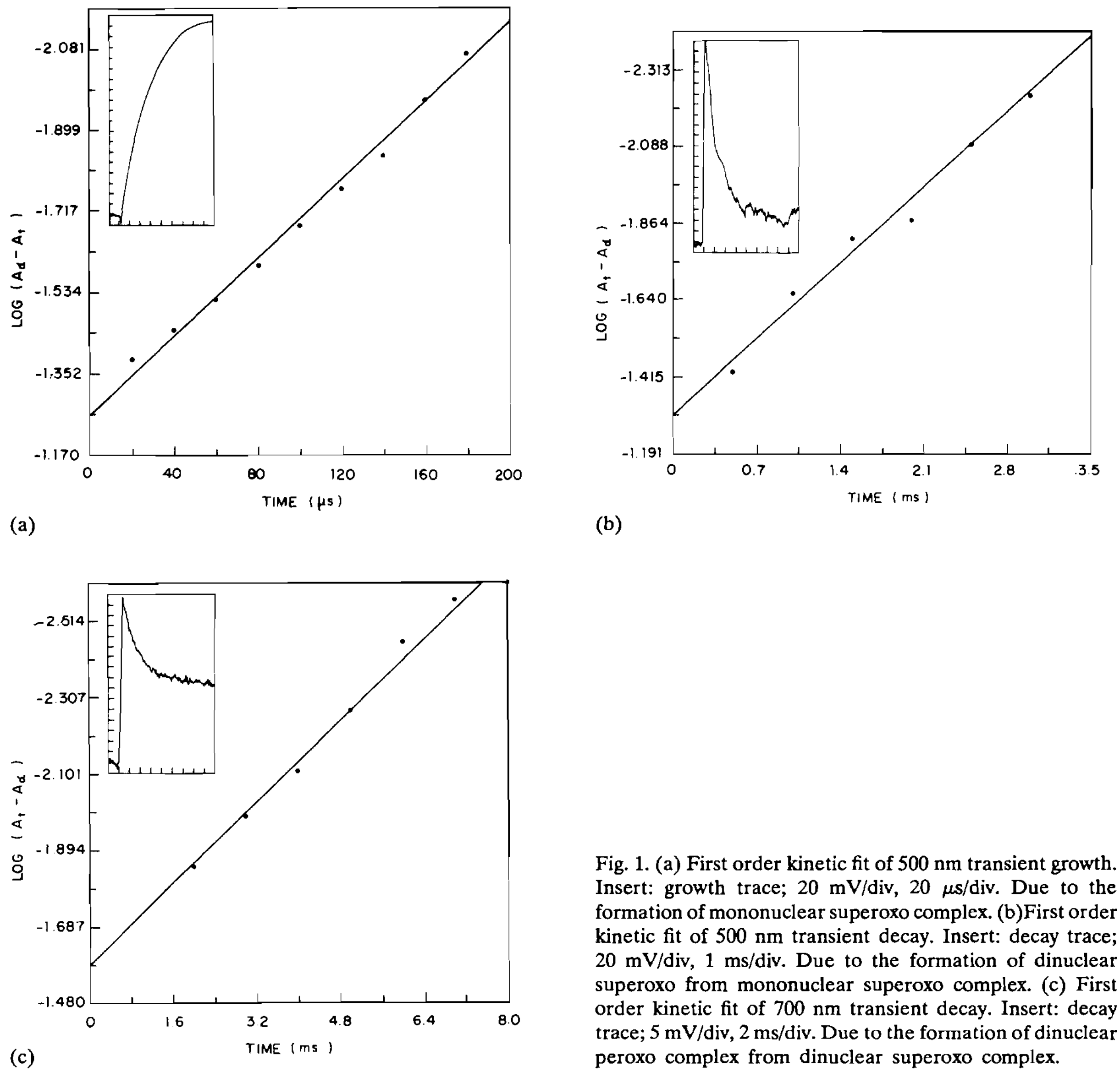

Fig. 1. (a) First order kinetic fit of 500 nm transient growth. Insert: growth trace; 20 mV/div, 20 μs/div. Due to the formation of mononuclear superoxo complex. (b)First order kinetic fit of 500 nm transient decay. Insert: decay trace; 20 mV/div, 1 ms/div. Due to the formation of dinuclear superoxo from mononuclear superoxo complex. (c) First order kinetic fit of 700 nm transient decay. Insert: decay trace; 5 mV/div, 2 ms/div. Due to the formation of dinuclear peroxo complex from dinuclear superoxo complex.

nm which are similar to those of the axial nitro dinuclear μ-peroxo cobalt(III) complexes with quadridentate macrocyclic ligands [8]. These above experimental observations are corroborated in the following scheme.

$$[\mathrm{Co(N_4)(NO_2)_2}]^+ \xrightarrow[\mathrm{CTTM}]{h\nu} [\mathrm{Co(N_4)(NO_2)}]^+ + \mathrm{NO_2}$$

$$[\mathrm{Co(N_4)(NO_2)}]^+ + \mathrm{O_2} \longrightarrow \underset{\mathbf{1}}{[\mathrm{Co(N_4)(NO_2)O_2}]^+}$$

$$\mathbf{1} + [\mathrm{Co(N_4)(NO_2)_2}]^+ \longrightarrow \underset{\mathbf{2}}{[\mathrm{(NO_2)(N_4)CoO_2{}^-Co(N_4)(NO_2)_2}]^{2+}}$$

$$\mathbf{2} \longrightarrow \underset{\mathbf{3}}{[\mathrm{(NO_2)(N_4)CoO_2{}^{2-}Co(N_4)(NO_2)}]^{2+}} + \mathrm{NO_2}$$

N_4 = tet-a or tet-b

A few mononuclear stable cobalt–amine complexes have been reported where the amine is bulky, but mostly they dimerise to result in the peroxo complex [17]. Due to the high reactivity of quadridentate macrocyclic ligand complexes, we are not able to observe well separated steps, as we observed in the case of cobalt(III)–amine complexes [10], for the formation of mononuclear and dinuclear superoxo complexes.

In compound **2** a seven coordinated cobalt centre is introduced and there has been evidence for an

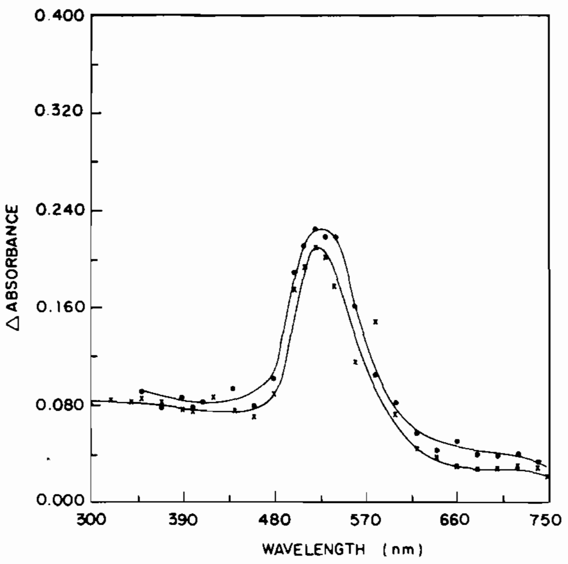

Fig. 2. Transient absorption spectrum recorded at 200 μs after flash for (●) tet-a and (×) tet-b complexes.

associative substitution at the cobalt(III) centre when electron withdrawing groups like NO_2^- are coordinated [18]. The redox couple of superoxo–peroxo is around 1.0 V and mild reducers like NO_2^-, SO_3^- and Fe^{2+} are known to reduce the superoxo bridge to a peroxo bridge [19]. Enhancement of reduction rates of superoxo-to-peroxo by the addition of nitrite ion has been observed.

In summary, the $Co^{II}(N_4)$ complexes undergo an oxygenation reaction resulting in the dinuclear peroxo complex as the final product via mononuclear superoxo and dinuclear superoxo complexes as intermediates.

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