Flash Photolysis Study of the Oxygenation of Cobalt(II)–Amine Complexes: Evidence for the Formation of a μ-Superoxo Dinuclear Complex

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cis-$[Co(pn)_2(NO_2)_2]^+$ ion (pn = 1,2-diaminopropane), after flash photolysis, reacts with dioxygen in two steps to form a μ-superoxo dinuclear cobalt(III) complex.

Cobalt(II)–amine complexes have been known for a long time to undergo both reversible and irreversible addition with molecular oxygen.[1] In these dioxygen–cobalt(III) systems, oxygen is co-ordinated to the cobalt(III) centre as the superoxo (O_2^-) or peroxo (O_2^{2-}) ligand.[2] Since the cobalt(II)–amine complexes are reactive, particularly in aqueous solution, a definitive picture of the co-ordination environment of the cobalt(II)–amine reacting with dioxygen is not always known. The general reaction mechanism proposed by Wilkins[3] involves reactions (1) and (2).

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

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

Recently we found[4] that, in acetonitrile, complexes of the type *cis*-$[Co(amine)_4(NO_2)_2]^+$ undergo charge-transfer photolysis to produce the corresponding cobalt(II) complex which reacts with dissolved oxygen. We now report the intermediate formation of the μ-superoxo dinuclear cobalt(III) complex. A solution of *cis*-$[Co(pn)_2(NO_2)_2]ClO_4$ (pn = 1,2-diaminopropane), prepared by the known method,[5] in pure acetonitrile (Aldrich) was irradiated with light from a xenon lamp. Irradiation of air-equilibrated solutions produced spectral changes at 440 (shoulder) and 325 nm (maximum, ε 4785) indicating the formation of a dinuclear μ-peroxo complex which did not show an e.s.r. signal. The spectral changes showed isosbestic points, for consecutive irradiations using white light, at 338 and 368 nm indicating an almost 100% photoredox reaction. In deaerated solutions none of the above spectral features were seen; a slight decrease in absorbance over the entire region was observed, showing net photodecomposition of the complex. Flash photolysis of the complex

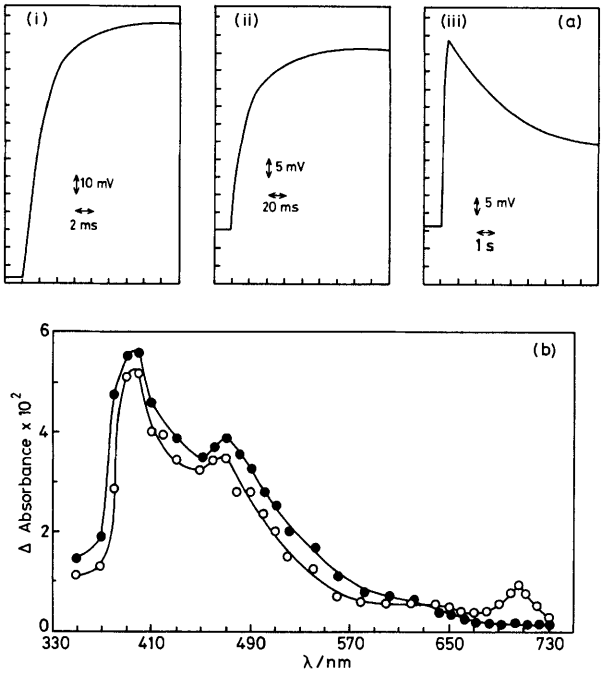

Figure 1. (a) Flash photolysis of *cis*-$[Co(pn)_2(NO_2)_2]ClO_4$ in MeCN, showing transient growth at (i) 400 and (ii) 700 nm, and (iii) transient decay at 700 nm. (b) Absorption spectrum of the transient on flash photolysis of *cis*-$[Co(pn)_2(NO_2)_2]ClO_4$ in MeCN recorded after a delay of (●) 10 and (○) 180 ms.

in air-equilibrated acetonitrile solution (using an Applied Photophysics flash system) showed a fast growth of the absorbance at 400 nm followed by a slower growth of the absorbance at 700 nm (Figure 1a). Dinuclear μ-superoxo cobalt(III) complexes show[6] a characteristic absorption band at ~700 nm (ε~600) which is not observed for the μ-peroxo complexes. The absorption spectra of the transients are shown in Figure 1b. The rate constant for the faster reaction with oxygen was calculated to be 480 ± 20 s^{-1}. The rate constant for the slower growth of absorbance at 700 nm depends on the concentration of the starting complex and the second order rate constant was calculated to be $1.0 \pm 0.02 \times 10^3$ dm^3 mol^{-1} s^{-1}. The absorbance at 700 nm decayed on a slower time scale and the first-order rate constant for the decay was calculated to be 2.0 ± 0.1 s^{-1}.

In aqueous solution, photolysis of cobalt(III)–amine complexes is known to produce the cobalt(II) complex, which, being labile, is rapidly converted into the cobalt(II) aquo ion, while in non-aqueous solutions the photo-produced cobalt(II)–amine complex reacts with molecular oxygen to form the mononuclear superoxo complex. The reaction between the mononuclear superoxo complex and the cobalt(III)–amine complex to produce the μ-superoxo dinuclear complex (**1**) is reported for the first time in this communication. The μ-superoxo complex is subsequently converted into the stable μ-peroxo complex (**2**). The observed results are consistent with the reactions in Scheme 1.

The mononuclear superoxo cobalt(III) complex is not very stable, with a high tendency to form the dimer. Except in a few cases[7] with bulky amines, a mononuclear superoxo complex has not been reported. In the present study, since the reactions occur on different time scales, we were able to monitor the three steps during the course of the formation of the dinuclear μ-peroxo complex (**2**). The mononuclear superoxo complex is able to react with *cis*-$[Co(pn)_2(NO_2)_2]^+$ ion to

$$cis\text{-}[Co(pn)_2(NO_2)_2]^+$$
$$\downarrow h\nu$$
$$[Co(pn)_2(NO_2)]^+ + NO_2$$
$$\downarrow O_2$$
$$[Co(pn)_2(NO_2)(O_2)]^+$$
$$\downarrow cis\text{-}[Co(pn)_2(NO_2)_2]^+$$
$$[(O_2N)(pn)_2Co\text{–}O_2\text{–}Co(pn)_2(NO_2)_2]^{2+}$$
(1)
$$\downarrow$$
$$[(O_2N)(pn)_2Co\text{–}O_2\text{–}Co(pn)_2(NO_2)]^{2+} + NO_2$$
(2)

Scheme 1

form the dinuclear μ-superoxo complex. The rate constants observed for substitution reactions at a cobalt(III) centre in acetonitrile[8] are much lower than those we have observed. We propose that one end of the superoxo group of the mononuclear cobalt(III) complex binds with the starting complex *cis*-$[Co(pn)_2(NO_2)_2]^+$ and the final dinuclear μ-peroxo complex results by intramolecular reduction of the superoxo centre by the nitrite ligand. 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^{2+} are known[9] to reduce the superoxo centre. Reduction by free NO_2^- ion present in the medium is ruled out, since the decay of the absorbance at 700 nm follows first-order, and not second-order, kinetics.†

The flash photolysis study of the oxygenation thus gives a more detailed picture on the individual steps. Preliminary results have indicated that other amine complexes of cobalt(III) show a similar behaviour in acetonitrile, methanol, and ethanol.

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† However, addition of nitrite ion to the medium accelerates the decay of the signal observed at 700 nm indicating that nitrite ion does reduce (**1**).