# Dismutation of Superoxide Ion in an Aprotic Solvent by 5,10,15,20-Tetra-*p*-tolylporphyrinatocobalt(II)†

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The reactions of superoxide ion, $O_2^-$, with 5,10,15,20-tetra-*p*-tolylporphyrinatocobalt(II), [Co(tptp)], were investigated by spectroscopic methods (u.v.–visible and e.s.r.). The visible spectrum of [Co(tptp)] in dimethyl sulphoxide (dmso) was red shifted upon successive addition of $O_2^-$ solutions. The initial reaction product is the superoxo-complex $[Co(tptp)(O_2)]^-$, the formation of which was confirmed by e.s.r. measurements. The superoxo-complex subsequently reacts *via* intramolecular electron transfer to give $[Co(tptp)]^+$ and $HO_2^-$. In turn, $[Co(tptp)]^+$ oxidizes superoxide ion, present in the medium, to yield $O_2$. These results reveal that this cobalt porphyrin complex, in dmso, may function as an efficient catalyst for dismutation of superoxide ($2O_2^- \xrightarrow{HX} O_2 + HO_2^-$ : HX = proton source).

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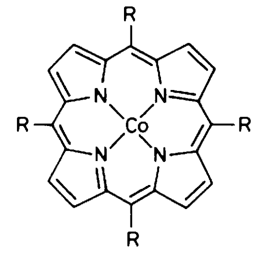
The formation of dioxygen complexes of metalloporphyrins is of great interest in relation to the transport and storage of dioxygen by haemoglobin and myoglobin and the activation of dioxygen by cytochrome $P_{450}$. Superoxide (hyperoxide) ion, $O_2^-$, probably contributes to an important resonance configuration for oxygenated haemoglobin and cytochrome $P_{450}$.[1] Cobalt porphyrins, as well as iron porphyrins, may serve as suitable models with which the nature of the interaction between $O_2$ and these haemoproteins might conveniently be probed. In fact, reversible binding of dioxygen to both five-co-ordinate iron(II) and cobalt(II) porphyrins has been demonstrated.[1–3] From the numerous e.s.r. studies, it is believed that the dioxygen complex of cobalt(II) porphyrins may formally be represented as $Co^{III}–O_2^-$, *i.e.* a superoxo-complex.[2] In a preliminary communication[4] we reported that the cobalt(III) complex of 5,10,15,20-tetra-*p*-tolylporphyrin, $[Co(tptp)]^+$, was stoicheiometrically reduced to [Co(tptp)] by $O_2^-$ in dimethyl sulphoxide (dmso) solution and that the [Co(tptp)] subsequently reacted with $O_2^-$ present in excess.

In the present paper we describe the results of a more thorough investigation, using spectroscopic methods at room temperature, of the reaction between [Co(tptp)] and $O_2^-$.

## Experimental

*Materials.*—The complex [Co(tptp)] was synthesized by a method similar to that described in the literature for the corresponding tetraphenylporphyrin (tpp) complex.[5] Potassium superoxide ($KO_2$) was purchased from Alfa Products. Dicyclohexyl-18-crown-6 (eicosahydrodibenzo[*b*,*k*]-[1,4,7,10,13,16]hexaoxacycloctadecine) (Nippon Soda Co.) was used without further purification. Other reagents were commercially available. Dimethyl sulphoxide (dmso) was distilled at reduced pressure from $CaH_2$ and stored over freshly activated 4 A molecular sieves under argon gas. Dichloromethane was distilled and then passed through an alumina column to remove impurities. Other solvents were distilled immediately prior to use.

*Preparation of Solutions of Superoxide Ion.*—A solution of superoxide ion was prepared as described previously.[6,7] The concentration of $O_2^-$ was determined by the method involving titration with ferricytochrome c, as described by Bielski and co-workers.[8]



R = Ph [Co(tpp)]
R = $C_6H_4Me$-*p* [Co(tptp)]

*Reaction of* [Co(tptp)] *with Superoxide Ion.*—*Visible spectral experiments.* Using a microsyringe, aliquots of $10^{-3}$—$10^{-2}$ mol dm$^{-3}$ $KO_2$–dicyclohexyl-18-crown-6 were introduced into a solution (2 cm$^3$) of [Co(tptp)] ($10^{-5}$—$10^{-6}$ mol dm$^{-3}$) in a capped quartz cuvette with a light path of 1 cm. The reactions were started by shaking the cuvette vigorously, and spectra in the visible region were then recorded immediately. In anaerobic experiments, a Thunberg cell with a light path of 1 cm was used.

*E.s.r. experiments.* Aliquots of $10^{-3}$—$10^{-2}$ mol dm$^{-3}$ $KO_2$–dicyclohexyl-18-crown-6 were added to a solution (1 cm$^3$) of $10^{-3}$ mol dm$^{-3}$ [Co(tptp)] dissolved in $CH_2Cl_2$–dmso (4:1). After transferring this reaction mixture to the quartz e.s.r. tube, the solution was rapidly frozen to 77 K. The e.s.r. spectra were recorded at the same temperature. In anaerobic experiments a two-armed quartz tube (one arm is 25 cm long and other 5 cm) was used. Aliquots of [Co(tptp)] and superoxide solutions were transferred with Pasteur pipettes into the separate arms. Each solution was then frozen and evacuated and the e.s.r. spectra of [Co(tptp)] were recorded. After warming to room temperature, the samples were then mixed and the e.s.r. spectrum of the reaction product was recorded at 77 K.

*Spectroscopy.*—Visible spectra were recorded with a Union Giken SM-401 spectrophotometer at room temperature. Equilibrium constants ($K_{eq}$) were estimated by the method of Miller and Dorough[9] with corrections for volume changes. E.s.r. spectra were measured at room temperature or at 77 K with a JEOL-PE-1X (*X*-band) spectrometer with 100-kHz field modulation, and calibrated by comparison with a standard sample of $Mn^{2+}$-doped MgO and 2,2-diphenyl-1-picrylhydrazyl (dpph, $g$ = 2.0036).

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† *Non-S.I. unit employed:* G = $10^{-4}$ T.

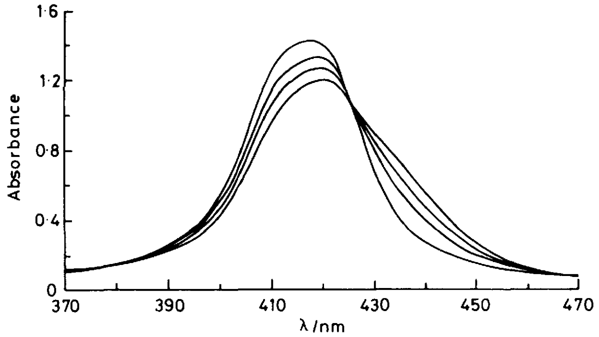

Figure 1. Visible spectral changes resulting from the successive addition of $O_2^-$ to [Co(tptp)] in dmso. Only the Soret band is shown. Starting concentration of complex: 2.90 × $10^{-5}$ mol dm$^{-3}$. Final spectrum corresponds to the addition of 4.9 equivalents of $O_2^-$

## Results and Discussion

Metal-free $H_2$tptp in dmso solution did not undergo any spectral change in the presence of $O_2^-$ or molecular oxygen dissolved in the medium. Dicyclohexyl-18-crown-6 did not affect the spectral pattern of [Co(tptp)] even though the mixtures were allowed to stand for 3 d at room temperature in the dark. These observations indicate that $O_2^-$ does not react with $H_2$tptp and that neither $O_2$ nor crown ether reacts at room temperature with [Co(tptp)] in dmso.

The visible absorption spectrum of [Co(tptp)] in dichloromethane at room temperature has two absorption bands, the Soret band at 414 nm and another at 528 nm. When dmso was added dropwise to this dichloromethane solution these bands gradually shifted to 418 and 533 nm, respectively. This spectral shift is ascribable to the formation of a dmso complex, [Co(tptp)(dmso)] [equation (1)]. In anhydrous dmso solutions

$$[\mathrm{Co(tptp)}] + \mathrm{dmso} \longrightarrow [\mathrm{Co(tptp)(dmso)}] \qquad (1)$$

the axial ligand is dmso. The equilibrium constant ($K_{eq}$) for this reaction is calculated to be 5.1 × $10^4$ dm$^3$ mol$^{-1}$. Upon successive addition of $O_2^-$ solutions to [Co(tptp)] in dmso the absorption peaks at 418 and 533 nm of [Co(tptp)(dmso)] shifted to 420 and 535 nm, respectively (Figure 1). This observation suggests that [Co(tptp)(dmso)] undergoes either ligand exchange or a redox reaction in the presence of $O_2^-$.

Upon addition of methanol, known[10] to react with $O_2^-$, this new species reverted to [Co(tptp)(dmso)], confirmed spectrophotometrically. The spectrum of [Co(tptp)(dmso)] did not change after continuously bubbling $O_2$ through the solution. Thus, the compound formed upon addition of $O_2^-$ to [Co(tptp)(dmso)] can be assigned as the $O_2^-$ adduct, $[\mathrm{Co(tptp)(O_2)}]^-$ with $K_{eq}$ estimated to be 3.3 × $10^5$ dm$^3$ mol$^{-1}$. Superoxide ion thus has a higher affinity for [Co(tptp)] than does dmso and can easily replace dmso [equation (2)].

$$[\mathrm{Co(tptp)(dmso)}] + O_2^- \longrightarrow [\mathrm{Co(tptp)(O_2)}]^- + \mathrm{dmso} \qquad (2)$$

The visible spectrum of the initially formed $O_2^-$ adduct changes irreversibly with time; good isosbestic behaviour was observed. The final spectrum ($\lambda_{max.}$ 435, 550, and 590 nm) is identical to that of $[\mathrm{Co(tptp)}]^+$, which was synthesized independently.[4] The latter is not likely to form a stable dioxygen adduct by reaction with $O_2^-$.[4] It is therefore suggested that the cobalt(III) species is generated from the oxidation of $[\mathrm{Co(tptp)(O_2)}]^-$ by molecular oxygen as in equation (3) or by intramolecular electron transfer from Co$^{II}$ to $O_2^-$ [equation (4)]

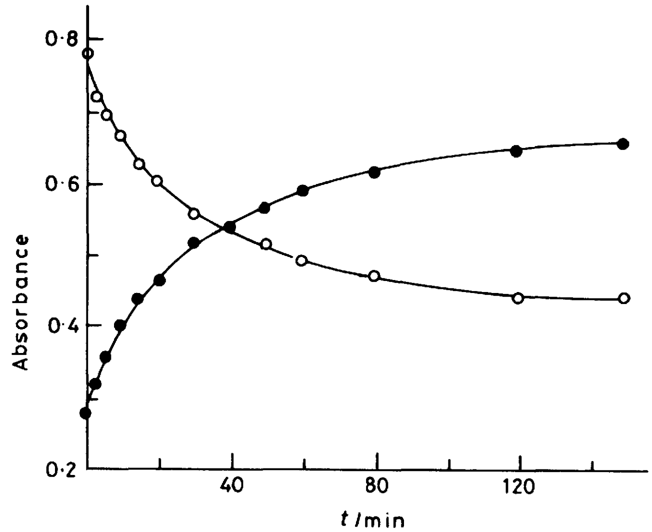

Figure 2. Time course of the spectral changes occurring upon intramolecular reaction of $[\mathrm{Co(tptp)(O_2)}]^-$ to give $[\mathrm{Co(tptp)}]^+$ in the absence of oxygen. Initial concentrations: $O_2^-$, 2.89 × $10^{-4}$; [Co(tptp)], 1.89 × $10^{-5}$ mol dm$^{-3}$. $\lambda_{max.}$ = 420 (○) and 433 nm (●)

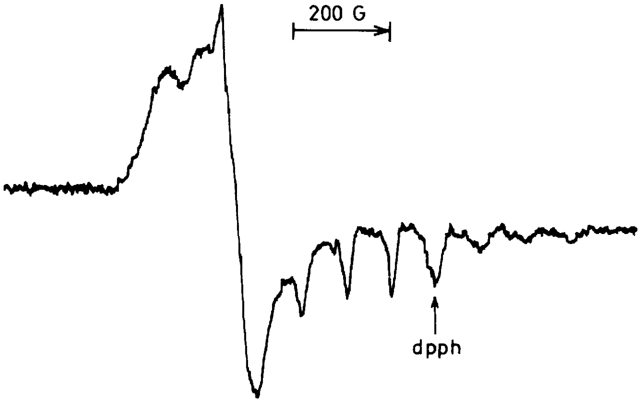

Figure 3. E.s.r. spectrum observed for the reaction of $O_2^-$ with [Co(tptp)(dmso)] upon evacuation at 77 K. The complex [Co(tptp)] was dissolved in $CH_2Cl_2$–dmso (4:1). Initial concentrations prior to mixing: $O_2^-$, 4.5 × $10^{-3}$; [Co(tptp)], 4.0 × $10^{-3}$ mol dm$^{-3}$

$$[\mathrm{Co(tptp)(O_2)}]^- + O_2 \longrightarrow [\mathrm{Co(tptp)}]^+ + 2O_2^- \qquad (3)$$

$$[\mathrm{Co(tptp)(O_2)}]^- \xrightarrow{HX} [\mathrm{Co(tptp)}]^+ + HO_2^- \qquad (4)$$

where HX represents a proton source such as dmso and/or traces of water in solution. In equation (4), $O_2^{2-}$ instead of $HO_2^-$ is not realistic, because $O_2^{2-}$ is an extremely unstable, highly basic ion that has never been identified in non-aqueous media.

In order to determine the predominant reaction process an experiment under anaerobic conditions was performed. When $O_2^-$ solutions were mixed with [Co(tptp)(dmso)] after evacuation (see Experimental section), spectral changes similar to those in the presence of oxygen were observed (Figure 2). Specifically, Figure 2 shows the time course of the decay of [Co(tptp)] ($\lambda_{max.}$ = 420 nm) and the formation of $[\mathrm{Co(tptp)}]^+$ ($\lambda_{max.}$ = 433 nm) under anaerobic conditions. This result strongly suggests that $[\mathrm{Co(tptp)}]^+$ is formed *via* an intramolecular electron transfer in the $O_2^-$ adduct as shown in equation (4).

This suggestion is substantiated by the results of the e.s.r. experiments. When [Co(tptp)] in dmso was mixed with $O_2^-$ solution upon evacuation an e.s.r. spectrum due to the five-co-ordinated species [Co(tptp)(dmso)] ($g_{\parallel} = 2.017$, $g_{\perp} = 2.277$; $A_{\parallel} = 93.8$, $A_{\perp} = 16.4$ G), was replaced by a new spectrum (Figure 3; $g_{\parallel} = 2.014$, $g_{\perp} = 2.264$; $A_{\parallel} = 90.8$, $A_{\perp} = 38.5$ G) with parameters similar to those observed for many five-co-ordinated cobalt(II) porphyrins.[2] Therefore, the new paramagnetic species observed can be assigned to five-co-ordinated $[Co(tptp)(O_2)]^-$. The e.s.r. spectrum of the latter gradually disappeared with time, when the reaction solutions were maintained under evacuated anaerobic conditions. This indicates that reaction (2) is succeeded by reaction (4).

Similar results have been reported in the reaction of $O_2^-$ with synthetic iron(III) porphyrins in non-aqueous media.[11–14] In this case, the first reaction is reduction as shown in equation (5)

$$[FeL]^+ + O_2^- \longrightarrow [FeL] + O_2 \qquad (5)$$

$$[FeL] + O_2^- \longrightarrow [FeL(O_2)]^- \qquad (6)$$

(L = porphyrinate). Addition of excess of $O_2^-$ to [FeL] thus formed appears to favour formation of the iron(III) peroxide species *via* an oxidative coupling as shown in equation (6).

While the peroxoiron(III) complex was formed in the reaction of $O_2^-$ with [FeL], the peroxocobalt(III) complex could not be obtained by the reaction of $O_2^-$ with [Co(tptp)]. This is suggested on the basis of the following experiment: the reaction of [Co(tptp)Cl] with $O_2^{2-}$ (probably existing as $HO_2^-$), prepared from $BaO_2$–dicyclohexyl-18-crown-6 in dmso, was monitored by spectroscopic methods, but no spectral changes were observed.

In a previous paper[4] we reported that $[Co(tptp)]^+$ was stoicheiometrically reduced by $O_2^-$ to yield [Co(tptp)] and $O_2$ [equation (7)]. By combining equations (1), (2), (4), and (7), equation (8) can be derived. This corresponds to the

$$[Co(tptp)]^+ + O_2^- \longrightarrow [Co(tptp)] + O_2 \qquad (7)$$

$$O_2^- + O_2^- \xrightarrow{HX} O_2 + HO_2^- \qquad (8)$$

dismutation of $O_2^-$. Therefore, on this basis we suggest that [Co(tptp)] may function as an effective catalyst for the dismutation of superoxide ion. Further studies on this interesting system are in progress.

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