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SPECTROSCOPIC STUDIES OF THE REACTION OF SUPEROXIDE ION WITH COBALT(III) TETRA-p-TOLYLPORPHYRIN COMPLEX

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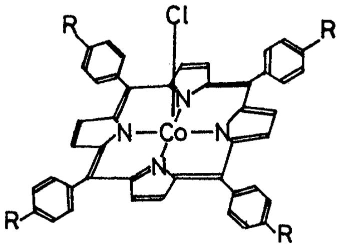
The reaction of superoxide ion, O_2^-, with chloro-5,10,15,20-tetra-p-tolylporphinatocobalt(III), [Co(III)(TTP)Cl], was investigated by spectroscopic methods (UV/vis and ESR) in dimethyl sulfoxide (DMSO). Spectral data show that O_2^- does not bind to Co(III)(TTP)Cl to give the O_2^- complex, but reduces it directly to Co(II)(TTP) at room temperature.

KEYWORDS——chloro-5,10,15,20-tetra-p-tolylporphinatocobalt(III); Co(III)(TTP)Cl; superoxide ion; O_2^-; visible spectrum; ESR spectrum

The dioxygen complexes of metalloporphyrins are biologically of importance, because they are involved in a variety of biological processes. Until now there are many reports concerned with the model reactions of hemoglobin and myoglobin. Cobalt porphyrin is considered to be a good model to investigate such model reactions. Reversible binding of dioxygen to five-coordinate cobalt(II) porphyrins has been reviewed.1) On the basis of numerous ESR studies, it is indicated that the unpaired spin is localized in the axial d_{z^2} orbital ($^2A_1$ state) and the binding state is represented by Co(III)--O_2^- (superoxo complex).2,3) Then, if Co(III) porphyrins are used instead of Co(II) porphyrins, it is expected that the direct reaction with O_2^- to form the superoxo complex occurs. Therefore, we intended to investigate the reactions of O_2^- with cobalt(III) porphyrins. The results of the reaction of O_2^- with Co(III)(TTP)Cl are reported here.

Co(III)(TTP)Cl (Fig. 1b) was synthesized by a method similar to that described in the literature for the tetraphenylporphyrin (TPP) complex (Fig. 1a).4) The O_2^- ion was prepared by dissolving potassium superoxide (KO_2) in DMSO using dicyclohexyl-18-crown-6, and its concentration was estimated from the reduction of ferricytochrome c by O_2^-.5) Visible and ESR spectra were recorded on a Union Giken SM-401 spectrophotometer and JEOL-PE-1X (X-band) spectrometer, respectively.

Co(III)(TTP)Cl is thought to have a structure similar to Co(III)(TPP)Cl; that is, it has a five-coordinate square-pyramidal structure as shown in Fig. 1, and is diamagnetic.6) It is known that in the noncoordinating solvent or in the absence



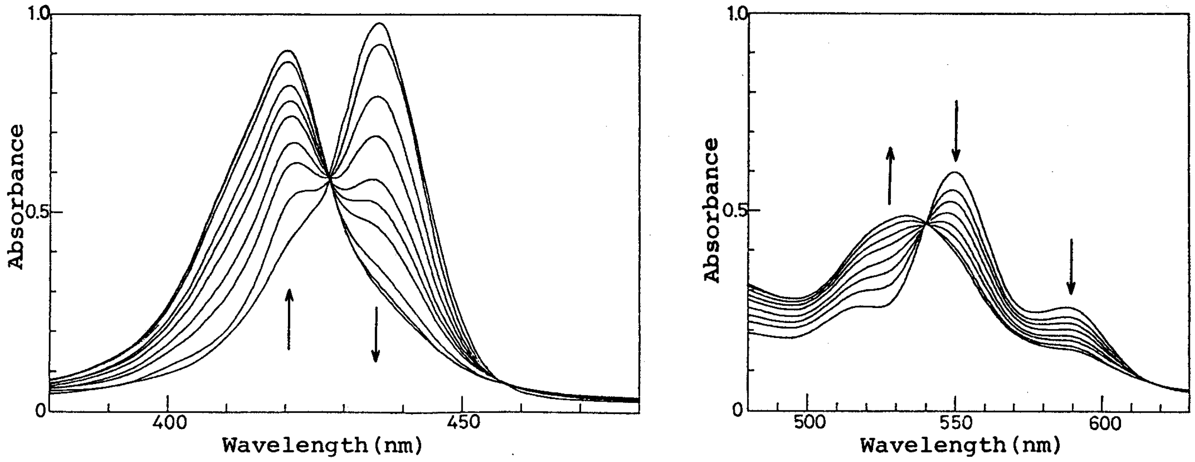
a) TPP; R=H
b) TTP; R=CH_3

Fig. 1. Structure of Cobalt(III) Porphyrins

of an added ligand, Co(III)(TTP) coordinates with an anionic ligand for the requirement of electroneutrality.$^{7)}$ But in noncoordinating solvents such as dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$) and 1,1,2,2-tetrachloroethane ($CHCl_2CHCl_2$), Co(III)(TPP)Cl is partly paramagnetic to give π-cation radical.$^{8)}$ In the same noncoordinating solvents mentioned above, Co(III)(TTP)Cl also showed the ESR spectrum (g=2.0028) similar to that of Co(III)(TPP)Cl,$^{8)}$ indicating that it becomes partly paramagnetic. Then, it is not relevant to examine the reactions of O_2^- with Co(III)(TTP)Cl in such solvents, because of possible interaction of O_2^- with π-cation radical. On the other hand, Co(III)(TPP)Cl is readily converted into six-coordinate complexes, Co(III)(TPP)Cl(solvent), in coordinating solvents such as ether, alcohol and pyridine.$^{6)}$ Co(III)(TTP)Cl is also converted into a six-coordinate complex, [Co(TTP)Cl(DMSO)], in DMSO, since the visible spectrum of Co(III)(TTP)Cl in CH_2Cl_2 (λmax(nm): 420.0, 520.0, 546.5, 587.0(sh)) underwent the red shift (λmax(nm): 421.0, 435.0, 517.0, 557.0, 591.0) on addition of DMSO, suggesting the coordination of DMSO as a sixth ligand.

When O_2^- solution was added to Co(III)(TTP)Cl in DMSO, rapid reduction of Co(III)(TTP)Cl to Co(II)(TTP) was observed. Co(II)TTP, which is presumed to dissociate chloride ion, was identified by its characteristic visible spectral properties in DMSO (λmax(nm): Co(III)(TTP)Cl, 436.5, 515.0 (sh), 550.0, 588.0; Co(II)(TTP), 420.5, 533.0) (Fig. 2). A titration curve of Co(III)(TTP)Cl with O_2^- indicated that it was reduced to Co(II)(TTP) stoichiometrically by superoxide ion (Fig. 3). Moreover, the presence of isosbestic points showed the absence of any long-lived intermediate (Fig. 2). Further spectral changes were observed upon addition of more than 2 equivalent of O_2^- to Co(III)(TTP)Cl. Similar spectral changes were also observed by successive addition of O_2^- to the DMSO solution of Co(II)(TTP). Therefore, it is suggested that the spectral changes observed upon addition of more than 2 equivalent of O_2^- to Co(III)(TTP)Cl reflect a result of the reaction between O_2^- and the reduction product, Co(II)(TTP). We are now investigating the reaction of O_2^- with Co(II) porphyrins in detail.

The similar reactions were followed by the ESR spectroscopy. The ESR spectrum due to O_2^- ($g_{/\!/}$=2.104, $g_{\perp}$=2.007) disappeared upon addition of approximately 1 equivalent of Co(III)(TTP)Cl, but no new spectrum could be observed. When the concentration of O_2^- exceeded that of Co(III)(TTP)Cl, the spectrum due to O_2^- was



(a) (b)

Fig. 2. Visible Spectra resulting from Successive Additions of O_2^- to Co(III)(TTP)Cl in DMSO.
Starting concentration of Co(III)(TTP)Cl is 2.97×10^{-5} M. 1 μl of O_2^- (2.90×10^{-3} M) was successively added to 2 ml of the Co(III)(TTP)Cl solution.
(a) Soret band (ordinate scale is reduced to 1/10); (b) β and α band.

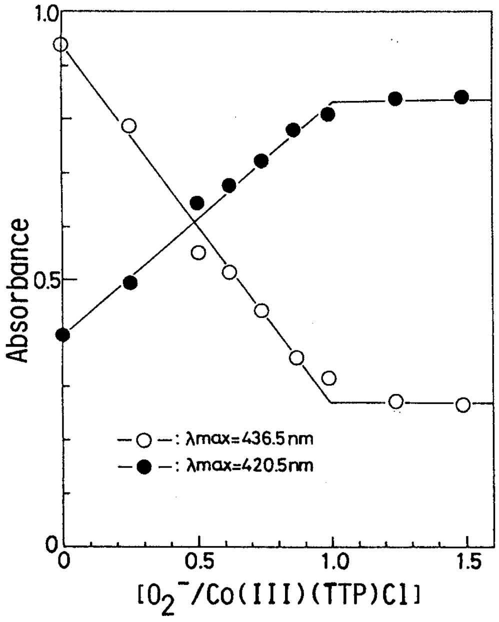


Fig. 3. Titration of Co(III)(TTP)Cl with O_2^- in DMSO at Room Temperature
Absorptions of λmax=436.5 nm and 420.5 nm are due to Co(III)(TTP)Cl and Co(II)(TTP), respectively.

observed and spectral pattern was also unchanged, suggesting that the O_2^- adduct[9] was not present under the experimental conditions.

Two mechanisms have been proposed for the reaction of the metalloporphyrins against O_2^-.[10] The first is known as an outer-sphere electron transfer mechanism in which the metal cation is directly reduced (reaction 1):[11]

$$M(n)Por + O_2^- \longrightarrow M(n-1)Por + O_2 \qquad (1)$$

where M and Por indicate the metal and porphyrin, respectively.
The second mechanism is the reduction via the formation of an intermediate, a metal-O_2^- complex (reaction 2):

$$M(n)Por + O_2^- \longrightarrow M(n)Por{-}{-}O_2^- \longrightarrow M(n-1)Por + O_2 \qquad (2)$$

Reaction (2) is known as an inner-sphere electron transfer mechanism.[11] Pasternack et al.[12] suggested that the reaction of O_2^- with Co(III) complex of tetrakis-(4-N-methylpyridyl)porphyrin (Co(III)TMPyP) follows an outer-sphere mechanism. On the other hand, it has been reported that the Co(III) complex of aquocobalamin (vitamin B_{12a}) reacts with O_2^- in dimethyl formamide at -50° C to give superoxocobalamin.[13] From our experimental finding that the O_2^- adduct was not detected, we now believe that the reaction of Co(III)(TTP)Cl with O_2^- proceeds via an outer-sphere mechanism.

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