# Reactions of Cr(III) Tetraphenylporphyrin Complex with Superoxide Ion: ESR Evidence for the Formation of a New Superoxide Adduct of Cr(IV) Porphyrinate and its Reactive Character

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## Abstract

The electron spin resonance (ESR) spectrum of the reaction product of superoxide ion, $O_2^-$, with chloro-5,10,15,20-tetraphenylporphyrinatochromium(III) [Cr(III)(TPP)Cl] shows strong hyperfine interactions with the metal nucleus and the metal ligand, indicating the formation of a superoxide adduct, Cr(IV)(TPP)(Cl)($O_2^-$). The formation of this superoxide adduct was also confirmed by UV–Vis spectroscopy. The reactive character of this superoxide adduct was investigated by ESR spectrometry. It was found that Cr(IV)(TPP)(Cl)($O_2^-$) can oxidize t-butylamine and triphenylphosphine to give the corresponding radical species, respectively, but not pyridine, 4-cyanopyridine or imidazole. These results indicate that the reactive character of Cr(IV)(TPP)(Cl)($O_2^-$) resembles that of the free superoxide ion.

## Introduction

Chromium porphyrins have been extensively investigated since their first description in 1966 [1]. Under aerobic conditions, the oxidation state of chromium incorporated into porphyrins is III. It is known that Cr(III) porphyrins are not readily reduced to Cr(II) porphyrins [2]. Cr(IV) porphyrins were first postulated from their cyclic voltammograms [3]. Recently, three groups independently succeeded in isolating oxochromium(IV) porphyrins [4–9]. However, there have been no reports concerning the formation of chromium(IV) porphyrins, supported by ligands other than oxo. In a previous paper [10], we reported on the basis of UV–Vis spectroscopic studies that a superoxide adduct is formed at the initial step of reaction of superoxide ion, $O_2^-$, with chloro-5,10,15,20-tetraphenylporphyrinatochromium(III) [Cr(III)(TPP)Cl]. We have now further studied the reaction of $O_2^-$ with Cr(III)(TPP)Cl by both electron spin resonance (ESR) and UV–Vis spectroscopy and have confirmed the formation of such a superoxide adduct. We now wish to report the evidence that a new chromium(IV) porphyrin, Cr(IV)(TPP)(Cl)($O_2^-$), is formed by the reaction of $O_2^-$ with Cr(III)(TPP)Cl and that this species can oxidize some organic substrates.**

## Experimental

### *Materials*

Potassium superoxide ($KO_2$) was purchased from Alfa Products, Inc. (Danvers, Massachusetts). Dicyclohexyl-18-crown-6 (Nippon Soda Co. Ltd., Tokyo, Japan) was used without further purification. Imidazole (Im), pyridine (Py), 4-cyanopyridine (4-CNPy), t-butylamine and triphenylphosphine ($PPh_3$) were purchased from Nakarai Chemicals, Ltd. (Kyoto, Japan). Hydrogen peroxide ($H_2O_2$, 30%) was obtained from Mitsubishi Gas Chemicals, Ltd. (Tokyo, Japan). Other reagents were commercially available. Dimethyl sulfoxide (DMSO) was distilled at reduced pressure from $CaH_2$ and stored over freshly activated 4 Å molecular sieves under dry argon. Dichloromethane ($CH_2Cl_2$) was distilled, and then passed through an alumina column to remove stabilizers. Other solvents were distilled immediately prior to use.

### *Preparation of Chromium Porphyrins*

*meso*-Tetraphenylporphyrin ($TPPH_2$) was prepared [11] and purified [12] by literature methods. Cr(III)(TPP)Cl was prepared by the reaction of anhydrous chromium(II) chloride with $TPPH_2$ under refluxing in dimethylformamide [13]. The crude product was

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**Abbreviations used here: $TPPH_2$, *meso*-tetraphenylporphyrin; Cr(III)(TPP)Cl, chloro-5,10,15,20-tetraphenylporphyrinatochromium(III); $O_2^-$, superoxide ion; Im, imidazole; Py, pyridine; 4-CNPy, 4-cyanopyridine; $PPh_3$, triphenylphosphine; DMSO, dimethyl sulfoxide; $H_2O_2$, hydrogen peroxide; Cr(IV)O(TPP), (tetraphenylporphyrinato)oxochromium(IV); Cr(V)N(TPP), nitrido(tetraporphyrinato)chromium(V); TTP, *meso*-tetra-*p*-tolylporphyrin; HX, proton source.

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purified by the method of Basolo *et al.* [14]. Oxochromium(IV) porphyrin, Cr(IV)O(TPP), was prepared by the method of Buchler *et al.* [15]. Nitrido(porphyrinato)chromium(V), Cr(V)N(TPP), was synthesized by the same method as described by Groves *et al.* [16].

### *Preparation of Solution of Superoxide Ion*

Potassium superoxide was ground to a fine powder with a mortar and pestle in a dry atmosphere. Powdered $KO_2$ and dicyclohexyl-18-crown-6 were dissolved in dry DMSO as described previously [17–20]. The concentration of $O_2^-$ was determined by the method of Bielski *et al.* [21].

### *Spectral Measurements*

#### *ESR measurements*

The ESR measurements were carried out on a JEOL-PE-1X ESR spectrometer (X-band) with 100 kHz field modulation. ESR parameters were calibrated by comparison with the standard sample of $Mn^{2+}$ doped on MgO and 2,2-diphenyl-1-picrylhydrazyl (DPPH, $g = 2.0036$).

#### *UV–Vis spectral measurements*

UV–Vis spectra were recorded on a Union Giken SM-401 spectrophotometer at room temperature.

## Results and Discussion

### *Identification of the Reaction Product of Cr(III)(TPP)Cl with Superoxide Ion*

When DMSO solutions of Cr(III)(TPP)Cl were mixed with DMSO solutions containing a six-fold excess concentration of superoxide ion at room temperature, an ESR spectrum having two absorption lines ($g = 1.956$ and $1.970$) was observed as shown in Fig. 1. These two absorption lines are quite similar to those of a relatively stable chromium(V) intermediate observed during the reaction of chromic acid with oxalic acid [22]. Thus, the two absorption lines having a separation of 0.98 mT are not hyperfine components, but, rather, two unidentified chromium(V) species, which may be merely resonance structures for which large activation barriers are not expected, are probably present. If the solutions were kept at room temperature for 10 min after the reaction, the higher-field signal ($g = 1.956$) completely disappeared and the lower-field signal ($g = 1.970$) became reduced in intensity. Moreover a new signal centred at $g = 1.981$ appeared. Finally, after 30 min of the reaction, only a well resolved nine-line pattern was observed as shown in Fig. 2. These nine lines are assigned to the superhyperfine structure ($a^N(4) = 0.237$ mT) arising from the interactions of four nitrogen nuclei coordinated to $^{50}Cr$, $^{52}Cr$, and $^{54}Cr$ ($I = 0$). However, no absorption lines due to a superhyperfine which might be caused by interactions between four nitrogen and a paramagnetic chromium, $^{53}Cr$ ($I = 3/2$, natural abundance 9.5%), were observed. When this reaction solution was measured at 77 K, an ESR spectrum due to $O_2^-$ ($g_\parallel = 2.104$, $g_\perp = 2.007$) [18], which was observed before mixing with Cr(III)(TPP)Cl, completely disappeared and only a broad singlet line ($\Delta H_{msl} = 1.823$ mT) was observed at $g = 1.981$. From the $g$ values of this broad line, it is suggested that there is considerable Cr interaction. The ESR spectrum shown in Fig. 2 did not exhibit the peak height intensities expected for four equivalent nitrogen ligands. This ESR spectrum may show evidence of incomplete averaging of anisotropic couplings which yield an unresolved single line at 77 K. The absence of a spectrum identifiable with $^{53}Cr$ in Fig. 2 could be explained by the fact that the larger anisotropic $^{53}Cr$ hyperfine couplings will be even broader.

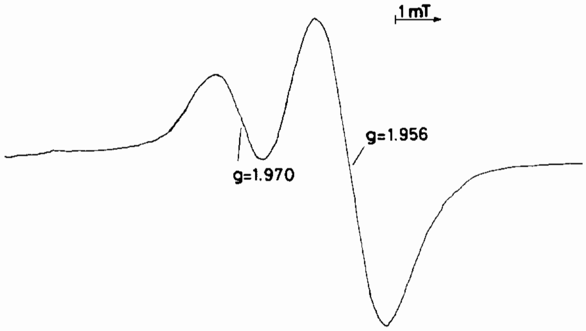


Fig. 1. ESR spectrum observed during the reaction of $O_2^-$ with Cr(III)(TPP)Cl in DMSO at room temperature. This spectrum was recorded immediately after mixing of two solutions. Concentrations: Cr(III)(TPP)Cl, $5.40 \times 10^{-3}$ mol $dm^{-3}$; $O_2^-$, $3.20 \times 10^{-2}$ mol $dm^{-3}$.

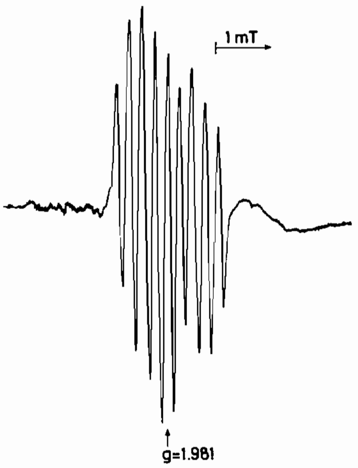


Fig. 2. ESR spectrum observed in the reaction of $O_2^-$ with Cr(III)(TPP)Cl in DMSO at room temperature. This ESR spectrum was recorded after 30 min of the mixing of two solutions. Concentrations: Cr(III)(TPP)Cl, $5.40 \times 10^{-3}$ mol $dm^{-3}$; $O_2^-$, $3.20 \times 10^{-2}$ mol $dm^{-3}$.

TABLE I. ESR Parameters of Chromium Porphyrins

| Chromium porphyrin | $g$ | $a^N$ (porphyrin) (mT) | $a^{Cr}$ (mT) |
|---|---|---|---|
| This radical species | 1.981 | 0.237 | |
| Cr(V)TPP(O)(Cl)[a] | 1.982 | 0.285 | 2.3 |
| Cr(V)N(TPP)[b] | 1.983 | 0.275[c] | 2.85 |
| Cr(V)N(TPP)[d] | 1.9825 | 0.27[c] | 2.83 |
| Cr(V)N(TTP)[e] | 1.985 | 0.279[c] | 2.85 |
| Cr(III)(TPP)(NO)[f] | 1.993 | 0.315 | 2.12 |

[a] Ref. 5. [b] This work. [c] Hyperfine splitting constant due to ligand N is the same value with the porphyrin ring N. [d] Ref. 23. [e] Ref. 16; TTP, *meso*-tetra-*p*-tolylporphyrin. [f] Ref. 24.

We have further measured the ESR spectrum at a higher temperature than room temperature to remove anisotropic $g$ tensor and hyperfine couplings. However, no spectral changes were observed up to 80 °C. If paramagnetic Cr(III) or Cr(V) complexes were to interact with paramagnetic $O_2^-$, no ESR spectra would be observed. Moreover, the ESR spectrum shown in Fig. 2 is different from that of Cr(V)O(TPP)Cl [5], Cr(V)N(TPP) [16, 23] or Cr(III)(TPP)(NO) [24] as shown in Table I. Further, it is known that Cr(III) porphyrins are not readily reduced to Cr(II) porphyrins [2].

From these results, the oxidation state of the chromium ion of the radical species obtained by the reaction of $O_2^-$ with Cr(III)(TPP)Cl is assumed to be IV. Furthermore, a chromium(IV) porphyrin $\pi$ cation-radical would be expected to show significant proton hyperfine interactions and a $g$ value near free spin ($g = 2.0023$). Also, when $H_2O_2$ or $H_2O$, both of which can destroy $O_2^-$, was added to the radical-containing solution, the ESR signal shown in Fig. 2 rapidly decreased in intensity and then disappeared completely.

These results indicate that the radical species observed in Fig. 2 is the superoxide adduct of Cr(IV) porphyrin, Cr(IV)(TPP)(A)($O_2^-$) [A = Cl or $O_2^{2-}$]. Since there are no examples known of $O_2^{2-}$ coordinated to Cr(IV) porphyrins in the absence of any oxo ligand, one of the postulated products, Cr(IV)(TPP)($O_2^{2-}$)($O_2^-$), may be excluded, and then the observed radical species is assignable to the other suggested product, Cr(IV)(TPP)(Cl)($O_2^-$). In this case, $O_2^-$ acts as a $1e^-$ oxidant as shown in the reaction scheme. However, it is known that in aprotic media, $O_2^-$ is unlikely to act as a $1e^-$ oxidant, producing $O_2^{2-}$ due to the instability of $O_2^{2-}$ [25]. Probably, traces of water in solution may act as a proton source for $O_2^{2-}$ [19].

The above ESR results are supported by the UV–Vis spectral data (Table II). From Table II, it is apparent that the product obtained from the reaction of Cr(III)(TPP)Cl with excess $O_2^-$ is a chromium(IV) complex. A typical UV–Vis spectrum of the ESR samples mentioned above is shown in Fig. 3.

TABLE II. Visible Spectral Data of Chromium Porphyrins in DMSO

| Cr complex | $\lambda_{max}$ (nm) |
|---|---|
| Cr(III)(TPP)Cl | 396, 448, 522, 568, 608 |
| Cr(III)(TPP)(Cl)($O_2^-$) | 415sh, 438, 525, 566, 608 |
| Cr(IV)O(TPP) | 393, 445, 526, 566, 603 |
| Cr(V)N(TPP) | 424, 550 |
| Cr(IV)(TPP)(Cl)($O_2^-$) | 391, 445, 526, 566, 604 |

sh, shoulder.

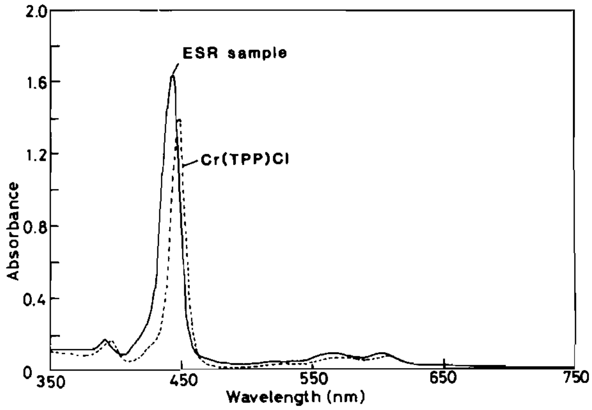
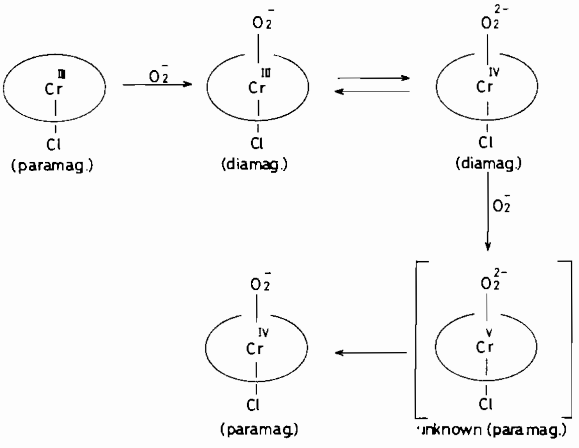


Fig. 3. UV–Vis spectrum of the ESR sample shown in Fig. 2. The ESR sample solutions were diluted 500 times with DMSO.

Since Cr(III)(TPP)(Cl)($O_2^-$) is formed at the initial step of reaction between $O_2^-$ and Cr(III)(TPP)Cl [10], this radical species might be formed by the oxidation of Cr(III)(TPP)(Cl)($O_2^-$) with the excess $O_2^-$, as shown in Scheme 1.

### *Reactive Character of Cr(IV)(TPP)(Cl)($O_2^-$)*

The superoxide adduct, Cr(IV)(TPP)(Cl)($O_2^-$), is very stable and its lifetime is greater than 2 days at room temperature in the dark. This radical species can oxidize t-butylamine to give the corresponding cation radical, $[(CH_3)_3CNH_2]^{+\cdot}$. By contrast, in



Scheme 1.

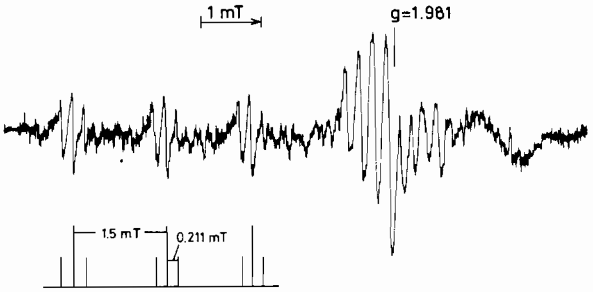


Fig. 4. ESR spectrum observed during the reaction of Cr(IV)-(TPP)(Cl)($O_2^-$) with t-butylamine in DMSO.

Cr(V)O(TPP)Cl the axial ligand, Cl, was replaced by t-butylamine to yield Cr(V)O(TPP)(t-butylamine) [5]. The ESR spectrum ($a^N(1) = 1.50$ mT, $a^H(2) = 0.211$ mT) of the cation radical obtained from the reaction of Cr(IV)(TPP)(Cl)($O_2^-$) with t-butylamine is shown in Fig. 4. In this case, a residual ESR spectrum due to Cr(IV)(TPP)(Cl)($O_2^-$) is still observed. Its signal intensity, however, is substantially reduced. The cation radical may be formed by the following reaction (1)

$$(CH_3)_3CNH_2 + Cr(IV)(TPP)(Cl)(O_2^-) \longrightarrow [(CH_3)_3CNH_2]^{+\cdot} + Cr(IV)(TPP)(Cl)(O_2^{2-}) \qquad (1)$$

Triphenylphosphine is also oxidized by Cr(IV)(TPP)-(Cl)($O_2^-$) to yield the corresponding radical, the ESR signal of which is too weak to analyze. Imidazole, Py and 4-CNPy did not react with Cr(IV)(TPP)(Cl)-($O_2^-$). Both $H_2O_2$ and $H_2O$ reacted with Cr(IV)-(TPP)(Cl)($O_2^-$), as mentioned above.

From these reaction patterns, it is assumed that the reactive character of Cr(IV)(TPP)(Cl)($O_2^-$) resembles that of the free superoxide ion [25–29]. These data also support the assumption that the reaction product of Cr(III)(TPP)Cl with $O_2^-$ has a superoxide ion as axial ligand.

We are now trying to isolate Cr(IV)(TPP)(Cl)-($O_2^-$).

## Conclusions

The reaction of Cr(III)(TPP)Cl with superoxide ion gives the superoxide adduct, Cr(III)(TPP)(Cl)-($O_2^-$), at the first step of the reaction. When a six-fold excess $O_2^-$ was added to this reaction solution, a new superoxide adduct, Cr(IV)(TPP)(Cl)($O_2^-$), is formed. This superoxide adduct has a reactive character similar to that of free superoxide ion. It can oxidize some organic substrates, notably tertiary phosphines and primary amines.

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