

Spectroscopic Studies on the Reactions of Copper(II) Ion with Quinone Form of Polyvalent Porphyrin

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Reactions of Cu(II) ion with quinone, 5,15-di-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-10,20-di-(3,5-di-*tert*-butyl-4-quinomethene)porpho-10,20-dimethene (2) were investigated using UV/vis and electron spin resonance (ESR) spectroscopic methods.

Formation of tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrinatocopper(II) [Cu(II)T'BHPP, 4] from the reaction of Cu(II) ion with 2 was determined by UV/vis and ESR measurements. However, the direct reaction product, Cu(II)-quinone complex (3), was not detected. These results suggest that 3 which may be formed at the initial reaction step between Cu(II) ion and 2 is gradually reduced by excess Cu(II) ion to yield 4. The reaction scheme between Cu(II) ion and the quinone is discussed.

Keywords polyvalent porphyrin; quinone; UV/vis; ESR; copper(II) ion

In recent years there have been many reports concerning the facile aerial oxidation of porphyrins *meso*-substituted with redox active groups.²⁾ Polyvalent porphyrin, tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin (H₂T'BHPP, 1), for example, undergoes facile two-electron oxidation to the quinone, 5,15-di-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-10,20-di-(3,5-di-*tert*-butyl-4-quinomethene)porpho-10,20-dimethene (2). Reduction back to 1 may be achieved either chemically^{2a)} or electrochemically.^{2f)}

In previous papers, we described that 2 was obtained in high yield by the oxidation of 1, with superoxide ion

(O₂⁻)³⁾ or with the Mn²⁺-O₂ system.⁴⁾ We also showed⁵⁾ that the Cu(II)-quinone complex (3) may be formed by the reaction of tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrinatocopper(II) [Cu(II)T'BHPP, 4] with O₂⁻. Further, in order to get 3 directly, we have investigated the reaction of Cu(II) ion with 2 using UV/vis and electron spin resonance (ESR) spectroscopic methods to obtain 3. In this paper, we describe the reaction scheme between Cu(II) ion and 2.

Experimental

Materials Quinone (2) was prepared by the method described

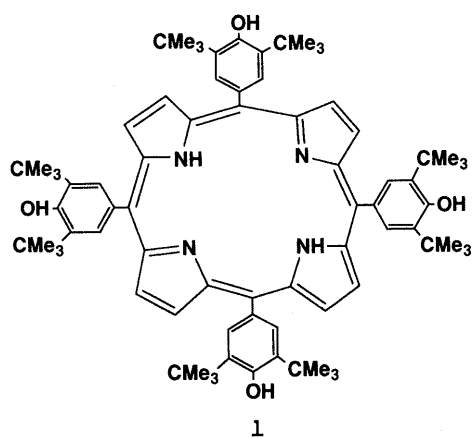


Chart 1

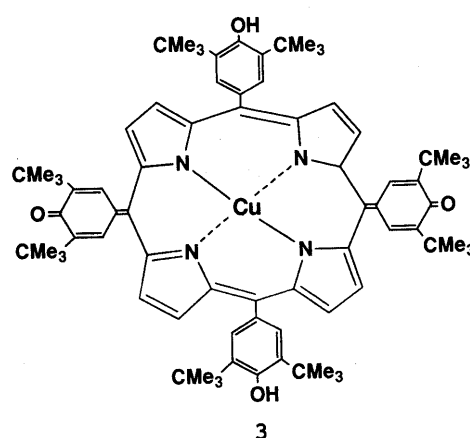


Chart 3

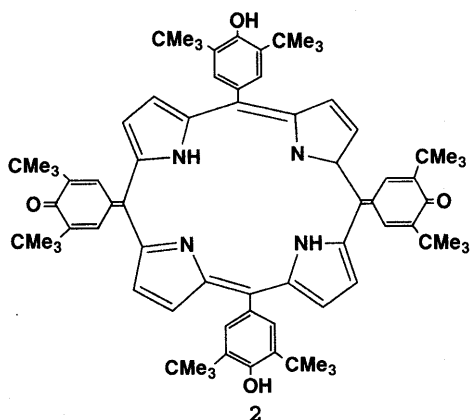


Chart 2

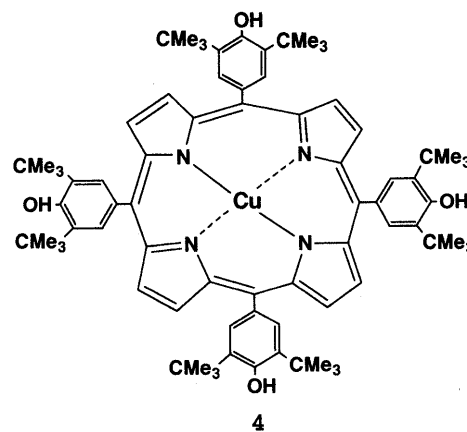


Chart 4

previously.^{3,4,6} Cu(II)T'BHPP (**4**) was synthesized as described previously.⁷ CuCl₂·2H₂O was purchased from Wako Pure Chemical Ind., Ltd. Other reagents were commercially available. Chloroform (CHCl₃) was distilled and passed through a neutral alumina column (Wolem) prior to use. Other solvents were distilled prior to use.

Spectral Measurements Absorption spectra were measured at room temperature with a Union Giken SM-401 spectrophotometer. ESR spectra were measured at room temperature or at 77 K with a JEOL-RE-1X (X-band) spectrometer with 100 kHz field modulation. ESR parameters were calibrated by comparison with the standard sample of Mn²⁺ doped on MgO and 2,2-diphenyl-1-picrylhydrazyl (DPPH, $g = 2.0036$). For more accurate calibration a nuclear magnetic resonance (NMR) field meter (JEOL ES-FC 5) and a microwave counter (Advantest) were used.

Results and Discussion

Quinone (**2**) shows a very broad absorption spectrum ($\lambda_{\max} = 522$ nm, $\log \epsilon = 5.09$) in CHCl₃ (spectrum 1 in Fig. 1). When Cu(II) ion in CHCl₃ was added to a CHCl₃ solution of **2**, spectral changes were observed as shown in Fig. 1. Spectrum 2 in Fig. 1 was observed immediately after mixing of Cu(II) ion with **2**. This spectrum gradually changed with time to spectrum 14 having the isosbestic points (388 and 445 nm). The final spectrum 14 obtained 2 d after the reaction shows four absorption bands ($\lambda_{\max} = 426, 477, 550$ and 590 nm). There was no further spectral change after the final change of spectrum 14. The visible spectrum with three absorption bands ($\lambda_{\max} = 426,$

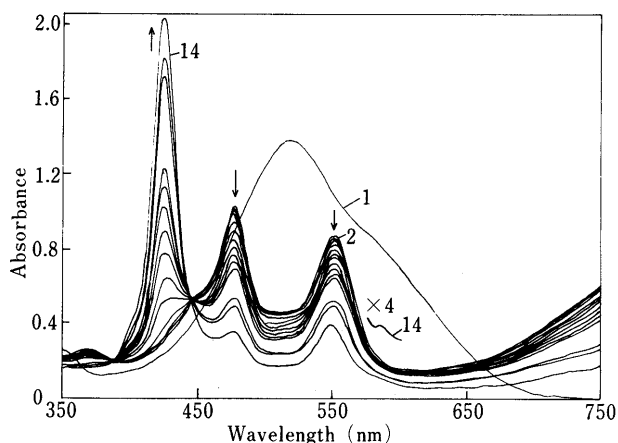


Fig. 1. Visible Spectral Changes Accompanying the Reaction of Cu(II) Ion with Quinone **2** in CHCl₃ Solution at Room Temperature

Concentrations: quinone, 1.34×10^{-2} mM; Cu(II) ion, 2.25×10^{-2} mM. Time after mixing (min): 0, 0.33, 2, 30, 60, 120, 180, 240, 300, 360, 420, 480, 22 (h), 30 (h) and 50 (h). The final spectrum was recorded after 50 h.

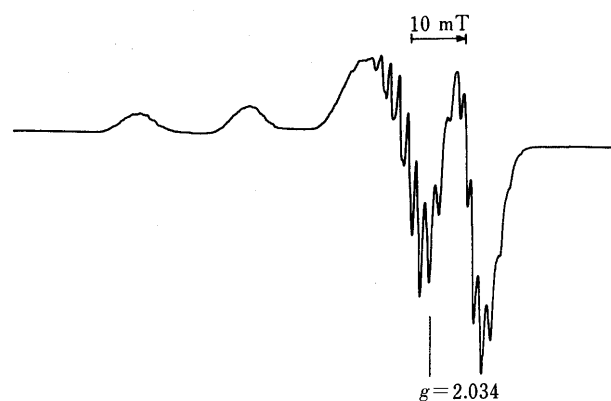


Fig. 2. ERS Spectrum Observed at 77 K from the Reaction Solution Which Gave the Visible Spectrum 14 in Fig. 1

Instrument settings: microwave power, 10 mW; modulation amplitude, 0.5 mT; amplitude, 1.0×10 ; time constant, 0.03 s; scan time, 4 min.

550 and 590 nm) resembles that obtained from **4** in CHCl₃. Further, when the reaction mixture showing spectrum 14 in Fig. 1 was measured by ESR at 77 K, the ESR spectrum shown in Fig. 2 was observed. This ESR spectrum ($A_{\parallel}^{\text{Cu}} = 20.18$ mT, $A_{\perp}^{\text{Cu}} = 3.61$ mT, $A_{\parallel}^{\text{N}} = 1.68$ mT, $g_{\parallel} = 2.181$ and $g_{\perp} = 2.049$) was identical to that obtained from a CHCl₃ solution of **4** at 77 K.⁵ Thus, the chemical species which gave the final spectrum 14 in Fig. 1 is assignable to **4**.

The absorption spectrum 2 in Fig. 1 did not show the Soret band. It is known that the Soret band is found in all tetrapyrroles in which the nucleus is fully conjugated and can therefore be regarded as a characteristic of this macrocyclic conjugation.⁸ Thus, it is thought that the chemical species showing the spectrum 2 does not have a porphyrin skeleton which is fully conjugated. Since the quinone form (**2**) of **1** is not fully conjugated, it does not show the Soret band. Absorption spectrum 2 in Fig. 1 differed greatly from spectrum 1 which was obtained from **2**. Therefore, the chemical species which gives the absorption spectrum 2 ($\lambda_{\max} = 477$ and 552 nm) in Fig. 1 is assignable to **3**.

The absorption maximum observed at 477 nm in spectrum 2 in Fig. 1 was also observed in spectrum 14. This result indicates that a small amount of **3** still exists in the reaction solution even 2 d after mixing of Cu(II) ion with **2**.

When the reactions of Cu(II) ion with **2** were done in the absence of oxygen, the same spectral changes as shown in Fig. 1 were observed. This implies that oxygen does not affect the formation of **4**. Thus, the quinone moiety of **3** may be reduced by a slight excess of Cu(II) ion to yield **4**.

From these results, the following reaction schemes may be assumed:



In conclusion, **4** was obtained from the reaction of **2** with Cu(II) ion, instead of **3**.

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References and Notes

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