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Synthesis and Reactivity of Bis(porphyrinato-Cobalt(II)) Complexes Linked by a Flexible Polyatomic Chain

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In the previous papers [1–3] we revealed that reactivities of binuclear copper(II) complexes are quite different from those of planar mononuclear copper(II) complexes in the reaction with two-electron donors, such as ascorbic acid or catechol, *etc.* In order to obtain more detailed knowledge on the reactivity of binuclear metal complexes, in this study we have prepared new binuclear cobalt(II) complexes, in which two cobalt(II) porphyrin rings are linked by a flexible polyatomic chain (cf. Fig. 1) and investigated the reactivity with 3,5-di-*t*-butylcatechol.

The ligands cited in Fig. 1 were prepared according to the method described by Little [4]. The preparation of the metal complexes were carried out by general methods, and were purified by the column chromatography (metal ion = Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+} and Mn^{3+}).

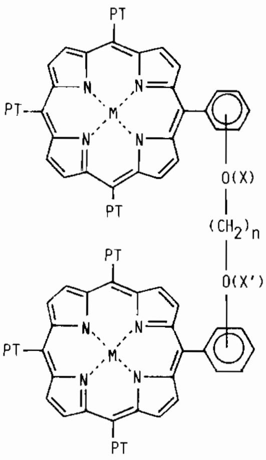

Fig. 1. Structures of the metal complexes cited in this paper. These ligands are abbreviated as H$_4$(p-X-n-X'-p), for example, H$_4$(p-2-3-4-p) represents 5,10,15-tri-*p*-tolyl-20-[2-[3-[*p*-(10,15,20-tri-*p*-tolyl-5-porphinyl)phenoxy]propox]phenyl]porphine. PT represents *p*-tolyl group.

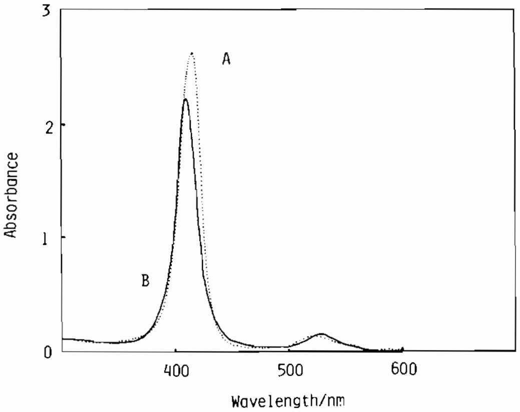

Fig. 2. Absorption spectra of A(– – –), [Co(ttp)] and B(———), Co$_2$(p-2-4-4-p) (in CHCl$_3$ at room temperature, [Co^{2+}] = 1 × 10^{-6} mol dm^{-3}).

In Fig. 2, the absorption spectra of Co$_2$(p-2-4-4-p) (for the abbreviation, see Fig. 1) and [Co(ttp)](H$_2$(ttp) represents α,β,γ,δ-tetra-*p*-tolylporphyrin) are shown, the spectral data of other complexes being listed in Table I. The Soret bands of [Co(ttp)] and Co$_2$(p-2-4-4-p) were observed at 417 and 410 nm, respectively. Several authors have pointed out that the shift of the Soret band and the visible (around 525 nm) bands can be used to diagnose the presence of the interaction between two porphyrin units [5, 6]. It is well known that Soret and visible bands are blue- and red-shifted when the interaction occurs between two porphyrin units, the shift of the Soret band being 15 nm in the case of 'face-to-face' porphyrins prepared by Chang *et al.* [6]. Thus, the data in Table I show that there is an interaction between two cobalt(II) porphyrin rings in some compounds, such as Co$_2$(p-2-n-4-p) (n = 3,4,5,6) and Co$_2$(p-2-3-2-p). An examination using the Dreiding model predicts that two porphyrin rings cannot stack in the case of Co$_2$(p-4-3-4-p). This is consistent with the

TABLE I. Spectral Data of the Complexes.

Complex	Soret (nm)	Visible (nm)
[Co(ttp)]	417	523
Co$_2$(p-4-6-4-p)	412	527
Co$_2$(p-4-5-4-p)	415	525
Co$_2$(p-4-4-4-p)	412	528
Co$_2$(p-4-3-4-p)	417	522
Co$_2$(p-2-6-4-p)	411	528
Co$_2$(p-2-5-4-p)	411	528
Co$_2$(p-2-4-4-p)	410	528
Co$_2$(p-2-3-4-p)	411	528
Co$_2$(p-2-3-2-p)	410	528

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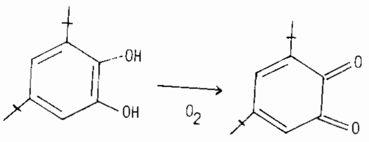
fact that there is no appreciable shift in the Soret and the visible bands of this complex relative to those of [Co(ttp)]. The ESR spectra showed that one unpaired electron resides in the d_{z^2} orbital in the ground state [7] for these complexes.

The catalytic activities of these cobalt(II) complexes for the oxidation of 3,5-di-*t*-butylcatechol by dioxygen molecule (reaction (I)), can be evaluated in



(I)

terms of the measurements of increase of absorbance at 400 nm, because 3,5-di-*t*-butylcatechol is colorless, whereas formed *o*-quinone shows strong absorption band at 400 nm [2]. Fig. 3 shows the time course of the absorbance at 400 nm in the reaction mixtures of cobalt(II) complex, triethylamine and catechol with the ratio 1:3.75:75 in $CHCl_3$, the concentration of cobalt(II) ion being fixed at 5.7 X 10^{-5} mol dm^{-3}. These results clearly indicate that the presently prepared bis(porphyrinatocobalt(II) complexes show high catalytic activity for the reaction (I) in contrast to the low catalytic activity of mononuclear [Co(ttp)]. This fact can be accounted for on the assumption of the formation of an 'intermediate' complex shown in Fig. 4, followed by the 'concerted' two-electron transfer reaction between catechol and a dimeric cobalt(II) complex.

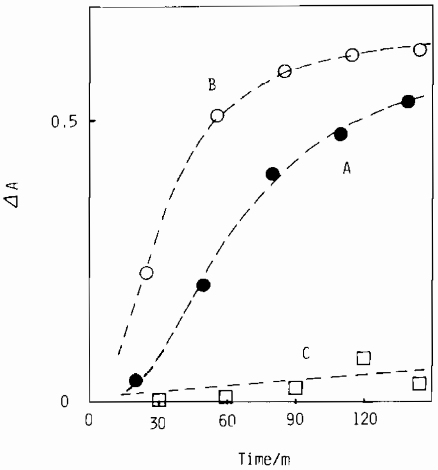


Fig. 3. Time course of the absorbance at 400 nm of the reaction mixtures of 3,5-di-*t*-butylcatechol and (A) Co_2(p-4-3-4-p), (B) Co_2(p-2-3-4-p), and (C) [Co(ttp)] (in $CHCl_3$, 298 K).

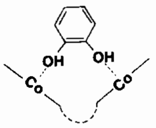


Fig. 4. Assumed 'intermediate' complex between bis(porphyrinatocobalt(II) and catechol.

It was also found that the intensities in the fluorescence spectra are greatly reduced in some bis(porphyrinatozinc(II)) complexes compared with that of the monomeric [Zn(ttp)]. More detailed results on the photochemical behaviour of these dimeric zinc(II) complexes will be reported in a separate paper.

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