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SYNTHESIS OF NEW BINUCLEATING LIGANDS CONTAINING A PORPHYRIN

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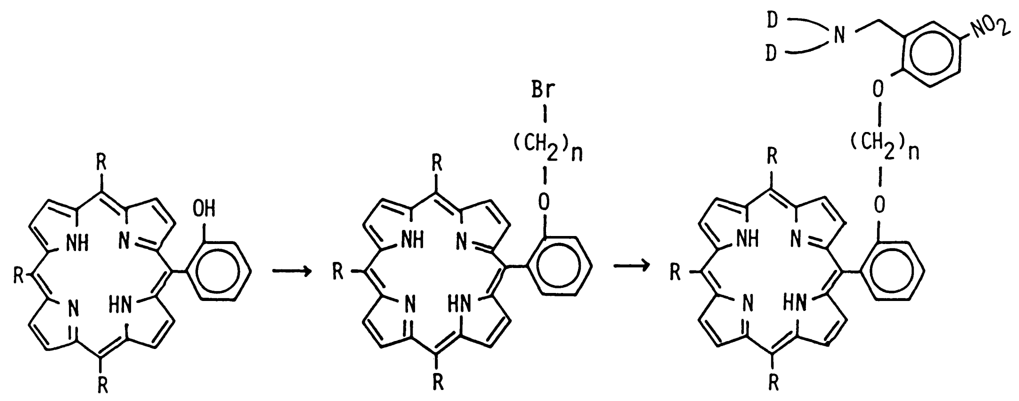
New binucleating ligands containing a porphyrin and another coordination site in close proximity, and their metal complexes were prepared and characterized.

Cytochrome c oxidase is the enzyme which mediates the four-electron reduction of molecular oxygen to water.1) The enzyme contains four metal centers (cytochrome a, cytochrome a_3, Cu_A and Cu_B). One conceptual model which is capable of accounting for a wide range of spectroscopic and magnetic data is based on the hypothesis that the oxygen reduction site is an antiferro-magnetically coupled cytochrome a_3-Cu_B binuclear ion. This proposal2) has stimulated considerable activity for the synthesis of simple mixed-metal binuclear ions which might serve as structural analogues of the site, and several examples have been reported.3-7) In view of providing new models for cytochrome c oxidase, we have in this study prepared new binucleating ligands containing a porphyrin and another coordination site in close proximity, according to the scheme shown below.

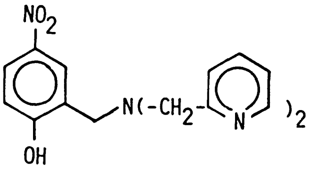
Compound **2** was prepared from compound **1**, 5-(2-hydroxyphenyl)-10,15,20-tri(p-tolyl)porphyrin and $Br(CH_2)_nBr$(n=3,4,5,6).8) The N,N-dimethylformamide solution containing **2** (2 mmol), **4-a** (10 mmol)9) and K_2CO_3(1 mmol) was stirred for a week at room temperature. The solvent was evaporated by a rotary evaporator, and the residue was treated with $CHCl_3$. The $CHCl_3$ solution was eluted on a alumina column(Nakarai Chemicals, Alumina Activated 200, CHR-10). The desired porphyrin was collected and purified on a silicagel column(Wakogel C-200). The eluted $CHCl_3$ solution was collected, and to this was added methanol to give the porphyrin as deeply colored needles(**3-a** , these porphyrins are abbreviated as H_2(p-n-Npy$_2$)). Instead of **4-a** , **4-b** 10) was also used to obtain the binucleating ligands, **3-b** , which are abbreviated as H_2(p-n-NS$_2$). The analytical data of the compounds **3-a** are given in Table 1.

For the preparation of the hetero-binuclear metal complexes, for example, Co(p-n-NS$_2$)CuCl$_2$(in these cases, cobalt(II) ion is coordinated by the porphyrin and copper(II) ion is in another coordination site), we have started with the cobalt(II) complex of **1** . By a method similar to that described in the scheme,

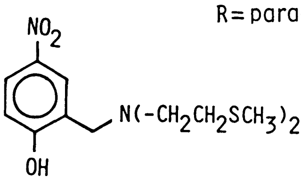


1 2 3

3-a: D= (2-pyridylmethyl)
3-b: D= (2-methylthioethyl)
R= para-tolyl



4-a



4-b

the cobalt(II) complexes of 3-b (n=3,4,5,6) were prepared and purified by the column chromatography. Adding a methanol solution of $CuCl_2 \cdot 2H_2O$(0.1 mmol) to a $CHCl_3$ solution of the cobalt(II) complex of 3-b (0.1 mmol), the hetero-binuclear complexes, Co(p-n-NS_2)$CuCl_2$ were obtained, the analytical data of these compounds being listed in Table 1.

Table 1. The analytical data of new compounds

compound	C(%) found(calcd)	H(%) found(calcd)	N(%) found(calcd)
H_2(p-3-Npy_2)	77.58(77.94)	5.62(5.50)	10.39(10.54)
H_2(p-4-Npy_2)	77.89(78.04)	5.65(5.61)	10.37(10.40)
H_2(p-5-Npy_2)	77.76(78.14)	5.76(5.73)	10.06(10.26)
H_2(p-6-Npy_2)	78.01(78.24)	5.90(5.83)	9.96(10.14)
Co(p-3-NS_2)	69.36(69.66)	5.52(5.38)	7.63(7.74)
Co(p-5-NS_2)	70.17(70.06)	5.77(5.71)	7.48(7.54)
Co(p-3-NS_2)$CuCl_2$	61.64(61.99)	4.82(4.79)	6.59(6.88)
Co(p-4-NS_2)$CuCl_2$	62.68(62.26)	5.00(4.90)	6.81(6.81)
Co(p-6-NS_2)$CuCl_2$	62.95(62.78)	5.21(5.11)	6.64(6.66)

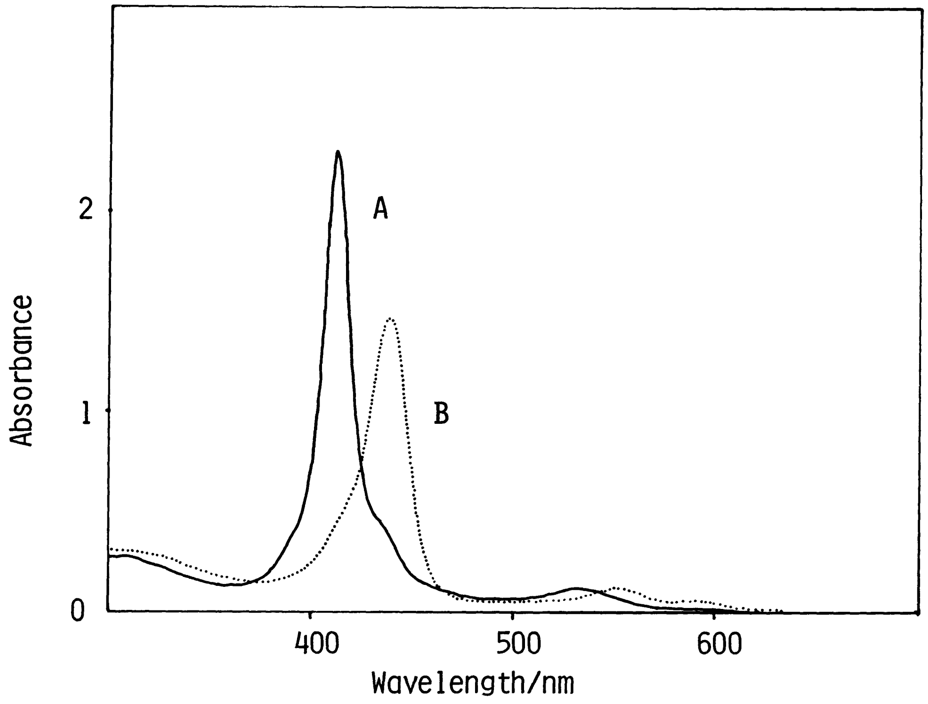


Fig. 1 Absorption spectra(in $CHCl_3$) of A: Co(p-3-NS_2) and B: Co(p-3-NS_2)$CuCl_2$($[Co^{2+}]=10^{-6}$ mol dm^{-3})

The spectral data are summarized in Table 2. The Soret band of [Co(ttp)] is observed at 417 nm(in $CHCl_3$). In the cases of H_2(p-n-Npy_2) and Co(p-n-NS_2) (n=3,4,5,6), the Soret bands are observed in the range 412∼419 nm, the shift of the absorption maximum being small. On the other hand, the Soret bands in the hetero-binuclear complexes(Co(p-n-NS_2)$CuCl_2$) are observed in the range 434 ∼ 439 nm(cf. Fig. 1 and Table 2), which greatly shift to longer wavelength region relative to that of [Co(tpp)]. These facts are suggesting that there are some interactions between the cobalt and the copper coordination units.

Table 2. Spectral data of the compounds(in $CHCl_3$)

compound	Soret(nm)	visible(nm)
H_2(ttp)*	419	515
H_2(p-5-Npy_2)	419	515
H_2(p-6-Npy_2)	419	515
Co(ttp)	417	523
Co(p-3-NS_2)	412	532
Co(p-5-NS_2)	412	533
Co(p-3-NS_2)$CuCl_2$	439	552
Co(p-4-NS_2)$CuCl_2$	436	548
Co(p-6-NS_2)$CuCl_2$	434	552

*H_2(ttp)=α,β,γ,δ-tetra(p-tolyl)porphyrin.

Each component complex in the hetero-binuclear complexes(Co(p-n-NS_2)$CuCl_2$), e.g., [Co(ttp)] and Cu(NS_2)Cl_2, does not catalyze only by itself the oxidation[11)] of TMPD(N,N,N',N'-tetramethyl-p-phenylenediamne) by molecular oxygen, where(NS_2) represents bis(2-methylthioethyl)amine. However, the hetero-binuclear complexes showed remarkably high activity for the oxidation reaction. We are making effort to prepare more hetero-binuclear complexes of this type with a variety of metal ions, and more detailed studies on the reaction mechanism of the catalytic function of these hetero-binuclear complexes are now in progress.

Acknowledgement

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