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^{1}H-Nuclear Magnetic Resonance Studies on Cobalt(II) Complexes of N-Alkyl-octaethylporphyrins

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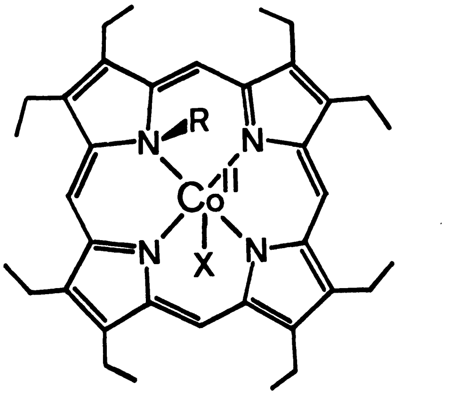
High-spin cobalt(II) complexes of N-alkyl-octaethylporphyrin have been characterized by ^{1}H-NMR measurements. Proton signals of N-alkyl groups and aromatic meso-protons were assigned by deuteration method. Axially coordinated imidazole resonance appeared at very low magnetic field.

Abnormal heme metabolism caused by xenobiotic reaction of reactive organic species in heme enzymes and hemoproteins gives rise to formation of the green pigment, which has been determined as N-substituted porphyrin.$^{1)}$ It is most likely that iron complex of N-substituted porphyrin is important key intermediate involved in these suicide reactions of prosthetic heme. Although autoxidation rate of iron(II) complex of N-alkyl-porphyrin to the iron(III) complex is slower than that of usual ferrous porphyrin,$^{2)}$ we have noticed that its faster oxidation takes place in organic solvent under aerobic condition.$^{3)}$ Cobalt(II) complexes of N-substituted-porphyrins seem to be appropriate model for intermediate complex in the heme reaction, because of their high stability toward dioxygen. We wish to report ^{1}H-NMR spectra of the high spin cobalt(II) complexes of N-alkyl-octaethylporphyrins and facile identification of axially coordinated imidazole and unligated base.



1; $R=CH_3$, $X=AcO^-$
2; $R=CD_3$, $X=AcO^-$
3; $R=CH_3$, $X=AcO^-$ meso-d_4
4; $R=CH_3$, $X=Im$
5; $R=C_2H_5$, $X=AcO^-$
6; $R=C_2D_5$, $X=AcO^-$
7; $R=C_2H_5$, $X=Im$

N-alkylation of porphyrins was carried out by a newer method reported by Jackson and his coworkers.$^{4)}$ N-CD_3-octaethylporphyrin, N-CD_3-OEPH, was obtained from reaction of octaethylporphyrin, $OEPH_2$, with CD_3I in $CHCl_3$-CH_3COOH. Meso-protons of N-CH_3-OEPH were deuterated by the mixture of D_2SO_4-CF_3COOD. The cobalt(II) complexes were obtained by addition of CH_3OH solution of cobalt(II) acetate to a $CHCl_3$ solution of

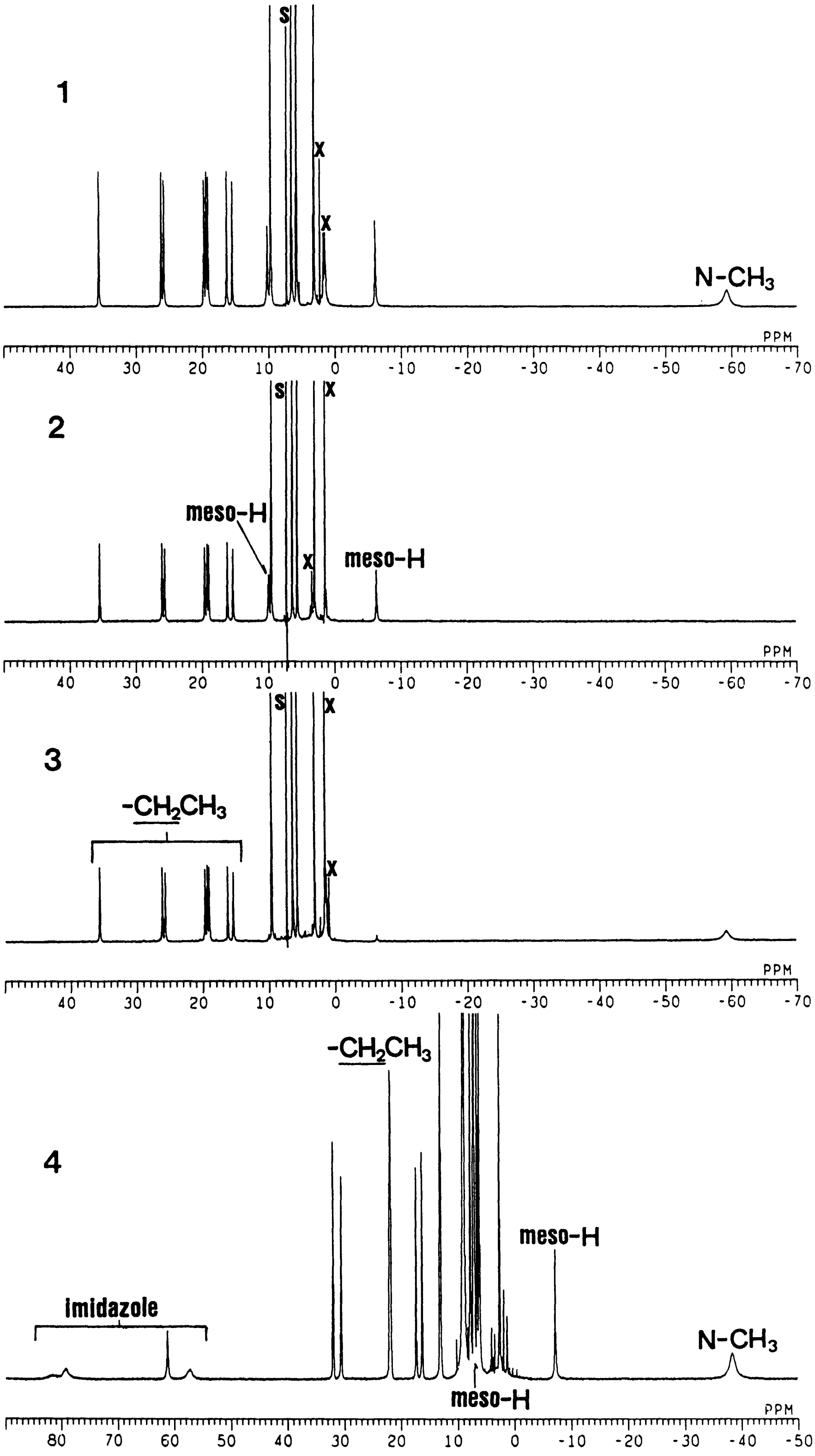


Fig. 1. 270 MHz ^{1}H-NMR spectra of (1)(N-CH$_3$-OEP)Co(II)OAc, (2)(N-CD$_3$-OEP)Co(II)-OAc, (3)(N-CH$_3$-OEP-meso-d$_4$)Co(II)OAc, and (4)(N-CH$_3$-OEP)Co(II)Im (Imidazole/(N-CH$_3$-OEP)Co(II)OAc = 15/1) in CDCl$_3$ at 25 °C. S, solvent; X, impurities.

N-alkyl-octaethylporphyrins.[5] Crude crystals of the cobalt(II) complexes were treated with $CHCl_3$ containing small amount of acetic acid to complete axial coordination of acetate anion and recrystallized from hexane-$CHCl_3$.

Figure 1 shows 270 MHz ^1H-NMR spectra of the cobalt(II) complexes 1-4 in $CDCl_3$ at 25 °C. Spectral feature of 1 is almost identical with that reported by Latos-Grazynski.[6] Assignment of two kinds of the meso-protons at -6.2 and 10.2 ppm is clearly verified by comparing the spectrum of 1 with that of the meso-deuterated complex 3. Eight signals distributed from 15 to 35 ppm are due to the CH_2 protons of four kinds of peripheral ethyl groups. Each resonance is split to two peaks by atropism of the porphyrin ring above and below. Four signals at 3.0, 5.8, 6.6, and 9.8 ppm are readily assigned to the CH_3 protons of ethyl groups. Since the signal disappears upon deuteration of the N-CH_3 group as is shown in Fig. 1. A broad resonance at markedly upfield of -60 ppm is unambigously assigned to the N-CH_3 group.

The cobalt(II) complex of N-ethyl derivative 5 reveals a sharp signal at -45 ppm and a very broad signal at -122 ppm which are assignable to the methyl and methylene protons of the N-ethyl group respectively. It is noted that the CH_3 group of N-ethyl is subjected to large isotropic effect derived from paramagnetic cobalt(II) ion and its line width is smaller than that of the CH_2 group. Magnetic susceptibility and ESR spectrum of 1 is characteristic of high-spin state (s = 3/2).[7] It is particularly interesting to compare the N-CH_3 resonance of 1 with the high-spin ferrous complex of N-CH_3-porphyrin (s = 2). The N-CH_3 signal of ferrous complex is observed at extremely downfield (δ = 150 ppm).[8] This marked shift is attributed to predominant contribution of contact term. The opposite magnetic field shift of N-CH_3 proton of 1 is required to be explain in different mechanism from that of the iron(II) complex. Anomalous resonance of 1 is probably due to both σ-spin transfer and dipolar term.

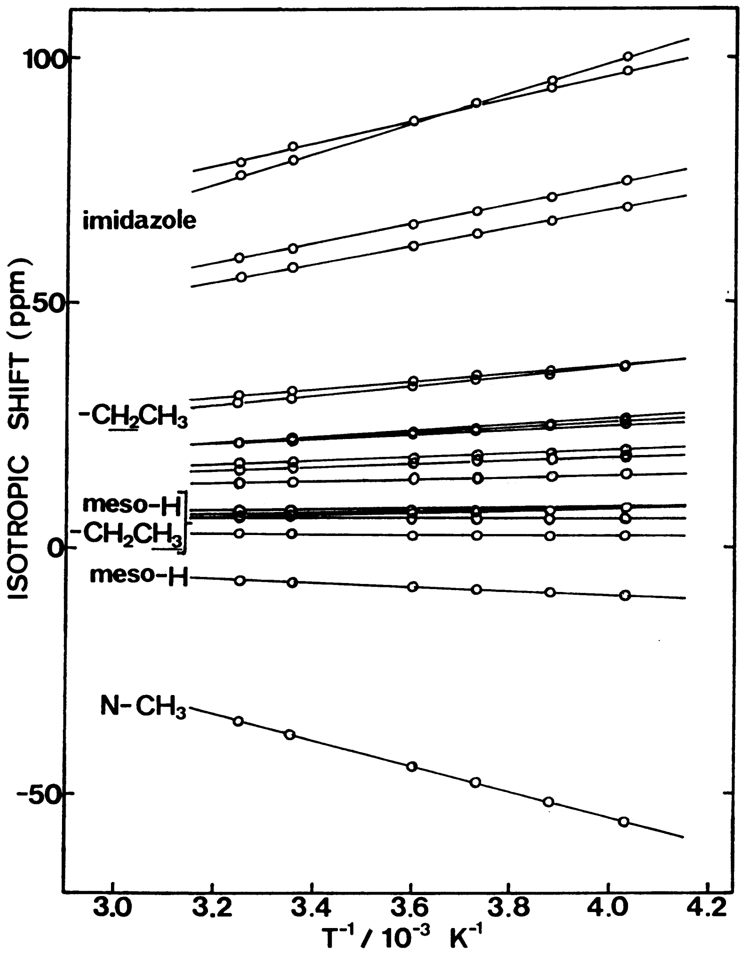


Fig. 2. Plot of the temperature dependencies of the shifts of (N-CH_3-OEP)Co(II)Im (4) in $CDCl_3$.

Latos-Grazynski has reported that the resonance of axially coordinated imidazole could not be observed due to fast exchange with non-coordinated base.$^{6)}$ However, chemical shifts due to axially ligated imidazole are clearly observable at very low magnetic field in the present study. Four protons of imidazole appeared as a sharp signal at 61.2 and three broad ones at 57.3, 79.3, and 81.5 ppm. A resonance at the lowest magnetic field is assignable to the imidazole N-H proton based on its disappearance upon addition of trace amount of D_2O. Relatively sharp signal at 61.2 ppm is probably due to the 5-H of imidazole which is far from the paramagnetic metal ion. Figure 2 shows the temperature dependence of the ^{1}H-NMR signals of 4. Among resonances, both chemical shifts of N-CH_3 group and axially coordinated imidazole show larger temperature dependencies. Former signals shift toward downfield as temperature increases, whereas latter one shows upfield shift. Mechanism of spin transfer of the high-spin complex 1 is different from that of the low-spin cobalt(II) porphyrins.$^{9)}$ Theoretical treatment is required to explain the isotropic shift of the high-spin complex. Recent investigation on the mechanism of model heme reaction has suggested similarity in iron and cobalt series.$^{10)}$ Therefore, ^{1}H-NMR study on the cobalt(II) complexes of N-substituted porphyrins seems to provide a useful nuclear probe to investigate the key intermediate complex in the abnormal heme reaction.

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