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MAGNETIC BEHAVIOR OF FIVE-COORDINATE COBALT(III) COMPLEX OF α,β,γ,δ-TETRAPHENYLPORPHIN

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^{1}H NMR spectrum of chloro-α,β,γ,δ-tetraphenylporphinatocobalt(III) in inert solvent was found to show unusual temperature dependence. The signals became broad by raising the temperature in reversible manner. The compound is diamagnetic in solid state, and the observed temperature dependence was attributed to the partial transformation of the compound in the solution to a paramagnetic species with increased temperature. The formation of paramagnetic species was verified by magnetic moment measurement in the same solution.

It has been reported previously that chloro-α,β,γ,δ-tetraphenylporphinatocobalt(III) (ClTPPCo, Fig. 1) is a five-coordinate Co(III) complex ([Co(N)$_4$Cl]) of TPP having square-pyramidal structure with chlorine atom at the apex, and is diamagnetic.1) This complex is readily converted into solvent-coordinated six-coordinate complexes in ether, alcohol, and pyridine.2,3) However, the five-coordinate structure persists in inert solvent such as chloroform, dichloromethane, or benzene.3) We now report that ClTPPCo in such solutions becomes partly paramagnetic when the temperature is raised. Many instances4) of temperature-dependent spin-state conversion have been already known for clearly definable Werner type complexes of iron(II), iron(III), cobalt(II), and nickel(II). There are also several reports of similar dependence of Co(III) complexes, i.e., a [Co(N)$_4$X] type,5) a [Co(S)$_4$]$^+$ type,6) and a [Co(N)$_4$(C)(L)] type complex.7)

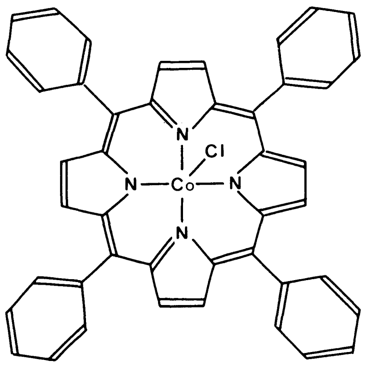

Fig. 1

Solutions of ClTPPCo8) in chloroform, dichloromethane, and 1,1,2,2-tetrachloroethane (TCE) showed unusual temperature-dependent ^{1}H NMR spectra. The dependence was reversible and well reproducible. A typical example of 100 MHz ^{1}H FT-NMR spectra of ClTPPCo in TCE-d$_2$ measured at temperatures between -50 and 145 °C is shown in Fig. 2.9) The spectra at low temperatures are similar to

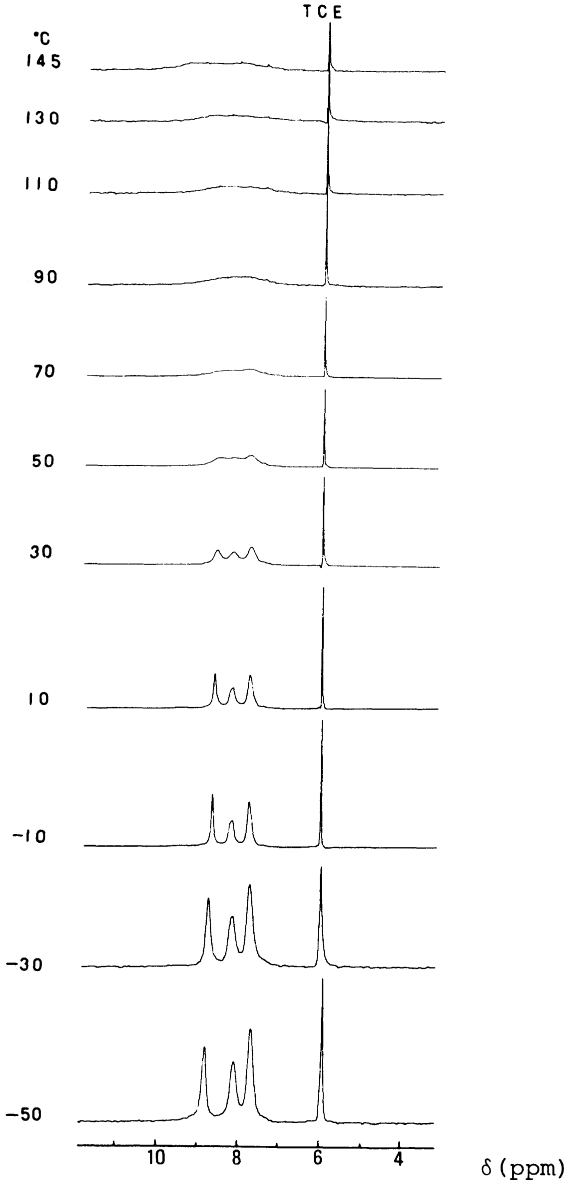

Fig. 2. The 100 MHz ^{1}H FT-NMR spectra of ClTPPCo in TCE-d_2 as a function of temperature.

that of diamagnetic Co(III)TPP complexes,[2)] and the signals were assigned to phenyl-m,p-protons (12H), phenyl-o-protons (8H), and pyrrole-β-protons (8H), respectively, in the order of shifting toward lower field.[10)] When the temperature was raised, signals were broadened and were accompanied by small shifts with respect to the TMS signal, although the signal of TCE-protons varied scarcely in both its profile and position. These broadened signals were the only signals that were observed in the region extending 100 ppm above and below the TCE signal. Furthermore, the intensity of TPP-protons, when examined by CW spectra, was almost constant in the temperature range from -50 to 145 °C. The observed broadening of signals with temperature increase can be attributed to the proton exchange between the newly formed paramagnetic species and the original diamagnetic species.

The formation of paramagnetic species was verified by magnetic moment measurements by the method of Evans11) using NMR spectra, in TCE or dichloromethane at various temperatures between -50 and 145 °C.12) Magnetic moments (μ_{eff}) of 1.66 BM (averaged value in eight experiments) were observed at room temperature in both solvents and, 1.7_2 BM (single value),13) at 73 °C in TCE. Below 0 °C, the moment was too small to be detected. These moments were considerably smaller than those expected for high-spin states (triplet and quintet), indicating that ClTPPCo in the solution changes only partly into paramagnetic species by temperature increase.

The X-ray diffraction study1) showed that the cobalt atom in ClTPPCo is scarcely deviated, i.e., only 0.05 Å away from the porphinato plane formed by four nitrogen atoms, and also that the observed distance of Co–Cl bond of 2.149 Å is shorter by about 0.1 Å than those in ordinary Co(III) complexes. The fact that ClTPPCo, which is diamagnetic in solid state, shows paramagnetic behavior in inert solvents would be the result of slight change in geometry of ClTPPCo in the solutions, i.e., the slight displacement of the cobalt atom from the porphinato plane, and/or the elongation of Co–Cl bond. It has been reported that, in resonance Raman spectra of metalloporphyrins, the shift to the lower frequencies of the anomalously polarized 1590 cm^{-1} line indicates the out-of-plane positioning of the metal atom.14) Resonance Raman spectra of ClTPPCo in TCE produce such line at 1567 cm^{-1} at room temperature, and at 1568 cm^{-1} at dry ice-methanol temperature.15) These values indicate that the cobalt atom is out-of-plane. In this connection, it may be noted that five-coordinate Co(III) complex $[Co(N)_4Cl]$,16) whose coordination polyhedron is square-pyramidal, is paramagnetic. The cobalt atom in this compound is situated 0.19 Å out-of-plane of the N_4 plane, in the direction of the axial chlorine atom, and the distance of Co–Cl bond (2.507 Å) is longer than those in ordinary Co(III) complexes.

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8) ClTPPCo was prepared by the method previously reported1) and identified by visible spectra and analysis (Found: C,72.63; H,4.12; N,7.78; Co,7.48; Cl,5.50%).

9) The sample was prepared as follows: 5 mg ClTPPCo was dissolved in 1 ml TCE-d_2 and degassed by successive freeze-thaw pumping cycle, then sealed under reduced pressure. The ^{1}H FT-NMR spectra were measured by a JEOL FX-100 Spectrometer, using TMS as the internal reference.

10) The relative intensity was measured by using a Varian HA-100D Spectrometer.

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12) Exactly weighed amount of ClTPPCo which was close to 2 mg was dissolved in 1 ml TCE (or dichloromethane) containing 5% TMS. The solvent was purified by repeated distillation just before use. Sample cell was a co-axial double cell. The sample solution and TCE containing 5% TMS were respectively placed in the inner and the outer cell, and were degassed. The cell was then sealed under reduced pressure. Proton resonance of TCE contained in the two compartments of the cell was measured by Varian HA-100D Spectrometer, with field/frequency locked with the TMS signal.

13) The measurements of peak separation at elevated temperatures were extremely difficult due to lowered resolution of peaks.

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