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Formation of Antiferromagnetically Coupled Dimer of [N,N'-o-Phenylenebis-(salicylaldiminato)]cobalt (II) in DMF Solution

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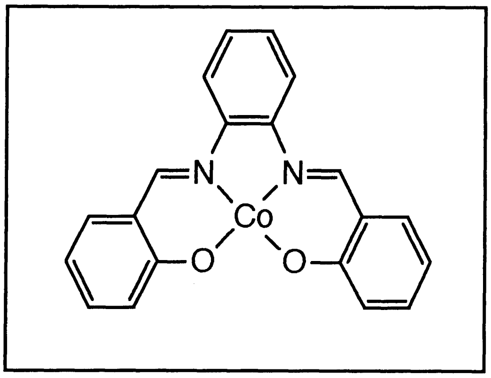
The ^{1}H NMR signals of [N,N'-o-phenylenebis(salicylaldiminato)]cobalt (II), [Co(II)(saloph)], showed an anti-Curie behavior in DMF-d_7 solution. Temperature dependence in magnetic moments suggested the formation of antiferromagnetically coupled dimeric species at low temperature.

Cobalt(II) Schiff-base complexes have been investigated as reversible oxygen carriers in aprotic solvents.$^{1)}$ On the other hand, irreversible oxidation of cobalt(II) takes place in alcohol to give the corresponding alcoholatocobalt(III) complexes.$^{2)}$ Thus, the chemical behavior of these complexes varies to a great extent depending upon solvents. We have been interested in the solvent effects on the spectroscopic properties of [N,N'-o-phenylenebis(salicylaldiminato)]cobalt(II), [Co(II)(saloph)], one of these Co(II) complexes. In the previous paper, we reported on a transient absorption which was detected when the CH_2Cl_2 solution of [Co(II)(saloph)] was irradiated by 337 nm light.$^{3)}$ The absorption was ascribed to a solvated complex in which CH_2Cl_2 molecule is supposed to bind weakly to phenolic oxygen atoms of the ligand. In the case of dimethylformamide (DMF) solution, the absorption spectra of both the ground and transition states exhibited a time dependence with similar isosbestic points.$^{4)}$ Since DMF is a solvent frequently used for the oxygenation reactions of Co(II) Schiff-base complexes, we were interested in the molecular species formed in DMF solutions. In this paper, we would like to report the formation of antiferromagnetically coupled dimeric species of [Co(II)(saloph)] in DMF-d_7 solution.

The ^{1}H NMR spectra were measured in DMF-d_7 solution on a JEOL FX90Q spectrometer operating at 89.55 MHz. Samples were prepared under argon and the sample concentration was adjusted to 70 mM. Figure 1 shows the ^{1}H NMR spectra of [Co(II)(saloph)] taken at various temperatures. In accordance with the molecular symmetry, seven signals with equal integral intensities were clearly observed outside the diamagnetic positions at 151 °C. The small peaks at around 7 ppm were ascribed to those of the diamagnetic Co(III)



[Co(II)(saloph)]

complex formed by the action of molecular oxygen during the measurement. When the temperature was lowered to 99 °C, these signals moved to further lower or higher magnetic fields as signified by the dotted lines. The ^{1}H NMR spectra of the same complex were taken in CD_2Cl_2 solution (27 mM). Although six signals were observed outside the diamagnetic positions, the other one overlapped with the signals of the Co(III) complex. The chemical shifts of these signals were -52.0, -24.8, 1.9, 14.0, 16.9, 29.1 ppm at 47 °C. The large difference was observed in the ^{1}H NMR spectra of these two solutions; the peak at -52 ppm in CD_2Cl_2 solution was absent in the spectra taken in DMF-d_7 solution. The difference could be ascribed to the axial coordination of the solvent in the former case to form [Co(II)(saloph)(DMF)]. Formation of the solvated species was further supported by a large difference in electronic spectra between these two solvents.[3,4)]

The solvated species noted by [Co(II)(saloph)(DMF)] is, however, not the single species in DMF solution. When the temperature of the DMF-d_7 solution was further lowered, each signal unexpectedly moved toward its diamagnetic position. At -35 °C, all the signals appeared in the narrow magnetic region, 0 to 15 ppm, as shown in Fig. 1. It should be noted that some of the signals, especially the signal at the lowest magnetic field, showed considerable broadening as the temperature was lowered. The tem-

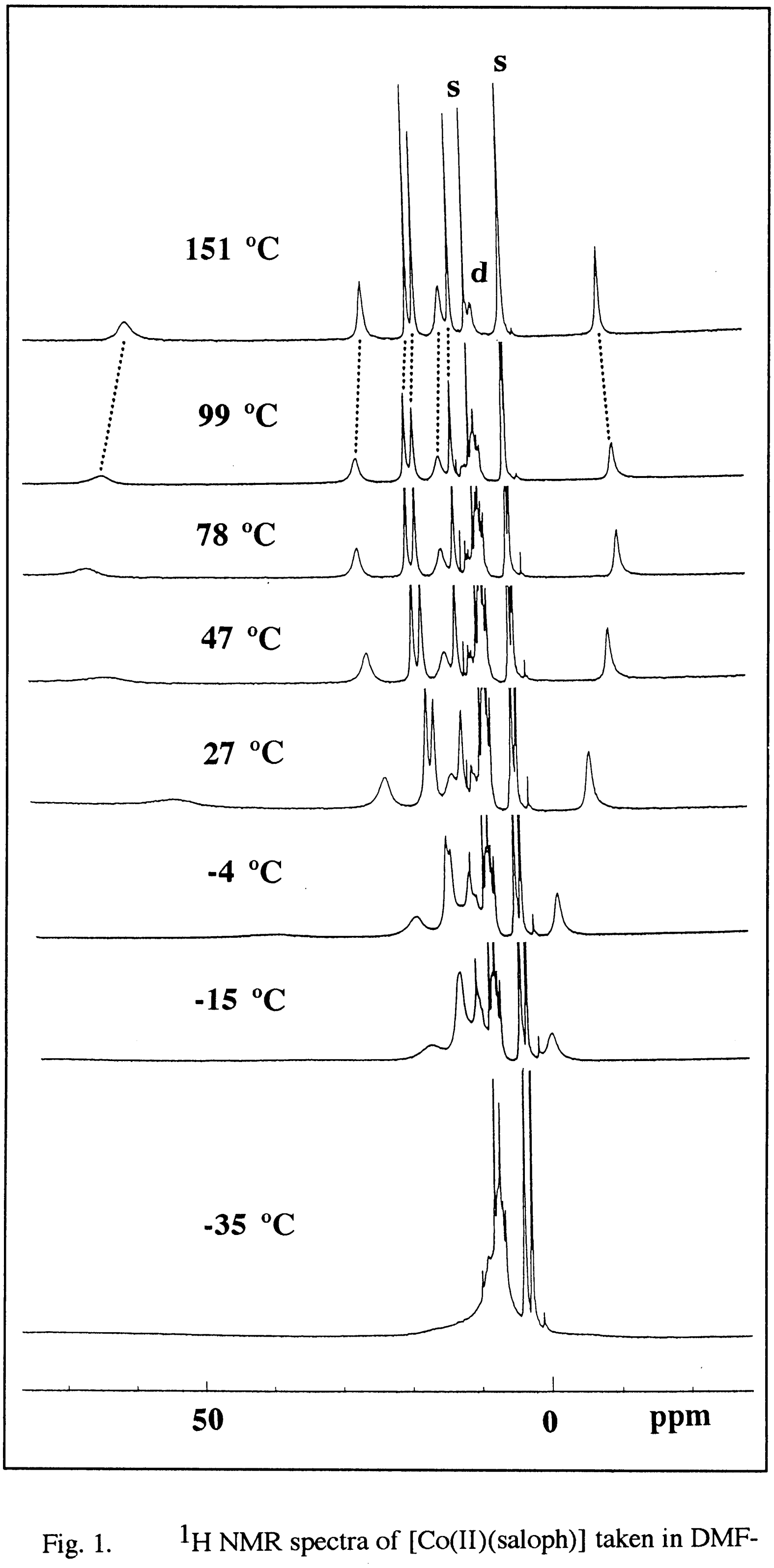


Fig. 1. ^{1}H NMR spectra of [Co(II)(saloph)] taken in DMF-d_7 solution (70 mM). Labels s and d stand for the signals due to solvent and diamagnetic complex, respectively.

perature dependence of the signals was summarized in Fig. 2(a) as Curie plot, which clearly exhibited a curvature at ca. 70 °C. The temperature dependence of the chemical shifts varied by the sample concentration; the sample with smaller concentration exhibited a curvature at lower temperature. The anti-Curie behavior strongly suggests that the spin state changed depending upon the temperature.[5] Migita and coworkers reported the anti-Curie behavior of the analogous [Co(II)(salen)][6] complex in N-heterocyclic solvents(B) such as aniline, pyridine and 1-methylimidazole.[7,8] The result was ascribed to the equilibrium between five coordinated low spin (S = 1/2) [Co(II)(salen)(B)] and six coordinated high spin (S = 3/2) [Co(II)(salen)(B)$_2$] complexes.

In contrast to the case of [Co(II)(saloph)] in DMF solution, the temperature dependence of the chemical shifts was quite normal in CD_2Cl_2 solution as shown in Fig. 2(b); all the signals obeyed Curie law, though the temperature range examined was rather narrow due to the low solubility of the complex toward CD_2Cl_2.

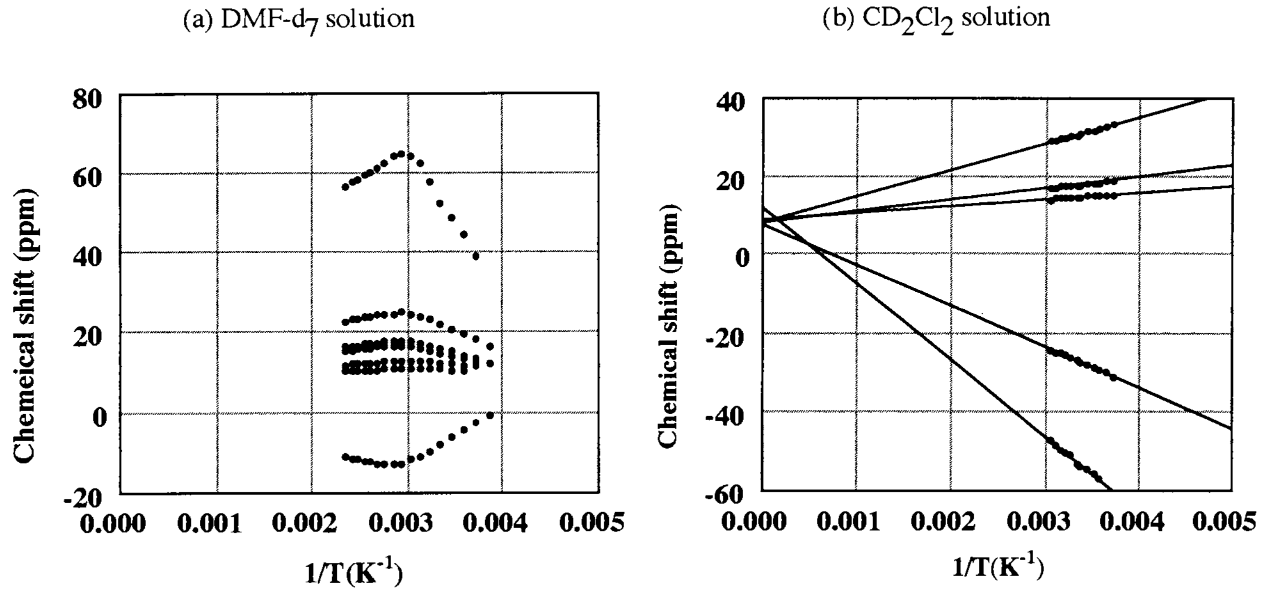


Fig. 2. Curie plots of [Co(II)(saloph)] in (a) DMF-d_7 (70 mM) and (b) CD_2Cl_2 (27 mM).

In order to find out the reasons for the anti-Curie behavior of the complex in DMF solution, magnetic moments were measured by the Evans method[9,10] at various temperatures using CH_2Cl_2 as reference substance. The results are given in Fig. 3. In the case of DMF solution (51 mM), magnetic moment was ca. 2.0 B.M. in the temperature range between 89 and 68 °C and decreased to 0 B.M. below -35 °C. Since the change in magnetic moments was reversible, the irreversible formation of diamagnetic complexes such as Co(III) species can be ruled out. In fact, the ^1H NMR spectrum of diamagnetic [Co(III)(saloph)]I in DMF-d_7 solution was completely different from that of [Co(III)(saloph)] at -35 °C. The most reasonable explanation for

$$2\,[\mathrm{Co(II)(saloph)(DMF)}] \rightleftharpoons [\mathrm{Co(II)(saloph)(DMF)}]_2 \qquad (1)$$

the anomalous temperature dependence in DMF solution is the transformation of the low spin (S = 1/2) monomeric species to an antiferromagnetically coupled dimeric species at lower temperatures as shown in equation (1). Concentration dependence in Curie plots also support the equilibrium between monomeric and dimeric species. The crystallographic study of the analogous [Co(II)(salen)] revealed that the complex exists as a discrete five coordinate dimer.[11] Broadening of the signals observed at low temperature might suggest either that the solution viscosity increases or that the rate of interconversion between these species decreases on the NMR time scale.

In contrast to the case in DMF solution, the magnetic moments of [Co(II)(saloph)] in CH_2Cl_2 (26 mM) were nearly constant, 1.4 B.M., in the temperature range between -35 °C and 37 °C. The result suggests that the complex exists as the low spin monomer in non-coordinating solvents at least in this temperature range and at this concentration. Further work is in progress to elucidate the structure and dynamics behavior of this new species.

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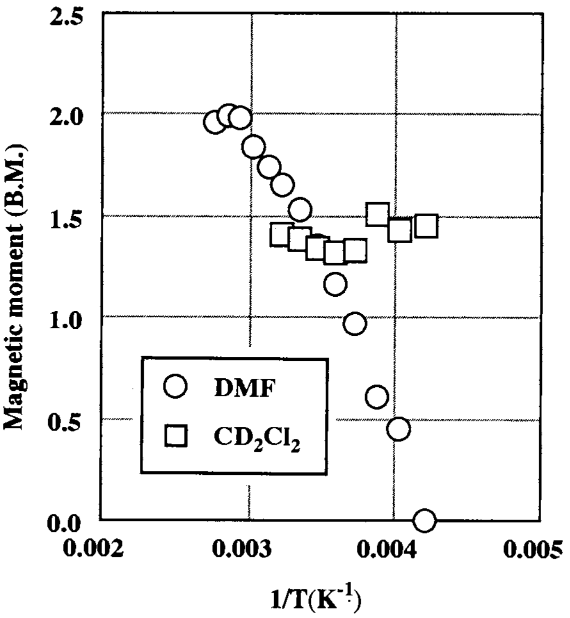

Fig. 3. Temperature dependence in magnetic moments of [Co(II)(saloph)] in DMF and CH_2Cl_2 solutions. Sample concentrations are 51 mM and 26 mM, respectively.

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