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# ESR STUDIES OF THE SPIN-EXCHANGE INTERACTION AND THE DIMERIC STRUCTURE OF N,N'-BIS(3-NITROSALICYLIDENE)-iso-BUTYLENEDIAMINO-COPPER(II) IN FROZEN NITROETHANE SOLUTIONS

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The temperature variation of the intensity of $\Delta M = 2$ transitions over the range 4.2 to 1.7 K indicates that the triplet state lies $2.2 \pm 0.2\ \mathrm{cm}^{-1}$ above the ground singlet state. The computer simulations of the ESR spectra indicates that the dimeric structure has markedly changed from those of the other quadridentate Schiff base complexes of copper(II) in frozen solutions.

In our previous paper,$^{1),2)}$ it has been revealed that the angles ($\xi$) between the $g_{/\!/}$ axes and the copper-copper axes of the dimers of various quadridentate salicylaldehyde Schiff base complexes of copper(II) in frozen toluene solutions are considerably smaller than those of the bidentate ones. However, new experimental results are obtained that the dimeric structures have markedly changed with the nitro-groups at the positions of 3 in the phenyl rings of the Schiff bases. Though the complexes of the type generally represented as Cu($3NO_2$-SalB) (see Fig. 1) are scarcely soluble in toluene, they are considerably soluble in various nitroalkanes and exhibit intense ESR signals due to triplet dimers. Nitroalkane solutions of many other Cu(nX-SalB) which are soluble in toluene did not exhibit the triplet ESR signals.

The 77 K ESR spectra of Cu($3NO_2$-Salibn) in nitroethane are shown in Fig. 2. The magnetic parameters of the triplet dimers were defined in the same manner as previously described and listed in Table 1 with the previously obtained parameters of Cu(Salpn) in toluene.$^{2)}$ In contrast to the parameters of the doublet state monomers, those of the triplet state dimers have markedly changed with the 3-nitro-groups. The parameters of the triplet dimers of Cu($3NO_2$-Salibn) exhibited the characteristics of the non-coaxial g and fine-structure tensors, that is, $g_{M/\!/} > g_2$ and $A_{M/\!/}/2 > A_1 > A_h$, whereas those of Cu(Salpn) exhibited the characteristics of the coaxial ones, that is, $g_{M/\!/} \approx g_2$ and $A_{M/\!/}/2 \approx A_1 \approx A_h$. Moreover, $D_2$ value of Cu($3NO_2$-Salibn) is considerably larger than that of Cu(Salpn) in toluene. These experimental results suggest that the structure of the triplet dimers has changed with the 3-nitro-groups.

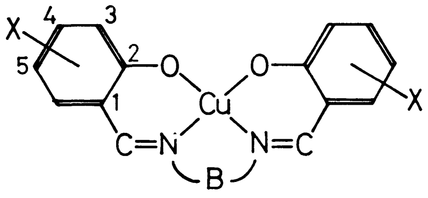


Fig. 1. Cu(nX-SalB).
B; ibn = $C(CH_3)_2CH_2$
pn = $C(CH_3)HCH_2$
en = $CH_2CH_2$

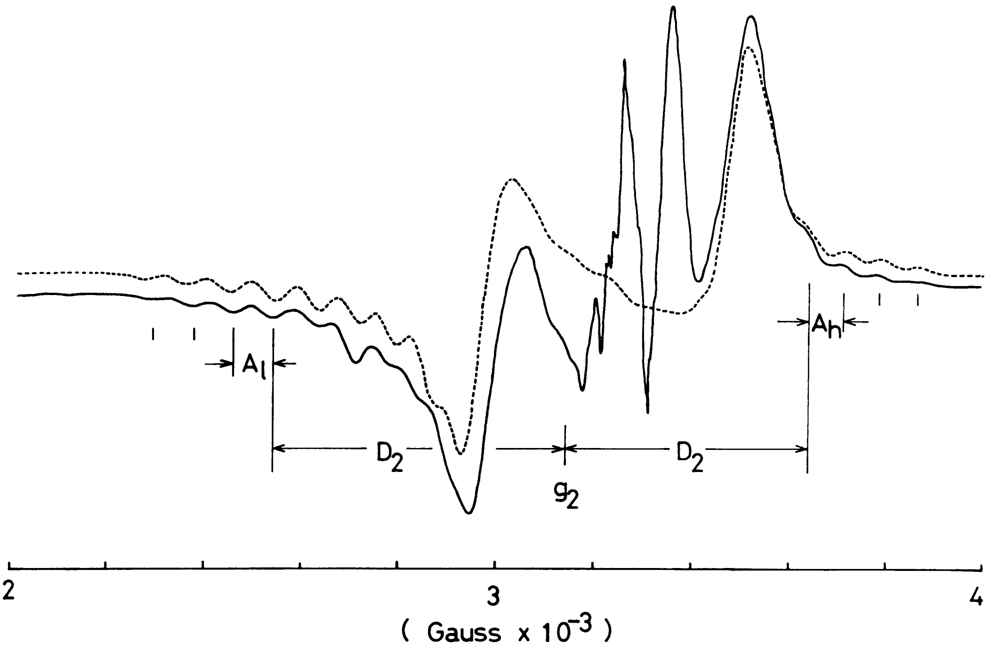
Generally, the fine-structure tensors of the triplet dimers are the sums of the spin-dipole interaction ($D_{dd}$) and the pseudo-dipole interaction ($D_{pseudo}$)

which can be estimated from Eqs.(1) and (2),[3),4)]

$$D_{dd} = - \frac{0.65 g_2^{\,2}}{r^3} \tag{1}$$

$$D_{pseudo} = \frac{J}{8} \left\{ \frac{1}{4} (g_{/\!/} - 2)^2 - (g_{\perp} - 2)^2 \right\} \tag{2}$$

where $J$ is the energy difference between a triplet state and a singlet state, and where r is the distance between the two copper ions. In order to estimate the dimeric structure from the computer simulations of the ESR spectra, it is necessary to evaluate the magnitude of the $J$ value. However, no $J$ values for the dimers of copper(II) complexes of this type in frozen solutions have ever been reported. Therefore, we have determined the $J$ value of Cu(3$NO_2$-Salibn) in nitroethane by the method described below.



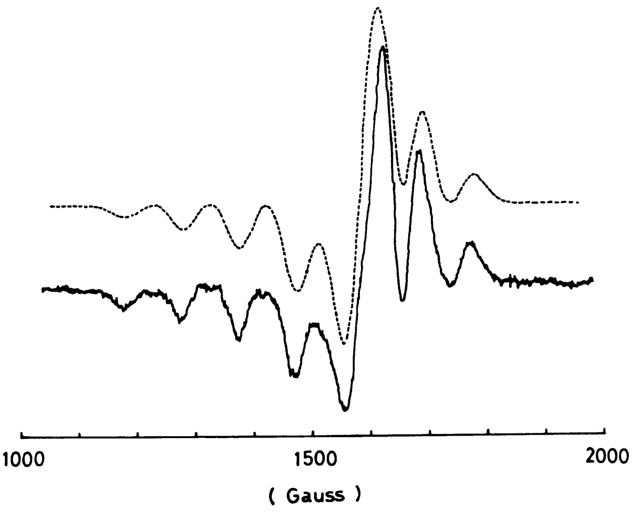


Fig. 2. ESR spectra of Cu(3$NO_2$-Salibn). full lines: observed spectra at 77 K for saturated nitroethane solution. dotted lines: simulated spectra with the parameters, $g_{/\!/} = 2.20$, $g_{\perp} = 2.045$, $A_{/\!/} = 0.0100\ cm^{-1}$, $A_{\perp} = 0.0010\ cm^{-1}$, $r = 3.8$ Å, and $\xi = 35°$. Convolution functions are Gaussian. $\Delta H = 25$ Gauss for $\Delta M = 1$, and $\Delta H = 22$ Gauss for $\Delta M = 2$.

TABLE 1. MAGNETIC PARAMETERS AT X-BAND

| | Dimer | | | | Monomer | |
|---|---|---|---|---|---|---|
| | $g_2$ | $D_2$(Gauss) | $A_1$(Gauss) | $A_h$(Gauss) | $g_M$ | $A_M$ (Gauss) |
| Cu(3$NO_2$-Salibn) | 2.153 | 544 | 84 | 77 | 2.212[a)] | 196[a)] |
| Cu(Salpn) | 2.190 | 428 | 100 | 100 | 2.197 | 207 |

a) these values were determined from the spectra of nitromethane solutions.

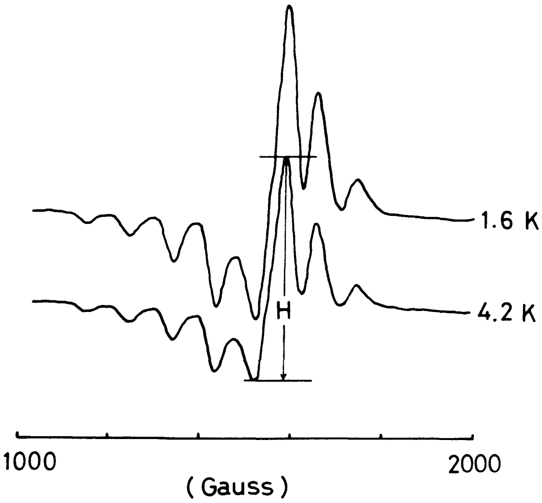


Fig. 3. ESR spectra ($\Delta M = 2$) of the saturated nitroethane solutions at 4.2 K and 1.6 K.

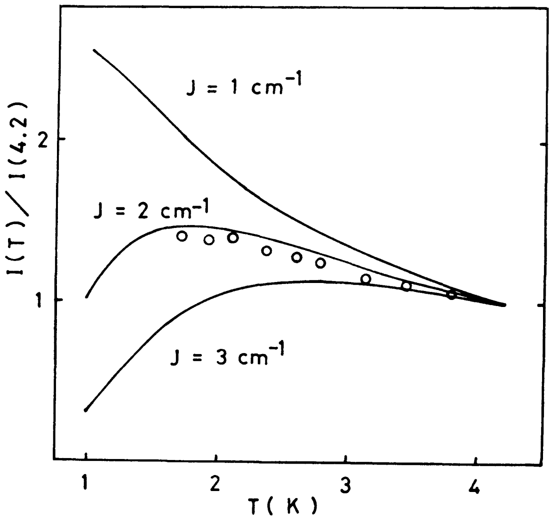


Fig. 4. Temperature variations of relative intensities. full lines: calculated from Eq. (3), o: experimentally obtained values.

The spectral intensity of triplet dimers is proprtional to the paramagnetic susceptibility of the dimer systems, and expressed as Eq. (3),

$$I = \frac{c}{T\left\{3 + \exp\left(\frac{J}{kT}\right)\right\}} \tag{3}$$

where c is a proportionality constant. Therefore, J values can be estimated from the temperature dependence of the spectral intensity due to the triplet dimers. As the peaks of $\Delta M = 2$ transitions are well separated from those of $\Delta M = 1$ transitions, the I in Eq. (3) is well represented by the integrated intensity of the $\Delta M = 2$ transitions. Figure 3 shows the spectra of $\Delta M = 2$ transitions at 4.2 K and 1.6 K. These spectra were measured with an improved insertion type liquid helium dewar in conjunction with the room temperature cavity of a Hitachi 771 spectrometer.[5)] The temperature of the smaple was determined by the vapour pressure of liquid helium. As the linewidths of these spectra did not change between 1.6 K and 4.2 K, the relative integrated intensity for these spectra can be calculated from the peak height (H) in the first derivative spectra. It was observed that the spectral intensity at 1.6 K increased proportionally to the square root of the magnitude of the microwave powers. This phenomenon indicates that the signals at 1.6 K are not saturated. Therefore, the validity of Eq. (3) for the determination of the J values has been justified. Figure 4 shows the calculated and experimentally obtained relative intensity changes of $\Delta M = 2$ transitions in the unit of the spectral intensity at 4.2 K. The J value of Cu($3NO_2$-Salibn) dimers in nitroethane was estimated from this figure at $2.2 \pm 0.2$ $cm^{-1}$. This J value clearly indicates that the contribution of the pseudo-dipole interaction to the observed fine-structure splittings of the triplet ESR spectra can be neglected.

Simulations of the triplet ESR spectra for the non-coaxial spin-Hamiltonian expressed as Eq. (4) were performed as previously described.$^{1)}$

$$\mathcal{H} = \beta g_{/\!/}(S_xH_x + S_yH_y) + g_{\perp}S_zH_z + A_{/\!/}(S_xI_x + S_yI_y) + A_{\perp}S_zI_z + H_{dd} \qquad (4)$$

$H_{dd}$ in Eq. (4) is the spin-dipole interaction tensor. The perturbation calculations were made to the second order for both the fine-structure and hyperfine-structure tensors. As is shown in Fig. 2, the observed spectra can well be simulated by the following spin-Hamiltonian parameters; $g_{/\!/} = 2.20$, $g_{\perp} = 2.045$, $A_{/\!/} = 0.0100$ $cm^{-1}$, $A_{\perp} = 0.0010$ $cm^{-1}$, $r = 3.80$ Å, and $\xi = 35°$. The best fit set of the parameters was chosen by the method described before.$^{1)}$ Thus, the r and $\xi$ values of Cu($3NO_2$-Salibn) are rather similar to those of the dimers of many bidentate salicylaldehyde Schiff base complexes of copper(II) in toluene than to those of the other quadridentate ones in toluene.$^{1),2)}$ It should be also noted that the J value of Cu($3NO_2$- Salibn) is small and antiferromagnetic. It had been reported that the J value of Cu(Salen) in crystals is -5 $cm^{-1}$.$^{6)}$ These facts suggest that the J values or the dimeric structure in solutions may possibly be different from those in crystals. Further experiments are now in progress for the determinations of the dimeric structure and the J values of the other copper(II) complexes in solutions.

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