ESR Studies of the Structures and Spin-exchange Interactions of the Dimers of Nitro-substituted Salicylaldehyde Schiff-base Complexes of Copper(II) in Frozen Solutions*

Makoto Chikira and Taro Isobe

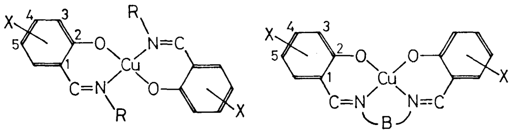
Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira, Sendai 980

(Received March 3, 1975)

The computer simulations of the ESR spectra for the triplet-state dimers of the title complexes in frozen solutions revealed that the dimeric structures change markedly upon nitro-substitutions at the positions of 3 or 5 in the phenyl-rings of the Schiff bases. It was also found that some of these nitro-substituted copper(II) complexes form 1:1 molecular complexes with bis(*N*-salicylideneisopropylaminato)copper(II) in toluene. The dependence of the ESR spectral intensities for the $\Delta M=2$ transitions upon the temperature in the range of 1.57–4.2 K indicated that the intra-dimer spin-exchange interactions are weakly anti-ferromagnetic (0.7—2.2 cm^{-1}).

Recently, many mononuclear copper(II) complexes have been found to be dimerized in solutions.[1–10] In our previous paper, it has been revealed that the angle (ξ) between the $g_{//}$ axis and the copper-copper axis for the dimers of various quadridentate salicylaldehyde Schiff-base complexes of copper(II) in frozen toluene solutions is considerably smaller than that for the bidentate ones.[6] However, we have now obtained a new experimental result that the dimeric structures of the Schiff-base complexes of copper(II) in frozen solutions change markedly upon the introduction of nitro-groups into the phenyl-rings of the Schiff bases at the 3 or 5 position. Moreover, it has been found that the nitro-substituted bidentate Schiff-base complexes of copper(II) form 1:1 molecular complexes in toluene with bis(*N*-salicylideneisopropylaminato)copper(II), which has no ability to be dimerized in toluene.

The purpose of this paper is to estimate the dimeric structures and intra-dimer spin-exchange interaction energies for these dimers and to investigate the nature of these dimerizations in solutions.



Cu(nX-RSal) Cu(nX-SalB)

Fig. 1. Schematic illustrations of salicylaldehyde Schiff-base complexes of copper(II). Following abbreviations were made.
Me=CH_3, Et=C_2H_5, *n*-Pr=C_3H_5, *iso*-Pr=$(CH_3)_2CH$, *t*-Bu=$C(CH_3)_3$, MeO=CH_3O, en=C_2H_4, pn=(CH_3)-$CHCH_2$, ibn=$(CH_3)_2CCH_2$, tren=$(CH_2)_3$.

Experimental

Materials. The copper(II) complexes generally represented as Cu($n$$NO_2$-RSal) and Cu($n$$NO_2$-SalB) (see Fig. 1) were prepared according to the method of Sacconi and Ciampolini.[11] Commercial toluene and nitroalkanes were purified by the usual methods.[12]

Measurements. The ESR spectra were measured at 77 K and in the range of 1.57—4.2 K. An improved insertion-type liquid helium Dewar in conjunction with a room-temperature cavity of a HITACHI 771 X-band ESR spectrometer was used for the measurements in the low-temperature range. The temperature below 4.2 K was obtained by pumping on liquid helium by means of a vacuum pump (150 l/min) and a manostat.

The sample solutions were transferred into thin quartz tubes (o.d. 2.0 mm). In order to secure thermal contact between the sample and liquid helium, the upper parts of the tubes were made open so that the tubes could be filled with the liquid helium. The relation between the microwave power and the intensity was examined at the lowest temperature of the measurement in every case in order to remove the effect of saturation in the measurement of the ESR spectral intensity.

Results and Discussion

Figure 2 shows the observed ESR spectra of Cu(5NO_2-EtSal) in toluene at 77 K. In general, the introduction of nitro-groups into the phenyl-rings of the Schiff base resulted in a decrease in the solubility of the copper(II) complexes in toluene. On the other hand, the ratio of dimers to monomers considerably increased with the nitro-substitutions. We have previously reported that, in the case of bidentate Schiff-base complexes of copper(II) in toluene, the dimer formations are seriously inhibited by methyl or methoxy groups at the 3 positions in the phenyl-rings of the Schiff bases.[6] However, 3-nitro-groups did not hinder the dimerization at all. Moreover, the ratio of the triplet-state spectral intensity to the doublet-state one for Cu(3NO_2-EtSal) in toluene was larger than that for Cu(EtSal) at the same concentration. A similar correlation between the solubility and the ratio of dimers to monomers in solutions has been reported by Yokoi for bis(*t*-butylacetoacetato)-copper(II) in hydrocarbon solvents.[3]

The magnetic parameters for triplet-state dimers were defined in the manner previously described;[5,6] they are listed in Table 1, together with the data previously obtained for unsubstituted complexes.[5] In contrast to the parameters for the doublet-state monomers, those for the triplet-state dimers changed markedly with the nitro-substitutions. The triplet-state dimers of Cu(3NO_2-EtSal) and Cu(5NO_2-EtSal) have the magnetic parameters characteristic of coaxial g and fine-structure tensors, that is, $g_2 \approx g_{M//}$ and $|A_{M//}/2| \approx A_1 \approx A_h$. In order to estimate the distance between the two copper ions and the ξ angle for theses dimers, the simulation

---

* Part of this report was preliminarily published in *Chem. Lett.*, **1974**, 865.

of the triplet ESR spectra was performed as has previously been described5,10) on the basis of the spin-Hamiltonian expressed as:

$$\mathscr{H} = \beta g_{\perp}(S_xH_x+S_yH_y) + \beta g_{//}S_zH_z + A_{\perp}(S_xI_x+S_yI_y) + A_{//}S_zI_z+H_{dd}-JS_1\cdot S_2 \qquad (1)$$

where H_{dd} is the point-spin-dipole interaction tensor; the other symbols have their usual meanings. The resonance magnetic fields were calculated by means of the perturbation calculations to the second order for both H_{dd} and hyperfine terms. The angular dependence of the transition probability was calculated by the use of the spin functions obtained from the first-order perturbation calculations only for H_{dd}.

As Fig. 2 shows, the observed spectra for Cu(5NO$_2$-EtSal) in toluene can be well simulated with the following spin-Hamiltonian parameters: $g_{//}=2.225$, $g_{\perp}=2.05$, $|A_{//}|=0.0095$ cm^{-1}, $|A_{\perp}|=0.0010$ cm^{-1}, r(copper–copper distance)$=4.02$ Å, and $\xi=15°$. The estimated values of r and ξ are very close to those for the dimers of Cu(EtSal) in methylcyclohexane9) and for various quadridentate Schiff-base complexes of copper(II) in toluene.6)

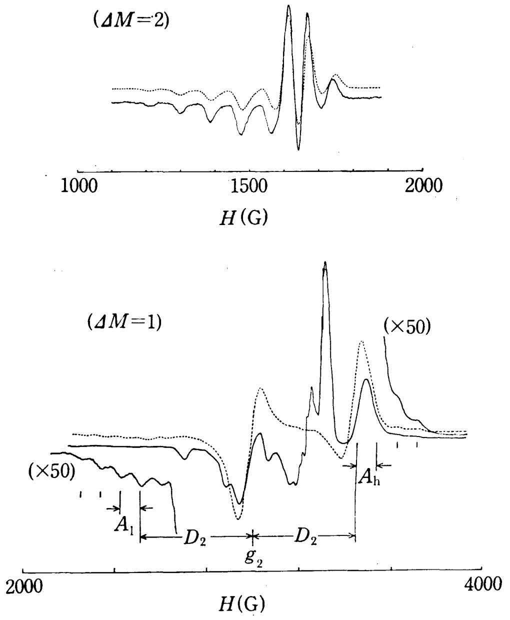


Fig. 2. ESR spectra of Cu(5NO$_2$-EtSal) in toluene at 77 K.
Broken lines: calculated spectra with the parameters, $g_{//}=2.225$, $g_{\perp}=2.050$, $|A_{//}|=0.0095$ cm^{-1}, $|A_{\perp}|=0.0010$ cm^{-1}, $r=4.02$ Å, $\xi=15$ °, ΔH (Gaussian)$=30$ G ($\Delta M=1$) and 15 G ($\Delta M=2$). Microwave frequency; $\nu=9.2576$ GHz.

The triplet ESR spectra of Cu(nNO$_2$-RSal) in toluene markedly changed in their line-shape upon the addition of a large excess of Cu(*iso*-PrSal). Figures 3 and 4 show the ESR spectra of Cu(5NO$_2$-EtSal) and Cu(5NO$_2$-*iso*-PrSal) respectively with a large excess of Cu(*iso*-PrSal) in toluene. The A_1 values (70 G) for these spectra are considerably smaller than those (87 G) for the dimers of Cu(5NO$_2$-EtSal) in toluene. The peaks near 3500 G are markedly broadened. It should be noted that neither Cu(*iso*-PrSal) nor Cu(5NO$_2$-*iso*-PrSal) in toluene exhibited triplet-sate ESR signals. Therefore, these triplet signals may be due to 1 : 1 molecular complexes of Cu(5NO$_2$-RSal) with Cu(*iso*-PrSal), although it remains uncertain whether these 1 : 1 complexes are the dimers of mixed-ligand complexes or the associated complexes of Cu(nNO$_2$-RSal) and Cu(RSal).

Since the magnetic parameters for the monomers of Cu(5NO$_2$-*iso*-PrSal) are almost equal to those of Cu-(*iso*-PrSal), Eq. (1) may still be a good approximated spin-Hamiltonian for the analysis of the triplet ESR

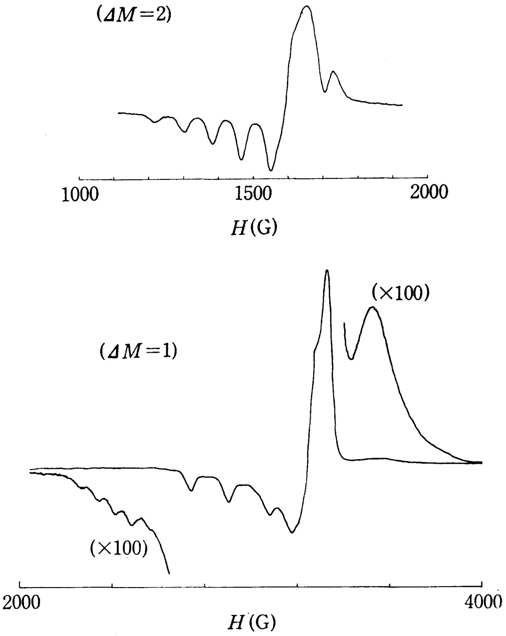


Fig. 3. ESR spectra of Cu(5NO$_2$-EtSal) with a large excess of Cu(*iso*-PrSal) in toluene at 77 K. $\nu=9.258$ GHz.

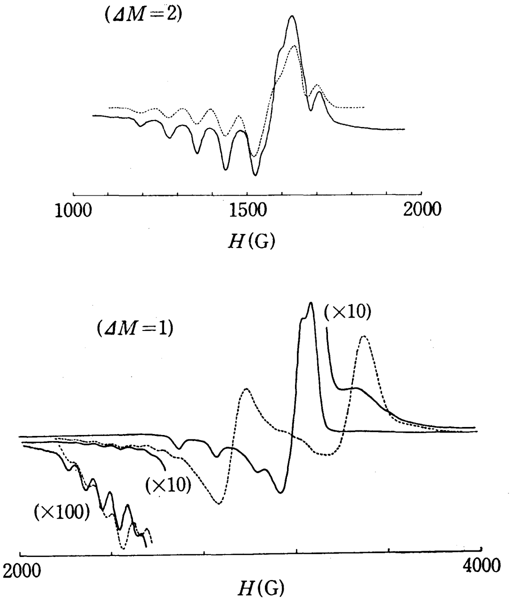


Fig. 4. ESR spectra of Cu(5NO$_2$-*iso*-PrSal) with a large excess of Cu(*iso*-PrSal) in toluene at 77 K. Broken lines: calculated spectra with the parameters, $g_{//}=2.230$, $g_{\perp}=2.040$, $|A_{//}|=0.0085$ cm^{-1}, $|A_{\perp}|=0.0015$ cm^{-1}, $r=3.75$ Å, $\xi=35$ °, ΔH(Gaussian)$=30$ G ($\Delta M=1$) and 20 G ($\Delta M=2$).

spectra of the 1: 1 molecular complexes. The best fit between observed and calculated spectra could be obtained with the following parameters: $g_{//}=2.23$, $g_{\perp}=2.04$, $|A_{//}|=0.0087\ \mathrm{cm}^{-1}$, $|A_{\perp}|=0.0015\ \mathrm{cm}^{-1}$, $r=3.75$ Å, and $\xi=35°$. These parameters are close to those of the dimers of Cu(*iso*-PrSal) in methylcyclohexane.[9]

In contrast with Cu(*iso*-PrSal), Cu(*t*-BuSal) did not form such 1: 1 complexes with Cu(nNO$_2$-RSal) in toluene; the excess of Cu(*t*-BuSal) in the toluene solutions of Cu(5NO$_2$-RSal) did not alter the observed parameters of the triplet ESR spectra due to the dimers of Cu(5NO$_2$-RSal). In this case, only the broadenings of the spectra were observed. It has been reported by Yokoi that two species with different degrees of tetrahedral deformation exist for Cu(*iso*-PrSal) in toluene, while only one species with a high degree of that deformation exists for Cu(*t*-BuSal) in toluene.[14] It is of interest that the $g_{//}$ and $|A_{//}|$ values for the 1: 1 complexes of Cu(5NO$_2$-RSal) with Cu(*iso*-PrSal) are closer to those for the species of Cu(*iso*-PrSal) with a lower degree of tetrahedral deformation. The difference between Cu(*t*-BuSal) and Cu(*iso*-PrSal) in the ability to form 1: 1 complexes with Cu(nNO$_2$-RSal) is probably due to the differences in the tetrahedral deformation of the ligand coordination. A similar tendency in the dimer formation has been observed for Cu(RSal) in methylcyclohexane.[9]

The copper(II) complexes generally represented as Cu(nNO$_2$-SalB) are scarcely soluble in toluene, while Cu(3NO$_2$-Salpn) and Cu(3NO$_2$-Salibn) are considerably soluble in various nitroalkanes and exhibit intense ESR signals due to triplet dimers. The nitroalkane solutions of many other Cu(nX-SalB) complexes (X= H, Me, Br, and MeO) which were soluble in toluene did not exhibit the triplet ESR signals. The effect of the bridges between the iminoic nitrogens on the dimer formations of the 3-nitro-substituted Schiff-base complexes in nitroalkanes was quite analogous to that of the unsubstituted complexes in toluene:[6] Cu(3NO$_2$-Salen) is insoluble in nitroalkanes, and the amount of the dimers of Cu(3NO$_2$-Salpn) in nitroalkanes is larger than that of Cu(3NO$_2$-Salibn), while Cu(3NO$_2$-Saltren) is scarcely dimerized in nitroalkanes.

The ESR spectra of Cu(3NO$_2$-Salibn) in nitroethane at 77 K are shown in Fig. 5. In contrast with the dimers of Cu(nNO$_2$-RSal) in toluene, those for Cu-(3NO$_2$-SalB) in nitroalkanes have the parameters characteristic of the non-coaxial spin-Hamiltonian tensors- that is, $g_{\mathrm{M}//}>g_2$ and $|A_{\mathrm{M}//}/2|>A_{\mathrm{l}}>A_{\mathrm{h}}$. In addition, the D_2 values of Cu(3NO$_2$-SalB) is considerably larger than that of Cu(SalB) in toluene.[6] As Fig. 5 shows, the observed spectra could be simulated with those parameters: $g_{//}=2.20$, $g_{\perp}=2.045$, $|A_{//}|=0.0100$ cm^{-1}, $|A_{\perp}|=0.0010\ \mathrm{cm}^{-1}$, $r=3.80$ Å, and $\xi=35°$. These r and ξ values are closer to those of Cu(RSal) in toluene than to those of Cu(SalB) in toluene.[6] However, it is still uncertain whether the phenolic oxygen atoms in the Schiff base coordinate to the adjacent copper ions in the dimer at their apical positions, because we simulated the observed spectra with axially symmetric g and A tensors.

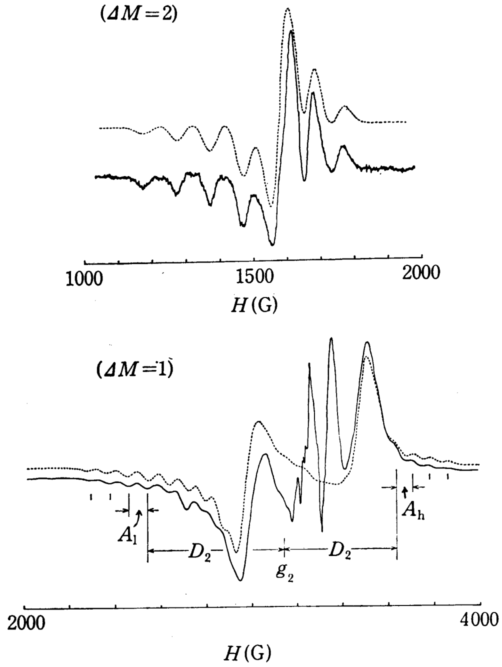


Fig. 5. ESR spectra of Cu(5NO$_2$-Salibn) in nitroethane at 77 K. Broken lines: calculated spectra with the parameters, $g_{//}=2.20$, $g_{\perp}=2.045$, $|A_{//}|=0.0100$ cm^{-1}, $|A_{\perp}|=0.0010$ cm^{-1}, $r=3.80$ Å, $\xi=35$ °, ΔH (Gaussian) =25 G (ΔM=1) and 22 G (ΔM=2). ν=9.297 GHz.

Table 1. Magnetic parameters for copper(II) dimers (X-band)

Ligand	g_2	D_2 (G)	A_{l} (G)	A_{h} (G)	$g_{\mathrm{M}//}$	$A_{\mathrm{M}//}$ (G)
5NO$_2$-EtSal	2.221	469	87	87	2.221	186
3NO$_2$-EtSal	2.222	466	86	86	2.226	184
(EtSal)[a]	2.171	564	80	67	2.227	180
5NO-n-PrSal			83		2.227	180
3NO$_2$-Salpn	2.156	548	89	80		
3NO$_2$-Salibn	2.153	544	84	77	2.212	196
(Salpn)[a]	2.190	428	100	100	2.197	207

a) Ref. 6.

Intra-dimer Spin-exchange Interactions. When an ESR spectrum due to triplet-state dimers is not saturated, the spectral intensity (I) is proportional to the paramagnetic susceptibility of the dimer system; it can be expressed as:

$$I = c/T(3+\exp(-J/kT)) \qquad (2)$$

where c is an appropriate proportionality constant. Since the $\Delta M=2$ spectra for the present dimers are quite different in position from the allowed spectra due to both dimers and monomers, the I in Eq. (2) can be estimated from the intensity of the $\Delta M=2$ spectra alone.

Figure 6 shows the $\Delta M=2$ spectra of Cu(3NO$_2$-Salibn) in frozen nitroethane at 1.6 and 4.2 K. Since the line-shapes or linewidths of these spectra did not vary over this temperature range, the relative intensity of the triplet ESR spectra is equal to the relative peak height of a certain line (H) in the first derivative $\Delta M=2$ spectra. On the other hand, the shape of the $\Delta M=2$ spectra for Cu(5NO$_2$-EtSal) in toluene changed with the temperature even at the minimum level of microwave power (0.48 mW) at which the $\Delta M=2$ spectra can be obtained with a satisfactory signal-to-noise ratio on our spectrometer. The examination of the relation between the spectral intensity and the microwave power revealed that the $\Delta M=2$ spectra at 4.2 K were saturated to some extent even at this microwave power. A similar change in the line-shape at 4.2 K could be observed at a stronger microwave power. These phenomena suggest that the modulations of the intradimer spin-exchange or spin-dipole interaction by thermal vibrations in this temperature range are not sufficient to make the spin-lattice relaxation time short enough to remove the saturation of the ESR signals. Because of the low solubility of Cu(5NO$_2$-EtSal) in toluene, the concentration of the sample cannot be made so high as that of Cu(3NO$_2$-Salibn) in nitroethane. Therefore, the modulation of the interdimer or dimer-monomer spin-dipole interaction in the toluene solutions of only Cu(5NO$_2$-EtSal) may be too weak to recover the spin-lattice relaxation.

This problem, however, could be solved by the addition of a large excess of Cu(*t*-BuSal) to the toluene solutions of Cu(5NO$_2$-EtSal). When an excess of Cu(*t*-BuSal), which does not combine with Cu(5NO$_2$-EtSal), coexists in the solution, the shape of the $\Delta M=2$ spectra no longer depends on the temperature and the intensity increases linearly with the square root of the microwave power over the range of 0.48—4.8 mW (see Fig. 7). This phenomenon indicates that the thermal contact between the spin system of Cu(5NO$_2$-EtSal) and that of Cu(*t*-BuSal) could recover the spin-lattice relaxations. Consequently, the *J* value for the dimers of Cu(5NO$_2$-EtSal) in toluene could be estimated in the way described above by the addition of excess Cu(*t*-BuSal) to the solutions.

In the case of the 1 : 1 complexes of Cu(5NO$_2$-RSal) with Cu(*iso*-PrSal) in toluene, the line shapes of the $\Delta M=2$ spectra depend on the temperature in a more complicated manner. Figure 8 shows the $\Delta M=2$ spectra for the 1 : 1 complexes of Cu(5NO$_2$-EtSal) with Cu(*iso*-PrSal) in toluene at 4.2 and 1.57 K. The linewidth at 1.57 K is quite broad compared to that at 4.2 K. In this case, the broadening of the spectrum is not due to the saturation effect, because the intensity of the $\Delta M=2$ spectra at 1.57 K increased linearly with the microwave power over the range of 0.48—4.8 mW. A similar change in the line-shape was observed for the 1 : 1 complexes of Cu(5NO$_2$-*iso*-PrSal) with Cu(*iso*-PrSal). These changes in the line-shape may be attributed to a considerable decrease in the T_2 (spin-spin relaxation time) and/or in the degree of the structural homogeniety of the 1 : 1 complexes, including their surroundings. Since the line-shape varied in a complicated manner, we did not attempt to estimate the *J* values for these complexes.

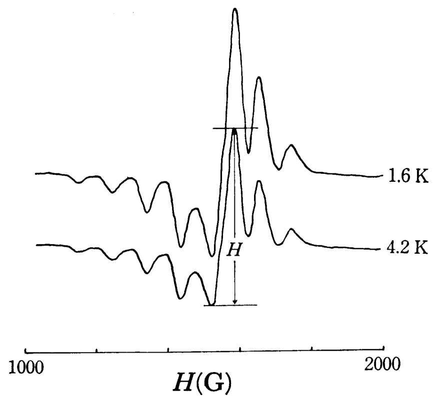


Fig. 6. $\Delta M=2$ spectra of Cu(5NO$_2$-Salibn) in nitroethane at 4.2 and 1.6 K.

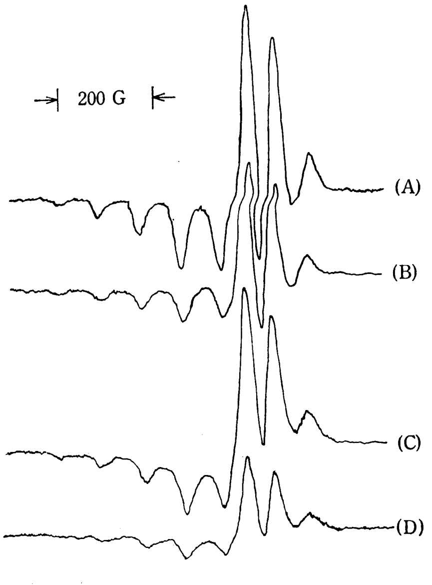


Fig. 7. $\Delta M=2$ spectra of Cu(5NO$_2$-EtSal) in toluene. (A): 1.57 K, (B): 4.2 K without Cu(*t*-BuSal). (C): 1.57 K, (D): 4.2 K with a large excess of Cu(*t*-BuSal).

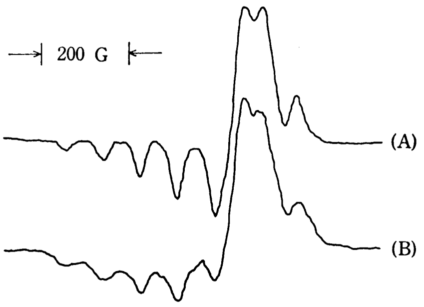


Fig. 8. $\Delta M=2$ spectra of Cu(5NO$_2$-EtSal) with a large excess of Cu(*iso*-PrSal) in toluene. (A): 4.2 K, (B): 1.57 K.

Figure 9 shows the calculated and experimentally determined relative intensity changes of the triplet ESR spectra for the dimers of Cu(5NO$_2$-EtSal) in toluene and of Cu(3NO$_2$-Salibn) in nitroethane, in units of the intensity at 4.2 K. The *J* values estimated from this figure are listed in Table 2, together with the *r* and *ξ* values determined by computer simulations. In this table, the corresponding parameters for the dimers of Cu(MeSal) and Cu(3Me-Salpn) in toluene are also listed. The *J* values for the dimers of Cu(5NO$_2$-EtSal) and Cu(3NO$_2$-Salibn) were antifer-

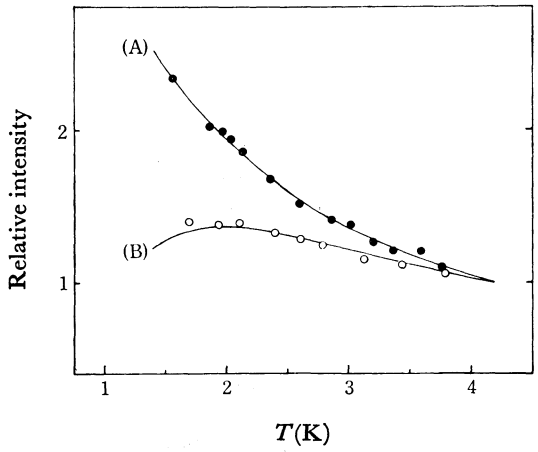


Fig. 9. Temperature dependence of relative intensities for $\Delta M=2$ spectra.
●: Cu(5NO_2-EtSal) with a large excess of Cu(*t*-BuSal) toluene, ○: Cu(3NO_2-Salibn) in nitroethane.
Full lines: calculated curves from Eq. (2). (A) $J=-0.7$ cm^{-1}, (B) $J=-2.2$ cm^{-1}.

TABLE 2. THE J, r, AND ξ VALUES FOR COPPER(II) DIMERS

	Medium	J(cm^{-1})	r(Å)	ξ(°)
Cu(5NO_2-EtSal)	Toluene	-0.7 ± 0.2	4.02	15
(Cu(MeSal))[a]	Toluene	-2.3 ± 0.2	3.75	35
Cu(3NO_2-Salibn)	Nitroethane	-2.2 ± 0.2	3.80	35
(Cu(3Me-Salpn)[a]	Toluene	-1.5 ± 0.3	4.05	15

a) Refs. 7 and 10.

romagnetic, as in the case of the other Schiff-base complexes of copper(II) in frozen solutions.[7,9,10]

We have previously reported that many Cu(*n*X-RSal) and Cu(*n*X-SalB) complexes (X=H, Me, MeO, Br; R=Me, Et, *n*-Pr; B=pn, ibn) in toluene are similar in dimeric structure to Cu(MeSal) and Cu(Salpn) in toluene respectively.[6] Corresponding to the changes in the *r* and ξ values with the nitro-substitutions, marked changes in the J values were observed. Since the nitro-groups in phenyl-rings have a strong electron-attracting power, the π-electron distribution over the copper(II) chelates will be severely modified with these groups. In particular, the affinity of the phenolic oxygen for the adjacent copper(II) ions at their apical positions may be reduced because of a decrease in the π-electron density on the oxygen atoms. Therefore, the contribution of such apical coordinations of the phenolic oxygen atoms to the spin-exchange interactions may decrease upon the nitro-substitutions. However, this is merely one possible explanation for the changes in the dimeric structure and in the J values with the nitro-substitutions. The fact that the dimer formation was markedly promoted by the nitro-groups suggests that the change in the dispersion or polarization forces between the ligands may play an important role in determining the dimeric structure and spin-exchange interactions.

Since the dimeric structures have still not been revealed in detail, it is impossible to discuss the mechanisms of the intradimer spin-exchange interactions further. However, the results obtained above support the previous conclusion that dimeric structures for copper(II) chelates in frozen solutions are determined by the subtle balance of many kinds of interactions between monomeric halves in the dimers and between the dimers and solvents.[3,6,9,10]

The authors wish to express their thanks to Dr. Hiroshi Yokoi for his valuable discussions and suggestions during this work.

References

1) T. D. Smith and J. R. Pilbrow, *Coordin. Chem. Rev.*, **13**, 173 (1974), and the references therein.
2) W. E. Hatfield, *Inorg. Chem.*, **11**, 216 (1972), and the references therein.
3) H. Yokoi and T. Isobe, This Bulletin, **44**, 1446 (1971); *ibid.*, **46**, 447 (1973); *ibid.*, **47**, 497 (1974).
4) H. Yokoi and T. Isobe, *Chem. Lett.*, **1972**, 95.
5) M. Chikira and T. Isobe, This Bulletin, **45**, 3006 (1972).
6) M. Chikira, H. Yokoi, and T. Isobe, *ibid.*, **47**, 2208 (1974).
7) M. Chikira and T. Isobe, *Chem. Phys. Lett.*, **30**, 498 (1975).
8) H. Yokoi and M. Chikira, *J. Amer. Chem. Soc.*, in press.
9) H. Yokoi and M. Chikira, *J. Chem. Soc.*, in press.
10) M. Chikira and T. Isobe, to be published.
11) L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, **1964**, 276.
12) J. A. Riddick and W. B. Bunger, "Organic Solvents," John Wiley & Sons, New York, 1970.
13) Z. Matsumura, M. Chikira, S. Kubota, and T. Isobe, *Rev. Sci. Instrum.*, **45**, 596 (1974).
14) H. Yokoi, This Bulletin, **47**, 3037 (1974).