A Re-investigation of the Dimer ESR Spectra in Several Quadridentate Schiff Base Complexes of Copper(II)

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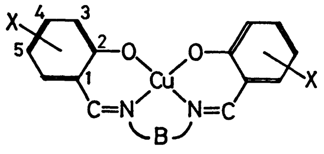
The angle between the $g_{/\!/}$ axis and the copper-copper axis in most parallel planar dimers of the quadridentate salicylaldehyde Schiff base complexes of copper(II) in toluene or xylene has been reconfirmed to be not $\approx 35°$, but $\approx 17°$, by a computer simulation of the dimer ESR spectra at both the K and X-bands. In order to remedy the shortcomings of the so-called point-dipole approximation generally used in the simulation, a delocalization model, in which the delocalization of each unpaired electron on the copper atom and its surrounding four ligand atoms is explicitly taken into consideration, has been discussed in some detail. The delocalization effect has been proven to be highly significant in estimating dimeric structures reliably. An application of this model to the structural estimation of several dimers in solutions has also been made.

A number of mono-nuclear planar copper(II) complexes have been found to exist as dimers in crystals[1–4] and in solutions.[5–11] The structures of dimers in solutions have been estimated by the computer simulation of the dimer ESR spectra.[6–11,13–16] We have previously reported that many quadridentate salicylaldehyde Schiff base complexes of copper(II) (hereafter abbreviated as Cu(nX-SalB), Fig. 1) in toluene form dimers with almost coaxial g and fine-structure tensors,[12] together with the fact that the dimeric structures of Cu(SalB) in solution are markedly different from those of Cu($3NO_2$-SalB).[13]



Cu(nX-SalB)

Fig. 1. Quadridentate salicylaldehyde Schiff base complexes of copper(II).
Abbreviations: Me=$-CH_3$, en=$-CH_2CH_2-$, pn=$-CH(CH_3)CH_2-$, ibn=$-C(CH_3)_2CH_2-$, MeO=$-OCH_3$, tn=$-CH_2CH_2CH_2-$.

Recently, Cookson *et al.* have reported that the angle, ξ, between the $g_{/\!/}$ axis and the copper-copper axis in the dimers of Cu(nX-SalB) (nX=H or 3MeO and B=pn or tn) in frozen xylene is estimated to be 35° by the computer simulation of the X-band ESR spectra, suggesting that these dimers are similar in structure to that of Cu(Salen) in crystals.[2,14] This value, however, is very different from the value (15°) we ourselves previously estimated for similar systems.[12] More reliable information on the mutual orientation of these axes can often be obtained by investigating simultaneously the dimer ESR spectra at different microwave frequencies. In this study, therefore, the dimeric structures for Cu(3Me-Salpn) in toluene, Cu(Salpn) in xylene, and Cu($3NO_2$-Salibn) in nitroethane were examined by the computer simulation of the K-band ESR spectra as well as the X-band ones.

In most studies so far reported on the computer simulation of dimer ESR spectra, the magnetic dipole interaction has been calculated using the so-called point-dipole approximation.[6,15,16] Actually, however, each unpaired electron in a dimer is delocalized on the copper atom and its surrounding ligand atoms. It has been suggested that there is a tendency for the Cu–Cu distance, r, and the ξ value in the dimer to be over- and under-estimated respectively by the use of the point-dipole approximation.[17,18] A notable example of the delocalization effect has recently been presented for the dimer of bis(dialkyldithiocarbamato)copper(II) (Cu(dtc)$_2$) by Van Rens and De Boer.[19] By calculating the fine-structure tensor of the dimer from the results of extended Hückel molecular orbital calculations, they have indicated that the delocalization reduces the dipolar interaction by a factor of two, and that one of the principal axes of the fine-structure tensor bisects the angle between the $g_{/\!/}$ and Cu–Cu axes.

Although the metal-ligand bondings of Cu(dtc)$_2$ are strongly covalent,[20] the question still comes to our minds whether or not the delocalization effect can be neglected in many other cases. In order to obtain detailed information on errors inherent in the point-dipole approximation, a delocalization model was discussed and checked by applying the model to two dimeric systems of known structures in the title complexes. Using the results, an attempt was made to reestimate the structures of several dimers in solution more reliably.

Experimental

All the quadridentate salicylaldehyde Schiff base complexes of copper(II) used here had been prepared and purified in previous works.[12,13] The Cu(Salen)·$CHCl_3$ was prepared by the recrystallization of Cu(Salen) from chloroform.[21] The sample of Cu(Salen) diluted in the nickel complex was prepared by the recrystallization of a 5: 1 mixture of Ni(Salen) and Cu(Salen) from nitrobenzene, and the Ni(Salen) was prepared by the same method. All the solvents used were purified by the usual methods.[22]

The ESR spectra at 77 K were recorded on Hitachi 771 X-band and MES-4001 K-band ESR spectrometers and analyzed by computer simulation. All the calculations in the simulation were carried out at the Computer Center of Tohoku University on a NEAC 2200 computer, using fundamentally the same program as in previous works,[7,13] except that the delocalization of each unpaired electron was taken into consideration, as will be described later. The co-ordinate system for the present dimers is shown in Fig. 2.

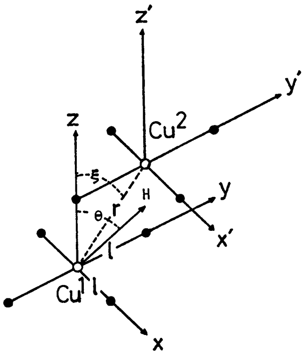


Fig. 2. Co-ordinate system for the dimers.

Results and Discussion

Combined Use of K and X-Band ESR Spectral Simulations. The observed ESR spectra of Cu(3Me-Salpn) in toluene at X and K-bands and of Cu(Salpn) in xylene at K-band are shown in Figs. 3, 4, and 5 respectively, together with the calculated spectra. The $\Delta M=2$ transition probability is inversely proportional to the square of microwave frequency,[15] so that, unfortunately, we have not observed any well-defined $\Delta M=2$ spectra at K-band with our spectrometer because of the low signal-to-noise ratios. The observed X-band and K-band dimer ESR spectra of Cu(3Me-Salpn) in toluene were almost the same as those of Cu(Salpn) in xylene, so their dimeric structures are similar. In this section, only the magnetic and structural parameters estimated by the computer simulation of the dimer ESR spectra using the point-dipole approximation will be discussed.

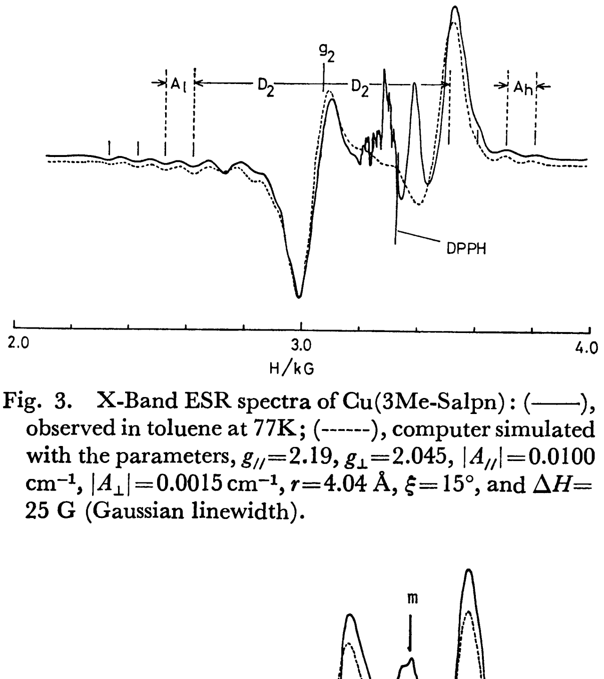


Fig. 3. X-Band ESR spectra of Cu(3Me-Salpn): (——), observed in toluene at 77K; (------), computer simulated with the parameters, $g_{//}=2.19$, $g_{\perp}=2.045$, $|A_{//}|=0.0100$ cm^{-1}, $|A_{\perp}|=0.0015$ cm^{-1}, $r=4.04$ Å, $\xi=15°$, and $\Delta H=$ 25 G (Gaussian linewidth).

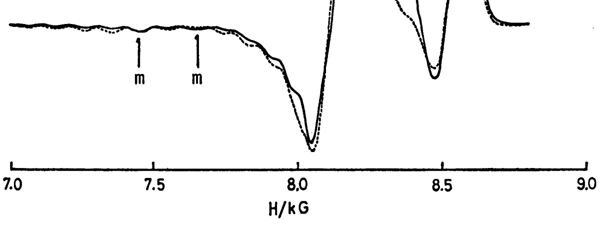


Fig. 4. K-Band ESR spectra of Cu(3M-Salpn): (——), observed in toluene at 77 K; (------), computer simulated with the parameters, $g_{//}=2.19$, $g_{\perp}=2.045$, $|A_{//}|=$ 0.0100 cm^{-1}, $|A_{\perp}|=0.0015$ cm^{-1}, $r=4.04$ Å, $\xi=15°$, and $\Delta H=30$ G. m represents absorption line due to monomers.

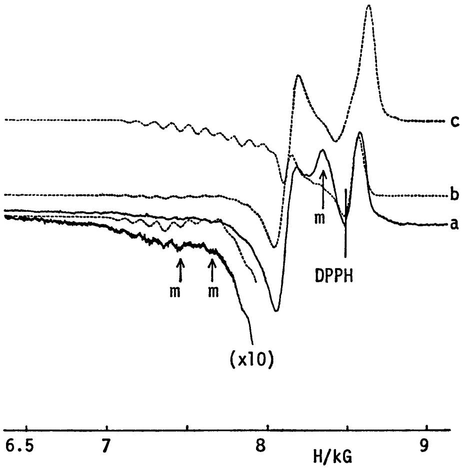


Fig. 5. K-Band ESR spectra of Cu(Salpn): a (solid lines), observed in xylene at 77 K; b and c, computer simulated with the parameters, (b) $g_{//}=2.19$, $g_{\perp}=2.045$, $|A_{//}|=0.0100$ cm^{-1}, $|A_{\perp}|=0.0015$ cm^{-1}, $r=4.05$ Å, $\xi=$ 15°, $\Delta H=25$ Gauss, and (c) $g_{//}=2.18$, $g_{\perp}=2.03$, $|2A_{//}|$ $=0.0225$ cm^{-1}, $|2A_{\perp}|=0.0010$ cm^{-1}, $r=3.95$ Å, $\xi=35°$, $\Delta H=30$ G m represents absorption line due to monomers.

The parameters of (b) and (c) in Fig. 5, which have been estimated from the X-band spectra by us and by Cookson *et al.* respectively for the dimer of Cu(Salpn), are considerably different, especially in ξ. On the basis of the fact that both the A_l and A_h values and the g_2 value are almost equal to the monomer's $A_{//}/2$ and $g_{//}$ values respectively in many quadridentate Schiff base complexes, we have previously concluded that the $g_{//}$ and Cu–Cu axes in these complexes almost coincide; namely, the ξ value is close to 0°,[6,12,13] where the parameters of A_l, A_h, and g_2 are as defined in Fig. 3. Two calculated $\Delta M=1$ spectra (b and c) of Cu(Salpn) at K-band, which we obtained with their respective sets of parameters, are shown in Fig. 5, together with the observed one. It should be noted that no complicated progression of the hyperfine structure in the 7.5—8 kG range (1 G$=10^{-4}$ T) can be seen in the observed K-band spectra of either Cu(3Me-Salpn) in toluene or of Cu-(Salpn) in xylene, but such a progression can be seen in the calculated spectrum of c. The appearance of such a hyperfine structure, therefore, was found to be characteristic of non-coaxial g and fine-structure tensors. In addition, the calculated spectrum of c as a whole is shifted to a little higher magnetic field than the observed one. As one can see in Fig. 5, a much better fit between the calculated and observed spectva at K-band is obtained with the parameters of (b) than with those of (c). We may conclude, therefore, that the ξ value of

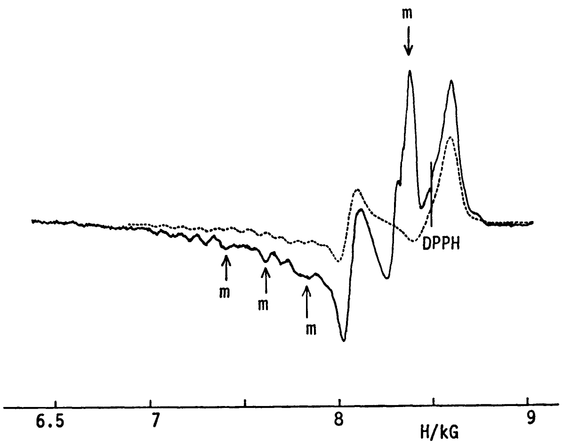


Fig. 6. K-Band ESR spectra of Cu(3NO$_2$-Salibn): (——), observed in nitroethane at 77 K; (------), computer simulated with the parameters, $g_{//}=2.20$, $g_{\perp}=2.045$, $|A_{//}|=0.0100\ \text{cm}^{-1}$, $|A_{\perp}|=0.0010\ \text{cm}^{-1}$, $r=3.8$ Å, $\xi=35°$, $\Delta H=30$ G. m represents absorption line due to monomers.

35° is too large for the present dimer, as far as the point-dipole approximation is concerned.

On the other hand, the dimer of Cu(3NO$_2$-Salibn) in nitroethane is a typical dimer with a larger ξ value. The observed and calculated K-band spectra of this dimer are shown in Fig. 6, in which the parameters used in the calculation were the same as those previously chosen for the X-band spectrum ($\xi=35°$).[13] Although the hyperfine structures due to the monomer were also simultaneously observed in the 7—8 kG range, every peak in the range can be well assigned by comparison with the simulated spectrum. Accordingly, we are led to the conclusion that the dimeric structure of Cu(3NO$_2$-Salibn) in nitroethane is remarkably different from those of many other quadridentate salicylaldehyde Schiff base complexes in toluene.

Errors Inherent in the Point-dipole Approximation. In order to obtain information on errors inherent in the point-dipole approximation, we first simulated the ESR spectra for the dimers of a known structure. The observed X-band spectrum of Cu(Salen)·CHCl$_3$ in the powder state at 77 K is shown in Fig. 7. This spectrum is obviously due to typical $\Delta M=1$ transitions in copper(II) pairs, although no hyperfine structure was observed in it. According to Baker *et al.*,[21] the molecules of Cu(Salen) in Cu(Salen)·CHCl$_3$ crystals exist as dimers with $r=3.37$ Å and $\xi=34°$. The best calculated spectrum, which is also shown in Fig. 7, was obtained with the parameters listed there, in which the g and A values were taken from the monomer spectrum of Cu(Salen) in chloroform and in which the ξ value mentioned above was adopted. The difference of 0.28 Å between the true and estimated r values is probably responsible for the point-dipole approximation used.[17,18]

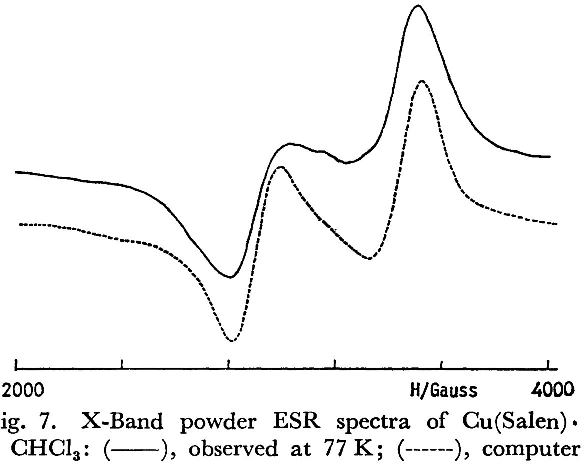


Fig. 7. X-Band powder ESR spectra of Cu(Salen)·CHCl$_3$: (——), observed at 77 K; (------), computer simulated with the parameters, $g_{//}=2.19$, $g_{\perp}=2.04$, $|A_{//}|=0.0100\ \text{cm}^{-1}$, $|A_{\perp}|=0.0010\ \text{cm}^{-1}$, $r=3.65$ Å, $\xi=34°$, and $\Delta H=60$ G.

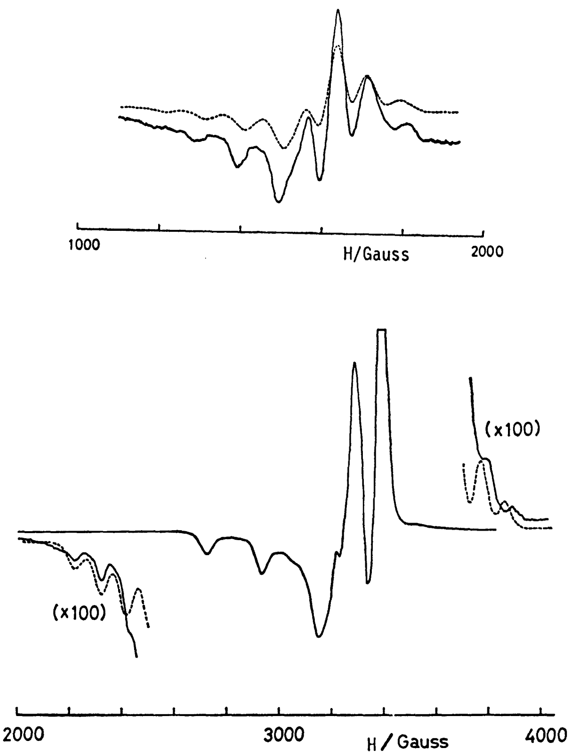


Fig. 8. X-Band powder ESR spectra of Cu(Salen) in Ni(Salen) crystals: (——), observed at 77 K; (------), computer simulated with the parameters, $g_{//}=2.19$, $g_{\perp}=2.04$, $|A_{//}|=0.0100\ \text{cm}^{-1}$, $|A_{\perp}|=0.0010\ \text{cm}^{-1}$, $r=3.8$ Å, $\xi=15°$, and $\Delta H=25$ G.

The powder X-band ESR spectra of Cu(Salen) doped in a high concentration in Ni(Salen) crystals are shown in Fig. 8. According to Shkol'nikova *et al.*,[23] the Ni(Salen) molecules in crystals are also present as dimers with $r=3.22$ Å and $\xi=15°$. This ξ value is much closer to those estimated for the dimers of Cu(Salpn) and Cu(3Me–Salpn) in frozen solutions than those for Cu(Salen) in crystals of Cu(Salen) itself ($\xi=40°$) and Cu(Salen)·CHCl$_3$. In the $\Delta M=1$ spectrum shown in Fig. 8, it is noteworthy that the hyperfine splittings at both edges are equal ($\approx$100 G), being the same as one half of the monomer's $|A_{//}|$ value. This fact indicates that the principal axes of the g and fine-structure tensors are almost coincident and, therefore, that the dimeric structure of Cu(Salen) in Ni(Salen) crystals is similar to that of the host nickel complex. The best fit for the $\Delta M=1$ spectrum at both sides and for the $\Delta M=2$

spectrum was obtained with the same g and A values as in Fig. 7 and with $r=3.80$ Å and $\xi=15°$. The difference of 0.58 Å between the true and estimated r values for the dimer of Cu(Salen) in Ni(Salen) crystals is larger than that in Cu(Salen)·$CHCl_3$ crystals. This fact suggests that the error in r inherent in the point-dipole approximation depends upon both r and ξ. Such might also be the case with the error in ξ.

In order to check these errors more systematically, we calculated the fine-structure splittings in the $\Delta M=1$ spectra, assuming that, in each of the monomeric halves in the dimers, the fractions of the unpaired electron on the copper atom and on each of its four coordinating ligand atoms are given by α^2 and $(1-\alpha^2)/4$ respectively, where α^2 is a covalency parameter which has its usual meaning in the metal-ligand bondings.[24,25] As may be seen in Fig. 2, the x′ and y′ axes are parallel to the x and y axes respectively, and the Cu^2 atom is located on the xz plane. It is obvious from a symmetry consideration of the dimer that the maximum principal value axis of the fine-structure tensor is on the xz plane. We calculated the fine-structure splitting D, setting the static magnetic field on the xz plane and changing θ from 0 to 90° at intervals of 1°. The maximum principal value, D_H, and the direction, θ_{max}, of the D tensor were determined graphically from the plots of D against θ.[26]

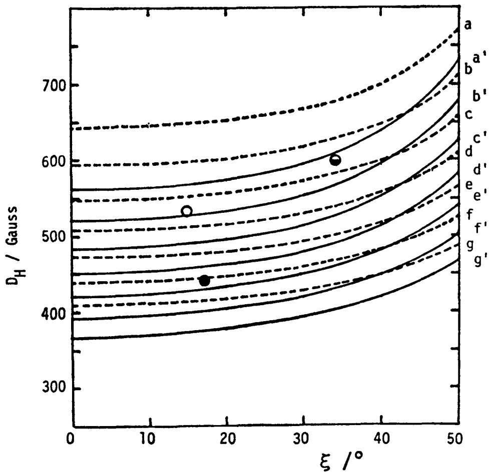


Fig. 9. Dependence of D_H on ξ and r: (——), $\alpha^2=0.65$; (------), $\alpha^2=0.75$.
a and a′, $r=3.2$ Å, b and b′, $r=3.3$ Å; c and c′, $r=3.4$ Å; d and d′, $r=3.5$ Å; e and e′, $r=3.6$ Å; f and f′, $r=3.7$ Å; g and g′, $r=3.8$ Å. D_H was calculated for $g_{//}=2.19$, $g_\perp=2.045$, and microwave frequency=9.23 GHz. ○, Cu(Salen) in Ni(Salen) crystals; ◒, Cu(Salen) in Cu(Salen)·$CHCl_3$ crystals; ●, Cu(3Me-Salpn) in toluene.

Figure 9 shows the dependence of D_H on ξ and r for $\alpha^2=0.65$ and 0.75. This figure clearly indicates that D_H increases with ξ and α^2, and that the increment of D_H *vs.* α^2 decreases with an increase of r. These results are in agreement with the intuitively acceptable fact that the point-dipole approximation becomes a better one as α^2 or r increases. This figure also explains why the error in r inherent in the point-dipole approximation is smaller for the dimer of Cu(Salen) in Cu(Salen)·$CHCl_3$ crystals than for the one in Ni(Salen) crystals. The open and half-darkened circles shown in Fig. 9 are for the dimers of Cu(Salen) in Ni(Salen) and Cu(Salen)·$CHCl_3$, to which the D_H values estimated and the ξ values taken from the crystal data were assigned, respectively. A closer inspection of these circles with regard to r indicates that the above-mentioned dimers can have their actual r value when $\alpha^2=\approx 0.65$ and 0.75 respectively are assumed for them. Both of the α^2 values are smaller than 0.82,[27] which was calculated from the monomer's ESR parameters by the usual method.[25] These small inconsistencies in α^2, however, do not seem significant because all the procedures involved are originally rough. We would like to emphasize here that, in order to get more fruitful results from the dimer ESR spectra, an explicit consideration of the delocalization effect in the simulation is necessary.

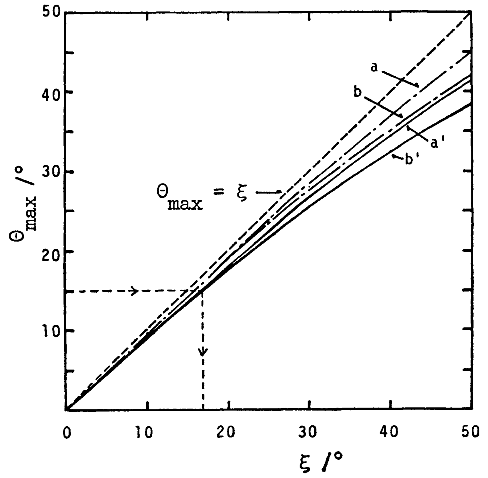


Fig. 10. Dependence of θ_{max} on ξ for $g_{//}=2.19$ and $g_\perp=2.045$.
a, $r=3.8$ Å and $\alpha^2=0.75$; b, $r=3.2$ Å and $\alpha^2=0.75$; a′, $r=3.8$ Å and $\alpha^2=0.65$; b′, $r=3.2$ Å and $\alpha^2=0.65$.

Figure 10 shows the dependence of θ_{max} on ξ, r, and α^2. Apparently, the value of $\Delta\xi=\xi-\theta_{max}$ increases with ξ and decreases with increases in α^2 and r. When each unpaired electron is completely localized on the copper nucleus, θ_{max} is equal to ξ. For a dimer with a considerable delocalization of the unpaired electron, therefore, the ξ value estimated by the use of the point-dipole approximation should approach the θ_{max} value rather than the actual ξ one. As has been described above, the ξ ($\simeq\theta_{max}$) values for the dimers of Cu(Salpn) in xylene and of Cu(3Me-Salpn) in toluene have been estimated to be 15° using the point-dipole approximation. These results suggest that their dimeric structures are similar to that of Cu(Salen) in Ni(Salen) crystals, in which the D_H value has been satisfactorily explained on the assumption of $\alpha^2=0.65$. By applying the case of $\theta_{max}=15°$ and $\alpha^2=0.65$ to Fig. 10, we can estimate $\xi=17°$ for these dimers in solution. Furthermore, by re-plotting their estimated D_H values at $\xi=17°$ as darkened circles in Fig. 9, we can estimate their r values more reliably as ≈3.55 Å. In the same way, $r=\approx 3.50$ Å and $\xi=\approx 38.5°$ have been estimated for the dimer of Cu(3NO_2-Salibn) in nitroethane. The result of $\xi=17°$ thus re-estimated for the dimers of Cu(Salpn) in xylene and of Cu(3Me-Salpn) in toluene supports our previous conclusion that these dimers are remarkably different in structure from that of Cu(Salen) in crystals.

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26) The approximate determination of D_H begins by plotting the resonance magnetic field for $\Delta M=1$ transitions against θ. Since $2D_H$ is defined as the maximum difference between two resonance fields at the same θ value, θ_{max}, D_H is graphically determined from the plot. D_2 is generally different from D_H, because $2D_2$ is defined as the difference between the maximum and minimum magnetic fields at different θ values (see Ref. 6).
27) The value of 0.82 is likely to decrease slightly if we regard the α^2 value as the metal orbital population in the anti-bonding molecular orbital occupied by an unpaired electron. See R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).