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ESR Studies of the Triplet State Dimers of the Salicylaldehyde Schiff Base Complexes of Copper(II) in Toluene and in Chloroform

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The ESR spectra of triplet-state dimers have been obtained for various bidentate and quadridentate salicylaldehyde Schiff base complexes of copper(II) in frozen solutions. The spectra have been analysed on the basis of the previously-obtained results concerning the non-coaxial g and fine-structure tensors. The results indicate that the angles between the $g_{\parallel}$ axis and the copper-copper axis of the dimers for the quadridentate Schiff base complexes are considerably smaller than those for the bidentate ones. Each of the actually-measured ESR spectra, however, consisted of two mutually-overlapping spectra; one is due to dimers (M_2), and the other, to monomers (M). The equilibrium constant for $2M \rightleftharpoons M_2$ has been estimated by comparing the ESR spectral intensities of the two species. The factors which govern the dimer formations have been discussed in some detail.

In our previous paper,[1] it has been revealed, through computer simulations of the triplet ESR spectra that the dimeric structure of Bis-(N-salicylidenemethylaminato)copper(II) in toluene is similar to that in its γ-form crystals,[2] and that it is necessary to take into account the non-coincidence of the principal axes of the g tensor with those of the fine-structure tensor in order to estimate such dimeric structures. A considerable number of copper(II) chelates are known to have dimeric structures in crystals such as those shown schematically in Fig. 1. Hatfield and his co-workers extensively studied the magnetic interaction within the dimers of this type by means of ESR and magnetic susceptibility measurements.[3] The factors which govern the dimer formations, the nature of the dimerization forces, and the mechanisms of the spin-exchange interaction within the dimers, however, have not yet been established in full detail. In order to study these problems, we systematically measured the ESR spectra of various salicylaldehyde Schiff base complexes of copper(II) in toluene and in chloroform, and discussed the influence of various substituent groups at the iminoic nitrogens and in the phenyl-rings on the dimer formation and dimeric structure.

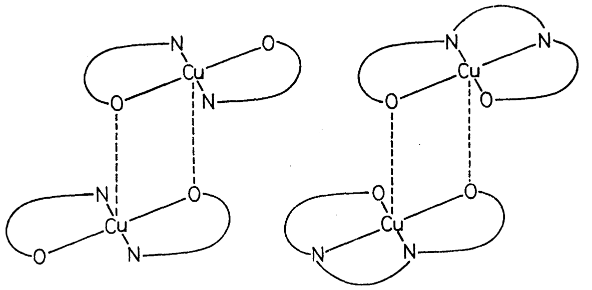
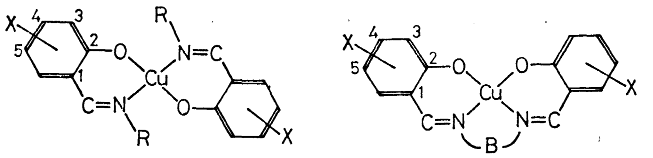


Fig. 1. Schematic illustrations of dimeric structure.



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

Fig. 2. Schematic illustrations of salicylaldehyde Schiff base complexes of copper(II). Following abbreviations were made respectively.

X: Me–, CH_3–; MeO–, CH_3O–

R: Me, CH_3; Et, C_2H_5; n-Pr, C_3H_6

B: en, C_2H_2; pn, $(CH_3)CHCH_2$; bn, $(CH_3)CHCH(CH_3)$; ibn, $(CH_3)_2CCH_2$

Experimental

The salicylaldehyde Schiff base complexes of copper(II) with the general formulae of Cu(nX-RSal) and Cu(nX-SalB) (see Fig. 2) were prepared, where X, R, and B are the generalized ring, nitrogen, and bridging group substituents respectively, and where n represents the position of X in the phenyl ring. These complexes were obtained by refluxing salicylaldehyde or X-substituted salicylaldehyde copper(II) complexes with the appropriate amines or diamines in ethanol. The methyl-substituted salicylaldehyde was synthesized by Duff's reaction.[4] The other salicylaldehyde derivatives were commercially obtained.

The toluene and chloroform were purified according to the usual method,[5] and the chloroform was used immediately after the purification. The ESR of the quadridentate Schiff base complexes in chloroform solutions were measured at 77 K after the frozen solutions had been crushed to fine powders according to a method described previously.[6]

Results and Discussion

The Magnetic Parameters and the Dimeric Structure. The g and A values observed for the monomers of the salicylaldehyde Schiff base complexes of copper(II) were not changed greatly with the substituents ether at the iminoic nitrogens or in the phenyl rings. These magnetic parameters for the bidentate salicylaldehyde Schiff base complexes of copper(II) are in the range of $2.23 > g_{\parallel} > 2.21$, $2.06 > g_{\perp} > 2.04$, and $0.0195\ \mathrm{cm}^{-1} > |A_{\parallel}| > 0.0185\ \mathrm{cm}^{-1}$, while those for the quadridentate ones are in the range of $2.20 > g_{\parallel} > 2.18$, $2.06 > g_{\perp} > 2.04$, and $0.0215\ \mathrm{cm}^{-1} > |A_{\parallel}| > 0.0205\ \mathrm{cm}^{-1}$.

The ESR spectra of Cu(5Br–MeSal) and Cu(3Me–Salpn) in toluene are shown in Fig. 3. The magnetic parameters of the triplet-state dimers are defined in Fig. 3 as has been previously described,[1] and their values are tabulated in Table 1. The values of g_1 and g_2 are defined from the centers of the so-called full-field perpendicular and parallel lines respectively. The A_1 and A_h values express the hyperfine-splittings of the low-field and high-field parallel lines respectively. The D_1 and D_2 values express the observed fine-structure splittings of the perpendicular and parallel lines respectively. As Table 1 shows, the magnetic parameters of the triplet dimers do not change markedly with the substituents. The line shapes and the magnetic parameters of the bidentate Schiff base complexes are characterized by the non-coaxial g and fine-structure tensors; that is, $(A_{\parallel}/2) > A_l > A_h$, and $g_2 < g_{\parallel}$. Therefore, the dimeric structures of the bidentate complexes are considered to be similar to those of Cu(MeSal) in γ-form crystals, where the angle between the $g_{\parallel}$ axis and the copper-copper axis is about 30°.[1] On the other hand, the triplet-state dimers of the quadridentate Schiff base complexes show the typical ESR line shapes for the indication of the near co-axial g and fine-structure tensors; that is, A_l and A_h are almost equal to the $A_{\parallel}/2$ of the monomers, while g_2 is almost equal to the $g_{\parallel}$ of the monomers.

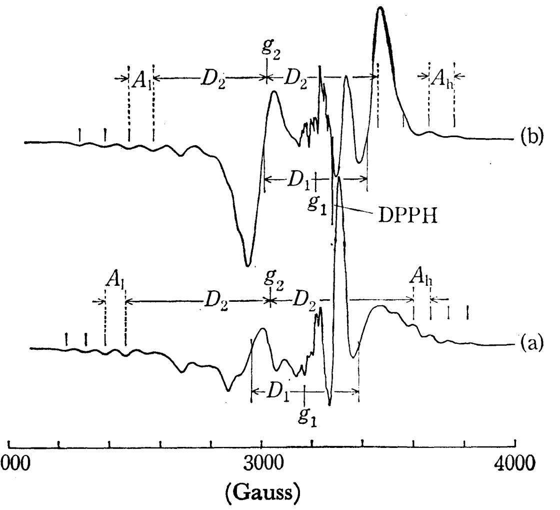


Fig. 3. ESR spectra of 77 K frozen toluene solutions of a) Cu(5Br–MeSal), b) Cu(3Me–Salpn).

TABLE 1. MAGNETIC PARAMETERS OF TRIPLET DIMERS

Ligand	g_1	g_2	A_l	A_h	D_1	D_2	Frequency (MHz)
				(gauss)			
MeSal	2.069	2.170	79	65	409	563	9220
3Me-			83		400		9224
4Me-	2.065	2.172	79	66	414	565	9293
5Me-	2.07	2.170	80	67	400	568	9285
5Br-	2.073	2.174	80	70	420	566	9288
EtSal	2.061	2.171	79	68	390	564	9135
5Br-	2.066		80		405		9182
nPrSal		2.171	75	67		563	9324
Salen		2.180	100	100		432	9139[a]
Salpn	2.042	2.190	100	100	380	428	9327
		2.185	103	103		434	9329[a]
3Me-	2.050	2.184	99	100	408	444	9230
4Me-		2.188	100	100		420	9249
5Me-	2.052		100		380		9284
5Br-	2.052		100		400		9211
Salbn		2.186	100	100		423	9210

a) Medium; chloroform. All the other data were obtained in frozen toluene solutions.

It is well known that Cu(Salen) has a dimeric structure in crystals similar to that of Cu(MeSal).[2,7] There are two possible explantions for the near coincidence between the principal axes of the g and fine-structure tensors. One is that the dimeric structure in the frozen solutions is so different from those in the crystals of Cu(Salen) or Cu(MeSal) that the $g_{\parallel}$ axis almost coincides with the copper-copper axis. The other is that, although the dimeric structure similar to that found in the crystals of Cu(Salen) is retained even in frozen solutions, the so-called pseudo-dipole interaction whose principal axes coincide with those of the g tensor cancels the effect of the non-coaxial g and fine-structure tensors in the spin-dipole interaction.

The magnitudes of the pseudo-dipole and spin-dipole interaction can be estimated from Eqs. (1) and (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.

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

$$D_{\text{dd}} = \frac{-0.65 g_2^2}{r^3} \qquad (2)^{9)}$$

The J value for the dimers of Cu(Salen) in crystals had been estimated at 5 cm^{-1}.[10] From this J value and the magnetic parameters for the triplet dimers of Cu(Salen), that is, $g_{\parallel} = g_2 = 2.19$, $g_{\perp} = 2.05$, and $r = 3.5$ Å, D_{pseudo} and D_{dd} can be estimated at -0.0041 and -0.0700 cm^{-1} respectively. It is clear that the obtained value of D_{pseudo} is too small to cancel the effect of the spin-dipole interaction. It may be concluded, therefore, that the first explanation is more reasonable than the second one in this case. It has been reported that the dimeric structure of Cu(Etacest)$_2$ in toluene is also different from that in crystals,[11] where Etacest is the anion of ethylacetoacetate. These facts indicate that the dimeric structures in crystals are often different from those in solutions: the dimeric structures in crystals depend to a greater or lesser degree upon the ways of molecular packing. The polymorphism of Cu(MeSal) is regarded as an example of such phenomena.

Two papers have appeared during the preparation of our report concerning the triplet-state dimers of the salicylaldehyde Schiff base complexes of copper(II) in solutions.[10,12] In both papers, the parameters of the spin Hamiltonian tensors were estimated on the basis of the computer simulations of the ESR spectra only for $\Delta M = 2$ transitions. Toy *et al.* estimated the copper-copper distance and the angle between the $g_{\parallel}$ axis and the copper-copper axis for the Cu(Salen) dimers in chloroform at 4.55 Å and 40±5° respectively.[12] However, it is evident from the results of our computer simulation previously described that the spectral patterns for the $\Delta M = 1$ transitions of Cu(Salen) cannot be reproduced by the use of such non-coaxial g and spin-dipole interaction tensors. On the other hand, Hatfield *et al.* concluded that the principal axes of the g and fine-structure tensors are coincident with each other. This conclusion is in accord with our results. However, they had previously assumed that the dimeric

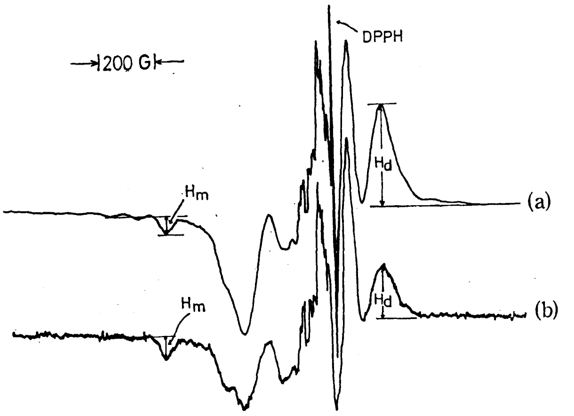


Fig. 4. Concentration dependence of ESR spectra of Cu(Salpn) in toluene at 77 K. a) 3.1×10^{-3} M, b) 0.5×10^{-3} M.

structure of Cu(Salen) in crystals is retained in frozen chloroform solutions, and had estimated the contribution of the spin-dipole interaction to the observed fine-structure splittings at 0.036 cm^{-1}.[13] This value seems too small to agree with the value calculated from Eq. (2). A further detailed report on the relation between the dimeric structure and the relative orientations of the g and fine-structure tensors will soon be published.

The Equilibrium between Dimers and Monomers. In order to obtain quantitative information on the effects of various substituents on the dimer formations, we have estimated the equilibrium constants for $2\text{M}\rightleftarrows\text{M}_2$, where M and M_2 represent monomer and dimer species respectively. In our previous paper, we have already presented the following relation:[11]

$$2Q^2 + qQ = Kq^2c^\circ \tag{3}$$

where the equilibrium constant, K, is expressed as follows:

$$K = \frac{[\text{M}_2]}{[\text{M}]^2} \tag{4}$$

where c° is the initial concentration of a complex and where the Q and q values are defined as:

$$Q = \frac{H_\text{d}}{H_\text{m}} = q\frac{[\text{M}_2]}{[\text{M}]} \tag{5}$$

H_d and H_m in Eq. (5) are the peak heights of certain absorption lines due to the dimers and monomers respectively in the first derivative ESR spectra, as is shown in Fig. (4) in the case of Cu(Salpn) in toluene. It may reasonably be supposed that the magnitude of the spin exchange interaction within the present dimers is much smaller than the thermal energy at 77 K. Then, we can derive Eq. (6):

$$\frac{I_\text{d}}{I_\text{m}} = \frac{2[M_2]}{[M]} \tag{6}$$

where I_d is the total integrated intensities of the ESR spectra due to the dimers, and I_m, the total of those due to the monomers, respectively. I_d and I_m were obtained as has been described previously.[11]

The plots of $(2q^2+qQ)/q^2$ *vs.* c° for the toluene solutions of Cu(MeSal), Cu(EtSal), Cu(nPrSal), and Cu(Salpn) are shown in Figs. 5 and 6. Since the magnetic parameters of the triplet dimers of the salicylaldehyde Schiff base complexes of copper(II) do not change markedly with the substituents, it may reasonably be supposed that the q values do not change with the substituents. Then, we can estimate the values of K using the Q values obtained from the ESR spectra measured at only one concentration. The K values thus obtained for other salicylaldehyde Schiff base complexes by the use of the q values determined for Cu(MeSal) and Cu(Salpn) are listed in Tables 2 and 3. The salicylaldehyde Schiff base complexes of copper(II) employed here are soluble in many coordinating solvents, such as methanol, ethanol, and pyridine. However, the ESR signals due to the triplet dimers were not observed in these solutions. In general, the K values of the quadridentate complexes are much larger than those of the bidentate ones. The chloroform solutions of the bidentate complexes did not exhibit any signals due to triplet dimers, but those of the quadridentate ones did, though the spectral intensities due to the dimers were very weak as compared with those due to the monomers.

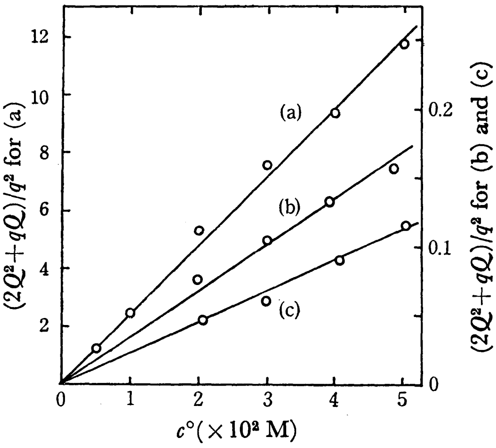


Fig. 5. The plot of $(2Q^2+qQ)/q^2$ *vs.* c° for the 77 K frozen toluene solutions. (q=2.0)
a) Cu(MeSal), b) Cu(EtSal), c) Cu(nPrSal)

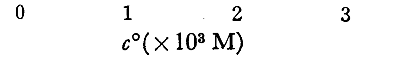


Fig. 6. The plot of $(2Q^2+qQ)/q^2$ *vs.* c° for the 77 K frozen toluene solutions of Cu(Salpn). (q=4.0)

Table 2 indicates the variation in the K values with the substituents at the iminoic nitrogens. In the case of the bidentate complexes, it is clear that the more bulky the substituent at the iminoic nitrogen becomes, the less the K value becomes. When the R in Fig. 2 was replaced by the isopropyl or *tert*-butyl group, no signals due to the triplet-state dimers could be detected.

TABLE 2. THE DEPENDENCE OF THE K VALUES ON THE SUBSTITUENT GROUPS AT THE IMINOIC NITROGENS OF SALICYLALDEHYDE SCHIFF BASES

	Toluene	Chloroform
Cu(MeSal)	2.4×10^2	0
Cu(EtSal)	3.2	0
Cu(nPrSal)	2.3	0
Cu(Salen)	—a)	41
Cu(Salpn)	1.3×10^3	28
Cu(Salbn)	1.1×10^3	0
Cu(Salibn)	7.8×10^2	0

a) Cu(Salen) is scarcely soluble in toluene.

TABLE 3. THE DEPENDENCE OF THE K VALUES ON THE SUBSTITUENT GROUPS AT THE PHENYL RINGS OF THE SALICYLALDEHYDE SCHIFF BASES

X	MeSal Toluene	Salpn Toluene	Salpn Chloroform	Salen Chloroform
H	2.4×10^2	1.3×10^3	28	41
3Me	21	1.2×10^4	28	24
4Me	4.7×10^2	2.4×10^2	49	1.2×10^2
5Me	1.8×10^2	6.6×10^3	54	54
5Br	2.3×10^3	3.2×10^4	71	—b)
3MeO	0	—c)	8.4×10^2	1.3×10^3
5MeO	2.1×10^3	—c)	94	76

a) The q values for bidentate Schiff base complexes were put equal to that for Cu(MeSal) (2.0), and those for quadridentate ones, to that for Cu(Salpn) (4.0) in toluene. b) Cu(5Br-Salen) is scarcely soluble in chloroform. c) The spectral patterns correspond to crystalline powders were obtained.

On the other hand, when the R was replaced by proton, no evidence for the dimer formation could be obtained because of the low solubility of the complex in toluene. The K values for the quadridentate complexes in toluene were not changed by the methyl groups at the ethylene bridge. When the iminoic nitrogens were bridged with the trimethylene group, however, no signals due to the triplet-state dimers could be detected. These experimental facts suggest that the dimer formations are inhibited by the direct steric hindrance of bulky substituents near the first coordination sphere and/or by the tetrahedral deformation of coordination due to such bulky substituents.

Table 3 indicates the changes in the K values with substituents in the phenyl rings. We may clearly recognize large differences between the bidentate and quadridentate complexes in the effect of substituents in the phenyl rings on the K values. The 3-methyl and 3-methoxy groups of the bidentate complexes severely inhibited the dimer formation, whereas those of the quadridentate ones did not. For instance, the K values of Cu(3MeO–Salpn) and Cu(3Me–Salpn) become larger than those of the unsubstituted complexes. It should be further noticed that the influence of the substituents on the K values are markedly dependent upon the solvents. For instance, the K values for the toluene solutions of Cu(3Me–Salpn) and Cu(5Me–Salpn) were considerably larger than that of Cu(Salpn), whereas those of the chloroform solutions of the former did not increase so much as that of the latter. It may naturally be supposed that toluene molecules have a strong affinity for the phenyl rings of the complexes rather than for the copper ions and coordinating atoms. It seems likely that the dependence upon solvents for such changes in the influence of substituents in the phenyl rings is to be attributed to the changes in solvation. These experimental results suggest that the phenyl rings of the salicylaldehyde Schiff bases play an important role in determining the dimer formation. These estimations are further supported by the fact that no ESR signals of the triplet dimers were observed for a toluene solution of N,N'-ethylenebis(4-amino-3-penten-2-ono)copper(II) at 77 K. Recently, Yokoi indicated that the K values of bis(t-butylacetoacetato)copper(II) and Cu(Etacest)$_2$ change markedly with slight changes in the properties of the solvents.14) Thus, it seems natural that the K values change greatly with a slight change in the properties of the substituents and the solvents.

Conclusion

In the solutions of various Schiff base complexes of copper(II), the K values for $2M \rightleftharpoons M_2$ depend on many delicate factors, although the triplet-state ESR spectral patterns do not change markedly with the substituents. It was also revealed that the dimeric structure of the quadridentate Schiff base complexes in frozen solutions is different from that of Cu(Salen) in crystals. These facts, besides similar results previously obtained, suggest that the dimerization force must be weak, and that the forces are generated not only by the coordination of the oxygen atoms to the apical positions of adjacent complexes, as is shown schematicaly in Fig. 1, but also by the wholly-molecular electric dipole or dispersion interaction between the monomeric halves in the dimers. It may be expected, accordingly, that the dimeric structures of these types of complexes change sensitively with the nature of such dimerization forces and with their environments.

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