Electron Spin Resonance Study of Dimer Formation in some Bis(*N*-alkylsalicylideneiminato)copper(II) Complexes in Inert Solvents

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The complexes [Cu(*N*-R-sal)$_2$] (R = Et, Pr^n, Pr^i, Bu^n, n-hexyl, cyclohexyl, and n-octyl) show well defined triplet-state e.s.r. spectra in methylcyclohexene for both $\Delta M = 1$ and 2 transitions with the zero-field splitting due to dipolar interaction between the copper(II) pairs. Computer analysis of the spectra has revealed that these complexes adopt various dimeric structures according to R which do not require apical co-ordination of the phenolic oxygen atoms, and that the structures in methylcyclohexane are different from those in toluene. Intradimer spin-exchange interactions for these dimers are weakly antiferromagnetic (1.1—4.5 cm^{-1} from the temperature dependence of intensity for $\Delta M = 2$ transitions in the range 1.57—4.2 K). Thermodynamic constants for dimer formation in methylcyclohexane have been estimated as $\Delta H \approx -3$ kcal mol^{-1} and $\Delta S \approx -9$ cal K^{-1} mol^{-1} and are discussed.

RECENTLY a number of e.s.r. and susceptibility studies of various dicopper(II) systems with considerably weak magnetic interactions between the Cu^{II} pairs have been carried out, with the aim of determining their structural properties or of revealing the mechanisms of the magnetic interactions.[1-5] One of the main systems consists of dimers formed from stable mononuclear Cu^{II} complexes in solution. Interest in these dimers is further developed by the fact that dimer formation, as well as the association or aggregation of molecules, is of fundamental significance in both physical chemistry and biochemistry.[6,7] The problem of which factors are important in dimer formation, however, remains unsolved because of insufficient data.[8] We have found a series of bis(*N*-alkylsalicylideneiminato)copper(II) complexes, [Cu(*N*-R-sal)$_2$], which adopt various dimeric structures depending on the hydrocarbon solvent used. The present paper describes a detailed e.s.r. study of this dimer formation from new points of view.

EXPERIMENTAL

Materials.—Seven new [Cu(*N*-R-sal)$_2$] complexes, together with the known R = Me derivative, were prepared and purified according to the usual method,[9] using commercial reagents (Table 1). Commercial methylcyclohexane and toluene were purified in the usual way.[10]

E.S.R. Measurements.—E.s.r. spectra were recorded on a Hitachi 771 *X*-band spectrometer over the field range 0—5 000 G in the temperature ranges 326—77 and 4.2—1.57 K.† For measurements in the lower temperature range, an insertion-type liquid-helium Dewar in conjunction with a room-temperature cavity was used with microwave power low enough to remove the saturation effect on intensity measurements;[11] the appropriate power was determined beforehand for every sample.[4] Sample solutions were as concentrated as possible in order to weaken the saturation effect.

The intramolecular spin-exchange interaction energy J was evaluated from the spectral intensity I for $\Delta M = 2$ transitions using the equation $I = (C/T)\ [3 + \exp(-J/kT)]^{-1}$, where C is a proportionality constant. Since linewidths did not change over the temperature range 4.2—1.57 K for each $\Delta M = 2$ spectrum, the relative peak height of a line in the first-derivative spectrum was used as a substitute for I in the above equation.

TABLE 1

Observed parameters for the dimeric species of [Cu(*N*-R-sal)$_2$] in methylcyclohexane

R	Spectral type *	g_D	$10^2\|D\|$ (cm^{-1})	$10^2\|A_L\|$ (cm^{-1})
Et	A	2.207	4.60	0.99
Pr^n	A	2.200	4.93	1.00
Bu^n	B	2.187	4.84	0.82
Pr^i	B	2.187	4.84	0.82
n-Hexyl	B	2.189	4.86	0.81
n-Octyl	B	2.189	4.86	0.78
Pr^i	C	2.166	5.94	0.74
Cyclohexyl	C	2.170	6.07	0.74

* The representative e.s.r. spectra A, B, and C are shown in Figures 1, 2, and 3 respectively.

RESULTS AND DISCUSSION

Triplet-state E.S.R. Spectra of Dimers.—Representative e.s.r. spectra at 77 K for the [Cu(*N*-R-sal)$_2$] complexes in methylcyclohexane are shown in Figures 1—3. All other spectra in this solvent could be roughly classified into three types corresponding to these Figures respectively (Table 1). The Figures show that the e.s.r. line shapes are of a triplet-state type.[1-5] A weak extra absorption near the diphenylpicrylhydrazyl (dpph) signal in each spectrum, although exceptionally intense in Figure 3, is due to polymers or microcrystals of the

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† 1 G = 10^{-4} T; 1M = 1 mol dm^{-3}; 1 cal = 4.184 J.

[1] T. D. Smith and J. R. Pilbrow, *Co-ordination Chem. Rev.*, 1974, **13**, 174 and refs. therein.

[2] H. Yokoi and T. Isobe, *Bull. Chem. Soc. Japan*, 1971, **44**, 1446; *ibid.*, 1973, **46**, 447; *Chem. Letters*, 1972, 95.

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[8] H. Yokoi, *Bull. Chem. Soc. Japan*, 1974, **47**, 497; unpublished work.

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[10] J. A. Riddick and W. B. Bunger, 'Organic Solvents,' Wiley, New York, 1970.

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complex concerned since only this absorption decreased in intensity with a decrease in concentration.* It is, accordingly, obvious that the main species in these frozen solutions at concentrations of 0.01M or less are dimers. The magnetic parameters, g_D, D, and A_L, which are defined in Figures 1—3, are summarized in Table 1.

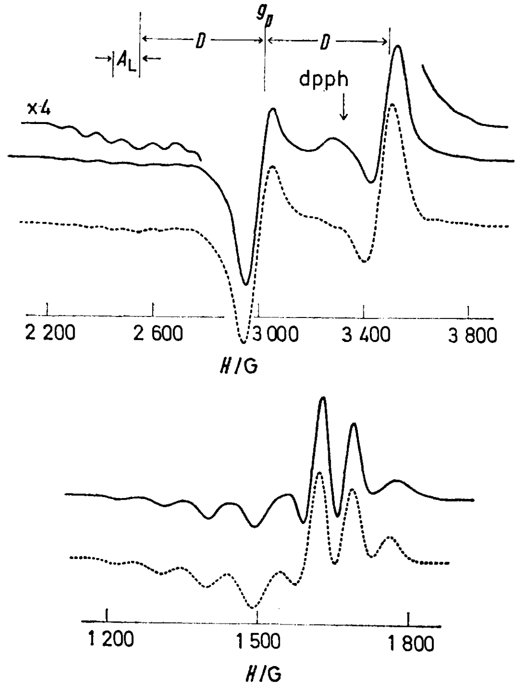

Figure 1 X-Band e.s.r. spectra of $[Cu(N\text{-}Pr^n\text{-}sal)_2]$: (——), observed in methylcyclohexane (1.0×10^{-2}M) at 77 K; (— — —), computer simulated with the parameters listed in Table 2

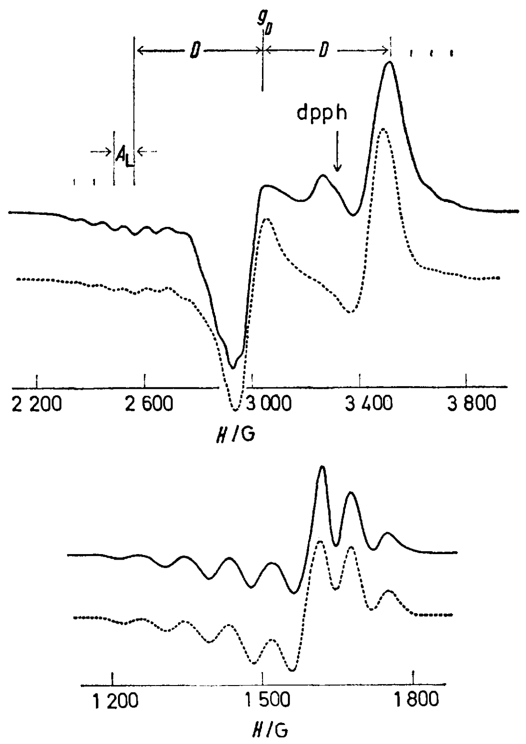

Figure 2 X-Band e.s.r. spectra of $[Cu(N\text{-}Bu^n\text{-}sal)_2]$. See Figure 1 for key

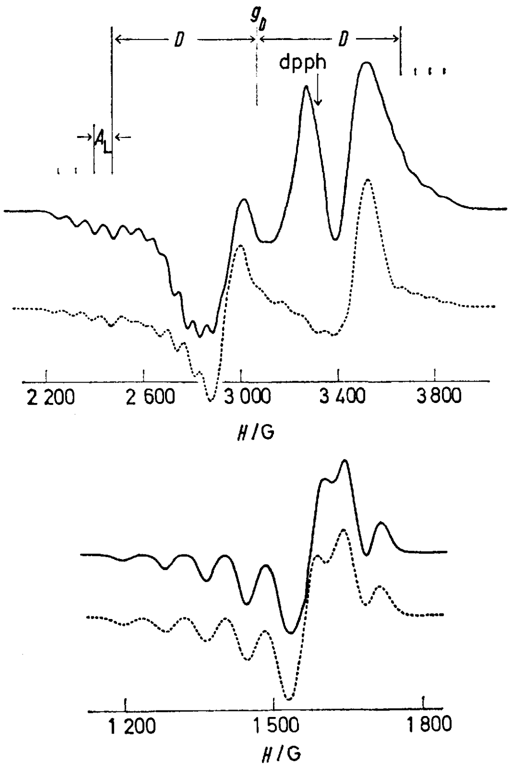

Figure 3 X-Band e.s.r. spectra of $[Cu(N\text{-}Pr^i\text{-}sal)_2]$. See Figure 1 for key

As will be described in detail later, intradimer spin-exchange interactions for the present dimers are weak enough for their contribution to zero-field splitting to be neglected. The observed triplet-state e.s.r. spectra were analyzed by the computer-simulation method

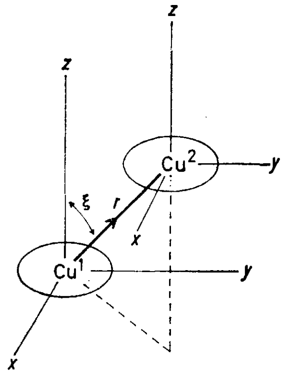

Figure 4 Co-ordinate system for the dimers

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* The equilibrium $n(\text{dimer}) \rightleftharpoons (\text{dimer})_n$ with a small constant is considered to exist in each frozen solution (see refs. 2 and 5).

previously developed,[3] using the co-ordinate system shown in Figure 4. The relations $g_x = g_y$ ($\equiv g_\perp$) and $A_x = A_y(\equiv A_\perp)$ were assumed, since it was difficult to determine the parameters of non-axiality in g and A tensors, as has already been pointed out for the A tensor by Smith and Pilbrow,[1] and it is thought that the assumption does not make a serious error in the computational results. A point-dipole model with each electron spin located on a copper nucleus was used in calculating dipolar interaction between the $\mathrm{Cu^{II}}$ pairs. The analysis was based on the use of perturbation theory to second order in the fine and hyperfine terms and, of course, it was corrected for the angular dependence of transition probability.[12,13] Gaussian line shapes with the half-widths ΔH_1 and ΔH_2 in $\Delta M = 1$ and 2 spectra respectively were used throughout.

An important characteristic of the above triplet-state e.s.r. spectra is that both well defined $\Delta M = 1$ and 2 spectra with well resolved hyperfine structures were simultaneously observed; such spectra have scarcely been observed so far in spite of their importance to an examination of methods for spectral analysis. Computer simulations were carried out for variations in the parameters at the following intervals: 0.05 Å (r); 3° (ξ); 0.005 ($g_\parallel$ and $g_\perp$); 0.0003—0.0005 cm^{-1} ($A_\parallel$ and $A_\perp$); and 3—5 G (ΔH_1 and ΔH_2). Some of the results are shown as dotted lines in Figures 1—3. Best fits were selected by visual fitting of the experimental and computed results (Table 2). In general, better correlations were obtained for $\Delta M = 2$ than for $\Delta M = 1$ spectra, as pointed out by Smith and Pilbrow.[1] In addition, the $\Delta M = 2$ spectra were much more insensitive to the values of the parameters. Accordingly, the results obtained only by analysis of $\Delta M = 2$ spectra probably lack precision.

TABLE 2

Calculated parameters for the dimeric species of [Cu(N-R-sal)$_2$] in methylcyclohexane

R	Spectral type	r Å	ξ °	$g_\parallel$	$g_\perp$	$10^3\lvert A_\parallel\rvert$ cm^{-1}	$10^3\lvert A_\perp\rvert$ cm^{-1}	ΔH_1 G	ΔH_2 G
Et	A	4.05	15	2.220	2.045	9.5	1.5	30	22
Pr^n	A	3.95	15	2.220	2.045	9.5	1.5	30	22
Bu^n	B	3.95	27	2.215	2.045	9.0	1.5	30	22
Pr^i	C	3.70	37	2.240	2.050	8.7	1.5	23	22

It is quite reasonable to obtain each simulated curve with the principal g and A values close to those of the monomers, if the binding energy between the monomeric halves is not large; as to the A values, this means $2\,A^{\mathrm{d}} \approx A^{\mathrm{m}}$ in this study, where d and m represent the dimer and monomer respectively. This is the case for the present dimers, as will be described later.

Dimeric Structures.—The r and ξ values in Table 2 clearly indicate that the dimeric structures for the above three types of spectra are considerably different. This result is in conflict with the general belief that dimeric structures for Schiff-base and related complexes are always of a parallel planar type with a square-pyramidal configuration around $\mathrm{Cu^{II}}$ due to the apical co-ordination of phenolic oxygen atoms [Figure 5(a)].[14] The $\Delta M = 1$ spectra of the [Cu(N-R-sal)$_2$] complexes with R = Me and Et in toluene and of the latter in methylcyclohexane are shown in Figure 6. Both $\Delta M = 1$ spectra of the complexes in toluene were the same, showing their dimeric structures to be of the above type ($r \approx 3.7$ Å and $\xi \approx 35°$).[3] On the other hand, the spectrum of the latter complex in methylcyclohexane, from which $r = 4.05$ Å and $\xi = 15°$ were estimated (Table 2), was quite different from that in toluene. In addition, a comparison between Figures 6(b) and (c) reveals that the R = Et complex is dimerized in methylcyclohexane more easily than in toluene. These results are surprising in view

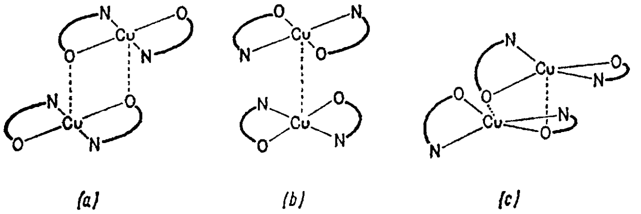

FIGURE 5 Possible structures of the dimers

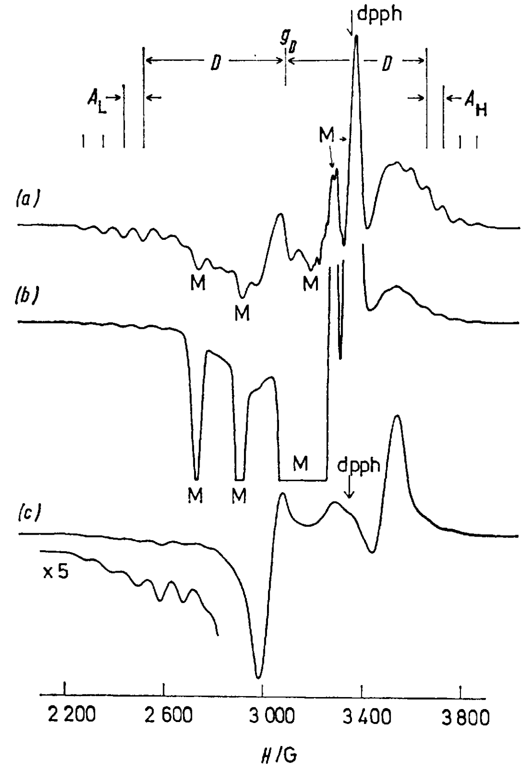

FIGURE 6 X-Band e.s.r. spectra for $\Delta M = 1$ transitions at 77 K: (a) [Cu(N-Me-sal)$_2$] in toluene; (b) [Cu(N-Et-sal)$_2$] in toluene; (c) [Cu(N-Et-sal)$_2$] in methylcyclohexane; M represents the absorption line due to monomers

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[12] B. Bleaney, *Proc. Phys. Soc.*, 1960, **A75**, 621.

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of the fact that both methylcyclohexane and toluene are hydrocarbon solvents with similar properties,[10] the former being saturated with the carbon skeleton of the latter. It is of particular importance that the dimer formation is markedly affected by small changes in solvent properties.

A molecular arrangement of the R = Me complex in the α form is shown in Figure 5(*b*).[15] It is interesting that only this complex in methylcyclohexane at 77 K showed a crystalline powder e.s.r. spectrum, which is close in line shape to that for the α rather than the γ form.

From Table 2, it is clear that dimeric structures for the spectra A and B are intermediate between those in Figures 5(*a*) and (*b*). Table 2 suggests that there may be a tendency for ξ to decrease with an increase in r for the present dimers in hydrocarbon solvents. In conclusion, the present dimer formation does not always need apical co-ordination of oxygen atoms. Furthermore, it is suggested that there may be no large differences in stabilization energy among the various dimeric structures mentioned. This is presumably responsible in part for the polymorphism of this series of complexes.[16]

The R = Pr^i complex has been shown to adopt a tetrahedrally distorted configuration around Cu^{II} in the solid state due to the bulkiness of the alkyl group.[17] Such is also the case for this complex in solution, although there exists in toluene a configurational equilibrium between two species with different degrees of tetrahedral distortion.[18] It is unusual that the dimers of this complex have the same r and ξ values as the parallel planar dimers of the R = Me derivative in toluene (Table 2). The r and ξ values, however, can be interpreted in terms of a dimeric structure with a distorted square-pyramidal configuration around Cu^{II} [Figure 5(*c*)]. This structure satisfies all the steric requirements, and both ligand planes of the monomeric halves are parallel to each other as in the other dimeric structures.

Intradimer Spin-exchange Interactions.—The intradimer spin-exchange interaction energy J has always come into question in magnetic investigations of dimeric Cu^{II} complexes or related systems. Recently, we established a method of determining J values ranging from -0.5 to -20 cm^{-1} with a considerable degree of accuracy; this method is based on the relative-intensity measurements of a $\Delta M = 2$ spectrum over the temperature range 4.2—1.57 K (see Experimental section). Some experimental data on this subject are shown in Figure 7. The determined J values (Table 3) indicate that all the present dimers in solution are weakly antiferromagnetic, despite the fact that dimers of [Cu(*N*-Me-sal)$_2$] in the γ form in the solid state are ferromagnetic.[19] $|J|$ Values for dimers of spectral types A and B are almost the same, but smaller than those of type C. On the grounds of Table 3 only, however, it is difficult to obtain a definite correlation between J and a structural property because of insufficient data.

The $|J|$ values in Table 3 satisfy the condition $3\,h\nu \leqslant |J| \leqslant 30$ cm^{-1}, where $h\nu$ is the microwave energy at *X* band. In this condition, pseudo-dipolar corrections can be neglected in the estimation of the zero-field splitting energy and, in addition, the spectrum can be treated as arising simply within the triplet state because of sufficiently large splitting between the triplet and singlet states.[1] Therefore, the computer-simulation method used above is fundamentally valid in the present cases, as has been noted above.

TABLE 3

Intradimer spin-exchange interaction energies (J) for dimeric species of [Cu(*N*-R-sal)$_2$]

R	Spectral type	J [a] / cm^{-1}
Et	A	-1.5 [b]
Pr^n	A	-1.6 [b]
Bu^n	B	-1.1 [b]
n-Hexyl	B	-1.5 [b]
Pr^i	C	-4.2 [b]
Cyclohexyl	C	-4.5 [b]
Me		-2.3,[c] 8 [d]

[a] The error was ±0.2 except R = Me. [b] In methylcyclohexane. [c] In toluene (ref. 4). [d] In the solid state as the γ form (ref. 19).

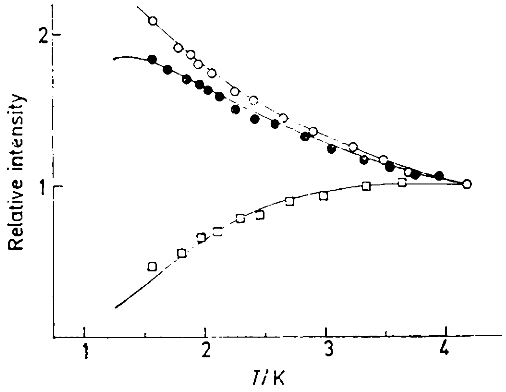

FIGURE 7 Temperature variations of relative intensities in $\Delta M = 2$ spectra: (●), for [Cu(*N*-Et-sal)$_2$]; (○), for [Cu-*N*-Bu^n-sal)$_2$]; (□), [Cu(*N*-Pr^i-sal)$_2$]; (——), calculated with the J values in Table 3

Thermodynamics of Dimer Formation.—We investigated the equilibrium $2\,M \rightleftharpoons M_2$ (M = monomer) quantitatively for dimers of spectral types A and B. Mononuclear Cu^{II} complexes in solution give a hyperfine structure of four equally intense lines with different linewidths. On the other hand, their dimers apparently show no e.s.r. signals because of extremely large anisotropy in the triplet-state spectra. The equilibrium constant, accordingly, can be determined from the decrease in intensity of the e.s.r. spectrum due to the

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[15] E. C. Lingafelter, G. L. Simmons, B. Morosin, C. Scheringer, and C. Freiburg, *Acta Cryst.*, 1961, **14**, 1222.

[16] L. M. Shkol'nikova and E. A. Shugan, *Zhur. strukt. Khim.*, 1964, **5**, 590.

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[19] W. E. Hatfield, *Inorg. Chem.*, 1972, **11**, 216.

monomers. The temperature dependence of ordinary (not first-derivative) e.s.r. spectra for [Cu(N-Pr^n-sal)$_2$] in methylcyclohexane is shown in Figure 8. The integrated intensity (the shaded area in the Figure) directly read from the spectrum observed at T K was corrected for temperature dependences of concentration or solvent density and of transition probability by multiplying by the factor T/d_T, where d_T is the density of methylcyclohexane at T K, which was estimated from the equation $d_T = 0.7651 + 0.00087\ (298 - T)$.[10] All the experimental data are in Table 4. In Figure 8, the non-linearity of the baseline observed at lower temperatures is perhaps due to the absorption of triplet-state dimers.

TABLE 4

Data on the equilibrium 2 [Cu(N-R-sal)$_2$] $\rightleftharpoons$ [{Cu(N-R-sal)$_2$}$_2$] in methylcyclohexane [a]

R = Pr^n				R = Bu^n			
T/K	R.i.[b]		log K	T/K	R.i.[b]		log K
326	73.3	av. 75.0 [c]		324	74.4	av. 75.4 [c]	
310	75.5			309	75.8		
295	76.4			295	76.4		
281	74.8			281	76.0		
236	62.0		1.10 ± 0.20	238	62.6		1.00 ± 0.23
213	59.6		1.21 ± 0.16	214	60.4		1.16 ± 0.16
187	47.8		1.64 ± 0.12	187	44.3		1.76 ± 0.12
169	32.7		2.16 ± 0.10	169	31.3		2.22 ± 0.10
158	27.4		2.36 ± 0.10	158	24.5		2.50 ± 0.10
150	22.9		2.56 ± 0.10	149	20.6		2.68 ± 0.10

[a] [Complex] = 1.00 × 10^{-2}M. [b] R.i. = relative integrated intensity (±1.1), corrected for temperature dependences of concentration and transition probability (see text). [c] A large error, ±3.0, was adopted for extra safety.

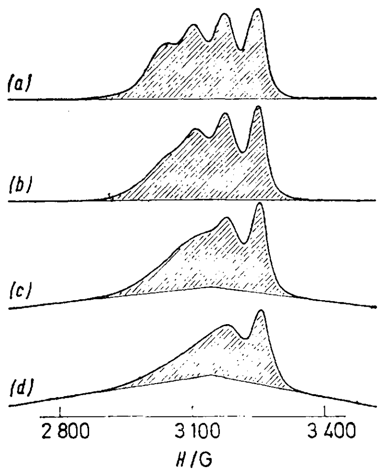

FIGURE 8 X-Band e.s.r. spectra of [Cu(N-Pr^n-sal)$_2$] in methylcyclohexane (1.00 × 10^{-2}M) at 295 (a); 236 (b); 169 (c); and 150 K (d)

Table 4 shows that the relative integrated intensities in the range 0—60 °C are almost constant. Therefore their average is considered to correspond to the situation in which only monomers exist in solution. The thermodynamic constants for this equilibrium in methylcyclohexane were determined to be $\Delta H = -3.0 \pm 0.3$ kcal mol^{-1} and $\Delta S = -8.0 \pm 1.6$ cal K^{-1} mol^{-1} for [Cu(N-Pr^n-sal)$_2$] and $\Delta H = -3.3 \pm 0.4$ kcal mol^{-1} and $\Delta S = -9.8 \pm 1.9$ cal K^{-1} mol^{-1} for [Cu(N-Bu^n-sal)$_2$]. Solvent contributions to these values are small, since methylcyclohexane is an inert saturated hydrocarbon. These results indicate that entropy, rather than enthalpy, changes play an important role in determining the stability of the present dimers; the $|\Delta S|$ values are much larger than $5R/2$, which corresponds to the constant loss of translational entropy per mol accompanied by any kind of dimerization.

The above $|\Delta H|$ values are not large, compared with that for pyridine-adduct formation of bis(pentane-2,4-dionato)copper(II) in benzene ($\Delta H = -6.1$ kcal mol^{-1}).[20] Combined with the fact that [Cu(N-R-sal)$_2$] are generally much more stable than the β-diketone complex, the small $|\Delta H|$ values for dimer formation indicate that there are no large differences in the principal g and A values between the dimers and monomers,[18] as has been noted above. Our computed results are therefore reliable.

[5/446 *Received, 5th March,* 1975]

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