Factors Affecting the Line-width of Nitrogen Superhyperfine Structure in the ESR Spectra of Copper(II) Complexes

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ESR spectra were measured for several series of copper(II) complexes in an attempt to find the best-observable condition for ^{14}N-superhyperfine structure. It was demonstrated that in addition to the temperature and the dilution factors the line-width of ^{14}N-superhyperfine structure is broadened out by the following factors; 1) deviation from square planar configuration around a copper ion, *i. e.*, deformation to elongated octahedron or square pyramid due to weak bonding along the tetragonal axis and/or distortion of coplanality of the coordination bond effected by some steric condition, and 2) the presence of protons that can couple with an unpaired electron and ^{14}N-nuclei.

Although variable informations of coordination bonds are obtainable from an observation of ^{14}N-superhyperfine structure (=^{14}N-shfs) in ESR spectra of copper(II) complexes, there are known rather few examples which give ESR spectra with well-resolved ^{14}N-shfs useful for the discussion of nature of coordination bond. In this study, therefore, it was attempted to investigate under what condition ^{14}N-shfs is observed with a good resolution.

It has been known that broadening of ESR line-width is effected mainly by 1) spin-lattice interaction and 2) spin-spin interaction.[1] Since the spin-orbit coupling plays an essential role at the mechanism, 1), the spin-lattice relaxation time depends very markedly on the energy separation between the ground state and the first excited state capable of coupling with the ground state *via* spin-orbit interaction.[2] Among the various symmetries of copper(II) complexes, the separation between the ground and the first excited states is largest for a square planar complex. Accordingly, deformation of square planar structure to eleongated octahedron, square pyramid or flattered tetrahedron should cause broadening of ESR line-width.

For the mechanism, 2), there are two kinds of spin-spin interactions, that is, intermolecular interaction between paramagnetic ions and interaction between an unpaired electron and nuclear spins. The effect due to the former interaction can be reduced by diluting a sample in diamagnetic host lattice or solvent. The latter interaction sometimes gives a hyperfine or superhyperfine structure with many sharp lines, but when there are so many nuclear spins to interact with an electron spin and line-width are not narrow enough to separate each line, the lines are superposed on each other, making the line-width of the original spectrum broader. Therefore, the effect of ligand protons may play an important role for the resolution of ^{14}N-shfs of copper(II) complexes.

Among the various factors on which ESR line-width is dependent, the two effects, *i. e.*, the effect of deviation from square planar configuration around copper ion and the effect of protons in the ligand capable of coupling with an electron spin, are mainly investigated in the present study.

Experimental

Bis(*N*-alkylsalicylaldiminato)copper(II),[3] bis(*N*,*N*-dialkylglycinato)copper(II),[4] sodium bis(*N*,*N*'-dialkyloxamidato)-cuprate(II),[5] *N*,*N*'-bis(2-aminoethyl)malonamidatocopper-(II),[6] bis(2-hydroxyacetophenone)ethylenediiminatocopper-(II)[7] and bis(salicylaldehyde)ethylenediiminatocopper(II)[7] were prepared according to the methods described in the literatures.

The ESR spectra were measured with a JEOL ESR-apparatus model JES-ME-3X at 130 K and at room temperature using the X-band, DPPH being used as a standard marker.

Absorption and reflectance spectra in the visible region were measured with Hitachi EPS-2 and EPS-3T spectrophotometers, respectively.

Abbreviations of the compounds are tabulated in Table 1.

TABLE 1. THE COMPOUNDS AND THE ABBREVIATIONS

Compound	Abbreviation
Bis(*N*-methylsalicylaldiminato)copper(II)	Cu $msaln_2$
Bis(*N*-ethylsalicylaldiminato)copper(II)	Cu $esaln_2$
Bis(*N*-iso-propylsalicylaldiminato)copper(II)	Cu $psaln_2$
Bis(*N*-tert-butylsalicylaldiminato)copper(II)	Cu $bsaln_2$
Bis(glycinato)copper(II)	Cu gly_2
Bis(*N*,*N*-dimethylglycinato)copper(II)	Cu $dmgly_2$
Bis(*N*,*N*-diethylglycinato)copper(II)	Cu $degly_2$
Bis(*N*,*N*-di-*n*-propylglycinato)copper(II)	Cu $dpgly_2$
N,*N*'-Bis(2-aminoethyl)malonamidato-copper(II)	Cu malen
Sodium bis(oxamidato)cuprate(II)	Cu oxd_2
Sodium bis(*N*,*N*'-dimethyloxamidato)-cuprate(II)	Cu $dmoxd_2$
Sodium bis(*N*,*N*'-diethyloxamidato)cuprate(II)	Cu $deoxd_2$
Bis(2-hydroxyacetophenone)ethylene-diiminatocopper(II)	Cu oapen
Bis(salicylaldehyde)ethylenediiminato-copper(II)	Cu salen

Results and Discussion

Spin-Hamiltonian parameters were obtained from the observed spectra according to the methods of Kneubühl[8] and Sands[9] and are listed in Table 2.

Table 2. ESR parameters and peaks of electronic spectra

Compound	Solvent	g_0	$g_\parallel$	$g_\perp$	A_0	$A_\parallel$	$A_\perp$	A_0^N	$1/2(A_\parallel^N+A_\perp^N)$	$A_\perp^N$	ν_{max} (mμ)
					($\times 10^4$ cm^{-1})						
Cu msaln$_2$	TCE[1]	2.110	2.225	2.053	71.8	171.6	21.9	—	—	—	—
Cu esaln$_2$	TCE	2.113	2.220	2.060	70.3	161.1	24.9	—	—	—	—
Cu psaln$_2$	TCE	2.121	2.229	2.067	62.8	164.9	11.8	—	—	—	—
Cu bsaln$_2$	TCE	—	2.273	—	—	119.3	—	—	—	—	—
Cu gly$_2$	W+E[2]	2.120	2.232	2.065	61.2	152.1	15.8	—	—	—	630
Cu dmgly$_2$	W+E	2.117	2.217	2.067	63.1	157.7	15.8	10.4	—	—	598
Cu degly$_2$	W+E	2.113	2.220	2.060	70.5	161.3	25.0	9.3	—	—	590
Cu dpgly$_2$	W+E	2.111	2.219	2.057	74.2	163.2	29.7	7.4	—	—	583
Cu malen	D_2O	2.090	—	—	83.1	—	—	—	—	11.5	—
	M[3]	2.086	—	—	84.9	—	—	—	—	—	—
Cu oxd$_2$	Ni[4]	—	2.168	—	—	189.1	—	13.0	—	—	520[5]
Cu dmoxd$_2$	Ni	—	2.202	—	—	166.9	—	11.9	—	—	560[5]
Cu deoxd$_2$	Ni	—	2.201	—	—	148.4	—	—	—	—	605[5]
Cu oapen	TCE	2.097	2.198	2.047	85.0	188.1	33.5	13.1	10.9	11.9	555
Cu salen	TCE	2.092	2.173	2.052	82.6	182.5	34.7	—	—	—	570

1) 1,1,2,2-tetrachloroethane, 2) water+ethanol (1 : 1), 3) methanol, 4) corresponding nickel(II) complex, 5) reflectance spectrum

The spectra of a series of bis(*N*-alkylsalicylaldiminato)copper(II), (where, alkyl=methyl, ethyl, *i*-propyl, and *t*-butyl) are shown in Fig. 1. For the methyl homologue ^{14}N-shfs was observed in a perpendicular component of the spectra, though the resolution was rather poor. With the increase of bulkiness of the alkyl group ^{14}N-shfs becomes unresolved as seen in Fig. 1. This is compatible with the trend[10] that the increase of the size of a substituent on the imine nitrogen sterically effects a distortion of the planar configuration around the copper ion. On the contrary to the above results, as shown in Fig. 2, the resolution of ^{14}N-shfs becomes better with the increase of bulkiness of alkyl group for the series of bis(*N*,*N*-dialkylglycinato)copper(II), (where, alkyl=H, methyl, ethyl, and *n*-propyl). Since in these compounds the alkyl groups block the axial coordination sphere from the attack of solvent molecules, the increase of the size of alkyl group reduces the axial perturbation, effecting a good resolution of the ESR line-width. As shown in Table 2, frequency of visible absorption band increases with the increasing order of bulkiness of alkyl groups *i.e.*, $H<CH_3<C_2H_5<n\text{-}C_3H_7$. This fact is supporting the above discussion, since it is well known that d-d band of a copper complex shifts to higher frequency with the change from elongated octahedron to square planar configuration.

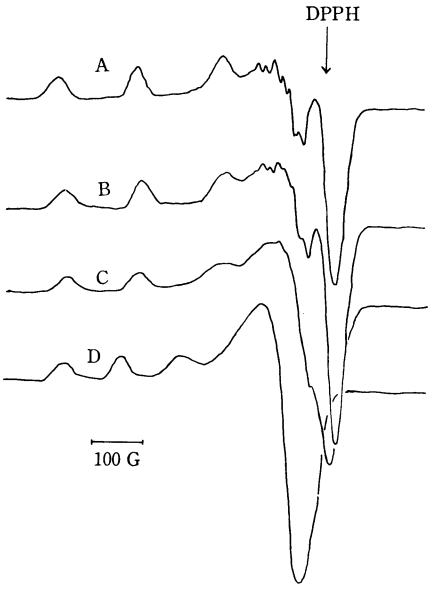

Fig. 1. ESR spectra of bis(*N*-alkylsalicylaldiminato)-copper(II) in 1,1,2,2-tetrachloroethane at room temperature
A: methyl, B: ethyl, C: *i*-propyl, D: *t*-butyl

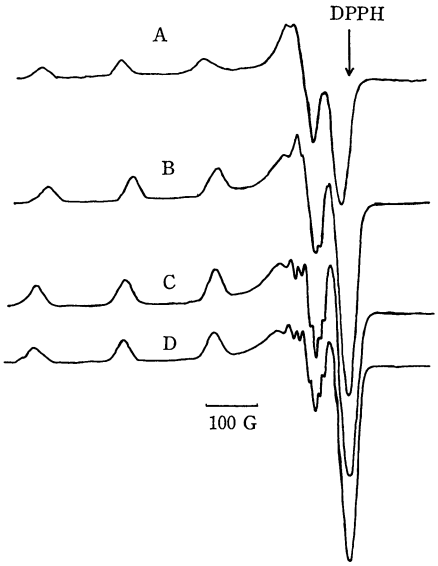

Fig. 2. ESR spectra of bis(*N*,*N*-dialkylglycinato)-copper(II) in water-ethanol (1 : 1) at 133 K
A: H, B: methyl, C: ethyl, D: *n*-propyl

In the series of bis(*N*,*N'*-dialkyloxamidato)copper(II) complexes, frequency of visible band of powder reflectance spectrum decreases with the increase of bulkiness of alkyl group, *i.e.*, $H > CH_3 > C_2H_5$, (*cf.* Table 2), quite reverse to the bis(*N*,*N*-dialkylglycinato)copper(II) series. This fact implies that in this case the alkyl groups function as to twist the planar configuration around the copper ion by steric hindrance.

Accordingly, one might expect that the resolution of ^{14}N-shfs becomes poor with the increase of the size of the substituent. This is true for the methyl and the ethyl derivatives, as obviously seen in Fig. 3. However, the oxamidato complex shows much poorer ^{14}N-shfs than the methyl derivative (Fig. 3). This rather complex result seems to be only interpretable in terms of the line-broadening effect of protons on nitrogen atoms of oxamide, *i. e.*, further coupling with the hydrogen nucleus tends to increase the number of ESR lines,[11] but line-width is not so sharp as to separate each line, and as a result, smoothening out the original ^{14}N-shfs.

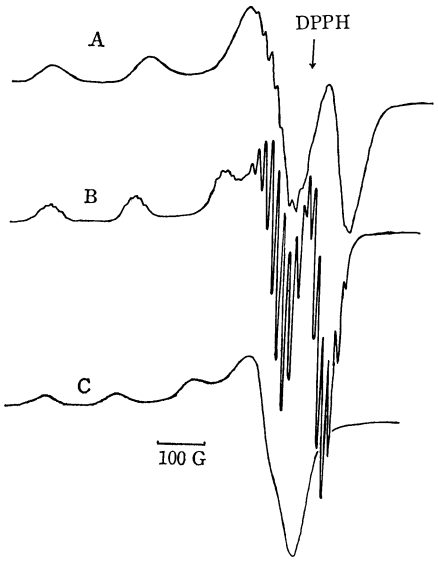

Fig. 3. ESR spectra of sodium bis(*N*,*N'*-dialkyloxamidato)cuprate(II) doped in the corresponding nickel(II) complexes at 130 K
A: H, B: methyl, C: ethyl

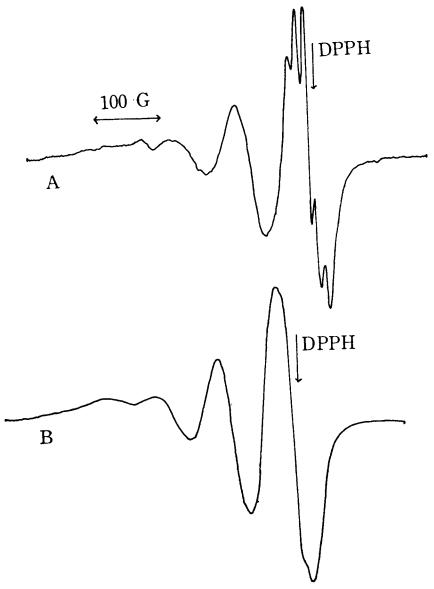

Fig. 4. ESR spectra of bis(salicylaldehyde)ethylenediiminatocopper(II) (B) and its methyl derivative (A) in 1,1,2,2-tetrachloroethane at room temperature.

A similar effect is seen in bis(salicylaldehyde)ethylenediminatocopper(II) (=[Cu salen]) and its methyl derivative (=[Cu oapen]). As evidently seen in Fig. 4, the ^{14}N-shfs was much better resolved in the methyl homologue than that in [Cu salen]. This is also attributed to the line-broadening effect of methine protons which are very close to the C═N═Cu π-bond system.

The effect of protons on ^{14}N-shfs is clearly elucidated by comparison of the spectra of *N*,*N'*-bis(2-aminoethyl)-malonamidatocopper(II) (= [Cu malen]) in methanol and D_2O. As shown in Fig. 5, ^{14}N-shfs was observed in D_2O solution,[12] but hardly observable in methanol solution. This is because the spin-spin interaction between electron and nucleus is much weaker for $^2H(\mu_I=0.857)$ compared to that for ^1H $(\mu_I=2.793)$ and therefore, ^{14}N-shfs of [Cu malen] was observed only in D_2O, where the amino hydrogens are substituted with deuterium.

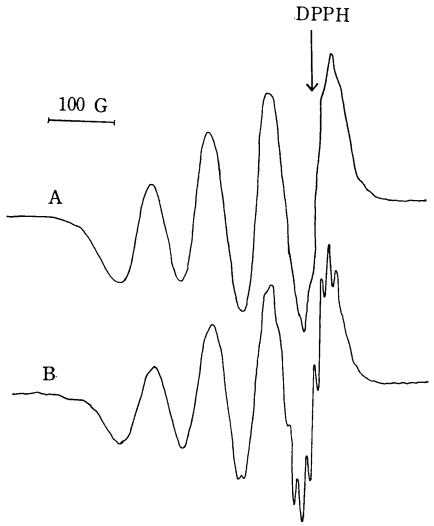

Fig. 5. ESR spectra of *N*,*N'*-bis(2-aminoethyl)malonamidatocopper(II) in methanol (A) and in D_2O (B) at room temperature.

All the above facts support our initial assumption that a deviation from square planar configuration and a presence of protons to couple with an unpaired electron spin are both important factors for the interference of observation of well-resolved ^{14}N-shfs.

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