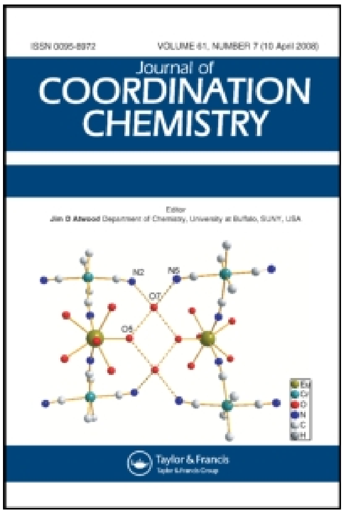

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ESR SPECTRA OF THE SQUARE PLANAR COPPER(II) COMPLEXES WITH VARIOUS N_4-MACROCYCLIC LIGANDS

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ESR SPECTRA OF THE SQUARE PLANAR COPPER(II) COMPLEXES WITH VARIOUS N_4-MACROCYCLIC LIGANDS

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The ESR parameters were determined for copper(II) complexes with various 14-, 15- and 16-membered N_4-macrocyclic ligands. Of these ESR parameters $g_{\parallel}$ has the most simple relation to the covalency of the coordination bonds in the present compounds, i.e., the smaller the $g_{\parallel}$ value the larger the covalency. The order of covalencies derived from the $g_{\parallel}$ values nicely matches with that supposed from the size of macrocyclic rings and the charge of the ligands. The approach to the estimation of covalency of the coordination bonds by use of copper hyperfine coupling constant was examined, but it was found that this approach gives rather unreliable results for the present compounds.

INTRODUCTION

Recently a large number of metal complexes with macrocyclic ligands have been synthesized, and their properties have been discussed in terms of the effects of the macrocyclic ligands, i.e., ring size, π-conjugation, electric charge and substituents.[1–4] In this study, we have measured ESR spectra of copper(II) complexes with various N_4-macrocyclic ligands in frozen solutions or in analogous nickel(II) complexes, and determined ESR parameters. On the basis of these data we have tried to estimate covalency of the coordination bonds for these complexes.

Many investigations have been undertaken for the determination of covalency of copper(II) complexes by use of ESR parameters. So far, three different approaches have been employed; they are based on the theoretical interpretation of (1) g-values[5,6], (2) ^{Cu}A as well as g-values[7,8] and (3) ^{N}A-values[5], where ^{Cu}A and ^{N}A represent the hyperfine coupling constants due to copper atom and coordinated nitrogen atoms, respectively. However each method has met considerable criticism on the theoretical interpretation and the evaluation of the necessary parameters for the calculation.[9,10] Accordingly we must be careful in applying these methods, and assess the method in a practical situation.

In this study, the compounds are limited to copper(II) complexes with N_4-macrocyclic ligands, so that the theoretical expression can be much simplified (see later section). Accordingly we tried to determine the relative magnitude of σ-covalency from $g_{\parallel}$-values of the complexes. We also determined the covalency parameters from g- and ^{Cu}A-values by conventional methods[7,8], and assessed the validity of the methods, comparing the results with those from $g_{\parallel}$-values.

EXPERIMENTAL

The ligands (see Fig. 1) and their nickel(II) and copper(II) complexes were prepared according to the methods described in the literature. H_2(*a*-14, 15, 16)[11], H_2(*b*-14, 15, 16)[12], H_2(*c*-14, 15, 15′, 16)[13], H_2(*d*-14)[14], (*e*-14)[15], H(*f*-14)[16], H_2(*g*-14, 14′)[17] and (*h*-16)[18]. ESR spectra were obtained with a JEOL ESR apparatus JES-ME-3X using the X-band at room temperature and liquid nitrogen temperature. DPPH was used as a standard marker.

RESULTS AND DISCUSSION

Investigation of g-values.

According to Maki and McGarvey[5], $g_{\parallel}$ and $g_{\perp}$ of square planar copper(II) complexes are expressed as

$$g_{\parallel} = 2 - \frac{8\lambda\alpha\beta_1}{E_{xy} - E_0}\left(\alpha\beta_1 - \tfrac{1}{2}\alpha'(1 - \beta_1^2)^{1/2}T(n)\right) \qquad (1)$$

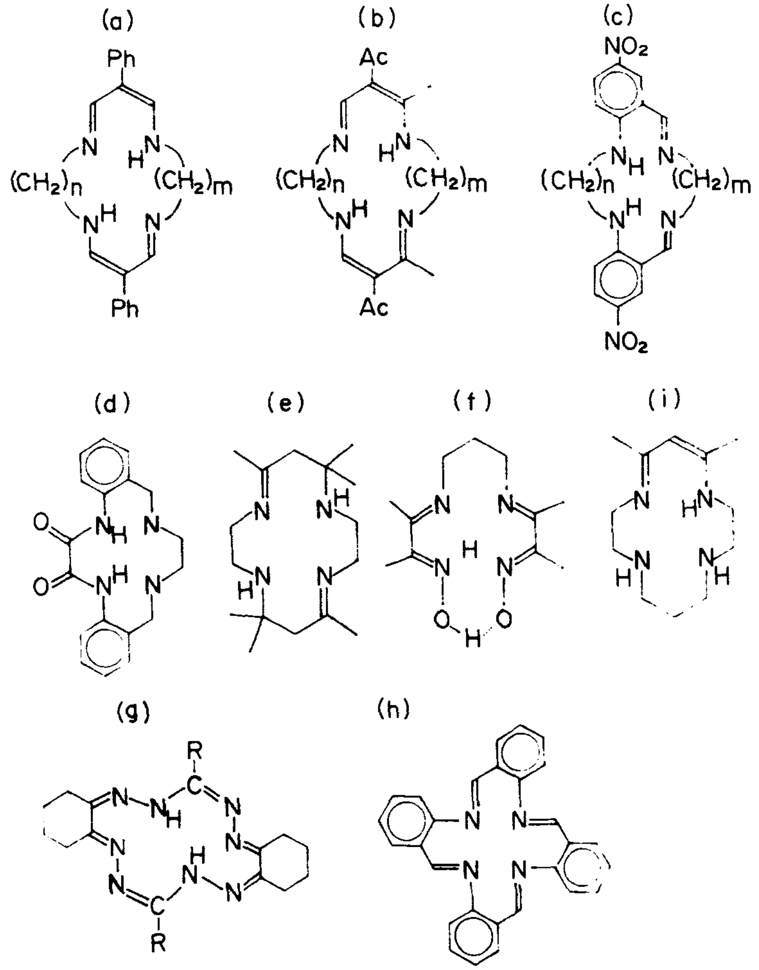

FIGURE 1 The N_4-macrocyclic ligands used in this study. The abbreviations are: (*a*) H_2(*a*-14); $n = m = 2$, H_2(*a*-15); $n = 2$, $m = 3$, H_2(*a*-16); $n = m = 3$ (*b*) H_2(*b*-14); $n = m = 2$, H_2(*b*-15); $n = 2$, $m = 3$, H_2(*b*-16); $n = m = 3$ (*c*) H_2(*c*-14); $n = m = 2$, H_2(*c*-15); $n = 2$, $m = 3$, H_2(*c*-15′); $n = 3$, $m = 2$, H_2(*c*-16); $n = m = 3$ (*d*) H_2(*d*-14) (*e*) (*e*-14) (*f*) H (*f*-14) (*g*) H_2 (*g*-14); $R{=}CH_3$ H_2(*g*-14′); $R{=}C_2H_5$ (*h*) (*h*-16) (*i*) H(*i*-14).

$$g_\perp = 2 - \frac{2\lambda\alpha\beta}{E_{xz,yz} - E_0}\,(\alpha\beta - (1/\sqrt{2})\alpha'(1-\beta^2)^{1/2}T(n)) \qquad (2)$$

where λ is the spin-orbit coupling constant for the free copper(II) ion, E_n is the energy of the appropriate molecular orbital and α, α', β and β_1 are the coefficients of the molecular orbitals;

$$b_{1g} \quad \alpha\, d_{x^2-y^2} - \frac{\alpha'}{2}(-\sigma^a + \sigma^b + \sigma^c - \sigma^d) \qquad (3)$$

$$b_{2g} \quad \beta_1 d_{xy} - \frac{(1-\beta_1^2)^{1/2}}{2}(\pi_y^a + \pi_x^b - \pi_y^c - \pi_x^d) \qquad (4)$$

$$a_{1g} \quad \alpha_1 d_{z^2} - \frac{\alpha_1'}{2}(\sigma^a + \sigma^b + \sigma^c + \sigma^d) \qquad (5)$$

$$e_g \quad \beta d_{xz} - \sqrt{\frac{(1-\beta^2)}{2}}(\pi_z^a - \pi_z^c) \qquad (6)$$

$$\beta d_{yz} - \sqrt{\frac{(1-\beta^2)}{2}}(\pi_z^b - \pi_z^d) \qquad (7)$$

for $T(n)$ refer to reference 5.

In this study, our discussion is limited to copper(II) complexes with N_4-macrocyclic ligands, where no π_x and π_y orbitals exist. Hence we may regard β_1 as unity. Thus, the equation (1) is reduced to

$$g_\parallel = 2 - \frac{8\lambda\alpha^2}{E_{xy} - E_0}\,. \qquad (8)$$

TABLE I

ESR parameters of copper(II) complexes with N_4-macrocyclic ligands****

Complexes	$g_{\parallel}$	$\lvert A_{\parallel} \rvert$ (10^{-4} cm^{-1})
[Cu(*b*-14)] **	2.136	221
[Cu(*b*-15)] **	2.149	213
[Cu(*b*-16)] *	2.161	199
[Cu(*c*-14)] *	2.135	217
[Cu(*c*-15)] *	2.151	206
[Cu(*c*-15′)] *	2.160	199
[Cu(*c*-16)] *	2.184	177
[Cu(*d*-14)] *	2.133	212
[Cu(*e*-14)] $(Bph_4)_2$ *	2.161	199
[Cu(*f*-14)] ClO_4 *	2.149	210
[Cu(*g*-14)] **	2.082	212
[Cu(*g*-14′)] **	2.076	212
[Cu(*h*-16)] $(ClO_4)_2$ *	2.200	178
Cu-phthalocyanine[28]	2.160	217
Cu-TPP[29],***	2.187	218

*in nickel(II) complexes (295 K)

**in $CHCl_3$ solution (77 K)

***TPP represents $\alpha, \beta, \gamma, \delta$-tetraphenylporphyrin.

****For the ESR parameters of the complexes with ligands (a), see Ref. 20.

It is evident that an increase of σ-covalency results in the increase of $E_{xy} - E_0$ and decrease of α. Therefore, we conclude that $g_{\parallel}$-value is a good measure of σ-covalency of square planar copper(II) complexes with N_4-macrocycles, i.e., the smaller the $g_{\parallel}$-value the larger the σ-covalency. On the other hand, it is not easy to estimate the covalency of π-interaction, because β is apparently less than unity, so that equations (6) and (7) can not be reduced to such simple formulas.

The $g_{\parallel}$-values of various copper(II) complexes with N_4-macrocycles are listed in Table I. Among these [Cu(*g*-14)] and [Cu(*g*-14′)] have the smallest $g_{\parallel}$-values. This is in good accordance with the fact that the macrocyclic radii of (*g*-14) and (*g*-14′) are smaller than any other N_4-macrocycles listed in Fig. 1,[19] indicating that our criterion based on $g_{\parallel}$-value is working satisfactorily so far.

It is obvious from Table 1 that the largest $g_{\parallel}$-value of the 14-membered macrocycles is that of [Cu(*e*-14)] $(Bph_4)_2$, and the second largest $g_{\parallel}$-value is that of [Cu(*f*-14)] ClO_4, which are followed by several non-charged complexes of 14-membered N_4-macrocycles. This fact indicates that the negatively charged ligands have stronger σ-donor strengths than those of neutral ligands. The same trend is also seen in the series of 16-membered N_4-macrocycles in Table 1. The extent of the axial ligation for copper(II) atom is dependent upon the donor strengths of the counter ions and the solvents. They do profoundly effect the energy level of the d_{z^2} orbital and to a monor extent the other orbitals. However, $g_{\parallel}$-value is not effected by the energy of d_{z^2} orbital (see eq. 8) and the ESR measurements of the copper(II) complexes of neutral ligands were performed in analogous nickel(II) complexes (see Table 1), the effects due to the axial ligation were neglected in the interpretation of the ESR parameters.

In this connection, it is interesting to see the d-d bands. The frequencies of the lowest-energy d-d bands of some copper(II) complexes with N_4-macrocycles are listed in Table II. The cationic complexes, for example, [Cu(*e*-14)] $(Bph_4)_2$ and [Cu(*f*-14)] ClO_4, dissolve only in polar solvents, such as acetone, DMF and CH_3OH. For these cases, the axial ligation due to the solvents may occur, which leads to the lowering of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition energy. However, as seen in the Table, the bands of the complexes with negatively charged ligands locate at lower-energy region than those of complexes with non-charged ligands of similar ring size. This fact may appear to be strange in view of the preceding discussion on the ESR parameters. The above facts can be reasonably explained in terms of the d-d splitting scheme by

TABLE II

Spectral data (d-d bands) of some copper(II) complexes with N_4-macrocyclic ligands

Complex	$\bar{\nu} \cdot 10^3$ cm^{-1} (ϵ)	solvent	Ref.
[Cu(*a*-14)]	16.0(240)	CH_2ClCH_2Cl	20
[Cu(*a*-15)]	13.0(209)	CH_2ClCH_2Cl	20
[Cu(*b*-14)]	18.1(358)	CH_2ClCH_2Cl	This work
[Cu(*b*-15)]	18.4(298)	CH_2ClCH_2Cl	This work
[Cu(*e*-14)] $(Bph_4)_2$	19.0(143)	DMF	20
[Cu(*f*-14)] ClO_4	21.9(235)	acetone	20
[Cu(*i*-14)] $(PF_6)_2$ *	20.0(150)	methanol	23
[Cu(*i*-14)] PF_6	16.0(100), 23.5(200)	methanol	23

*In this case, the N_4-macrocycle is neutral.

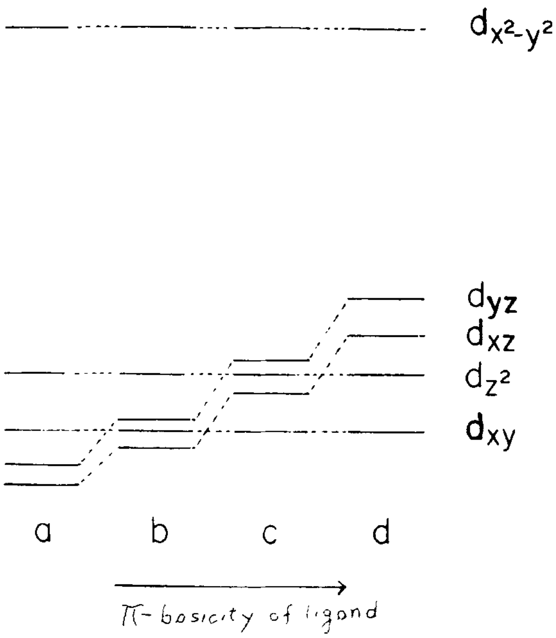

FIGURE 2 The splitting schemes of d-orbitals in the square planar metal complexes. For the sake of simplicity, the energy gap between d_{xy} and $d_{x^2-y^2}$ orbitals is fixed at a constant value.

Nishida et al.[20,21] proposed for square planar complexes (cf. Fig. 2).

In these studies, Nishida et al. investigated the ESR spectra of low-spin square planar cobalt(II) complexes, and assigned the $(a_{1g})^1(b_{1g})^2$ electronic configuration to the ground state of [Co(e-14)]$(Bph_4)_2$ and [Co(f-14)]ClO_4, whereas, $(e_g)^1(b_{1g})^2$ was assigned to those of the complexes with dinegatively charged ligands, except for phthalocyanine and porphyrins.[20,22] On this basis Nishida et al. proposed a d-d splitting scheme for square planar complexes illustrated in Fig. 2.[21] According to the results obtained from the cobalt(II) complexes, it is shown that the metal $e_g(d_{xz}, d_{yz})$ orbitals are considerably lifted through π-interaction in the complexes of dinegatively charged ligands. Thus, the complexes of dinegatively charged ligands correspond to the case of (d) in Fig. 2, whereas the case (a) or (b) was assumed for the complexes with non-charged ligands.[21] If we assign the lowest-energy band to $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transition, these orbital energy schemes explain the experimental fact that the lowest-energy bands of the copper(II) complexes with negatively charged ligands are generally lower in energy than those of the complexes with non-charged ligands.

According to our scheme, the $d_{xy} \rightarrow d_{x^2-y^2}$ transition is expected at a higher energy region for the complexes of negatively charged ligands. In fact, as shown in Table 2, two splitted d-d bands are observed for the [Cu(i-14)]PF_6 complex.[23] Unfortunately, however, in other cases of the ligands such as H_2(a-14) and H_2(b-14), etc, intense charge-transfer bands mask the highest d-d bands.

Approach from the g- and ^{Cu}A-values

The most simplified theoretical expression for ^{Cu}A was obtained by Kivelson and Neiman[7]:

$$A_{\parallel} = P[-\alpha^2(4/7 + \kappa) + (g_{\parallel} - 2) + 3/7(g_{\perp} - 2) + 0.04] \qquad (9)$$

It is evident that the largest contribution term is $-(4/7 + \kappa)$ in equation (9), because it is known that $A_{\parallel}$ usually assumes a negative value[10], where κ is Fermi hyperfine coupling constant.[24] Therefore, $|A_{\parallel}|$ is expected to decrease with the increase of σ-covalency of coordination bonds. As seen in Table 1, the experimentally obtained $|A_{\parallel}|$ decreases with the increase of the ring size. Hence, we might interpret this result as that the σ-covalency of the coordination bonds increase with the increase of the *ring size*. However, it is obvious that this interpretation is in conflict with the generally accepted view. This suggests that the discussion on the covalency of coordination bonds in terms of ^{Cu}A-values is not reliable. This view is also supported by the fact that $|A_{\parallel}|$ values in Table 1 show no systematic trend for the ring size and the charge on the ligands.

TABLE III
Bonding parameters (α^2) obtained from the ESR spectra*[1]

Complex	A*[2]	B*[3]
[Cu(a-14)]	0.639	0.792
[Cu(a-15)]	0.605	0.790
[Cu(a-16)]	0.618	0.779
[Cu(b-14)]	0.709	0.836
[Cu(b-15)]	0.636	0.843
[Cu(f-14)]ClO_4 *[4]	0.682	0.733
[Cu(g-14)]	0.571	0.705
[Cu(h-16)]$(ClO_4)_2$ *[4]	0.625	0.762

*[1] For the calculations, P and κ were fixed at 0.036 cm^{-1} and 0.4, respectively.

*[2] Calculated from the equation (10).

*[3] Calculated from the equation (11).

*[4] The g_{ave} and $|A_{ave}|$ of [Cu(f-14)]ClO_4 and [Cu(h-16)]$(ClO_4)_2$ were obtained from the spectra in a acetone and a acetonitrile solution (295 K), respectively. For other complexes, the ESR data in $CHCl_3$ solutions (295 K) were used.

The bonding parameter, α^2 can be evaluated by using ^{Cu}A- and g-values according to equations (10) and (11).[7,8,10]

$$\alpha^2 = \tfrac{7}{4}[-A/P - \kappa + (g_{\parallel} - 2) + \tfrac{3}{7}(g_{\perp} - 2) + 0.04] \quad (10)$$

$$\alpha^2 = -A_{\mathrm{ave}}/P\kappa + (g_{\mathrm{ave}} - 2) \quad (11)$$

As seen in Table III, however, there is no good accodance between the α^2 values obtained from equation (10) and (11) and neither series of α^2 show any systematic trends. Thus, we concluded that ^{Cu}A-values give no reliable information about the covalency of the coordination bonds in square planar copper(II) complexes with N_4-macrocyclic ligands.

Approach from the ^{N}A-value

Approaches to the estimation of covalency of coordinate bonds by utilizing superhyperfine coupling constant, ^{N}A, were reported by several authors.[5,25] However, it is not easy to obtain the precise $^{N}A_{\parallel}$ and $^{N}A_{\perp}$-values experimentally. In addition to this, this approach has another difficulty, i.e., in order to evaluate the σ-covalency of the coordinate bonds in terms of ^{N}A-values, we have to estimate the degree of contribution from 2s and 1s orbitals to the ^{N}A-values,[26,27] which would considerably vary depending on the ligands. For these reasons the application of the approach from ^{N}A-value is limited.

In the present study the superhyperfine structures due to the coordinated nitrogen atoms were observed for only few complexes and the results are summarized in Table IV. As shown in the Table, the $|^{N}A_{\mathrm{ave}}|$ values are almost the same in copper(II)-porphyrin and [Cu(g-14)], on the other hand, the $g_{\parallel}$-values of these complexes are greatly different from each other. In conclusion, $g_{\parallel}$-values can be used as the most reliable and convenient measure of σ-covalency of coordinate bonds for copper(II) complexes with N_4-macrocyclic ligands.

TABLE IV
Data of superhyperfine structures of some copper(II) complexes with macrocyclic ligands

Complex	$\lvert ^{N}A_{\mathrm{ave}} \rvert$ (10^{-4} cm^{-1})	$g_{\parallel}$
[Cu(g-14)]	15.2	2.082
[Cu(g-14′)]	15.2	2.076
Cu-TPP[29],*	15.9	2.187
Cu-etioporphyrin[30]	14.6	2.169

*TPP represents α, β, γ, δ-tetraphenylporphyrin.

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