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ESR Studies of Copper(II) Complexes of Ethylenediamine and Its Analogues

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The ESR spectra of the copper(II) complexes of ethylenediamine, 1,2-diaminopropane, *meso*-2,3-diaminobutane, 1,3-diaminopropane, and ammonia were measured in methanolic and aqueous solutions at room temperature and in frozen solutions at the temperature of liquid nitrogen. The covalency of the bonding of the copper atom to the ligand atoms in these complexes was evaluated from the *g* values, the copper hyperfine constants, and the nitrogen super-hyperfine constants. Even in the case of amino groups which were coordinating groups, the π bonding seemed to be as important in determining the properties of the complexes as the σ bonding.

ESR has been proved effective for investigating the bonding in copper(II) complexes.[1-6] However, ESR studies of the copper(II) chelate complexes of ethylenediamine and its analogues have not been carried out in full detail. In these complexes the central copper atom is coordinated to the amino groups, one of best known kinds of coordinating groups; the investigation of the bonding character of copper-amino group bonds is very important in coordination chemistry. The purpose of this work is to obtain the magnetic parameters, neamely, the *g* values, the copper hyperfine constants, and the nitrogen super-hyperfine constants of the copper(II) complexes of ethylenediamine, 1,2-diaminopropane, *meso*-2,3-diaminobutane, 1,3-diaminopropane, and ammonia in solutions at room temperature and at the temperature of liquid nitrogen, and to discuss the covalency of the bonding of the copper atom to amino groups as evaluated from these magnetic parameters.

Experimental

The copper(II) complexes employed in this study were [I] $[Cu(en)_2](ClO_4)_2$, [II] $[Cu(pn)_2](ClO_4)_2$, [III] $[Cu(m\text{-}bn)_2](ClO_4)_2$, [IV] $[Cu(tn)_2](ClO_4)_2$, and [V] $[Cu(am)_4](ClO_4)_2$, where en, pn, m-bn, tn, and am are ethylenediamine, 1,2-diaminopropane, *meso*-2,3-diaminobutane, 1,3-diaminopropane, and ammonia respectively. All the amines were commercially

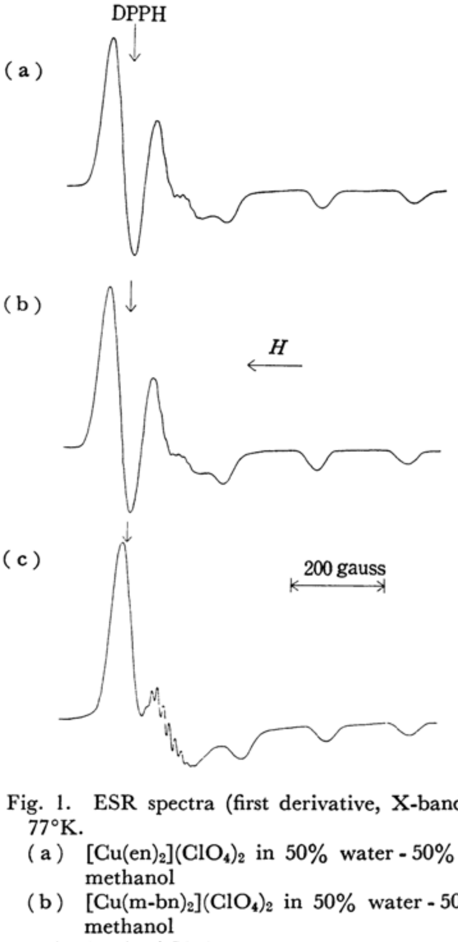

Fig. 1. ESR spectra (first derivative, X-band) at 77°K.

(a) $[Cu(en)_2](ClO_4)_2$ in 50% water - 50% methanol
(b) $[Cu(m\text{-}bn)_2](ClO_4)_2$ in 50% water - 50% methanol
(c) $[Cu(am)_4](ClO_4)_2$ in methanol

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[1] K. W. H. Stevens, *Proc. Roy. Soc. (London)*, **A219**, 542 (1953); J. Owen, *ibid.*, **A227**, 183 (1955).

[2] A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31, 35 (1958).

[3] D. Kivelson and R. Neiman, *ibid.*, **35**, 149 (1961).

[4] E. M. Robert and W. S. Koski, *J. Am. Chem. Soc.*, **82**, 3006 (1960); F. R. Gersman and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962); S. J. T. Owen, K. J. Standley and A. Walker, *ibid.*, **40**, 183 (1964); B. G. Malmstom and T. Vanngard *J. Mol. Biol.*, **2**, 118 (1960).

[5] A. K. Wiersma and J. J. Windle, *J. Phys. Chem.*, **68**, 2316 (1964); W. Schneider and A. v. Zelewsky, *Helv. Chim. Acta*, **48**, 1529 (1965).

[6] S. E. Harrison and J. M. Assour, *J. Chem. Phys.*, **40**, 365 (1964); S. E. Harrison and J. M. Assour, "Paramagnetic Resonance," ed. by W. Low, Academic Press, New York (1963), p. 861; H, A. Kuska, F. M. D'itri and A. I. Popov, *Inorg. Chem.*, **5**, 1272 (1966).

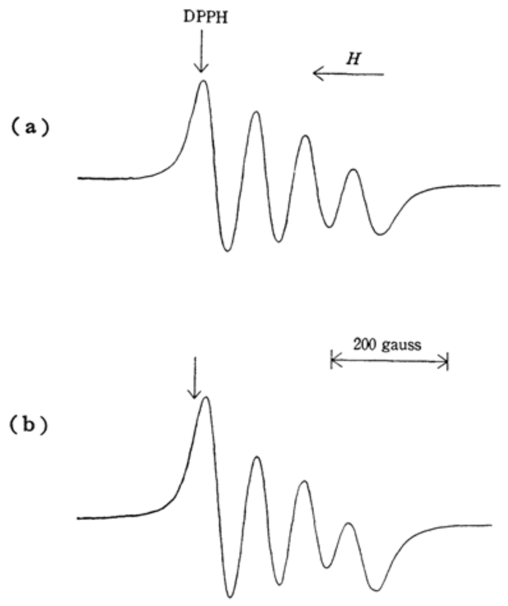

Fig. 2. ESR spectra (X-band) at room temperature in 50% water - 50% methanol.
(a) $[Cu(en)_2](ClO_4)_2$
(b) $[Cu(tn)_2](ClO_4)_2$

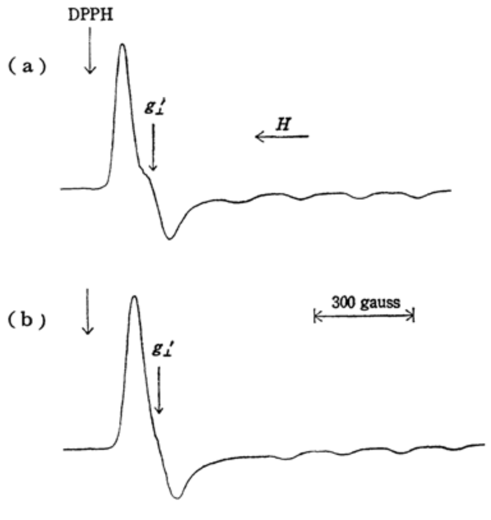

Fig. 3. ESR spectra (first derivative, K-band) on frozen solutions.
(a) $[Cu(pn)_2](ClO_4)_2$ in 50% water - 50% methanol
(b) $[Cu(am)_4](ClO_4)_2$ in methanol

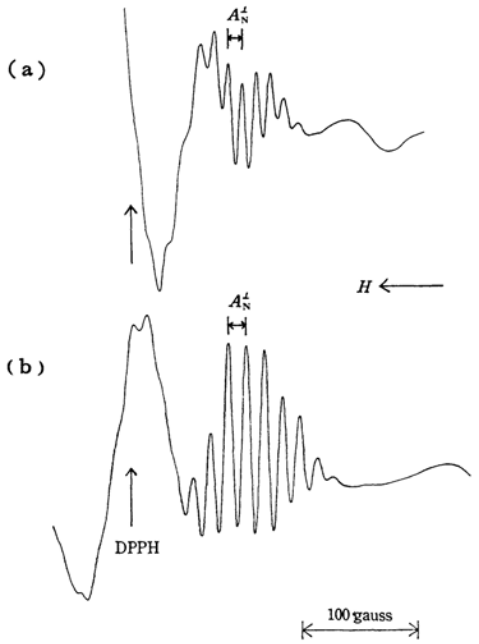

Fig. 4. The high field part of ESR spectra (second derivative, X-band) at 77°K.
(a) $[Cu(pn)_2](ClO_4)_2$ in 50% water-50% methanol
(b) $[Cu(am)_4](ClO_4)_2$ in methanol

available except for m-bn, which was prepared and purified according to the method of literature.[7] The solvents were methanol and a 50% water - 50% methanol mixture (per cent in volume). The ESR spectra of the complexes were measured in solutions at room temperature and on frozen solutions at the temperature of liquid nitrogen with a Hitachi X-band and K-band ESR spectrometer, model MES-4001, equipped with a 100 kc/s field modulation unit. Furthermore, the second derivative ESR spectra were obtained using 100 kc/s-40 c/s field modulations in order clearly to resolve the nitrogen super-hyperfine structure. The field was calibrated with an NMR probe and then with a benzene solution of vanadyl acetylacetonate or with Mn(II) ions in MgO powder. Some of the ESR spectra observed are shown in Figs. 1—4. The optical absorption spectra of the complexes in solutions were measured with a Cary model 14 spectrometer.

Results and Discussion

Magnetic Parameters. As may be seen in Fig. 1, the copper(II) complexes employed in this work show broad ESR absorption lines. This is due to the poor resolution of the nitrogen super-hyperfine strcture, which is, however, observed on $g_\perp$ components in the high-field part of the spectra of Fig. 1. Figure 4 exibits the second derivative of the super-hyperfine lines, from which the super-hyperfine constants can be obtained with considerable accuracy. The problem of determining the magnetic parameters from the ESR spectra of polycrystalline samples or rigid glass solutions has been studied extensively by several authors.[8]

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[7] F. Basolo, Y. T. Chen and R. K. Murmann, *J. Am. Chem. Soc.*, **75**, 1478 (1953).

[8] R. H. Sands, *Phys. Rev.*, **99**, 1222 (1955); R. Neiman and D. Kivelson, *J. Chem. Phys.*, **35**, 156 (1961); T. Vanngard and R. Aasa, Proc. 1st. Intern. Congr. "Paramagnetic Resonance," Jerusalem, 1962, Academic Press, New York (1963), p. 509.

TABLE 1. MAGNETIC PARAMETERS

Copper(II) complex		Solvent[a]	$g_{//}$	$g_\perp$[b]	$g'_\perp$[c]	$A_{//}$ $\times 10^4$ cm^{-1}	$A_\perp$[b] $\times 10^4$ cm^{-1}	g_0[d]	A_0[d] $\times 10^4$ cm^{-1}	$A_N^\perp$ $\times 10^4$ cm^{-1}
[I]	Ethylenediamine	M	2.209			207				
		MH	2.206	2.050	2.052	209	25	2.102	86	10.5
[II]	1,2-Diaminopropane	M	2.209			206				
		MH	2.208	2.050	2.051	210	26	2.103	87	10.7
[III]	*meso*-2,3-Diaminobutane	M	2.203			204				
		MH	2.203	2.050	2.050	205	27	2.101	86	11.3
[IV]	1,3-Diaminopropane	M	2.219			202				
		MH	2.222	2.052	2.052	201	21	2.109	81	12.6
[V]	Ammonia	M	2.242	2.056	2.055	199	17	2.118	77	12.7

a) M: methanol, MH: 50% water-50% methanol (volume %).
b) $g_\perp$ was calculated using the following equation, $g_0=1/3\ (g_{//}+2g_\perp)$.
$A_\perp$ was also calculated in the same way.
c) $g'_\perp$ was directly obtained from the ESR spectrum measured at K-band.
d) Measured at room temperature.

However, it is difficult to analyze completely such ESR spectra as are shown in Fig. 1. The ESR measurements of the copper(II) complexes of ethylenediamine and ammonia in single crystals have revealed that the complexes have axial symmetry (two distinct g values).[9,10] It is now desirable to ascertain whether or not the complexes under discussion have axial symmetry in solutions. Since ESR measurements at both the K-band and X-band are often used to distinguish between two lines of different g values, the ESR spectra were measured at the K-band in this study; some of the ESR spectra are shown in Fig. 3. This figure indicates that, in solutions, axial symmetry is approximately maintained; approximate $g_\perp$ values can be obtained directly from the ESR spectra shown in this figure.

The spin Hamiltonian is expressed as follows:

$$\begin{aligned} H = \beta_0[g_{//}H_zS_z + g_\perp(H_xS_x + H_yS_y)] \\ + A_{//}S_zI_z + A_\perp(S_xI_x + S_yI_y) \\ + A_N^{//}S_zI_z^N + A_N^\perp(S_xI_x^N + S_yI_y^N) \end{aligned} \tag{1}$$

The experimental data are listed in Table 1. It is interesting to see in this table that $g_\perp \doteqdot g'_\perp$; therefore, $A_\perp$ was also calculated using the values of $A_{//}$ and A_0 in the same way as in calculating $g_\perp$.

Chemical Bonding. The experimentally determined quantities, $g_{//}$, $g_\perp$, $A_{//}$, $A_\perp$, and $A_N^\perp$ can be used to estimate the character of the chemical bonding of the copper atom to ligand nitrogen atoms by means of the molecular orbital theory. In the complexes of amines, the σ orbitals of ligand nitrogen atoms are the lone-pair electron orbitals formed by sp^3 hydridization. Therefore, these nitrogen atoms do not have pure π orbitals such as the oxygen atoms of acetylacetonate anion have. However, in this study the complexes of amines have been treated on the assumption that amino groups have a kind of π orbital; we used the same procedure as did Maki and McGarvey,[2] and Kivelson and Neiman[3] in treating Cu(II) bisacetylacetonate. The notation of Maki and McGarvey for a square planar complex will be used here. The following antibonding molecular orbitals, in the order of increasing energy, can be formed for the "hole" configuration:

$$\left.\begin{aligned} \Psi_{b_{1g}} &= \alpha d_{x^2-y^2} - \alpha'(-\sigma_x^{(1)} \\ &\quad + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)})/2 \\ \Psi_{b_{2g}} &= \beta_1 d_{xy} - \beta_1'\phi_L(xy) \\ \Psi_{a_{1g}} &= \alpha_1 d_{z^2} - \alpha_1'(\sigma_x^{(1)} \\ &\quad + \sigma_y^{(2)} - \sigma_x^{(3)} - \sigma_y^{(4)})/2 \\ \Psi_{e_g} &= \begin{cases} \beta d_{xz} - \beta'\phi_L(xz) \\ \beta d_{yz} - \beta'\phi_L(yz) \end{cases} \end{aligned}\right\} \tag{2}$$

where $\sigma^{(i)}=np^{(i)}\mp(1-n^2)^{1/2}s^{(i)}$, in which $0\leq n\leq 1$, and where $\varphi_L(xy)$, $\varphi_L(xz)$, and $\phi_L(yz)$ are pseudo-π orbitals of amino groups which have been assumed to interact with the d_{xy}, d_{xz} and d_{yz} of copper orbitals respectively. $\Psi_{b_{2g}}$ and Ψ_{e_g} represent the in-plane π bonding and the out-of-plane π bonding respectively. The normalization of the $\Psi_{b_{1g}}$ orbital yields:

$$\alpha^2 + \alpha'^2 - 2\alpha\alpha'S = 1 \tag{3}$$

where S is the overlap integral between the $d_{x^2-y^2}$ of the copper atom and the σ orbitals of ligand nitrogen atoms.

The second-order perturbation calculation results in the following approximate expressions for the spin Hamiltonian parameters in Eq. (1):

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9) H. Abe and K. Ono *J. Phys. Soc. Japan*, **11**, 947 (1956).

10) E. H. Carlson and R. D. Spence, *J. Chem. Phys.*, **24**, 471 (1956).

$$\left.\begin{aligned} g_{/\!/} &= 2.002 - \frac{8\lambda}{\Delta E_{xy}}\,\alpha^2\beta_1{}^2(1-f_1) \\ g_{\perp} &= 2.002 - \frac{2\lambda}{\Delta E_{xz}}\,\alpha^2\beta^2(1-f_2) \\ A_{/\!/} &= P\Big[-\alpha^2\Big(\frac{4}{7}+\kappa_0\Big)+(g_{/\!/}-2) \\ &\qquad +\frac{3}{7}(g_{\perp}-2)+f_3\Big] \\ A_{\perp} &= P\Big[\alpha^2\Big(\frac{2}{7}-\kappa_0\Big)+\frac{11}{14}(g_{\perp}-2)+f_4\Big] \end{aligned}\right\} \quad (4)$$

Furthermore, $A_{\mathrm{N}}^{\perp}$ is expressible in the form:(2,6)

$$A_{\mathrm{N}}^{\perp} = \left(\frac{\alpha'}{2}\right)^2 (2\beta_0\beta_{\mathrm{N}}\gamma_{\mathrm{N}})\left[\frac{8\pi}{3}(1-n^2)\rho_{2s}(0) + \frac{2}{5}n^2\langle r^{-3}\rangle_{2p}\right] \quad (5)$$

where $P=2\gamma\beta_0\beta_{\mathrm{N}}\langle d_{x^2-y^2}|r^{-3}|d_{x^2-y^2}\rangle$, where κ_0 is the Fermi contact term, where $\Delta E_{xy}=E_{xy}-E_{x^2-y^2}$ and $\Delta E_{xz}=E_{xz}-E_{x^2-y^2}$, where $\rho_{2s}(0)$ is the value of the ligand $2s$ function at the nitrogen nucleus, where r is the radius of the $2p$ ligand orbital, and where f_1, f_2, f_3 and f_4 are small and almost constant values for a variety of copper(II) complexes (f_1, $f_2 \leqq 0.04$, $f_3 \leqq 0.33$, and $f_4 \leqq 0.005$).

Next, the values of ΔE_{xy} and ΔE_{xz} must be determined in order to calculate β_1 and β. The visible absorption spectrum of a square planar copper(II) complex generally consists of three component absorption bands, corresponding to ΔE_{xy}, ΔE_{xz} and ΔE_{z^2}, where $\Delta E_{z^2}=E_{z^2}-E_{x^2-y^2}$. However, the visible absorption spectra of the copper(II) complexes employed in this study show in solutions only a single broad band, the position of the peak of which is tabulated in Table 2, so that it is not easy to determine accurately the values of ΔE_{xy} and ΔE_{xz} for the complexes. The absorption spectral data of the single crystal of bis(ethylenediamine)copper(II) complex are not sufficient to determine the energy values.[11]

The circular dichroism measurements of various metal complexes have been used to estimate the structure of their electronic absorption spectra.[12] 1,2-Diaminopropane contains an optically-active asymmetric carbon. Recently Gillard observed the circular dichroism of $[\mathrm{Cu}(-\mathrm{pn})_2]^{2+}$ in an aqueous solution, and showed two bands corresponding to 657 mμ and 510 mμ.[13] The two bands are thought to be due to components of ${}^2T_2 \leftarrow {}^2E$ from the symmetry arguments of the magnetic dipole transition. Therefore, it may reasonably be considered that the ΔE_{xy} and ΔE_{xz} of $[\mathrm{Cu(pn)_2}](\mathrm{ClO_4})_2$ in an aqueous solution correspond approximately to 657 mμ and 510 mμ respectively. The energy values of the ΔE_{xy} and ΔE_{xz} of the other copper(II) complexes under discussion could be estimated roughly on the assumption that there is the same relationship in energy values among ΔE_{xy}, ΔE_{xz} and the maximum absorption peak for these complexes as with the copper(II) complexes of 1,2-diaminopropane. The estimate ligand field energy values of ΔE_{xy} and ΔE_{xz} are listed in Table 2.

TABLE 2. LIGAND FIELD ENERGIES

Copper(II) complex	λ_{max}* (mμ)	log ε	Estimated ligand field energies (cm^{-1})	
			ΔE_{xy}	ΔE_{xz}
[I]	547	1.80	15200	19600
[II]	547	1.84	15200	19600
[III]	546	1.85	15200	19600
[IV]	568	2.02	14600	18900
[V]	598	1.70	13900	17900

* Solvents were MH for [I]—[IV] and M for [V]. The description of MH and M is in the footnote of Table 1.

The values of the bonding parameters, namely, α, β_1, β, and κ_0 were calculated using Eq. (4), where $P=0.036\ \mathrm{cm}^{-1}$; they are listed in Table 3. Furthermore, the values of α were also calculated from the nitrogen super-hyperfine constants using Eq. (5), where $n=\sqrt{3}/2$ for sp^3 hybrid ligand orbitals, $\rho_{2s}(0)=33.4\times 10^{24}\ \mathrm{cm}^{-3}$, $\langle r^{-3}\rangle_{2p}=21.1\times 10^{24}\ \mathrm{cm}^{-3}$, and $S=0.08$.

There are several points of interest in the results shown in Table 3. Values of $\beta_1{}^2$ and β^2 which are indicated to be considerably smaller than unity, namely, $\beta_1{}^2=0.6$ and $\beta_2=0.7$, are found for all the copper(II) complexes in this work. This implies that remarkably covalent π bonding is

TABLE 3. BONDING PARAMETERS[a)]

Copper(II) complex	From Eq. (4)				From Eq. (5)[b)]	
	α^2	$\beta_1{}^2$	β^2	κ_0	α'^2	α^2
[I]	0.83	0.58	0.72	0.42	0.29	0.79
[II]	0.84	0.58	0.70	0.42	0.30	0.78
[III]	0.82	0.58	0.72	0.43	0.31	0.77
[IV]	0.84	0.60	0.70	0.41	0.35	0.73
[V]	0.87	0.59	0.68	0.39	0.35	0.73

a) Calculated from the experimental data measured in solvent MH for [I]—[IV] and solvent M for [V]. The description of M and MH is in the footnote of Table 1.

b) $n^2=3/4$ (sp^3 hybrid) was assumed in Eq. (5).

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[11] S. Yamada and R. Tsuchida, This Bulletin, **29**, 289 (1956).

[12] A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963); B. E. Douglas, R. A. Haines and J. B. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963); T. Yasui, J. Hidaka and Y. Shimura, *J. Am. Chem. Soc.*, **87**, 2762 (1965).

[13] R. D. Gillard, *J. Inorg. Nucl. Chem.*, **26**, 1455 (1964).

found in the copper-amino group bonds of the complexes. This finding, to which little attention has yet been paid, is considered to be reliable from the point of ESR. Rajan also suggested the existence of π bonding in $[\mathrm{Cu(en)_2}](\mathrm{NO_3})_2$, on reasoning a simple basis.[14] It has generally been believed that the metal-ligand bonding in the metal complexes of amines is almost equivalent to σ bonding, where the ligand orbitals concerned with the bonding are the lone-pair electron orbitals of amines formed by sp^3 hybridization. The values of α^2 in Table 3 indicate that the σ bonding in the copper(II) complexes of amines is also covalent, but the degree of the covalency of the bonding is not very different from that reported for many common copper(II) complexes.[2-6] Accordingly, it is characteristic of the copper(II) complexes of amines that such covalent π bonding as that indicated in Table 3 is present. Now, a very important but difficult problem is that of considering what orbitals of amino groups are used as π orbitals, which are expressed, for convenience, in Eq. (2) as $\varphi_L(xy)$,φ_L (xz), and $\varphi_L(yz)$. One of most probable answers to the problem is that amino groups fulfil such a function of hyperconjugation as does the methyl group of toluene molecule. The fact that the convalent π bonding is present in the metal complexes of amines has much meaning for coordination chemistry and biochemistry, because it suggests that charge transfer, which is thought to be initial step of reactions, may occur easily between the metal atom and ligand molecules through amino groups.

The values of κ_0 in Table 3 are about 0.42 for [I]—[IV], but 0.39 for [V]. The former value is equal to the one reported for some copper(II) complexes,[2,3] and the value of κ_0 has been assumed to be essentially constant for all copper(II) complexes.[15] However, we must bear our mind in cases which the κ_0 value in some copper(II) complexes like [V] in Table 3 deviates from 0.42.[16]

Another point of interest is the values of α^2 calculated from the nitrogen super-hyperfine constants using Eqs. (5) and (3). The super-hyperfine constants listed in Table 1 are almost equal in magnitude to those reported for many nitrogen-bonded copper(II) complexes whose nitrogen valence orbitals are clearly known to be sp^2 hybridized orbitals;[2,3,5,6] therefore, the nitrogen super-hyperfine constants listed in Table 1 seem to be rather too large considering that the nitrogen valence orbitals of amines are nearly sp^3 hybridized orbitals. In Table 3 the values of α^2 calculated from Eq. (5) are compared with those calculated from Eq. (4). The agreement for [I]—[III] in Table 3 is comparatively good considering the various assumptions involved in Eqs. (4) and (5). However, the former is much smaller than the latter for [IV] and [V] in Table 3. This implies that there are slight differences in the characters of copper-amino group bonds between the first three complexes and the last two complexes in Table 3. [IV] in the table is more similar to [V] in chemical and physical properties, for instance, in stability constants,[17] optical absorption spectra and magnetic parameters, than to the first three complexes. This seems to be because the amino groups of 1,3-diaminopropane can be bonded to the copper atom with the same bonding nature as ammonia because of the structural flexibility of the trimethylene group in 1,3-diaminopropane. Since the values of α^2 calculated from Eq. (5) are alway smaller than those calculated from Eq. (4), it seems that the nitrogen orbitals of the copper(II) complexes of amines are not pure sp^3 hybridized orbitals, but, rather, orbitals with a greater degree of s-character. However, further studies of these problems are desirable in order to make the nature of chemical bonding in the complexes clearer.

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[14] R. Rajan, *J. Chem. Phys.*, **37**, 1901 (1962).

[15] A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc.*, **A206**, 164 (1951); A. Abrgam, J. Horowitz and M. H. L. Pryce, *ibid.*, **A230**, 169 (1955).

[16] B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967); H. A. Kuska and M. T. Rogers, *J. Chem. Phys.*, **43**, 1744 (1965); H. Yokoi and T. Isobe, This Bulletin, **39**, 2054 (1966).

[17] L. G. Sillen and A. E. Martell, "Stability Constants of Metal-ion Complexes" (Special Publication No. 7), The Chemical Society, Burlington House, London (1964).