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ESR and Optical Absorption Studies of the Copper(II) Complexes of Ethylenediamine and Its Alkyl Derivatives

Hiroshi Yokoi and Taro Isobe

Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira-cho, Sendai

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The ESR and the optical absorption of the copper(II) complexes of ethylenediamine and a series of alkylated ethylenediamines have been investigated in order to estimate the character of the chemical bonding in the copper(II) complex. The covalency of the bonding of the copper atom to the ligand nitrogen atoms in the complexes has been discussed in connection with the chemical and physical properties of the complexes or of their ligand molecules themselves. The ESR results indicate that the σ bonding of the complexes becomes more covalent as the number of alkyl groups in their ligand molecules increases; furthermore, the tendency toward the σ bonding becomes more pronounced when the alkyl groups are ethyl rather than methyl and when they are *N*-substituted alkyl groups rather than *C*-substituted ones. It is also indicated that there is a linear relationship between the energies of the ultraviolet absorption band for the complexes and the relative ionization potentials estimated for their ligand molecules, and that absorption band can be assigned to an electron transfer from a ligand σ orbital to an antibonding orbital associated with the copper atom. From these results, it may be concluded that, as the σ bonding becomes more covalent, this charge transfer band shifts to a longer wavelength.

The ESR spectra of a variety of copper(II) complexes have been measured in order to investigate the bonding character of copper-ligand bonds in the complexes. The bonding parameters showing the degree of covalency for the bonds have been estimated from the magnetic parameters, namely, the g and A values, determined from their ESR spectra.[1-4] Little attention has been paid to the interesting and important problem of finding some correlation between the degree of covalency thus obtained and the chemical and physical properties of the complexes or their ligand molecules themselves. However, it is not easy to do this because of the fact that the ESR of the complexes is substantially concerned with only the antibonding orbitals associated with the copper atom.

In the present work the copper(II) complexes of ethylenediamine and a series of alkylated ethylenediamines were examined systematically by the usual methods of ESR and optical absorption, and an attempt was made to find the above-mentioned correlation. Since only a few papers have been published on the behavior of the optical absorption bands of the complexes, the assignment of the bands in the ultraviolet region was also discussed.

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] $[Cu(d'men)_2](ClO_4)_2$, [V] $[Cu(eten)_2](ClO_4)_2$, [VI] $[Cu(d'een)_2](ClO_4)_2$, [VII] $[Cu(dmen)_2](ClO_4)_2$, and [VIII] $[Cu(deen)_2](ClO_4)_2$, where en, pn, *m*-bn, d'men, eten, d'een, dmen, and deen are ethylenediamine, 1,2-diaminopropane, *meso*-2, 3-diaminobutane, *N,N'*-dimethylethylenediamine, *N*-ethylethylenediamine, *N,N'*-diethylethylenediamine, *N, N*-dimethylethylenediamine, and *N,N*-diethylethylenediamine respectively. The first three copper(II) complexes had already been dealt with in our previous paper.[4] The ligand molecules were commercially available except for *m*-bn, eten, and d'een, which were prepared and purified according to the methods of the literature.[5]

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,

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

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

[3] 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); 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); S. E. Harrison and J. M. Assour, *J. Chem. Phys.*, **40**, 365 (1964); D. Kivelson and S. Lee, *ibid.*, **41**, 1896 (1964).

[4] H. Yokoi and T. Isobe, This Bulletin, **41**, 2835 (1968).

[5] F. Basolo, Y. T. Chen and R. K. Murmann, *J. Am. Chem. Soc.*, **75**, 1478 (1953); R. C. O'Gee and H. M. Woodburn, *ibid.*, **73**, 1370 (1951).

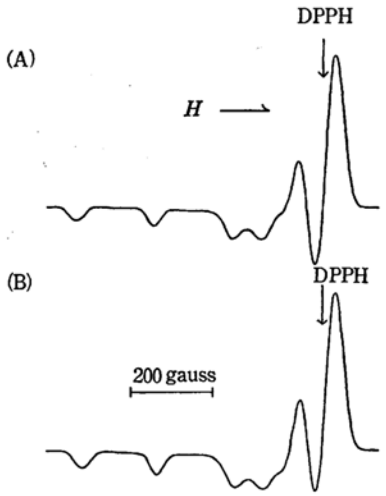

Fig. 1. ESR spectra (X-band) measured in 50% water - 50% methanol at 77°K.
(A) [Cu(d'men)$_2$](ClO$_4$)$_2$
(B) [Cu(dmen)$_2$](ClO$_4$)$_2$

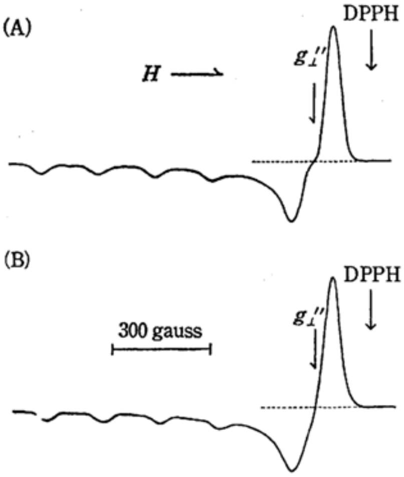

Fig. 2. ESR spectra (K-band) measured in 50% water-50% methanol at rigid state.
(A) [Cu(d'men)$_2$](ClO$_4$)$_2$
(B) [Cu(dmen)$_2$](ClO$_4$)$_2$

equipped with a 100 kc field modulation unit. The solvents were methanol and a 50% water - 50% methanol mixture (volume %). 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—3. The optical absorption spectra of the complexes in an aqueous solution were measured with a Cary model 14 spectrometer; some of them are shown in Figs. 4 and 5.

Results and Discussion

Magnetic Parameters. The spin Hamiltonian and the methods of determining the magnetic parameters, the g and A values, had already been described in one of our previous papers.[4] It

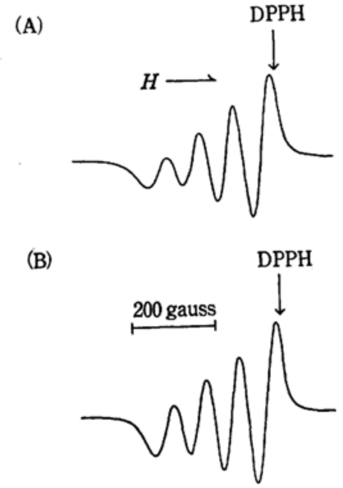

Fig. 3. ESR spectra (X-band) measured in 50% water - 50% methanol at room temperature.
(A) [Cu(d'men)$_2$](ClO$_4$)$_2$
(B) [Cu(dmen)$_2$](ClO$_4$)$_2$

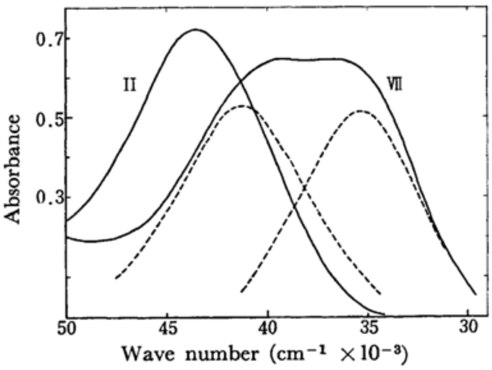

Fig. 4. The ultraviolet absorption spectra measured in aqueous solution at room temperature. Dotted lines represent the possible component bands obtained by approximate Gaussian analysis.

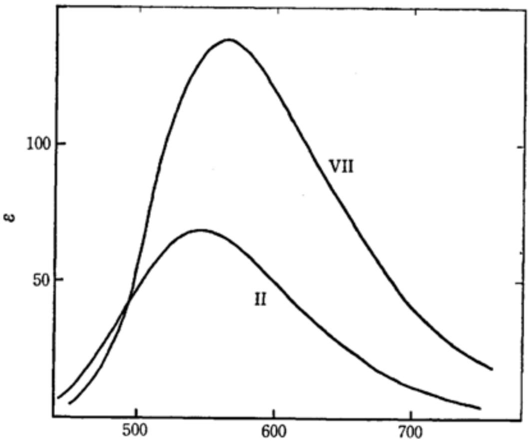

Fig. 5. The visible absorption spectra measured in aqueous solution at room temperature.

TABLE 1. MAGNETIC PARAMETERS

Copper(II) complex[a]		Solvent[b]	$g_{//}$	$g'_{\perp}$[c]	$g''_{\perp}$[d]	$A_{//}$ $\times 10^4$ cm^{-1}	$A_{\perp}$[c] $\times 10^4$ cm^{-1}	g_0[e]	A_0[e] $\times 10^4$ cm^{-1}
[I]	$[Cu(en)_2](ClO_4)_2$	MH	2.206	2.050	2.052	209	25	2.102	86
		M	2.209			207			
[II]	$[Cu(pn)_2](ClO_4)_2$	MH	2.208	2.050	2.051	210	26	2.103	87
		M	2.209			206			
[III]	$[Cu(m\text{-}bn)_2](ClO_4)_2$	MH	2.203	2.050	2.050	205	27	2.101	86
		M	2.203			204			
[IV]	$[Cu(d'men)_2](ClO_4)_2$	MH	2.216	2.053	2.050	201	26	2.107	84
		M	2.210			205			
[V]	$[Cu(eten)_2](ClO_4)_2$	MH	2.213	2.052	2.044	202	27	2.106	85
		M	2.210			204			
[VI]	$[Cu(d'een)_2](ClO_4)_2$	MH	2.217	2.052	2.050	196	23	2.107	81
		M	2.214			198			
[VII]	$[Cu(dmen)_2](ClO_4)_2$	MH	2.209	2.053	2.048	198	24	2.105	82
		M	2.218			185			
[VIII]	$[Cu(deen)_2](ClO_4)_2$	MH	2.212	2.055	2.049	184	21	2.107	75
		M	2.208			186			

a) The data for the complexes [I], [II] and [III] were quoted from our previous paper.[4]

b) M: methanol, MH: 50% water, 50% methanol (volume %).

c) $g'_{\perp}$ was calculated using the following equation, $g_0=(1/3)(g_{//}+2g'_{\perp})$. $A_{\perp}$ was also calculated in the same way.

d) $g''_{\perp}$ was directly obtained from the ESR spectrum measured in rigid solution at K-band.

e) Measured at room temperature.

seems that the ligand field can not always be of an axial symmetry for the complexes [V], [VII], and [VIII], because, in their ligand molecules, alkyl groups are not substituted symmetrically on the two nitrogen atoms; this fact is certainly reflected in their ultraviolet absorption spectra, which will be discussed below. However, judging from the line shapes of such K-band ESR spectra as are shown in Fig. 2, it may well be said that the ligand field for the complexes does not deviate greatly from axial symmetry. Therefore, the average value, expressed as $g_{\perp}$, for two slightly different perpendicular g values was adopted for use in the following discussions. The $g_{\perp}$ value was determined according to the following two methods. One is the method of using the parameters, g_0 and A_0, obtained from the ESR spectra of a solution at room temperature, and the equation $g_0=(1/3)(g_{//}+2g_{\perp})$, where the $g_{\perp}$ value thus obtained is expressed as $g'_{\perp}$ in Table 1. The other is the method of determining the $g_{\perp}$ value directly from the K-band ESR spectra in the way shown by the arrow in Fig. 2. The $g_{\perp}$ value thus obtained is expressed as $g''_{\perp}$ in Table 1. All the magnetic parameters obtained in this work are listed in Table 1.

Bonding Parameters. The experimentally-determined magnetic parameters listed in Table 1 can be used for estimating the nature of the chemical bonding between the copper atom and the ligand nitrogen atoms in the complexes by means of the molecular orbital theory. This method had already been outlined in our previous paper on the copper(II) complexes of amines whose ligand field is of axial symmetry.[4] On the other hand, it is convenient to know that almost the same method for obtaining the bonding parameters is substantially applicable to the copper(II) complexes in which ligand field deviates to some extent from axial symmetry. The following wave functions can generally be written for the antibonding molecular orbitals associated with the copper atom;

$$\psi(x^2-y^2) = \alpha d_{x^2-y^2} - \alpha'\phi_L(x^2-y^2)$$

$$\psi(xy) = \beta_1 d_{xy} - \beta_1'\phi_L(xy)$$

$$\psi(z^2) = \alpha_1 d_{z^2} - \alpha_1'\phi_L(z^2)$$

$$\psi(xz) = \beta_x d_{xz} - \beta'_x\phi_L(xz)$$

$$\psi(yz) = \beta_y d_{yz} - \beta_y'\phi_L(yz)$$

The expressions which relate the experimental ESR data to the covalency parameters, α, β_1, β_x, and β_y, are:

$$g_z = 2 - \frac{8\lambda}{\Delta E_{xy}}(\alpha^2\beta_1^2 - f_1) \tag{1}$$

$$g_x = 2 - \frac{2\lambda}{\Delta E_{xz}}(\alpha^2\beta_x^2 - f_2) \tag{2}$$

$$g_y = 2 - \frac{2\lambda}{\Delta E_{yz}}(\alpha^2\beta_y^2 - f_3) \tag{3}$$

$$A_z = P\left\{-\frac{4}{7}\alpha^2 - \kappa + (g_z - 2) + \frac{3}{14}[(g_x - 2) + (g_y - 2)] + f_4\right\} \tag{4}$$

$$A_x = P\left\{\frac{2}{7}\alpha^2 - \kappa + (g_x - 2) - \frac{3}{14}(g_y - 2) + f_5\right\} \tag{5}$$

$$A_y = P\left\{\frac{2}{7}\alpha^2 - \kappa + (g_y - 2) - \frac{3}{14}(g_x - 2) + f_6\right\} \tag{6}$$

where κ is the Fermi contact term, $P=0.036\ \mathrm{cm}^{-1}$, $\lambda=-828\ \mathrm{cm}^{-1}$, f's are small constants (f_1, f_2, $f_3 \leq 0.04$, $f_4 \leq 0.03$, f_5, $f_6 \leq 0.005$), and $\Delta E_s = E_{x^2-y^2} - E_s$ ($s=xy$, xz, yz). From the above equations, it can be understood that the values of α^2 and κ ($\kappa=\alpha^2\kappa_0$[2]) can be calculated by the same method as we used previously if we can experimentally obtain the average values of g_x and g_y, and of A_x and A_y, expressed here as $g_\perp$ and $A_\perp$ respectively.[4] Furthermore, the average value of β_x^2 and β_y^2, expressed as β^2, can also be estimated by the above procedure. The approximate ligand field energies of the complexes under discussion were determined by the procedure in our previous paper,[4] assuming that the ligand field for the complexes is of axial symmetry; they are listed in Table 4. The bonding parameters thus calculated are listed in Table 2.

TABLE 2. BONDING PARAMETERS[a]

Copper(II) complex[b]	α^2	β_1^2	β^2	κ_0
[I]	0.83	0.58	0.72	0.42
[II]	0.84	0.58	0.70	0.42
[III]	0.82	0.58	0.72	0.43
[IV]	0.82	0.61	0.71	0.42
[V]	0.82	0.60	0.66	0.42
[VI]	0.81	0.58	0.70	0.42
[VII]	0.81	0.59	0.70	0.41
[VIII]	0.77	0.60	0.68	0.41

a) The parameters were calculated using the experimental data measured in the solvent MH. The mean of $g'_\perp$ and $g''_\perp$ listed in Table 1 were used for convenience as the essential $g_\perp$ value for calculation of the parameters.

b) The listed values for the complexes [I], [II] and [III] were quoted from our previous paper.

The results in Table 2 indicate that there is a clear correlation between the value of α^2 (the covalency parameter of σ bonding) and the structure of the ligand molecule. The more alkyl groups (methyl or ethyl groups) a ligand contains, the smaller the value of α^2 for its complex becomes. Especially, the *N*-substituted alkyl group shows a stronger tendency to make the value of α^2 decrease than the *C*-substituted alkyl group; furthermore, the tendency is more pronounced in the ethyl group than in the methyl group. This tendency can be simply explained in terms of the inductive effect of alkyl groups, which increases the electron-donating power of the ligand nitrogen σ orbitals and, consequently, makes the σ orbitals interact more strongly with the $d_{x^2-y^2}$ orbital of the copper atom. The acid dissociation constants of the ligand molecules and the stability constants of their copper(II) complexes are cited in Table 3 from the literature.[6] From a comparison between the results of Tables 2 and 3, it follows that there seems to be little correlation between the acid dissociation constants of the ligand molecules and the values of α^2 for their complexes, but the stability constant decreases as the value of α^2 decreases, that is, as the σ bonding becomes more covalent. However, since the stability constant must be substantially related to the total energy of stabilization for complex formation, it is suggested that more important factors than the σ bonding contribute to the stability of the complex.

TABLE 3. ACID DISSOCIATION CONSTANTS p$K_{\mathrm{BH^+}}$ OF ETHYLENEDIAMINE AND ITS ALKYL DERIVATIVES AND STABILITY CONSTANTS β_2 OF THE COPPER(II) COMPLEXES OF THESE LIGAND MOLECULES[a]

Ligand molecule	p$K_{\mathrm{BH^+}}$	β_2
en	10.18	20.13
pn	10.00	20.06
m-bn	9.97	20.06
d'men	10.29 (10.16)	18.10 (16.34)
eten	10.56	18.57
d'een	10.46	15.62
dmen	10.00 (9.53)	19.58 (15.96)
deen	(10.02)	(13.72)

a) These data were cited from the literatures.[6] The measurements were carried out at 25°C in aqueous 0.5 N $\mathrm{KNO_3}$ medium by the method of glass electrode. The values in parentheses are the data measured in aqueous 0.1 N KCl medium.

The values of β_1^2 and β^2 for all the complexes listed in Table 2 are much smaller than unity. This implies, as has been indicated previously,[2] that in-plane and out-of-plane π bondings must play an important role in determining the properties of the copper(II) complexes of amines.

Optical Absorption Spectra. The spectral data obtained for the complexes employed in this work are listed in Table 4. There have been fewer reports about the spectroscopy of copper(II) complexes than on other metal complexes, and

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6) L. G. Sillen and A. E. Martell, "Stability Constants of Metal-ion Complexes" (Special Publication No. 7), The Chemical Society, Burlington, London (1964); F. Basolo, R. K. Murmann and Y. T. Chen, *J. Am. Chem. Soc.*, **75**, 1478 (1953); F. Basolo and R. K. Murmann, *ibid.*, **76**, 211 (1954); F. Basolo, Y. T. Chen and R. K. Murmann, *ibid.*, **76**, 956 (1954); H. Irving and J. M. M. Griffiths, *J. Chem. Soc.*, **1954**, 213, 4370.

TABLE 4. OPTICAL ABSORPTION SPECTRA[a)] AND ESTIMATED LIGAND FIELD ENERGIES[b)]

Copper(II) complex	λ_{max} (mμ): log ε			ΔE_{xy} (cm^{-1})	ΔE_{xz} (cm^{-1})
[I]		228 : 3.78	547 : 1.80	15200	19600
[II]		230 : 3.81	547 : 1.84	15200	19600
[III]		234 : 3.90	546 : 1.85	15200	19600
[IV]		262 : 3.77	566 : 1.98	15000	19300
[V][c)]	242 : 3.49	265 : 3.40	558 : 1.96	14900	19200
[VI][c)]	244 : 3.43	272 : 3.43	581 : 1.98	14200	18300
[VII]	243 : 3.56	283 : 3.55	563 : 2.14	14800	19000
[VIII][c)]	244 : 3.32	283 : 3.41	588 : 2.12	14100	18200

a) The measurement was carried out in aqueous solution at room temperature.
b) The method for estimating these energy values had been described in our previous paper.[4)]
c) Ultraviolet absorption bands were determined by approximate Gaussian analysis.

only a few papers on the ultraviolet spectroscopy for the copper(II) complexes of ethylenediamine and its analogues have been published so far. Basu and Basu reported that the intense absorption bands of the copper(II) complexes of amines in the 200—250 mμ region are the charge-transfer bands between the copper ion and the amines.[7)] On the other hand, the single broad band generally observed in the visible region for copper(II) complexes in solution has been ascertained to be due to *d–d* absorption bands and to consist of three or four components.[8)] The visible spectral bands of the copper(II) complexes of ethylenediamine and its analogues have already been discussed in our previous paper.[4)]

The ultraviolet absorption spectrum of the complex [VII] in an aqueous solution, as is shown in Fig. 5, clearly consists of two absorption bands. For the complexes [V], [VIII], and also [VI] the observed ultraviolet absorption spectra may reasonably be considered to consist of two bands. The data listed in Table 3 for these complexes were obtained from their spectra by approximate Gaussian analysis. Since the structures of these complexes are considered to be lower in symmetry than those of the complexes [I], [II], and [III], the above-mentioned spectral fact seems to result from this decrease in symmetry; the ligand field for the complexes [V], [VI], [VII], and [VIII] deviates to some extent from axial symmetry.

The energy of the ultraviolet absorption band decreases in going from [I] to [VIII] in Table 3 when the lower energy band of the two ultraviolet bands is chosen in [V], [VI], [VII], and [VIII]. This tendency suggests that there is a correlation between the energies of the ultraviolet absorption band for the complexes and the structure of their ligand molecules; furthermore, the value of α^2 also decreases in the same order, as has been indicated above.

Molecular Orbitals and Chemical Bondings. The ESR results obtained for the copper(II) complexes of ethylenediamine and a series of alkylated ethylenediamines revealed that there is a clear correlation between the covalency of σ bonding for the complexes and the structure of their ligand molecules. However, the ESR method can not explain why there is such a correlation, because only antibonding molecular orbitals associated with the copper atom are treated in obtaining bonding parameters from the ESR data, whereas bonding and other antibonding orbitals are not entirely necessary in doing so. Ligand field energies themselves also reflect various aspects of the electronic structure of complexes. However, some of the ligand field energies determined experimentally from optical absorption are used for calculating bonding parameters using Eqs. (1)—(6) without deeply considering the original meanings of the ligand field energies themselves.

The molecular orbitals of the copper(II) complexes are built up by linear combinations of the 3*d*, 4*s*, and 4*p* atomic orbitals or the copper atom and the hybrid orbitals of the ligand atoms directly coordinated to the copper atom. It has generally been accepted that the ligand nitrogen atoms of amines have sp^3 hybrid orbitals or orbitals near to sp^3 hybrid orbitals.

The amount of mixing of atomic orbitals in the molecular orbitals, which shows the degree of covalency directly, is proportional to the atomic orbital overlap and inversely proportional to their Coulomb-energy difference.[9,10)] Now, it was assumed that for all the complexes under considera-

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7) G. Basu and S. Basu, *Anal. Chim. Acta*, **21**, 187 (1959).

8) J. Bjerrum, C. J. Ballhausen and C. K. Jorgensen, *Acta Chem. Scad.*, **8**, 1275 (1954); R. L. Belford, M. Calvin and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957); S. Yamada and R. Tsuchida, This Bulletin, **29**, 289 (1956).

9) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1841 (1955); M. Wolfsberg and L. Helmholz, *ibid.*, **20**, 837 (1952).

10) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962); C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York (1964), p. 102.

TABLE 5. IONIZATION POTENTIALS (IN UNITS OF eV) OF VARIOUS ALKYL AMINES[a)]

Alkyl amine	R					
	H	CH_3	CH_2CH_3	$(CH_2)_2CH_3$	$CH(CH_3)_2$	$(CH_2)_3CH_3$
RNH_2	10.15	8.97	8.86	8.78	8.72	8.71
R_2NH		8.24	8.01	7.84	7.73	7.69
R_3N		7.82	7.50	7.23		

a) These were cited from Watanabe's data.[11)]

tion the values of the overlap integral, *S*, for the σ bonding are almost equal and that the Coulomb energies of copper atomic orbitals with which ligand orbitals mix to from molecular orbitals are not very different form each other; thus, we do not introduce such a complicated and refined concept as valence-state ionization energy.[10)] On the above assumption, the degree of covalency of the σ bonding for the complexes depends only upon the Coulomb energies of their ligand σ orbitals. As has already been mentioned in the foregoing paragraph, there is a clear correlation between the energies of the ultraviolet absorption band for the complexes and the structure of their ligand molecules. It can, therefore, be expected from this fact that all the ultraviolet absorption bands are of the same type, and that the Coulomb energies of the ligand orbital concerned with the ultraviolet absorption band undergo regular change in the order given in Table 3. Watanabe measured the ionization potentials of various small and simple molecules.[11)] We selected the ionization potentials of various amines from his data; they are listed in Table 5. It is clearly indicated in this table that the ionization potential of alkyl amine becomes smaller as the alkyl group changes from methyl to butyl and as the number of alkyl groups in the amine increases. The ionization potentials of the amines may be considered, on a first approximation, to correspond to the Coulomb energies of the nitrogen lone-pair electron orbital which is used as the ligand σ orbital in their complexes. It is reasonable to expect that the ionization potentials of ethylenediamine and its alkyl derivatives, which have not yet been measured, vary in just the same way as those of alkyl amines. As a trial, the relative values of the ionization potentials for ethylenediamine and its alkyl derivatives were estimated by the following procedure. The ionization potentials of ethylenediamine, 1,2-diaminopropane, *N*-ethylethylenediamine, and *N*,*N*-diethylethylenediamine were assumed to be equal to those of ethylamine, isopropylamine, diethylamine, and triethylamine respectively. The ionization potentials of other alkylated ethylenediamines were also estimated from the corresponding two alkyl amines, with a proportional allotment. The relative values of the ionization potentials thus estimated are listed in Table 6.

TABLE 6. THE RELATIVE IONIZATION POTENTIALS (IN UNITS OF eV) ESTIMATED FOR ETHYLENEDIAMINE AND ITS ALKYL DERIVATIVES

en	$NH_2CH_2CH_2NH_2$	8.86
pn	$NH_2CH_2CH(CH_3)NH_2$	8.72
m-bn	$NH_2CH(CH_3)CH(CH_3)NH_2$	8.62
d'men	$CH_3NHCH_2CH_2NHCH_3$	8.13
eten	$NH_2CH_2CH_2NHCH_2CH_3$	8.01
d'een	$CH_3CH_2NHCH_2CH_2NHCH_2CH_3$	8.01
dmen	$NH_2CH_2CH_2N(CH_3)_2$	7.71
deen	$NH_2CH_2CH_2N(CH_2CH_3)_2$	7.50

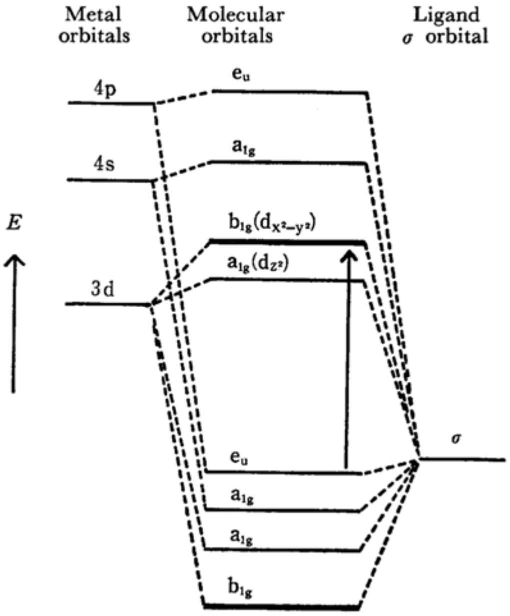

Fig. 6. Molecular orbital energy level scheme for square planar copper(II) complex (D_{4h} symmetry) in which ligand has a σ orbital system.

The energy-level scheme of the molecular orbitals concerned with ligand σ orbitals for the copper(II) complex whose ligand field has a D_{4h} symmetry is shown in Fig. 6. The ground state of the complex is, then, B_{1g}. From symmetry arguments, two allowed charge-transfer transitions may be anticipated for the complex, corresponding to the one-electron transitions:

$$e_u \leftarrow b_{1g}\ (B_{1g} \rightarrow E_u) \text{ and } b_{2u} \leftarrow b_{1g}\ (B_{1g} \rightarrow B_{2u})$$

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11) K. Watanabe, *J. Chem. Phys.*, **26**, 1773 (1957).

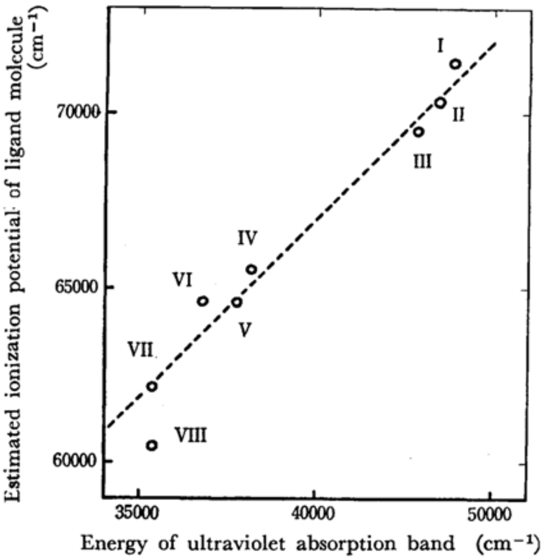

Fig. 7. Shifts in energies of ultraviolet absorption bands with changes in the estimated ionization potentials of ligand molecules.

These are transitions from molecular orbitals essentially localized on the ligands to molecular orbitals essentially localized on the metal atom. In order to ascertain whether or not the ultraviolet absorption band corresponds to the former charge-transfer band, the energies of the band were plotted against the ionization potentials estimated above, where the lower energy band of the two ultraviolet absorption bands was chosen for the complexes [V]—[VIII]; this is shown in Fig. 7. It is obvious in this figure that there is a linear relationship between the energies of the band and the ionization potentials with a slope of about 45°. This relationship is a characteristic feature of the charge-transfer band; it suggests that a dominant factor in determining the energy of the charge-transfer band is the energy difference between the Coulomb energies of copper 3*d* orbitals and ligand σ orbitals. Therefore, the band is assigned to the $B_{1g} \rightarrow E_u$ charge-transfer transition.

As has already been mentioned, the charge transfer bands of the complexes in Table 3 appear at lower energies as the number of alkyl groups in their ligand molecules increases; furthremore, the tendency of the band becomes more pronounced when the alkyl groups are ethyl rather than methyl and when they are *N*-substituted alkyl groups rather than *C*-substituted ones. The fact that the charge-transfer band shifts to a longer wavelength indicates that the energy difference between the levels of the copper 3*d* orbital and the ligand σ orbital becomes smaller and that, accordingly, the σ bonding becomes more covalent. This tendency toward covalency is perfectly consistent with the one derived from the ESR results. Therefore, it may be concluded that, for the metal complexes of ethylenediamine and its analogues, the σ bonding becomes more covalent as the charge-transfer bands appear at longer wavelengths.