

# Electron Paramagnetic Resonance Study of Copper(II)-tetrammine Nitrate in Solution

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The electron paramagnetic resonance of copper(II)-tetrammine nitrate in solution of methanol and water has been investigated. The data obtained from the spectra at room temperature and 97 °K together with the optical transition energies determined from single crystal polarized absorption spectra at 77 °K by other authors were used to calculate the LCAO-MO bonding parameters. The bonding orbital of the ammonia molecule cannot be described by the concept of  $sp^2$  hybridization which was exclusively used in the theory. Therefore a calculation of the overlap integral  $S(n)$  for  $\sigma$  bonding and of the superhyperfine splitting was carried out in terms of an arbitrary hybridization parameter  $n$ . For ammonia,  $n$  was taken from the Duncan-Pople hybrid wave function for the lone pair orbital. The  $\sigma$  bonding and the out-of-plane  $\pi$  bonding appear to have a moderate degree of covalency ( $\alpha=\delta=0.91$ ;  $\alpha'=0.49$ ). The covalent in-plane  $\pi$  bonding is somewhat stronger ( $\beta=0.87$ ) but is by no means so strongly covalent as is observed in compounds with ligands which do not exclusively coordinate through the lone pair electrons.

At low temperature nine ligand nuclear superhyperfine structure lines corresponding to the interaction of four magnetically equivalent nitrogen nuclei have been observed. The value of  $\alpha'$  derived from the superhyperfine splitting is in excellent agreement with that obtained from the copper nucleus hyperfine structure.

## Introduction

The LCAO-MO theory of copper(II)-coordination compounds developed by MAKI and MCGARVEY<sup>1</sup> and KIVELSON and NIEMAN<sup>2</sup> permits the experimental determination of the covalent bonding parameters for different orbitals by measuring the EPR spectrum of the complex in solution at room temperature and at low temperature and by the measurement of some optical absorption properties.

The EPR spectra of the copper(II) tetrammine complex have hitherto been obtained from single crystals, e.g.,<sup>3,4</sup>  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ , and from a solution in glycerine<sup>5</sup>. GERSMAN and SWALEN<sup>6</sup> investigated the EPR spectrum of a copper(II) ammine complex in a solution of chloroform and toluol but it is not made clear whether the tetrammine complex was formed or not. Nevertheless, the authors used the above theory for the determination of the bonding parameters. This was the first attempt of this kind concerning a copper tetrammine compound.

It is not possible, however, to apply the theory of Maki, MCGARVEY, KIVELSON and NIEMAN immediately to this complex because exact  $sp^2$  hybridization of the ligand wave function was generally assumed. For many ligands this is quite a good approximation but for ammonia it is not. The wave function of the ground state of the  $\text{NH}_3$  molecule is approximately given by the concept of  $sp^3$  hybridization. But the values of the overlap integral  $S(n)$  for  $\sigma$  bonding, the parameter  $T(n)$  and the superhyperfine splitting are quite strongly dependent on the hybridization parameter  $n$  used in the ligand wave function. Actually, in the work of Gersman and Swalen, the agreement of the results derived from the hyperfine spectra and independent of this from the superhyperfine splitting is quite bad.

Furthermore, a difficulty in applying the theory arise from the fact that in many cases the required optical data are not known exactly and are not easily obtained, as well. For the most part the optical absorption spectrum of the copper(II) coordination compounds reveal only one band in the

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<sup>1</sup> A. H. MAKI and B. R. MCGARVEY, J. Chem. Phys. **29**, 31, 35 [1958].

<sup>2</sup> D. KIVELSON and R. NIEMAN, J. Chem. Phys. **35**, 149 [1961].

<sup>3</sup> H. ABE and K. ONO, J. Phys. Soc. Japan **11**, 947 [1956].

<sup>4</sup> E. H. CARLSON and R. D. SPENCE, J. Chem. Phys. **24**, 471 [1956].

<sup>5</sup> E. LUTZE and D. BÖSNECKER, Z. Naturforsch. **14 a**, 755 [1959].

<sup>6</sup> H. R. GERSMAN and J. D. SWALEN, J. Chem. Phys. **36**, 3221 [1962].



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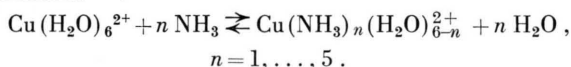
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red region instead of the three expected bands and a charge transfer band in the UV region. Several assignments of the three bands expected at  $D_{4h}$  symmetry are possible. Gersman and Swalen obviously assumed that the unsymmetrical red band at about  $16\,600\text{ cm}^{-1}$  contains the two lower lying transitions  $B_{1g} \rightarrow A_{1g}$  and  $B_{1g} \rightarrow B_{2g}$  unresolved and that the third transition  $B_{1g} \rightarrow E_g$  is hidden by the charge transfer band. Its assignment is highly speculative.

Meanwhile, polarized absorption spectra of single crystals of several copper(II) tetrammine complexes have been measured at  $77^\circ\text{K}$ <sup>7</sup>. The results show that the above assumptions of Gersman and Swalen are wrong. Therefore, the chemical bonding in the copper tetrammine complex was again investigated by the EPR method. In order to interpret the spectra quantitatively a slight extension of the theory incorporating an arbitrary hybridization parameter  $n$  in the overlap integral  $S$  and in the superhyperfine splitting was necessary.

## Experimental

Five different ammine complexes are formed in aqueous solution of the Cu(II) ion by addition of ammonia<sup>8,9</sup>.



At a free ammonia concentration of  $10^{-1.5} \approx 0.032\text{ M/L}$  the formation of the tetrammine complex prevails<sup>10</sup>. At room temperature its absorption spectrum exhibits a peak at about  $600\text{ nm}$ <sup>11</sup> the position of which is distinctly different from that of other ammine complexes<sup>11</sup>. Absorption spectra can be used for the identification of these compounds.

But hyperfine interactions are not well resolved in aqueous solution EPR spectra. Therefore a mixture of methanol and water was used as a solvent. By addition even of little amounts of water the thermodynamic equilibrium of the glassy solution is reached very quickly at low temperatures.

The investigated solution had the composition:

$$[\text{Cu}^{2+}] = 1.1 \times 10^{-3}\text{ M/L as } \text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}, \\ [\text{NH}_3] = 5.2 \times 10^{-2}\text{ M/L}, \\ [\text{H}_2\text{O}] = 3.6\text{ M/L}, \quad [\text{CH}_3\text{OH}] = 23.2\text{ M/L}.$$

All substances used were of analytical grade. The formation constant of the tetrammine complex in the

above solution is not known. In aqueous solution its value<sup>7</sup> is  $120\text{ L/M}$ . But with the total cupric ion and ammonia concentrations chosen the exact value of the formation constant has only extremely little influence on the calculation of the free ammonia concentration in the above solution. Comparing its extinction\* ( $E=0.242$ ) with that of an aqueous solution with the same ammonia and cupric ion concentrations ( $E=0.193$ ) the formation constant is found somewhat higher in the methanol-water solution as is expected from the polarized ionic model of coordination compounds. The free ammonia concentration in the investigated solution is calculated using the aqueous solution formation constant to  $0.048\text{ M/L}$  which is within the tetrammine formation range. This can be demonstrated by two independent methods. The absorption spectrum of the above solution measured at room temperature exhibits the typical peak at  $608\text{ nm}$  which is observed in aqueous solution at  $607\text{ nm}$  with a very small solvent shift.

The EPR spectrum of the solution at the same temperature consists of the four well known hyperfine lines of the copper nucleus with a line separation of  $77\text{ Gauss}$ . SAMARAEV and TIKHOMIROVA<sup>10</sup> have shown that the line distance is strongly dependent on the number of ammonia ligand molecules. The value of the hyperfine splitting obtained from the methanolic solution agrees well with the result of these authors for the tetrammine complex in aqueous solution. Finally, the formation of this compound is confirmed by the fact that actually nine superhyperfine lines are observed as expected from the theory if an interaction of the magnetic electron on the copper ion with four nitrogen atoms with a nuclear spin of  $I=1$  is assumed.

The EPR spectra were measured with the Varian X-band spectrometer V-4502 with  $100\text{ Kc}$  modulation. The dual cavity V-4532 with pitch as standard probe ( $g=2.0028$ ) was used for the determination of the  $g$ -values. The static magnetic field was measured with the help of an AEG-proton resonance gaussmeter connected to a Racal frequency counter (type 806 R). The solution was cooled to  $97^\circ\text{K}$  by a stream of cold nitrogen in the V-4557 cooling setup. Room temperature spectra were obtained using the usual Varian aqueous solution sample cell.

## Results

The EPR parameters derived from the room temperature spectra are

$$g_0 = 2.122 \pm 0.002, \quad |A_0| = 77 \pm 2\text{ G}.$$

The analysis of the line shapes of the EPR spectrum of copper(II) compounds carried out by VÄNN-

<sup>7</sup> B. J. HATHAWAY and A. A. G. TOMLINSON, *Coord. Chem. Rev.* **5**, 1 [1970].

<sup>8</sup> J. BJERRUM and E. J. NIELSON, *Acta Chem. Scand.* **2**, 297 [1948].

<sup>9</sup> J. BJERRUM, *Metal Ammine Formation in Aqueous Solution*, P. Haase & Son, Copenhagen 1957.

<sup>10</sup> I. SAMARAEV and N. N. TIKHOMIROVA, *Zh. strukt. Khimii* **5**, 691 [1964].

<sup>11</sup> J. BJERRUM, C. J. BALLHAUSEN, and C. K. JØRGENSEN, *Acta Chem. Scand.* **8**, 1275 [1954].

\* Absorption spectra were measured with the Cary 15 spectrophotometer.

GARD and AASA<sup>12</sup> reveal that  $g_{||}$  and  $A_{||}$  can easily be obtained from the low temperature solution spectra whereas  $g_{\perp}$  and  $A_{\perp}$  usually cannot be determined experimentally with sufficient accuracy. These parameters were calculated using the relations

$$g_0 = \frac{1}{3} (g_{||} + 2g_{\perp}), \quad (1)$$

$$A_0 = \frac{1}{3} (A_{||} + 2A_{\perp}). \quad (2)$$

It can be assumed that these equations are excellent approximations for the complex under study because rotations of this relatively small molecule in solution at room temperature presumably are not all hampered. The low temperature spectrum (Fig. 1) yields

$$g_{||} = 2.245 \pm 0.001, \\ |A_{||}| = 0.0192 \pm 0.0002 \text{ cm}^{-1}.$$

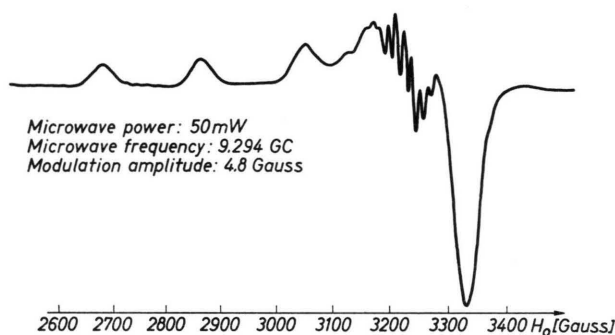


Fig. 1. EPR spectrum of Cu(II) tetramine nitrate in methanol and water at 97 °K.

Then Eqs. (1) and (2) give

$$g_{\perp} = 2.061 \pm 0.002, \\ |A_{\perp}| = 0.00232 \pm 0.00003 \text{ cm}^{-1}.$$

$$\Psi_{B_{1g}} = \alpha d_{x^2-y^2} - \frac{1}{2} \alpha' (-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)}), \quad (3)$$

$$\Psi_{B_{2g}} = \beta d_{xy} - \frac{1}{2} (1 - \beta^2)^{1/2} [p_y^{(1)} + p_x^{(2)} - p_y^{(3)} - p_x^{(4)}], \quad (4)$$

$$\Psi_{E_g} = \begin{cases} \delta d_{xz} - (1 - \delta^2)^{1/2} [p_z^{(1)} - p_z^{(3)}] \frac{1}{\sqrt{2}}, \\ \delta d_{yz} - (1 - \delta^2)^{1/2} [p_z^{(2)} - p_z^{(4)}] \frac{1}{\sqrt{2}}. \end{cases} \quad (5)$$

The only overlap considered is that in the  $B_{1g}$  ground state

$$\alpha^2 + \alpha'^2 - 2\alpha\alpha'S = 1 \quad (7)$$

with the overlap integral  $S$  given by

$$S = 2 \langle d_{x^2-y^2} | -\sigma_x^{(1)} \rangle. \quad (6)$$

<sup>12</sup> T. VÄNNGÅRD and R. AASA, in: W. LOW, edit., Paramagnetic Resonance, Vol. II, Academic Press, New York 1963, p. 509.

At low temperature a superhyperfine structure consisting of nine equally spaced lines is observed (Fig. 2). The magnitude of the splitting is

$$A_{||}^N = 13.0 \pm 0.2 \text{ G}.$$

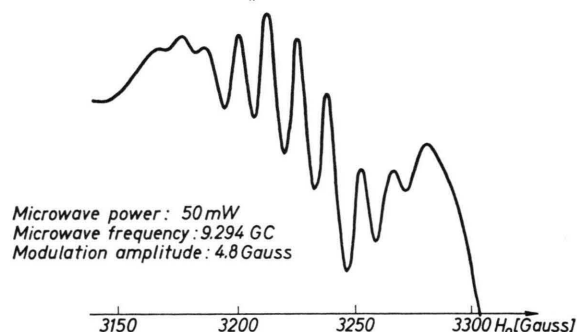


Fig. 2. Superhyperfine structure in the EPR spectrum of Cu(II) tetramine nitrate in methanol and water at 97 °K.

The measurement of the polarized absorption spectra of the  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  crystal whose structure is assumed to be quite close to that of the coppertetrammine ion in solution shows that<sup>7</sup>

$$E(E_g) - E(B_{1g}) = \Delta E_{xz} = 18\,000 \text{ cm}^{-1}, \\ E(B_{2g}) - E(B_{1g}) = \Delta E_{xy} = 15\,900 \text{ cm}^{-1}.$$

## Theory

With these data it is possible to calculate the LCAO-MO bonding parameters accurately. First the results of the theory will be given in the notation of GERSMAN and SWALEN<sup>6</sup>. By use of group theoretical considerations the following LCAO-MO scheme for the antibonding orbitals can be set up for  $D_{4h}$  symmetry (the  $A_g$  orbital has been omitted)

The  $\sigma$  orbitals are hybridized nitrogen sp-orbitals of the type

$$\sigma = n p \mp (1 - n^2)^{1/2} S \quad (8)$$

where the minus sign refers to the ligands on the negative  $x$  and  $y$  axes.

Thus the  $B_{1g}$  state describes  $\sigma$  bonding in the complex. The  $B_{2g}$  and  $E_g$  states represent, respectively, inplane — and out-of-plane  $\pi$  bonding.

Calculation of the spin Hamiltonian using these wave functions yields the results <sup>1, 2, 6</sup>:

$$g_{||} = 2.0023 - \frac{8\lambda}{\Delta E_{xy}} [\alpha^2 \beta^2 - f(\beta)], \quad (9)$$

$$g_{\perp} = 2.0023 - \frac{2\lambda}{\Delta E_{xz}} [\alpha^2 \delta^2 - g(\delta)], \quad (10)$$

$$A_{||} = P \left[ -\alpha^2 \left( \frac{4}{7} + k \right) - 2\lambda \alpha^2 \left( \frac{4\beta^2}{\Delta E_{xy}} + \frac{3\delta^2}{7\Delta E_{xz}} \right) \right] \quad (11)$$

$$A_{\perp} = P \left[ \alpha^2 \left( \frac{2}{7} - k \right) - \frac{22\lambda \alpha^2 \delta^2}{14\Delta E_{xz}} \right], \quad (12)$$

$$f(\beta) = \alpha \alpha' S \beta^2 + \frac{1}{2} \alpha \alpha' T(n) \beta (1 - \beta^2)^{1/2}, \quad (13)$$

$$g(\delta) = \alpha \alpha' S \delta^2 + \frac{1}{\sqrt{2}} \alpha \alpha' T(n) \delta (1 - \delta^2)^{1/2}. \quad (14)$$

The parameter  $P$  is

$$P = 2\gamma \beta_0 \beta_N \langle d_{x^2-y^2} | r^{-3} | d_{x^2-y^2} \rangle = 0.036 \text{ cm}^{-1}.$$

$\gamma$  is the gyromagnetic ratio for the copper nucleus,  $\beta_0$  is the Bohr magneton,  $\beta_N$  is the nuclear magneton. The parameter  $T(n)$  is given by

$$T(n) = n - \frac{8(1-n^2)^{1/2} (Z_p Z_s)^{5/2} (Z_s - Z_p)}{(Z_s + Z_p)^5} \frac{R}{a_0}. \quad (15)$$

Here  $n$  is the hybridization parameter,  $Z_p$  and  $Z_s$  are the effective charges for the hydrogenlike 2p and 2s states of nitrogen, respectively.  $R$  is the central ion-ligand distance,  $a_0$  the Bohr radius.  $\lambda$  is the spin orbit coupling parameter of the free cupric ion ( $\lambda = -828 \text{ cm}^{-1}$ ) and  $k$  is a constant introduced to correct for the Fermi contact term of excited configurations containing unpaired s-electrons, which have a finite electron density at the nucleus. Its value is  $k = 0.43$  for the free cupric ion.

The values for the overlap integral  $S(n)$  and for the parameter  $T(n)$  given by Maki and McGarvey cannot be used for the tetrammine complex because the assumptions of  $sp^2$  hybridization in the ligand wave function and the bonding distance of  $R = 3.62 a_0$  are not valid. Because of the structural similarity between the  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  crystal

and the copper (II) tetrammine ion a value of  $R = 3.88 a_0$  was chosen which was found by X-ray analysis of the crystal <sup>13</sup>.

For the lone pair orbital the simple Duncan-Pople hybrid function <sup>14, 15</sup>

$$\Psi = 0.62362 \Psi_{2s} - 0.78172 \Psi_{2p_z} \quad (16)$$

was used in our calculation\*. The hybridization parameter is  $n = 0.78172$ . For to have the same system used in the original papers the coordinate system of (16) was rotated so that  $z \rightarrow -x$ . Then (16) transforms to

$$\Psi' = 0.62362 \Psi_{2s} + 0.78172 \Psi_{2p_x}. \quad (17)$$

With these values of  $n$  and  $R$  the parameters  $S(n)$  and  $T(n)$  were calculated (see appendix):

$$S(n) = 0.067 \quad \text{for } n = 0.78172, \\ T(n) = 0.221.$$

The system of Eq. (9) – (12) can be solved by an iteration procedure as suggested by KIVELSON and NIEMAN <sup>2</sup>.

From these equations the following expression for  $\alpha$  is derived

$$\alpha^2 = -A_{||}/P + g_{||} - 2 + \frac{3}{2} (g_{\perp} - 2) + a \quad (18)$$

with the small correction term

$$a = -2\lambda \left[ \frac{4f(\beta)}{\Delta E_{xy}} + \frac{3}{7} \frac{g(\delta)}{\Delta E_{xz}} \right]. \quad (19)$$

The value of  $a$  was generally estimated to 0.04 by Kivelson and Nieman.

In our calculation a slightly different procedure was used. At first the constant  $a$  was determined using estimated values for the bonding parameters:  $\alpha = 0.9$ ;  $\alpha' = 0.5$ ;  $\beta = \delta = 1$  ( $a = 0.0138$ ). In a first approximation the values of  $\alpha$ ,  $\alpha'$ ,  $\beta$ ,  $\delta$  were then calculated using the Eqs. (6), (10), (9) and (18). With this result a new value of the constant  $a$  was received:  $a = 0.0202$ . The second approximation for the bonding parameters yields

$$\alpha = 0.91, \quad \alpha' = 0.49, \quad \beta = 0.87, \quad \delta = 0.91.$$

According to Eq. (12) one obtains with these values

$$|A_{\perp}| = 24.5 \cdot 10^{-4} \text{ cm}^{-1}.$$

<sup>13</sup> Tables of interatomic distances and configurations in molecules and ions, London, The Chemical Society, Burlington House, W 1 [1958].

<sup>14</sup> A. B. F. DUNCAN and J. A. POPLE, Trans. Faraday Soc. **49**, 217 [1953].

<sup>15</sup> A. B. F. DUNCAN, J. Chem. Phys. **27**, 423 [1957].

\* This wave function was obtained by adjusting the hybridization parameter  $n$  in the trial function

$$\Psi = n \Psi_{2p_z} + (1-n^2)^{1/2} \Psi_{2s},$$

so that the theoretical value for the dipole moment of ammonia derived from this function agreed with the experimental one <sup>14</sup>.

The experimental value derived from Eq. (2) is

$$|A_{\perp}| = 23.2 \cdot 10^{-4} \text{ cm}^{-1}$$

in good agreement with the theoretical one.

This result shows that the constant  $k$  in (11) and (12) has only a slightly different value from that of the free ion. One actually obtains the same results for the bonding parameters within the experimental error of  $\pm 1$  per cent if Eq. (12) with the experimental value of  $A_{\perp}$  is incorporated in the iteration procedure. This means that instead of using Eq. (18)  $\alpha$  has to be calculated from

$$\alpha^2 = \frac{7}{6} \frac{A_{\perp} - A_{\parallel}}{P} + \frac{7}{6} (g_{\parallel} - 2) + \frac{1}{2} (g_{\perp} - 2) + b \quad (19)$$

with

$$b = -\lambda \left[ \frac{28}{3} \frac{f(\beta)}{\Delta E_{xy}} + \frac{g(\delta)}{\Delta E_{xz}} - \frac{11}{6} \frac{\alpha^2 \delta^2}{\Delta E_{xz}} \right]. \quad (20)$$

### Ligand Nuclear Superhyperfine Structure

The measurement of the superhyperfine splitting establishes a method independent from that used up to now for the determination of the bonding parameter  $\alpha'$ . Since the value of the superhyperfine splitting is dependent on the hybridization parameter the result of Maki and McGarvey could not be used. Therefore a calculation of the interaction energy as a function of  $n$  was carried out.

Using the  $B_{1g}$  ground state wave function (3) and neglecting higher multipole terms than dipole one obtains in a first approximation by comparison of the calculated interaction energy with the expected form of the spin Hamiltonian (see appendix)

$$A_{\parallel}^N(n) = \gamma \beta_0 \beta_N \alpha'^2 \cdot \left[ \frac{4\pi}{3} (1 - n^2) |\Psi_{2s}(0)|^2 + \frac{2}{5} n^2 \langle r^{-3} \rangle_{2p} \right], \quad (21)$$

$$A_{\perp}^N(n) = \gamma \beta_0 \beta_N \alpha'^2 \cdot \left[ \frac{4\pi}{3} (1 - n^2) |\Psi_{2s}(0)|^2 - \frac{1}{5} n^2 \langle r^{-3} \rangle_{2p} \right]. \quad (22)$$

For the case of  $sp^2$  hybridization these equations lead to the well known result of Maki and McGarvey except for a factor 4 in the dipolar term of Eq. (22)\*\*.

Using the values

$$|\Psi_{2s}(0)|^2 = 33.4 \cdot 10^{-24} \text{ cm}^{-3}$$

and

$$\langle r^{-3} \rangle_{2p} = 21.1 \cdot 10^{24} \text{ cm}^{-3}$$

estimated by Maki and McGarvey and  $n = 0.78172$  the superhyperfine splitting  $A_{\parallel}^N = 13 \text{ G}$  gives according to Eq. (21)  $\alpha' = 0.49$  in excellent agreement with the result derived from the hyperfine structure.

The use of the *free* ammonia lone pair orbital can be justified by the reasonable assumption that the value of the wave function at the nitrogen nucleus is not considerably affected by the bonding in the complex.

### Discussion

The covalent bonding parameters, distinctly different from those of Gersman and Swalen, show that chemical bonding in the copper(II) tetrammine complex is predominantly ionic as was expected but that there is also considerable covalent  $\sigma$  and  $\pi$  bonding. The covalent out-of-plane  $\pi$  bonding is as strong as the covalent  $\sigma$  bonding in the ground state and the inplane  $\pi$  bonding is even stronger. This result which is clearly inconsistent with the assumption of the theory that the  $\pi$  overlap integrals can be neglected has been observed on most Cu(II) coordination compounds some of which are quoted in Table 1. Only compounds with ligands which coordinate through the nitrogen atom are given.

Table 1. LCAO-MO parameters of some Cu(II) coordination compounds. Abbreviations: GH=Glycyl-L-histidine, AcG<sub>2</sub>HG=Acetyl-glycyl-L-histidylglycine. The value of  $\alpha'$  in the fifth column is calculated from the superhyperfine splitting.

Compound	$\alpha$	$\alpha'$	$\beta$	$\delta$	$\alpha'$	Ref.
Cu(II)-Na-chlorophyllin	0.91	0.51	0.81	0.85	0.55	17
Cu(II)-Phthalocyanin	0.88	0.55	—	—	0.55	2
Cu(II)-Etio-porphyrin II	0.86	0.59	0.82	—	0.55	18
Cu(II)-AcG <sub>2</sub> HG	0.91	0.52	0.82	0.83	0.52	19
Cu(II)-GH	0.90	0.52	0.86	0.87	0.46	19
Cu(NH <sub>3</sub> ) <sub>4</sub> -(CH <sub>3</sub> OH) <sub>2</sub> <sup>2+</sup>	0.91	0.49	0.87	0.91	0.49	this work
Cu(II)-tetra-pyridin	0.87	0.57	0.93	$\approx 1$	?	6

\*\* This factor is also found in the expression for the interaction energy in the case of  $sp^2$  hybridization given by HARRISON and ASSOIR<sup>16</sup>.

<sup>16</sup> S. E. HARRISON and J. M. ASSOIR, in: W. Low, edit., Paramagnetic Resonance, Vol. II, Academic Press, New York 1963, p. 861.

<sup>17</sup> G. SCHOFFA, Z. Naturforsch. **23a**, 550 [1968].

<sup>18</sup> E. M. ROBERTS and W. S. KOSKI, J. Amer. Chem. Soc. **82**, 3006 [1960].

<sup>19</sup> G. F. BRYCE, J. Phys. Chem. **70**, 3549 [1966].



To a first approximation these complexes should have some common features. The values for  $\alpha$  and  $\alpha'$  are quite close, indeed. The strength of the covalent  $\sigma$  bonding is obviously only slightly dependent on the different nature of the ligand molecules. The  $\beta$  and  $\delta$  values of the compounds with ligands which do not exclusively coordinate through the lone pair electrons of the nitrogen atom, however, are by far lower than those of the Cu(II) tetrammine- and the tetra-pyridine complex although in the latter case the values are probably too high because the assignments of the optical transition energies  $\Delta E_{xy}$  and  $\Delta E_{xz}$  made by Gersman and Swalen have to be doubted. The work of TOMLINSON and HATHAWAY<sup>7</sup> indicated that in most Cu(II) coordination compounds the three optical transitions expected at  $D_{4h}$  symmetry are contained in the broad band in the red region of the visible spectrum so that the energies  $\Delta E_{xy}$  and  $\Delta E_{xz}$  are expected to be considerably lower than assumed by the authors.

The compound Cu(II)-GH three ligands of which use the lone pair orbital for chemical bonding has  $\beta$  and  $\delta$  values intermediate between the first group of compounds in Table 1 (only two lone pair coordinations) and the last two complexes (four lone pair orbitals involved in the bonding).

VAN HEUVELEN and GOLDSTEIN<sup>20</sup> attribute the observation that  $\pi$  bonding is usually much stronger than  $\sigma$  bonding in copper (II) coordination compounds to several shortcomings of the theory: the neglect of the reduction of the parameter  $P$ , the spin orbit parameter  $\lambda$  and the Fermi contact parameter  $k$  in the ligand field, neglect of low lying ligand states and the use of estimated values for the unknown optical transition energies. These shortcomings, however, do not influence the results for the complex under study. As was shown above there was no significant change of the Fermi contact parameter  $k$  of the central ion in the complex. Since in the ammonia molecule only  $\sigma$  bonding occurs no low lying ligand states are expected.

The reduction of the spin orbit parameter in the ligand field (relativistic nephelauxetic effect) is caused by two effects<sup>21</sup>: the symmetry restricted

covalency (reduction of the density of the central ion electrons by covalent bonding) and the central field covalency (reduction of the effective nuclear charge of the central ion caused by additional shielding of the nucleus by the ligand electrons). The first effect has been incorporated in the theory but the second has not. But MCGARVEY<sup>22</sup> pointed out that the neglect of the charge dependence of  $\lambda$  should not influence the results for the bonding parameters significantly since the value of  $\lambda$  for the cupric ion ( $\lambda = 828 \text{ cm}^{-1}$ ) and for the copper atom ( $\lambda = 818 \text{ cm}^{-1}$ ) are only slightly different. Therefore, assuming a total shielding of the copper (II) ion by two charge units (a much stronger shielding is not very probable) a reduction of  $\lambda$  by about 1 per cent would result. According to Eq. (18) this would cause an increase of  $\alpha$  of about 1 per cent, as well. This is within experimental error. The same argument holds for the change of the parameter  $P$  because  $P$  is proportional to  $\langle d_{x^2-y^2} | r^{-3} | d_{x^2-y^2} \rangle$  as is  $\lambda$ .

Because of some inevitable uncertainties (e. g. the unknown optical transition energies) inherent in the experimental results most workers confine themselves on the Fermi contact part of the superhyperfine interaction when calculating the bonding parameter  $\alpha'$ . In many cases the agreement of the results for  $\alpha'$  obtained from the hyperfine- and the superhyperfine structure is satisfactory but may be casual. In quantitative calculations, however, besides the anisotropic dipolar part higher multipole contributions to the interaction energy have to be considered as was pointed out by MARSHALL and STUART<sup>23</sup> and MARSHALL<sup>24</sup>. Correction terms usually are in the order of 1 per cent but can contribute up to 10 per cent in some cases. No explicit calculation of the higher multipole terms has yet been carried out for a copper (II) compound although the deviations from spherical symmetry of the charge distribution in the  $3d^9$  configuration should give rise to non-negligible corrections. Therefore, the complete agreement the values of  $\alpha'$  for the complex under study calculated by the two independent methods should not be overestimated. The maximal change of the

<sup>20</sup> A. VAN HEUVELEN and L. GOLDSTEIN, J. Phys. Chem. **72**, 481 [1968].

<sup>21</sup> C. K. JØRGENSEN, Progr. Inorg. Chem. **4**, 73 [1962].

<sup>22</sup> B. MCGARVEY, in: R. L. CARLIN, Transition Metal Chemistry, Vol. 3, Edward Arnold Ltd., London/Marcel Dekker, Inc., New York 1966, p. 89.

<sup>23</sup> W. MARSHALL and R. STUART, Phys. Rev. **123**, 2048 [1961].

<sup>24</sup> W. MARSHALL, in: W. LOW, edit., Paramagnetic Resonance, Vol. I, Academic Press, New York 1963, p. 350.

interaction energy of 10 per cent would cause the same change in  $\alpha'^2$  but the value of  $\alpha'$  which was used for comparison is affected only by 5 per cent. Therefore, even under these circumstances, no serious disagreement is to be expected if multipole effects are included in the Eq. (21) and (22).

## Appendix

### 1. Calculation of the overlap integral $S(n)$

According to Eq. (7) and (8)

$$S = -2[n \langle d_{x^2-y^2} | p_x^{(1)} \rangle + (1-n^2)^{1/2} \langle d_{x^2-y^2} | s^{(1)} \rangle].$$

Hydrogenlike functions with values for  $Z_p$  and  $Z_s$  given in<sup>2</sup> were used in the evaluation of the two-center integrals. By transforming to elliptical coordinates<sup>25</sup> these integrals can be expressed by the auxiliary integrals

$$A_n(p) = \int_1^\infty e^{-px} x^n dx,$$

$$B_n(p, t) = \int_{-1}^1 e^{-ptx} x^n dx$$

which have extensively been tabulated<sup>26, 27</sup>. One obtains

$$S = 2nJ_1 - 2(1-n^2)^{1/2}J_2$$

with

$$J_1 = \frac{Z_{3d}^{7/2} Z_{2p}^{5/2}}{3^4 \cdot 2^9} \left( \frac{R}{a_0} \right)^6 [A_1(B_3 + B_5) + A_2(3B_0 + B_4) - A_3(B_1 + 3B_5) - A_4(B_0 + B_2) - A_5(B_1 - 3B_3) - A_0(3B_2 - B_4)]$$

and

$$J_2 = \frac{Z_{2s}^{3/2} Z_{3d}^{7/2}}{3^4 \cdot 2^7} \left( \frac{R}{a_0} \right)^5 \left\{ 4A_1B_3 + 3A_2(B_0 - B_4) - 4A_3B_1 + A_4(3B_2 - B_0) - A_0(3B_2 - B_4) - \frac{Z_{2s}}{4} \frac{R}{a_0} [A_0(B_5 - 3B_3) + A_1(-3B_2 + 5B_4) + A_2(3B_1 + 4B_3 - 3B_5) + A_3(3B_0 - 4B_2 - 3B_4) + A_4(-5B_1 + 3B_3) + A_5(-B_0 + 3B_2)] \right\}.$$

For  $R = 3.88 a_0$  one obtains  $J_1 = 0.0299116$  and  $J_2 = -0.0162963$ . With  $n = 0.78172$  the result for  $S$  is  $S = 0.067$ .

### 2. Calculation of the superhyperfine splitting

The Hamiltonian for the superhyperfine interaction is

$$\hat{H} = 2\gamma\beta_0\beta_N \left\{ \frac{\mathbf{I} \cdot \mathbf{I}}{r^3} + \frac{-\mathbf{S} \cdot \mathbf{I} + 3(\mathbf{r}_0 \cdot \mathbf{S})(\mathbf{r}_0 \cdot \mathbf{I})}{r^3} + \frac{8\pi}{3} \delta(\mathbf{r}) \mathbf{I} \cdot \mathbf{S} \right\}$$

Neglecting higher multipole terms than dipole the Hamiltonian can be replaced by the following equivalent operator<sup>28</sup>

$$\hat{H} = 2\gamma\beta_0\beta_N \left\{ \langle r^{-3} \rangle_l \left[ \mathbf{I} \cdot \mathbf{I} + \frac{2}{(2l-1)(2l+3)} \cdot [l(l+1) \mathbf{I} \cdot \mathbf{S} - \frac{3}{2} (\mathbf{I} \cdot \mathbf{I})(\mathbf{I} \cdot \mathbf{S}) - \frac{3}{2} (\mathbf{I} \cdot \mathbf{S})(\mathbf{I} \cdot \mathbf{I})] \right] + \frac{8\pi}{3} \delta(r) \mathbf{I} \cdot \mathbf{S} \right\}.$$

The spin Hamiltonian is then calculated from

$$\hat{H}_{Sp} = \langle \Psi_{B_{1g}} | \hat{H} | \Psi_{B_{1g}} \rangle$$

using the wave function (3) of the ground state of the complex. By comparison with the expression expected at axial symmetry in our coordinate system

$$\hat{H}_{Sp} = A_{||} \hat{S}_x \hat{I}_x + A_{\perp} (\hat{I}_y \hat{S}_y + \hat{I}_z \hat{S}_z)$$

the result (21) and (22) is obtained.

<sup>25</sup> C. J. BALLHAUSEN, Introduction to Ligand Field Theory, McGraw-Hill Book Co., Inc., New York 1962, p. 174.

<sup>26</sup> H. PREUSS, Integraltafeln zur Quantenchemie, I.

<sup>27</sup> M. KOTANI, A. AMEMIYA, E. ISHIGURO, and T. KIMURA, Tables of Molecular Integrals, Maruzen Co., Ltd., Japan 1955.

<sup>28</sup> A. ABRAGAM and B. BLEANEY, Electron Paramagnetic Resonance of Transition Ions, Clarendon Press, Oxford 1970, p. 692.