Electron Paramagnetic Resonance Study of Copper(II) Dimethylglyoxime.   I. Theoretical and Experimental Study of the Effect of Axial Ligands

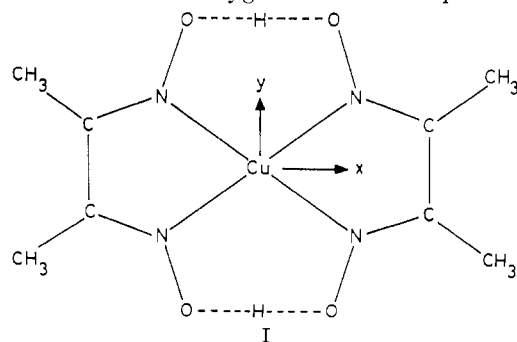By KARL-ERIK FALK,[1a] ELENA IVANOVA,[1b] BJÖRN ROOS,[1c] and TORE VÄNNGÅRD[1a]

Epr parameters of copper(II) dimethylglyoxime ($Cu(HD)_2$) are calculated and the values are compared with those experimentally obtained from solutions of $Cu(HD)_2$. The method used for the calculations is an open-shell SCF–MO method with the zero differential overlap (ZDO) approximation and inclusion of semiempirical parameters. Epr parameters are computed using second-order perturbation theory and as a consequence of the ZDO approximation the resulting expressions for the *g* values contain no overlap integrals. It is found that charge-transfer transitions give appreciable contributions to the *g* values. The covalency decreases (*g* values increase) as electron-donating ligands are added along the *z* axis, although the total number of 3d electrons is constant due to a balance between donation and back-donation. Epr parameters are reported for $Cu(HD)_2$ dissolved in benzene, benzene–pyridine mixtures, chloroform, chloroform–pyridine mixtures, and water. Resolved epr spectra of frozen solutions could only be obtained when axial ligands were present. The calculated *g* values and the anisotropy of the hyperfine coupling are compared with the experimental values. The agreement is found to be satisfactory. In addition spectra of some species obtained in a pH titration of $Cu(HD)_2$ are given, and possible structures of the complexes are suggested.

Introduction

Copper(II) normally coordinates with four strong bonds to neighbors approximately situated in a plane and with weaker bonds to one or two axial ligands. In electron paramagnetic resonance (epr) studies of copper(II) complexes one is mostly concerned with the effect of the close ligands on the resonance parameters. In particular, the unpaired electron appears in an orbital that can interact strongly with orbitals of these ligands, in favorable cases giving rise to hyperfine interaction with the ligand nuclei. For example, an earlier epr investigation[2] on the copper(II)–triglycylglycine system gave important information about the coordination of the closest ligands in the various complexes formed in a potentiometric titration.

Some influences of axial ligands on epr spectra have been reported for copper acetylacetonates[3] and copper *t*-butylacetoacetate,[4] but the adduct formation is rather weak for these oxygen-chelated complexes.

I

Copper(II) dimethylglyoxime ($Cu(HD)_2$, I) has been chosen for our study. The metal ion in this complex has a stable coordination to its closest neighbors, four nitrogens in the two dimethylglyoxime ligands. The structure of the complex is further stabilized by two strong hydrogen bonds. Furthermore, it is well established from work by Dyrssen, *et al.*,[5,6] and by Fleischer and Freiser[7] that $Cu(HD)_2$ can form adducts with organic compounds containing basic nitrogen in organic solvents and with H_2O and OH^- in aqueous solutions. This tendency to form adducts also governs the solid structure.[8] In addition, the electronic structure of $Cu(HD)_2$ and its adducts with water and amines has been subject to a theoretical investigation,[9] in which epr parameters were calculated for the complex without any adduct. Previously, experimental epr parameters have been reported by Schübel and Lutze[10] and by Wiersema and Windle[11] and the theoretical values in ref 9 were compared to those of Wiersema and Windle. However, their measurements were restricted to polar solvents and the results thus refer to a case where adduct formation has occurred.

In this work we have analyzed the epr spectra of $Cu(HD)_2$ and some of its adducts in solution both at room temperature and in frozen solutions. Owing to the low solubility of $Cu(HD)_2$ inert solvents like carbon tetrachloride or heptanes could not be used (the estimated solubility is 5×10^{-6} *M*). The solvents employed were benzene, chloroform, and water, where the solubilities at 25° are 4.1×10^{-5}, 1.24×10^{-3}, and 5.7×10^{-3} *M*, respectively (E. Ivanova, unpublished work). These solubilities are large enough for room-temperature studies. The experimental values

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(2) K.-E. Falk, H. C. Freeman, T. Jansson, B. G. Malmström, and T. Vänngård, *J. Am. Chem. Soc.*, **89**, 6071 (1967).

(3) (a) H. A. Kuska, M. T. Rogers, and R. E. Drullinger, *J. Phys. Chem.*, **71**, 109 (1967); (b) H. A. Kuska and M. T. Rogers, *J. Chem. Phys.*, **43**, 1744 (1965).

(4) A. F. Garito and B. B. Wayland, *J. Am. Chem. Soc.*, **91**, 866 (1969).

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(6) D. Dyrssen and D. Petković, *ibid.*, **19**, 653 (1965).

(7) D. Fleischer and H. Freiser, *J. Phys. Chem.*, **66**, 389 (1962).

(8) E. Frassen, R. Bardi, and S. Bozzi, *Acta Cryst.*, **12**, 201 (1959).

(9) B. Roos, *Acta Chem. Scand.*, **21**, 1855 (1967).

(10) W. Schübel and E. Lutze, *Z. Angew. Phys.*, **17**, 332 (1964).

(11) A. K. Wiersema and J. J. Windle, *J. Phys. Chem.*, **68**, 2316 (1964).

of the epr parameters could then be compared to the theoretical values for the complex and its adducts. In addition, epr parameters were measured for complexes obtained by hydrolysis of $Cu(HD)_2$, one of which is believed to be the cuprate ion $Cu(OH)_4{}^{2-}$.

The epr spectra can also be used for the determination of stability constants of adduct formation. This will be dealt with in a subsequent publication.[12]

Experimental Section

Chemicals.—The chloroform used was washed three times with an equal amount of distilled water to remove ethanol and then dried overnight with anhydrous sodium sulfate. Other organic solvents were only dried with the anhydrous salt. Copper-63 was obtained from Oak Ridge National Laboratory in the form of CuO. The ^{13}CN was purchased from Bio-Rad Laboratories as KCN with 61% enrichment of the carbon isotope.

Preparation of Samples.—Copper(II) dimethylglyoxime with isotopically pure ^{63}Cu was prepared according to the following procedure. A 0.0516-g (0.0653-mmol) amount of ^{63}CuO was dissolved in ~0.5 ml of concentrated HCl. The excess of HCl was evaporated, the residue was dissolved in 0.8–1 ml of 25% NH_3, and 0.1546 g (0.133 mmol) of dimethylglyoxime in absolute ethanol was added. The solution was allowed to stand for 1 hr at room temperature after which it was chilled overnight at −20° in a deep freezer. The dark brown precipitate was separated from the solution, washed with 1 ml of cold water, and dried in the air. The saturated chloroform and benzene solutions of Cu(HD)₂ were prepared by shaking the solid sample with the solvents overnight. The concentration of copper was determined spectrophotometrically with a Beckman DB spectrophotometer equipped with 1-cm cells. The absorbance was measured at 400 nm and the concentration was calculated using the values log ϵ = 3.222 and log ϵ = 3.272 for Cu(HD)₂ in chloroform and benzene, respectively.[6] The molar absorptivity for benzene was checked by adding a 0.004 or 0.0004 M solution of Cu(HD)₂ in absolute ethanol to dry benzene, keeping the ethanol concentration constant at 10% by volume. Nitrogen was bubbled through all organic solutions to avoid the broadening of the epr signal caused by dissolved oxygen.

For the aqueous solutions of Cu(HD)₂, the copper concentration was checked by measurements of the atomic absorption at 3247 Å with a Perkin-Elmer 303 spectrometer with a recorder read-out using a copper sulfate solution as a standard or by spectrophotometric determinations of the copper complex with bathocuprein prepared in a procedure involving reduction of Cu(II) to Cu(I) and chloroform extraction. All aqueous solutions contained 1 M NaClO₄ which improves the resolution of the low-temperature spectra.[2] The water used for solutions with pH higher than 10 was boiled for 1 hr, cooled under argon, and thereby freed from carbon dioxide. For the preparation of the cyanide samples a special procedure had to be used, as CN⁻ was found to reduce the copper if the concentration of KCN was too high, resulting in no epr signal. On the other hand, too small amounts did not produce any detectable adduct formation. Best results were obtained with a CN⁻:Cu ratio of 4:1 and with the samples being frozen 1 min after mixing. KCN was added at pH 9.1.

Measurements of pH.—The pH values were measured with a Beckman glass electrode, Type G 202B, and a Radiometer calomel electrode using a digital voltmeter "Dynamco, Module 02," equipped with an operational amplifier. The electrode system was standardized with 0.001 M NaOH–0.999 M NaClO₄ at pH 10.77.

Epr Measurements.—The epr measurements were carried out using a Varian E-3 spectrometer. The microwave frequency was measured with a Systron Donner 1018 frequency counter, and the magnetic field strength was obtained with an AEG nmr gaussmeter and an HP 5245 L counter.

For chloroform solutions at room temperature quartz tubes with an i.d. of 3 mm were used. The benzene solutions, however, were poured directly into a quartz dewar vessel (i.d. 6 mm) in order to obtain a better signal at room temperature. The aqueous solutions were contained in quartz tubes with an i.d. of 1 mm. All room-temperature spectra were recorded at about 25° which gave the best resolution. At liquid nitrogen temperature all spectra were recorded with the samples in quartz tubes with an i.d. of 3 mm.

Theory

A theoretical investigation of the electron structure and excited states of Cu(HD)₂ and Cu(HD)₂B$_x$ (where B is H_2O or $(C_2H_5)_2NH$ and x = 1 or 2) was reported in an earlier paper.[9] This calculation was based on the zero differential overlap (ZDO) approximation with inclusion of semiempirical parameters.[13] The parameter scheme was obtained from a study[14] of the ionic complexes $Cu(NH_3)_6{}^{2+}$ and $Cu(H_2O)_6{}^{2+}$. In this earlier report the molecular orbitals and excited states obtained for Cu(HD)₂ were used in a calculation of the epr parameters.

The theoretical calculation of the epr parameters has in this paper been extended to include a study of the shifts of g and A values, when axial ligands are added. Four cases have been investigated: addition of one or two water molecules and addition of one or two molecules of diethylamine.

The method used is the second-order perturbation theory of Abragam and Pryce,[15] with molecular orbitals introduced by Maki and McGarvey[16] and Kivelson and Neiman.[17]

The molecular orbitals for Cu(HD)₂, relevant in this context and corresponding to the molecular point group D$_{2h}$, are

$$\nu a_g = \beta_{1\nu}(4s) + \beta_{2\nu}(3d_{z^2}) + \beta_{3\nu}(3d_{x^2-y^2}) + \beta_{4\nu}\sigma_N(a_g)$$

$$\nu b_{1g} = \alpha_{1\nu}(3d_{xy}) + \alpha_{2\nu}\sigma_N(b_{1g}) \qquad (1)$$

$$\nu b_{2g} = \gamma_{1\nu}(3d_{xz}) + \gamma_{2\nu}\pi_N(b_{2g}) + \gamma_{3\nu}\pi_C(b_{2g}) + \gamma_{4\nu}\pi_O(b_{2g})$$

$$\nu b_{3g} = \delta_{1\nu}(3d_{yz}) + \delta_{2\nu}\pi_N(b_{3g}) + \delta_{3\nu}\pi_C(b_{3g}) + \delta_{4\nu}\pi_O(b_{3g})$$

where $\sigma_N(\gamma)$ is a linear combination of nitrogen lone-pair orbitals corresponding to the irreducible representation γ, and $\pi(\gamma)$ are similarly constructed linear combinations of atomic π orbitals for the N, C, and O atoms. In what follows the coefficient for $3d_{xy}$ in $2b_{1g}$ (the antibonding orbital containing the odd electron), α_{12}, will simply be called α. The molecular orbital coefficients for Cu(HD)₂ were given in Table II of ref 9.

The excited states have been computed with superposition of all singly excited configurations. A wave function for the ith excited state of symmetry type Γ can thus be written

$$\psi_i(\Gamma) = \sum_\nu C_i(\nu\gamma)\Phi(\nu\gamma, 2b_{1g}) + \text{other terms} \qquad (2)$$

(12) D. Dyrssen, E. Ivanova, and K.-E. Falk, to be submitted for publication.

(13) B. Roos, *Svensk Kem. Tidskr.*, **80**, 204 (1968).
(14) B. Roos, *Acta Chem. Scand.*, **20**, 1673 (1966).
(15) A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc.* (London), **A205**, 135 (1951).
(16) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31 (1958).
(17) D. Kivelson and R. Neiman, *ibid.*, **35**, 149 (1961).

TABLE I
ELECTRON POPULATION AND COVALENCY FOR $Cu(HD)_2B_x$

B	x	R^a	$q(3d)^b$	$q(4s)^b$	$q(4p)^b$	$q(n_B)^b$	α^2	$N(\sigma_N)^c$
...	0	...	9.206	0.517	0.423	...	0.714	0.361
H_2O	1	2.60	9.200	0.499	0.428	1.965	0.723	0.351
H_2O	1	2.40	9.199	0.494	0.433	1.955	0.726	0.348
H_2O	2	2.60	9.194	0.483	0.431	1.967	0.732	0.341
H_2O	2	2.40	9.192	0.472	0.438	1.959	0.738	0.335
$(C_2H_5)_2NH$	1	2.50	9.210	0.517	0.465	1.927	0.716	0.359
$(C_2H_5)_2NH$	1	2.30	9.213	0.513	0.477	1.908	0.717	0.358
$(C_2H_5)_2NH$	2	2.50	9.214	0.518	0.500	1.930	0.718	0.356
$(C_2H_5)_2NH$	2	2.30	9.220	0.510	0.516	1.912	0.720	0.354

[a] Cu–B distance in ångströms. [b] Gross atomic populations; n_B is the lone pair of the axial ligands. [c] Net atomic population of the odd electron on the nitrogen lone-pair orbitals.

where $C_i(\nu\gamma)$ is the coefficient of the configuration $\Phi(\nu\gamma, 2b_{1g})$. This configuration corresponds to an excitation of an electron from a doubly occupied orbital $\nu\gamma$ to $2b_{1g}$ or from $2b_{1g}$ to an empty orbital $\nu\gamma$. These are the only configurations which contribute to the epr parameters. The "other terms" in (2) contain all other types of excitations. It was found necessary to include configuration interaction in a calculation of the epr parameters since the so-called ligand field transitions are not purely metal transitions but heavily mixed with charge-transfer transitions from the ligand π system to the metal.[9]

Using the nomenclature introduced in (1) and (2) we can write down the expressions for g_{ii} and A_{ii} as follows ($\Delta g_{ii} = g_{ii} - 2.0023$)

$$\Delta g_{zz} = -8\lambda_0\alpha^2 R_{33}$$

$$\Delta g_{xx} = -2\lambda_0\alpha(\alpha P_{11} + t P_{12}(\sin\theta)\sqrt{1-\alpha^2}) \quad (3)$$

$$\Delta g_{yy} = -2\lambda_0\alpha(\alpha Q_{11} + t Q_{12}(\cos\theta)\sqrt{1-\alpha^2})$$

$$A_{zz} = P\left\{-\varkappa - \frac{4}{7}\alpha^2 + \Delta g_{zz} - \frac{3}{7}\lambda_0\alpha^2(P_{11} + Q_{11})\right\}$$

$$A_{xx} = P\left\{-\varkappa + \frac{2}{7}\alpha^2 - 2\lambda_0\alpha^2 P_{11} + \frac{3}{7}\lambda_0\alpha^2 Q_{11} - \frac{8\sqrt{3}}{7}\lambda_0\alpha^2 R_{23}\right\} \quad (4)$$

$$A_{yy} = P\left\{-\varkappa + \frac{2}{7}\alpha^2 - 2\lambda_0\alpha^2 Q_{11} + \frac{3}{7}\lambda_0\alpha^2 P_{11} + \frac{8\sqrt{3}}{7}\lambda_0\alpha^2 R_{23}\right\}$$

where

$$R_{kl} = \sum_i[\sum_\nu C_i(\nu a_g)\beta_{k\nu}][\sum_\nu C_i(\nu a_g)\beta_{l\nu}]/\Delta E_i(A_g)$$

$$P_{kl} = \sum_i[\sum_\nu C_i(\nu b_{2g})\gamma_{k\nu}][\sum_\nu C_i(\nu b_{2g})\gamma_{l\nu}]/\Delta E_i(B_{2g}) \quad (5)$$

$$Q_{kl} = \sum_i[\sum_\nu C_i(\nu b_{3g})\delta_{k\nu}][\sum_\nu C_i(\nu b_{3g})\delta_{l\nu}]/\Delta E_i(B_{3g})$$

The formulas above do not contain any overlap integrals. It is easy to see that in the ZDO approximation, which works with formally orthogonalized atomic orbitals, the molecular orbital coefficients correspond to gross atomic populations rather than net atomic populations. The overlap terms in the g-value expressions of Kivelson and Neiman[17] are obtained

if α^2 is replaced by the gross atomic population in a nonorthogonal basis. The A values, however, depend on net atomic populations, and should in the ZDO formalism contain overlap integrals. A numerical check shows that these terms are small and can safely be omitted. It should further be noted that in-plane π bonding was not taken into account in the model proposed for the electronic structure of $Cu(HD)_2$.[9]

For the spin–orbit coupling constant λ_0 the free-atom value -828 cm^{-1} has been used. The constant t is the degree of p character in the nitrogen lone-pair orbital. Here sp^2 hybridization has been assumed, in which case $t = (^2/_3)^{1/2}$. The angle N–Cu–N, where the two nitrogen atoms belong to the same dimethylglyoxime molecule, is 2θ. The x axis bisects this angle. For P the value 388×10^{-4} cm^{-1}, reported by McGarvey[18] for $^{63}Cu^{2+}$, has been used.

The calculations of the epr parameters were performed for nine different cases: $Cu(HD)_2$ with no axial ligands, $Cu(HD)_2(H_2O)_x$ with $x = 1$ or 2 and a Cu–O distance of 2.60 or 2.40 Å, $Cu(HD)_2((C_2H_5)_2NH)_x$ with $x = 1$ or 2 and a Cu–N distance of 2.50 or 2.30 Å. In each case the added ligand molecules were placed on the z axis perpendicular to the molecular plane.

In a first step the molecular orbitals and the excited states for the complexes were computed. The molecular orbital coefficients of $Cu(HD)_2$ have been published previously.[9] Table I gives the variations in electron population when the axial ligands are added. The results shown in this table can be summarized as follows.

1. The covalency of the odd electron decreases (α increases) as electron-donating ligands are added along the z axis. This effect was also found for copper acetylacetonates in various solvents.[3] The donation of electrons to copper from the axial ligands causes a back-donation to the in-plane ligands, which results in an increase in α (the number of electrons in $3d_{xy}$ is $2 - \alpha^2$). Qualitatively this is in agreement with the observed shifts of the epr parameters (see below).

2. The balance between donation and back-donation, discussed above, is also reflected in the total number of 3d electrons, $q(3d)$. This number is almost constant, with a slight decrease for the water complex and a small increase for the amine complex.

3. It has been suggested[3,18] that the variations

(18) B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967).

TABLE II
SPECTRAL TRANSITIONS CONTRIBUTING TO
THE g VALUES IN $Cu(HD)_2$

Excd state	Config[a]	Type	ΔE[b]	Contribution to g_{ii}
$^{II}A_g$	$3a_g \rightarrow 2b_{1g}$	d–d	22.22	$\Delta g_{zz} = 0.018$
$^{III}A_g$	$2a_g \rightarrow 2b_{1g}$	d–d	27.02	$\Delta g_{zz} = 0.158$
$^{I}B_{2g}$	$1b_{2g} \rightarrow 2b_{1g}$	d–d + CT	26.84	$\Delta g_{xx} = 0.041$
$^{IV}B_{2g}$	$2b_{2g} \rightarrow 2b_{1g}$	CT + d–d	72.99	$\Delta g_{xx} = 0.001$
$^{I}B_{3g}$	$1b_{3g} \rightarrow 2b_{1g}$	d–d + CT	22.90	$\Delta g_{yy} = 0.028$
$^{II}B_{3g}$	$3b_{3g} \rightarrow 2b_{1g}$	CT + d–d	30.53	$\Delta g_{yy} = 0.013$
$^{IV}B_{3g}$	$3b_{2g} \rightarrow 2b_{1g}$	CT + d–d	64.38	$\Delta g_{yy} = 0.002$

[a] Dominating configuration. [b] Theoretical transition energy in kilokaisers.

TABLE III
CALCULATED EPR PARAMETERS FOR $Cu(HD)_2B_x$
(HYPERFINE SPLITTINGS $\times 10^4$ CM^{-1})

B	x	R[a]	$g\|$	$g\perp$	g_0[b]	$-(A\|- A\perp)$	A_N[c]
...	0	...	2.179	2.044	2.089	174.7	15.6
H_2O	1	2.60	2.186	2.046	2.093	175.5	15.2
H_2O	1	2.40	2.188	2.046	2.094	175.6	15.0
H_2O	2	2.60	2.193	2.047	2.096	176.0	14.7
H_2O	2	2.40	2.197	2.048	2.098	176.4	14.5
$(C_2H_5)_2NH$	1	2.50	2.181	2.045	2.090	174.8	15.5
$(C_2H_5)_2NH$	1	2.30	2.182	2.045	2.091	174.8	15.5
$(C_2H_5)_2NH$	2	2.50	2.183	2.045	2.092	174.2	15.4
$(C_2H_5)_2NH$	2	2.30	2.185	2.046	2.092	174.8	15.3

[a] Cu–B distance in ångströms. [b] $g_0 = \frac{1}{3}(g\| + 2g\perp)$. [c] Nitrogen isotropic hyperfine structure.

of the total charge in the 4s orbital, $q(4s)$, might be one of the reasons for the variation of the Fermi contact term $\varkappa$. The results obtained here indicate no considerable change in this charge. This point will be further discussed below.

4. About half of the net donation of charge from the axial ligands is transmitted through the $4p_z$ orbital into the lone pairs and π system of the chelate ring, while the rest stays in the $4p_z$ orbital.

5. The ret atomic population on the nitrogen ligands, $N(\sigma)$, is given in the last column. This quantity is, to the first order in the overlap integral, obtained as

$$N(\sigma) = 1 - \alpha^2 + S\alpha\sqrt{1 - \alpha^2} \qquad (6)$$

where S is the overlap integral $\langle 3d_{zy}|\sigma_N(b_{1g})\rangle$ (note that $1 - \alpha^2$ corresponds to the gross atomic population for orthogonalized atomic orbitals). From $N(\sigma)$ the spin density at the nitrogen nucleus is obtained, which gives the isotropic ligand hyperfine structure constant.

The detailed results of the configuration interaction treatment for the excited states have been published earlier.[9] Of interest here is the contribution from the different excited states to the epr parameters. Table II gives an example of this for $Cu(HD)_2$. The

with large charge-transfer character will give non-negligible contributions to the g values.

Table III gives the calculated epr parameters. Since the in-plane components were found to be almost equal (negligible deviation from C_{4v} symmetry), only their mean values $g_\perp$ and $A_\perp$ are reported. Also, as the hyperfine constants contain the Fermi contact interaction term $\varkappa$, which cannot be calculated in the present scheme, the table only gives the difference $A_\perp - A_{\||}$, which is independent of $\varkappa$. The values will be discussed and compared to the experimental results in the Discussion.

Results

$Cu(HD)_2$ in Organic Solvents.—The room-temperature recording of a 4×10^{-5} M benzene solution of $Cu(HD)_2$ is shown in Figure 1A. The solution giving the spectrum in Figure 1B in addition contained 10^{-1} M pyridine. With chloroform instead of benzene one gets very similar spectra. In addition to the hyperfine splitting due to the copper nucleus, all spectra have a superhyperfine structure. This consists of nine lines in the intensity ratios expected for equal coupling to four nitrogen nuclei. Hyperfine constants ($|A_0|$ and $|A_N|$) and g_0 values are given in Table IV.

TABLE IV
EXPERIMENTAL EPR PARAMETERS OF DOMINATING SPECIES OBTAINED WITH $Cu(HD)_2$
IN VARIOUS SOLVENT SYSTEMS (HYPERFINE SPLITTINGS $\times 10^4$ CM^{-1})

Solvent system	Low-temp spectra			Room-temp spectra		Nitrogen hfs		$\|A\||- \|A\perp\|$[b]	$\varkappa = (\|A_0\|/P) + \Delta g_0$
	$g\|$	$g\perp$	$\|A\||$	g_0	$\|A_0\|$	No. of nitrogens	$\|A_N\|$		
C_6H_6 $\}$[c] $CHCl_3$	...[a]	...[a]	...[a]	2.069	89	4	15.9	...	0.30
C_6H_6–0.1 M C_5H_5N $\}$[c] $CHCl_3$–0.1 M C_5H_5N	2.155	2.040	184	2.081	71	4	15.3	170	0.26
$CHCl_3$–$(C_2H_5)_2NH$[c]	2.163	2.052	182	2.086	68	...[a]	16.0	171	0.26
H_2O (pH ~6.5)	2.157	2.040	204	2.084	83	4	15.5	182	0.30
H_2O (pH ~10.6)	2.176	2.053	196	2.094	81	4	15.6	173	0.30
H_2O (pH ~11.7)	2.206	2.054	201	2.105	86	2	16.3	173	0.33
H_2O (pH ~14.0)	2.273	2.055	194	2.136	75	0	...	179	0.33
H_2O–CN^- (pH ~9.0)	2.172	2.040	177						

[a] These entries could not be measured due to low resolution. [b] As $|A_0| = (|A_{\||}| + 2|A_\perp|)/3$ we obtain $|A_{\||}| - |A_\perp|$ from $|A_{\||}| - |A_\perp| = 3(|A_{\||}| - |A_0|)/2$. [c] For calculated values see Table III.

symmetry assignments corresponding to D_{2h} have been kept, even though the actual symmetry is decreased to C_{2v} if one axial ligand is added. It should be noted from this table that not only pure ligand field states (d–d transitions) but also excited states

Unfortunately, no resolved spectrum could be obtained from frozen benzene or chloroform solutions of $Cu(HD)_2$. Rapid-freeze experiments and other inert solvents (isopentane, heptane, octane, and naphthalene) were tried but did not produce any considerable
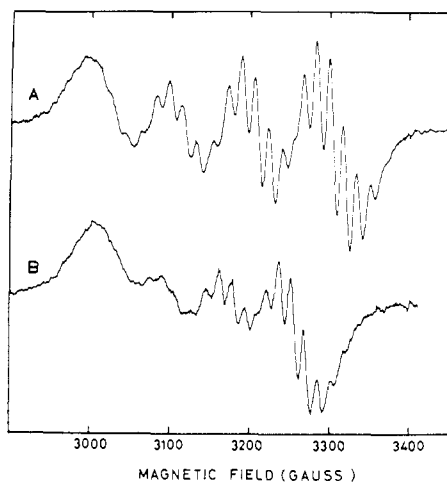
Figure 1.—Room-temperature epr spectrum of Cu(HD)$_2$ dissolved in benzene (A) and benzene containing 9.9×10^{-2} M pyridine (B). The copper concentration was 4×10^{-5} M. The modulation amplitude was 9 G, microwave power, 5 mW, microwave frequency, 9154 MHz, time constant, 3 sec, and sweep time, 0.5 hr.
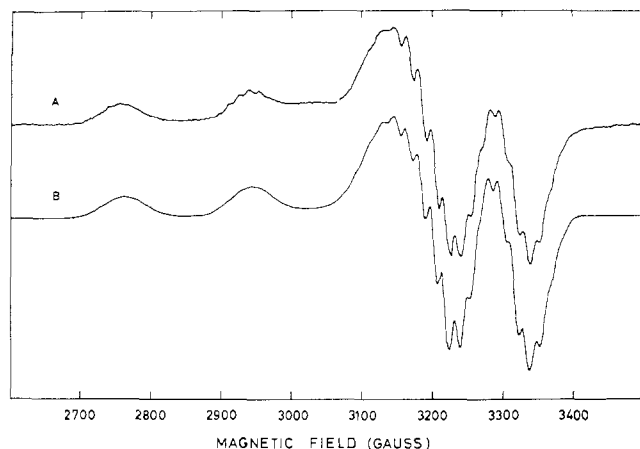

Figure 2.—(A) Epr spectrum recorded at 77°K of Cu(HD)$_2$ dissolved in chloroform containing 0.2 M pyridine. The microwave power was 5 mW, microwave frequency, 9151 MHz, modulation amplitude, 9 G, time constant, 0.3 sec, and sweep time, 4 min. (B) Simulated epr spectrum with the parameters of Cu(HD)$_2$ dissolved in chloroform containing 0.2 M pyridine, as given in Table IV. A line width of 16 G for the individual lines was used.

increase in resolution. Most likely, the Cu(HD)$_2$ molecules aggregate on freezing, which results in a dipolar broadening. However, addition of bulky axial ligands, like pyridine, makes this aggregation more difficult and results in resolved spectra.[19] This is illustrated in Figure 2, which gives the spectrum of the pyridine adduct in chloroform. With other solvents, like ethanol, one can get higher resolution but only with such solvents which are believed to form adducts.

The parameters of the spectra from the adducts with pyridine and diethylamine are listed in Table IV. The $g_{||}$ and $|A_{||}|$ values were calculated directly from the spectra, whereas $g_\perp$ values were obtained
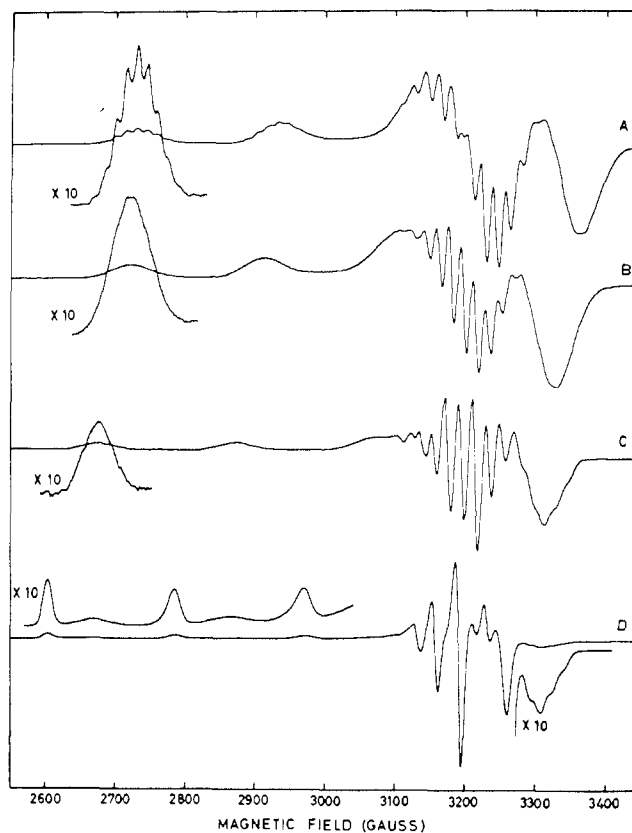

Figure 3.—Epr spectra recorded at 77°K of Cu(HD)$_2$ dissolved in H$_2$O of various pH values. The copper concentration was 1.0 $\times 10^{-3}$ M. pH values and recorder gain settings were (A) 6.5 and 2.5×10^4, (B) 10.5 and 4×10^4, (C) 11.6 and 5×10^4, and (D) $\sim$14 and 2.5×10^5, respectively. The microwave power was 5 mW, microwave frequency, 9152 MHz, modulation amplitude, 9 G, time constant, 0.3 sec, and sweep time, 4 min. For the magnified parts of the spectra the time constant was 1 sec and the sweep time was 8 min. All samples contained 1 M NaClO$_4$.

from comparisons with spectra simulated on an IBM 360-50 computer. A simulated curve is shown in Figure 2 together with the corresponding experimental one. Values of $|A_\perp|$ are not given, but good agreement with the experimental curves resulted if, for the simulations, the value of $|A_\perp|$ was calculated from the relation[20] $|A_\perp| = (3|A_0| - |A_{||}|)/2$. With pyridine, equal coupling to four nitrogens is again seen, but with diethylamine the resolution is too low to allow any conclusion about the number of nitrogens interacting.

Cu(HD)$_2$ in Aqueous Solutions.—Figures 3 and 4 show the low- and room-temperature spectra, respectively, of the species obtained in a titration to higher pH of Cu(HD)$_2$ dissolved in water. At neutral pH a coupling to four equivalent nitrogens is seen, particularly clearly resolved in the low-field peak in the low-temperature spectrum (Figure 3A) where the relative intensities are very close to those predicted (1:4:10: 16:19:16:10:4:1). At pH 10.5 (Figures 3B and 4B) a new species is formed which has somewhat less resolved lines but which still shows coupling to four equivalent nitrogens, as seen in the room-temperature

(19) A. MacCragh, C. B. Storm, and W. S. Koski, *J. Am. Chem. Soc.*, **87**, 1470 (1965).

(20) M. E. Foglio, *Nuovo Cimento*, **50** (10), 158 (1967).

spectrum. The species dominating at pH 11.6 (Figures 3C and 4C) has a spectrum with splitting only to two nitrogens. At even higher pH, above 14 (3 M NaOH, Figures 3D and 4D), the species that dominated at pH 11.6 still exists, but an entirely new spectrum now has appeared with narrow lines and no nitrogen hyperfine structure. The same spectrum is obtained from a solution of copper sulfate in 3 M NaOH. The resonance parameters of all species were calculated as described above and are presented in Table IV. The values reported here differ considerably from those given by Wiersema and Windle.[11]

With cyanide added, spectra could only be recorded of the frozen solutions, as the reaction proceeded too rapidly at room temperature. The spectra were fairly broad (the line at lowest field about 70 G) with no well-resolved nitrogen hyperfine splitting and were identical whether $K^{12}CN$ or $K^{13}CN$ was used. The epr parameters are found in Table IV.

In Table IV the anisotropic part of the experimental hyperfine coupling constants is given as $|A_{||}| - |A_{\perp}|$. This is calculated using the relation[20] $|A_0| = (|A_{||}| + 2|A_{\perp}|)/3$ and the observed values of $|A_0|$ and $|A_{||}|$. In the same table empirical values of the Fermi contact term $\varkappa$ are presented as obtained according to

$$\varkappa = \frac{|A_0|}{P} + \Delta g_0 \qquad (7)$$

$|A_0|$ is the hyperfine splitting of the room-temperature spectra and the relation is valid provided $A_{||}$ and $A_{\perp}$ have the same sign, which seems very probable (see below).

Discussion

Structure of Complexes in Organic Solvents.—One

of the aims of this study is to provide epr data of Cu-(HD)$_2$ as undisturbed as possible by the solvent in order to make comparisons with the theoretical results more correct. The fact that the solubilities in benzene and chloroform are higher than in solvents like carbon tetrachloride does indicate that some interaction exists in the former two solvents, in benzene probably through π bonding to Cu and in chloroform through hydrogen bonding to N or O in the dimethylglyoxime. However, we believe that this interaction is weak, particularly as both solvents give very similar spectra, and that comparisons with theoretical results are justified. As described in the Results, they are limited to the isotropic couplings.

The equal coupling to four dioxime nitrogens in the pyridine adduct shows that the planar structure is essentially intact. As the unpaired electron still is in a d_{xy} orbital, no appreciable coupling to an axial nitrogen is expected. Thus, from epr data we cannot say whether one or two pyridine molecules are bound, but other investigations[5,6,12] show that one molecule coordinates. This might cause a displacement of the metal ion out from the plane through the four nitrogens, as in the crystal state.[8]

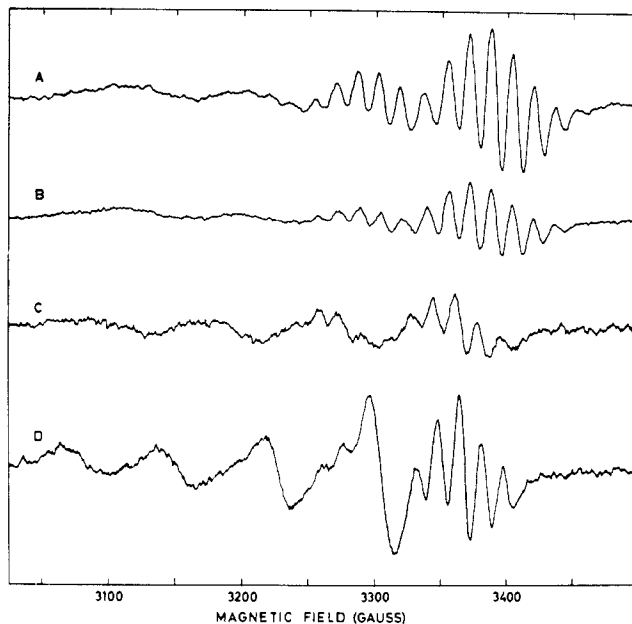### Structure of Complexes Formed in Aqueous Solutions.

Figure 4.—Room-temperature epr spectra of Cu(HD)$_2$ dissolved in H$_2$O of various pH values. The copper concentration was 1.2×10^{-3} M. The pH values and recorder gain settings were (A) 6.9 and 2.5×10^5, (B) 10.5 and 2.5×10^5, (C) 11.6 and 5×10^5, and (D) $\sim$14 and 5×10^5, respectively. The microwave power was 5 mW, microwave frequency, 9525 MHz, modulation amplitude, 9 G, time constant, 0.3 sec, and sweep time, 2 min. All samples contained 1 M NaClO$_4$.

—The interaction of Cu(HD)$_2$ with water is quite complicated, as water molecules cannot only bind to Cu but also form hydrogen bonds to the ligand molecules. It has been suggested[5] that two water molecules form axial bonds to the metal, and proton relaxation rate measurements at 60 MHz (K.-E. Falk, E. Ivanova, unpublished work) are consistent with this geometry. The rate obtained with Cu(HD)$_2$ was found to be about half of that with Cu(H$_2$O)$_6{}^{2+}$.

In the species appearing when the pH is raised to about 10.5, the Cu is still coordinated to four nitrogens (Figure 4B). The structure is likely to be Cu(HD)$_2$-(H$_2$O)(OH)$^-$. The g values increase relative to neutral pH (Table IV) which is expected when stronger electron-donating ligands are added.

The pH was increased further in an attempt to see the second water being replaced by an hydroxyl ion. However, at higher pH only two nitrogens coordinate with copper. Thus, the planar structure with four nitrogens is broken and the structure probably is CuD(OH)$_y$(H$_2$O)$_x{}^{y-}$ with $x + y \le 4$. Again the g values increase which can be related to the replacement of the in-plane nitrogens with oxygens.

Above pH 14, the spectrum obtained is that of copper sulfate dissolved in NaOH which shows that the chelate structure is completely disrupted. Thus, we believe that this spectrum represents the cuprate ion Cu(OH)$_4{}^{2-}$.

When cyanide is added to Cu(HD)$_2$ in water, pH 9, a new complex is formed. There is no well-resolved nitrogen splitting to tell something about the structure, but nevertheless we think that cyanide is an axial

ligand. With cyanide in the plane we would have expected a difference between the ^{12}C and ^{13}C cyanides due to coupling to the carbon nucleus.

Comparisons between Theoretical and Experimental Epr Parameters. g Values. The overall agreement between the calculated (Table III) and observed (Table IV) values is satisfying, in particular as they are calculated without the use of experimental optical energies of the complexes. In the following, special attention will be paid to the shifts occurring on adduct formation.

As expected, there is an increase in the theoretical g values, particularly in $g_{||}$, as axial ligands are added. This is partly due to the decreased covalency discussed above and partly to a red shift in the transitions of type A_g and B_{2g}. The transitions of type B_{3g} undergo a blue shift which, however, is too small to affect this general trend.

Experimentally, the g values also become larger on adduct formation. In water solution the isotropic g value (g_0) is 2.084, 0.015 higher than the value obtained from benzene solution. Theoretically, a smaller shift results (0.004–0.009). The reason for this very likely is that our model does not take into account any interactions between solvent molecules and the dimethylglyoxime ligands. These effects will draw electrons away from the metal, thereby decreasing the covalency and causing a shift in the g values in the same direction as electron-donating ligands along the z axis. However, of the four cases of water addition studied theoretically the best agreement with the experimental results is obtained with the previously suggested[9] structure for the water adduct having two water molecules coordinated with the Cu–O distance about 2.4 Å.

The experimental shift of g_0 for the complex Cu(HD)$_2$B$_x$ (B = (C$_2$H$_5$)$_2$NH or C$_5$H$_5$N) is of the same order as for Cu(HD)$_2$(H$_2$O)$_2$. Theoretically only a very small shift is obtained. This might be due to the assumption that the Cu(HD)$_2$ part of the complex remains planar. It is known that five-coordinate complexes Cu(HD)$_2$B are formed if B is an amine or pyridine.[5,6] It is therefore very probable that the copper atom moves out of the plane as the fifth ligand is added. This would decrease the in-plane binding and thereby also the covalency. The result would be a positive shift of the g values. As will be seen below this model might also explain the low values of the Fermi contact term $\varkappa$ obtained for the amine and pyridine complexes.

A Values.—*A priori* calculations of the hyperfine structure constants cannot be done, since the Fermi contact term $\varkappa$, which depends on the spin polarization of the metal s orbitals, is not obtained in the present model. However, the anisotropic part of the coupling can be obtained both in the present theory and experimentally. The predicted values of $A_\perp - A_{||}$ agree very satisfactorily with the value of $|A_{||}| - |A_\perp|$ determined from the spectra. This is also a very strong indication that the observed hyperfine constants both are of the same sign. An assumption of opposite

signs leads to much less agreement. Theoretically there is an increase in the hyperfine anisotropy on adduct formation but the shifts are quite small and will not be further discussed.

The experimentally determined contact hyperfine interaction is given in Table IV. The complex itself and the water adduct both have $\varkappa$ equals 0.30 whereas the adducts with pyridine and amine both have a value of 0.26. A comparison with the results of Wiersema and Windle[11] shows that their value of $\varkappa$ is much lower. Our values illustrate that $\varkappa$ is neither a constant nor simply proportional[17] to α^2. In complexes of sufficiently low symmetry a direct mixing[18] of 4s orbital into the orbital of the unpaired electron can affect $\varkappa$. This mechanism has been used by Garito and Wayland[4] to explain a decrease in $\varkappa$ of about 0.03 on formation of the pyridine adduct to copper *t*-butylacetoacetate. However, in our case the symmetry is so high that such mixing is not allowed and it would seem that a different mechanism is operative. It has been suggested[3,21] that the variation of the contact term in copper complexes is due to changes in a vibronic interaction placing part of the unpaired electron into the 4s orbital. This mechanism does not readily explain why only the pyridine and the amine adducts and not the water adduct show shifts in $\varkappa$ and therefore we favor still another explanation. An increase in the charge density in the 4s orbital should lead to a decrease in $\varkappa$ through spin polarization of this orbital.[18] From Table I it would appear that there is no appreciable shift in this density on adduct formation which would be consistent only with the results for the water adduct and not for the other adducts. However, it is likely that the square-pyramidal configuration suggested above for the amine and pyridine adducts would increase the axial bonding and thereby also increase the 4s density through sp^z hybridization of the acceptor orbital. This is consistent with the molecular orbital scheme for Cu(HD)$_2$, which places the empty orbitals 3b$_{1u}$ (with 4p$_z$ character) and 4a$_g$ (predominantly 4s) close together at low energies (*cf.* Table II in ref 9).

The isotropic nitrogen hyperfine structure constant A_N has been calculated by means of the formula of Maki and McGarvey[16]

$$A_N = -(4\pi/9)\gamma\beta_0\beta_N N(\sigma)\delta(\bar{r}) \tag{8}$$

The good agreement between calculated and observed values indicates that the assumed sp^2 hybridization of the nitrogen lone pair is correct. It is also a good check on the calculated values of α^2.

(21) T. Chiang, *J. Chem. Phys.*, **48**, 1814 (1968).