# Electron Paramagnetic Resonance Study of Copper(II)

# Dimethylglyoxime. II. Determination of Adduct

# Formation Constants

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The adduct formation constants for copper(II) dimethylglyoxime
with pyridine in benzene and chloroform are determined using an
EPR method. The distribution of different complexes formed in
aqueous solution at different pH is determined by integrating the
EPR spectra.

In Part I[1] an investigation of the effect of axial ligands on the EPR spectra
of copper(II) dimethylglyoxime $(Cu(HD)_2)$ was presented. It was shown
that adduct formation causes significant shifts in the EPR parameters of the
metal ion. The complexes present in solution have different EPR spectra and
it is therefore possible to draw some conclusions from the data about the
stoichiometry of the complexes and calculate the stability constants for the
adduct formation in organic solvents, and the distribution of hydroxo com-
plexes formed in aqueous solutions at different pH. Although some determina-
tions of adduct formation constants have already been made,[2,3] we found it
worth while to compare earlier results with another, independent, method.
So far there is little experience in using the EPR method for determination
of stability constants and the stoichiometry of metal complexes in solution
$(Ti(III) - EDTA,[4]$ $Mo(V) - Cl^-,$ $Br^-,$ $I^-,[5]$ $Cu(II) - acetylacetone,$ $TTA -$
pyridine [6]).

## EXPERIMENTAL

*Chemicals.* The chemicals used and the preparation procedure are as described in
Part I.[1]

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*Measurement of pH.* The pH values were measured with a Beckman glass electrode Type 202B and a radiometer calomel electrode using a digital voltmeter "Dynamco, model 02" equipped with an operational amplifier. The electrode system was standardized against a solution of 0.001 M NaOH + 0.999 M NaClO$_4$. ($-\log$ [OH$^-$] = $-3.000$ and $-\log$ [H$^+$] = 10.77 from p$K_w$ = 13.77.) From the measurements of the potential $E$ of a standard and investigated solutions the pH-values were calculated according to the formula: pH = $(E - E_{st})/59.16 + 10.77$.

*EPR measurements.* In addition to what is described in Part I [1] a time averaging computer (C-1024) was utilized in some of the experiments.

## DETERMINATIONS OF STABILITY CONSTANTS

*Symbols.* In order to make a short concise description a list of symbols used in the text is first presented.
$a$    concentration of Cu(HD)$_2$
$b$    concentration of the adduct forming ligand L
$c$    concentration of Cu(HD)$_2$L
$C$   total concentration of copper
$B$   total concentration of adduct forming ligand L
$K = c/ab$ stability constant to be determined
$I$    EPR signal height at a certain field
$E_a$   EPR signal height of Cu(HD)$_2$ per mol of Cu(HD)$_2$
$E_c$   EPR signal height of Cu(HD)$_2$L per mol of Cu(HD)$_2$L
Comment: The EPR signal height is measured as the first derivative of the intensity with respect to the magnetic field.

*Calculations.* If one assumes that only two species are present in the solution, the total EPR signal height is given from the relation

$$I_{calc} = aE_a + cE_c$$

By eliminating $a$ and $c$, using the relations $c = Kab$, $C = a + c$, and $B = b + c$ one arrives at the following expression for the calculated EPR intensity

$$I_{calc} = E_a(\sqrt{q^2 + C/K} - q) + E_c(C - \sqrt{q^2 + C/K} + q)$$

where $q = (B - C + 1/K)/2$.

The values of $I_{calc}$ were computed for the different concentrations used and the function $W = (I_{calc} - I_{exp})^2$ was minimized by varying the parameters $E_a$, $E_c$, and $K$ according to a standard program in the IBM 360/65 library.

## RESULTS AND DISCUSSION

*Organic solvents.* The spectra obtained from Cu(HD)$_2$ in a benzene pyridine mixture and in a chloroform pyridine mixture are given in Fig. 1 of Part I.[1] The transition from the planar Cu(HD)$_2$ to the pyridine adduct is demonstrated in Fig. 1 of the present paper. In this figure is shown the high field part of the room temperature spectra where the concentration of pyridine is varied. (The concentration figures are given in the figure caption.) The intermediate are mixtures of the two extremes. This was proved by the fact that it was possible to synthesize the intermediate spectra by addition of proper amounts
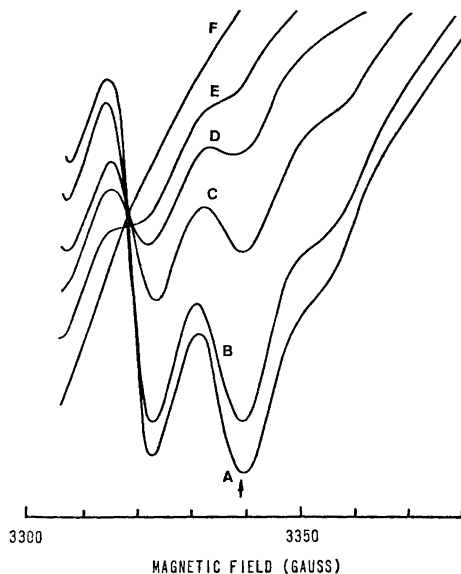
Fig. 1. Details of EPR spectra of $5.13 \times 10^{-5}$ M copper(II) − dimethyl-glyoxime in benzene. Curve A contains no pyridine, curve B $3.46 \times 10^{-5}$ M pyridine, curve C $4.8 \times 10^{-4}$ M pyridine, curve D $9.64 \times 10^{-4}$ M pyridine, curve E $1.98 \times 10^{-3}$ M pyridine and curve F $9.64 \times 10^{-3}$ M pyridine. The microwave frequency was 9153 MHz, the microwave power 5 mW and the modulation amplitude 8 gauss. The whole spectra have been published in Part I [1] (Fig. 1).

MAGNETIC FIELD (GAUSS)

of the spectra from $Cu(HD)_2$ in benzene (Fig. 1A) and in benzene containing $10^{-2}$ M pyridine (Fig. 1F). *The exchange rate of the pyridine is thus slow enough to give a simple additivity of the spectra.* From the difference in the positions of the highest lines the exchange frequency between the free and bound pyridine is estimated to be slower than $10^8$ Hz. The stability constants for the pyridine adducts in benzene and chloroform calculated according to the described procedure are given in Table 1. Similar measurements of the adduct formation with ethanol instead of pyridine gave only low values of $K$ (in the order of $10 - 20$).

The values of $K$ obtained by EPR are of the same order of magnitude as those obtained by measurements of distribution ratios [2,3] and UV-VIS spectra.[3] However, the values for benzene are lower than for chloroform contrary to previous measurements,[2,3] and we can at present offer no good explanation for this contradiction, which should be further investigated.

The amplitudes of the signal that are used in the computation of the adduct formation constants are taken at the magnetic field where there is a maximum change in signal height. This is indicated in Fig. 1.
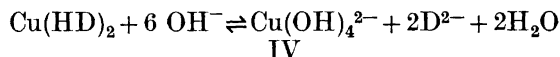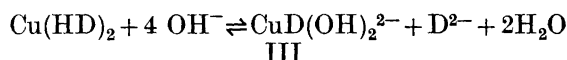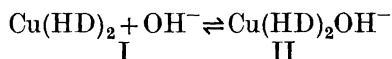
Table 1.

| System | $K$ (M$^{-1}$) |
|---|---|
| $C_6H_6$, $C_5H_5N$ | $1790 \pm 100$ |
| $CHCl_3$, $C_5H_5N$ | $2970 \pm 150$ |

*Aqueous solutions.* The possible structures of the complexes formed in water solutions are discussed in Part I.[1] The number of dioxime nitrogens given in this discussion can be seen from the hyperfine splittings. In the present paper is given a qualitative estimation of the relative amounts of the complexes at different pH values. The concentration of copper is calculated by integrating only the low field line of the EPR spectrum [7] and the results
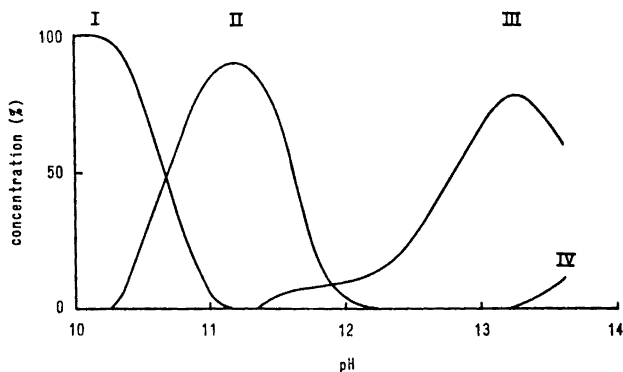


*Fig. 2.* Relative amounts of various complexes I−III (see text) of copper dimethyl-glyoxime and $Cu(OH)_4{}^{2-}$ (IV) in water as a function of pH obtained from an integration of the low field lines of the EPR spectra. The concentrations are normalized to 100 at pH 10. The shoulder at pH 11.7 may indicate small amounts of $Cu(HD)_2(OH)_2{}^{2-}$. Due to the precipitation of CuO the aqueous solubility of copper(II) is low around pH 12.

are presented in Fig. 2. The stepwise decrease in the number of copper-nitrogen bonds can be explained by the following reactions.

$$Cu(HD)_2 + OH^- \rightleftharpoons Cu(HD)_2OH^-$$
$$\phantom{Cu(HD)_2 + OH^-}\ \ \text{I}\phantom{+ OH^- \rightleftharpoons}\ \ \text{II}$$

$$Cu(HD)_2 + 4\ OH^- \rightleftharpoons CuD(OH)_2{}^{2-} + D^{2-} + 2H_2O$$
$$\text{III}$$

$$Cu(HD)_2 + 6\ OH^- \rightleftharpoons Cu(OH)_4{}^{2-} + 2D^{2-} + 2H_2O$$
$$\text{IV}$$

For the first reaction a formation constant $\log K = 13.77 - 10.67 = 3.1$ can be estimated. This value agrees with an earlier determination by Dyrssen and Hennichs,[2] who obtained $\log K$ from a distribution study. The constants for the reactions leading to the complexes III and IV can only be very roughly estimated as $\log K = 1.3$ and $\log K = -3.8$.

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