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## PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY AT TULANE UNIVERSITY]

# Metallated Dye Complexes. IV. The Stereochemistry of Copper(II)–Dye Complexes

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An investigation of the hydroxide, quinoline and 8-hydroxyquinoline complex compounds of copper(II)-*o,o'*-dihydroxyazobenzene, -2-carboxyphenyl-azo-β-naphthylamine and -2-carboxyphenyl-azo-β-naphthol complexes has been made by means of stability, spectrophotometric and *p*H studies. It has been shown that 1:1 addition complexes form with the above, and that when 8-hydroxyquinoline is added a complex is formed in which the copper(II) ion exhibits a coördination number of at least five.

## Introduction

Although most complexes of the copper(II) ion are four coördinated, a coördination number greater than four also has been reported.[2–5]

Azo dyes substituted in the *ortho* positions can act as tridentate coördinating groups, effecting coördination through the two substituted groups and through the electron-rich nitrogen–nitrogen double bond of the azo group. Thus, when a dye molecule combines with the copper(II) ion three of the coördinating positions of the metal ion are occupied.

The copper–dye complex can then add another group to exhibit its characteristic coördination number of four. Under conditions where the electronic configuration is favorable, it should be possible to have the 8-hydroxyquinoline ion coördinate in two positions.

This work was undertaken as a direct result of the work of Wilson[6] in which he showed the possibility of existence of a coördination number of five for $[Cu(OH)_5]^{-3}$.

Stability studies, calculations of $\Delta H^0$, $\Delta F^0$ and $\Delta S^0$, spectrophotometric studies and *p*H studies were undertaken.

## Experimental

**A. Reagents.**—The dyes were prepared according to methods outlined in the literature and their melting points were in very good agreement with these reported.[6] Synthetic quinoline was purchased from Matheson, Coleman and Bell. The 8-hydroxyquinoline and all inorganic chemicals were C.P. grade J. T. Baker Analyzed. Lithium perchlorate was used as a supporting electrolyte and was prepared by neutralizing lithium carbonate with perchloric acid. Triply distilled mercury and electrolytic sheet copper of high purity were used in preparing the copper amalgam electrodes for the concentration cells.

**B. Apparatus.**—1. **Concentration Cells.**—To calculate the instability constants, the concentration of copper(II) ion in equilibrium with each complex was determined by concentration cell e.m.f. measurements. A copper(II) nitrate solution of known concentration was placed in one half-cell and a solution of the complex in the other. The half-cells were connected by means of a saturated agar–potassium chloride salt bridge and the resultant voltage was measured with a Leeds and Northrup Type K2 potentiometer, connected to a Rubicon box galvanometer having a sensitivity of one microvolt per millimeter. All measurements utilized for the standard cell, a Weston cell, Model 4 Unsaturated, Certified, which had been calibrated by the Bureau of Standards.

2. **Electrodes.**—For the reversible copper electrode, a pool of copper amalgam was used, and electrical contact was established by means of a platinum wire sealed into a glass tube. The copper amalgam was 2% copper by weight and was prepared by a slight modification of the method of Dawson.[7] The amalgam was tested for uniformity by preparing two half-cells having the same concentration of copper(II) nitrate. In a number of measurements the voltage thus developed did not exceed 0.0005 volt, which is too small to affect the accuracy of the *pK* values. In testing for reversibility the cell made up of half-cells containing different, but known, concentrations of copper(II) nitrate was momentarily shorted, and the time for equi-

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[1] Abstracted in part from a dissertation submitted by James R. Oliver to Tulane University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] J. Bjerrum and E. J. Nielson, *Acta Chem. Scand.*, **2**, 297 (1948).

[3] J. G. Breckenridge, *Can. J. Research*, **26**, 11 (1948).

[4] H. B. Jonassen, R. B. LeBlanc and R. B. Rogan, THIS JOURNAL, **72**, 4968 (1950).

[5] S. Kirschner, *ibid.*, **78**, 2372 (1956).

[6] H. B. Jonassen, M. Cook and J. S. Wilson, *ibid.*, **73**, 4683 (1951).

[7] J. E. Dawson and C. K. N. Nair, *Soil Sci.*, **69**, 239 (1950).

librium to be re-established was measured. In no case was more than 30 seconds required.

Because this amalgam is easily oxidized, the solutions were saturated with oxygen-free nitrogen. The purified nitrogen was also bubbled through the solutions in the half-cells while the e.m.f. measurements were being made, halting it only during the instant of measurements.

3. **Spectrophotometer.**—Spectrophotometric measurements were made with a Beckman spectrophotometer, model B, using matched Corex cells.

4. ***p*H Meter.**—All *p*H measurements were made using a Beckman *p*H meter, model G. Prior to each set of measurements the meter was standardized against standard Beckman buffers of *p*H, 7 and 10.

C. **Preparations of Solutions.**—1. **Solvent.**—The stability studies were performed in 50% aqueous solutions of ethanol. Constant ionic strength was maintained by making the solvent 0.5 *M* in $LiClO_4$. Dissolved oxygen was displaced from the solvent by saturating it for two hours with deoxygenated nitrogen.

2. **Dyes.**—Stock solutions of the potassium salts of *o,o'*-dihydroxyazobenzene and 2-carboxyphenyl-azo-β-naphthylamine dyes 0.005 *M* were prepared. Since the 2-carboxyphenyl-azo-β-naphthol dye is much less soluble, 0.0005 *M* solution had to be prepared.

3. **Other Reagents.**—A primary stock solution of copper(II) nitrate was prepared and standardized electrolytically; this was diluted as needed.

The quinoline and 8-hydroxyquinoline were used as obtained and 0.100 and 0.001 *M* stock solutions were prepared by weighing.

4. **Complexes.**—In preparing solutions of the complexes with *o,o'*-dihydroxyazobenzene and 2-carboxyphenyl-azo-β-naphthylamine, the concentration of copper(II) was $4.0 \times 10^{-5}$ *M* in all cases. Excess dye was present in the cells which contained dye concentrations of $4.0 \times 10^{-4}$, $6.0 \times 10^{-4}$, $8.0 \times 10^{-4}$ and $10 \times 10^{-4}$ *M*. For the 2-carboxyphenyl-azo-β-naphthol, however, due to its limited solubility, the concentrations of all components except the hydroxide ion were one-tenth of the values given for the other two dyes. The concentrations of quinoline and 8-hydroxyquinoline were the same as the dye concentrations.

D. **Stability Studies.** 1. **Determination of *pK* values.**—For the purpose of measuring the concentration of Cu(II) ions in equilibrium with the complex, a series of cells of the type

$$\begin{array}{ll|l} \text{Cu; Hg; } Cu(NO_3)_2 & M_1 & Cu(NO_3)_2 \quad 0.001\ M; \quad \text{Hg; Cu} \\ K_2 \text{ dye} & M_2 & \\ X & M_3 & \\ LiClO_4 & 0.5M & \quad LiClO_4 \quad 0.5\ M \end{array}$$

were prepared where X was either 0.00001 *M* hydroxide ion, or quinoline or 8-hydroxyquinoline with a concentration equal to that of the dye. When the dyes used were *o,o'*-dihydroxyazobenzene and 2-carboxyphenylazo-β-naphthylamine, the initial value of $M_1$ was $4 \times 10^{-5}$, and $M_2$ and $M_3$ were successively $4 \times 10^{-4}$, $6 \times 10^{-4}$, $8 \times 10^{-4}$ and $10 \times 10^{-4}$ in each of the four cells prepared. Due to the low solubility of 2-carboxyphenyl-azo-β-naphthol, the values of $M_1$, $M_2$ and $M_3$ were one-tenth of the values mentioned above, except when X was the hydroxide ion. For each variation in the identity of X this series of four cells was repeated for temperatures of 5, 15, 25 and 35°.

From the voltage developed in the above cells the concentrations of copper(II) ions remaining after complexing were calculated from the equation

$$E = \frac{RT}{nF} \ln \frac{C_2}{C}$$

where *E* is the electromotive force developed by the cell, *R* is the gas constant in joules, *T* is the absolute temperature, *n* is the electron change in the oxidation reaction, *F* is the number of coulombs per faraday, $C_2$ the known, and *C* the unknown concentrations of the metal ion.

The equilibrium constants were calculated for the reaction

$$[Cu(II) - \text{dye} - X] \rightleftharpoons Cu^{++} + \text{dye}^{=} + X$$

Where X = OH, quinoline, hydroxyquinoline, the equilibrium constant is given by the expression

$$pK = -\log \frac{[Cu^{++}][Dye^{=}][X]}{[Cu(II) - \text{dye} - X]}$$

Table I gives the *pK* values for each complex at each of the four temperatures investigated.

TABLE I

THERMODYNAMIC VALUES FOR [Cu(II)-DYE-X] COMPLEXES[a]

| | Temp., °C. X | Temperature, °C. 5 | 15 | 25 | 35 |
|---|---|---|---|---|---|
| | | Dye = *o,o*-dihydroxyazobenzene | | | |
| | OH | 24.29 | 23.17 | 22.34 | 21.40 |
| *pK* | qn | 24.58 | 23.45 | 22.52 | 21.54 |
| | hq | 25.65 | 24.51 | 23.51 | 22.45 |
| | OH | 30.90 | 30.65 | 30.44 | 30.17 |
| $\Delta F^0$ | qn | 31.29 | 30.90 | 30.70 | 30.34 |
| | hq | 32.65 | 32.29 | 32.04 | 31.63 |
| | OH | 0.023 | 0.023 | 0.023 | 0.023 |
| $\Delta S^0$ | qn | .031 | .031 | .031 | .031 |
| | hq | .033 | .033 | .033 | .033 |
| | OH | 37.37 | | | |
| $\Delta H^0$ | qn | 39.85 | | | |
| | hq | 41.76 | | | |
| | | Dye = 2-carboxyphenyl-azo-β-naphthylamine | | | |
| | OH | 20.22 | 19.64 | 19.05 | 18.55 |
| *pK* | qn | 20.61 | 19.93 | 19.21 | 18.64 |
| | hq | 21.68 | 20.91 | 20.22 | 19.69 |
| | OH | 25.74 | 25.89 | 25.97 | 26.13 |
| $\Delta F^0$ | qn | 26.24 | 26.27 | 26.19 | 26.25 |
| | hq | 27.59 | 27.57 | 27.57 | 27.74 |
| | OH | −0.012 | −0.013 | −0.013 | −0.013 |
| $\Delta S^0$ | qn | .000 | .000 | .000 | .000 |
| | hq | − .002 | − .002 | − .002 | − .002 |
| | OH | 22.12 | | | |
| $\Delta H^0$ | qn | 26.12 | | | |
| | hq | 27.08 | | | |
| | | Dye = 2-carboxyphenyl-azo-β-naphthol | | | |
| | OH | 17.30 | 16.91 | 16.45 | 16.00 |
| *pK* | qn | 17.61 | 17.08 | 16.66 | 16.08 |
| | hq | 18.68 | 18.13 | 17.67 | 17.00 |
| | OH | 22.02 | 22.29 | 22.42 | 22.55 |
| $\Delta F^0$ | qn | 22.42 | 22.52 | 22.71 | 22.66 |
| | hq | 23.78 | 23.91 | 24.08 | 23.96 |
| | OH | −0.024 | −0.024 | −0.023 | −0.023 |
| $\Delta S^0$ | qn | − .017 | − .017 | − .017 | − .016 |
| | hq | − .016 | − .016 | − .016 | − .015 |
| | OH | 15.44 | | | |
| $\Delta H^0$ | qn | 17.73 | | | |
| | hq | 19.45 | | | |

[a] OH = hydroxide ion; qn = quinoline; hq = 8-hydroxyquinoline.

2. **Thermodynamical Functions.**—Approximate functions, $\Delta H^0$, $\Delta F^0$ and $\Delta S^0$ were calculated for the complexes.

The *pK* values are plotted against the reciprocal of the absolute temperature for the hydroxy, quinoline and 8-hydroxyquinoline complexes of each of the three dyes in Fig. 1. Table I gives the $\Delta F^0$ and approximate $\Delta H$ and $\Delta S$ values for each complex.

E. **Spectrophotometric Studies.**—In these studies a slight modification of the method of continuous variation as developed by Vosburgh and Cooper[8] was used. The copper(II)-dye complex was used as one of the components and the X group as the other. The results of the continuous variation studies for the *o,o'*-dihydroxyazo complexes are plotted in Fig. 2. Similar results were obtained also for the other two dyes.

F. ***p*H Studies.**—A plot of *p*H *vs.* ml. of acid added in lowering the *p*H of a solution of the complex from an initial

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(8) W. C. Vosburgh and C. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

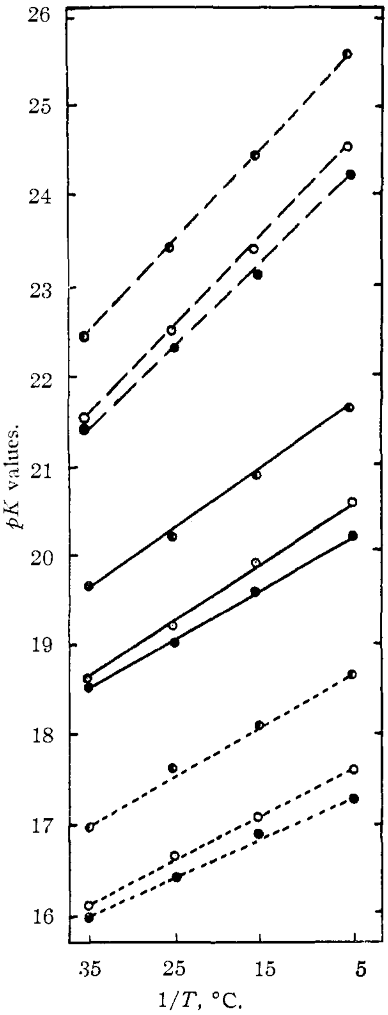

Fig. 1.—A plot of $pK$ values *vs.* $1/T$ for the Cu(II)-DYE-X complexes: — — —, dye = *o,o'*-dihydroxyazobenzene; ————, dye = 2-carboxyphenyl-azo-β-naphthylamine; - - - - - - - - -, dye = 2-carboxyphenyl-azo-β-naphthol; ◐, X = 8-hydroxyquinoline; ○, x = quinoline; ●, X = hydroxide ion.

$p$H of 10.00 showed that for all dyes studied, an abrupt change occurred at $p$H 7.2 to 7.7. In the case of the *o,o'*-dihydroxyazobenzene this change was accompanied by precipitation of the solid complex. This precipitation did not occur with the 2-carboxyphenyl-azo-β-naphthylamine, and no comparison was made with 2-carboxyphenyl-azo-β-naphthol because of its low solubility and correspondingly low concentration. Decomposition of the complex and precipitation of the acid form of the dye occurred at about $p$H 4.

## Discussion

**A. Stability Studies.**—The $pK$ values of the various complexes reveal that the stability decreases from *o,o'*-dihydroxyazobenzene to 2-carboxyphenyl-azo-β-naphthylamine to 2-carboxyphenyl-azo-β-naphthol. This order is in line with the work of Basolo and Murmann[9] in which they demonstrated that in the absence of steric effects the hydrogen ion affinity of ligands and their tendency toward complex formation are directly related. Any steric effect would be essentially constant in these dyes, since their structures are so similar.

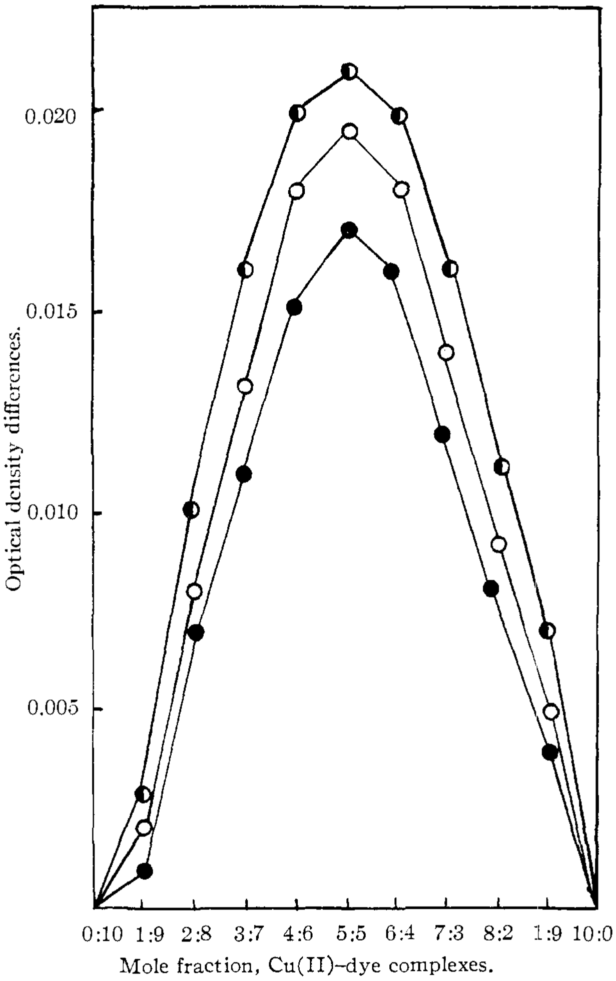

Fig. 2.—Continuous variation study of the *o,o'*-dihydroxyazobenzene–Cu(II) complex *vs.*: ◐, 8-hydroxyquinoline at 400 mμ; ○, quinoline at 400 mμ; ●, 8-hydroxyquinoline at 500 mμ.

However, in all cases a difference of approximately 1.0 $pK$ unit is observed in going from the quinoline to the corresponding complex with 8-hydroxyquinoline as opposed to the small difference between the hydroxy and quinoline complexes. This may be due to chelation for 8-hydroxyquinoline which would result in the formation of a pentacoördinated complex of the copper(II) ion.

A coördination number of four would require that one of the bonds by which the dye molecule is attached to the copper atom be broken. To break the linkage between the azo group and the copper(II) ion would require the changing from two chelate five-membered rings to one extremely large one. Haendler and Smith[10] have shown that for a coördinated azo dye, a peak in the absorption of visible light in the 4700–5300 Å. region occurs which is less than that obtained from the dye alone. Spectral investigation of these complexes indicated no absorption changes in this region had occurred, therefore no bond seems to have been broken.

The thermodynamic functions were studied to

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[9] F. Basolo and R. K. Murmann, THIS JOURNAL, **74**, 5243 (1952).

[10] H. M. Haendler and G. M. Smith, *ibid.*, **63**, 1371 (1941).

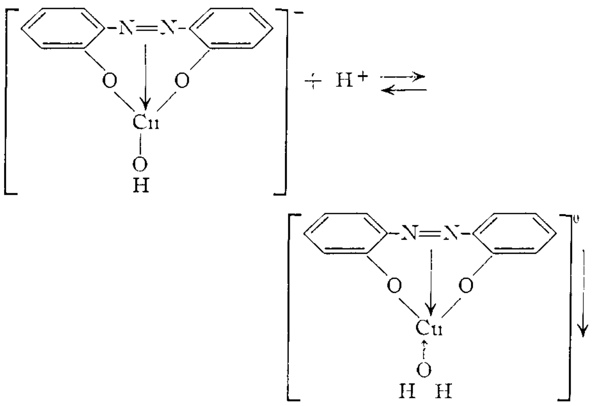
investigate some of the factors influencing the increased stability of the 8-hydroxyquinoline complexes. Bjerrum[11] stated that this increase is due to an increase in bond strength which arises from the formation of the chelate ring. However, Burkin[12] considers this increase in stability due to a statistical effect. A polyamine molecule with one end attached to the metal ion would have other coördinating positions of the molecule at a much closer proximity to the metal ion than those of other ligands in the solution.

However, in these complexes three of the coördinating positions are occupied by the dye molecule. If one end of the 8-hydroxyquinoline molecule were coördinated this would sterically inhibit the approach of any other molecule. The proximity of the coördinating groups would then only be a minor factor and the strength of the bond should then be the major factor. This increase in bond strength should be reflected in a definite increase in $\Delta H^0$ for the 8-hydroxyquinoline complex which is observed. The $\Delta S^0$ values, however, should be and are very nearly the same in all of the complexes studied.

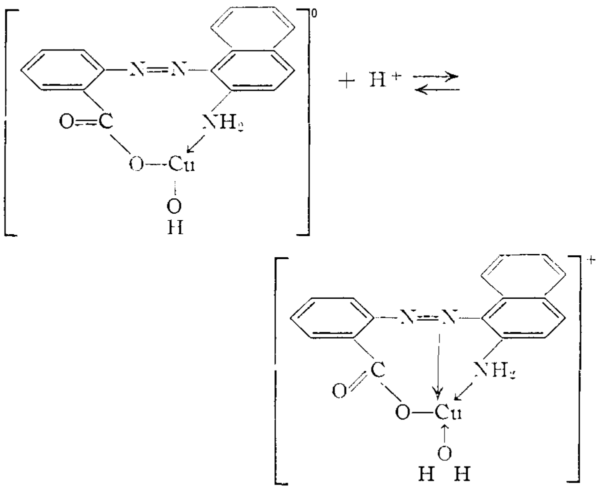
**B. Spectrophotometric Studies.**—Continuous variation studies gave a peak at a 1:1 ratio of quinoline to copper–dye complex indicating a 1:1 complex. A similar peak was noted at a 1:1 ratio of 8-hydroxyquinoline to copper–dye complex. However, this does not allow any deductions as to whether the 8-hydroxyquinoline coördinates through one position or two.

**C. *p*H Studies.**—An abrupt change in the titration curve was noted, in lowering the *p*H of the solution, when *p*H values of 7.7 to 7.2 were reached. This change seems to be due to the transformation from the hydroxy to the water complex and it becomes necessary therefore to maintain the solutions under study at a *p*H of 9.

It also was noted that for the complex of *o,o'*-dihydroxyazobenzene this decrease was accompanied by the precipitation of the solid complex as shown by the reaction given.



For 2-carboxyphenyl-azo-β-naphthylamine, however, a *p*H change did not decrease the solubility since a cationic complex is formed as indicated below



It was not possible to compare the complex involving 2-carboxyphenyl-azo-β-naphthol due to the difference in concentration used because of the low solubility of this dye and its complexes.

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(11) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, 1941.

(12) A. R. Burkin, *Quart. Revs.*, **5**, 1 (1951).