three complexes the maximum slope found in the *p*H regions of about 3 to 6 corresponded to a value of 3 for *z*.

Considering the species of the protonated amines existing in the *p*H regions of the study the following reactions are indicated:

For the Cu(II)–trien complexes with decreasing *p*H two reactions may occur

$$\begin{array}{l} \text{Complex}_1 + 3H^+ + 2e \longrightarrow Cu^0 + \text{trien } 4H^{4+} \\ \text{Complex}_2 + 3H^+ + 2e \longrightarrow Cu^0 + \text{trien } 3H^{3+} \end{array} \Big\uparrow$$

decreasing *p*H

This would fit the data if Complex$_1$ = [CuHtrien]$^{3+}$ and Complex$_2$ = [Cutrien]$^{2+}$

For the Cu(II)–tetren complex these three reactions fit the data.

$$\begin{array}{l} \text{Complex}_1 + 3H^+ + 2e \longrightarrow Cu^0 + \text{tetren } 5H^{5+} \\ \text{Complex}_2 + 3H^+ + 2e \longrightarrow Cu^0 + \text{tetren } 4H^{4+} \\ \text{Complex}_3 + 3H^+ + 2e \longrightarrow Cu^0 + \text{tetren } 3H^{3+} \end{array} \Big\uparrow$$

decreasing *p*H

if

Complex$_1$ = CuH$_2$tetren^{4+}
Complex$_2$ = CuHtetren^{3+}
Complex$_3$ = Cutetren^{2+}

For the Cu(II)–hexen system four reactions would explain the data

$$\begin{array}{l} \text{Complex}_1 + 3H^+ + 2e \longrightarrow Cu^0 + \text{hexen } 6H^{6+} \\ \text{Complex}_2 + 3H^+ + 2e \longrightarrow Cu^0 + \text{hexen } 5H^{5+} \\ \text{Complex}_3 + 3H^+ + 2e \longrightarrow Cu^0 + \text{hexen } 4H^{4+} \\ \text{Complex}_4 + 3H^+ + 2e \longrightarrow Cu^0 + \text{hexen } 3H^{3+} \end{array} \Big\uparrow$$

decreasing *p*H

If

Complex$_1$ = CuH$_3$hexen^{5+}
Complex$_2$ = CuH$_2$hexen^{4+}
Complex$_3$ = CuHhexen^{3+}
Complex$_4$ = Cuhexen^{2+}

This also seems to indicate that three of the copper to amine bonds in the copper(II) polyethyleneamine complexes are of about the same order of strength, far greater than the strength of the proton to amine bond. The other copper to amine bonds are of about the same order of strength as the proton to amine bond and an equilibrium is set up between them. At least three of the amine groups are bound to the copper(II) ion, the rest are protonated depending upon the *p*H of the medium.

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NEW ORLEANS, LA.

[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY AT TULANE UNIVERSITY]

Studies of Metallated Dye Complexes. III. Copper(II)-*o*-Azophenol Complexes

BY HANS B. JONASSEN AND ELWOOD J. GONZALES[1]

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Spectrophotometric and conductometric evidence indicates that the copper(II)-*o*-azophenol complex forms a copper(II) complex with propylene glycol in alkali in which the glycol and copper(II)-dye react in a 1:1 mole ratio. The complexes K[Cu-*o*-azophenol-OH] and Cu(II)-*o*-azophenol-H$_2$O were isolated from ethanolic solution.

Introduction

o-Azophenol, a dye containing hydroxy groups *ortho* to the azo group, readily forms a dye complex with transition metal ions in which the metal ion is bound to the two oxygen atoms and to the azo linkage as shown by investigations of Morgan and co-workers,[2-8] Drew and Landquist,[9] Wilson,[10] and Oliver.[11] In the present investigation dihydroxy compounds, propylene glycol (pngl) and *l*-2,3-butanediol, having free rotation of the hydroxy groups, are used to show their effect on the unsaturation of the copper(II) complex coördination sphere.

Experimental

A. **Reagents.**—Pngl (99+% pure), white label, Eastman Kodak Company was used without further purification.

A sample of dye prepared according to Willstätter and Benz[12] was kindly furnished by Mr. Gayle Strickland. The melting point was found to be 172–173° (lit. value 172°).

l-2,3-Butanediol, kindly furnished by Dr. R. E. Reeves, was used in polarimetric studies, $[\alpha]_D$ −12.8°.

Formamide, C.P. grade, Fisher Scientific Company, was distilled at 8 mm. pressure and the fraction boiling at 89–90° collected. The refractive index at 23° was 1.4468.

Molar solutions of pngl, *l*-2,3-butanediol, and the dye were prepared by direct weighing and dilution to volume with oxygen-free 95% ethanol prepared by bubbling nitrogen deoxygenated by alkaline pyrogallol into ethanol for at least one hour.

Aqueous molar solutions of copper(II) chloride were prepared by weighing directly reagent grade $CuCl_2 \cdot 2H_2O$, dried over partially dehydrated $CuSO_4 \cdot 5H_2O$, and diluting to volume.

A molar solution of copper(II) nitrate was prepared by dissolving reagent grade $Cu(NO_3)_2 \cdot 3H_2O$ in one liter of distilled water. A drop of C.P. concd. nitric acid was added to suppress hydrolysis. The copper(II) ion concentration was determined by electrolysis.

Aqueous molar potassium hydroxide solutions were prepared by weighing the appropriate quantities of potassium hydroxide. Standardization was against potassium acid phthalate using phenolphthalein as indicator.

B. **Spectrophotometric Studies.**—Absorption measurements in the visible spectral region were made with a Beckman Model B spectrophotometer using 1-cm. matched Corex cells. All solutions were diluted to 100 milliliters with oxygen-free 95% ethanol prepared by bubbling nitrogen deoxygenated by alkaline pyrogallol into ethanol for at least

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[1] Abstracted in part from a thesis submitted by Elwood J. Gonzales to the Tulane University in partial fulfillment of the requirements for the degree of Master of Science.

[2] G. T. Morgan and J. D. Main-Smith, *J. Chem. Soc.*, 704 (1921).

[3] G. T. Morgan and J. W. Porter, *ibid.*, 645 (1915).

[4] G. T. Morgan and E. D. Evans, *ibid.*, 1126 (1919).

[5] G. T. Morgan, *J. Soc. Dyers and Colourists*, **37**, 43 (1921).

[6] G. T. Morgan and J. D. Main-Smith, *J. Chem. Soc.*, 2866 (1922).

[7] G. T. Morgan, *ibid.*, 1731 (1924).

[8] G. T. Morgan and J. E. Moss, *J. Soc. Chem. Ind.*, 461T (1923).

[9] H. D. K. Drew and J. K. Landquist, *J. Chem. Soc.*, 292 (1938).

[10] J. S. Wilson, Doctoral Dissertation, Tulane University, 1952.

[11] J. Oliver, THIS JOURNAL, **79**, (1957).

[12] R. Willstätter and M. Benz, *Ber.*, **39**, 3492 (1906).

one hour. Absorbancy values were determined at the wave lengths noted in the figures at 25–26°.

C. Conductometric Studies.—An Heath oscilloscope and a signal generator were used as a null point indicator in connection with a Leeds and Northrup slide wire potentiometer and decade resistance box. The conductance cell used was a vertical dipping type with platinized platinum electrodes. All conductometric work was carried out at 30°, under nitrogen in a constant temperature bath. In all cases the volume of the solution at the start of the titration was 100 ml. and conductances were corrected for dilution effects.

D. Preparation of Complexes.—Attempts to isolate the pngl complex of the Cu(II)-dye compound were unsuccessful. Instead the complexes listed below were obtained.

(1) K(Cu-dye-OH).—A compound K(Cu-dye-OH) was prepared by mixing 84 ml. (0.008 mole) of KOH, 0.002 mole of $Cu(OH)_2$, made by Segal,[13] 0.002 mole of pngl and 0.002 mole of dye. The solution turned from blue to deep red on adding the pngl and dye. A dark brown precipitate resulted. This was filtered, washed with distilled water and 150 ml. of ether until the filtrate was colorless. The residue was dried in a 120° oven overnight.

Anal. Calcd. for K(Cu-dye-OH): C, 43.44; H, 2.73; N, 8.44; ash, 38.17 (based on CuO and K_2O). Found: C, 43.39; H, 2.88; N, 8.51; ash, > 36.14 (sample popped slightly on combustion due to the —N=N— linkage).

(2) [Cu(II)-dye-H_2O].—A second compound was isolated by mixing 50 ml. of the pure pngl and 0.6 g. of the dye. The whole was stirred until some of the dye dissolved in the pngl. Then 1 g. of $Cu(NO_3)_2$ in 20 ml. of distilled water and 40 ml. of 95% ethanol was added. The solution immediately turned deep red. The whole was stirred and dissolved on the hot plate for 15 minutes. Filtration and dilution to 300 ml. with distilled water with subsequent slow evaporation to 100 ml. gave a brownish-red solution. Dilution to 200 ml. with distilled water and cooling in an ice-salt bath gave a brownish-black precipitate. The filtered and washed precipitate was dried in a 110° oven for 2 hours.

Anal. Calcd. for [Cu(II)-dye-H_2O]: C, 49.06; H, 3.43; N, 9.54; ash, 27.08 (as CuO). Found: C, 49.18; H, 3.15; N, 9.54; ash, 27.00 (as CuO).

Discussion and Results

A. Spectrophotometric Studies.—The spectrophotometric titration in Fig. 1 indicates that no change in absorption occurs until the two hydrogen ions liberated in the copper(II)-*o*-azophenol interaction have been neutralized. No sharp break is noted after two equivalents of KOH have been added such as was observed in the Jonassen, Cook and Wilson investigation.[14] Hence seemingly no Cu(II)-dye-hydroxy complex forms in the presence of pngl.

The change in slope occurring near 2.5 equivalents KOH is similar to a weak acid-strong base type interaction which the pngl-KOH reaction is. The pngl thus seems capable of coördinating with the Cu(II)-dye complex.

Nine equivalents of KOH are necessary to produce maximum absorption without formation of a precipitate. In Wilson's studies,[14] in the absence of pngl, seven equivalents of KOH are needed to give the maximum absorption without precipitation. If the same reaction mechanism is assumed as in Wilson's investigation,[14] *i.e.*, addition of OH^- ions to give the hydroxy complex which then decomposes to $[Cu(OH)_5]^{3-}$, then the additional two hydroxide ions in this investigation must have reacted with the pngl giving first the [copper(II)-dye-pngl]$^{2-}$ complex which then decomposes at high OH^- ion concentration again to the $[Cu(OH)_5]^{3-}$ ion.

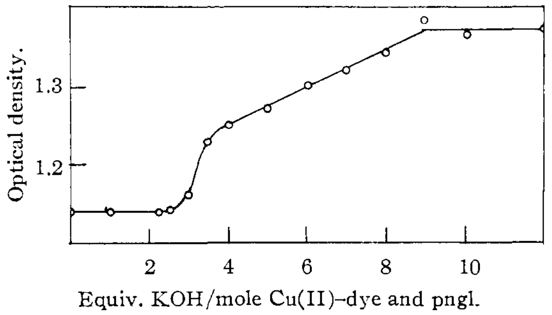

Fig. 1.—Spectrophotometric titration: 0.01 mmole copper(II)-*o*-azophenol + 0.01 mmole propylene glycol with 0.1119 *M* KOH; wave length, 525 mμ; temperature, 25–26°.

Although alcoholic hydrogens generally are not acidic, if the oxygen atoms coördinate, however, such as to a copper(II) ion in the dye complex, the resulting shift in electron density would weaken the oxygen-hydrogen bond giving enhanced acid characteristics such as reaction between tartrate and copper(II) ion in Fehling solution. If the other oxygen of the pngl behaves similarly, then two OH^- ions would be required if the pngl reacted as a bidentate ligand which would indicate a five coördinated [copper(II)-dye-pngl]$^{2-}$ complex proposed from the titration data. The sixth position of the copper(II) coördination sphere may be occupied by a solvent molecule.

The pngl and copper(II)-dye interaction with base may be shown as

$$\text{Cu(II)-dye} + \text{pngl} + 2OH^- \rightleftarrows [\text{Cu(II)-dye-pngl}]^{2-} + 2H_2O \quad \text{(I)}$$

with decomposition of the pngl complex as further OH^- ion is added

$$[\text{Cu(II)-dye-pngl}]^{2-} + 5OH^- \rightleftarrows [Cu(OH)_5]^{3-} + \text{dye ion} + \text{pngl ion} \quad \text{(II)}$$

Evidence for the presence of a copper(II)-dye-hydroxy complex in the absence of pngl is indicated by inspection of curve A, Fig. 2. The first value is

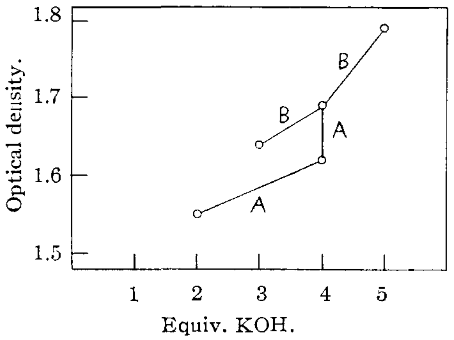

Fig. 2.—Effect of alkali on the copper(II)-*o*-azophenol and the copper(II)-*o*-azophenol + propylene glycol systems; wave length, 510 mμ; temperature, 25–26°. Curve A, points 1 and 2 contain 0.01 mmole copper(II)-*o*-azophenol; curve A, point 3 and curve B, points 1, 2, and 3 contain 0.01 mmole copper(II)-*o*-azophenol plus 0.01 mmole propylene glycol.

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[13] L. Segal, Doctoral Dissertation, Tulane University, 1954.

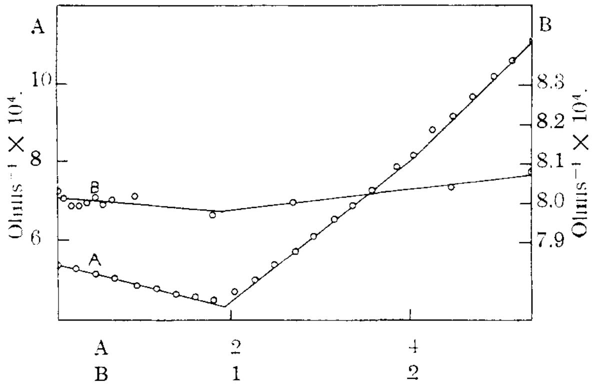
[14] H. B. Jonassen, M. M. Cook and J. S. Wilson, THIS JOURNAL, **73**, 4683 (1951).

the absorption for the copper(II)–dye complex after the two OH^- ions are added to neutralize the H^+ ions for the copper(II)–dye interaction. The second value shows increased absorption for this complex in basic solution where a copper(II)–dye–hydroxy species may be present.

When, however, pngl is added to the copper(II)–dye complex in the same concentration of alkali, the absorbancy increases again (point 3), suggesting a pngl complex.

Such interaction is also indicated in curve B, Fig. 2 where, to equivalent quantities of copper(II)–dye and pngl, additions of the same 4 equivalents of OH^- ion cause increases in absorption to the same value. Addition of 5 equivalents of OH^- ion leads to point 3, curve B.

B. Conductometric Titration Studies.—Titration for a 1:1 molar ratio of the copper(II)–dye and pngl with KOH (curve A, Fig. 3) exhibits two breaks: the first at the neutralization of the two hydrogen ions liberated in the copper(II)–dye reaction. The second break occurs at about four OH^- ions. This inflection after two more OH^- ions are added, which occurs also in the spectrophotometric titration, confirms the interpretation given for the titration data.



A = equiv. KOH/mole Cu(II)-dye and pngl.
B = moles pngl/mole Cu(II)-dye.

Fig. 3.—Conductometric titrations at 30°: curve A, 0.05 mmole copper(II)-*o*-azophenol in 0.05 mmole propylene glycol with 0.1119 *M* KOH; curve B, 0.05 mmole copper(II)-*o*-azophenol in 0.20 mmole KOH with 0.0236 *M* propylene glycol.

The reverse titration of a solution containing one mole of copper(II)–dye and four equivalents of KOH with the pngl (curve B, Fig. 3) shows a break after one mole of pngl has been added, confirming the above results.

C. Isolation of Complexes.—Attempts to prepare the pngl complex were unsuccessful. Conditions used resulted in the products K[Cu–dye–OH] and [Cu(II)–dye–H_2O].

In the preparation of K[Cu–dye–OH] small quantities of distilled water were used. High base concentration in the method results in the anionic complex having a coördinated OH group.

A second compound, [Cu(II)–dye–H_2O], isolated by using large amounts of water resulted in a coördinated H_2O molecule.

Depending on the method employed, the reactions may be

$$Cu(OH)_2 + dye + KOH \rightleftarrows K[Cu\text{–}dye\text{–}OH] + 2H_2O \qquad (III)$$

and

$$Cu(NO_3)_2 + dye + H_2O \rightleftarrows [Cu(II)\text{–}dye\text{–}H_2O] + 2HNO_3 \qquad (IV)$$

These compounds were found to be quite soluble in formamide and pngl. Determination of their absorption values at the wave length noted in Table I indicates the hydroxy complex in formamide has greater absorption than the aquo complex in the same solvent. This agrees with the data of curve A, Fig. 2, in which the dye complex in excess alkali also has greater absorption indicating a hydroxy complex.

TABLE I

System	mμ	Optical density
1 × 10^{-4} *M* K[Cu–dye–OH][a]	510	1.900
1 × 10^{-4} *M* [Cu(II)–dye–H_2O][a]	510	1.700
2 × 10^{-5} *M* K[Cu–dye–OH][a]	510	0.278
2 × 10^{-5} *M* K[Cu–dye–OH][b]	510	.382
2 × 10^{-5} *M* [Cu(II)–dye–H_2O][a]	510	.328
2 × 10^{-5} *M* [Cu(II)–dye–H_2O][b]	510	.337

[a] In formamide. [b] In pngl.

If the isolated compounds of same concentrations are dissolved in formamide and in pngl, the absorption values (Table I) are greater in both instances when pngl is added which might be another confirmation of pngl complexes. Furthermore, since the difference in optical densities in formamide and pngl for the hydroxy complex is at least tenfold over that of the aquo compound, this indicates the OH group is necessary in pngl ion formation.

It was also attempted to follow the complexing reaction polarimetrically by using *l*-2,3-butanediol, an optically active glycol. If the concentration of the glycol is kept constant, then the change in optical activity would be due to the optical activity of the [copper(II)–dye–glycol]$^{2-}$ complex. To facilitate visual observation solutions 1 × 10^{-5} *M* in copper(II)–dye and 3 × 10^{-4} *M* in glycol were used but the changes in activity were too small to be measured accurately.

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