# THE RELATION BETWEEN THE ABSORPTION SPECTRA AND CHEMICAL CONSTITUTION OF DYES. XVII. THE ABSORP-TION SPECTRA OF THE COPPER, NICKEL, AND COBALT COMPOUNDS OF SOME SIMPLE ortho-HYDROXY AND ortho-AMINO AZO DYES<sup>1</sup>

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In earlier published papers on the chemistry of the metal compounds of simple o-hydroxy and o-amino azo dyes (1, 2, 3, 4, 5, 6, 7, 8, 9), no data on the absorption spectra of compounds of this type have been included. The present paper discusses the absorption spectra of a representative group of such compounds.

#### EXPERIMENTAL

A. Metal compounds of o-hydroxybenzeneazo- $\beta$ -naphthol. The dye was prepared by the method of Charrier and Fererri (10). Its metal compounds were prepared by two methods: (a) The dye in alcoholic solution was treated with a solution of copper sulfate in excess ammonium hydroxide. A red-brown precipitate was formed which contained copper, was insoluble in water, soluble in alcohol and other organic solvents, and did not melt below 300°. Its visible spectrum differed from that of the dye. Attempts to purify it were unsuccessful. (b) ortho-Aminophenol was diazotized and to the solution of the diazonium salt was added an excess of a solution of a metal salt. The diazonium salt was then coupled to alkaline  $\beta$ -naphthol. The following salts were used: CuSO<sub>4</sub>, CrF<sub>3</sub>, CoCl<sub>2</sub>, NiSO<sub>4</sub>, and FeSO<sub>4</sub>. In every case a product was obtained which was insoluble in water and did not melt below 300°. The chromium and iron products showed no visible absorption maxima, but the visible absorption spectra of the copper, nickel, and cobalt compounds differed from the spectrum of the dye and from each other. This indicates that definite compounds were formed, although efforts to purify them were unsuccessful.

B. Metal compounds of mono-o-hydroxy and o-amino azo dyes. Three general methods were used in preparing these compounds. A preparation typical of each method is described below and in subsequent discussion these methods will be referred to by number.



<sup>1</sup> An abstract of a portion of a thesis submitted by Maurice L. Ernsberger in partial fulfilment of the requirements for the degree of Doctor of Philosophy at The Ohio State University in 1936.

zeneazo-*p*-cresol in 600 ml. of alcohol was treated with 3 g. of  $CuSO_4 \cdot 5H_2O$  in water to which was added 19 ml. of concentrated ammonium hydroxide. The solution was refluxed for one hour and filtered hot. The brown precipitate was washed successively with dilute ammonium hydroxide, alcohol, and water. The product was recrystallized from xylene.

#### II. Action of the Metal Acetate on the Dye in Alcoholic Solution

A solution of the metal acetate was made by dissolving the salt in a small amount of water and diluting with alcohol. This solution was added to a solution of the dye in hot alcohol. The metal compound of the dye precipitated immediately, was filtered, washed with alcohol, and dried.

## III. Coupling in the Presence of the Metal Salt (11)

Aniline (1.7 g.) was diazotized with an equivalent amount of sodium nitrite. A solution of 5 g. of  $CuSO_4 \cdot 5H_2O$  was added to the diazonium salt solution, which was then coupled to  $\beta$ -naphthol in alkaline solution. The insoluble product was filtered off, washed with alcohol and water, and dried.

*New compounds.* The following compounds not previously described were prepared.



By method II. The product was a brown

powder, insoluble in alcohol and only slightly soluble in chloroform; m.p. 228-229° with slight decomposition. Chlorine: calculated, 23.8; found, 23.7, 23.7.



By method II. The product was a

reddish-brown powder very insoluble in organic solvents; it decomposed without melting. Chlorine: calculated, 11.5; found, 11.0, 11.2.



By method II. A brown solid was

obtained but could not be purified.



By method I. The product was a brown

powder, soluble in organic solvents; m.p. 234°. Copper: calculated, 13.1; found, 12.8, 13.1; nitrogen: calculated, 11.5; found, 11.1, 11.9. This compound was prepared and analyzed in the present work in May, 1935, prior to its description by Elkins and Hunter (7). They give its melting point as 230°.



By method I. Green crystals were ob-

tained by recrystallizing the compound from xylene; m.p. 217-220°. Nickel: calculated, 12.2; found, 12.1, 12.2. Molecular weight: calculated, 480; found, 473. Elkins and Hunter (7) give the melting point of this compound as 216°.

No	COMPONEN	METHOD OF	<b>м.р.,</b> °С.						
NU.		PREPA- RATION	Found	Lit.	LIT. REF.				
	OH								
I			82.5-83.5	82.5-83	12, 8				
	Cu(dye) <sub>2</sub>	II	226	226	1, 8				
II			154–155						
	Cl Cl Cl Cl Cl	II	288-289		a				
III			140–143						
	Cl Cu(dye)2	II	Decomp.		a				
IV			175–180						
	NO <sub>2</sub> Cu(dye) <sub>2</sub>	11	Decomp.		a				
v			108	108					
	Cu(dye).	Т	234	230	7				
	Ni(dye) <sub>2</sub>	Ī	217-220	216	7				
	Co(dye) <sub>2</sub>	II	202–203	202	7				
VI			191	186					
	Cu(duo)	тт	Decomp		a				
	Ni(dve).	II	280-290		a				
	OH								
VII	CH <sub>8</sub> -N=N-		111–112	112-113					
	Cu(due)	TT	042 04E	949	7				
	Ni(dye) <sub>2</sub>	II	243-245 242-243	242-243	7				

#### TABLE I

COMPOUNDS INCLUDED IN THE PRESENT WORK. The metal compounds of each dye are listed immediately below the dye.

<sup>a</sup> Compound not previously described.



TABLE I-Concluded



By method II in acetone solution.

By recrystallizing it from xylene, the product was obtained as shiny black crystals, m.p. 280-290° with decomposition. Nickel: calculated, 10.3; found, 9.9.



By method I. A gray-green product

was obtained which was very insoluble in organic solvents. It could not be purified. All the compounds included in this study are listed in Table I.

Purity of the dyes was established by their melting points after they were recrystallized several times. The metal compounds, with the exception of one or two which were very well characterized, were analyzed for the metal and in some cases for nitrogen or chlorine, so that they were of known purity. Although some of the metal compounds decompose in solution, determinations of absorption spectra were made rapidly enough to be completed before this decomposition was appreciable.



FIG. II. ABSORPTION SPECTRA OF PHENYLAZO- $\beta$ -NAPHTHYLAMINE IN CHCl<sub>3</sub> 1. Dye 0.0001 M; 2. Cu (dye)<sub>2</sub> 0.00005 M; 3. Ni (dye)<sub>2</sub> 0.00005 M; 4. Co (dye)<sub>2</sub> 0.00005 M.

Absorption spectra. Solutions of the dyes were made up to 0.0001 M. in chloroform. Solutions of the metal compounds were made up to 0.00005 M. in chloroform, so that all solutions contained the same amount of azo nitrogen. All the visible absorption spectra were measured in a 1.0 cm. cell, and determined with a Bausch and Lomb spectrophotometer. A Bausch and Lomb quartz spectrograph with a Hilger rotating sector photometer was used for the ultraviolet spectra. The light source was a condensed tungsten spark under water. For a more detailed description of the apparatus see Brode (13) and others (14, 15). Instrumental errors involved in this method are discussed by Brode (13) and by Flexser and co-workers (16). For the broad bands studied in the present work instrumental errors are negligible.

The absorption curves are plotted with values of the extinction coefficient  $\left(k = \frac{1}{d} \log \frac{I_0}{I}\right)$  as ordinates, and wave length  $(m\mu = \text{meters} \times 10^{-9})$  or frequency  $\left(f = \frac{3 \times 10^{10}}{\text{cm}} \times 10^{12} = \frac{\text{vibrations}}{\text{seconds} \times 10^{12}}\right)$  as abscissae. The spectra of each dye and its metal compounds were plotted on the same graph so that they could be compared. Two typical graphs are shown (see Figures I and II).

# DISCUSSION

A. Methods of preparation. The reactions used in preparing these compounds may be represented in this manner:

Method I



The hydrogen ion formed is neutralized by the excess of ammonium hydroxide.

Method II



Although these compounds are unstable in the presence of acids, the concentration of acetic acid reached in the reaction is not sufficient to prevent the formation of the compounds. Method III. The nature of the reactions in which the metal compound is formed by carrying out the coupling in the presence of the metal salt is in doubt. There is a possibility that there is chemical combination between the metal and the diazonium salt (17, 18, 19).

Methods I and II were used for the preparation of several compounds in the present work. Elkins and Hunter (7) suggest that method I is unlikely to lead to salt formation, whereas method II (their method) should lead to salt formation. The copper and nickel compounds of benzeneazop-cresol were prepared in the present work by method I, and the compounds were found to be identical with those prepared by method II.

No record of the use of method III was found except in the patent literature and in a brief discussion by Georgievics and Grandmougin (11). In the present work several compounds were prepared by this method and were found to be the same as when prepared by other methods.

In general the new compounds described have properties similar to those of compounds of the type previously described. However, the copper compounds of *m*-chlorobenzeneazo-*p*-chlorophenol, *p*-nitrobenzeneazo-*p*chlorophenol, *p*-nitrobenzeneazo-*p*-cresol, and *p*-nitrobenzeneazo-*p*-nitrophenol were very insoluble in solvents such as chloroform, ether, benzene, etc., which is contrary to the usual behavior of compounds of this type.

B. Molecular Weights. Values were obtained for the molecular weights of



and

These are the first to be published for compounds of this type. They were determined cryoscopically in benzene, and although the limited solubility of the compounds in cold benzene made it possible to get only a small  $\Delta T_f$  (less than 0.1°), the values are reliable to within 5%. The nickel compound was found to be monomolecular and undissociated. The cobalt compound was found to be bimolecular; molecular weight, calculated, 553; found, 1080, 1040; 2 × 553 = 1106. Less reliable evidence by the boiling point method in chloroform indicates that



is also monomolecular and undissociated. The general behavior and absorption spectra of these particular copper and nickel compounds are typical of the other copper and nickel compounds, which indicates that all of the copper and nickel compounds are probably also monomolecular and undissociated. It was not possible to determine molecular weights of the other compounds because they are too insoluble in cold benzene. A possible explanation of the fact that the cobalt compound is bimolecular is that it may be a cobaltic compound. Other evidence in favor of this suggestion is the fact that Elkins and Hunter (7) recommend the addition of some hydrogen peroxide to the cobalt acetate solution used to prepare cobalt compounds. This causes the pink cobaltous solution to turn dark brown, indicating oxidation.

C. Absorption spectra. The absorption spectra of the products obtained by coupling diazotized o-aminophenol to  $\beta$ -naphthol in the presence of metal salts were only qualitative because no definite compounds were isolated. These spectra indicate that there are compounds formed. Further work should result in their isolation.

The absorption spectra of the metal compounds of mono-*ortho*-hydroxyazo dyes show very few differences from the absorption spectra of the corresponding dyes alone. For the compounds of the dyes with the hydroxyl group on a benzene nucleus the ultraviolet spectra of the dyes and the metal compounds are practically identical. In the visible region the spectra of the metal compounds show a weak band not found in the spectra of the dyes alone. The example given (Fig. I) is typical. For the compounds with the hydroxyl group on a naphthalene nucleus, the spectra are more complicated, but the general effect of the metal is about the same as for the simpler dyes. A new visible band is introduced, although at the same time the intensities, but not the positions, of the ultraviolet bands of the dye are altered.

The new band in the visible region shown by the nickel compounds is at about 590 m $\mu$  and by the copper compounds at about 490 m $\mu$  regardless of the dye with which the metal is combined. Table II gives the maxima of the new bands. Because of the difficulty of their preparation, few cobalt compounds could be obtained pure, so that generalizations about them cannot be made.

D. Conclusions. 1. The new band in the visible region of the absorption spectra of the metal compounds is due to the presence of the metal.

2. The metal has very little effect on the chromophore of the dye, since the dye bands appear unchanged in the absorption spectrum of the metal compound.

3. Because the new bands in the spectra of the dye-metal compounds occur at the same position for a given metal regardless of the dye with which it is combined, it must be concluded that the dye mass has little effect. Therefore the new band is not due to vibration of the entire molecule, since if it were, the change in mass caused by changing the dye would change the position of the band.

4. The only possibility which remains is that the new band is due to an electronic transition. Since the new band is characteristic of the metal rather than of the dye, the electrons must be associated with the metal, and under its influence. Since the characteristic absorption maxima of the new bands do not correspond to the absorption maxima of water solutions of simple salts of the metals, the electronic configuration must also be influenced by the dye.

5. It is likely, therefore, that the electron (or electrons) which undergoes transition is one of those in the covalent or coordinate covalent bonds

DYE	COPPER COMPOUND	NICKEL COMPOUND	COBALT COMPOUNI
I	475 mµ		
v	490 mµ	580 mµ	460 mµ
VI		$590 \text{ m}\mu$	
VII	490 mµ	590 mµ	
VIII	490 mµ	$580 \text{ m}\mu$	500 mµ
			480 mµ
х	$495 m\mu$	$600 \ m\mu$	600 mµ
		545 mµ	450 mµ

# TABLE II Visible Absorption Maxima in the Spectra of the Dye-Metal Compounds

Compounds included in Table I and not in Table II are those which were too

joining the dye and the metal, since those are the electrons directly influenced by both the dye and the metal.

# SUMMARY

1. Several copper, nickel, and cobalt compounds of o-hydroxy and o-amino azo dyes have been prepared and their absorption spectra have been determined.

2. In the ultraviolet region the absorption spectra of the metal compounds do not differ appreciably from the spectra of the corresponding dyes, but in the visible region a new weak band due to the metal is found.

3. It is suggested that this new absorption band may be due to transitions of one or more electrons in the bonds between the dye and the metal.

4. Data on the molecular weights of three of the compounds have been obtained.

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### REFERENCES

- (1) BAMBERGER, Ber., 33, 1939 (1900).
- (2) SCHAPOSCHNIKOFF AND SVIENTOSLAVSKI, Chem. Zentr., 1905, i, 97.
- (3) CHARRIER AND BERETTA, Gazz. chim. ital., 56, 865 (1926).
- (4) CREMONINI, Gazz. chim. ital., 58, 372 (1928).
- (5) CRIPPA, Gazz. chim. ital., 57, 20, 497, 593 (1927); 58, 716 (1928).
- (6) CRIPPA AND LONG, Gazz. chim. ital., 61, 99 (1931).
- (7) ELKINS AND HUNTER, J. Chem. Soc., 1935, 1600.
- (8) DREW AND LANDQUIST, J. Chem. Soc., 1938, 292.
- (9) HAENDLER AND SMITH, J. Am. Chem. Soc., 62, 1669 (1940).
- (10) CHARRIER AND FERERRI, Gazz. chim. ital., 41, 717 (1912).
- (11) GEORGIEVICS AND GRANDMOUGIN, "A Textbook of Dye Chemistry", Greenwood and Son, London, **1920**, p. 19.
- (12) MCPHERSON AND FISCHER, J. Am. Chem. Soc., 22, 143 (1900); MCPHERSON AND LUCAS, 31, 283 (1909).
- (13) BRODE, Bur. Standards J. Research, 2, 504 (1929).
- (14) MCNICHOLAS, Bur. Standards J. Research, 1, 939 (1928).
- (15) GIBSON et al., Bureau of Standards Sci. Papers 440, 18, 128 (1922).
- (16) FLEXSER, HAMMETT, AND DINGWALL, J. Am. Chem. Soc., 57, 2104 (1935).
- (17) BLUMBERGER, Rec. trav. chim., 49, 267 (1930).
- (18) NESMEIANOW et al., Ber., 68, 1877 (1935).
- (19) HIEBER AND SCHNACKIG, Z. anorg. allgem. Chem., 226, 209 (1936).