On the Structure of Condensation Products of o-Aminophenols with α-Dicarbonyl Compounds. III. Copper Chelates of 2,2′-Bibenzoxazoline Derivatives

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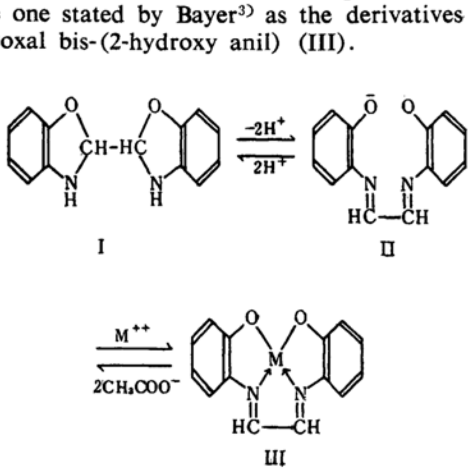
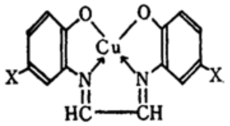
In previous papers[1,2], the condensation products of *o*-aminophenols (2 mol.) with α-dicarbonyl compounds (1 mol.) were determined to have the structure of 2,2′-bibenzoxazolines (I). In addition, 2,2′-bibenzoxazoline tautomerized to the corresponding Schiff base (II) in ethanol solution on addition of alkali, the formation of its metal chelates being explained by the scheme indicated below. The structure of metal chelates was thus in agreement with the one stated by Bayer[3] as the derivatives of glyoxal bis-(2-hydroxy anil) (III).



I II III

Here, the reaction of copper acetate with 2,2′-bibenzoxazoline derivatives was conducted, obtaining copper chelates of 5,5′-dinitro (IV), 5,5′-dimethyl (V) and 5,5′-dichloro (VI) derivative as deep violet or blue amorphous powder.



IV, $X=NO_2$ V, $X=CH_3$ VI, $X=Cl$

The absorption spectra in ethanol of these compounds were taken by the method indicated in the experimental part and they are shown in Fig. 1, where ε of each copper chelate was expediently calculated by means of concentrations of bibenzoxazolines dissolved.

Each spectrum did not represent the true feature of the copper chelate itself since the solution consisted of equilibrium mixture of bibenzoxazoline and copper chelate as suggested from the above scheme. However, the band at

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[1] I. Murase, This Bulletin, 32, 827 (1959).
[2] I. Murase, ibid., 33, 59 (1960).
[3] E. Bayer, *Ber.*, 90, 2325 (1957).

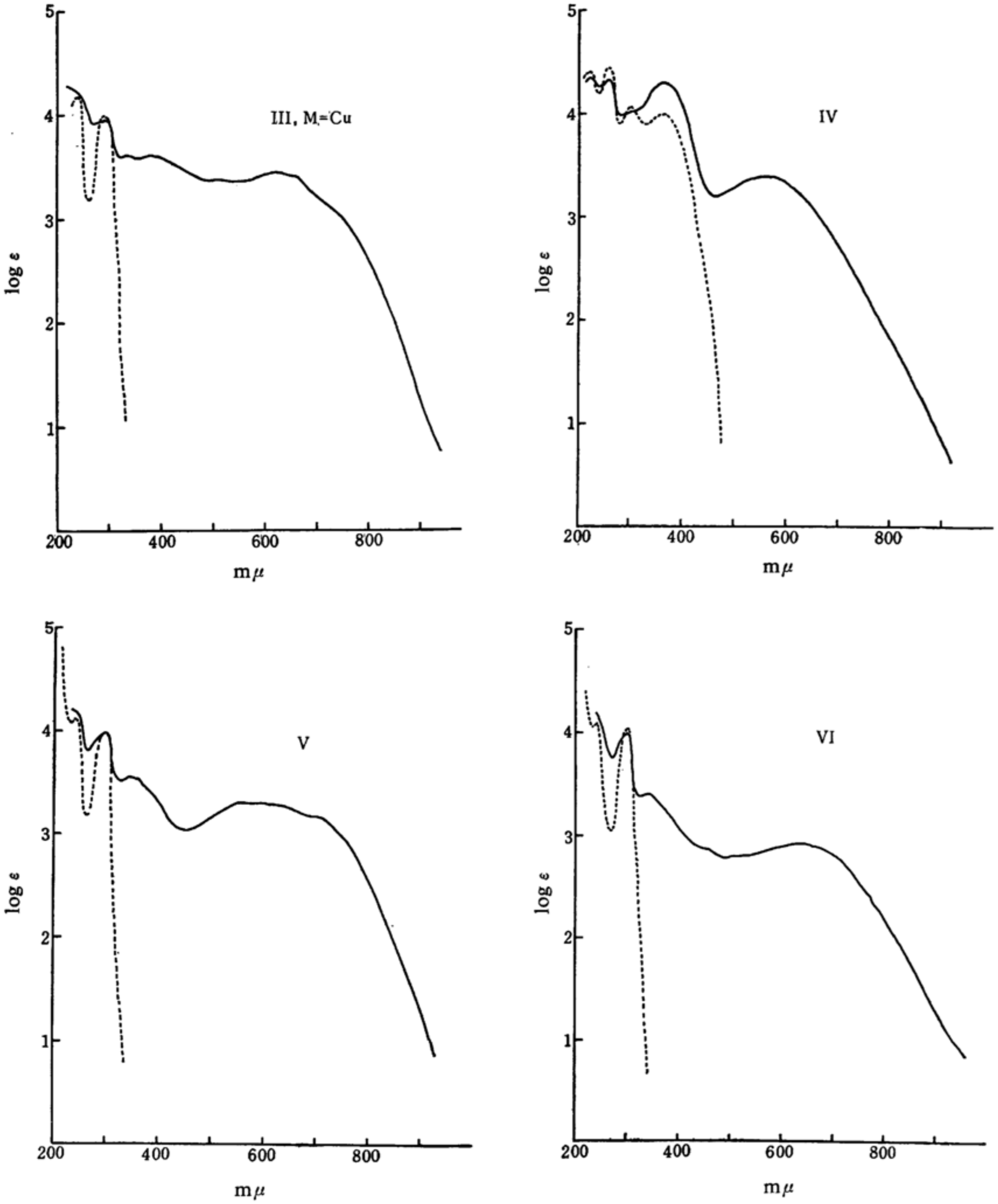
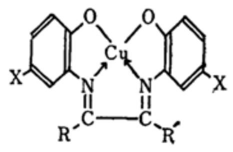


Fig. 1. Ultraviolet and visible absorption spectra of copper chelates of 2, 2′-bibenzoxazoline and its derivatives in ethanol, ——; copper chelate, ------; parent bibenzoxazoline or its derivative.

500~600 mμ in each spectrum should be due to metal-ligand linkage and it resembles the authentic one of glyoxal bis-(2-hydroxy anil)-copper (Fig. 1, III, M=Cu), the solution of which was prepared also in the same manner as other chelates. Therefore, it has been assumed from those spectra that these copper chelates have structures IV—VI.

In the case of 2-substituted and 2, 2′-disubstituted derivatives of 2, 2′-bibenzoxazoline such as 2-methyl-, 5, 5′-dinitro-2-methyl-, 2-methyl-2′-ethyl-2, 2′-diethyl- and 2-methyl-2′-phenyl-bibenzoxazoline, with the exception of 2, 2′-dimethyl derivative, deep violet or blue colored solutions were obtained by addition of copper acetate to their ethanol solutions. On concentration of these colored solutions, no copper chelates were isolated, instead the oxazolines were recovered unchanged. However, the presence of the chelates in solution was suggested by their coloration and was revealed by their absorption spectra which are shown in Fig. 2, where ε of each copper chelate was calculated in the same manner as in Fig. 1.

These spectra resemble those in Fig. 1 in having absorption bands at 500~600 mμ, though their absorption intensities varied with substituents in 2, 2′-positions. Thus, the presence of copper chelates in solution of similar structures VII—XII has been recognized.



VII, $R=CH_3$, $R'=X=H$
IIX, $R=CH_3$ $R'=H$, $X=NO_2$
IX, $R=R'=CH_3$, $X=H$
X, $R=CH_3$, $R'=C_2H_5$, $X=H$
XI, $R=R'=C_2H_5$, $X=H$
XII, $R=CH_3$, $R'=C_6H_5$, $X=H$

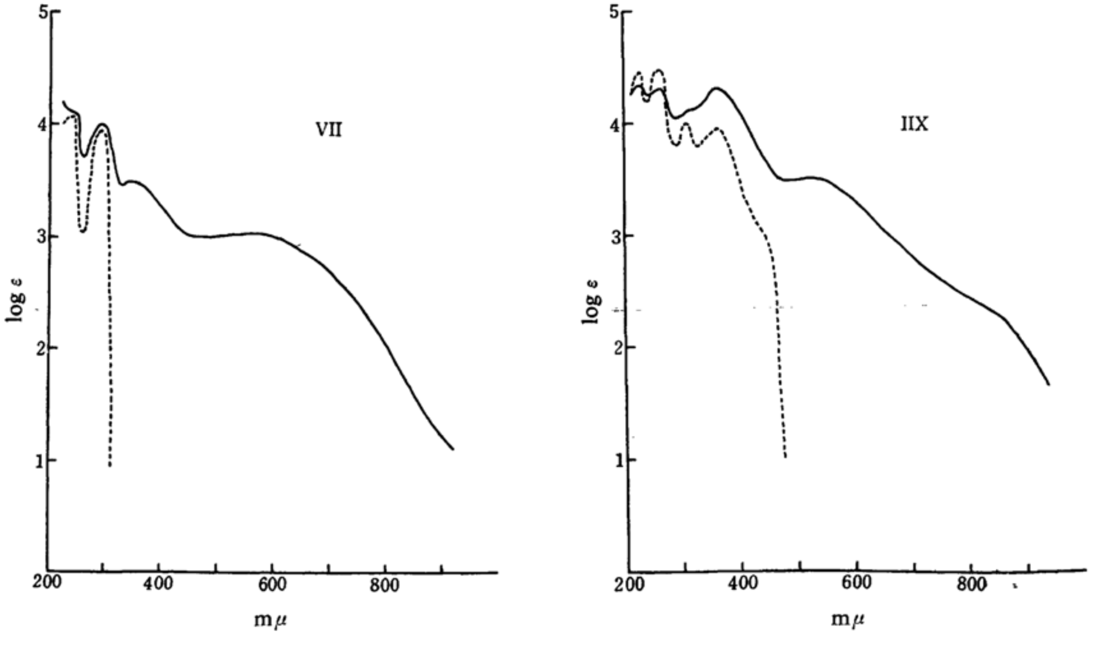
The reason why these copper chelates could not be isolated may be that their formation constant is considerably small. Since the formation constant in each case should be introduced from overall equilibrium consisting of oxazoline, Schiff base and chelate, the proportion of the tautomeric form of oxazoline in the mixture should be considered to be very small.

With respect to the condensation product of *o*-aminophenol with diacetyl, Bayer explained its inability to form metal chelate as the result of the hindrance of methyl groups in diacetyl bis-(2-hydroxy anil), but the author previously suggested, from the spectroscopic behavior toward alkali, that 2, 2′-dimethyl-2, 2′-bibenzoxazoline does not tautomerize to diacetyl bis-(2-hydroxy anil) and forms no metal chelates[1].

Apparently no deep coloration was observed when copper acetate was added to this compound in ethanol. Nevertheless, in this case also, the presence of the chelate in solution was suggested from the careful observation of its spectrum (Fig. 2, IX); an absorption maximum was observed at 560 mμ though in very weak intensity. Thus, it was found that 2, 2′-dimethyl-2, 2′-bibenzoxazoline still possesses a tendency of tautomerism and of formation of copper chelate in solution.

Thus, it is concluded that 2, 2′-bibenzoxazolines acquire an ability of metal chelate formation through tautomerism, which is most remarkable in the case of 2, 2′-unsubstituted derivatives and is hindered by substituents at 2, 2′-position, among which the methyl group is most effective and the phenyl group is not so much.

In the case of carboxy derivatives of bibenzoxazoline, it is interesting to note that 5, 5′-dicarboxy derivative gave reddish violet precipitates on reacting with an equimolar amount



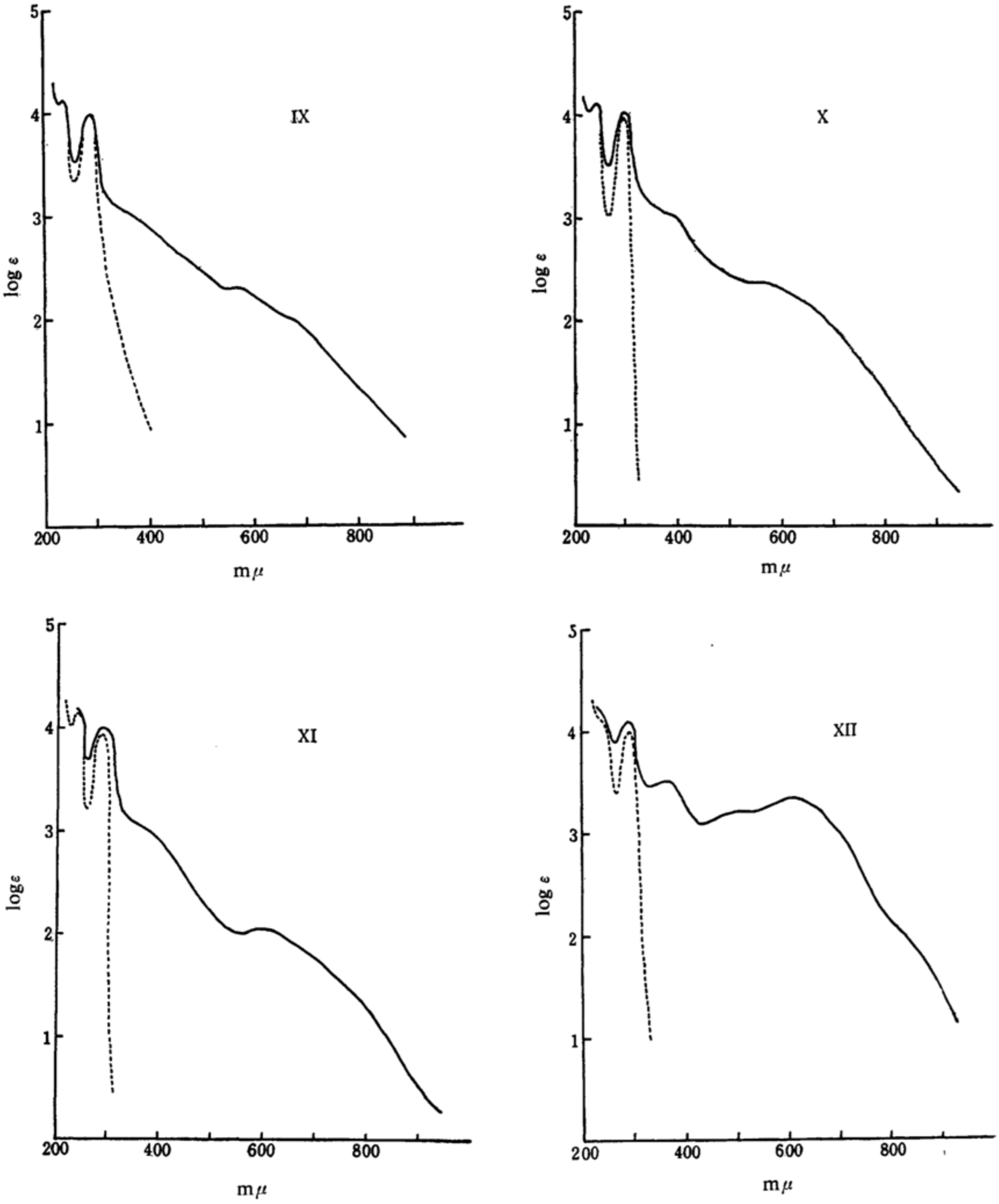


Fig. 2. Ultraviolet and visible absorption spectra of copper chelates of 2, 2′-bibenzoxazoline derivatives in ethanol, ——; copper chelate, ------; parent bibenzoxazoline derivative.

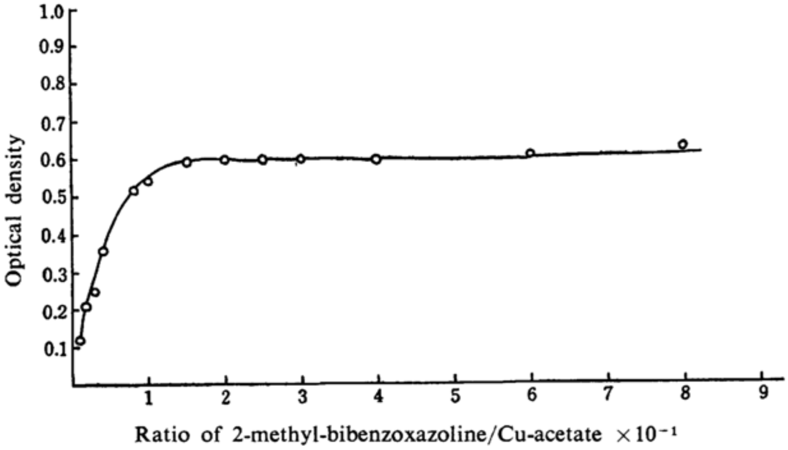


Fig. 3. Optical densities at 540 mμ of various solutions with excess 2-methyl-bibenzoxazoline present: Cu-acetate $=9.99\times10^{-5}$ M.

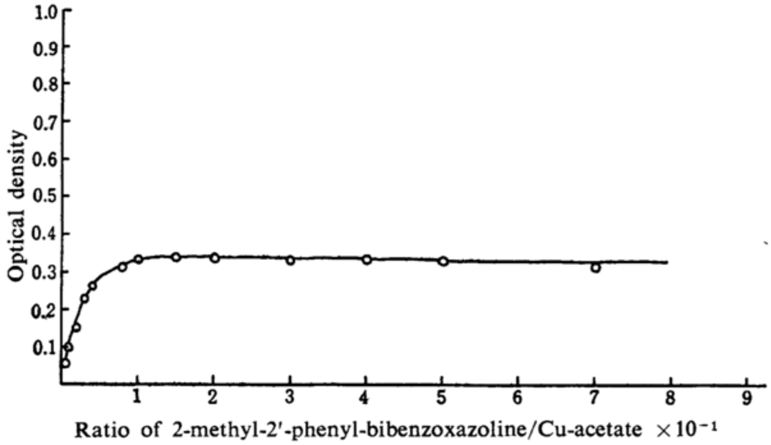
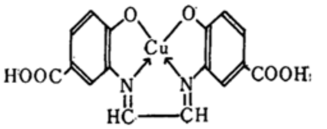
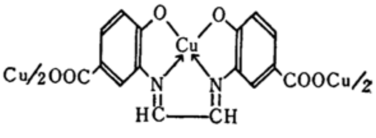


Fig. 4. Optical densities at 600 mμ of various solutions with excess 2-methyl-2′-phenyl-bibenzoxazoline present: Cu-acetate $=4.99\times10^{-5}$ M.

of copper acetate. Since a part of the precipitates was soluble in sodium hydrogen carbonate solution with a blue-violet coloration, the precipitates should contain copper chelate of structure XIII* in which the carboxyl groups are free and the copper atom is coordinated with the Schiff base ligand in the same manner as the other chelates. When this dicarboxy derivative reacted with bimolar amounts of copper acetate, blue-violet precipitates were obtained. This substance was insoluble in sodium hydrogen carbonate solution and consisted of two copper atoms to one molecule of ligand. The structure should be given as XIV in which one copper atom chelates and the other combines as carboxylate.



XIII



XIV

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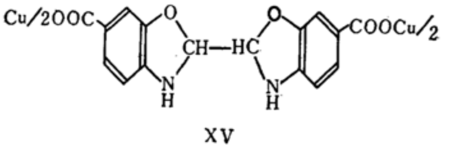
* The precipitates were treated with sodium hydrogen carbonate solution and the soluble part was reprecipitated by neutralization with acetic acid. The substance obtained did not show reasonable analytical results, possibly due to partial decomposition by this treatment.

Found: C, 44.26; H, 3.48; N, 7.04; Cu, 16.07. Calcd. for $C_{16}H_{10}N_2O_6\cdot2H_2O$: C, 45.13; H, 3.31; N, 6.58; Cu, 15.39%.

On the other hand, 6, 6′-dicarboxy derivative gave green precipitates with copper acetate. The substance may have the structure of simple salt of bibenzoxazoline carboxylic acid (XV), because they were insoluble in sodium hydrogen carbonate solution and consisted of one copper atom to one oxazoline molecule. The structure may further be supported by its green color which is seen in ordinary copper carboxylates. It seems that the carboxyl groups at 6, 6′-positions prevent the ring opening of oxazoline to form the Schiff base.



XV

For the determination of metal-ligand proportion in metal chelate in solution, the molar ratio method is known⁴⁾; it consists of the measurement of optical density at a typical wavelength at which an absorption is caused by metal chelate formation, the molar ratio of the ligand being varied to a constant metal ion concentration. If a formation constant of metal chelate is appreciably large, the optical density should reach a constant value at which the metal-ligand proportion is equivalent.

In the case of the above copper chelates, in which the metal-ligand ratio is naturally 1 : 1, the optical densities should be expected to give constant values over the range of more than this ratio.

The experiment was carried out on 2-methylbibenzoxazoline and 2-methyl-2′-phenyl-bibenzoxazoline**. The results are shown in Figs. 3 and 4, but they fell short of expectations.

The optical density of each solution gave almost constant value for ratios greater than 20. Since such poly-coordinate chelate is considered to be impossible, these curves should mean that stability constants of these copper chelates are small. Here again, it proved that the equilibrium between bibenzoxazoline and the Schiff base exists in favor of the former.

Experimental

Copper Chelate of 5, 5′-Dimethyl-2, 2′-bibenzoxazoline.—To a solution of 5, 5′-dimethyl-2, 2′-bibenzoxazoline (0.2 g.) in hot methanol (50 ml.), a solution of copper acetate (0.15 g.) in methanol (20 ml.) was added and the mixture was heated on a water bath for 30 min. The resulting deep violet-blue precipitates were centrifuged and washed with methanol and dried over phosphorus pentoxide in vacuo at 110°C.

Found: C, 55.43; H, 4.48; N, 7.98; Cu, 18.61. Calcd. for $C_{16}H_{14}N_2O_2Cu \cdot H_2O$: C, 55.24; H, 4.60; N, 8.04; Cu, 18.26%.

Copper Chelate of 5, 5′-Dichloro-2, 2′-bibenzoxazoline.—Prepared from 5, 5′-dichloro-bibenzoxazoline (0.2 g.) and copper acetate (0.13 g.) in the same manner as described in the case of the dimethyl derivative. Deep blue amorphous powder.

Found: C, 43.07; H, 2.71; N, 7.43; Cu, 15.96. Calcd. for $C_{14}H_8N_2O_2Cl_2Cu \cdot H_2O$: C, 43.26; H, 2.57; N, 7.20; Cu, 16.34%.

Copper Chelate of 5, 5′-Dinitro-2, 2′-bibenzoxazoline.—Prepared from 5, 5′-dinitro-bibenzoxazoline (0.5 g.) and copper acetate (0.4 g.) in the same manner as described in the case of the dimethyl derivative. Deep reddish violet crystalline powder.

Found: C, 41.12; H, 2.53; N, 13.55; Cu, 15.55. Calcd. for $C_{14}H_8N_4O_6Cu \cdot H_2O$: C, 40.97; H, 2.43; N, 13.65; Cu, 15.51%.

Copper Chelate of Copper-2, 2′-bibenzoxazoline-5, 5′-dicarboxylate.—To a solution of 5, 5′-dicarboxy-2, 2′-bibenzoxazoline (0.5 g.) in hot methanol (300 ml.), copper acetate (0.8 g.) in methanol (50 ml.) was added and the mixture was heated on a water bath for 1 hr. After cooling, resulting precipitates were filtered and washed with methanol and dried over phosphorus pentoxide in vacuo at 110°C. Deep blue-violet crystalline powder.

Found: C, 36.84; H, 3.00; N, 5.06; Cu, 24.91. Calcd. for $C_{16}H_8N_2O_6Cu_2 \cdot 4H_2O$: C, 36.71; H, 3.08; N, 5.35; Cu, 24.28%.

Copper-2, 2′-bibenzoxazoline-6, 6′-dicarboxylate.—To a suspension of 6, 6′-dicarboxy-2, 2′-bibenzoxazoline (0.2 g.) in ethanol (100 ml.), a solution of copper acetate (0.12 g.) in ethanol and 2 drops of acetic acid were added and the mixture was heated on a water bath for 4 hr. The crystals were gradually diminished and green precipitates were formed. After standing over-night, they were filtered and washed with ethanol and dried over phosphorus pentoxide in vacuo at 60°C.

Found: C, 45.62; H, 3.49; N, 6.21; Cu, 14.96. Calcd. for $C_{16}H_{10}N_2O_6Cu \cdot 2H_2O$: C, 45.13; H, 3.31; N, 6.58; Cu, 15.39%.

Absorption Spectra.—The copper chelates III∼VI, when once precipitated, were very difficult to dissolve in ethanol. To obtain the ultraviolet and visible absorption spectra in ethanol of these compounds, a method was devised in the preparation of the solution. To ethanol solutions of bibenzoxazolines (ca. 1/5000∼1/10000 M), equimolar amounts of copper acetate in ethanol were added and the solutions were heated at 70°C for ten minutes and cooled to room temperature. The coloration of each solution reached almost a maximum by this treatment and further heating resulted in decolorization by decomposition, thus clear colored solutions containing copper chelates being obtained.

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4) S. Miyakawa and T. Uemura, This Bulletin, **24**, 25 (1951); R. P. Yaffe and A. F. Voigt, *J. Am. Chem. Soc.*, **74**, 2503 (1952).

** Since their own spectra have no absorption at a visible region (refer to Fig. 2, VII and XII), the optical densities could be observed without any correction. For the measurements, the solution were prepared in the same manner as the case of the measurement of their spectra and the concentration of coppr acetate was used in place of the copper ion concentration to avoid the ambiguity of the latter in ethanol.

In the case of VII—XII, the solutions were prepared also in the same manner as indicated above.

The measurement of absorption spectra and optical densities in the molar ratio method were carried out using a Hitachi EPU-2A spectrophotometer with a 10 mm. quartz cell.

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