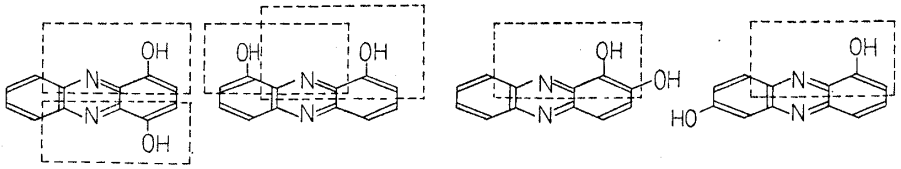
UDC 547.864-156 : 545.822

15. Yoshinori Kidani: Studies on Metal Chelate Compounds of Phenazine Derivatives. III.* Spectrophotometric Study of Copper Chelate Compounds of 1,2-, 1,4-, 1,7-, and 1,9-Dihydroxyphenazine.

(*International Christian University***)

In the previous papers,* it was reported that the phenazine derivatives which have two oxine-like functional groups form chelate compounds with copper. In the present work, copper chelates of the isomers which also have two functional groups, 1,4- and 1,9-dihydroxyphenazine, were studied. When a hydroxyl, which is a chelate-forming functional group, is located *peri* to a ring-nitrogen, and is in the α-position, all such compounds form chelates as have been studied. When such a hydroxyl is in the β-position, this hydroxyl group cannot take part in the formation of chelates, and instead they show specific characteristics. In this report, copper chelates of 1,2- and 1,7-dihydroxyphenazine are described, which have one hydroxyl group at the α-position and one extra hydroxyl group at the β-position.



I. 1,4- and 1,9-Dihydroxyphenazine-Copper Chelates

1. Absorption Spectra—Three varieties of properties in solution are shown in Figs. 1 and 2. Absorption maximum of 1,4-dihydroxyphenazine-copper chelate is 690 mμ in neutral solution (pH 8.0) and 700 mμ in acid medium (pH 4.5). In the case of 1,9-dihydroxyphenazine, absorption maximum of copper chelate is observed at 550 mμ in neutral and at 700 mμ in acid solution.

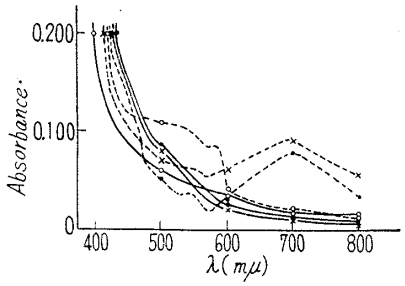


Fig. 1. Absorption Spectra of 1,4-Dihydroxyphenazine-Copper Chelate
(The solution contains $1\times10^{-4}M$ of 1,4-Dihydroxyphenazine)

	Reag.	Complex
pH 4.5	—●—	- - -●- - -
pH 8.0	—×—	- - -×- - -
pH 9.5	—○—	- - -○- - -

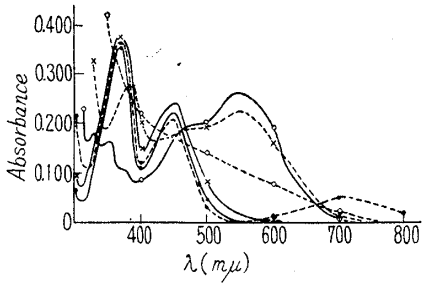


Fig. 2. Absorption Spectra of 1,9-Dihydroxyphenazine-Copper Chelate
(The solution contains $1\times10^{-4}M$ of 1,9-Dihydroxyphenazine)

	Reag.	Complex
Acid	—●—	- - -●- - -
Neut.	—×—	- - -×- - -
Alkali	—○—	- - -○- - -

* Part I: This Bulletin, **6**, 556(1958); Part II: *Ibid.*, **6**, 563(1958).

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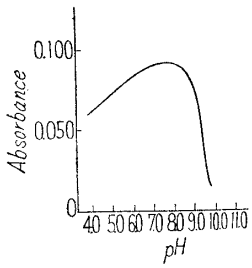


Fig. 3. Effect of pH Change on 1,4-Dihydroxyphenazine-Copper Chelate

(Measured at 690 mμ. The solution contains $1\times10^{-4}M$ of 1,4-dihydroxyphenazine)

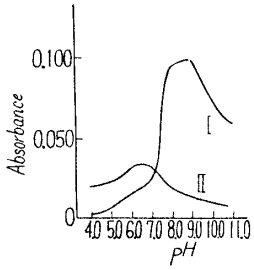


Fig. 4. Effect of pH Change on 1,9-Dihydroxyphenazine-Copper Chelate

(Measured at 550 mμ (I) and 700 mμ (II). The solution contains $1\times10^{-4}M$ of 1,9-dihydroxyphenazine)

2. Effect of pH Change—They are shown in Figs. 3 and 4. The maximum is measured at pH 8.0 in the case of 1,4-dihydroxyphenazine-copper chelate. The maxima for 1,9-dihydroxyphenazine-copper chelate appear at the wave length of 550 mμ at a pH of about 9.0, and at 700 mμ at a pH of about 6.0~7.0.

3. Composition of Chelate in Solution—(i) Job's Continuous Variation Method (Figs. 5 and 6): The experimental data of both 1,4- and 1,9-dihydroxyphenazine-copper chelates gave a composition of 1:1, only the normal complex, at 650 mμ and pH 8.0 in the case of 1,4-dihydroxyphenazine, and at 550 and 700 mμ at pH 7.8 in the case of 1,9-dihydroxyphenazine.

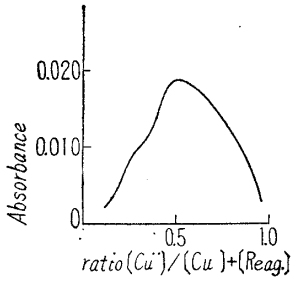


Fig. 5. Absorption Curve of 1,4-Dihydroxyphenazine-Copper Chelate (Job Method)

(Measured at 650 mμ and at pH 8.0. The total concentration is $1\times10^{-4}M$)

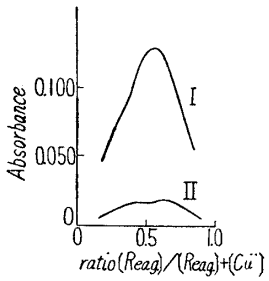


Fig. 6. Absorption Curves of 1,9-Dihydroxyphenazine-Copper Chelate (Job Method)

(Measured at 550 mμ (I) and 700 mμ (II), at pH 7.8. The total concentration is $1\times10^{-4}M$)

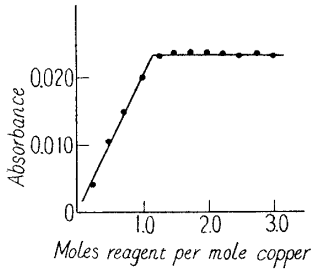


Fig. 7. Absorption Curve of 1,4-Dihydroxyphenazine-Copper Chelate (Molar Ratio Method)

(Measured at 650 mμ and at pH 8.0. The concentration of copper, $1\times10^{-4}M$)

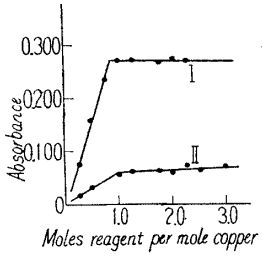


Fig. 8. Absorption Curves of 1,9-Dihydroxyphenazine-Copper Chelate (Molar Ratio Method)

(Measured at 550 mμ (I) and 700 mμ (II), at pH 7.8. Concentration of copper is $1\times10^{-4}M$)

(ii) Molar Ratio Method: Under a similar condition, similar results were obtained for both compounds (Figs. 7 and 8).

II. 1,2- and 1,7-Dihydroxyphenazine-Copper Chelates

1. Absorption Spectra (Figs. 9 and 10)—Copper chelate of 1,2-dihydroxyphenazine shows the λ_{max} at 600 mμ both in neutral and acid media, and this chelate compound is slightly affected by the reagent

absorption. In 1,7-dihydroxyphenazine chelate, λ_{max} of the first absorption region appears at 550 mμ in acid and neutral solutions, and at 550 mμ in alkaline solution.

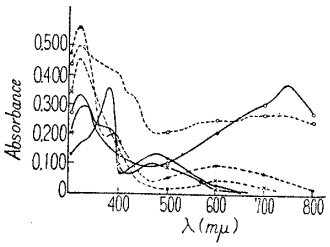


Fig. 9. Absorption Spectra of 1,2-Dihydroxyphenazine-Copper Chelate

(The solution contains $5\times10^{-5}M$ of 1,2-dihydroxyphenazine)

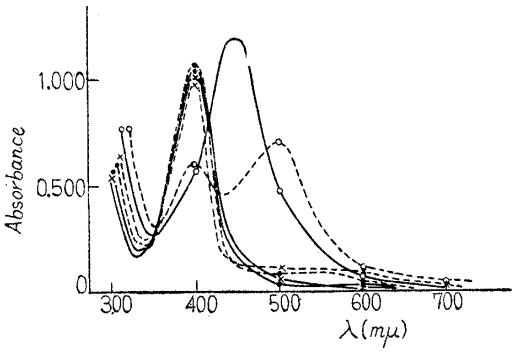


Fig. 10. Absorption Spectra of 1,7-Dihydroxyphenazine-Copper Chelate

(The solu tion contains $1\times10^{-4}M$ of 1,7-dihydroxyphenazine)

	Reag.	Complex
pH 4.4	—●—	---●---
pH 7.6	—×—	---×---
pH 9.5	—○—	---○---

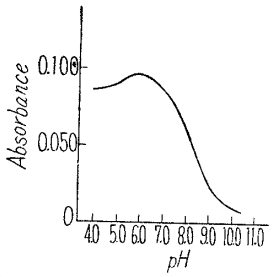


Fig. 11. Effect of pH Change on 1,2-Dihydroxyphenazine-Copper Chelate

(Measured at 600 mμ. The solution contains $5\times10^{-5}M$ of 1,2-dihydroxyphenazine)

	Reag.	Complex
pH 5.0	—●—	---●---
pH 7.4	—×—	---×---
pH 9.8	—○—	---○---

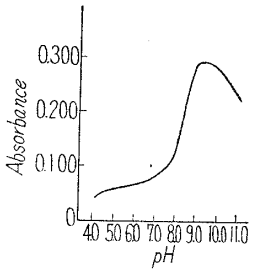


Fig. 12. Effect of pH Change on 1,7-Dihydroxyphenazine-Copper Chelate

(Measured at 500 mμ. The solution contains $6\times10^{-5}M$ of 1,7-dihydroxyphenazine)

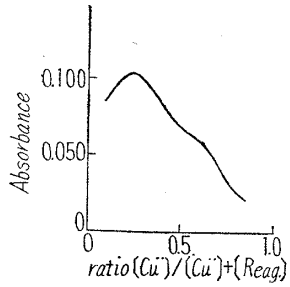


Fig. 13. Absorption Curve of 1,2-Dihydroxyphenazine-Copper Chelate (Job Method)

(Measured at 600 mμ and at pH 6.0. The total concentration is $5\times10^{-5}M$)

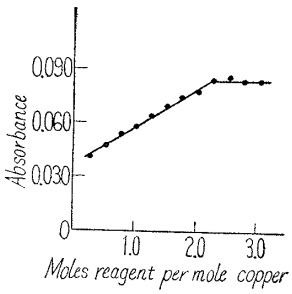


Fig. 14. Absorption Curve of 1,2-Dihydroxyphenazine-Copper Chelate (Molar Ratio Method)

(Measured at 600 mμ and at pH 6.0. The concentration of copper is $5\times10^{-5}M$)

2. Effect of pH Change—The peaks shown in Figs. 11 and 12 were measured at 600 mμ in 1,2-dihydroxyphenazine and at 500 mμ in 1,7-dihydroxyphenazine. The maxima were found at a pH of about 6.0 in the former chelate and at a pH of about 9.2~10.2 in the latter. This is quite different from the other chelates.

3. Composition of Chelate in Solution (Figs. 13~16)—By the two methods (i) and (ii) measured at pH 6.0 and at 600 mμ in the case of 1,2-dihydroxyphenazine, and at pH 9.2 and at 500 mμ in 1,7-dihydroxyphenazine. These results indicate composition to be 2:1 chelate (Reag.: Cu) which is a normal complex.

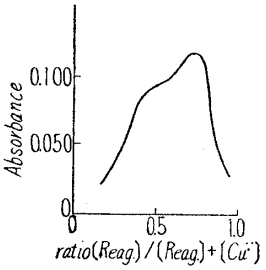


Fig. 15. Absorption Curve of 1,7-Dihydroxyphenazine-Copper Chelate (Job Method)

(Measured at 500 mμ and at pH 9.2. The total concentration is $2\times10^{-4}M$)

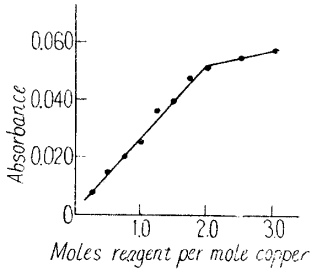


Fig. 16. Absorption Curve of 1,7-Dihydroxyphenazine-Copper Chelate (Molar Ratio Method)

(Measured at 500 mμ and at a pH 9.2. The concentration of copper is $2\times10^{-4}M$)

4. Degree of Dissociation (α) **and Dissociation Constant** (**K**)—In a work previously reported,* the degree of dissociation and dissociation constants of chelate compounds were determined by the following formula, which was measured spectrophotometrically by the molar ratio method.

$$\alpha=\frac{A_m-A_s}{A_m} \quad \cdots\cdots (1)$$

where A_m is the maximum extinction obtained from the horizontal portion of the curve, indicating that all the copper is present in the form of a chelate compound, and A_s is the extinction at the stoichiometric molar ratio.

The degree of dissociation mentioned above was used when the absorption of either the reagent or the metal calls for no careful consideration. Although the absorption of metal may be disregarded, that of reagent must be taken into consideration. The following formula[1] should then be used

$$\alpha=\frac{A_m-A_s}{A_m-A_1} \quad \cdots\cdots (4)^*$$

where A_1 is the absorption of the ligand itself.

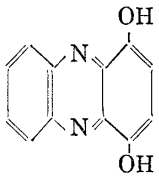
The experimental data, measured by the Molar Ratio Method are shown in Table I. In the case of 1,4- and 1,9-dihydroxyphenazine, they were calculated by the formula (1) and (3). In the case of 1,2- and 1,7-dihydroxyphenazine, calculations were made by the formula (3) and (4).

Compounds	α	-log K	pH
1,4-Dihydroxyphenazine	0.04	6.78	8.0
1,9-Dihydroxyphenazine	0.30	4.90	8.0
1,2-Dihydroxyphenazine	0.16	10.34	6.0
1,7-Dihydroxyphenazine	0.20	8.80	9.2

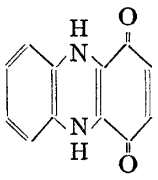
5. Structures and Discussions—It has been shown that all the compounds discussed here form a five-membered chelate ring. The structures are discussed below:

1) Y. Yamane: Yakugaku Zasshi, **77**, 393(1957); T. Sakaguchi, K. Taguchi, S. Fukushima, N. Obi: *Ibid.*, **78**, 179(1958).

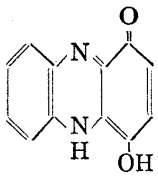
(a) 1,4-Dihydroxyphenazine-Copper Chelate:



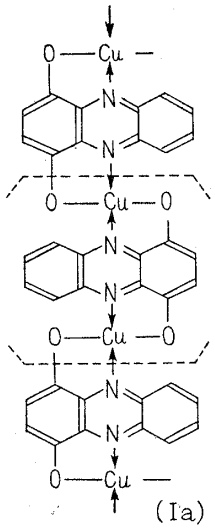
(I)



(IA)



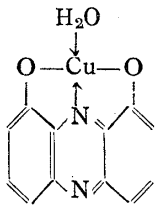
(IB)



(Ia)

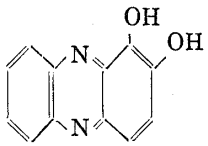
1,4-Dihydroxyphenazine is supposed to have isomeric structures (I) to (IB). Both (I) and (IA) are able to form a chelate but the semiquinoid form (IB), which is also considered to be present, has no ability to form a chelate. The structure of copper chelate is thought to be (Ia).

(b) 1,9-Dihydroxyphenazine-Copper Chelate:

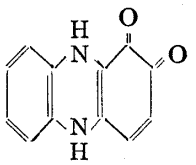


In this compound, as is shown, one mole of H_2O is coordinated to the central metal and it is rather difficult to expect formation of a cation complex.

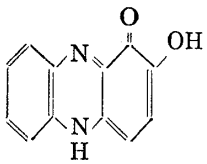
(c) 1,2-Dihydroxyphenazine-Copper Chelate:



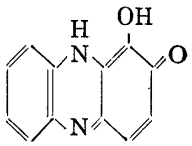
(II)



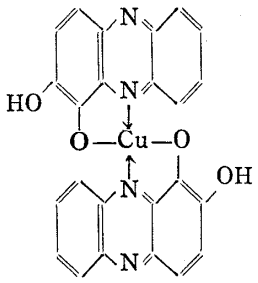
(IIA)



(IIB)



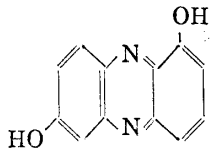
(IIC)



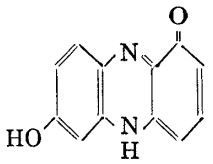
(IIa)

The above isomeric structures can be expected of 1,2-dihydroxyphenazine. The first two (II) and (IIA) form chelates in acid medium. This has a chelating function but at the same time, they have no possibility to form chelate compounds in the latter two forms (IIB) and (IIC). The structure of copper chelate is shown as (IIa).

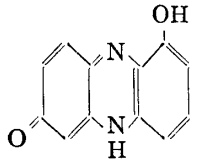
(d) 1,7-Dihydroxyphenazine-Copper Chelate:



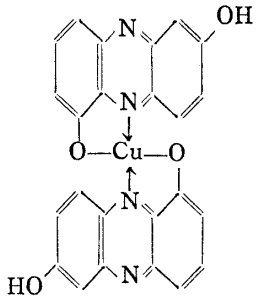
(III)



(IIIA)



(IIIB)



(IIIa)

The copper chelate of this compound has the structure (IIIa). This compound cannot form diketo form such as 1,2- and 1,4-dihydroxyl derivatives, and the first two (III and IIIA) have ability to form chelates, but the last form (IIIB) has no chelating ability at all. As far as this compound is concerned, it is a little different from other chelate compounds in that the chelate is formed in an alkaline solution at pH 9.2.

The author wishes to express his deep gratitude to Prof. M. Ishidate of the University of Tokyo for his encouragements and helpful advices. The author is also very grateful to Prof. T. Sakaguchi of the University of Chiba for his valuable suggestions and encouragements, and also indebted to Mr. N. Chiba of International Christian University for his helpful co-operations. A part of the expenses for this work was defrayed by the Grant-in-Aid for Scientific Research from the Ministry of Education to which the author's thanks are due.

Experimental

A $1\times10^{-4}\,M$ solution of each compound was prepared by dissolving 2.12 mg. of 1,2-, 1,4-, 1,7-, or 1,9-dihydroxyphenazine in 100 cc. of dehyd. EtOH.

Summary

Spectrophotometric investigations of copper chelates of 1,4- and 1,9-dihydroxyphenazines, which are isomers of the already reported compound having two oxine-like functional groups, have been carried out. The copper chelates of 1,2- and 1,7-dihydroxyphenazine, which have only one functional group, though they are dihydroxyl compounds and the other hydroxyl group located at the β-position, have been studied by spectrophotometric method on their properties, compositions, and dissociation constants. It was learned that all of the compounds formed a normal complex, with a five-membered chelate ring.

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