Studies on New Derivatives of 8-Quinolinol as Chelating Agents. II. Chelate Formation of Some Aminomethyl Derivatives Derived from 8-Hydroxyquinoline-2-carbaldehyde with Metal Ions

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The reactions of new oxine derivatives with additional coordinative sites, 8-hydroxyquinoline-2-carbaldehyde, 2-(*p*-chlorophenylaminomethyl)-, 2-(naphthylaminomethyl)-, 2-(*p*-tolylaminomethyl)-, and 2-(*o*-hydroxyphenylaminomethyl)-8-hydroxyquinoline, and *N,N'*-bis(8-hydroxy-2-quinolylmethyl)ethylenediamine (abbreviated as HQA, CAMHQ, NAMHQ, TAMHQ, PAMHQ, and BHQED respectively), with Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Mg^{2+}, and Ca^{2+} were investigated by potentiometric and spectrophotometric methods. The stability constants of the metal chelates were determined in a 50 v/v % aqueous dioxane solution at 25°C. The stability constants of metal chelates of HQA, NAMHQ, CAMHQ, and TAMHQ with a ligand-to-metal ratio of 2 : 1 are lower than those of oxine. In these ligands, steric hindrance due to the aminomethyl group results in lower stability constants of the metal chelates. PAMHQ reacts as a terdentate ligand with Cu^{2+}, Mn^{2+}, Mg^{2+}, and Ca^{2+} to form 1 : 1 chelates by coordination with quinoline nitrogen and two phenolate oxygens. BHQED reacts with Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, and Mn^{2+} to form a protonated chelate, MHL^+, in the acid region, while, in the neutral region, one proton is released from the protonated chelate to form a deprotonated chelate, ML, by coordination with six donor groups, namely, two imino and hydroxyl groups, and two quinoline nitrogens. BHQED acts as a sexadentate ligand to form the most stable chelates among these oxine derivatives.

In a previous paper,[1] we reported the syntheses of new oxine derivatives, such as 8-hydroxyquinoline-2-carbaldehyde(HQA), 2-(*p*-chlorophenylaminomethyl)-8-hydroxyquinoline(CAMHQ), 2-(naphthylaminomethyl)-8-hydroxyquinoline(NAMHQ), 2-(*p*-tolylaminomethyl)-8-hydroxyquinoline(TAMHQ), 2-(*o*-hydroxyphenylaminomethyl)-8-hydroxyquinoline (PAMHQ), and *N,N'*-bis-(8-hydroxy-2-quinolylmethyl)ethylenediamine(BHQED), with additional coordinative sites. Their color reactions with metal ions and acid dissociation constants were also reported.

The influence of the introduction of the additional groups into these ligands may be reflected in the stability of the metal chelates in the following way. If additional coordinative groups, such as aminomethyl, imino, and hydroxyl groups, participate in the coordination, the formation of stable multidentate chelates may be expected. On the contrary, the steric hindrance of these groups at the 2 position may lower the stability of the metal chelates. In this case, the effect of these groups may be greater than that of the alkyl and aryl groups, which have been known to lower the stability of the metal chelates by their steric hindrance. The effect of the additional coordinative groups on the chelate formation may be discussed through a comparison of the stability of the metal chelates formed from these ligands with that of the metal chelates of oxine. From these points of view, we investigated the chelate formation of the oxine derivatives in a 50 v/v % aqueous dioxane solution by potentiometric and spectrophotometric methods.

Experimental

Reagents. The preparations of 8-hydroxyquinoline-2-carbaldehyde, 2-(*p*-chlorophenylaminomethyl)-, 2-(naphthylaminoethyl)-, 2-(*p*-tolylaminomethyl)-, 2-(*o*-hydroxyphenylaminomethyl)-8-hydroxyquinoline, and *N,N'*-bis-(8-hydroxy-2-quinolylmethyl)ethylenediamine were described in the previous paper.[1] Stock solutions of metal chlorides and and perchlorates were standardized by titration with EDTA. All the other compounds used were of a reagent-grade purity.

Potentiometric Titration. The details of the experimental conditions and the method have been described previously.[1] As the ligands and the metal chelates are in soluble in water, the titrations were carried out in a 50 v/v % aqueous dioxane. A solution containing a ligand (10^{-3} M), perchloric acid (10^{-3} M for HQA, CAMHQ, NAMHQ, TAMHQ, and PAMHQ, and 2×10^{-3} M for BHQED), and metal chloride or perchlorates (from 5×10^{-4} M to 10^{-2} M) was titrated with a standard KOH solution.

Spectrophotometric Measurements. The absorption spectra were measured with a Hitachi recording spectrophotometer model 124, and measurements were made in a 50 v/v% aqueous dioxane solution. The pH of the solutions was adjusted with KOH and $HClO_4$ solutions or a Walpole buffer (CH_3COOH–CH_3COONa).

Results and Discussion

HQA, NAMHQ, CAMHQ, and TAMHQ. The results of the molar-ratio method showed that HQA, CAMHQ, and NAMHQ react with metal ions to form 2 : 1 ligand-to-metal chelates. Accordingly, the titration was carried out in the molar ratio of 2 : 1. With HQA, CAMHQ, and NAMHQ, similar curves were obtained. The titration curves of HQA in the presence and the absence of metal ions are shown in Fig. 1. In the cases of Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Mg^{2+}, and Ca^{2+}, each titration curve of the three ligands gives an inflection at $a=1$, indicating that the dissociation reaction of the proton from the ligand occurs between $a=0$ and $a=1$, and that the formation of metal chelates occurs between $a=1$ and $a=2$. However, as is shown in Fig. 2, the titration curves of TAMHQ-metal systems differ from those of HQA-, CAMHQ-, and NAMHQ-metal systems. With all the metal ions except for Cu^{2+} and Ni^{2+}, the titration curves

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[1] T. Hata and T. Uno, This Bulletin, **45**, 477 (1972)

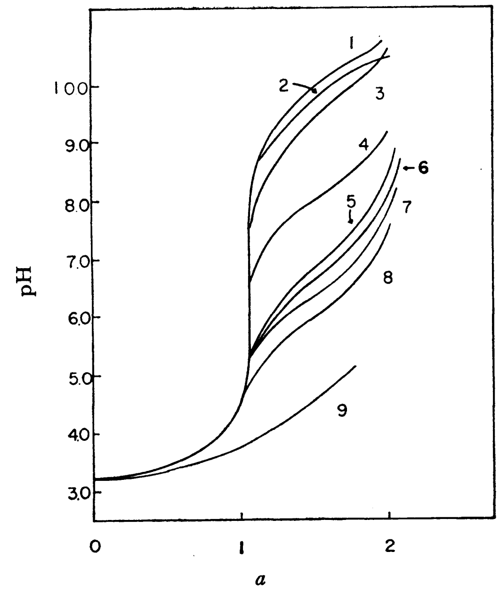

Fig. 1. Potentiometric titration curves of molar ratio of HQA to metal ions 2 : 1 in 50 v/v% aqueous dioxane solution at 25°C $\mu=0.1$(KCl); abscissa *a* represents moles of KOH added per mole of ligand; curve 1, ligand; 2, Ca^{2+}; 3, Mg^{2+}; 4, Mn^{2+}; 5, Cd^{2+}; 6, Ni^{2+}; 7, Co^{2+}; 8, Zn^{2+}; 9, Cu^{2+}.

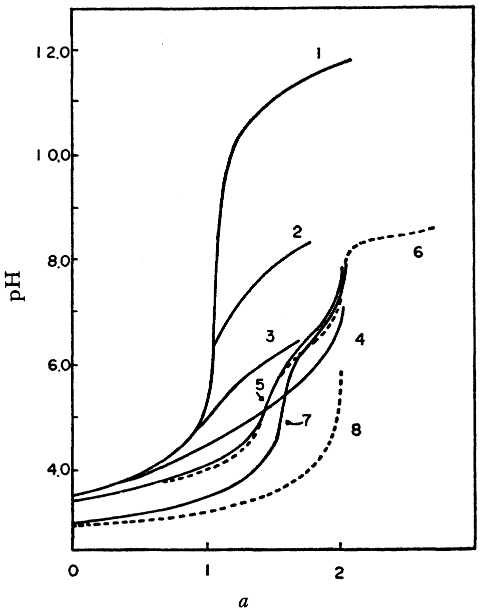

Fig. 2. Potentiometric titration curves of molar ratio of TAMHQ to metal ions 2 : 1 and 1 : 1; the solid line and broken line represent the curves of molar ratio 2 : 1 and 1 : 1, respectively; curve 1, ligand; 2, Mn^{2+}; 3, Cd^{2+}; 4, Zn^{2+}; 5 and 6, Ni^{2+}; 7 and 8, Cu^{2+}.

are analogous to those of HQA, CAMHQ, and NAMHQ, and they show an inflection at $a=1$. However, with Cu^{2+}, the curve of the 2 : 1 molar ratio gives an inflection at $a=1.5$, while in the curve of the 1 : 1 molar ratio, an inflection is no longer observed at $a=1.5$. The titration curves for the Cu^{2+} ion suggest the following reaction process. The dissociation reaction of the proton from the ligand and the formation reaction of the 1 : 1 chelate CuL^+ occur simultaneously between $a=0$ and $a=1.5$, and this chelate reacts with the second ligand to form the 2 : 1 chelate ML_2 in the 2 : 1 molar ratio solution. On the other hand, in the 1 : 1 solution, the ligand reacts with the Cu^{2+} ion to release two protons and form the 1 : 1 chelate in one step.

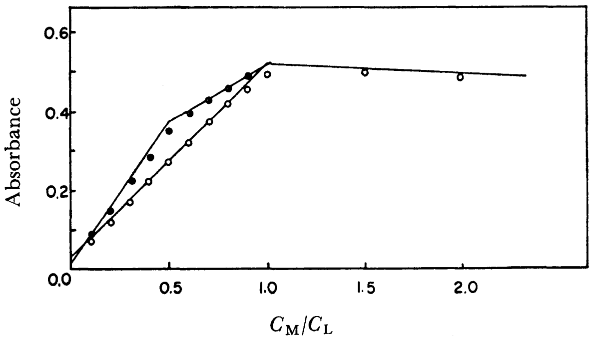

Fig. 3. The determination of molar ratio of TAMHQ to Cu^{2+} in 50 v/v% aqueous dioxane solution; abscissa represents the molar ratio of metal to ligand; ○, pH 4.80; ◑, pH 6.92.

$$H_2L^+ \rightleftarrows HL + H^+ \qquad K_2=\frac{[HL][H^+]}{[H_2L^+]} \qquad (1)$$

$$Cu^{2+} + L^- \rightleftarrows CuL^+ \qquad K_{ML}=\frac{[CuL^+]}{[Cu^{2+}][L^-]} \qquad (2)$$

$$CuL^+ + L^- \rightleftarrows CuL_2 \qquad K_{ML_2}=\frac{[CuL_2]}{[CuL^+][L^-]} \qquad (3)$$

In fact, the results of the molar-ratio method given in Fig. 3 show that TAMHQ forms the 1 : 1 chelate below pH 4.80 and the 2 : 1 chelate together with the 1 : 1 chelate at about pH 6.90. With Ni^{2+}, the titration curves of the 2 : 1 and 1 : 1 molar ratios are identical between $a=0$ and $a=2$, but the hydrolysis of the Ni^{2+} ion occurs at about $a=2$ in the 1 : 1 solution. From these facts, it is considered that TAMHQ reacts with the Ni^{2+} ion to form a protonated chelate, $M\cdot HL\cdot L$ between $a=0$ and $a=1.5$; then one proton is released to form a deprotonated 2 : 1 chelate, ML_2, between $a=1.5$ and $a=2$ in both solution:

$$Ni^{2+} + HL + L^- \rightleftarrows Ni\cdot HL\cdot L \quad K=\frac{[Ni\cdot HL\cdot L^+]}{[Ni^{2+}]\cdot[HL]\cdot[L^-]} \qquad (4)$$

$$Ni\cdot HL\cdot L^+ \rightleftarrows NiL_2 + H^+ \qquad K_C=\frac{[NiL_2]\cdot[H^+]}{[Ni\cdot HL\cdot L^+]} \qquad (5)$$

The equilibrium constants, K and K_C, given in Reactions (4) and (5) are calculated from the data in the regions between $a=0.3$ and $a=1.2$, and between $a=1.6$ and $a=1.9$, respectively. The results obtained from the 2 : 1 and 1 : 1 curves coincide to give $\log K=13.45$ and $pK_C=6.62$ respectively.

The stability constants of 2 : 1 ligand-to-metal chelates were calculated by Bjerrum's method,[2] as modified by Irving and Rossotti,[3] from the following equations:

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[2] J. Bjerrum, "Metal Ammine Formation in Aqueous solution," P. Haase and Sons, Copenhagen, 1941.

[3] G. Irving and H. S. Rossoti, *J. Chem. Soc.*, **1953**, 3397.

$$[\mathrm{L}]=\frac{C_\mathrm{L}+[\mathrm{HClO_4}]+[\mathrm{OH^-}]-[\mathrm{KOH}]-[\mathrm{H^+}]}{[\mathrm{P}]} \qquad (6)$$

$$\bar{n}=\frac{C_\mathrm{L}-Q\cdot[\mathrm{L}]}{C_\mathrm{M}} \qquad (7)$$

where $P=[\mathrm{H^+}]/K_1+2\cdot[\mathrm{H^+}]^2/K_1\cdot K_2$, and $Q=1+[\mathrm{H^+}]/K_1+[\mathrm{H^+}]^2/K_1\cdot K_2$; n is the average number of ligands bound per metal ion, C_L and C_M are the total ligand concentration and the total metal concentration respectively, and K_1 and K_2 are acid dissociation constants. The values of $\bar{n}$ and [L] at each point of the titration curves were calculated from Eqs. (6) and (7). From these data, the formation curves were plotted. The step-by-step stability constants, K_ML and K_{ML_2}, were calculated by the least-squares method by the use of Eq. (8):

$$\frac{\bar{n}}{(\bar{n}-1)\cdot[\mathrm{L}]}=\frac{(2-\bar{n})\cdot[\mathrm{L}]}{(\bar{n}-1)}K_\mathrm{ML}\cdot K_{\mathrm{ML}_2}-K_\mathrm{ML} \qquad (8)$$

When the precipitation was observed in the course of titration, the stability constants were estimated apporoximately from the values of pL at $\bar{n}=0.5$ and $\bar{n}=1.5$. From the values of K_ML, K_{ML_2}, and [L], $\bar{n}$ was recalculated by Eq. (9) and theoretical formation curves were plotted:

$$\bar{n}=\frac{K_\mathrm{ML}\cdot[\mathrm{L}]+2\cdot K_\mathrm{ML}\cdot K_{\mathrm{ML}_2}\cdot[\mathrm{L}]^2}{1+K_\mathrm{ML}\cdot[\mathrm{L}]+K_\mathrm{ML}\cdot K_{\mathrm{ML}_2}\cdot[\mathrm{L}]^2} \qquad (9)$$

The theoretical curve and the experimental plots of the TAMHQ metal chelates are shown in Fig. 4. The theoretical curve is in good agreement with the experimental plots. The stability constants are summarized in Table 1, along with the acid dissociation constants, and are compared with those of oxine.

As may be seen in Table 1, the stability constants of the metal chelates of four ligands, HQA, CAMHQ, NAMHQ, and TAMHQ, are lower than those of oxine. These results can be explained as follows. The basicity of these ligands is lower than that of oxine. These ligands do not behave as terdentate ligands, but as bidentate ligands toward metal ions; that is, the quinoline nitrogen and phenolate oxygen for four ligands participate in coordination to metal ions to form 2 : 1 chelates. Moreover, the aminomethyl group introduced at the 2 position induces a large steric hindrance. Accordingly, their metal chelates should be lower in stability than those of oxine, as is observed in the cases of 2-aryl- and 2-alkyl-8-hydroxyquinoline.[4,5]

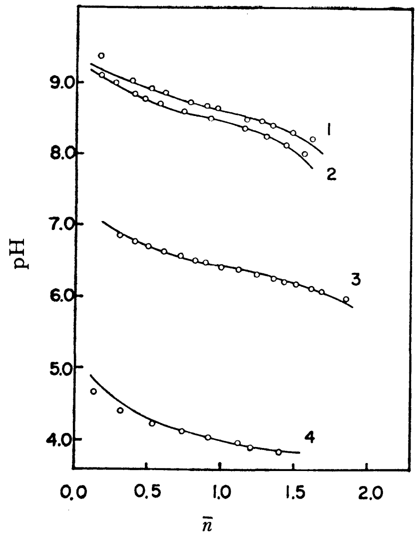

Fig. 4. The formation curves of TAMHQ-metal chelates; solid line represents the theoretical formation curves; curve 1, Zn^{2+}; 2, Co^{2+}; 3, Mn^{2+}; 4, Mg^{2+}.

The stability of metal chelates in these ligands decreases in the order of $Cu^{2+}>Zn^{2+}>Co^{2+}\sim Ni^{2+}>Cd^{2+}>Mn^{2+}$. It is noteworthy that this order is in agreement with that in 2-alkyl-8-hydroxyquinoline and is different from that of oxine, that is, Mellor-Mallery's order[6]: $Cu^{2+}>Ni^{2+}>Co^{2+}>Zn^{2+}>Cd^{2+}>Mn^{2+}$.

PAMHQ. The titration curves of the 1 : 1 and 2 : 1 molar ratios are shown in Fig. 5. In the presence of any metal ion except Zn^{2+}, the titration curves of the 2 : 1 molar ratio are almost identical

TABLE 1. THE STABILITY CONSTANTS OF METAL CHELATES OF HQA, TAMHQ, CAMHQ, AND NAMHQ $\mu=0.1$, 25°C

Ligand	Oxine[a]		HQA		TAMHQ		CAMHQ		NAMHQ	
Cation	log K_ML	log K_{ML_2}	log K_ML	log K_{ML_2}	log K_ML	log K_{ML_2}	log K_ML	log K_{ML_2}	log K_ML	log K_{ML_2}
Cu^{2+}	13.49	12.73	8.97	8.46	<12.00	8.06			10.7[b]	
Zn^{2+}	9.96	8.90	7.25	7.14	8.92	8.22	9.24	8.63	9.21	8.62
Ni^{2+}	11.43	9.94	6.58	6.62			8.9[b]		8.07	7.98
Co^{2+}	10.55	9.11	7.12	6.43	8.78	8.06	8.6[b]		8.6[b]	
Cd^{2+}	7.78		6.63	6.17	8.5[b]		8.4[b]			
Mn^{2+}	8.28	7.17	5.49	4.92	6.67	6.20	6.8[b]			
Mg^{2+}	6.38	5.43	3.45		4.2		4.5		4.6	
Ca^{2+}	3.2		4.0	2.6					3.5	
	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2	pK_1	pK
H^+	11.54	3.97	9.92	<3	11.11	3.62	11.10	3.19	11.11	3.39

a) W. D. Johnston and H. Freiser, *J. Amer. Chem. Soc.*, **74**, 5239 (1952). b) Precipitation occured.

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[4] W. D. Johnston and H. Freiser, *J. Amer. Chem. Soc.*, **74**, 5239 (1952).

[5] H. Kaneko and K. Ueno, This Bulletin, **39**, 1910 (1966).

[6] D. P. Mellor and L. Malley, *Nature*, **159**, 370 (1947); **161**, 436 (1948).

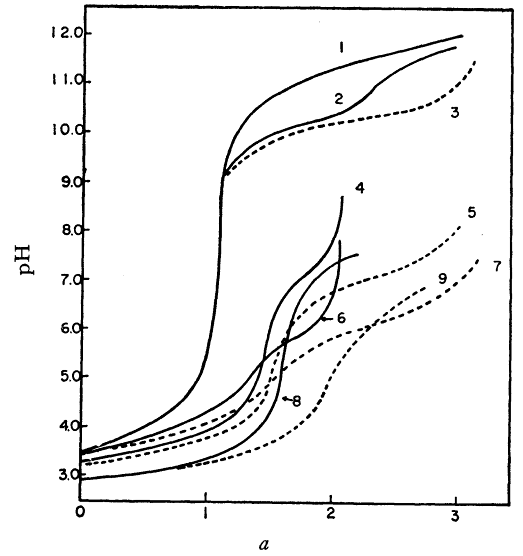

Fig. 5. Potentiometric titration curves of molar ratio of PAMHQ to metal ions 2 : 1 and 1 : 1; solid line and broken line represent the curves of molar ratio 2 : 1 and 1 : 1, respectively; curve 1, ligand; 2 and 3, Ca^{2+}; 4 and 5, Ni^{2+}; 6 and 7, Zn^{2+}; 8 and 9, Cu^{2+}.

TABLE 2. THE STABILITY CONSTANTS OF METAL CHELATES OF 2-(*o*-HYDROXYPHENYLAMINOMETHYL)-8-HYDROXYQUINOLINE(PAMHQ) $\mu=0.1$, 25°C

Cation	log K_{MHL}	log $K_{\mathrm{M(HN)_2}}$	log K_{ML}	
Cu^{2+}		8.07	17.44	log $K_{\mathrm{CuHL^+}}=12.47$
Co^{2+}	8.06	8.02		p$K_{\mathrm{CuHL^+}}^{\mathrm{H^+}}=6.54$
Cd^{2+}	6.80	6.70		
Mn^{2+}	6.36	5.94	9.50	
Mg^{2+}	4.52		5.17	
Ca^{2+}	4.51		6.10	
	pK_1	pK_2	pK_3	
H^+	11.53	10.86	3.72	

with the curves for TAMHQ. This observation indicates that PAMHQ reacts with metal ions to form 2 : 1 protonated chelates by the coordination of metal ions with quinoline nitrogen and phenolate oxygen in the quinoline ring in the same manner as TAMHQ. In fact, as is apparent from Table 2, the stability constants of 2 : 1 protonated chelates of PAMHQ are comparable with those of the four ligands described above, and are lower than those of oxine.

However, the curves of the 1 : 1 molar ratio differ from those of the 2 : 1 molar ratio. With Cu^{2+}, the titration curve gives an inflection at $a=2$, and at this point the color of the 1 : 1 molar ratio solution changes from green to a brownish red, while the color of the 2 : 1 molar ratio solution changes from light green to a brownish yellow. The absorption spectra of the 1 : 1 molar ratio solution at the various pH values given in Fig. 6 show that in the low pH region, only one band is observed, with an absorption maximum at 380 nm, whereas the absorption spectra change in accordance with the increase in pH to show two absorption bands with absorption maxima at 480 and 580 nm in the region above pH 6.0. From these facts, it is clear

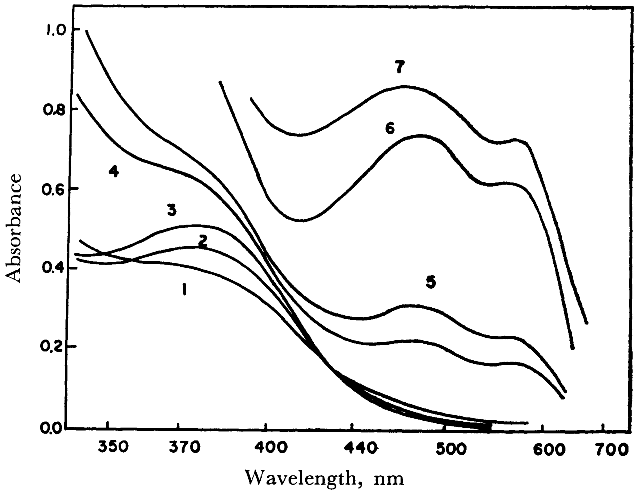

Fig. 6. Absorption spectra of molar ratio of PAMHQ to Cu^{2+} 1 : 1 solution in 50 v/v% aqueous dioxane at various pH; PAMHQ=$Cu^{2+}=2\times10^{-4}$ M; curve 1, pH 3.60; 2, 4.20; 3, 5.95; 4, 7.10; 5, 7.90; 6, 8.00; 7, 8.88.

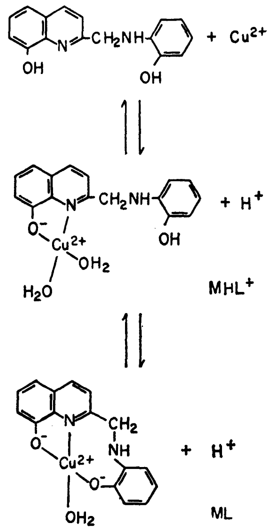

Chart 1. PAMHQ-Cu^{2+} chelate.

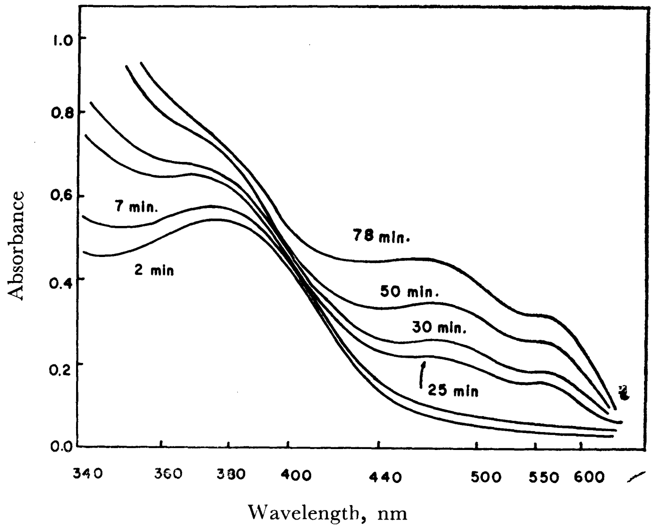

Fig. 7. Spectral change of molar ratio of PAMHQ to Cu^{2+} 1 : 1 solution with time at pH 7.40 (Walpole buffer) in 50 v/v% aqueous dioxane.

that two different chelating species exist in the 1 : 1 solution. That is, as may be seen in Chart 1, PAMHQ reacts with the Cu^{2+} ion to form the protonated chelate $CuHL^+$ between $a=0$ and $a=2$ by the coordination of the Cu^{2+} ion with quinoline nitrogen and phenolate oxygen in the quinoline ring, and then one proton is released from the protonated chelate and the CuL chelate is formed by coordination with phenolate oygen in benzene ring. The spectral change with the time shown in Fig. 7 reveals that the equilibrium of Reaction (10) is rapid, but Reaction (11), the conversion of $CuHL^+$ into CuL, is slow.

$$Cu^{2+} + HL^- \rightleftarrows CuHL^+ \quad K_{CuHL^+} = \frac{[CuHL^+]}{[Cu^{2+}]\cdot[HL^-]} \qquad (10)$$

$$CuHL^+ \rightleftarrows CuL + H^+ \quad K^{H^+}_{CuHL^+} = \frac{[CuL]\cdot[H^+]}{[CuHL^+]} \qquad (11)$$

Accordingly, the stability constants were calculated from the data of the curve which was obtained by the titration for 2.25 hr. The results are given in Table 2, together with the over-all stability constant, K_{CuL}; it is clear that the stability constants are higher than that of oxine.

However, with Ni^{2+}, and Zn^{2+}, the titration curves of the 1 : 1 and 1 : 10 molar ratios exhibit an inflection at $a=1.5$, indicating that three protons are displaced from the ligand in two steps. Judging from the fact that the three curves of the 2 : 1, 1 : 1, and 1 : 10 molar ratios give an inflection at $a=1.5$, it is considered that the same reaction occurs between $a=0$ and $a=1.5$ in each solution. That is, as was observed for the TAMHQ–Ni^{2+} system, PAMHQ reacts first with the Ni^{2+} ion to form a 2 : 1 protonated chelate, $Ni\cdot H_2L\cdot HL$, between $a=0$ and $a=1.5$, and then this chelate reacts with the free Ni^{2+} ion to release 1.5 protons and to form a 1 : 1 chelate, NiL, between $a=1.5$ $a=3$ in the 1 : 1 solution.

With Mn^{2+}, Mg^{2+}, and Ca^{2+}, the initial reaction, that is, the one-proton dissociation reaction from the ligand, is followed by the two-proton displacement reaction in the 1 : 1 and 1 : 10 molar ratios solutions. This fact indicates that PAMHQ reacts with these metal ions to form a 1 : 1 terdentate chelate by coordination with two phenolate oxygens and quinoline nitrogen. The stability constants of 1 : 1 deprotonated chelates are higher than those of oxine, as is shown in Table 2.

Although the reaction mechanism of PAMHQ–Ni^{2+} and Zn^{2+} has not been completely clarified, it is obvious from the above discussion that PAMHQ reacts with Cu^{2+}, Mn^{2+}, Mg^{2+}, and Ca^{2+} to form terdentate chelates and that their stabilities are higher than those of the chelates of oxine.

BHQED. This ligand has two hydroxyl and imino groups, and two quinoline nitrogens, and is expected to act as a multidentate ligand toward metal ions to form 1 : 1 ligand-to-metal chelates. The titration curves obtained in the equivalent (1 : 1) and excess (1 : 10) molar ratios of ligand to metal are shown in Fig. 8. The shapes of the curves clearly show the different types of reactions observed, involving the formation of deprotonated chelates as well as various protonated chelates.

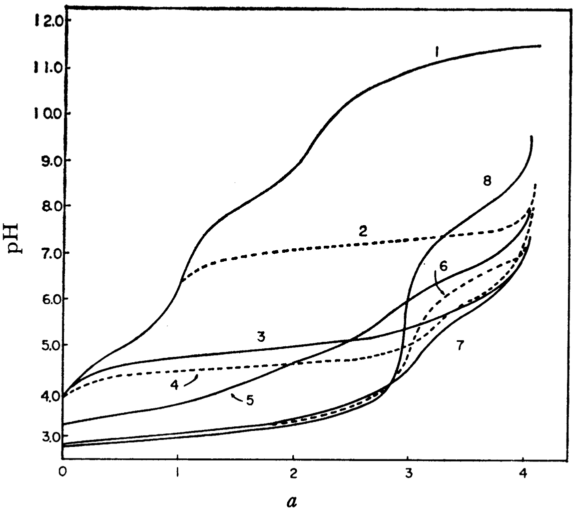

Fig. 8. Potentiometric titration curves of the equivalent and the excess molar ratio of BHQED to metal ions; solid line and broken line represent the equivalent and excess curves, respectively; curve 1, ligand; 2, Mg^{2+}; 3 and 4, Mn^{2+}; 5 and 6 Ni^{2+}; 7, Co^{2+}; 8, Cu^{2+}.

In the cases of Cu^{2+} and Mn^{2+}, the equivalent curves have an inflection at $a=3$ and, moreover, a flat buffer region between $a=0$ and $a=3$. These facts indicate that three protons are displaced from the ligand in one step to form a monoprotonated chelate, MHL^+, and that one proton is then dissociated from this chelate to form a deprotonated chelate, ML:

$$M^{2+} + HL^- \rightleftarrows MHL^+ \quad K^{M}_{ML_2} = \frac{[MHL]}{[M^{2+}]\cdot[HL^-]} \qquad (12)$$

$$MHL^+ \rightleftarrows ML + H^+ \quad K^{H^+}_{MHL^+} = \frac{[ML]\cdot[H^+]}{[MHL^+]} \qquad (13)$$

The equilibrium constants were calculated by the use of Eqs. (14) and (15) from the data in the regions between $a=0.5$ and $a=2.5$, and between $a=3.2$ and $a=3.9$, respectively.

$$K_{MHL^+} = \frac{C_L\cdot(\varepsilon-\sigma)\cdot\varepsilon+\alpha\cdot\sigma\cdot\varepsilon}{\{\varepsilon\cdot(C_M-C_L)+\sigma(C_L-\alpha)\}\cdot(C_L-\alpha)} \qquad (14)$$

$$K^{H^+}_{MHL^+} = \frac{(\alpha-C_M)\cdot[H^+]}{(2\cdot C_M-\alpha)} = \frac{(\alpha-C_L)\cdot[H^+]}{(2\cdot C_L-\alpha)} \qquad (15)$$

Where $\varepsilon=[H^+]/K_2+2\cdot[H^+]^2/K_2\cdot K_3+3\cdot[H^+]^3/K_2\cdot K_3\cdot K_4$, $\sigma=1+[H^+]/K_2+[H^+]^2/K_2\cdot K_3+[H^+]^3/K_2\cdot K_3\cdot K_4$, and $\alpha=[KOH]+[H^+]-[OH^-]-[HClO_4]$; C_M and C_L are the total ligand concentration and the total metal concentration respectively, and K_2, K_3, and K_4 are the respective acid dissociation constants. With Co^{2+}, Ni^{2+}, and Cd^{2+}, the initial reaction is a two-proton displacement to form a diprotonated chelate:

$$M^{2+} + H_2L \rightleftarrows MH_2L^{2+} \quad K^{M}_{ML_2} = \frac{[MH_2L^{2+}]}{[M^{2+}]\cdot[H_2L]}$$

This is followed by a dissociation reaction:

$$MH_2L^{2+} \rightleftarrows MHL^+ + H^+ \quad K^{H^+}_{MH_2L} = \frac{[MHL^+]\cdot[H^+]}{[MH_2L^{2+}]}$$

$$MHL^+ \rightleftarrows ML + H^+ \quad K^{H^+}_{MHL^+} = \frac{[ML]\cdot[H^+]}{[MHL^+]}$$

The equilibrium constants for each step can be calculated because there is a suitable buffer region.

With Mg^{2+}, the excess curve shows that Mg^{2+} is not bound until at least one proton is displaced from the ligand because of the weaker binding ability of this metal ion to the ligand; this follows the displacement of three protons to form a deprotonated chelate between $a=1$ and $a=4$. The data of the excess curve were employed in the previous paper for the evaluation of the stability constants by the use of Schwarzenbach's method.[7] The equilibrium constants are summarized, along with the overall stability constants, in Table 3.

TABLE 3. THE STABILITY CONSTANTS OF METAL CHELATES OF N,N'-BIS(8-HYDROXY-2-QUINOLYLMETHYL)ETHYLENEDIAMINE(BHQED), $\mu=0.1$, 25°C

Cations	log $K^{H^+}_{MH_2L}$	log $K^{H^+}_{MHL^+}$	log $K^{M}_{MH_2L}$	log $K^{M}_{MHL^+}$	log K_{ML}
Cu^{2+}		7.89		20.0	23.5
Co^{2+}	3.59	5.99	12.49	19.0	22.5
Ni^{2+}	5.20	6.79	9.59	14.2	18.9
Cd^{2+}	3.91	7.78	10.62	17.4	22.0
Mn^{2+}		6.20		12.4	17.6
Mg^{2+}					10.2
	pK_1	pK_2	pK_3	pK_4	
H^+	11.38	10.81	8.15	5.12	

In the presence of Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, and Mn^{2+}, but not Mg^{2+}, BHQED reacts with these metal ions to form a monoprotonated chelate, MHL^+, and this reaction is followed by the dissociation of one proton from this chelate to form a deprotonated chelate, ML. As is shown in Table 3, the dissociation constants, $K^{H^+}_{MHL^+}$ of these metal chelates decrease in the order: $Cu^{2+} > Cd^{2+} > Ni^{2+} > Mn^{2+} > Co^{2+}$. This order shows that the $K^{H^+}_{MHL^+}$ values of Co^{2+} and Mn^{2+} chelates, which are considered to have an octahedral structure, are lower than those of the Cu^{2+}, Ni^{2+}, and Cd^{2+} chelates, which have square planar, or tetrahedral structures. As is indicated in Figs. 9 and 10, in the BHQED-Cu^{2+} system the spectral change is not observed in the region from pH 3.1 to 6.0, but as the pH is increased above 6.0 the intensity of the band (max. 389 nm) increases with an increase in the pH and remains constant above pH 9.0. In the BHQED-Co^{2+} system, the absorption band changes gradually with the change of pH in the region from pH 2.0 to 4.0 and greatly at about pH 6.0. These facts indicate that the one-proton displacement reaction is not the dissociation of the proton from the coordinated water, but the dissociation of the proton from the free hydroxyl group in the quinoline ring. Moreover, with Cu^{2+}, the conversion of MHL^+ into ML does not occur with ease in the acid region from about pH 2.5 to 6.0 because the protonated chelate exists stably in this pH region as a square planar chelate by coordination of the Cu^{2+} ion with two imino nitrogens and phenolate oxygen. Above pH 6.0, this chelate rearranges to have a distorted octahedral structure by coordination with another phenolate oxygen and also by weaker coordination with two quinoline nitrogens in the fifth and the sixth positions above and below the plane. The reaction scheme is given in Chart 2. With Co^{2+}, the conversion occurs readily in a lower pH region than Cu^{2+}, because the Co^{2+} chelate tends to be arranged

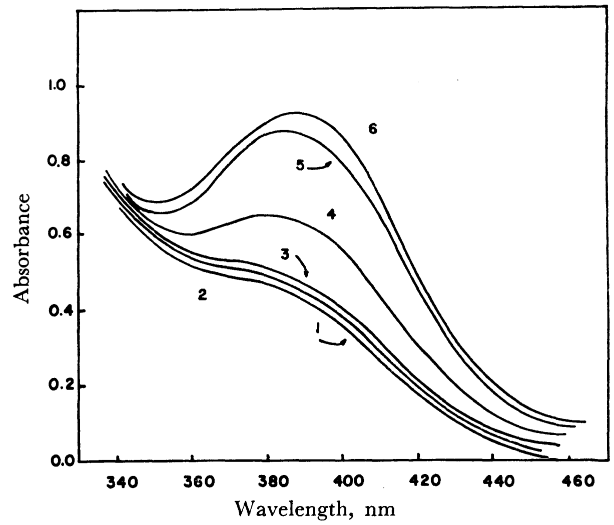

Fig. 9. Absorption spectra of BHQED-Cu^{2+} chelate at various pH in 50 v/v% aqueous dioxane solution; BHQED=$Cu^{2+}=2\times10^{-4}$ M; curve 1, pH 3.12; 2, 3.72; 3, 6.00; 4, 7.32; 5, 8.08; 6, 10.66.

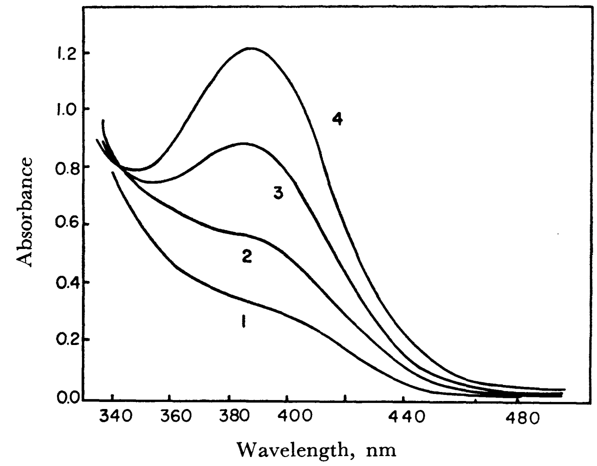

Fig. 10. Absorption spectra of BHQED-Co^{2+} chelate at various pH in 50 v/v% aqueous dioxane solution; BHQED=$Co^{2+}=2\times10^{-4}$ M; curve 1, pH 3.09; 2, 3.92; 3, 5.45; 4, 8.05.

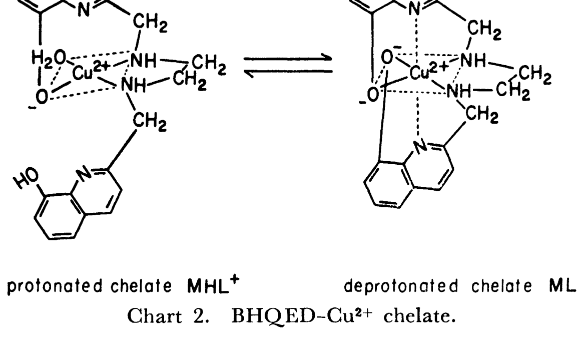

Chart 2. BHQED-Cu^{2+} chelate.

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[7] G. Schwarzenbach, *Helv. Chem. Acta*, **33**, 947 (1950).

Table 4. Comparison of stability constants of BHQED, HBED, EDAMP, and Trien metal chelates

Cation	BHQED log K_{ML}	HBED log K_{ML}	EDAMP log K_{ML}	Trien log K_{ML}	ΔK (BHQED-HBED)	ΔK (BHQED-EDAMP)	ΔK (BHQED-Trien)
Cu^{2+}	23.5	21.38	16.3	20.5	2.1	7.3	8.1
Co^{2+}	22.5	19.89	12.8	11.0	2.7	11.0	12.8
Ni^{2+}	18.8	19.31	12.7	14.1	−0.4	6.1	4.7
Cd^{2+}	22.0	17.52	9.9	10.0	4.5	12.1	12.0
Mn^{2+}	17.6	14.78	5.9	4.9	3.8	11.7	6.6

from the structure formed by coordination with three donor groups to a more stable octahedral structure by coordination with two imino nitrogens and phenolate oxygens and by equivalent coordination with two quinoline nitrogens in the fifth and the sixth positions above and below the plane. From the above discussion, it is clear that BHQED behaves as a sexadentate ligand toward metal ions.

This conclusion is supported by a comparison of the BHQED-metal chelate with triethylenetetramine (trien),[8] ethylenebis-(2-aminomethyl)pyridine (EDAMP)-,[9] and *N*,*N*′-di(2-hydroxybenzyl)ethylenediamine-*N*,*N*′-diacetic acid(HBED)[10]-metal chelates. The stability constants of these metal chelates are given in Table 4. From the increment of the stability constants of BHQED-metal chelates over the trien and EDAMP metal chelates seen in Table 4, the importance of the contribution of quinoline nitrogens to the stabilities of the chelates may be roughly estimated. The metal ions of a higher coordination number, Co^{2+}, Cd^{2+}, and Mn^{2+}, show a large increment of the stability for the BHQED-metal chelates, causing the more favorable steric arrangement of the quinoline nitrogens. On the other hand, the smaller increment observed for the Cu^{2+} ion indicates that these three ligands react with the Cu^{2+} ion to form a stable, square, planar chelate, although there is also a contribution of the quinoline nitrogens in the BHQED chelate, as is shown in Chart 3. Moreover, HBED acts as a sexadentate ligand toward metal ions in the same manner as does BHQED. With Cu^{2+}, HBED forms a stable, distorted, octahedral chelate by coordination with two amino nitrogens and two phenolate oxygens and by weaker coordination with two carboxylate oxygens in the fifth and the sixth positions above and below the plane. In fact, the stability constant of the BHQED-Cu^{2+} chelate is slightly higher than that of the HBED-Cu^{2+} chelate compared with that of the trien- and EDAMP-Cu^{2+} chelates.

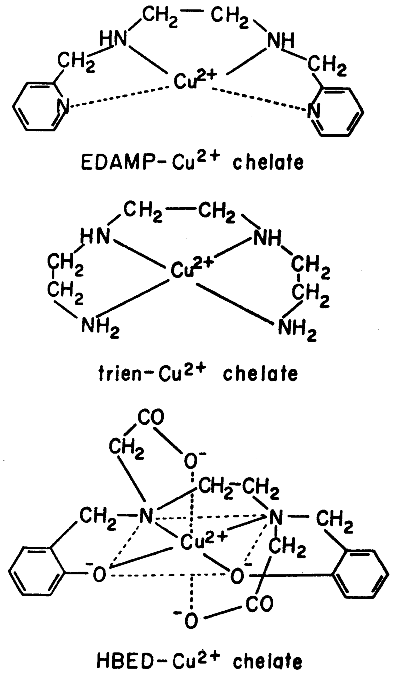

Chart 3. Cu^{2+} chelate of EDAMP, trien, and HBED.

The fact that BHQED forms the most stable chelates among various oxine derivatives is probably due to the sterically-favorable arrangement of bonds when all six donor groups of the ligand are involved in the coordination of metal ion.

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[8] F. Nakashima and K. Sakai, *Bunsekikagaku*, **10**, 89 (1961).

[9] R. G. Lacoste and A. E. Martell, *Inorg. Chem.*, **3**, 881 (1964).

[10] F. L'Epilattennier, I. Murase, and A. E. Martell, *J. Amer. Chem. Soc.*, **89**, 837 (1967).