Diprotonated Bimetallic Complex between Copper(II) with 3,3′-Bis[*N*,*N*-bis(carboxymethyl)aminomethyl]-*o*-cresolsulfonphthalein*

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(Received November 25, 1975)

The solution chemistry for complexes of copper(II) with 3,3′-bis[*N*,*N*-bis(carboxymethyl)aminomethyl]-*o*-cresolsulfonphthalein(XO) is studied by spectrophotometric measurement. Copper(II) is found to form a diprotonated bimetallic complex with XO in weakly acidic medium. Stability constant and molar absorptivity of the complex are evaluated to be log $K_{Cu_2LH_2}=9.86\pm0.05$ and $\varepsilon_{574\text{nm}}=3.73\times10^4$ M^{-1} cm^{-1}, respectively, at 25.0 °C and $I=0.1$ M. Thermodynamic parameters are calculated to be $\Delta H=4.3$ kcal·mol^{-1} and $\Delta S=64$ eu at 25.0 °C and $I=0.1$ M.

Xylenol Orange forms mononuclear 1 : 1, 1 : 2 or binuclear 2 : 2 complexes with various metal ions in solution.[1] Nickel(II) and cobalt(II) have been found to form mononuclear monoprotonated 1 : 1 complexes[2] in the presence of an excess of the metal ions to the ligand at pH 3.5—4.4.

However, copper(II) does not form mononuclear 1 : 1 complex but bimetallic 2 : 1 complex in the presence of an excess of the metal ion to the ligand at pH 3.5—5.5. In the present paper the anomalous behavior in copper(II) complex of XO is discussed in terms of the degree of protonation, the stability constant and the thermodynamic parameters of the bimetallic 2 : 1 complex. The structure of the complex is estimated, whose structure would give an important suggestion to the reaction mechanisms of complexation between XO and metal ions.[3,4]

Experimental

Materials. *Reagents*: All the chemicals used were of analytical grade, unless otherwise specified. Water was deionized and distilled.

Xylenol Orange: The acid from of the "*pure*" specimen[5,6] was used. 1.0×10^{-3} M stock solution of XO was prepared by weight. The solution was very stable in a refrigerator.

Copper(II) Perchlorate: Copper(II) perchlorate was prepared from recrystallized copper(II) chloride by heating with a small excess of perchloric acid. Perchlorate was further recrystallized twice from water. The solution was standardized by EDTA titration using PAN as indicator.

Sodium Perchlorate: The purified salt[2] was heated at *ca.* 200 °C to prepare anhydrous salt. The concentration of the solution was determined by weight. The ionic strength of the solution was adjusted to 0.1 M with the sodium perchlorate.

Buffer Solutions: They were prepared from 1.0 M acetic acid and 1.0 M sodium acetate.

Measurements. The equilibria of complexation were measured with a Hitachi 139 spectrophotometer at 574 nm of the maximum absorption for copper(II) complex. Absorption spectra were recorded with a Hitachi recording spectrophotometer Model EPS-3T. A 1-cm glass or quartz cell was used.

The pH values of the solutions were measured with a Radiometer pH Meter 4d (Copenhagen) equipped with a glass electrode Type G 202B and a saturated calomel electrode Type K 401. Temperature of the solution was maintained constant by circulating thermostated water from a Coolnics Model CTR-1B with a circulator CTE-1A.

Results

Absorption Spectra. Figure 1 shows the absorption spectra for the total concentrations of copper(II) and XO, $T_{Cu}=(0.40—1.20)\times10^{-4}$ M and $T_L=1.60\times10^{-5}$ M, at pH 4.308±0.005, at 25.0 °C and $I=0.1$ M.

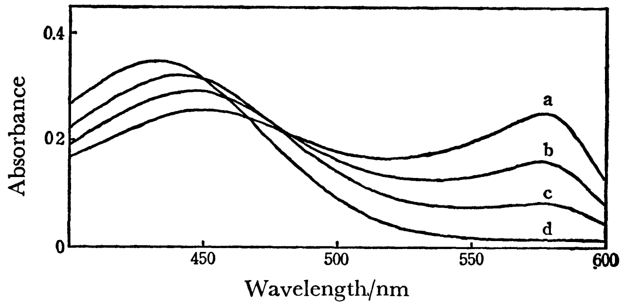

Fig. 1. Absorption spectra of copper(II) complex at various concentrations of copper(II).
T_{Cu}: a) 1.20×10^{-4} M, b) 2.00×10^{-5} M, c) 1.28×10^{-5} M, and d) 0 M. $T_L=1.60\times10^{-5}$ M. pH=4.308±0.005, $I=0.1$ M, 25.0 °C.

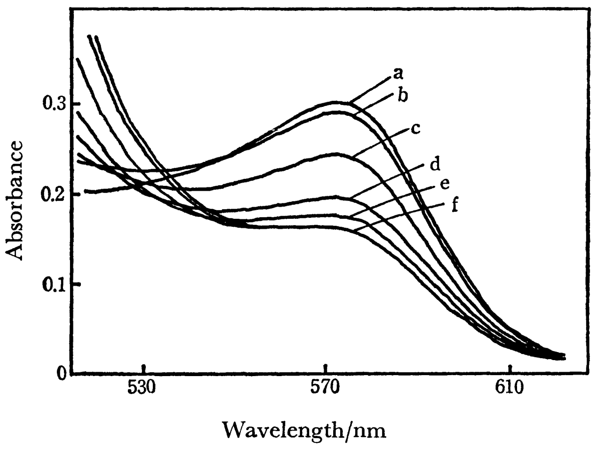

Fig. 2. Absorption spectra of copper(II) complex at various concentrations of XO.
T_L: a) 2.00×10^{-5} M, b) 3.00×10^{-5} M, c) 4.00×10^{-5} M, d) 6.00×10^{-5} M, e) 8.00×10^{-5} M, and f) 1.80×10^{-4} M. $T_{Cu}=4.00\times10^{-5}$ M. pH=4.284±0.024, $I=0.1$ M, 25.0 °C.

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* Presented in part at the 25th Annual Meeting on Coordination Chemistry, Tokyo, October 8, 1975, Abstract, p. 161.

The absorption maximum of copper(II) complex is 574 nm, while those of nickel(II) and cobalt(II) are 584 nm.[2] Surprisingly, there is only a little increase in the absorbance at the absorption maximum with the increase of the copper(II) concentration compared with the case of nickel(II) and cobalt(II) complexes with XO.[2] Figure 2 indicates that a successive reaction occurs for $T_{Cu}=8.00\times10^{-5}$ M and $T_L=(0.20—1.80)\times10^{-4}$ M at pH 4.284±0.024 and at 25.0 °C and $I=0.1$ M.

The Composition of the Complex. The method of molar ratio at 574 nm at pH 4.308±0.005 indicates that the complex species contains 2 copper(II) and 1 XO and that another species of different composition exists as expected in Fig. 2. The curve exhibits an inflection at lower mole fractions of copper(II) (Fig. 3).

Degree of Protonation, Molar Absorptivity and Stability Constant of the Bimetallic Complex. Figure 4 shows pH-dependence of the absorbance of Cu_2XO at 574 nm for $T_{Cu}=2.00\times10^{-4}$ and $T_L=1.60\times10^{-5}$ M at pH 3.458—5.498 at 25.0 °C and $I=0.1$ M. Under these conditions the ligand and the complex exist predominantly in the form of LH_3^{3-}[7] and Cu_2XO, respectively. So the following equilibrium is postulated for the copper(II) complex. (Charges on the metal and the ligand ions are omitted.)

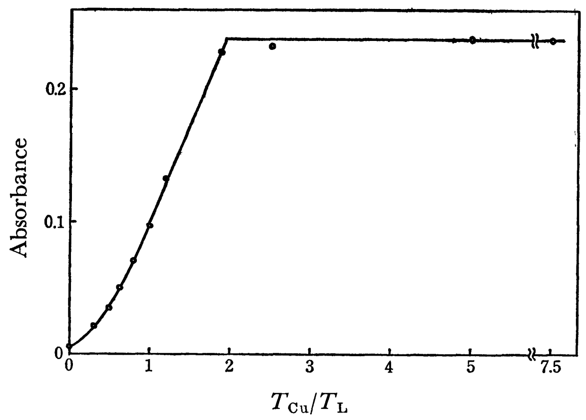

Fig. 3. Curve of molar ratio for copper(II) complex at 574 nm. pH=4.308±0.005, $I=0.1$ M, 25.0 °C.

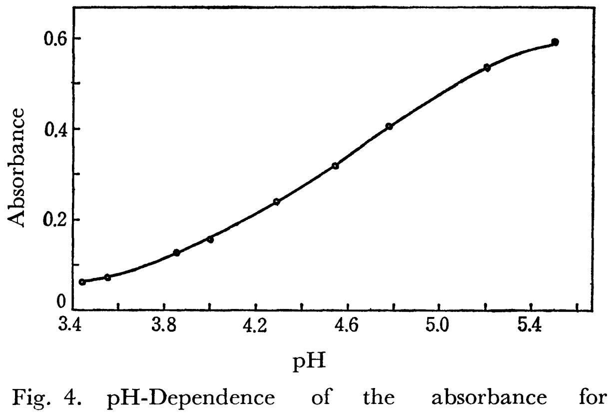

Fig. 4. pH-Dependence of the absorbance for copper(II) complex at 574 nm.
$T_{Cu}=2.00\times10^{-4}$ M and $T_L=1.60\times10^{-5}$ M. $I=0.1$ M, 25.0 °C.

$$2Cu + LH_3 \rightleftharpoons Cu_2LH_i + (3-i)H \tag{1}$$

Applying the law of mass action, we obtain

$$K = [Cu_2LH_i][H]^{3-i}/[Cu]^2[LH_3] \tag{2}$$

and the absorbance of the solution is given by

$$A = \varepsilon_L[LH_3] + \varepsilon_1[Cu_2LH_i], \tag{3}$$

where ε_L and ε_1 are molar absorptivities of LH_3 and Cu_2LH_i, respectively. Analytical concentrations of copper(II) ion and XO are

$$T_{Cu} = [Cu] + 2[Cu_2LH_i] \tag{4}$$

$$T_L = [LH_3] + [Cu_2LH_i]. \tag{5}$$

Combining Eqs. 2—5, and rearranging one leads to

$$\frac{T_L}{A-\varepsilon_L T_L} = \frac{1}{\varepsilon_1-\varepsilon_L} + \frac{[H]^{3-i}}{(\varepsilon_1-\varepsilon_L)K\left\{T_{Cu}-\dfrac{2(A-\varepsilon_L T_L)}{\varepsilon_1-\varepsilon_L}\right\}^2} \tag{6}$$

Under the experimental conditions, Eq. 6 is approximated to Eq. 6′

$$\frac{T_L}{A-\varepsilon_L T_L} = \frac{1}{\varepsilon_1-\varepsilon_L} + \frac{[H]^{3-i}}{\varepsilon_1-\varepsilon_L K T_{Cu}^2} \tag{6′}$$

The plot of $T_L/(A-\varepsilon_L T_L)$ against $[H]^{3-i}$ using the data obtained in Fig. 4 gives a straight line for $i=2$ for copper(II) complex (Fig. 5).

The complex is found to be the diprotonated bimetallic species Cu_2LH_2. The intercept gives 0.313×10^{-4} M cm. From this value and Eq. 6, the exact value 0.270×10^{-4} M^{-1} cm^{-1} is obtained by plotting $T_L/(A-\varepsilon_L T_L)$ against $[H]/\{T_{Cu}-2(A-\varepsilon_L T_L)/(\varepsilon_1-\varepsilon_L)\}^2$. ε_L is evaluated to be 300 M^{-1} cm^{-1} at 574 nm. The molar absorptivity at 574 nm is calculated to be $(3.70+0.03)\times10^4=3.73\times10^4$ M^{-1} cm^{-1} for Cu_2LH_2.

The stability constant of the complex Cu_2LH_2 is determined as follows,

$$2Cu + LH_2 \rightleftharpoons Cu_2LH_2 \tag{7}$$

$$K = [Cu_2LH_2]/[Cu]^2[LH_2] \tag{8}$$

$$A = \varepsilon_L' C_L + \varepsilon_1[Cu_2LH_2], \tag{9}$$

where ε_L' and C_L are the apparent molar absorptivity and the total concentration of the free XO, respectively. Total concentrations of copper(II) and XO are

$$T_{Cu} = [Cu] + 2[Cu_2LH_2] \tag{10}$$

$$T_L = C_L + [Cu_2LH_2] \tag{11}$$

and

$$C_L = [LH_2] + [LH_3] + [LH_4]. \tag{12}$$

Combination of Eqs. 7 to 12 and a rearrangement lead to

$$K = \frac{(A-\varepsilon_L' T_L)\alpha}{(\varepsilon_1-\varepsilon_L')\left\{T_{Cu}-\dfrac{2(A-\varepsilon_L' T_L)}{\varepsilon_1-\varepsilon_L'}\right\}^2\left(T_L-\dfrac{A-\varepsilon_L' T_L}{\varepsilon_1-\varepsilon_L'}\right)} \tag{13}$$

and

$$\alpha = 1 + K_1[H] + K_1K_2[H]^2 \tag{14}$$

$$LH_2 + H \rightleftharpoons LH_3;\quad K_1 = 10^{6.74\ 7)} \tag{15}$$

$$LH_3 + H \rightleftharpoons LH_4;\quad K_2 = 10^{2.85\ 7)} \tag{16}$$

The result is summarized in Table 1. The stability

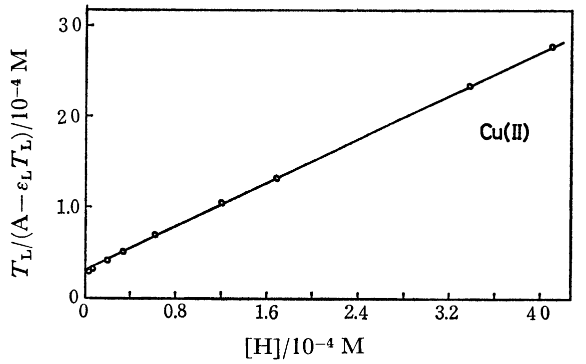

Fig. 5. Plot of $T_L/(A-\varepsilon_L T_L)$ for copper(II) complex against $[H]^{3-\iota}$ for $\iota=2$.

Table 1. Stability constant and molar absorptivity for Cu_2LH_2

pH	−log [H]	log *K*
3.458	3.377	9.91
3.552	3.471	9.89
3.854	3.773	9.86
4.000	3.919	9.83
4.288	4.207	9.81
4.548	4.467	9.81
4.778	4.697	9.84
5.204	5.123	9.91
5.498	5.417	9.85

av. $\log K=9.86\pm0.05$
$\varepsilon_{574\,\mathrm{nm}}=3.73\times10^4\ \mathrm{M^{-1}\,cm^{-1}}$

constant of the diprotonated bimetallic complex of copper(II) and XO is found to be $\log K=9.86\pm0.05$.

The thermodynamic parameters are spectrophotometrically determined for $T_{Cu}=8.00\times10^{-5}$ M and $T_L=1.60\times10^{-5}$ M and at 15.0, 20.0, 25.0 and 30.0 °C and I=0.1 M. Since the acid-association constants K_1's of XO at 15.0—30.0 °C are spectrophotometrically determined, the calculation of the stability constant $K_{Cu_2LH_2}$ is carried out at higher pH region where it is possible to neglect the concentration of LH^{2-1}. At the higher pH region, $\alpha=1+K_1[H]$.

$K_{Cu_2LH_2}$ is a little larger than 9.86. ΔH is determined to be 4.3 kcal·mol^{-1} by a graphical solution[8] of the following equation

$$\log K = (\Delta S-\Delta H/T)/2.303R$$

and

$$\begin{aligned}\Delta S_{298} &= (\Delta H-\Delta G)/T\\ &= (4.3+14.7)\times10^3/298\\ &= 64\ \text{e.u.}\end{aligned}$$

Discussion

Xylenol Orange forms mononuclear 1 : 1, 1 : 2 or binuclear 2 : 2 complexes with many metal ions but it is found that XO forms bimetallic 2 : 1 complex with copper(II) ion. Low stability constant of the 2 : 1 copper(II) complex implies the existence of a larger-membered chelate ring than five. Formation of the diprotonated complex species indicates that amine protons of XO do not dissociate but a phenolic proton dissociates on complexation. It is also supported by the fact that a bathochromic shift upon complexation between XO and metal ions is due to the dissociation of a phenolic proton.[9] Furthermore, the endothermicity of the complexation of copper(II) with XO ($\Delta H=4.3$ kcal·mol^{-1}) strongly supports that copper(II) atoms do not coordinate to the nitrogen atoms.[10]

As the amine proton does not dissociate in the experimental pH region, the copper(II) atom in the complex could not be in a plane of three oxygen atoms—a phenolic or a quinoidal and two carboxylic oxygen atoms, but would be a little above or below the plane. Therefore, the copper(II) atom could not take an octahedral or a square-planar structure but a more or less distorted tetrahedral structure.

The structure of Cu_2LH_2 with four nine-membered rings and two eight-membered rings is proposed (Fig. 6). The resonance stabilization due to the bimetallic structure of the complex may contribute to the stability of such structure.

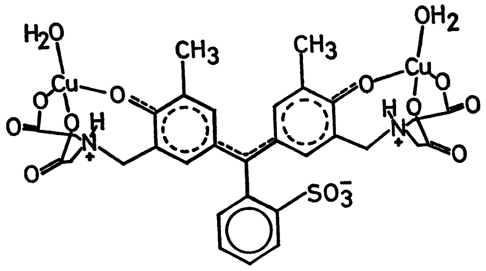

Fig. 6. Proposed structure of Cu_2LH_2 complex.

Despite of large-membered chelate rings, a large positive entropy 64 eu is obtained. It may be due to the reduction of the ordered arrangement of the inner-sphere water molecules around the reactant ions by the formation of the uncharged bimetallic species. The decrease in the coordination number of copper(II), presumably from six to four, also contributes to the positive entropy. The increase in entropy is sufficiently large to overcome the endothermicity of this complexation reaction.

The formation of large chelate rings is also kinetically supported:[4] The overall rate constant of the complex formation of copper(II) with XO is smaller approximately by 3 orders of magnitude than the value expected from the normal substitution reactions of aqua copper(II) ion. Therefore, the complexation reaction of copper(II) ion and XO is a sterically controlled substitution reaction.

The bimetallic diprotonated species Cu_2LH_2 shows reversible thermochromism at pH about 4. The aqueous solution containing $T_{Cu}=2.0\times10^{-4}$ M and $T_L=1.60\times10^{-5}$ M is orange at room temperature and changes reddish purple at about 70 °C and green at 77 K. The phenomena relate to the configurational change around the copper(II), which affects in turn the π-electron system of the coordinated XO. The thermochromism of Cu_2LH_2 would provide a support for the proposed structure of bimetallic complex Cu_2LH_2. The further details are now in progress.

The author should like to thank to Professor M. Fujimoto for general discussion and reading this manuscript and to Professor T. Ito for the valuable discussion on the configuration of the complex Cu_2LH_2.

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