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Equilibria of Complex Formation between Bivalent Metal Ions and 3,3′-Bis[*N*,*N*′-bis(carboxymethyl)aminomethyl]-*o*-cresolsulfonphthalein

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The complex formation equilibria between several bivalent metal ions and 3,3′-bis[*N*,*N*′-bis(carboxymethyl)-aminomethyl]-*o*-cresolsulfonphthalein (XO) have been investigated potentiometrically and spectrophotometrically. The metal ions studied here were Co(II), Ni(II), Cu(II), Zn(II), Pb(II), and Cd(II). The formation constants and visible-absorption-spectrum parameters of these metal complexes have been determined. It has been found that all these metal ions form 1: 1 and 2: 1 (metal: XO) complexes with XO. Moreover, the complex of each composition changes into one of several protonated ones depending on the pH of the solution. The probale structures of the complexes in solution are discussed.

Xylenol Orange (abbreviated as XO or H_6L; Formula I) forms stable and colored complexes with metal ions, and it has been widely used as an indicator in the chelatometric and spectrophotometric determinations of numerous metal ions.[1–5] However, despite many interesting findings concerning the solution chemistry of its metal complexes, serious discrepancies have often been noted among the data and/or conclutions reported by different authors. These discrepancies are primarily caused by the use of commercial or incompletely purified XO.[6] Recently, new methods for the purification of XO have been established,[6–9] pure XO has been used, in particular, in the investigation of the solution chemistry of XO. However, discrepancies among the data and conclusions reported seem to remain. The following two facts may be offered as explanations of this problem:

1) The metal complexes of XO have a visible absorption spectrum. The compositions and the stability constants of these complexes have, therefore, often been determined only by spectrophotometry.

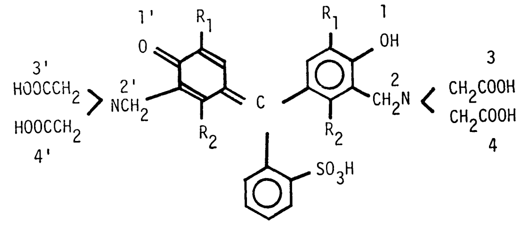
2) The XO molecule has two chelating groups on each side of its large sulfonphthalein nucleus, and each chelating group reacts with metal ions independently of the other;[3] hence, several complex species have various ratios of metal and XO.[3,5] Moreover, the complex of each component changes into different types of protonated or hydroxo complexes, depending on the pH of the solution.[10–12] The complex formation equilibria between metal ions and XO must, therefore, be complicated.

The change in the visible absorption spectrum of XO accompanying its complex formation is smaller than that of 3,3′-bis[*N*,*N*′-bis(carboxymethyl)aminomethyl]-thymolsulfonphthalein,[12–14] MTB, similar sulfonphthalein indicator (Formula I), and the difference in color between XO and its complexes, especially in neutral and alkaline solutions, not clearly distinguishable except in the case of metal ions with valences of 3 or more.[1,3,12] This may be due to differences in electron-donation effects of the substituent groups, R_1 and R_2, on the sulfonphthalein nucleus, as seen in Formula I.[15] Moreover, no clearly visible change in the spectrum is observable in the metal complex formation with sulfonphthalein indicators when the metal ions combine with coordinating donors other than phenolic or quinolic oxygen (1 or 1′ in Formula I).[10,12,14–21] In such a case, no information can be obtained spectrophotometrically. Also, most of the measurements have been limited to the narrow pH range of the solution (pH 3 to 6) in which the spectrum change is remarkable. The following points may be made regarding on investigation of XO chemistry in solution:

i) Measurement over a wide pH range should be under taken.

ii) The results by spectrophotometry should be compared with those obtained by other instrumental methods.

The present work is a study of the complex formation equilibria of XO with several bivalent metal ions in aqueous solutions over the pH range of 1 to 14 by spectrophotometry and potentiometry, refering to the results of research by ESR[22] and electrochemical (polarography and potential sweep voltametry)[23] techniques. The metal ions examined were Co(II), Ni(II), Cu(II), Zn(II), Pb(II), and Cd(II). The results obtained were compared with those reported by other authors: Co(II),[24] Ni(II),[24] Cu(II),[11,24,25] Zn(II),[26,27] Pb(II),[28] and Cd(II).[29]



	R_1	R_2
XO	CH_3	H
MTB	$CH(CH_3)_2$	CH_3

I XO or MTB

Experimental

Xylenol Orange. XO was synthesized and purified by cellulose-column chromatography and by ion exchange using the batch method, as has been described previously.[8,16] The product was the free acid form of XO, and the purity was nearly 100%, as measured by potentiometric titration with standard sodium hydroxide. This XO was weighed and dissolved in water in each experiment.

Metal Ion Solutions. The commercial perchlorate salt of each metal ion was dissolved in water without further purification. Each solution was standardized by EDTA titration.[1)]

The other reagents and apparatus for the potentiometric and spectrophotometric experiments were the same as have been described earlier.[14,16)] All the measurements were performed at 25±0.2 °C. The ionic strength of the solutions was maintained at 0.1 with sodium perchlorate. The pH values of the strongly acidic and alkaline media ($pH < ca.$ 1.5 and $pH > ca.$ 12) are difficult to measure by means of a pH meter using a glass electrode. The pH values of such media were determined directly from the concentrations of perchloric acid or sodium hydroxide, one of which was added to adjust the hydrogen ion concentrations, without account being taken of the activity coefficient.

Formation Constants. The formation constants of the complexes were calculated from the mass balances and the electroneutrality, utilizing the successive approximation method previously described in detail.[14–16)] The acid formation constants of XO used in the foregoing calculations were those determined previously[8)] ($\log k_i$: 12.23, 10.56, 6.74, 2.85, 2.32, and 1.5 from $i=1$ to 6 respectively).

Results

Complex Formation Equilibria. Potentiometric titrations of XO solutions containing 1 : 1, 2 : 1, and 3 : 1 molar ratios of Co(II), Ni(II), Cu(II), Zn(II), Pb(II), and Cd(II) to XO were performed (the molar ratios of the metal ion to the ligand will be, hereinafter, referred to as "1/1", "2/1", and "3/1"). The visible absorption spectra of the 1/1 and 2/1 solutions for each metal ion at different pH values (pH 1—14) were measured between 350 and 700 nm, and the variation in the spectrum with the pH was investigated.

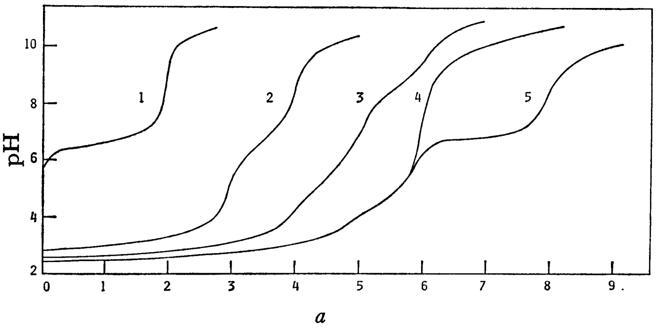


Fig. 1. Potentiomitric titration curves of Cu(II)–XO solutions.
1-Cu(II), 2-XO, 3, 4, and 5-1/1, 2/1, and 3/1 solutions, respectively. [XO]=about 1×10^{-3} mol/l and [Cu(II)] is varied.

Cu(II) Complexes. Figure 1 shows the foregoing titration curves for the Cu(II) complexes, together with the curves for the Cu(II) and XO solutions. The 1/1 Curve 3 exhibits three inflections at $a=4$, 5, and 6, indicating the formation of these three stable 1 : 1 complex species: CuH_2L^{2-}, $CuHL^{3-}$, and CuL^{4-}, where a is the number of moles of base added per mole of XO. The 2/1 Curve 4 shows two inflections at $a=$ 5 and 6 (the first one is not well-defined), probably with the formation of two 2/1 complexes, $CuHL^-$ and Cu_2L^{2-}, at the respective a values. The 3/1 Curve 5 is quite identical with the 2/1 Curve up to $a=6$, but beyond this a value up to $a=8$ there is a buffer region in which copper(II) hydroxide is precipitated; this precipatation reaction of copper(II) hydroxide is in the same pH range as when the Cu(II) aquo ion is hydrolyzed ($a=0$ to 2 on Curve 1). The 3/1 solution may, therefore, contain the free Cu(II) ion. The extent of the buffer region over two unit of a indicates that there exists one mole of free Cu(II) ion per mol of ligand in the 3/1 solution, and that not more than two Cu(II) ions can combine with one XO molecule.[14,16)]

The absorption spectra of the 1/1 and 2/1 solutions for Cu(II) at various pH values are shown in Figs. 2 and 3 respectively. The absorbances of these spectra at a given wavelength are shown as a funtion of pH in Fig. 4. The 1/1 solutions below pH 10 show two steps of change in their absorbance (Plot 1 in Fig. 4). The first step in the pH region from 4 to 6, and the second step, from 7 to 10. Moreover, an isosbestic point for

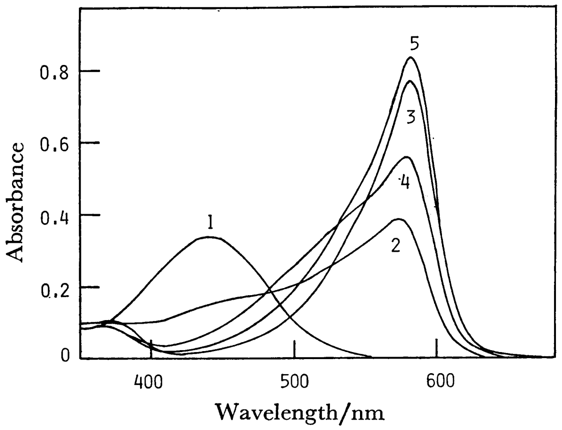


Fig. 2. Visible absorption spectra of 1/1 Cu(II)–XO solutions at various pH values.
pH: 1-2.75, 2-6.49, 3-11.20, 4-13.28, and 5-13.76.
[XO]=1.20×10^{-5} mol/l.

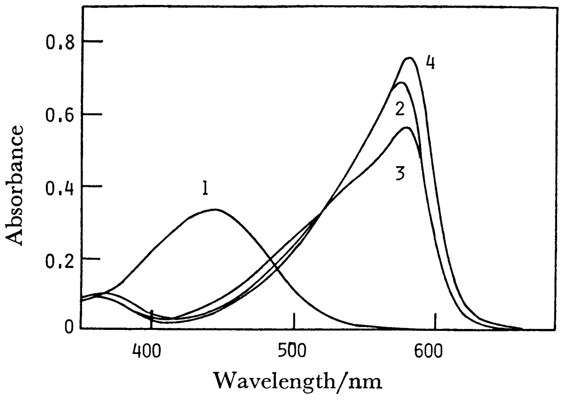


Fig. 3. Visible absorption spectra of 2/1 Cu(II)–XO solutions at various pH values.
pH: 1-2.62, 2-9.31, 3-13.42, and 4-13.57.
[XO]=1.20×10^{-5} mol/l.

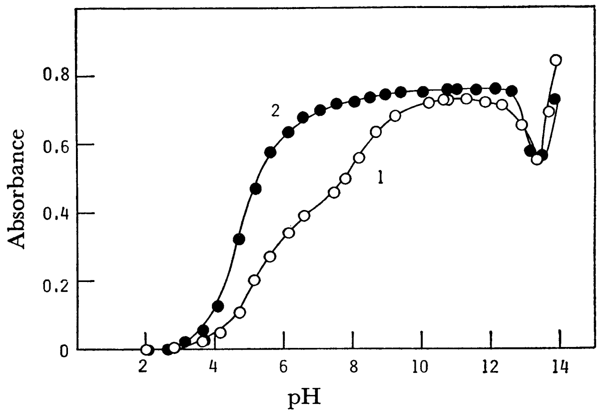


Fig. 4. Absorbances at 575 nm for Cu(II)-XO solutions as a function of pH.
1-1/1 and 2-2/1 solutions, respectively.
$[\mathrm{XO}]=1.20\times10^{-5}$ mol/l.

the spectra in each pH range was observed at 483 and 533 nm respectively (the intercept points of Spectra 1 and 2, and of Spectra 2 and 3, respectively in Fig. 2). These pH regions are similar to those for the buffer regions of the titration curve (Fig. 1) from $a=4$ to 5 and from $a=5$ to 6 respectively. In addition, for the following reaction:

$$\mathrm{CuH}_i\mathrm{L}^{-4+i} \rightleftarrows \mathrm{CuH}_{i-n}\mathrm{L}^{-4+i-n} + n\mathrm{H}^+$$

$$K^{n\mathrm{H}}_{\mathrm{MH}_i\mathrm{L}} = \frac{[\mathrm{CuH}_i\mathrm{L}]}{[\mathrm{H}]^n[\mathrm{CuH}_{i-n}\mathrm{L}]}.$$

The plot of $\log\{[\mathrm{CuH}_i\mathrm{L}]/[\mathrm{CuH}_{i-n}\mathrm{L}]\}$ *vs.* pH[30] gave a straight line with a slope of $n=1$ for each step of the absorbance change, as is seen in Fig. 5 for the proton dissociation from $\mathrm{CuH_2L^{2-}}$. The value of each $K^{\mathrm{H}}_{\mathrm{CuH}i\mathrm{L}}$ for $i=1$ and 2 was evaluated from the pH value when the log term was equal to zero (Table 1). In the 1/1 solutions, the formation of the three complex species $\mathrm{CuH_2L^{2-}}$, $\mathrm{CuHL^{3-}}$, and $\mathrm{CuL^{4-}}$ may be complete around pH 3, 6.5, and 11 respectively, taking into account the change in their absorbance (Fig. 4). Spectra 1, 2, and 3 in Fig. 2, therefore, may correspond to the foregoing complex species. The wavelength, $\lambda_{\max}$, and the absorptivity, ε, for the maximum absorbance of the spectrum attributed to each complex species were also determined (Table 2).

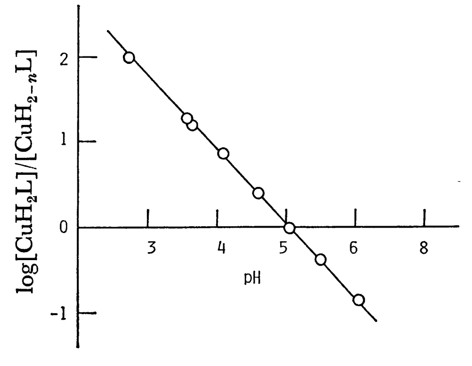


Fig. 5. Plot of $\log\{[\mathrm{CuH_2L}]/[\mathrm{CuH}_{2-n}\mathrm{L}]\}$ *vs.* pH.
Wavelength: 575 nm.

The 2/1 solutions show a single step of change in their visible absorbance below pH 8 (Plot 2 in Fig. 4), and the isosbestic point was at 486 nm for the spectra in this pH range (the intercept point of Spectra 1 and 2 in Fig. 3). The plot of $\log\{[\mathrm{Cu_2H}_i\mathrm{L}]/[\mathrm{Cu_2H}_{i-n}\mathrm{L}]\}$ *vs.* pH showed a straight line, with a slope of $n=1$. The pH region for the change in this absorbance may correspond to that from $a=5$ up to 6 (Curve 4 in Fig. 1). These facts suggest that a mono-protonated complex, $\mathrm{Cu_2HL^-}$, is almost complete around pH 3 (its corresponding spectrum may be seen in Curve 1 in Fig. 3). The change in the spectrum from pH 3 to 7 may be accompanied by a proton dissociation from $\mathrm{Cu_2HL^-}$.

Below pH 3, no remarkable change in the spectrum as a function of pH is observed, and no observable inflections are seen on the titration curves. However, the spectra of both the 1/1 and 2/1 solutions at pH 2—3 are at slightly longer wavelengths than that of the XO solutions of the same pH (*i.e.*, $\lambda_{\max}$ and ε for the XO, 1/1 and 2/1 solutions are 439, 443, and 443 nm, and 2.62, 2.75, and 2.75×10^4 l mol^{-1} cm^{-1}, respectively). The results of the mole-ratio method at pH 2—3 showed the existence of the 1: 1 and 2: 1 complex species, as may be seen in Plots 1 and 2 in Fig. 9. (The results of the mole-ratio methods will be discussed below in more detail.) The ESR spectra of the 1/1 solutions indicated the existence of stable 1: 1 complex species down to around pH 1.[22] This fact suggests that more highly protonated complex species, *i.e.*, $\mathrm{CuH}_i\mathrm{L}^{-4+i}$ ($i\geqslant3$), may be formed in such acidic solutions.[12,14] Around pH 1, the ESR spectra consisted of two overlapping lines attributed to the 1: 1 complex species and the Cu(II) aquo ion. Below pH 1, the spectra showed one line attributed to a Cu(II) aquo ion, indicating that the 1: 1 complex species $\mathrm{CuH}_i\mathrm{L}^{-4+i}$ dissociates to a Cu(II) ion and $\mathrm{H_6L}$ in such strongly acidic solutions. The ESR spectra of the 2/1 solutions around pH 4 showed the existence of the 2: 1 complex species, but around pH 2—3 they consisted of three overlapping lines, attributed to the 2: 1 and 1: 1 complex species, and a Cu(II) aquo ion. Around pH 1 the ESR spectra consisted of two lines attributable to the 1: 1 complex species and Cu(II) aquo ion. These facts indicate that the 2: 1 complex species, $\mathrm{Cu_2HL^-}$, begins to dissociate to $\mathrm{CuH}_i\mathrm{L}^{-4+i}$ and the Cu(II) aquo ion as the pH decreases from 3, its dissociation being complete around pH 1.

Above pH 13, the visible absorbances for both 1/1 and 2/1 solutions decrease and exhibit their minimum value at almost the same pH value (*ca.* 13.2); they then increase beyond this pH value, as are seen of Spectra 3, 4, and 5 in Fig. 2 and Spectra 2, 3, and 4 in Fig. 3 for the 1/1 and 2/1 solutions respectively and in Plots 1 and 2 in Fig. 4. No precipitate of the copper(II) hydroxide was observed in the solutions. The spectra for both 1/1 and 2/1 solutions around pH 14 are quite identical with that of the XO solutions around this pH value. The ESR spectra of the 2/1 and 1/1 solutions around pH 13.2 suggested the existence of hydroxo complex species of Cu(II) with XO, while those around pH 14 were similar to that of the tetrahydroxocuprate-

(II) ion, $Cu(OH)_4{}^{2-}$. These findings suggest that both the 1 : 1 complex, CuL^{4-}, and the 2 : 1 complex, Cu_2L^{2-}, dissociate to $Cu(OH)_4{}^{2-}$ and L^{6-} through an intermediate hydroxo complex species,[12,14,15,17,19,21] such as $Cu(OH)L^{5-}$ and $[Cu(OH)]_2L^{4-}$.

Co(II), Ni(II), Zn(II), and Pb(II) Complexes. These metal complexes showed similar types of titration curves and changes in the spectra with pH value. Accordingly, the Zn(II) system will be discussed. The 2/1 and 3/1 solutions behaved similarly in their titration curves and their spectra to the Cu(II) system. However, two 1/1 titration curves for Zn(II) have the inflections, at $a=4$ and $a=5$, although the Cu(II) 1/1 curve has three inflections, at $a=4$, $a=5$, and $a=6$, as are seen in the 1/1 Curve 3 in Fig. 1. These facts suggest that the formations of their 1 : 1 complexes, MH_2L^{2-} and MHL^{3-}, are complete at the respective a values, but that the dissociation of a proton from MHL^{3-} occurs in more alkaline solutions at $a>5$. The 1/1 solution for Zn(II) showed only one step of change in the absorbance below pH 9. However, the absorbances decreased slightly from about pH 9 up to 11. This change may correspond to the dissociation of a proton from the MHL^{3-} complex. Both 1/1 and 2/1 solutions for the Zn(II) complexes showed a minimum absorbance at 12.5, as high as was observed in the Cu(II) system (Fig. 4).

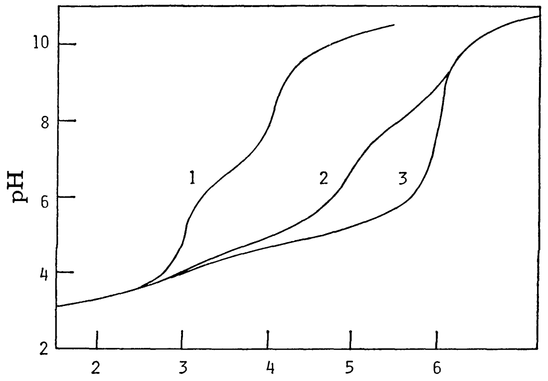


Fig. 6. Potentiometric titration curves of Cd(II)–XO solutions.
1-XO, 2-1/1, and 3-2/1 solutions, respectively.
[XO]=about 1×10^{-3} mol/l.

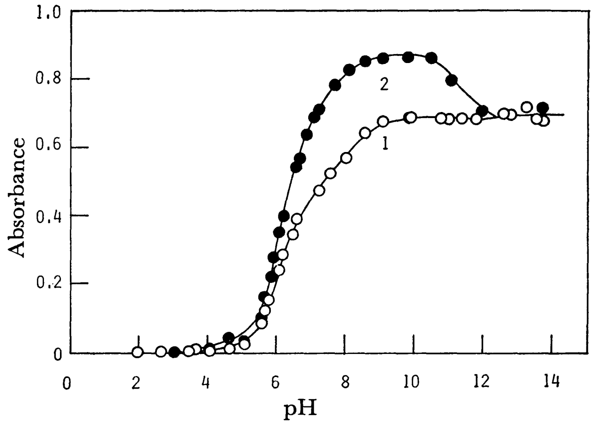


Fig. 7. Absorbances at 575 nm for Cd(II)–XO solutions.
1-1/1 and 2-2/1 solutions.
[XO]=1.20×10^{-5} mol/l.

These foregoing findings suggest that complex formation equilibria similar to those as found in the Cu(II) and XO system are also involved in both 1/1 and 2/1 (or 3/1) solutions of Co(II), Ni(II), Zn(II), and Pb(II), although the complex formation and proton dissociation reactions occur in different pH regions (see Table 1).

Cd(II) Complexes. Both the 1/1 and 2/1 titration curves for Cd(II) are identical to that for the XO solution up to around $a=3$ (Curves 1, 2, and 3 in Fig. 6). Cd(II), therefore, may not react with XO species, H_iL^{-6+i} ($i\geqslant3$),[8] in acidic media (pH 4). Beyond about $a=3$, these curves differ from that for XO and are terminated by an inflection at $a=5$ and $a=6$ for the 1/1 and 2/1 solutions respectively, indicating the formations of complex species, $CdHL^{3-}$ and Cd_2L^{2-}, at each a value. The 1/1 curve beyond $a=5$ is similar in type to that for Cu(II). The 1/1 solution showed two steps of change in the absorbance as a function of pH below 10, as is seen on Plot 1 in Fig. 7. The first step is from pH 4 to 7. The 1/1 curve shows the similar pH value between $a=3$ and 5. Accordingly, this change in absorbance may be ascribed to the complex formation of $CdHL^{3-}$. The plot of $\log\{[CdH_{3-n}L]/[H_3L]\}$ *vs.* pH gave a straight line with a slope of $n=2$ (XO exists as the H_3L^{3-} species in this pH region[8]), which suggests that a protonated complex, such as CdH_iL^{-4+i} ($i\geqslant2$), may not exist, and the complex formation reaction involved in the 1/1 solution from around $a=3$ to 5 may be as follows:

$$Cd^{2+} + H_3L^{3-} \rightleftarrows CdHL^{3-} + 2H^+.$$

The change in absorbance from pH 7 to 10 may correspond to the dissociation of a proton from $CdHL^{3-}$.

Up to about pH 6 the 2/1 solutions showed spectra almost identical with those of the 1/1 solutions (Fig. 7). In addition, the 2/1 titration curve is very similar in pH value to the 1/1 curve up to around $a=5$. These findings suggest that Cd(II) does not form the 2 : 1 complex until around pH 6. Beyond this pH value the 2/1 spectra differed from the 1/1 spectra. The change in the absorbance of the 2/1 solution from pH 4 to 6, therefore, may be accompanied by the formation of the 1 : 1 complex, $CdHL^{3-}$, while the change above pH 6 may be attributed to the formation of the 2 : 1 complex. The plot of $\log\{[CdH_iL]/[CdHL]\}$ *vs.* pH from 6 to 10 showed a straight line with a slope of $n=1$. Accordingly, the 1 : 1 protonated complex of Cd(II) does not exist until about pH 6, and the reaction involved in the 2/1 solution from pH 6 to 10 may be indicated as follows:

$$Cd^{2+} + CdHL^{3-} \rightleftarrows Cd_2L^{2-} + H^+.$$

Discussion

Problems in the Determination of the Complex Composition by Spectrophotometry. Otomo,[24,29] Hung *et al.*,[25] Studlar *et al.*,[26] Miyazima,[27] and Marchenko[28] have

TABLE 1. FORMATION CONSTANTS OF XO COMPLEXES AT 25 °C AND $\mu=0.1$ ($NaClO_4$)

Reaction		log *K*					
		Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Pb(II)
$M^{2+}+L^{6-} \rightleftharpoons ML^{4-}$	K_{ML}	12.63	12.37	12.52	13.41	9.67	13.68
$M^{2+}+HL^{5-} \rightleftharpoons MHL^{3-}$	K_{MHL}	10.58	10.52	10.54	10.44	7.84	11.63
$M^{2+}+H_2L^{4-} \rightleftharpoons MH_2L^{2-}$	K_{MH_2L}	4.64	4.84	4.99	4.55		5.39
$H^++ML^{4-} \rightleftharpoons MHL^{3-}$	K^H_{MHL}	10.18	10.38	8.15	9.27	8.03	10.08
				(8.21)		(7.96)	
$H^++MHL^{3-} \rightleftharpoons MH_2L^{2-}$	$K^H_{MH_2L}$	4.62	4.88	5.01	4.56		4.32
		(4.76)	(4.61)	(5.05)	(5.21)		(4.36)
$M^{2+}+ML^{4-} \rightleftharpoons M_2L^{2-}$	K_{M_2L}	11.61	11.36	11.43	11.63	8.54	12.45
$M^{2+}+MHL^{3-} \rightleftharpoons M_2HL^-$	K_{M_2HL}	5.43	5.18	7.58	6.96		6.47
$H^++M_2L^{2-} \rightleftharpoons M_2HL^-$	$K^H_{M_2HL}$	4.4	4.2	4.3	4.6		4.1
		(4.66)	(4.49)	(4.68)	(4.91)		(4.22)

Data in parentheses measured by spectrophotometry; the rest, by pH titration.

TABLE 2. THE WAVELENGTH AND ABSORPTIVITY AT THE MAXIMUM ABSORBANCE OF EACH COMPLEX SPECIES FOR BIVALENT METAL COMPLEXES WITH XO

Complex species	λ_{max}/nm						$\varepsilon/10^4$ l mol^{-1} cm^{-1}					
	Co	Ni	Cu	Zn	Pb	Cd	Co	Ni	Cu	Zn	Pb	Cd
MH_iL^{-4+i} ($i \geq 3$)	435	445	443	435	440							
MH_2L^{2-}	435	445	443	435	440		2.83	2.75	2.75	2.58	2.42	
MHL^{3-}	580	583	577	573	573	578	6.57	7.83	3.83	5.50	3.92	4.16
ML^{4-}	580	582	582	575	575	585	5.54	6.25	6.43	5.08	3.75	6.33
M_2HL^-	435	445	443	440	443		2.83	2.43	2.75	2.57	2.41	
M_2L^{2-}	587	585	578	574	578	578	8.75	9.58	6.42	7.58	7.50	7.42

concluded, from the results of the mole-ratio method and the continuous variation method, that Co(II),[24] Ni(II),[24] Zn(II),[26,27] Pb(II),[28] and Cd(II)[29] form only 1: 1 complexes with XO in weakly acidic solutions (around pH 5.5—6.5). On the other hand, Yamada and Fujimoto[11] have concluded, from the results of the mole-ratio method using spectrophotometry, that Co(II) and Ni(II) form only 1: 1 complexes at pH 3.5—4.5, but for Cu(II) only the 2: 1 complexes are formed at pH 3.5—4.5. In the present work, it has been found that all these metal ions form both 1: 1 and 2: 1 complexes in all the solutions from acidic to alkaline pH. The same conclusions as offered here have been reported from the studies by ESR[22] and electrochemical[23] techniques. Thus, there are serious discrepancies among the results by different authors. Some authors[24–29] used commercial XO without further purification. However, Yamada and Fujimoto[11] used pure XO,[6,9] and so the different results might be caused not only by the purity of the XO used, but also by the experimental method.

The present results from the continuous variation method for Cu(II), Zn(II), and Cd(II) complexes in weakly acidic solutions are shown in Fig. 8. The individual plot at a given wavelength in the continuous variation method indicates the formation of either a 1: 1 or 2: 1 complex for each metal ion; that is, the plots at 574, 570, and 578 nm for Cu(II), Zn(II), and Cd(II) respectively in Fig. 8 exhibit an inflection at [M]/([M]+[XO]) =2/3, but the plots at 498, 510, and 500 nm for these same metal ions show an inflection at 1/2. These facts indicate that the different conclusions are reached regarding the compositions of the complexes, depending on the wavelength used, in spite of testing the same metal ion at the same pH. The results of the mole-ratio method at various pH values for the Cu(II) system are shown in Fig. 9. The individual plot at a given pH exhibits either one inflection or two at [M]/[XO] = 1 and/or 2, depending on the pH of the solution.

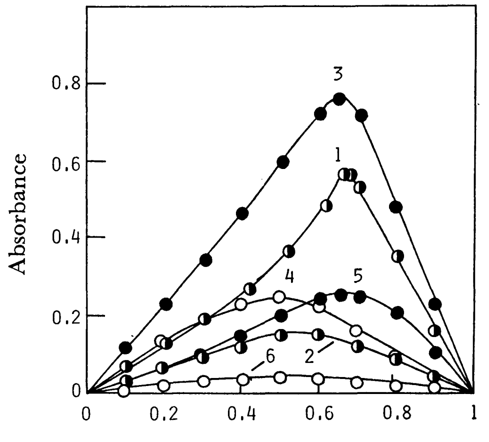


Fig. 8. Continuous variation method for Cu(II), Zn(II), and Cd(II) complexes with XO.
Cu(II): 1-574 and 2-498 nm at pH 5.86, Zn(II): 3-570 and 4-510 nm at pH 5.89, Cd(II): 5-578 and 6-500 nm at pH 6.20. [M]+[XO]=4.0×10^{-5} mol/l.

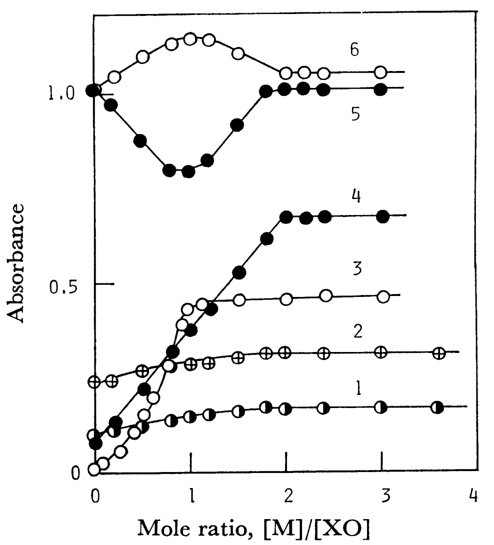


Fig. 9. Mole ratio method for Cu(II) complexes with XO at various pH values.
pH: 1-1.95, 2-3.12, 3-4.45, 4-5.58, 5-7.80, and 6-10.36.
Wavelength: 1-480, 2-500, 3-575, 4-540, 5-575, and 6-582 nm.

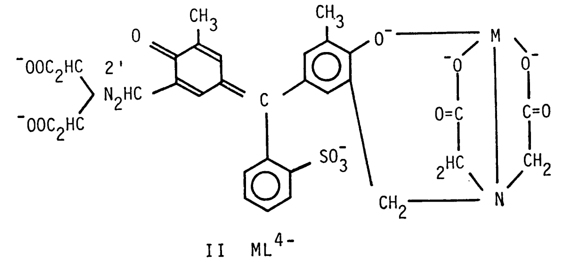
One of the explanations for this problem is that the 1: 1 and the 2: 1 complexes of XO formed in solutions of the same pH have absorption maxima at the same wavelength and differ only in absorptivity, as seen in Table 2. The complex of each component changes into a different type of protonated or hydroxo complex, therefore, the absorptivity, $\bar{\varepsilon}_1$ or $\bar{\varepsilon}_2$, is defined as $\bar{\varepsilon}=\sum\varepsilon_i x_i$ to express the apparent absorptivity of each component. ε_i and x_i are the absorptivity and the molar fraction of the complex species i, and the summation is performed on all the complex species of the same component which exist in the solution of a given pH. The subscript 1 or 2 indicates the 1: 1 or 2: 1 complex. The results of the mole-ratio method may be divided into the following three groups in terms of the relationship between $\bar{\varepsilon}$ and inflections on the plots:

(i) two inflections at [M]/[XO] = 1 and 2 when $\bar{\varepsilon}_1 \neq \bar{\varepsilon}_2$.
(ii) one inflection at 1 when $\bar{\varepsilon}_1=\bar{\varepsilon}_2$.
(iii) one inflection at 2 when $2\bar{\varepsilon}_1=\bar{\varepsilon}_2$.

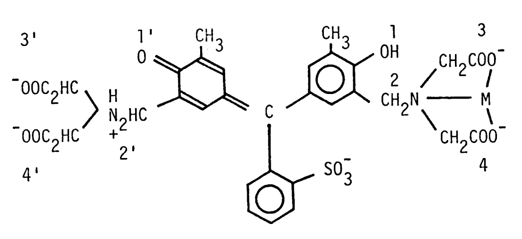
The 1, 2, 5, and 6 plots in Fig. 9 may be explained by (i), the 3 plot by (ii), the 4 plot by (iii). Accordingly, caution should be taken in determining the composition of the metal complexes with XO by spectrophotometry.

Arrangement of the Complex. The changes in the visible absorption spectrum of XO, accompanied by proton dissociation and/or complex formation, may be due to a change in the π-electron structure of its sulfonphthalein nucleus. Thus, the proton dissociation from the phenolic hydroxyl group (1 in Formula I) and the coordination of the phenolic (1) and/or quinolic oxygen (1′) lead to an important change in the absorption spectrum (the number in parentheses after the donor of the XO molecule, hereinafter, will refer to the donor, as indicated by its number in Formula I). Based on the visible absorption parameters, a discussion has been made of the coordination of the individual donor of XO, which is involved in the complex formation and/or in the proton dissociation from the acid group of the XO molecule of the protonated complex.

ML^{4-} dissociates all of the available protons; therefore, the arrangement of the complex may be presented as in Formula II. The mono-protonated complex, MHL^{3-}, dissociates its proton in alkaline solutions (with pH values of from 8 to 10.5, as seen in its acid dissociation constant in Table 1). In addition to this, the conversion from MHL^{3-} to ML^{4-} is accompanied by a slight change in ε, but almost no change in λ_{max} (Table 2). The protonated nitrogens (2 and 2′) of XO dissociate their protons in alkaline solutions, accompanied by a slight change in ε, but almost no change in λ_{max}.[8] Accordingly, the proton in MHL^{3-} may dissociate from the uncoordinating nitrogen (2′) in Formula II. The conversion from MH_2L^{2-} to MHL^{3-} accompanies the blue shift in the spectrum from around 440 to around 580 nm. This fact suggests that its proton dissociation is from phenolic oxygen (1) and that the coordinating donor involved in this reaction is the phenolic oxygen. MH_2L^{2-} exists in a weakly acidic medium. The uncoordinating phenolic oxygen (1) of XO in the MH_2L^{2-} complex would be protonated in such media, considering its p*K* value.[8] These considerations suggest the arrangement for the MH_2L^{2-} complex indicated in Formula III. The highly protonated complex species, H_iL^{-4+i} $(i \geqslant 3)$, which are thought to exist in an acidic solution (pH 1—4), have λ_{max} around 440 nm. No remarkable change in the spectrum on its complex formation was observed, as has been mentioned above. In strongly acidic solutions with pH values from 1 to 2, carboxylic groups (3′ and 4′), which are not coordinated to metal ions, may be protonated based on their p*K* values.[8] Accordingly, the maximum value of i may be 4; that is, the four protons in MH_iL^{-4+i} $(i=4)$ may be attached to two carboxylic oxygens (3′ and 4′) and the phenolic oxygen (1) and the amino nitrogen (2′)[12] in Formula III.



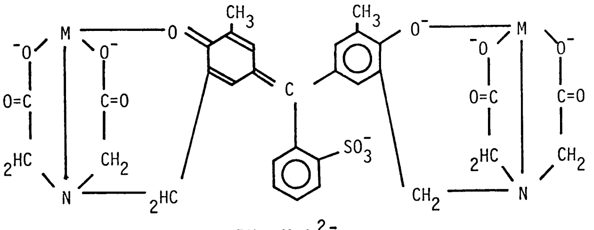
II ML^{4-}



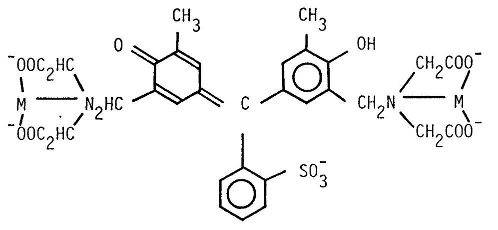
III MH$_2$L^{2-}

M_2L^{2-} dissociates all of the available protons; therefore, its arrangement may be offered as Formula IV. The spectra corresponding to the mono-protonated 2: 1

complex, M_2HL^-, for each metal ion have λ_{max} values of 435 to 445 nm and ε of 2.41 to 2.83×10^4 l mol^{-1} cm^{-1} respectively. There is not much difference in the spectra between this complex species and the XO species, H_iL^{-6+i} (i=3 to 6) the phenolic oxygen (1) of which is protonated, while its quinolic oxygen (1′) is not protonated (H_iL, i=3 to 6: λ_{max}=439—434 nm, ε=2.62×10^4 l mol^{-1} cm^{-1}). These facts suggest that neither phenolic nor quinolic oxygens coordinate to metal ions; the arrangement indicated in Formula V is suggested for M_2HL^-.



IV M_2L^{2-}



V M_2HL^-

Yamada *et al.*[11] have established the existence of the diprotonated 2:1 complex, Cu_2H_2L, at pH 3.5—5.5 from their spectrophotometric investigation. They have proposed that the phenolic and quinolic oxygens (1 and 1′) coordinate with Cu(II), but that the amino nitrogens (2 and 2′) do not coordinate and the nitrogens are protonated. Such a structure is, however, contradictory to the following two facts: i) If the Cu_2H_2L is formed at pH 3.5—5.5, the two protons might dissociate at a higher pH. However, the 2/1 titration curve indicates only one proton dissociation above pH 5.5. ii) Iminodiacetic acid, H_2L, forms ML with Cu(II) in weakly acidic media, and all the available protons in this ligand dissociate completely by pH about 5.[31] These facts suggest that all the donors of the bis(carboxymethyl)aminomethyl group in an XO molecule may coordinate to a Cu(II) ion in such weakly acidic solutions as are indicated in Formulas III and V for the MH_2L^{2-} and M_2HL^- complexes.

It is interesting to investigate whether the phenolic (or quinolic) oxygen (1 or 1′) coordinates to metal ions at a lower or higher pH than the amino nitrogen (2 or 2′). Among the metal complexes with SXO,[32] XO, SMTB,[33] MTB, and SGCR,[34] metal ions are, in general, divided into two groups in terms of the foregoing point: 1) Alkaline earth metal ions[10,18] and trivalent metal ions, such as Fe(III),[12] Cr(III),[21] and Al(III),[19] are coordinated by their phenolic oxygen at a lower pH than by their amino nitrogen. 2) Bivalent metal ions,[14—17,20] such as Co(II), Ni(II), Cu(II), Zn(II), Pb(II), and Cd(II), are coordinated by the amino nitrogen at lower pH and by the phenolic oxygen at higher pH. The metal ions of group (1) are hard metal ions, while those of group (2) are intermediate or soft metal ions, according to the hard and soft acid and base (HSAB) theory.[35,36] The phenolic oxygen, therefore, has more affinity to harder metal ions, and the amino nitrogen, to softer metal ions, in complexation in aqueous solutions.

Formation Constants. The formation constants were calculated utilizing the suceissive approximation method;[14,16] they are listed in Table 1. The formation constants of XO complexes with these metal ions have been determined by many authors. They have, however, assumed that only one reaction was involved in the solutions, as indicated in either of following equations:

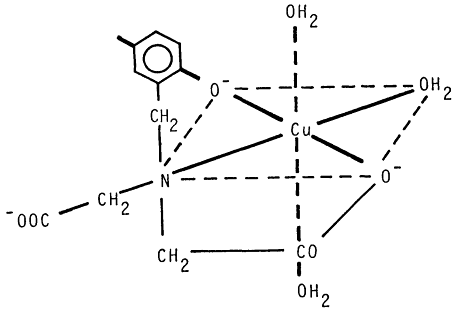
i) $M^{2+} + L^{6-} \rightleftharpoons ML^{4-}$: Refs. 24—29.

ii) $2M^{2+} + H_2L^{4-} \rightleftharpoons Cu_2H_2L$: Ref. 11.

However, several reactions may be assumed to be involved, as has been determined above. This may be one reason why there are discrepancies among the formation constants calculated by the different authors. The present formation constants were calculated by taking all the probable reactions involved into account.[14,16]

The stabilities of the complexes in aqueous solutions frequently observed for the ligands, which coordinate to metal ions through oxygen and/or nitrogen donor atoms, follow this sequence: i) Co(II)<Ni(II)<Cu(II)> Zn(II) and ii) Pb(II)>Zn(II)> Cd(II). The stabilities of the XO complex species, ML^{4-}, MHL^{3-}, and M_2L^{2-}, do not follow this sequence, but that of MH_2L^{3-} does. The relative stabilities of the former three complex species for Cu(II) is considered to be lower than would be expected from the foregoing sequence. XO has two chelating groups on each side of the sulfonphthalein nucleus, consisting of phenolic (1) or quinolic (1′), amino (2 or 2′), and two carboxylic oxygens (3 and 4 or 3′ and 4′). In general, XO might act as a branched tetradentate ligand centered on the nitrogen atom. Such ligands prefer a regular octahedral or tetrahedral structure rather than a planar or tetragonal structure arising from elongation along an axis.[37] However, Cu(II) frequently forms complexes with the latter structure.[38,39] Accordingly, either of the following interpretations for the relative instabilities of the XO complexes for Cu(II) may be suggested: (i) If all of the four donor atoms of each chelating group were coordinated to such a structure, the complexes would be distorted into a lower symmetry or converted into a more regular octahedral one, resulting in the Jahn-Teller destabilization.[37,39] (ii) If the Cu(II) complexes keep a planar or tetragonal structure, it may be sterically impossible for one of the three branching donor atoms, *i.e.*, phenolic oxygen (1 and/or 1′), two carboxylic oxygens (3 and 4 and/or 3′ and 4′), to coordinate into a *trans* coordination site of the Cu(II) ion, in which another *trans* site is coordinated by the central nitrogen atom (2 and/or 2′), because it is too far away from it.[14,17] Therefore, each chelating group of XO would act as a tridentate ligand, resulting in a decrease in the chelate effects.[39]

The relative instability of the Cu(II) complexes among the bivalent first transition metal ions has also been observed in other sulfonphthalein indicators, such as SXO,[15] MTB,[14] SMTB,[17] and SGCR.[20] Spectrophotometric and ESR studies of the Cu(II)-SXO complex[15] have suggested that the instability of this complex is explained by the foregoing interpretation (ii) and that the tetradentate ligand SXO acts as a tridentate one to Cu(II), to which one of the two carboxylic groups of SXO molecule remains uncoordinating. If the instabilities of the Cu(II)-XO complexes can be explained along the same lines as that for the Cu(II)-SXO complex, the sterical structure VI can be proposed for the $CuHL^{3-}$, CuL^{4-}, and Cu_2L^{2-} complex species. However, it still doubtful whether the explanation used for the SXO complex can also be applied to the XO complexes. The ESR study of the Cu(II)-complexes is being under taken: a valid discussion of these structure must await further investigation. The stabilities of the ML^{4-}, MHL^{3-}, and M_2L^{2-} complex species for Co(II), Zn(II), Cd(II), and Pb(II) exhibits the ordinary trend. This may be explained by the assumption that these metal ions probably take a regular octahedral or tetrahedral structure.[39] The Ni(II) complexes exhibit a property intermediate between Co(II) and Cu(II). Similar behavior of Ni(II) is encountered in connection with the other sulfonphthalein indicators.[14,15,17] The Ni(II) complexes frequently exhibit behavior similar in structure to that of the Cu(II) complexes as a result of the Jahn-Teller effect, although this effect is not so pronounced as that seen in the Cu(II) complexes.[40]



VI CuL^{4-}, $CuHL^{3-}$ and Cu_2L^{2-}

The stabilities of the MH_2L^{2-} and M_2HL^{-} complex species for all the metal ions exhibit the ordinary trend. The XO molecule in these complex species may act as a tridentate ligand; *i.e.*, the phenolic and/or quinolic oxygen may remain uncoordinated (Formulas III and V), so that its stability is not so much dependent on the coordination structures of the metal ions as the stabilities of ML^{4-}, MHL^{3-}, and M_2L^{2-} appear to be.

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