Mixed Ligand Complexes of Copper(II)-1-(2-Pyridylazo)-2-naphthol with Bidentate Ligands

Hiroko WADA,* Kazuyoshi IKUTA, and Genkichi NAKAGAWA*

Laboratory of Analytical Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466

(Received February 23, 1978)

Formation constants of mixed ligand complexes of copper(II)–1-(2-pyridylazo)-2-naphthol chelate (Cu(pan)) with bidentate ligands, which accelerate the rate of color change of 1-(2-pyridylazo)-2-naphthol (PAN) indicator in copper(II)–EDTA titrations, were determined by the spectrophotometric method in 5 or 10% v/v dioxane–H_2O at $\mu=0.1$ (KNO_3) and at 25 °C. The overall formation constants ($\log K^{\text{pan},\text{L}}_{\text{Cu(pan)L}}=\log$ ([Cu(pan)L]/[Cu][L][pan]) are 21.26 (5% dioxane) for 2,2′-bipyridine, 21.64 (10% dioxane) for ethylenediamine, 22.80 (5% dioxane) for 8-hydroxy-5-quinolinesulfonic acid, 19.39 (10% dioxane) for glycine, and 20.68 (10% dioxane) for iminodiacetic acid. These ligands coordinate with Cu(pan) chelate as bidentate ligands, and the mixed ligand complexes may have a distorted octahedron structure. Thus the Cu–pan bond in the mixed ligand complex is weakened.

In the EDTA-titration of copper(II), 1,10-phenanthroline, 2,2′-bipyridine, ethylenediamine, 8-quinolinol, glycine, and iminodiacetic acid accelerate the rate of the color change of 1-(2-pyridylazo)-2-naphthol (PAN) indicator.[1] In a previous work[2] the mechanism of the acceleration by 1,10-phenanthroline was elucidated: *i.e.* the mixed ligand complex of Cu(pan) chelate with 1,10-phenanthroline is formed and undergoes a faster substitution with EDTA than does Cu(pan) chelate. In the present paper the composition and the formation constants of the mixed ligand complexes of Cu(pan) chelate with 2,2′-bipyridine(bpy), ethylenediamine(en), 8-hydroxy-5-quinolinesulfonic acid(Hoxs), glycine (Hgly), and iminodiacetic acid (H_2ida) are reported.

Experimental

Reagents. The copper(II) solution and the Hpan solution were the same as those used in previous work.[2] Reagent grade chemicals were purified by recrystallization. A 2,2′-bipyridine dioxane solution, and ethylenediamine aqueous solution, a glycine aqueous solution, a 8-hydroxy-5-quinolinesulfonic acid alkaline aqueous solution, and an iminodiacetic acid aqueous solution were used. The ionic strength was maintained constant with potassium nitrate. Dioxane was purified as described in the previous paper.[2] Buffer solutions: 0.02 M 2-morpholino-1-ethanesulfonic acid (MES)–NaOH buffer for pH 4—7, and 0.01 M disodium tetraborate–HNO_3 or NaOH buffer for pH 7.5—11 were used.

Apparatus. A Hitachi 124 Spectrophotometer, a Hitachi 356 Two-wavelength Spectrophotometer, a Radiometer PHM 26 pH meter equipped with a Radiometer G202B glass electrode and a K401 calomel electrode (saturated KCl), and a Hitachi-Horiba F-5 pH meter equipped with an Orion 94-29A copper(II) ion-selective electrode or a Hitachi-Horiba 1026-05T glass electrode and a Hitachi-Horiba 2080-05T calomel electrode (3.3 M KCl) were used. These glass electrodes were calibrated with the two standard buffers: 0.025 M KH_2PO_4 +0.025 M Na_2HPO_4 and 0.05 M $KH_3(C_2O_4)_2\cdot 2H_2O$, 0.05 M $KHC_6H_4(COO)_2$, 0.05 M $Na_2B_4O_7\cdot 10H_2O$ or saturated (25 °C) $Ca(OH)_2$.

Procedure. All measurements were carried out in 5 or 10% v/v dioxane–water media, depending upon the solubility of mixed ligand complexes, at an ionic strength of 0.1 M (KNO_3) and at 25±1 °C. The acid dissociation constants and the formation constants of copper(II) complexes of the ligands (bpy, en, Hoxs, Hgly, H_2ida) were determined under the same conditions as those employed for the determination of the formation constants of mixed ligand complexes. All constants determined are written in the form of mixed constants involving hydrogen ion activity.

Determination of the Acid Dissociation Constants of the Ligands and the Formation Constants of the Cu(II) Complexes. The acid dissociation constant of protonated 2,2′-bipyridine (Hbpy) was determined by a spectrophotometric method. The acid dissociation constants of protonated ethylenediamine (H_2en), 8-hydroxy-5-quinolinesulfonic acid (H_2oxs), glycine (H_2gly), and iminodiacetic acid (H_2ida), and the formation constants of Cu–ida complexes were determined by the pH-tritration with a NaOH standard solution. The formation constants of Cu–bpy, Cu–en, Cu–oxs, and Cu–gly complexes were determined by the potentiometric method with a copper(II) ion-selective electrode.[3] The acid dissociation constants of the ligands and the formation constants of the copper(II) complexes are summarized in Table 1.

Determination of the Formation Constants of the Mixed Ligand Complexes. The formation constant of a mixed ligand complex is defined by Eq. 1. Charges are omitted for simplicity.

TABLE 1. EQUILIBRIUM CONSTANTS OF LIGANDS (L)
25 °C, $\mu=0.1$ (KNO_3)

Ligand (L)	pk_1	pk_2	Method[a)]	log β_{CuL}	log β_{CuL_2}	log β_{CuL_3}	Method[a)]	Dioxane (%)
bpy	4.37		3	8.59	14.09	17.84	2	5
en	7.14	9.98	1	10.56	19.55		2	10
Hoxs	3.90	8.82	1,3	11.86	21.87		2	5
Hgly	2.52	9.40	1	8.12	14.71		2	10
H_2ida	2.86	9.51	1	10.93	16.67		1	10

a) Method 1: pH titration, Method 2: potentiometry with Cu(II) ion-selective electrode, Method 3: spectrophotometry.

$$\beta_{\mathrm{Cu(pan)L}_n} = \frac{[\mathrm{Cu(pan)L}_n]}{[\mathrm{Cu(pan)}][\mathrm{L}]^n}, \tag{1}$$

where L represents the free ligand. The conditional formation constant of Cu–pan complexes, taking into account the formation of mixed ligand complexes, is given by

$$K_{\mathrm{(Cupan)'}} = \frac{[\mathrm{(Cupan)'}]}{[\mathrm{Cu'}][\mathrm{pan'}]} = \frac{K_{\mathrm{Cupan}}\alpha_{\mathrm{Cupan(L)}}}{\alpha_{\mathrm{Cu(L)}}\alpha_{\mathrm{pan(H)}}}, \tag{2}$$

where

$$[\mathrm{(Cupan)'}] = [\mathrm{Cu(pan)}] + [\mathrm{Cu(pan)L}] + [\mathrm{Cu(pan)L_2}] + \cdots + [\mathrm{Cu(pan)L}_n], \tag{3}$$

$$K_{\mathrm{Cupan}} = \frac{[\mathrm{Cu(pan)}]}{[\mathrm{Cu}][\mathrm{pan}]}, \tag{4}$$

$$\alpha_{\mathrm{Cupan(L)}} = 1 + \sum_{n=1}^{n} \beta_{\mathrm{Cu(pan)L}_n}[\mathrm{L}]^n, \tag{5}$$

$$\alpha_{\mathrm{Cu(L)}} = 1 + \sum_{m=1}^{m} \beta_{\mathrm{CuL}_m}[\mathrm{L}]^m, \tag{6}$$

$$\alpha_{\mathrm{pan(H)}} = 1 + \frac{[\mathrm{H}]}{k_2} + \frac{[\mathrm{H}]^2}{k_1k_2}. \tag{7}$$

β_{CuL_m} is the overall formation constant of CuL_m, and k_1 and k_2 are the acid dissociation constants of $\mathrm{H_2pan}$.

The total concentration of Cu–pan complexes [(Cupan)′] can be obtained from the absorbance at the wavelength where the absorbance of the mixed ligand complex is equal to that of Cu(pan) chelate. [Cu′] and [pan′] are calculated by means of the following equations:

$$[\mathrm{Cu'}] = C_{\mathrm{Cu}} - [\mathrm{(Cupan)'}], \tag{8}$$

$$[\mathrm{pan'}] = C_{\mathrm{Hpan}} - [\mathrm{(Cupan)'}], \tag{9}$$

where C_{Cu} and C_{Hpan} represent the analytical concentrations of Cu and Hpan, respectively. Thus the values of $K_{\mathrm{(Cupan)'}}$ are obtained at the various concentrations of the ligand and the various pHs of the solutions.

On the other hand the concentration of free ligand L is calculated by

$$[\mathrm{L}] = \frac{[\mathrm{L'}]}{\alpha_{\mathrm{L(H)}}}, \tag{10}$$

where

$$\alpha_{\mathrm{L(H)}} = 1 + \frac{[\mathrm{H}]}{k_p} + \frac{[\mathrm{H}]^2}{k_pk_{p-1}} + \cdots + \frac{[\mathrm{H}]^p}{k_p\cdots k_2k_1},$$

and [L′] represents the total concentration of the ligand not combined with copper, and k_1, k_2, $\cdots k_p$ are the acid dissociation constants of the ligand. In this work a large excess of the ligand compared with copper and Hpan was used; thus [L′] is approximately equal to the initial concentration of the ligand C_{L}. $\alpha_{\mathrm{Cu(L)}}$ and $\alpha_{\mathrm{pan(H)}}$ are calculated from the concentration of L and the pH of the solution by means of Eqs. 6 and 7, respectively.

Thus $K_{\mathrm{Cupan}}\alpha_{\mathrm{Cupan(L)}}$ can be written as Eq. 11 and evaluated from $K_{\mathrm{(Cupan)'}}$ by the use of Eq. 2.

$$K_{\mathrm{Cupan}}\alpha_{\mathrm{Cupan(L)}} = K_{\mathrm{Cupan}}(1 + \sum_{n=1}^{n}\beta_{\mathrm{Cu(pan)L}_n}[\mathrm{L}]^n) \tag{11}$$

From the plots of $\log K_{\mathrm{Cupan}}\alpha_{\mathrm{Cupan(L)}}$ *vs.* log [L] the formation constants of Cu(pan) and $\mathrm{Cu(pan)L}_n$ complexes were obtained by the curve fitting method.

Results

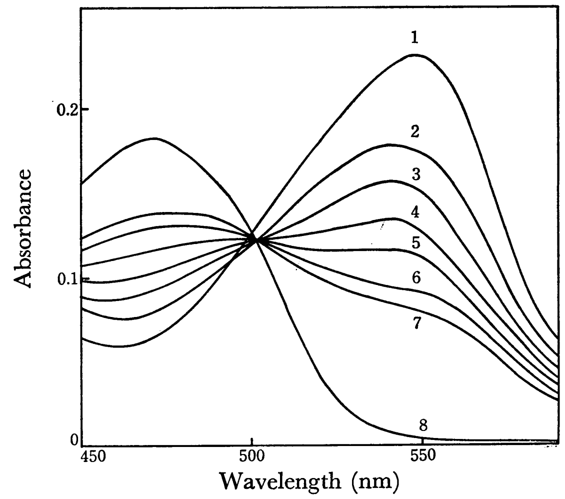

Fig. 1. Absorption spectra of Cu(pan)(bpy).
$C_{\mathrm{Cu}} = 1.11\times10^{-4}$ M, $C_{\mathrm{Hpan}} = 1.01\times10^{-5}$ M, pH 9.05, $C_{\mathrm{bpy}} =$: (1) 0 (pH 5.78), (2) 1.50×10^{-2} M, (3) 2.00×10^{-2} M, (4) 2.50×10^{-2} M, (5) 3.00×10^{-2} M, (6) 3.50×10^{-2} M, (7) 4.00×10^{-2} M, (8) only Hpan.

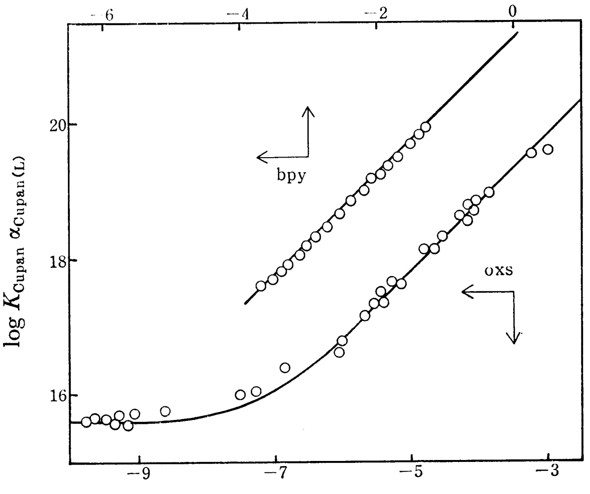

Fig. 2. Plots of $\log K_{\mathrm{Cupan}}\alpha_{\mathrm{Cupan(L)}}$ *vs.* log [L].
Solid lines are the theoretical curves calculated with the values obtained by curve fitting.

2,2′-Bipyridine. Under the conditions: $C_{\mathrm{Cu}} = 0.223$—11.1×10^{-5} M, $C_{\mathrm{Hpan}} = 1.01$—20.2×10^{-6} M, $C_{\mathrm{L}} = 3.00$—500×10^{-4} M, pH 8.18—9.07, dioxane 5% v/v, the absorption spectra were measured. Some of them are shown in Fig. 1. By the addition of 2,2′-bipyridine the absorption maximum of Cu(pan) chelate shifted from 550 to 540 nm, and the absorbance at λ_{max} decreased with increasing the concentration of 2,2′-bipyridine, because the replacement of Cu(pan) chelate by 2,2′-bipyridine proceeds together with the formation of the mixed ligand complex. The isosbestic point of the curves 2—8 at 502 nm indicates the existence of the mixed ligand complex and Hpan in the presence of 2,2′-bipyridine. From the absorbances at 545 nm the total concentration of Cu–pan complexes and then the values of $K_{\mathrm{(Cupan)'}}$ were calculated. A plot of $\log K_{\mathrm{Cupan}}\alpha_{\mathrm{Cupan(L)}}$ *vs.* the logarithm of free 2,2′-bipyridine concentration log [bpy] yielded a straight line with a slope of 1.0 (Fig. 2). Thus, over the concentration range of 2,2′-bipyridine from 10^{-4} to 10^{-1} M a mixed ligand complex

TABLE 2. FORMATION CONSTANTS OF THE MIXED LIGAND COMPLEXES OF Cu(pan)
25 °C, $\mu=0.1$ (KNO_3)

Ligand (L)	λ_{max} (nm)	log $K^{pan,L}_{Cu(pan)L}$	log $K^{pan}_{Cu(pan)L}$	log $K^{L}_{Cu(pan)L}$	$\Delta\log K$	dioxane (%)
phen	540	21.18	12.20	5.60	−3.38	5
bpy	540	21.26	12.67	5.68	−2.91	5
en	548	21.64	11.08	5.65	−4.91	10
Hoxs	550	22.80	10.94	7.22	−4.64	5
Hgly	545	19.39	11.27	3.40	−4.72	10
H_2ida	550	20.68	9.75	4.69	−6.24	10
H_2O	550	15.60$^{a)}$				5
		16.00$^{b)}$				10
		15.58$^{c)}$				5
		15.99$^{c)}$				10

Hpan: $pk_1=2.87$, $pk_2=11.55$ (dioxane 5%) $pk_1=2.90$, $pk_2=11.68$ (dioxane 10%). a) In the presence of Hoxs. b) In the presence of en, H_2ida, or Hgly. c) In the absence of auxiliary complexing agents.

Cu(pan)(bpy) is formed, as in the case of 1,10-phenanthroline. The value of log $K^{pan,bpy}_{Cu(pan)bpy}$ was obtained from the value of log $K_{Cupan}\alpha_{Cupan(L)}$ at log[bpy]=0 (Table 2).

Ethylenediamine. By the addition of ethylenediamine the absorption maximum of Cu(pan) chelate shifted to 548 nm. Increasing the concentration of free ethylenediamine caused the formation of the mixed complex and the substitution with ethylenediamine to proceed. Under the conditions: $C_{Cu}=2.14$—12.9×10^{-4} M, $C_{Hpan}=9.97$—10.2×10^{-6} M, $C_L=1.57$—12.1×10^{-2} M, pH 6.08—10.22, dioxane 10% v/v, the absorbances at 549 nm were measured. As shown in Fig. 3, the values of log $K_{Cupan}\alpha_{Cupan(L)}$ became higher than that of log K_{Cupan} when the concentration of free ethylenediamine exceeded 10^{-6} M, and a straight line with a slope of 1.0 was obtained at concentrations higher than 10^{-4} M. Thus a mixed ligand complex Cu(pan)(en) is formed.

8-Hydroxy-5-quinolinesulfonic Acid. In this case Cu–oxs chelate is extremely stable, so the substitution of Cu(pan) chelate with oxs proceeded even at a low concentration of oxs. Hence the following experimental conditions were employed: $C_{Cu}=1.6$—488×10^{-5} M, $C_{Hpan}=2.94$—32.2×10^{-6} M, $C_L=0.378$—113×10^{-4} M, pH 3.58—11.00, dioxane 5% v/v. A plot of log $K_{Cupan}\alpha_{Cupan(L)}$ *vs.* log [oxs] is shown in Fig. 2. The formation of a mixed ligand complex Cu(pan)(oxs) was observed.

Glycine. In this case the absorption maximum of Cu(pan) chelate shifted to the shorter wavelength (545 nm) with increase in the concentration of free glycine. The absorbances at 547.5 nm were measured under the conditions: $C_{Cu}=4.29\times10^{-6}$—1.07×10^{-3} M, $C_{Hpan}=3.00$—9.01×10^{-6} M, $C_L=1.62$—19.8×10^{-2} M, pH 5.84—9.28, dioxane 10% v/v. The results are shown in Fig. 3 and Table 2.

Iminodiacetic Acid. The absorption spectrum was slightly shifted to the shorter wavelengths compared with that of Cu(pan) chelate. The experiments were carried out under the conditions: $C_{Cu}=8.00$—80.0×10^{-5} M, $C_{Hpan}=0.923$—1.18×10^{-5} M, $C_L=3.62$—45.3×10^{-3} M, pH 5.14—9.66, dioxane 10% v/v. The results are shown in Fig. 3 and Table 2.

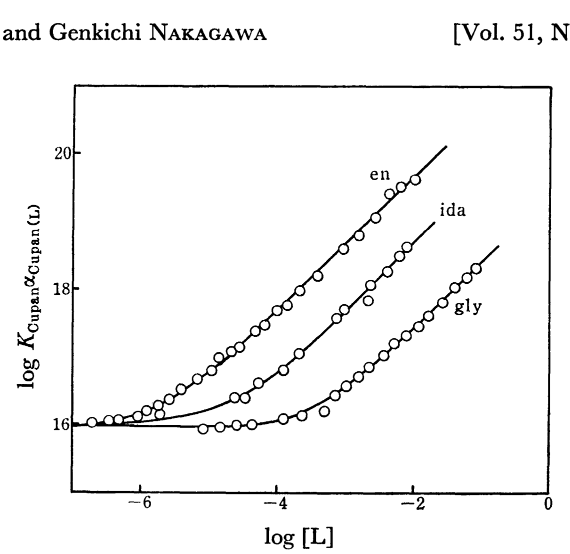

Fig. 3. Plots of log $K_{Cupan}\alpha_{Cupan(L)}$ *vs.* log [L].
Solid lines are the theoretical curves calculated with the values obtained by curve fitting.

Discussion

In all cases, the replacement of Cu(pan) chelate by auxiliary complexing agents takes place before the complete formation of the mixed ligand complex. Thus, it was assumed that the molar absorptivity of the mixed ligand complex is the same as that of Cu(pan) chelate at the middle wavelength of these two absorption maxima, as observed in the case of 1,10-phenanthroline.[2] Since the plots of log $K_{Cupan}\alpha_{Cupan(L)}$ *vs.* log [L] fitted well with a normalized curve plotting y *vs.* $\log x$ for $y=\log(1+x)$, and since in the case of 8-hydroxy-5-quinolinesulfonic acid, ethylenediamine, iminodiacetic acid, and glycine the formation constants of Cu(pan) chelate obtained from the horizontal parts of the curves were in good agreement with the values obtained in the absence of auxiliary complexing agents[4] (Table 2), the above assumption should be correct. In each case at higher concentrations of free ligand a straight line with a slope of 1.0 was obtained; hence one molecule of ligand coordinates with one molecule of Cu(pan) chelate.

To compare the formation constants of Cu(pan) and Cu(pan)L, $K^{pan}_{Cu(pan)L}$ was calculated from $K^{pan,L}_{Cu(pan)L}$, as

$$K^{pan}_{Cu(pan)L} = \frac{[Cu(pan)L]}{[CuL][pan]},$$

and values of Δlog K defined by Sigel[5] were calculated:

$$\Delta\log K = \log K^{pan}_{Cu(pan)L} - \log K_{Cupan}.$$

In all cases Δlog K are negative (Table 2). Therefore, by the formation of the mixed ligand complex the bonds between copper and pan may be weakened.

Tabata and Tanaka determined the formation constants of mixed ligand complexes of copper(II)-4-(2-pyridylazo)resorcinol (Cu(par)) chelate with unidentate ligands(L) such as SCN^-, Cl^-, Br^-, I^-, NH_3, pyridine, CH_3COO^- and N_3^-.[6] Comparing the values of $K^{L}_{Cu(pan)L}$ obtained in this work with those of $K^{L}_{Cu(par)L}$ by Tabata and Tanaka, $K^{L}_{Cu(pan)L}$ for 1,10-phenanthroline, 2,2'-bipyridine, and 8-hydroxy-5-quinolinesulfonic acid are much larger than $K^{L}_{Cu(par)L}$ for pyridine. $K^{L}_{Cu(pan)L}$ for ethylenediamine, and iminodiacitic acid are also greater than $K^{\mathrm{L}}_{\mathrm{Cu(par)L}}$ for NH_3, while in the case of glycine $K^{\mathrm{L}}_{\mathrm{Cu(pan)L}}(=10^{3.40})$ is of the same order as $K^{\mathrm{L}}_{\mathrm{Cu(par)L}}$ $(=10^{3.51})$ for NH_3. On the other hand, in the EDTA titration of copper(II) with PAN indicator the rate of the color change is accelerated with glycine,[1] but glycine methyl ester slows down the rate of color change, as does pyridine.** Thus glycine may coordinate with Cu(pan) chelate as a bidentate ligand. The calculated $\Delta\log K$ value for iminodiacetic acid was small, if iminodiacetic acid were to act as a terdentate ligand; thus iminodiacetic acid may coordinate as a bidentate ligand with the amine nitrogen and one of the carboxyl oxygen atoms.

All ligands examined in this study coordinate with Cu(pan) chelate as bidentate ligands and the mixed ligand complexes may have a distorted octahedron structure. This is the reason why 1,10-phenanthroline, 2,2′-bipyridine, ethylenediamine, 8-hydroxy-5-quinolinesulfonic acid, glycine, or iminodiacetic acid accelerates the rate of color change of PAN indicator in copper(II)-EDTA titrations.

** The formation constant of the mixed ligand complex of Cu(pan) with glycine methyl ester could not be determined, because of the small solubility in H_2O–dioxane.

References

1) G. Nakagawa and H. Wada, *Talanta*, **20**, 829 (1973).
2) G. Nakagawa and H. Wada, *Talanta*, **22**, 563 (1975).
3) G. Nakagawa, H. Wada, and T. Hayakawa, *Bull. Chem. Soc. Jpn.*, **48**, 424 (1975).
4) G. Nakagawa and H. Wada, *Nippon Kagaku Zasshi*, **84**, 639 (1963).
5) H. Sigel, *Chimia*, **21**, 489 (1967). R. Griesser and H. Sigel, *Inorg. Chem.*, **9**, 1238 (1970).
6) M. Tabata and M. Tanaka, *J. Inorg. Nucl. Chem.*, **38**, 1529 (1976).