

Contribution from the Department of Chemistry, Montana State University, Bozeman, Montana 59717

## Thermodynamic Study of the Formation of Some Mixed-Ligand Complexes of Copper(II)<sup>†</sup>

M. S. MOHAN, D. BANCROFT, and E. H. ABBOTT\*

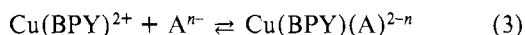
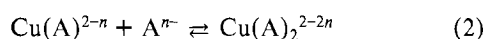
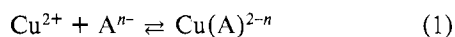
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The thermodynamics of formation for the mixed-ligand complexes of the type M(BPY)(A) (where M = Cu(II), BPY = bipyridyl, A = ethylenediamine, histamine, glycine, malonic acid, and pyrocatechol) have been investigated. Bipyridyl is found to enhance the ability of Cu(II) to bind the anionic but not the neutral ligands. Comparison of the enthalpies and entropies of formation shows that the enhancement is due to a more favorable enthalpy term for the interaction of an anion with Cu(BPY)<sup>2+</sup> than with Cu<sub>aq</sub><sup>2+</sup>. The discriminatory behavior of Cu(BPY)<sup>2+</sup> toward anionic and neutral donors is discussed in terms of an electrostatic model.

### Introduction

It has been recognized for many years that mixed-ligand Cu(II) complexes containing an aromatic amine and an anion as the second ligand are several orders of magnitude more stable than would be expected on statistical grounds.<sup>1</sup> It has been demonstrated with EPR that the aromatic ligand receives  $\pi$ -electron density from the metal ion and that this process is augmented by the binding of anionic ligands to the metal ion.<sup>2</sup> These electronic effects have been suggested to lead to the enhanced stability. In contrast to this, the stabilities of mixed-ligand Cu(II) complexes containing a neutral donor as the second ligand are of the order expected on statistical grounds.<sup>3</sup>

Very few thermodynamic studies<sup>4</sup> have been carried out on mixed-ligand systems, perhaps because of their complexity. In the present study we report a detailed thermodynamic analysis of reactions 1–3, where BPY = bipyridyl, and A =



ethylenediamine, histamine, glycine, malonic acid, and pyrocatechol. Values of the thermodynamic parameters  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  have been tabulated in order to determine the degree to which they contribute to the stability of a given complex and to see how this is affected by the charge on A.

### Experimental Section

**Reagents.** The  $\alpha, \alpha'$ -bipyridyl (BPY), glycine (GLY), ethylenediamine dihydrochloride (EN), histamine dihydrochloride (HS), and pyrocatechol (PYR) were obtained from Sigma Chemical Co. while malonic acid (MAL), copper(II) nitrate trihydrate, sodium hydroxide, ethylenediamine tetraacetic acid (EDTA), potassium hydrogen phthalate and potassium nitrate were Baker Analyzed grade. The purity of the ligands was checked and their molecular weights were determined by potentiometric titration with standard carbonate-free sodium hydroxide. All ligands were employed in the diprotonated form. A stock solution of Cu(II) was prepared and standardized by titrating with the disodium salt of EDTA<sup>5</sup> while the carbonate-free sodium hydroxide was prepared and standardized by titrating with potassium hydrogen phthalate.

**Methods.** Association constants for the free ligands and the metal complexes were determined by potentiometric titration with standard carbonate-free sodium hydroxide in the absence and presence of Cu(II), respectively. In binary systems a 1:2 metal:ligand ratio was employed, while in ternary systems a 1:1:1 molar ratio of BPY:Cu(II):secondary ligand was employed. The concentration of Cu(II) was ca.  $2.0 \times 10^{-3}$  M. Multiple titrations were carried out for each system at  $15.0 \pm 0.1$ ,  $25.0 \pm 0.1$ , and  $35.0 \pm 0.1$  °C in a 100-mL jacketed cell serviced by a constant-temperature bath. Carbon dioxide free nitrogen was bubbled through the experimental solutions whose ionic strength was initially adjusted to be 0.2 M by suitable addition of KNO<sub>3</sub>. Standard

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NaOH was added to the titration cell with a Metrohm Dosimat microburet, and the changes in the pH of the solution during the course of the titration were monitored with a digital Radiometer pH meter, PHM 52, in combination with a Radiometer combination electrode, GK2401C. The experimental data were obtained in homogeneous aqueous media.

The electrode system was calibrated by direct titration of acetic acid, the observed pH meter readings being compared with the actual hydrogen ion concentration calculated from data tabulated by Harned and Owen.<sup>6</sup> The pH regions below 3.5 and above 10.5 were calibrated by measurements in the HCl and NaOH solutions, respectively.

**Calculations.** The association constants for the free ligands and the stability constants for the various complexes formed in binary and ternary systems were calculated from the titration data using a corrected version of the computer program SCOGS.<sup>7</sup> In the case of the binary systems involving EN, HS, GLY, MAL, and PYR the stability constants for equilibria 1 and 2 were calculated by taking into consideration the species H<sub>2</sub>A, HA, A, Cu, Cu(A), and Cu(A)<sub>2</sub>. In titrations involving BPY and Cu(II) in a 2:1 molar ratio the initial pH of the solution corresponds to the presence of 3 mol of free acid/mol of metal ion indicating that the 1:1 Cu(BPY) complex is completely formed initially. The equilibrium constant for the bis complex (equilibrium 4) was therefore calculated by taking into account the species HBPY, BPY, Cu(BPY), and Cu(BPY)<sub>2</sub>.

The stability constants for the ternary complexes Cu(BPY)(A) were calculated by two different methods. In one approach the 1:1 Cu(BPY) complex was considered to be completely formed. The ternary constants were calculated by taking into consideration the species H<sub>2</sub>A, HA, A, Cu(BPY), and Cu(BPY)(A). The validity of these constants was checked by the second approach wherein no assumptions were made and the ternary constants were calculated by taking into consideration the species H<sub>2</sub>A, HA, A, HBPY, Cu, Cu(BPY), Cu(BPY)<sub>2</sub>, Cu(A), Cu(A)<sub>2</sub>, and Cu(BPY)(A). The constants for Cu(BPY) were taken from the work of Irving and Mellor.<sup>8</sup> As found in the previous studies,<sup>9</sup> the constants obtained by the two methods were found to be in very good agreement.

The values of enthalpy and entropy associated with the various equilibria were obtained by a graphical solution of the equation

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

Values of  $\Delta G$  were calculated using the equation

$$\Delta G(25.0 \text{ }^\circ\text{C}) = -1.364 \log K \text{ (kcal/mol)}$$

The association constants for the various equilibria are precise to the extent of  $\pm 0.02 \log K$  unit. The values of  $\Delta H$  and  $\Delta S$  are therefore precise to  $\pm 0.4$  kcal/mol and  $\pm 1$  eu, respectively.

### Results

**Protonation Constants of Free Ligands.** Potentiometric titration curves of GLY, MAL, EN, and HS in the diprotonated form exhibit two distinct buffer regions corresponding to the stepwise dissociation of the two protons. In the case of BPY the dissociation of the two protons overlap and further the initial pH of the solution indicates that the first proton is completely dissociated. The protonation constants  $K_{\text{HA}}^{\text{H}}$  and  $K_{\text{H}_2\text{A}}^{\text{HA}}$  for GLY, MAL, EN, and HS and the  $K_{\text{HBPY}}^{\text{H}}$  for BPY at 25 °C are reported in Table I along

**Table I.** Association Constants<sup>a</sup> and Corresponding Thermodynamic Functions for the Free Ligands at 25.0 °C and  $\mu = 0.2$  M (KNO<sub>3</sub>)

ligand	H + A $\rightleftharpoons$ HA				HA + H $\rightleftharpoons$ H <sub>2</sub> A			
	log K <sup>H</sup> <sub>HA</sub>	$\Delta H$ , kcal/mol	$\Delta S$ , cal/(mol deg)	$\Delta G$ , kcal/mol	log K <sup>HA</sup> <sub>H<sub>2</sub>A</sub>	$\Delta H$ , kcal/mol	$\Delta S$ , cal/(mol deg)	$\Delta G$ , kcal/mol
bipyridyl	4.45	-2.4	+12.4	-6.1				
ethylenediamine	10.03	-12.7	+3.3	-13.7	7.23	-11.3	-4.9	-9.9
histamine	9.88	-12.6	+3.1	-13.5	6.16	-7.7	+2.3	-8.4
glycine	9.60	-10.6	+8.4	-13.1	2.33	-2.3	+2.8	-3.2
malonic acid	5.22	+0.6	+26.1	-7.1	2.64	-0.5	+10.3	-3.6
pyrocatechol <sup>b</sup>	13.0	-5	+40	-17.7	9.23	-6.0	+22.0	-12.6

<sup>a</sup> All constants accurate to  $\pm 0.02$ . <sup>b</sup> Values taken from ref 9.

**Table II.** Association Constants<sup>a</sup> and Corresponding Thermodynamic Functions for the 1:1 Binary Metal-Ligand Complexes at 25.0 °C and  $\mu = 0.2$  M (KNO<sub>3</sub>)

equilibrium	log K <sup>M</sup> <sub>MA</sub>	$\Delta H$ , kcal/mol	$\Delta S$ , cal/(mol deg)	$\Delta G$ , kcal/mol
Cu <sup>2+</sup> + EN $\rightleftharpoons$ Cu(EN) <sup>2+</sup>	10.60	-13.6	+3.0	-14.5
Cu <sup>2+</sup> + HS $\rightleftharpoons$ Cu(HS) <sup>2+</sup>	9.59	-12.3	+2.8	-13.1
Cu <sup>2+</sup> + GLY <sup>-</sup> $\rightleftharpoons$ Cu(GLY) <sup>+</sup>	8.16	-6.6	+15.2	-11.1
Cu <sup>2+</sup> + MAL <sup>2-</sup> $\rightleftharpoons$ Cu(MAL)	4.81	+1.1	+25.6	-6.6
Cu <sup>2+</sup> + PYR <sup>2-</sup> $\rightleftharpoons$ Cu(PYR)	13.81	-5.2	+45.8	-18.8

<sup>a</sup> All constants accurate to  $\pm 0.02$ .

with the corresponding thermodynamic parameters. Due to experimental difficulties associated with the determination of the protonation constants for pyrocatechol, we have made use of the thermodynamic values reported earlier<sup>10</sup> in calculating the stability constants of the binary and ternary complexes for systems involving pyrocatechol.

**Binary Systems.** Potentiometric titration curves of systems containing a 1:2 molar ratio of Cu(II) and BPY, GLY, EN, or MAL exhibit a single steep inflection at  $m = 4$  (where  $m$  = moles of base added per mole of ligand) indicating that there is an overlapping formation of the 1:1 (MA) and 1:2 (MA<sub>2</sub>) metal-ligand complexes. In the case of BPY the initial pH corresponds to the presence of 3 mol of free acid/mol of metal ion indicating that the 1:1 metal-BPY complex is completely formed initially. The titration curves for systems containing Cu(II) and histamine or pyrocatechol in a 1:2 molar ratio exhibit a weak inflection at  $m = 2$  and a steep one at  $m = 4$  indicating that there is no extensive overlapping in the formation of the MA and MA<sub>2</sub> complexes. Association constants

**Table III.** Association Constants<sup>a</sup> and Corresponding Thermodynamic Functions for the 1:2 Binary Metal-Ligand Complexes at 25.0 °C and  $\mu = 0.2$  M (KNO<sub>3</sub>)

equilibrium	log K <sup>ML</sup> <sub>MA<sub>2</sub></sub>	$\Delta H$ , kcal/mol	$\Delta S$ , cal/(mol deg)	$\Delta G$ , kcal/mol	$\Delta \log K^b$
Cu(BPY) <sup>2+</sup> + BPY $\rightleftharpoons$ Cu(BPY) <sub>2</sub> <sup>2+</sup>	5.30	-6.5	+2.4	-7.2	
Cu(EN) <sup>2+</sup> + EN $\rightleftharpoons$ Cu(EN) <sub>2</sub> <sup>2+</sup>	9.11	-12.0	+1.4	-12.4	-1.49
Cu(HS) <sup>2+</sup> + HS $\rightleftharpoons$ Cu(HS) <sub>2</sub> <sup>2+</sup>	6.52	-9.8	-3.0	-8.9	-3.07
Cu(GLY) <sup>+</sup> + GLY <sup>-</sup> $\rightleftharpoons$ Cu(GLY) <sub>2</sub>	6.82	-6.9	+8.1	-9.3	-1.34
Cu(MAL) + MAL <sup>2-</sup> $\rightleftharpoons$ Cu(MAL) <sub>2</sub> <sup>2-</sup>	2.66	+2.3	+19.9	-3.6	-2.15
Cu(PYR) + PYR <sup>2-</sup> $\rightleftharpoons$ Cu(PYR) <sub>2</sub> <sup>2-</sup>	11.09	-5.5	+32.3	-15.1	-2.72

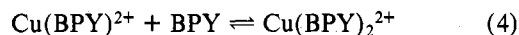
<sup>a</sup> All constants accurate to  $\pm 0.02$ . <sup>b</sup>  $\Delta \log K = \log K^{\text{ML}}_{\text{MA}_2} - \log K^{\text{M}}_{\text{MA}}$ .

**Table IV.** Association Constants<sup>a</sup> and Corresponding Thermodynamic Functions for the 1:1:1 Ternary Complexes at 25.0 °C and  $\mu = 0.2$  M (KNO<sub>3</sub>)

equilibrium	log K <sup>ML</sup> <sub>MLA</sub> <sup>b</sup>	$\Delta H$ , kcal/mol	$\Delta S$ , cal/(mol deg)	$\Delta G$ , kcal/mol	$\Delta \log K^{c,d}$
Cu(BPY) <sup>2+</sup> + EN $\rightleftharpoons$ Cu(BPY)(EN) <sup>2+</sup>	9.41	-11.1	+5.9	-12.8	-1.19 (-1.29)
Cu(BPY) <sup>2+</sup> + HS $\rightleftharpoons$ Cu(BPY)(HS) <sup>2+</sup>	7.15	-8.9	+2.9	-9.8	-2.44
Cu(BPY) <sup>2+</sup> + GLY <sup>-</sup> $\rightleftharpoons$ Cu(BPY)(GLY) <sup>+</sup>	7.74	-8.0	+8.6	-10.6	-0.42 (-0.35)
Cu(BPY) <sup>2+</sup> + MAL <sup>2-</sup> $\rightleftharpoons$ Cu(BPY)(MAL)	5.12	-1.8	+17.4	-7.0	+0.31 (+0.27)
Cu(BPY) <sup>2+</sup> + PYR <sup>2-</sup> $\rightleftharpoons$ Cu(BPY)(PYR)	14.12	-7.1	+40.9	-19.3	+0.31 (+0.43) <sup>e</sup>

<sup>a</sup> All constants accurate to  $\pm 0.02$ . <sup>b</sup> L = BPY. <sup>c</sup>  $\Delta \log K = \log K^{\text{ML}}_{\text{MLA}} - \log K^{\text{M}}_{\text{MA}}$ . <sup>d</sup> Values in parentheses were reported by Griesser and Sigel<sup>9</sup> at  $\mu = 0.1$  M (NaClO<sub>4</sub>). <sup>e</sup> L'Heureux and Martell<sup>1a</sup> report a value of  $\pm 0.36$  at  $\mu = 0.1$  M (KNO<sub>3</sub>).

for the 1:1 and 1:2 metal-ligand complexes formed in these binary systems according to equilibria 1 and 2 are reported in Tables II and III. The association constant for the addition of a second BPY molecule to the 1:1 Cu(II)-BPY chelate according to equilibrium 4 is also reported. The thermody-



amic parameters associated with the formation of the 1:1 and 1:2 metal-ligand complexes have been calculated from the stability constant data and are listed in Tables II and III.

**Ternary Systems.** Potentiometric titration curves for ternary systems containing BPY, Cu(II), and EN, HS, or PYR in a 1:1:1 molar ratio exhibit inflections at  $m = 2$  and  $m = 4$ , while in systems containing BPY, Cu(II), and MAL or GLY, a single steep inflection at  $m = 4$  was obtained. The computer analysis of the titration curves for the ternary systems in terms of the two methods discussed earlier indicates that ternary complexes are formed in all of the systems investigated. The stability constants of these complexes are listed in Table IV. The relative stability of mixed-ligand complexes as compared to that of corresponding binary complexes can be quantitatively expressed in many different ways. We have tabulated the difference in stability,  $\Delta \log K$ , for the addition of a ligand A to Cu<sup>2+</sup> and to the 1:1 Cu(BPY)<sub>2</sub><sup>2+</sup> complex according to eq 5.

$$\Delta \log K = \log K^{\text{Cu}(\text{BPY})_2}_{\text{Cu}(\text{BPY})(\text{A})} - \log K^{\text{Cu}}_{\text{Cu}(\text{A})} \quad (5)$$

The advantages of using  $\Delta \log K$  in comparing the stabilities of the binary and ternary complexes have been recently reviewed.<sup>11</sup> For the tetragonal complexes of Cu(II) with bidentate ligands the statistical value for  $\Delta \log K$  is expected to be -0.6. The  $\Delta \log K$  values listed in Table IV show that

ternary complex formation is favored when the second ligand is GLY, MAL, and PYR. The order of interaction of the 1:1 Cu(BPY) chelate with a second ligand is  $HS < EN < GLY > MAL \approx PYR$ .

The importance of careful studies of binary systems under conditions identical with those used for the ternary systems has been stressed.<sup>12</sup> This statement becomes more significant when thermodynamic parameters are being calculated from the temperature variation of the stability constant data. Therefore in order to ensure that the thermodynamic constants reported in this paper are reliable, the stability constants for the binary and ternary systems have all been determined under identical conditions. Where experimental conditions permit comparison, the values reported in this paper are in good agreement with those reported earlier.<sup>13</sup>

### Discussion

Due to statistical, steric, and electrostatic considerations, the stability constant for the stepwise formation of a 1:2 metal-ligand complex is expected to be smaller than that for the 1:1 complex. The large negative  $\Delta \log K$  values for the binary systems in Table III confirm this expectation. Comparison of the enthalpy and entropy data for the corresponding 1:1 and 1:2 systems shows that in most cases both enthalpy and entropy are unfavorable for the addition of a second ligand to the 1:1 complex. Extensive thermodynamic analysis has been carried out to identify the features of structure and charge which are responsible.<sup>14</sup>

Considering the results on the binary systems, one would also expect comparable negative  $\Delta \log K$  values for the ternary complexes. Examination of the values listed in Table IV reveals that the  $\Delta \log K$  values for systems involving the dianions MAL and PYR are positive; i.e., these bind Cu(II)-BPY better than they bind Cu(II) alone. In fact, the formation constants of the ternary complexes are 2.5-3.0 log  $K$  units higher than is considered normal for the addition of a second ligand.<sup>13</sup> On the other hand, the  $\Delta \log K$  values for ternary systems involving the neutral ligands EN and HS are negative while the value for the monoanion GLY lies between those found for the above cases. These results confirm the earlier findings regarding the discriminatory behavior of Cu(BPY) complexes toward oxygen and nitrogen donors.<sup>3</sup>

It is instructive to compare the data in Tables II and IV for reactions 1 and 3. First, it is noted by comparison of enthalpies that the enthalpy for reaction 3 is much less favorable than for reaction 1 when  $A = EN$  or  $HS$ . This is readily attributable to the steric requirements of BPY and its interaction with EN or HS in the mixed-ligand complexes. For GLY, a more favorable enthalpy term is observed for reaction 3 than for reaction 1. Evidently a strong stabilizing effect is coming into play and overcomes the steric effects noted as dominant for the neutral ligands. The dinegative ions MAL and PYR underscore the trend to still more favorable enthalpy for reaction 3.

The entropies behave differently. For EN and HS, the entropy of reactions 1 and 3 are similar and less negative than for reaction 2. This is in keeping with what is expected from statistical considerations. For GLY, MAL, and PYR, entropies of coordination are far more positive than for the neutral ligands, no doubt because the anions lose water of hydration upon coordination. By comparison of reactions 1 and 3, however, it is noted that the entropy change is significantly less positive for the mixed-ligand species than for the corresponding binary 1:1 complexes.

Thus, reaction 3 has a more favorable enthalpy and a less favorable entropy than reaction 1 when  $A$  is charged. These

effects may be rationalized as follows. If solvation effects are neglected,  $\Delta H$  is made up of two terms, one from covalent bond formation and the other from electrostatic attraction between metal ion and ligand. BPY withdraws  $\pi$ -electron density from Cu(II) making it more positive than it is in the aquo complex. This enhances its Coulombic interaction with the anions GLY, MAL, and PYR in the mixed-ligand complex but does not much affect the strength of binding of the neutral ligands water, EN, and HS. Now, when solvation is taken into consideration, the charge separation which leads to more favorable enthalpy of formation in Cu(BPY)(A) also causes the mixed-ligand complex to be more solvated when  $A = GLY$ , MAL, or PYR than when  $A$  is neutral. Increased solvation of these mixed-ligand species containing anionic ligands makes their entropies of formation less favorable than for the 1:1 binary complexes.

In arriving at this thermodynamic model, we considered many others. One of these is the possibility that Cu(BPY)<sup>2+</sup> is less hydrated than Cu(II) and therefore can react more easily with other ligands. Such a model is excluded because it implies that all mixed-ligand BPY complexes would be more stable than the corresponding 1:1 complexes, not just those involving anions. On balance, it appears that Cu(BPY)<sup>2+</sup> is not much different from Cu<sup>2+</sup> itself, in its reaction with neutral ligands

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**Registry No.** Bipyridyl, 366-18-7; ethylenediamine, 107-15-3; histamine, 51-45-6; glycine, 56-40-6; malonic acid, 141-82-2; Cu(EN)<sup>2+</sup>, 15488-87-6; Cu(HS)<sup>2+</sup>, 12352-69-1; Cu(GLY)<sup>+</sup>, 15488-81-0; Cu(MAL), 7268-92-0; Cu(PYR), 636-16-8; Cu(BPY)<sub>2</sub><sup>2+</sup>, 16787-11-4; Cu(EN)<sub>2</sub><sup>2+</sup>, 13426-91-0; Cu(HS)<sub>2</sub><sup>2+</sup>, 18346-87-7; Cu(GLY)<sub>2</sub>, 13479-54-4; Cu(MAL)<sub>2</sub><sup>2+</sup>, 22174-10-3; Cu(PYR)<sub>2</sub><sup>2+</sup>, 16674-39-8; Cu(BPY)(EN)<sup>2+</sup>, 28204-81-1; Cu(BPY)(HS)<sup>2+</sup>, 68238-10-8; Cu(BPY)(GLY)<sup>+</sup>, 18588-01-7; Cu(BPY)(MAL), 28204-82-2; Cu(BPY)(PYR), 15740-81-5; Cu(BPY)<sub>2</sub><sup>2+</sup>, 16482-45-4.

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