Structural Change and Hydrophobic Interaction as Related to Unusual Stability Constants of Copper(II) Complexes with 2,2′-Bipyridyl and Substituted 1,10-Phenanthrolines

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Unusual values of K_1 and K_2 for the formation of complexes CuL_2 with L = 2,2′-bipyridyl (bpy) and substituted 1,10-phenanthrolines (phen) have been discussed in relation to the structural change from CuL to CuL_2 and the hydrophobic interaction between the coordinated ligands. The free energy for the structural change from the distorted octahedral CuL_2 to the trigonal bipyramidal CuL_2 has been estimated to be 0.80 (-4.5 kJ mol^{-1}) for L = bpy and 0.47 (-2.7 kJ mol^{-1}) for L = phen.

2,2′-Bipyridyl, 1,10-phenanthroline, and their derivatives have been the subject of extensive research not only in analytical[1,2] and coordination chemistry[3–17] but also in bioinorganic chemistry.[18,19] A critical review of stability constants of metal complexes with these ligands has been compiled by McBryde.[20]

In Table 1 are listed stability constants of copper(II) complexes with 2,2′-bipyridyl (bpy) and substituted 1,10-phenanthrolines (phen). As is evident from the Table, steric hindrance occurs in complexes with 2- and 2,9-substituted phen, for which $\log K_1$ values are lower than for unsubstituted phen. For 2,9-dimethyl-phen a $\log K_2$ value higher than the $\log K_1$ value has been reported.[8]

Irving and Mellor[9] have noticed for the copper complexes with unsubstituted phen and bpy an abnormally high value of K_1/K_2 as compared to the ethylenediamine complexes. This was thought to be a piece of evidence for the steric effects of 2- and 9-hydrogen atoms of phen and 3,3′-hydrogen atoms of bpy. This steric effect makes it difficult for the 1:2 copper complexes to form the usual distorted octahedral structure.

The structure of the 1:2 bipyridyl complex in aqueous solution is known to be different from that of the 1:1 complex:[3] the 1:1 complex has the usual axially elongated octahedral structure with 4 additional water molecules, while the 1:2 complex has the five coordinated trigonal bipyramidal structure with an additional water molecule. Similar changes of crystal structure have been observed for the phen complexes.[4,5]

Now according to the mechanistic consideration of the stability constant,[21] $\log K_2$ can be estimated from corresponding $\log K_1$. The postulated structure of the copper(II) complex is the distorted octahedron for the 1:1 as well as the 1:2 complex. For the copper(II) complexes with heterocyclic diamines like bpy and phen, we have:

$$\log K_2\ (\text{calcd}) = \log K_1\ (\text{obsd}) - 1.86. \tag{1}$$

The $\log K_2$ (calcd) value may be regarded as a $\log K_2$ value to be observed for the 1:2 complex with a presumed structure of a distorted octahedron. Then $\log K_2$ (calcd) $-$ $\log K_2$ (obsd) (denoted as "Dif" in Table 1) is the logarithmic constant of formation of the fictitious distorted octahedral CuL_2 from the trigonal bipyramidal CuL_2. The average values of "Dif" are: 0.80 (-4.5 kJ mol^{-1}) for L = bpy and 0.47 (-2.7 kJ mol^{-1}) for L = phen.

The "Dif" value may be utilized to normalize the structural change from CuL to CuL_2. The normalized $\log K_2$ values for substituted phen are given by $\log K_2$ (calcd) $-$ 0.47 and they are listed in the column "norm. $\log K_2$" of Table 1. These values are utilized for consideration of the effect of substituents in the absence of any steric hindrance.

For 5-nitro-phen, two independent $\log K_2$ (obsd) values are available.[22] If the lower value is accepted, the situation is sim-

Table 1. Stability Constants of Copper(II) Complexes with 2,2′-Bipyridyl (bpy) and Substituted 1,10-Phenanthrolines (phen)

Ligand	$\log K_1$ (obsd)	$\log K_2$ (obsd)	$\log K_2$ (calcd)	norm. $\log K_2$	Dif.	Ref.
bpy	8.10	5.34	6.24	5.44	+0.90	6
	8.11	5.55	6.25	5.45	+0.70	15
	8.15	5.50	6.29	5.49	+0.79	9
phen	9.00	6.70	7.14	6.67	+0.44	6
	9.25	6.75	7.39	6.92	+0.64	7
	9.16	6.96	7.30	6.83	+0.34	8
2-Chloro-phen	5.07	5.00	3.22	2.75	−1.78	14
	5.60	4.85	3.74	3.27	−1.11	15
5-Nitro-phen	8.00	5.47	6.14	5.67	+0.67	13
	8.00	6.48	6.14	5.67	−0.34	16
2-Methyl-phen	7.40	6.45	6.54	6.07	+0.09	10
5-Methyl-phen	8.55	6.47	6.69	6.22	+0.22	11
2,9-Dimethyl-phen	5.20	5.8	3.34	2.87	−2.46	10
4,7-Dimethyl-phen	8.76	7.26	6.90	6.48	−0.36	12
5,6-Dimethyl-phen	8.71	6.99	6.85	6.38	−0.14	12

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Table 2. Comparison of ($\log K_2$ (obsd) − norm. $\log K_2$) with Hydrophobicity $\log\{K_D$ (PhX)/K_D (PhH)$\}$

Substituent of phen	5-NO_2	H	5-CH_3	4,7-$(CH_3)_2$	5,6-$(CH_3)_2$
$\log K_2$ (obsd) − norm. $\log K_2$	0.81, −0.20	0	0.25	0.83	0.61
$\log\{K_D$ (PhX)/K_D (PhH)$\}$	−0.28	0	0.60	1.20	1.20

ple: for 5-methyl-, 4,7-dimethyl-, and 5,6-dimethyl-phen, $\log K_2$ (obsd) is higher than norm. $\log K_2$ values, whereas reversely for 5-nitro-phen $\log K_2$ (obsd) is lower than norm. $\log K_2$. As a measure of hydrophobicity of a substituent X, we propose to utilize the logarithmic ratio of the partition constant K_D (between the organic and aqueous phases) of X-phenyl (PhX) against H-phenyl (PhH).[23]

$$\log\{K_D\ (\text{PhX})/K_D\ (\text{PhH})\}. \tag{2}$$

This value is compared with the value of ($\log K_2$ (obsd) − norm. $\log K_2$) in Table 2.

Evidently ($\log K_2$ (obsd) − norm. $\log K_2$) values are parallel to the hydrophobicity of the substituent X.

On the other hand, if we accept the higher value of $\log K_2$ (obsd) for 5-nitro-phen complex,[16] $\log K_2$ (obsd) is higher than norm. $\log K_2$. The nitro group is known as a hydrophile. Thus the 5-nitro-phen complex should be excluded as an exception from the $\log\{K_D$ (PhX)/K_D (PhH)] correlation.[24]

For 2- and 2,9-substituted phen, values of $\log K_2$ (obsd) are definitely higher than norm. $\log K_2$. For the 2,9-dimethyl-phen complex, $\log K_2$ (obsd) is higher than $\log K_1$ (obsd): steric hindrance appears to be less pronounced for the 1:2 complex (distorted trigonal bipyramid) than for the 1:1 complex (distorted octahedron).

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24 In this respect, it is noticed that for copper ternary complexes CuLA with L = phen or bpy and A = *para*-X-substituted DL-phenylalanine (X = F, Cl, and Br) and *para*-X-substituted L-phenylalanine (X = H, I, and NO_2),[19] $\{\log K(\text{CuL} + \text{A})$ (obsd) − $\log K(\text{CuL} + \text{A})$ (calcd)[21]$\}$ is almost linearly related to $\log\{K_D$ (PhX)/K_D (PhH)$\}$ (M. Tanaka, unpublished result).