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Formation Constant of Copper(II) Complexes with Aminobenzenes

MOTOHARU TANAKA* and BERND M. RODE

Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Nagoya, 464 Japan, and Institut für Anorganische und Analytische Chemie, Universität Innsbruck, A-6020 Innsbruck, Austria

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Complex formation with aminobenzenes has not been extensively studied. Recently Arena and others [1] have reported the results on the formation constants of ternary copper(II) complexes involving 1,2-diaminobenzene. Their main purpose was to see whether or not copper(II) complexes of 1,2-diaminobenzene form stable ternary complexes with ligands having oxygen donor atoms as copper(II) complexes with 2,2′-bipyridine do [2].

The mechanistic consideration enabled us to predict formation constants of a number of copper(II) complexes involving amines and amino-acids [3–7]. The enhanced formation constant of copper(II) complexes involving 2,2′-bipyridine and oxygen donor(s) has been quantitatively accounted in terms of donor atom–donor atom interaction, according to the mechanistic consideration [3].

The formation constants of the mixed ligand complex CuAL and higher complexes CuL_n is related to the formation constant of the 1:1 complex CuL as follows [3]:

$$\log K_{CuAL}{}^{L} = \log K_{CuL}{}^{L} + (\log K_{os(CuA,L)} - \log K_{os(Cu,L)}) + \sum_{I}^{I} {}_{<} \sum_{J}^{J} \delta_{ij} X_i(A) Y_j(L)$$

$$\log K_{CuL_n}{}^{L} = \log K_{CuL}{}^{L} + (\log K_{os(CuL_{n-1},L)} - \log K_{os(Cu,L)}) + \sum_{I}^{I} {}_{<} \sum_{J}^{J} \delta_{ij} X_i(L) Y_j(L) - \log n$$

where $K_{os(CuA,L)}$ and $K_{os(Cu,L)}$ denote formation constants of the outer-sphere complexes [CuA,L] and [Cu,L], respectively, δ_{ij} the effect of the donor atom X_i in the ligand A (or L) on the donor atom Y_j in the ligand L, and $X_i(A)$ (or $X_i(L)$) and $Y_j(L)$ the number of the donor atoms X_i in A (or L) and Y_j in L, respectively. The term log n provides the statistical correction for the number of ways that CuL_n can dissociate. Formation constants are defined as follows:

$$K_{CuAL}{}^{L} = [CuAL]\,[CuA]^{-1}\,[L]^{-1}$$

$$K_{CuL_n}{}^{L} = [CuL_n]\,[CuL_{n-1}]^{-1}\,[L]^{-1}$$

$$K_{CuL}{}^{L} = [CuL]\,[Cu]^{-1}\,[L]^{-1}$$

Charges are omitted for simplicity. Values of δ_{ij} have been estimated for various types of ligand involving oxygen and nitrogen as donors [3]:

$\delta_{N(AL)N(AL)} = -0.35(+2.00\ kJ)$;

$\delta_{N(AL)N(AR)} = -0.25(+1.43\ kJ)$;

$\delta_{N(AR)N(AR)} = -0.39(+2.23\ kJ)$;

$\delta_{N(AR)O} = +0.09(-0.51\ kJ)$;

$\delta_{N(AL)O} = -0.26(+1.48\ kJ)$;

$\delta_{OO} = -0.29(+1.65\ kJ)$ for oxygen donor not bound with pi-system;

$\delta_{OO} = -0.10(+0.57\ kJ)$ for oxygen donor directly connected with pi-system.

N(AL) and N(AR) denote aliphatic nitrogen and aromatic heterocyclic nitrogen, respectively. It is anticipated that the donor atom interaction term for anilinic nitrogen differs from that for aliphatic or aromatic heterocyclic nitrogen. Thus it may be interesting to estimate the interaction term of anilinic nitrogen denoted by N(AN).

Formation constants of copper(II) complexes containing anilinic nitrogen as a donor are summarized in Table I.

From these values the following interaction terms are evaluated:

$\delta_{N(AN)O} = -0.09(+0.51\ kJ)$;

$\delta_{N(AN)N(AN)} = -0.18(+1.03\ kJ)$;

$\delta_{N(AN)N(AR)} = -0.28(+1.60\ kJ)$;

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*Author to whom correspondence should be addressed.

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TABLE I. Formation Constants of Copper(II) Complexes Involving 1,2-Diaminobenzene and 2-Aminophenol.[a]

Ligand L	Ligand A	$\log K_{ML}{}^{L}$(obs)	$\log K_{MAL}{}^{L}$(obs)	$\log K_{MAL}{}^{L}$(calc)	Reference
DAB[b]	L	4.47	3.45	3.45	1
		4.44	3.42	3.42	8
		4.55	3.17	3.53	9
4-methoxy-DAB	L	4.78	3.64	3.76	9
4-methyl-DAB	L	4.74	3.76	3.72	9
4-chloro-DAB	L	3.32	2.44	2.30	9
succinate	DAB	2.59	2.20	2.23	1
malonate	DAB	5.05	4.69	4.69	1
maleate	DAB	3.40	3.11	3.04	1
oxalate	DAB	4.85	4.48	4.49	1
acetate	DAB	1.75	1.92	1.57	1
2-aminophenol	L	8.49	7.03	7.32[c]	8
		8.77[d]	7.37[d]	7.41[e]	10
DAB	bipyridine	4.44	3.26	3.32	8
2-aminophenol	bipyridine	8.49	8.18	8.11	8

[a] Ionic strength = 0.1 and 25 °C unless otherwise noted. [b] DAB = 1,2-diaminobenzene. [c] $\log K_{os(CuA,L)} - \log K_{os(Cu,L)} = -0.41$ (ref. 3). [d] Ionic strength = 0, 25 °C. [e] $\log K_{os(CuA,L)} - \log K_{os(Cu,L)} = -0.60$ (ref. 3).

With these δ values, formation constants of copper(II) complexes given in Table I can be reproduced. As seen from Table I, the agreement of the observed formation constant with the calculated one is satisfactory in most cases. The interaction of anilinic nitrogen with oxygen is endergic, while the interaction of aromatic heterocyclic nitrogen with oxygen is exergic.

Some preliminary *ab initio* MO-SCF calculations have been carried out for metal ions with one C=O coordinated ligand and a second N coordinated ligand. The results show that in the case of aniline the energy difference between *cis*- and *trans*-arrangements is significantly different from the case where the second ligand is pyridine. This result also indicates that the ligand–ligand interaction involving aromatic heterocyclic nitrogen is quite different from that involving anilinic nitrogen as a donor atom. Further quantum chemical studies on this subject are in progress [11].

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