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Ternary Complexes in Solution. X. The Influence of the Size of the Chelate Rings on the Stability of Mixed-Ligand Copper(II) Complexes[1]

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The influence of the ring size on the stability of ternary Cu^{2+} complexes was investigated (25°; $I = 0.1$). The differences $\Delta \log K = \log K^{\mathrm{CuA}}_{\mathrm{CuAB}} - \log K^{\mathrm{Cu}}_{\mathrm{CuB}}$ and the constants $\log X$ due to the equilibrium $\mathrm{Cu(2,2'\text{-}bipyridyl)_2 + CuL_2 \rightleftharpoons 2Cu(2,2'\text{-}bipyridyl)L}$ were compared for ligands forming five- and six-membered chelates: L = oxalate ($\log X = \sim 4.9$), glycinate (3.05), and ethylenediamine (1.10) or malonate (5.49), β-alaninate (2.68), and 1,3-propylenediamine (0.06). The same was done for the equilibrium $\mathrm{Cu(pyrocatecholate)_2 + CuL_2 \rightleftharpoons 2Cu(pyrocatecholate)L}$, with L = α-picolylamine ($\log X = 4.64$), 4-aminomethylimidazole (3.46), and ethylenediamine (2.65) or α-aminoethylpyridine (4.52), histamine (4.86), and 1,3-propylenediamine (4.11). It is concluded that the differences in stability between comparable pairs of ternary complexes are, at least, partly due to the different magnitudes of $\log K^{\mathrm{Cu}}_{\mathrm{CuL}} - \log K^{\mathrm{CuL}}_{\mathrm{CuL_2}}$ of the binary complexes with five- or six-membered chelates, the difference usually being greater for the latter ones. This especially favors the formation of ternary complexes containing a five- and a six-membered chelate ring. Besides this, however, it seems that mixed-ligand complexes containing two five-membered chelates are slightly favored compared to those with a five- and a six-membered ring.

Among the driving forces which lead to the formation of mixed-ligand–Cu^{2+} complexes in solution are statistical factors,[2–4] steric hindrance in one of the binary parent complexes,[5] and neutralization of charge in the ternary complex.[6] The latter favors the formation of a ternary complex by both enthalpy (coulombic interactions) and entropy (release of the orientation of solvent molecules) effects.[7] The importance of π bonds for the stability of ternary Cu^{2+} complexes was demonstrated recently.[1,8]

So far no systematic investigation has been made dealing with the influence of the size of the chelate ring on the stability of mixed-ligand complexes, although such an influence on the stability of binary complexes is well known.[9] Therefore, in the present study the stability of ternary Cu^{2+} complexes containing only five-membered chelate rings is compared with ones containing one five- and one six-membered ring. The stability constants of the following two series of complexes were determined or taken from earlier work: (a) 2,2′-bipyridyl–Cu^{2+}–L system with L = oxalate (ox) or malonate (mal),[8] glycinate (gly),[8] α-alaninate (α-al),[10] or β-alaninate (β-al), and ethylenediamine (en)[8] or 1,3-propylenediamine (prop);[11] (b) pyrocatecholate–Cu^{2+}–L system with L = α-picolylamine (pic)[1] or α-aminoethylpyridine (aep), 4-aminomethylimidazole (ami)[1] or histamine (ha),[12] and ethylenediamine (en)[1,12] or 1,3-propylenediamine (prop).[13]

Experimental Section

Materials.—2,2′-Bipyridyl and pyrocatechol were from Fluka AG, Buchs, Switzerland. β-Alanine and 1,3-propylenediamine were obtained from the British Drug Houses, Ltd., BDH Laboratory Chemicals Division, Poole, England. α-Aminoethylpyridine was from K & K Laboratories, Inc., Plainview, N. Y., and Hollywood, Calif. The respective dihydrochlorides were prepared from 1,3-propylenediamine and α-aminoethylpyridine. The other substances were used as purchased. For all other materials see ref 8.

Measurements and Determination of Constants.—All constants were measured by potentiometric titrations (25°; $I = 0.1$, $NaClO_4$) as described.[8] The acidity constants of the ligands and the stability constants of the binary complexes were determined as in earlier studies.[8] The stability constant $\beta^{\mathrm{Cu}}_{\mathrm{CuAB}}$ of the ternary systems was computed[8] from the data obtained by titrating solutions containing Cu–A–B in a ratio 1:1:1 and by taking into account the species H, H_2A, HA, A, CuA, CuA_2, H_2B, HB, B, CuB, CuB_2, Cu, and CuAB. By titrating solutions containing Cu^{2+} alone, Cu:A = 1:1, or Cu:B = 1:1, it was checked that hydrolysis could be omitted in the pH region used for the evaluation of the data. For the systems of 2,2′-bipyridyl–Cu^{2+}–1,3-propylenediamine and pyrocatecholate–Cu^{2+}–ethylenediamine, $\beta^{\mathrm{Cu}}_{\mathrm{CuAB}}$ was determined from solutions containing bipy–Cu^{2+}–prop in a ratio 1:1:(up to) 10 and pyr:Cu^{2+}:en = 1:1:2, respectively. This was done to make the concentration of the species of the mixed-ligand complex significant and also to obtain the complex formation in a pH region where hydrolysis could be omitted.

Results and Discussion

All constants were measured by potentiometric titrations. The computed stability constant $\beta^{\mathrm{Cu}}_{\mathrm{CuAB}}$ of the ternary complexes is due to the overall eq 1. However, for the discussion of the stability of the mixed-ligand complexes, the stability constants $K^{\mathrm{CuA}}_{\mathrm{CuAB}}$ or $K^{\mathrm{CuB}}_{\mathrm{CuBA}}$, according to eq 2 or 3, are more convenient. The connection between eq 1 and 2 or 3 is given by eq 4 and 5.

$$\mathrm{Cu + A + B \rightleftharpoons CuAB} \quad \beta^{\mathrm{Cu}}_{\mathrm{CuAB}} = [\mathrm{CuAB}]/[\mathrm{Cu}][\mathrm{A}][\mathrm{B}] \tag{1}$$

$$\mathrm{CuA + B \rightleftharpoons CuAB} \quad K^{\mathrm{CuA}}_{\mathrm{CuAB}} = [\mathrm{CuAB}]/[\mathrm{CuA}][\mathrm{B}] \tag{2}$$

$$\mathrm{CuB + A \rightleftharpoons CuBA} \quad K^{\mathrm{CuB}}_{\mathrm{CuBA}} = [\mathrm{CuAB}]/[\mathrm{CuB}][\mathrm{A}] \tag{3}$$

$$\log K^{\mathrm{CuA}}_{\mathrm{CuAB}} = \log \beta^{\mathrm{Cu}}_{\mathrm{CuAB}} - \log K^{\mathrm{Cu}}_{\mathrm{CuA}} \tag{4}$$

$$\log K^{\mathrm{CuB}}_{\mathrm{CuBA}} = \log \beta^{\mathrm{Cu}}_{\mathrm{CuAB}} - \log K^{\mathrm{Cu}}_{\mathrm{CuB}} \tag{5}$$

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(13) Additional abbreviations used: L, A, or B, general bidentate ligand; bipy, 2,2′-bipyridyl; pyr, pyrocatecholate.

One way to characterize the stability of a given ternary complex is according to eq 6, *i.e.*, by comparing the difference in stability between eq 2 and 8 or 3 and 7. The values expected for $\Delta \log K$ are negative, since usually $K^{\mathrm{Cu}}_{\mathrm{CuL}} > K^{\mathrm{CuL}}_{\mathrm{CuL_2}}$, because more coordination positions are available for bonding of the first ligand to a given metal ion than for the second ligand.[14]

$$\Delta \log K = \log K^{\mathrm{CuA}}_{\mathrm{CuAB}} - \log K^{\mathrm{Cu}}_{\mathrm{CuB}} = \log K^{\mathrm{CuB}}_{\mathrm{CuBA}} - \log K^{\mathrm{Cu}}_{\mathrm{CuA}} \quad (6)$$

$$\mathrm{Cu} + \mathrm{A} \rightleftharpoons \mathrm{CuA} \quad K^{\mathrm{Cu}}_{\mathrm{CuA}} = [\mathrm{CuA}]/[\mathrm{Cu}][\mathrm{A}] \quad (7)$$

$$\mathrm{Cu} + \mathrm{B} \rightleftharpoons \mathrm{CuB} \quad K^{\mathrm{Cu}}_{\mathrm{CuB}} = [\mathrm{CuB}]/[\mathrm{Cu}][\mathrm{B}] \quad (8)$$

Another way of characterizing the stability of mixed-ligand complexes is according to eq 9–11. The value expected for X on statistical reasons is 4, *i.e.*, $\log X = 0.6$.[2,3]

$$\mathrm{CuA_2} + \mathrm{CuB_2} \rightleftharpoons 2\mathrm{CuAB} \quad X = [\mathrm{CuAB}]^2/[\mathrm{CuA_2}][\mathrm{CuB_2}] \quad (9)$$

$$\log X = 2 \log \beta^{\mathrm{Cu}}_{\mathrm{CuAB}} - (\log \beta^{\mathrm{Cu}}_{\mathrm{CuA_2}} + \log \beta^{\mathrm{Cu}}_{\mathrm{CuB_2}}) \quad (10)$$

$$\log X = (\log K^{\mathrm{CuA}}_{\mathrm{CuAB}} - \log K^{\mathrm{CuB}}_{\mathrm{CuB_2}}) + (\log K^{\mathrm{CuB}}_{\mathrm{CuBA}} - \log K^{\mathrm{CuA}}_{\mathrm{CuA_2}}) \quad (11)$$

Of the mentioned mixed-ligand–Cu^{2+} systems, bipy–Cu^{2+}–ox, bipy–Cu^{2+}–β-al, bipy–Cu^{2+}–prop, pyr–Cu^{2+}–aep, and pyr–Cu^{2+}–prop have not been investigated so far. The acidity constants of the ligands which occur in these ternary systems and the stability constants of the corresponding binary Cu^{2+} complexes are given in Table I. They were used for the calculations of the stability constants of the ternary complexes given in Table II.

TABLE I

NEGATIVE LOGARITHMS OF THE ACIDITY CONSTANTS OF THE LIGANDS AND LOGARITHMS OF THE STABILITY CONSTANTS OF THEIR BINARY Cu^{2+} COMPLEXES ($I = 0.1$; 25°)[a]

L	$pK^{H}_{H_2L}$	pK^{H}_{HL}	Log K^{Cu}_{CuL}	Log $K^{CuL}_{CuL_2}$	Log $\beta^{Cu}_{CuL_2}$
bipy[b]	−0.2[c]	4.49	8.00	5.60	13.60
pyr[1,8,12]	9.32	13.00[d]	13.96	11.07	25.03
ox[e]	1.37	3.81	4.84	3.6	8.44
β-al	3.56 ± 0.01	10.22 ± 0.01	7.07 ± 0.03	5.61	12.68
prop	8.85[f]	10.62[f]	9.82 ± 0.02	7.22	17.04
aep	3.97 ± 0.01	9.75 ± 0.01	7.59 ± 0.01	5.70	13.29

[a] For the data of the other ligands occurring in the systems of Table III see ref 1, 8, 10, and 12. [b] G. Anderegg, *Helv. Chim. Acta*, **46**, 2397 (1963). [c] R. H. Linnel and A. Kaczmarczyk, *J. Phys. Chem.*, **65**, 1196 (1961). [d] D. D. Perrin, *Nature (London)*, **182**, 741 (1958); C. A. Tyson and A. E. Martell, *J. Amer. Chem. Soc.*, **90**, 3379 (1968). [e] A. McAuley and G. H. Nancollas, *Trans. Faraday Soc.*, **56**, 1165 (1960). [f] The buffer regions of these two constants are slightly overlapping; the constants were calculated using the method of G. Schwarzenbach, A. Willi, and R. O. Bach, *Helv. Chim. Acta*, **30**, 1303 (1947).

TABLE II

LOGARITHMS OF STABILITY CONSTANTS OF TERNARY Cu^{2+} COMPLEXES ($I = 0.1$; 25°)[a]

2,2′-Bipyridyl–Cu^{2+}–L Systems

L	Log $\beta^{Cu}_{Cu(bipy)L}$	Log $K^{Cu(bipy)}_{Cu(bipy)L}$	Log $K^{CuL}_{CuL(bipy)}$
ox	13.5[b]	5.5[b]	8.7[b]
β-al	14.48 ± 0.03	6.48	7.41
prop	15.35 ± 0.11	7.35	5.53

L–Cu^{2+}–Pyrocatecholate Systems

L	Log $\beta^{Cu}_{CuL(pyr)}$	Log $K^{CuL}_{CuL(pyr)}$	Log $K^{Cu(pyr)}_{Cu(pyr)L}$
aep	21.42 ± 0.02	13.83	7.46
prop	23.09 ± 0.02	13.27	9.13

[a] For the data of the other ternary systems occurring in Table III see ref 1, 8, 10, and 12. [b] These values are only estimated.[15]

The stability constant of the ternary 2,2′-bipyridyl–Cu^{2+}–oxalate complex could not be determined, since under the conditions needed for potentiometric titrations, even at very low pH, a precipitate is formed.[7,8] However, the titration curves revealed that $\Delta \log K$ (eq 6) for this system has a positive value. This is in agreement with the results obtained for other 2,2′-bipyridyl–Cu^{2+}–O-ligand systems[7,8] and also with the estimations of the constants due to the bipy–Cu^{2+}–ox complex.[15]

The values used for the characterization of the stability of the ternary complexes, $\Delta \log K$ (eq 6) and $\log X$ (eq 9–11), are given in Table III for all the mentioned mixed-ligand–Cu^{2+} systems. A comparison of the stability data due to the 2,2′-bipyridyl–Cu^{2+}–L systems confirms the discriminating qualities[8] of the Cu^{2+}–2,2′-bipyridyl 1:1 complex. The latter preferably coordinates ligands containing O as donor atoms.

TABLE III

COMPARISON OF THE STABILITIES AND VALUES OF Δ LOG K (EQ 6) AND LOG X (EQ 9) OF SOME TERNARY Cu^{2+} COMPLEXES CONTAINING TWO FIVE-MEMBERED RINGS OR A FIVE- AND A SIX-MEMBERED CHELATE RING ($I = 0.1$; 25°)

Five-, five-membered chelates			Five-, six-membered chelates		
L	Δ log K	Log X	L	Δ log K	Log X
2,2′-Bipyridyl–Cu^{2+}–L Systems					
ox	+0.7[a]	4.9[a]	mal[8]	+0.27	5.49
gly[8]	−0.35	3.05	β-al	−0.59	2.68
α-al[10]	−0.26	3.08			
en[8]	−1.29	1.10	prop	−2.47	0.06
L–Cu^{2+}–Pyrocatecholate Systems					
pic[1]	−0.11	4.64	aep	−0.13	4.52
ami[1]	−0.35	3.46	ha[12]	−0.48	4.86
en[1,12]	−0.76	2.65	prop	−0.69	4.11

[a] These values are only estimated.[15]

Within a pair of the systems, *e.g.*, bipy–Cu^{2+}–ox and bipy–Cu^{2+}–mal, the binding sites are of the same kind, the only difference being the number of links within the chelate rings. Therefore, the $\Delta \log K$ values due to the six 2,2′-bipyridyl–Cu^{2+}–L systems suggest that the formation of five-membered chelates is somewhat favored compared to the formation of six-membered ones. However, this conclusion is hardly supported by the $\Delta \log K$ values of the L–Cu^{2+}–pyrocatecholate systems.

Indeed, a comparison of the $\log X$ values of Table III suggests that the matter is more complicated and that additional effects may be responsible for the order of the data. From eq 11 it can be seen that the order of the stability of the binary Cu^{2+}–L 1:2 complex has an intrinsic influence on the size of $\log X$, *i.e.*, on the stability of the ternary complex. The larger the difference is

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[14] As one of the reviewers pointed out, $\Delta \log K$ is also the constant due to the equilibrium $\mathrm{MA} + \mathrm{MB} \rightleftharpoons \mathrm{MAB} + \mathrm{M}$.

[15] The $\log X$ values (eq 9–11) of the 2,2′-bipyridyl–Cu^{2+}–ethylenediamine and 2,2′-bipyridyl–Cu^{2+}–glycinate complexes are 1.10 and 3.05, respectively.[8] This means the replacement of one amino group by one carboxylate group increases the stability of the complex by 1.95 log units. Therefore, if both amino groups are replaced by carboxylate groups, the expected increase in stability is 3.90 log units; *i.e.*, the estimated value for $\log X$ due to bipy–Cu^{2+}–ox is 5.0. A similar extrapolation is possible by comparing the systems ethylenediamine–Cu^{2+}–pyrocatecholate ($\log X = 2.65$)[1,12] and ethylenediamine–Cu^{2+}–oxalate ($\log X = 1.3$).[6] The replacement of pyrocatecholate by oxalate lowers the stability of the complex by 1.35 log units; therefore, using 2,2′-bipyridyl–Cu^{2+}–pyrocatecholate ($\log X = 6.15$)[8] as a basis, a value of 4.8 is obtained for $\log X$. In other words, the average value of 4.9 given in Table III seems to be a reasonable estimation for $\log X$ of the 2,2′-bipyridyl–Cu^{2+}–oxalate complex. Using this estimated value, the constants of Table I, and eq 4, 5, and 10, the values given in Table II could be calculated.

between the stability of the binary 1:1 and 1:2 complexes, the larger is the stability of the mixed-ligand complex. The differences log $K^{Cu}{}_{CuL}$ − log $K^{CuL}{}_{CuL_2}$ are given in Table IV. For the most cases these differences are significantly greater (within a pair of comparable ligands) for the six-membered chelates. This favors especially the stability of the L–Cu^{2+}–pyrocatecholate complexes containing a six-membered chelate.

TABLE IV

DIFFERENCE BETWEEN THE LOGARITHMS OF THE STABILITY CONSTANTS OF THE BINARY 1:1 AND 1:2 COMPLEXES

(I = 0.1; 25°)

Five-membered chelates		Six-membered chelates	
L	Log $K^{Cu}{}_{CuL}$ − log $K^{CuL}{}_{CuL_2}$	L	Log $K^{Cu}{}_{CuL}$ − log $K^{CuL}{}_{CuL_2}$
ox[a]	1.24	mal[8]	2.55
gly[8]	1.35	β-al[a]	1.46
α-al[10]	1.20		
en[1,8,12]	1.28	prop[a]	2.60
pic[1]	1.97	aep[a]	1.89
ami[1]	1.27	ha[12]	2.93
en[1,8,12]	1.28	prop[a]	2.60

[a] See Table I.

TABLE V

DIRECT COMPARISON OF THE STABILITY CONSTANTS FOR SOME TERNARY Cu^{2+} COMPLEXES CONTAINING FIVE- AND SIX-MEMBERED CHELATE RINGS (I = 0.1; 25°)

2,2′-Bipyridyl–Cu^{2+}–L Systems

Five-, five-membered chelates			Five-, six-membered chelates		
L	Log $K^{Cu(bipy)}{}_{Cu(bipy)L}$	Log $K^{CuL}{}_{CuL(bipy)}$	L	Log $K^{Cu(bipy)}{}_{Cu(bipy)L}$	Log $K^{CuL}{}_{CuL(bipy)}$
ox	5.5[a]	8.7[a]	mal[8]	5.37	8.27
gly[8]	7.92	7.65	β-al	6.48	7.41
α-al[10]	7.99	7.74			
en[8]	9.15	6.71	prop	7.35	5.53

L–Cu^{2+}–Pyrocatecholate Systems

Five-, five-membered chelates			Five-, six-membered chelates		
L	Log $K^{CuL}{}_{CuL(pyr)}$	Log $K^{Cu(pyr)}{}_{Cu(pyr)L}$	L	Log $K^{CuL}{}_{CuL(pyr)}$	Log $K^{Cu(pyr)}{}_{Cu(pyr)L}$
pic[1]	13.85	9.61	aep	13.83	7.46
ami[1]	13.61	8.87	ha[12]	13.48	9.19
en[1,12]	13.20	9.68	prop	13.27	9.13

[a] These values are only estimated.[15]

Therefore, a comparison of the data of Table III for the two pairs of ternary complexes containing ligands with about equal differences, as given in Table IV (gly and β-al or pic and aep), suggests that mixed-ligand complexes with two five-membered chelates may be a little more favored than those with a five- and a six-membered one. However, this fact is often suppressed by the greater difference log $K^{Cu}{}_{CuL}$ − log $K^{CuL}{}_{CuL_2}$ for the ligand forming the six-membered chelate, which favors the formation of the ternary complex containing a five- and a six-membered ring.

So far, only the parameters Δ log K and log X for the various systems were considered. In this way the differences in basicity of the ligands are taken into account and it proves possible to consider directly the special properties of ternary complexes, but for the systems under investigation it is of additional interest to examine the values of $K^{Cu(bipy)}{}_{Cu(bipy)L}$ for closely analogous systems as was done for binary complexes.[9] For the latter it had been determined that the decrease in stability in replacing five- by six-membered rings of the same type (*i.e.*, aliphatic diamines, amino acids, and carboxylic acids) is a general phenomenon shown by all metal ions and all polydentate ligands of a given kind; the base strength of the ligand forming a six-membered chelate ring is frequently greater than that for a ligand forming a five-membered ring. For example, the following orders may be written for base strength: mal > ox, β-al > gly, prop > en, aep > pic, and ha > ami. Yet the values for $K^{Cu(bipy)}{}_{Cu(bipy)L}$ and $K^{Cu(pyr)}{}_{Cu(pyr)L}$ are greater for the ligands forming five-membered chelate rings in all cases but one (*cf.* Table V). When the values of $K^{CuL}{}_{CuL(bipy)}$ or of $K^{CuL}{}_{CuL(pyr)}$ are compared, one sees that there is virtually no difference between having a five-membered or a six-membered ring in the inner coordination sphere when adding an additional ligand except again for one counter example. Therefore, we conclude that the "chelate effect" found for binary systems is operable for ternary systems as well and is a manifestation of the relative difficulty in closing a six-membered chelate ring.[16]

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