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Study of Various Factors Affecting the Stability of Ternary Cu(II) and Ni(II) Complexes

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The stability constants of the ternary M(II) complexes [MAL], where M(II) refers to Cu(II) and Ni(II), A refers to 2,6-pyridinedicarboxylic acid (dpa) and iminodiacetic acid (imda) and L refers to glycine, α-alanine, phenylalanine, tyrosine, tryptophan, ethylenediamine, 1,3-propanediamine, oxalic acid, catechol, catechuic acid, tiron, pyrogallol, *o*-aminophenol, and *o*-phenylenediamine, have been determined potentiometrically by using SCOGS computer programme. Probable reasons for less negative $\Delta\log K$ values of the ternary complexes have been discussed.

The nature of the two ligands involved in the formation of the ternary complex greatly affects its stability constant.[1,2]

These effects vary with the nature of the metal ion involved. The interesting comparisons have been made of Cu(II) and Ni(II) ternary complexes.[3,4] Five main nonstatistical factors have been observed to be of significance in determining the stability of a ternary complex.

i) The charges on the two ligands leading to electrostatic repulsion.[5,6]

ii) π Acid character of one of the ligands.[7,8]

iii) Tridentate character of one of the ligands.[9,10]

iv) Large groups in the vicinity of the coordinating atoms leading to steric hindrance between the ligands.[11,12]

v) Intramolecular interligand interactions.[13,14]

It was thought of interest to study the ternary complexes involving 2,6-pyridinedicarboxylic acid (dpa=AH_2), as one of the ligands, which is subject to the effect of four of the above factors. Complexes of the type MAL have been studied where, M=Cu(II) and Ni(II) and L=glycine, α-alanine, phenylalanine, tyrosine, tryptophan, ethylenediamine, 1,3-propanediamine, oxalic acid, catechol, catechuic acid, tiron, pyrogallol, *o*-aminophenol, *o*-phenylenediamine and AH_2=dpa or iminodiacetic acid (imda). Formation constants of some of the M-imda complexes have been reported eariler,[15] but they have been redetermined to get the values under similar experimental conditions.

Experimental

All the reagents used were of A.R. grade and the titrations were carried out in aqueous medium using a G.P. Electronics pH meter (No. 8021, accuracy±0.01 pH unit). The proton-ligand formation constant of the ligands and the formation constants of the binary complexes CuL, CuL_2, NiL, NiL_2, and NiL_3 were determined in aqueous medium at 25 °C and I=0.2 M ($NaClO_4$) (1 M=1 mol dm^{-3}) using the SCOGS[16] computer programme (charges on the species have been omitted for simplicity). In the case of proton-ligand formation constants L, LH, and LH_2 and for formation constants of the binary complexes L, LH, LH_2, M, ML, ML_2 species were considered. ML_3 species was also considered in case of Ni(II) complexes. These refined values are in close agreement with the values reported earlier in literature.[17—19] These values were used as fixed parameters for the refinement of the formation constants of the ternary complexes [MAL]. For the determination of the formation constant of the ternary complexes MAL, the following sets of solutions (50 cm^3) having M : A : L in the ratio 1 : 1 : 1 and 1 : 2 : 2 were prepared and titrated against standard alkali:

i) 0.02 M $HClO_4$, 0.002 M metal perchlorate, 0.002 M ligand (A), 0.002 M ligand (L) and 0.174 M $NaClO_4$.

ii) 0.02 M $HClO_4$, 0.002 M metal perchlorate, 0.004 M ligand (A), 0.004 M ligand (L) and 0.170 M $NaClO_4$.

Titrations of each set were carried out twice to check the reproducibility of the data. In case of catechol and its derivatives titrations were carried out under nitrogen atmosphere. The pH range selected for the computer programme was 3—7 for [CuAL] and 5—9 for [NiAL] complexes. The experimental values of pH and volume of alkali used in this range were fed to the computer. Calculations were carried out using the computer programme SCOGS. The species considered for the calculation of formation constants of the ternary complexes were A, AH, AH_2, L, LH, LH_2, M, MA, MA_2, ML, ML_2, and MAL. ML_3 species were also considered in case of Ni(II) complexes. The formation constants $\log K^{M}_{MAL}$, $\Delta\log K$ and $\Delta(\Delta\log K)$ have been presented in Tables 1 and 2. The deviations in the $\log K^{M}_{MAL}$ values have been shown in brackets. These indicate random errors in the titration, dependent on the precision of the instruments.

Discussion

The stability of the ternary complexes can be quantitatively evaluated in terms of $\Delta\log K$.

$$\Delta\log K = \log K^{MA}_{MAL} - \log K^{M}_{ML}$$
$$= \log K^{ML}_{MAL} - \log K^{M}_{MA}.$$

Alternatively it can be shown as

$$\Delta\log K = \log \beta^{M}_{MAL} - (\log K^{M}_{MA} + \log K^{M}_{ML}).$$

It is observed, that in general, $\Delta\log K$ for the MAL complexes studied is negative, as expected from the statistical considerations. $\Delta\log K$ becomes more negative with increasing charge on the ligand L, e.g. oxalate$\geqslant$glycinate$\sim$ethylenediamine. This is because imda and dpa have two negative charges. The second negatively charged ligand faces electrostatic repulsion in

Table 1. Stability Constants of Ligand Complexes in Aqueous Medium and I=0.2 M ($NaClO_4$) at 25±1 °C with Standard Deviation in Parentheses

Ligand (L)	2,6-Pyridinedicarboxylic acid-Ni-L		2,6-Pyridine carboxylic acid-Cu-L		($\Delta\log K_{Ni}-\Delta\log K_{Cu}$)
	$\log K^{Ni}_{NiAL}$	$\Delta\log K$	$\log K^{Cu}_{CuAL}$	$\Delta\log K$	$\Delta(\Delta\log K)$
Glycine	12.20 (0.04)	−0.59	15.84 (0.03)	−0.98	+0.39
α-Alanine	11.90 (0.04)	−0.56	16.00 (0.05)	−0.83	+0.27
Phenylalanine	11.78 (0.07)	+0.01	16.10 (0.06)	−0.29	+0.30
Tyrosine	11.90 (0.01)	+0.19	15.92 (0.02)	−0.28	+0.47
Tryptophan	12.39 (0.01)	+0.14	16.69 (0.02)	−0.19	+0.33
Ethylenediamine	14.36 (0.05)	−0.58	18.02 (0.04)	−0.91	+0.33
1,3-Propanediamine	13.42 (0.04)	−0.97	17.60 (0.05)	−1.01	+0.04
Oxalic acid	10.35 (0.07)	−0.69	11.69 (0.06)	−2.05	+1.36
Catechol	14.82 (0.01)	−0.51	20.90 (0.03)	−1.66	+1.15
Catechuic Acid	14.32 (0.01)	−0.71	19.98 (0.03)	−1.71	+1.00
Tiron	15.05 (0.07)	−1.50	20.89 (0.05)	−1.83	+0.33
Pyrogallol	13.40 (0.06)	−0.97	20.66 (0.07)	−1.04	+0.07
o-Aminophenol	10.50 (0.07)	−0.84	16.46 (0.07)	−0.93	+0.09
o-Phenylenediamine	—	—	12.62 (0.06)	−0.72	—

Table 2. Stability Constants of Mixed Ligand Complexes in Aqueous Medium and I=0.2 M ($NaClO_4$) at 25±1 °C with Standard Deviation in Parentheses

Ligand (L)	Iminodiacetic acid-Ni-L		Iminodiacetic acid-Cu-L		($\Delta\log K_{Ni}-\Delta\log K_{Cu}$)
	$\log K^{Ni}_{NiAL}$	$\Delta\log K$	$\log K^{Cu}_{CuAL}$	$\Delta\log K$	$\Delta(\Delta\log K)$
Glycine	13.55 (0.04)	−0.79	15.71 (0.06)	−1.73	0.94
α-Alanine	13.31 (0.04)	−0.70	15.76 (0.06)	−1.69	0.99
Phenylalanine	12.80 (0.01)	−0.52	15.73 (0.05)	−1.28	0.76
Tyrosine	12.86 (0.01)	−0.40	15.52 (0.02)	−1.30	0.90
Tryptophan	13.37	−0.43	16.14	−1.36	0.93
Ethylenediamine	15.77 (0.02)	−0.72	18.31 (0.04)	−1.24	0.52
1,3-Propanediamine	14.78 (0.01)	−1.14	16.97 (0.07)	−2.26	1.12
Oxalic acid	—	—	—	—	—
Catechol	15.42 (0.02)	−1.46	—	—	—
Tiron	15.78 (0.02)	−2.32	—	—	—
Pyrogallol	14.39 (0.04)	−1.53	—	—	—
o-Aminophenol	11.15 (0.05)	−1.74	—	—	—
o-Phenylenediamine	—	—	—	—	—

forming the ternary complex. Hence, the tendency of L^{n-} to get bound to neutral MA will be less than to get bound with charged M^{2+} ion in the formation of binary complex ML, leading to negative $\Delta\log K$ value. The electrostatic replusion is more with increasing charge on L^{n-}, resulting in more negative $\Delta\log K$ values.

However, it is observed that $\Delta\log K$ in [M–dpa–L] complexes is less negative than [M–imda–L]. This is attributable to the fact that dpa coordinates from two carboxylates and one tertiary amine nitrogen. There is π acidic character in the ligand, due to the possibility of $M\rightarrow N\pi$ bond formation. On the other hand imda coordinates from two carboxylates and one σ bonding secondary amine nitrogen. Due to the π acidic character of dpa $\Delta\log K$ is less negative as observed in [M–dipyridyl–L] complexes.[7,8]

It is interesting to observe that $\Delta\log K$ is more negative in case of Cu(II) complexes compared to Ni(II) complexes. This is due to the tridentate character of dpa and imda.

In the binary complex the tridentate ligand dpa or imda occupy the three equatorial positions around the metal ion. Hence in the formation of the termary complex, the bidentate ligand(L) has to occupy one equatorial and one axial position,[20] or the tridentate ligand has to change to two equatorial and one axial position, and there may be equilibrium between the two forms. Due to Jahn Teller effect, in case of CuAL complexes either ligand is strained in occupying the axial position and hence its tendency to coordinate with the MA is much less than in the binary complex, hence $\log K^{\mathrm{MA}}_{\mathrm{MAL}}$ is much less than $\log K^{\mathrm{M}}_{\mathrm{ML}}$ and $\Delta\log K$ is more negative. In the absence of Jahn Teller distortion in Ni(II) complexes, the bidentate or the tridentate ligand does not feel any strain in occupying one equatorial and one axial position, and hence $\Delta\log K$ is less negative.

It is interesting to observe that $\Delta(\Delta\log K)(=\Delta\log K_{\mathrm{NiAL}}-\Delta\log K_{\mathrm{CuAL}})$ is less in MdpaL complexes than MimdaL complexes. This can be explained by considering the fact that the stabilizing effect of π acidic character of ligand (A) is more pronounced in CuAL complexes than in NiAL complexes. Hence the destabilization of the Cu–dpa–L complexes due to J. T. effect, is compensated by the increase in stability due to greater π acidic character of dpa. Hence $\Delta(\Delta\log K)$ $(=\Delta\log K_{\mathrm{NiAL}}-\Delta\log K_{\mathrm{CuAL}})$ is less in case of MdpaL complexes, compared to M–imda–L complexes.

It is observed that for the complexes Cu–dpa–L and Ni–dpa–L, where L=phenylalanine, tyrosine and tryptophan, $\Delta\log K$ value is less negative than the complexes where L=glycine or α-alanine. This is because of intramolecular interligand interaction as observed by Sigel[21] in complexes of the type $M(phen)(pheCA)^+$ where $M=Cu^{2+}$, Zn^{2+}, phen=1,10-phenanthroline and pheCA =phenylalkane carboxylates as also by Yamauchi[22] in complexes of the type Cu(DA)(AA), where AA=amino acids with side chains and DA= diamines. In the present complexes, the amino acids are bidentate, hence occupy one equatorial and one axial position or both equatorial positions as in case of glycinate and α-alaninate. Model building shows that in case where the amino acid occupied both equatorial positions, the non-coordinated side group, phenyl, hydroxyphenyl, and indole ring of phenylalanine, tyrosine, and tryptophan respectively, come over the pyridyl ring of dpa and hence non-covalent hydrophobic interaction stabilizes the ternary complex, leading to less negative $\Delta\log K$ values. Thus in cases of M–dpa–L complexes, the bidentate amino acid L should prefer two equatorial positions.

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