

Quantification of intramolecular interactions in the metal complexes of beta-hydroxy ketone derivatives (O-O donors) and benzotriazole derivatives (N-O donors) in solution

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Abstract- The stabilities of ternary complexes of metal ions (copper, nickel, zinc and cobalt) with beta-hydroxy ketone (BHK) derivatives and benzotriazole (BTAZ) derivatives in 50% water + 50% dioxane medium in 0.1 M KNO_3 ionic strength at 25°C using potentiometric pH titrations have been established. The data reveal that the copper forms more stable complexes, which is followed by zinc ion complexes with these ligands. Both nickel and cobalt form complexes with similar stabilities. The stabilities of these complexes are further quantified with $\Delta \log K$ values, intra-molecular equilibrium constants and percentage of stacking interaction in the ternary systems. The observed positive $\Delta \log K$ values suggest that the flexible side chain alkyl moiety (butyl group) or aromatic moiety (phenyl group) in BHK ligand overlaps with the fixed aromatic moiety of BTAZ ligand in the ternary complex, which results in the enhanced stabilities for the (BHK-Bu)-Metal(II)-BTAZ and (BHK-Ph)-Metal(II)-BTAZ systems. Interestingly, the positive $\Delta \log K$ values for both BHK-Bu and BHK-Ph ligands in their corresponding ternary complexes are about the same. This suggests the flexible butyl or phenyl sidechain of BHK is overlapping with the triazole ring, but not the phenoxy ring of the BTAZ ligand.

Index Terms- Ternary complexes, mixed ligand complexes, stability constants, intramolecular interactions, stacking interactions.

I. INTRODUCTION

Metal-ligand complexes have several applications in various fields. Some of the utilities include in the biological systems¹ development of luminescent materials^{2,3} color stabilizing agents for toners in color photography^{4,5} and catalysts⁶. In these applications, the metal ligand complexes act as charge controlling agents, because the metal-ligand complexes are excellent in heat resistance and environment resistance in the medium. These properties of metal complexes directly depend on (i) the structure of the ligand and (ii) the stability of metal-ligand complexes against the heat, light and their solubility properties. For example, in order to develop a luminescent material with excellent properties, the first requirement is the investigation of the stabilities of metal-ligand complexes. The easy and quick technique to find out the properties of metal ligand complexes is

potentiometric technology⁷ and is being used in exploring the interactions of metal ligand(s) complexes in solution^{8,9,10}.

In general the stability of metal ligand complexes is estimated by the strength of the interaction between the metal ion and the ligands. However, in some cases, the intramolecular non-covalent interactions between ligands can contribute a significant role in the overall binding energy of the complex. These interactions include hydrogen bonding, hydrophobic interactions, and stacking interactions between the ligands of the complex. Most of the time the predicted stabilities of the metal ligand complexes, based on the pK_a values of the ligands, differ from the experimental values. This is because of the fact that the intramolecular interactions present between the coordinated ligands in the metal complex and also these interactions are depend on the orientation of the side chains of the ligands.

In order to get more information on the intramolecular interactions and their contribution towards the overall stability of metal ligand complexes, in this investigation, we selected beta-hydroxy ketone (BHK) derivatives and benzotriazole(BTAZ) derivatives as ligands, and Cu(II), Ni(II), Zn(II) and Co(II) as metal ions in the formation of metal ligand complexes.

The metal complexes of beta-hydroxy ketone (BHK) and benzotriazole (BTAZ) derivatives have several industrial applications. For example, metal complexes of BHK are known to use as a fluorescent probes or insecticides¹¹ whereas metal complexes of BTAZ used as catalysts in organic synthesis¹².

The selected beta-hydroxy ketone derivative has a methyl or ethyl or butyl or aromatic substitution in a flexible side chain and this side chain is not involved in the metal coordination. The selected second ligand, benzotriazole derivative, which has benzotriazole ring connected to ethanol or phenol side chain, and this side chain involved in the coordination with the metal ion. In this report we show that the flexible butyl and phenyl side chain of beta-hydroxy ketone involves in the intramolecular interaction with the benzotriazole ring, but not phenoxy ring of benzotriazole derivative.

The objective of this investigation is to identify the intramolecular interactions and their contributions towards the overall stabilities of metal-ligand complexes. In this investigation we explore, how the side chain groups from BHK interact with fixed aromatic moieties of bound BHK ligand to the metal ion and its effect on the overall stability of the ternary metal-ligand complexes in solution.

II. EXPERIMENTAL

The ligands from beta-hydroxy ketone (BHK) derivatives are shown in Figure 1 (a)-(d). The BHK ligands consisting of trifluoromethyl group in the compound. The listed ligands differ from each other at their terminal positions. The formula (a) is abbreviated as BHK-Me, the formula (b) is abbreviated as BHK-Et, the formula (c) is abbreviated as BHK-Bu, and the formula (d) is abbreviated as BHK-Ph, where BHK is $\text{CF}_3\text{-C(OH)=CH-C(=O)-CH}_2\text{-}$, Me is methyl, Et is ethyl, Bu is butyl and Ph is $\text{-CH}_2\text{-phenyl}$ group.

The ligands from benzotriazole (BTAZ) derivatives are shown in Figure 1 (e) and (f). The listed two ligands differed by the nature of substituted alcohol group. The formula (e) is abbreviated as BTAZ-Alk-OH, and the formula (f) is abbreviated as BTAZ-Ph-OH, where Alk is $\text{-CH}_2\text{-CH}_2\text{-}$ and Ph is -phenyl group.

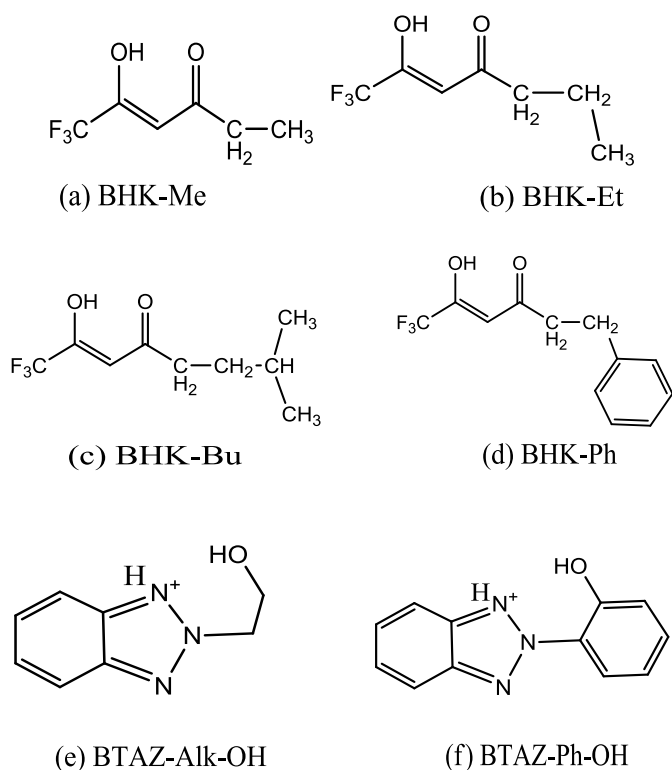


Figure 1. Beta-hydroxy ketone (BHK) derivatives (a)-(d) and Benzotriazole (BTAZ) derivatives (e) and (f).

The above ligands are synthesized and purified in our laboratory (unpublished data).

Metal salts of Cu(II), Ni(II), Co(II) and Zn(II) were AR grade chemicals. All the metal ions were standardized with disodium salt of EDTA¹³. Carbonate free sodium hydroxide was prepared and standardized by titration with potassium acid phthalate¹⁴.

Stock solutions of metal ion were prepared from double distilled water. For every titration, fresh solid ligand was weighed out into the reaction cell to avoid possible hydrolysis.

The experimental method consisted of potentiometric titration of the free ligands with standard sodium hydroxide in the absence and in the presence of above mentioned metal ions being investigated. The titrations were carried out in a

magnetically stirred double-walled reaction cell maintained at 25°C. The ionic strength was maintained constant by using 0.10M KNO_3 as a supporting electrolyte and relatively low concentration of the ligand and metal ion ($1 \times 10^{-3}\text{M}$). During the course of titration a stream of nitrogen was passed over the solution to eliminate the adverse effect of atmospheric carbon dioxide. For every titration, fresh solid ligand was weighed out into the reaction cell to avoid possible concentration effects.

A digital pH meter with a combination electrode was used to determine the hydrogen ion concentration. The electrode system was calibrated by direct titration of acetic acid, and the observed pH meter reading was compared with the actual hydrogen ion concentration. The pH regions below 3.5 and above 10.5 were calibrated by measurement in HCl and NaOH solutions, respectively.

All the titrations were conducted in dioxane-water (50:50) solvent system. The pK_w^c values were validated for 25°C and 0.1 M ionic strength using the Debye-Huckel equation for water and dioxane mixture¹⁵. The pK_w values, the dielectric constants and densities were obtained from Harned and Owen¹⁶. No turbidity or precipitation was noticed at any time during the titration of metal ions with the ligands.

III. CALCULATIONS

The ionization constants of various ligands were calculated using the computer program PKAS⁷. Entire pH range from the titration data has been given for the calculation of pK_a values using the computer program. All the formation or stability constants were subjected to refinement using the computer program BEST⁷. The refinement of the stability constants of binary and ternary systems were done by considering all possible species present in the solution, i.e., HL^+ , HA, L⁻, A⁻, ML, ML_2 , MA, MA_2 and MAL etc, where L and A are different ligands in the complex. The refined values for these complexes thus obtained are given in Tables 1-3. The error limits in these constants were minimized (sigma fit is 0.001).

Table 1 – Ionization constants (pK_a) of Beta-hydroxy ketone derivatives and Benzotriazole derivatives, $\mu = 0.10 \text{ mol dm}^{-3}$ (KNO_3) at Temp = 25°C, Solvent 50% water + 50% dioxane

Ligand	pK_a	pK_{2a}
(a) BHK-Me	9.88 ± 0.04	-
(b) BHK-Et	9.99 ± 0.04	-
(c) BHK-Bu	10.16 ± 0.04	-
(d) BHK-Ph	10.36 ± 0.03	-
(e) BTAZ-Alk-OH	6.55 ± 0.02	9.82 ± 0.02
(f) BTAZ-Ph-OH	6.74 ± 0.04	10.22 ± 0.04

Table 2 – Stability constants[†] ($\log K$) for the metal(II)-ligand (1:1) binary complexes, $\mu = 0.10 \text{ mol dm}^{-3}$ (KNO_3) at Temp = 25°C, Solvent 50% water + 50% dioxane

Ligand	Cu(II)	Ni(II)	Zn(II)	Co(II)
(a) BHK-Me	6.62	4.45	3.62	3.56
(b) BHK-Et	6.33	4.24	3.33	3.25
(c) BHK-Bu	6.03	3.92	3.13	2.89

(d) BHK-Ph	6.01	3.81	3.12	2.92
(e) BTAZ-Alk-OH	8.71	5.98	6.28	5.83
(f) BTAZ-Ph-OH	8.65	5.78	6.01	5.63

†standard deviation ±0.02 to ±0.04

Table 3 – Stability constants[†] (log K) for the BHK-metal(II)-BTAZ(1:1:1) ternary complexes, $\mu = 0.10 \text{ mol dm}^{-3}$ (KNO_3) at Temp = 25°C, Solvent 50% water + 50% dioxane

Ternary Complex	Metal ion			
	Cu(II)	Ni(II)	Zn(II)	Co(II)
(BHK-Me)-(Metal (BTAZ-AlkOH))-	14.98	9.82	9.52	8.68
(BHK-Me)-Metal-(BTAZ-Ph-OH)	14.91	9.72	9.42	8.67
(BHK-Et)-(Metal (BTAZ-Alk-OH))-	14.82	9.71	9.38	8.38
(BHK-Et)-Metal-(BTAZ-Ph-OH)	14.72	9.62	9.22	8.29
(BHK-Bu)-(Metal (BTAZ-Alk-OH))-	14.91	9.88	9.52	8.75
(BHK-Bu)-Metal-(BTAZ-Ph-OH)	14.83	9.74	9.28	8.55
(BHK-Ph)-(Metal (BTAZ-Alk-OH))-	15.39	9.92	9.79	8.88
(BHK-Ph)-Metal-(BTAZ-Ph-OH)	15.34	9.75	9.54	8.71

†standard deviation ±0.02 to ±0.04

IV. RESULTS AND DISCUSSION

Dissociation constants of ligands

The potentiometric titration of BHK ligands took one mole of base per mole of ligand to complete deprotonate the ligand. The dissociation constant (pK_a) for these ligands were calculated from the experimental points taken between $a=0$ and $a=1$ (a is moles of bases added per mole of ligand). The pK_a values for BHK ligands were calculated by taking into consideration of species HA and A, where HA is protonated ligand and A is a deprotonated ligand. The pK_a values for these ligands are listed in Table 1. The single pK_a value from the dissociation of H^+ is from the $-\text{OH}$ group on the ligand.

The potentiometric titration curve of BTAZ ligands show an inflection at $a=1$ followed by buffer region at high pH. The pK_a and pK_{2a} for these ligands were calculated between $a=0$ and $a=1$, and $a=1$ and $a=2$ respectively and the constants are listed in Table 1. The protonation constants were calculated by taking into consideration of the species, H_2L , HL and L, where H_2A and HL are protonated ligand and L is deprotonated ligand.

The calculated pK_a values for these ligands are listed in Table 1. The pK_a values for BHK ligands increase in the order $-\text{CH}_3 < -\text{CH}_2-\text{CH}_3 < \text{butyl} < -\text{CH}_2-\text{Ph}$. This increase can be explained based on the fact that increase in hydrophobicity of the ligand increases pK_a value. In this case, the hydrophobicity increases from $-\text{CH}_3$ to $-\text{CH}_2-\text{Ph}$, which weakens the ionization

of proton and therefore increases the pK_a value the ligand. Similar trend is noticed in the pK_a values of BTAZ ligands.

Stabilities of binary complexes

The interaction of metal ions (Cu^{2+} , Ni^{2+} , Zn^{2+} and Co^{2+}) with BHK ligands in a 1:1 ratio at 25°C took one mole of base per mole of metal ion, i.e., $m=1$ (m is moles of based added per mole of metal ion) followed by buffer region till $m=3$, indicating simultaneous formation of 1:1 metal ligand complex between $m=0$ and $m=1$. The formation constants for the metal-ligand complexes were calculated in the upper buffer region taking into consideration of pK_a value of the ligand. All the stability constants for the binary complexes are listed in Table 2.

The interaction of metal ions (Cu^{2+} , Ni^{2+} , Zn^{2+} and Co^{2+}) with BTAZ ligands in a 1:1 ratio at 25°C gave inflection at $m=2$ (m is moles of based added per mole of metal ion) followed by buffer region till $m=5$, indicating simultaneous formation of 1:1 metal ion complex with BTAZ ligands in between $m=0$ and $m=2$. All the stability constants for the binary complexes are listed in Table 2.

Stabilities of Ternary Complexes

The interaction of metal ions (Cu^{2+} , Ni^{2+} , Zn^{2+} and Co^{2+}) with BHK and BTAZ ligands in a 1:1:1 ratio at 25°C gave inflection at $m=3$ indicating simultaneous formation of 1:1:1 mixed ligand complex between $m=0$ and $m=3$. This was further confirmed by the species distribution curves (Figure 2).

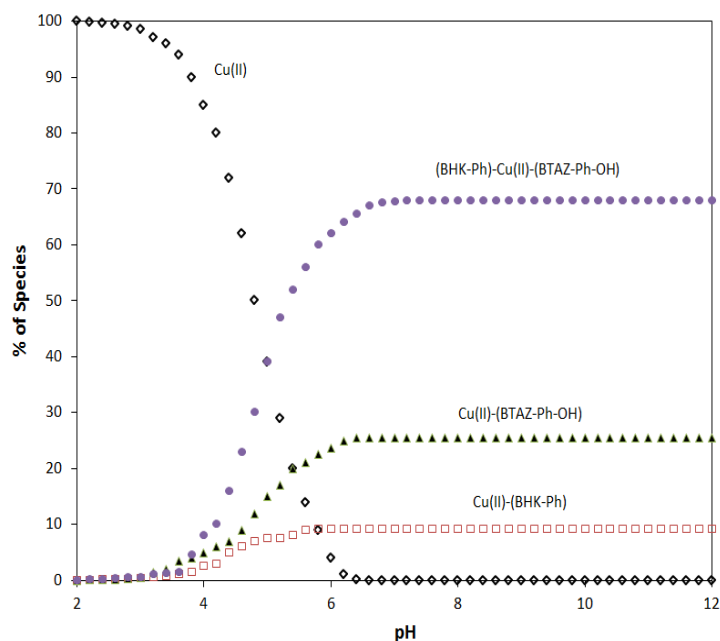


Figure 2. Distribution of various species present in the ternary complex formation between Cu(II), BHK-Ph and BTAZ-Ph-OH over the pH range from 2-12

The stability constants for the mixed ligands and metal ion complexes were calculated in the upper buffer region taking into consideration of pK_a value of both the ligands. All the constants so calculated are listed in Table 3.

Quantification of the Stabilities of Ternary Complexes

The ligand-ligand interactions between the alkyl and aromatic side chain of the bound ligands to metal ion in the ternary complex may result in an enhancement of stability of the complex, relative to the stabilities of their corresponding binary complexes. This kind of stability in the ternary complexes can be quantified in terms of $\Delta \log K$ values (the difference between the overall ternary complexes and the corresponding binary complexes), and these values are listed in Table 4.

Table 4 –Stabilities of BHK-metal(II)-BTAZ (1:1:1) ternary complexes in terms of $\Delta \log K$ values

Ternary Complex	Metal ion			
	Cu(II)	Ni(II)	Zn(II)	Co(II)
(BHK-Me)-(Metal)-(BTAZ-AlkOH)	-0.35	-0.61	-0.38	-0.71
(BHK-Me)-Metal-(BTAZ-Ph-OH)	-0.36	-0.51	-0.21	-0.52
(BHK-Et)-(Metal)-(BTAZ-Alk-OH)	-0.22	-0.51	-0.23	-0.70
(BHK-Et)-Metal-(BTAZ-Ph-OH)	-0.26	-0.40	-0.12	-0.59
(BHK-Bu)-(Metal)-(BTAZ-Alk-OH)	0.17	0.02	0.11	0.03
(BHK-Bu)-Metal-(BTAZ-Ph-OH)	0.15	0.04	0.14	0.03
(BHK-Ph)-(Metal)-(BTAZ-Alk-OH)	0.67	0.13	0.39	0.13
(BHK-Ph)-Metal-(BTAZ-Ph-OH)	0.68	0.16	0.41	0.16

It appears that the $\Delta \log K$ values are positive for (BHK-Bu)-Metal(II)-(BTAZ) and (BHK-Ph)-Metal(II)-(BTAZ) system and where $\Delta \log K$ values are negative for BHK ligands having aliphatic side chain with methyl and ethyl groups. This clearly suggests that the flexible butyl and aromatic moiety in BHK ligand overlaps with the aromatic moiety of fixed BTAZ ligand in the ternary complex (Figure 3), which results in the enhanced stabilities for the (BHK-Bu)-Metal(II)-BTAZ and (BHK-Ph)-Metal(II)-BTAZ systems.

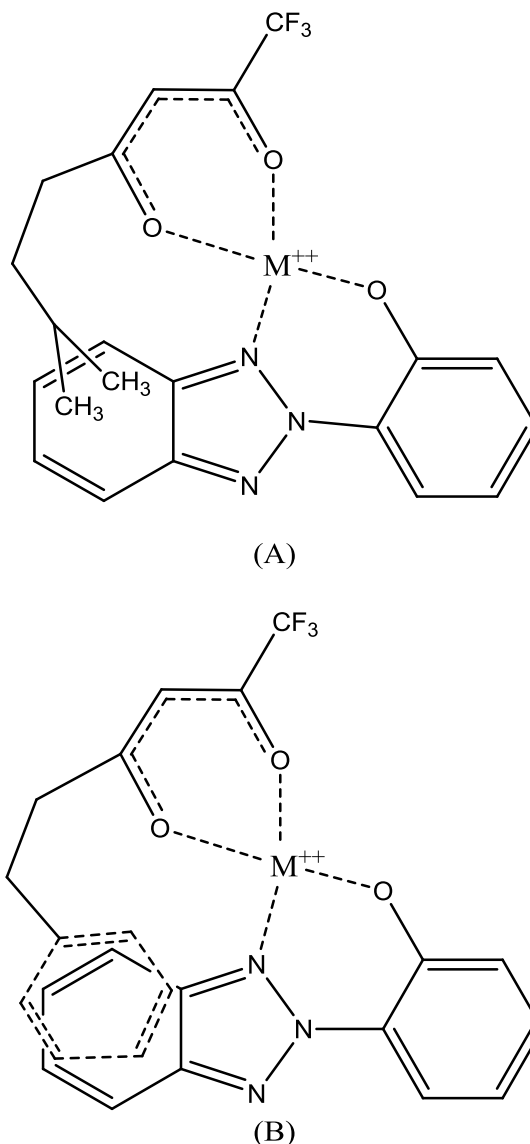


Figure 3. Tentative and simplified structure of ternary complex of (A) (BHK-Bu)-Metal(II)-(BTAZ-Ph-OH), and (B) (BHK-Ph)-Metal(II)-(BTAZ-Ph-OH), showing the intramolecular interaction between flexible side chain of BHK ligand with the heterocyclic ring of fixed BTAZ-Ph-OH ligand

Interestingly, the $\Delta \log K$ values for both (BHK-Bu)/(BHK-Ph)-Metal(II)-(BTAZ-Alk-OH) and (BHK-Bu)/(BHK-Ph)-Metal(II)-(BTAZ-Ph-OH) are about the same. This suggests that butyl and phenyl moiety of BHK is overlapping with the triazole ring, but not the phenoxy ring of the BTAZ ligand. The copper complexes exhibit larger positive $\Delta \log K$ or lower negative $\Delta \log K$ values, which is followed by zinc. The cobalt and nickel show about the same $\Delta \log K$ values.

The positive $\Delta \log K$ values are transformed into intramolecular equilibrium constant and percentage of stacking interaction in the ternary system, and these values are listed in Tables 5 and 6. The intra-molecular equilibrium and percentage of stacking between the butyl and phenyl moieties of the BHK

and BTAZ ligands in the ternary complex are calculated with the following equations (1) and (2):

$$K_1 = (10^{\Delta \log K}) - 1 \quad (1)$$

$$\% \text{ of (TernaryComplex)}_{\text{stacking}} = (K_1 / (1 + K_1)) * 100 \quad (2)$$

where K_1 is intra-molecular equilibrium constant, which is a dimensionless constant.

Table 5 – Quantification of ligand-ligand interactions in (BHK-Bu)-metal(II)-BTAZ (1:1:1) ternary complexes in terms of $\Delta \log K$, Intra-molecular equilibrium constant (K_1) and Percentage of Stacking[‡]

Metal(II)	(BHK-Bu)-Metal-(BTAZ-AlkOH)			(BHK-Bu)-Metal-(BTAZ-Ph-OH)		
	$\Delta \log K$	K_1	% of Stacking	$\Delta \log K$	K_1	% of Stacking
Cu(II)	0.17	0.48	32.39	0.25	0.41	29.21
Ni(II)	0.02	0.05	4.51	0.04	0.09	8.79
Zn(II)	0.11	0.29	22.38	0.14	0.38	27.56
Co(II)	0.03	0.07	6.67	0.03	0.07	6.67

[‡]overlap between the butyl side chain of BHK over the heterocyclic ring of benzotriazole.

Table 6 – Quantification of ligand-ligand interactions in (BHK-Ph)-metal(II)-BTAZ (1:1:1) ternary complexes in terms of $\Delta \log K$, Intra-molecular equilibrium constant (K_1) and Percentage of Stacking[‡]

Metal(II)	(BHK-Ph)-Metal-(BTAZ-AlkOH)			(BHK-Ph)-Metal-(BTAZ-Ph-OH)		
	$\Delta \log K$	K_1	% of Stacking	$\Delta \log K$	K_1	% of Stacking
Cu(II)	0.67	3.67	78.62	0.68	3.78	79.11
Ni(II)	0.13	0.35	25.87	0.16	0.44	30.81
Zn(II)	0.39	1.45	59.26	0.41	1.57	61.09
Co(II)	0.13	0.35	25.87	0.16	0.44	30.82

[‡]overlap between the phenyl side chain of BHK over the heterocyclic ring of benzotriazole.

According to the data in Tables 5 and 6, the intra-molecular equilibrium constant is high for copper complexes compared to other metal ternary complexes. The percentage of stacking is also high for copper complexes, followed by zinc complexes and about the same for nickel and cobalt complexes.

V. CONCLUSIONS

We report stabilities of ternary complexes of metal ions (copper, nickel, zinc and cobalt) with beta-hydroxy ketone derivatives and benzotriazole derivatives in 50% water + 50%

dioxane medium using potentiometric technology. The calculated data suggests that copper forms more stable complexes, which is followed by zinc ion complexes with these ligands. Both nickel and cobalt form about the same stable complexes. The stabilities of these complexes are quantified with $\Delta \log K$ values, intra-molecular equilibrium constants and percentage of stacking interaction in the ternary systems. The striking positive $\Delta \log K$ values suggest that side chain butyl and phenyl moiety in BHK ligand overlaps with the aromatic moiety of BTAZ ligand in the ternary complex, which results in the enhanced stabilities for the (BHK-Bu)/(BHK-Ph)-Metal(II)-BTAZ system. Interestingly, the $\Delta \log K$ values for both (BHK-Bu)/(BHK-Ph)-Metal(II)-(BTAZ-Alk-OH) and (BHK-Bu)/(BHK-Ph)-Metal(II)-(BTAZ-Ph-OH) are about the same. This suggests the aromatic moiety of BHK is overlapping with the triazole ring, but not the phenoxy ring of the BTAZ ligand.

In view of the utilities of metal complexes of beta-hydroxy ketone and benzotriazole derivatives in the chemical and biochemical fields, the established unexpected stabilities, from the intramolecular interactions, for the reported ternary complexes may serve as good model complexes in the design and development of chemical probes. The ligand-ligand interactions in the metal-ligand complexes are directly related to the overall stability of the chemical probe. Our data also suggest that copper and zinc complexes may be superior to the nickel and cobalt complexes.

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