

# Metal mediated intramolecular interactions in the ternary complexes of beta-hydroxy ketone derivatives (O-O donors) and benzotriazole derivatives (N-N and N-O donors) with transitional metal ions

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**Abstract-** The metal mediated intramolecular interactions and their stabilities have been established for the ternary complexes of metal ions (copper, nickel, zinc and cobalt) with beta-hydroxy ketone (BHK) derivatives (O-O donor atoms) and benzotriazole (BTAZ) derivatives (N-N and N-O donor atoms) in 50% water + 50% dioxane medium in 0.1 M  $\text{KNO}_3$  ionic strength at 25°C using potentiometric pH titrations. The intramolecular interactions and the stabilities of these complexes are quantified in terms of  $\Delta \log K$  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 in BHK ligand having butyl and phenyl ring overlaps with the fixed aromatic moiety of BTAZ ligand in the ternary complex, which results in the enhanced stabilities for the ternary complexes. Based on the experimental data we conclude that, (i) the flexible side chains of BHK ligand having butyl and phenyl ring interacts with the heterocyclic ring of BTAZ ligand in the ternary metal-ligand complex, but not with aniline ring, (ii) ternary complexes with BTAZ having N-N donor atoms form more stable complexes over the BTAZ having N-O donor atoms and (iii) ternary complexes with copper forms more stable complexes, which is followed by zinc ion complexes with the ligands, and both nickel and cobalt form complexes with similar stabilities.

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

## I. INTRODUCTION

The scientific research in the identification of mixed ligand metal complexes or ternary complexes has been constantly growing for the last several decades, because of their broad arrays of applications in various scientific fields. The metal-ligand complexes have unique properties such as charge controlling agents or stabilizing agents or can act as liquid crystals etc., given the fact that the metal-ligand complexes are excellent in heat resistance and environment resistance in the medium. In view of their unique properties, the metal-ligand complexes have several applications in numerous fields from biotechnology to electronic devices. Some of the utilities include in the biological systems<sup>1</sup> development of luminescent materials<sup>2,3,4</sup> color stabilizing or charge controlling agents for

toners in photography<sup>5,6,7</sup> catalysts in chemical synthesis<sup>8</sup> in the photonic and optoelectronic devices<sup>9</sup> and liquid crystals<sup>10</sup>.

In the above mentioned utilities of metal-ligand complexes, the criticality is in the stabilities of metal-ligand complexes for a given medium. These stabilities are directly depending on (i) the structure of the ligand, (ii) nature of the metal ion, (iii) intramolecular interactions between the bound ligands in the metal mediated complex, and (iv) the medium for the complex formation. For example, in order to develop a metal-ligand complex for therapeutic applications with excellent properties, the first requirement is to investigation of the stabilities of metal-ligand complexes in the medium of interest. As we mentioned above, several factors influence the stability of the metal ligand complex. Therefore, understanding the factors those contribute towards the overall stabilities of metal-ligand complexes is essential in the development of a metal-ligand complex system. A mechanistic understanding of how metal complexes achieve extra stability is crucial to their utility, as well as the rational design of new complexes with improved potency.

The stability of metal ligand complexes can be estimated or predicted based on the ligand coordination atoms, the charges of coordinated atoms and metal ions, and the chelate ring size in the complex. 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  $\text{pK}_a$  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 designed beta-hydroxy ketone (BHK) derivatives having flexible side chains of methyl, ethyl, butyl and phenyl groups and benzotriazole (BTAZ) derivatives having to side chains, and Cu(II), Ni(II), Zn(II) and Co(II) as metal ions in the formation of metal ligand complexes. The objective of this investigation is to explore, how the side chain groups from BHK interact with fixed aromatic moieties of bound BHK ligand to the metal ion.

The BHK derivative has a methyl or ethyl or butyl or aromatic substitution in a flexible side chain and this side chain does not involve in the metal coordination. In BHK O-O atoms are the donor atoms and these atoms coordinate to the metal ion. The BTAZ derivative has a benzotriazole ring connected to ethylene amine or aniline, and nitrogen atom from benzotriazole ring and amine group from the side chain involve in the coordination to the metal ion.

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 insecticides<sup>11</sup> whereas metal complexes of BTAZ used as catalysts in organic synthesis<sup>12</sup>. However, there is no stability data available in the literature for these metal ligand complexes. Therefore, our report is certainly provides a valuable information in the development of metal-ligand probes using BHK and BTAZ ligands.

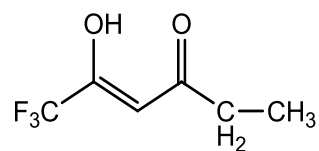
In addition to the above, the data from this report, i.e., the ternary complexes of transitional metal ions with BHK ligands (O-O donor atoms) and BTAZ ligands (N-N donor atoms) is compared with our previous communicated data for the ternary complexes of metal ions with BHK ligands (O-O donor atoms) and BTAZ ligands having N-O donor atoms (communicated to International Journal of Scientific and Research Publications Vol.4, Issue 7, July 2014) to establish the stabilities of ternary complexes with various donor atoms.

To achieve our above objectives, we chose potentiometric methodology, because it is the most convenient method and more economical to measure the stabilities of the metal-ligand complexes in solution<sup>13</sup> and is being used in exploring the interactions of metal ligand(s) complexes in solution in the scientific field<sup>14,15,16</sup>. In this report we adopted the potentiometric methodology to explore the stabilities of the metal-ligand complexes in solution.

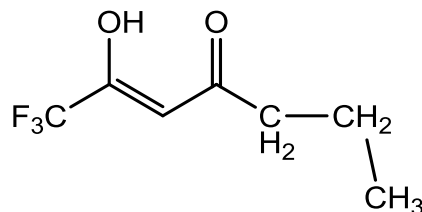
## II. EXPERIMENTAL

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.

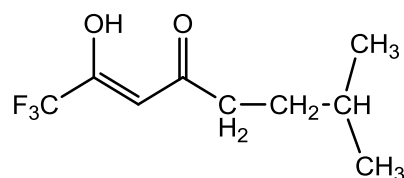
The ligands from benzotriazole (BTAZ) derivatives are shown in Figure 1 (e) and (f). The listed two ligands differed by the nature of the substituted amino side chain on the benzotriazole ring. The formula (e) is abbreviated as BTAZ-Alk-NH<sub>2</sub>, and the formula (f) is abbreviated as BTAZ-Ph-NH<sub>2</sub>, where Alk is  $\text{-CH}_2\text{-CH}_2\text{-}$  and Ph is  $\text{-phenyl}$  group.



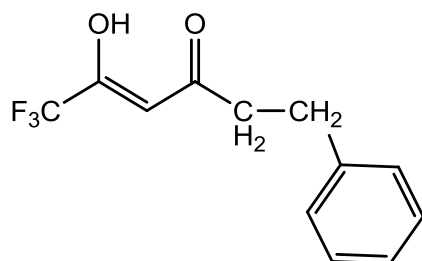
(a) BHK-Me



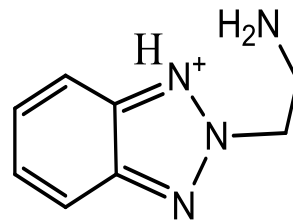
(b) BHK-Et



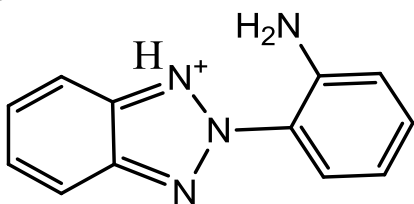
(c) BHK-Bu



(d) BHK-Ph



(e) BTAZ-Alk-NH<sub>2</sub>



(f) BTMZ-Ph-NH<sub>2</sub>

**Figure 1. Beta-hydroxy ketone (BHK) derivatives (a)-(d) and Benzotriazole (BTMZ) 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 EDTA<sup>17</sup>. Carbonate free sodium hydroxide was prepared and standardized by titration with potassium acid phthalate<sup>18</sup>

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<sub>3</sub> as a supporting electrolyte and relatively low concentration of the ligand and metal ion (1x10<sup>-3</sup>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<sub>w</sub><sup>c</sup> values were validated for 25°C and 0.1 M ionic strength using the Debye-Huckel equation for water and dioxane mixture<sup>19</sup>. The pK<sub>w</sub> values, the dielectric constants and densities were obtained from Harned and Owen<sup>20</sup>. No turbidity or precipitation was noticed at any time during the titration of metal ions with the ligands.

### Calculations

The ionization constants of various ligands were calculated using the computer program PKAS<sup>13</sup>. Entire pH range from the titration data has been given for the calculation of pK<sub>a</sub> values using the computer program. All the formation or stability constants were subjected to refinement using the computer program BEST<sup>13</sup>. 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<sup>+</sup>, HA, L<sup>-</sup>, A<sup>-</sup>, ML, ML<sub>2</sub>, MA, MA<sub>2</sub> and MAL etc, where L and A are different ligands in the complex. The refined values for these complexes thus obtained are provided in the Tables. The error limits in these constants were minimized (sigma fit is 0.001).

## III. 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<sub>a</sub>) 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<sub>a</sub> 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 calculated pK<sub>a</sub> value for BHK-Me is 9.88±0.04, for BHK-Et is 9.99±0.04, for BHK-Bu is 10.16±0.04 and BHK-Ph is 10.36±0.03. The single pK<sub>a</sub> value from the dissociation of H<sup>+</sup> is from the -OH group on the ligand.

The potentiometric titration curve of BTMZ ligands show an inflection at a=1 followed by buffer region at high pH. The pK<sub>a</sub> and pK<sub>2a</sub> for these ligands were calculated between a=0 and a=1, and a=1 and a=2 respectively. The calculated pK<sub>a</sub> and pK<sub>2a</sub> values for BTMZ-Alk-NH<sub>2</sub> are 6.51±0.02 and 9.22±0.02, and for BTMZ-Ph-NH<sub>2</sub> are 6.72±0.03 and 9.33±0.03. The pK<sub>a</sub> is corresponds to the release of protonated nitrogen from the heterocyclic ring, whereas the pK<sub>2a</sub> is corresponds to the release of protonated amino group from the side chain in the BTMZ ligand. The protonation constants were calculated by taking into consideration of the species, H<sub>2</sub>L, HL and L, where H<sub>2</sub>A and HL are protonated ligand and L is deprotonated ligand.

The pK<sub>a</sub> values for BHK ligands increase in the order -CH<sub>3</sub> < -CH<sub>2</sub>-CH<sub>3</sub> < -butyl < -CH<sub>2</sub>-Ph. This increase can be explained based on the fact that increase in hydrophobicity of the ligand increases pK<sub>a</sub> value. In this case hydrophobicity increases from -CH<sub>3</sub> to -CH<sub>2</sub>-Ph, which increases the pK<sub>a</sub> value of the ligand. Similar trend is noticed in the pK<sub>a</sub> values of BTMZ ligands.

### Stabilities of binary complexes

The interaction of metal ions (Cu<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup> and Co<sup>2+</sup>) 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 ligand BHK coordinates to the metal ion through its oxygen atoms (O-O donor atoms) in the formation of metal-ligand complex. The formation constants for the metal-ligand complexes were calculated in the upper buffer region taking into consideration of pK<sub>a</sub> value of the ligand. All the stability constants for the binary complexes are listed in Table 1.

**Table 1 – Stability constants<sup>†</sup> (log K) for the metal(II)-ligand (1:1) binary complexes,  $\mu = 0.10 \text{ mol dm}^{-3}$  (KNO<sub>3</sub>) 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-NH <sub>2</sub>	8.92	6.91	6.47	6.03
(f) BTAZ-Ph-NH <sub>2</sub>	8.68	5.98	6.28	5.93

<sup>†</sup>standard deviation  $\pm 0.02$  to  $\pm 0.04$

The interaction of metal ions (Cu<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup> and Co<sup>2+</sup>) with BTAZ ligands in a 1:1 ratio at 25°C gave inflection at m=2 (m is moles of base 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. The ligand BTAZ coordinates to the metal ion through its nitrogen atoms (N-N donor atoms) in the formation of metal-ligand complex. All the stability constants for the binary complexes are listed in the Table 1.

**Table 2 – Stability constants<sup>†</sup> (log K) for the BHK-metal(II)-BTAZ(1:1:1) ternary complexes,  $\mu = 0.10 \text{ mol dm}^{-3}$  (KNO<sub>3</sub>) 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-Alk-NH <sub>2</sub> )	15.13	9.99	9.72	8.78
(BHK-Me)-Metal-(BTAZ-Ph-NH <sub>2</sub> )	15.01	9.89	9.61	8.71
(BHK-Et)-Metal -(BTAZ-Alk-NH <sub>2</sub> )	14.92	9.93	9.52	8.62
(BHK-Et)-Metal-(BTAZ-Ph-NH <sub>2</sub> )	14.79	9.82	9.42	8.52
(BHK-Bu)-Metal-(BTAZ-Alk-NH <sub>2</sub> )	15.29	10.22	9.82	9.04
(BHK-Bu)-Metal-(BTAZ-Ph-NH <sub>2</sub> )	15.04	10.02	9.62	8.93
(BHK-Ph)-Metal -(BTAZ-Alk-NH <sub>2</sub> )	15.74	10.26	10.14	9.24
(BHK-Ph)-Metal-(BTAZ-Ph-NH <sub>2</sub> )	15.51	10.04	9.92	9.12

<sup>†</sup>standard deviation  $\pm 0.02$  to  $\pm 0.04$

### Stabilities of Ternary Complexes

The interaction of transitional metal ions (Cu<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup> and Co<sup>2+</sup>) 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. The

stability constants for the mixed ligands and metal ion complexes were calculated in the upper buffer region taking into consideration of pK<sub>a</sub> values of both the ligands. All the stability constants so calculated are listed in the Table 2.

**Table 3 – Stabilities of BHK-metal(II)-BTAZ(1:1:1) ternary complexes in terms of  $\Delta \log K$  values**

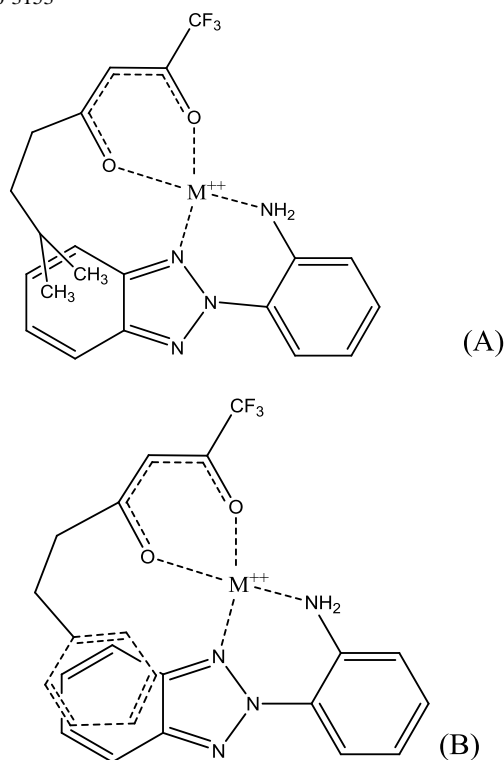
Ternary Complex	Metal ion			
	Cu(II)	Ni(II)	Zn(II)	Co(II)
(BHK-Me)-Metal -(BTAZ-AlkNH <sub>2</sub> )	-0.41	-0.65	-0.37	-0.81
(BHK-Me)-Metal-(BTAZ-Ph-NH <sub>2</sub> )	-0.29	-0.54	-0.29	-0.78
(BHK-Et)-Metal -(BTAZ-Alk-NH <sub>2</sub> )	-0.33	-0.50	-0.28	-0.66
(BHK-Et)-Metal-(BTAZ-Ph-NH <sub>2</sub> )	-0.22	-0.40	-0.19	-0.66
(BHK-Bu)-Metal -(BTAZ-Alk-NH <sub>2</sub> )	0.34	0.11	0.22	0.12
(BHK-Bu)-Metal-(BTAZ-Ph-NH <sub>2</sub> )	0.33	0.12	0.21	0.11
(BHK-Ph)-Metal -(BTAZ-Alk-NH <sub>2</sub> )	0.81	0.26	0.55	0.29
(BHK-Ph)-Metal-(BTAZ-Ph-NH <sub>2</sub> )	0.82	0.25	0.52	0.27

<sup>†</sup>standard deviation  $\pm 0.02$  to  $\pm 0.04$

### Quantification of the Stabilities of Ternary Complexes

The ligand-ligand interactions between the alkyl and aromatic groups 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 3.

In the analysis of stabilities of ternary complexes, specifically the role of BHK ligand, where the side chain is flexible, and is not involved with the metal ion coordination. It appears that the  $\Delta \log K$  values are positive (Table 3), if the ligand BHK having the side chain of butyl and phenyl group, whereas  $\Delta \log K$  values are negative for the ternary complexes, if the ligand BHK having the side chain of methyl and ethyl group. This clearly suggests that the flexible butyl and phenyl side chain from BHK ligand overlaps with the aromatic moiety of fixed BTAZ ligand in the ternary complex (Figure 2), which results in the enhanced stabilities for the (BHK-Bu)-Metal(II)-BTAZ and (BHK-Ph)-Metal(II)-BTAZ systems.



**Figure 2.** Tentative and simplified structure of ternary complex of (A): (BHK-Bu)-Metal(II)-(BTAZ-Ph-NH<sub>2</sub>), and (B): (BHK-Ph)-Metal(II)-(BTAZ-Ph-NH<sub>2</sub>), showing the intramolecular interaction between flexible side chain of BHK ligand with the heterocyclic ring of fixed BTaz-Ph-NH<sub>2</sub> ligand

In the further analysis of stabilities of ternary complexes, specifically the role of BTaz ligand, it appears that there is no effect of aniline ring on the BTaz on the overall stability of the ternary complexes, because the  $\Delta \log K$  values for both BTaz having either -Alk-NH<sub>2</sub> or -Ph-NH<sub>2</sub> systems are about the same (Table 3). This suggests that the butyl and phenyl side chain of BHK ligand is overlapping with the heterocyclic ring, but not the aniline 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 intra-molecular equilibrium constant and percentage of stacking interaction in the ternary system, and these values are listed in Tables 4 and 5. The intra-molecular equilibrium and percentage of stacking between the aromatic 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.

According to the data from Tables 4 and 5, 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.

**Table 4 – 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<sup>‡</sup>**

Metal(II)	(BHK-Bu)-Metal-(BTaz-Alk-NH <sub>2</sub> )			(BHK-Bu)-Metal-(BTaz-Ph-NH <sub>2</sub> )		
	$\Delta \log K$	$K_1$	% of Stacking	$\Delta \log K$	$K_1$	% of Stacking
Cu(II)	0.34	1.19	54.29	0.33	1.14	53.23
Ni(II)	0.11	0.29	22.38	0.12	0.32	24.14
Zn(II)	0.22	0.66	39.74	0.21	0.62	38.34
Co(II)	0.12	0.32	24.14	0.11	0.28	22.38

<sup>‡</sup>overlap between the butyl side chain of BHK over the heterocyclic ring of benzotriazole.

**Table 5 – Quantification of stacking 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<sup>‡</sup>**

Metal(II)	(BHK-Ph)-Metal-(BTaz-Alk-NH <sub>2</sub> )			(BHK-Ph)-Metal-(BTaz-Ph-NH <sub>2</sub> )		
	$\Delta \log K$	$K_1$	% of Stacking	$\Delta \log K$	$K_1$	% of Stacking
Cu(II)	0.81	5.45	84.51	0.82	5.61	84.86
Ni(II)	0.26	0.82	45.04	0.25	0.78	43.77
Zn(II)	0.55	2.55	71.81	0.52	2.31	69.81
Co(II)	0.29	0.95	48.71	0.27	0.86	46.29

<sup>‡</sup>overlap between the phenyl side chain of BHK over the heterocyclic ring of benzotriazole

In the above mentioned ternary systems, where BHK having O-O donor atoms and BTaz having N-N donor atoms

are involved in the coordination of metal ions. It is important to compare the above data with their corresponding ternary complexes where BTAZ having N-O donor atoms (communicated to International Journal of Scientific and Research Publications Vol.4, Issue 7, July 2014). This comparison data is listed in Table 6 and 7. In this report we compared, in Table 6 and 7, the ternary systems with only BHK having side chains butyl and phenyl group with BTAZ (N-O donor atoms) *versus* BTAZ (N-N donor atoms) to evaluate the effect of overall charge on the complex formation and its role on the stability of the ternary complexes in addition to the existing ligand-ligand interactions.

The data from the Table 6 and 7 reveals that the ternary complexes with BTAZ having N-N donor atoms forming more stable complexes (higher  $\Delta \log K$  and higher % of stacking values) compared to that of complexes with BTAZ having N-O donor atoms. This is because of the absence of electrostatic repulsion between the donor atoms of the two ligands, ternary complexes involving N-N donor ligands from BTAZ ligands are destabilized to a lesser extent than the corresponding complexes containing dinegative oxygen donor ligands from BHK ligands. The decreased stability is attributable to the electrostatic repulsion arising from the negatively charged oxygen atoms.

#### IV. CONCLUSION

We quantified the metal mediated intramolecular interactions and their stabilities for the ternary complexes of the ternary complexes of metal ions (copper, nickel, zinc and cobalt)

with beta-hydroxy ketone (BHK) derivatives (O-O donor atoms) and benzotriazole (BTAZ) derivatives (N-N and N-O donor atoms) in terms of  $\Delta \log K$ , intra-molecular equilibrium constant and % of stacking (for both alkyl and aromatic groups). Our experimental data suggest that, (i) the flexible side chains of BHK ligand having butyl and phenyl ring interacts with the heterocyclic ring of BTAZ ligand in the ternary metal-ligand complex, but not with aniline ring, (ii) ternary complexes with BTAZ having N-N donor atoms form more stable complexes over the BTAZ having N-O donor atoms and (iii) ternary complexes with copper forms more stable complexes, which is followed by zinc ion complexes with the ligands, and both nickel and cobalt form complexes with similar stabilities.

In view of the importance of metal complexes of beta-hydroxy ketone and benzotriazole derivatives in the chemical and biochemical fields, the established unexpected stabilities for the reported ternary complexes may be good model complexes in the design and development of chemical probes. The chemical probe can be a luminescent material or charge controlling agent or an ionic liquid crystal or a catalyst. The stability and the extra stability contributions from 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.

**Table 6- Comparison of intramolecular interactions in between BHK-Bu (O-O donor atoms) and BTAZ (N-O and N-N donor atoms) in metal mediated ternary complexes**

BTAZ with N,O donor atoms <sup>§</sup>			BTAZ with N,N donor atoms					
(BHK-Bu)-Metal-(BTAZ-Alk-OH)			(BHK-Bu)-Metal-(BTAZ-Ph-OH)		(BHK-Bu)-Metal-(BTAZ-Alk-NH <sub>2</sub> )		(BHK-Bu)-Metal-(BTAZ-Ph-NH <sub>2</sub> )	
	$\Delta \log K$	% of Stacking	$\Delta \log K$	% of Stacking	$\Delta \log K$	% of Stacking	$\Delta \log K$	% of Stacking
Cu(II)	0.17	32.39	0.15	29.21	0.34	54.29	0.33	53.23
Ni(II)	0.02	4.51	0.04	8.79	0.11	22.38	0.12	24.14
Zn(II)	0.11	22.38	0.14	27.56	0.22	39.74	0.21	38.34
Co(II)	0.03	6.67	0.03	6.67	0.12	24.14	0.11	22.38

<sup>§</sup>Data is from sridarala et al ( submitted to International Journal of Scientific and Research Publications)

**Table 7- Comparison of intramolecular interactions in between BHK-Ph (O-O donor atoms) and BTAZ (N-O and N-N donor atoms) in metal mediated ternary complexes**

BTAZ with N,O donor atoms <sup>§</sup>			BTAZ with N,N donor atoms					
(BHK-Ph)-Metal-(BTAZ-Alk-OH)			(BHK-Ph)-Metal-(BTAZ-Ph-OH)		(BHK-Ph)-Metal-(BTAZ-Alk-NH <sub>2</sub> )		(BHK-Ph)-Metal-(BTAZ-Ph-NH <sub>2</sub> )	
	$\Delta \log K$	% of Stacking	$\Delta \log K$	% of Stacking	$\Delta \log K$	% of Stacking	$\Delta \log K$	% of Stacking
Cu(II)	0.67	78.62	0.68	79.11	0.81	84.51	0.82	84.86
Ni(II)	0.13	25.86	0.16	30.81	0.26	45.04	0.25	43.76
Zn(II)	0.39	59.26	0.41	61.09	0.55	71.81	0.52	69.81
Co(II)	0.13	25.86	0.16	30.81	0.29	48.71	0.27	46.29

<sup>§</sup> Data is from Sridarala et al (submitted to International Journal of Scientific and Research Publications)

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