

## Synthesis and Studies of New Ternary Complexes of Transition, Lanthanides and Actinides Metal Ions with some Organic Ligands

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**Abstract:** Potentiometric studies of interaction between transition metal ions, Cu(II), Ni(II), Co(II), Zn(II) and Cd(II), F-block ions UO<sub>2</sub>(VI), Th(IV) Sm(III) and Er(III) and mixed ligands are described. Benzyl-monohydrazone-3-hydrazino-4-Benzyl-6-phenyl Pyridazine (BHP) used as primary ligand and 8-hydroxy quinolone (8-HQ), 2-Amino-4-methyl pyridine (2-AMP) or 1,10-phenanthroline (1,10-Phen) used as secondary ligand. Mixed complexes are formed in 75% (v/v) dioxane-water and 1:1:1 molar ratio of M<sup>n+</sup> to BHP as a primary ligand and 8-HQ, 2-AMP or 1,10-Phen as a secondary ligand. It was found that the order of stability constant for complexes of transition metal ions runs according to: Cu(II) > Co(II) > Ni(II) > Cd(II) > Zn(II). While the order that obtained for F-block complexes are runs according to: Th(IV) > UO<sub>2</sub>(VI) > Sm(III) > Er(III). Also, Ni(II), Co(II) and Cu(II) ternary complex systems in solid states were isolated and characterized by different techniques.

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**Key words:** BHP ligand; secondary ligand; ternary complexes; solid complex; thermal analysis; ternary complexes.

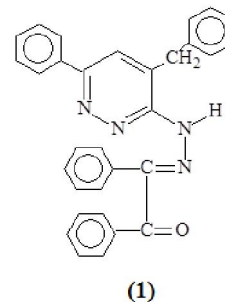
### 1. Introduction

Previous studies have been done in our laboratory [1], concerning with preparation and properties of benzyl derivative of 3-hydrazino-4-benzyl-6-phenylpyridazine (BHP) structure (1), with transition and lanthanide metal ions. The ligand have demonstrated quantitatively the capability of forming 1:1 and 1:2 (M:L), with a ligand behaves as bidentate mono-protic. A series of mono-nuclear complexes were formed in solution and their formation constants, enthalpies and entropies were determined. The solid metal complexes and corresponding thermal products were elucidated by elemental analysis, conductance, IR and electronic spectra, magnetic moments, <sup>1</sup>H-NMR and TG-DSC measurements as well as mass spectroscopy. The use of BHP as analytical reagent for the determination of copper(II), nickel(II) and cobalt(II) as well as extracting agent for these metal ions were discussed.

The purpose of the present investigation was to determine those mixed ligand chelation of Cu(II), Co(II), Ni(II) UO<sub>2</sub>(VI), Th(IV), Sm(III) and Er(III) formed in solution of 1:1:1 molar ratios of M:L<sub>1</sub>:L<sub>2</sub>. BHP served as primary ligand (L<sub>1</sub>) and 8-hydroxyquinoline (8-HQ), 2-amino-6-methyl pyridine (2-AMP) or 1,10-phenanthroline (1,10-Phen) used as secondary ligand (L<sub>2</sub>). An additional purpose was to determine the stabilities of these mixed ligand chelates in 75% (v/v) dioxane-water solvent.

Also, some of mixed complexes in solid state were prepared for Cu(II), Co(II) and Ni(II). The structure of mixed complexes was confirmed using

TGA, DTA, conductivity measurements, mass spectra and infrared spectra.



### 2. Experimental:

#### 2.1. Reagent and Materials:

8-HQ, 2-AMP and 1,10-Phen are supplied as B.D.H. and used as obtained. Copper, nickel, cobalt, zinc, cadmium, thorium, samarium and erbium nitrates stock solutions are prepared in distilled water and standardized using EDTA in the presence of suitable indicator [2]. Dioxane was purified by refluxing it with Na/LiAlH<sub>4</sub> for 8-10 hs., followed by distillation. The procedure was repeated twice to insure the disappearance of acetals.

#### 2.2. Preparation of Solid Ligands:

BHP ligand was prepared by refluxing an ethanolic solution of 3-hydrazino pyridazine derivatives with stoichiometric amount by benzyl solution in ethanol for one hour [3]. The yellow crystals separated on hot were filtered, washed with

ethanol and crystallized from benzene. Results of elemental analysis are shown in Table 1.

### 2. 3. Preparation of Mixed Solid Complexes:

BHP ligand was used as a primary, 2-AMP, 8-HQ or 1,10-Phen were used as secondary ligand. A mixture of equimolar amounts of ethanolic solution of BHP, secondary ligand and metal nitrate was refluxed for 8 hours. Separated solid was filtered off, washed with aqueous ethanolic solution and dried under vacuum. The prepared solid are [Ni(BHP)(8-HQ)], [Ni(BHP)(1,10-Phen)], [Cu(BHP)(8-HQ)], [Cu(8-HQ)(2-AMP)] and [Co(BHP)(8-HQ)], the full analysis of C%, N%, H% and M% were given in Table 1.

### 2. 4. Procedures:

An appropriate amount of standard solution of metal nitrates and ligands in 75% (v/v) dioxane-water and 0.1M KNO<sub>3</sub> were titrated potentiometrically with standard KOH solution also in 75% (v/v) dioxane-water. The pH of the solution was recorded using Orion Research Expandable Ion Analyzer EA-940 fitted with a combined glass-calomel electrode. The pH meter was calibrated using buffer pH=4.01 before and after use. The correction for pH values in 75% (v/v) dioxane-water was taken as 0.28 [4]. The temperature was maintained at 40°C by the use of jacketed cell with water circulated from a constant temperature bath, purified nitrogen was passed through the solution during measurements. The ionic strength of the medium was kept constant at 0.1M KNO<sub>3</sub> as a back ground electrolytes. All titrations were repeated at least twice.

In mixed-ligand mixture ratio was kept at 1:1:1 molar ratio of M<sup>n+</sup>: BHP: secondary ligand with metal concentration equals to 2x10<sup>-3</sup>M. IR spectra were recorded on Perkin-Elmer (4000-400 cm<sup>-1</sup>) spectrometer using KBr discs. Magnetic susceptibilities of the complexes were measured by Goy method at room temperature using Johnson Matthey; Alfa products model MKI magnetic susceptibility balance. The effective magnetic moments were calculated from the expression  $\mu_{eff.} = 2.828(X_M T)^{1/2} B.M.$ , where X<sub>M</sub> the molar susceptibility is corrected using Pascal's constants [5] for the diamagnetism of all atoms in the compounds.

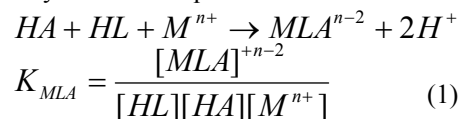
Mass spectra were recorded at 70 eV and 300°C on a MS 5988-Hewlett packed mass spectrometer. Conductivities were measured for complexes solutions in DMF (10<sup>-3</sup>M) using model LBR WIWD-812 Wilhelm Conductivity meter fitted with a model LTA 100 cell.

## 3. Results and Dissection;

### 3. 1. Complexes in solution state:

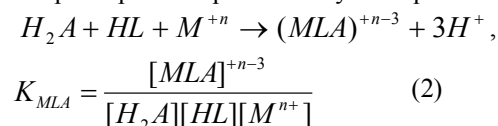
Titration curves of 1:1:1 (M<sup>n+</sup>:BHP:8-HQ) ternary complex systems are plotted in Figs. 1 and 2, the two curves (1, 2) show the titration curves for

metal complexes with BHP and 8-HQ at 40°C and constant ionic strength of 0.1M KNO<sub>3</sub> in 75% (v/v) dioxane-water and have been discussed before [1]. Curve 3 show a long buffer region point at m=0 to m=2 followed by an inflection point at m=2 which may due to the equilibrium:



(M = Cu<sup>+2</sup>, Ni<sup>+2</sup>, Co<sup>+2</sup>, Zn<sup>+2</sup> and Cd<sup>+2</sup>). The titration curves in case of Sm<sup>3+</sup>, Th<sup>4+</sup> and Er<sup>3+</sup> show additional mole of the base is consumed due to deprotonation of the ternary complex species [M<sup>n+</sup>LA]<sup>n-2</sup> and the formation of a hydroxo-complex [MAL(OH)<sup>n-3</sup>].

In the ternary complex system, when 2-AMP is used as a secondary ligand as dihydro and is protonated by adding two moles of nitric acid. The protonation constants are determined by titrating 30 ml of 0.003M 2-AMP against 0.06M HNO<sub>3</sub>, the ionic strength kept constant at 0.1M using KNO<sub>3</sub> and 75% (v/v) dioxane-water is used as solvent. The values of protonation constants obtained are  $pK_1^H = 2.27 \pm 0.03$  and  $pK_2^H = 5.84 \pm 0.05$ . Titration curves of 1:1:1 (M<sup>n+</sup>:BHP:2-AMP) are presented in Figures 3-5, the curve show long buffer region between m=0 and m=3 followed by inflection point at m=3 due to the formation of [MLA]<sup>n-3</sup> complex species represented by the equilibrium:



The formation of mixed ligand complexes are inferred in the studied systems from qualitative evidence. The absence of any kind of precipitation during the titration indicates that a complex which is more resist hydrolysis is produced when two ligands are mixed. The formations of mixed complexes are also substantiated by the lowering of the original pH in 1:1:1 titration curve compared to the curves of binary complexes ML and MA (L=BHP and A=2-AMP). In addition the mixed ligands curve does not coincide with either ML or MA curve. This indicates that the mixed complexes formation taking place simultaneously not stepwise and both ligands are attached simultaneously to the metal ion.

Formation constants for the 1:1:1 mixed ligand chelate was calculated using Condike and Mortell [6] relationship where:

$$K_{MAL} = \frac{(T_M - [A^{2-}]X_A)}{[A^{2-}]^3(X_A)^2} x (X_L - K_{ML}[A^{2-}]X_A)$$

where,  $K_{ML}$  are the formation constants of  $M^{n+}$ -8-HQ or  $M^{n+}$ -2-AMP complexes. In case of 2-AMP as a secondary ligand  $A = A^{2-}$  and  $X$  is  $X_A$ , it is obtained from the following relationship:

$$X = \frac{[H^+]^2}{K_1^H K_2^H} + \frac{[H^+]}{K_2^H} + 1$$

where,  $K_1^H$  and  $K_2^H$  are the protonation constants of 2-AMP, while in case of 8-HQ as a secondary ligand  $X = X_A$  and is obtained from the relationship:

$$X = \frac{[H^+]}{K^H} + 1,$$

where  $K^H$  is the protonation constant of 8-HQ.

$$[A^{2-}] = \frac{2T_{OH} - T_{OH} - [H^+] + [OH^-]X_L}{X_A(2X_L - 1) - X_L},$$

$T_{OH}$  is the total concentration of the base added after neutralization of the first equivalent of acids.

The calculated values of the formation constants for the two complexes  $[M^{n+}(\text{BHP})(2\text{-AMP})]$  and  $[M^{n+}(\text{BHP})(8\text{-HQ})]$  complexes are recorded in Tables 2 and 3. It was found that the order of  $\text{Log}K_{MLA}^M$  for transition metal complexes runs according to:  $\text{Cu}^{+2} > \text{Co}^{+2} > \text{Ni}^{+2} > \text{Cd}^{+2} > \text{Zn}^{+2}$ , while for the f-block complexes is:  $\text{Th}^{+4} > (\text{UO}_2)^{+4} > \text{Sm}^{+3} > \text{Er}^{+3}$ . The general order of stability of binary and ternary complexes is:  $\text{Log}K_{MLA}^M > \text{Log}K_{ML}^M > \text{Log}K_{MA}^M$ .

The values of  $\Delta\text{Log}K = [\text{Log}K_{MAL}^M - (\text{Log}K_{ML}^M + \text{Log}K_{MA}^M)]$ , presented in Tables 2 and 3 are positive in all  $[M^{n+}(\text{BHP})(2\text{-AMP})]$  ternary complex systems, while it is negative for  $[M^{n+}(\text{BHP})(8\text{-HQ})]$  ternary systems. The values of  $\Delta\text{Log}K$  depend on the geometry of the complex and basicity of the ligands. In case of ternary complex systems, the basicity of the ligands plays a very important role on the value of  $\Delta\text{Log}K$ . The higher values of the stability for  $[M^{n+}(\text{BHP})(2\text{-AMP})]$  compared to that for  $[M^{n+}(\text{BHP})(8\text{-HQ})]$  complex systems, is related to:

- i. The basicity of 2-AMP ( $\Sigma pK^H = 8.11$ ) with respect to the corresponding value of 8-HQ ( $\Sigma pK^H = 12.41$ ).
- ii. The size of the chelating ring, it has more effect on the values of  $\Delta\text{Log}K$ , 2-AMP forms four membered ring while 8-HQ forms five membered rings.

So, the expected trend from Bayer's strain theory will be: 2-AMP > 8-HQ.

Percentage relative stabilization (%R.S.) is a new parameter has been introduced to compare the

different mixed ligand complexes. The %R.S. factor may be defined as:

$$\%R.S. = \left\{ \frac{\text{Log}K_{MLA}^M - \text{Log}K_{ML}^M}{\text{Log}K_{ML}^M} \right\} X 100$$

As it seen from Tables 2 and 3, the values of %R.S. ranged between (57.01-93.29%) and (4.73-39.6%) for  $[M^{n+}(\text{BHP})(2\text{-AMP})]$  and  $[M^{n+}(\text{BHP})(8\text{-HQ})]$  ternary complex systems respectively. The higher values of 2-AMP system reflect the greater stability of this ternary system, which could be tentatively explained on the bases of a cooperative effect between primary and secondary ligands [7]. The possibilities of stereo selectivity, indirect cooperative effect, intra covalent bond formation being ruled out and hydrophobic interaction takes place and consequently greater stabilization of mixed complexes results.

### 3. 2. Solid Complexes in ternary system:

Five ternary complexes of  $\text{Ni}^{+2}$ ,  $\text{Cu}^{+2}$  and  $\text{Co}^{+2}$  were prepared and characterized using different techniques. BHP is used as primary ligand and 8-HQ, 1,10-Phen or 2-AMP was used as secondary ligand.

#### 3.2.1. Mixed ligands-Ni(II) complexes:

The reaction of Ni(II) with BHP and other chelating agent such as 1,10-Phen or 8-HQ resulted in isolation of the complexes listed in Table 1. These complexes are  $[\text{Ni}(\text{BHP})(8\text{-HQ})]$  (2) and  $[\text{Ni}(\text{BHP})(1,10\text{-phen})]$  (3), with molecular formula  $[\text{Ni}(\text{C}_{31}\text{H}_{23}\text{N}_4\text{O})(\text{C}_9\text{H}_6\text{NO})(\text{H}_2\text{O})]$  (2) and  $[\text{Ni}(\text{C}_{31}\text{H}_{23}\text{N}_4\text{O})(\text{C}_{12}\text{H}_7\text{N}_2)(\text{H}_2\text{O})_2] \text{NO}_3 \cdot \text{H}_2\text{O}$  (3).

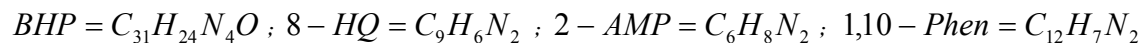
Complex (2) showed a low value of conductance  $18 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  which indicates that it is a non electrolyte. The mass spectra of the complex showed that the highest mass peak at  $m/e = 667$  agree with the formula weight of anhydrous complex  $[\text{Ni}(\text{C}_{31}\text{H}_{23}\text{N}_4\text{O})(\text{C}_9\text{H}_6\text{NO})]$  (M. wt. = 669.7). The fragments show a base peak (100%) at  $m/e = 105$  corresponding to the elimination of  $\text{C}_6\text{H}_5\text{CO}$  molecule. The structure of the complex is further substantiated through thermal decomposition. This study was carried out using the thermo-gravimetric technique (TG) with a heating rate of  $10^\circ\text{C}/\text{min}$ . The complex is decomposed in seven resolved and well-defined steps, which indicated in Table 4. The important step is the fourth one, which occurred in the temperature range,  $210\text{-}344^\circ\text{C}$  with a net weight loss of 20.13% (Calc. 20.36%). This weight loss was consistent with elimination of 8-HQ molecule, which exhibits an exothermic peak at  $225.3^\circ\text{C}$ . and  $\Delta H = -185.2 \text{ J/g}$  in the DSC curve.

In the thermo gram of complex (3), there are weight lost 5.55% of its weight at  $32.4\text{-}116.1^\circ\text{C}$ , corresponding to  $\text{NO}$  and  $\text{H}_2\text{O}$  molecules (Calc. 5.85%) and exothermic peak in DSC curve with  $H = -15.8 \text{ J/g}$ . The second process was at  $117.1\text{-}209.3^\circ\text{C}$



**Table 1: Analytical and physical data for ternary metal complexes**

Molecular formula [F.W.T.]	Elemental analysis %Found, (Calc.)			$\mu$ B.M.	Conductance $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$
	C	H	N		
(1) $\text{C}_{31}\text{H}_{24}\text{N}_4\text{O}$ [468]	79.80 (79.46)	5.10 (5.16)	11.50 (11.96)	-----	
(2) $[\text{Ni}(\text{BHP})(8\text{-HQ})(\text{H}_2\text{O})]$ 687.7	69.20 (69.80)	4.02 (4.22)	10.08 (10.18)	2.68	18
(3) $[\text{Ni}(\text{BHP})(1,10\text{-phen})(\text{H}_2\text{O})_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ [820.7]	63.01 (62.87)	4.45 (4.39)	12.05 (11.94)	2.72	88.2
(4) $[\text{Cu}(\text{BHP})(8\text{-HQ})(\text{H}_2\text{O})_2]\text{NO}_3$ 772.5	62.33 (62.14)	4.32 (4.27)	10.96 (10.87)	1.67	75.20
(5) $[\text{Cu}(\text{BHP})(2\text{-AMP})]\text{NO}_3 \cdot \text{H}_2\text{O}$ [718.5]	61.95 (61.80)	4.39 (4.31)	13.80 (13.64)	1.89	70.40
(6) $[\text{Co}(\text{BHP})(8\text{-HQ})(\text{H}_2\text{O})_2]$ [704.9]	68.40 (68.09)	4.73 (4.68)	10.02 (9.93)	3.89	18

**Table 2: Stability constants of single and mixed ligands chelates.**[T = 40°C, 75% (v/v) dioxane-water,  $\mu = 0.1\text{M KNO}_3$ ]

$\text{M}^{n+}$	$\log K_{ML}^M$	$\log K_{MA}$	$\log K_{MLA}^{ML}$	$\Delta \log K$	%R.S.
$\text{Cu}^{2+}$	11.82	4.33	19.23	3.08	62.70
$\text{Ni}^{2+}$	11.56	4.10	18.15	2.49	57.01
$\text{Co}^{2+}$	11.23	4.22	19.68	4.21	75.07
$\text{Zn}^{2+}$	9.72	3.88	17.78	4.18	82.92
$\text{Cd}^{2+}$	9.40	3.88	17.11	3.83	82.02
$(\text{UO}_2)^{2+}$	10.60	3.81	18.44	4.03	73.96
$\text{Th}^{4+}$	11.99	3.98	19.01	3.04	58.55
$\text{Sm}^{3+}$	9.68	3.88	18.71	5.15	93.29
$\text{Er}^{3+}$	10.15	3.76	18.90	4.99	86.21

L = BHP ; A = 2-amino-4-methyl pyridine (2-AMP)

**Table 3: Stability constants of single and mixed ligands chelates.**[T = 40°C, 75% (v/v) dioxane-water,  $\mu = 0.1\text{M KNO}_3$ ]

$\text{M}^{n+}$	$\log K_{ML}^M$	$\log K_{MA}$	$\log K_{MLA}^{ML}$	$-\Delta \log K$	%R.S.
$\text{Cu}^{2+}$	11.82	12.54	16.50	7.86	39.60
$\text{Ni}^{2+}$	11.56	11.51	14.27	8.80	23.44
$\text{Co}^{2+}$	11.23	11.16	15.64	6.75	39.26
$\text{Zn}^{2+}$	9.72	10.97	13.25	7.44	36.31
$\text{Cd}^{2+}$	9.40	10.18	11.27	8.31	19.89
$(\text{UO}_2)^{2+}$	10.60	9.91	12.67	7.84	19.53
$\text{Th}^{4+}$	11.99	11.28	14.58	8.69	21.60
$\text{Sm}^{3+}$	9.68	8.88	11.46	7.10	18.39
$\text{Er}^{3+}$	10.15	9.63	10.63	9.15	4.73

L = BHP ; A = 8-hydroxy quinolone (8-HQ)

**Table 4: Thermal analysis data for ternary complexes**

Compound	Temperature range °C	% loss in wt.		DSC peak °C		$\Delta H$ j/g	Assignment
		Found	Calc.	Endo	Exo		
Comp. (2) [Ni(BHP)(8HQ)(H <sub>2</sub> O)] M. wt. = 687.7	1. 29.6-70.2	1.54	1.31	---	60.2	-69.9	½ H <sub>2</sub> O
	2. 71.2-126.2	5.94	5.38	---	105.7	-35.1	CO ; ½ H <sub>2</sub> O
	3. 126.2-208.9	9.87	9.89	---	131.8	-124.1	2N <sub>2</sub> ; C
	4. 210.9-344.9	20.13	20.36	---	225.3	-185.2	8-HQ
	5. 345.8-454.2	13.61	13.38	310.9	---	56.2	C <sub>6</sub> H <sub>5</sub> -CH <sub>3</sub>
	6. 456.2-588.4	6.45	7.56	---	418.7	-44	2(CH≡CH)
	7. 589.4-794.3	17.04	18.90	---	503.5	-10.6	2(CH≡CH) ; C <sub>6</sub> H <sub>6</sub>
	Above 794.3	24.31	25.96				NiO ; C <sub>6</sub> H <sub>6</sub> ; (CH≡CH)
Comp. (3) [Ni(BHP)(1,10-Phen)(H <sub>2</sub> O) (NO <sub>3</sub> )]·NO <sub>3</sub> ·H <sub>2</sub> O M. wt. = 820.7	1. 32.9-116.1	5.55	5.85	---	61.9	-15.8	NO ; H <sub>2</sub> O
	2. 117.1-209.3	11.48	11.70	---	104.5	-52.9	H <sub>2</sub> O ; C <sub>6</sub> H <sub>6</sub>
	3. 211.3-377.4	25.13	25.22	---	225.8	-162.6	N <sub>2</sub> ; 1,10-Phen
				---	290.3	-15.9	
				---	352.4	-40.7	
	4. 379.4-477.5	10.8	11.20	---	392.8	-30.7	C <sub>6</sub> H <sub>6</sub> ; ½ N <sub>2</sub>
	5. 478.5-574.8	4.33	4.87	---	503.9	-11.4	CO ; C
			---	529.5	-8.7		
6. 576.8-793.6	15.29	15.84				2(CH≡CH) ; C <sub>6</sub> H <sub>6</sub> ;	
Above 793.6	27.40	27.26				NiO ; C <sub>7</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub>	
[Cu(BHP)( 2-AMP)]NO <sub>3</sub> H <sub>2</sub> O M.wt.=	1. 36-128	2.59	2.51	101	---	63.5	H <sub>2</sub> O
	2. 129-272	11.05	10.86	---	244	-70.3	C <sub>6</sub> H <sub>6</sub>
	3. 274-587	47.03	47.88	---	503	-14.7	2-AMP ; C <sub>13</sub> H <sub>8</sub> N <sub>4</sub> O
				533	-13.0		
Comp.(6) [Co(BHP)(8HQ)(H <sub>2</sub> O) <sub>2</sub> ] M.wT. = 704.9	1. 48.5-141.4	5.48	5.11	---	109.7	-60.7	2 H <sub>2</sub> O
					123.9	-14.9	
	2. 142.1-258.0	22.55	22.13	---	206	-148.2	2C <sub>6</sub> H <sub>6</sub>
	3. 260.0-338.2	11.47	11.06	---	360.1	-72.2	C <sub>6</sub> H <sub>6</sub>
	4. 339.2-501.7	16.61	15.32	310.9	425.5	-76.2	2(CH≡CH) ; 2N <sub>2</sub>
	5. 502.8-568.6	12.71	12.77	---	505.9	-49.4	C <sub>6</sub> H <sub>6</sub> ; C
	6. 570.5-798.5	20.61	20.43	---	541.9	-1.9	8-HQ
Above 798.5	11.50	12.19				CoO ; C	

**Table 5: Important IR spectral bands (cm<sup>-1</sup>) and their tentative assignment of ternary complexes.**

BHP	8-HQ	Ni-BHP-8HQ	Ni-BHP-1,10Phen	Assignment
		3392 sb	3385 sb	V <sub>OH</sub> ; V <sub>N-H</sub>
3313 s				V <sub>OH</sub> ; V <sub>N-H</sub>
3052 m	3131 bs			V <sub>C-H</sub> phenyl
3025 m	3066 m	2955 sh		
2919 w	3046 m	2922 s	2923 s	V <sub>C-H</sub> ; -CH <sub>2</sub> -
2850 w		2852 w	2855 w	
1664 vs			2370 m	V <sub>C=N</sub>
1629 s		1631 m	1623 w	
1587 w				V <sub>C=C</sub> ; phenyl
1569 s	1578 s			
1516 m	1471 vs	1530 m	1524 w	
1492 s	1471 m			
1443 s	1435 w			V <sub>N-N</sub> ; C-H bending
1427 s				

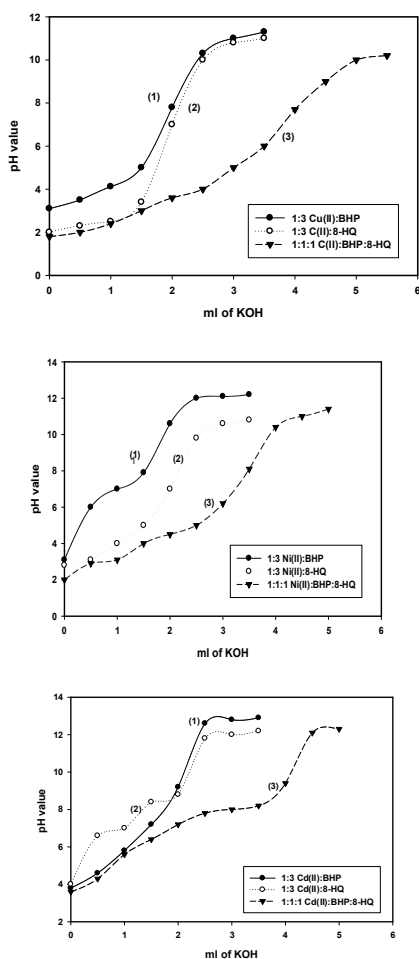
1394 w	1409 s			$V_{NO_3^-}$
		1386 vs	1386 vs	
1325 w	1379 s			$V_{C-C}$ ; phenyl aromatic carbon
1259 w	1282 vs			
1223 vs	1224 s	1227 m	1230 m	
	1204 s	1196 m	1170 m	
1176 w	1167 m	1169 m		$V_{C-C}$ ; $V_{C-O}$ and $V_{C-N}$
	1139 vw			
	1094 m	1095 m	1094 m	
1064 s	1058 w	1071 w		
1028 w		1024 w		
1005 vs				
935 vs	974 w	938 w	936 w	
		912 w		
	895 m	876 w		$V_{Ar-H}$ bending (out of plane)
	847 w	854 w	854 w	
829 w	815 s	821 w		
773 m	780 vs	758 w		
730 vs	741 vs	729 w	730 vw	
695 vs	709 vs	692 m	692 m	
641 m	636 m			$V_{M-O}$
622 s		612 w		
	576 m	580 w		
	544 m	510 w		
498 m	491 vw			$V_{M-N}$
456 m	467 m	470 w		
	422 w	429 w		

Table 5: continue

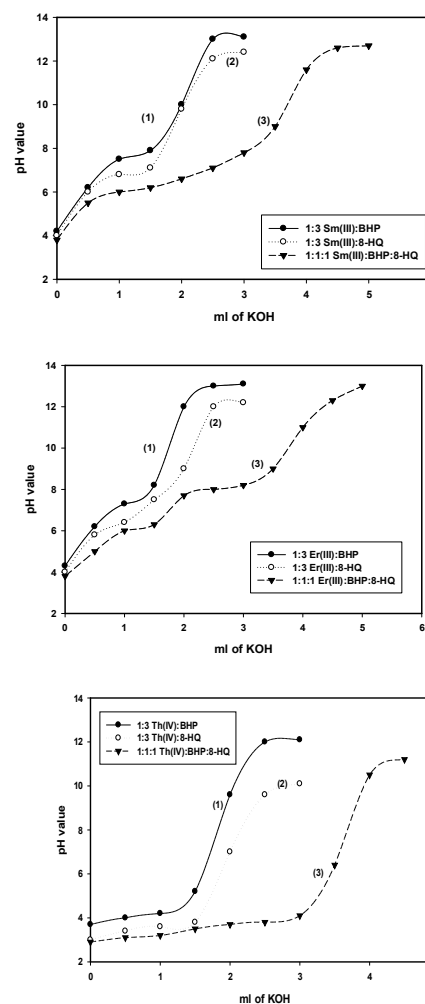
BHP	2-AMP	Cu-BHP-2-AMP	Assignment
3313 s	3445 s	3420 sb	$V_{OH}$ ; $V_{N-H}$ ; intramolecular H-bond; coord. $H_2O$
	3304 m		
	3237.9 w		$V_{C-H}$ phenyl
3052 m	3167 b		
3025 m	3070 w		
	2955 w	2955 sh	
		2922 s	$V_{C-H}$ ; $-CH_2-$
	2322 w	2852 m	
1664 vs		1666 s	
1629 s	1630 s	1628 m	$V_{C=O}$ ; $V_{C=N}$
1587 w	1598 w	1595 w	
1569 s	1559 s		
1516 m		1520.5 w	$V_{C=C}$ ; phenyl
1492 s	1489 s		
1443 s	1440 vs		$V_{N-N}$
1427 s			
1394 w			
1325 w	1335 m	1384 vs	$V_{C-C}$ ; phenyl aromatic carbon; $V_{NO_3^-}$
1223 vs	1276 m	1238 s	
		1197 m	
1176 w		1169 s	$V_{C-C}$ ; $V_{C-O}$ and $V_{C-N}$
	1138 s	1095 s	

1064 s		1052 s	
1028 w	1038 w	1023 w	
1005 vs			
935 vs	986 s	939 w	
		915 w	
824 w		826 m	$V_{Ar-H}$ ; bending (out of plane)
773 m	769 s	767 s	
730 vs	737 m		
695 vs	667 m	695 s	
641 m			
622 s	627 w	624 w	$V_{M-O}$
549 s		587 w	
498 s		470 w	$V_{M-N}$
460 m			

v = very ; b = broad ; s = strong ; w = weak ; m = medium ; sh = shoulder

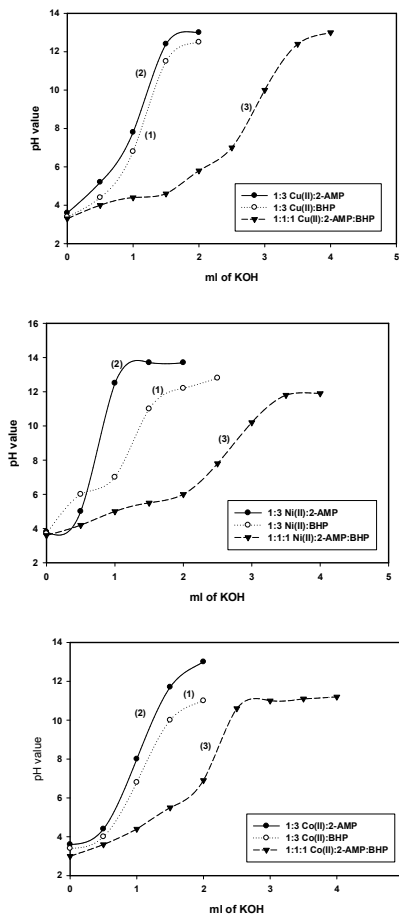


**Fig. 1:** Potentiometric titration of BHP and 8-HQ in the presence of  $M^{+2}$  ions at  $40^{\circ}C$ ,  $\mu=0.1M$   $KNO_3$

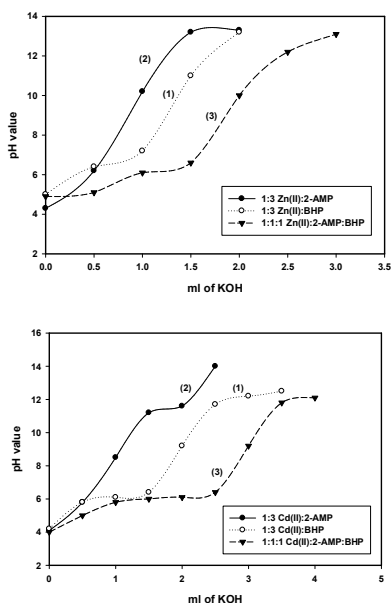


**Fig. 2:** Potentiometric titration of BHP and 8-HQ in the presence of  $Ln^{n+}$  ions at  $40^{\circ}C$ ,  $\mu=0.1M$   $KNO_3$

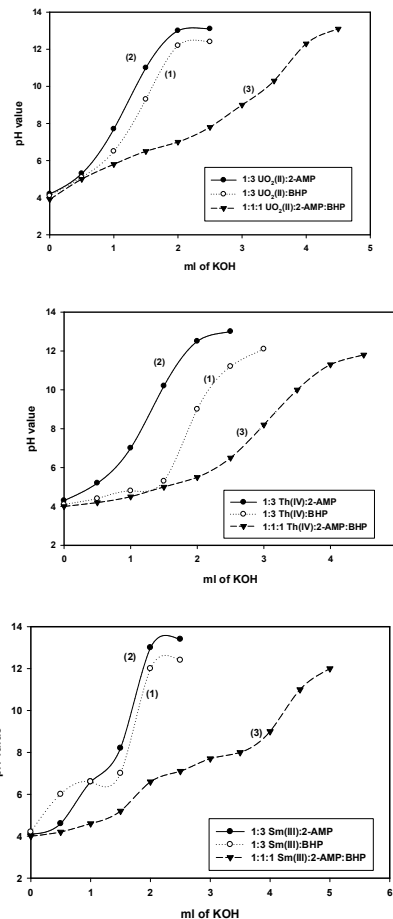




**Fig. 3:** Potentiometric titration of BHP and 2-AMP in the presence of  $M^{2+}$  ions at  $40^{\circ}\text{C}$ ,  $\mu=0.1\text{M KNO}_3$



**Fig. 4:** Potentiometric titration of BHP and 2-AMP in the presence of  $M^{2+}$  ions at  $40^{\circ}\text{C}$ ,  $\mu=0.1\text{M KNO}_3$



**Fig. 5:** Potentiometric titration of BHP and 2-AMP in the presence of  $\text{Ln}^{n+}$  ions at  $40^{\circ}\text{C}$ ,  $\mu=0.1\text{M KNO}_3$

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