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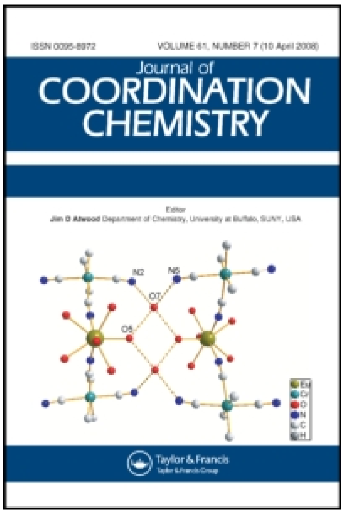

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Synthesis and properties of transition and lanthanide complexes with benzyl monohydrazone-3-hydrazine-4-benzyl-6-phenyl pyridazine ligand (BHP)

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Synthesis and characterization of benzyl-monohydrazone-3-hydrazino-4-benzyl-6-phenyl pyridazine (BHP) and its complexes with copper(II), nickel(II), cobalt(II), zinc(II), manganese(II), cadmium(II), thorium(IV), dioxyuranium(VI), samarium(III) and erbium(III) are presented. The protonation equilibrium of BHP ion and complex formation equilibrium with the metal ions have been studied by potentiometry in 75% (v/v) dioxane-water and 0.10M KNO_3 at different temperatures (10, 20, 30 and 40°C). A series of mononuclear complexes $[ML_n]^{(1-z)+}$ ($L^- = BHP$ and $n = 1 - z$) were found 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, ^1H NMR and TG-DSC measurements as well as by mass spectroscopy. The use of BHP as analytical reagents for the determination of copper(II), nickel(II) and cobalt(II) as well as extracting agents for these metal ions are discussed.

Keywords: Potentiometric titration; BHP complexes; BHP as an indicator; BHP as an extracting agent

1. Introduction

Heterocyclic diazines, such as pyrazine, pyrimidine and pyridazine are excellent bidentate ligands [1] and pyridazine derivatives are good sequestering agents. In particular pyridazine substituted by hydrazine can undergo condensation with ketonic or aldehydic groups.

In earlier studies [2–4] the sequestering properties of condensation products of 3-hydrazino-4-benzyl-6-phenylpyridazine with benzoyl acetone (BAHP) [2], benzil (BHP) [3] and pyrovic (PHP) and hippuric acid (HIPHP) [4] with transition and lanthanide metal ions were studied. BAHP demonstrated the capability of forming bis-chelates as a monoprotic acid. Under reflux with copper salts, the ligand

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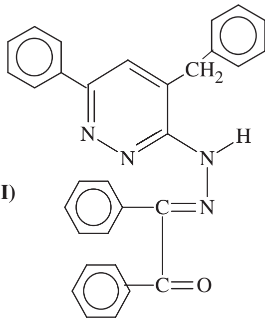
loses two protons, probably those of the enolic and hydrazo groups and is a diprotic species.

BHP has been prepared, characterized, and its acid-base properties and its equilibrium with transition metal ions in 75% (v/v) dioxane-water solvent at 30°C investigated by pH-meter. The role of proton and metal ion solvation by dioxane is discussed in comparison to lanthanide-BHP systems in different media. The probable structure was given based on potentiometric data and spectral data for solid copper chelates.

Complexes with PHP and PIPHP were inferred from electronic and vibrational spectral results. Evidence was presented for formation of protonated complexes with PHP [4]. Similar series of compounds were prepared and their complexation with different metal ions studied [5–7]. Complexes of trivalent lanthanide [5] and divalent metal ions [6] with 3-hydrazino-6-phenylpyridazine (HPP) and its condensation with benzyl (BHPP) and methoxy acetophenone (p-MeOPHPP) [5] have been investigated by pH-metric titration in 75% (v/v) dioxane-water medium at 30°C.

The present communication reports complex formation of BHP with different metals. The complexes have been isolated and structurally characterized from various physico-chemical techniques in order to have insight into bonding of these important chelating agents (I).



(I)

2. Experimental

2.1. *Preparation of the solid ligand*

BHP was prepared by refluxing an ethanolic solution of 3-hydrazino-pyridazine derivatives [8] with the stoichiometric amount of benzil solution in ethanol for one hour. The yellow crystals separated while hot, were filtered, washed with ethanol and crystallized from benzene (yield 70%). Results of elemental analysis are shown in table 1.

2.2. *Preparation of the solid complexes*

An equimolar amount of BHP and metal nitrate in 75% (v/v) dioxane-water solvent was refluxed for 1 h (for copper, nickel and cobalt) and 2.5 h for other metals. The solid complexes separated while hot, were filtered, washed with ether and dried under vacuum. Metal contents were determined using standard method [9].

Table 1. Analytical and physical data for BHP and its metal complexes.

	Elemental analysis% found [Cald.]						
Formula [M. w.]	C	H	N	M	μ (B.M.)	Conductance (Ohm^{-1} $cm^2 mol^{-1}$)	Color
($C_{31}H_{24}N_4O$) [468]	79.80 [79.46]	5.10 [5.16]	11.50 [11.96]	–	–	–	Yellow
[($C_{31}H_{24}N_4O$)(H_2O)$_3$Ni]NO_3 [641.7]	58.00 [59.97]	4.30 [4.52]	11.00 [10.91]	9.08 [9.15]	2.78	82.50	Red
[($C_{31}H_{24}N_4O$)(H_2O)$_2$(NO_3)Co]NO_3 [685.9]	54.10 [54.24]	4.96 [3.94]	–	8.61 [8.95]	zero	86.00	Greenish
[($C_{31}H_{24}N_4O$)(H_2O)Cu]NO_3 [648.5]	60.55 [60.93]	4.40 [4.10]	–	10.04 [9.97]	1.70	80.10	Wine red
[($C_{31}H_{24}N_4O$)(H_2O)$_2$(NO_3)Cd]NO_3 [739.4]	50.66 [50.31]	5.00 [3.65]	–	–	zero	81.10	Pale red
[($C_{31}H_{24}N_4O$)(H_2O)$_2$(NO_3)Zn]NO_3 [698.4]	53.25 [53.70]	4.20 [3.89]	–	–	zero	76.80	Pale red

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2.3. *Reagents and materials*

Stock solutions of the metal nitrates were prepared and standardized using EDTA in the presence of suitable indicator [9]. Dioxane was purified according to the Eigenberger method [10].

2.4. *Procedures*

Potentiometric titration is described [3]; temperatures were 10, 20, 30 and 40°C and the ionic strength was maintained at 0.10M KNO_3. In all cases the metal to ligand ratio was kept at 1 : 3 with the metal concentration 1×10^{-3} M. The pH of the solution was recorded using an Orion Research Expandable Ion Analyzer EA-940 fitted with a combined glass electrode. The temperature was maintained at ±0.05°C with constant temperature water circulated through a sealed jacketed cell. Purified nitrogen presaturated in 75% (v/v) dioxane-water was purged during titrations. Titrations of BHP in the absence and presence of different metal ions were performed in 75% (v/v) dioxane-water and the pH was recorded after each increment of base added. The correction factor for pH-value in 75% (v/v) dioxane-water was taken as +0.28 [11].

Electronic spectra were recorded on a Spectronic 21-Bausch & Lomb spectrometer. IR spectra were recorded on a Perkin-Elmer (4000–400 cm^{-1}) spectrometer using KBr discs and polyethylene was used as calibrant. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a Johnson Mathey, Alfa products, model MKI magnetic susceptibility balance. The effective magnetic moments were calculated using the relation $\mu_{eff} = 2.828(X_m T)^{1/2}$ B.M., where X_m is the molar susceptibility correction using Pascal's constants. ^1H NMR spectra (DMSO-d_6) were recorded at room temperature on a 90 MHz model FT-296 Varian spectrometer using TMS as an internal standard. TG-DSC measurements were carried out on a Shimadza Thermogravimetric Analysis using the TA-SO WSI program. Mass spectra were recorded at 70 eV and 300°C on a MS 5988 Hewlett-Packard mass spectrometer. Conductivities were measured in DMF (10^{-3} M) solutions using a model LBR

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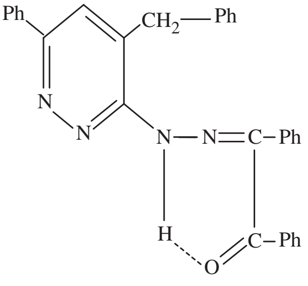
WIWD-812 Weilheim conductivity meter fitted with a model LTA 100 cell. Carbon, hydrogen and nitrogen microanalyses were carried out at the Microanalytical Centre, Cairo University, Cairo, Egypt.

3. Results

3.1. *The ligand*

The mass spectrum of BHP (Supplementary data) showed the M peak at *m*/*e* 468 corresponding to the formula $C_{31}H_{24}N_4O$ ($F_w = 468$). In addition, the base peak at *m*/*e* 77(100%) represents C_6H_5. The other peaks of appreciable intensity for the major fragments possible are shown in supplementary data. The ^{1}H NMR spectrum (DMSO-d$_6$) of BHP exhibited signals at $\delta = 3.4$ (s, 2H, CH_2 of benzyl group), 6.9–7.8 (m, 21H, Ar–H and 4H of pyridazine ring) and 12.9 ppm (s, 1H, NH). The electronic spectrum of the ligand in 75% (v/v) dioxane-water shows absorption bands at 260 and 360 nm. The band at 260 nm ($\log \varepsilon = 4.81$) may be assigned to π–π^* transitions through the conjugated system, while the band at 360 nm ($\log \varepsilon = 4.48$) is due to the n-π^* transition.



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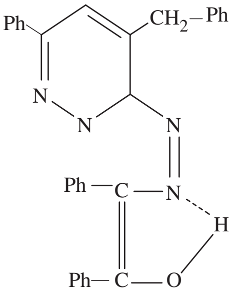

(III)

3.2. *Protonation equilibrium*

The pH-titration curves for the free and complexed BHP at 10, 20, 30 and 40°C are shown in figure 1. Between $a = 0$ and $a = 1$ in the presence of different metal ions only one proton dissociates (a = number of moles of base added per mole of ligand present). This suggests that under these conditions the ligand is monoprotic, with dissociation of the hydrazo proton. The acid dissociation constant K^H was calculated using the following relationship,

$$\log K^H = \frac{aC_L - [H^+] - [OH^-]}{(a-1)C_L + [H^+] + [OH^-]} + pH \qquad (1)$$

Since the ionic product of water, pK_w is approximately 18.7 [12] both the hydrogen and hydroxyl ion concentration terms in equation 1 are negligible in the region of proton dissociation. The obtained pK^H values are presented in table 2.

The variation of pK^H with $1/T$ (T absolute temperature) using linear regression method always gives straight lines with correlation coefficient $(R) = 0.99$, indicating that raising of temperature increases the acidity of BHP. The linear change of pK^H with $1/T$

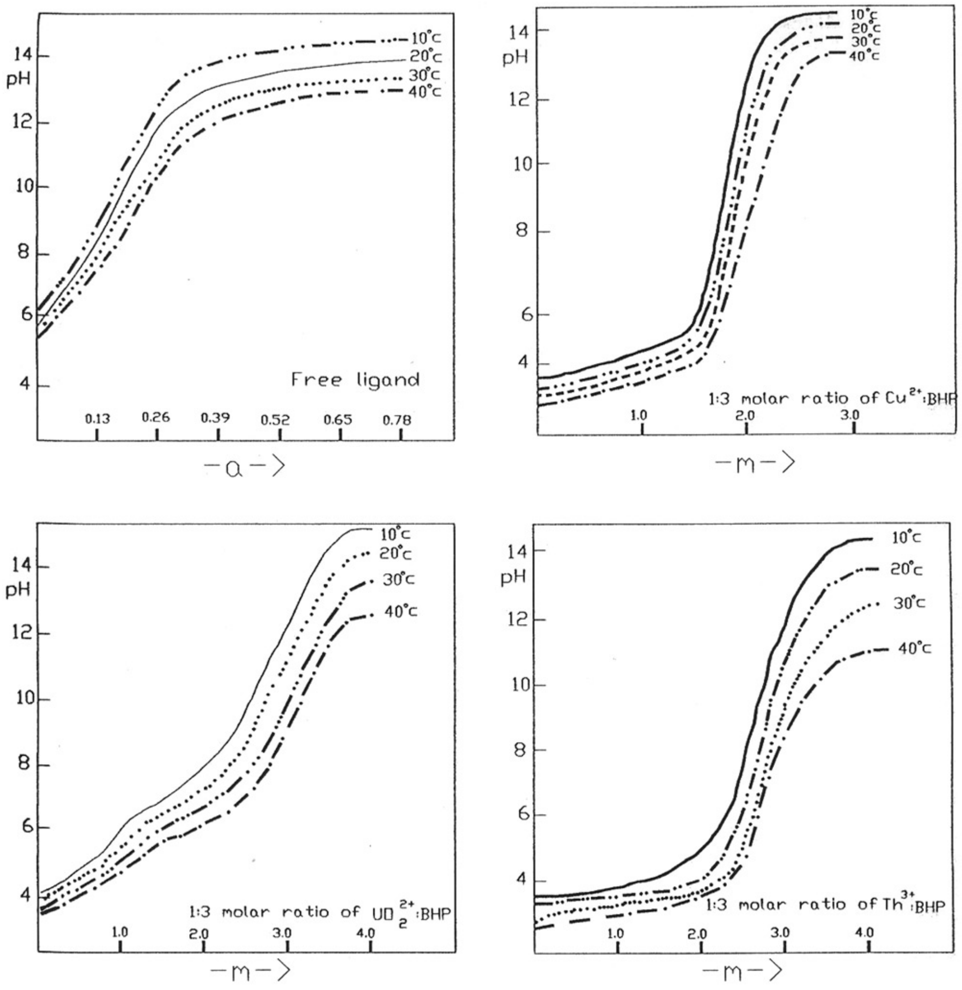

Figure 1. Potentiometric equilibrium curves of free and complexed BHP at different temperatures [75% (v/v) dioxane-water, $\mu = 0.1$M KNO_3]. a: number of moles of base added per mole of ligand. m: number of moles of base added per mole of ligand.

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permits the calculation of the enthalpy (ΔH) of protonation by the use of Van't Hoff equation: ($\mathrm{dlog}\,K/\mathrm{d}T = \Delta H/2.303RT^2$).

The values of ΔH are calculated in each case by least-squares fit of the data to the relationship:

$$\log K = -\left\{\frac{\Delta H}{(2.303\mathrm{RT})}\right\} + \text{constant}$$

The free energy ΔG and entropy ΔS are calculated from the known relationships:

$$-\Delta G = 2.303\mathrm{RT}\ \log K \text{ and } \frac{\Delta S = (\Delta H - \Delta G)}{T}$$

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Table 2. Protonation constants and thermodynamic parameters of BHP at different temperatures [75% (v/v) dioxane-water, $\mu = 0.1\text{M KNO}_3$].

	Temperatures				ΔG	ΔH	
Symbol of proton constant	10°C	20°C	30°C	40°C	k · (Cal mole^{-1})		ΔS (Cal mole^{-1} · K^{-1})
pK^{H}	14.21	13.58	13.02	12.61	18.06	21.74	12.41

Thermodynamic parameters for the ligand are listed in table 2.

The titration curves obtained in the presence of bivalent metal cations at different temperatures (10, 20, 30 and 40°C) (figure 1) show an inflection point at $m = 2$ ($m =$ moles of base added per mole of metal ion present) corresponding to the formation of bis-chelates represented by the equilibrium:

$$M^{2+} + 2HL \rightarrow ML_2 + 2H^+$$

In the titration curves for $UO_2^{2+}$and Th^{4+} the inflection point occurred at $m = 3$ corresponding to formation of ML_3. Calculation of overall equilibrium constants was carried out using standard procedures based on the average number of ligands bound per metal ion $n^{\backslash}_L$ and the free ligand concentration, $[L^-]$ then minimizing the residuals in the equation:

$$\frac{n^{\backslash}_L}{(1 - n^{\backslash}_L)[L^-]} + \beta_1 \frac{(n^{\backslash}_L - 2)[L^-]}{(1 - n^{\backslash}_L)} - K_1 = 0 \tag{2}$$

$$\frac{n^{\backslash}_L}{(2 - n^{\backslash}_L)[L^-]^2} + \frac{K_1(n^{\backslash}_L - 1)}{(2 - n^{\backslash}_L)[L^-]} = \beta_2 \frac{(3 - n^{\backslash}_L)}{(2 - n^{\backslash}_L)} + \beta_1 \tag{3}$$

where $\beta_1 = K_1K_2$ and $\beta_2 = K_1K_2K_3$. Using a least squares method, summary of these constants at different temperatures are given in table 3.

The linear plots of $\log K_n$ ($n = 1$, 2 and 3) against $1/T$ gives straight lines of slope $= (-\Delta H/4.57)$, from which ΔH is obtained. The values of ΔH are calculated in each case by least-squares fit of the data to equation 1. The thermodynamic parameters, ΔH, ΔG and ΔS, are shown in table 3.

4. Discussion

A comparison of pK^{H} value (13.00) for BHP with those obtained for BHPP (pK$^{H} = 12.62$) [5] under similar experimental conditions, reflects the basicity (ΣpK^{H}) of hydrazo nitrogen in BHP compared to that in BHPP. The difference of 0.38 log unit could be related to the presence of C_6H_5–CH_2– group in BHP, in addition to the difference in ionic strength. Comparsion of stability constants of the formed complexes (log β) shows that BHP > BHPP for Ni(II), Co(II), Zn(II), Cd(II) and nearly the same for Cu(II) and UO_2(VI) complexes in accord with the basicity order.

From the stability constants of BHP complexes, it is clear that the stepwise and overall stability constants decrease with rise in temperature indicating that formation equilibria are exothermic, confirmed by the fact that ΔG and ΔH are both negative.

Table 3. Equilibrium constants and thermodynamic parameters for interaction of BHP with some metal ions.

	$\log K_1$				$\log K_2$				$\log K_3$			
Cation	10°C	20°C	30°C	40°C	10°C	20°C	30°C	40°C	10°C	20°C	30°C	40°C
Cu^{2+}	12.68	12.27	11.99	11.82	12.17	11.81	11.49	11.31	–	–	–	–
Ni^{2+}	12.36	12.06	11.76	11.56	11.32	11.07	10.84	10.70	–	–	–	–
Co^{2+}	12.06	11.66	11.37	11.23	9.62	9.40	9.33	9.31	–	–	–	–
Zn^{2+}	9.92	9.73	9.60	9.72	8.49	8.19	8.12	8.14	–	–	–	–
Cd^{2+}	9.28	9.07	9.18	9.40	7.80	7.68	7.63	8.02	–	–	–	–
Sm^{3+}	9.86	9.76	9.58	9.68	9.07	9.05	8.91	9.08	8.92	9.02	8.97	9.16
Er^{3+}	10.95	10.68	10.36	10.15	9.14	8.99	8.66	8.49	8.87	8.78	8.38	8.20
Th^{3+}	12.94	12.55	12.17	11.99	12.96	12.58	12.21	12.05	12.12	12.40	12.22	11.95
UO_2^{2+}	11.44	11.07	10.75	10.60	9.62	9.43	9.26	9.27	6.44	7.03	7.39	7.70

	ΔG_1	ΔH_1		ΔG_2	ΔH_2		ΔG_3	ΔH_3	
Cation	k Cal mole^{-1}		ΔS_1 (Cal mole^{-1} K)	k Cal mole^{-1}		ΔS_2 (Cal mole$^{-1}\cdot$K^{-1})	k Cal mole^{-1}		ΔS_3 (Cal mole^{-1} K^{-1})
Cu^{2+}	−16.63	−11.64	16.47	−15.94	−11.77	13.76	–	–	–
Ni^{2+}	−16.14	−10.95	17.13	−15.04	−8.49	21.62	–	–	–
Co^{2+}	−15.77	−9.05	22.18	−12.94	−5.70	23.89	–	–	–
Zn^{2+}	−13.32	−3.04	33.93	−11.26	−4.62	21.91	–	–	–
Cd^{2+}	−12.72	−6.89	64.75	−10.52	−3.34	23.70	–	–	–
Sm^{3+}	−13.29	−5.47	25.81	−12.36	−3.10	30.56	−12.44	2.87	50.53
Er^{3+}	−14.37	−11.03	11.02	−12.01	−9.21	9.24	−11.62	−9.73	6.24
Th^{3+}	−16.88	−13.13	12.38	−16.94	−12.59	14.36	−16.95	−9.41	24.88
UO_2^{2+}	−14.91	−9.89	16.57	−12.85	−4.99	25.94	−10.25	16.83	89.37

The higher ΔH values could be explained by the increase of solvent basicity [13], which causes the transfer of metal ions from aqueous state to dioxane to be exothermic. The enthalpy change for transfer processes from water to organic solvent mixture (ΔH_{trans}) is made up of the partial transfer enthalpies for the individual species.

The ΔH dependence on the solvent can be ascribed primarily to the different hydration-solvation conditions of the metal ions. On the basis of a published report [14], high dioxane concentration (i.e. 75% dioxane-water) strengthening the interaction between metal ion and solvent is more than offset by decrease in hydration of the bulky ligand anion. Thus, only a minor proportion of the energy released on formation of the strong coordination bond is utilized against the interaction between the ion and the solvent molecules. Therefore, complex formation will be exothermic, to a greater or lesser extent, in comparison with the process in aqueous medium. The large enthalpy contribution as a major driving force for metal ligand coordination is substantiated by the relatively large magnitude of ΔS_1 and ΔS_2, compared with ΔH_1 and ΔH_2 (table 4).

The entropy changes for metal-chelate formation are relatively high and positive for the 1 : 1, 1 : 2 and 1 : 3 M:L complexes (table 4), attributed to: (i) an increase in ΔS from release of waters of hydration, (ii) a decrease in entropy of translation of one chelate from two species, and (iii) a decrease in configuration entropy of the ligand on complex formation. For reactions with charged donor groups (i.e. L^-), the entropy changes associated with (i) predominate because of neutralization of charge on the metal ion, resulting in greater release of waters of hydration and hence, greater disorder of the partially immobilized and oriented water dipoles.

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Table 4. Important IR spectral bands (cm^{-1}) and their tentative assignment for BHP and its metal complexes.

BHP	Co-BHP	Ni-BHP	Cu-BHP	Zn-BHP	Cd-BHP	Assignment
	3431 sh	3420 sh	3432 sh	3450 sh	3451 sh	ν_{OH}; intra-molecular H-bond; cord H_2O
3313 s				3316 m	3314 m	$\nu_{O–H}$; $\nu_{N–H}$
3052 m	3060 w			3058 w	3058 w	
3025 m				3029 sh	3023 sh	$\nu_{(C–H)}$ Phenyl
2919 w	2924 m	2923 m	2925 s	2922 s	2922 s	
2850 w	2855 w	2855 w	2855 w	2859 w	2854 w	$\nu_{(C–H)}$; $–CH_2–$
	2362 m	2363 s	2367 w			
1664 vs	1648 s	1638 s	1629 s	1663 w	1662 w	$\nu_{C=O}$; $\nu_{C=N}$
1629 s	1540 w	1523 w	1565 vw	1630 w	1630 w	
1587 w	1457 w	1448 w		1575 w	1573 w	$\nu_{C=C}$; Phenyl
1569 s				1539 w	1542 w	
1516 m				1492 w	1489 w	
1492 s						
1443 s						$\nu_{C–C}$; Phenyl aromatic C; Ionic ν_{NO3}; $\nu_{N=N}$
1427 s	1405 w					
1394 w						
		1385 vs	1385 vs	1384 vs	1386 vs	
1325 w	1323 m		1326 w			
1259 w	1232 w	1230 m	1235 w	1231 m	1227 m	$\nu_{C–C}$; $\nu_{C–O}$ and $\nu_{C–N}$
1223 vs	1162 s	1171 w	1168 w	1175 vw	1178 vw	
1176 w	1105 w	1050 m	1097 w	1080 m	1075 w	
1064 s						
1028 w	981 m	936 w	925 w	1006 w	1004 w	Ar–H bonding (out of plane)
1005 vs				932 s	932 s	
935 vs						
829 w	842 w	824 w	826 w	828 w	826 w	$\nu_{Ar–H}$ bending (out of plane)
773 m	773 w	774 w	776 w	770 w	772 m	
730 vs				731 w	731 w	
695 vs	695 s	692 m	694 m	693 m	692 m	$\nu_{M–O}$
641 m		620 w		630 w	629 w	
622 s	591 w			583 w	583 w	
549 s		553 w	546 w	551 w	551 w	$\nu_{M–N}$
498 m	469 w	517 w	469 w	508 w	505 w	
456 m		467 w	419 w	461 w	460 w	

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

Dioxane breaks down the hydrogen bonded structure of water [15]. Water molecules liberated from the coordination sphere of a complex behave more freely in dioxane-water mixture in which the hydrogen bonded structure of water is partially destroyed and increase of the entropy of any metal ion-BHP complex in 75% (v/v) dioxane-water mixture is attributable to an entropy gain of water liberated.

4.1. *Metal complexes in the solid state*

BHP consists of a pyridazine hydrazo group condensed with benzyl, existing in different tautomeric forms (II) and (III). The existence (and strength) of intramolecular hydrogen bonds between the hydrazo hydrogen and ketonic oxygen(II) or enolic OH group and azo-nitrogen(III) are important. The absence of strong carbonyl stretching band at 1700 cm^{-1} and the presence of a sharp strong band at 3312 cm^{-1} agree with structure (II), but it was difficult to decide from infrared spectra alone, where the hydrazo-hydrogen is located. Thus, the IR bands could be associated with both tautomeric isomers (II) and (III). The $\nu_{(NH)}$, $\nu_{(C=N)}$ and $\nu_{(C=O)}$ of tautomer(II) were detected at 3312, 1629 and 1663 cm^{-1}, respectively. The latter is shifted to longer frequency as a result of hydrogen bonding with NH. Evidence for tautomer(III) is derived from the IR bands for $\nu_{(N=N)}$ and $\nu_{(C=C)}$ which appear at 1442 and 1222 cm^{-1}, respectively.

The IR spectra of complexes of BHP with copper(II), nickel(II), cobalt(II), cadmium(II) and zinc(II) show systematic shift of $\nu_{(C=C)}$, $\nu_{(C=N)}$ and $\nu_{(CO)}$ or the disappearance of $\nu_{(NH)}$ absorption bands. The band at 1663 ($\nu_{(C=O)}$) observed in the spectrum of BHP shifts for the complexes. The IR spectra of the complexes indicate participation of ketonic oxygen and hydrazo nitrogen in bonding to the metal. Table 4 presents the IR spectral bands (cm^{-1}) and their assignment for the free ligand and its metal complexes.

The participation of the hydrazo nitrogen in complexation with Cd(II) and Zn(II) ions does not take place through deprotonation since the NH band is still observed in the IR spectra of those complexes. The non deprotonation of hydrazo proton is further evidenced from ^{1}H NMR spectra of Zn(II)- and Cd(II)-BHP complexes, with the NH (observed at $\delta = 12.94$ ppm in BHP) almost unchanged (at $\delta = 12.96$ ppm and $\delta = 12.94$ ppm) for the Zn(II)- and Cd(II)-BHP complexes. The magnetic properties, molar conductances and elemental analyses for Cu^{2+}–, Ni^{2+}, Co^{2+}– and Zn^{2+}–BHP complexes are in table 1.

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4.1.1. Ni(II) complex. The mass spectrum of Ni(II)–BHP complex showed that the highest mass peak agrees with the formula weight of $[Ni(L)(H_2O)_3]^+$ (M.w. 579, m/e 579). Conductance in DMF is indicative of 1 : 1 electrolyte. The magnetic moment is 2.82 B.M. indicating two unpaired electrons for Ni(II). The broad band at 3420 cm^{-1} assigned to $\nu_{(OH)}$ indicates the presence of water molecule. The intense band at 1385 cm^{-1} is characteristic of ionic nitrate [16].

The TG-DSC studies of Ni(II)–BHP complex are summarized in table 5 up to 800°C, at 20°C per minute. Thermal decomposition indicates five steps from room temperature to 597.8°C. The second weight loss step (131–166°C) is correlated with the elimination of three water molecules, confirmed by endothermic change at 140°C (DSC). The fifth process at 444.2–597.0°C for loss of CH_3–CH_3, $2C_6H_6$, NO and NO_2 (table 5) is associated with an exothermic DSC peak at 431.9 and ($\Delta H = -2.79$ j g^{-1}), probably due to liberation of the flammable benzene and ethane. Thus on the basis of elemental analysis, molar conductance, IR spectrum, magnetic moment and thermal analysis the geometry of Ni(II)–BHP complex is proposed to be octahedral.

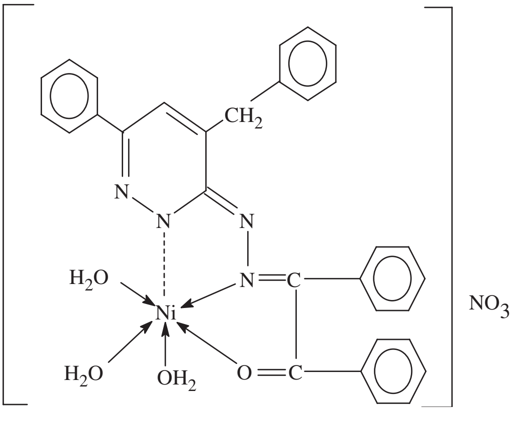

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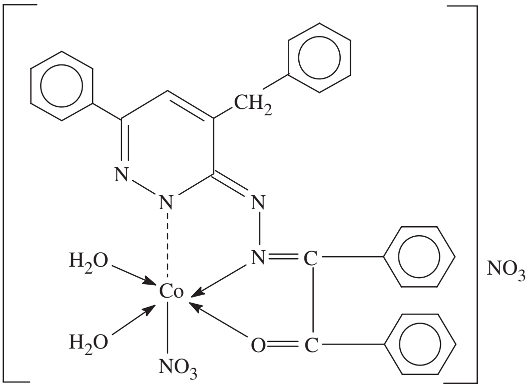
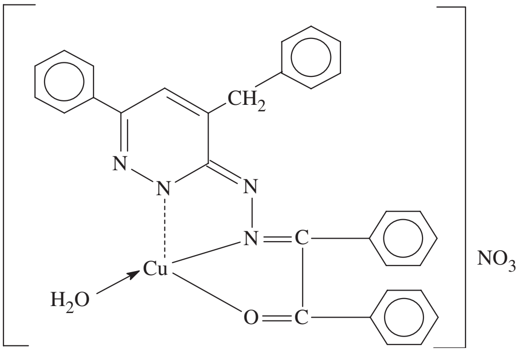
Table 5. Thermal analysis data for Ni(II)- and Co(II)-complexes.

Compound	Temperature range (°C)	% Loss in weight		DSC peak (°C)		ΔH J g^{-1}	Assignment
		Found	Calc	Endo	Exo		
[Ni(BHP)(H_2O)$_3$]NO_3	34.2–131.6	6.29	6.31	–	97.8	−55.3	½ N_2; CO
M.w. 641.7	131.6–166.7	8.69	8.42	140.4	–	122.2	$3H_2O$
	168.6–279.2	14.08	14.34	–	201.4	−34.9	C_6H_6; ½ N_2
	281.2–442.6	22.8	22.44	294.9	–	14.5	C_6H_6; 2(CH≡CH); ½ N_2
	444.2–597.8	39.85	40.82	–	431.9	−2.79	CH_3–CH_3; NO; $2C_6H_6$; NO_2
	Above 597.8	8.29	9.45	–	–	–	Ni
[Co(BHP)(H_2O)$_2$(NO_3)]NO_3	26.3–89.8	1.38	1.31	–	73.6	−32.5	½ H_2O
M.w. 685.9	94.5–274.3	12.25	12.98	200.5	–	148.9	$1.5H_2O$; NO_3
	275.9–370.4	16.19	15.75	–	248.1	−82.8	C_6H_6; NO
	370.4–581.4	31.97	31.49	–	–	–	$2C_6H_6$; CH_4; N_2O
	581.6–793.6	28.82	29.45	–	–	–	2(CH≡CH); N_2; C_6H_6; CO_2
	Above 793.6	10.00	12.67	–	–	–	CoO; C

4.1.2. Co(III) complex. The magnetic moment Co(III)-BHP complex is nearly zero, indicating the low spin cobalt(III). The molar conductance of the complex in DMF, 86 $\mathrm{Ohm^{-1}\,cm^2\,mol^{-1}}$, indicates a 1 : 1 electrolyte. Thermal analysis data (table 5) supports the existance of coordinated water and ionic nitrate. The second step of the thermal decomposition gives loss in weight corresponding to 1.5 H_2O andNO_3^-, confirmed by an endothermic DSC peak at 200.5°C and $\Delta H = 148.9\,\mathrm{J\,g^{-1}}$. The mass spectra of the complex show the highest mass peak in accordance with the formula weight of the cationic species $[Co(L)(H_2O)_2(NO_3)]^+$ (F.W. = 605.9; $m/e = 604$). The IR of the solid complex showed a shift of the absorbance of the $\nu_{(C=N)}$ to a higher frequency, indicating participation of this group in chelate formation. All the previous data indicate that Co(III) is octahedral, as represented in the following diagram:



4.1.3. Cu(II) complex. The molar conductance of $[Cu(L)(H_2O)]NO_3$ in DMF = 80 $\mathrm{Ohm^{-1}\,cm^2\,mol^{-1}}$ indicates a 1 : 1 electrolyte. The ESR spectrum at room temperature gives a g_{eff} value (2.85) indicating tetrahedral geometry around Cu(II) [17]. The shape of the ESR spectrum together with the g_{eff} value indicate an elongated tetrahedron. The electronic spectra in DMF show a shift in the $\pi \rightarrow \pi^*$ band in the free ligand to 376 nm as a shoulder due to complex formation. The shoulder arises from the non-symmetrical coordinating sites in the ligand. An additional band at 350 nm is due to L → M transition. The proposed Cu(II)-BHP complex is shown in the following diagram:



4.1.4. Cd(II) and Zn(II) complexes. Cd(II)- and Zn(II)-BHP complexes are confirmed through elemental analysis, conductance measurements, IR, ^1H NMR and

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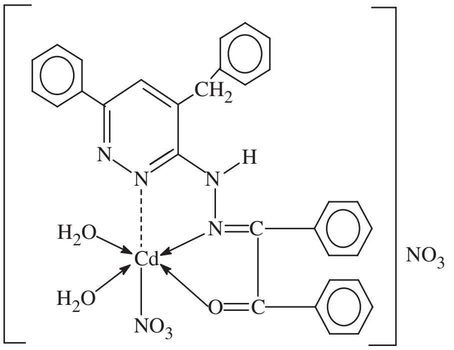
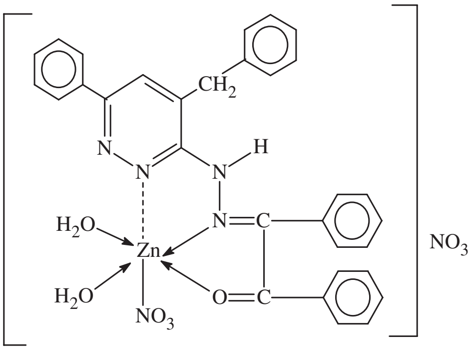
mass spectra. The values obtained for the electrical conductance are 76.8 and 81.1 $\mathrm{Ohm^{-1}\,cm^2\,mol^{-1}}$, which indicate 1 : 1 electrolytes. The IR spectra support the ionic nature of the nitrate group in these complexes due to the bands at 1384 and 1388 $\mathrm{cm^{-1}}$ [16]. The NH absorption observed at 3312 $\mathrm{cm^{-1}}$ in the IR spectrum of free BHP is still observed at 3315 and 3314 $\mathrm{cm^{-1}}$ in the spectra of the two complexes, indicating NH coordination to the metal without deprotonation. The ^{1}H NMR of the diamagnetic Zn(II) and Cd(II) complexes supports the presence of the NH after coordination, since the NH at δ 12.99 ppm is still in ^{1}H NMR spectra of Zn(II)- and Cd(II)-BHP complexes. The mass spectra reveals the existence of a molecular ion peak at $m/e = 661$ and 565 corresponding to the formula $[\mathrm{Cd(L)(H_2O)_2(NO_3)}]^+$ and $[\mathrm{Zn(L)(H_2O)_2}]^{2+}$ of molecular weights 659.4 and 568.4. The structures are presented in the diagram below:





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4.2. *Analytical application*

The rate of complexation of Cu(II), Ni(II) and Co(II) with BHP ligand were spectrophotometrically determined in 75% (v/v) dioxane-water solution at 25°C. A solution of ligand (1×10^{-4} M) and equimolar amount of each metal ion were mixed and the absorption spectrum measured in the range 220–750 nm. The 1 : 1 ($\mathrm{M^{n+}}$:BHP) where M = Cu(II), Ni(II) and Co(II) spectra show extensive changes compared to the free ligand ($\lambda_{\max}$ 250 nm, $\log\varepsilon = 4.74$ $\pi \rightarrow \pi^*$ and $\lambda_{\max} = 360$ nm, $\log\varepsilon = 4.45$ $n \rightarrow \pi^*$) supporting coordination. The two bands show a marked bathochromic shift with the appearance of additional bands. On mixing BHP with copper nitrate in 75% (v/v) dioxane-water, a pink solution was obtained. For nickel and cobalt a wine-red and bluish-green color develop. BHP was used as indicator for copper [3]. In this study, the use of BHP as indicator for Ni(II) and Co(II) ions by spectrophotometric methods was examined. In addition this chelating agent as an extracting agent for copper, nickel and cobalt ions was investigated using spectrophotometric titration.

A series of 5 mL solutions containing 5×10^{-5} M of $\mathrm{M^{2+}}$ and 5×10^{-5} M BHP in 75% dioxane-water are prepared and an equivalent of EDTA is gradually added to the solutions keeping the volume of the reaction mixture at 5 mL. The absorption spectra of these solutions were recorded using 75% (v/v) dioxane-water as a reference solution. As shown in figure 2, the band maxima at 530, 580 and 520 nm assigned to $\mathrm{d} \rightarrow \pi$ transition in the complexes gradually decreased and disappear with complete addition of an equivalent of EDTA. This indicates that BHP could act as an indicator in EDTA titration of Cu(II), Co(II) and Ni(II) ions. The complete changes from purple to pale

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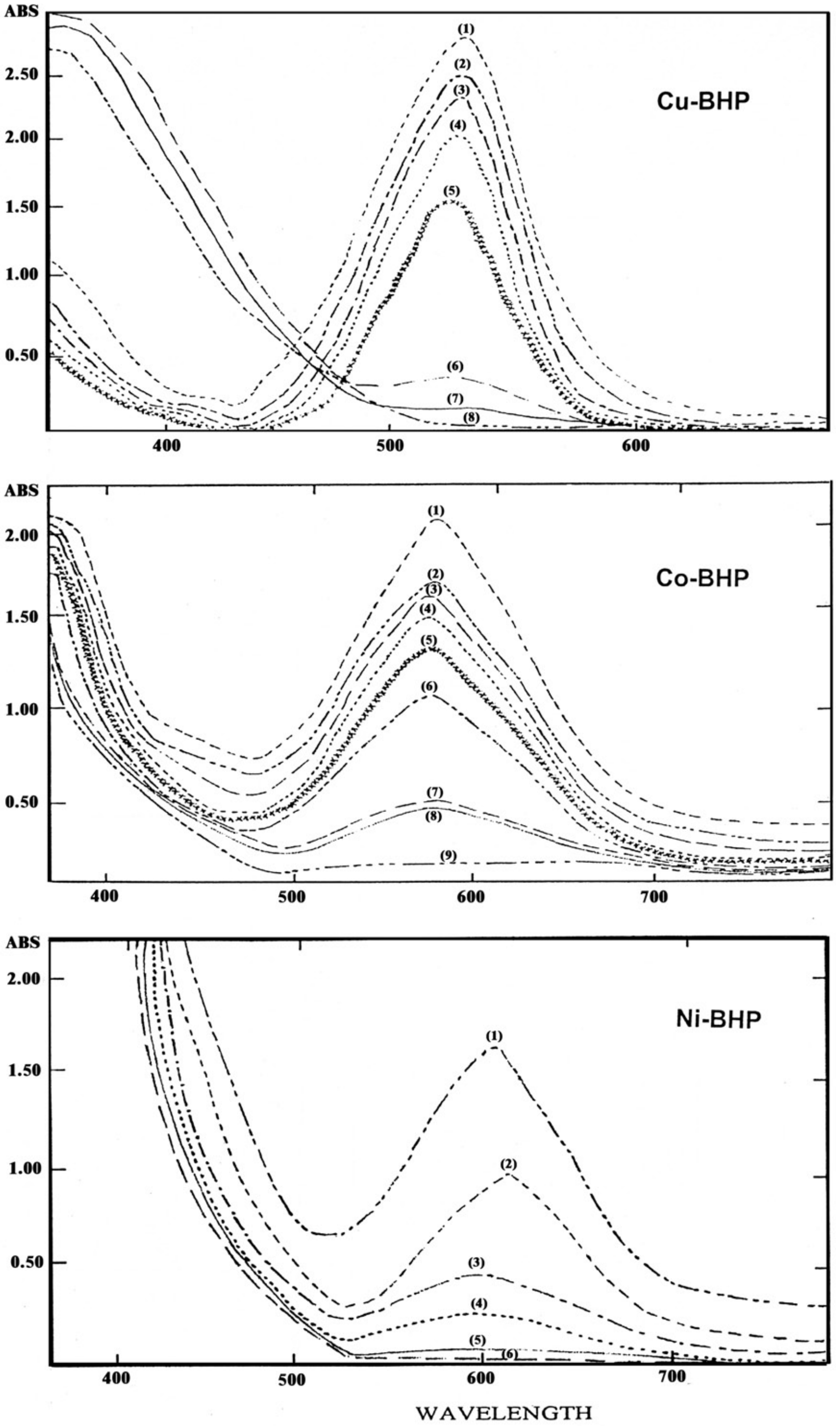

Figure 2. Electronic absorption spectra of M^{+2}-BHP complex in 75% (v/v) dioxane-water at different volumes of EDTA.

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green, bluish-green to pale yellow and wine-red to pale green for Cu(II)-, Co(II)- and Ni(II)-BHP EDTA at the equivalent points supports the use of BHP ligand as indicator to these cations.

4.3. *Solvent extraction of transition metal ions by BHP (HL)*

Solvent extraction was carried out using 10 cm^3 tube with a stopper in which an aqueous solution (5 mL) of the metal nitrate (Cu^{2+}, Ni^{2+} and Co^{2+}) and benzene solution (5 mL) of the ligand were put as aqueous and organic phases. The test tube was shaken for an adequate time (2 to 6 h) at room temperature. The concentration of metal complexes transferred into organic phase was determined by measuring the visible absorption spectra of the benzene layer. The effect of shaking time, pH, ionic strength and molar ratio on the extent of extraction are studied.

4.3.1. Effect of shaking time. Figure 3(a) shows the plots of absorbance (A) against shaking time. The concentration of both the extracting BHP in benzene and the metal ion in water was 1×10^{-3} M and the pH of the aqueous phase were adjusted at 3.5 without using buffer solution. The maximum rate of extraction of Cu(II) by BHP was found to be much faster (1 h) than those of Ni(II) and Co(II) (4 and 5 h, respectively).

4.3.2. Effect of pH. The effect of pH of the aqueous phase on the extraction of Cu(II), Ni(II) and Co(II) by BHP were made under the following conditions:

The concentration of each of the extracting and the metal ions was 1×10^{-3} M and the shaking times were 1, 4 and 5 h for Cu(II), Ni(II) and Co(II) ions, respectively. It was found that the maximum extraction of these ions by BHP occurred around

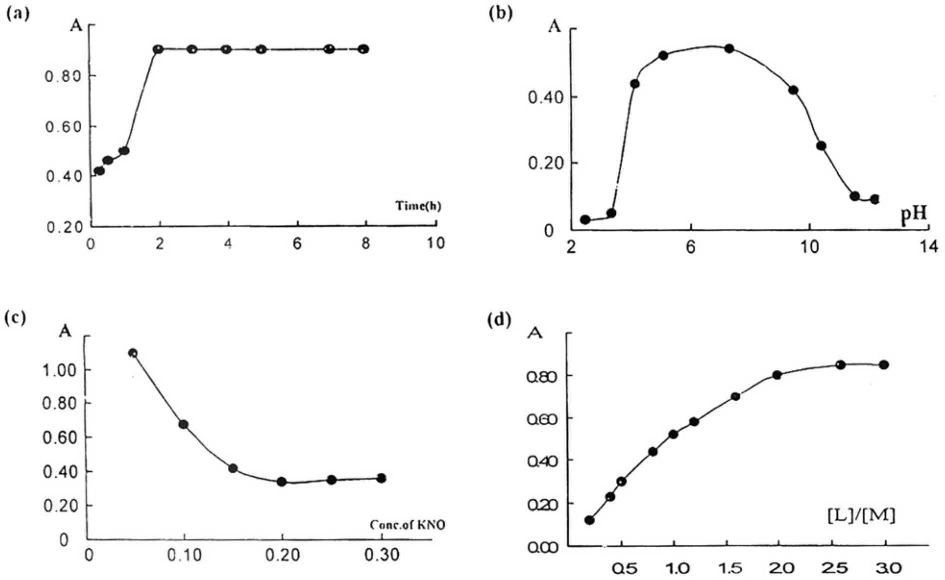

Figure 3. Factors affecting the extent of extraction of Cu^{2+} by BHP ligand. (a) effect of shaking time (b) effect of pH (c) effect of ionic strength (d) effect of mole ratio.

the pH range (5 to 7) for copper, (4 to 6) for nickel and (5 to 6) for cobalt. The similar pH maxima indicate that BHP possesses a similar extractability to these ions (figure 3b).

4.3.3. Effect of ionic strength. Extraction where $[\mathrm{BHP}]=[\mathrm{M}^{2+}]=1\times10^{-3}\,\mathrm{M}$, the pH of aqueous solution was 5.0 and the shaking time were 1, 4 and 5 for Cu(II)–, Ni(II)- and Co(II)-BHP systems, respectively, and the ionic strength of the aqueous phase was varied from 0.05 M to 0.30 M by addition of KNO_3. The extraction of copper was strongly influenced by ionic strength of the aqueous phase with absorbance (which is directly proportional to the percentage of the extracted metal ion) decreasing from 1.10 to 0.34 as the ionic strength increased from 0.05 to 0.20 M. Extractions of Ni(II) and Co(II) were not affected by change of ionic strength from 0.05 to 0.20 M. The absorbance change is 0.19 to 0.07 for nickel and 0.24 to 0.08 for cobalt when ionic strength changes from 0.05 to 0.20 M. Thus, BHP can be used for extraction of these ions from aqueous solutions containing large amounts of alkali metals.

4.3.4. Effect of molar ratio of [L] : [M]. From the relationship of the molar ratio of $[\mathrm{BHP}]:[\mathrm{M}^{2+}]$ it was apparent that appreciable extraction started at $[\mathrm{L}]/[\mathrm{M}^{2+}]$ ratio above 2.0 and reached a maximum value at 2.5 molar ratio for all ions (figure 3d).

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4.4. *Validity of Beer's law*

A series of solutions containing a constant BHP in benzene $(1\times10^{-3}\,\mathrm{M})$ and metal concentrations varied from 5×10^{-5} to $1\times10^{-3}\,\mathrm{M}$ were prepared; the pH was adjusted at 5.0 and the absorbance of each solution was measured at $\lambda=530\,\mathrm{nm}$. These systems obey Beer's law in metal concentration range from 5×10^{-5} to $4.5\times10^{-4}\,\mathrm{M}$, 5×10^{-5} to $8\times10^{-4}\,\mathrm{M}$ and 5×10^{-5} to $9.5\times10^{-4}\,\mathrm{M}$ with molar absorptivities of 7837.8, 7916.9 and $6000\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1}$ for Cu(II)-, Ni(II)- and Co(II)-BHP complexed systems, respectively.

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