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THERMODYNAMICS, FORMATION CONSTANTS, SPECTROPHOTOMETRY AND INFRARED SPECTROSCOPY OF COMPLEXES BETWEEN SOME DIVALENT METAL IONS AND 3-HYDRAZINO-6-PHENYLPYRIDAZINE AND RELATED LIGANDS

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ABSTRACT

The stepwise formation constants of complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Cd(II) and UO_2(II) ions with 3-hydrazino-6-phenylpyridazine (HPP) and its condensation products with benzil (BHPP) and *p*-methoxyacetophenone (*p*-MeOAHPP) were determined in a 75% (v/v) dioxane–water mixture at $\mu = 0.05$ M (KNO_3). The effect of temperature (at 10, 20, 30 and 40 °C) was also examined for Cu(II) and UO_2(II)–BHPP complexes. The overall changes in ΔG, ΔH and ΔS have been calculated. The solid complexes of Cu(II)-, Co(II)- and Ni(II)–BHPP were prepared and examined by elemental analysis and IR spectroscopy. Analysis of the data indicates chelation of the BHPP ligand through the nitrogens of both hydrazone and the pyridazine ring and the carbonyl oxygen group. The spectrophotometric studies were performed on solutions of Cu(II), Ni(II) and Co(II) with BHPP in order to obtain the optimum pH values for complex formation. The compositions of the chelates formed were determined. Analytical determinations of the micro amounts of Cu(II), Ni(II) and Co(II) were also done using BHPP as the complexing agent.

INTRODUCTION

The class of compounds under investigation is related structurally to the corresponding azo-pyrazolone dyes [1–3]. The parent compound (6-phenyl-3-hydrazinopyridazine) was condensed with benzil and *p*-methoxyacetophenone. The pharmacological properties of hydralazine, dihydrazine and some related compounds were studied by Kirpekar and Lewis [4]. Hydrazine (I) and dihydralazine (II) cause adrenaline (III) reversal and antagonize the pressor effects of noradrenaline (IV) on cat blood pressure. (I) and (II)

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antagonize vasoconstriction caused by (III), (IV), histamine (V), 5-hydroxytryptamine (VI) or $BaCl_2$ in isolated perfused preparations of rat hindquarters or rabbit ear.

The present paper deals with the determination of formation constants for the complexes of Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and UO_2(II) with BHPP and other related organic ligands. The solid complexes were prepared, and then investigated using elemental analysis and IR spectroscopy.

Spectrophotometric studies were carried out individually on Cu(II), Ni(II) and Co(II) with BHPP and metal ions were analytically determined at the appropriate pH values in universal buffer solution using BHPP as the complexing agent.

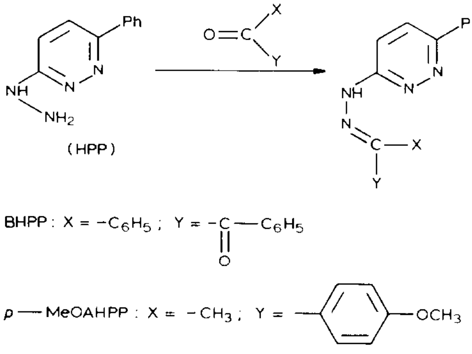
EXPERIMENTAL

Preparation of the solid organic ligands

BHPP and *p*-MeOAHPP were prepared by refluxing an ethanolic solution of 3-hydrazino-6-phenylpyridazine (HPP) with the stoichiometric amounts of benzil and *p*-methoxyacetophenone in ethanol as previously described [5]; the structures of the ligands are shown in Scheme 1.

Reagents and materials

Stock solutions of the metal nitrate salts (BDH and Merck) were prepared and standardized using EDTA in the presence of suitable indicators [6]. Dioxane was purified as described previously. Uranyl ion was standardized gravimetrically [6] as the oxide (U_3O_8). Universal buffer solutions were prepared using standard methods. Potassium hydroxide free from CO_2 was prepared and standardized using the reagent potassium hydrogenphthalate.



Scheme 1

Doubly distilled water was used in all solution preparations.

Preparation of the solid complexes

Copper nitrate solution was mixed with benzil (at a metal-to-ligand ratio of 1 : 2) in ethanol at 70 °C and then refluxed for a few minutes. Then a saturated KCl solution was used to separate the soluble complex from the solution. The Cu(II)–BHPP complex was precipitated as a deep violet solid, which was collected, washed several times with an alcohol–water mixture and then dried in air and stored in a vacuum desiccator. The elemental analysis and physical properties are given in Table 1.

Ni(II)–BHPP was obtained from nickel(II) nitrate (0.1 M) after mixing with a 2×10^{-2} M solution of benzil ligand (at a metal-to-ligand ratio of 1 : 2) in ethanol at 70 °C; after refluxing for 10 min, the solution turned deep pink in colour. The solid complex was isolated by salting out using a saturated solution of KCl. Deep pink crystals were separated and collected, washed and dried in air.

The Co(II)–BHPP complex was obtained as bluish-black crystals on mixing cobalt nitrate solution and the BHPP ligand in ethanol (at a metal-to-ligand ratio of 1 : 2) and refluxing for about 10 min. The elemental analysis and physical properties are tabulated in Table 1.

Measurement and procedures

pH metric titrations and all other experimental conditions were essentially the same as previously described [5]. The temperature was 30 °C and ionic strength was maintained at 0.05 M with KNO_3. In all cases the metal-to-ligand ratio was kept at 1 : 2, with a metal concentration of 1.5×10^{-3} M.

TABLE 1

Elemental analysis of the organic ligands and their metal complexes

Compound	Found (calculated)			Colour, melting point
	C	H	N	
BHPP($C_{24}H_{18}ON_4$)	76.60 (76.19)	4.80 (4.76)	14.70 (14.81)	Yellow, 170° [5]
Cu–(BHPP)	70.50 (70.50)	4.20 (4.30)	13.70 (13.60)	Violet, 146–148°
Ni–$(BHPP)_2 \cdot 2H_2O$	67.70 (67.90)	4.50 (4.50)	14.80 (14.20)	Dark pink, decomposed at 250°
Co–$(BHPP)_2$	69.20 (70.90)	4.20 (4.20)	12.80 (13.80)	Bluish-black, decomposed at 125°

All measurements were taken in 75% (v/v) dioxane–water. Stability constants of Cu(II) and UO_2(II)–BHPP chelates were determined at various temperatures (10, 20, 30 and 40 °C) in order to calculate the thermodynamic constants. In the dioxane–water mixture measurements, the value of the hydrogen ion concentration was derived from the pH after adding [7] a correction factor of 0.28. pH measurements and calculations of the thermodynamic functions were obtained as previously described [6]. The electronic spectra were recorded using a Perkin-Elmer 550S spectrophotometer with the ligand solution as a reference. The IR spectra were recorded using a Perkin-Elmer spectrophotometer (4000–200 cm^{-1}) using the potassium bromide discs technique.

RESULTS AND DISCUSSION

Thermodynamics and formation constants

pH metric technique

Representative plots for HPP–metal ion mixtures are shown in Fig. 1. Representative plots for the titration curves of the BHPP ligand in the absence and in the presence of divalent metal ions are shown in Fig. 2. The curves obtained for the titration of divalent metal–HPP mixtures are very similar to those obtained for divalent metal–*p*-methoxy-AHPP mixtures. In all titrations, the ligands under investigation appear to behave as monoprotic through the dissociation of the hydrazone hydrogen, since the metal–ligand titration curves show the presence of an inflection at $m = 1$ (where m = number of moles of base added per mole of ligand). The values of the dissociation constants K_1^H were calculated and they are summarized in Table 2. The titration curves for the *p*-MeOAHPP and HPP ligands in the presence of copper(II) ion showed a distinct, sharp inflection at $m = 1$ (here m = number of moles of base added per mole of metal ion) in addition to that at $m = 2$, thus accounting for the stepwise formation of ML and ML_2 species (Fig. 1). Such features were however not observed with other cations, where only one overlapping buffer zone was observed between $m = 0$ and $m = 2$. However, different behaviour was observed in the titration curves of BHPP ligand–metal ions. In the presence of zinc(II) and cadmium(II) ions with BHPP ligand, a sharp inflection was observed at $m = 1$, indicating the formation of the ML species only (Fig. 1). In the case of both Ni(II) and Co(II) with BHPP, the titration curves show a distinct inflection at $m = 1$ and $m = 2$, in line with the stepwise formation of the ML and ML_2 species. Such features were not observed with Cu(II) and UO_2(II) metal ions, where only one overlapping buffer region was observed between $m = 0$ and $m = 2$, indicating the formation of the ML_2 species. The stepwise formation constants and the associated thermodynamic quantities were calculated as

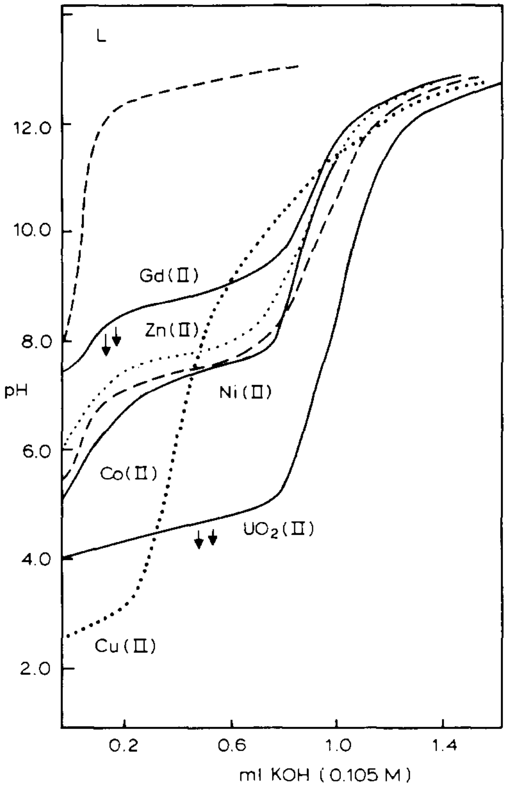


Fig. 1. pH titration curves of HPP ligand and its metal complexes at 30 °C in 75% (v/v) dioxane–water solvent: $[L]$ = free ligand (3×10^{-3} M), $V_0 = 30$ ml, μ = zero.

previously described [5]. The values of log K_1 and log β (the overall formation constant) of the metal complexes studied are listed in Table 2.

Values of log β for bis chelates of the UO_2(II) ion with either the

TABLE 2

Formation constants for BHPP, *p*-MeOAHPP and HPP complexes with the divalent metal ions at 30 °C ($\mu = 0.05$ MKNO_3 in 75%(v/v) dioxane–water solvent)

Metal ion	BHPP [a], $pK^H = 12.69$ [5]		*p*-MeOAHPP, $pK^H = 13.25$ [5]		HPP, $pK^H = 13.08$ [5]	
	log K_1	log β	log K_1	log β	log K_1	log β
Co(II)	10.60	19.00	8.74	17.19	8.58	16.88
Ni(II)	11.33	19.66	8.54	16.84	8.28	16.37
Cu(II)	12.00	22.27	12.51	19.92	12.15	–
Zn(II)	9.15	–	8.47	16.74	8.01	15.68
Cd(II)	8.00	–	7.17	14.08	–	–
UO_2(II)	11.30	22.30	11.47	–	11.02	↓↓

[a] Ionic strength zero.

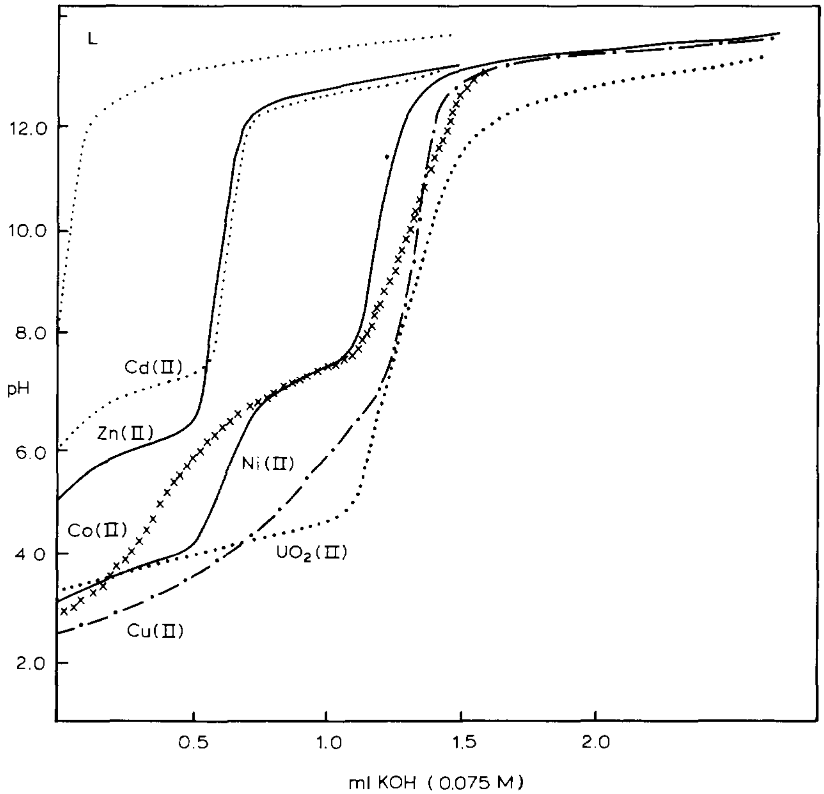


Fig. 2. pH titration curves of BHPP ligand and its metal complexes at 30 °C in 75% (v/v) dioxane-water solvent: [L] = free ligand (3×10^{-3} M), $[M]=1.5\times10^{-3}$ M, $V_0 = 30$ ml, μ = zero.

p-MeOAHPP or the HPP ligands are not included here because of the tendency of these species to hydrolyse in the region of their formation. log K_1 and log β could also not be calculated for the Cd-HPP chelate, because of the precipitation occurring at the beginning of the titration. In the case of the Zn(II) and Cd(II)-BHPP complexes, only the 1 : 1 chelate compounds are formed since the highest values of $\bar{n}$ obtained were less than 1.5. For the same reason, only values of log K_1 were obtained for the Cu(II)-HPP chelate compound (Table 2).

The hydrazone-group nitrogen of the ligands can coordinate with the metal ions, particularly when additional complex stabilization is afforded by the presence of a second donor atom in a position favourable for chelation. Thus, in isostructural PAR complexes (PAR = 4-2-(pyridylazo)resorcinol) [8], there is coordination through the pyridine nitrogen, the azo nitrogen farthest from the pyridine nitrogen and the *ortho* phenolic group, forming a tridentate 1 : 1 chelate. Also, BHP and DAHP [3], which are similar in structure to the studied ligand, are expected to form complexes of a similar nature. With transition metal ions, the relative stabilities of the 1 : 1 metal complexes are the same for the three ligands and are in agreement with the order found for other ligands, namely Cu(II) > UO_2(II) > Ni(II) > Co(II) > Zn(II) > Cd(II), except with HPP and *p*-MeOAHPP where Ni(II) and Co(II) exchange positions in the order.

The general trend in the formation constants of the metal complexes (Table 2) follows the order BHPP > *p*-MeOAHPP > HPP, except in the case of the Cu(II) complexes, for which the stabilities are proportional to the values of log K_1^H (Table 2).

Effect of temperature

The values of ΔH, ΔG and ΔS have been calculated using the Gibbs–Helmholtz equation from the formation constants of chelates of both Cu(II) and UO_2(II) with BHPP obtained at different temperatures (10, 20, 30 and 40 °C) and they are given in Table 3. The ΔH values were obtained from plots of log K_1 vs. $1/T$. The negative values of ΔH show that the reactions of these metals with the BHPP ligand are exothermic. Since the complex formation reaction is not favoured by higher temperature, the values of both log K_1 and log β decrease with increasing temperature. The ΔG values are negative for all the chelates, showing that these reactions are spontaneous. The ΔS values are positive for all the chelates, showing that entropy considerations favour complex formation [9].

Spectrophotometric studies

Absorption spectra of metal–BHPP solutions

The absorption spectra of 50% dioxane–water solutions of these complexes were measured against that of a BHPP ligand reference solution. On

TABLE 3

Thermodynamic functions and stepwise formation constants for 1 : 1 and 1 : 2 Cu(II)– and UO_2(II)–BHPP chelates at various temperatures

Metal ion	Temperature (°C)	pK_1^H	Formation constants		$-\Delta G$ (kcal mol^{-1})	$-\Delta H$ (kcal mol^{-1})	ΔS (cal mol^{-1}
			log K_1	log β			
Cu(II)	10	13.44	11.43	21.33	28.54	18.42	33.96
	20	12.98 [5]	11.31	20.90			
	30	12.62 [5]	11.30	20.88			
	40	11.94 [5]	11.19	20.11			
UO_2(II)	10	13.44	11.05	22.14	29.57	11.52	61.60
	20	12.98 [5]	10.97	21.97			
	30	12.62 [5]	10.84	21.65			
	40	11.94 [5]	10.53				

adding metal ion (5×10^{-5} M) to the ligand solution (2×10^{-4} M), a deep violet colour developed in the case of Cu(II), a deep violet colour for Ni(II) and a bluish-purple colour for Co(II). The characteristic bands appearing on complex formation were as follows: 475 nm (strong) with a shoulder at 375 nm in the case of Cu(II); 495 nm (strong) in the case of Ni(II); and 570 nm (strong), 440 nm (weak) and 375 nm (medium) in the case of Co(II).

Determination of Co(II), Ni(II) and Cu(II) metal with BHPP ligand

Spectrophotometric study of the effect of pH on the formation of the various metal chelates with BHPP revealed that cobalt(II), nickel(II) and copper(II) form coloured chelates over the pH range 2–8. The optimum pH range for complex formation was found to be 3.0–5.0, with a sharp maximum at pH 4.0 for Co(II), 5–8 for Ni(II) and 6–8 for Cu(II) ions (Fig. 3). The chelate spectra, shown in Fig. 3, are sufficiently different, which may be of great use in the simultaneous determination of the pairs Co(II) + Ni(II) and Co(II) + Cu(II), which will be the subject of future work.

Validity of Beer's law

Absorbance measurements at around 475, 495 and 570 nm for solutions of the chelates of Cu(II), Ni(II) and Co(II), respectively, follow Beer's law and provide high sensitivity for the determination of each of these ions (Fig. 4).

Composition

The compositions of the complexes were determined spectrophotometrically following Job's continuous variation method [10], the slope ratio [11] and the molar ratio [12] at various wavelengths. Measurements were carried out using a 50% dioxane–water solvent at the optimum pH value previously determined. As may be seen from Fig. 5 which illustrates the Job method,

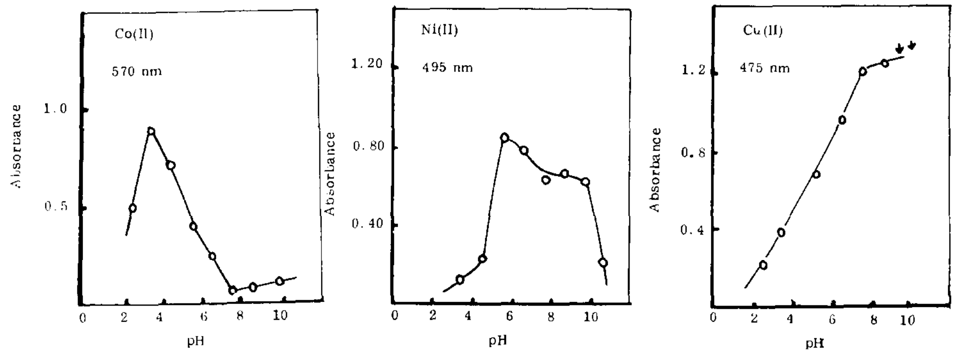


Fig. 3. Absorbance vs. pH for metal chelates at concentrations of 1.5×10^{-4} M of BHPP and 3×10^{-5} M of metal ion in 50% (v/v) dioxane–water solvent (with BHPP used as a blank).

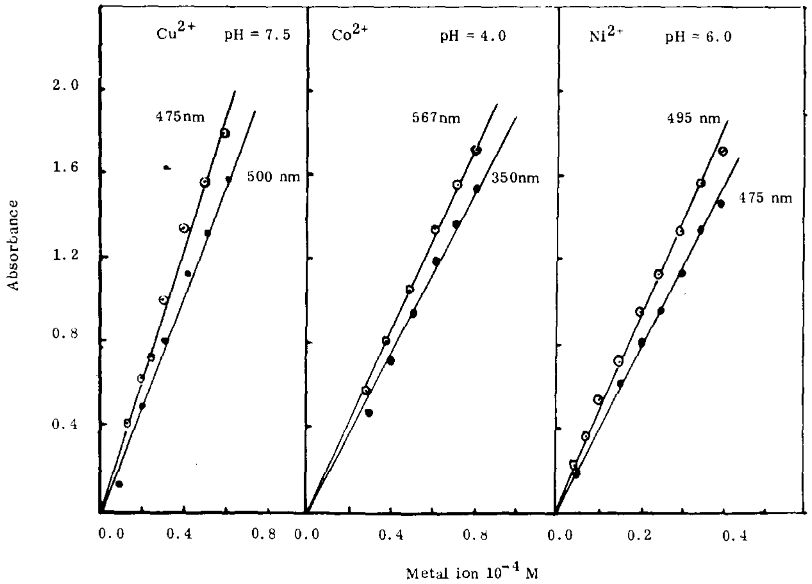


Fig. 4. Validity of Beer's law for M(II)-BHPP complexes.

the Cu–BHPP complex at pH 7.5 has a 1 : 2 composition which is also confirmed by other methods. The composition of the Ni–BHPP complexes were determined at pH 6.0, revealing that both 1 : 2 and 1 : 1 compositions are present in solution (Fig. 5). In the Co–BHPP mixture the 1 : 2 composition is observed to be the predominate species in the solution (Fig. 5).

Isolation of solid complexes

The copper(II) complex of BHPP was isolated from the solution as the 1 : 2 chelate (Table 1). The absence of both keto carbonyl stretching bands

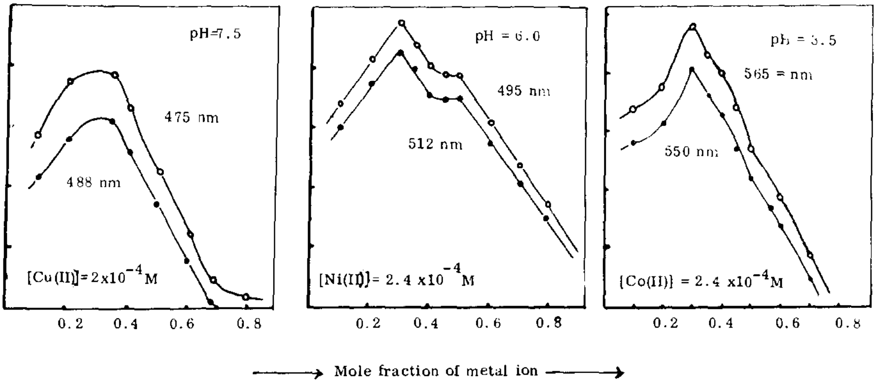


Fig. 5. Job's method [10] for M(II)-BHPP complexes in 50% (v/v) dioxane–water.

TABLE 4

Selected bands (cm^{-1}) [a] in the IR spectra and tentative assignments

Assignment	BHPP	Cu–BHPP	Ni–BHPP	Co–BHPP
$\nu(\mathrm{HOH})$	–	–	2690–3005 (vs, br)	–
$\nu(>\mathrm{NH})$	3308 (m)	–	–	–
$\nu(\mathrm{CH})$	3025 (m)	3025 (m)	3025 (m)	3025 (m)
$\nu(>\mathrm{C{=}O})$	1655 (vs)	–	1628 (vs)	1630 (s)
$\delta(\mathrm{H_2O})$	–	–	1520 (vs)	
$\nu(\mathrm{-N{=}N-})$	1390 (m)	1404 (m)	1400 (m)	1410 (m)
$\pi(\mathrm{H_2O})$	–	–	860 (s)	–
$\nu(\mathrm{M{-}O})$	–	585 (m)	600 (s)	605 (m)
$\nu(\mathrm{M{-}N})$	–	422 (m)	540 (m)	540 (m)

[a] Abbreviations: vs, very strong; s, strong; m, medium; br, broad.

$\gamma(\mathrm{C{=}O})$ and $\nu(>\mathrm{N{=}H})$ and the observed shift in $\nu(\mathrm{N{=}N})$ frequencies [13,14] in the IR spectra of both the copper complex itself and its ligand (Table 4), suggests the formation of a chelate similar in structure to that proposed. The appearance of new Cu–N [14,15] and Cu–O [14,16] bands indicates that the ligand may behave as a bidentate N,O-donor. Further evidence is obtained from both potentiometric and spectrophotometric data for the presence of the 1 : 2 species in solution. The isolated solid state Ni(II) complex of BHPP has been found as the $\mathrm{ML_2}$ dihydrated species. The structure of this species can be inferred from the changes in the infrared absorption bands of the free ligand and its metal chelate (Table 4), namely the shift in the $\nu(>\mathrm{C{=}O})$ band and the absence of $\nu(\mathrm{N{-}H})$ frequencies, as well as the appearance of M–N and M–O bond frequencies which suggest the sharing of the two donor centers (carbonyl oxygen and either the azo or the pyridazine ring nitrogen). The three different modes for coordinated water [14], $\nu(\mathrm{H_2O})$, $\delta(\mathrm{H_2O})$ and $\pi(\mathrm{H_2O})$, were all observed (Table 4). Results obtained in solution from both pH and spectrophotometric studies confirmed the presence of ML and $\mathrm{ML_2}$ species (Figs. 2 and 5). The probable structures of the solid complexes are shown in Fig. 6.

In the case of the Co(II)–BHPP solid complex, the results obtained indicate that the coordination may be through >NH, >C=O and N=N

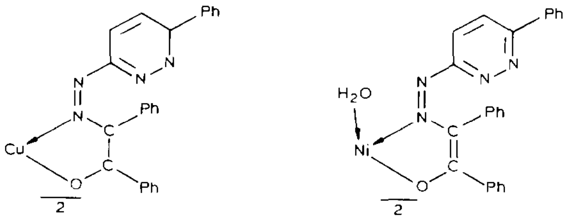


Fig. 6. Proposed structure of the solid complexes.

groups (Table 4), as evidenced by their absence or the shift in their frequencies in the infrared spectrum of the ligand. The pH and spectrophotometric data reveal that the ML_2 species is predominant, while the species ML is also present (Figs. 2 and 5).

Analytical studies

The BHPP ligand was used successfully as an analytical reagent for the determination of cobalt(II), nickel(II) and copper(II) ions in two different methods. All measurements were carried out using 50% dioxan–water in the presence of universal buffer solution at the pH value appropriate for the metal ion concerned.

In the first method, absorbances were recorded for the divalent metal ions in concentrations of 0.5–6 μg ml^{-1}, in the presence of sufficient excess of the reagent at suitable wavelengths and pH values (Fig. 4). The results obtained followed very closely the Beer–Lambert relationship (Fig. 4).

In the second method, the deep violet, deep pink and bluish-purple solutions of the Cu–BHPP, Ni–BHPP and Co–BHPP (1 : 5) mixtures were titrated spectrophotometrically at the same wavelength as was used in the first method using standard EDTA (1×10^{-4} M) solution as the titrant, and both the titrant and titrand were buffered to the optimum pH values mentioned earlier, namely 7.5 for Cu(II), 4.0 for Co(II) and 6.0 for Ni(II).

REFERENCES

1 F.A. Snavely, W.C. Fernelius and B.P. Block, J. Am. Chem. Soc., 79 (1957) 1028.
2 F.A. Snavely, B.D. Krecker and C.G. Clark, J. Am. Chem. Soc., 81 (1959) 2337.
3 E.N. Rizkalla, A.T. Ramadan and M.H. Seada, Polyhedron, 2 (1983) 1155.
4 S.M. Kirpekar and J.J. Lewis, J. Pharm. Pharmacol., 9 (1957) 877.
5 B.A. El-Shetary, M.S. Abdel-Moez and H.S. Sleem, Thermochim. Acta, 113 (1987) 21.
6 A.I. Vogel, Quantitative Inorganic Analysis, 4th edn., Longman, London, 1978.
7 H.M.N. Irving and U.S. Mohnot, J. Inorg. Nucl. Chem., 30 (1968) 1215.
8 U. Casellato, M. Vidali and P.A. Vigato, Inorg. Chim. Acta, 18 (1976) 77.
9 R.N. Kasi Viswanathan and M.G. Reddy, J. Indian Chem. Soc., 61 (1984) 856.
10 P. Job, Ann. Chim., 9 (1928) 113, 11 (1936) 97.
11 A.E. Harvey and D.L. Manning, J. Am. Chem. Soc., 72 (1950) 4488.
12 J.H. Yoe and A.L. Jones, Ind. Eng. Chem. Anal. Edn., 16 (1944) 111.
13 L.J. Bellamy, Advances in Infrared Group Frequencies, Methuen, London, 1968.
14 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 2nd edn., Wiley-Interscience, 1969.
15 E.B. Powell and N. Shepard, J. Chem. Soc., (1961) 1112.
16 K. Nakamoto and A.E. Martell, J. Chem. Phys., 32 (1960) 588.