Synthesis, Spectral, Magnetic and Thermal Studies of the Complexes of Co^{II} and Ni^{II} With Some Bidentate and Tridentate Hydrazone Ligands

CHETAN K. MODI¹, ASHWIN S. PATEL² AND BHARAT T. THAKER^{3*}

¹Department of Chemistry, Sardar Patel University,
Vallabh Vidyanagar 388 120, India.

²Department of Chemistry, Navyug Science College, Rander Road,
Surat 395 009, India.

³Department of Chemistry, Veer Narmad South Gujarat University,
Surat 395 007, India.

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Abstract The reaction of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with hydrazones derived from 1-phenyl-3-methyl-4-acyl-5-pyrazolone (where acyl = acetyl, propionyl, butyryl and benzoyl) with 2-picolinic acid hydrazide have been studied and characterized on the basis of elemental analysis, magnetic moments, molar conductivity measurements, IR and electronic spectral studies and thermogravimetric analysis. Various ligand field parameters have been calculated. Electronic spectral data and the magnetic moment values suggest an octahedral structure for all cobalt(II) and nickel(II) complexes.

Key words: Synthesis, Transition metal complexes, Hydrazone ligands, Spectral, magnetic and thermal studies

Introduction

In the last two decades, much interest has been focused on compounds containing hydrazide and hydrazone moieties and their complexes with first row transition metals¹⁻⁶. Such interest has been growing due to their use in medicine⁷ (for treatment of tuberculosis), biological systems⁸ and analytical chemistry⁹.

The present study is concerned with the preparation of hydrazone ligands (**Scheme 1**) from 1-phenyl-3-methyl-4-acyl-5-pyrazolone (where acyl = acetyl, propionyl, butyryl and benzoyl) with 2-picolinic acid hydrazide, which are capable of multidentate behavior by virtue of having a large number of donor atoms. Different modes of chelation are proposed. In view of this and the cobalt(II)

and nickel(II) complexes of these hydrazone ligands have been synthesized and characterized. The results of these studies are presented in this paper.

Experimental

All the solvents and chemicals were commercial reagent grade or better and were used without further purification. 1-phenyl-3-methyl-4-acyl-5-pyrazolone (PMAcP) (Where acyl =acetyl, propionyl, butyryl and benzoyl) was prepared using $\text{Ca}(\text{OH})_2$ as catalyst modified by B.S. Jensen method¹⁰ and the synthesis of 2-picolinic acid hydrazide was reported earlier¹¹. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ used were BDH make.

$\text{R} = -\text{CH}_3$,	1-phenyl-3-methyl-4- [α -(2-picolinoyl hydrazono)] ethyl -5- hydroxy pyrazole (PHE)
$\text{R} = -\text{CH}_2-\text{CH}_3$,	1-phenyl-3-methyl-4- [α -(2-picolinoyl hydrazono)] propyl-5- hydroxy pyrazole (PHP)
$\text{R} = -\text{CH}_2-\text{CH}_2-\text{CH}_3$,	1-phenyl-3-methyl-4- [α -(2-picolinoyl hydrazono)] butyl-5-hydroxy pyrazole (PHBy)
$\text{R} = -\text{C}_6\text{H}_5$	1-phenyl-3-methyl-4- [α -(2-picolinoyl hydrazono)] benzyl-5-hydroxy pyrazole (PHBz)

Scheme – 1

Synthesis of hydrazone ligands

A quantity of 3.42 g (0.025 M) of 2-picolinic acid hydrazide was dissolved in ethanol (150 ml) and then 0.025 M of PMAcP [where Ac = acetyl (5.40 g), propionyl (5.75 g), butyryl (6.10 g) and benzoyl (6.95 g)] was added in it. The reaction mixture was refluxed on a water bath for 1-2 h. The colour of the initial solution was changed. After cooling to room temperature a large amount of yellowish or yellowish orange precipitate was obtained. The precipitate was filtered and washed with excess of ethanol and dried over fused CaCl_2 .

Preparation of complexes

0.01 M of hydrazone ligands [PHE (3.35 g), PHP (3.49 g), PHBy (3.63 g) and PMBz (3.97 g)] was added to DMF (15 ml) and a solution of 0.005 M of the metal salts [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.455 g)] or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.45 g)] dissolved in minimum quantity of methanol. Both the solutions were mixed together with constant stirring and pH raised up to 6-7 by the addition of sodium acetate solution. The resulting mixture was refluxed for 3-4 h. The complexes which separated out were collected by filtration, washed with distilled water and small quantity of methanol and dried over fused CaCl_2 . Microanalytical data were performed at RSIC, CDRI, Lucknow. The metal contents of the complexes were analyzed by EDTA titration¹² after decomposing the organic matter with a mixture of HClO_4 , H_2SO_4 and HNO_3 (1: 1.5: 2.5). The vibrating sample magnetometer (VSM), model 7304 (4-inch electromagnet VSM system), Lake Shore Cryotronics Inc., USA was used to characterize magnetic properties of the metal chelates at Department of Chemistry, Sardar Patel University, Vallabh

Vidyanagar. The infrared spectra were recorded as KBr pellets using a Perkin-Elmer 3010 spectrophotometer. The ^1H NMR spectra were recorded at RSIC, IIT, Mumbai on a Perkin-Elmer 300 MHz instrument using TMS as internal standard. Electronic spectra of the complexes were recorded on a Shimadzu UV-160 A spectrophotometer using quartz cell of 1 cm^3 optical path.

Results and Discussion

The hydrazone ligands used in the present investigation are the condensation products of 2-picolinic acid hydrazide and respective PMAcP ligands (Where Ac=acetyl, propionyl, butyryl and benzoyl) in 1:1 molar ratio. The reaction leading to the formation of the hydrazone ligands can be represented according to the **scheme-1** as shown above. The hydrazone ligands have been characterized by elemental analysis, i.r. and ^1H NMR spectral studies. Analytical and physical data are collected in **Table 1**.

The ^1H n.m.r. spectra of PHE, PHP, PHBy and PHBz in CDCl_3 and $\text{DMSO}-d_6$ show low field signals respectively at δ 12.48, 12.56, 12.68 and 12.38 ppm for the -OH proton of pyrazoline ring. The -NH proton of hydrazide residue observed at δ 11.57, 10.20, 10.00 and 10.03 ppm in PHE, PHP, PHBy and PHBz ligand respectively. In the n.m.r. spectra of PHE ligand, two methyl (-CH₃) protons are observed at δ 2.34 and 1.26 ppm for pyrazoline ring -CH₃ and 4-ethyl group -CH₃ respectively. In the spectra of PHP, PHBy and PHBz, pyrazoline ring -CH₃ proton is observed at δ 2.40, 2.44 and 1.62 ppm, respectively. Signals due to pyridine ring ($\text{C}_5\text{H}_4\text{N}$) protons occur as multiplets between δ 8.03 – 9.10 ppm.

Characterization of metal complexes

Reaction of corresponding hydrazone ligands with metal(II) salts yielded complexes having 1:2 metal-ligand stoichiometries. Formation of the complexes has been shown below.

Where $\text{M} = \text{Co}^{\text{II}}$ and Ni^{II}
 $\text{HL}^1 = \text{PHE, PHP and PHBy}$
 $\text{HL}^2 = \text{PHBz}$

All the complexes are microcrystalline solids, stable at room temperature, non-hygroscopic. They are insoluble in water, sparingly soluble in common organic solvents but completely soluble in coordinating solvents like DMF and DMSO. 10^{-3} M DMF solutions were subjected to conductivity measurements. The molar conductance values for Co^{II} and Ni^{II} complexes lie in the range 11.79-13.64 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ and 11.89-14.58 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$, respectively. These values suggest the non-electrolytic nature of all the complexes.

Magnetic moments and electronic spectra

The magnetic moments of cobalt(II) complexes with PHE, PHP, PHBy and PHBz ligands (**Table 1**) are respectively found to be 4.86, 4.90, 4.92 and 4.88 B.M. suggesting a high spin octahedral geometry with a very high orbital contribution attributable to the three fold degeneracy of the $^4\text{T}_{1g}(\text{F})$ ground state term^{13,14}. The electronic spectra of cobalt(II) complexes were recorded in DMF. Two distinct bands in the range 9327-9381 and 18761-18867 cm^{-1} were observed in the electronic spectra of cobalt(II) complexes (**Table 3**) attributable to the $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{v}_1)$ and $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{P})(\text{v}_3)$ transition respectively in an octahedral field. Besides the d-d transitions, the band also observed at 25573-37735 cm^{-1} in the UV region, attributable to charge transfer transitions.

Important ligand field parameters are presented in **Table 3**. Racah interelectronic repulsion parameter (B), covalent factor (β_{35}) and 10Dq values were calculated using standard equation¹⁵. The ratio $\text{v}_3(\text{obs.})/\text{v}_1(\text{obs.})$ and $\text{v}_3(\text{calc.})/\text{v}_1(\text{calc.})$ were found to be in the range 2.00-2.02 as required for octahedral cobalt(II) complexes. The reduction of the Racah parameter from the free ion value 971 cm^{-1}

to 700.33 cm^{-1} and β value of 28% are taken as evidence of considerable covalence in the complex.

The electronic spectral data of nickel(II) complexes are given in **Table 3**. The electronic spectra of these paramagnetic complexes show two bands in visible region in the range 9832 – 9861 cm^{-1} and 16528 – 16806 cm^{-1} attributable to the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ (ν_1) and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (F) (ν_2) transition respectively are in conformity with octahedral arrangements for Ni^{II} ion and also show the bands in the UV region in the range 25641-26315, 28571-29411 and 32258-32786 cm^{-1} , attributable to charge transfer transitions.

The spectral bands are utilized to compute important ligand field parameter using the ligand field theory of spin allowed transition in d^8 configuration¹⁶. The value of 10 Dq and B are employed to calculate ν_2 and ν_3 (**Table 3**) leading to the following conclusion. Comparison of 10 Dq and B values for these Ni^{II} complexes indicates that the ligands give reasonably strong fields and form strong covalent bonds. The high values of Dq and B are also consistent with coordination of azomethine nitrogen. The ratio of ν_2/ν_1 , lies in the range 1.68-1.70 expected for octahedral geometry for nickel (II) complexes¹⁷. Also, the present nickel(II) complexes exhibit magnetic moments in the range 2.84-2.87 B.M. (**Table 1**) indicating an octahedral geometry¹⁸.

Infrared spectra

Some important bands observed (**Table 2**) in the infrared spectra of PHE, PHP, PHBy and PHBz and their metal complexes are considered for the identification of donor sites of the ligands. The IR spectra of the free ligands viz. PHE, PHP and PHBy, exhibit $\nu(\text{N-H})$ absorbance bands at ca.3190 cm^{-1} and $\nu(\text{C=O})$ bands at ca.1695 cm^{-1} indicating that the ligands exist in keto form in the solid state. However in solution, the ligands probably exist in equilibrium with tautomeric enol form. By the loss of proton, the enolic form may act as a uninegative ligand. The bands appearing in the spectra of ligands ~ 1695, 1640, 1535, 1015 cm^{-1} are attributed¹⁹ to amide I [$\nu(\text{C=O})$], $\nu(\text{C=N})$, amide II [$\beta(\text{N-H})$] + (C-N)] modes respectively.

Cobalt(II) and nickel(II) complexes of PHE, PHP and PHBy

Bands due to $\nu(\text{N-H})$ and $\nu(\text{C=O})$ stretching vibrations are not observed in the spectra of complexes. Instead, they show new bands characteristic of $\nu(\text{NCO})$ in the spectra of these complexes. The appearance of $\nu(\text{NCO})$ stretching vibration in the spectra of these complexes suggest the presence of $>\text{C=N-N=C}<$ residues of the stoichiometry and hence destruction of keto group via enolisation and bonding through resulting enolate oxygen. A strong band observed in the spectra of these ligands at 1640 cm^{-1} is shifted to lower wave number suggesting the participation of azomethine nitrogen in coordination²¹. In the spectra of free ligand, the band observed at ca.3440 and ca.1590 cm^{-1} are attributed to $\nu(\text{O-H})$ and $\nu(\text{C=N})$ ²² of pyrazoline ring, respectively. Which were remain unaltered in the spectra of complexes, indicating that non-participation of this groups. The appearance of bands at 875-870 and 688-680 cm^{-1} in spectra of the complexes attributed to $\rho_r(\text{H}_2\text{O})$ and $\rho_w(\text{H}_2\text{O})$, indicates the presence of coordinated water²³. The non-ligand bands observed in the 530-470 and 460-420 cm^{-1} regions are tentatively assigned to $\nu(\text{M-O})$ and $\square(\text{M-N})$ vibrational modes respectively.

Cobalt(II) and nickel(II) complexes of PHBz

The presence of $\nu(\text{N-H})$ in the spectra of these complexes suggests that PHBz remain protonated in chelation. A band observed in the spectra of PHBz at 1628 cm^{-1} is shifted to lower wave number in the spectra of complexes suggesting the participation of azomethine nitrogen in bonding. Similarly, the red shift of the $\nu(\text{C=O})$ band in the IR spectra of these complexes suggest the participation of carbonyl oxygen in complex formation. A broad band observed at 3410 cm^{-1} in the spectra of PHBz is due to $\nu(\text{O-H})$ of the pyrazoline ring. This band was disappeared in the spectra of these complexes suggesting enolisation exist at $-\text{OH}$ group of the pyrazoline ring by replacing hydrogen forming covalent bond with the metal ions.

Table 1. Physical and analytical data of hydrazone ligands and its Co^{II} and Ni^{II} complexes

Compounds Empirical Formula	Formula weight	Colour	Found(Calcd.) %				M.P. (^o C)	μ_{eff} (B.M.)	Conductance (U) ^b	% yield
			C	H	N	Metal				
PHE	335.43	Yellowish	64.52	5.04	21.08	-	230	-	-	72
C ₁₈ H ₁₇ N ₅ O ₂		orange	(64.47)	(5.06)	(21.07)					
PHP	349.36	Yellowish	65.26	5.29	20.32	-	183	-	-	74
C ₁₉ H ₁₉ N ₅ O ₂		orange	(65.31)	(5.28)	(20.34)					
PHBy	363.39	Yellowish	65.16	6.08	19.55	-	184	-	-	72
C ₂₀ H ₂₁ N ₅ O ₂		orange	(65.10)	(6.06)	(19.52)					
PHBz	397.41	Orange	69.63	4.65	17.82	-	180	-	-	80
C ₂₃ H ₁₉ N ₅ O ₂			(69.59)	(4.70)	(17.86)					
[Co(PHE) ₂ .(H ₂ O) ₂]	762.93	Golden	56.82	4.79	18.48	7.84	262	4.86	12.23	68
C ₃₆ H ₃₆ N ₁₀ O ₆ Co		brown	(56.76)	(4.73)	(18.39)	(7.75)				
[Co(PHP) ₂ .(H ₂ O) ₂]	790.93	Golden	58.12	5.34	17.79	7.58	238	4.90	11.79	72
C ₃₈ H ₄₀ N ₁₀ O ₆ Co		brown	(57.65)	(5.05)	(17.70)	(7.45)				
[Co(PHBy) ₂ .(H ₂ O) ₂]	818.93	Golden	58.82	5.46	17.23	7.26	212	4.92	13.64	70
C ₄₀ H ₄₄ N ₁₀ O ₆ Co		brown	(58.61)	(5.37)	(17.09)	(7.19)				
[Co(PHBz) ₂]	850.93	Brown	64.92	4.33	16.52	6.96	258	4.88	12.89	74
C ₄₆ H ₃₆ N ₁₀ O ₄ Co			(64.87)	(4.23)	(16.45)	(6.92)				
[Ni(PHE) ₂ .(H ₂ O) ₂]	760.71	Yellowish	56.79	4.84	18.60	7.82	251	2.85	14.58	72
C ₃₆ H ₃₆ N ₁₀ O ₆ Ni		Green	(56.78)	(4.73)	(18.40)	(7.71)				
[Ni(PHP) ₂ .(H ₂ O) ₂]	790.69	Yellowish	57.73	5.12	17.97	7.58	229	2.87	11.89	68
C ₃₈ H ₄₀ N ₁₀ O ₆ Ni		Green	(57.67)	(5.05)	(17.70)	(7.42)				
[Ni(PHBy) ₂ .(H ₂ O) ₂]	818.69	Yellowish	58.72	5.39	17.19	7.23	214	2.84	12.72	62
C ₄₀ H ₄₄ N ₁₀ O ₆ Ni		Green	(58.63)	(5.37)	(17.10)	(7.16)				
[Ni(PHBz) ₂]	850.69	Yellowish	64.90	4.26	16.54	6.95	238	2.86	14.23	76
C ₄₆ H ₃₆ N ₁₀ O ₄ Ni		Green	(64.88)	(4.23)	(16.45)	(6.89)				

$$(U) = \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Table 2. Important IR spectral data (cm⁻¹) of hydrazone ligands and its Co^{II} and Ni^{II} complexes

Compounds	ν O-H	ν N-H	ν C=O	ν C=N ^a	ν C=N ^b	ν C-O	ν N-N
PHE	3435	3190	1695	1635	1590	-	998
PHP	3435	3192	1695	1640	1590	-	990
PHBy	3440	3220	1696	1640	1592	-	995
PHBz	3410	-	1690	1628	1590	-	996
[Co(PHE) ₂ .(H ₂ O) ₂]	3415	-	-	1608	1590	1347	1010
[Co(PHP) ₂ .(H ₂ O) ₂]	3410	-	-	1625	1595	1353	1008
[Co(PHBy) ₂ .(H ₂ O) ₂]	3410	-	-	1620	1595	1350	1010
[Co(PHBz) ₂]	-	3270	1676	1605	1595	-	1005
[Ni(PHE) ₂ .(H ₂ O) ₂]	3420	-	-	1622	1595	1355	1012
[Ni(PHP) ₂ .(H ₂ O) ₂]	3410	-	-	1608	1590	1342	1005
[Ni(PHBy) ₂ .(H ₂ O) ₂]	3422	-	-	1625	1590	1350	1005
[Ni(PHBz) ₂]	-	3255	1660	1618	1588	-	1008

^acyclic; ^bazomethine stretching*Thermal analysis*

The DTA thermogram of [Co(PHE)₂.(H₂O)₂] in the temperature range 53-226 °C shows an endothermic peak at 110 °C accompanied by a weight loss of 4.35% as shown by the TG thermogram. This may be due to loss of two H₂O molecules. In the temperature range 226-310 °C shows an exothermic peak was observed at 292 °C showing a 4.75% loss in weight of the compound. This may be due to loss of the -OH group of the pyrazoline ring. On increasing the temperature further, the residue decomposes, resulting in a loss of 46.08% in the temperature range 310-545 °C with exothermic peak at 365 °C, due to the loss of pyrazoline ring moiety and a loss of 34.12% in the temperature range 545-787 °C with exothermic peak at 695 °C due to loss of pyridine ring moiety and methyl group (**Table 4**). No loss in weight was observed beyond 740 °C, indicating the formation of stable metal oxide.

The DTA thermogram of [Ni(PHBy)₂.(H₂O)₂] in the temperature range 57-193 °C shows an endothermic peak at 174 °C accompanied by a weight loss of 4.42%. This may be due to loss of two water molecules. In the temperature range 193-358 °C with endothermic peak at 321 °C showing a 34.94% loss in weight of the compound. This may be due to loss of the pyrazoline ring moiety. Two exothermic peaks at 387 and 605 °C shows loss in weight of 27.86 and 23.36% which may be accounted for by considering the loss of pyridine ring moiety and (CH₃-CH₂-CH₂-C=N-, -CH₃ and -OH groups), respectively (**Table 4**). On increasing the temperature further, no loss in weight occurred up to 800 °C which indicates the formation of a stable metal oxide.

Table 3. Electronic spectral data and ligandss field parameters of Co^{II} and Ni^{II} hydrazone complexes

Complexes	Band Obs./ Calc.	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	ν_3 (cm ⁻¹)	B (cm ⁻¹)	β_{35}^*	$B^0(\%)^{**}$	δv^{***}	10Dq	$\nu_2-\nu_1$	ν_2/ν_1	ν_3/ν_1	LFSE K.cal.mol ⁻¹
[Co(PHE) ₂ .(H ₂ O) ₂]	Obs.	9367	-	18761	-	-	-	-	-	-	-	2.00	-
	Calc.	8376	-	16786	700.33	0.72	28	1975	10470	-	-	2.00	25.16
[Co(PHE) ₂ .(H ₂ O) ₂]	Obs.	9327	-	18867	-	-	-	-	-	-	-	2.02	-
	Calc.	8352	-	16945	718.60	0.73	27	1922	10480	-	-	2.02	25.29
[Co(PHE) ₂ .(H ₂ O) ₂]	Obs.	9363	-	18796	-	-	-	-	-	-	-	2.00	-
	Calc.	8378	-	16825	707.48	0.72	28	1971	9759	-	-	2.00	23.42
[Co(PHE) ₂ .(H ₂ O) ₂]	Obs.	9381	-	18796	-	-	-	-	-	-	-	2.00	-
	Calc.	8400	-	16977	711.80	0.73	27	1819	10500	-	-	2.02	25.37
[Co(PHE) ₂ .(H ₂ O) ₂]	Obs.	9842	16778	-	-	-	-	-	9842	6936	1.70	-	26.62
	Calc.	-	17712	24332	835.00	0.81	19	934	-	-	-	-	-
[Co(PHE) ₂ .(H ₂ O) ₂]	Obs.	9852	16528	-	-	-	-	-	9852	6676	1.68	-	26.38
	Calc.	-	17730	23955	809.00	0.78	22	1202	-	-	-	-	-
[Co(PHE) ₂ .(H ₂ O) ₂]	Obs.	9861	16666	-	-	-	-	-	9861	6805	1.69	-	26.52
	Calc.	-	17694	23667	789.00	0.76	24	1062	-	-	-	-	-
[Co(PHE) ₂ .(H ₂ O) ₂]	Obs.	9832	16806	-	-	-	-	-	9832	6974	1.70	-	26.63
	Calc.	-	17694	23901	807.00	0.78	22	888	-	-	-	-	-

β_{35}^* = Ratio of the complex and free ion, $B^0(\%)^{**}$ = Percentage covalency and δv^{***} = Difference in observed and the calculated values

Table 4. Thermo analytical data of some Co^{II} and Ni^{II} complexes

Complex	% Wt. Loss		Temp. range (°C)	DTA peak	Possible leaving group(s).
	Observed	Calculated			
[Co(PHE) ₂ .(H ₂ O) ₂]	4.35	4.71	53-226	110 ^a	2 H ₂ O
	4.75	4.45	226-310	292 ^b	2 (-OH)
	46.08	47.71	310-545	365 ^b	2 (Pyrazoline ring + CH ₃ CN)
	34.12	35.38	545-787	695 ^b	2 (C ₅ H ₄ N-CON + -CH ₃)
[Co(PHBz) ₂]	36.90	39.25	160-387	358 ^b	2 (Pyrazoline ring + >C=N-)
	35.10	35.72	387-530	471 ^b	2 (C ₅ H ₄ N-CON + -CH ₃)
	19.33	18.09	530-636	567 ^a	2 (-C ₆ H ₅)
	4.42	4.39	57-193	174 ^a	2 H ₂ O
[Ni(PHBy) ₂ .(H ₂ O) ₂]	34.94	34.44	193-358	321 ^a	2 (Pyrazoline ring)
	27.86	25.89	358-493	387 ^b	2 (C ₅ H ₄ N-CON)
	23.36	24.67	493-673	605 ^b	2 (CH ₃ -CH ₂ -CH ₂ -C=N- + -OH + -CH ₃)
	35.35	35.97	61-383	343 ^a	2 (Pyrazoline ring + >C=N-)
[Ni(PHBz) ₂]	55.49	53.83	383-622	446 ^b	2 (C ₅ H ₄ NCON + -CH ₃)

a= endothermic, b= exothermic peak

On the basis of analytical and physical data, the probable structure of Co^{II} and Ni^{II} complexes as shown in **Figure. 1**.

Where M = Co^{II} or Ni^{II}R = -CH₃, -CH₂-CH₃, -CH₂-CH₂-CH₃

Figure 2 The probable structure of the complexes

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