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SYNTHESIS AND CHARACTERIZATION OF TRANSITION METAL COMPLEXES OF N'-[(2Z, 3E)-3-(HYDROXYIMINO) BUTAN-2-YLIDENE] BENZOHYDRAZIDE

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Keywords:

Bidentate, Pyridine,
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ABSTRACT: Synthesis and characterization of Co(II), Ni(II), Cu(II) and Pd(II) complexes of ligand *N'*-[(2*Z*,3*E*)-3-(hydroxyimino) butan-2-ylidene] benzohydrazide are reported. The ligand is monobasic and bidentate in nature. The molar conductivities reveal that all the metal complexes are non-electrolyte. The metal complexes have been characterized on the basis of spectral and magnetic studies. Co(II) ion forms brown complex $Co(BBH)_2$ which has low spin square planar geometry. The diamagnetic nature and the spectral features of the brown $Ni(BBH)_2$ complex suggests the square planar environment for the Ni(II) ion. $Ni(BBH)_2$ adds on two molecules of pyridine to form a high spin six coordinate adduct. The room temperature magnetic susceptibility measurements of the pyridine adduct of $Ni(BBH)_2$ indicates octahedral nature of the complex which is further supported by the absorption spectrum. The magnetic data in case of $Cu(BBH)_2$ indicates presence of one unpaired electron in Cu(II) ion. The EPR spectrum of $Cu(BBH)_2$ suggests the square planar geometry which is further supported by electronic absorption spectrum of the complex. Studies reveal square planar geometry for $Pd(BBH)_2$ complex.

INTRODUCTION: Oximes and hydrazones belong to an important class of compounds, are studied extensively [1 - 9] and have drawn significant attention due to their remarkable biological [2] and analytical [3] properties. The presence of several coordination sites in these compounds has also developed an increasing interest in the study of their complexing abilities towards various metal ions. Recently, the compounds containing both oxime and hydrazone functional groups are under remarkable study and are expected to show interesting functional and structural properties. These ligands are further expected to show an immense promise to act as polydentate ligands and show great structural variations in their metal complexes. These interesting structural variations have led us to investigate and report the structural features of the metal complexes of ligand *N'*-[(2*Z*,3*E*)- 3- (hydroxyimino) butan- 2- ylidene] benzohydrazide with the Co(II), Ni(II), Cu(II) and Pd(II) ions.

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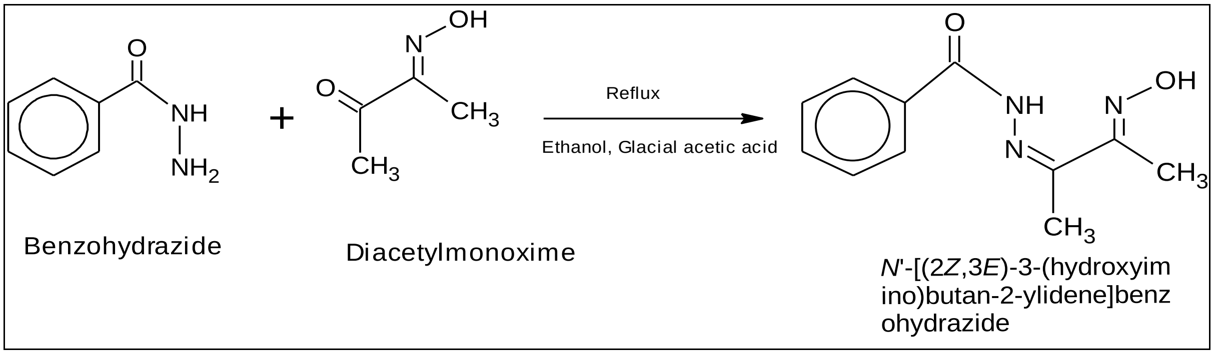
MATERIAL AND METHODS: All chemicals used were of AR grade. The organic solvents used were purified by standard methods prescribed by Vogel. Volumetric glass wares were calibrated before use. An Equiptronics Conductivity-meter (EQ-665) was used for conductivity measurements, which was calibrated using 0.1M KCl solution. The magnetic susceptibility measurement of the complexes were recorded on Guoy balance with $Hg[Co(SCN)_4]$ as the standard. Molar conductivity of the metal complexes was measured using 1×10^{-3} M solution in nitrobenzene. The electronic absorption spectra of complexes were recorded on Equiptronics EQ-824 spectrophotometer with 1 cm quartz cell in chloroform as solvent. FTIR spectrum of ligand and its complexes were recorded in the range of 4000 - 400 cm^{-1} in KBr disk on Perkin Elmer instrument. PMR spectra were recorded using Bruker 300 MHz spectrometer in deuteriated DMSO solution.

Synthesis of Ligand (HBBH):



Procedure: The ligand N'-[(2Z,3E)-3-(hydroxyimino) butan-2-ylidene] benzohydrazide (HBBH) was synthesized by treating Biacetyl-monoxime (7.37 g, 0.07 mol) with Benzoic Hydrazide (10.00 g, 0.07 mol) in 50 cm^3 ethanol, followed by adding 4 - 5 drops of glacial acetic acid. The resulting solution was refluxed for 8 hours. Completion of reaction was confirmed by TLC. The white crystalline plates of ligand HBBH obtained were filtered, washed with water and dried in oven at 110 °C. It was recrystallized from ethanol and analyzed for C, H, and N.

Co(II), Ni(II) and Cu(II) complexes were synthesized by mixing hot ethanolic solution of ligand (0.004 mol) with aqueous solution of metal chloride (0.002 mol) followed by dropwise addition of dilute NaOH solution till complete complex formation. The complexes on precipitation were filtered through whatman filter paper no. 1, washed with water and dried in oven at 110 °C. Ni(II) complex of HBBH on dissolution in minimum quantity of hot pyridine and gradual evaporation gave the adduct $Ni(BBH)_2Py_2$. Pd(II) complex was precipitated in acidic medium. The yields obtained were 62 - 86%. The melting points of ligand and all the complexes were determined by open capillary method. The metal content of the complexes were determined by the reported methods [10]. The solubility of the complexes was determined in various polar and non-polar solvents.

RESULTS AND DISCUSSION:

Characterization of Ligand: Ligand was characterized using analytical data obtained from FTIR, PMR, UV-VISIBLE spectroscopy, elemental analysis *etc*. The molecular weight of ligand is 219 $gmol^{-1}$ determined by Rast method. The melting point of the ligand is 191 °C. It is white crystalline solid, highly soluble in chloroform, acetone, DMF, DMSO, Nitrobenzene, partially soluble in dilute alkali, methanol and ethanol *etc*. Several resonating structures of ligand are possible, however, computational studies reveal that the structure shown in **Fig. 1** has least energy *i.e.* most stable.

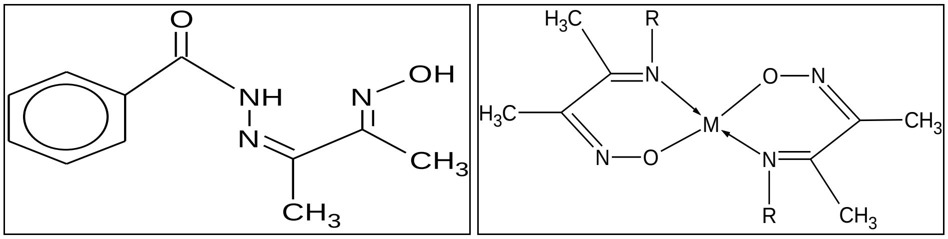

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FIG. 1: PROPOSED SQUARE PLANAR STRUCTURE FOR Co(II), Ni(II), Cu(II), Pd(II) METAL COMPLEXES (M = Co, Ni, Cu, Pd)

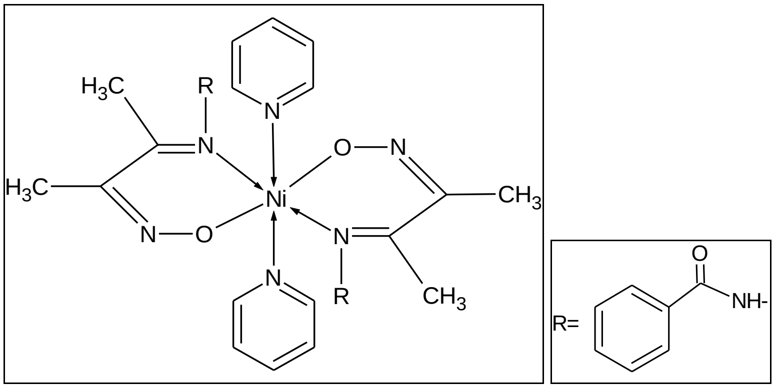

FIG. 2: PROPOSED STRUCTURE FOR SIX COORDINATE Ni(II) PYRIDINE ADDUCT

TABLE 1: PHYSICAL AND ANALYTICAL DATA OF LIGAND AND METAL COMPLEXES

Compound (Colour)	M.W.	Yield (%)	Λ_mScm^{2}mol^{-1}	Elemental analysis in % found (calculated)					μ_{eff} (B.M.)
				C	H	O	N	Metal	
HBBH	219	76.20	---	60.19	5.89	14.53	19.11	---	---
(White)				(60.27)	(5.94)	(14.61)	(19.18)		
Co(BBH)$_2$	494.93	79.24	0.39	53.21	4.77	12.86	16.87	11.23	2.12
(Brown)				(53.34)	(4.85)	(12.93)	(16.97)	(11.90)	
Ni(BBH)$_2$	494.71	78.22	0.76	53.29	4.79	12.85	16.86	11.11	Dimagnetic
(Brown)				(53.36)	(4.86)	(12.94)	(16.98)	(11.87)	
Ni(BBH)$_2$Py$_2$	652.71	77.11	0.78	58.74	5.19	9.73	17.07	8.34	3.12
(Green)				(58.83)	(5.25)	(9.80)	(17.15)	(8.98)	
Cu(BBH)$_2$	499.55	84.11	0.85	52.77	4.44	12.72	16.73	12.19	1.81
(Green)				(52.85)	(4.80)	(12.81)	(16.82)	(12.72)	
Pd(BBH)$_2$	542.42	82.66	0.81	48.61	4.35	11.70	15.41	19.15	Diamagnetic
(Yellow)				(48.67)	(4.42)	(11.80)	(15.49)	(19.61)	

The metal complexes are insoluble in water and are soluble in methanol, ethanol, chloroform, carbon tetrachloride, acetone, DMF, DMSO nitrobenzene. The elemental analysis shows the stoichiometry 1: 2 (metal: ligand) for all the metal complexes. All complexes exhibit low molar conductivities (0.39–0.85 Scm^{2}mol^{-1}) which indicate their non-electrolyte nature [11]. The analytical data and physical properties of ligand and its metal complexes are given in **Table 1**.

Electronic Spectrum and Magnetic Susceptibility: The electronic absorption spectrum of the methanolic solution of the ligand HBBH in the ultra-violet region shows two high intensity bands at 43.47 kK (ε = 22,619 dm^{3}mol^{-1}cm^{-1}) and 32.25 kK (ε = 35,952 dm^{3}mol^{-1}cm^{-1}). This may be attributed to intra ligand $(\pi \rightarrow \pi^*)$ (allowed) transitions of azomethine environment in the molecule. In isonitrosopropiophenone and many other isonitrosoketones [1 - 2, 5 - 7], a band at similar positions and intensity, is reported to be the $(\pi \rightarrow \pi^*)$ transitions in the ligand [6]. The ultra-violet spectrum of the ligand HBBH in dilute alkali solution (0.1N NaOH) solution reveals that the band observed at 43.47 kK (ε = 22619 dm^{3}mol^{-1}cm^{-1}) and 32.25 kK (ε = 35,952 dm^{3}mol^{-1}cm^{-1}) in the methanolic solution spectrum are somewhat suppressed and shifted to the higher wavelength *i.e.* 37.03 kK (ε = 11,190 dm^{3}mol^{-1}cm^{-1}) and 29.41 kK (ε = 12,380 dm^{3}mol^{-1}cm^{-1}). The bathochromic shift in the band and the lowering of intensity suggests formation of anion in the alkaline solution due to the deprotonation of the oximino group [5, 7].

The electronic spectra of all the metal complexes were recorded in Chloroform as solvent. The electronic spectrum of the Co(II) complex exhibits two bands at 17.85 kK and at 20.60 kK. The square planar Co(II) complexes are normally expected to exhibit transitions in these regions [12 - 15]. The magnetic moment value 2.12 BM also corroborates the expected low-spin square planar geometry for Co(II) ions [15].

The electronic spectrum of Ni(II) complex exhibits two bands at 23.81 kK and 27.78 kK. These bands are typical for square planar d^8 complexes [16]. The square planar geometry for the Ni(II) complex is also corroborated by the diamagnetic nature of the complex. Ni(BBH)$_2$Py$_2$ reveals a peak at 10.20 kK and a hump near 16.47 kK which are attributed to spin allowed transitions $3_{T2g} \leftarrow 3_{A2g}$ (v_1), $3_{T1g} \leftarrow 3_{A2g}$ (v_2) respectively. The value v_2/v_1 = 1.62 lies in the usualrange (1.60 - 1.82), reported for the majority of octahedral Ni(II) compounds [17]. From the observed positions of these two transitions, the frequency of the third transition 3_{T1g} (P) $\leftarrow$ 3_{A2g} (v_3) has been calculated by using the equation [18],

$$v_3 = (225B^2 + 100Dq^2 + 180DqB)^{1/2}$$

This band is expected to occur at 25.51 kK. However, it is not observed in the spectrum of the complex probably due to its masking by the tail end of the high intensity charge transfer band around 29.4 kK. The spectral parameters for $[Ni(BBH)_2]$ Py_2 are Dq = 1.02 kKB' = 0.869, B'/B=, β=0.84 and β% = 16%. Reduction of Racah parameter from 1.03 kK (free ion value) to 0.869 kK and the β% value 19% indicate the covalent nature of the compound. The $Ni(PPBH)_2Py_2$ shows magnetic moment value of 3.12 B.M. which lies in the range of 2.8 – 3.5 B.M. and is consistent with the octahedral geometry of the complex [19]. For square planar Cu(II) complexes, the expected transitions are $2_{A1g} \leftarrow 2_{B1g}$ and $2_{Eg} \leftarrow 2_{B1g}$ with the respective absorption bands [17]. The square planar Cu(II) complexes are expected to exhibit a broad absorption band between 16.66 kK and 14.28 kK due to Jahn-Teller distortion. The electronic spectrum of $[Cu(BBH)_2]$ exhibits a broad band at 15.38 kK which indicates square planar geometry. The magnetic moment of Cu(II) complex is 1.81 B.M. A characteristic feature of palladium complexes is the absence of any appreciable absorption beyond 14.00 kK and it is typical for square planar d^8complexes. Such complexes are expected to show at least three closely spaced *d-d* transition weak bands [16]. However, due to the high intensity charge transfer transitions, these bands are masked. The $Pd(BBH)_2$ shows two transitions at 28.57 kK and 22.72 kK and are attributed to charge transfer transitions.

IR Spectral Studies: The infrared spectral data of the ligand (HBBH) and its metal complexes are presented in **Table 2**. On the basis of the reported FTIR spectra of several isonitrosoketones and aromatic hydrazides an attempt has been made to assign some of the important bands. The spectrum shows a broad band at 3220 cm^{-1} and 3176 cm^{-1} due the presence of oximino –OH group and NH group in the ligand respectively. Assignment of these bands was based on comparisons with other Isonitrosoketones and aromatic hydrazides [1, 9].

TABLE 2: IR SPECTRAL BANDS OF THE LIGAND (HBBH) AND ITS METAL COMPLEXES (cm^{-1})

Tentative assignments	Ligand	$Co(BBH)_2$	$Ni(BBH)_2$	$Ni(BBH)_2Py_2$	$Cu(BBH)_2$	$Pd(BBH)_2$
-OH (oximino)	3220	---	---		---	---
-NH	3176	3129	3129	3130	3130	3131
>C=N(oximino)	1499	1464	1466	1467	1466	1468
N=CH (azomethine)	1587	1534	1534	1535	1536	1538
C=O	1662	1661	1662	1660	1661	1661
N-O	1020	1009	1009	1007	1008	1005
M-N	---	528	541	546	549	555
M-O	---	492	494	496	497	499
C=CH (Aromatic)	3048	3047	3046	3047	3048	3048

In isonitrosopropiophenone (HINPP) band at 3244 cm^{-1} is attributed to oximino (-OH) group. The band observed at 3048 cm^{-1} in the FTIR spectrum of the ligand is due to the aromatic C-H stretching vibrations. The band at 1662 cm^{-1} may be attributed to carbonyl (C=O) group. The band at 1562 cm^{-1} and 1499 cm^{-1} may be ascribed to >C=N- stretching vibrations of the azomethine (>C=N) and oximino (>C=N) groups respectively. In isonitrosopropiophenone a peak at 1000 cm^{-1} is attributed to N-O. The band in the region 1020 cm^{-1} may be assigned to the N-O vibrations [20].

The broad peak observed at 3220 cm^{-1} in the IR spectrum of the ligand assigned to oximino (OH) group is found to have disappeared in all the complexes which indicates the deprotonation of oximino group. In all the metal complexes the carbonyl (>C=O) group is nearly in the same position which indicates its non-participation in coordination. The coordination of azomethine nitrogen is confirmed by the shift in the position of the band at 1587 cm^{-1} in the ligand to lower frequency in all complexes [21]. The appearance of a new band in the region 460 - 490 cm^{-1} and 520 -

560 cm^{-1} in all complexes is attributed to M-O bond and M-N bonds respectively. The IR spectra of all the complexes reveal that ligand HBBH behaves as a mono-negative bidentate ligand coordinating through (C=N) imine and the deprotonated oximino oxygen. This mode of chelation is expected due to the disappearance of oximino – OH group, the shift of imine (C=N) group to lower frequency and with the (C=O) stretch nearly in the same position indicates its non-participation in coordination.

PMR: The PMR spectrum of ligand HBBH in deuteriated DMSO shows two singlets at δ10.72 ppm and δ11.62 ppm which disappeared on adding D_2O. This may be attributed to NH and NOH protons. The down field shift of these resonances may be related to amide-imide tautomeric form (NH-C=O)⟷(N=C-OH). The peaks at δ7.4 – δ7.8 ppm and 2.0 ppm may be assigned to phenyl ring protons and methyl protons respectively.The comparison of the spectra of $Ni(BBH)_2$ and $Pd(BBH)_2$ with that of ligand spectrum reveals that the peak for oximino proton of the ligand (δ11.62 ppm) disappeared in the PMR spectrum of both $Ni(BBH)_2$ and $Pd(BBH)_2$ complexes which corroborates the deprotonation of oximino proton and involvement of oximino group in coordination with metal ions.

EPR Spectrum Studies: The room temperature EPR spectrum of green $Cu(BBH)_2$ gave poor resolution. The EPR spectrum at LNT gave better resolution to allow the calculations of various EPR parameters. EPR spectrum of $Cu(BBH)_2$ complex was recorded at LNT in chloroform solution, on the *x*-band at 9.1 GHz, under the magnetic field strength 3000 G. The analysis of spectra gave $g_{\|}$ = 2.1928 and $g_{\perp}$ = 2.0406. The trend $g_{\|} > g_{\perp} > 2.0023$, indicates that the unpaired electron is localized in dx^2-y^2 orbital which is the characteristics of square planar geometry. It is reported that compounds having $g_{\|} > 2.3$ are ionic in nature while those with $g_{\|} < 2.3$ are covalent in character [22]. For the complex under study $g_{\|} < 2.3$ indicates the covalent character of the metal-ligand bond. The G value (G = 4.74) is greater than 4 which indicates that there is negligible Cu-Cu interaction [23, 24] in the Cu(II) complex.

CONCLUSION: The present study shows that the synthesized ligand (HBBH) coordinates to central metal ion through azomethine nitrogen and oximino oxygen. The synthesized ligand and its metal complexes have been confirmed by the analytical data, electronic spectra, IR, PMR, ESR spectral data, magnetic susceptibility. From the analytical data and spectral studies, we propose square geometry for the Co(II), Ni(II), Cu(II) and Pd(II) complexes and octahedral geometry for $Ni(BBH)_2Py_2$ complex.

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CONFLICT OF INTEREST: Nil

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