

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

Mr S.Khaja Shamshuddin, Mrs. Mala Sridevi, Mrs. Jamalpuri Jhansi
Assistant professor^{1,2,3}

Department of Pharmaceutics

Global College of Pharmacy, Hyderabad. Chilkur (V), Moinabad (M), Telangana- 501504.

ABSTRACT: The ligand N'-[(2Z,3E)-3-(hydroxyimino)butan-2-ylidene]benzohydrazide complexes with Co(II), Ni(II), Cu(II), and Pd(II) have been synthesized and characterized. It is bidentate in nature and the ligand is monobasic. It is revealed by the molar conductivities that all the metal complexes are ar-sodium chloride. Based on spectroscopic and magnetic research, the metal complexes have been described. The low-spin square planar geometry brown complex is formed by the Co(II) ion. It is suggested that the Ni(II) ion occupies a square planar environment by the spectrum characteristics and diamagnetic nature of the brown Ni(BBH)₂ complex. Two molecules of pyridine are added to Ni(BBH)₂ to generate a high spin-six coordinated adduct. The absorption spectra and room-temperature magnetic susceptibility studies of the pyridine adduct of Ni(BBH)₂ both point to an octahedral complex structure. In the instance of Cu(BBH)₂, the magnetic data suggests that the Cu(II) ion has one unpaired electron. The complex's electronic absorption spectra corroborate the square planar shape, which is corroborated by the EPR spectrum of Cu(BBH)₂. New research shows that the Pd(BBH)₂ complex has a square planar shape.

Keywords: Bidentate, Pyridine, Adduct, Metal complexes

INTRODUCTION:

Due to their outstanding biological and analytical characteristics, oximes and hydrazones—an important family of compounds—have attracted considerable interest and have been the subject of intensive research (1–9). Because these compounds have several coordination sites, researchers are very interested in studying how they bind with different metal ions. In recent times, there has been much research into molecules that include both oxime and hydrazone functional groups. It is anticipated that these compounds would exhibit intriguing structural and functional characteristics.

It is anticipated that these ligands would exhibit remarkable structural diversity in their metal complexes and have considerable potential as polydentate ligands. Because of these intriguing structural differences, we searched for and documented the properties of metal complexes

involving the ligand N'-[(2Z,3E)-3-(hydroxyimino)butan-2-ylidene]benzohydrazide and the ions Cu(II), Pd(II), Ni(II), and Co(II).

The chemicals utilized were all of the AR grade. Vogel recommended specific procedures for purifying the organic solvents. All glassware with a volume measurement was calibrated before to use. The conductivity measurements were taken using a calibrated Equiptronics Conductivity-meter (EQ-665), which was immersed in a 0.1M KCl solution. Using Hg[Co(SCN)₄] as a reference, the complexes' magnetic susceptibility measurements were recorded on a Guoy balance. Molecular conductivity

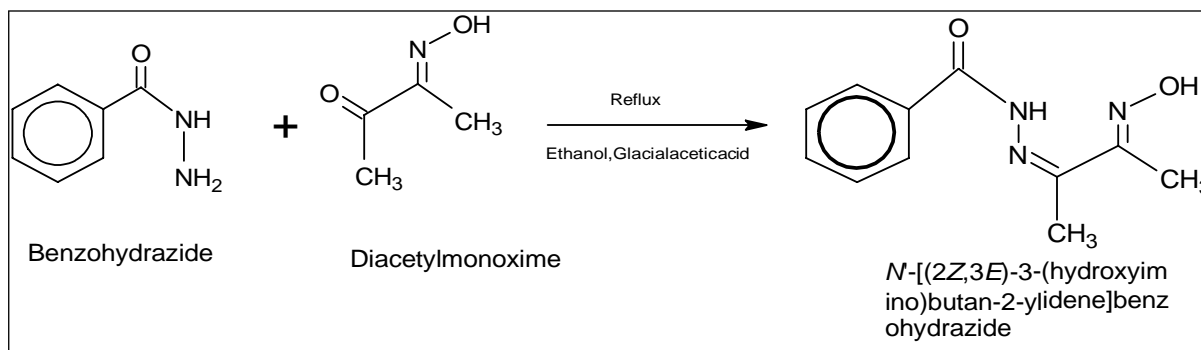
utilizing a 1×10⁻³ M solution in nitrobenzene, the

concentration of the metal complexes was determined. Using a 1 cm quartz cell in chloroform solvent, the electronic absorption

spectra of the complexes were recorded using an Equiptronics EQ-824 spectrophotometer. FTIR absorption spectra

HBBH Ligand Synthesis:

of the ligand and its complexes were detected in the KBr disk using the Perkin Elmer instrument between the 4000 - 400 cm⁻¹ range. The PMR spectra were captured in a deuterated DMSO solution using a Bruker 300 MHz spectrometer.



Procedure: The ligand N'-[(2Z,3E)-3-(hydroxyimino)butan-2-ylidene]benzohydrazide (HBBH) was synthesized by treating Biacetylmonoxime (7.37 g, 0.07 mol) with Benzoic Hydrazide (10.00 g, 0.07 mol) in 50 cm³ 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 methanol 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 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)₂Py₂. 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 methods¹⁰. 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.

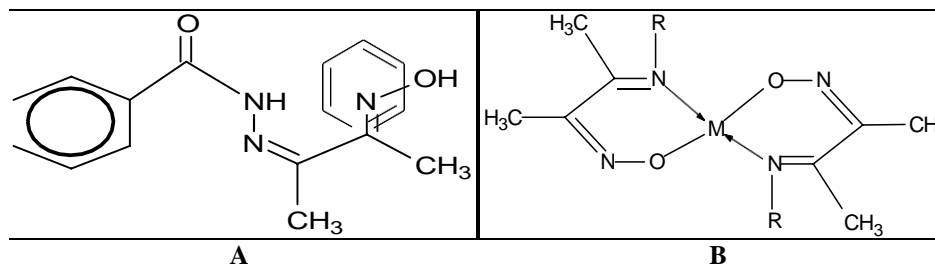


FIG.1:PROPOSEDSQUAREPLANARSTRUCTUREFORCo(II),Ni(II),Cu(II),Pd(II)METALCOMPLEXES(M=Co,Ni,Cu,Pd)

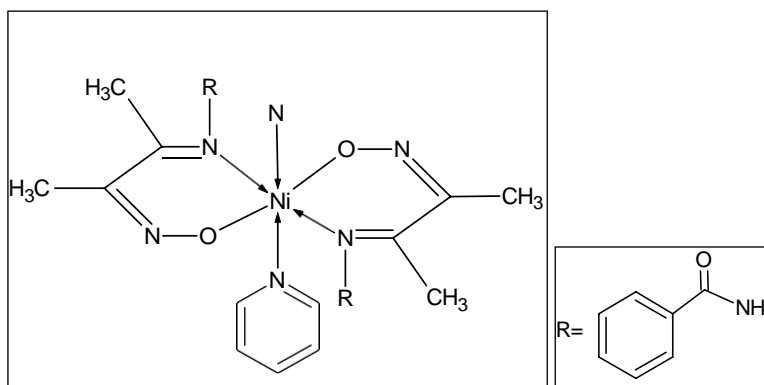


FIG.2:PROPOSEDSTRUCTUREFORSIXCOORDINATENi(II)PYRIDINEADDUCT

PHYSICAL AND ANALYTICAL DATA OF LIGAND AND METAL COMPLEXES

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

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 $\text{Scm}^2 \text{mol}^{-1}$) which indicate their non- electrolyte nature¹¹. 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 ($\epsilon = 22,619 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and

32.25 kK ($\epsilon = 35,952 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). This may be attributed to intraligand ($\pi \rightarrow \pi^*$) (allowed) transitions of azomethine environment in the molecule. In isonitrosopropiophenone and many other isonitroso ketones^{1-2,5-7}, a band at similar

positions and intensity, is reported to be the ($\pi \rightarrow \pi^*$) transitions in the ligand⁶. 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 ($\epsilon = 22,619 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 32.25 kK ($\epsilon = 35,952 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in the methanolic solution spectrum are somewhat suppressed and shifted to the higher wavelength *i.e.* 37.03 kK ($\epsilon = 11,190 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 29.41 kK ($\epsilon = 12,380 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). 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 regions¹²⁻¹⁵. The magnetic moment value 2.12 BM also corroborates the expected low-spin square planar geometry for Co(II) ions¹⁵.

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 complexes¹⁶. The square planar geometry for the Ni(II) complex is also corroborated by the diamagnetic nature of the complex. Ni(BBH)₂Py₂ reveals a peak at 10.20 kK and a hump near 16.47 kK which are attributed to spin allowed transitions $3T_{2g} \leftarrow 3A_{2g}(v_1), 3T_{1g} \leftarrow 3A_{2g}(v_2)$ respectively. The value $v_2/v_1 = 1.62$ lies in the usual range (1.60 - 1.82), reported for the majority of octahedral Ni(II) compounds¹⁷. From the observed positions of these two transitions, the frequency of the third transition $3T_{1g}(P) \leftarrow 3A_{2g}(v_3)$ has been calculated by using the equation¹⁸,

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

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]Py₂ are $Dq = 1.02 \text{ kK}$, $B' = 0.869$, $B'/B = \beta = 0.84$ and $\beta\% = 16\%$. Reduction of Racah parameter from 1.03 kK (free ion value) to 0.869 kK and the

$\beta\%$ value 19% indicate the covalent nature of the compound. The Ni(PPBH)₂Py₂ 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 complex¹⁹. For square planar Cu(II) complexes, the expected transitions $2A_{1g} \leftarrow 2B_{1g}$ and $2E_g \leftarrow 2B_{1g}$ with the respective absorption bands¹⁷. 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^8 complexes. Such complexes are expected to show at least three closely spaced $d-d$ transition weak bands¹⁶. 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 to 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) ₂ Py 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 $>\text{C}=\text{N}$ -stretching vibrations of the azomethine ($>\text{C}=\text{N}$) and oximino ($>\text{C}=\text{N}$) 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 vibrations²⁰. 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 ($>\text{C}=\text{O}$) 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 complexes²¹. The appearance of a new band in the region $460\text{-}490\text{ cm}^{-1}$ 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 $\delta 10.72$ ppm and $\delta 11.62$ 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 $(\text{NH}-\text{C}=\text{O}) \leftrightarrow (\text{N}=\text{C}-\text{OH})$. The peaks at $\delta 7.4\text{-}\delta 7.8$ ppm and 2.0 ppm may be assigned to phenyl ring protons and methyl protons respectively. The comparison of the spectra of $\text{Ni}(\text{BBH})_2$ and $\text{Pd}(\text{BBH})_2$ with that of ligand spectrum reveals that the peak for oximino proton of the ligand ($\delta 11.62$ ppm) disappeared in

the PMR spectrum of both $\text{Ni}(\text{BBH})_2$ and $\text{Pd}(\text{BBH})_2$ 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 $\text{Cu}(\text{BBH})_2$ gave poor resolution. The EPR spectrum at LNT gave better resolution to allow the calculations of various EPR parameters. EPR spectrum of $\text{Cu}(\text{BBH})_2$ 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 $g_{\parallel} = 2.1928$ and $g_{\perp} = 2.0406$. The trend $g_{\parallel} > g_{\perp} > 2.0023$, indicates that the unpaired electron is localized in 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 $\text{Ni}(\text{BBH})_2\text{Py}_2$ complex.

CONCLUSION: The data presented here demonstrate that the synthetic ligand (HBBH) binds to the central

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