



Synthesis and Characterization of Co(II), Ni(II), Cu(II) and Pd(II) Complexes of *N*-[(1*Z*,2*E*)-2-(hydroxyimino)-1-phenylpropylidene]benzohydrazide

N. M. Bahuguni

Konkan Gyanpeeth Karjat College of Arts, Science and Commerce, Karjat, Dist. Raigad, Maharashtra 410201, India.

Abstract : Synthesis and characterization of ligand *N*'-[(1*Z*,2*E*)-2-(hydroxyimino)-1-phenylpropylidene]benzohydrazide and its metal complexes are reported. The ligand is monobasic bidentate/tridentate in nature depending upon the coordinating metal ion. The molar conductivities show that all the metal complexes are non-electrolyte. The bonding and probable structures of the metal complexes are discussed on the basis of spectral and magnetic data. Studies reveal that ligand behaves as tridentate in Ni(II) complex whereas in Co(II), Cu(II) and Pd(II) complexes it acts as bidentate ligand. Ni(II) complex have octahedral geometry while Co(II), Cu(II) and Pd(II) complexes have square planar structure.

Keywords : azomthine, oximino, bidentate, tridentate, metal complexes.

Introduction

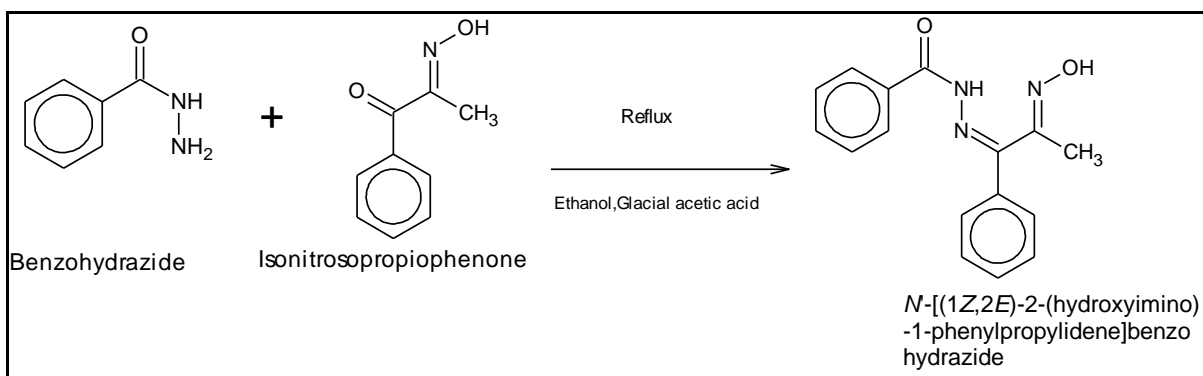
Hydrazones and oximes form a special class of compounds and act good polydentate chelating agents that can form a variety of complexes with various transition metals. Although transition metal complexes of oximes and hydrazones have been studied extensively¹⁻⁷, the compounds containing both these functional groups have developed an increasing interest in the study of the complexing abilities towards various metal ions due to the presence of several potential coordinating sites. Thus the study of ligands containing both hydrazone and oxime moieties, as ligands containing mixed functional groups are expected to show interesting structural and functional properties.

2. Experimental:

2.1. 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 of the complexes. It was calibrated using 0.1M KCl solution. The magnetic susceptibility measurement of the complexes were done on Guoy balance using Hg[Co(SCN)₄] as the standard. Molar conductivity of the ligand and its complexes were measured using 1 x 10⁻³ M solution in nitrobenzene on Equiptronics Conductivity-meter (EQ-665). The electronic absorption spectra of complexes were recorded using chloroform as solvent on Equiptronics EQ-824 spectrophotometer with 1 cm quartz cell. FTIR spectrum of ligand and its complexes were recorded in the range of 4000-400cm⁻¹ in KBr disk on Perkin Elmer instrument. PMR spectra were recorded in deuteriated DMSO solution using Bruker 300MHz spectrometer.

2.2. Synthesis of ligand (HPPBH):



2.3. Procedure

The ligand *N*'-[(1*Z*,2*E*)-2-(hydroxyimino)-1-phenylpropylidene]benzohydrazide (HPPBH) was synthesized by treating isonitrosopropiophenone (11.89g, 0.07mol) with Benzoic Hydrazide (10.00g, 0.07mol) in 50cm³ ethanol, followed by adding 4-5 drops of glacial acetic acid. The resulting solution was refluxed for 10 hours. Completion of reaction was confirmed by TLC. The off white crystalline plates of ligand HPPBH obtained were filtered, washed thoroughly with water and dried in oven at 110^oC. It was recrystallized from ethanol and analyzed for C, H, and N.

All metal complexes except Pd(II) were synthesized by mixing hot ethanolic solution of ligand (0.004 mol) with aqueous solution of metal chloride (0.002 mol) and dilute NaOH solution was added dropwise till complex formation. The precipitated complexes were filtered through whatman filter paper no. 1 and washed with water and dried in an oven at 110^oC. Pd(II) complex was precipitated in acidic medium. The yields obtained were 65-85%. The melting points of ligand and all the complexes were determined by open capillary method. The metal content of the metal complexes were determined by the reported methods⁸. The solubility of the complexes were examined in different polar and non-polar solvents.

3. Results and discussion:

3.1. Characterization of ligand:

Characterization of the ligand was done by using analytical data obtained from FTIR, PMR, UV-VISIBLE spectroscopy, GC-MS, elemental analysis etc. The molecular weight of ligand is 281 gmol⁻¹ determined by Rast method. It is off white crystalline solid, highly soluble in chloroform, acetone, DMF, DMSO, Nitrobenzene, partially soluble in dilute alkali, methanol and ethanol etc. Several structures of ligand are possible but computational studies reveals that the structure shown in Fig.1 has least energy i.e. most stable.

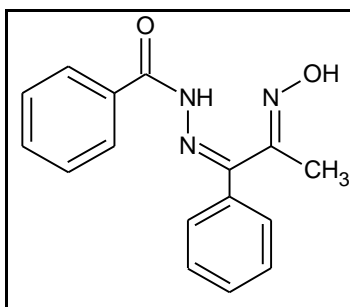


Fig.1.

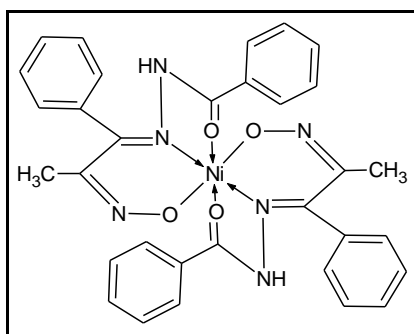


Fig.2. Proposed structure of octahedral Ni(II) complex

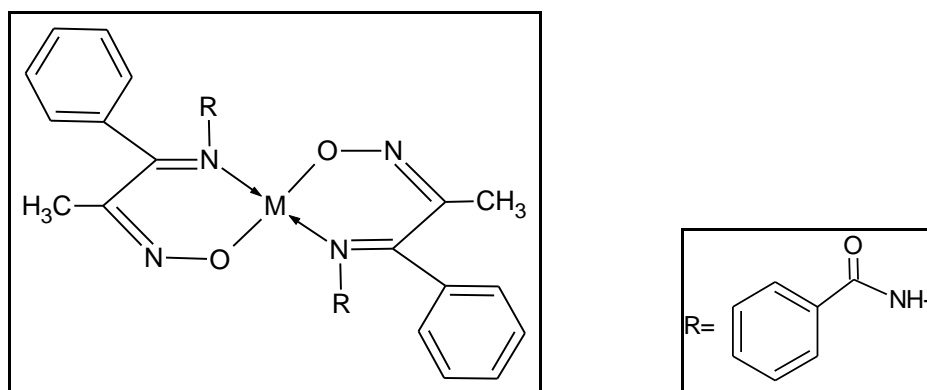


Fig.3. Proposed structure of Co(II), Cu(II), Pd(II) metal complexes (Square Planar, M=Co, Cu, Pd).

Table 1: Physical and analytical data of ligand and metal complexes

Compound (Colour)	M.W.	Elemental Analysis					Magnetic Moments B.M.	Conductance $\text{Scm}^2\text{mol}^{-1}$
		% M Found (Calculated)	% C Found (Calculated)	% H Found (Calculated)	% O Found (Calculated)	% N Found (Calculated)		
HPPBH (offwhite)	281	----	68.26 (68.33)	5.29 (5.34)	11.33 (11.39)	14.87 (14.95)	----	----
Co(PPBH) ₂ (Orange brown)	618.93	9.17 (9.41)	61.96 (62.04)	4.47 (4.52)	10.26 (10.34)	13.50 (13.57)	2.11	0.18
Ni(PPBH) ₂ (Green)	618.71	9.39 (9.48)	61.99 (62.06)	4.47 (4.53)	10.29 (10.35)	13.51 (13.58)	3.03	0.23
Cu(PPBH) ₂ (Dark green)	623.55	9.71 (10.17)	61.50 (61.58)	4.44 (4.49)	10.21 (10.26)	13.42 (13.47)	1.79	0.68
Pd(PPBH) ₂ (Orange)	666.42	15.35 (16.01)	57.56 (57.62)	4.14 (4.20)	9.56 (9.60)	12.55 (12.60)	Dimagnetic	0.36

The metal complexes are insoluble in water but are soluble in methanol, ethanol, chloroform, carbon tetrachloride, acetone, DMF, DMSO. The elemental analysis shows 1:2 (metal:ligand) stoichiometry for all the metal complexes. The low molar conductivities of all the metal complexes ($0.18\text{--}0.36 \text{ Scm}^2\text{mol}^{-1}$) indicate their nonelectrolyte nature⁹. The physical properties and analytical data of ligand and metal complexes are given in table 1.

3.2. Electronic Spectrum and Magnetic Susceptibility:

The electronic absorption spectrum of the methanolic solution of the ligand HPPBH in the ultra-violet region shows two high intensity bands at 45.45 kK ($\epsilon=23,745 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$) and 35.71 kK ($\epsilon=28,115 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$). This may be due to intra ligand ($\pi \rightarrow \pi^*$) (allowed) transitions of azomethine environment in the molecule. In many isonitrosoketones¹⁻⁵ including isonitrosopropiophenone, a band occurring at similar positions and intensity, is reported to be the ($\pi \rightarrow \pi^*$) transitions in the ligand⁴. The ultra-violet spectrum of the ligand HPPBH in dilute alkali solution (0.1N NaOH) solution reveals that the band observed at 45.45 kK ($\epsilon=23,745 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$) and 35.71 kK ($\epsilon=28,115 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$) in the methanol solution spectrum are somewhat suppressed and shifted to the higher wavelength i.e. 41.66 kK ($\epsilon=25,666 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$) and 33.33 kK ($\epsilon=29,466 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$). 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 group¹⁻⁵.

The electronic spectral data of metal (II) complexes were recorded in Chloroform. The electronic spectrum of the Co(II) complex displayed weak intensity band at 15.38kK and a hump at 19.60kK. The square planar Co(II) chelates often exhibit transitions that are normally expected in these regions¹⁰⁻¹⁵. This is also corroborated by the magnetic moment value 2.11 BM, expected for the low-spin square planar geometry around Co(II) ions¹⁰. [Ni(PPBH)₂] reveals a peak at 10.42 kK and a broad hump near 16.68kK which are attributed to spin allowed transitions $3T_{2g} \leftarrow 3A_{2g} (v_1)$, $3T_{1g} \leftarrow 3A_{2g} (v_2)$ respectively. The value $v_2/v_1 = 1.79$ lies in the usual range (1.60–1.82), reported for the majority of octahedral Ni(II) compounds¹⁶. 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 equation¹⁷,

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

This band is expected to occur at 23.04kK. However, it is not observed in the spectrum of the complex probably because it is masked by the tail end of the high intensity charge transfer band around 29.4 kK. The spectral parameters for [Ni(PPBH)₂] are $Dq = 1.042 \text{ kK}$, $B'/B = 0.749$, $B'/B = \beta = 0.73$ and $\beta\% = 19\%$. Reduction of Racah parameter from 1.03 kK (free ion value) to 0.749 kK and the $\beta\%$ value 19 % indicate the covalent nature of the compound. The [Ni(PPBH)₂] shows magnetic moment value of 3.03 B.M. which lies in the range of 2.8–3.5 B.M. and is consistent with the octahedral geometry of the complex. For square planar Cu(II) complexes, the expected transitions are $2A_{1g} \leftarrow 2B_{1g}$ and $2E_g \leftarrow 2B_{1g}$ with the respective absorption bands¹⁶. The square planar Cu(II) complexes due to Jahn–Teller distortion give a broad absorption band between 16.66 kK and 14.28 kK. The electronic spectrum of [Cu(PPBH)₂] exhibits a broad band centered at 15.62 kK indicating square planar geometry. The magnetic moment of Cu(II) complex is 1.79 B.M. The absence of any appreciable absorption beyond 14000 cm^{-1} is a characteristic feature of palladium complexes. This is typical for square planar d^8 complexes. Gray and Ballhausen¹⁸ have reported that such complexes are expected to show at least three closely spaced $d-d$ transition weak bands. However these bands are masked due to the high intensity charge transfer transitions. The Pd(PPBH)₂ shows high intensity transitions at 21.42kK and 17.85kK and are suggested to be charge transfer transitions.

3.3. IR Spectral Studies:

The infrared spectral data with the tentative assignments of the ligand (HPPBH) and its Co(II), Ni(II), Cu(II), and Pd(II) complexes are presented in Table 2. An attempt to assign some of the important bands has been made on the basis of the reported FTIR spectrum of several isonitrosoketones and aromatic hydrazides. The spectrum shows a broad band at 3387 cm^{-1} and 3287 cm^{-1} due to the presence of oximino–OH group and NH group respectively in the ligand. Assignment of these bands was based on comparisons with other Isonitrosoketones and aromatic hydrazides¹⁻⁷. The IR spectrum of isonitrosopropiophenone (HINPP) shows band due to oximino (-OH) group at 3244 cm^{-1} . The band observed at 3055 cm^{-1} in the FTIR spectrum of the ligand is ascribed to the aromatic C-H stretching vibrations. The band at 1668 cm^{-1} may be assigned to carbonyl (C=O) group. The band at 1562 cm^{-1} and 1501 cm^{-1} may be attributed 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 1018 cm^{-1} may be assigned to the N-O vibrations¹⁹.

The broad peak observed at 3387 cm^{-1} in the IR spectrum of the ligand assigned to oximino (OH) group is found to have disappeared in all the complexes indicating deprotonation of oximino group. In Ni(PPBH)₂ the carbonyl ($>C=O$) group is shifted to lower frequency suggesting that the carbonyl oxygen is also a potential site for bonding. In Co(PPBH)₂, Cu(PPBH)₂ and Pd(PPBH)₂ the ($>C=O$) stretch is nearly in the same position which indicates its non-participation in coordination. The coordination of azomethine nitrogen is confirmed by the presence of band at 1610 cm^{-1} in the ligand which is shifted to lower frequency in all complexes²⁰. This reveals the involvement of oximino group in coordination. The appearance of a new band at $460-490 \text{ cm}^{-1}$ and $520-550 \text{ cm}^{-1}$ in all complexes corresponds to M-O bond and M-N bonds respectively. The IR spectra of Co(PPBH)₂, Cu(PPBH)₂ and Pd(PPBH)₂ complexes shows that ligand HPPBH behaves as a mononegative 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, with the (C=O) stretch nearly in the same position indicates its non-participation in coordination.

Table 2: IR spectral bands of the ligand (HPPBH) and its metal complexes (cm⁻¹)

Tentative assignments	Ligand	Co(PPBH) ₂	Ni(PPBH) ₂	Cu(PPBH) ₂	Pd(PPBH) ₂
-OH	3387	---	---	---	---
-NH	3287	3176	3180	3176	3195
>C=N(oximino)	1501	1470	1472	1477	1481
N=CH(azomethine)	1562	1530	1533	1537	1539
C=O	1668	1640	1643	1667	1668
N-O	1018	1010	1008	1004	1001
M-N	---	520	532	540	552
M-O	---	490	492	493	498
C=CH (Aromatic)	3057	3048	3027	3033	3021

3.3.PMR:

The PMR spectrum of ligand HPPBH in deuteriated DMSO shows two singlets at δ 11.78 ppm and δ 11.139 ppm which disappeared on adding D₂O. 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) \leftrightarrow (N=C-OH). The peaks at δ 7.2 – δ 7.8 ppm and 2.1 ppm may be attributed to phenyl ring protons and methyl protons respectively.

3.5. EPR Spectrum studies:

EPR spectrum of Cu(PPBH)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 $g_{\parallel} = 2.2768$ and $g_{\perp} = 2.0632$. The trend $g_{\parallel} > g_{\perp} > 2.0023$, indicates that the unpaired electron is localized in $d_{x^2-y^2}$ orbital which is the characteristics of square planar geometry. It is reported that g_{\parallel} value is less than 2.3 for covalent character and is greater than 2.3 for ionic character of the metal ligand bond in the complex²¹. For the complex under study $g_{\parallel} < 2.3$ which suggests the covalent character of the metal-ligand bond. The G value of the complex (G=4.38) is greater than 4 suggesting that there is negligible Cu-Cu interaction²² in the complex.

4. Conclusion:

The present study shows that the synthesized ligand (HPPBH) acts as tridentate/bidentate ligand coordinating through azomethine nitrogen and oximinooxygen. The synthesized ligand and its metal complexes have been confirmed by the analytical data, IR, electronic, mass spectrometry, PMR, ESR spectral data, magnetic susceptibility, molar conductivity. From the analytical data and spectral studies, we propose octahedral geometry for the Ni(II) complex and square planar geometry for Co(II), Cu(II) and Pd(II) complexes.

Acknowledgement:

The Author is grateful to the chemistry department, KonkanGyanpeethKarjat College (ASC), Karjat for providing the necessary facilities and their support.

References:

1. Patel N.J. and Haldar B.C. *J. Inorg. Nucl. Chem.* 1967; 42:843.
2. Talwar U.B. and Haldar B.C. *J. Indi. Chem. Soc.* 1972;49:785.
3. Deshmukh R.G. and Thakkar N.V. *Ind. J. Chem.* 1985; 24A:1066.
4. Deshmukh R.G. Ph.D. Thesis, University of Bombay, 1992
5. Thakkar N.V. and Haldar B.C. *J. Inorg. Nucl. Chem.* 1980;42:843
6. M. M. Bekheit, *Synth. Reac. Inorg. Met.-Org. Chem.*, 1991, 21, 681

7. Chakrabarti A. and Sahoo B. *Ind. J. Chem.* 1981;20A:431.
8. G. H. Jeffery, J. Bassett, J. Mendham, and R. C. Deney, *Vogel's Textbook of Quantitative Chemical Analysis*, Longman, London,UK, 5th edition, 1989.
9. W. J. Geary, "The use of conductivity measurements in organic solvents for the characterization of coordination compounds," *Coordination Chemistry Reviews*, vol. 7, no. 1, pp. 81–122, 1971.
10. N.V. Loginova et al. *Polyhedron*, 2008, 27, 985–991
11. A. Pui, J.-P. Mahy, *Polyhedron* 26 (2007) 3143.
12. B.K. Singh, R.K. Sharma, B.S. Garg, *Spectrochim. Acta* 2006,63A, 96.
13. H. Nishikawa, S. Yamada, *Bull. Chem. Soc. Jpn.* 1964, 37, 8.
14. Y. Nishida, S. Kida, *Bull. Chem. Soc. Jpn.* 1972, 45, 461.
15. M.J. Carter, D.P. Rillema, F. Basolo, *J. Am. Chem. Soc.* 1974, 96, 392.
16. A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, the Netherlands, 2nd edition, 1984.
17. *Konig E, Structure and Bonding*, 1971, 9, 175-212.
18. H.B. Gray and C.J. Ballhausen, *J. Am. Chem. Soc.*, 85, 260 (1963)
19. P.P. Bhargava and M. Tyagi, *Ind. J. Chem.*, 1986,25A, 193.
20. B. H. Mehta and J. A. Shaikh, *J. Ind. Council Chem.*, 2009,26,1,1-6.
21. Kivelson, D.; Neiman, R. ESR Studies on the Bonding in Copper Complexes. *J. Chem. Phys.* 1961, 35, 149-155.
22. M. Joseph, V. Suni, M.R.P. Kurup, M. Nethaji, A. Kishore, S.G. Bhat, *Polyhedron* 2004,23 2069.
