IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)
An International Open Access, Peer-reviewed, Refereed Journal

“SYNTHESIS AND SPECTRAL CHARACTERIZATION OF NOVEL SCHIFF BASE COMPLEXES DERIVED FROM 2-HYDROXYBENZALDEHYDE DERIVED OF BENZILMONOXIMETHIOCARBOHYDRAZIDE ”

Deepak Patekar[1], Kalpana Patankar-Jain[2], Raj Badekar[3*] and Rama Lokhande[1]

1. School of Basic Sciences, Jaipur National University, Jaipur-India-302 017.
2. Dept of Chem, BNN College, Bhiwandi, Dist:Thane-Maharashtra, India.
3. *Riva Industries, Ambernath MIDC, Dist-Thane-Maharashtra, India-421 505, badekarrr@gmail.com.

Abstract:

A new thiocarbahydrazide Schiff based *N*''-[(1*E*, 2*E*)-2-(hydroxyimino)-1,2-diphenylethylidene]-*N*'''-[(*E*)-(2-hydroxyphenyl)methylidene] thiocarbohydrazide prepared by condensing 2-hydroxybenzaldehyde and benzilmonoximethiocarbohydrazide. Its Fe(II), Ni(II), Pd(II) and Co (II) complexes are synthesized and characterized on the basis of physical characteristics, micro-analytical data, PMR, FTIR spectrum and electronic spectrum data. The spectrum data suggest coordination of Schiff base ligand with metal through nitrogen of azomethine and oximino groups.

Key words: Schiff base, Metal complexes, Spectroscopic study, Thiocarbahydrazide

1. INTRODUCTION:

Schiff base (azomtehine group), named after Hugo Schiff, is functional group that contains a >C=N- bond. Some chemical abstract covered this research under the categories imines and Schiff base. Generally Schiff bases are formed by condensation reaction [1-2]. A number of reviews on Schiff base synthesis are available a Schiff bases compounds are commonly referred to by their names abbreviations. Schiff bases could be bidenate, tridenate, tetradentate or polydentate ligand forming very stable complexes with various transition metals. These types of ligands if they bear a functional group like hydroxyl, sufficiently near the site of condensation in such a way that a 5 or 6 member ring can be formed when coordinated with central metal ion.

Schiff bases derived from aromatic aldehydes have a wide variety of applications of many fields e.g. analytical, inorganic, biological and organic chemistry [3-4]. Primary amine as well as carbonyl compound derived Schiff bases highly used in analytical determination. Schiff base also play an essential role in the coordination chemistry due to their ability to most of the stable transition metal complexes [5].

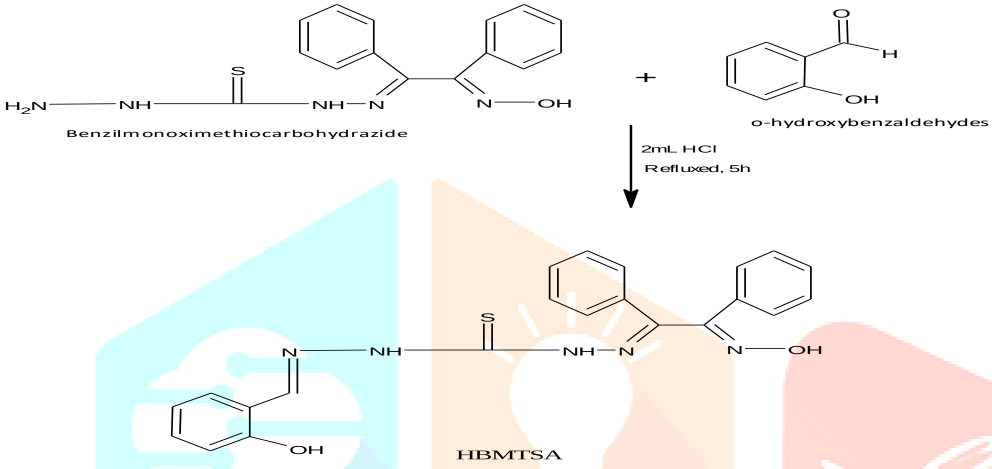
In the present study, Schiff base of α-benzilmonoximethiocarbohydrazidesalicylidene was synthesized and their Fe(II), Co(II), Ni(II) and Pd(II) metal complexes were prepared. These ligand and its metal complexes were further characterized on the basis of spectral analysis.

2. MATERIALS and METHODS:

All chemicals were used by AR grade and were used without further purification. Melting points were determined in an Electrothermal 9200. ^{1}H-NMR spectra in $CDCl_3$ were recorded on Brucker AV300 NMR spectrometers using TMS as internal standard. The FT-IR spectra were recorded in the range 400–4000 cm^{-1} by KBr pellet using a ‘Perkin- Elmer spectrum 100’ model FT-IR spectrophotometer. The UV–Vis spectra in methanol were recorded with a JASCO V-650 Spectrophotometer.

2.1. Preparation of o-hydroxybenzaldehyde derivatives of benzilmonoximethiocarbohydrazide:

Benzilmonoximethiocarbohydrazide were prepared by reported method [**6**]. A mixture of 0.100mol of o-hydroxybenzaldehydes in 50mL ethanol was added to alcoholic solution of 0.125mol of benzilmonoximethiocarbohydrazide und agitation and added dropwise 2ml of conc. HCl. The final mixture was refluxed continuously for 4h and then allowed to cool. The yellow compound was collected and purified by crystallization method using 70% methanol (yield: 80%).



2.2. Preparation of metal complexes of α-Benzilmonoximethiocarbohydrazone-o-Hydroxybenzaldehyde (HBMToHB):

2.2.1. Bis(α-Benzilmonoximethiocarbohydrazone-o-Hydroxybenzaldehyde)Ferrous(II), $[Fe(BMToHB)_2]$:

To a solution of 0.76g ferrous sulfate (5mmol) in 10cm^3 water was added gradually with stirring a solution of 3.71g (10mmol) of HBMToHB in 20cm^3 ethanol. The pH of the mixture was raised slowly to 5.5 with dilute (0.10N) NaOH, when an ink blue colored complex separated. It was filtered, washed with hot water (50cm^3) and dried at 110^{0}C. It was recrystallized from methanol.

2.2.2. Bis(α-Benzilmonoximethiocarbohydrazone-o-Hydroxybenzaldehyde)Cobalt(II), $[Co(BMToHB)_2]$:

To solution of 0.85g cobalt chloride hexahydrate (5mmol) in 10cm^3 water was added gradually with stirring a solution of 3.71g (10mmol) of HBOSTH in 20cm^3 ethanol. The pH of the mixture was raised slowly to 6.5 with dilute (0.10N) NaOH, when an orange colored complex separated, which was digested for 15 minutes on a hot water bath and then filtered, washed with hot water(50 cm^3) and dried at 110^{o}C. It was recrystallized from methanol.

2.2.3. Bis(α-Benzilmonoximethiocarbohydrazone-o-Hydroxybenzaldehyde)Nickel(II), [Ni(BMToHB)$_2$]:

To a solution of 0.85g nickel sulfate hepahydrate (5mmol) in 10cm^3 water was added gradually with stirring a solution of 3.71g (1mmol) of HBMToHB in 20cm^3 ethanol. The pH of the mixture was raise to 8.0 slowly with dilute (0.10N) NaOH, when an light green colored complex separated, which was digested for 15 minutes on a hot water bath and then filtered, washed with hot water (50cm^3) and dried at 110^{0}C. It was recrystallized from methanol.

2.2.4. Bis(α-Benzilmonoximethiocarbohydrazone-o-Hydroxybenzaldehyde)Palladium(II), [Pd(BMToHB)$_2$]::

To an acidic solution of 0.50g of palladium chloride (28mmol) was added a solution of 2.08g HBMToHB (56mmol) in 10cm^3 ethanol. The pH of the solution was raised to 8.0 with dilute(0.10N) NaOH, when a green complex separated, which was digested on a hot water bath for 15 minutes and then filtered, washed with hot water (50cm^3) and dried at 110^{0}C. It was recrystallized from methanol.

3. RESULTS AND DISCUSSIONS:

In the present paper we described the synthesized and characterization of HBMToHB ligand and its neutral complexes of the type ML$_2$ (M = Fe, Co, Ni, Pd; L = HBMToHB). The analytical and physical data represented in **Table-1**. The resulting complexes are isolated as yellow color solids. All complexes are soluble in common organic solvents and low molar conductance of complexes, indicating their non-ionic nature [**7**]. High decomposition points indicated that they have high thermal stability and strong metal-liagnd bond.

Table-1: Analytical and Physical data HBMToH Ligand and its metal complexes

Compound	Color	% Yield	MP /DP ºC	Elemental Analysis: Expected (Found)						Molar Conductance	agnetic Moment
				C	H	N	O	S	M		
HBMToHB	Yellow	80.00	190	63.29(62.92)	4.59(4.51)	16.98(16.29)	7.66(7.53)	7.68 (7.29)	-	-	-
Fe(BMToHB)$_2$	Ink Blue	79.38	203	59.47(59.01)	4.05(4.00)	15.77(15.09)	7.21(7.00)	7.21 (7.02)	6.29(6.15)	0.5	5.18
Co(BMToHB)$_2$	Brown	82.63	200	59.26(58.91)	4.04(4.08)	15.71(15.56)	7.18(7.01)	7.18 (7.00)	6.62(6.58)	3.6	5.02
Ni(BMToHB)$_2$	Brown	81.99	202	59.28(59.00)	4.04(3.98)	15.72(17.28)	7.19(7.21)	7.19 (7.11)	6.59(6.23)	9.2	3.17
Pd(BMToHB)$_2$	Green	80.12	205	56.26(55.99)	3.84(3.79)	14.92 (14.33)	6.82(6.77)	6.82 (6.80)	11.34(11.15)	9.6	Dia

3.1. Magnetic moments:

Magnetic moments of all metal complexes of HBMToHB are measured at room temperature, Fe(II), Co(II) and Ni(II) complexes paramagnetic susceptibilities (5.18, 5.02 and 3.17BM) respectively of the high spin octahedral geometry and palladium (II) complex is square planar in nature.

3.2. Electronic Spectra:

Electronic spectra of HBMToHB displayed in methanol solution and its Fe(II), Co(II), Ni(II) and Pd(II) transition metal ion complexes were displayed in chloroform solution. Electronic spectra of HBMToHB shows three absorption bands in UV region at 339, 297 and 221nm with high intensities which indicated $\pi \rightarrow \pi^*$ transitions of oximino and two azomethine groups of HBMToHB [8].

The electronic spectra of $[Co(BMToHB)_2]$ complex shows two bands at 597 and 488nm. This is due to ${}^4T_{2g}(F) \rightarrow {}^4A_{2g}$ and ${}^4T_{2g}(F) \rightarrow {}^4T_{2g}(P)$ respectively, which indicates presence of octahedral geometry of Co(II) complex [9]. The Fe(II) complex shows two energy bands at 598 and 483nm is due to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ transition. The electronic spectra of Fe(II) complex of HBMToHB ligand suggested an octahedral geometry [10]. The electronic spectra of Ni(II) complex shows absorption band at 1040 and 583nm assigned to ${}^5T_{2g} \rightarrow {}^5E_g$ and ${}^5E_g \rightarrow {}^5B_{1g}$ transitions, which indicates Ni(II) complex have high spin octahedral geometry [11]. The Pd(II) complex shows high energy bands at 366, 298 and 225nm due to metal-ligand charge transfer transition of Pd(II) complex [12].

Table-2: Electronic Absorption spectra of HBMToHB Ligand and its metal complexes

Compound	**Solvent**	λ_{nm}	ε	**Transition**
HBMToHB	Methanol	339	13166	Oximino $\pi \rightarrow \pi^*$
		297	20899	Azomethine $\pi \rightarrow \pi^*$
		221	12218	Azomethine $\pi \rightarrow \pi^*$
	0.1N NaOH	384	9033	Oximino $\pi \rightarrow \pi^*$
		307	9156	Azomethine $\pi \rightarrow \pi^*$
		230	6589	Azomethine $\pi \rightarrow \pi^*$
$Fe(BMToHB)_2$	Chloroform	598	233	$^5T_{2g} \rightarrow {}^5E_g$
		483	2256	$^5E_g \rightarrow {}^5B_{1g}$
$Co(BMToHB)_2$	Chloroform	597	300	$^4T_{2g}(F) \rightarrow {}^4A_{2g}$
		488	600	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
$Ni(BMToHB)_2$	Chloroform	1040	5	$^3A_{2g} \rightarrow {}^3T_{2g}$
		583	988	$^3A_{2g} \rightarrow {}^3T_{1g}$
		511	3989	d-d transition
$Pd(BMToHB)_2$	Chloroform	366	25122	M→L Charge Transfer
		298	10830	M→L Charge Transfer
		225	9060	M→L Charge Transfer

3.3. PMR Spectra:

The PMR spectra has provide the evidence for the structural characteristics of oxime base ligand and its Pd(II) metal complex. The spectrum of the HBMToHB ligand showed a signet single at 11.20ppm due to the oximino –OH, absent in its Pd(II) complex deprotonation of oximino proton during complex formation and oxime group coordinated Pd(II) metal ion through nitrogen atom. Phenolic -OH peak observed at 10.40ppm, this is un-shifted, because non-involvement of phenolic –OH group in coordination. Multiplet observed at 6.90-7.50ppm and singlet at 9.10-9.20ppm assignable of aromatic and methane protons respectively of HBMToHB ligand Pd(II) complex [13-14].

Table-3: PMR data of HBMToHB and its Pd(II) metal ion complxes in ppm

Compounds	**-OH**	**Phenolic -OH**	**>C=N-NH-**	**-SH/-NH**	**-CH=**	**Phenyl rings**
HBMToHB	11.20	10.30	8.20	8.60	9.10	6.90-7.30
Pd(BMToHB)$_2$	-	10.40	8.20	8.60	9.20	6.90-7.50

3.4. FT(IR) Spectra:

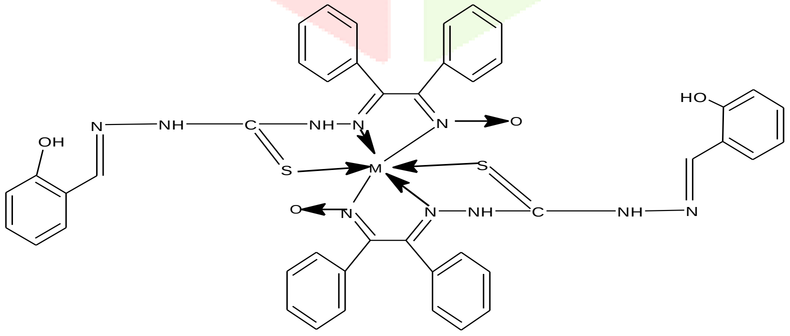
The infrared spectra of free ligand HBMToHB broad band shown at 3287cm^{-1} is absent in its transition metal complexes, suggested that hydroxyl group deprotonated and involvement of oximino group in complexation and formation of N→O and observed at around 1200cm^{-1} in its metal complexes [15-17]. The IR frequencies at 1644 and 1616cm^{-1} had indicated the existence of azomethine and oximino groups respectively of HBMToHB ligand and it was shifted to lower side in metal complexes. It was shown the existence of coordination bond formation with metals through nitrogen atoms of azomethine and oximino group [18-20]. Another sharp band observed at 2848cm^{-1} in spectrum of HBMToHB is shifted higher sight in Fe(II), Co(II) and Ni(II) metal complexes, indicated this group also involved in coordination [21-22]. The new bands observed in metal complexes of HBMToHB ligand in the region 505-536cm^{-1} which can be assigned as M-N or M→N. The strong bands at 3200, 1531 and 742cm^{-1} are assignable to phenolic-OH, νNH and benzene ring respectively in HBMToHB. These groups unchangeable or slightly shifted in metal complexes indicated these groups non-coordinated to central metal atoms.

Table-4: FT(IR) spectral bands of the ligands and its metal complexes (cm^{-1})

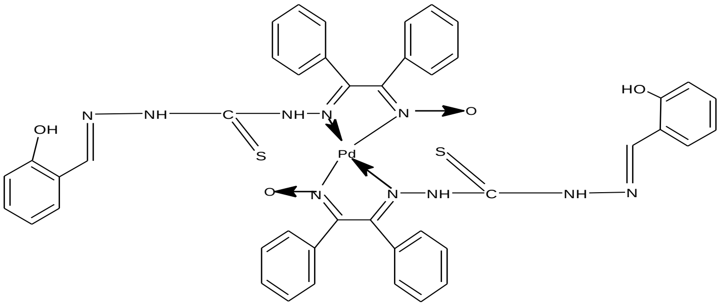
Compounds	-OH	Phe OH	ν(C-S-H)	ν(C=NO)	ν(C=NN)	ν(N-H)	ν(N-O)	ν(N-N)	Benz ring	M-N
HBMToHB	3287	3200	2848	1616	1644	1531	1010	1093	742	--
[Fe(BMToHB)$_2$]	-	3205	2861	1535	1602	1506	1008	1150	754	536,509
[Co(BMToHB)$_2$]	-	3216	2853	1507	1600	1471	1008	1149	754	531,505
[Ni(BMToHB)$_2$]	-	3216	2862	1505	1603	1473	1009	1152	754	533, 505
[Pd(BMToHB)$_2$]	-	3226	2865	1540	1598	1470	1009	1150	754	528, 508

4. Conclusion:

In this paper, we have explored the synthesis and characterization of HBMToHB and Fe(II), Co(II), Ni(II) and Pd(II) metal complexes. The HBMToHB and its metal complexes were synthesized and evaluated, according to the UV-visible, IR and NMR data. FT(IR) data of HBMToHB and its metal complexes suggested that, HBMToHB coordinated through nitrogen atom of azomethine and oximino group and sulphur atom of –C=S group and form MN_4S_2 combination. High decomposition points of coordinate compounds indicated high thermal stability and strong metal-liagnd bond and also they are non-electrolyte in nature. On the basis of spectral data structures of the metal complexes tentatively assigned as;



(Where M = Fe(II), Co(II) and Ni(II)



5. References:

1. Anand P, Patil V, Sharma V, Khosa R, Masand N., *Int J Drug Des Discov*, 2012; **3(3)**:851-866.
2. Somani R, Dandekar R, Shirodkar P, Gide P, Tanushree P, Kadam V., *Int J ChemTech Res*, 2010*;* **2(1):**172-179.
3. Ashraf M, Mahmood K, Wajid A, Maah M, Yusoff I, *Int Conf Chem Ads Chem Process*, 2011; **10**:1-7.
4. Kumar N, Sharma P., *Int J Appl Res study*, 2013*;* **2(2)**:1-6.
5. Turki A, *J Kerbala Univeristy*, 2012; **10(3)**:259–266.
6. Kulkarni S, Badekar R, Gore G, and Shimpi P, *JETIR*, 2019; **6(2)**; 494-499.
7. Singh V, Kamble P and Badekar R, *International Journal of Research and Analytical Reviews*, 2018; **5(3I)**; 910y-913y
8. Dhanraj, C and Nair M, *J. of Coordination Chem*, 2009*;* **62(24)**: 4018-4028.
9. Chandra S, Gupta R., and Bawa S, *Spectrochimica Acta A, Molecular and Biomolecular Spectroscopy*, 2005*;* **62(1-3)**: 552-556.
10. Bayoumi H, Alaghaz A and Aljahadali M, *Int. J. Eletrochem. Sci*, 2013; **8**: 9399-9413.
11. El-Sherif A, Eldebss T and Taha M, *Spectrochimica Acta A*, 2011; **79(5)**: 1803-1814.
12. Lever A.B.P, "Inorganic electronic spectroscopy"; *Elsevier Amsterdam*, 1994.
13. Kurtoğlu M, Ispir E, Kurtoğlu N and Serin S, Dyes Pigm, 2008; **77:**75.
14. Silverstein R, Bassler G, Morrill T, Spectrometric Identification of Organic Compounds, 5th ed., Wiley, New York, 1991.
15. Badekar R, Kulkarni S, Thawkar B and Lokhande R, *IJAR*, 2016; **2(9)**: 175-179.
16. Badekar R, Lokhande R, Kulkarni S and Patil R, *International Journal of Advanced Research*, 2016; **4:**8.
17. Badekar R, Lokhande R, Kulkarni S and Patil R, *International Journal of Advanced Research*, 2016; **4:**7.

18. Krishnankutty K, Ummathur M and P. Ummer, *J. Serb. Chem. Soc*, 2009*;* **74**:1273
19. Dahikar P and Kedar R, *International Journal of Scientific and Research Publications*, 2013; **3(5)**:1-3.
20. Soleimani E, *Journal of the Chinese Chemical Society*, 2011; **58**:53-59.
21. Soleimani E, Sayed A and Sargolzaei M, *J. Chi. Chem. Soc*, 2017; **62, 4**: 3731-3740.
22. Kulkarni S, Badekar R, Gore G, and Shimpi P, *JETIR*, 2019; **6(2)**.
23. Thube A, Badekar R, Kamble P and Lokhande R, Accepted, 2020.
24. Amol Thube, 'Studies on some nitro- and chloro- benzaldehydes derivatives of N''-[(1E, 2E)-2-(hydroxyimino)-1,2-diphenylethylidene] thiocarbohydrazide'; *PhD Thesis;* Jaipur National University, 2020.
25. Belavale P, Badekar R, Kulkarni S and Lokhande R, *International Journal of Advance and Innovative Research*, 2019; **6(2)(IX)**: 139-141.
26. Singh V, Kamble P and Badekar R, Synethsis and characterization of novel coordination compound of Cr(III), Fe(III), with α-Benzilmonoximethiocarbohydrazide; International Journal of Research and Analytical Reviews, 2018; **5(3)**:910y-913y.
27. Deepak S, Raj B and Rama L, *International Journal of Advance and Innovative Research*, 2018; **5(4)**(XIII): 11-14.
28. Pingale S, "Synthesis and characterization of some transition metal complexes of α-benzilmonoximethiosemicarbazone"; *M.Sc. Thesis, University of Mumbai*, 2005.
29. Priya B, Raj B, Rama L and Vijay G; Synthesis and Spectral Characterization of Ni(II) and Pd(II) complexes of Benzilmonoximethiocarbhydrazide-p-dimethylaminobenzaldehyde: Communicated.