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Synthesis and Characterization of Novel Compound derived from α-Benzilmonoximehydrazone with 4, 4-dimethylaminobenzaldehyde and its Fe(II), Ni(II) and Pd(II) Complexes

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Abstract: L The α-benzilmonoximehydrazone-4, 4-dimethylaminobenzaldehyde (HBMHBB) was prepared in Methanol from the reaction of α-benzilmonoximehydrazone with 4, 4-dimethylaminobenzaldehyde in the presence of hydrochloric acid and also prepared its Fe(II), Ni(II) and Pd(II) complexes. The UV spectrum, PMR spectral data elucidate the structure of synthesized compounds. All prepared compounds are non-electrolyte in nature. On the basis of spectral analysis suggests that Fe(II) and Ni(II) complexes are high spin octahedral and Pd(II) is square planar geometries in environment.

Keywords: α-benzilmonoximehydrazone, 4,4-dimethylaminobenzaldehyde, Ni(II), Pd(II) and Fe(II)

I. INTRODUCTION

Schiff base derivatives attract significant interest and occupy an important role in the development of coordination chemistry. Moreover, Schiff bases complexes containing transition metals have been studied in several research areas such as structural chemistry[1]. The Schiff base ligands and their corresponding metal complexes have expanded enormously and include a vast area of organometallic compounds and various aspects of bioinorganic chemistry[2-4]. Schiff bases ligands have been reported to sow a variety of biological actions by virtue of the azomethine linkage, which is responsible for various antibacterial, antifungal, herbicidal, clinical and analytical activities[5-7]. Transition metal complexes with nitrogen donor atom of Schiff bases are of particular interest[8-10], because of their ability to possess unusual configuration[11]. On the other hand, Schiff bases containing α-benzilmonoxime known to better coordinating ligand[12-13]. Quite recently, the Schiff base ligand derived from the condensation of α-benzilmonoximehydrazone was previously prepared and characterized[14-17]. As a continuation to our work, a new Schiff base such as α-benzilmonoximehydrazone-4,4-dimethylaminobenzaldehyde derived from α-benzilmonoximehydrazone condense with 4,4-dimethylaminobenzaldehyde in the presence of hydrochloric acid and also prepared its Fe(II), Ni(II) and Pd(II) complexes. IUPAC name of the prepared ligand is 4-[(*E*)-{(2*E*)-[(2*E*)-2-(hydroxyimino)-1, 2-diphenylethylidene] hydrazinylidene}methyl]-*N*,*N*-dimethylaniline, abbreviated as HBMHDAB. The title ligand and its synthesized metal complexes were characterized on the basis of elemental analysis, ^{1}H NMR, FT(IR), Electronic absorption spectra, Mass and EPR spectra, Magnetic susceptibility measurement.

II. EXPERIMENTAL

All the chemicals used were of AR grade. The solvents were dried and distilled before use according to standard procedure[18]. FT(IR) spectra were recorded in KBr medium on a ‘Perkin- Elmer spectrum 100’. The pmr spectra recorded on a ‘Brucker AV300 NMR Spectrometer’ instrument in d_6 DMSO solvent using TMS as internal standard. The UV-visible spectra of ligand and its all metal complexes were recorded on JASCO spectrophotometer V650. Magnetic susceptibility measurements of the complexes in the solid state were determined by Gouy balance using $[Ni(en)_3S_2O_3]$ as callibrants. Molar conductance of the complexes was measured in nitrobenzene at room temperature using Synchronic conductivity bridge type 305.

A. Synthesis of Schiff base Ligand:

α-Benzilmonoximehydrazone was prepared by reported method[19]. The title ligand was synthesized by the condensation of α-benzilmonoximehydrazone and 4, 4-dimethylaminobenzaldehyde (1:1 molar ratio) dissolved in ethanol. The resulting reaction mixture was refluxed for 5h the yellow solid precipitate was obtained through filtered, wash with hot distilled water dried, recryatallised from ethanol. Yield: 78% (M.P. 191^{0}C).

B. Synthesis of Metal Complexes

An ethanolic solution of title ligand (0.02mol) was mixed with aqueous solution of metal (II) chloride (0.01mol), pH was adjusted to 7.5-8.0 by using 0.1N NaOH, colored precipitated was separate out. Filtered and washed with hot distilled water and recrystallized from methanol.

III. RESULTS AND DISCUSSIONS

The analytical data along with some physical properties of the ligand and its various metal complexes are summarized in Table-1. The ligand on interaction with Fe(II), Ni(II) and Pd(II) chlorides, yields complexes corresponding to the general formula ML_2. The analytical data show that the metal to ligand ratio is 1:2. They are insoluble in water, soluble in common organic solvents. The low molecular conductance value of the complexes reveals their non-electrolytic nature[20]. High melting points of all metal complexes suggests strong metal-ligand bond.

Table-1: Analytical and physical data for HBMHDAB and its Fe(II), Ni(II), Pd(II) metal complexes

Compound	Color	% Yield	Percentage Expected	(Found)				Conductance	Magnetic
	(M.P. in °C)		C	H	N	O	M	Ω^{-1}	Moment in BM
HBMHDAB	Yellow	79.03	74.59	5.95	15.40	4.32	-	-	-
	(191)		(73.88)	(5.98)	(15.00)	(4.39)			
Fe(BMHDAB)$_2$	Blue	83.12	69.53	5.30	14.11	4.03	7.04	1.80	5.17
	(238)		(67.99)	(4.81)	(14.29)	(4.01)	(6.98)		
Ni(BMHDAB)$_2$	Brown	79.63	71.71	5.46	14.55	4.16	7.63	2.00	3.08
	(243)		(70.91)	(4.99)	(14.03)	(4.28)	(7.62)		
Pd(BMHDAB)$_2$	Brown	79.99	65.40	4.98	13.27	3.79	12.56	1.30	-
	(260)		(64.75)	(4.92)	(12.90)	(3.18)	(12.02)		

A. FT(IR) Spectra

Absence of any band between 3300-3400cm^{-1} in present ligand, in α-benzilmonoximehydrazone reported[19] at 3287cm^{-1} for –NH$_2$ group indicating successfully replacement of amino group during condensation. In order to study the binding modes of Schiff base to metal in the complexes, IR spectrum of the free ligand was compared with the spectra of the metal complexes. The band at 3267cm^{-1} in the ligand was disappeared in all complexes, indicating this hydroxyl group deprotonated during complex formation. The bands at 1645cm^{-1} and 1745cm^{-1} due to the azomethine and oximino group respectively of the ligand underwent to Shift to lower frequency (Table-2) after complexation, indicating the coordination of azomethine and oximino nitrogen to metal ion and this can be explained by the donation of electrons from nitrogen to the empty *d*-orbitals of the metal atom. The nature of metal-ligand bonding is confirmed by the newly formed bands at the region 490-555cm^{-1} in the spectra of the complexes which is tentatively assigned to M-N vibration. On the basis of FT(IR) spectra of ligand and its all complexes, suggested that HBMHDAB ligand coordinated to metal ion through nitrogen atoms only. The formation of metal to ligand is M-N$_4$ type of composition.

Table: - 2: FT(IR) spectral data for HBMOH and its metal complexes

Compound	υ(O-H)	Ar. C-H	C=NO	C=NN	>CH-	N - O	N-N	M-N
HBMHDAB	3267	3058	1645	1745	1690	1000	1072	-
Fe(BMHDAB)$_2$	-	3069	1600	1690	1691	1025	1093	492, 458
Ni(BMHDAB)	-	3025	1603	1710	1695	1017	1099	482, 555
Pd(BMHDAB)$_2$	-	3012	1608	1705	1690	1018	1100	515, 490

B. ^{1}H NMR spectra:

The ^{1}H NMR spectra of the ligand and its Pd(II) complex done in d_6 DMSO solvent. The ^{1}H NMR spectrum of the prepared ligand exhibits a multiplet signal at 6.7-8.50δ (m, 14H) suggests that the aromatic groups present in ligand. This band is unshifted in Pd(II) complexes, indicate non-involvement of aromatic group in the coordination and also two methane group observed in the region 1.2-1.6δ are unshifted in complex, suggests they are not involve in coordination. A sharp and singlet band observed at 10.20δ (s, 1H) in title ligand is absent in the palladium (II) complex, confirm the oximino group is deprotonated during complex formation. Other bands are unchanged in complex, suggests non-involvement of these group in coordination.

Table -3: PMR spectral data of the HBMOH

Compound	-OH	Phenyl Rings	N-CH_3	-CH=
HBMHDAB	10.28	6.70-8.50	1.20-1.60	0.38
Pd$(BMHDAB)_2$	-	6.80-8.40	1.20-1.60	0.39

C. Magnetic Moment

Room temperature magnetic susceptibility measurements indicate that the Pd(II) complex is diamagnetic suggesting absence of unpaired electron in this complex as expected for square planar (d^8) geometry of Pd(II) complex. Ink blue colored Fe$(BMHDAB)_2$ exhibits paramagnetic moment of 5.17 BM at room temperature. The Fe(II) ion shows little tendency to form four coordinate complexes[21]. Most ferrous complexes are found to be octahedral showing either diamagnetism or paramagnetism corresponding to four unpaired electrons. The observed magnetic moment for Fe$(BMHDAB)_2$ complex, suggests high spin octahedral environment for this complex. The brown colored Ni$(BMHDAB)_2$ complex shows room temperature magnetic moment of 3.08BM. High spin Ni(II) complexes expected to be paramagnetic properties due to two unpaired electrons. Octahedral Ni(II) complexes have magnetic moments between 3.0-3.3BM, which indicates a small but definite orbital contribution to the magnetic moment. Tetrahedral complexes, however, range from 3.45-4.0BM, the larger the distortion from a regular tetrahedron, the lower the magnetic moment. Square planar Ni(II) complexes usually have no unpaired electrons, are diamagnetic and thus magnetic moment of zero. The observed magnetic moment for Ni$(BMHDAB)_2$ complex is in the range expected for octahedral Ni(II) complexes.

D. Electronic Absorption Spectra

The electron absorption spectra of the ink blue [Fe$(BMHDAB)_2$] in chloroform solution shows a symmetrical broad band around 646nm, along with a small band at around 555nm. The spectrum also shows a high intensity band at 380nm. The position of the last band along with the high intensity shown, suggests that it originated from a charge transfer phenomenon. While, the earlier two bands could be said originate from the intra metal transitions. For Fe(II) high spin case, the ground state (^{5}D) is supported to split into ^5E_g and $^5T_{2g}$ states, as such are d-d transition corresponding to $^5T_{2g} \rightarrow {}^5E_g$ may be expected. However, the ^5E_g state is expected to further split into $^5B_{1g}$ and $^5A_{1g}$ owing perhaps, to Jahn-Teller distortion. As such Fe(II) high spin octahedral complexes could show two, fairly closely spectral bands. The electronic spectrum of the light green Ni(II) complex in chloroform solution exhibits a peak at 980nm which assigned to $^3A_{2g} \rightarrow {}^3T_{2g}(\upsilon_1)$ transition, this value assigned to 10Dq of the Ni(II) complex. Another broad band is observed at 620nm which assigned to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)(\upsilon_2)$. The ratio υ_2/υ_1, is found to be 1.55, which falls in the range the octahedral complexes of Ni(II)[22]. From the observed position of these two transitions, the frequency of the third d-d transitions $^3A_{2g} \rightarrow {}^3T_{1g}(P)(\upsilon_3)$ and B values has been calculated employing the following equations[23].

$$B = [(\upsilon_2 - 2\upsilon_1)\ (\upsilon_2 - \upsilon_1)]/(15\upsilon_2 - 27\upsilon_1)$$

$$\upsilon_3 = (225B^2 + 100Dq^2 + 180DqB)^{1/2}$$

The third band, υ_3 is expected to occur at 16160cm^{-1}. However, this band is not observed in the solution spectrum of the complex probably because, it is masked by the tail-end of the strong charge transfer band around 25970cm^{-1}(ε = 5668 dm^3/mol/cm). The value of the Racah interelectronic repulsion parameter B is 0.7420cm^{-1}, calculated with the help of the appropriate equations[24]. The expression $B = 15B'$ is found to be 11143cm^{-1} and the ratio $\beta = \frac{B\ (found)}{B'(free\ ion)}$, the covalency factor is found to be 0.8216cm^{-1} and is in close agreement octahedral Ni(II) complexes[25].

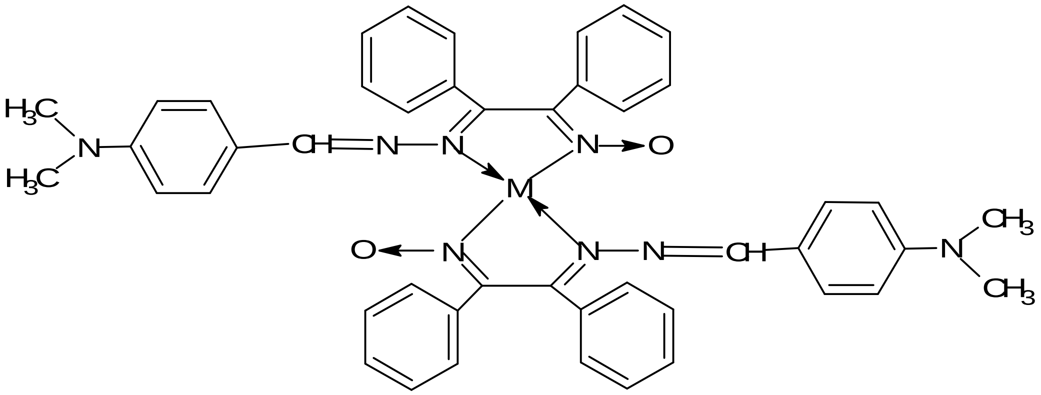
The green Pd(II) complex in chloroform shows charge transfer bands at 440nm. The ligand field transitions are not clearly observed.

Table -4: Electronic spectral data for HBMHDAB and its metal complexes

No.	Compound	Solvent	Band position in nm	Intensity ε	Assignment
1	HBMHDAB	Methanol	339	12252	□ximino □→□* transition
			249	11181	Azomethine □→□* transition
		0.1N NaOH	356	12116	Oximino □→□* transition
			256	11288	Azomethine □→□* transition
2	Fe(BMHDAB)$_2$	Methanol	221	23600	Charge transfer M→L transition
		Chloroform	646	271	${}^5T_{2g} \rightarrow {}^5E_g$ *transition*
			555	5444	Charge transfer M□Ltransition
			380	27899	Charge transfer M□Ltransition
3	Ni(BMHDAB)$_2$	Methanol	328	29100	Charge transfer M→Ltransition
			225	18190	Charge transfer M→Ltransition
		Chloroform	980	10	${}^3A_2g \rightarrow {}^3T_1g$transition
			620	328	${}^3A_2g \rightarrow {}^3T_1g$(F)transition
			523	14371	Charge transfer M□Ltransition
5	Pd(BMHDAB)$_2$	Methanol	333	1811	Charge transfer M□Ltransition
		Chloroform	578	1910	Charge transfer M□Ltransition
			449	13530	Charge transfer M□Ltransition

IV. CONCLUSION

In the present paper, coordination chemistry of a Schiff base ligand obtained from the condensation reaction of α-benzilmonoximehydrazone and 4,4-dimethylaminobenzaldehyde is described. Fe(II), Ni(II) and Pd(II) metal complexes have been synthesized using the title schiff base ligand and characterized on the basis of analytical, magnetic and spectral data. The ligand coordinates through its oximino and azometine nitrogen atoms to the metal ions and acts as a neutral bidentate ligand. All complexes are non-electrolyte, high thermal stability and strong metal-ligand bond. On the basis of spectral and magnetic moment analysis, Fe(II) and Ni(II) complexes are high spin octahedral and Pd(II) is square planar geometry. On the basis of FT(IR) spectra of ligand and its all complexes, suggested that HBMHDAB ligand coordinated to metal ion through nitrogen atoms only. The proposed structure of metal complexes of HBMHDAB fallows;



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

V. ACKNOWLEDGMENTS

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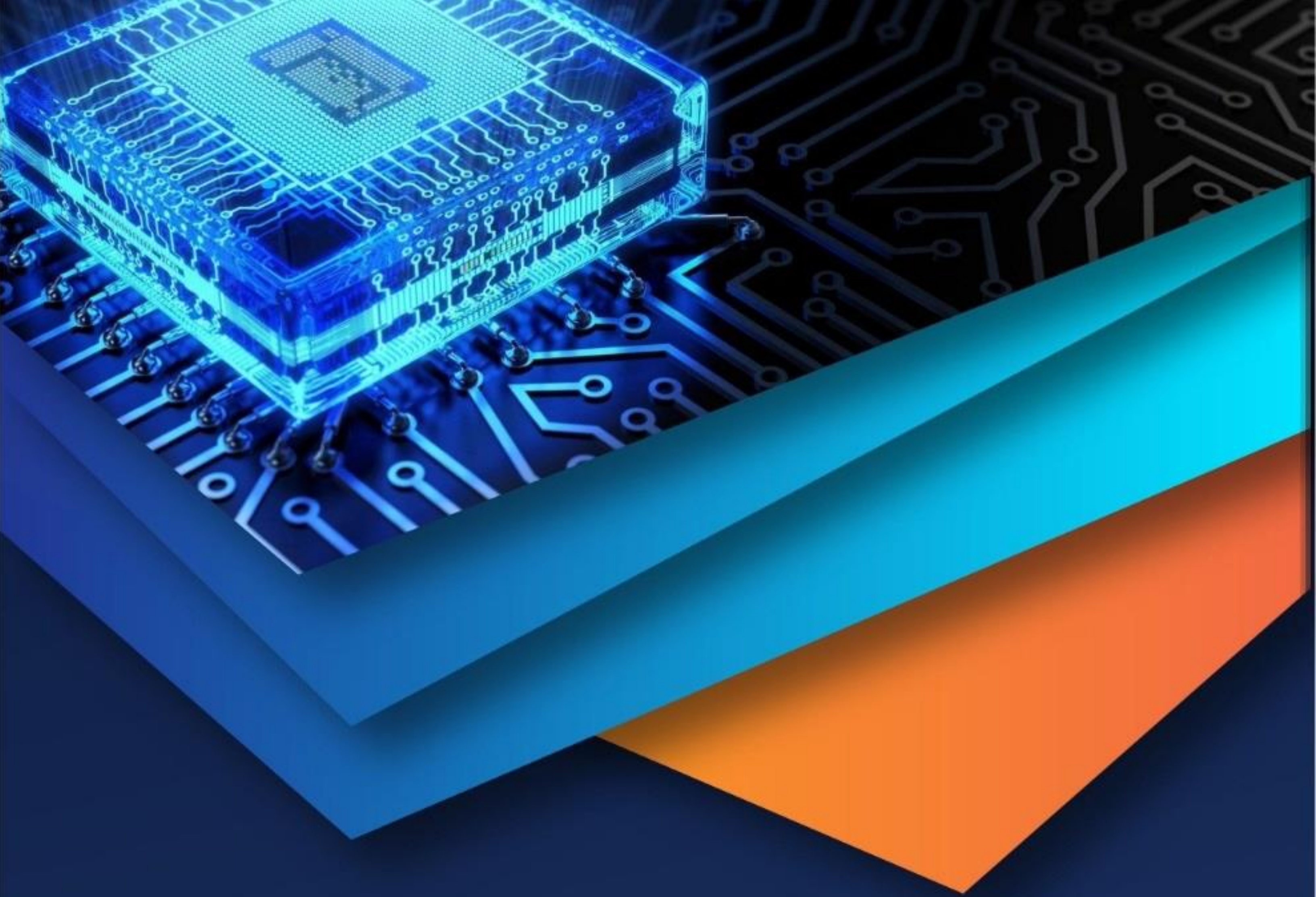

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