

Synthesis, Spectroscopic, And Magnetic Properties Of Some Transition Metal Complexes With 4-[(E)-{(2E)-[(3E)-3-(Hydroxyimino)Butan-2-Ylidene]hydrazinylidene}Methyl]Phenol

Dr. Sharad Sankhe^{1*}, Mr. Farhan Moosa²

^{1*,2}Department of Chemistry, Patkar-Varde College, Goregaon West, Mumbai-62, India.

Abstract

Complexes of diacetylmonoximehydrazide-4-hydroxybenzaldehyde (HDMHpHB) [IUPAC name: 4-[(E)-{(2E)-[(3E)-3-(hydroxyimino)butan-2-ylidene]hydrazinylidene}methyl]phenol] have been synthesized and characterized by elemental analyses, molar conductance, spectral (IR, visible, and NMR), and magnetic moment measurements. These complexes are Fe(II), Mn(II), Pd(II), Co(II), Ni(II), Cu(II), Zn(II), Hg(II), and Cd(II). Infrared spectra reveal that the ligand exhibits bidentate behavior. For the complexes [Fe(DMHpHB)₂], [Mn(DMHpHB)₂], [Ni(DMHpHB)₂], and [Cu(DMHpHB)₂] are high spin octahedral geometry, a square-planar structure is recommended for [Pd(DMHpHB)₂] complex and tetrahedral geometries for [Cd(DMHpHB)₂], [Hg(DMHpHB)₂], and [Zn(DMHpHB)₂] complexes.

Keywords: Diacetylmonoximehydrazide, 4-hydroxybenzaldehyde, elemental analyses, and molar conductance

INTRODUCTION

Oxime hydrazones [1-3] have an intriguing coordination chemistry since they combine donor sites like protonated/deprotonated oximino oxygen, an imine nitrogen of the hydrazone moiety, and an extra donor site (often N or O) supplied by the Schiff base [4-5]. Aspects of oxime complex coordination behavior that have been the subject of extensive structural studies are quite remarkable [6]. It has the potential to form coordination complexes with metal ions through the nitrogen and oxygen atoms, respectively. Therefore, it is capable of forming a proximate-bridged extended network [7-8]. The hydrogen atom of an oxime-OH group can create strong hydrogen bonds with other atoms or groups within or between molecules [9, 10]. Since metal complexes with non-deprotonated oximes can form extensive supramolecular networks through intermolecular hydrogen bonds, they can be regarded as supramolecular synthons. The dimensionality of the extended network is greatly affected by the orientation of the oxime group in these molecules [11]. Because of their biological effects, trivalent oxime-hydrazones have been the subject of much research into their coordination chemistry [12–15]. We synthesized Schiff bases of diacetylmonoximehydrazide with *p*-hydroxybenzaldehyde to examine their supramolecule-forming abilities. In this study, authors discuss the synthesis, characterization, and spectroscopic investigations of a few metal (II) complexes of the type [M(DMHpHB)₂] that were produced by reacting a *p*-hydroxybenzaldehyde derivative of diacetylmonoximehydrazide with metal (II) ions.

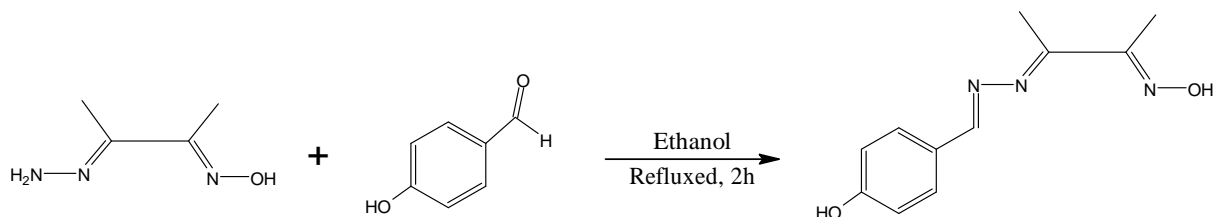
EXPERIMENTAL

Instrumentation

C, H, and N elemental studies were carried out using a PE 2400 Series II CHNSIO Analyzer. 10 mm quartz cells were used to record electronic spectra at room temperature using a UV JASCO V650 UV-spectrophotometer. KBr pellets were subjected to infrared spectra recording in the 4000–370 cm⁻¹ spectral region using a Brucker FT-IR Spectrometer. A Sherwood Scientific MSBMK I magnetic susceptibility balance was used to measure magnetic susceptibilities at room temperature. Using a Bruker spectrometer operating at 400 MHz, ¹H NMR measurements were made. PPMs are used to express chemical changes with respect to the internal TMS (tetramethylsilane).

Preparation of the Ligand

As previously reported, diacetylmonoximehydrazide-4-hydroxybenzaldehyde (HDMHpHB) was produced [16].



Preparation of the Metal Complexes

HDMHpHB (0.30 g, 1.2 mmol) and the hydrated metal salts (1.2 mmol), such as sulfates and chloride, were refluxed in 30 mL of ethanol or 15:15 mL of aqueous ethanol for two hours to prepare all the complexes. The resultant solid complexes were dried in a vacuum over CaCl_2 , filtered while still hot, and then rinsed with ethanol and diethyl ether.

RESULTS AND DISCUSSION

Table 1 lists the metal complexes' analytical and physical data. The complexes are soluble in DMSO, acetonitrile, nitrobenzene, and DMF, but fairly stable in air and insoluble in typical organic solvents. For every complex, the molar conductivities in the nitrobenzene solution (**Table 1**) at 25 °C fall within the range that suggests a non-electrolytic nature [17].

According to **Table 1** of the analytical results, the complexes showed stoichiometry of type ML_2 , where M stands for metal ions and L for Schiff base HDMHpHB ligand. The complexes showed color, were stable at room temperature, did not absorb moisture, and broke down when heated. Normal organic solvents also failed to dissolve the complexes, in addition to water. The complexes are not electrolytic, as evidenced by their low observed molar conductance values ($0.85\text{--}1.80\ \Omega^{-1}\text{ cm}^2\text{ mole}^{-1}$). The possibility of complex dissociation in nitrobenzene is refuted by these findings [18–19].

Table 1: Physical and Analytical data of HDMHpHB ligand and its metal complexes

Compound	Color	% Yield	MP/D P in °C	% Element Content, expected (Observed)					Molar Cond	Magnetic Moments
				C	H	N	O	M		
HDMHpHB	Yellow	78.67	198	60.26 (60.20)	5.98 (5.96)	19.17 (19.14)	14.60 (14.55)	-	-	-
[Fe(DMHpHB) ₂]	Blue	79.63	229	53.68 (53.30)	4.88 (4.83)	17.08 (17.00)	13.00 (12.90)	11.40 (11.33)	2.25	5.67
[Co(DMHpHB) ₂]	Brown	73.29	218	53.33 (52.93)	4.85 (4.70)	16.97 (16.67)	12.90 (12.75)	11.90 (11.87)	1.68	4.56
[Ni(DMHpHB) ₂]	Brown	76.89	226	53.37 (53.15)	4.85 (4.81)	16.98 (16.74)	12.90 (12.38)	11.90 (11.81)	0.50	3.31
[Pd(DMHpHB) ₂]	Orange	84.58	233	48.71 (48.61)	4.43 (4.38)	15.50 (15.33)	11.80 (11.73)	19.56 (19.43)	0.85	-
[Cu(DMHpHB) ₂]	Brown	79.44	220	52.85 (52.28)	4.80 (4.75)	16.82 (16.78)	12.80 (12.70)	12.70 (12.54)	1.71	2.12
[Mn(DMHpHB) ₂]	Brown	80.14	208	53.88 (53.56)	4.89 (4.70)	17.11 (16.90)	13.04 (12.71)	11.19 (11.03)	1.74	5.12
[Zn(DMHpHB) ₂]	Yellow	70.23	215	52.65 (52.44)	4.79 (4.71)	16.75 (16.66)	12.80 (11.66)	13.00 (12.98)	2.87	-
[Cd(DMHpHB) ₂]	Yellow	75.99	219	48.14 (48.03)	4.38 (4.35)	15.32 (15.31)	11.70 (11.61)	20.50 (20.17)	1.11	-
[Hg(DMHpHB) ₂]	Yellow	80.79	237	41.51 (41.46)	3.77 (3.71)	13.21 (13.19)	10.06 (10.02)	31.54 (31.45)	1.87	-

IR Spectra:

The FT(IR) spectra of the synthesized ligand and its complexes with Mn (II), Co (II), Ni (II), Pd (II), Cu (II), Zn (II), Hg (II), and Cd (II) transition metal ions are displayed in **Table 2**. A band at 3216 cm^{-1} , which is associated with phenolic -OH, was seen in the free HDMHpHB ligand FT(IR) spectra. The fact that this band moved downwards across the complexes shows that the phenolic OH group is engaged in bonding [20–21]. The title ligand's oximino -OH is responsible

for the prominent band observed at 3216 cm^{-1} . It was evident that the hydroxyl group had deprotonated during complexation [22] since this band was absent from all of the complexes. The $>\text{C}=\text{NN}-$ stretch of the azomethine group was responsible for the free ligand's noticeable band at 1590 cm^{-1} [23]. In all of the complexes, this band moved to the side with the lowest wavenumber, which means that the oxygen in the azomethine made connections with metal ions [24]. An intense band with a medium-to-strong intensity at 1512 cm^{-1} in the free ligand [25] was found to originate from the $\square(\text{C}=\text{NO})$ stretch of the oximino group. The coordination of the Schiff base to the metal ions through the nitrogen atom [26] is expected to cause a decrease in the electron density in the azomethine link and the $>\text{C}=\text{N}-$ stretching absorption frequency. All of the complexes now have this band on the lower wavenumber, which means that oximino nitrogen is coordinating with metal ions [27]. The new weak intensity nonligand bands observed in the complex's spectra in $532\text{--}607\text{ cm}^{-1}$ and $511\text{--}527\text{ cm}^{-1}$ are caused by the stretching frequencies of the $\square(\text{M}-\text{O})$ and $\square(\text{M}-\text{N})$ bonds, respectively.

Table 2: FT(IR) spectral bands of the ligand (HDMHpHB) and its metal complexes (cm^{-1}):

Assignments	HDMH pHB	Fe(II)	Co(II)	Ni(III)	Pd(II)	Cu(II)	Mn(II)	Zn(II)	Cd(II)	Hg(II)
Oximino -OH	3294	-	-	-	-	-	-	-	-	-
Phenolic -OH	3216	3293	3340	3352	3211	3342	3295	3384	3300	3302
-CH=	2926	2930	3018	2976	2933	2977	2935	2978	2947	2957
vC=NN	1590	1550	1513	1512	1511	1512	1509	1509	1513	1517
vC=NO	1512	1503	1448	1441	1448	1442	1471	1488	1491	1467
vN-N	968	1017	978	1009	1001	1076	1003	1002	1000	967
vO→M	-	513	527	517	-	511	512	-	-	-
vM-N	-	581	607	610	525	561	555	532	595	530
vM→N	-	519	560	533	512	525	548	506	534	509

Electronic absorption spectra:

At room temperature, in a freshly developed chloroform solution, the electronic absorption spectra of all the HDMHpHB ligand and their metal complexes were measured. Shown in **Table 3** are the HDMHpHB ligand field parameters and spectral data. The electronic spectra of the Fe(II) complex showed an absorption band at 597 nm, which is characteristic of the $^5\text{T}_{2g} \rightarrow ^5\text{E}_g$ transition in an octahedral environment [28]. It is possible to observe bands 900 and 609 nm in the electronic spectra of the Co(II) complex. The $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{A}_{2g}(\text{F})$ (\square_2) and $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{P})$ (\square_3) transitions are responsible for these two bands in an octahedral geometry [20]. The instrument's limited range prevented us from seeing the lowest band, \square_3 , but we were able to calculate it using the band-fitting approach proposed by Underhill and Billing [30]. Three absorption bands at 978, 580, and 490 nm were seen in the Ni(II) complex in an octahedral setting; these bands correspond to the $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\square_1)$, $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{F})$ (\square_2) and $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{P})$ (\square_3) transitions, respectively.

A square-planar geometry surrounding the palladium (II) ion is indicated by this complex's electronic spectra [31]. A single broad asymmetric band between 625 and 447 nm was seen in the Cu(II) complex, which exhibited a light green hue. The breadth of the band indicates that there is just one broad absorption band, which is the result of an identically energy-transferred transition: $^2\text{T}_{2g} \rightarrow ^2\text{E}_g$. Jahn-Teller's distortion in motion can be the source of the band's breadth. Based on these findings, the octahedral geometry surrounding the Cu(II) ion is distorted. The octahedral Mn(II) complex transitions $^6\text{A}_{1g} \rightarrow ^4\text{T}_{1g}(\text{F})$, $^6\text{A}_{1g} \rightarrow ^4\text{E}_g(\text{D})$, $^6\text{A}_{1g} \rightarrow ^4\text{T}_{1g}(\text{P})$, and $^6\text{A}_{1g} \rightarrow ^4\text{E}_g(\text{G})$ are corresponding to weak absorption bands at 754nm (\square_1), 515nm (\square_2), 393nm (\square_3), and 282nm (\square_4), respectively, and indicate octahedral geometry. A magnetic moment in the range of 5.12 B.M. [32] is displayed by the complex. The electronic spectra of the complexes with Zn(II) show bands at 383 and 278 nm, whereas those with Cd(II) and Hg(II), respectively, show bands at 362 and 278 nm. Possible origin of these bands33: metal-to-ligand charge transfer.

Table 3: UV-visible spectral data of HDMHpHB ligand and its Ln(III) metal complexes

Compound	λnm	$\epsilon\text{ (dm}^3\text{/mol/cm)}$	Transition
HDMHpHB	317	12664	$\pi^* \leftarrow \pi$
	276	7980	$\pi^* \leftarrow \pi$
	245	7198	$\pi^* \leftarrow \pi$
[Fe(DMHpHB)₂]	597	3	$^5\text{T}_{2g} \leftarrow ^5\text{E}_g$
[Co(DMHpHB)₂]	900	721	$^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{A}_{2g}(\text{F})$
	609	814	$^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{P})$
[Ni(DMHpHB)₂]	978	596	$^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{F})$
	580	5499	$^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{P})$
[Pd(DMHpHB)₂]	380	347	$^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$
	321	587	$^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$
	283	1058	$^1\text{A}_{1g} \rightarrow ^1\text{E}_g$

[Cu(DMHpHB) ₂]	625	319	² B _{1g} → ² A _{1g} (v ₁)
	447	536	² B _{1g} → ² B _{2g} (v ₂)
	365	947	² B _{1g} → ² E _g (v ₃)
[Mn(DMHpHB) ₂]	754	356	⁶ A _{1g} → ⁴ T _{1g} (⁴ G)
	515	963	⁶ A _{1g} → ⁴ E _g (⁴ D)
	393	1056	⁶ A _{1g} → ⁴ T _{1g} (⁴ P)
	282	3547	⁶ A _{1g} → ⁴ E _g (G)

PMR spectra:

The synthesized ligand was characterized by the ¹H NMR (400 MHz and ppm) in DMSO-d₆. The spectra all corroborate the ligand structure that has been suggested. The ligand that was synthesized exhibited distinct NMR signals in its ¹H NMR spectrum. A singlet at 11.59 ppm is observed in the ¹H NMR spectra of the prepared ligand, which is attributed to the oximino-OH proton. It was determined that the oximino group engaged in complexation via deprotonation because this band vanished in produced diamagnetic metal complexes. At 11.21 ppm, the proton that is diagnostic of phenol was detected. At 9.08 ppm, you may detect the CH signal. Aromatic protons are those that fall within the 6.44-7.19 ppm range.

Table 4: PMR spectrum of HDMHpHB and its metal complexes in d₆ DMSO

Compound	Oximino -OH	Phenolic -OH	-CH=	Phenyl Ring	-CH ₃
HDMHpHB	11.59	11.21	9.08	6.44-7.19	2.39
[Pd(DMHpHB) ₂]	-	10.56	7.99	7.47-7.53	2.53
[Zn(DMHpHB) ₂]	-	10.69	8.02	6.99-7.53	2.54
[Cd(DMHpHB) ₂]	-	10.66	9.03	7.01-7.38	2.49
[Hg(DMHpHB) ₂]	-	10.58	9.00	7.08-7.42	2.53

Conclusion:

Diacetylmonoximehydrazide and 4-hydroxybenzaldehyde were mixed to synthesize the new ligand. The reactions of metal salts with certain ions resulted in the formation of complexes of different colors. The synthesized compounds were defined by measuring their elemental abundance, physicochemical properties, FTIR, NMR, UV-Vis, and molar conductivity. The complexes have different shapes depending on the elements they are made of, for Pd(II) complexes, the shapes could be square planar, for Zn (II), Hg(II), and Cd(II) complexes, tetrahedral, and for Fe(II), Mn(II), Co(II), Ni(II), and Cu(II) complexes, octahedral. All of the synthesized metal compounds were found to be mononuclear.

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