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Synthesis, Complexation And Spectral Study Of Benzilmonoximehydrazide-M-Bromobenzaldehyde Ligand

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ABSTRACT

In this newly approached method a novel series of transition metal complexes were synthesized by the reaction of 3-bromobenzaldehyde react with benzilmonoximehydrazide in ethanolic solution under refluxed condition. Mononuclear complexes were synthesized by reaction with Fe(II), Zn(II), Cd(II) and Hg(II) metal salts. The complexes were characterized by elemental analysis, electronic absorption, FT(IR) and PMR spectral studies.

Keywords: benzilmonoximehydrazide, metals, complexes, elemental analysis and 3-bromobenzaldehyde

1. INTRODUCTION

In recent years, the chemistry of coordination compounds has shown rapid development in diverse disciplines as a result of possible use of these new compounds in biological applications. Transition metal complexes with potential biological activity are the main focus of extensive investigation. The biological importance of oximes and their complexes is very well known. Metal complexes with ligands containing nitrogen, sulfur and oxygen donor atoms have act as the fungicidal agents. Synthesis of oximes, and their complexes with different transition metals are reported in the literature¹⁻⁹ and found to be active as antibacterial, antitubercular⁸, antilepral¹⁰, antiviral¹¹, antimalarial¹² and active against certain kinds of tumours^{13,14}. In this paper, a novel series of transition metal complexes with oxime were synthesized.

2. EXPERIMENTAL METHODS

The chemicals such as 3-bromobenzaldahyde, ferrous sulfate, cadmium chloride, mercury chloride and zinc chloride were procured from s. d. chem. Melting points were observed in open capillaries and were uncorrected. FT(IR) spectra of all compounds were recorded in Perkin-Elmer spectrum 100 using KBr pellets. Electronic absorption spectra were recorded on JASCO 650 spectrophotometer using methanol/0.1N NaOH solvents for ligands and methanol/ chloroform solvents for all metal complexes. Bohr magnetic properties recorded at The Institute of Science, Madam Kama road, Mumbai using Gouy electromagnetic balance at 4 amp and 6 amp at room temperature using Hg[Co(SCN)₄] and Ni(en)₃S₂O₃] as a calibrant. The diamagnetic corrections were made by Pascal's constant¹⁵. PMR spectra were recorded a Brucker AV300 NMR spectrometer using TMS an internal standard.

Synthesis of benzilmonoximehydrazide-m-bromobenzaldehyde

The ethanolic solution of 3-bromobenzaldehyde (12.5 mM) was refluxed with benzilmonoximehydrazide (10 mM) add the glacial acetic acid for 10h, the volume of the solution was reduced to one third. On cooling, a white solid was separated, filtered and recrystallised from ethanol.

Synthesis of complexes with the ligand

An ethanolic solution of the ligand (20 mM) was refluxed with FeSO₄ (10 mM) for ~ 8h. The mixture was kept at room temperature for ~24h, a microcrystalline complex was separated. It was filtered under suction, and the crystals were washed with cold ethanol and finally with anhydrous diethyl ether and kept in a desiccators over fused CaCl₂. The other complexes were also precipitated by a similar procedure in ethanol medium.

3. RESULTS AND DISCUSSION

Metal (II) salts react with α -benzilmonoximehydrazone-m-bromobenzaldehyde ligand in 1:2 molar ratios in alcoholic medium. The ligand and its complexes are stable at room temperature, indicated they are thermally stable and strong metal-ligand bond and they are also non-hygroscopic. The ligand is soluble in common polar organic solvents, such as ethanol, methanol, nitrobenzene and chloroform. The Schiff base complexes are relatively well soluble in DMF and DMSO. The synthesized ligand and its complexes were characterized by elemental analysis, spectra, and molar conductivity measurements. The geometry of the newly synthesized compounds has been elucidated based on their elemental analysis, molar conductivity and spectral data. The values of molar conductance, suggest that all prepared complexes are non-electrolytes in nature.

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			M.P.	Elemental Analysis				Magnetic	Electrical	
			/						Moments	Conductance
Compound	Color	Yield	Dec.p	% M	% C	% H	% N	%0	(B.M.)	10 ⁻³ M(in DMF)
		%	oint ^o	Found	Found	Found	Found	Found		mhos
			С	(Calcd)	(Calcd)	(Calcd)	(Calcd)	(Calcd)		
HBMHmBB	Yellow	77.64	222		62.08	3.97	10.34	3.94	7.7	-
					(61.71)	(3.90)	(10.22)	(3.90)		
	Blue	75.22	265	6.45	58.17	3.46	9.69	3.69	5.41	1.33
Fe(BMHmBB) ₂				(6.11)	(58.09)	(3.38)	(9.61)	(3.61)		
					· · · · · · · · · · · · · · · · · · ·					
Pd(BMHmBB) ₂	Green	73.65	255	11.56	54.96	3.27	9.16	3.49	-	1.89
				(11.43)	(54.90)	(3.20)	(9.11)	(3.42)		
Zn(BMHmBB) ₂	Yellow	74.55	256	7.47	57.54	3.42	9.59	3.65	-	0.96
				(7.21)	(57.49)	(3.37)	(9.49)	(3.62)		
Cd(BMHmBB) ₂	Yellow	73.96	275	12.18	54.61	3.25	9.10	3.47	-	1.79
				(12.11)	(54.60)	(3.19)	(9.00)	(3.42)		
Hg(BMHmBB) ₂	Green	77.26	280	19.84	49.85	2.97	8.31	3.17	-	0.45
				(19.66)	(49.71)	(2.90)	(8.11)	(3.11)		

Table 1: Analytical and physical data of the ligand and its metal complexes.

Infrared spectra

The infrared spectrum of free ligand shown broad band at 3239 cm⁻¹ which correspond to –OH group of oxime, this broad band is disappearing in its metal complexes, indicated ligand coordinated to metal ion through oximino nitrogen. The sharp band at 1605 cm⁻¹ which correspond to >C=NO group of oxime. The FT(IR) frequency of all the complexes was shifted to higher frequencies for to >C=NO group of oxime group to metal. The FT(IR) frequency at 1605 cm⁻¹ had indicated the existence of –C=NN-azomethine group. The FT(IR) spectra of all metal complexes of –C=N group of azomethine had also

shifted to higher frequencies and it was shown the existence of coordinate bond formation with metals through nitrogen atom of azomethine group¹⁵.

Compound	υ(O-H)	Ar(C=C)	Ar. C-H	C=NN	C=NO	N - O	N-N	M-N
HBMHmBB	3229	3154	3110	1605	1545	1067	1154	-
Fe(BMHmBB) ₂	-	3155	3111	1671	1593	1010	1155	520, 548
Pd(BMHmBB) ₂	-	3150	3109	1669	1594	1007	1153	507, 525
Zn(BMHmBB) ₂	-	3175	3107	1670	1594	1008	1154	515, 551
Cd(BMHmBB) ₂	-	3133	3110	1672	1595	1006	1142	512, 538
Hg(BMHmBB) ₂	-	3149	3115	1673	1595	1009	1138	509, 525

Table 2: FT(IR) data of the ligand and its metal complexes

Magnetic Moments

Magnetic measurements of the complexes are measured at room temperature. The Fe(II) complex magnetic moment μ_{eff} value is 5.41 suggest the octahedral geometry^{8,14}. Pd(II) complex is dimagnetic and suggest square planer geometry but that Zn(II), Cd(II) and Hg(II) complexes are zero magnetic moment of the tetrahedral geometries.

Electronic Spectra

The electronic absorption spectra of the ligand and its complexes were recorded in chloroform solution in the range of 200 to 900 nm regions and the data are presented in **Table-3**. The electronic spectra of the Fe(II) complex in chloroform solution shows absorption bands at 566 and 478nm. The first band may be assigned to ${}^{6}A_{1} \rightarrow {}^{4}A_{1} {}^{4}E(G)$, transition, while the second band would be due to ${}^{6}A_{1} \rightarrow {}^{4}T_{2(G)}$ transition, suggesting an octahedral arrangement around the Fe(II) ion^{18,20}.

The Pd(II) complex, displays two bands at 521 and 450 nm assigned to metal to ligand charge transfer transitions of 4-coordinate square planar geometry²¹. The Zn(II), Cd(II) and Hg(II) complexes are observed two absorption bands in the region 572-611nm and 357-396nm, typical of a 4-coordinate tetrahedral geometry and is assigned to ${}^{3}T_{1(F)} \rightarrow {}^{3}T_{1(P)}$ and ${}^{3}T_{1} \rightarrow {}^{3}A_{2}$ transitions^{8,14}.

Table-3 : UV-Visible spectral data of HBMHmBB ligand and its metal complexes							
Compound	λnm	ε (dm ³ /mol/cm)	Probable Transition				
HBMHmBB	339	12723	$\pi \rightarrow \pi^*$				
	249	20905	$\pi { ightarrow} \pi^*$				
[Fe(BMHmBB) ₂]	566	1005	$^{6}A_{1} \rightarrow {}^{4}A_{1} {}^{4}E(G)$				
	478	1965	$^{6}A_{l} \rightarrow {}^{4}T_{2(G)}$				
[Pd(BMHmBB) ₂]	521	1167	MLCT				
	450	20634	MLCT				
[Zn(BMHmBB) ₂]	572	2964	MLCT				
[Cd(BMHmBB) ₂]	608	3156	${}^{3}T_{1(F)} \rightarrow {}^{3}T_{1(P)}$				
	595	2156	${}^{3}T_{1} \rightarrow {}^{3}A_{2}$				
[Hg(BMHmBB) ₂]	611	288	${}^{3}T_{1(F)} \rightarrow {}^{3}T_{1(P)}$				
	590	24537	$^{3}T_{1} \rightarrow ^{3}A_{2}$				

Nuclear magnetic resonance spectral studies:

The PMR spectra have provide the evidence for the structural characteristics of the oxime ligand. The PMR chemical shift at 8.50 ppm with sharp singlet had indicated the presence of aldehydic proton. The spectrum of the title ligand and its metal complexes exhibited multiplet signals at 7.0-7.70ppm due to aromatic protons¹⁸. In addition, the spectrum of the title ligand showed a singlet signal at 10.50 ppm due to the hydrogen of the –OH group, which is disappearing in all synthesized complexes. Indicated that this proton deprotonated during complexation.

Table-4: PMR spectrum of 3-Bromobenzaldehyde derivatiove of α-Benzilmonoximehydrazone ligands

Compound	-OH	-CH=	Phenyl Ring
HBMHmBB	10.50	8.50	7.0-7.70
Pd(BMHmBB) ₂	-	8.40	7.0-7.70
Zn(BMHmBB) ₂			
	-	8.50	7.0-7.70
Cd(BMHmBB) ₂		00	
	-	8.60	7.0-7.70
Hg(BMHmBB) ₂	-	8.35	7.0-7.70

Conclusion

In this paper new Schiff Base ligand complexes with the general formula $[ML_2 \text{ where Ligand}=L, M= Fe(II), Zn(II), Cd(II) and Hg(II) were synthesized. The molar conductivity of the complexes in nitrobenzene solution was non-electrolyte and the configurations were performed to coordinate the Schiff base through the nitrogen atoms of azomethine and oximino group. Therefore, from the presented results the complexes have tetrahedral for Zn(II), Cd(II), Hg(II) complexes, square planer with Pd(II) complex and octahedral geometry with Fe(II) configuration. On the basis of magnetic and spectral data, structure of Fe(II), Pd(II), Zn(II), Cd(II) and Hg(II) complexes tentatively assigned as;$



Where M = Pd(II), Zn(II), Cd(II), Hg(II)

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