

Synthesis, Spectroscopic, and Biological Studies of Complexes of Unsymmetrical Thiosemicarbohydrazide ligand

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Abstract- A new unsymmetrical p-fluorobenzaldehyde derivative of α -benzilmonoximethiosemicarbohydrazide (HBMTSpFB) ligand is prepared via condensation of α -benzilmonoximethiosemicarbohydrazide and p-fluorobenzaldehyde in the 1:1 ratio. Metal complexes of Fe(II), Co(II), Cu(II), Zn(II), Hg(II) and Ni(II) have been prepared. These prepared compounds were characterized by physicochemical study, PMR, FT(IR), electronic absorption, and magnetic moment, and the purity of the HBMTSpFB ligand was analyzed by thin layer chromatography study. All prepared compounds are color-solid, air-stable, and soluble in common organic solvents. On the basis of elemental analysis metal to ligand and stoichiometry is 1:2 ratio for all complexes. Comparison of the FT(IR) spectra of the HBMTSpFB ligand and its trivalent metal complexes confirm that the HBMTSpFB ligand is a monobasic, tridentate ligand towards the central trivalent metal ion with an ONS and sequence.

Keywords- α -Benzilmonoxime, thiosemicarbohydrazide, metal complex, magnetic moments, and tridentate ligand.

I. INTRODUCTION

Thiosemicarbohydrazide transition metal complexes are of interest particularly to inorganic chemists because their chemical, spectral, and structural properties are dependent strongly on the nature of the structure of ligands¹⁻⁵. The substituted ketones coordination complexes have shown diverse structural and generating properties, a stereochemistry variety, and a wide range of interactions bonding⁶. The symmetrical coordination complex's construction interest in reacting trivalent transition metal ions with tridentate has been constantly growing over the years⁷⁻⁸. Within this increased knowledge and understanding lies molecular self-assembly, complexation of metal ligands, and metal binding sites disposition⁹.

By mastering these areas, improved new systems related to the field of bio-engineering¹⁰, supramolecular chemistry¹¹, and catalysis¹² can be achieved due to this coordination of complex applications. The preparation and characterization of some symmetrical tridentate thiosemicarbohydrazide-based ligand complexes have been thoroughly studied but less study comparatively seems to have been done on complexes of unsymmetrical thiosemicarbohydrazide derived from α -benzilmonoxime¹³. A review of the literature revealed that no work has been done on trivalent transition metal complexes of the unsymmetrical thiosemicarbohydrazide bases ligand derived from p-fluorobenzaldehyde and α -

benzilmonoximethiosemicarbohydrazide. The complexes of Fe(II), Co(II), Cu(II), Zn(II), Hg(II), and Ni(II) with this HBMTSpFB ligand are also synthesized in the solid state and characterized by various physico-chemicals and spectral techniques.

Experimental:

All required chemicals and solvents of AR grade and used as received. All metal chlorides were of S. D. fine Chemicals and used as received.

Synthesis of HBMTSpFB ligand:

The α -benzilmonoximethiosemicarbohydrazide was prepared by the reported method¹³. The HBMTSpFB ligand was synthesized by the following method. A mixture of α -benzilmonoximethiosemicarbohydrazide (29.3g, 0.10mol) and p-fluorobenzaldehyde (18.6g, 0.15mol) in ethanol was refluxed for about 15h. The reaction mixture was cooled to 301K and the yellow-colored solid was separated, filtered, and washed with hot distilled water and then dried over anhydrous calcium chloride under vacuum.

Preparation of metal complexes:

To a hot alcoholic solution of 25ml of HBMTSpFB ligand (2 mol), an aqueous solution of 15ml of the desired metal (II) chloride (1 mol) was added by constant stirring. The final reaction mixture was refluxed for 3 h, and on cooling to 301K the color for separation, was filtered, washed with hot distilled water, and then dried over anhydrous calcium chloride.

II. RESULTS AND DISCUSSION

Physical measurement:

Carbon, hydrogen, nitrogen, and sulfur elements analyses were obtained by using a Thermo-fining FLASH-1112 series analyzer. The FT(IR) spectra of the prepared compounds were recorded on a Perkin-Elmer-100 FT(IR) spectrometer using KBr pellets. PMR spectra were obtained using JEOL (Japan) ECZR-series 600MHz spectrometer deuterated dimethyl sulfoxide solvent. The electronic absorption spectra were recorded on a JASCO V650 spectrophotometer (double beam). The room temperature magnetic moments were measured by Gouy's method using calibrants as Hg[Co(NCS)₄] and the diamagnetic corrections were made using the Pascal constant. The electrical conductivity measurements of prepared trivalent metal complexes at room temperature were measured by ELICO-CM 180 conductivity meter.

The physical-chemical and analytical data of the HBMTSpFB ligand and its trivalent metal complexes are listed in Table 1. Prepared compounds are colored, non-hygroscopic, and soluble in common organic solvents. Thus, it can be concluded that the HBMTSpFB ligand behaves as a monobasic, tridentate ligand coordinating via the nitrogen atoms of the oximino and azomethine groups and the Sulphur atom of the thiosemicarbohydrazide group¹⁴⁻¹⁵. Molar conductivity studies of the prepared trivalent metal complexes at room temperature in nitrobenzene (10⁻³ M) suggest that non-electrolytic in nature¹⁶⁻¹⁷.

Table 1: Physico-chemical and analytical data of HBMTSpFB ligand and its metal complexes

Comp	Color	MW	% Yield	MP/DP	Element Content							Cond	MM
					M	C	H	N	O	S	F		
HAMTSpFB	Yellow	404.46	73.57	189	-	65.33	4.24	13.85	3.96	7.93	4.70	-	-
Fe(AMTSpFB) ₂	Blue	862.76	81.26	208	6.47	61.20	3.71	12.98	3.71	7.42	2.20	1.29	5.49
Co(AMTSpFB) ₂	Brown	867.91	80.99	207	6.80	60.84	3.69	12.90	3.69	7.37	2.19	4.25	4.37
Ni(AMTSpFB) ₂	Brown	867.61	75.89	202	6.76	60.86	3.69	12.91	3.69	7.38	2.19	2.21	3.14
Cu(AMTSpFB) ₂	Green	872.47	81.98	207	7.28	60.52	3.67	12.84	3.67	7.34	2.18	1.49	1.95
Zn(AMTSpFB) ₂	Yellow	874.31	80.79	208	7.48	60.39	3.66	12.81	3.66	7.48	2.17	2.35	-
Hg(AMTSpFB) ₂	Yellow	1008.92	82.56	207	19.88	52.33	3.17	11.10	3.17	6.34	1.88	1.56	-

FT(IR) spectra:

To study the HBMTSpFB ligand bonding mode to the trivalent metal ions in the coordination complexes. The prepared trivalent metal complex's FT(IR) spectra were interpreted by comparing the free HBMTSpFB ligand spectrum as shown in Table 2. The broadband revealed at 3140cm⁻¹ FT(IR) spectra of HBMTSpFB ligand due to oximino $\square(-OH)$ group, disappeared this band in all prepared trivalent metal complexes, suggesting the coordination of HBMTSpFB ligand through oximino nitrogen via deprotonation¹⁸. The bands at 1516 and 1500cm⁻¹ due to azomethine $\square(>C=NN-)$ and oximino $\square(>C=NOH)$ groups respectively shifted their position to lower frequencies on complexation¹⁹⁻²⁰. The $\square(NH)$ band of 3260cm⁻¹ does not change its position after complexation. In addition, all the divalent metal complexes displayed the new bands in the region 552-584 and 513-517cm⁻¹ were assigned to $\square(M-N)$ and $\square(M-S)$ vibrations respectively²¹⁻²².

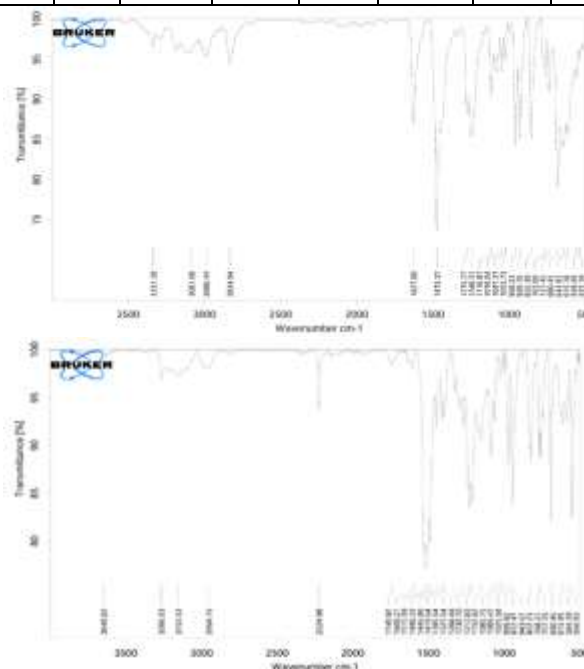


Figure 1: FT(IR) spectrum of HBMTSpFB ligand and its complex

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

Comp	-OH	-NH-	-CH=	>C=NN-	>C-NOH	C-F	C-S	N→M	S→M
HAMTS _p FB	3140	3260	2971	1516	1500	1212	1252	-	-
Fe(AMTS _p FB) ₂	-	3266	2954	1510	1490	1230	1210	584	550
Co(AMTS _p FB) ₂	-	3265	2994	1514	1491	1233	1222	619	551
Ni(AMTS _p FB) ₂	-	3267	3060	1518	1492	1236	1217	553	513
Cu(AMTS _p FB) ₂	-	3266	3055	1485	1438	1238	1216	552	522
Zn(AMTS _p FB) ₂	-	3266	2979	1516	1493	1232	1226	552	-
Hg(AMTS _p FB) ₂	-	3263	2979	1520	1493	1236	1221	517	-

III. ELECTRONIC SPECTRA AND MAGNETIC PROPERTIES

Table 3 shows that the HBMTSpFB ligand's electronic spectra feature two prominent broad bands at 265 and 283 nm. Two absorption bands are observed for Schiff bases because of their diastereomeric (keto and imine) structure^{23, 24}. All the complexes exhibit a band of elevated energy absorption between 445 and 285 nm. This change is attributable to the charge transfer band²⁵⁻²⁶.

The effective magnetic moment of the Fe(II) complex is 5.49 BM, which is consistent with the presence of five unpaired electrons in the octahedral structure. The electronic spectra of the iron(II) complex revealed absorption bands at 585nm that correspond to the ${}^5T_{2g} \rightarrow {}^5E_g$ electronic transition, indicating the presence of an octahedral iron(II) complex²⁷⁻²⁸.

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The cobalt(II) complex exhibits the *d-d* transition bands at 900, 635, and 435 nm in its electronic spectrum. These transitions correspond to the ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ν_1 , the ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ν_2 , and the ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ ν_3 , respectively²⁹⁻³⁰. The transitions correspond to the complexes' octahedral geometry. The nickel (II) complex exhibits three *d-d* transition bands at 970, 620, and 529 nm in its absorption spectrum. The transitions correspond, respectively, to the ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ν_1 , ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ν_2 and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ ν_3 . These transitions demonstrate the nickel complex has an octahedral structure and *D_{4h}* symmetry³¹⁻³².

For the Co(II) and Ni(II) complexes, the ligand field parameters Racah inter-electronic repulsion parameter B, ligand field

splitting stabilization energy 10 Dq, covalency factor, and ligand field stabilization energy (LFSE) have been calculated. Using the ν_3/ν_1 ratio, the values of B and Dq of Co(II) complexes were calculated from the transition energy ratio diagram. The value of **Table 4** accounts for the covalent nature of the complexes under study containing the evaluated parameters. Cu(II) complex exhibited two absorptions at 686 and 490 nm, which correspond to ${}^2B_{1g} \rightarrow {}^2E_g$ versus ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transitions, corresponding to a deformed octahedral geometry surrounding copper(II)³³⁻³⁴.

The complex's spectrum displays three bands due to three *d-d* spin-allowed transitions. These are the transitions between the three lower d orbitals and the vacant $d_{x^2-y^2}$ orbital. The ground state is ${}^1A_{1g}$, and the excited states corresponding to the above transitions are, in order of increasing energy, ${}^1A_{2g}$, ${}^1B_{1g}$, and ${}^1E_{1g}$. **Table 3** displays three *d-d* transition bands at 392, 319, and 283 nm. These bands are attributed to the transitions ${}^1A_{1g} \rightarrow {}^1A_{2g}$, ${}^1A_{1g} \rightarrow {}^1B_{1g}$, and ${}^1A_{1g} \rightarrow {}^1E_{1g}$, respectively. These complexes' electronic spectra indicate a square planar geometry.

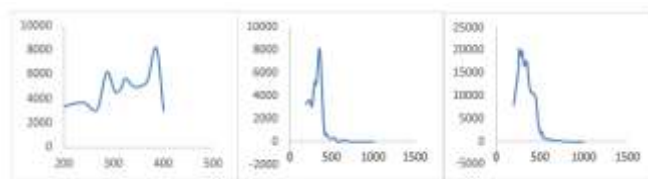


Figure 2: Electronic spectral data of HBMTSpFB ligand and its metal complexes

Table 3: Electronic spectral data of HBMTSpFB ligand and its metal complexes

Compound	λ nm	Transition
HAMTS _p FB	265	$\pi \rightarrow \pi^*$
	283	$\pi \rightarrow \pi^*$
Fe(AMTS _p FB) ₂	585	${}^5T_{2g} \rightarrow {}^5E_g$
	442, 368, 273	L → M charge transfer
Co(AMTS _p FB) ₂	~900	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1)

Ni(AMTSpFB) ₂	635	${}^4T_{1g(F)} \rightarrow {}^4T_{2g(P)} (v_2)$
	970	${}^3A_{2g(F)} \rightarrow {}^3T_{2g(F)} (v_1)$
	620	${}^3A_{2g(F)} \rightarrow {}^3T_{1g(F)} (v_2)$
Cu(AMTSpFB) ₂	686	${}^2B_{1g} \rightarrow {}^2A_{1g} (v_1)$
Zn(AMTSpFB) ₂	392, 307, 384	L → M charge transfer
Hg(AMTSpFB) ₂	373, 330, 285	L → M charge transfer

NMR Spectra:

The ligand HBMTSpFB and its metal complexes in DMSO-d₆ are shown in Table 4, along with their respective ¹H NMR spectra (ppm). D₂O neutralizes the acidic oximino -OH protons (□12.494 ppm) in the HBMTSpFB ligand, suggesting that the hydroxyl group participates in metal ion interaction. ligand HBMTSpFB ¹H-NMR spectrum shows a singlet at □10.56 ppm (s, 1H, Ar-NH), and one singlet at □8.09 ppm (s, 1H, -CH=), caused by a methyl group attached to the azomethine group, as well as multiplets at □7.472-7.919ppm. Due to the absence of the oximino -OH proton in the Hg(II) complex, the spectrum of the HBMTSpFB ligand displays a broad signal. The absence of this signal indicates that this proton was lost during complexation, and oxygen coordination has occurred 35-36. The multiplets in the region □7.472-7.919ppm ppm due to aromatic protons, the singlet in the region □10.56 ppm due to the Ar-NH group, and the singlet in the region □8.09 ppm due to -CH= protons of the ring do not change in the metal complexes, indicating that these groups are not involved in coordination (□).

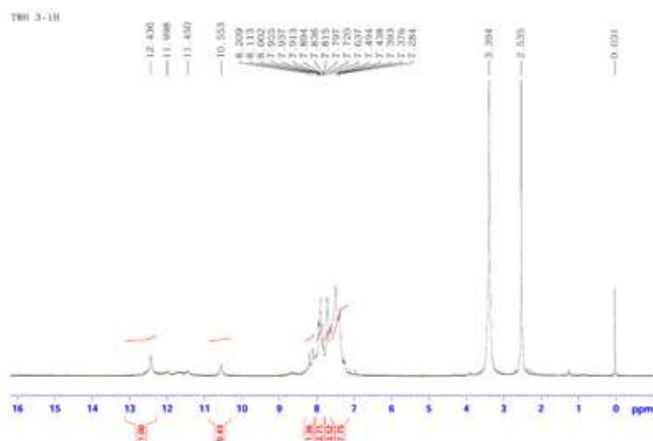


Figure 3: ¹H NMR spectrum of HBMTSpFB ligand

IV. CONCLUSION

Analytical, IR, electronic, magnetic, and magnetic moments all pointed to the HBMTSpFB ligand's binding to metal. The present study revealed that HBMTSpFB, a Schiff base, was monobasic tridentate concerning transition metal ions. The

tetrahedral geometry was attributed to the Zn(II), and Hg(II) complexes, while the octahedral geometry was allocated to the Co(II), Cu(II), Ni(II), and Fe(II) complexes were determined by analytical and physicochemical research. Based on spectral studies, the structures of complexes are assigned as follows;

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

Where M = Zn(II) and Hg(II)

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