

## "Synthesis, And Characterization Of Several Transition Metal Complexes Derived From $\alpha$ -Benzilmonoximethiosemicarbohydrazide And *m*-Chlorobenzaldehyde."

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### Abstract

Several complexes derived from thiosemicarbohydrazide, specifically  $\alpha$ -benzilmonoximethiosemicarbohydrazide-*m*-chlorobenzaldehyde (HBMTSmCB) and its complexes with Fe(II), Ni(II), Cu(II), and Co(II), have been synthesized and meticulously characterized. The characterization employed a range of analytical techniques including elemental analysis, conductivity measurements, and magnetic susceptibility assessments. Spectroscopic methods such as Proton Magnetic Resonance (PMR), Fourier Transform Infrared (FTIR) spectroscopy, and electronic absorption spectra were also utilized to elucidate the structural and bonding characteristics of these complexes. It was determined that all trivalent metal complexes synthesized exhibit octahedral geometries.

**Keywords:** Octahedral geometry,  $\alpha$ -benzilmonoximethiosemicarbohydrazide, and *m*-chlorobenzaldehyde.

### 1. Introduction:

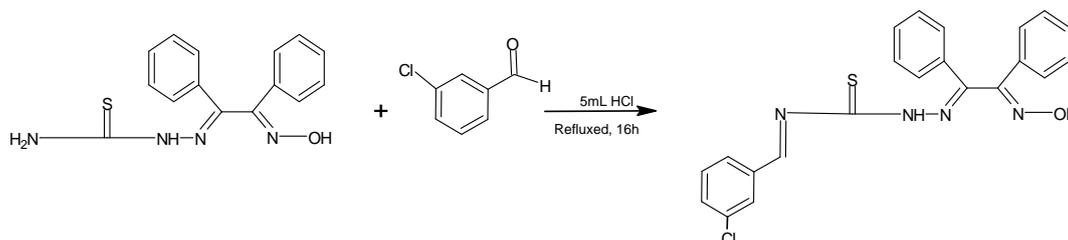
Thiosemicarbohydrazide and its derivatives are extensively used in synthesizing inorganic ligands and their complexes with transition and inner transition metals [1-3]. Thiosemicarbohydrazide-based compounds are synthesized by condensation with amino groups, allowing the introduction of amino functionalities at various positions within the thiosemicarbohydrazide framework [4-5]. The ligands derived from thiosemicarbohydrazide contain multiple donor atoms, including nitrogen (N), oxygen (O), and sulfur (S). Depending on the ligand structure, these donor sites exhibit diverse topologies and coordination modalities [6-8]. The formation of a wide range of complexes has been well-documented, and thiosemicarbohydrazide motifs are noted for their antimicrobial properties [9-10]. The biological activity of thiosemicarbohydrazide-based ligands and complexes is influenced by the chemical groups attached to the carbon atom of the (>C=S) group [11-13]. These compounds exhibit antiviral [14], anti-HIV [15], antifungal [16], antibacterial [17], anti-inflammatory [18], and anticancer properties [19]. The choice of metal ions can enhance the biological characteristics of these complexes compared to the unbound ligands. Metal ions such as Fe(II), Ni(II), Cu(II), and Co(II) are essential trace elements found in metalloenzymes, where they function as catalysts. This study focuses on the synthesis and characterization of Schiff bases formed by the reaction of *m*-chlorobenzaldehyde with  $\alpha$ -benzilmonoximethiosemicarbohydrazide-*m*-chlorobenzaldehyde (HBMTSmCB), as well as their respective complexes with Fe(II), Ni(II), Cu(II), and Co(II).

### 2. Experimental:

All chemicals were procured from S. D. Fine Chem and used without further purification. These chemicals included commercially available *m*-chlorobenzaldehyde, chloroform, ethanol, nitrobenzene, copper chloride, ferrous chloride, cobalt chloride, and nickel chloride. Thiosemicarbohydrazide was synthesized following a previously reported procedure. The concentrations of carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and chlorine (Cl) were analyzed using specialized instrumentation. Fourier Transform Infrared (FTIR) spectra were recorded by preparing KBr disc samples and using a Bruker FT-IR spectrometer. The molar conductance of the metal complexes in a 10<sup>-3</sup> M solution was measured at 301K with a conductivity meter equipped with a conductivity cell in nitrobenzene. The electronic spectra were obtained using a JASCO V650 UV-visible spectrophotometer at room temperature.

#### 2.1. Synthesis of the HBMTSmCB ligand:

*m*-Chlorobenzaldehyde (10 mmol) and  $\alpha$ -benzilmonoximethiosemicarbohydrazide (10 mmol) were subjected to reflux in ethanol for 16 hours. Upon cooling, a yellow precipitate formed, which was subsequently collected through filtration. The resulting yellow solid was thoroughly washed with distilled water and then dried under vacuum conditions.



Scheme 1: Preparation of HBMTSmCB ligand

## 2.2. Synthesis of the complex:

An ethanolic solution of the HBMTSmCB ligand (10 mmol) was combined with an ethanolic solution of the corresponding metal chloride (0.1 mol) to produce a suspension. This mixture was then refluxed for 3-5 hours. Upon cooling, the resulting precipitate was filtered, thoroughly washed with hot distilled water, and subsequently dried under vacuum conditions.

## 3. Results and discussion:

The reaction between  $\alpha$ -benzilmonoximethiosemicarbohydrazide and m-chlorobenzaldehyde in a 1:1 molar ratio yields the HBMTSmCB ligand, which is isolated as a yellow powder following condensation. When an ethanolic solution of a metal(II) chloride is combined with the HBMTSmCB ligand in a 1:2 molar ratio, a solid of specific coloration is formed. The development of these compounds was supported by elemental analysis and various physicochemical studies. The composition of all synthesized compounds was confirmed through spectroscopic investigations.

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

Comp	Color	MW	% Yield	MP	Element Content						Cond	MM	
					M	C	H	N	Cl	O			S
HBMTSmCB	Yellow	120	73.65	189	-	62.78	4.07	13.31	8.42	3.80	7.62	-	-
Fe(BMTSmCB) <sub>3</sub>	Blue	895	80.66	213	6.24	58.95	3.95	12.50	3.96	3.57	7.15	0.35	5.61
Co(BMTSmCB) <sub>2</sub>	Brown	900	73.47	219	6.55	58.61	3.55	12.43	3.94	3.55	7.10	1.33	4.66
Ni(BMTSmCB) <sub>2</sub>	Green	900	69.98	212	6.52	58.63	3.55	12.44	3.94	3.55	7.11	2.78	3.25
Cu(BMTSmCB) <sub>2</sub>	Green	905	71.71	227	7.02	58.32	3.53	12.37	3.92	3.53	7.07	5.73	2.00

### 3.1. FT(IR) spectrum:

Table 2 presents the infrared spectra of the Schiff base ligands and their corresponding metal complexes. This table elucidates the coordination sites of the metals involved in chelation by comparing the infrared spectrum of the free HBMTSmCB ligand with those of its complexes. The infrared spectral analysis of the Schiff base HBMTSmCB ligand revealed an -OH absorption band at 3293 cm<sup>-1</sup> [21-22]. The absence of this band in the metal complexes indicates that the oxygen in the Schiff base ligand has been chelated. Additionally, the -NH<sub>2</sub> bands present in the infrared spectra of o-chlorobenzaldehyde and  $\alpha$ -benzilmonoximethiosemicarbohydrazide were not observed in the Schiff base ligand, replaced instead by a new band at 1543 cm<sup>-1</sup> attributed to the azomethine ( $\nu$ (CH=N)) group. This band indicates the condensation of the aldehyde moiety of o-chlorobenzaldehyde and the amino group of thiosemicarbohydrazide.

The coordination of metals with the ligands resulted in a shift of the azomethine group's band to a lower frequency, mapping the coordination of the nitrogen atoms in this group. In the infrared spectra, faint bands at 511–545 cm<sup>-1</sup>, 547–576 cm<sup>-1</sup>, and 609–622 cm<sup>-1</sup> were observed, corresponding to the stretching vibrations of N→M, N→M, and O→M bonds, respectively. These bands signify the chelation of the metals with the nitrogen atom in the azomethine group and the coordination with the oxygen atom in the oximino anions group [23-24].

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

Comp	-OH	-NH	-CH=	>C=NN-	>C=NO	C=S	C-Cl	O-M	N→M	S→M
HBMTSmCB	3293	3133	2989	1543	1517	1211	833	-	-	-
Fe(BMTSmCB) <sub>3</sub>	-	3138	2969	1517	1499	1196	831	609	547	511
Co(BMTSmCB) <sub>2</sub>	-	3131	2983	1522	1493	1195	830	622	576	545
Ni(BMTSmCB) <sub>2</sub>	-	3135	2982	1532	1496	1190	830	613	570	519
Cu(BMTSmCB) <sub>2</sub>	-	3130	2983	1529	1497	1191	827	617	553	543

### PMR spectra:

The Proton Magnetic Resonance (PMR) spectrum of the HBMTSmCB ligand, recorded in deuterated dimethyl sulfoxide (d<sub>6</sub> DMSO), exhibits a broad signal at  $\delta$  10.63 ppm in the HBMTSmCB ligand, which is attributed to the oximino -OH

group. Additionally, the signals observed at  $\delta$  8.13 ppm and  $\delta$  12.53 ppm are assigned to the  $>C=N-NH-$  and  $-CH=$  groups, respectively, of the thiosemicarbohydrazone moiety.

**Table 3:**  $^1H$  NMR spectral data of HBMTSmCB ligand and its metal complexes

Comp	-OH	-NH	-CH=	Aromatic Protons
HBMTSmCB	10.63	12.53	8.13	7.47-8.06

#### Electronic absorption spectra:

The Co(II) complex spectrum displayed peaks at 289 nm and 353 nm attributable to ligand field effects, while the absorption at 393 nm was ascribed to charge transfer phenomena. Additional peaks observed at 659 nm, 746 nm, and 799 nm corresponded to electronic transitions of the types  $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ ,  $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ , and  $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ , respectively. In the Ni(II) complex, the absorption spectrum revealed a peak at 257 nm arising from ligand field interactions. Three further peaks observed at 387 nm, 544 nm, and 777 nm were attributed to electronic transitions of type  $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$  involving charge transfer,  $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ , and  $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ , respectively.

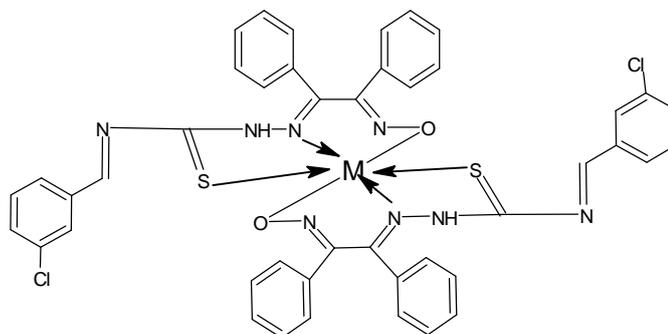
The electronic absorption spectrum of the  $[Cu(BMTmCB)_2]$  complex in chloroform solution exhibited an absorption band at 639 nm. The complex exhibited a magnetic moment value of 2.00 BM, confirming its distorted octahedral geometry. The observed electronic band was assigned as a  $^3E_g \rightarrow ^3T_{2g}$  transition.

**Table 4:** Electronic spectral data of HBMTSmCB ligand and its metal complexes

Compound	$\lambda_{nm}$	Transition
HBMTSmCB	277	$\square\square\square\square$
	313	$\square\square\square\square$
Fe(BMTSmCB) <sub>2</sub>	587	$^5T_{2g} \rightarrow ^5E_g$
	444, 369, 274	L $\rightarrow$ M charge transfer
Co(BMTSmCB) <sub>2</sub>	799	$^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ ( $\nu_1$ )
	746	$^4T_{1g}(F) \rightarrow ^4T_{2g}(P)$ ( $\nu_2$ )
	659	$^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ ( $\nu_3$ )
Ni(BMTSmCB) <sub>2</sub>	289, 353, 393	L $\rightarrow$ M charge transfer
	777	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ ( $\nu_1$ )
	544	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ ( $\nu_2$ )
Cu(BMTSmCB) <sub>2</sub>	257, 387	L $\rightarrow$ M charge transfer
	639	$^2E_g \rightarrow ^2T_{2g}$ ( $\nu_1$ )

#### Conclusion:

This study focuses on the synthesis of Schiff bases through the condensation reaction of  $\alpha$ -benzilmonoximethiosemicarbohydrazone with m-chlorobenzaldehyde. These Schiff bases are capable of coordinating with several transition metals such as Fe(II), Ni(II), Cu(II), and Co(II) using the oximino oxygen and nitrogen atoms of the azomethine group. The resulting complexes exhibit two distinct geometries. However, based on various spectral analyses including infrared spectroscopy, nuclear magnetic resonance, and chemical shift spectroscopy, octahedral geometry has been suggested for the Ni(II), Fe(II), and Co(II) complexes. These complexes are electrically neutral and non-electrolytic, as indicated by their low molar conductance values.



**Scheme 2:** Where M = Fe(II), Ni(II), Cu(II), and Co(II)

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