

Synthesis, Characterization and Biological Studies of Some Transition Metal Complexes of α - Benzilmonoximethiosemicarbohydrazide-O- Chlorobenzaldehyde

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Abstract- Some thiosemicarbohydrazide derived α - benzilmonoximethiosemicarbohydrazide - o chlorobenzaldehyde (HBMTSoCB) and its Fe(II), Ni(II), Cu(II), Zn(II), Hg(II), and Co(II) complexes have been synthesized and analyzed. These analytical (elemental analysis, physical conductivity, and magnetic susceptibility measurements) and spectral (PMR, FT(IR), and electronic absorption spectra) properties were used to infer the complex structures and bonding in nature. All prepared trivalent metal complexes have octahedral geometries. Antibacterial activities against two gram-positive species, *S. aureus* (MCC 2408) and *B. subtilis* (MCC 2010), and two gram-negative species, *P. aeruginosa* (MCC 2080) and *E. coli* (MCC 2412), as well as in vitro antifungal activities against *Candida albicans* (MCC 1439), and *Saccharomyces cerevisiae* (MCC 1039).

Keywords: Electronic spectra, α -benzilmonoximethiosemicarbohydrazide, and o-chlorobenzaldehyde.

I. INTRODUCTION

Thiosemicarbohydrazide and its derivatives have extensive use in synthesizing inorganic ligands and their complexes with transition and inner transition metals¹⁻³. Thiosemicarbohydrazide-based compounds are synthesized by condensing with an amino group and introducing an amino group to various regions of the thiosemicarbohydrazide group⁴⁻⁵. The ligands produced from thiosemicarbohydrazide have many donor atoms, including nitrogen (N), oxygen (O), and sulfur (S). These donor sites can vary depending on the ligand and exhibit diverse topologies, with the coordination occurring in multiple modalities⁶⁻⁸. The generation of numerous complexes is extensively documented. Thiosemicarbohydrazide motifs are recognized for their antimicrobial properties⁹⁻¹⁰. The biological

action of thiosemicarbohydrazide-based ligands and complexes is determined by the chemical group linked to the carbon atom of the (>C=S) group¹¹⁻¹³. They possess antiviral¹⁴, anti-HIV¹⁵, antifungal¹⁶, antibacterial¹⁷, anti-inflammatory¹⁸, and anticancer¹⁹ properties. The choice of metal ions can enhance the biological characteristics of the complexes in comparison to the unbound ligand.

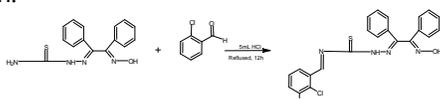
The metal ions Fe(II), Ni(II), Cu(II), Zn(II), Hg(II), and Co(II) are vital trace elements found in metalloenzymes, where they can serve as catalysts. This study focuses on the synthesis, and characterization of Schiff bases formed by combining o-chlorobenzaldehyde with α -benzilmonoximethiosemicarbohydrazide-o-chlorobenzaldehyde (HBMTSoCB), along with their respective complexes with Fe(II), Ni(II), Cu(II), Zn(II), Hg(II), and Co(II).

1. Starting Materials and Instrumentation:

All chemicals were obtained from S. D. Fine Chem and used without undergoing any purification: commercially available o-chlorobenzaldehyde, chloroform, ethanol, nitrobenzene, copper chloride, ferrous chloride, zinc chloride, mercuric chloride, cobalt chloride, and nickel chloride. The thiosemicarbohydrazone is synthesized using a reported procedure²⁰. The analysis of carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and chlorine (Cl) concentrations was conducted using specialized instruments. The FT(IR) spectra were obtained by recording KBr disc samples using the Bruker FT-IR spectrometer. The molar conductance of the metal complex in a 10⁻³ M solution was determined at 301K using a conductivity meter equipped with a conductivity cell in nitrobenzene. The electronic spectra were measured using a JASCO V650 UV-visible spectrophotometer at the standard temperature of the room.

2. Synthesis of the HBMTSoCB Ligand:

O - Chlorobenzaldehyde (10 mmol) and α -benzilmonoximethiosemicarbohydrazone (10 mmol) was refluxed during 12h in ethanol. On cooling a yellow-colored precipitate appeared and was collected by filtration. The yellow-colored solid was washed with distilled water and dried under a vacuum.



Scheme 1: Preparation of HBMTSoCB ligand

3. Synthesis of the Complex:

An ethanolic solution of HBMTSoCB ligand (10 mmol) was mixed with an ethanolic solution of the appropriate metal chloride (0.1mol) to give a suspension. The resulting mixture refluxed for 3-5 hours on cooling the precipitate was filtered and washed with hot distilled water, and dried under vacuum.

II. RESULTS AND DISCUSSION

1. General Study:

The reaction between α -benzilmonoximethiosemicarbohydrazone and o-chlorobenzaldehyde in a 1:1 molar ratio produces

the HBMTSoCB ligand, which is obtained as a yellow powder after condensation. When an ethanolic solution of metal (II) chloride is mixed with the HBMTSoCB ligand at a molar ratio of 1:2, a solid of a certain hue is formed. The elemental analysis and physicochemical research facilitated the development of the compounds. The formulation of all produced compounds was validated using spectroscopic investigations.

Table 1: Physico-chemical and analytical data of

Comp	Color	MW	% Yield	MP	Element Content								
					M	C	H	N	Cl	O	S		
HBMTSoCB	Yellow	120	77.81	183	-	62.78	4.07	13.31	8.42	3.80	7.62	-	-
Fe(BMTSoCB) ₃	Blue	895	83.47	209	6.24	58.95	3.95	12.50	3.96	3.57	7.15	2.11	5.65
Co(BMTSoCB) ₂	Brown	900	79.09	210	6.55	58.61	3.55	12.43	3.94	3.55	7.10	2.27	4.69
Ni(BMTSoCB) ₂	Green	900	83.14	207	6.52	58.63	3.55	12.44	3.94	3.55	7.11	0.72	3.17
Cu(BMTSoCB) ₂	Green	905	79.46	213	7.02	58.32	3.53	12.37	3.92	3.53	7.07	3.27	2.04
Zn(BMTSoCB) ₂	Yellow	907	77.18	207	7.21	58.20	3.53	12.35	3.91	3.53	7.05	2.28	-
Hg(BMTSoCB) ₂	Yellow	1041	80.56	215	19.25	50.68	3.07	10.36	6.81	3.07	6.14	0.89	-

2. FT(IR) Spectrum:

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

Comp	-O H	-N H	-C H =	>C =N N	>C =N O	C =S	C -Cl	O -M	N →M	S →M
HBM TSoC B	3 2 6 5	3 1 3 7	2 9 8 8	1 5 3 5	1 5 1 0	1 2 2 9	8 2 9	-	-	-
Fe(B MSo CB) ₃	-	3 1 4 3	2 9 6 6	1 5 1 2	1 4 9 2	1 1 5	8 3 0	6 1 9	5 7 2	5 1 5
Co(B MSo CB) ₂	-	3 1 4 3	2 9 9 6	1 5 1 2	1 4 9 2	1 1 5	8 3 0	6 1 8	5 7 0	5 4 2
Ni(B MSo CB) ₂	-	3 1 4 3	2 9 9 7	1 5 1 2	1 4 9 2	1 1 5	8 3 1	6 1 8	5 7 3	5 1 0
Cu(B MSo CB) ₂	-	3 0 5 8	2 9 9 2	1 5 1 5	1 4 4 1	1 2 0	8 4 7	6 0 6	5 5 9	5 2 3
Zn(B MSo CB) ₂	-	3 1 4 3	2 9 9 7	1 5 1 2	1 4 9 2	1 2 4	8 3 0	6 1 8	5 7 3	-
Hg(B MSo CB) ₂	-	3 1 5 5	2 9 6 5	1 5 1 9	1 4 9 3	1 2 4	8 3 5	6 2 0	5 4 0	-

Table 2 displays the spectra of Schiff base ligands and the complexes they form. The coordination sites of the metals that could be involved in chelation are described in this table by comparing the infrared spectrum of the free HBMTSoCB ligand with those of its complexes. The Schiff base HBMTSoCB ligand infrared spectral analysis revealed the presence of a -OH absorption band at 3265 cm⁻¹. When complexed with metals, this band is absent, which indicates that the oxygen in the Schiff base ligand has been chelated²¹⁻²². Unlike o-chlorobenzaldehyde and α-benzilmonoximethiosemicarbohydrazide, the -NH₂ bands seen in the infrared spectra of Schiff base ligand were not present. The presence of

azomethane (CH=N) was instead attributed to a new band at 1535 cm⁻¹. The presence of this band in the Schiff base ligand suggests that the aldehyde moiety of o-chlorobenzaldehyde and the amino group of the thiosemicarbohydrazide under study are condensed. The coordination of metals with ligands caused a shift in the azomethane group's band to a lower frequency, which mapped out the coordination of the nitrogen atoms in the group. In the infrared spectra, there are faint bands at 510–542, 540-573, and 606-620 cm⁻¹, which represent the stretching vibrations of the N•M, N•M, and O–M bonds, respectively. These bonds describe the chelation of the studied metals with the nitrogen atom in the azomethane group, as well as the coordination of the metals with the oxygen atom in the oximino anions group²³⁻²⁴.

3. PMR Spectra:

The PMR spectra of the HBMTSoCB ligand and its Zn(II), and Hg(II) complexes recorded in d₆ DMSO reveal of broadband signal at 10.59ppm in HBMTSoCB ligand assigned as oximino -OH group disappeared in its metal complexes, suggested that HBMTSoCB ligand coordinated to metal ion via deprotonated oximino proton. The signals at 8.09 and 12.48ppm are assigned to the >C=N-NH- and -CH= transitions respectively of the thiosemicarbohydrazide moiety.

Table 3: 1H NMR spectral data of HBMTSoCB ligand and its metal complexes

Comp	-OH	-NH	-CH=	Aromatic Protons
HBMTSoCB	10.592	12.481	8.090	7.377-8.054
Zn(BMSoCB) ₂	-	11.410	8.195	7.430-8.063
Hg(BMSoCB) ₂	-	11.602	8.212	7.424-7.914

III. ELECTRONIC ABSORPTION SPECTRA

The Co(II) complex spectra exhibited peaks at 275 nm and 322 nm as a result of the ligand field. The peak observed at a wavelength of 389 nm was

attributed to charge transfer. Three further peaks were observed at wavelengths of 643 nm, 737 nm, and 786 nm. These peaks can be attributed to electronic transitions of the $4T_{1g}(F) \rightarrow 4T_{1g}(P)$, $4T_{1g}(F) \rightarrow 4A_{2g}(F)$, and $4T_{1g}(F) \rightarrow 4T_{2g}(F)$ types, respectively. The absorption spectrum of the Ni (II) complex exhibited a peak at 233 nm, which can be attributed to the ligand field. Additionally, three other peaks were observed at 366 nm, 539 nm, and 776 nm, corresponding 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 25-26. The electronic absorption spectrum of [Cu(BMTmCB)₂] complex in chloroform solution exhibited that at 630nm. The magnetic moment value of this complex is 2.04 BM, which confirms the distorted octahedral geometry of this complex. The observed electronic band is assigned as $3E_g \rightarrow 3T_{2g}$ transition. The Zn (II) and Hg(II) complexes exhibited absorption peaks at the region 330-340 nm and 380-390 nm in their spectra, which can be attributed to charge transfer. The lack of absorption peaks in the visible area suggests the absence of any (d-d) electronic transitions, which is a favorable outcome for a complex with octahedral geometry 27-28.

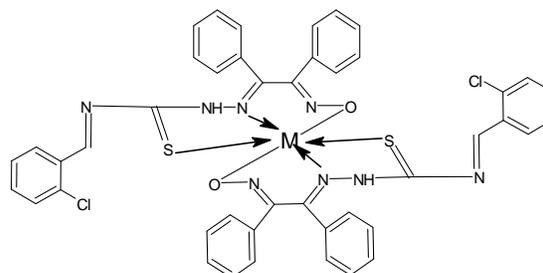
Table 4: Electronic spectral data of HBMTSoCB ligand and its metal complexes

Compound	λ nm	Transition
HBMTSoCB	265
	283
Fe(BMTSoCB) ₂	585	$^5T_{2g} \rightarrow ^5E_g$
	442, 368, 273	L → M charge transfer
Co(BMTSoCB) ₂	786	$^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ (ν_1)
	737	$^4T_{1g}(F) \rightarrow ^4T_{2g}(P)$ (ν_2)
	643	$^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ (ν_3)
	275, 322, 359	L → M charge transfer
Ni(BMTSoCB) ₂	776	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ (ν_1)
	539	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ (ν_2)
	233, 366	L → M charge transfer
Cu(BMTSoCB) ₂	630	$^2E_g \rightarrow ^2T_{2g}$ (ν_1)
Zn(BMTSoCB) ₂	330, 380	L → M charge transfer
Hg(BMTSoCB) ₂	340, 390	L → M charge transfer

IV. CONCLUSION

The primary objective of this article is on the process of synthesizing Schiff bases, which involves the

condensation of α -benzil- mono - xime thiosemi carbohydrazide with o-chlorobenzaldehyde. A number of transition metals, including Fe(II), Ni(II), Cu(II), Zn(II), Hg(II), and Co(II), can be coordinated with the synthesized Schiff bases by means of the oximino oxygen and nitrogen of the azomethane group. For these complexes, two distinct geometric kinds have been suggested. The initial geometries indicated that the Zn(II), and Hg(II) complexes were tetrahedral. Utilizing several spectral studies such as infrared, nuclear magnetic resonance, and chemical shift spectroscopy, octahedral geometry has been suggested for Ni(II), Fe(II), Fe(II), and Co(II) complexes. The complexes are neutral and non-electrolyte based on their low molar conductance.



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

REFERENCES

1. Kumar, G., Devi, S., & Johari, R. (2012). Synthesis and spectral characterization of Schiff base Cr (III), Mn (III), and Fe (III) novel macrocyclic complexes derived from thiocarbohydrazide and dicarbonyl compound. *Journal of Chemistry*, 9, 2255-2260.
2. Chachkov, D. V., & Mikhailov, O. V. (2011). The relative stability of macrotricyclic metal complexes in M (II)-thiocarbohydrazide-acetone (M= Mn, Fe, Co, Ni, Cu, Zn) ternary systems according to the data of quantum-chemical calculations. *Russian Journal of Physical Chemistry A*, 85, 152-155.
3. Shebl, M., Khalil, S. M., & Al-Gohani, F. S. (2010). Preparation, spectral characterization and antimicrobial activity of binary and ternary Fe (III), Co (II), Ni (II), Cu (II), Zn (II), Ce (III) and UO₂ (VI) complexes of a thiocarbohydrazone ligand. *Journal of Molecular Structure*, 980(1-3), 78-87.
4. Momidi, B. K., Tekuri, V., & Trivedi, D. R. (2017). Multi-signaling thiocarbohydrazide based

- colorimetric sensors for the selective recognition of heavy metal ions in an aqueous medium. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 180, 175-182.
- Mosa, A. I., Emara, A. A., Yousef, J. M., & Saddiq, A. A. (2011). Novel transition metal complexes of 4-hydroxy-coumarin-3-thiocarbohydrazone: Pharmacodynamic of Co (III) on rats and antimicrobial activity. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 81(1), 35-43.
 - Fouad, R., Shaaban, I. A., Ali, T. E., Assiri, M. A., & Shenouda, S. S. (2021). Co (ii), Ni (ii), Cu (ii) and Cd (ii)-thiocarbonohydrazone complexes: Spectroscopic, DFT, thermal, and electrical conductivity studies. *RSC advances*, 11(60), 37726-37743.
 - Asadollahi, P., Bikas, R., Krawczyk, M. S., Siczek, M., & Lis, T. (2022). The effect of azide and thiocyanate anions on the coordination mode of thiocarbohydrazone ligand in preparing Mn (II) coordination compounds. *Inorganic Chemistry Research*, 6(1), 17-25.
 - Aly, A. A., Hassan, A. A., & AbdEl-latif, E. S. S. (2018). An update of the use of thiocarbohydrazides and thiosemicarbazides in the preparation of heterocycles and their biological importance. *Journal of Heterocyclic Chemistry*, 55(10), 2196-2223.
 - Demirbas, N., Demirbas, A., Karaoglu, S. A., & Celik, E. (2005). Synthesis and antimicrobial activities of some new [1, 2, 4] triazolo [3, 4-b][1, 3, 4] thiadiazoles and [1, 2, 4] triazolo [3, 4-b][1, 3, 4] thiadiazines. *Arkivoc*.
 - Ramadan, S. K., & El-Helw, E. A. (2018). Synthesis and antimicrobial activity evaluation of some novel heterocycles derived from chromonyl-2 (3 H)-furanone. *Journal of Chemical Research*, 42(6), 332-336.
 - Dzah, C. S., Duan, Y., Zhang, H., Wen, C., Zhang, J., Chen, G., & Ma, H. (2020). The effects of ultrasound assisted extraction on yield, antioxidant, anticancer and antimicrobial activity of polyphenol extracts: A review. *Food Bioscience*, 35, 100547.
 - Santos, J. D., Branco, A., Silva, A. F., Pinheiro, C. S., Neto, A. G., Uetanabaro, A. P., ... & Osuna, J. T. (2009). Antimicrobial activity of Agave sisalana. *African Journal of Biotechnology*, 8(22).
 - Azaz, D., Demirci, F., Satil, F., Kürkçüoğlu, M., Hüsni, K., & Başerb, C. (2002). Antimicrobial activity of some Satureja essential oils. *Zeitschrift für Naturforschung C*, 57(9-10), 817-821.
 - Abbas, S. Y., Farag, A. A., Ammar, Y. A., Atrees, A. A., Mohamed, A. F., & El-Henawy, A. A. (2013). Synthesis, characterization, and antiviral activity of novel fluorinated isatin derivatives. *Monatshefte für Chemie-Chemical Monthly*, 144, 1725-1733.
 - Hassan, A. A., & Makhlof, M. M. (2018). Thiazolidine-4-ones from Thiocarbohydrazides. *Journal of Heterocyclic Chemistry*, 55(11), 2480-2506. Zhang, X., Lei, P., Sun, T., Jin, X., Yang, X., & Ling, Y. (2017). Design, synthesis, and fungicidal activity of novel thiosemicarbazide derivatives containing piperidine fragments. *Molecules*, 22(12), 2085.
 - Kaushik, N., Kumar, N., Kumar, A., & Sharma, V. (2021). Synthesis and Biological Activity of 3-(substitutedphenyl)-6-(4-methoxy phenyl)-7H-[1, 2, 4] triazolo [3, 4-b][1, 3, 4] thiadiazine: Part II. *Anti-Infective Agents*, 19(2), 162-168.
 - Rubčić, M., Pisk, J., Pičuljan, K., Damjanović, V., Lovrić, J., & Vrdoljak, V. (2019). Symmetrical disubstituted carbohydrazides: From solid-state structures to cytotoxic and antibacterial activity. *Journal of Molecular Structure*, 1178, 222-228.
 - Ahmed, M. S., Metaib, A. T., & Al-Ghabban, S. L. (2022). TRIAZOLOTHIADIAZOLES DRIVED FROM IBUPROFEN AND THIOCARBOHYDRAZIDE: Synthesis, Characterization, docking studies, and Preliminary Pharmacological assessment. *Journal of Pharmaceutical Negative Results*, 111-119.
 - Narkhede, H. I., Dhake, A. S., & Surana, A. R. (2022). Synthesis and screening of thiosemicarbazide-dithiocarbamate conjugates for antioxidant and anticancer activities. *Bioorganic Chemistry*, 124, 105832.
 - Sawant, D. C., Pingale, S. G., & Deshmukh, R. G. (2008). Stability studies of some transition metal chelates of alpha-benzilmonoximethiosemicarbazone. *Asian Journal of Chemistry*, 20(3), 2464.

21. Zhao, G. J., & Han, K. L. (2007). Novel infrared spectra for intermolecular dihydrogen bonding of the phenol-borane-trimethylamine complex in electronically excited state. *The Journal of chemical physics*, 127(2).
22. Smidt, E., Eckhardt, K. U., Lechner, P., Schulten, H. R., & Leinweber, P. (2005). Characterization of different decomposition stages of biowaste using FT-IR spectroscopy and pyrolysis-field ionization mass spectrometry. *Biodegradation*, 16, 67-79.
23. Norman, J. J. (1962). OXIMES: II. The infrared spectra of some complex oximes. *Canadian Journal of Chemistry*, 40(10), 2023-2029.
24. Wahba, M. A., El-Saied, F. A., Al-Hakimi, A. N., & Shakdofa, M. M. (2017). Preparation, Characterization and Antimicrobial Activities of N'-(3-(hydroxyimino) butan-2-ylidene)-2 (phenylamino) acetohydrazide and Its Metal Complexes. *Egyptian Journal of Chemistry*, 60(1), 124.
25. Yu, X., Wang, N., He, H., & Wang, L. (2014). Theoretical investigations of the structures and electronic spectra of Zn (II) and Ni (II) complexes with cyclohexylamine-N-dithiocarbamate. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 122, 283-287.
26. Angelusiu, M. V., Barbuceanu, S. F., Draghici, C., & Almajan, G. L. (2010). New Cu (II), Co (II), Ni (II) complexes with aroyl-hydrazone based ligand. Synthesis, spectroscopic characterization and in vitro antibacterial evaluation. *European journal of medicinal chemistry*, 45(5), 2055-2062.
27. Chai, L. Q., Tang, L. J., Chen, L. C., & Huang, J. J. (2017). Structural, spectral, electrochemical and DFT studies of two mononuclear manganese (II) and zinc (II) complexes. *Polyhedron*, 122, 228-240.
28. Mobin, S. M., Saini, A. K., Mishra, V., & Chaudhary, A. (2016). A series of new heteroleptic Hg (II) complexes: synthesis, crystal structures and photophysical properties. *Polyhedron*, 110, 131-141.