



Synthesis, Spectral and Antibacterial Studies of Fe(III), Cr(III), Mn(III), Ti(III) and Pt(IV) complexes derived from benzilmonoximethiocarbohydrazide and *o*- bromobenzaldehyde

Dr. Uttam Yadav, Dr. Nazar Abbas Jafry, Dr. Sharad Sankhe, Dr. Prashant Kamble

Abstract

A new thiocarbohydrazide based N'' -{(E)-(2-bromophenyl)methylidene}- N''' -{(1E,2E)-2-(hydroxyimino)-1,2-diphenylethylidene} thiocarbohydrazide prepared by condensing benzilmonoximethiocarbohydrazide and *o*-bromobenzaldehyde. Its complexes of Fe(III), Cr(III), Mn(III), Ti(III), and Pt(IV) are produced and described using physicochemical studies, elemental analysis, PMR, electronic absorption, and FT(IR) spectrum data. The spectral data suggested that coordination of thiocarbohydrazide based ligand with central metal ion through azomethine and oximino groups nitrogen atoms and sulfur atom of thiocarbo group. The produced ligand and its transition metal complexes are screened against gramme negative and positive bacteria utilising the disc diffusion technique, which reveals that the components have better antibacterial comparable to the thiocarbohydrazide base ligand against the bacteria tested.

Keywords: Thiocarbohydrazide, Benzilmonoxime, *o*-Bromobenzaldehyde, Metal complexes, Biological activity.

Introduction:

Thiocarbohydrazide is described by condensation between hydrazine hydrate and carbondisulfide¹. Thiocarbohydrazide is good ligands as are able to coordinates with transition metals through azomethine and oximino nitrogen and thiocarbo sulfur atoms²⁻³. Thiocarbohydrazides are important class of ligand in coordination chemistry⁴⁻⁵. Thiocarbohydrazide-oximino based ligands are considered to be the important class of chelating agents especially when -OH functional group also present with azomethine group⁶. Many

Researchers in recent years shows much obsession with the preparation and identification of thiocarbohydrazide-oximino complexes of metals due to their importance in many reactions as catalyst⁷⁻⁹. The products obtained from condensation of thiocarbohydrazide with oximino are biological active and also have good complexation ability with transition metals¹⁰. It is also noted that their activity enhanced by complexation with transition metal¹¹. The transition metal complexes of thiocarbohydrazide derived from oximino group has enhanced activity led to considerable interest in coordination chemistry. Undertaken of many analyses of the metal ion interaction with ligand containing nitrogen, sulfur and oxygen as donor atom, It was also established that the thiocarbohydrazide biological activity is altered many folds on coordination with transition metal ions¹².

In this research work, benzilmonoximethiocarbohydrazide-*o*-bromobenzaldehyde (HBMT*o*BB), IUPAC name N'''-{(E)-(2-bromophenyl) methylidene} - N'''- {(1E,2E)-2-chydroxyimino) -1, 2-diphenylethylidene} thiocarbohydrazide synthesized by refluxing *o*-bromobenzaldehyde and benzilmonoximethiocarbohydrazide and its transition metal complexes with Fe(III), Cr(III) Mn(III) Ti(III) and Pt(IV) were synthesized. The structure of HBMT*o*BB ligand and its transition metal complexes had been studied absorption of electromagnetic waves ligand its transition metal complexes also studied their biological activity against both Gram-positive and Gram-negative bacteria

Materials and Procedures:

Experimental work:

Every chemical and reagents are analytical grade materials were employed and of the highest purity obtainable, and they were not purified further. *o*-Bromobenzaldehyde, chloroform; methanol, nitrobenzene etc were obtained from S. d. fine chem, before being used, the solvents were distilled and purified.

Synthesis of HBMT*o*BB ligand:

0.10 M solution of *o*-bromobenzaldehyde was added to 0.15 M solution of benzilmonoximethiocarbohydrazide in ethanol than 2mL of conc. HCl added to reaction mixture, after that, the reaction mass is heated for 8 hours under reflux at 60-70⁰C, after cooling, the precipitated reaction mass was recovered after filtration. The HBMT*o*BB ligand precipitate forms a yellow colour solid once the reaction process is completed.

Metal complexes synthesis:

The transition complexes of metals of HBMT*o*BB ligand were synthesized by mixing 0.3M of HBMT*o*BB ligand in ethanol with Fe(III), Cr(III), Mn(III), Ti(III), and Pt(IV) chloride keeping ligand- metal ration 3:1 in ethanol. On a water bath, the resulting solution was further concentrated using distilled water.

Solid complexes precipitated after 3 hours of refluxing the reaction material. The complex was cooled, filtered, and washed with ethanol after each time.

Results and discussion:

The HBMT_oBB ligand is prepared by using 1:1:5 molar quantities of *o*- bromobenzaldehyde and benzilmonoximethiocarbohydrazide. The HBMT_oBB transition metal complexes are stable at open atmosphere, non-hygroscopic and are colored solids¹⁴. **Table-1** summarizes the HBMT_oBB ligand and its transition metal complexes' analytical and physical properties.

Table-1: Physical and analytical data for HBMT_oBB ligand and its trivalent complexes of metals.

Compound	DP (°C)	% Yield	% Expected (Found)							Cond Ω ⁻¹	Magnetic Moment (BM)
			C	H	N	O	S	Br	M		
[Ti(BMT _o BB) ₃]	257	81.00	53.57 (53.00)	3.63 (3.61)	14.12 (14.07)	3.23 (3.11)	6.46 (6.43)	16.07 (15.43)	3.22 (3.11)	5.65	1.71
[Mn(BMT _o BB) ₃]	256	78.03	53.36 (52.87)	3.50 (3.41)	13.62 (13.57)	3.11 (3.10)	6.22 (6.13)	15.50 (15.43)	3.56 (3.50)	0.89	4.80
[Cr(BMT _o BB) ₃]	255	78.02	53.12 (53.01)	3.62 (3.60)	14.08 (14.01)	3.22 (3.18)	6.44 (6.33)	16.03 (15.99)	3.49 (3.30)	0.54	3.89
[Fe(BMT _o BB) ₃]	257	76.03	51.39 (61.01)	3.50 (3.41)	13.61 (13.55)	3.11 (3.06)	6.22 (6.13)	15.49 (15.40)	3.62 (3.57)	0.18	4.93
[Pt(BMT _o BB) ₃]Cl ₂	266	75.33	43.10 (42.91)	2.94 (2.91)	11.42 (11.20)	2.61 (2.51)	5.22 (5.00)	15.92 (15.88)	15.92 (15.69)	1.36	Dia

FT(IR) spectra:

To confirm their structures, the FT(IR) spectra of HBMT_oBB ligand and its transition metal complexes were recorded¹⁴. Table-2 shows the FT(IR) spectra of HBMT_oBB and its metal complexes. The sharp band observed at 1699 cm⁻¹ for the HBMT_oBB ligand is due to the azomethine (>C=NN-) linkage, which shifts to a lower frequency (1650-1665 cm⁻¹) as one moves from the HBMT_oBB ligand to its transition metal complexes due to the coordination of the azomethine group's nitrogen atom with metal ion¹⁵. Another sharp band observed at 1611 cm⁻¹ of oximino group in HBMT_oBB ligand, lower frequencies are shifted, suggested that oximino group involvement in coordination. The broad band observed in HBMT_oBB ligand at 3226 cm⁻¹ disappearance of this broad band in all prepared complexes, indicated oximino proton deprotonated during complexation, observed metal-ligand vibration in the far-IR region frequently contains information about the ligand's bonding with the metal ion¹⁶. The now band is appear in the region of 503-513 cm⁻¹ due to the M-N/M→N.

Table-2: FT(IR) Spectral parameters in cm^{-1} for trivalent complexes of metals

Compound	$\nu(\text{OH})$	$\nu(\text{NH})$	$\nu(\text{C-S-H})$	C=NN	C=NO	$\nu\text{C=S}$	$\nu(\text{N-H})$	N-O	N-N	M-N
HBMT oBB	3226	3318	2346	1699	1611	1288	1690	1000	1072	-
[Ti(BMT oBB) $_3$]	-	3311	2344	1660	1588	-	1695	1022	1091	503
[Mn(BMT oBB) $_3$]	-	3319	2343	1650	1581	-	1693	1026	1085	504
[Cr(BMT oBB) $_3$]	-	3312	2347	1652	1583	-	1695	1021	1090	513
[Fe(BMT oBB) $_3$]	-	3309	2349	1665	1587	-	1692	1023	1088	509
[Pt(BMT oBB) $_3$] Cl_2	-	3313	2346	1663	1582	-	1693	1022	1087	506

PMR spectra:

In DMSO- d_6 solvent, HBMT oBB and its transition metal complexes were recorded and internal standard used as TMS. The disappearance of oximino $-\text{OH}$ signal at δ 11.50 ppm, confirms oximino group coordination with metal ion. The azomethine proton ($>\text{C}=\text{N}-\text{NH}$) appears at δ 10.07 ppm, it has shifted to down field in Pt(IV) complex, confirm coordination nitrogen¹⁷. The phenolic proton in HBMT oBB appears at δ 7.60-8.44 ppm.

Table-3: PMR information about the HBMT oBB ligand and its Pt(IV) complexes of metals

Compound	$>\text{C}=\text{N}-\text{OH}$ (δ)	$=\text{N}-\text{NH}-$ (δ)	Phenyl ring (δ)
HBMTCH	11.50	10.07	7.60-8.44
[Pt(BMT oBB) $_3$] Cl_2	-	9.60	7.58-8.45

Electronic absorption spectra:

The HBMT oBB ligand UV-spectrum was recorded in ethanolic solution showed absorption bands 370, 289 and 221 nm assigned for $\pi \rightarrow \pi$ transitions with in the azomethine and oximino group.

The electronic absorption spectrum of [Fe(BMT oBB) $_3$] showed broad band's at 698 and 722nm, which can be assigned as ${}^6\text{A}_{19} \rightarrow {}^4\text{T}_{29}(\text{G})$ and ${}^6\text{A}_{19} \rightarrow {}^4\text{T}_1(\text{G})$ transition respectively. 5.39 BM is the magnetic moment of the Fe(III) complex., which is consistent with the magnetic moment reported for octahedral geometry around Fe(III) ions¹⁸.

Intensity is low, as a result of the d-d transition with spin allowed, two transitions were seen in the spectra of [Cr(BMT oBB) $_3$] complex. The t_{2g}^3 configuration of Cr(III) octahedral complexes was confirmed by 3.40 B.M. observed magnetic moment of this complex. The Tanabe-Sugano diagram for the t_{2g}^3 setup shows the observed bands in electronic absorption spectrum of [Cr(BMT oBB) $_3$] complex at the region 545nm (18349 cm^{-1}) and 421nm (23753 cm^{-3}) were assigned to the transitions ${}^4\text{A}_{29} \rightarrow {}^4\text{T}_{29} (\nu_1)$ and ${}^4\text{A}_{29} \rightarrow {}^4\text{T}_{19} (\text{F}) (\nu_2)$ respectively¹⁹.

In the $[\text{Cr}(\text{BMT}o\text{BB})_3]$ complex $\nu_2 = 23753\text{cm}^{-1}/18349\text{cm}^{-1} = 1.29$, and ratio of this corresponds to Δ_0 being equal to 33. By using this value in the calculation of the nephelauxetic parameter, undetected third transition for splitting energy and The following results were obtained using the Racah parameter for the $[\text{Cr}(\text{BMT}o\text{BB})_3]$ complex $\nu_3=36965\text{ cm}^{-1}$ (270nm) $B=0.62$ $\Delta_0=18489\text{ cm}^{-1}$ and $B= 563\text{ cm}^{-1}$.

The moment of magnetic attraction of $[\text{Mn}(\text{BMT}o\text{BB})_3]$ complex is 4.45 B.M is lower than the spin-only value. The electronic spectrum of this complex displays a shoulder at 606nm assignable to ${}^5\text{E}_g \rightarrow {}^5\text{T}_{2g}$ transition as expected for octahedral geometry and charge transfer transition bands at 531nm, 366nm and 271nm. The $[\text{Ti}(\text{BMT}o\text{BB})_3]$ electronic spectra show broad band at 552nm (18100 cm^{-1}) due to ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ transition, which suggested by octahedral shape surrounding the metal ion Ti(III). The spectrum of UV-visible of $[\text{Pt}(\text{BMT}o\text{BB})_2]\text{Cl}_2$ shows a band at 397nm assigned the transition $n \rightarrow \pi^*$ while the band at 416nm, the charge transfer shift from ligand to metal is to responsibility. Pt(IV) complexes, previous studies reported that the band at 400-420nm was assigned for $\text{S}(\sigma) \rightarrow \text{M}$ transition and the band at 485nm was due to $\text{s}(\pi) \rightarrow \text{M}$ transition²⁰.

Table-4: HBMT o BB ligand electronic spectrum data and trivalent metal complexes

Compound	Band (nm)	Transition
HBMT o BB	370, 289, 211	MLCT, MLCT, MLCT
$[\text{Ti}(\text{BMT}o\text{BB})_3]$	552	${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$
$[\text{Mn}(\text{BMT}o\text{BB})_3]$	531, 366, 271	${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$, MLCT, MLCT
$[\text{Cr}(\text{BMT}o\text{BB})_3]$	545, 421	${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$, ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ (F)
$[\text{Fe}(\text{BMT}o\text{BB})_3]$	698, 722	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$ (G), ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_1$ (G)
$[\text{Pt}(\text{BMT}o\text{BB})_3]\text{Cl}_2$	438, 485	$\text{S}(\sigma) \rightarrow \text{M}$, $\text{s}(\pi) \rightarrow \text{M}$

Antibacterial activity:

Table-4 shows the data on antibacterial activity for the metal complexes of HBMT o BB ligands. By disc diffusion, the produced compounds were tested on gram negative bacteria *S. aureus* and *S. pneumonia*, as well as gram positive bacteria *E. coli* and *P. aeruginosa*. The diameter of the susceptibility zone measured in millimetres. The data were recorded after a 24 hour incubation period at 30⁰C with a 6mm diameter filter paper disc. The HBMT o BB ligands, as well as its transition metal complexes, were studied. evaluated by observing the zone of inhibition around the substance. HBMT o BB shown a considerable active range on the growth of all bacteria strains tested. The findings show that complexes boost antibacterial activity²¹.

Table-5: Antibacterial screening (500ppm) for HBMT_oBB ligand and metal complexes in (mm)

Compound	<i>B. subtilis</i>	<i>P. aeruginosa</i>	<i>S. aureus</i>	<i>S. typhi</i>	<i>E. coli</i>	<i>K. pneumoniae</i>
HBMT _o BB	14	13	17	11	09	12
[Ti(BMT _o BB) ₃]	16	16	22	14	12	16
[Mn(BMT _o BB) ₃]	16	16	19	20	17	15
[Cr(BMT _o BB) ₃]	16	15	23	19	19	18
[Fe(BMT _o BB) ₃]	18	14	18	13	11	13
[Pt(BMT _o BB) ₃]Cl ₂	17	14	18	13	11	13
DMF (Solvent)	-	-	01	03	-	-
Streptomycin	22	21	13	20	18	21

Conclusion:

A new thiocarbohydrazide based has been synthesized as a result of condensing *o*-bromobenzaldehyde and benzilmonoximethiocarbohydrazide. Physicochemical analyses, elemental analysis, PMR, electronic absorption, and FT(IR) spectral data reveal the HBMT_oBB proposed coordination is bidentate and linked by oximino and azomethine groups nitrogen atoms and creating stable chelates. The metal chelate of the HBMT_oBB ligand has been structurally studied, and it has been determined complexes of metals have coordinated octahedral geometry with the exception of the Pt(IV) complex, which geometry has square planar. Biological studies demonstrate that metal complexes have far more activity than the ligand.

References:

1. Thangadural T and Natarajan K; Tridentate Schiff base complexes of ruthenium(III) containing ONS/ONO donor atoms and their biocidal activities; *Trans Met Chem*; **2001**, 26(6), 717-722.
2. Sharma R, Singh R and Tondon J; Biscyclopentadienyl titanium(IV) complexes of monofunctional bidentate ketamines; *J of Inorg and Nucl Chem*; **1980**, 42(9), 1382-1384.
3. Natarajan K and Agarwaa U; Some new β -diketone complexes of ruthenium(III) with triphenylphosphine and triphenylarsine; *Bull Chem Soc*; **1976**, 49, 2877-2878.
4. Aranha P, Santos M, Romera S and Dockal E; Synthesis, characterization and spectroscopic studies of tetradenate Schiff base chromium(III) complexes; *Polyhedron*; **2006**.
5. Prakash A and Ahmed S; Synthesis and characterization of Schiff base complexes with Ti(III), Cr(III) and Ni(II); *Ori J of Chem*; **2009**, 25(4), 1035-1040.
6. Suresh M and Prakash V; Preparation and characterization of Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) chelates of Schiff base derived from vanillin and 4-amino antipyrine; *Int J of the Sci*; **2010**, 5(14), 2203-2211.

7. Vogel A. I.; "A Textbook of Quantitative Inorganic Analytical"; Longmans Green and Co. Ltd., 3rd Ed., London, (1964).
8. R. L. Dutta and A. Syamal; *Elements of magnetochemistry*; S. Chand and Comp. Ltd, (2009).
9. Kamble P, Badekar R and Singh V; Synthesis and characterization of novel coordination compounds of Cr(III), Fe(III), with α -Benzilmonoximethiocarbohydrazide; *IJRAR*; 5(3), (2018); 911y-913y.
10. Nishina C, Enolci N, Tawata S, Mori A, Kobryashi K and Fukushima M; *Agric Bio. Chem*; **1987**, 51, 139.
11. Grover R and Moore J; *Phytopathology*; **1962**, 52, 879.
12. Migh M, Ahmad H, Sharma N, Ali A and Miah S; *Bangladesh J Bot*; **1990**, 195.
13. Prakash A and Ahmed S; Synthesis and characterization of Schiff base complexes with Ti(III), Cr(III) and Ni(II); *Ori J of Chem*; **2009**, 25(4), 1035-1040.
14. Al-Nahary T; Synthesis and characterization of metal complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Ru(III), Rh(III) and Pd(II) with derivatives of 1, 3, 4-thiadiazole-2, 5-dithiole as new ligand; *J of Saudi Chem Soc*; **2009**, 13(3), 253-257.
15. Chandra s and Singh R; Pd(II), Pt(II), Rh(III), Ir(III) and Ru(III) complexes of some nitrogen-oxygen donor ligands; *Ind J of Chem*; **1988**, 27, 417-420.
16. Arun N, Hasaan S, Saad E, Butler I and Mostafa S; Preparation, characterization and pHmetric measurements of 4-hydroxysalicylidene chitosan Schiff base complexes of Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ru(III), Rh(III), Pd(II) and Au(III); *Carbohydrate Research*; **2011**, 346(6), 775-773.
17. Laila A, Ahmed M, Rafet M and Shimag M; Sonochemical synthesis, DNA binding, antimicrobial evaluation and *in vitro* anticancer activity of three new nano-sized Cu(II), Co(II) and Ni(II) chelates based on tridentate NOO imine ligands as precursors for metal oxides; *J of Photochem and Photobiology*; **2016**, 162, 298-308.
18. Joshi S and Habib S; Synthesis, characterization and antimicrobial evaluation of benzoin oxime transition metal complexes; *J of Chem and Pharma Res*; **2014**, 6(6), 1085-1088.
19. Aswale S, Mandlik P, Aswale S and Aswar A; *Ind J of Chem*; **2003**, 42, 322-326.
20. Joshi S and Habib S; Co(II) and Zn(II) metal complexes of heterocyclic Schiff bases: a Synthesis, spectral and antimicrobial study; *Ori J of Chem*; **2014**, 30(3), 1343-1348.
21. Kumar B, Prasad K and Srivastava S; Synthesis of oxygen bridged complexes of Cu(II) or Ni(II) salicylaldehyde with alkali metal salts of some organic acids and studies on their antimicrobial activities; *Ori J of Chem*; **2010**, 26(4), 1413-1418.