



SYNTHESIS, CHARACTERIZATION AND STUDY OF MICROBIOLOGICAL ACTIVITY OF RHODIUM (III) COMPLEX WITH, 2-(5- BROMO-2- OXOINDOLIN-3- YLIDENE) HYDRAZINECARBOTHIOAMIDE

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ABSTRACT

A Schiff base ligand derived from 5-Bromoisatin with thiosemicarbazide, [2-(5-Bromo -2-Oxoindolin-3-ylidene) Hydrazine Carbothioamide], [HBITSC] and its complex with Rh (III) has been synthesized which was characterized by elemental analysis, molar conductance, electronic spectra, IR and NMR spectroscopy. The metal complex is coloured and solid in nature. The Schiff base ligand exhibits bidentate nature, coordination through azomethine nitrogen and thioketo sulphur to the metal ion. On the basis of electronic spectral analysis geometry of complex was proposed to be octahedral. The molar conductivity data of complex suggests its non - electrolytic nature. On the basis of above studies three ligands were suggested to be coordinated to rhodium atom by thioketo sulphur and azomethine nitrogen to form diamagnetic octahedral complexes. The ligand and Rh (III) complex have been screened for their microbiological activity.

KEYWORDS: Schiff base (HBITSC), Spectra, Metal Complex and Microbiological activity.

INTRODUCTION

Schiff bases are an important class of ligand in the field of coordination chemistry.^[1] During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donor atoms.^[2-5] A large number of Schiff bases and their metal complexes have been found to possess important biological and catalytic activity.^[6-8] Schiff bases are also used as an efficient reagent in trace analysis of some metal cations.^[9-10]

In the present paper, complex of Rh(III), with Schiff base ligand derived from 5-Bromoisatin and thiosemicarbazide, [2-(5-Bromo -2-Oxoindolin-3-ylidene)HydrazineCarbothioamide], [HBITSC] have been synthesized and characterized by elemental analysis, molar conductivity measurement, electronic, IR, and ESR spectrum to determine the mode of bonding and geometry. The microbiological activities of the ligand and its metal complex have also been studied.

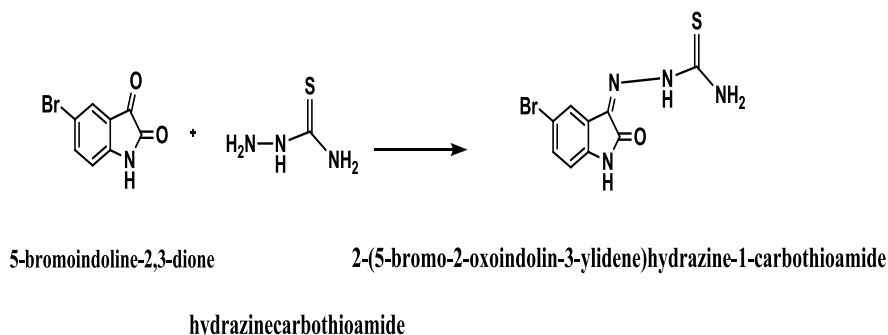
MATERIALS AND METHODS

Instrumentation: All the used chemicals and solvents were of AR grade and were used without further purification. The percentage compositions of the

elements (CHNO) of the compounds were determined using an element analyzer CHNO model Flash EA 1112 series. The metal contents of the complex was analyzed by ICPAES (Inductive coupled plasma atomic emission spectroscopy). The Infrared spectra were recorded as potassium bromide (KBr) discs using a 8400 FTIR Perkin Elmer Spectrophotometer. The electronic Spectrum of complex was recorded on ELICO SL -159 UV-Vis Spectrophotometer. Melting point of ligand and its Rhodium (III) complex were recorded. The molar conductivity measurement was made on ELICO SL - 303 model using methanol as the solvent.

Synthesis of 2-(5-Bromo -2-Oxoindolin-3-ylidene) Hydrazine Carbothioamide [HBITSC].

Schiff base ligand HBITSC was synthesized by refluxing equimolar amount of ethanolic solution of 5-Bromoisatin with thiosemicarbazide for 4 - 5 hours. On cooling the reaction mixture, a sharp yellow crystal product separated out (80%, yield) which was collected by filtration. The resulting HBITSC was recrystallized using aqueous ethanol as the procedure recommended by Vogel.^[11] The product was characterized by elemental and spectral analysis.



Preparation of complex with Schiff base ligand (HBITSC): The complex of Rh (III) was prepared by refluxing aqueous solution of hydrated Rhodium chloride with solution of ligand prepared in dimethyl formamide in molar ratio of 1:3 at pH 5.0 to 6.5 on boiling water bath for 2 - 3 hrs. After cooling at room temperature, dark brown colored solid separated out which was filtered, washed with water. The resulting product was recrystallised and dried in vacuum desiccator over CaCl_2 anhydrous (yield 60 - 70%).

Biological Studies: Antibacterial and antifungal activity of ligand and its complex has been determined by cup plate method. The stock solution of Rh (III) complex was prepared by dissolving 20 mg of compound in methanol and the volume was made up to 10ml with same solvent. The stock solution of 2000ppm of each compound thus

prepared on active ingredient basis was kept at room temperature till used. Sterile Mueller Hinton agar plates for bacterial test cultures and Sabourauds agar plates for fungus *Candida albicans* were seeded with 1ml of 24 hour old, 0.1 O.D. cultures. The compounds to be tested (50 μl) were added to the wells punched in the above media. The plates were incubated at 37°C / R.T. for 48 hours depending on the cultures. The zone of inhibition around the wells was measured in millimeters.

RESULTS AND DISCUSSION

The Rhodium (III) complex is colored, solid, stable at room temperature. The Analytical and physical data of ligand and Rh (III) complex is recorded in Table - 1. The Rhodium (III) complex exhibits 1:3 (rhodium (III)-ligand) stoichiometry.

Table - 1. The Analytical and physical data of ligand and its Rh(III) complex

Compounds (Colour)	Molecular Weight	M.P. $^\circ\text{C}$	% Elemental Analysis Found (Calculated)							$\Lambda_m \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
			C	H	N	Br*	O*	S	M	
HBITSC (Yellow)	299.64	278	36.42 (36.1)	2.46 (2.67)	18.5 (18.72)	26.71 (26.7)	4.99 (5.2)	10.92 (10.6)	-	-
[Rh(HBITSC) ₃]Cl ₃ (Dark Brown)	1106.86	>300	29.85 (29.17)	1.894 (1.897)	15.257 (15.178)	21.93 (21.656)	4.327 (4.336)	8.130 (8.673)	9.34 (9.297)	35.3

*By difference

Infrared Spectral Analysis

Infrared spectra was recorded with a Perkin Elmer FTIR -8400S Spectrometer ($4000\text{--}400\text{cm}^{-1}$) using KBr pellets. On the basis of this, the presence of important functional groups in the compound can be identified. The Infrared spectrum of the ligand was compared with the spectra of its Rh(III) complex. The typical IR spectra were shown in "Fig. 1 and 2". Data was summarized in Table-2 along their assignment.

The IR spectrum of the ligand shows broad band at 1603.81cm^{-1} , which was assigned to due ν (C=N) stretching of azomethine group.^[12] In complexes this band was shifted to higher regions, 1607.35cm^{-1} for Rh(III) complex, suggesting the coordination of azomethine nitrogen to metal atom in complexation^[13,14] This was due to the donation of electron density from Nitrogen to metal.

The strong bond observed at 856.00cm^{-1} in ligands is mainly due to the (C=S) stretching vibration which

shifted towards lower frequency 853.0 in metal complex indicating the coordination of thioketo sulphur to metal atom.^[13-15]

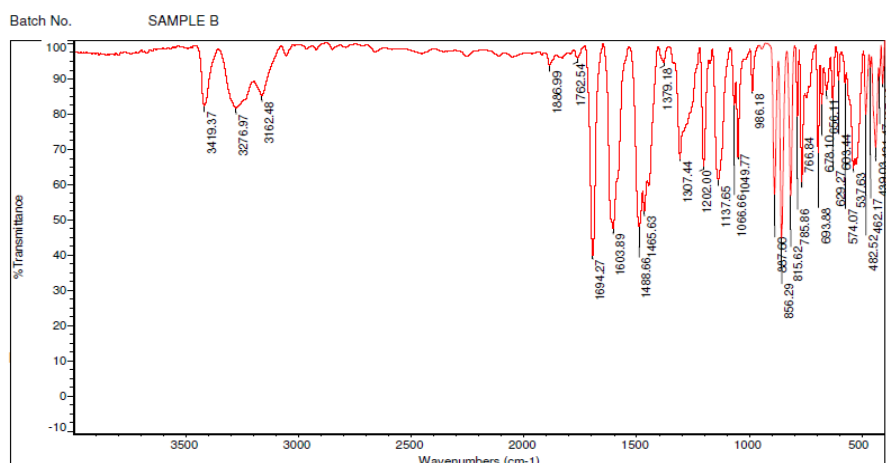
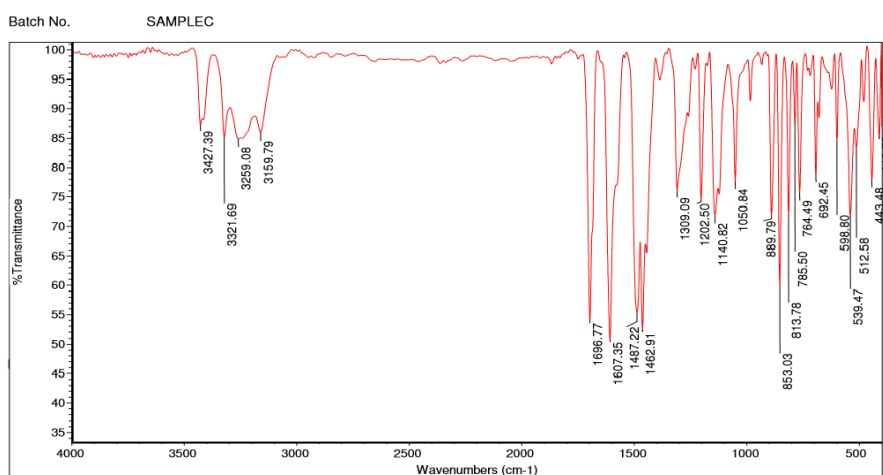
New bands were observed between $400 - 600\text{cm}^{-1}$ region in the complex, which were absent in the spectrum of ligand. The band at 443.48cm^{-1} is assigned to stretching frequencies of $\nu(\text{M-S})$ and the band at 512.58cm^{-1} have been assigned to the stretching frequencies $\nu(\text{M-N})$ respectively.^[15-17]

The IR spectrum of the ligand and complex shows band at $3276\text{--}3259\text{cm}^{-1}$, which was assigned to $\nu(\text{N-H})$ stretching.^[18]

Therefore from IR spectra it is concluded that ligand behaves as bidentate ligand co-ordinated to metal ion via azomethine (N) and thioketo sulphur.

Table-2: The Important IR bands of Ligand and Their Metal Complexes

Compound	$\nu(\text{N-H}) \text{ cm}^{-1}$	$\nu(\text{N-N}) \text{ cm}^{-1}$	$\nu(\text{C=N}) \text{ cm}^{-1}$	$\nu(\text{C-S})$ stretching cm^{-1}	$\nu(\text{M-N})$ cm^{-1}	$\nu(\text{M-S})$ cm^{-1}
HBITSC	3276	1137.65	1603.81	856.00	-	-
$[\text{Rh}(\text{HBITSC})_3]\text{Cl}_3$	3259 Broad band	1140.82	1607.35	853.00	512.58	443.48

**Fig 1: Spectra of Ligand****Fig 2: IR Spectra of Rh (III) Complex**

Molar Conductance: The molar conductance values of 1×10^{-3} M solution of Rhodium(III) complex in methanol was measured at room temperature (Table - 1) using an ELICO Conductivity meter (cell constant 1.0 cm^{-1}). The value was compared with known molar conductivities^[19-20] which indicates the non - electrolytic nature^[21] of the complex.

Electronic Spectra of Complex

In UV-Visible electromagnetic radiation, the transitions are associated with the electronic energy levels of the compound under investigation. The electronic spectra were recorded on ELICO SL - 159 UV-Visible Spectrophotometer. The transition metal ions occur in a variety of structural environments. Because of this, the electronic structures are extremely varied. The electronic structures have been identified with UV-Visible

spectroscopy. The nature of ligand field around the metal ion and the geometry of complex have been deduced from the electronic spectra.

The Rh (III) complex display band at 20202.20 cm^{-1} (495nm) and which may be assigned to

$^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ transition suggesting octahedral geometry and diamagnetic nature of complex.^[22-23]

^1H NMR: Coordination of thiosemicarbazones in the Rh(III) complexes are further confirmed by ^1H NMR spectra (see Table 6). Significant azomethine proton signal, due to $\text{CH}=\text{N}$, was observed at $\delta 8.74 \text{ ppm}$ in the Schiff base ligand. On complexation the position of this peak shifted to $\delta 8.835 \text{ ppm}$, indicating involvement of nitrogen in coordination. The proton peak of N-H group

at δ 11.321 ppm in complex remains same as in the ligand which is at δ 11.31 ppm, it suggested that deprotonation do not occur and it has also shown keto form of the ligands.^[15 and 22] The multiplet as strong band

in the region 6.87-7.88 ppm were assign to aromatic ring protons, which also shifted downfield in the complex.^[15 and 22]

Table-3 NMR spectral data (δ , ppm) of the thiosemicarbazones and their complexes

Compound	$\delta(\text{CH}=\text{N})$	$\delta(\text{N}-\text{H})$	$\delta(\text{Ar}-\text{H})$
HBITSC	8.740	11.310	6.87-7.88
[Rh(HBITSC) ₃]Cl ₃	8.835	11.321	6.89-7.94

Proposed Structure of Complexes: The present study clearly indicates that the ligand forms stable coordination compound with the rhodium (III), under investigation which is evidenced by micro - analytical

and spectroscopic data. The probable structure of the complex under investigation on the basis of the above experimental evidence can be shown as “Fig-3”

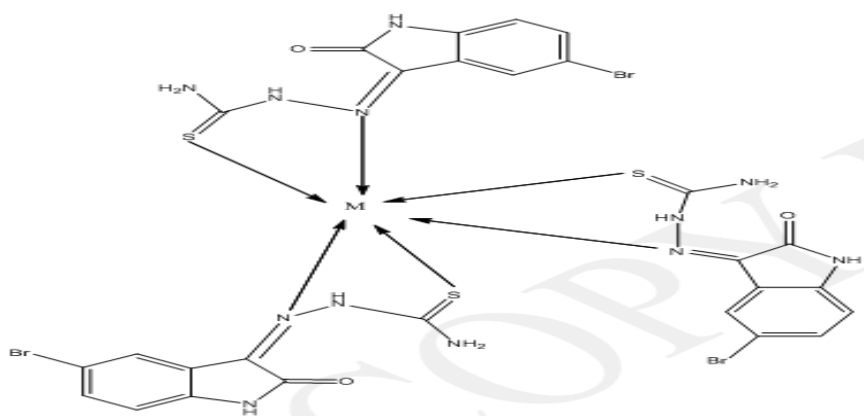


Fig -3: M = Rh (III)

Biological Activity

Table 5: Zone of inhibition of growth in millimeters after 48 hours of incubation

Complexes	Cultures			
	S.a	E.c	K.p	C.a
HBITSC	12	08	10	13
[Rh(HBITSC) ₃]Cl ₃	24	15	14	18
SOLVENT	-	-	-	-

Schiff base ligand and its Rh(III) complex were screened for antibacterial activity against gram positive bacteria (staphylococcus aureus), gram negative bacteria (Escherichia coli and Klebsiella pneumonia) and antifungal activity against (Candida albicans and aspergillus species) by cup plate method.^[23] The results of the biological activity of the metal complexes indicated the following facts. A comparative study of the ligand and their complexes indicates that Rh (III) chelate exhibited higher antibacterial and antifungal activity than that of the free ligand recorded in Table – 5. The increase in the biological activity of Rh (III) chelate was found due to the effect of Rh (III) on the chelate which could be explained on the basis of overtones concept and chelation theory. On chelation the polarity of the Rh (III) reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charges of Rh (III) with donor groups. It was further noted that the delocalization of electrons over the whole chelate ring

enhanced the lipophilicity of the complex. This increased lipophilicity^[24] enhanced the penetration of the complex into lipid membrane and blocking the metal sites on enzymes of microorganism. The activity was compared with zone of inhibition was measured in millimeters.

CONCLUSIONS

It can be concluded from the results of above study that Schiff base ligand 2-(5-Bromo -2-Oxoindolin-3-ylidene) Hydrazine Carbothioamide, [HBITSC] acts as a very good bidentate complexing agent towards Rh (III) during complexation. Analytical data of complex is in good agreement with its molecular formula. The involvement of azomethine (N), thioketo (S) of the bidentate Schiff base to the Rh (III) was confirmed by comparing electronic, IR and NMR spectral data of the ligand with that of its Rh(III) complex. Further conclusive evidence of the coordination of these Schiff-base with Rh (III) was

shown by the appearance of new bands due to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{S})$ in the Rh(III) complex. The electronic spectra is used for assigning the geometry of Complex of Rh(III) with HBITSC was proposed to be octahedral in nature. On the basis of these findings the structures have been proposed for the complex which are in good agreement with theoretical consideration.(Fig.-3)

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