

---

# INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN CHEMISTRY AND PHARMACEUTICAL SCIENCES

(p-ISSN: 2348-5213; e-ISSN: 2348-5221)

[www.ijcrcps.com](http://www.ijcrcps.com)

(A Peer Reviewed, Referred, Indexed and Open Access Journal)

DOI: 10.22192/ijcrcps

Coden: IJCROO(USA)

Volume 9, Issue 10 - 2022

---

## Research Article



DOI: <http://dx.doi.org/10.22192/ijcrcps.2022.09.10.001>

## Synthesis spectral study of novel series of Schiff base ligands and its metal complexes

**Gopalkrushna H. Murhekar\* and Supriya Belsare**

PG Department of Chemistry, Government Vidarbha Institute of Science and Humanities,

Amravati, Maharashtra, India- 444602

E-mail: [gopalmurhekar@gmail.com](mailto:gopalmurhekar@gmail.com)

---

### Abstract

Heterocyclic chemistry is fundamental to biology and medicine. It is not impossible to say that we are living in the age of heterocyclic chemistry. It constitutes a large group of organic molecules exhibiting a wide range of biological activities which is basis of life and society [1]. Transition metals have numerous and unique biological, chemical, and physical properties due to the availability of d electrons in valence shells [2]. Schiff's bases are important class of ligands in coordination chemistry and find extensive application in different fields. Schiff's base ligands and their complexes have been extensively studied for their structures and applications [3]. Metal complexes of the Schiff's bases are generally prepared by treating metal salts with Schiff's base ligands under suitable experimental conditions [4]. The present work represents the synthesis, spectral characterization, Thermal properties and antimicrobial activity of Novel series of Schiff base derived from 2, 4-bis (hydrazino)-6-substituted triazine and their Schiff base derivatives. A series of metal complexes of Ti (II), Cr (III), Mn (II), and Cu (II) have been synthesized with newly derived biologically active ligands. The probable structure of the complexes has been proposed on the basis of elemental analyses and spectral data. All the complexes of Ti (II), Cr (III), Mn (II) and Cu (II) were screened for their antimicrobial, thermal and optical properties.

**Keywords:** Metal Complexes, Optical Properties, Schiff's base, Thermal Properties.

---

### Introduction

The rapid development of pathogen resistance to most of the known antibiotics is becoming a serious health problem. One possible long-term solution is the development of agents that act on unexploited bacterial targets. S-triazine

derivatives have received considerable attention due to their potent biological activity such as anticancer, estrogen receptor modulators, antivirals, and anti-malarial. It has been reported that triazine derivatives possess potent antimicrobial activity [5]. Schiff's bases are important class of ligands in coordination

chemistry and find extensive application in different fields. Schiff's base ligands and their complexes have been extensively studied for their structures and applications. Schiff's bases derived from the carbonyl compounds and ethylenediamine are well known polydentate ligands forming neutral complexes [6]. However, for some catalytic application the Schiff's base metal complexes are prepared in situ in the reaction system [7]. The interactions of these donor ligands with metal ions give complexes of different geometries which are potentially biologically active. Thus, in recent years metal complexes of Schiff's bases have attracted considerable attention due to their remarkable antifungal, antibacterial, antitumor and anticancer activities [8]. Many biologically important Schiff's bases have been reported in the literature possessing, antibacterial, antifungal, anti-inflammatory, anticonvulsant, antitumor and anti HIV activities [9,10]. Transition metal complexes with Schiff's bases have expanded enormously and embraced wide and diversified subject comprising vast areas of bio-organic compounds. Many studies have been done on transition metal complexes of Schiff's bases due to the fact that Schiff's bases offer opportunities for inducing substrate chirality, tuning metal centered electron factor, enhancing the solubility and stability of either homogenous or heterogeneous catalyst [11]. Schiff's base ligands are able to coordinate many different metals and stabilize them in various oxidation states [12].

Metal ions play very important role in biological systems by influencing the functions of enzymes, polypeptides and amino acids. These can act as energy reacting catalysts by coordinating to the donor atoms of the ligands, e.g., Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> may coordinate through oxygen and carry out biological functions such as charge transfer, trigger reactions, hydrolysis etc. Heavy metal ions such as manganese, iron, cobalt, copper, zinc, cadmium and molybdenum coordinate to the ligands containing the nitrogen and sulphur atoms and help to control the pH, hydrolysis and redox reactions. Coordination compounds also recognize electron transport in

living cells through a number of steps involving some oxidation-reduction enzymes in conjugation with sulphur proteins [13].

## Materials and Methods

All chemicals and solvents used were of AR grade.

X-ray diffraction (XRD) is a powerful technique used to uniquely identify the crystalline phases present in materials and to measure the structural properties (strain state, grain size, epitaxy, phase composition, preferred orientation, and defect structure) of these phases. XRD is also used to determine the thickness of thin films and multilayer and atomic arrangements in amorphous materials (including polymers) and at interfaces. Figure 2.10, shows the basic features of XRD experiment set up; the diffraction angle  $2\theta$  is the angle between the incident and diffracted X ray. From  $2\theta$  values for reflection, 'd' values were calculated using Bragg equation and average crystallite size calculated by Scherrer's equation [14]. The thermogravimetric analysis of all newly synthesised compounds was carried out using a Netzsch STA 409 thermal analyzer at our institute in the temperature range 40-800°C with a heating rate 10°C/min [15].

### 1) Synthesis of Hydrazino-Trazine derivative (HTD):

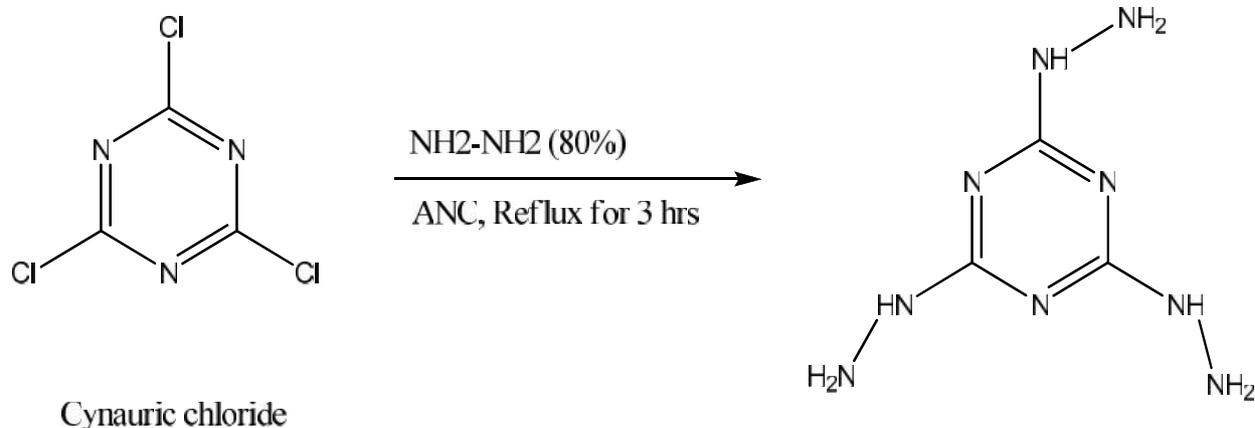
#### Chemical Required:

Cynuaric chloride, Acetonitrile, Hydrazine hydrate

#### Method:

Cynuaric chloride (0.05 M) dissolved in acetonitrile (10 ml). Hydrazine hydrates (0.05 M) dissolved in acetonitrile (10 ml). The mixture was refluxed for 3- 4 hrs. The product as white solid mass started appearing after 3 hrs. The Precipitate was filtered and dried. Melting point – 238°C

**Reaction:**



Cynauric chloride

HTD

**Scheme 1:1: Synthesis of Hydrazino-Triazine derivatives. (HTD)**

**2) Synthesis of Hydrazino - Triazine Schiff Base (HTDSB):**

**Chemical Required:**

Hydrazino -Triazine derivative, m-Hydroxy acetophenone, Ethanol

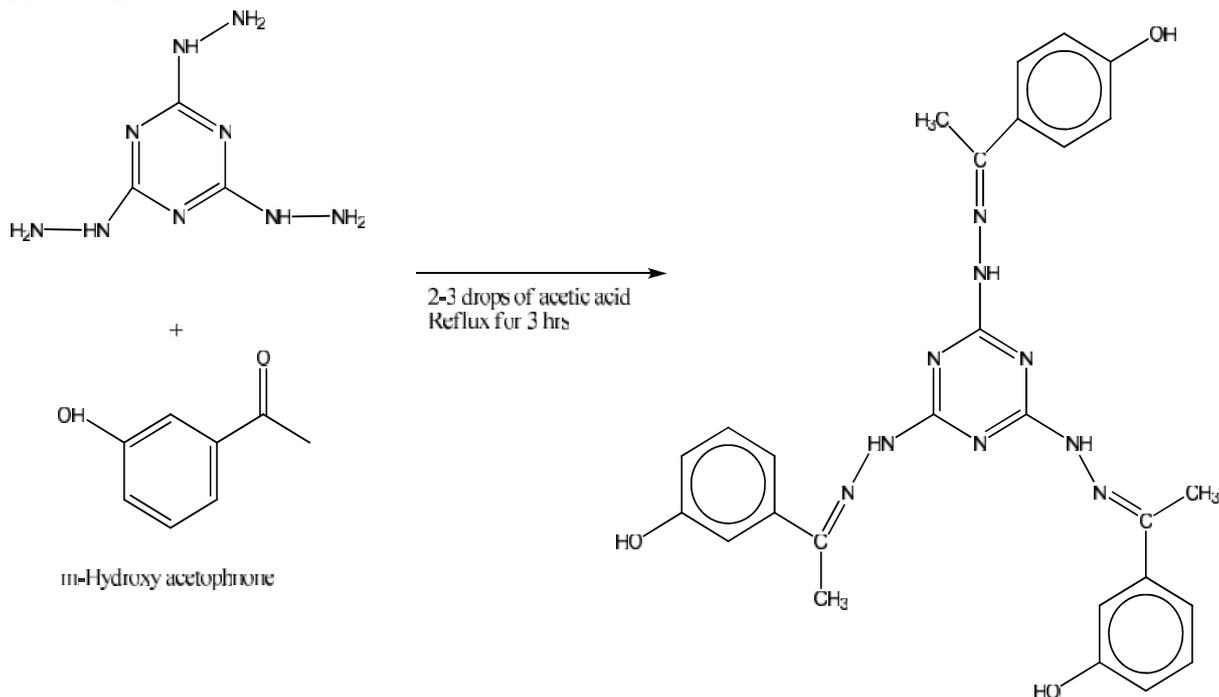
**Method:**

Hydrazino-Triazine derivative (0.01M) dissolved in ethanol (15ml) and m-Hydroxy acetophenone

(0.01m) dissolved in ethanol (15ml). The Hydrazino -Triazine derivative and m- Hydroxy acetophenone was given in 1:3 Proportions. Then mixture was reflux for 3 – 4 hrs. The product as solid mass started appearing after 3hrs. The precipitate was filtered and dried.

Melting Point - 252°C

**Reaction:**



m-Hydroxy acetophenone

HTDSB

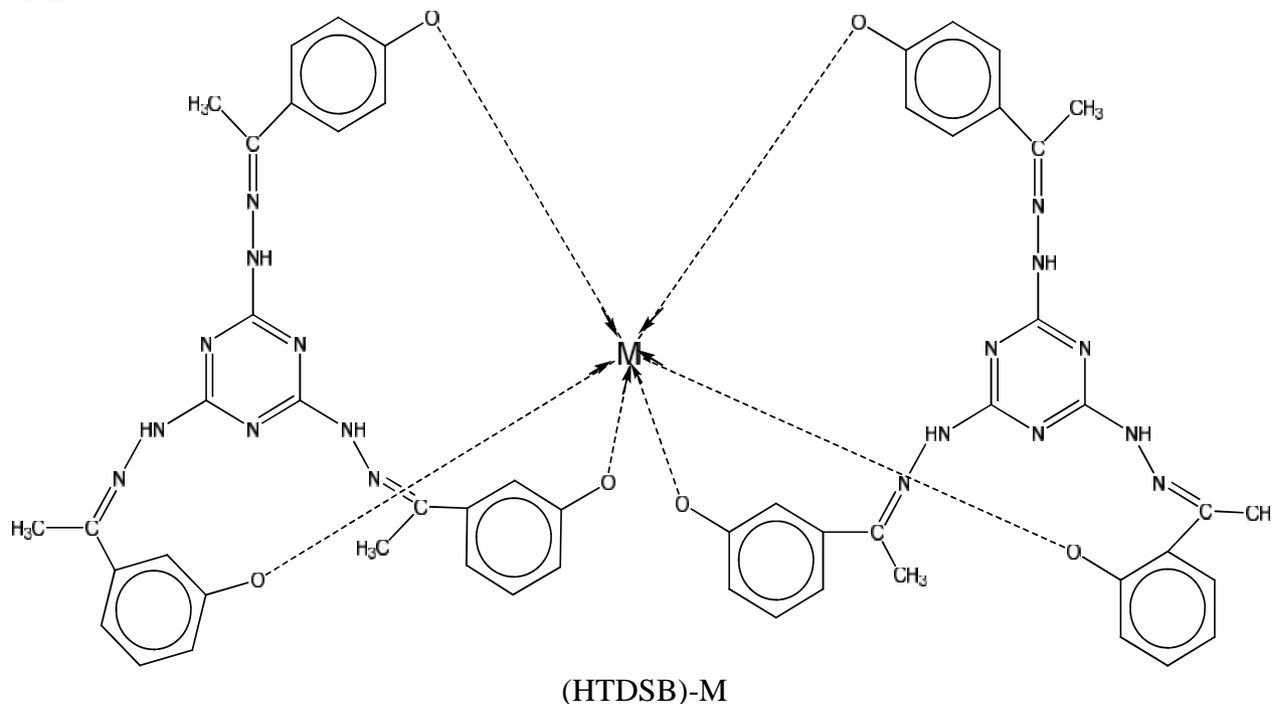
**Scheme 1.2: Synthesis of Hydrazino – Triazine Schiff Base (HTDSB).**

### 3) Synthesis of Transition metal complexes with Hydrazino-Triazine Schiff Base

#### Chemical Required:

Hydrazino-Triazine Schiff Base, Dimethyl Sulphoxide, anhydrous metal halides, Sulphate (CuSO<sub>4</sub>, NiSO<sub>4</sub>, MnSO<sub>4</sub>)

#### Reaction:



**Scheme 1.3: Structure of Hydrazino-Triazine Schiff Base-M (II) Complexes. (HTDSB)-M (II)**

#### Antifungal Activity

Antifungal activity [16-18] was determined based on the growth inhibition rates of the mycelia of *Aspergillus niger* and *Candida albicans* strains grown in potato dextrose broth medium (PDB). Under aseptic conditions, one mL of spore suspension ( $5 \times 10^6$  cfu/mL) of the fungus being tested was added to 50 mL of PDB medium in a 100 mL Erlenmeyer flask. Appropriate volumes of tested metal complexes were added to produce concentrations ranging from 10 to 100  $\mu\text{g mL}^{-1}$ . The flasks were incubated at  $27 \pm 1^\circ\text{C}$  in the dark

#### Method:

The coordination compounds Hydrazino-Triazine Schiff Base (0.01 M) in DMSO under reflux with the anhydrous metal halides, sulphate (Cu, Ni and Mn) in two different compositions. Thus, metal complexes formed are filtered and washed with the corresponding solvents and yielded metal complexes in high yield.

for 5 days, at which time the mycelia were collected on filter papers. The filter papers were dried to a constant weight, and the level of inhibition relative to the control flasks was calculated from the following formula:

$$\text{Percentage of Inhibition} = \frac{C-T}{C} \times 100$$

Where  $T$  is the weight of mycelia from the test flasks and  $C$  represents the weight of mycelia from the control.

## Antioxidant activity

*In vitro* antioxidant activities of the synthesized compounds were assessed according to a reported method. In brief, 0.01 mg/mL (0.001% (w/v)) solution of DPPH in methanol and DMSO was prepared, 1 mL of this solution was poured into 4 mL of the synthesized samples in methanol to furnish four different concentrations (1.25, 2.5, 5, 10 µg/mL). The control was made by adding 1 mL of DPPH solution to 4 mL of methanol or 4 mL of DMSO. Absorbance was measured against blank at  $\lambda_{max}$  of 517 nm using UV-Visible Spectrophotometer (SM-1600 Spectrophotometer, India). Ascorbic acid was used as a positive control. The activity was expressed in  $IC_{50}$  in which the concentration of the compounds is required to give a 50% decrease in absorbance compared to that of the control solution. The percentage inhibition of the synthesized

compounds against DPPH was calculated using [19-20].

$$\% \text{ Inhibition} = [(A_{\text{control}} - A_{\text{sample}}) / A_{\text{control}}] \times 100$$

Where,  $A_{\text{control}}$  is the absorbance of the control,  $A_{\text{sample}}$  is the absorbance of the test compounds.

## Results and Discussion

The Schiff bases synthesized from HTD with substituted acetophenone and metal (II) complexes of copper (II), nickel (II) and Manganese (II) of HTDSB were obtained in good yield with the corresponding substituted acetophenone and metal salts. The analytical data and physical properties of Schiff bases synthesized from HTD with substituted acetophenone with transition metal (II) complexes are listed in Table-1.

**Table – 1: Physical Data of Newly Synthesized compounds**

SR.NO.	Name of Compound	Compound	Molecular Weight	Color	% Yield	M.Pt.(°C)
1.	HTD	CH <sub>3</sub> NH <sub>9</sub>	171	White	68 %	238° C
2.	HTDSB	CH <sub>27</sub> N <sub>14</sub> O <sub>3</sub>	525	Yellow	89 %	252° C
3.	HTDSB-Cu(II)	CH <sub>54</sub> N <sub>28</sub> O <sub>6</sub> Cu	1117.54	Green	96 %	185° C
4.	HTDSB-Ni(II)	CH <sup>54</sup> N <sub>28</sub> O <sub>6</sub> Ni	1112.69	Yellow	87 %	196° C
5.	HTDSB-Mn(II)	CH <sub>54</sub> N <sub>28</sub> O <sub>6</sub> Mn	1108.93	Black	93 %	189° C

## X-Ray Diffraction

### Interpretation

The XRD characterised data of Schiff bases synthesised from HTD with substituted acetophenone and ligand HTDSB with transition metal (II) complexes are shown in Table-2. X-ray diffraction of Schiff bases synthesised from HTD with substituted acetophenone samples at room

temperature in the scanning range  $5^\circ \leq 2\theta \leq 85^\circ$ . Spectrum of HTD shows an intense reflection peak at  $2\theta = 32^\circ$  diffused in the hallow amorphous region. The appearance of sharp reflections and diffuse scattering is characteristic of crystalline and amorphous phases of conventional semi-crystalline compounds. However, spectrum of complexes shows a broad amorphous hallow with a scattered intensity, maximum corresponding to  $2\theta = 22.5^\circ$  to  $25.1^\circ$ .

Table – 2: XRD data Triazine Compounds

SR.NO	Compounds	2 $\theta$
1	HTD	22.5, 25.1, 27.7, 32.0, 34.0
2	HTDSB	19.4,25.1,29.5,32.1,39.6
3	HTDSB-Cu(II)	21.6,28.3,34.2
4	HTDSB-Ni(II)	17.9,25.7,28.2,37.9,44.6
5	HTDSB-Mn(II)	19.3,26.8,34.4,

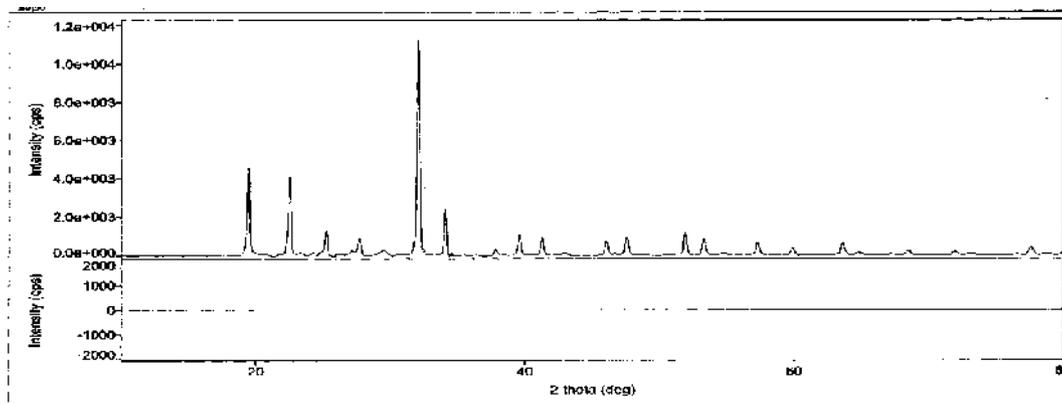


Fig. 1.1: XRD of Complex HTD

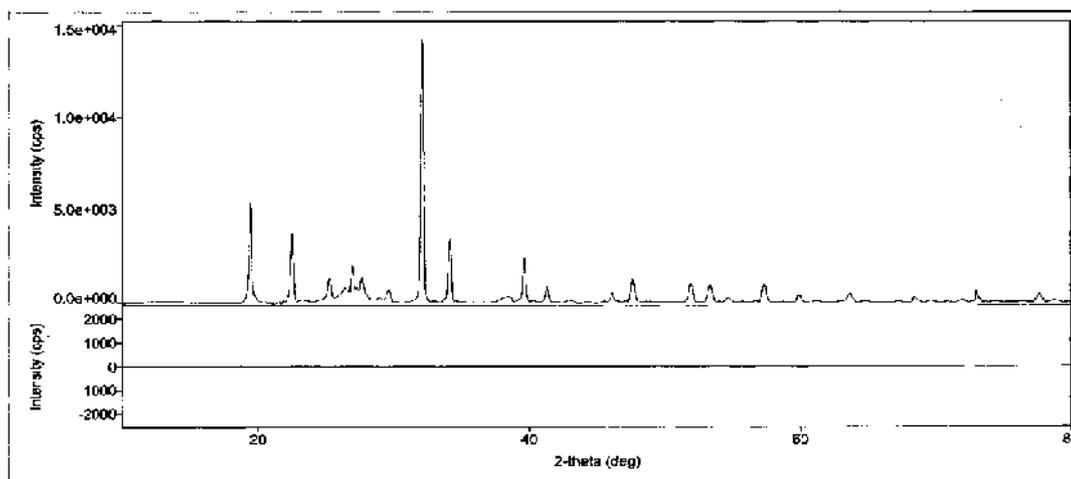


Fig. 1.2: XRD of Complex HTDSB

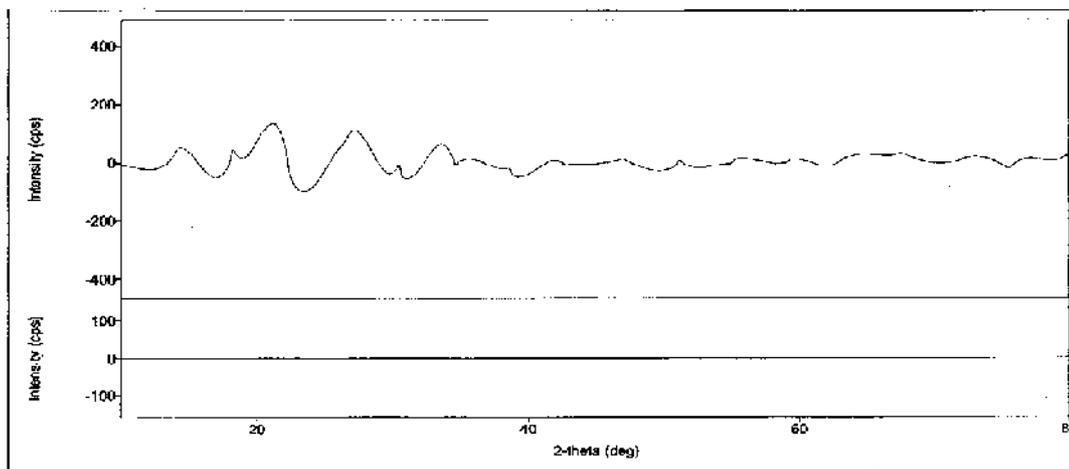


Fig. 1.3: XRD of Complex HTDSB-Cu (II)

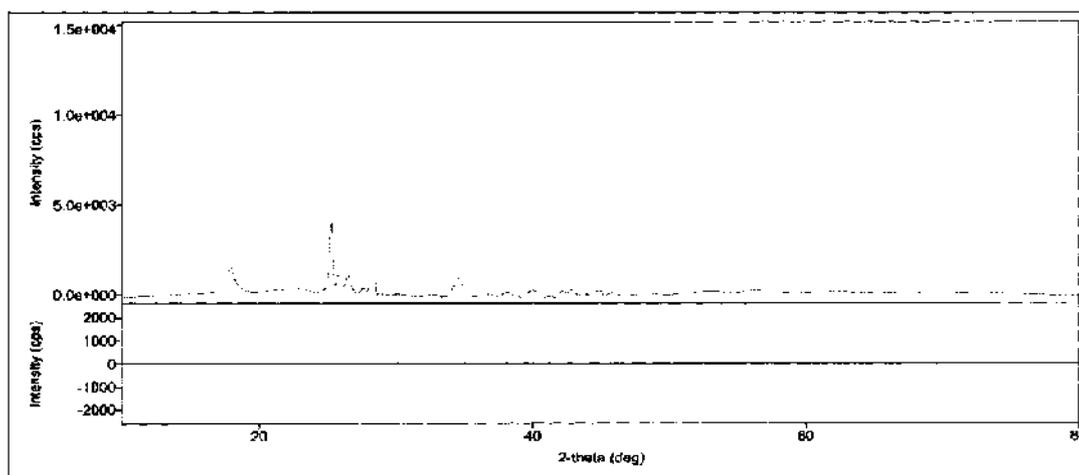


Fig. 1.4: XRD of Complex HTDSB-Ni (II)

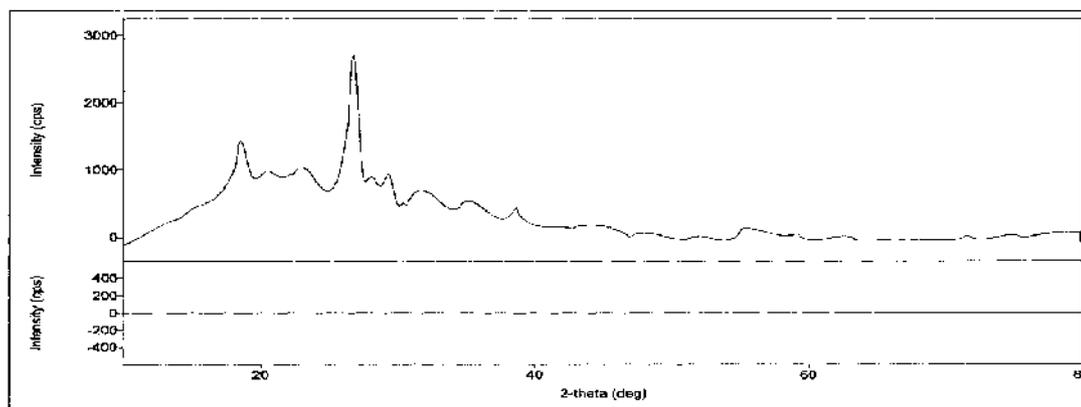


Fig. 1.5: XRD of Complex HTDSB-Mn (II)

### Thermal study of modified HTD and its metal complexes

The thermograms of modified HTD and its metal complexes are shown in Fig. 1.6. All the modified HTD and its metal complexes show a gradual weight loss indicating decomposition by fragmentation with increase in temperature. The thermograms of the HTD and its metal complexes show nearly the same pattern of decomposition reflecting their isostructural characteristics. An analysis of the thermograms of all HTD and its metal complexes indicates that these undergo single step decomposition after dehydration, while HTDSB undergo two steps decomposition. One coordinated water in HTD and its metal complexes [%wt. loss obs. /calcd.: 13.81/13.85]. An examination of the thermograms of modified

HTD and its metal complexes indicates that they are with varying thermal stability undergoing decomposition at different temperature. In all the modified HTD and its metal complexes rapid weight loss has been observed at around 300°C, indicative of decomposition of free part of the modified HTD and its metal complexes. A gradual increase in temperature above 600°C was accompanied by degradation of organic part content of the modified HTD and its metal complexes, leading to the formation of stable residue. The thermal data of the compounds is given in Table -3. On the basis of half decomposition temperature, the thermal stability order of compounds was found to be HTD < HTDSB < HTDSB Cu < HTDSB Ni < HTDSB Mn.

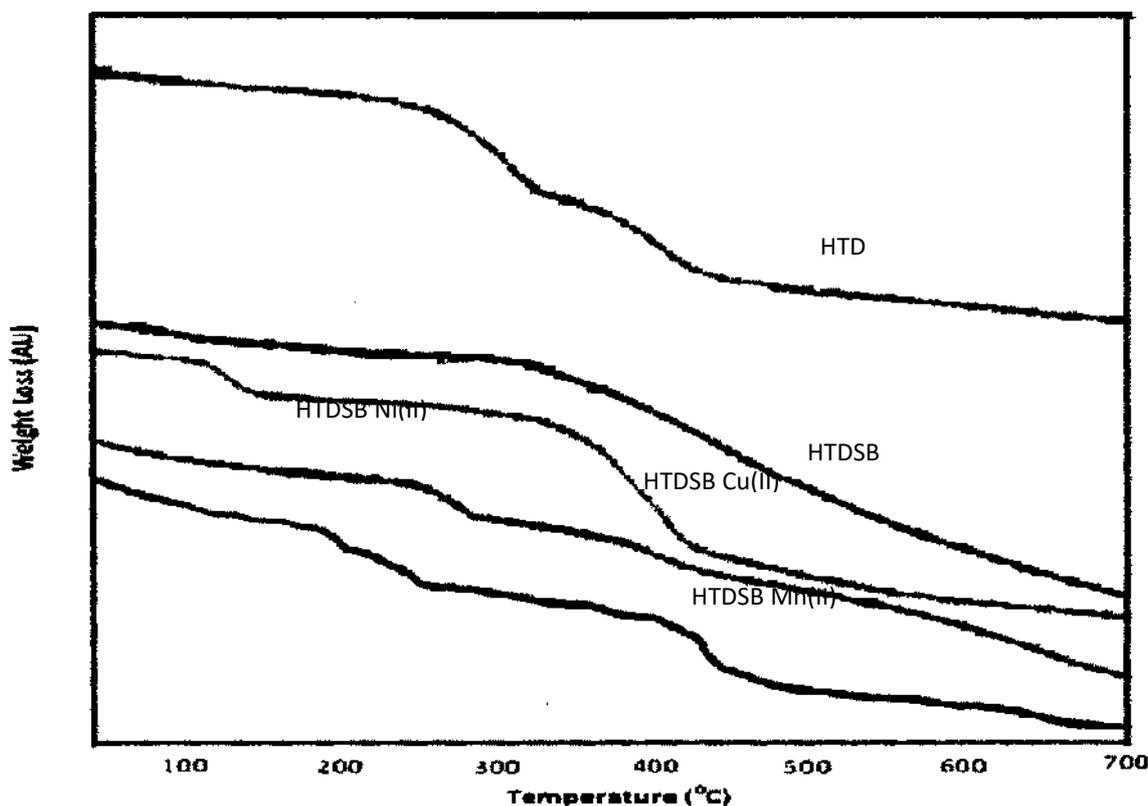


Fig. 1.6: Thermograms of HTD and its metal complexes

Table - 3: Thermal data of the compounds of HTD and its metal complex

Samples	Half Decomposition Temperature ( $^{\circ}\text{C}$ )	Activation Energy ( $\text{KJ mole}^{-1}$ )	Frequency Factor Z ( $\text{Sec}^{-1}$ )	Entropy Change - US ( $\text{J mol}^{-1}\text{K}^{-1}$ )	Free Energy Change UG ( $\text{k J Mol}^{-1}$ )
HTD	274	74.00	16.98	949	548.48
HTDSB	520	25.01	26.40	228.10	148.42
HTDSBCu(II)	386	35.89	79.36	216.80	119.71
HTDSBNi(II)	633	22.40	156.00	200.68	164.28
HTDSBMn(II)	306	18.18	142.38	206.26	78.00

### Antifungal activity

Table-4: Antifungal Activity of Newly Synthesized Compound

Compound	Diameter of zones showing complete inhibition of growth (mm)			
	<i>Aspergillus niger</i>	<i>Aspergillus flavus</i>	<i>Candida albicans</i>	<i>Tricocytum calcium</i>
HTD	18	16	22	19
HTDSB	16.2	19	20	15.2
HTDSB Cu(II)	17	15	18	18
HTDSB Ni(II)	22	20.5	13	20
HTDSBMn(II)	15	22	24.5	15.5

### Antioxident activity

Table-5: DPPH scavenging activity of newly synthesized compounds

Concentration ( $\mu\text{g/mL}$ )	Ascorbic Acid	HTD	HTDSB	HTDSBCu(II)	HTDSBNi(II)	HTDSBMn(II)
1.25	22.66%	14.74%	16.13%	17.4%	22.60%	16.40%
2.5	35%	56.14%	40.71%	64.25%	28.20%	24.00%
5	74.10%	72.34%	44.80%	70.00	58.82%	54.15%
10	92.20%	80.81%	76.78%	62.00	74.40%	86.60%
IC <sub>50</sub>	3.96	3.76	5.65	3.56	5.40	5.16

## Conclusion

In the present investigation, synthesis and characterization of Schiff bases synthesized from HTD with substituted m-Hydroxy acetophenone and derivative HTDSB with transition metal (II) complexes have been attempted due to their wide range of applications in various fields of science. The present investigation is summarized in the form of the following conclusions. In modification and complexation process positive change is occur in HTD backbone and this change is most important for further characterization. The spectral data shows the remarkable and positive change occur in HTD after reaction with substituted m-Hydroxy acetophenone. Also spectral data shows the remarkable and positive change occur in HTD compounds after complexation of HTDSB.

Thermogram of the Schiff bases synthesized from HTD with substituted m-hydroxy acetophenone and derivation HTDSB with transition metal (II) complexes indicate that they have varying degree of thermal stability and undergo decomposition at different temperature. The percent weight loss as computed from the thermo grams of the Schiff base synthesized from HTD with substituted m-Hydroxy acetophenone and derivative HTDSB with transition metal (II) complexes.

The experimental studies in the present investigation shows that the uses of HTD and HTDSB brings some change in structure and enhances thermal properties of the HTD compounds

## Acknowledgments

The authors gratefully acknowledge the Department of Chemistry, Government Vidarbha Institute of Science and Humanities.

## References

1. MohamadArshad, Taki Ahmed Khan and Alam Khan, *International Journal of PharmaSciences and Research (IJPSR)*, Vol. 5, No. 04, (Apr. 2014).
2. Supun Katugampala, Inoka C. Perera, Chandrika Nanaya Kkara and Theshini Perera, *Bioinorganic Chemistry and Applications*, Vol. 20188, Article ID 2530851, No, 07, (Aug. 2018).
3. Sonmez, M. and M.Sekerci, *Polish J. Chem*, Vol. 76, No. 907-914 (2002).
4. Keypour, H. S. Salehzadeh and R.V. Parish, *J. Molecules*, Vol. 7, NO. 140-144, (2002).
5. R. Shanmugakala, P. Thamaraj, C.D. Sheela and C. Anitha, *International Journal of Inorganic Chem.*, Vol. 2012, No.7, (Nov. 2012).
6. Liu, Y.-T.; Sheng, J.; Yin, D.-W.; Xin, H.; Yang, X.-M.; Qiao, Q.-Y.; Yang, Z.-J., *J. Organomet. Chem.*, 856, 27–33, (2018).
7. Reddy, V.N. Patil and S.D. Angadi, *E-J. Chem.*, Vol. 5(3), No. 577-583, (2008).
8. Hanna W.G. and M.M. Moaeed, *Transition Metal Chemistry*, Vol. 26, No. 644, (2001).
9. Pandeya, S.N., D. Sriram, G. Nath and E. Clercq De, *Pharma Acta Helv*, Vol. 74, No. 11, (1999).
10. Ravanassiddappa M.T. Suresh K. Syed, S.C. Radhavendray C. Basavaraj and S.D. Angadi, *E-J. Chem.*, Vol. 5(2), No. 395-403, (2008).
11. Del Paggio, A.A., D.R. McMillin, *Inorg Chem.*, Vol. 22, No. 691, (1983).
12. Canpolat, E. and M. Kaya, *J. Coord. Chem.*, 123, (2004).
13. R.J. Angellici, *Synthesis and Techniques in Inorganic Chemistry*, W.B. Saunders Company (1969).
14. Hassib H., Razik A.; *Solid State Commun*, 147, 346, (2008).
15. Daw ZY, EL-Baroty GS, Mahmoud AE. *Chemie, Mikrobiologie, Technologie der Lebensmittel.* , Vol.16, 129–135(1994).
16. Myiut S, Daud WRW, Mohamed AB, Kadhum AAH., *Journal of Chromatography B*, Vol.76, 193–195,(1996).
17. Al-Amiery AA., *Medicinal Chemistry Research*, Vol.21, 3204–3213,(2012).

19. Fitsum Lemilemu, Mamaru Bitew, Taye B. Demissie, Rajlakshmanan Eswaramoorthy & Milkyas Endale, *Chemistry Central Journal*, Vol. 15,67, (2021).
20. Sayed Suliman Shah, Dawood Shah, Ibrahim Khan, Sajjad Ahmad, Umar Ali, Atiqur Rahman, *Platinum Open Access Journal*, Vol. 10, Issue 6, 6936 – 6963, (2020).

Access this Article in Online	
	Website: <a href="http://www.ijcrcps.com">www.ijcrcps.com</a>
	Subject: Chemistry
Quick Response Code	
DOI: <a href="https://doi.org/10.22192/ijcrcps.2022.09.10.001">10.22192/ijcrcps.2022.09.10.001</a>	

How to cite this article:

Gopalkrushna H. Murhekar and Supriya Belsare. (2022). Synthesis spectral study of novel series of Schiff base ligands and its metal complexes. *Int. J. Curr. Res. Chem. Pharm. Sci.* 9(10): 1-11.

DOI: <http://dx.doi.org/10.22192/ijcrcps.2022.09.10.001>