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SYNTHESIS AND CHARACTERIZATION OF NOVEL SERIES OF TRIZINES SCHIFF BASE COMPLEXES WITH TRANSITION METAL IONS

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ABSTRACT

Schiff bases played a special role as chelating ligands in main group and transition metal chemistry because of their stability under a variety of redox condition. In addition they have different biological activity for example; antimicrobial activity and insecticides and further their metal complexes show more enhancements in all these activities. 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 Ni (II), 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 Ni (II), Mn (II) and Cu (II) were screened for their antimicrobial properties.

KEYWORDS

Antimicrobial properties, Triazine, Analysis, Thermal properties, Schiff base complexes and Transition metal ions.

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INTRODUCTON

Heterocyclic chemistry is fundamental to biology and medicine. It is not implausible to say that we are living in the age of heterocyclic chemistry. The constitutes of heterocyclic compounds have a large group of organic molecules exhibiting a wide range of biological activities which is basis of life and society. Triazines are nitrogen containing heterocycles. In the field organic chemistry, the term heterocycle refers to a ring system (or cyclic compound) that contains at least two different elements that make up the ring. A triazine is a heterocyclic structure that contains three nitrogen

atoms and three carbon atoms. There are three different triazine isomers and they differ from one another in the order of the nitrogen atoms relative to the carbons. The isomers have a organic compounds that have the same chemical formula but different atom connectivity. The isomers are 1, 2, 3-triazine, 1, 2, 4-triazine and 1, 3, 5-triazine[1-4].

Triazines have planar six-membered benzene-like ring but with three carbons replaced by nitrogen. The three isomers of the triazine are distinguished by the positions of their nitrogen atoms and are referred to as 1, 2, 3-triazine, 1, 2, 4-triazine, and 1, 3, 5-triazine[5-6]. The pyridine is a aromatic nitrogen heterocycles with one ring nitrogen atom, diazines with 2 nitrogen atoms in the ring, triazoles with 3 nitrogens in a 5 membered ring and tetrazines with 4 are well known. They are substituted at the carbon and ring nitrogen atoms. Triazine derivatives nitrogen atoms. Melamine is a derivative of 1, 3, 5-triazine and contains three -NH_2 groups, one bonded to each of the carbon atoms of the ring. Melamine is mostly used as a fire-retardant agent and also is used as a pesticide in some cases. A triazine is a well-known melamine (2, 4, 6-triamino-1, 3, 5-triazine). With three aminosubstituents, melamine is a precursor to commercial resins[7-9]. Guanamines are closely related to melamine, except with one amino substituent replaced by an organic group. This difference is exploited in the use of guanamines to modify the cross linking density inmelami[10].

The cyanuric chloride is another important triazine derivative. The derivative of 135 trizines is chlorinated at each of the three carbon atoms of the triazine ring and finds application as a precursor (building block or starting material) to a lot of popular pesticides. Chlorine-substituted triazines are components ofreactive dyes. These compounds react through a chlorine group with hydroxyl groups present in cellulose fibers innucleophilic substitution, the other triazine positions contain chromophores. Triazines compounds are often used as the basis for various herbicides. Some commercially important guanamines are benzoguanamine and acetoguanamone[11,12].

Transition metals ions have large numbers and unique biological, chemical and physical properties due to the availability of d electrons in valance shells. More attention has been focused on copper complexes due to their various potential biological activities out of which antimicrobial and an antiviral activity is paramount. Since triazine is a well-known natural material which possesses many biological properties, it is not surprising that organometallic complexes of triazine with first row transition metal ions Mn, Co, Ni, Cu and Zn, with second row transition metals Ru, Pd, Ag and Cd and with third row transition metals Re and Pt have been synthesized and their activities explored as catalysts and biological agents such as antibacterial, anticancer, antifouling, antifungal, anti-HIV, antimicrobial, antiproliferative, antiviral and DNA binding agents[13-15].

Metal complexes with potentially tridentate and tetra dentate ligands have evoked much interest in coordination chemistry. Schiff base complexes of transition metals have played prominent role in the development of coordination chemistry. Various Schiff base metal complexes have been studied because of their industrial and biological applications. The Schiff bases containing polyfunctional groups offer many practical advantages and unique structural environment for complexation. Literature survey reveals that many benzothiophene derivatives are known to possess good biological activities like antimicrobial, anti-inflammatory, analgesic, diuretic and antiviral activities[16-17]. Hence in the present work Novel series of Schiff bases derived from 2, 4-bis (hydrazine)-6-substituted Triazines has been synthesized and characterized by elemental analysis, Antimicrobial properties and further confirmed by UV, FTIR spectroscopic studies.

MATERIAL AND METHODES

All chemicals and solvents used were of AR grade. The infra-red spectra of the compounds were recorded in the conventional region (400-4000cm^{-1}) as KBr pellets. The infra-red spectral measurements were done using FT-IR Shimadzu spectrometer. The UV spectra of title compound and its complex

were recorded inthe conventional region (200-800nm) using DMSO as solvent. The UV spectra measurements were done in the UV-1800 Spectrophotometer. 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. The melting or points decomposition temperature were determined by placing a finely powdered sample in a glass capillary and heating by using digital melting point Apparatus.

Synthesis of Hydrazino-Trazine derivative (HTD)

Chemical Required

Cynuaric chloride, Acetonitrile, Hydrazine hydrate.

Method

Dissolved Cynuaric chloride (0.05M) in acetonitrile (90%) solution (10ml) in 250ml beaker, then dissolved Hydrazine hydrates (0.05M) in acetonitrile (90%) solution (10ml) in 250ml round bottom flask. Add the cynuaric chloride solution in RB at room temperature. Refluxed the mixture for 3- 4 hrs at constant temperature. Then the excess of hydrazine and solvent was removed under vacuum and the crude white precipitate was filtered off, washed with acetonitrile and ether and then dried to afford the desired products with high yields and purities. The products were used directly in the next step.

Melting point - 238^{o}C

Reaction

Synthesis of Hydrazino Triazine Schiff Base (HTDSB)

Chemical Required

Hydrazin - Triazine derivative (HTD), m-Hydroxy acetophenone, Ethanol

Method

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

Melting Point - 252^{o}C

Reaction

Synthesis of Transition metal complexes with Hydrazino - Triazine Schiff Base

Chemical Required

Hydrazino-Triazine Schiff Base, Dimethyl Sulphoxide, anhydrous metal halides, Sulphate (CuSO4, NiSO4, MnSO4)

Method

[VO (II) SO4. H2O, CoCl2.6H2O, RhCl3.XH2O, PdCl2 and HAuCl3.H2O] ethanol solution of 2N-salicylidene-5-(p-nitro phenyl)-1, 3, 4thiadiazole,

An DMSO solution of the metal ions (Cu, Ni and Mn) was added to Hydrazino - Triazine Schiff Base (0.01M) in DMSO HL in 1:2 (metal: ligand) molar ratio. Then, the mixture was heating under reflux for half an hour and coloured precipitates were obtained. Later, the precipitates were filtered out, washed with distilled water and finally recrystallized from DMSO.

Reaction

Antimicrobial Study

The disc diffusion method is based on the fact that for a given antibiotic, the size of the zone of inhibition is inversely related to the MIC (determined by the dilution method) of strain being tested when the conditions are held constant. Antimicrobial susceptibility testing with discs is a simple and rapid method and provides a reproducible means of testing bacterial sensitivity to various antibiotics and chemotherapeutical agents[18,19].

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 No.1.

FT-IR Spectral Interpretation

Infrared absorption spectrum of newly synthesized compound and its complexes is recorded with potassium bromide (pelletization). The corresponding spectra are shown in Figure No.1 HTD with substituted acetophenone and ligand HTDSB with transition metal (II) complexes at different frequencies HTD absorb at 1.64 values. It gives characterized peak at 2175cm-1 due to C=N. Whereas HTDSB gives characterized peak at 2360cm-1 respectively. Also complexes HTDSB with Co (II), Cu (II) and Ni (II) gives peak at 3896, 3340, 3279. The IR data of newly synthesized compounds is shown in Table No.2.

UV-Spectral Interpretation

UV-Visible spectra of Schiff bases synthesized from HTD with substituted acetophenone and ligand HTDSB with transition metal (II) complexes were recorded on Shimadzu UV-1800 spectrophotometer, all newly synthesized compounds by placing an uncoated identical conducting glass substrate in the reference beam ranging from 200 to 1100nm. Wavelength for maximum absorbance λmax and corresponding optical band gap for all samples are presented in Table No.3. All compounds have a conjugate system of double bonds on their backbone, such as σ-σ*, Π-Π*, n-Π* etc. The σ-σ* transition of conjugated double bonds is related to near UV regions around 200nm, UV-visible spectra of the spectrum of pure HTD is characterized by an absorption edge at wavelength 258nm. This absorption edge can be attributed for >C=N in backbone of compound[18-19]. Also, absorbance increases Schiff bases synthesized from HTD with substituted acetophenone and HTDSB and transition metal (II) complexes.

Antimicrobial Properties

Liquefied sterile Muller-Hilton agar (pH 7.3± 0.1) was poured into sterilized Petri plates. The Petri plates were allowed to stand for some time, until the agar medium gets same time, until the agar medium get solidified, the bacterial cultures (*Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Pseudomonas fluorescence*) After that the bacterial culture medium was lawned on the surface of the medium using a sterilized cotton swab. The newly synthesized compound was loaded on sterilized discs in different concentrations. These discs were carefully placed on the surface of the medium with the forceps. The Petri plates were incubated for 16-18 hrs at +35 to +37^{o}C in inverted position[20-22]. After that the zone of inhibition was measured in mm. On the basis of result / antimicrobial testing it is noted that the given compound Cu (II) found to be Antimicrobial against *Bacillus subtilis* (11mm), *Escherichia coli* (11mm), *pseudomonas fluorescence* (11mm). Compound Mn (II) having Antimicrobial against *Staphylococcus aureus* (12mm), *Bacillus subtilis* (11mm). Compound Ni (II) found to be no antimicrobial activity represented in Observation Table No.4.

Table No.1: Physical Data of Newly Synthesized compounds

S.No	Name of Compound	Compound	Molecular Weight	color	% Yield	M. Pt. (ºC)
1	HTD	CH_3NH_9	171	White	68%	238ºC
2	HTDSB	$CH_{27}N_{14}O_3$	525	Yellow	89%	252ºC
3	HTDSB-Cu(II)	$CH_{54}N_{28}O_6Cu$	1117.54	Green	96%	185ºC
4	HTDSB-Ni(II)	$CH^{54}N_{28}O_6Ni$	1112.69	Yellow	87%	196ºC
5	HTDSB-Mn(II)	$CH_{54}N_{28}O_6Mn$	1108.93	Black	93%	189ºC

Table No.2: FTIR data of Triazine compound

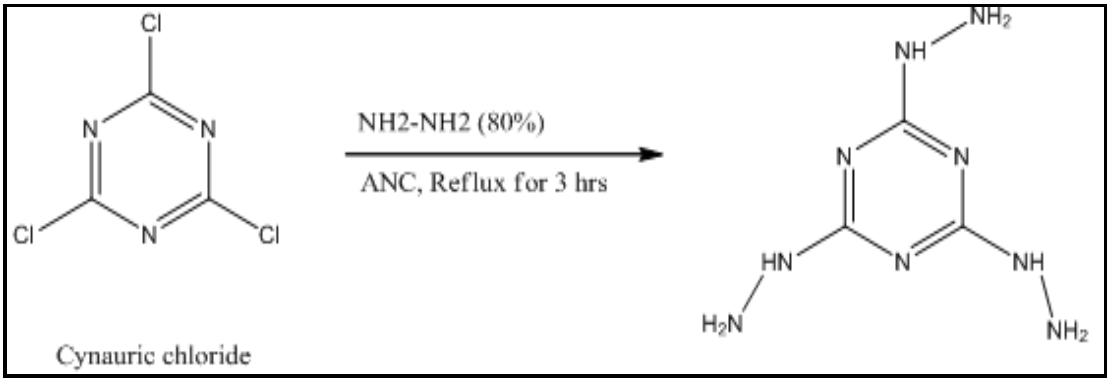
S.No	Compound	IR frequency in cm-1
1	HTD	3811, 3742, 3209, 2962, 2704, 2615, 2360, 2175, 1709, 1593, 1253, 1099
2	HTDSB	3892, 3738, 3201, 2978, 2360, 2175, 1944, 1612, 1496, 1219, 999
3	HTDSB Cu(II)	3896, 3811, 3738, 3194, 2360, 2110, 1739, 1546, 1396, 1203, 949
4	HTDSB Ni(II)	3340, 3005, 2920, 2218, 1496, 1315, 1284, 821
5	HTDSB Mn(II)	3279, 2928, 2380, 2204, 1518, 1485, 1111, 871

Table No.3: UV-Visible absorption values Triazine Compound

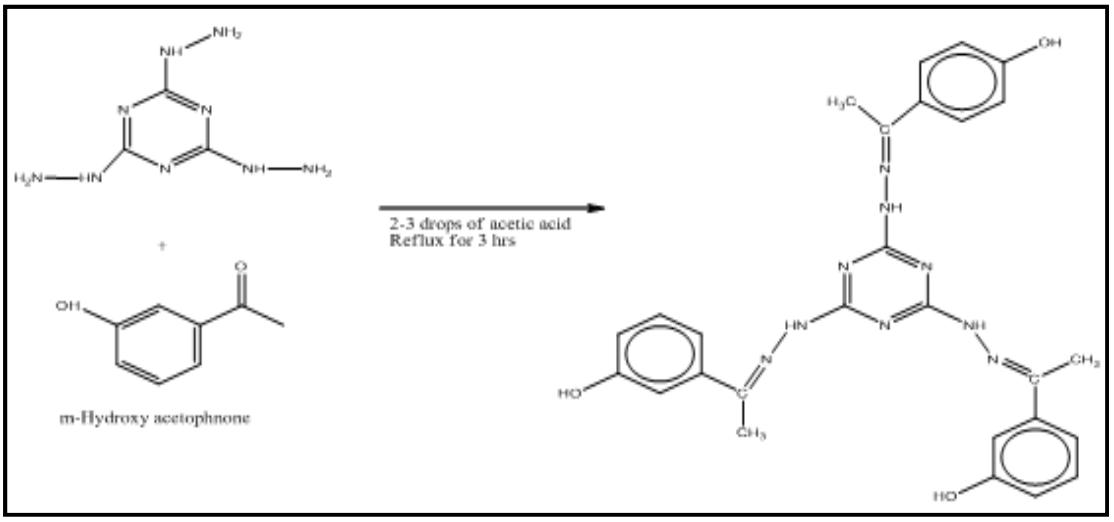
S.No	Material	λmax nm	Absorbance(au)
1	HTD	258	2.696
2	HTDSB	307	0.459
3	HTDSB-Cu(II)	307	0.727
4	HTDSB-Ni(II)	342, 310, 266, 318, 283	0.388, 0.328, 0.325, 0.314, 0.263
5	HTDSB-Mn(II)	336, 311, 271, 280	0.337, 0.341, 0.285, 0.280

Table No.4: Antimicrobial Activity of HTD and its metal complexes

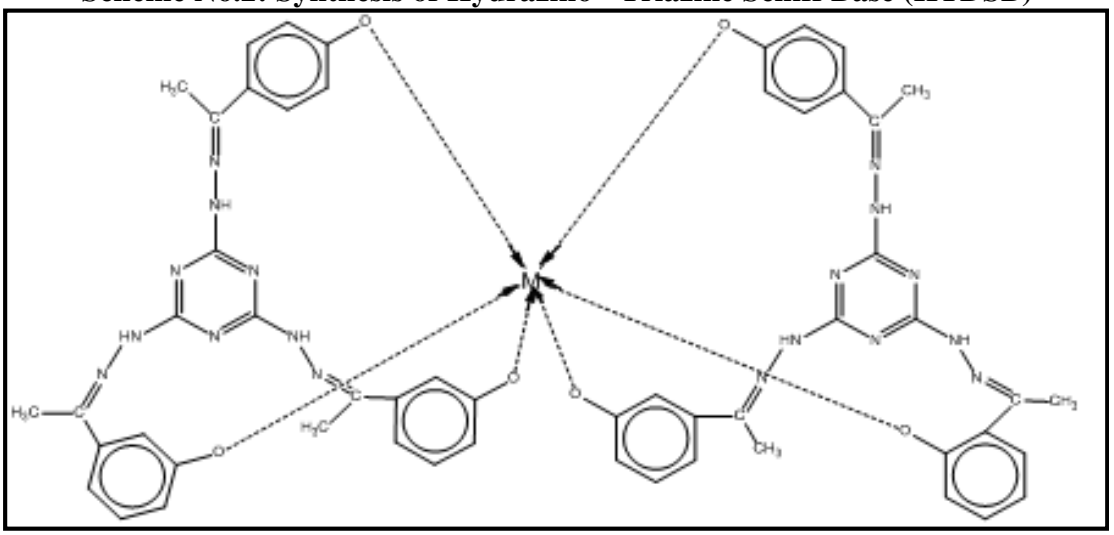
S.No	Test Compound	Zone for inhibition in mm			
		GM + VE Bacteria		GM - VE Bacteria	
		Staphylococcus aureus	*Bacillus subtilis*	*Escherichia coli*	*Pseudomonas fluorescence*
1	HTDSB-Cu(II)	----	11mm	11mm	11mm
2	HTDSB-Ni(II)	----	----	----	----
3	HTDSB-MN(II)	12mm	11mm	----	----
4	Reference Antibiotic	32mm (Ofloxacin)	35mm (Ofloxacin)	20MM (Ofloxacin)	45MM (Ofloxacin)
5	Control Disc	--	--	--	--



Scheme No.1: Synthesis of Hydrazino-Triazine derivatives (HTD)



Scheme No.2: Synthesis of Hydrazino - Triazine Schiff Base (HTDSB)



Scheme No.3: Structure of Hydrazino–Triazine Schiff Base-M(II) Complexes. (HTDSB)-M (II)

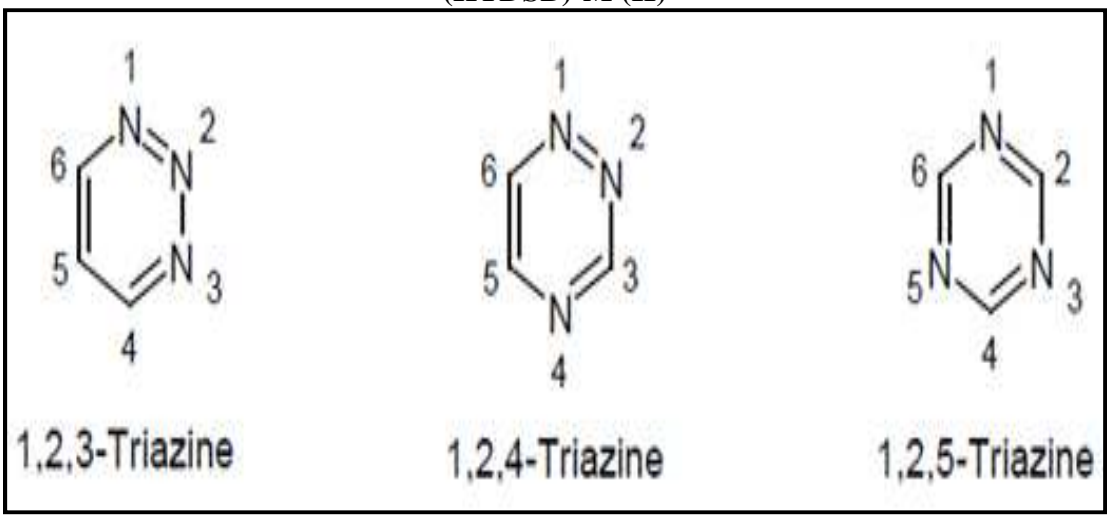


Figure No.1: Isomers of Triazine

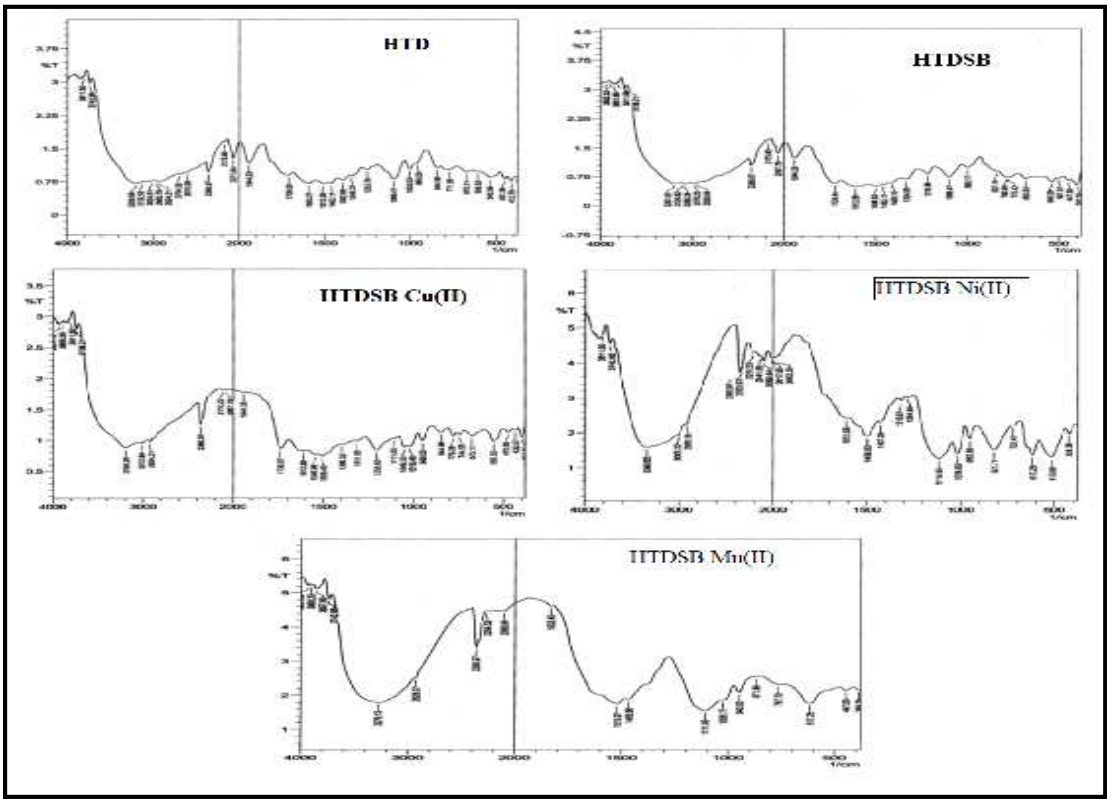


Figure No.2: IR Spectra of compounds

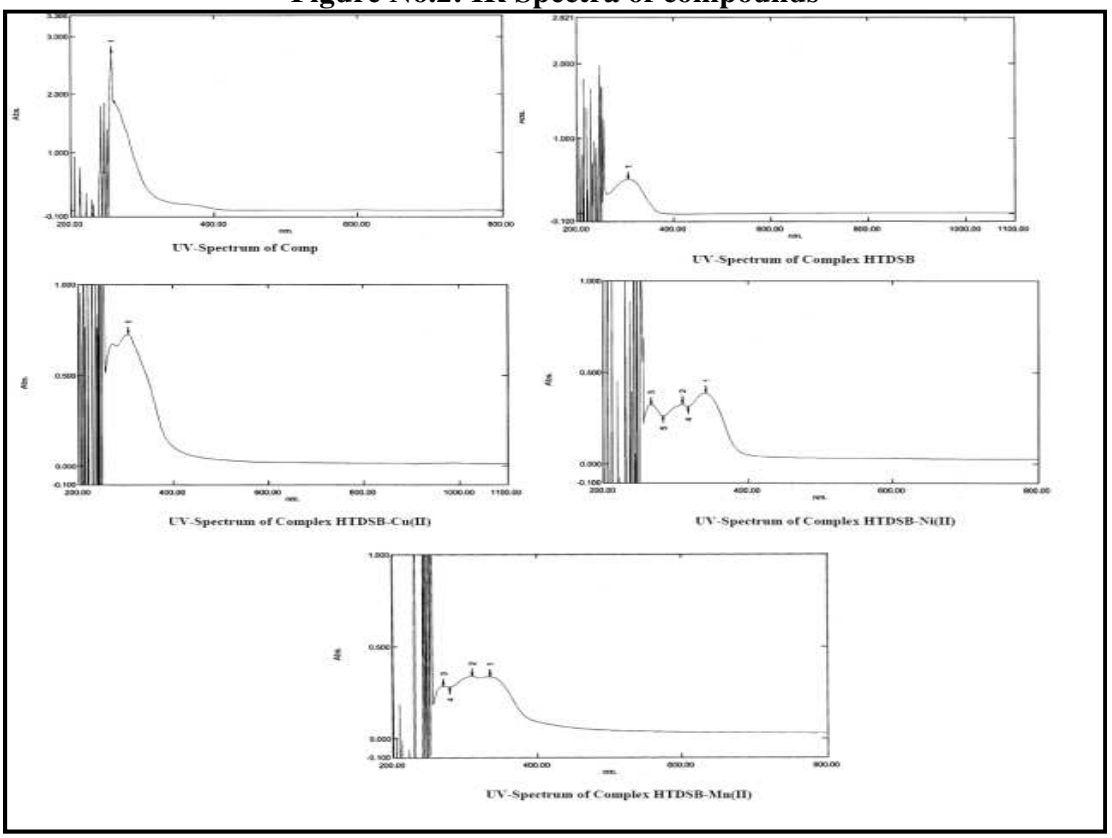


Figure No.3: UV- Spectra of Triazine Compound

FOR ANTIMICROBIAL SENSITIVITY TEST (After 24 hrs at 37°C)

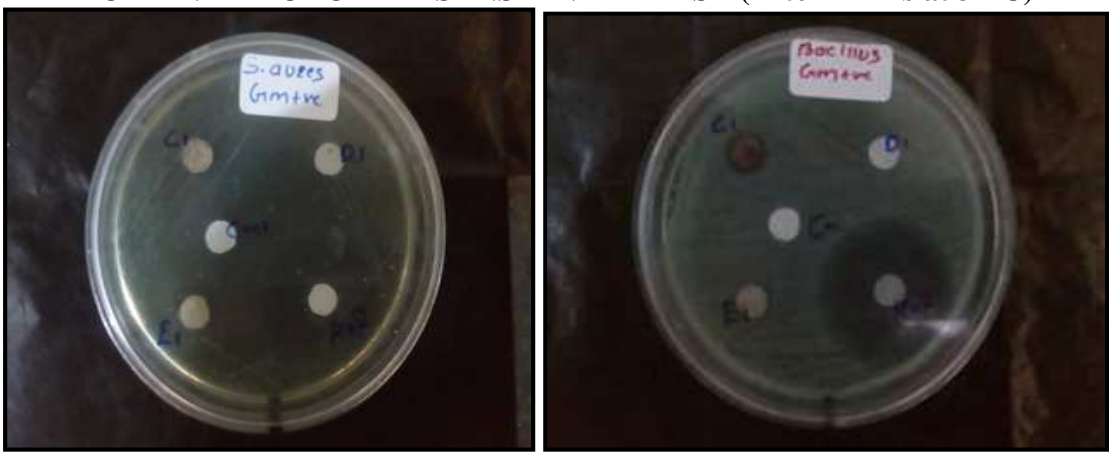


Figure No.4: Antibacterial activity of Schiff base Cu (II), Ni (II) and Mn (II) Complex against Gram + ve bacteria *Staphylococcus aureus* and *Bacillus subtilis*

Figure No.5: Antibacterial activity of Schiff base Cu (II), Ni (II), Mn (II) Complex against Gram - ve bacteria *Escherichia coli* and *Pseudomonas fluorescence*

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 complexion 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 complexion of HTDSB.

The antimicrobial activities of all the synthesized compounds are given in solvent DMSO. Different Gram positive and Gram negative strains are used for antimicrobial study. All compound shows different zone of inhibition.

The experimental studies in the present investigation shows that the uses of HTD and HTDSB brings some change in structure and enhances the various properties of the Trizine compounds[23-25].

ACKNOWLEDGEMENT

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CONFLICT OF INTEREST

We declare that we have interest. Following research areas, organic synthesis, Polymer drug delivery, heterocyclic chemistry, etc.

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