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Synthesis, Characterization, and Antibacterial Activity of the Schiff Base derived from P-Toluic hydrazide and 2-hydroxy-4-methoxy Acetophenone (HMAPPTH Ligand) and their Mn (II), Co (II), Ni (II) and Cu (II) Complexes

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ABSTRACT

Metal complexes of a novel Schiff base derived from condensation of p-toluic hydrazide and 2-hydroxy-4-methoxy acetophenone are reported and characterized based on elemental analyses, FT-IR, ¹H-NMR, UV-Visible, VSM, Molar conductance, and micro analytical data and also found to be an anti bacterial activity. From the elemental analyses data, 1:2 metal complexes are formed. The magnetic properties of these Mn (II), Co (II), Ni (II) and Cu (II) complexes are 5.40 B.M., 4.89 B.M., 3.18 B.M and 1.61 B.M respectively. This result clearly indicates that the metal complexes of this ligand show octahedral geometry. The IR spectrums of these Schiff base metal complexes shows bands at 1612 cm⁻¹, 1590 cm⁻¹, 1585cm⁻¹, and 1602cm⁻¹ respectively, which is assigned to (C=N) stretching vibrations, a fundamental feature of azomethine group. The anti bacterial results also indicate that the metal complexes are better antibacterial agents as compare to the Schiff base. All the metal chelates are found to be non-electrolytes.

Keywords: Schiff base, p-Toluic hydrazide, 2-hydroxy-4-methoxy Acetophenone, Anti bacterial activity and characterization.

INTRODUCTION

There is a continuing interest in transition metal complexes of Schiff bases because of the presence of both nitrogen and oxygen donor atoms in the backbones of these ligands, some of these complexes have been exhibit interesting physical and chemical properties and potentially useful biological activities [1-4]. Schiff base have also been used for analytical purposes in the determination of metal ions, and some Schiff base derivatives have been used in the extraction of metal solvents. The applications of such complexes depend to a large extent on their molecular structure. Schiff base ligands are able to coordinate many different metals, and to stabilize them in various oxidation states [5-7]. The Schiff base complexes have been used in catalytic reactions and as models for biological systems. During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donors. This may be attributed to their stability, biological activity and potential applications in many fields such as oxidation catalysis, and electrochemistry. Schiff base ligands have an affinity for transition

metals such as Cu, Mn, Co, Ni and Fe. Some of these complexes have been studied [8-10] in great deal for their various structures, steric effects and their coordination chemistry.

The present paper deals with a new series of metal complexes of Mn (II), Co (II), Ni (II) and Cu (II) with Schiff base ligand (HMAPPTH) derived from P-Toluic hydrazide and 2-hydroxy-4-methoxy acetophenone. These complexes were characterized by elemental analysis, IR, NMR, UV, ESR spectroscopy, TG-DTA, Powder X-Rd, VSM and Conductivity measurements to determine the mode of bonding, geometry and biological activities of the metal complexes were also studied.

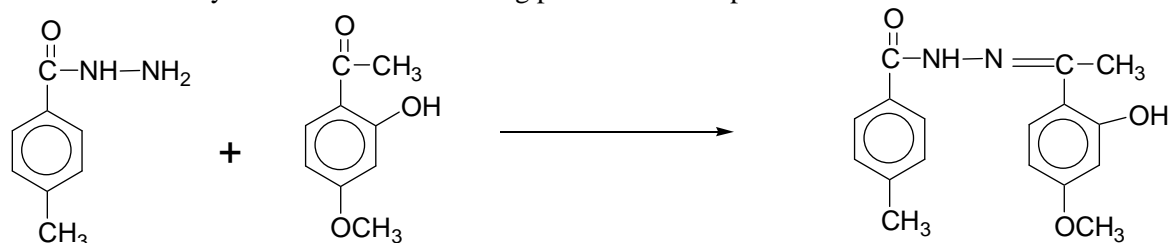
MATERIALS AND METHODS

All materials used in this investigation were purchased from AR Sd fine, AR Loba, AR (Qualigenes), Sigma/Aldrich and SRL (Sisco) and used as received. They include Sodium Meta Vanadate, Sodium hydroxide, p-Toulic hydrazide, 2- hydroxyl -4-methoxy acetophenone, methanol and double distilled water was used during the experimental procedures.

IR spectra were recorded with a Perkin-Elmer IR-598 spectrometer ($4000-400\text{ cm}^{-1}$) using KBr pellets. The ^1H NMR spectra of the ligands and their metal complexes are recorded on an AV-400 M-HZ NMR spectrometer in IICT, Hyderabad in DMSO-D_6 and CDCl_3 solvents at room temperature. The absorbances are measured on Elico SL UV-Visible spectrophotometer. Magnetic susceptibility data was recorded on an EG and G-155 magneto meter. Thermo gravimetric analyses of the metal complexes were carried out by using the Perken Elmar System in thermal analysis center: STIC KOCHIN. The molar conductance measurements were carried out in DMF using conductivity meter model CM Elico-185.

Synthesis of p-Toluic hydrazide and 2-Hydroxy-4-Methoxy Acetophenone Schiff base (HMAPPTH):

Mixture of p-Toluic hydrazide (1.5018g) and 2-Hydroxy-4-Methoxy Acetophenone (1.6617g) were dissolved in 30 ml ethanol and added few drops of dil HCl. The whole mixture was transferred in to 250 ml round bottom flask. The mixture was refluxed about for 2 hours on water bath. When the reaction mixture was allowed to cool yellow crystals were obtained. The compound was recrystallized from ethanol. The % of yield was 78% and melting point of the compound was $190-192^\circ\text{C}$.



P-Toluic hydrazide 2-Hydroxy-4-Methoxy Acetophenone

HMAPPTH Ligand

Scheme: Synthesis of HMAPPTH Ligand

Synthesis of V (IV), Mn (II), Co (II), Ni (II) and Cu (II) metal complexes of p-Toluic hydrazone and 2-hydroxy-4-methoxy acetophenone Schiff base (HMAPPTH): These complexes were prepared by adding required 2g (0.0067 moles) amount of Schiff base in 50ml of 50% methanol to the Mn (II), Co (II), Ni (II) and Cu (II) metal ions (0.0067 moles) in distilled water in the presence of Sodium acetate and stirred about 12 hours. Yellow, greenish black, dark brown and green color precipitates of metal complexes were obtained respectively with good yield. These products were washed several times with hot water and cold methanol to free from unreacted metal salts and ligand respectively and finally with ether and dried in vacuo over calcium chloride desiccator.

RESULTS AND DISCUSSION

IR & NMR Spectral Studies: IR & NMR data gives further useful information on the structure HMAPPTH ligand and its metal complexes. IR & NMR spectrum of the free ligand was compared with the spectrum of the metal complexes. The structurally significant IR & NMR Spectral data of free HMAPPTH ligand and its metal complexes have been reported in table 1 and 2. The IR & NMR spectra are shown in fig 1a-f.

In NMR spectrum a signal observed at 11.13ppm due to N-H proton in the ligand is shifted to δ 11.42, 11.21ppm respectively [11-12] for HMAPPTH-Co and HMAPPTH-Cu metal complexes. A broad band exhibited at 3294 cm^{-1} in the IR spectrum of the ligand is due to N-H stretching vibration. On complexation this band shifted to 3309, 3308, 3305 and 3306 cm^{-1} for Mn (II), Co (II), Ni (II) and Cu (II) complexes respectively. The IR spectrum of the ligand has shown a sharp band at 1706 cm^{-1} due to C=O stretching vibration. On complexation this band shifted to 1664, 1668, 1659 and 1672 cm^{-1} for Mn (II), Co (II), Ni (II) and Cu (II) Complexes respectively. These results indicate the formation of complexes. The IR spectra of Mn (II), Co (II), Ni (II) and Cu (II) complexes exhibited broad bands at 3441 cm^{-1} , 3530 cm^{-1} , 3510 cm^{-1} and 3450 cm^{-1} respectively which can be assigned to the OH stretching vibration of the coordinated water molecules [13-15]. These results indicate that the ligand coordinates with the metal ion through the azomethine nitrogen and the oxygen of the deprotonated hydroxyl group. The suggested structures of the complexes are given in Fig 4.0

Table 1. Important IR bands of HMAPPTH ligand and its metal complexes

Compound	OH Water	OH Phenolic	C=N	N-H	C=O	M-O	M-N
HMAPPTH	-	3227	1642	3294	1706	-	-
HMAPPTH-Mn	3441	-	1612	3309	1664	648	454
HMAPPTH-Co	3530	-	1590	3308	1668	644	421
HMAPPTH-Ni	3510	-	1585	3305	1659	607	448
HMAPPTH-Cu	3450	-	1602	3306	1672	637	452

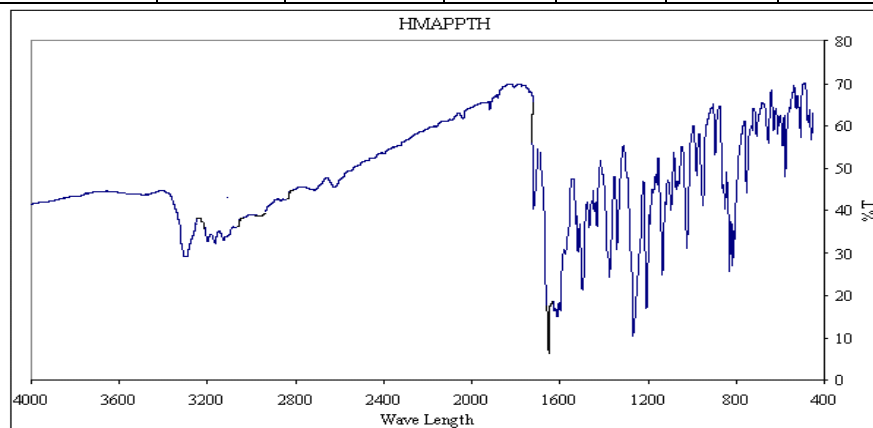


Fig. 1a. IR Spectrum of HMAPPTH Ligand

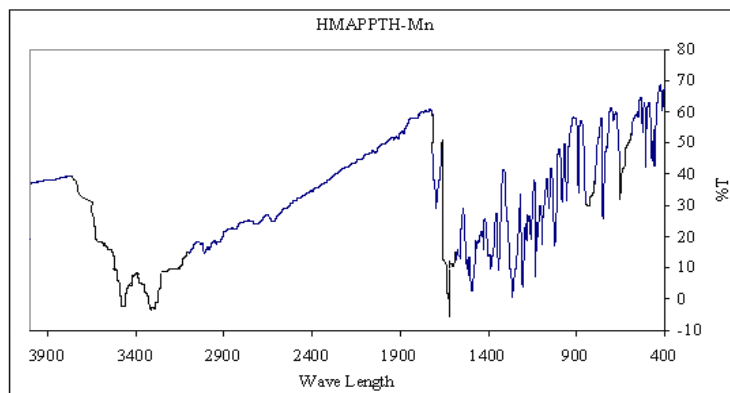


Fig. 1b. IR Spectrum of HMAPPTH- Mn (II) Complex.

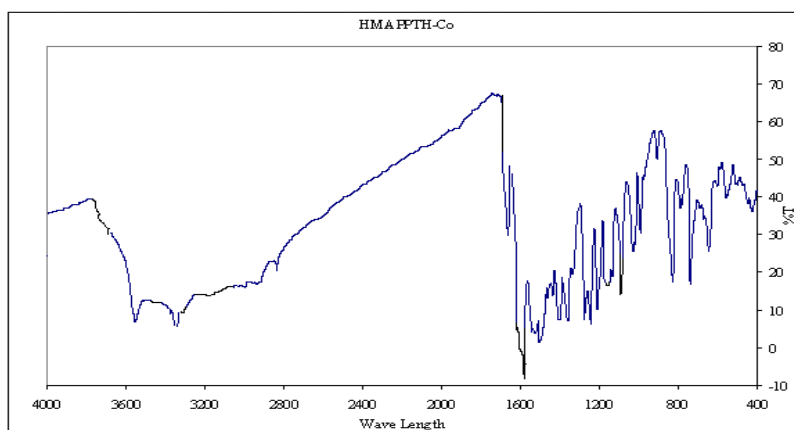


Fig. 1c. IR Spectrum of HMAPPTH- Co (II) Complex.

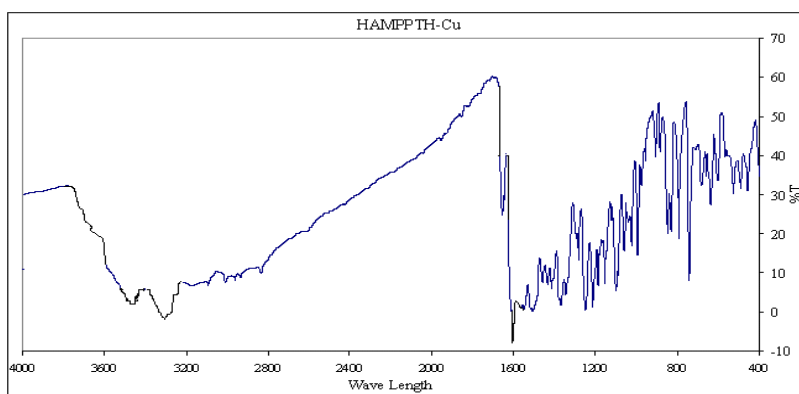


Fig. 1d. IR Spectrum of HMAPPTH- Cu (II) Complex.

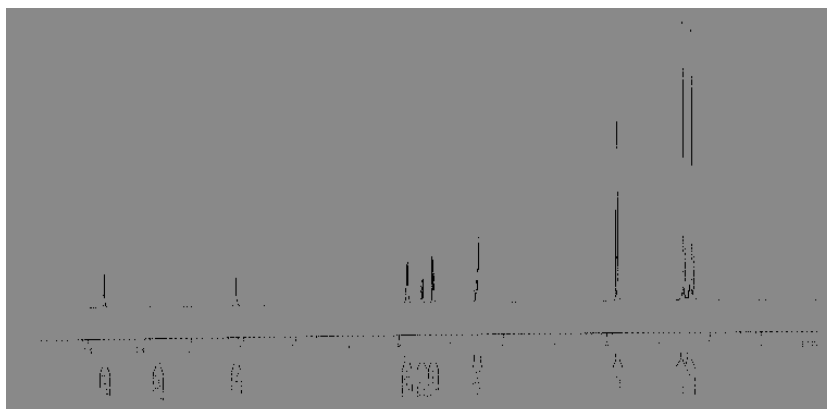


Fig. 1e. NMR Spectrum of HMAPPTH Ligand.

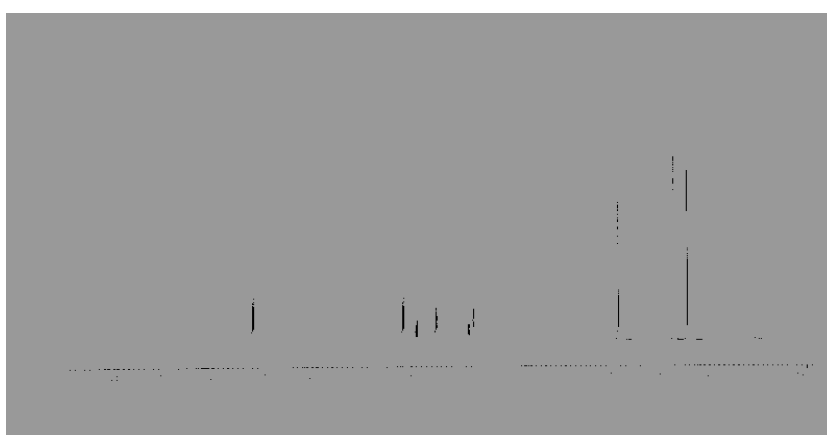
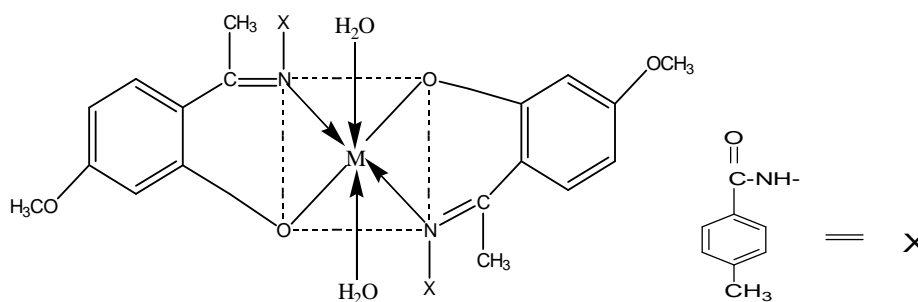


Fig. 1f. NMR Spectrum of HMAPPTH -Cu (II) Complex.

Table.2 ¹HNMR spectral data of HMAPPTH ligand and its metal complexes in DMSO-d₆ (ppm)

Compound	H ₃ C-C=N	Ar-H	CH ₃	OCH ₃	Ar-OH	N-H
HMAPPTH	2.57	6.42-7.89	2.35	3.82	13.70	11.13
HMAPPTH-Co	2.62	6.40-8.02	2.44	3.86	-	11.42
HMAPPTH-Cu	2.73	6.75-8.21	2.46	3.89	-	11.21

Fig 2. HMAPPTH Metal Complexes M=Cu⁺², Co⁺², Ni⁺², Mn⁺²

UV Spectral studies & Magnetic susceptibility measurements of HMAPPTH complexes: The electronic spectral data of RAPPPTH and its metal complexes are given in table.3. By UV spectral studies the transition for the ligand occurred at 298 nm. But on complexation with the different metal ions like Mn (II), Co (II), Ni (II) and Cu (II) new bands appeared at 390 nm, 383 nm, 378 nm and 392 nm respectively corresponding to the transitional charge transfer from the ligand to the different metal ions. Bands occurred in the region of 370-395 nm for all complexes [18-19] are assigned to charge transfer transition (L→M). Based on the results octahedral structure is proposed for Mn^{+2} , Co^{+2} , Ni^{+2} and Cu^{+2} complexes. The magnetic moments of the present HMAPPTH Mn (II), Co (II), Ni (II) and Cu (II) Complexes are 5.40, 4.89, 3.18 and 1.61BM. The magnetic moments of this ranges are suggest octahedral geometry for Mn (II), Co (II), Ni (II) and Cu (II) complexes [19].

Thermal behavior of Mn (II), Co (II), Ni (II) and Cu (II) Metal complexes of HMAPPTH: The Thermo gravimetric studies of all the complexes were carried out in air at a heating rate of 10° C per minute. The thermo analytical data is summarized in table.3. The thermal analysis curves of the complexes are given in fig 3a and 3b. The thermal decomposition of the complexes proceeds in three stages. The Mn (II), Co (II), Ni (II) and Cu (II) complexes [20-21] are thermally stable up to 131, 130, 111 and 140°C respectively. The first stage of decomposition corresponding to endothermic dehydration of complexes by the loss of two water molecules occurs in the temperature range 131-200°C, 130-276°C, 111-210°C and 140-217°C respectively. The intermediates formed [22-23] are stable up to 311, 340, 284 and 260°C. The second decomposition with exothermic peak by the loss of ligand moiety occur in the temperature range 311-540°C, 340-592°C, 284-509°C and 263-630°C. The solid residues above 665, 716, 530 and 680°C were identified as Mn, Co, Ni and Cu metal oxides respectively. In all the complexes, the final products are metal oxides.

Table 3: Thermal Analytical Data of the HMAPPTH metal complexes

Complex X=H ₂ O	M.Wt in g	Wt of the complex in mg	Stage	Temp in range °C	Probable assignment	Mass loss (%)	Total loss (%)
MnL ₂ 2X L=C ₁₆ H ₁₆ O ₃ N ₂	685.61	8.00	1	131-200.90	Loss of 2H ₂ O molecule	5.46	91.61
			2	311.43-538.47	Loss of 2L molecule	86.14	
			3	Above 665.86	Corresponds to MnO	8.40	
CoL ₂ 2X L=C ₁₆ H ₁₆ O ₃ N ₂	689.60	7.50	1	130.-276.54	Loss of 2H ₂ O molecule	5.22	90.388
			2	340-592.12	Loss of 2L molecule	85.168	
			2	Above 716.18	Corresponds to CoO	9.10	
NiL ₂ 2X L=C ₁₆ H ₁₆ O ₃ N ₂	689.309	8.00	1	111-210.27	Loss of 2H ₂ O molecule	5.22	89.55
			2	284.97-509.01	Loss of 2L molecule	84.328	
			3	Above 530	Corresponds to NiO	10.45	
CuL ₂ 2X L=C ₁₆ H ₁₆ O ₃ N ₂	694.126	8.00	1	140-217.52	Loss of 2H ₂ O molecule	5.18	88.64
			2	262.08-630.28	Loss of 2L molecule	83.46	
			3	Above 680.05	Corresponds to CuO	11.14	

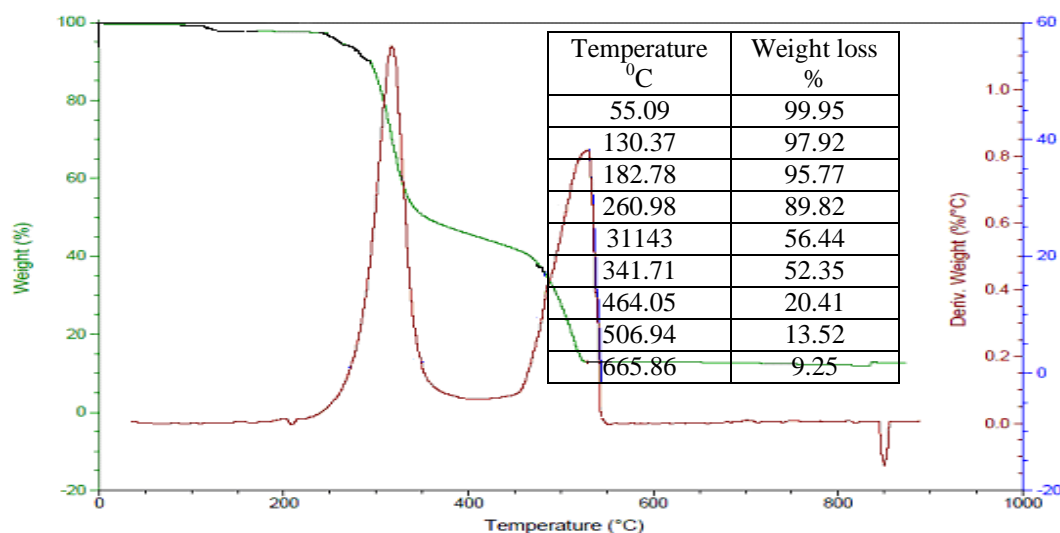


Fig.3a. HMAPPTH-Mn (II) Complex.

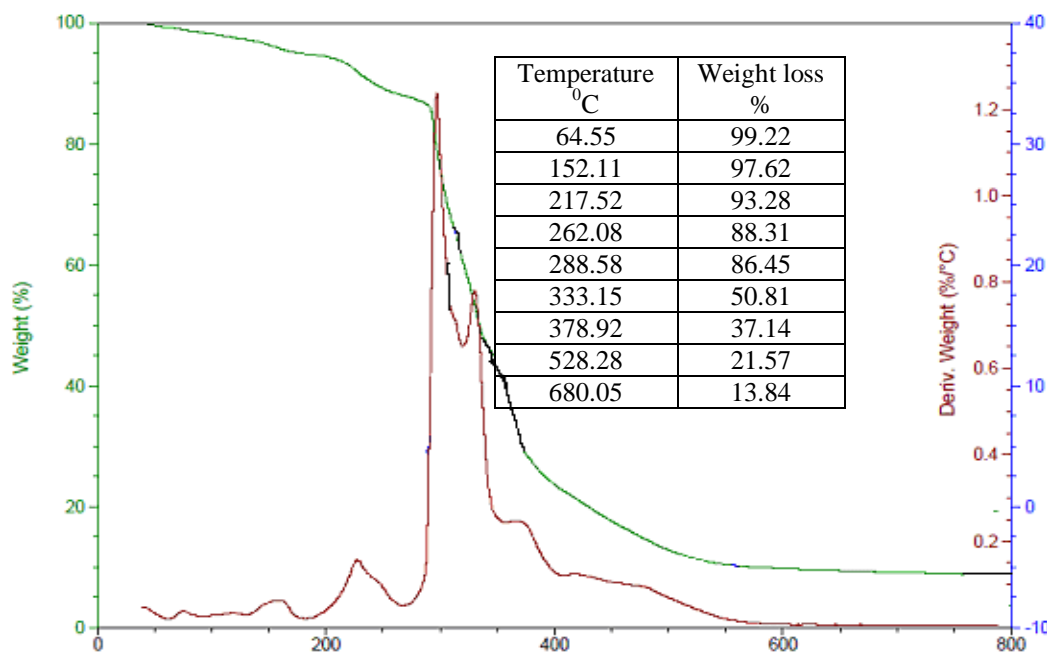


Fig 3b. HMAPPTH-Cu (II) Complex.

Conductivity Measurements of HMAPPTH metal complexes: The molar conductance of complexes in DMF (~10⁻³ M) was determined at 27±2°C using systronic 303 reading conductivity bridge. Mn (II), Co (II), Ni (II) and Cu (II) complexes of azomethine compound formed due to the condensation of 2-hydroxy-4-methoxy acetophenone and p-Toluic hydrazide (HMAPPTH) ligand is prepared. The complexes of HMAPPTH ligand are highly soluble in dimethyl formamide (DMF). Therefore these metal chelates are dissolved in DMF to perform conductivity measurements. A known amount of solid complex was transferred into 25 ml standard flask and dissolved in DMF. The contents were made up to the mark with DMF. The complex solution is transferred into a clean and dry 100 ml beaker. The molar conductance

values of these metal complexes which are residual are given in table .4. These values suggest non-electrolytic nature of the present complexes [24-27].

Table.4.Molar conductivity of Manganese, Cobalt, Nickel and Copper complexes

Metal complexes	Molar conductance(ohm ⁻¹ cm ² mol ⁻¹)
RAPPTH-Mn	6.50
RAPPTH-Co	5.00
RAPPTH-Ni	7.20
RAPPTH-Cu	4.80

Table-5. Analytical data of the HMAPPTH ligands and its metal complexes

Molecular Formula X=H ₂ O	Molecular Weight	Colour	Yield in %	Melting Point in °C	Elemental analysis							
					Carbon %		Hydrogen %		Nitrogen %		Metal %	
					Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
L=C ₁₆ H ₁₆ O ₃ N ₂ HMAPPTH	298.335	Light yellow	85	198-200	68.38	67.97	6.04	5.67	9.38	9.01	-	-
[Mn L ₂] ₂ X (HMAPPTH-Mn)	685.61	Dark green	69	320-330	59.50	59.23	5.54	5.13	8.16	8.03	8.01	7.76
[Co L ₂] ₂ X (HMAPPTH-Co)	689.60	Dark red	74	298-315	59.16	58.91	5.51	5.04	8.12	7.59	8.54	8.09
[Ni L ₂] ₂ X (HMAPPTH-Ni)	689.319	Light green	72	315-325	59.19	58.42	5.51	4.97	8.12	7.93	8.50	8.23
[Cu L ₂] ₂ X (HMAPPTH-Cu)	694.126	Green	72	302-310	58.78	58.64	5.47	5.12	8.06	7.63	9.14	8.87

APPLICATIONS

Anti bacterial activity: The biological activity of the Schiff base ligand and their metal complexes and streptomycin (as a standard compound) were tested against bacteria because bacteria can achieve resistance to antibiotics through biochemical and morphological modifications [28-30]. The organisms used in the present investigations included *Staphylococcus aureus* and *Bacillus subtilis* (as gram positive bacteria) and *Pseudomonas aereuginosa* and *Escherichia coli* (as gram negative bacteria).The diffusion agar technique was used to evaluate the antibacterial activity of synthesized ligand and its metal complexes. The results of the bacterial screening of the synthesized compounds are recorded in table 6. The data obtained reflect that the Schiff base ligand shows moderate activity in comparison with *Staphylococcus aureus*, *Bacillus subtilis* and less active in comparison with *Pseudomonas aereuginosa*, *Escherichia coli*. Antibacterial activity of all the complexes [30-35] at low concentration towards gram positive and negative bacteria is not detected or low. The activity of the Schiff base ligand and its metal complexes increases as the concentration increases because it is well known fact that concentration plays a vital role in increasing the degree of inhibition. The antibacterial activity results indicate that most of the metal chelates exhibited good to moderate antibacterial activity [36-37] when compared to Ligand. Among the synthesized metal complexes HMAPPTH-Cu showed high activity.

Table 6. Antibacterial Activity of HMAPPTH Schiff base Ligand and its metal complexes

Compound	Gram positive						Gramnegative					
	Staphylococcus aureus			Bacillus subtilis			Pseudomonas aereuginosa			Escherichia coli		
	5	2.5	1	5	2.5	1	5	2.5	1	5	2.5	1
L=C ₁₆ H ₁₆ O ₃ N ₂ . (HMAPPTH)	++	++	nd	++	++	+	+	+	nd	++	+	+
[Mn L ₂] ₂ X. (HMAPPTH-Mn)	+++	++	+	++	++	nd	++	++	+	++	+	+
[Co L ₂] ₂ X.(HMAPPTH-Co)	++	++	nd	++	++	+	++	++	+	++	nd	nd
[Ni L ₂] ₂ X.(HMAPPTH-Ni)	++	++	+	++	+	nd	++	++	nd	++	+	+
[Cu L ₂] ₂ X. (HMAPPTH-Cu)	++	++	+	+++	++	+	++	++	+	++	++	+
Streptomycin(standard)	+++	++	++	+++	++	++	++	++	++	++	++	++

Inhibition values = 0.1- 0.5cm beyond control = + (less active); inhibition values = 0.6- 1.0cm beyond control = ++ (moderate active);

Inhibition values = 1.1- 1.5cm beyond control = +++(high active).Concentration in mg/ml. nd:non detected.

CONCLUSIONS

The design and synthesis of a new family of bidentate Schiff base ligands for use in octahedral complexes have been successfully demonstrated. In this paper, the coordination chemistry of a Schiff base ligand obtained from the reaction of p-toulic hydrazide and 2-hydroxy-4-methoxy acetophenone is described Mn (II), Co (II), Ni (II), and Cu (II) complexes have been characterized by spectral and analytical data. The IR, & electronic transition data lead to the conclusion that the Mn (II), Co (II), Ni (II), and Cu (II) metal complexes are octahedral in nature and hence the structure of HMAPPTH Schiff base metal complexes are given in fig 4. In all the complexes, the ligand acts as bidentate. The results of in – vitro biocidal activities of the ligand and its metal complexes clearly show antibacterial activity against the tested organisms. On the basis of chelation theory, metal complexes have more biological activity than free ligand. All the metal chelates are found to be non-electrolytes. The present work points to the future work that HMAPPTH can be exploited as precursor for the synthesis of new complexes and it would be fruitful to obtain complexes with promising antibacterial activity. Further coordination chemistry needs to explore in these chemically rich systems.

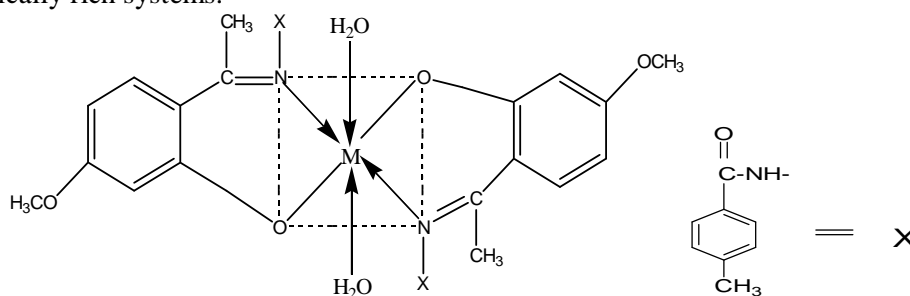


Fig.4.HMAPPTH Metal Complexes M=Cu⁺², Co⁺², Ni⁺², Mn⁺²

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