



SYNTHESIS, SPECTROSCOPIC AND MICROSCOPIC STUDIES OF METAL COMPLEXES OF SCHIFF BASE DERIVATIVE (2-CARBOXYBENZALDEHYDE-THIOSEMICARBAZONE) AND ITS NANOPARTICLES

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ABSTRACT

The Schiff base ligand (L) has been prepared using thiosemicarbazide and carboxybenzaldehyde. The composition of Ni(II) and Cu(II) were synthesized as complexes $M(L)_X(H_2O)_2$ (for $M = Ni(II), Cu(II)$ and $X = Cl^-, NO_3^-, CH_3COO^-$). Silver [Ag(I)] complex was synthesized with the ligand composition $[Ag_2(L)_2(H_2O)_2](NO_3)_2 \cdot 4H_2O$ and its nanoparticles (M-Nps) were also prepared using a plant extract, a green approach. The octahedral geometry for Ni(II), tetragonal geometry for Cu(II) complexes and tetrahedral structure for Ag complex was shown in spectral studies. The conventional chemical method for synthesis is not used rather environment friendly biological approach has been utilized by nutmeg plant extract. Furthermore, elementary analytical, IR, Mass, ^1H NMR techniques were used to characterize the ligand and metal complexes while for Silver nanoparticles, electron microscopy studies were performed.

KEYWORDS: Ligands, Carboxybenzaldehyde thiosemicarbazone, metal complexes, Silver Nanoparticles, Cu, Ni and Nobel Metal complexes, environment friendly approach.

INTRODUCTION

Metals and its pharmacological importance were traced back almost 500 years (Molavi, 2003). Due to the lack of researches in the insight of biologically active metal complexes, traditional medicinal chemists and pharmacologists was failed to identify important active metals. (Fujii *et al.* 2005). It delays the evolution of metal complexes and their role in pharmaceuticals. However, it anticipates the brilliant chemists to pioneer the development of new drugs (Gomez-Bosquet *et al.*, 1998).

The synthesis of thiosemicarbazones and their metal complexes are of considerable interest due to their pharmacological potential and large range of uses in bonding and stereochemistry (Vinod *et al.*, 2006). Thiosemicarbazones are the most widely studied ligand (Marina *et al.*, 2007) and have emerged as important sulphur containing ligands in the last two decades (Chen-Jie *et al.*, 1999; Sampath *et al.*, 2003; Martin *et al.*, 2007; Tudor *et al.*, 2007) as well as their metal complexes have been the subject of great interest of many researchers for a number of years (Martin *et al.*, 1997; Chen-Jie *et al.*, 1999; Sampath *et al.*, 2003; Leovac *et al.*, 2005; Vinod *et al.*, 2006; Marina *et al.*, 2007; Tudor *et al.*, 2007).

The advent of resistant virus strains and adverse side effects associated with extended use in the crossroads of medications used for viral disease treatment are major barriers that are hard to circumvent. Multidisciplinary research activities are therefore crucial to the production of improved antivirals through alternative methods, which are embedded in classical epidemiology and clinical approaches.

Nanotechnology has arisen to re-explore the biological properties, by manipulating their proportions, of proven antimicrobial substances including metals.

Due to their synthetic stability, selectivity and sensitivity towards the central metal atom, structural similarity with natural biological substances, and the presence of an imine group ($N=CH-$), Schiff bases are a significant class of ligands. Condensation of primary amine with carbonyl compounds, typically in an alcoholic medium, produces Schiff's base ligands.

Nanoparticles have sparked a lot of interest in recent years due to their distinct chemical and physical properties that set them apart from bulk materials and single atoms. SEM provided information on the sample's

surface and composition, while TEM provided information on the sample's inner structure, such as crystal structure and morphology. Nanoscale materials have emerged as novel antiviral agents in the current scenario due to the possibilities provided by their specific chemical and physical properties.

Silver nanoparticles have been researched primarily for their antimicrobial potential against bacteria, however they have also been shown to be effective against viruses such as the human immunodeficiency virus, hepatitis B virus, herpes simplex virus, respiratory syncytial virus, and monkey pox virus. The use of metal nanoparticles in antiviral therapies presents an intriguing opportunity. Metals have a lower risk of developing resistance than traditional antivirals because they can strike a wide variety of targets in the virus.

The emphasis of this review is on the development of methods for producing metal complexes, nanoparticles,

and analyzing them. CHN analysis and spectroscopic techniques such as IR, mass spectrum, and ¹H NMR spectrum confirm the ligand's elemental analysis. Following the synthesis of M–Nps metal salts, precise research was carried out using optical spectroscopy and electron microscopy.

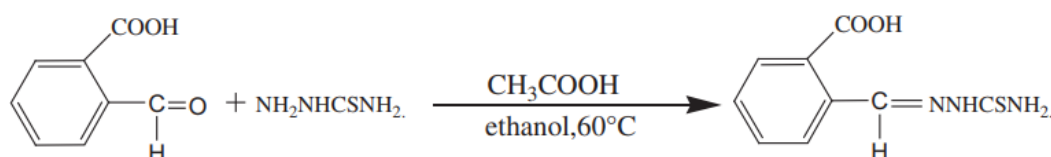
Finally, scanning electron microscopy (SEM) was used to demonstrate nano-size dimension magnification, which is 100 to 100000 times more efficient than optical microscopy and has a resolution of 3 to 100 nm.

MATERIALS AND METHODS

The analytical grade (AR) and maximum purity of all chemicals used were available. This contained thiosemicarbazide, carboxybenzaldehyde, silver(I) nitrate Ni(II) chloride, Cu(II) chloride, copper acetate or nickel acetate (Merck), ethanol, nutmeg plant extract. (Merck).

Experiment

Synthesis and characterisation of 2-Carboxybenzaldehyde thiosemicarbazone.



Thiosemicarbazide (0.115 g, 0.01 mole) alcoholic solution (20 mL) was taken in the round bottom flask with carboxybenzaldehyde (1.50, 0.01 mol), refluxed for 7-8 hours at 75°C and brown crystals have been precipitated during cooling. The precipitate have been removed, washed with cold EtOH and vacuum dried on P₄O₁₀. Melting point observed as 183°C with 67% yield. Elemental processing was used to verify the purity of the ligand. The ligand synthesis is presented (Fig 1), followed by metal complexes and its nanoparticles.

IR

Direct Ligand Synthesis Followed by Complexation

This method is used to isolate and purify the Schiff's base before complexing. The complexes are then processed by the various metal ions and Schiff's bases. The benefit of this procedure is that spectral characterization of complexes can be carried out by comparing them with spectral ligand results.

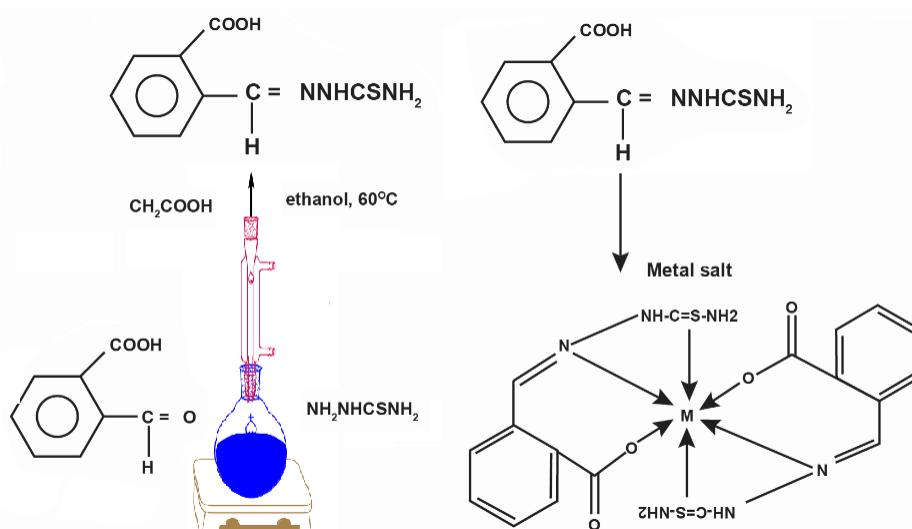


Figure 1.

Preparation of the complexes

The round bottom flask was taken with a hot ethanol solution of 15 mL (0.001 mol) and heated at 70°C for around 10 min to form a clear solution. The resulting metal salt was then heated under reflux with

continuous stirring in hot ethanol solution (15 mL, 0.001 mol) for approximately 12 to 15 h. The solid substance was precipitated when cooled at room temperature. The solid product obtained after filtration is washed several times with ethanol and vacuum dried over P₄O₁₀.



Figure 2.

Direct Ligand Synthesis Followed by Complexation For Silver complex formation

This method is used to isolate and purify the Schiff's base before complexing. The complexes are then processed by the various metal ions and Schiff's bases. The benefit of

this procedure is that spectral characterization of complexes can be carried out by comparing them with spectral ligand results. The method is utilized for Ag metal complex synthesis given in Figure 2.

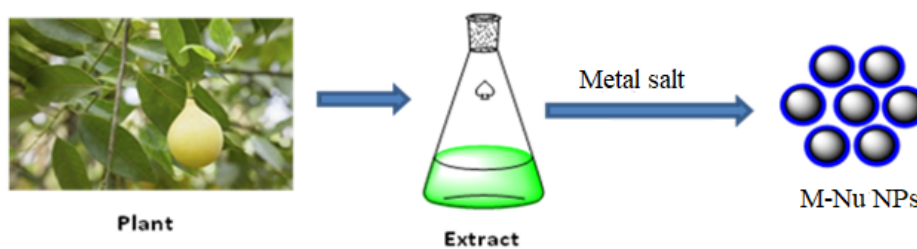


Figure 3.

Synthesis of nanoparticles using nutmeg plant extract (Ag, Cu, Ni-Nu Nps)

An environment friendly green approach is used to prepare M-Nu nanoparticle shown in Figure 3 at room temperature. In order to perform reactions with the respective metal salt, appropriate amount of powdered plant product must be extracted in fixed amount of hot water. The plant extract will function as a reducing and capping agent and prepared the nanoparticles with colour variations between pale yellow and dark brown.

Instruments

ANALYSIS INSTRUMENTS

MALDI MS - ABI Sciex 5800 TOF/ TOF System with LC-MALDI, FT-IR/ Raman Spectrometer with Microscope - Varian 7000 FTIR, Varian FT-Raman and Varian 600 UMA, Electron Paramagnetic Resonance (EPR) Spectrometer Bruker Model EMX MicroX, Elemental analysis Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometer - PANalytical Epsilon 5. Transmission electron microscope (tem) Jeol 2100F, and scanning electron microscope (sem) Zeiss EVO 40, Transmission electron microscope (tem) Jeol

2100F, and scanning electron microscope (sem) Zeiss EVO 40.

RESULTS AND DISCUSSIONS

Metal complexes were produced by reaction of respective metal salts and ligand. The metal complexes were sparingly soluble in water, ethanol, acetone and most organic solvents, but completely soluble in DMSO

and DMF. The stability of the complexes was shown and proven by their observed larger melting point than the free ligand. Analytically, all the complexes possessed 1:1 metal to ligand stoichiometry, and it was confirmed by elemental analysis. Elemental studies were carried out on the schiff base. Table 1 shows the effects of elementary analysis, molecular formulas and melting points.

Table 1.

Sl no	Metal complex with ligand	Colour	M. Wt	M P ($^{\circ}\text{C}$)	Molar conductance ($\text{X}^{-1} \text{cm}^2 \text{mol}^{-1}$)	Yield (%)	Elemental analyses data (%) calculated (found)			
							M	C	H	N
1.	$\text{L}:\text{C}_9\text{H}_9\text{N}_3\text{O}_2\text{S}$	Off white	223	188	-----	70	-----	48.43 (48.22)	4.03 (4.08)	18.83 (18.67)
2.	[ML]: $[\text{Ag}_2(\text{L})_2(\text{H}_2\text{O})_2](\text{NO}_3)_{2.4}\text{H}_2\text{O}$ $\text{C}_9\text{H}_9\text{N}_3\text{O}_2\text{S}\text{Ag}$	Metallic Grey	330	>300	15.43	69	28.86(28.73)	3.01 (3.12)	8.41 (8.45)	21.62 (21.68)
3.	[Ni L Cl(H_2O) $_2$] $\text{NiC}_9\text{H}_{12}\text{N}_3\text{O}_4\text{SCl}$	Grey green	352	290	14	60	16.66 (16.62)	30.60(30.57)	2.27 (2.24)	11.92 (11.88)
4.	[CuLCl(H_2O) $_2$] $\text{CuC}_9\text{H}_{12}\text{N}_3\text{O}_4\text{SCl}$	Brown	357	280	12	67	17.78 (17.71)	30.25 (30.23)	2.24 (2.20)	11.76(11.66)

The results obtained correspond well to those estimated for the proposed formula.

Conductivity Measurements

The synthesised compounds have been tested at a room temperature and molar conductance values of 10^{-3} M

DMSO. The synthesized compounds' conductance values were below $50 \text{ Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, suggesting their non-electrolytic properties. This indicated that no anions were present beyond the coordination sphere of the complexes.

IR SPECTRA OF LIGAND

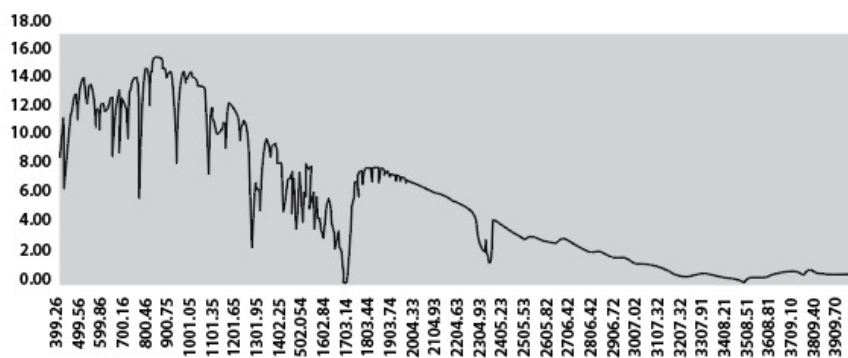


Figure 3.

Table 2.

Bond	Functional groups containing the bond	Absorption range (In wavenumbers/ cm^{-1})	Appearance of peak (s=strong, w=weak)
C=N	Azomethine	1606	s
C=S	Thiocyanate	786-800	s
COO ⁻	Carboxylate ion	1577-1707	v asym
COO ⁻	carboxylato group monodentate binding with Ag metal	167-243	w
M-O	Metal complex with oxygen stretching vibration	507-525	w
M-N	Metal complex with nitrogen stretching vibration	437-466	w

H ₂ O	coordinated water molecules	3310–3473	W
NO ₃ ⁻	Metal nitrate complex	1401-1476	w
CH ₃ COO	The acetate Anions	1474, 1460	w

Infrared Spectra: Table 2 shows the significant IR bands of the ligand and its metal complex.

The wide spectrum of all the complexes analyzed shows the presence of water molecules in the range 3157-3500 cm⁻¹ allocated to $\nu(\text{OH})$. The bands at 673-889 cm⁻¹ and 1023-1049 cm⁻¹, are attributed to $\nu(\text{CS})$ and $\nu(\text{CS})+\nu(\text{CN})$ respectively, in the free ligand either shifted or split indicating that the S atom is involved in complex forming 1 (Casas et al 1995). The $\nu(\text{C}=\text{N})$ band is also suggested to be synchronised with the azomethine

N to the metal ion (Kovala-Demertzi et al 2001). The N-bonding is also demonstrated by the 1234 cm⁻¹ change of heavy bands for this spectrum, assigned to the high or lower frequencies in their complexes, by (Casas -1 1 2 et al 1995, Fabretti and Peyronel 1978). The M-L complex shows major changes for $\nu(\text{C}=\text{O})$ bands to lower frequencies, showing that the ion is coordinated through the carbonyl oxygen atom (Casas et al 1995)

Mass spectra of the ligand.

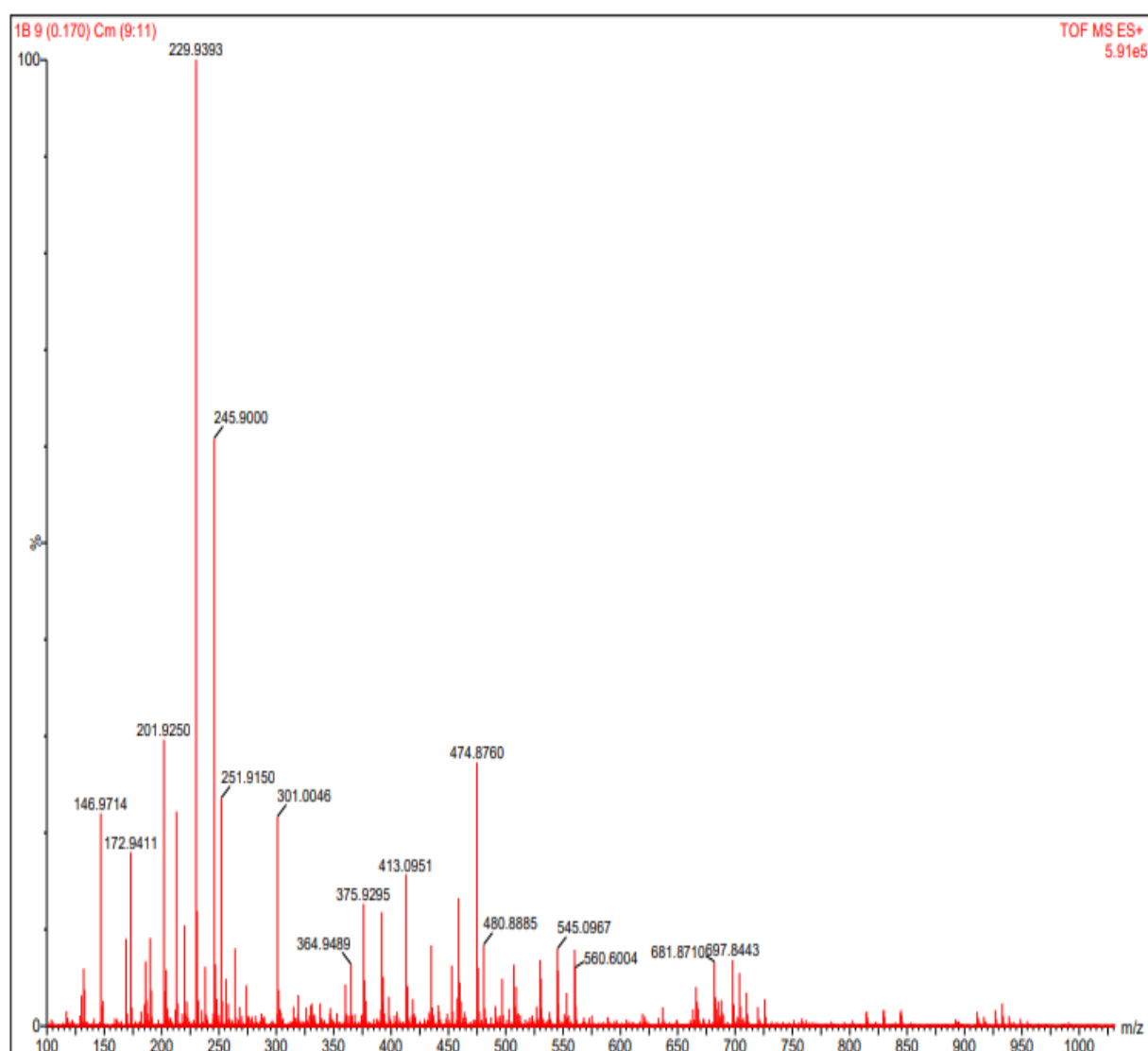


Figure 4.

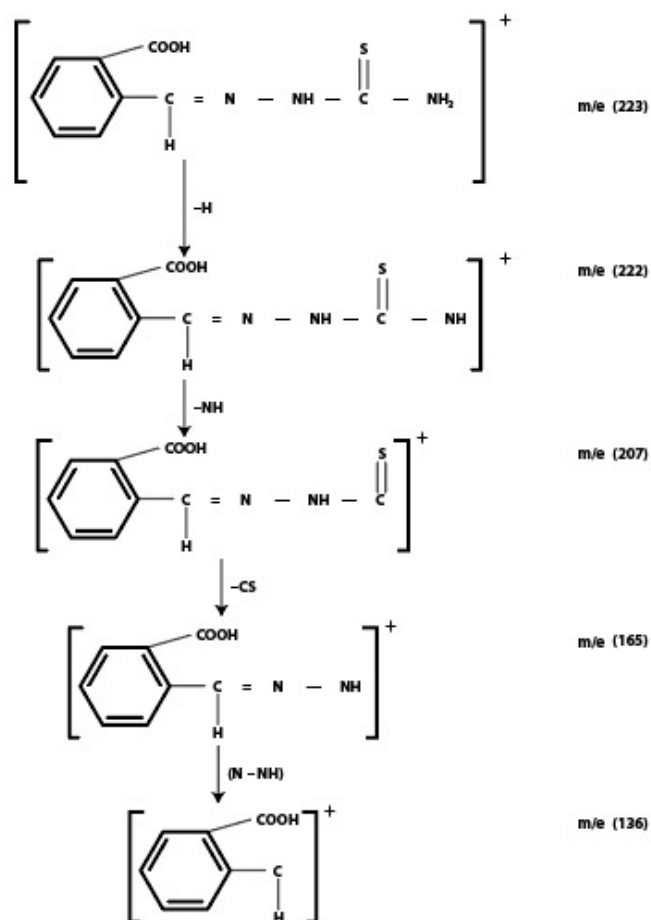


Figure 5.

Ligand L: The appearance of peak at $m/e=229$ ($\text{C}_9\text{H}_9\text{O}_2\text{SN}_3$) [calculated molecular mass at 223] and other peaks at 222, 207, 165, and 136 may be due to

different fragments. The intensities of remaining peaks are in accordance with their abundances and stability of these fragments.

NMR Spectra of the Ligand

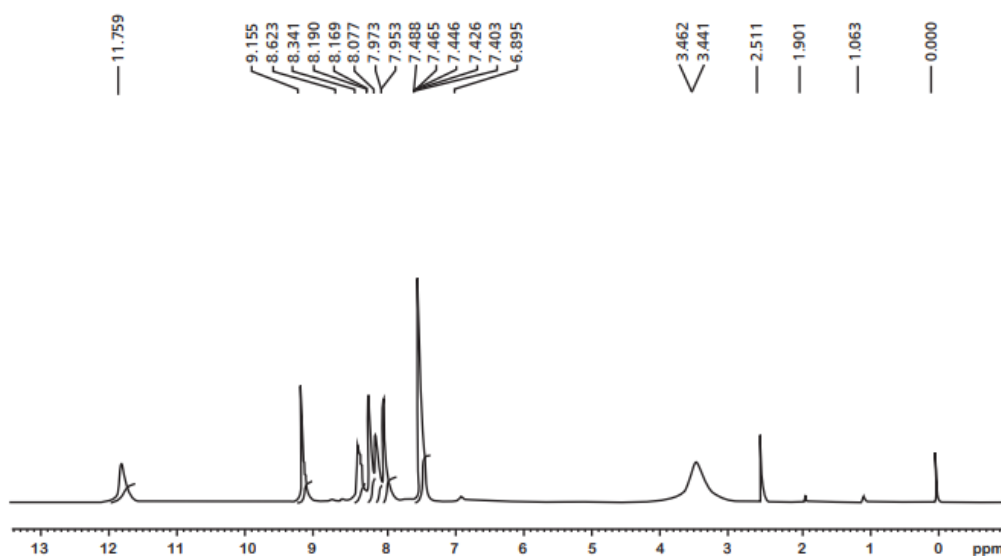


Figure 6.

NMR of Ligand

¹H NMR of ligand was done in DMSO on 44–300 MHz NMR given in Table 3. In ¹H NMR of ligand the aromatic proton appears as a singlet in the range 7.40–8.78 ppm. The singlet for NH proton appears at 12.1 ppm, while two NH₂ protons resonate as a multiplet at

7.34–7.38 ppm. For ligand L, signals for NH and C HC of the indole mode are 12.1 and 8.7 ppm, respectively, and azomethine proton at 8.1 and 8.9 for ligand L. The NH₂ and NH protons are confirmed by their D₂O spectra. All the protons are found in their expected region.

Table 3.

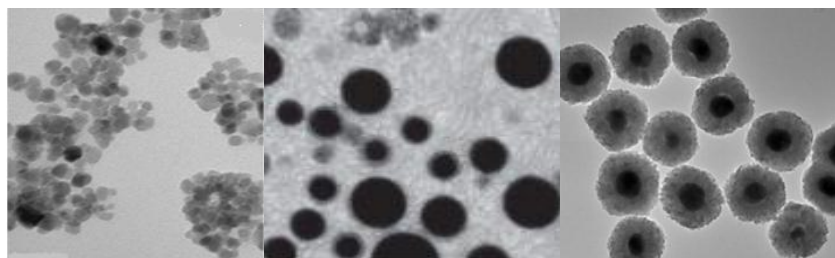
Ligand	Carboxylic COOH	CH of the ring	NH	NH ₂	CH	CH=N	Aromatic protons
δ, ppm	10.1	4.1	12.1	7.34-7.38	8.7	8.1	7.40-8.78

IR and ¹H NMR spectra also validate the configurations of Schiff's bases. Mass spectral results validate the ligand's composition as shown by its molecular mass peaks.

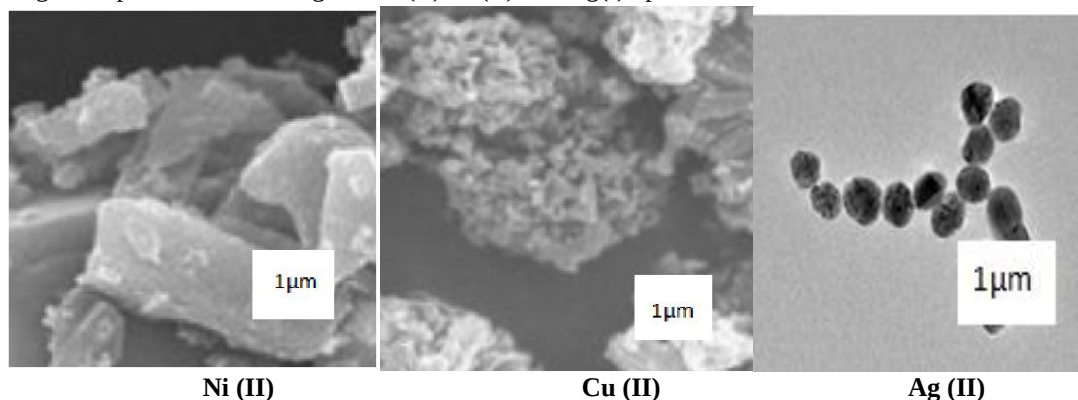
which demonstrated the formation of irregular Cu and Ni NPs with average size of 25, 27 and regular and 28 nm, respectively.

TEM Analysis

The size and morphology of the as-prepared Ni, Cu and Ag NPs were characterized using TEM as shown in Fig. 7

**Figure 7.****SEM analysis**

The given figure 8, presents SEM image of Ni (II), Cu(II) and Ag(I) NPs.

**Figure 8.****ACKNOWLEDGMENT**

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