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SYNTHESIS, SPECTROSCOPIC AND MICROSCOPIC STUDIES OF METAL COMPLEXES OF SCHIFF BASE DERIVATIVES (2-CARBOXYBENZALDEHYDE SEMI CARBAZONE, 3-METHYL 2-THIOPHENE CARBOXALDEHYDE SEMICARBAZONE) AND ITS NANOPARTICLES

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ABSTRACT
Schiff base ligands and its corresponding copper, nickel and silver complexes were synthesized. Ligand (L1) 2-carboxybenzaldehyde semicarbazone has been prepared using semicarbazide and carboxybenzaldehyde; ligand (L2) 3-methyl 2-thiophene carboxaldehyde semicarbazone is prepared by semicarbazide and 3-methyl-2-thiophene carboxaldehyde .The composition of Ni(II) and Cu(II) were synthesized as complexes $M(L1)_X(H_2O)_2$ Silver [Ag(I)] complex was synthesized with the ligand composition $[Ag_2 (L1)_2 (H_2 O)_2](NO_3)_2 .4H_2O$ 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 spctral studies. Complexes with L2 have general composition [M(L2)2X2], where M = Ni(II) and Cu(II), X = Cl^-, $NO3^-$, $CH3COO^-$ and ½SO_4^{2-} for both ligand M -complexes.On the basis of above spectral studies, an octahedral geometry has been assigned for Ni(II) complexes and tetragonal geometry for Cu(II) complexes except [Cu(L2)2-SO4] which possesses five coordinated trigonal bipyramidal geometry. ‘’Furthermore, elementary analytical, IR, Mass, $_H$NMR techniques were used to characterize the ligand and metal complexes while for Silver nanoparticles, electron microscopy studies were performed.. Also, we reported a green method for synthesis of their nanoparticles using nutmeg plant extract.

KEYWORDS: Synthesis, characterization, Cu, Ni and Nobel Metal Ag (I) complex of 2-Carboxybenzaldehyde semicarbazone, 3-methyl 2-thiophene carboxaldehyde semicarbazone, Nanoparticles, Environment friendly cleaner approach.

INTRODUCTION
Metal compounds with Schiff base ligands represents the significant class of compounds to produce and study spectral and analytical data for the development of novel metal NPs. Schiff bases have played a special role as chelating ligands in main group and transition metal coordination chemistry be- cause of their stability under a variety of redox conditions and because imine ligands are borderline Lewis bases (De Souza et al., 2003). The important physical and biological properties of the Schiff bases are directly related to intermolecular hydro- gen bonding and proton transfer equilibria (Przybylski et al., 2002). Schiff bases also offer opportunities for inducing sub- strate chirality, tuning metal-centered electronic factors and enhancing the solubility and stability of homogenous or hetero- geneous catalysts (Kannan and Ramesh, 2005). Transition met- als are involved in many biological processes which are essential to life process. The metals can coordinate with O-orN-terminals from proteins in a variety of models and play a crucial role in the conformation and function of biological macromolecules (Colacio et al., 2000; Karaliota et al., 2001) Schiff bases have played a special role as chelating ligands in main group and transition metal coordination chemistry be- cause of their stability under a variety of redox conditions and because imine ligands are borderline Lewis bases (De Souza et al., 2003). The important physical and biological properties of the Schiff bases are directly related to intermolecular hydro- gen bonding and proton transfer equilibria (Przybylski et al., 2002). Schiff bases also offer opportunities for inducing sub- strate chirality, tuning metal-centered electronic factors and enhancing the solubility and stability of homogenous or hetero- geneous catalysts (Kannan and Ramesh, 2005). Transition met- als are involved in many biological processes which are essential to life process.

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The Schiff bases played a particular significance as chelating ligands in principal group and metal coordinating chemistry due to its stability under several redox situations and because imine ligands are borderline Lewis foundations (De Souza et al., 2003). The key biological and physical qualities of the schiffs bases are linked directly to intermolecular hydrogen connection and the transmission of proton balance (Przybylski et al., 2002). The schiffs bases also provide the opportunity for induction of sub-shaped chirality, the adjustment of electronic parameters centring on metals and increasing the solubility and stability of homogeneous or heterogeneous catalysts (Kannan and Ramesh, 2005).

Furthermore, tetradentate and tridentate Schiff base complexes are increasingly important for designing metal complexes related to synthetic and natural oxygen carriers. Copper complexes of tridentate Schiff base type especially with dimeric units are considered as bioinorganic model compounds.

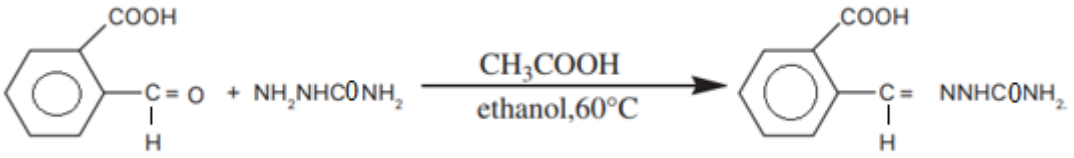
Transition metals are seen as fundamental to the life process in many biological systems. Metals can coordinate protein with O- or N-terminals in different models.

In recent years, many classes of indole derivative chemicals have been intensively investigated. Many of them have important biological characteristics, such as antibacterial and analgesic.

MATERIALS AND METHODS

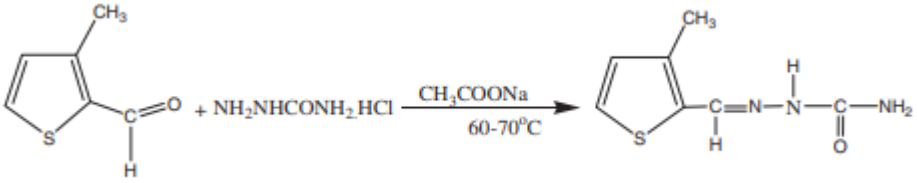
The analytical grade (AR) and maximum purity of all chemicals used were available. This contained semicarbazide, carboxybenzaldehyde, Semicarbazide hydrochloride , sodium acetate, 3-methyl-2-thiophene carboxaldehyde and silver(I)nitrate Ni(II)chloride, Cu(II) chloride, copper acetate or nickel acetate ,ethanol , nutmeg plant extract. (Merck)

Synthesis of Ligands and metal complexes 2-Carboxybenzaldehyde semicarbazone.



Semicarbazide (0.115 g, 0.01 mole) alcoholic solution (20 mL) was taken in the round bottom flask with carboxybanzaldehyde (1.50 , 0.01 mol) ,refluxed for 7-8 hours at 75 ^{o}C , yellow colored precipitate was isolated after cooling . The precipitate have been removed, washed with cold EtOH and vacuum dried on P_4O_{10}. Melting point observed as 220^{0} 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. $C_7H_9N_3OS$: Elemental Analysis: C;45.90 (45.87) H;4.91(4.86), N;22.95 C (found) (%) (22.89).

3-methyl 2-thiophene carboxaldehyde semicarbazone

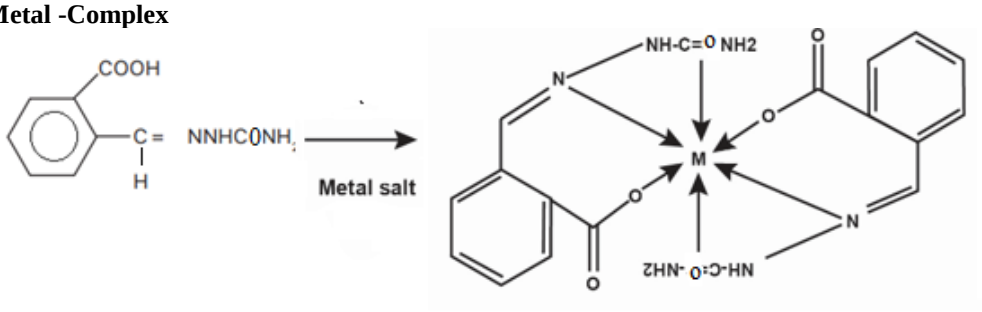


Synthesis and characterization of ligand(L) An aqueous solution in 20 mL of semicarbazide hydrochloride (1.11 g, 0.01 M) and sodium acetate (0.82 g, 0.01 M) of water was taken in a round bottom flask. To this solution 3-methyl-2-thiophene carboxaldehyde (1.17 mL, 0.01 M) was added drop wise with constant stirring. On cooling, brown colored crystals were precipitated out. Those were filtered off, washed with cold EtOH, and dried under vacuum over P_4O_{10}. Yield (67%), Melting point 183 C. The purity of the ligand was checked by elemental analysis. Synthesis of ligand is given in (Scheme 1). Elemental analysis calculated (found) (%) for $C_7H_9N_3OS$: C; 45.90(45.87) H; 4.91(4.86), N; 22.95 (22.89). Preparation of the complexes A hot ethanolic solution (15 mL, 0.001 mol) of ligand was taken in a round bottom flask and heated for about 10 min at 70 C to make the clear solution. Then hot ethanolic solution (15 mL, 0.001 mol) of the corresponding metal salt was added with continuous stirring and the resulting solution was refluxed for about 12– 15 h. The resulting solid product was filtered off, washed several times with ethanol, and dried in vacuum over P4O10.

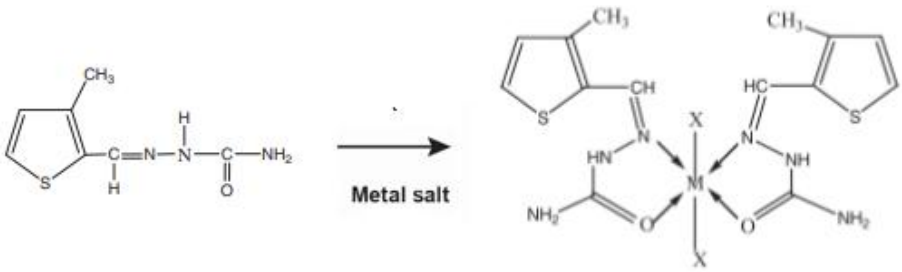
Preparation of the complexes

The round bottom flask was taken with a hot ethanol solution of 15 mL (0,001 mol) and heated at 70^0 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 P_4O_{10}.

Ligand1-Metal -Complex



Ligand 2-Metal-Complex



Synthesis of nanoparticles using nutmeg plant extract (M-Nu Nps)

An eco-friendly green approach in Figure for the synthesis of nanoscale particles of Ni,Cu Ag-Nu at room temperature would be used. Suitable quantity of powdered plant parts would be extracted in fixed quantity of hot water and will then use to carry out the reaction with Metal salt. The plant extract would work as a reducing and capping agent and prepare the nanoparticles with the indication of color changes from pale yellow to dark brown.

Figure:1

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 by a larger melting point than the free ligand. Analytically, all the complexes possessed 1:1 metal to ligand stoichiometry, confirmed by elemental analysis.

Elemental studies were carried out on the schiff base. Table shows the effects of elementary analysis, molecular formulas and melting points. The results obtained correspond well to those estimated for the proposed formula. IR and HNMR spectra also validate the configurations of schiffs bases. Mass spectral results validate the ligand's composition as shown by its molecular mass peaks.

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 $Ohm^{-1}cm^2mol^{-1}$, suggesting their non-electrolytic properties. This indicated that no anions were present beyond the coordination sphere of the complexes.

Table 1: The results obtained correspond well to those estimated for the proposed formula.

Sl no	Metal complex with ligand	Colour	M. Wt	M P (^{0}C)	Molar conductance (X^{-1} cm^2 mol^{-1})	Yield (%)	Elemental analyses data (%) calculated (found) M C H N
1.	L1:$C_9H_9N_3O_3$	Off white	207	188	---------- --	70	----- 48.43 (48.22) 4.03 (4.08) 18.83 (18.67)
a.	[ML]: Ligand 1 $[Ag_2 (L)_2 (H O)_2](NO_3)_2.4H_2 O$ $C_9H_9N_3O_3Ag$	Metallic Grey	314	>300	14.34	69	28.86(28.73) 3.01 (3.12) 8.41 (8.45) 21.62 (21.68)
b.	[Ni L $Cl(H_2O)_2$] $NiC_9H_{12}N_3O_5Cl$	Grey green	346	280	12	60	16.66 (16.62)30.60(30.57) 2.27 (2.24) 11.92 (11.88)
c.	[CuLCl$(H_2O)_2$] $CuC_9H_{12}N_3O_5Cl$	Brown	351	280	15	67	17.78 (17.71) 30.25 (30.23) 2.24 (2.20) 11.76(11.66)
2.	L2:$C_7H_9N_3OS$	Brown	183	178	--------	67	------ 45.90 (45.87) 4.91 (4.86) 22.95 (22.89)
a.	[ML]: Ligand 2 $[Ni(L)_2(Cl)_2]$ $NiC_{14}H_{18}N_6O_2S_2Cl_2$	Green	498	276	18	57	11.84 (11.77) 33.89 (33.82) 3.63 (3.60) 16.94 (16.89)
b.	[Ni(L)2(NO3)2] $NiC_{14}H_{18}N_8O_8S_2$	Brown	549	298	21	54	10.69 (10.63) 30.61 (30.57) 3.28 (3.24) 20.41 (20.37)
c.	$[Cu(L)_2(CH_3COO)_2]$ $CuC_{18}H_{24}N_6O_6S_2$	Brown	547	300	22	60	11.59 (11.51) 39.45 (39.41) 4.38 (4.35) 15.34 (15.29)

Mass Spectra of Ligand 1

Mass spectra of the ligands [Figure: 3and 4] give the important information regarding the proposed formula of the synthesized compounds. Mass spectra of ligands L1 and L2 show a molecular ion peak at m/z = 251 and 184 amu corresponding to species $[C_9H_{11}N_3O_3]^+$ .Figure:4 gives detail information of the fragments observed in the MS. These values favour the proposed formulae of the ligands under study.

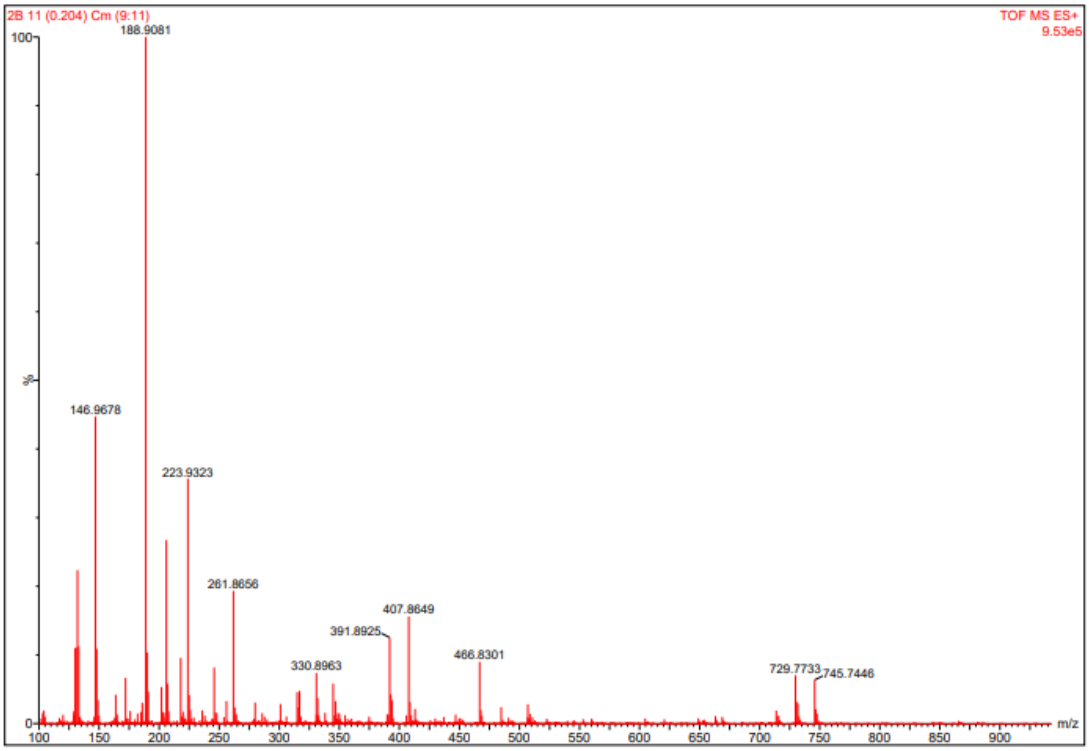


Figure: 3.

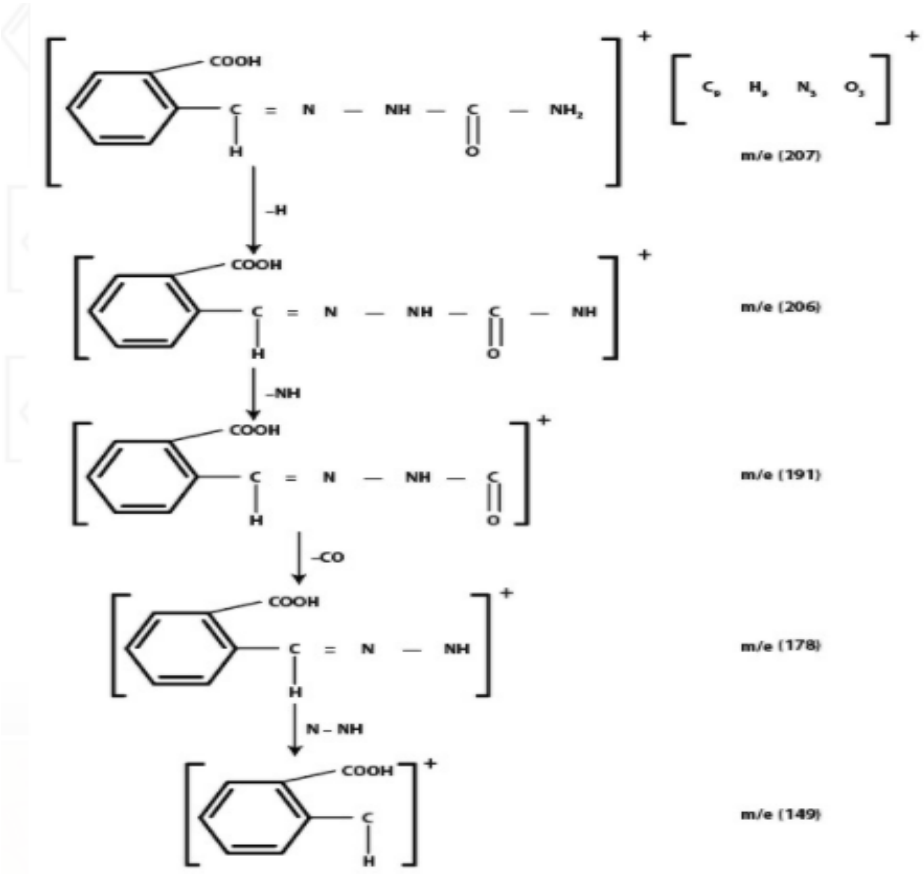


Figure: 4.

Mass Spectra of Ligand 2

The peak (Fig. 4) obtained at 184 corresponds to molecular ion peak (M)+ . Atomic mass of molecule is calculated as 184 amu for molecular formula $[C_7H_9N_3OS]$ +. Large number of peaks of varying intensity present in the spectrum corresponds to 169, 166, 140, 125 and 84 fragments generated during the analysis.

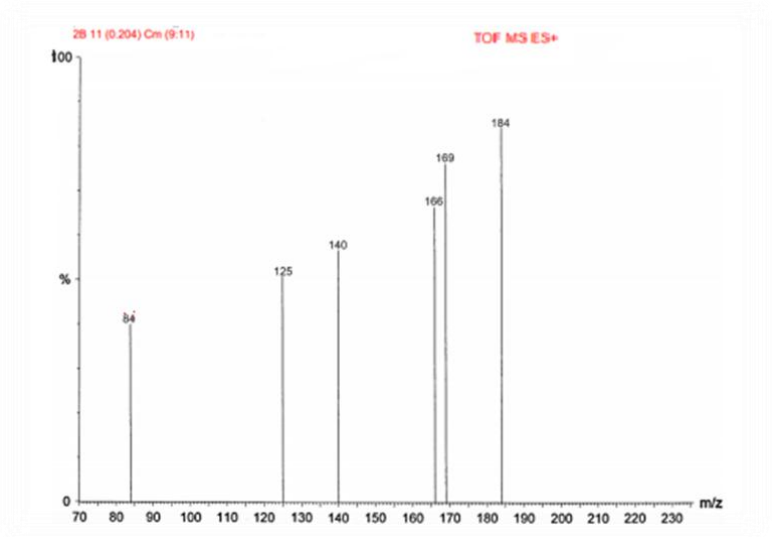


Figure 4.

1_H NMR of Ligands

1H NMR of ligands (L1and L2) was done in DMSO on 44–300 MHz NMR. In 1H NMR of ligands (L1 and L3) [Figure 1 and Figure 2], the aromatic proton appears as a set of singlet, doublet, and multiplet in the range 7.40–8.78 ppm. The NH_2 and NH protons are confirmed by their D_2O spectra. All the protons are found in their expected region.

The HNMR spectra of the free ligand [2], 5-methylene protons at 4.3 ppm and the azomethine proton at 8.1 and 8.9, in case of ligands L and HL , respectively. The phenolic OH proton has a signal at 10.7- 1 2 ppm in case, whereas in case of ligand L2 the signals due to NH and CH of the indole moiety appear at 12.1 and 8.7ppm, respectively.

Table: 2.

Ligand	Carboxyllic COOH	CH of the ring	NH	NH_2	CH	CH=N	Aromatic protons
δ,ppm L1	10.4	4.1	12.1	7.34-7.38	8.7	8.1	7.40-8.78
δ,ppm L2	-------	3.06	12.29	8.08-8.10	8.5	7.91	7.40-8.78
δ,ppm L2	3.02 (-CH3)	7.72 (-thiophene ring)	8.29 (-NHCO)	8.08 (-NH2)			

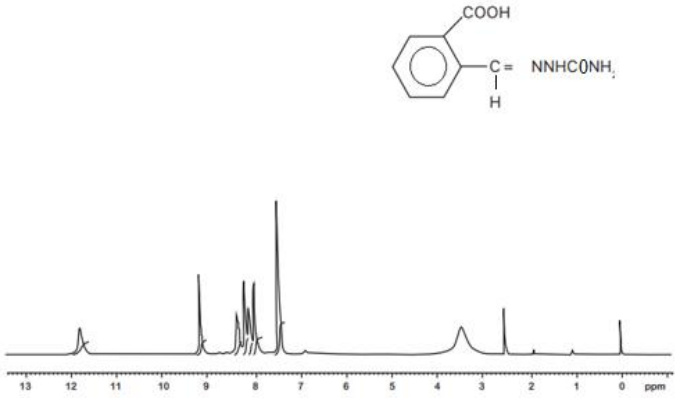


Figure 5.

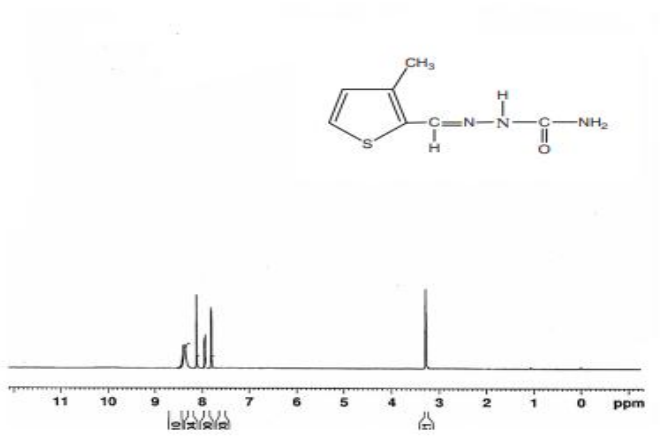


Figure 6.

Infrared Spectra: The significant IR bands of the ligand and their metal complex is given in Table 2.

The spectra of all studied complexes show a broad band in the range 3157-3500 cm assigned to -1 n(OH), suggesting the presence of water molecules . The bands due to n(CSO) and n(CS) + n(CN) at 673-889 cm and 1023-1049 cm respectively, in the free ligand either shifted or split, indicating the participation of the S atom in complex formation 1 (Casas et al 1995). Moreover, coordination of the azomethine N to the metal ion is suggested by the shift of the í(C=N) band (Kovala-Demertzi et al 2001). The N–bonding is also indicated by the shift of the strong bands at 1234 cm in case of this spectra, assignable to a (C-N-C) mode (Casas -1 1 2 et al 1995, Fabretti and Peyronel 1978), to high or lower frequencies in their complexes. The M-L complex show significant shifts to lower frequencies for í(C=O) band, suggesting coordination of the metal ion through the carbonyl oxygen atom (Casas et al 1995). The strong phenolic υ (C-O) band (Chatterjee and Ghosh 1998) at 1202 cm^{-1} in the free L ligand is shifted towards lower wave numbers in its complexes, consistent with -1 2 coordination via the deprotonated phenolic oxygen (Jayabalakrishnan and Natarajan 2001).

IR spectra

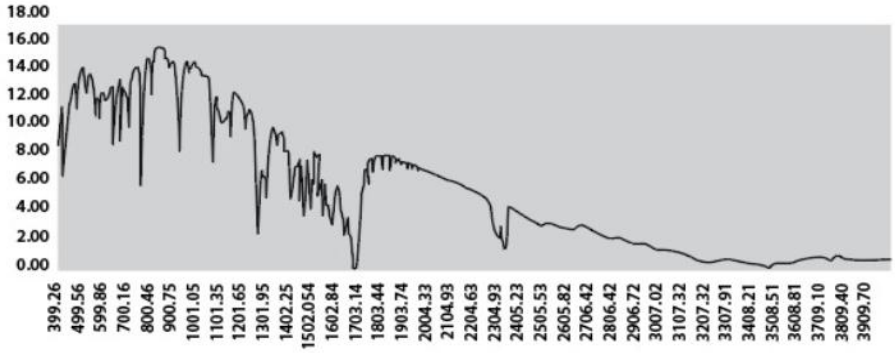


Figure 7.

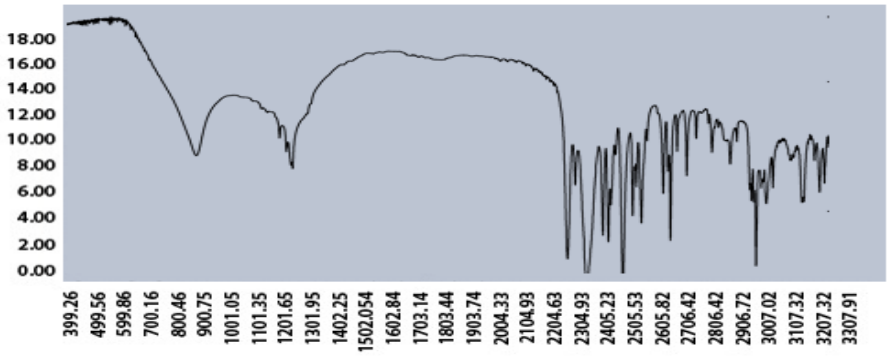


Figure 8.

Table 3.

Bond	Functional groups containing the bond	Absorption range (In wavenumbers/cm^{-1})	Appearance of peak (s=strong,w=weak)
C=N	Azomethine	1606	s
coo-	Carboxylate ion	1577–1638	υ 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_2O	coordinated water molecules	3310–3473	W
NO_3^-	Metal nitrato complex	1401-1476	w
CH3COO	The acetateanions	1474, 1460	w

SEM analysis

The given figure 9 and 10 , presents SEM image of Ni (II),Cu(II) and Ag(I)Nps.(1µm).
M-L-Nps with L1 and L2 respectively:

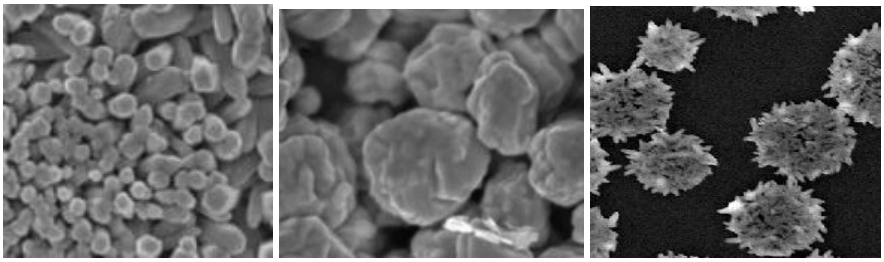


Figure 9 : ML_1Nps ; Ni SEM image Cu SEM image Ag SEM image.

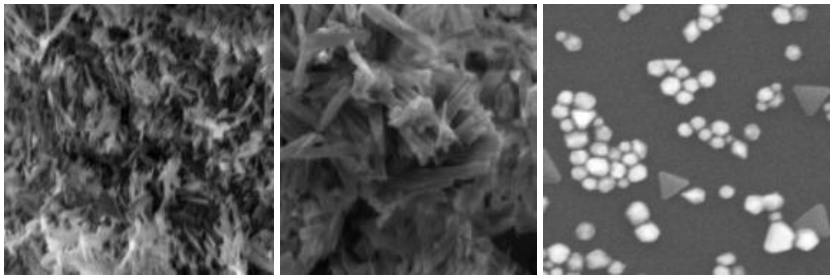


Figure 10: ML_2Nps ; Ni SEM image Cu SEM image Ag SEM image.

TEM analysis

TEM Analysis

The size and morphology of the as-prepared Ni, Cu and Ag NPs were characterized using TEM as shown in Figure 10 and 11 for L_1 and L_2 which demonstrated the formation of irregular Cu and Ni NPs with average size of 25, 27 and regular and 28 nm, respectively.

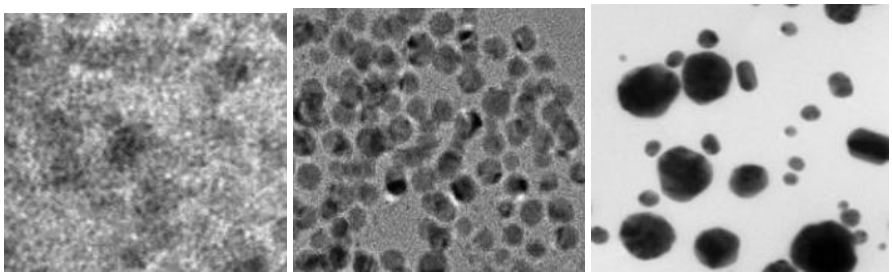


Figure 10: ML_1Nps: Ni TEM image Cu TEM image Ag TEM image.

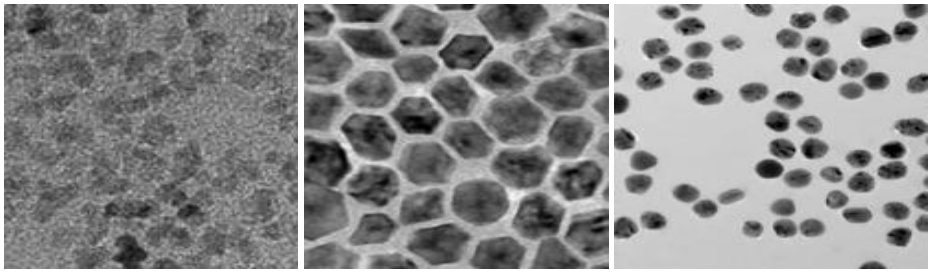


Figure 11: ML_1Nps: Ni TEM image Cu TEM image Ag TEM image.

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