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Research Article

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Synthesis, spectroscopic investigation and antimicrobial studies on some Schiff base complexes of Cu(II) and Ni(II)

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ABSTRACT

Two new metal complexes of Cu (II) and Ni (II) ions with a Schiff base derived from Glutaraldehyde and L-Valine have been investigated. The resulting complexes were characterized by elemental analysis, X-ray Diffraction studies, thermogravimetric analysis, Uv/vis IR, ^{1}H NMR spectral studies, molar conductance, magnetic susceptibility measurements and antimicrobial activity. The molar conductance measurements indicates that the complexes are non electrolytes. The IR data demonstrate the tetradentate binding of the ligand. The XRD data shows that CuL_1 and NiL_1 complexes were microcrystalline in nature. The invitrio antimicrobial activity of the compounds is tested against the bacteria Klebsiella sps, Escherichia coli, Staphylococcos aureus and fungi Candida sps, Aspergillus niger and Aspergillus fumingatus by the Disc diffusion method. The complexes show stronger antimicrobial activity than the free ligands.

Keywords: Schiff base , ^{1}H NMR, magnetic susceptibility, metal complexes, antimicrobial activity

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INTRODUCTION

Metal complexes play an essential role in agriculture, pharmaceutical and industrial chemistry. Ligand, a metal surrounded by a cluster of ions or molecule, is used for preparation of complex compounds named as Schiff bases[1], which are condensation products of primary amines and aldehydes or ketones (RCH= NR$'$, where R&R' represents alkyl and / or aryl substituents). Metal coordination complexes have been widely studied for their antimicrobial and anticancer properties[2]. Many drugs possess modified pharmacological and toxicological properties when administered in the form of metallic complexes [3]. This inspires synthetic chemists to search for new metal complexes for bioactive compounds. Various Copper and Nickel complexes have been reported to inhibit bacterial, fungal, yeast, algal, mycoplasma, and viral growth, as well as to cause the death of these organisms[4,6]. This prompted us to investigate some novel Copper (II) and Ni (II) complexes using Schiff base ligands. For, the coordination chemistry of Schiff base ligands is of considerable interest due to their biological importance [7,8] . A literature search revealed that no work has been done on the metal complexes of Schiff base ligand derived from L-Valine and Glutaraldehyde. Hence in this paper we describe the synthesis of the ligand and the metal complexes. Further insight into the bonding and possible geometrical structure has been made by micro analytical, IR, UV-vis, ^{1}H NMR, and XRD spectral studies, as well as magnetic, thermo gravimetric and conductivity data. The in vitrio antimicrobial activity of the compounds is also tested against few bacteria and fungi.

EXPERIMENTAL SECTION

Analytical grade nickel (II) nitrate, Copper (II) nitrate was used as such without further purification. Glutaraldehyde and L-Valine were obtained from Sigma Aldrich. Cu (II) nitrate and Ni (II) nitrate were obtained from Merck (LTD). Solvent was distilled and purified according to standard procedures. [9,10] . The metal contents of the complexes were determined by EDTA titration. Elemental analysis was carried out in a Vario EL 111 elemental analyzer at Sophisticated Analytical Instruments facility, CUSAT, Kochi. The molar conductance values were measured in DMSO (10^{-3} M) solutions using a Systronic digital conductivity meter. The room temperature magnetic susceptibility measurements of the complexes reported in the present study were made by the Guoy's method using copper sulphate as calibrant. The electronic spectra of all the complexes in DMSO solution (10^{-3}M) in the visible region were recorded on Shimadzu double beam visible spectrophotometer, using a quartz cell of 1 cm optical path. Infrared spectra of all the ligands and their metal complexes were recorded in KBr disc on a Perkin Elmer FT-IR spectrometer model 1600 in the region 4000-400 cm^{-1}. The pellets were prepared by taking necessary precautions inorder to avoid moisture. The instrument calibration with respect to wave number and present transmission was confirmed by recording the spectrum of standard polystyrene film. From the spectra, the characteristic groups were assigned the respected frequencies [11] . ^{1}H-NMR spectra (300 MHz) of the samples were recorded in DMSO-d_6 by employing TMS as internal standard at NIIST Trivandrum. XRD was recorded on a computer controlled X-ray diffractometer system JEOL JDX 8030. Double distilled water was used throughout the experimental work.

Thermal Analysis (TG and DTA) were carried out in controlled nitrogen atmosphere on a Perkin-Elmer Diamond thermal analysis at NIIST, Trivandrum, by recording the change in weight of the complexes on increasing temperature upto 900^oc at the heating rate of 10^o c/min. The antimicrobial activities of ligands and their mixed ligand complexes were screened by Disc Diffusion method [12].

Synthesis of Schiff base:-
The ligand under investigation was prepared by the condensation of the corresponding aldehyde and amine in 1:2 molar ratio by refluxing in distilled methanol[13].

The Schiff base was synthesized by the condensation of glutaraldehyde and L-Valine (1:2 molar ratio), in 150 ml of absolute methanol. The resulting reaction mixture was refluxed for 1 hour. The yellow solid precipitate of Schiff base obtained was filtered, washed with distilled water dried, recrystallised and finally preserved in a desiccators.

Synthesis of Schiff base complexes:-
A metal (II) nitrate (1.0 mmol) dissolved in methanol was added slowly with constant stirring to a solution of Schiff base ligand (1.0 mmol). The resulting mixture was refluxed and stirred for 8 hours. The product was digested on a hot water bath for half an hour. The complex thus formed was filtered out, washed with aqueous alcohol followed by distilled water and dried in vaccum over fused $CaCl_2$.

RESULTS AND DISCUSSION

The analysis data along with some physical properties of the complexes are summarized in table. Metal (II) salts react with Schiff base ligand in 1:1 molar ratio in alcoholic medium to afford dark green and greenish yellow complexes. The analytical data show that the metal to ligand ratio is 1:1. They are soluble in common organic solvents. The low molar conductance values of the complexes reveal their non-electrolytic nature [14].

IR spectra:
In order to study the binding mode of Schiff base to metal in the complexes, IR spectrum of the free ligand was compared with the spectra of the metal complexes. The Schiff base ligand show V(C=N) azomethine band observed at 1625 cm^{-1}. On complexation, this band was shifted to 1598 and 1619 cm^{-1} regions due to the coordination of azomethine nitrogen to the Cu (II) ion and Ni (II) ions. The IR spectra of the complexes also shows some other bands at 1320 and 1330 cm^{-1}, which may be ascribed to the presence of free NO_3 group. The spectra of the complexes illustrate broad bands in 3320 and 3318 cm^{-1} assigned to the presence of water molecules [15] in CuL_1 and NiL_1 complexes. The coordination through nitrogen of azomethine and oxygen of (C-O) group of ligands are further evidenced by the appearance in the complexes of non-ligand bands in 544 and 564 cm^{-1} which is due to M-O bond and bands in 428 and 446 cm^{-1} is due to M-N bond.[16]

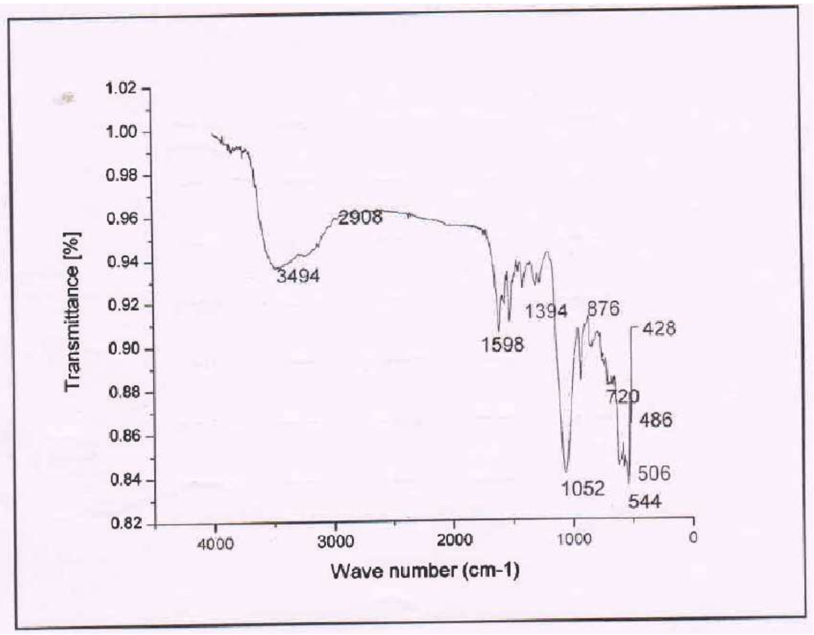


Fig -1: IR spectrum of Cu Complex

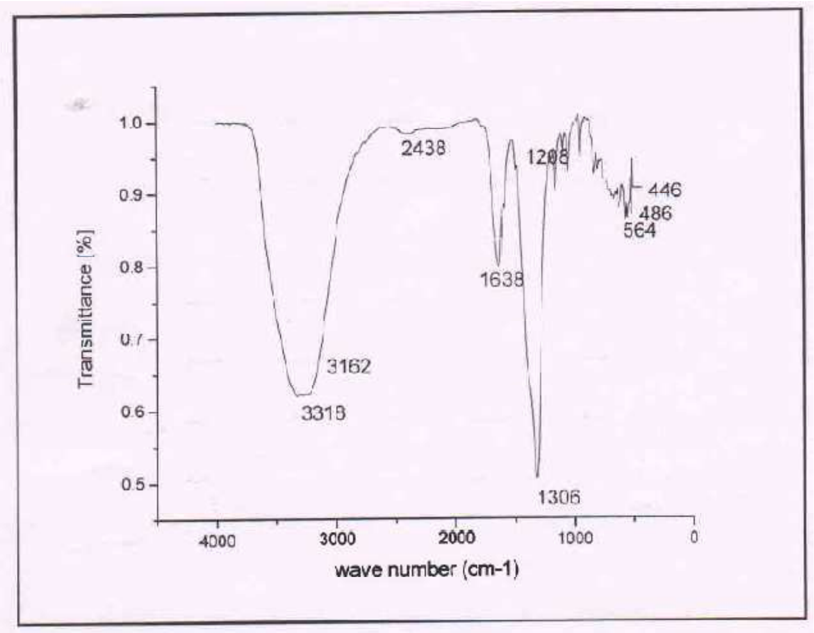


Fig -2 : IR spectrum of Ni Complex

UV/Vis Spectra:

The electronic spectral studies of Schiff base ligand complexes of Cu (II) and Ni (II) was carried out in DMSO solution. The electronic spectra of the metal complexes recorded in UV region exhibit intra ligand and charge transfer transitions. The Schiff base ligand L_1 show the absorption band at 260 nm which is assigned to π-π^* transition of the C=N chromophore. On complexation, this band was shifted to lower wave length region at 234 nm and 240 nm suggesting the co-ordination of azomethine nitrogen with Cu (II) and Ni (II) ions [17]. The spectra also shows the other transitions in the range of 340-400 nm and 310-450 nm which can be assigned to n- π^* transition. The spectra of metal complexes in DMSO recorded in the visible region show transitions in the range 400-500 nm, ascribed to charge transfer transition. Transitions around 600-650 nm may be ascribed to d-d transitions which are characteristic feature of transition metal complexes [18].

Fig -3 UV Spectrum of Cu complex

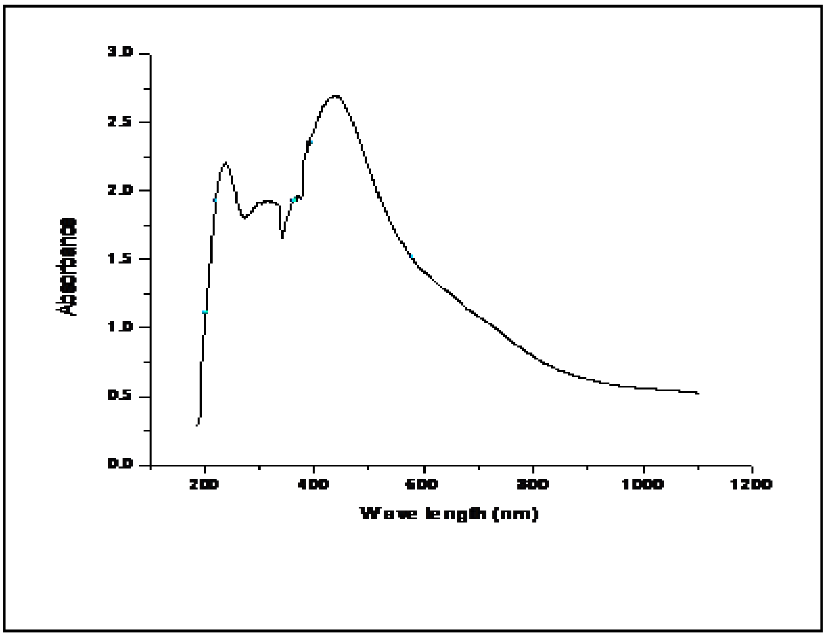
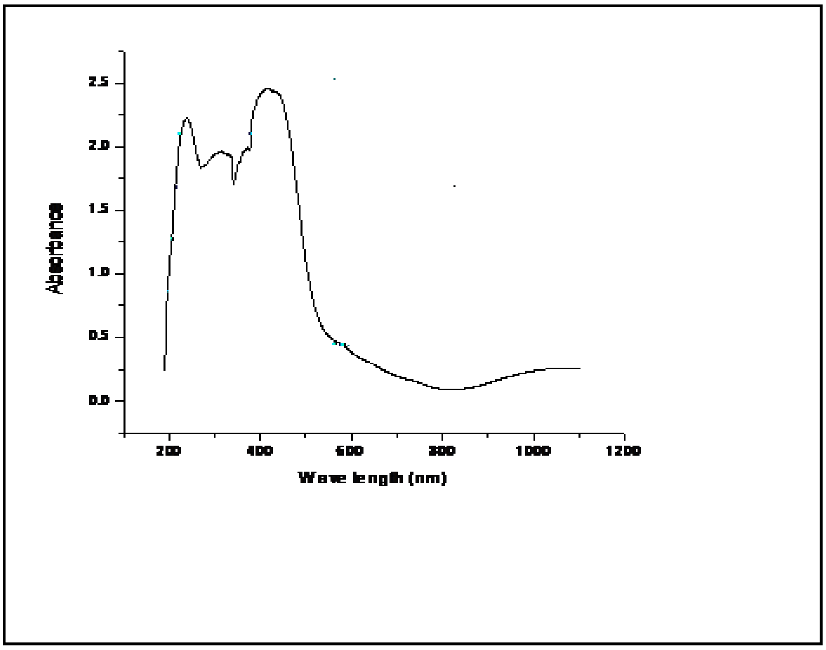


Fig -4 UV Spectrum of Ni complex



Magnetic Studies:

The magnetic moments of the metal complexes were calculated from the measured magnetic susceptibilities after employing diamagnetic corrections. The observed u_{eff} values presented in Table 1 suggest the octahedral geometry for Cu (II) and Ni (II) complexes. The magnetic moments of the compounds investigated support the conclusions.

^{1}H NMR spectra:

^{1}H NMR spectra of the Ligand L_1 recorded in DMSO solution. It shows a multiplet at 2.5, 1.6 ppm due to the methyl protons. The ^{1}H NMR spectra of the Schiff base complexes in DMSO exhibits signals at 8.2, 7.3 ppm and 8.4, 7.5 ppm, attributed to CH=N- and – NH protons respectively. The azomethine proton signal in the spectrum of the corresponding complexes is shifted down field compared to the free ligand, suggesting deshielding of the azomethine group due to the coordination with the metal ion. There is no appreciable change in all other signals of the complexes. The n.m.r results obtained further supports the i.r inferences. [19].

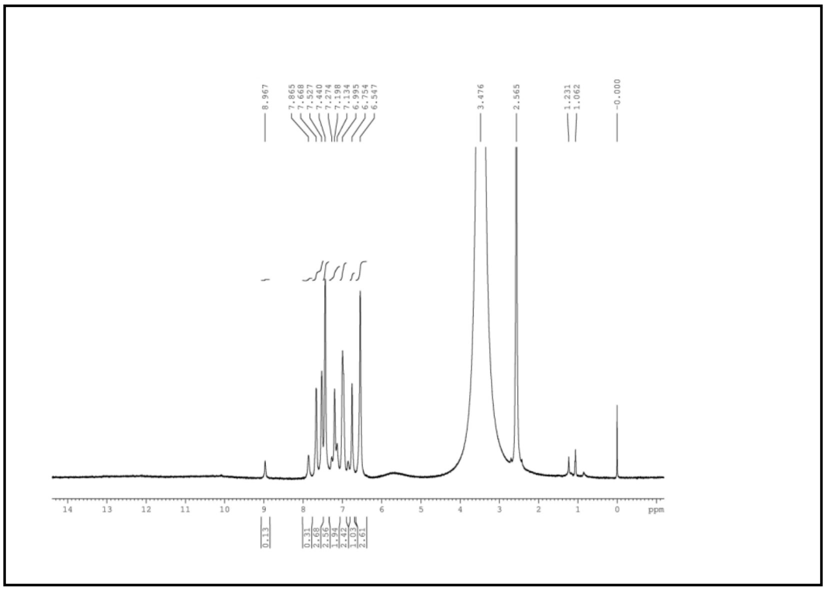


Fig -5 : ^{1}H NMR Spectrum of Cu complex

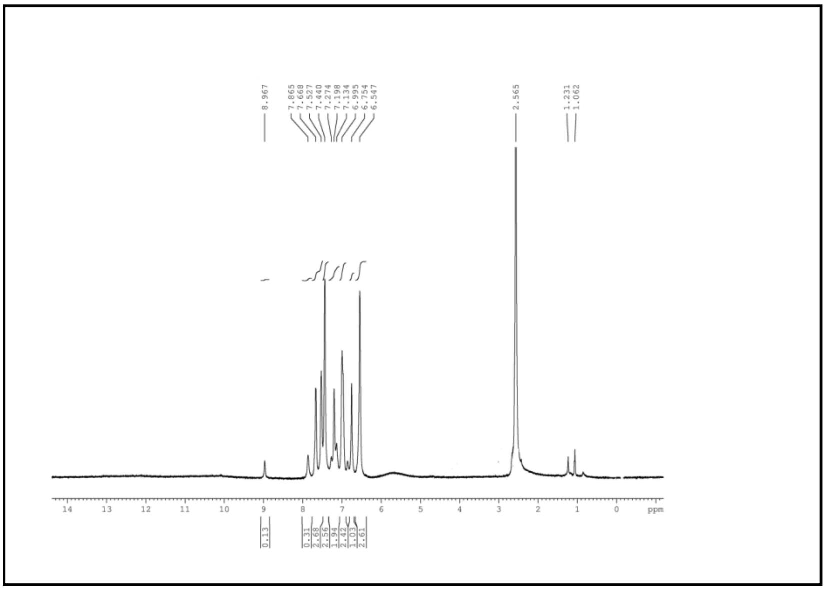


Fig -6 : ^{1}H NMR Spectrum of Ni complex

Thermogravimetric analysis:

The TG and DTA studies of the complexes have been recorded in the nitrogen atmosphere at the constant heating rate of 10^o c/ minute.

Thermal study on the ligand metal complexes in controlled nitrogen atmosphere was carried out to understand the stages and temperature range of decomposition.

The most probable decomposition pattern of the complexes is proposed on the basis of the careful examination of TG and DTA curves. The TG of the complexes shows that they are thermally quite stable but to varying degree. The complexes show gradual loss in weight due to decomposition by fragmentation with increasing temperature. The complexes lose their weight in the temperature range 170-210^o c and 150-300^o corresponding to two coordinated water molecules with an endothermic peak in DTA curve. After the total loss of water, the organic moiety decomposes on further increasing of temperature. The complete decomposition of ligands occurs at ~ 900^{o}c and 600^o c and the observed residue corresponds to the respective oxide. The occurrence of endothermic peak and elimination of the two water molecules at comparatively higher temperature unambiguously confirm our earlier observation based upon the IR spectrum that the water molecules are coordinated in the metal complexes.

Table 1. Physical and analysis data of the Schiff base ligand of its complexes

Compound	Formula	Colour	Elemental analysis found [calc] (%)				Molar Conductance (nm) Scm^2 mol^{-1}	U_{eff} (B.M)
			C	H	N	M		
L_1	$C_{12}H_{26}N_2O_4$	Yellow	59.83 [60.36]	8.31 [8.78]	8.92 [9.38]	-	-	-
$[Cu(L_1)(H_2O)_2]$	$C_{15}H_{30}N_2O_6Cu$	Pale green	44.54 [45.26]	7.2 [7.6]	6.9 [7.04]	15.01 [15.96]	13	1.79
$[Ni(L_1)(H_2O)_2]$	$C_{15}H_{30}N_2O_6Ni$	Greenish Yellow	45.12 [45.81]	7.15 [7.68]	6.89 [7.12]	14.05 [14.94]	15	3.08

XRD study:-

Single crystals of the complexes under study could not be obtained because the metal complexes were isolated as powder rather than single crystals, in addition to their insolubility in most organic solvents, thus no definitive structure can be described [20]. The X-ray powder diffraction pattern throws light only on the fact that each solid represents a definite compound of a definite structure which is not contaminated with starting materials.

X-ray diffraction patterns of Cu(II) and NI (II) complex shows sharp crystalline peaks. The above complexes have specific 'd' values which can be used for its characterization. The crystallite size of the complexes d_{XRD} could be estimated from XRD patterns by the Scherre's formula,

$$D_{XRD} = 0.9 \lambda / \beta (\cos \theta)$$

Where λ is the wavelength, β is the full width at half maxima and θ is the diffraction angle. The X-ray analysis shows the complexes were microcrystalline in nature.

Antimicrobial activity:

The in vitrio biological screening effects of the investigated compounds were tested against some bacterial and fungal species by the disc diffusion method [21]. The results of the antibacterial and antifungal activities are given in Table 2. The results show that the Schiff base ligand have moderate activity in the antibacterial species.

Table 2: Anti microbial data of the ligand and their mixed ligand complexes

Schiff base/ Complex	Zone of inhibition					
	Klebsiella sps	*E.coli*	*Staphylococcus aureus*	*Candida sps*	*Aspergillus niger*	*Asp fumingatus*
L_1	-	-	-	2.5	2.0	1.5
CuL_1	11.5	13.5	10.5	13.5	11.5	11.5
NiL_1	12.5	15.5	13.5	26.5	22.0	21.0

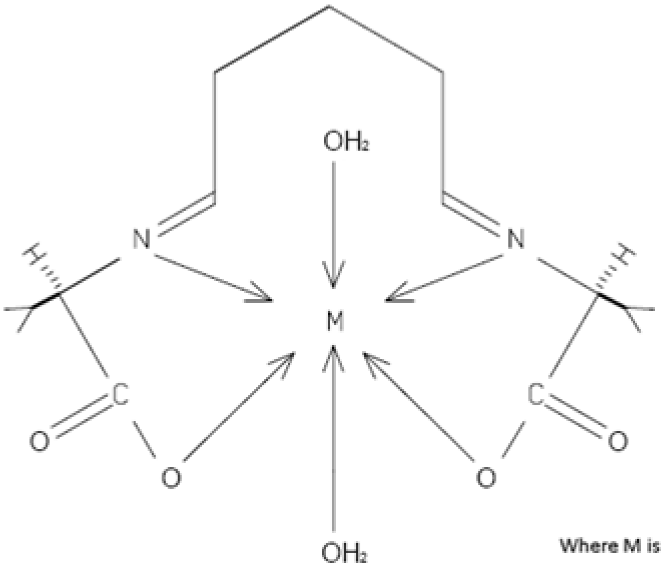
The Schiff base ligand doesnot show any activity against all the bacterial species. The complex CuL_1 exhibits high activity against all the tested bacteria expect for staphylococcus aureus. It shows high activity against the bacteria E-coli However, the complex NiL_1 had the highest effect against E-coli and moderate effect against Klebsiella sps.

The results on antifungal activity of the ligands show very less activity towards all the fungal species such as candida asps, Aspergillus niger and Aspergillus fumingatus. However, both CuL_1 and NiL_1 complexes shows higher activity in Candida sps and quite lesser activity in Aspergillus niger and Aspergillus fumingatus.

From the observation it is understood that the higher inhibition of microbial growth is due to uncoordinated hetero atoms and carboxylic moieties present in complexes.

CONCLUSION

Novel tetradentate Schiff base ligands derived from glutaraldehyde and L-Valine and also their complexes have been characterized by analytical and spectral techniques. From the electronic absorption absorption spectra and the stoichiometric analysis, Octahedral geometry was assigned for the synthesized complexes. The very low conductivity values indicate that all the complexes are non-electrolytes. From the microbial screening observation and from the available literature knowledge, the possible ways to inhibit the microbial growth using the complexes were explained. The redox properties of metal ion, the presence of >C=N group, carboxylate moiety and also substituents are responsible for their increased antimicrobial activity.



Where M is Ni, Cu or Co

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