Synthesis, Characterization and Antimicrobial Activity of Metal Complexes with Diethanolamine and Nitro Ligands

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Abstract:

 Cu(II) and Ni(II) metal complexes derived from diethanolamine and nitro ligands have been prepared. The newly synthesized compounds have been confirmed on the basis of elemental analysis, melting points, conductivity, IR, UV-VIS and NMR(1H) spectral methods .The metal complexes have been tested for their antimicrobial activity in Mueller Hinton Media, (MH Media) .
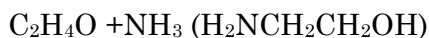
Key words: Synthesis, characterization, antibacterial and antifungal activity.

Introduction:

Ethanolamines are a class of organic compounds containing amine and alcohol groups.

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The reaction of ethylene oxide with aqueous ammonia first produces ethanolamine.

$$C_2H_4O + NH_3 \ (H_2NCH_2CH_2OH)$$

Which reacts with a second and third equivalent of ethylene oxide to give diethanolamine and triethanolamine.

$$C_2H_4O + H_2NCH_2CH_2OH = HN(CH_2CH_2OH)_2$$
$$C_2H_4O + HN(CH_2CH_2OH) = N(CH_2CH_2PH)_3$$

Diethanolamine is a tridentate ligand and readily forms co-ordination complexes with almost all metal ions and behave as nitrogen and oxygen donor ligands and their transition metal complexes were synthesised (1,2)

In some cases, diethanolamine loses its ethanolic hydrogen being as diethanolaminate anion, which also behave as a ligand similar to diethanolamine and diethanolaminate derivatives of metals have been reported (3-6.).

Diethanolamine is used in the production of diethanolamides , which are common ingredients in cosmetics and shampoos added to confer a creamy texture and foaming action . Diethanolamine is also a common material used in the chemical and pharmaceutical industries as an intermediates for the production of detergents,drugs,textile finishing agents and as an absorbent for acidic gases.(Sutton,1963)

Nitrite being a strong ligand never acts as a non – coordinating or ionic ligand in co-ordination compounds. It can bond through the nitrogen to give nitro complexes or through one of the oxygen to give the less common nitrito species. It can also act as a bridging ligand bonding through the nitrogen and one of the oxygens (7).

Materials and Methods:

All chemicals used were of analytical grade (AR) reagents and of the highest purity available. They included cupric chloride dihydrate (fisher scientific), nickel chloride hexahydrate

(Qualigens fine chemicals), diethanolamine (MERCK) and sodium nitrite (s.d.fine chem.ltd.)

The elemental analysis was performed using an elemental analyser. The measurement of conductance of the complexes were measured using a conductometer at 30 deg. Celcius. The IR spectra were recorded in a spectrometer (4000-400 cm-1). The UV-VIS electronic spectra (200-800nm) were performed using a double beam spectrophotometer .The geometries of the metal complexes were determined using molecular calculations.

Synthesis of the metal complexes:

An ethanolic solution of MX_2 (0.005 moles,) M=Cu and Ni, is added slowly to an ethanolic Solution of diethanolamime (0.005 mole,) with constant stirring. The mixture is refluxed for 5 hours at 60 deg. Celsius. Then an aqueous solution of sodium nitrite (0.005 mol) is added drop wise and the mixture is refluxed for 2 hours at 60 deg. Celsius. The mixture is filtered, washed with ethanol and dried the residue.

Result and Discussion:

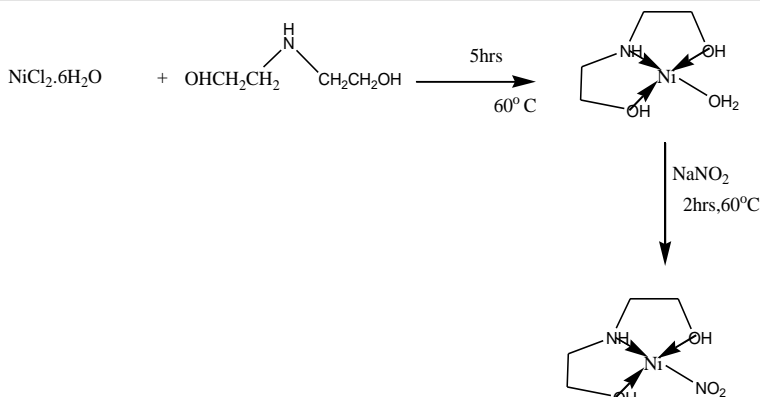The synthetic route of the metal complexes were outlined in scheme 1:
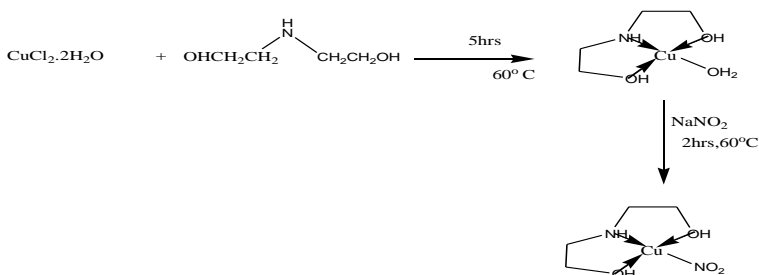
Fig 1: Reactions for the synthesis of Cu and Ni complexes.

Elemental analysis and molecular conductance:

The metal complexes are insoluble in water but soluble in DMSO. The analytical data and physical properties of the complexes are presented in the following table. The data are consistent with the calculated results from the empirical formula of each compound.

Table1: Elemental analysis, specific conductance and melting points of the complexes.

Complex	Emperical formula	Mol.wt g/mol	Elemental analysis found(calculated)%			Specific conductance mS/cm (30deg.C)	Melting point Deg C
			C	H	N		
Cu-complex	$C_4H_{11}O_4N_2Cu$	214.64	20.81 (22.36)	4.86 (5.167)	12.27 (13.05)	0.03	>300
Ni-complex	$C_4H_{11}O_4N_2Ni$	209.84	21.73 (22.87)	5.02 (5.284)	12.67 (13.34)	0.02	>300

Conductance of Cu-complex: A milimolar solution of the complex is prepared by dissolving 0.0022 g. of the complex in 1ml DMSO and diluted to 10ml with double distilled water.

Conductance of Ni-complex: 1milimolar solution of the complex is prepared by dissolving 0.0021g. of the complex in 1ml DMSO and diluted to 10ml with double distilled water.

Conductance of Cu-complex =0.03 mS/cm at 30 deg. C

Conductance of Ni –complex =0.02 mS/cm at 30 deg. C

The low conductance values indicates that the above complexes are non electrolytes.(8)

IR spectra:

The significant IR bands for the complexes are compiled and presented in table-2. The IR spectrum of the complexes, a sharp band observed at 1600 cm^{-1} is assigned to the υ(C-N) mode. This shifts to a lower wavenumber suggesting the co-ordination of the nitrogen to the metal centre. A strong sharp band observed at 3400cm^{-1} is assigned to υ (>N-H) of the ligand.

Table: 2 IR spectral data for the metal complexes:

COMPLEX	υ(M-N)	υ (C-N)	υ (C-O)	υ (>N-H)	υ (M-O)
Cu-complex	457-464	1600	1100	3400	537-555
Ni- complex	457-464	1600	1100	3400	537-555

Fig 2: IR spectrum of Ni- complex.

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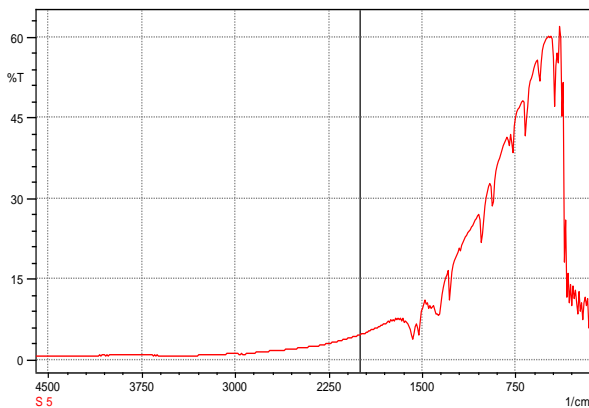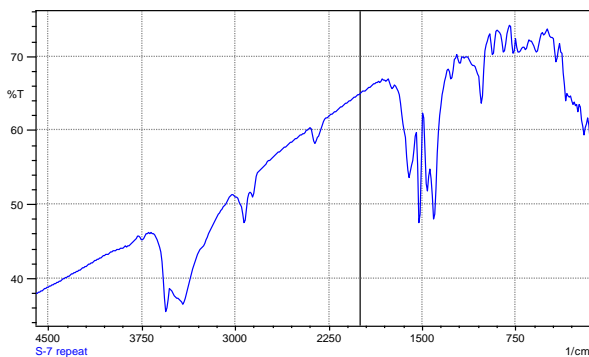**Fig 3: IR spectrum of Cu –complex.**

UV-VIS spectra:

The UV-VIS spectral data of the complexes are presented in
Table-3. The electronic   absorption spectra of both the
complexes of Copper and Nickel was made in DMSO and then
diluting the solution with double distilled water in the range
190- 700 cm^{-1} . For the Cu-complex, absorption peak was found
at 248.5 nm, 228.0 nm and 199.0 nm. And for the Ni-complex,
absorption peak was found at 283.5 nm and 232.5 nm.

Table -3: Electronic spectral data for the metal complexes.

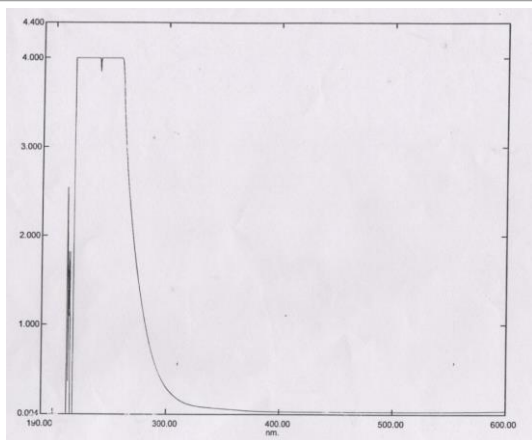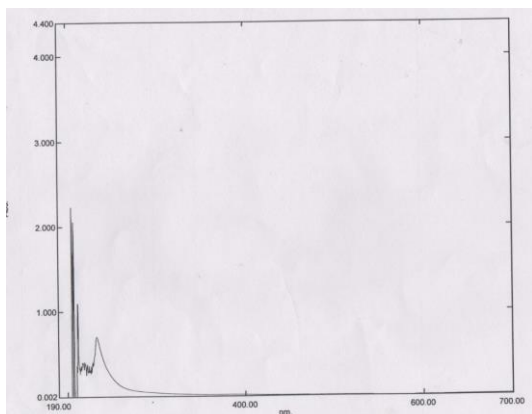| COMPLEX	Absorbance (nm)	Assignment	Geometry
Cu- complex	248.5	Squre planner	Squre planner
-do-	228.0	π- π *	-do-
-do-	199.0	π - π *	-do-
Ni- complex	283.5	Squre planner	Squre planner
-do-	232.5	π - π *	-do-

Fig 4:UV-VIS-Spectrum of Cu-complex.

Fig 5: UV-VIS-Spectrum of Ni-complex.

NMR spectra:

Here NMR spectra of Ni-complex is discussed. In the spectrum graph report we found three signals given by the complex in proton (H-1) NMR.

At 3.757 ppm the signal is corresponding to proton (H-1) attached to the secondary nitrogen atom. At 3.133 ppm, the signal is corresponding to two protons (H-1) near to the hydroxyl group. The signal corresponding to 2.162 ppm is due to two protons (H-1) near to the secondary nitrogen atom.
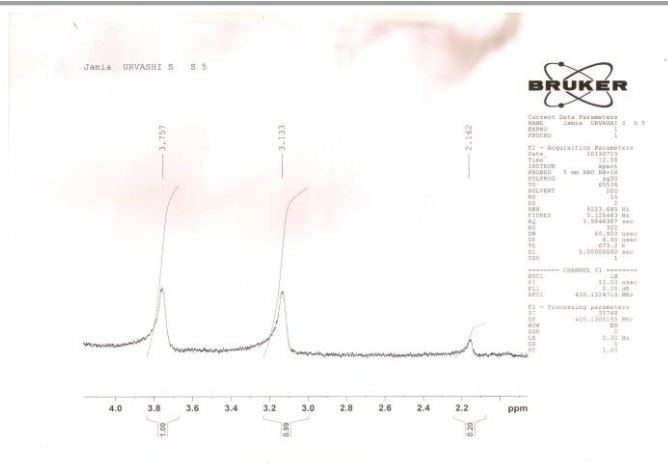
Fig 6: NMR-Spectrum of Ni-complex.

Applications:

Antimicrobial activity: An antimicrobial is a substance that kills or inhibits the growth of micro-organism such as bacteria, fungi or protozoans. The discovery of antimicrobials like penicillins by Alexender Fleming and tetracyclines paved the way for better health for millions around the world.

The in vitro biological screening effects of the investigated compounds were tested against the bacteria Salmonella typhi and Klebsiella pneumonie and fungi. Stock solution of 2mg/ml concentration were prepared by dissolving the compounds in dimethyl sulphoxide (DMSO) and serial dilution of the compounds were prepared in sterile distilled water to determine the minimum inhibition concentration (MIC).The nutrient Mueller Hinton media was poured into petriplatis. Different dilution of the stock solutions were applied on the 10mm diametis staile disc. The discs were placed in an incubator for 3 days. Antibacterial and antifungal potential of the complexes were assessed in terms of zone of inhibition of bacterial and fungal growth in figures 1,2. The minimum inhibitory concerntration (MIC) were calculated on

the highest dilution showing complete of the tested bacterial and gungal strain and we reported in table 4,5.
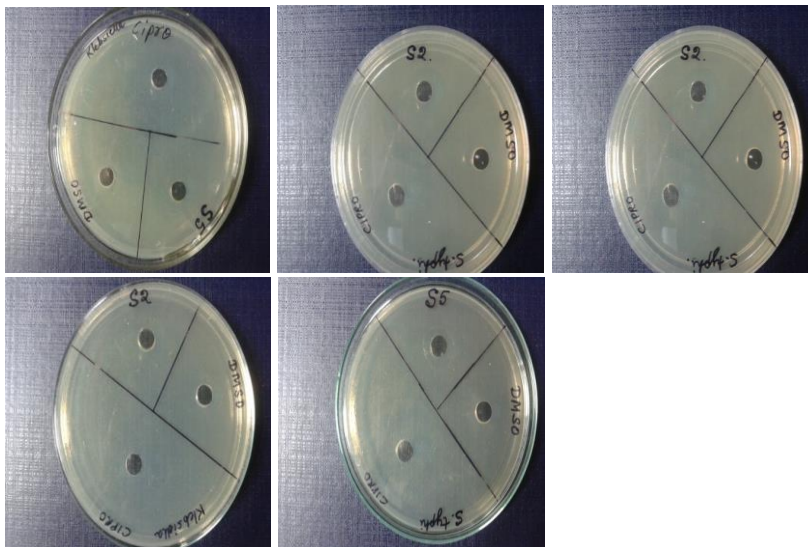
S-2=Cu-complex, S-5=Ni-complex
Fig 6: Disk diffusion assay showing zones of inhibition in the presence of compounds

Table-4: Determination of MIC for antibacterial and antifungal activities of the complex Cu-complex.

Micro-organism	2.0 m g/mi	1.7mg/ml	1.5mg/ml	1.2 m g/ml	1.0 m g/ml	0.7 m g/ml	0.5 m g/ml	0.1 m g/ml
S. typhi	-	-	-	+	+	+	+	+
K. pneu-monie	-	-	-	+	+	+	+	+
Fungi	-	-	-	+	+	+	+	+

Table-5: Determination of MIC for antibacterial and antifungal activity of the complex Ni- complex.

Micro-organism	2.0mg /ml	1.7 m g/ml	1.5mg /ml	1.2mg /ml	1.0 m g/ml	0.7mg /ml	0.5mg /ml	0.1mg /ml
S. typhi	-	-	-	-	+	+	+	+
K. pneu-monie	-	-	-	-	+	+	+	+
Fungi	-	-	-	-	+	+	+	+

Table -6: Antibacterial and antifungal activity of the complexes : MIC value.

Micro-organism	Complex	MIC value
Bacteria	Cu- complex	1.5mg/ml
Fungi	Cu- complex	1.5mg/ml
Bacteria	Ni – complex	1.2mg/ml
Fungi	Ni- complex	1.2mg/ml

The complexes were effective against both bacteria and fungi. It is evident from the table - 6 that MIC values (9) for the Cu-complex was 1.5mg/ml for both bacteria and fungi while that of Ni-complex was 1.2mg/ml.

Conclusion:

In this paper, we have reported the synthesis of Cu(II) and Ni(II) metal complexes with diethanolamine and nitro ligands. The complexes were characterized by spectral methods and analytical data. Based on these, a square planner geometry has been assigned for both the complexes. The antimicrobial studies carried out with the complexes confirms that they are antibacterial and antifungal agents with their MIC values.

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