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SYNTHESIS, CHARACTERISATION AND ANTIMICROBIAL ACTIVITY OF NICKEL(II) COMPLEXES DERIVED FROM PENTADENTATE SCHIFF BASE LIGAND

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Abstract:

Two different para substituted dinuclear nickel(II) complexes [$Ni_2L(O_2CC_6H_4\text{-p-X})$] [X= NO_2, Cl] were synthesized by the reaction of corresponding precursor withpentadentate Schiff base ligand.The ligand was characterized by UV-Visible,FTIR, NMRstudies.The synthesized complexes were characterized by molar conductance, UV- Visible, FTIR spectral studies.The ligand and its complexes screened for antimicrobial activity.

Key Words: Penta-Dentate Schiff Base Ligand, Nickel(II) Precursors, Nickel(II) Complexes & Antimicrobial Activity

Introduction:

The coordination chemistry of dinucleating ligands is currently an area of great activity[1]. One reason for this is the facile synthesis of dinuclear species toward model compounds of metallo-enzymes[2].On the other hand, these multidentate ligands are useful as building blocks for high-nuclearity compounds. Lately, we have explored ways to design the synthesis of dinuclear metal complexes by multidentate ligands. In this study, we have found that it is possible to use symmetrical pentadentate Schiff base ligand 1,3-bis-(5-nitro salicylideneamino)propan-2ol (H_3L), which affords a dinuclear species for Ni^{II} to generate dinuclear metal complexes.

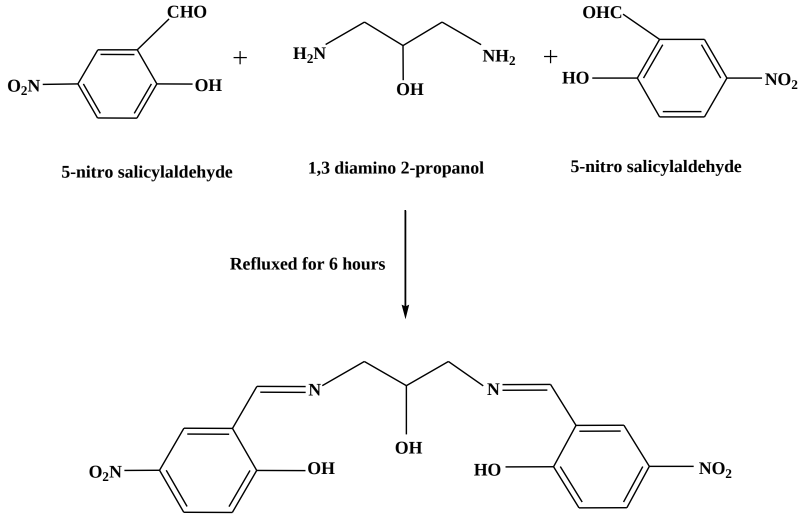
Experimental:

Materials and Methods:

1,3-diamino-2-propanol was purchased from Alfa Aesar, all other chemicals and solvents were purchased from commercial sources and were used after purification. Conductance of complexes was recorded using Elico conductometer. UV-Visible spectra were recorded using Systronics spectrophotometer operating in the range of 200-800 nm with quartz cell. FT-IR spectra of ligand and complexes were obtained on a Schimadzu IR-Affinity-I spectrometer and samples were prepared using KBr. ^1H NMR spectrum of Schiff base ligand was recorded using Bruker 400 MHz model.

Synthesis of Ligand:

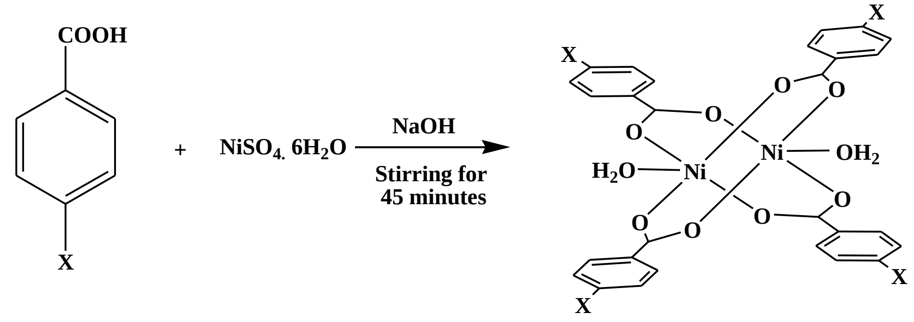
The ligand was synthesized using 1,3-diamino-2-propanol (10mmol; 0.9g) and 5-nitro salicylaldehyde (20mmol; 3.342g) in the ratio of 1:2 using ethanol as a solventand the mixture was refluxed for 6 hours. Colour change was observed and the reaction was monitored by TLC primarily using hexane as eluent. The product obtained was washed repeatedly with the minimum quantity of ethanol in order to remove the impurities and it was filtered and dried. The crude product obtained was characterised by techniques like UV-Visible, FT-IR, ^1H NMR spectra respectively.



Schematic representation of Ligand (H_3L)

Synthesis of Nickel(II) Precursors:

The Nickel(II) precursors were synthesized by using organic acids namely para-nitro benzoic acid and para-chloro benzoic acid with NaOH are stirred for 10 minutes and $NiSO_4.6H_2O$ was added to the above mixture and magnetically stirred with 45 minutes. The ratio of metal, organic acid and base was taken as 1:2:2 for the synthesis of nickel(II) precursors. The crude green nickel(II) precursors obtained was washed thoroughly with water and dried well. The nickel(II) precursors obtained was used for the synthesis of nickel(II) complexes as such.



X =NO_2, Cl

General schematic representation of nickel(II) precursors

Synthesis of Nickel (II) Complexes:

A general method was adopted for the preparation of Nickel(II) complexes. The synthesis of Nickel(II) complexes was prepared by taking the Schiff base ligand (H_3L), KOH and various Nickel(II) precursors in the stoichiometric ratio of 1:3:1. The ligand (1mmol; 0.388g) with KOH (3mmol; 0.1683g) and nickel p-nitro benzoate (1mmol; 0.8178g) was refluxed for 6 hours using ethanol as a solvent. Colour change was observed from yellow to light green. The crude product so obtained was washed repeatedly with a minimal amount of ethanol in order to remove the impurities, filtered and dried. Similarly complex-II was synthesised with nickel p-chloro benzoate The nickel(II) complexes obtained was characterised by conductivity measurement, UV-Visible, FT-IR, LC-MS spectral studies.

Scheme of the Complex:

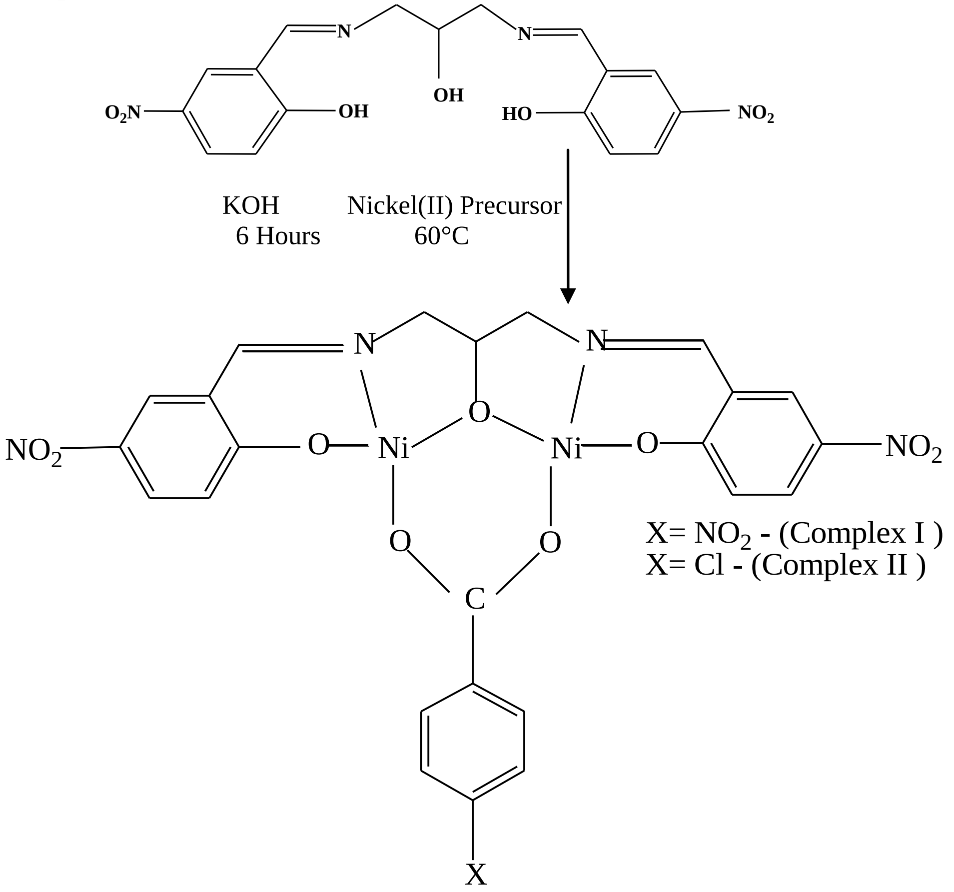


Table 1: Physical properties and Conductance of the metal complexes

Compound	**Molecular formula**	**Colour**	**Molar Conductance ($\text{Mho cm}^2\ \text{mol}^{-1}$)**
Complex-I	$C_{25}H_{17}N_5O_{11}Ni_2$	Light Green	18.9
Complex-II	$C_{24}H_{17}N_4O_9\,ClNi_2$	Light Green	11.7

Table 2 : IR data for ligand and its complexes

Functional group	Ligand (cm^{-1})	Complex-I (cm^{-1})	Complex-II (cm^{-1})
υ(C=N)	1633	1610	1618
υ(C-O)	1246	1307	1315
υ(-OH)	3421	3469	3496
υ(Ni-N)	-	540	532
υ(Ni-O)	-	466	469
υ(Ni-OCO)	-	1556,1479	1585, 1487

Results and Discussion:

Conductance Measurements:

Molar Conductivity measurements values revealed non-electrolytic nature of Nickel(II) complexes[3].

UV-Visible Spectra:

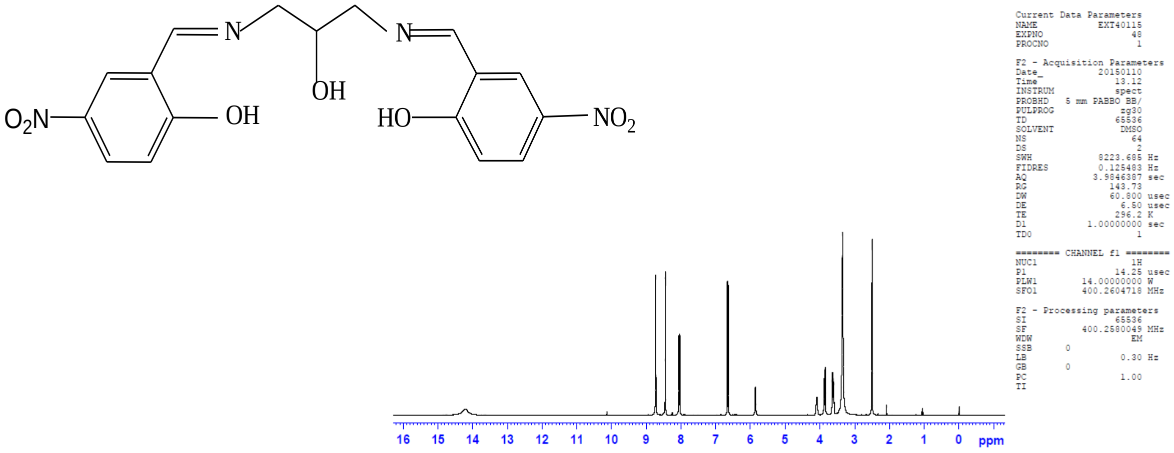
The UV-Visible spectra of the ligand was recorded in ethanol in the wavelength range 200-800 nm. The complexes were recorded in the ethanol solution in the above wave length range. The band observed at 280nm is due to π-π* transition of the benzene ring present in the ligand and it shifted to higher wavelength(red shift) upon complexation and the band was observed at 285 and 287 nm respectively for complex-I & II. The band at 360 nm is due to π-π* transition of the azomethine group present in the ligand and it shifted to higher wave length which was observed at 365 and 378 nm.This shows the coordination of metal with the azomethine nitrogen[4]. The band at 440 nm was assigned to n-π* transition of the ligand and it shifted to higher wave length which was observed at 442 and 450nm. The weak band at 665 and 650 nm is due to d-d transistion of complex-I & II.

Infrared Spectra:

In order to study the binding mode of ligand to metal in the complexes, IR spectrum of the free Schiff base ligand was compared with the spectra of the metal complexes. The free ligand exhibits IR peaks at 3421 cm^{-1} (O-H), 1633 cm^{-1} (C=N) and 1246 cm^{-1}Phenolic(C-O)[5,6]. In complexes the peak due to (O-H) of the ligand disappeared indicating the co-ordination of phenolic oxygen to the metal ion via deprotonation. This was further supported by upward shift to the phenolic (C-O) mode. The peak at 1633 cm^{-1} was dueto azomethine group of the ligand and it shifted to lower frequency after complexation. This shows the co-ordination of metal with azomethine nitrogen[7]. The peaks at 3469, 3496 cm^{-1}assignable to co-ordinated water or unco-ordinated water molecules associated with the complex. The difference between the carboxyl stretching frequency $\Delta\upsilon = \upsilon_{as}-\upsilon_s$ is in the range of 77 – 98 cm^{-1} which is less than that of $\Delta\upsilon$ of the free carboxylate anion (195 cm^{-1}), which indicates the bidentate binuclear bridging of the carboxyl group present in the complexes. Some new bands have also appeared indicating the complexation of metal with the ligand corresponds to (Ni-N), (Ni-O) .

^{1}H-NMR of the Ligand:

The ligand was characterized by ^{1}H-NMR and the values were obtained at 4.2δ for secondary alcohol proton; 3.3 δ for methylene proton; 6.6 δ for azomethine group; 8.78 δ for phenolic proton.



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PROCNO                  1

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PULPROG              zg30
TD                  65536
SOLVENT              DMSO
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DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ              3.9846387 sec
RG                 143.73
DW                 60.800 usec
DE                   6.50 usec
TE                  296.2 K
D1             1.00000000 sec
TD0                     1

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P1                  14.25 usec
PLW1          14.00000000 W
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F2 - Processing parameters
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WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
TI
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Mass Spectra:

The mass spectrum of complex (II) exhibited peak at m/z 658.96. This data is in good agreement with the proposed molecular formula.The mass spectra confirms the formation of the complexes. The complexes are found to be non-ionic in nature.

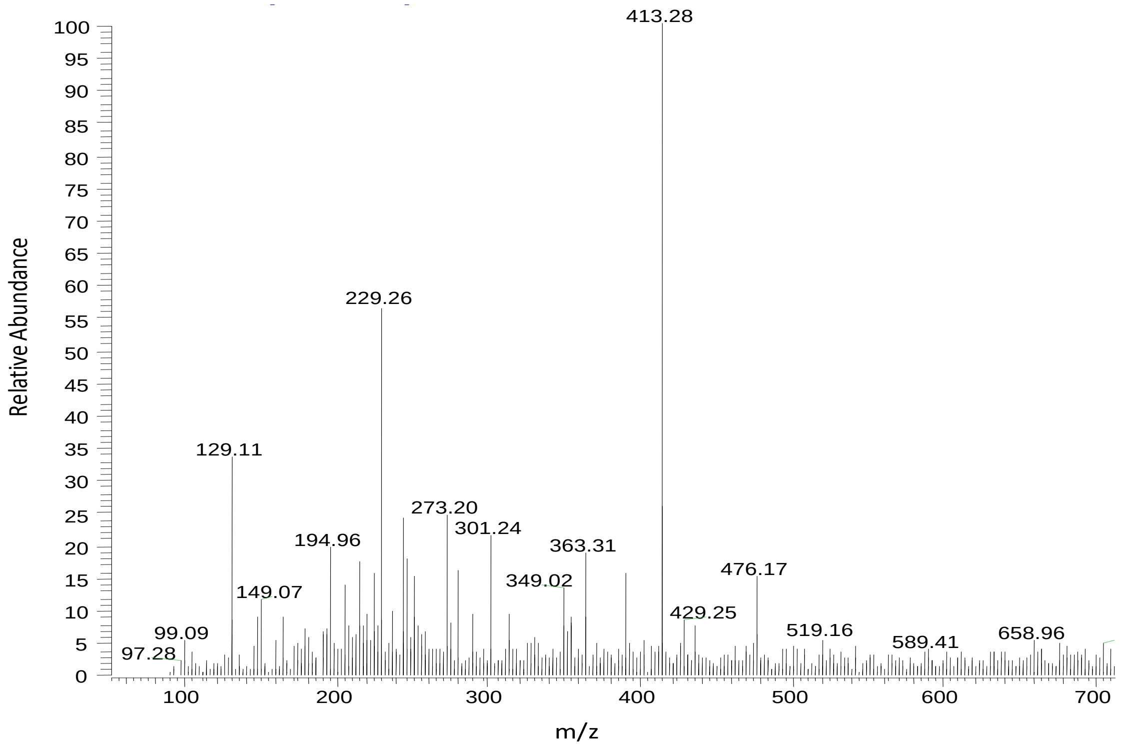


Figure 1: Mass spectrum of complex II

Biological Activity:

The *in vitro* growth inhibitory activities of the Schiff base ligand and its complexes (1-2) were tested against bacteria such as*vibrio cholera, staphylococcus epidermidis, escherichia, bacillus subtilis* by the agar well diffusion assay[8].The *in vitro* growth inhibitory activities of the Schiff base ligand and its complexes (1-2) were tested against fungai such as *Candida albicans,Aspergillus niger,Aspergillus flavus.* The antibacterial activity are listed in table-3.The antifungal behavior of ligand and its metal complexes shown in table-4. The result indicates that all the synthesised compounds varying degree of inhibitory effect on the growth of all the microorganisms. In general the antibacterial and antifungal activities of the synthesiszed compounds followed the order L> ComplexII > ComplexI

Table 3: Antibacterial activity of Schiff base Ligand and its complexes (Concentration 50 mcg)

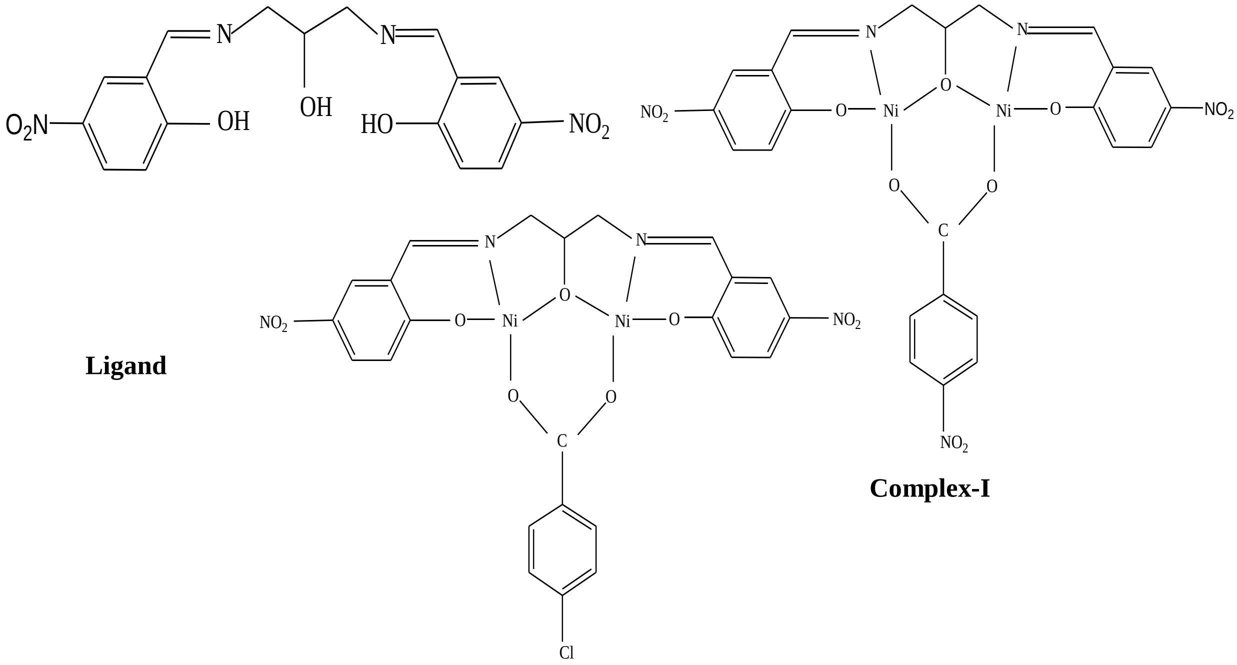
Compounds	Diameter of inhibition zone (in mm)			
	Vibrio cholerae	*Staphylococcus epidermidis*	*Escherichia coli*	*Bacillus subtilis*
L	10	9	15	12
Complex I	8	8	10	7
Complex II	5	10	12	10
DMSO	-	-	-	-
Ciprofloxacin	18	19	10	18

Table 4:Anti fungal activity of Schiff base Ligand and its complexes (Concentration 50 mcg)

Compounds	Diameter of inhibition zone (in mm)		
	Candida albicans	*Aspergillus niger*	*Aspergillus flavus*
L	25	30	05
Complex I	-	10	-
Complex II	-	10	-
DMSO	-	-	-
Amphotericin - B	24	16	08

Conclusion:

This chapter explains the synthesis and investigation of a Schiff base ligand 1,3-bis-(5-nitro salicylideneamino)propan-2-ol derived from1,3-diamino propan-2-ol and 5-nitro salicylaldehyde and its two complexes with various nickel(II) precursors. From the LC-MS data, the molecular formula of the complexes were obtained which confirms the formation of complexes. The molar conductance value of the complexes show that they are non-electrolyte or neutral which is well supported by LC-MS spectra. The electronic spectra and vibrational spectra confirm the presence of functional group in the ligand and its complexes. Especially, the vibrational spectra illustrates the coordination mode of the ligand and the bidentate binuclear bridging of the carboxylate group obtained from precursors towards the complexes. Antimicrobial studies confirmed that ligand is biologically active and their nickel(II) compleses show less activity against different microorganisms. Based on the above characterisation, the structure of the ligand and complexes are proposed as follows.



Ligand

Complex-I

Complex-II

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