



COMPLEXES OF NICKEL (II) WITH THE SCHIFF BASES DERIVED FROM CONDENSATION OF SALICYLALDEHYDE AND BIS-Ni (AMUH)₂Cl₂

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ABSTRACT

The nickel (II) complexes with Schiff base ligand derived from the condensation of Bis (1-amidino-O-methylurea) Ni(II) chloride and salicylaldehyde have been prepared and investigated using different chemical techniques such as elemental analysis, molar conductance, infra-red, electronic spectra, EPR, NMR and magnetic moment. The obtained chemical analysis data showed the formation of 1:1 (metal: ligand) ratio and octahedral geometry was suggested on the basis of magnetic moment and spectral data studies. The free ligand and its metal complexes have been tested in vitro against a number of bacteria in order to assess their antibacterial activities.

Keywords: Schiff base ligand, 1-amidino-O-alkylurea (AMUH), antibacterial activity.

INTRODUCTION

Transition metal complexes with Schiff base as ligand have been amongst the widely studied coordination compounds in the past few years, since they are found to be widely applicable in many fields such as biochemical, analytical and antimicrobial fields¹⁻⁵. It is well known from the literature that much work have been done on the synthesis and characterization of this compounds⁶⁻⁸ with Schiff base ligand formed from salicylaldehyde or substituted salicylaldehyde and various aromatic amines⁹⁻¹³.

Heterocyclic ring containing sulphur, nitrogen, and oxygen impart special biological activity to these Schiff bases and their metal complexes¹⁴. In view of the above applications, the present work describes the results of our investigations on the synthesis, structural studies and antibacterial studies of nickel (II) complexes of Schiff base ligand.

EXPERIMENTAL

Materials

All the chemicals used were of AR- grade and procured from Sigma-Aldrich and Fluka. Metal salts were purchased from E. Merck and used as received. Nutrient agar was purchased from Tulip diagnostics (P) LTD. Company as a ready made paste.

Experimental Details

Elemental analysis was carried out on a Perkin Elmer 240 C. Metal contents were determined by gravimetric method.

IR spectra were recorded on shimadzu FT-IR 8400s by using KBr Disks. The electronic spectra of the compound were recorded in DMF on a Beckmann DU-640 spectrophotometer. EPR experiments were conducted using a BRUKER ESP-300 spectrometer operated at X-band frequency (9.5 GHz) with 100 KHz field modulation. DPPH was used as a field marker. The room temperature magnetic moment (μ_{eff}) was measured using a PAR vibrating sample magnetometer (VSM) model 155 and also at Gouy balance at room temperature using Hg [Co(SCN)₄] as a calibrant. Molar conductance were measured at room temperature in methanol on an Elico conductivity bridge type CM-82 T.

Synthesis of ligand (L)

The complex Bis (1-amidino-O-methylurea) Ni (II) chloride were prepared according to Dutta and Ray¹⁵. The Schiff base ligands were prepared by refluxing the methanol solution of salicylaldehyde and

methanolic solution of Bis (1-amidino-O-amethylurea) Ni (II) chloride in 2:1 molar ratio on a steam water bath for about 40 hours. The solution mixture was made alkaline by adding 2N NaOH solution. The p^H value of the solution mixture was adjusted up to 8-12 range of p^H value.

On concentration and cooling in freeze for overnight, the bright orange colour Schiff base ligand was obtained. The compound was filtered off, washed several times with water. Water is used for washing because the starting compound Bis (1-amidino-O-methylurea) Ni (II) Cl_2 is soluble only in water. Then the compound was washed again with methanol and dried in air.

Synthesis of Compound

Hot methanolic solution (30ml) of the corresponding metal salts (0.001mol) was added to the hot methanolic solution of the Schiff base ligand (0.01mol). The solution mixture was refluxed in water bath with constant stirring for about 48 hours. On concentration and cooling in freeze for overnight, lustrous orange colour crystals were precipitated out. It was filtered, washed several times with acetone and dried in air. The acetone solvent is used because the Schiff base ligand is soluble in acetone but the complex is insoluble in acetone.

Antibacterial screening

The antibacterial activity of the synthesized complexes and Schiff base ligand were screened against *Klebsiella Pneumonia*, *Escherichia Coli*, *Staphylococcus aureus*, and *Pseudomonas aerogens*. The paper disk diffusion method was adopted for the determination of antibacterial activity¹⁶⁻¹⁹. The test solution was prepared at different concentration. Twenty five millilitre nutrient agar media was poured in each Petri plate and kept in refrigerator for 24 hours for prediffusion. After solidification, 0.1mL of test bacteria spread over the medium using a spreader. The discs of Whatman no.1 filter paper having the diameter 5.00mm, each containing $1.5mgcm^{-1}$ of compounds were placed at four equidistant places at a distance of 2 cm from the centre in the inoculated Petri plates. All determination was made in duplicate for each of the compounds. Finally, Petri plates were incubated for 26-30 hours at 37°C.

RESULTS AND DISCUSSION

The complex was synthesized by reacting ligand with the metal ion in 1:1 molar ratio in methanolic medium. The nickel (II) complex is paramagnetic in nature. The ligand and complex are stable at room temperature and are non-hygroscopic. The compounds generally do not melt up to approx. 250°C. Analytical data and general behaviour of the compounds are given in table 1 and solubility data in table 2.

Molar conductance measurement

The molar conductance data of the complex in DMF lies in the range of $20\Omega^{-1}cm^2mol^{-1}$ which are too low to account for any dissociation of the complexes in DMF. It indicates that the complex can be regarded as non electrolyte in nature.

Magnetic susceptibility

The best summary of the results on the magnetic behaviour of nickel compound was given by Figgis and Nyholm²⁰. The observed values of magnetic moment for complexes are generally diagnostic of the coordination geometry about the metal ion. Ni (II) has the electronic configuration $3d^8$ and should exhibit a magnetic moment higher than that expected for two unpaired electrons in octahedral (2.8-3.2 B.M) and tetrahedral (3.4-4.2 B.M.) complexes, whereas its square planar complexes would be diamagnetic. The magnetic moment observed for the nickel (II) complex is 2.95 B.M which is consistent with the octahedral stereochemistry of the complex.

Infrared spectra

The spectrum of the ligand shows a band at $1552cm^{-1}$ which is shifted to lower frequencies in the spectra of the complexes at $1539cm^{-1}$ indicating the involvement of $-C=N$ nitrogen in co-ordination to the metal ion²¹⁻²³. A band at $1616cm^{-1}$ is assigned to $\nu_{C=O}$ stretching frequency which appeared at $1683cm^{-1}$ in the spectra of free Schiff base. The shifting of this band to lower region indicates the involvement of oxygen atom of salicylaldehyde in complexation²⁴. The infrared spectrum of the complex under investigation displays a band at $953cm^{-1}$ which is due to the presence of a coordinate OH group of salicylaldehyde to Ni(II) ion²⁵. The band at $3306cm^{-1}$ is due to the presence of OH group in the complex²⁶. New bands which are not present in the spectrum of free Schiff base appeared at 497 and $750cm^{-1}$ are attributed to ν_{M-N} and

ν_{M-O} vibrations respectively. The appearance of ν_{M-N} and ν_{M-O} vibrations supports the involvement of nitrogen and oxygen atom in complexation with metal ion under investigation²⁷.

Electronic spectra

The electronic spectra of nickel (II) complexes display three absorption bands in the range of $14,725\text{cm}^{-1}$, $15,083\text{cm}^{-1}$, and $23,148\text{cm}^{-1}$. The ground state nickel (II) in an octahedral coordination is ${}^3A_{2g}$. Thus, these bands may be assigned to three spin-allowed transition ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(v_1)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(v_2)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(v_3)$ respectively. The position of bands suggest mostly of octahedral geometry²⁸.

EPR Study

The room temperature EPR spectra of nickel (II) complex show a strong single line peak without any hyperfine splitting. The compound present a very intensive EPR spectrum with isotropic parameter of g value = 2.026. The absence of any hyperfine splitting for the solution spectra of the compound even at liquid nitrogen temperature can be due to dipolar line broadening and to the much reduced nuclear hyperfine coupling. These results may be accounted for by assuming predominantly dimeric or polymeric structure of the complex.

Antibacterial study

The antibacterial activity of the Schiff base ligand and its metal complex were studied against *Klebsiella Pneumonia*, *Escherichia Coli*, *Staphylococcus aureus*, and *Pseudomonas aerogens*. The inhibition zone were measured in diameter mm as 6-10 as (27-45%), 10-14 as (45-64%), 14-18 as (64-82%) and 18-22(82-100%).

Percent inhibition values are relative to the inhibition zone 22mm with 100% inhibition. Nickel (II) complex are more active than the parent ligand because the metal complex may serve as a vehicle for activation of ligand as the principle cytotoxic species²⁹. The nickel (II) complex was found to have 15mm inhibition against *Pseudomonas aerogens*, 14mm against *Escherichia Coli*, 8mm against *Klebsiella pneumonia*, and 8mm against *Staphylococcus aureus*. It is known that chelating tends to make the ligand acts as more powerful and potent bactericidal agents, thus killing more of the bacteria than the ligand³⁰. There are other factors which also increase the activity, which are solubility, conductivity and bond length between the metal and the ligand.

¹H NMR Studies

The Schiff base shows ¹H NMR signal at δ 10.32 due to $-N=CH-$ group. The evidence for the bonding mode of the ligand is provided by the ¹H NMR spectrum of the nickel (II) complex.

The observed signal at δ 7.45 (H – 4 proton) are assigned for the aromatic group. The signal of the phenolic proton in the free ligand of δ 12.7ppm (intramolecularly H-bonded phenolic group) is absent in the spectrum of the complex thus confirming the deprotonation of the phenolic group on complex formation³¹.

The NH – group of ligand showed a sharp singlet at 6.559 ppm but after complexation to the nickel (II) ion, it showed a weak broad signal at 5.74ppm corresponding to the decrease in the electron density on N H proton³². The appearance of ¹H NMR spectra as a new multiplet peak at 3.25 – 3.50 ppm is assigned due to the presence of C-O-C group which is also supported by IR studies³³. The medium singlet peak at δ 4.15 ppm corresponds to OCH_3 of the Ni – complexes³⁴.

The signal at δ 2.5 ppm corresponds to $-CH$ group.

CONCLUSIONS

The analytical results show 1:1 metal: ligand stoichiometry. The molar conductance value reveals the presence of non-electrolytic compound with no inorganic anion outside the coordination sphere. The magnetic moment and electronic spectra studies suggest an octahedral structure. The spectral data shows that the complexation takes place through oxygen and nitrogen atom. The antibacterial activity of the Schiff base complex became more pronounced when coordinated with the metal ions.

In view of the above facts, an octahedral structure is proposed for nickel (II) Schiff base complex

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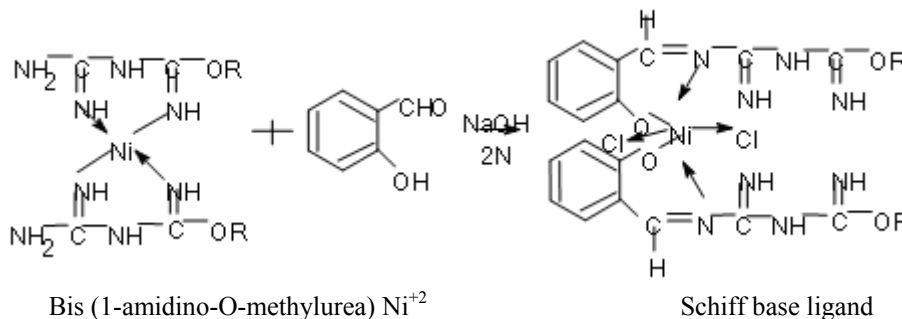
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Table-1: Analytical data and general behaviour of the compound.

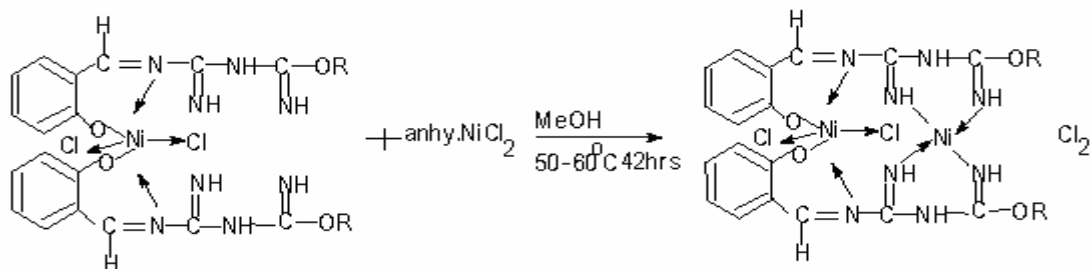
Compound	Colour	M.P. °C	μ_{eff}	% C Found (Cal.)	% H Found (Cal.)	%N Found (Cal.)	%Ni Found (Cal.)
Bis-Ni (1- amidino – O methylurea) ₂ Cl ₂	Orange	260	Diamagnetic	19.78 (19.9)	4.10 (4.42)	30.65 (30.96)	16.0 (16.2)
Schff base ligand	Bright orange	>280	Diamagnetic	48.51 (48.31)	4.70 (4.42)	22.90 (22.54)	11.5 (11.8)
[Ni(schiffbaseligand) ₂ Cl ₂]	Bright lustrous orange crystal	>255	2.95	38.35 (38.31)	3.24 (3.42)	17.55 (17.88)	18.57 (18.73)

Table-2: Solubility data.

Compound	H ₂ O	Acetone	DMF	DMSO	MeOH
BisNi (1- amidino – O methylurea) ₂ Cl ₂	Soluble	Insoluble	Insoluble	Insoluble	Insoluble
Schff base ligand	Insoluble	Soluble	Soluble	Soluble	Soluble
[Ni(schiffbaseligand) ₂ Cl ₂]	Soluble	Insoluble	Soluble	Soluble	Soluble



Scheme-1: Synthesis of Ligand



Scheme-2: Synthesis of compound

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