

Studies of Co(II) and Ni(II) Complexes with Polydentate Schiff base ligand.

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ABSTRACT

All over the world wide intersection which provide to comparative studies on macrocyclic metal Co(II) and Ni(II) complexes with macrocyclic ligand. Consequently due to under the present communication in coordination of our earlier interest. Very recently there has been a phenomenal growth in studies of Co(II) and Ni(II) complexes. The Schiff base ligand, 1,2-diimino bis(p-methoxy o-hydroxy acetophenonyl) ethane—1,2-dione has been prepared by the condensation of p-methoxy o-hydroxy acetophenone and ethane-1,2-diamine at room temperature. The complexes $[M(L)(B)_2]$ of a new macrocyclic ligand derived from metal ion catalysed template synthesis of 1,2-diimino bis(p-methoxy o-hydroxy acetophenonyl) ethane—1,2-dione with Co(II) and Ni(II) have been synthesized. Analyses with characterizations have been done on the basis of their elemental analyses, conductivity, magnetic moment, electronic transition and IR spectra. On the basis of electronic spectra and magnetic moment data suggest that the metal complexes have high spin octahedral paramagnetic more stable macrocyclic ring structure. Spectroscopic studies indicate that the coordination occurs with metal ions through two equatorial oxime-amine chelating ligand by neutral poly dentate donor azomethine nitrogen with two oxygen atom of phenolic group while other position of metal ions satisfied by two facial and axial mode of water, ammonia, quinoline etc with Co(II) and Ni(II). The Co(II) and Ni(II) complexes and ligands have been screened for antibacterial, antimicrobial activity and in the applied medicinal chemistry with other area of industries.

Keyword- Phenolic group, Conductivity, Medicinal Chemistry, Macrocyclic ligand, Facial and axial mode.

INTRODUCTION

Coordination chemistry has received great attention in the field of coordination chemistry during present time in all over the world. The reasons due to this interest are the fundamental importance in exchange interaction reaction with theory of bonding in new magnetic materials research and in understanding their important roles which play in large number of widely different processes of technological and biological importance¹⁻⁵. Consequently in the present communication in continuation of our earlier interest in the area. The metal complexes were prepared by refluxing hot ethyl alcohol solution of metal halide salts with the components of the ligand namely 1,2-diimino bis(p-methoxy o-hydroxy acetophenonyl) ethane—1,2-dione The stoichiometry of the complexes have been found to be of the $[M(L)(B)_2]$. The chelating of ligand with Co(II) and Ni(II) are expected to form complexes with different three dimensional cyclic ring geometry⁶⁻⁹. It may enhance their biological activity as antibacterial and antimicrobial activity after chelation¹⁰⁻¹⁴. Which may find their importance in the applied medicinal chemistry with antibacterial and antimicrobial activity and other area of chemical industries.

Materials and method

The acetate chloride of Co(II), Ni(II), ammonia, quinoline, phenyl isocyanide, pyridine and α -picoline used were of AR grade and purified by standard suitable method while dry before use in laboratory. Electrical conductivity of solution of complexes was measured by conductivity Meter Bridge. The electronic absorption spectra of the complexes were recorded with Hitachi-320 Spectrophotometer. The infra red spectra were recorded on Parkin Elemer 577 Spectrophotometer using KBr pellets in the range of 4000-400 cm^{-1} at C.D.R.I. Lucknow. While measurement of magnetic susceptibilities of the complexes were determined by Gouy's method.

Ligand synthesis

The Schiff base ligand 1,2-di-imino bis(p-methoxy o-hydroxy acetophenonyl) ethane-1,2-dione has been prepared by the condensation of p-methoxy o-hydroxy acetophenone and ethane-1,2-diamine at room temperature. The expected chemical reaction for the proposed Schiff ligand taking place during the course of the condensation of the condensation process is given below in Figure - 1

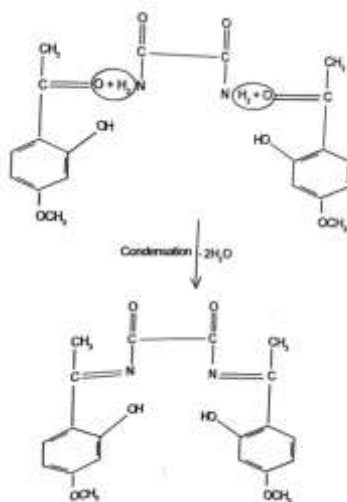


Figure -1

Preparation of complexes

1. Preparation of Co(II) Complexes with the ligand in presence of aqueous medium

A suspension of 0.4 gm of the ligand and 0.23 gm of Cobalt(II) chloride hexahydrate was also dissolved in aqueous ethanolic solution and it was diluted up to 20 ml. The molar ratio of the metal and the ligand was always kept into 1:1 ratio respectively. The resulting solution was heated under reflux on a hot water bath for about 2.5 hours when a light brown crystalline solid was obtained which was separated by filtration. The crystalline solid was washed with small quantity of alcohol followed by ether and dried over KOH pallets placed in desiccators.

2. Preparation of Co(II) Complexes with the ligand in presence of ammoniacal medium

A suspension of 0.4 gm of the ligand and 0.23 gm of Cobalt(II) chloride hexahydrate was also dissolved in aqueous ethanolic solution and it was diluted up to 20 ml with the addition of 2-4 drops of ammonium hydroxide. The molar ratio of the metal and the ligand was always kept into 1:1 ratio respectively. . The

resulting solution was heated under reflux on a hot water bath for about 2.5 hours when a faint brown crystalline solid was obtained which was separated by filtration. The crystalline solid was washed with small quantity of alcohol followed by ether and dried over KOH pallets placed in desiccators

3. Preparation of Co(II) Complexes with the ligand in presence of quinoline

A suspension of 0.4 gm of the ligand and 0.23 gm of Cobalt(II) chloride hexahydrate was also dissolved in aqueous ethanolic solution and it was diluted up to 20 ml with the addition of 2-4 drops of quinoline. The molar ratio of the metal and the ligand was always kept into 1:1 ratio respectively. The resulting solution was heated under reflux on a hot water bath for about 2.5 hours when a brown crystalline solid was obtained which was separated by filtration. The crystalline solid was washed with small quantity of alcohol followed by ether and dried over KOH pallets placed in desiccators

4. Preparation of Co(II) Complexes with the ligand in presence of phenyl-isocyanide

A suspension of 0.4 gm of the ligand and 0.23 gm of Cobalt(II) chloride hexahydrate was also dissolved in aqueous ethanolic solution and it was diluted up to 20 ml with the addition of 2-4 drops of phenyl isocyanide. The molar ratio of the metal and the ligand was always kept into 1:1 ratio respectively. The resulting solution was heated under reflux on a hot water bath for about 2.5 hours when a deep brown crystalline solid was obtained which was separated by filtration. The crystalline solid was washed with small quantity of alcohol followed by ether and dried over KOH pallets placed in desiccators

5. Preparation of Ni(II) Complexes with the ligand in presence of aqueous medium

A suspension of 0.4 gm of the ligand and 0.23 gm of Ni(II) chloride hexahydrate was also dissolved in aqueous ethanolic solution and it was diluted up to 20 ml. The molar ratio of the metal and the ligand was always kept into 1:1 ratio respectively. The resulting solution was heated under reflux on a hot water bath for about 2.5 hours when a green crystalline solid was obtained which was separated by filtration. The crystalline solid was washed with small quantity of alcohol followed by ether and dried over KOH pallets placed in desiccators

6. Preparation of Ni(II) Complexes with the ligand in presence of ammoniacal medium

A suspension of 0.4 gm of the ligand and 0.23 gm of Ni(II) chloride hexahydrate was also dissolved in aqueous ethanolic solution and it was diluted up to 20 ml with the addition of 2-4 drops of ammonium hydroxide. The molar ratio of the metal and the ligand was always kept into 1:1 ratio respectively. The resulting solution was heated under reflux on a hot water bath for about 2.5 hours when a faint green crystalline solid was obtained which was separated by filtration. The crystalline solid was washed with small quantity of alcohol followed by ether and dried over KOH pallets placed in desiccators

7. Preparation of Ni(II) Complexes with the ligand in presence of quinoline

A suspension of 0.4 gm of the ligand and 0.23 gm of Ni(II) chloride hexahydrate was also dissolved in aqueous ethanolic solution and it was diluted up to 20 ml with the addition of 2-4 drops of quinoline. The molar ratio of the metal and the ligand was always kept into 1:1 ratio respectively. The resulting solution was heated under reflux on a hot water bath for about 2.5 hours when a green crystalline solid was

obtained which was separated by filtration. The crystalline solid was washed with small quantity of alcohol followed by ether and dried over KOH pallets placed in desiccators

8. Preparation of Ni(II) Complexes with the ligand in presence of phenyl-isocyanide

A suspension of 0.4 gm of the ligand and 0.23 gm of Ni(II) chloride hexahydrate was also dissolved in aqueous ethanolic solution and it was diluted up to 20 ml with the addition of 2-4 drops of phenyl isocyanide. The molar ratio of the metal and the ligand was always kept into 1:1 ratio respectively. The resulting solution was heated under reflux on a hot water bath for about 2.5 hours when a deep green crystalline solid was obtained which was separated by filtration. The crystalline solid was washed with small quantity of alcohol followed by ether and dried over KOH pallets placed in desiccators

Results and discussion

The complexes $[M(L)(B)_2]$ of a new macrocyclic ligand derived from metal ion catalysed template synthesis of 1,2-diimino bis(p-methoxy o-hydroxy acetophenonyl) ethane—1,2-dione with Co(II) and Ni(II) have been synthesized. Characterizations have been done on the basis of their elemental analyses, conductivity, Magnetic moment with spectral data of I.R and UV-visible.

Magnetic Behaviour of Co(II) and Ni(II) Complexes

The magnetic moment values of Co(II) ($3d^7$) complexes fall into two classes. In one the magnetic moments lie in the range 4.3-5.6 B.M. Whilst in the other the moments occurs in the range 1.8-2.9 B.M. Co^{2+} ion contains three unpaired electrons in the ground state and the spin only magnetic moment value is 3.88 B.M. In the present investigation the magnetic moment values obtained for complexes $[M(L)(B)_2]$ are in the range of 4.90-5.10 B. M. While the magnetic moment of Ni(II) complexes values are in the range of 2.84 to 3.34 B.M. When the complex is outer d-orbital octahedral structure. Which unambiguously suggests the high spin six coordinated octahedral arrangement of the ligand molecules around the metal ion.

Magnetic moment data of Co(II) complexes with the ligand 1,2-diimino bis(p-methoxy o-hydroxy acetophenonyl) ethane—1,2-dione

Complexes	Colour	μ_{eff} in B.M.	Magnetic nature
$[Co(C_{20}H_{18}N_2O_6)(H_2O)_2]$	Faint brown	4.98	Paramagnetic
$[Co(C_{20}H_{18}N_2O_6)(NH_3)_2]$	Pinkish brown	4.88	Paramagnetic
$[Co(C_{20}H_{18}N_2O_6)(C_9H_7N)_2]$	Light brown	4.90	Paramagnetic
$[Co(C_{20}H_{18}N_2O_6)(C_6H_5NC)_2]$	Deep brown	5.00	Paramagnetic
$[Co(C_{20}H_{18}N_2O_6)(C_5H_5N)_2]$	Light brown	5.10	Paramagnetic

Table -1

Magnetic moment data of Ni(II) complexes with the ligand 1,2-diimino bis(p-methoxy o-hydroxy acetophenonyl) ethane—1,2-dione

Complexes	Colour	μ_{eff} in B.M.	Magnetic nature
$[Ni(C_{20}H_{18}N_2O_6)(H_2O)_2]$	Green	3.36	Paramagnetic
$[Ni(C_{20}H_{18}N_2O_6)(NH_3)_2]$	Light green	3.24	Paramagnetic
$[Ni(C_{20}H_{18}N_2O_6)(C_9H_7N)_2]$	Yellowish green	3.40	Paramagnetic
$[Ni(C_{20}H_{18}N_2O_6)(C_6H_5NC)_2]$	Deep green	3.22	Paramagnetic
$[Ni(C_{20}H_{18}N_2O_6)(C_5H_5N)_2]$	Light green	3.30	Paramagnetic

Table -2

Electrical Conductivity of Co(II) and Ni(II) Complexes

The values of electrical conductivity obtained in the range of 12-24 for Co(II) while the value of electrical conductivity obtained for Ni(II) complexes in the range of 12-30 indicate both are non-electrolyte nature of the complexes. The related data is given below.

Electrical Conductivity data of Co(II) Complexes with the ligand 1,2-diimino bis(p-methoxy o-hydroxy acetophenonyl) ethane—1,2-dione

Complexes	Ohm ⁻¹ cm ² mole ⁻¹	Solvent
[Co(C ₂₀ H ₁₈ N ₂ O ₆)(H ₂ O) ₂]	16	DMF
[Co(C ₂₀ H ₁₈ N ₂ O ₆)(NH ₃) ₂]	18	DMF
[Co(C ₂₀ H ₁₈ N ₂ O ₆)(C ₉ H ₇ N) ₂]	24	DMF
[Co(C ₂₀ H ₁₈ N ₂ O ₆)(C ₆ H ₅ NC) ₂]	18	DMF
[Co(C ₂₀ H ₁₈ N ₂ O ₆)(C ₅ H ₅ N) ₂]	22	DMF

Table- 3

Electrical Conductivity data of Ni(II) Complexes with the ligand 1,2-diimino bis(p-methoxy o-hydroxy acetophenonyl) ethane—1,2-dione

Complexes	Ohm ⁻¹ cm ² mole ⁻¹	Solvent
[Ni(C ₂₀ H ₁₈ N ₂ O ₆)(H ₂ O) ₂]	18	DMF
[Ni(C ₂₀ H ₁₈ N ₂ O ₆)(NH ₃) ₂]	24	DMF
[Ni(C ₂₀ H ₁₈ N ₂ O ₆)(C ₉ H ₇ N) ₂]	20	DMF
[Ni(C ₂₀ H ₁₈ N ₂ O ₆)(C ₆ H ₅ NC) ₂]	16	DMF
[Ni(C ₂₀ H ₁₈ N ₂ O ₆)(C ₅ H ₅ N) ₂]	22	DMF

Table- 4

Electronic spectra of complexes

In all the complexes the highest band obtained in the ligand molecule at 3430 cm⁻¹ due to phenolic frequency disappears in all the complexes supporting the deprotonation of phenolic and coordination of phenolic oxygen to the bond formation with the metal ion. The strong and sharp band around 1690 cm⁻¹ obtained in the ligand molecule has been found to be intact in the complexes indicating that condensation of C=O group of the ligand molecule could not take place during the course of complex formation with the ligand. The UV-visible spectra of the complexes were recorded for their solutions in ethyl alcohol and DMSO solvents in the range (200-1000) nm. The ligand field spectra of Co(II) complexes exhibit two bands in the region 624 and 455 nm which are assignable to ⁴A_{2g} → ⁴T_{2g} and ⁴A_{2g} → ⁴T_{1g} transition the ν₂/ν₁ ratio is 1.35 which is very close of value of 1.42 obtained for pure octahedral Ni(II) complexes¹⁵⁻¹⁷. Electronic spectra and magnetic moment data of Co(II) and Ni(II) complexes support paramagnetic high spin octahedral geometry. These Schiff base ligand and their metal complexes have been investigated as potential antibacterial and antimicrobial agents in long history of medical application. Recently greater variety of these ligand and their complexes containing hetero atoms represent good antimicrobial and antibacterial activity.

Elemental analysis

The physical and analytical data of the complexes are given in table-5. This is in satisfactory agreement with the calculated values. The suggested molecular formula are supported by the subsequent spectral as well as magnetic moment, molar conductivity in 10^{-3} M solution of DMSO, the value of λ_m show that Co(II) and Ni(II) complexes are non-electrolytic in nature.

Physical and analytical data for the complexes

Complexes	Colour	Yield %	Elemental analysis Calculation. (Found)			
			M%	N%	C%	H%
[Co(C ₂₀ H ₁₈ N ₂ O ₆)(H ₂ O) ₂]	Faint brown	78	11.75(11.74)	18.27(18.26)	36.56(36.54)	3.48(3.47)
[Co(C ₂₀ H ₁₈ N ₂ O ₆)(NH ₃) ₂]	Pinkish brown	77	9.08(9.07)	14.13(14.12)	28.27(28.26)	2.71(2.68)
[Co(C ₂₀ H ₁₈ N ₂ O ₆)(C ₉ H ₇ N) ₂]	Light brown	73	9.83(9.82)	22.90(22.89)	30.53(30.52)	2.90(2.89)
[Co(C ₂₀ H ₁₈ N ₂ O ₆)(C ₆ H ₅ NC) ₂]	Deep brown	79	8.29(8.28)	12.87(12.86)	25.74(25.74)	2.46(2.45)
[Co(C ₂₀ H ₁₈ N ₂ O ₆)(C ₅ H ₅ N) ₂]	Light brown	96	13.12(13.10)	19.68(19.66)	39.32(39.32)	3.74(3.73)
[Ni(C ₂₀ H ₁₈ N ₂ O ₆)(H ₂ O) ₂]	Green	91	10.86(10.83)	16.27(16.26)	32.55(32.54)	3.12(3.11)
[Ni(C ₂₀ H ₁₈ N ₂ O ₆)(NH ₃) ₂]	Light green	92	11.68(11.65)	23.32(23.31)	35.05(34.01)	3.32(3.31)
[Ni(C ₂₀ H ₁₈ N ₂ O ₆)(C ₉ H ₇ N) ₂]	Yellowish green	79	9.08(9.06)	15.24(14.89)	31.23(31.32)	3.01(3.00)
[Ni(C ₂₀ H ₁₈ N ₂ O ₆)(C ₆ H ₅ NC) ₂]	Deep green	82	13.12(12.78)	16.32(15.78)	32.21(31.56)	3.12(3.08)
[Ni(C ₂₀ H ₁₈ N ₂ O ₆)(C ₅ H ₅ N) ₂]	Light green	85	14.32(14.04)	16.78(15.89)	31.56(30.89)	3.14(3.12)

Table – 5

Infrared spectra of the ligand and the complexes

In case of our present investigation the Co(II) complexes display three bands in each case around 8920-9050 cm^{-1} , 16440-17500 cm^{-1} and 20400-21300 cm^{-1} due to ${}^2A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition while In case of our present investigation the Ni(II) complexes display three bands in each case around 8400 cm^{-1} , 14200 cm^{-1} and 21800 cm^{-1} due to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition indicating the octahedral geometry for the complexes. The silent bands of the IR spectra of the ligand 1,2-diimino bis(p-methoxy o-hydroxy acetophenonyl) ethane—1,2-dione with their probable assignment in cm^{-1} have been listed in the table-6 given below.

Ligand	Complexes	Nature	Probable assignments
3400	1860	Strong & sharp	ν O-H group
1690	1690	Strong & sharp	ν C=O
1640	1590	Strong & sharp	ν C=N
1480	1450	Medium & sharp	ν C-N
1420	1440	Medium & sharp	ν C-O
1150	1120	Medium & sharp	ν C-O
XX	550	Medium & sharp	ν M-O
XX	440	Medium & sharp	ν M-N

Table -6

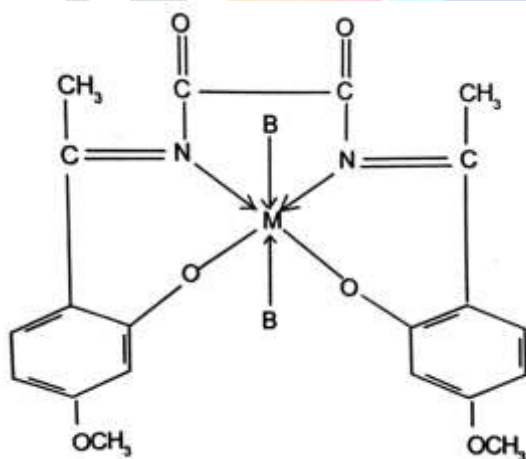
Biological activity

On the basis of experimental the Co(II) and Ni(II) complexes have work more effective action as compared to free ligands and its metal ions.. The antibacterial and antimicrobial activity of the synthesized Co(II) and Ni (II) complexes was tested against both Gram-negative and Gram-positive bacteria and other microorganism.. The tested solutions of complexes were prepared in suitable solvent. It seems that enhanced biological activity for the complex compound of Co(II) and Ni (II) is due to its electron donating group and the poly-conjugated nature of the compound. On the basis of conjugation compounds provide large surface areas which enhance greater extent of lipophilic and absorbing nature. The complexes are more active as compared to the greater dissolving ability in fats, oils, lipids and non-polar suitable organic solvent with more absorbing nature of the complexes as a result which controls the growth or increases the ratio of death of the bacteria and other microorganism.. Therefore the results indicated that chelating improved the effect of antibacterial and antimicrobial activity compared to the ligand and free metal ions, known as antibiotic drugs.¹⁸⁻²⁰

CONCLUSION

On the basis of above experimental studies it is concluded that the Schiff base ligands acts as a polydentate manner and coordination is proposed through equatorial oxime N moiety with two oxygen atom of phenolic group while other position of metal ions satisfied by two facial and axial mode of water, ammonia, quinoline etc with Co(II) and Ni(II). The Co(II) and Ni(II) complexes and ligands have been screened for antibacterial, antimicrobial activity and in the applied medicinal chemistry with other area of industries. On the basis of physicochemical and spectroscopic observation it is proposed that the geometry of the type Co(II) and Ni (II) metal ion complexes are monomeric high spin octahedral paramagnetic macrocyclic stable ring structure of the metal complexes. Which provide the extra stability of complexes.

On the basis of electronic spectra and magnetic moment data suggest that the high spin octahedral paramagnetic macrocyclic stable ring structure of the metal complexes can be proposed to have the following structures



M = Co(II) and Ni(II) B= Water, ammonia, quinoline, phenylisocyanide, pyridine.....etc. Octahedral structure of the metal complex.

Figure -2

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