



Preparation of Nickel (II) Complexes with Tetra Dentate derivative of 1,3 di-amino propane

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ABSTRACT: The Complexes of Nickel (II) Cations have been prepared with Tetra Dentate derivative of 1,3 di-amino propane in presence of bases which have oxygen and nitrogen atoms as their donor sites. On the basis of characterization of the ligand and the complexes by usual physico chemical methods such as elemental analysis, measurement of electrical conductance, magnetic moment, electronic transition and the infra-red spectroscopy, all the complexes have been found to be monomeric, non-electrolyte paramagnetic and octahedral in nature.

Key Words:- Complex, ligand, donor, characterization, monomeric, paramagnetic, octahedral, transition metal, divalent, donor etc.

INTRODUCTION: A considerable amount of research work has been carried out between divalent transition metals and the Schiff bases containing nitrogen and oxygen atoms as their donor sites. But at least work has been done for the formation of complex compounds between divalent transition metals and the Schiff bases containing Br-atom in its moiety. Therefore, We have undertaken to prepare the complexes of divalent Cobalt, Nickel and Copper (II) metals with Schiff base ligand 1, 3-bis (5-bromo salicyl-imino) propane in presence of bases like, water, ammonia, quinoline, phenylisocyanide, pyridine and α -Picoline.

Procedure:

About 2.4 grams (0.01 mole) of Nickel (II) chloride hexa hydrate was completely dissolved in minimum volume of aqueous-ethanoic solution and 4.4 grams (0.01 mole) of the ligand 1,3-bis (5-bromo salicyl imino) propane was also completely dissolved in ethyl alcohol. Both the solutions were mixed together gradually with regular.

shaking. Then, the resulting solution was refluxed on water bath for one and half an hour at room temperature. During the course of the reflux, the colour of the solution was gradually changed and the crystals of light green colour was separated out by allowing the solution to stand over night. The product was separated by filtration and washed with a small amount of cold ethyl alcohol and then dried over KOH pellets placed in a dessicator.

The complexes of Nickel (II) Cation have been prepared separately with the schiff base ligand in presence of bases like water, ammonia, quinoline, phenyl isocyanide, pyridine and α Picoline. In each case the ratio of metal and the ligand was always maintained 1:1 respectively.

Elemental analysis of Nickel (II) Complexes

Found - % (Calculated %)

Compounds	Metal	Carbon	Hydrogen	Nitrogen	Bromine
1. $[\text{Ni}(\text{C}_{17}\text{H}_{14}\text{N}_2\text{Br}_2\text{O}_2)_2(\text{H}_2\text{O})_2]$	10.78 (11.01)	37.90 (38.29)	3.40 (3.37)	5.30 (5.25)	29.80 (30.03)
2. $[\text{Ni}(\text{C}_{17}\text{H}_{14}\text{N}_2\text{Br}_2\text{O}_2)_2(\text{NH}_3)_2]$	10.88 (11.06)	37.98 (38.43)	3.78 (3.76)	10.62 (10.55)	29.76 (30.14)
3. $[\text{Ni}(\text{C}_{17}\text{H}_{14}\text{N}_2\text{Br}_2\text{O}_2)_2(\text{C}_9\text{H}_7\text{N})_2]$	7.56 (7.77)	55.34 (55.56)	3.73 (3.71)	7.50 (7.42)	21.00 (21.20)
4. $[\text{Ni}(\text{C}_{17}\text{H}_{14}\text{N}_2\text{Br}_2\text{O}_2)_2(\text{C}_6\text{H}_5\text{NC})_2]$	8.10 (8.35)	52.36 (52.93)	3.46 (3.41)	8.10 (7.96)	22.60 (22.76)
5. $[\text{Ni}(\text{C}_{17}\text{H}_{14}\text{N}_2\text{Br}_2\text{O}_2)_2(\text{C}_5\text{H}_5\text{N})_2]$	8.67 (8.96)	48.90 (49.48)	3.68 (3.66)	8.66 (8.55)	24.12 (24.43)
6. $[\text{Ni}(\text{C}_{17}\text{H}_{14}\text{N}_2\text{Br}_2\text{O}_2)_2(\text{C}_5\text{H}_4\text{NCH}_3)_2]$	8.30 (8.59)	50.36 (50.97)	4.12 (4.10)	8.30 (8.20)	23.23 (23.43)

Which corresponds the molecular formula $[\text{Ni}(\text{L})(\text{B})_2]$ where L= Ligand and B= bases.

Chemicals required:- Nickel(II) acetate/chloride, 1,3-diamino propane, 5-bromo salicylaldehyde, ethyl alcohol, ether, DMF, ammonia, quinoline, phenyl isocyanide, pyridine, α -picoline

All the chemicals used in present research work were obtained either from E. Merck extra pure or BDH (AR) quality. There were used without further purification.

Analytical Methods : The estimation of metal and non-metals present in the complexes has been done by standard methods.

- Nickel:** Nickel has been estimated gravimetrically by dimethyl glyoximate method.
- Carbon Hydrogen and Nitrogen:** The estimation of Carbon hydrogen and nitrogen have been done by semi-micro combustion method.
- Bromine:** Bromine is gravimetrically estimated as silver bromide. **Conductivity Method:** The measurement of electrical conductivity of the solutions of the complexes has been done by conductivity meter bridge manufactured by Wiss-Techen Warch Stathen type- LBR at room temperature. Pure DMF and conductivity water were used as solvents. **U.V.-visible spectra**

photometric measurement:

Hitachi - 320 spectrophotometer were used to record the electronic spectra of the complexes.

I.R.: Perkin elmer 577 spectrophotometer has been used to record the infra-red spectra of the ligand

and the complexes.

Magnetic susceptibility:

The measurement of the magnetic susceptibilities of the complexes was done by Gouy's method by using mercury tetra cyanato cobaltate, $[\text{Hg Co (S CN)}_4]$ as calibrant.

Result and discussion:

The value of the electrical conductance obtained in the range of 12-22 clearly indicates non-electrolyte nature of the complexes.

The elements analysis of the complexes indicates monomeric nature of the complexes.

The value of magnetic moments of Nickel(II) complexes obtained in the range of 3.30-3.42 B.M. clearly suggest octahedral geometry for all the complexes.

The value of μ_{eff} has been obtained greater than μ_s due to partially orbital contribution and negative value of λ for more than half filled configuration.

In our present investigation, three d-d bands have been obtained due to the following transitions, $\text{U}_1 = {}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ at 9250-10250 cm^{-1} , $\text{U}_2 = {}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{A}_{2g}(\text{F})$ at 13850 - 14850 cm^{-1} and $\text{U}_3 = {}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{P})$ at 22450 - 23250 cm^{-1}

The positions of all the three d-d bands indicate octahedral nature for all Nickel (II) complexes.

I.R. spectra of the ligand and the complexes:

There are so many bands in the ligand and the complexes but most of them have no importance. Only two bands obtained at 3460- cm^{-1} and at 1630 cm^{-1} due to the vibrations of phenolic -OH group and azomethine group ($>\text{C} = \text{N}-$) respectively in the ligand molecule have been appreciably changed after complex formation. The band obtained at 3460 cm^{-1} in the ligand has disappeared in all the complexes indicating deprotonation of phenolic -OH group. A medium and sharp band obtained at 1540 in the ligand due to phenolic (C - O) group has been increased to 1570 cm^{-1} in the complexes. This increase in the bond length of phenolic (-C-O) group indicates the deprotonation of phenolic - OH group. A broad and sharp bands obtained at 1630 cm^{-1} in the ligand molecule due to the vibration of azomethine group ($>\text{C} = \text{N}-$) has been reduced to 1580 cm^{-1} in the complexes. This reduction in the band position obtained due to the vibration of azomethine group ($>\text{C}=\text{N}-$)

indicates the participation of aldimino nitrogen atom in the bond formation with the metal ion.

On the basis of the comparison of I.R. spectral behaviour of the ligand molecule and the complexes, it has been concluded that the ligand behaves as bi-anionic tetradentate molecule. Thus two phenolic oxygen atoms and two aldimino nitrogen atoms are the bonding sites of the ligand. This indicates that oxygen atoms of phenolic-OH groups and azomethine ($>\text{C}=\text{N}-$) group have taken part in the bond formation with the metal cation.

In aquo and amino complexes, no separate band obtained for the coordination of H_2O and NH_3 molecules. A broad and medium band is obtained at 3480 cm^{-1} due to the over lapp of both the bands obtained for H_2O and NH_3 molecule. A band obtained in the range of $740\text{--}770\text{ cm}^{-1}$ in aquo-complexes has been found due to rocking mode of coordinated water. In case of quinoline complexes a medium and sharp band obtained around 1450 cm^{-1} due to the ring vibration indicates the involvement of N-atom of quinoline in the bond formation with the metal cations.

A medium and sharp band obtained around 2180 cm^{-1} in free ligand due to the vibration of iso-cyanide group ($-\text{C}\equiv\text{N}$) of phenyl iso cyanide has been increased to 2220 cm^{-1} in the complexes. This increase in the band position indicates the participation of N-atom of phenyl iso-cyanide in the bond formation with the metal cation.

The pyridine and Picoline complexes display bands in the finger print and far infra-red region. A sharp and medium band obtained around $940\text{--}10220\text{ cm}^{-1}$ in complexes have been found as the characteristic vibration of the co-ordinated pyridine and α picoline.

A sharp and medium band obtained in the range of $530\text{--}560\text{ cm}^{-1}$ in the complexes due to the vibration of (M-O) bonds further confirms the coordination of two phenolic oxygen atoms in the bond formation with the metal cation.

A sharp and medium band obtained in the range of $410\text{--}430\text{ cm}^{-1}$ due to the vibration of (M-N) bonds further confirms the coordination of two aldimino nitrogen atoms in the bond formation with the metal cation.

Thus, on the basis of elemental analysis of the ligand and the complexes measurement of electrical conductance, magnetic moments, electronic transition of the complexes and I.R. spectral behaviour of the ligand and the complexes, octahedral geometry may be suggested for all the complexes of Nickel(II) cations with the ligands in presence of bases with general molecular formula $[\text{Ni}(\text{L})\text{B}_2]$

Where M=Nickel(II) cation, L=Ligand, 1, 3- bis (5-Bromo salicyl-imino) propane, B= Bases like water, ammonia propane quinoline. phenylisocyanide, pyridine and α picoline.

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