Preparation of some Complexes of Nickel(II) and Copper (II) Metals with Macrocyclic Ligand, 1,7,9,15 tetra-aza-3,5,11,13 difurano-cyclo-1,6,9,14-hexa-deca tetra ene

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A R T I C L E I N F O

A B S T R A C T

The complexes of Nickel(II) and Copper(II) metals have been prepared with the macrocyclic ligand-1,7,9, 15-tetra-aza-3, 5,11,13- - difurano-cyclo-1,6,9,14-hexa deca tetra-ene. The complexes of both the metals have been characterised by usual physico-chemical methods such as elemental analysis, measurement of electrical conductance, magnetic moment and electronic transition spectra of the complexes and I.R. spectral behaviour of both ligands and the complexes. All the complexes of both the metals have been found to be non-electrolyte, mono-meric, paramagnetic with octahedral geometryy . T he general molecular formula of the complexes have been found to be [M(L) (X)2] Where M= Nickel(II) and Copper(II)

Cations, L= ligand and X= monodentate anions.

Keywords : Macrocyclic Ligand, Complex, Paramagnetic, Magnetic Moment, Mono-Meric, Octahedral, Geometry

I.   INTRODUCTION

A considerable amount of research work in the field of coor- dination compounds with macroocyclic ligand has been carried out. But at least work has been done with the macrocyclic ligand which contains 2.5 furan dicarboxaldehyde in its moiety. In this paper, we report the forma- tion of complexes of Nickel(II) and Copper(II) metals with a such macro- cyclic ligand which contains 2, 5-furan dicarboxaldehyde in its moiety.

Preparation of the complexes:

Procedure- Equirnolar mixture (0.001) of Nickel(II) chloride hexa hy- drate, methylene diamine and 2.5-furan diicarboxaldehyde was completely dissolved in minimum volume of ethyl alcohol and the resulting solution was refluxed continuouslyy under a condenser fitted with a running water tap for 5 to 6 hours . Then the solution was cooled and trasferred in a petri- dish and allowed to stand for over night for slow-evaporation which pro- duced greenish crystalline solid which was separated by filteration and washed with a small amount of cold water and a small amount of acetone.

Then the solid was dried over CaCl2 pellets placed in a desiccator . There coompound was found to be insoluble in cold water and common organic

solvents. The ratio of the metal, methylene diamine and 2.5-furan discarboxaldehyde was alwayys kept into 1:1:2 respectively.

The similar procedure was adopted for the preparation of Bro- mide, nitrate, acetate and perchlorate salts of Nickel and Copper metals . In case of copper metal, the colour of the complexes was found to quite different than those of Nickel metal.

The compoound was further analysed and found to contain.

Table No.1

Elements	Culculated	Found
1.Nickel	14.75	14.45
Carbon	42.24	42.02
Hydrogen	3.01	3.02
Nitrogen	14.08	14.11
Chlorine	17.85	17.47
2. Nickel	12.06	11.75
Carbon	34.51	34.17
Hydrogen	2.46	2.48
Nitrogen	11.50	11.54
Bromine	32.87	32.48
3. Nickel	13.02	12.81
Carbon	37.27	37.05
Hydrogen	2.66	2.67
4.Nitrogen	18.63	18.68
Nickel	13.19	12.97
Carbon	48.57	48.29
Hydrogen	4.04	4.06
Nitrogen	12.59	12.66
5.Nickel	11.16	11.00
Carbon	31.95	31.1
Hydrogen	2.28	2.30
Nitrogen	10.65	10.70
Chlorine	13.50	13.23
6.Coppper	15.77	15.52
Carbon	41.73	41.41
Hydrogen	2.98	3.00
Nitrogen	13.91	13.96
Chlorine	17.63	17.32
7.Copper	12.91	12.68
Carbon	34.18	33.82
Hydrogen	2.44	2.45
Nitrogen	11.39	11.46
Bromine	32.55	32.27
8.Copper	13.94	13.36
Carbon	36.88	36.44
Hydrogen	2.63	2.64
Nitrogen	18.44	18.48
9.Copper	14.12	13.91
Carbon	48.05	47.81
Hydrogen	4.00	4.02
Nitrogen	12.45	12.51
10.Copper	11.96	11.72
Carbon	31.66	31.33
Hydrogen	2.26	2.30
Nitrogen	10.55	10.61
Chlorine	13.38	13.13

which corresponds the general molecular formula $[M\ C_{14} H_{12} N_4 O_2) (X)_2]$ Where M= divalent Nickel(II) and Copper(II) metals.

L= $C_{14} H_{12} N_4 O_2$ = macrocyclic ligandX= Unidentate anions.

Chemical required:

Acetates/ Chlorides, Bromide, Nitrate and Perchlorate of Nickel(II) and Copper(II) metals, Dimethylformamide, ethyl alcohol, sodium hydroxide , Methylene diamine, 2.5-difurandicarboxaldehyde, calcium chloride, Common organic solvents, silver nitrate, etc. All chemicals were taken either of BDH (A.R.) quality or E.Merk extra pure. They were used without further purification.

II. ANALYTICAL METHODS

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

(i) Nickel :- Nickel has been estimated by gravimetrically by dimethoyl glyoximato method

(ii) Copper has been estimated by iodiometrically.

(iii) Hydrogen, Carbon and Nitrogen:- Hydrogen, Carbon and Nitrogen was estimated by semi-macro-duma's method.

(iv) Chlorine- Chlorine was gravimetrically estimated as AgCl

(-v) Bromine-Bromine was estimated gravimetrically as AgBr

CONDUCTIVITY MEASUREMENT:

The measurement of electrical conductivity of the solutions of the complexes was done by conductivity meter bridge manufactured by Wiss-Techen Wearch Stathen type-LBR-at room temperature . Pure DMF and conductivitywater were used as solvent.

U.V. –VISIBLE SPECTRA PHOTOMETRIC MEASUREMENT:-

Hitachi-320 spectrophotometer were

I.R. Spectra:- Perkin Elemer 577 spectrophotometer was used to recordthe infra-red spectra of the complexes and the ligand in nujol mull.

Characteristics peaks shown by Nujol mull as such sharp peaks at 2960 cm^1 to 2800 cm^1 and at 1460 cm^1 and a small peak at about 700 cm^1 has been excluded while recording the I.R. spectra for the complexes and the ligand.

MAGNETIC SUSCEPTIBILITIES:

For the measurement of the magnetic susceptibilities of the complexes was done by Gouy's method by using Mercury tetra thio cyanato coballtate , $(Hg\ Co\ (SCN)_4]$ as calibrant.

Result and discussion:

The values of electrical conductance obtained for the Nickel(II) and Copper(II) complexes have been found to be in the range of 14-32 Am and 18-36 Am reepctively which clearly indicates the non-electro- lyte nature of all the complexes.

The values of magnetic moment obtained for Nickel(II) and Copper(II) complexes have been found to be in the range of 3.20-8.38 BM and 1.88-2.10 BM respectively clearly indicates distorted octahe dral geometry for all the complexes of Nickel(II) and Copper(II)cations.

The values of electronic transition spectra obtained for Copper(II) complexes in the range of 14140-14350 cm^{-1} which with- out any fail indicate the distorted octahedral geometry of all the complexes of Copper(II) cations. The nature of the band was broad and unsymetrical which support the distortated octahydral geometry.

In case of Nickel(II) complexes, three bands have been obtained due to the following

$v_1 = {}^3A_{2g}\ (F) \rightarrow {}^3T_{2g}(F)$, 8100-82350- cm^{-1}

$v_2 = {}^3A_{2g}\ (F) \rightarrow {}^3T_{1g}(F)$, 16250- 17100 cm^{-1} and

used to record theelectronic absorption spectra of

$v_3 = {}^3A_{2g}\ (F) \rightarrow {}^3T_{1g}(P)$, 21260- 23180 cm^{-1}

transitions which clearly indicate the distortted octahedral geometry of all the complexes.

I.R. spectra of the macrocyclic ligand (L_1)1, 7, 9, 15,-tetra-aza 3, 5,11, 13, difurano-cyclo 1, 6,9, 14 hexa deca tetra-ene:- For the for- mation of complexes with this macrocyclic ligand methylene di-

amne, 2, 5 furan dicarboxaldehyed, and metal (II) salts have been taken. Free Methylene di-amine contains primary amino group (- NH_2)which

should give a medium and sharp band around 3480-3520

cm^{-1} and due to the presence of carbonyl group (>C=O) a band in the

range of 1740-1760 cm^{-1} should be obtained in the ligand. But no such bands have been obtained in ligand molecule. This indicates complete condensation of two carbonyl groups and two primary amino groups with the formation of four-azo methine group. A new

broad band obtained in the renge of 1630-1650 cm$_{-1}$ indicates the presence of azomethine group in the ligand. The band position iis

reduced by 40 to 50 cm^{-1} in the complexes supporting the coordina- tion of nitrogen atom of azomethine group in the bond formation with the metal cation. This means that this macrocyclic ligand is tetradentate molecule.

Thus four nitrogen atoms of four azo-methine groups are capable to form coordination compound with the central metal cation. Thus the microcyclic ligands are tetra-dentate molecule. Out of six coordination sites, of the metal cations, four coordination sites (secondary valency) are satisfiied by the four nitroogen atom of four azomethine groups present in the microcyclic ring.

In case of metal (II) chloride, a band obtained in the range of 315-320 cm^{-1} due to the vibration of (M-Cl) bond indicates the coordination of chloride ion in the bond formation with the metal cation. In case of metal (II) bromide a sharp and medium band has been obtained in the range of 280-300 cm^{-1} due to the vibration of M-Br bond. This indicates the participation of bromide ion in the complex formation with metal ion.

I.R. spectra of the nitrate complexes display three (N-O) stretching bands in the range of 1420-1460 cm^{-1} (v)1310-1320 cm^{-1} (v) and 1020-1030cm^{-1} (v

). The separation of two highest frequencies bands (v -v) suggest that both the nitrate groups are coordinated in a unidentate manner. This has been supported by the presence of bands obtained in the range of 215-225 cm^{-1} due to the vibration of (M-O) bonds in the all nitrate complexes. Thus it is concluded that bond formation between the metal ion and the ligand take place through one oxygen atom of nitrate ion.

In case of acetate complexes two bonds have been ob-tained in the range of 1635-1645 cm^{-1} (v) and 1385-1395 cm^{-1} (v). This indicates that acetate group is coordinated to the metal cation in a unidentate manner.

In case of perchlorate complexes two bands have been obtained in the range of 1210-1220cm^{-1} (v) 1125-1135 cm^{-1}(v). The presence of these two bands indicate that in perchlorate complexes, perchlorate groups are coordinated to the metal cation in a unidentate manner.

Thus by the perusal of I.R. pectra of anions such as chlo-ride ion (Cl$^-$), bromide ion (Br$^-$) nitrate ion (NO_3^-)] macetate ion(CH3COO$^-$) and

perchlorate ion, (ClO_4^-) it is suggested that all the anions are coordiinated to the metal cation in a unidentate manner to satisfy the two primary valencies (charge of the metal cation) of the metal cation in the complex formation in the macrocyclic com- plexes.

Thus on the basis of elemental analysis, measurement of electrical conductance, magnetic moment and electronic transition spectra of the complexes and I.R. spectral behaviour of both ligand and the complexes, octahedral geometry of Nickel(II) and Copper(II) complexes has been suggested with both the microcyclic ligand complexes and have been found to be non-electrolyte mono-

meric , paramagnetic with their general molecular formula [M(L) (X)$_2$]. M= Nickel(II) and

Copper(II) cations, L= Macrocyclic ligands and X= Monodentate

anions.

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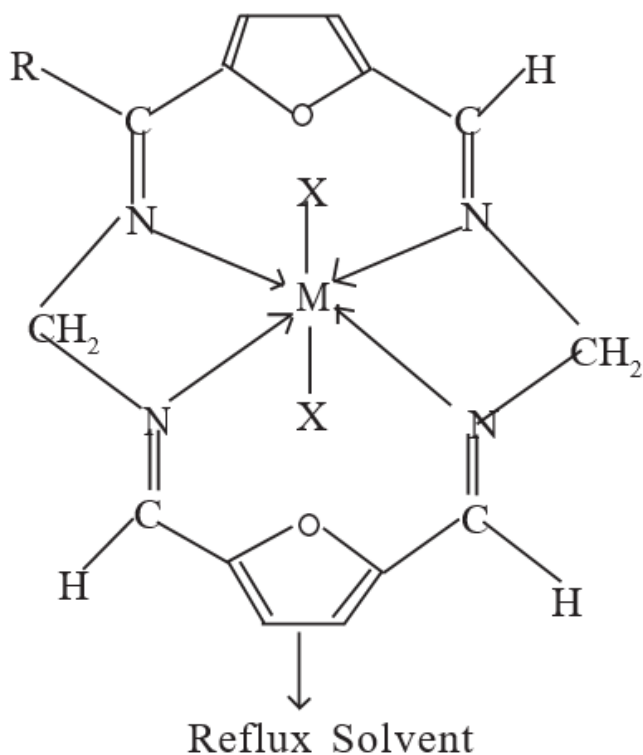
M=Nickel (II) & Copper (II) metals

X = Monodentate ligand such as Cl^-, Br^-, NO_3^-,

CH_3COO^- and ClO_4^-

X' = - (CH$_2$) -

Macrocyclic ligand 1, 7, 9, 15 tetra-aza, 3,5, 11 ,13, difurano-cyclo-1,6,9,14 -hexa-deca tetra-ene

III. ACKNOWLEDGEMENTS

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