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STUDY OF PREPARATION OF NI (II)

COMPLEXES AND DETERMINATION OF THEIR STRUCTURES.

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ABSTRACT :- The present paper is related with preparation of Ni(ii) complexes and determination of their structures. The present paper “Synthesis and characterization of Ni(II) Complexes of transition metals with 1,3-bis(o-hydroxy aniline) propane” as ligand (LH_2) and the determination of the structures of the complexes by employing various physico chemical methods like elemental analysis, electrical conductance and magnetic moment measurements. I.R. and electronic behaviour of the complexes.

KEYWORDS:- Complexes of Ni(II),Electrical conductance, Magnetic, Crystal, Spectra.

1. Preparation of Ni(II) Complexes :-

Preparation of Ni(II) complexes with 1, 3-bis(o-hydroxy anilino) propane as ligand (LH_2) were carried out of various bases like water, an oxygen donor molecule, water, ammonia, quinoline, pyridine, phenyl isocyanide and different picolines, nitrogen donor molecules by a general procedure detailed here under :

0.23 gram (0.001 mole) of Ni(II) chloride hexa hydrate (BDH) dissolved in ethanolic aqueous solution was added to 2.6 gram (0.001) of the ligand dissolved in the minimum volume of ethyl alohol with regular shaking and stirring. The resulting solution was then refluxed for two and half hour on water bath. The colour of the solution was gradually changed and crystals having the light green colour separated out by allowing the solution to stand for two days. The product was separated by filteration washed with a small amount of acetone and then dried over KOH placed in the desiccator.

The complexes of Ni(II) cations with ligand (LH_2) 1, 3- bis(O-hydroxy aniline) propane were prepared separately with nitrogen doner bases like ammonia, Pyridine isocyanide, α-picoline, β-picoline and γ-picoline having the metal ligand ration as 1:1 in each case.

On the basis of elemental analysis the complexes were found to posses the general molecular formula $[Ni(L)B_2]$.

Where,

B = Water

= Ammonia

= Quinoline

=Phenyl isocyanide

=Pyridine

$= \alpha = picoline$

$= \beta - picoline$

And $= \gamma - picoline$

TABLE-1

Elemental analysis of Ni(II) complexes with 1, 3-bis (o-hydroxy anilino) propane.

Complex	Metal	Carbon	Hydrogen	Nitrogen
1. $[Ni(C_{15}H_{16}N_2O_2)(H_2O)_2$	16.40 (16.73)	51.56 (51.32)	5.68 (5.70)	8.00. (7.98)
2. $[Ni(C_{15}H_{16}N_2O_2)(NH_3)_2$	16.60 (16.83)	51.30 (51.62)	6.32 (6.30)	16.10 (16.05)

3. $[Ni(C_{15}H_{16}N_2O_2)\ (C_9H_2N)_2]$ Quinoline	10.10 (10.24)	68.76 (69.14)	5.25 (5.23)	9.85 (9.77)
4. $[Ni(C_{15}H_{16}N_2O_2)\ (C_6\ H_5NC)_2]$ (Phenyl isocyanide)	11.10 (11.27)	66.54 (66.83)	5.04 (4.99)	10.80 (10.75)
5. $[Ni(C_{15}H_{16}N_2O_2)\ (C_5\ H_5N)_2]$ (Pyridine)	12.12 (12.41)	63.30 (63.46)	5.48 (5.50)	11.86 (11.84)
6. $[Ni(C_{15}H_{16}N_2O_2)\ (C_5\ H_4\ NCH_3)_2]$ (α-Picoline)	11.40 (11.72)	64.32 (64.70)	6.00 (5.99)	11.22 (11.18)
7. $[Ni(C_{15}H_{16}N_2O_2)\ (C_5\ H_4NCH_3)_2]$ $\beta - picoline$	11.40 (11.72)	64.32 (64.70)	6.00 (5.99)	11.22 (11.18)
8. $[Ni(C_{15}H_{16}N_2O_2)\ (C_5\ H_4NCH_3)_2]$ $\gamma - picoline$	11.36 (11.72)	64.40 (64.70)	5.98 (5.99)	11.24 (11.18)

2. Slectrical Conductance of the $[Ni\ (L)(B_2)]$ complexes :-

These complexes are isoluble in common organic solvent viz, carbon tetrachloride, methanol, ethanol, dioxane, THF (terahedrafuran), pyridine, acetone but they are partially soluble in DMSO (dimethyl sulphoxide) and appreciably in DMF (dimethly ormamide). The molar conductance of the complexes of Ni(II) ions with 1, 3-bis(o-hydroxy anilino) propane at 10^3 M DMF solution at room temperature.

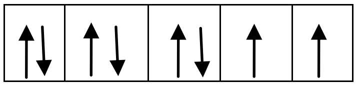
Table-2
Electrical conductance of the complexes $[Ni(L)B_2]$

Complex	Am ($ohm^{-1}\ cm^2$ $Mole^{-1}$)	Solvent
1. $[Ni(C_{15}H_{16}N_2O_2)\ (H_2O)_2$	20	D M F
2. $[Ni(C_{15}H_{16}N_2O_2)\ (NH_3)_2$	14	D M F
3. $[Ni(C_{15}H_{16}N_2O_2)\ (C_9H_2N)_2]$ Quinoline	18	D M F
4. $[Ni(C_{15}H_{16}N_2O_2)\ (C_6\ H_5NC)_2]$	12	D M F

(Phenyl isocyanide)		
5. $[Ni(C_{15}H_{16}N_2O_2)\ (C_5\ H_5N)_2]$ (Pyridine)	16	D M F
6. $[Ni(C_{15}H_{16}N_2O_2)\ (C_5\ H_4\ NCH_3)_2]$ (α-Picoline)	18	D M F
7. $[Ni(C_{15}H_{16}N_2O_2)\ (C_5\ H_4NCH_3)_2\ ]$ $\beta - picoline$	12	D M F
8. $[Ni(C_{15}H_{16}N_2O_2)\ (C_5\ H_4NCH_3)_2\ ]$ $\gamma - picoline$	14	D M F

3. Magnetic Properties of Nickel (II) Complexes :-

Determination of Ground term for Ni^{2+} free ion.

$Ni^{2+} \longrightarrow d^8$ System $\longrightarrow$ 

ML=L = Resultant of M_1 Values

= ε M^1 =2X2+1X2+2X0+-1X1+-2X1

=3

When ML = L = 0 1 2 3 4

Spectroscopic Symbol = SPDFG

The Value of ML =3

Thus the Symbol =F

Ms = S =Resultant of ms values

$= \varepsilon\ Ms = +\frac{1}{2} + \frac{1}{2} = +1 = 1$

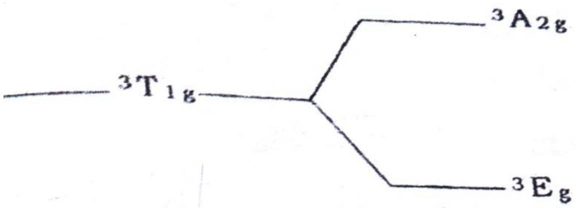
Spin Multiplicity = (2S+1) = 2X1+) =3

Then the ground term for Ni^{2+} = ^3F

The Valence shell electronic configuration of nickel is $3d^24s^2$. Thus Ni^{2+} is a $3d^8$ system. It has ^3F as free ion ground term. In tetrahedral crystal field, $^3T_1$ and in octahedral crystal field $^3A_{2g}$ are the ground term for Ni (II).

Table-3
Data of magnetic moment of the [Ni(L)B_2] Complexes :-

Complex	COLOUR	Self (B.M)	Magnetic Properties
1. [Ni($C_{15}H_{16}N_2O_2$) (H_2O)$_2$	Faint Green	3.24	Paramagnetic
2. [Ni($C_{15}H_{16}N_2O_2$) (NH_3)$_2$	Greenish White	3.12	Paramagnetic
3. [Ni($C_{15}H_{16}N_2O_2$) (C_9H_2N)$_2$] Quinoline	Yellowish Green	3.18	Paramagnetic
4. [Ni($C_{15}H_{16}N_2O_2$) (C_6H_5NC)$_2$] (Phenyl isocyanide)	Light Green	3.10	Paramagnetic
5. [Ni($C_{15}H_{16}N_2O_2$) (C_5H_5N)$_2$] (Pyridine)	Dirty Green	3.16	Paramagnetic
6. [Ni($C_{15}H_{16}N_2O_2$) ($C_5H_4NCH_3$)$_2$] (α-Picoline)	Yellowish Green	3.12	Paramagnetic
7. [Ni($C_{15}H_{16}N_2O_2$) ($C_5H_4NCH_3$)$_2$] $\beta - picoline$	Yellowish Green	3.14	Paramagnetic
8. [Ni($C_{15}H_{16}N_2O_2$) ($C_5H_4NCH_3$)$_2$] $\gamma - picoline$	Yellowish Green	3.22	Paramagnetic



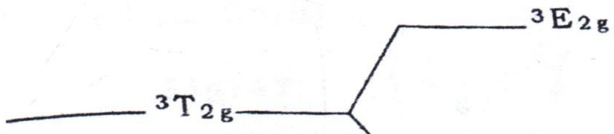


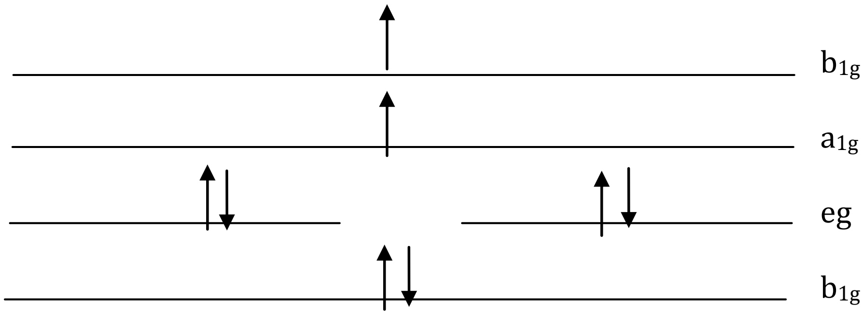
Fig-1

In strong crystal field, the ground term of Ni(II) is $^3A_{2g}$ but next excited term of is $^3A_{2g}$ is is $^1E_{g.}$

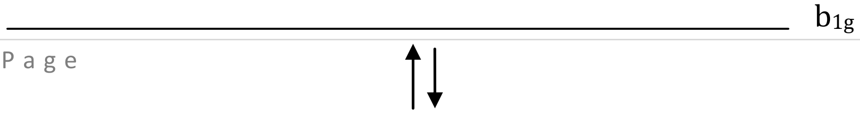
$T^6_{2g}e_2 \equiv A_{1g} . a_{2g} = {}^2A_{2g}$ (ground term)

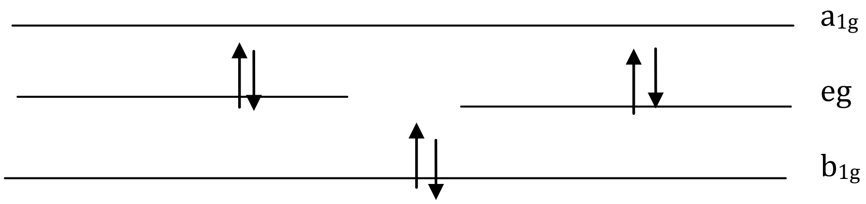
$T^6_{2g}e_2 \equiv E_g . E_g = {}^3A_{2g} + {}^1E_g + {}^1A_{1g}$

Square planar Ni (II) complexes are of high spin and low spin :-



(High Spin)
Fig-2





(Low Spin)

Fig-3

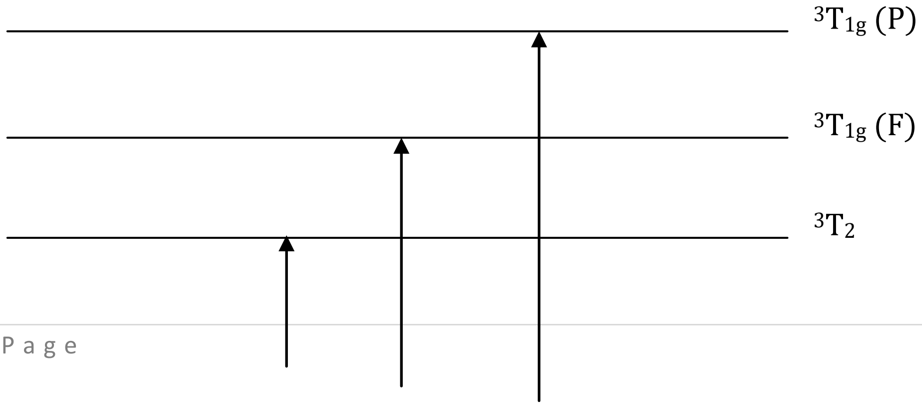
The ground term for low spin Ni^{2+} ion is $^1A_{1g}$ the square planer Ni(II) Complexes are formed due to dsp^2 hydbridisation leading to spin paired complexes. Hence in the absence of unpaired electron, square planer Ni(II) complexes are formed due to dsp^2 hybridisation leading to spin paired complexes Hence in the absence of unpaired electrons, Square Planer Ni(II) Complexes are thus diamagnetic. The magnetic behavior of square planar Ni(II) Complexes have been investigated by Reddy et. Al[17.] as expected found to be diamagnetic.

The ground term is case of Ni (II) tetrahedral complexes is $^3T_1$ and μeff is expected to be greater than μs due to orbital contribution. High spin Ni(II) complexes has $\mu s = 2.83\ B.M.$ and due to Mixing of High Energy term $^2b_{2g,}$ $^3e_{g\,,}\,{}^2a_{1g}$ $^2b_{1g}\,({}^3E_g)$ with $^2b_{2g,}$ $^4e_{g\,,}\,{}^1a_{1g}$ $^1b_{1g}\,({}^3E_g)$ first order Zeeman effect gives μeff greater than μ.

In the present investigation, all the complexes of Ni(II) ions, $[Ni(L)B_2]$, Were found to be paramagnetic. The values of magnetic moment of the complexes were found in the range of 3.10-3.24 B.M. indicating octahedral nature of Ni(II) complexes.

4. Electronic Spectra of Ni (II) Complexes :-

The free ion term of Ni(II) ion has the ^3F ground term with the first excited term 3P. Under the influence of cubic field the ^3F splits into $^3T_{1g}$ (F), $^3T_{2g}$ (F), and $^3T_{2g}$ (F), states and the 3P transforms to



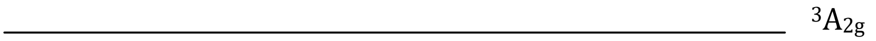


Fig-4

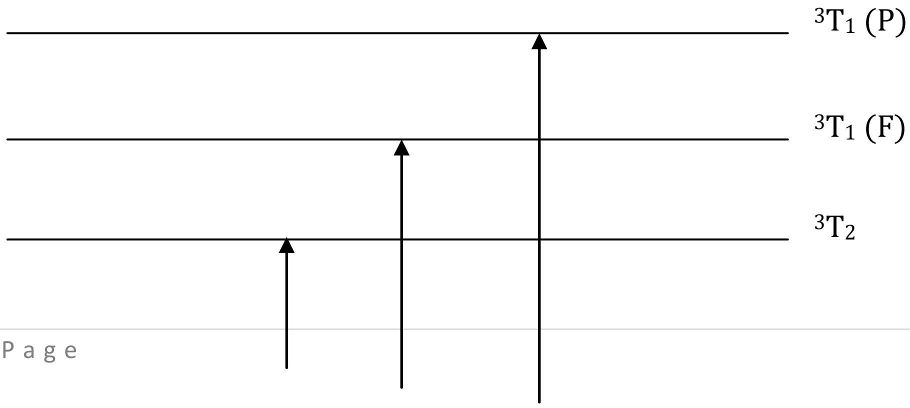
$^3T_{1g}$(P) state only. Nickel (II) complexes, in weak octahedral crystal field, is expected to give three d-d bands corresponding to corresponding to $^3A_{2g}$ (F) → $^3T_{2g}$(F), $^3A_{2g}$ (F) → $^3T_{1g}$(F) and $^3A_{2g}$ (F) → $^3A_{2g}$ (P)

TABLE-4

Data of Electronic Spectra of the [Ni(L)B_2]

Complex	**^{0}1cm^{-1}**	**ε_1**	**^{0}2cm^{-1}**	**ε_2**	**^{0}3cm^{-1}**	**ε_3**
1. [Ni($C_{15}H_{16}N_2O_2$) (H_2O)$_2$	10515	7.2	14990	7.1	21640	11.2
2. [Ni($C_{15}H_{16}N_2O_2$) (NH_3)$_2$	10340	6.6	14550	6.6	21800	11.0
3. [Ni($C_{15}H_{16}N_2O_2$) (C_9H_2N)$_2$] Quinoline	10135	6.8	15050	7.1	21400	11.2
4. [Ni($C_{15}H_{16}N_2O_2$) (C_6H_5NC)$_2$] (Phenyl isocyanide)	10310	6.6	14750	6.8	2700	11.4
5. [Ni($C_{15}H_{16}N_2O_2$) (C_5H_5N)$_2$] (Pyridine)	9510	5.5	15250	7.3	21650	11.0
6. [Ni($C_{15}H_{16}N_2O_2$) ($C_5H_4NCH_3$)$_2$] (a-Picoline)	9710	5.5	14950	7.4	21700	11.8
7. [Ni($C_{15}H_{16}N_2O_2$) ($C_5H_4NCH_3$)$_2$] $\beta - picoline$	9970	5.6	14250	6.7	21500	11.6
8. [Ni($C_{15}H_{16}N_2O_2$) ($C_5H_4NCH_3$)$_2$] $\gamma - picoline$	9660	5.4	14150	6.6	21500	11.6

In case of Ni(II) tetrahedral complexes three d-d bands are also expected corresponding to following transitions



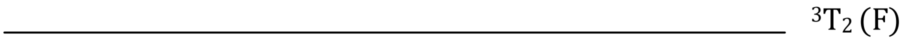


Fig-5

$^3T_1$ (F) → $^3T_2$ (F), $^3A_{2g}$ (F) → $^3A_2$(F) and $^3T_1$ (F) → $^3T_1$ (P) Respectively

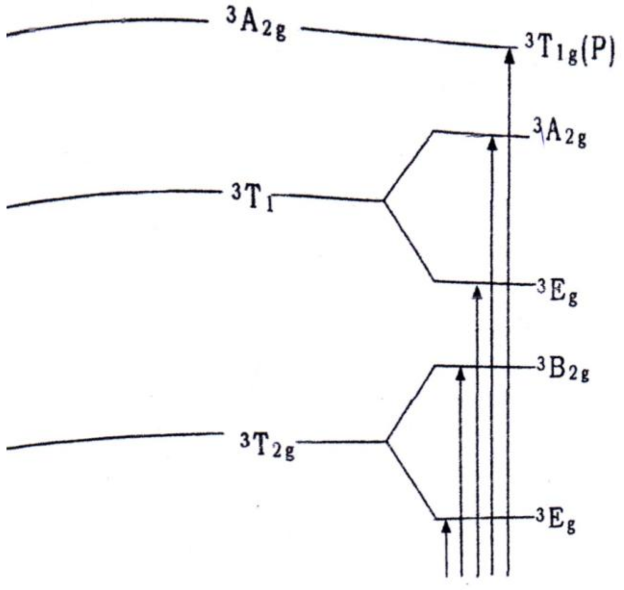


Fig. 6

Distorted octahedral Ni(II) complex is expected to give four d-d bands corresponding to $^3B_{1g}$ → ^3E_g, $^3B_{1g}$ → $^3B_{2g}$ $^3B_{1g}$ → $^3T_{1g}$ (^3E_g . $^3A_{2g}$)

And $^3B_{1g}$ → $^3T_1$ (P) Respectively .

Low spin Ni(II) square planar complexes should give two d-d bands but these occurs at high energy in charge transfer region and have not been satisfactorily interpreted. In high spin square planar two transitions corresponding to $^1A_{1g}$ → $^1B_{2g}$ and $^1A_{1g}$ → ^1E_g are expected.

In our present investigation in the electronic spectra of Ni(II) Complexes, three bands are obtained in each case. The probable assignment of band positions obtained due to the electronic transition of the complexes are given below.

(1). ϑ_1 = $^3A_{2g}$ $^3T_{2g}$ 9510-10515 cm^{-1}
(2). ϑ_2 = $^3A_{2g}$ $^3T_{1g}$ 14250-15250 cm^{-1}
(3). ϑ_3 = $^3A_{2g}$ ^3T_g (P) 21400-21650 cm^{-1}

The band positions of electronic spectra indicate the octahedral nature of the Ni(II) complexes.

5. I.R. Spectra of Nickel (II) complexes :-

By the proper examination of the I.R. spectra of the Ni(II) complexes and their comparison with that of the ligand, It is concluded that in almost all Complexes Phenolic $\vartheta(OH) imine$ ϑ(NH)and azomithine $\vartheta(C \equiv N)$ bands of the legend molecules are appreciably changed after complex formation. The strong and sharp band due to the vibrations of (O-H) and (N-H) bond of the ligand obtained at 3230 cm^1 disappears in all the complexes with a formation of new broad band in the complexes at about 3430 cm^1 indication the presence of the free –NH group even in the complexes . the disappearance of the strong band located at 3230 cm^1 further suggests the deprotonation of the phenolic (OH) proton present in ligand moiety. The azomethine band at 1650 cm^1 in the ligand molecule is also shifted to lower frequency in almost all the complexes by 60 to 50 cm^1 this shift of ϑ(C=N) band towards lower frequency in the complexes suggests the coordination of the azomethine nitrogen of the ligand in the formation of the complexes. The strong and sharp band due to imine group (N-H) of the ligand located at 3430 cm^1 is also shifted to higher frequency by 35-50 cm^{-1}indicationg the coordination of imine-nitrogen in the complex formation.

A strong and sharp band obtained at 1450-1470 cm^{-1} due to ϑ (C-N) vibration has been reduced by 20-25 cm^{-1} in the complexes supporting the coordination of imine nitrogen in the bond formation with metal cations.

The medium and sharp band located at 1300 cm^{-1} in the ligand obtained due to the deformation vibration of phenolic –OH disappears in all the complexes supporting the deprotonation of the phenolic –OH and coordination of phenolic oxygen to the metal atom. The ϑ (C-O) vibration of phenolic –(C-O) group shifts to higher frequency in the complexes suggesting increase in the bond order of (C-O) group in the complexes. The appearance two bands at around 450-460 cm^{-1} and 510-550 cm^{-1} due to ϑ (M-N) and ϑ (M-O) vibrations in the complexes further suggests the coordination of nitrogen and oxygen atoms of the ligand in the complex formation.

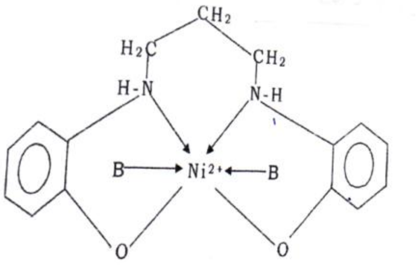
The case of aquo-complexes, the appearance of one more band in the range of 750-830 cm^{-1} due to the rocking the wagging made of vibrations auggests that H_2O is present in the coordination sphere A separate band for water molecule is not obtained due to overlapping ϑ (o-H)vibration.

Thus on the basic of elemental analysis measurement of electrical conductance and magnetic moment, I.R. and electronic spectral behaviour, It may be suggested that Ni (II) ions forms octahedral complexes with the ligand 1, 3-bis (o-hydroxy anilino) propane (LH_2) in presence of water, ammonia, quinoline, phenyl-isocyanide, pridine and different picolines.

Where

B= Water, ammonia, quinoline, pheny-lisocyanide pyridine, α, β *and* γ -picolines.

CONCLUSINN :- In this paper we get on the basis of elemental analysis, measurement of electrical conductance magnetic, moment, electronic and I.R. spectral behaviours of the complexes Ni(II) cation from octahedral complexes with the ligand 1, 3-bis(o-hydroxy anilino) propane in presence of bases containg oxygen and nitrogen atoms as their donor Sites.



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