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STUDY OF PREPARATION OF CO(II)
COMPLEXES AND DETERMINATION OF THEIR STRUCTURES

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ABSTRACT :- This paper is related to preparation of Co(II) Complexes and determination of their structures. In this paper Co (II) complexes, One broad and unsymmetrical band obtained around 20750-21850 cm^{-1} due to $^4T_{1g}$(F) $^4T_{1g}$(P) indicates octahedral nature of the complexes the probable assignment of band positions obtained due to the electronic transition of the complex.

The (C-O) Vibration of phenolic (C-O) group shifts to ligher frequency in the complexes suggesting increase of bond order of (C-O) group in the complexes.

Keywords :- Prepartion, determination, procedure, analysis magnetic behavior electronic spectra.

Preparation of Co(II) complexes and determination of their structures :-

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

Procedure :-

2.6 gram (0.001 mole) of the ligand was dissolved in a minimum volume of ethyl elcohal (20ml) and 0.23 gram (0.001 mole) of Co(II) chloride hexahydrate was dissolved separately in dry acetone. Both the solutions were gradually mixed and allow to react on water bath for two and half hour with regular shaking. The complexes were prepared separately in presence of different bases keeping the molar ratio of the metal ion and the ligand 1:1 respectively. A brownish solid separated out on cooling under tap water. The solid was separated by filteration and washed with acetone. The crud product of he complexes were crystallized with methyl alcohol and dried over KOH pillets placed in a desiccator.

On the basis of elemental analysis the complexes were found to possess the general molecular formula $[Co(L)(B)_2]$

Where :-

B=water

= ammonia

=pyridine

=phenyl isocyanide

=quinoline

=$\alpha - Picoline$

=$\beta - Picoline\ and$

=$\gamma - Picoline$

on the basis of elemental analysis and measurement of molar conductance of the complexes, all the complexes Co(II) cations with the Schiff base ligand , 1, 3-bis(o-hydroxy aniline) propane have been found to be monomeric and non-electrolyte in nature.

TABLE -1

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

Complex	**Metal**	**Carbon**	**Hydrogen**	**Nitrogen**
1. $[Co(C_{15}H_{16}N_2O_2)\ (H_2O)_2]$	16.34 (16.78)	51.00 (51.29)	5.70 (5.69)	8.00. (7.97)
2. $[Co(C_{15}H_{16}N_2O_2)\ (NH_3)_2]$	16.46 (16.88)	51.18 (51.59)	6.32 (6.30)	16.10 (16.05)
3. $[Co(C_{15}H_{16}N_2O_2)\ (C_9H_2N)_2]$ Quinoline	10.10 (10.28)	68.80 (69.12)	5.24 (5.23)	9.90 (9.77)
4. $[Co(C_{15}H_{16}N_2O_2)\ (C_6\ H_5NC)_2]$ (Phenyl isocyanide)	11.10 (11.30)	66.46 (66.80)	5.04 (4.99)	10.82 (10.75)
5. $[Co(C_{15}H_{16}N_2O_2)\ (C_5\ H_5N)_2]$ (Pyridine)	12.21 (12.45)	63.10 (63.43)	5.48 (5.49)	11.90 (11.84)
6. $[Co(C_{15}H_{16}N_2O_2)\ (C_5\ H_4\ NCH_3)_2]$ (a-Picoline)	11.58 (11.75)	64.30 (64.68)	6.00 (5.98)	11.20 (11.17)
7. $[Co(C_{15}H_{16}N_2O_2)\ (C_5\ H_4NCH_3)_2\ ]$ $\beta - picoline$	11.50 (11.75)	64.22 (64.68)	5.96 (5.98)	11.18 (11.17)
8. $[Co(C_{15}H_{16}N_2O_2)\ (C_5\ H_4NCH_3)_2\ ]$	11.46	64.28	5.94	11.22

$\gamma - picoline$	(11.75)	(64.68)	(5.98)	(11.17)

The values of electrical conductivity for cabalt (II) Complexes obtained in the range of 12-22 indicates non-electrolyte in the nature.

Table -2

Data of electrical conductance of the [Co(L)B_2] Complexes.

Complex	**Ohm^{-1}cm^{2} mole^{-}**	**Solvent**
1. [Co($C_{15}H_{16}N_2O_2$) (H_2O)$_2$	22	DMF
2. [Co($C_{15}H_{16}N_2O_2$) (NH_3)$_2$	14	DMF
3. [Co($C_{15}H_{16}N_2O_2$) (C_9H_2N)$_2$] Quinoline	16	DMF
4. [Co($C_{15}H_{16}N_2O_2$) (C_6H_5NC)$_2$] (Phenyl isocyanide)	18	DMF
5. [Co($C_{15}H_{16}N_2O_2$) (C_5H_5N)$_2$] (Pyridine)	20	DMF
6. [Co($C_{15}H_{16}N_2O_2$) ($C_5H_4NCH_3$)$_2$] (a-Picoline)	12	DMF
7. [Co($C_{15}H_{16}N_2O_2$) ($C_5H_4NCH_3$)$_2$] $\beta - picoline$	14	DMF
8. [Co($C_{15}H_{16}N_2O_2$) ($C_5H_4NCH_3$)$_2$] $\gamma - picoline$	16	DMF

Magnetic Behaviour of Co(II) Complexes:-

The magnetic moment values of Co(II) 3d^1 Complexes fall into two clases in one the magnetic moments lie in the range 4.3- 5.6 B M While in the other the 18.29 B.M. Co^2 +ion contains three unpaired electrons in the ground state and the spin only magnetic moment calculated by the expression $\mu = \sqrt{4S(S+1)}$ gives a value of 3.88 B.M and excess value of the magnetic moment over μ is attributed to the various degree of orbital contribution. The Spin only magnetic moments and the same associated with orbital contributions for different stereochemistry of Co(II) complexes are tabulated below :

Table :-3

Complex	Bonding	Unpaired electron	**μ (B.M)**	**μeff (B.M.)**
Co^2 free ion	Ionic	3	3.88	4.3-4.32
Tetrahedral (sp^3)	Ionic	3	3.88	4.3 -4.88
Octahedral (sp^{3}d^2)	Ionic	3	3.88	4.88-5.20
Planar (dsp^2)	Covalent	1	1.73	2.10-2.90
Octahedral (d^{2}sp^3)	Covalent	1	1.73	1.73-2.90

Co(II) forms tetrahedral, Planar and octahedral (inner or outer orbital type) complexes and all are paramagnetic, but it is possible to distinguish spin paired and spin free complexes from magnetic moment value Nyholm[2] has postulated that the magnitude of the orbital contribution may be diagnostic of the stereochemistry of the metal ion.

Table-04

Complex	**Colour**	**μeff (B.M)**	**Magnetic Properties**
1. [Co($C_{15}H_{16}N_2O_2$) (H_2O)$_2$]	Chocalate brown	4.96	Paramagnetic
2. [Co($C_{15}H_{16}N_2O_2$) (NH_3)$_2$]	Brownish pink	4.90	Paramagnetic
3. [Co($C_{15}H_{16}N_2O_2$) (C_9H_2N)$_2$] Quinoline	Brownish Yellow (10.28)	4.92	Paramagnetic

4. $[Co(C_{15}H_{16}N_2O_2)(C_6H_5NC)_2]$ (Phenyl isocyanide)	Pinkish Brown	4.98	Paramagnetic
5. $[Co(C_{15}H_{16}N_2O_2)(C_5H_5N)_2]$ (Pyridine)	Yellowish brown	4.88	Paramagnetic
6. $[Co(C_{15}H_{16}N_2O_2)(C_5H_4NCH_3)_2]$ (a-Picoline)	Brownish Yellow	5.10	Paramagnetic
7. $[Co(C_{15}H_{16}N_2O_2)(C_5H_4NCH_3)_2]$ $\beta - picoline$	Faint brown	4.96	Paramagnetic
8. $[Co(C_{15}H_{16}N_2O_2)(C_5H_4NCH_3)_2]$ $\gamma - picoline$	Light Brown	4.92	Paramagnetic

The ground state of spin free octahedral and tetragonally distorted octahedral complexes is $^4T_{1g}$ due this ,a large orbital contribution is expected in the magnetic moment and hence high spin octahedral complexes display μeff value higher than spin only value to an extent to over 0.8 to 1.3 B.M experimental results 4, 5 also support this idea. In the spin free octahedral cases the observed moments are larger than the tetrahedral complexes as in the former case the ground state itself contributes to the magnetic moment.

Some authors [6,] 7 have reported the magnetic moments of Co(II) octahedral complexes in the range of 5.0-5.22 and 4.46-4.59 B.M. The lower value of the magnetic moment in the latter cases due to some quenching of orbital angular momentum[8].

In our present investigation the magnetic moment values obtained for $Co(L)(B)_2$ Complexes are in the range of 4.88 to 5.10 B.M which unambiguously suggests the high spin six coordinated octahedral arrangement of ligand molecules around the metal ion.

Table- 5

Complexes	ϑ_1 cm^{-1}	ε_1	ϑ_1 cm^{-1}	ε_2	ϑ_1 cm^{-1}	ε_3	**C.T. band**
1. $[Co(C_{15}H_{16}N_2O_2)(H_2O)_2]$	8800	1.9	17600	0.3	21650	4.0	33150
2. $[Co(C_{15}H_{16}N_2O_2)(NH_3)_2]$	8450	1.6	17650	0.4	21600	3.6	33450
3. $[Co(C_{15}H_{16}N_2O_2)(C_9H_2N)_2]$	8650	1.8	17150	1.1	21150	2.9	33650

Quinoline							
4. $[Co(C_{15}H_{16}N_2O_2)(C_6H_5NC)_2]$ (Phenyl isocyanide)	8550	1.7	16550	0.9	20750	2.7	33550
5. $[Co(C_{15}H_{16}N_2O_2)(C_5H_5N)_2]$ (Pyridine)	8450	1.6	16650	1.1	21850	2.9	33450
6. $[Co(C_{15}H_{16}N_2O_2)(C_5H_4NCH_3)_2]$ (a-Picoline)	8250	1.4	16350	1.0	21250	2.7	33350
7. $[Co(C_{15}H_{16}N_2O_2)(C_5H_4NCH_3)_2]$ $\beta - picoline$	8600	1.8	16550	1.1	21450	2.3	33450
8. $[Co(C_{15}H_{16}N_2O_2)(C_5H_4NCH_3)_2]$ $\gamma - picoline$	8500	1.7	16500	1.2	21400	2.4	33300

Spectral Behaviour of Co (II) Complexes :-

The free ion term of Co(II) ion has the ^4F ground term with the first excited term ^4P under the influence of cubic field the 4F splits into $^4T_{1g}$ (F), $^4T_{2g}$ (F), and $^4TA_{2g}$ (F) states and the ^4P transforms of $^4T_{1g}$ (P), state only.

In the tetrahedral field the splitting of ^4F and ^4P may be given as follows according to orgel diagram.

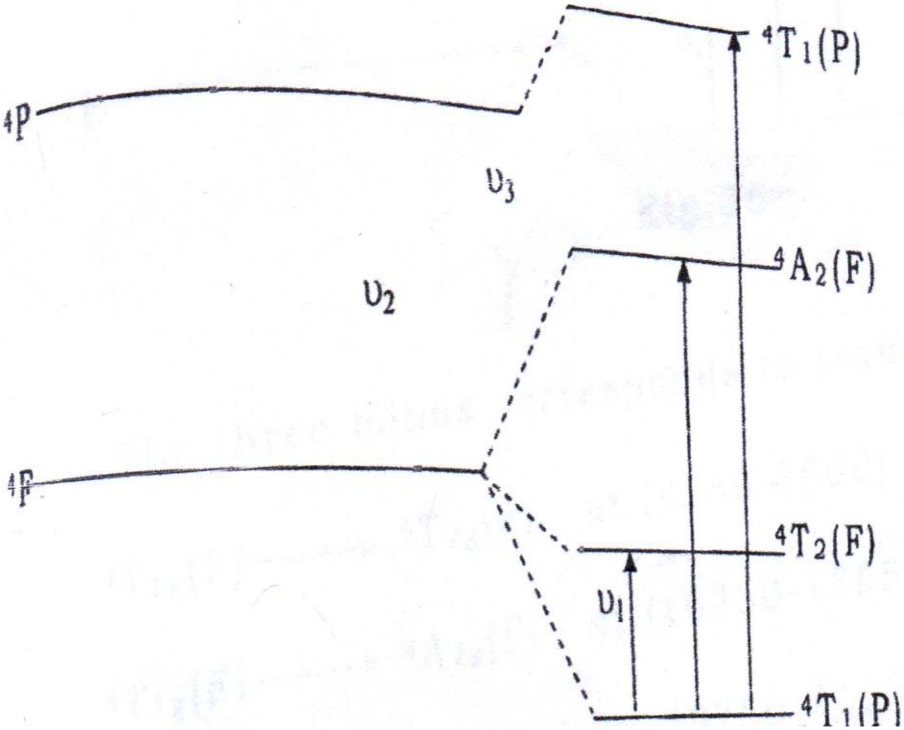

Fig-1

Splitting in tetrahedral field

Thus three bands are possible due to the corresponding Transitions are possible.

$^4A_2$ (F) → $^4T_2$ (F) at 4200 cm^{-1}

$^4A_2$ (F) → $^4T_1$ (F) at 7400 cm^{-1}

$^4A_2$ (F) → $^4T_1$ (F) at 15800 cm^{-1}

In the octahedral field the splitting of ^4F and ^4P takes place as :-

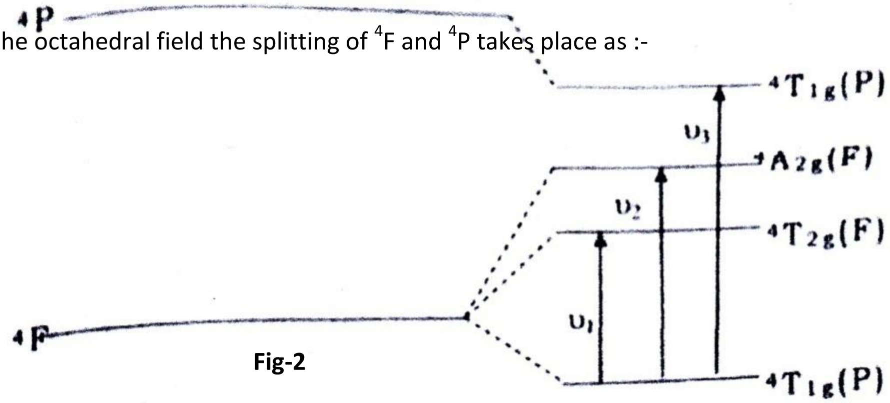

Fig-2

The three bands corresponds to transitions8

$^4T_{1g}$(F) → $^4T_{2g}$ (F) at (8250-8800) cm^{-1}

$^4T_{1g}$ (F) → $^4A_{2g}$ (F) at (16350-17650) cm^{-1}

$^4T_{1g}$(F) → $^4T_{1g}$ (P) at (20750-21850) cm^{-1}

In the present investigation a schiff base ligand 1, 3-bis (o-hydroxy anilino) propane has been synthesized by the condensation of 1, 3-dibromo propane and 2-amino phenol.

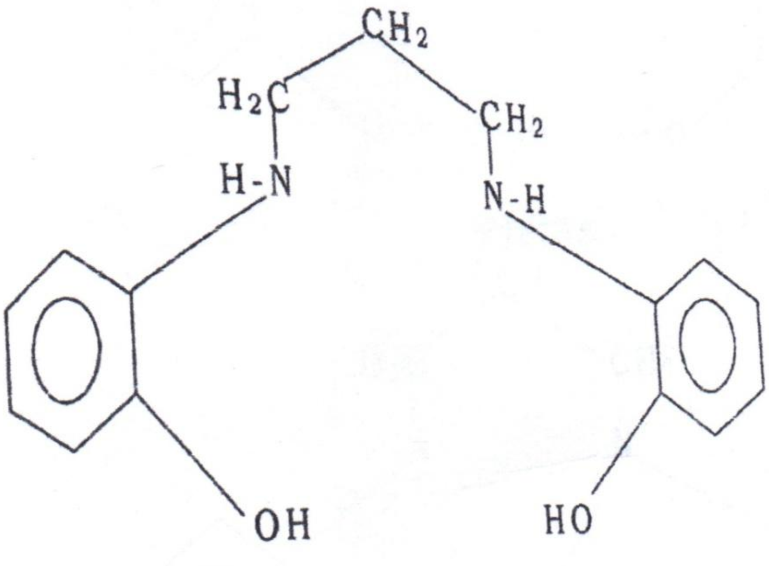

Fig -3

In the Ligand molecule, there is good probability for the formation of strong intra-hydrogen bonding between two phenolic (-OH) groups, one phenolic (OH) and one imino (NH) group of the ligand molecule. In view of the above possibilities of hydrogen bonding within the ligand molecules, it is expected that ϑ(NH) and ϑ(OH) frequencies of the ligand molecule would sharply fall below the expected range of ϑ(NH) and ϑ(OH) vibrations[11]

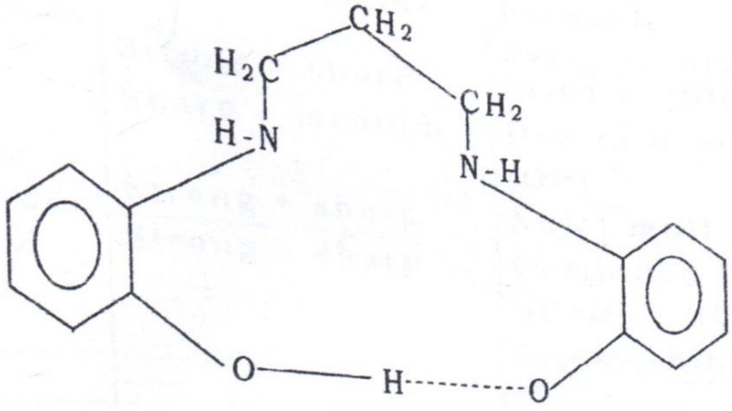

Fig-4

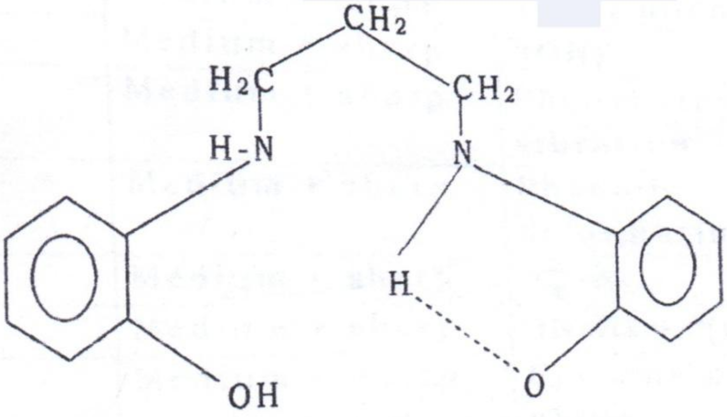

Fig-5

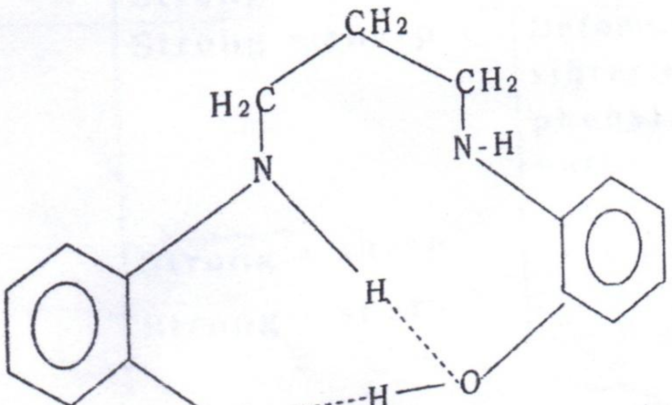

Table-6

I.R. bands of the ligand 1, 3-bis (hydroxyl aniline) propane (LH_2)

Sl	I.R. band Positions (cm^{-1})	Nature of Bands	Probable assignments
1	3430	Strong +Sharp	U(OH)+u(NH)
2	3230	Sharp +medium	Due to H-bonded(OH)
3	2930-2850	Strong +sharp	Nujol mull
4	1670-1640	Strong+sharp	Combined band of ^{u}(C=N) + ^{u}(c=c) (azomethine)
5	1460-1480		
6	1450-1370	Strong +sharp	Nujol mull
7	1430	Medium +sharp	^{u}(C-O) phenolic
8	1310	Medium + sharp	^{u}(OH)
9	1250	Medium + sharp	Phenyl ring vibration
10	1220	Medium + sharp	Phenolic deformation
12	980	Medium +sharp	^{u}(C-N)
13	810	Medium + sharp	^{u}(N-H) + ^{u}(C-H)
14	770	Medium + sharp	Benzene out of plane
15	710	Medium + sharp	Nujol Mull
16	560	Strong + sharp	
17	490	Strong + sharp	Deformation vibrations due to phenyl ring part
18	460	Strong + sharp	
19	410	Strong + sharp	

The I.R. spectrum of the ligand molecule 1, 3-bis (o-hydroxy anilino) propane, (LH_2) displays the highest I.R. band at 3430 cm^{-1} which may be obtained due to combined (OH) and (NH) vibrations. A weak and medium band obtained at 3230 cm^{-1} due to hydrogen bonded bonded (OH) group the ^{u}(OH) of the the phenolic ϑ(C-OH) shifts from 3430-3230 cm^{-1} due to strong hydrogen bonding. The ligand displays a sharp and strong band between 2930-2850 cm^{-1} due to Nujol mull. The important bands in the infrared spectrum of the ligand are at 1650-1620 cm^{-1} due to combined ϑ (C=N) azomethine and

ϑ (C=C), at 1460-1380 cm^{-1} due to Nujol mull, at 1430 cm^{-1} due to ϑ (C-O) phenolic, at 1310

cm^{-1} due to ϑ (OH) at 800 cm^{-1} due to Nujol mull

I.R. Spectra of the [$Co(L)B_2$) Complexe :-

In case of the ligand 1, 3 bis(b-hydroxy anilino) propane it is expected that two phenolic (OH) protons of the ligand molecule will be deprotonated forming bi-anionic tretradentate molecule. In this case two protons of the bhenoxy (OH) groups are lost producing binegative ion. The resulting ligand behaves as tetradentated molecule which coordinates through two deprotonated phenolic Oxygen and two aldimine or azomethine nitrogen atoms in the complex formation with metal cations.

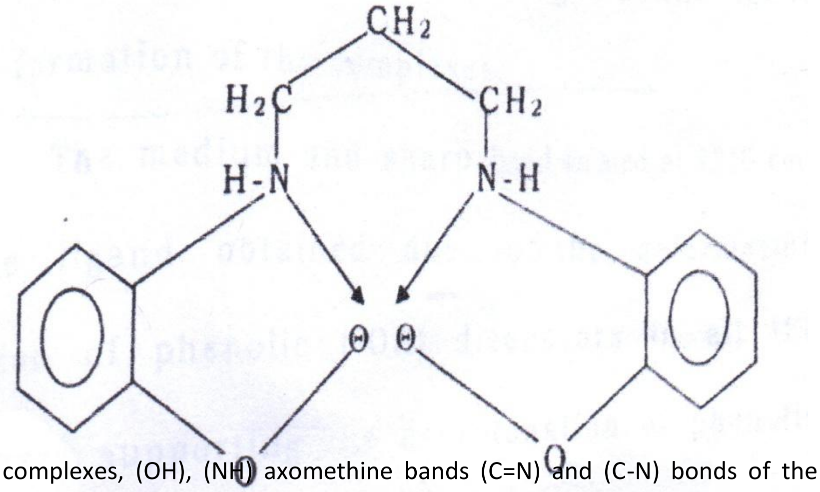

Fig – 7

In almost all the complexes, (OH), (NH) axomethine bands (C=N) and (C-N) bonds of the ligand molecule are appreciably changed after the complex formation.

The medium and sharp band located at 1310 cm^{-1} in the ligand obtained due to the deformation vibrations of phenolic (-OH) disappears in all the complexes supporting the deprotonation of phenolic (OH) and coordination of phenolic oxygen to the metal atom. The (C-O) vibration of phenolic (C-O) group shifts to higher frequency in the complexes suggesting increase of bond order of (C-O) group in the complexes as noticed by sin et. al. [13] the (M-N) and (M-O) stretching vibrations appear in the lower frequency rigions indicating the coordination of the nitrogen and oxygen atoms of the ligand in the complex formations.

Thus from the above discussion, it is suggested that two deprotonated phenolic oxygen, and two azomethine or aldimine (C=N) nitrogen atoms are the bonding sites of the Schiff base ligand 1, 3-bis (o-hydroxy anilino) propane and probable form of the ligand to form complexes is bi-anionic tetradentate molecute.

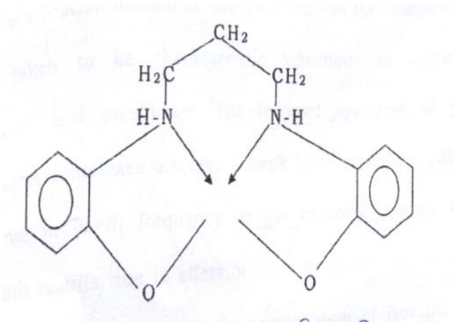

Fig-8

Vibrations suggests that H_2O is present in the coordination sphere[14]

The coordination through nitrogen atom of the ligand molecule, ammonia, quinoline, phenyl isocyanide, pyridine and different picolines groups have been further confirmed by the appearance of a new band at 450-460 cm^{-1} due to (M-N) vibrations.

The coordination through phenolic oxygen atom has been further confirmed by the appearance of a new band at 510-540 cm^{-1} due to (M-O) vibrations.

Thus on the basis of elemental analysis, measurement of electrical conductance, magnetic moment, electronic and I.R. spectral behaviours of the complexes it may be suggested that Co(II) cations form octahedral complexes with the ligand 1, 3-bis(o-hydroxy anilino) propane in presence of bases containing oxygen and nitrogen atoms as their doner sites.

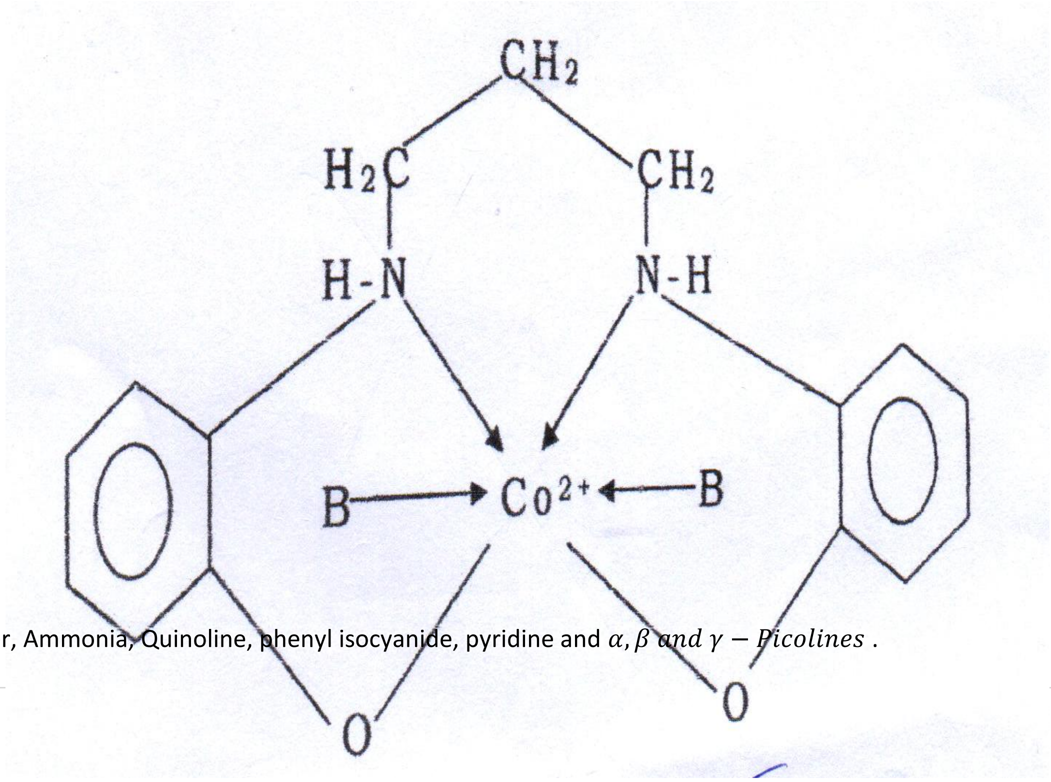

Fig – 9

B= water, Ammonia, Quinoline, phenyl isocyanide, pyridine and α, β *and* $\gamma -$ *Picolines* .

Conclusion :- in this present paper we get on the basis of elemental analysis , measurement of electrical conductance magnetic moment electrical and I.R. spectral behaviours of the complexes Co(II) Cation forms tetrahedral, planer and octahedral complexes with the ligand, 1, 3- bis (o-hydroxy anilino) propane in atoms as their doner sites.

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