JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Studies of spectral and magnetic behaviour of some complexes of Cobalt (II) and Iron (II) metals with tridentate derivative of benzohydroxamic acid

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Abstract:

A Schiff base ligand, 2(2-hydroxy pyridine-3-carbalidene imino) benzohydroxamic acid has been prepared by the condensation of 2-amino benzohydroxamic acid and 2-hydroxy Pyridine-3-Carbaldehyde under suitable conditions. On the basis of elemental analysis and I.R. spectral data this compound, was found to be bi-anionic tridentate. The complexes of Cobalt(II) and Iron (II) metals have been prepared with this ligand separately in presence of various bases containing oxygen and nitrogen atoms as their donor sites. On characterization by usual physico-chemical methods, all the complexes have been found to be non-electrolyte, monomeric and paramagnetic with octahedral geometry. The general molecular formula of the complexes have been found to be {M(L) $(B)_3$] Where M=Cobalt (II) and Iron(II) metals, L=ligand and B=Bases.

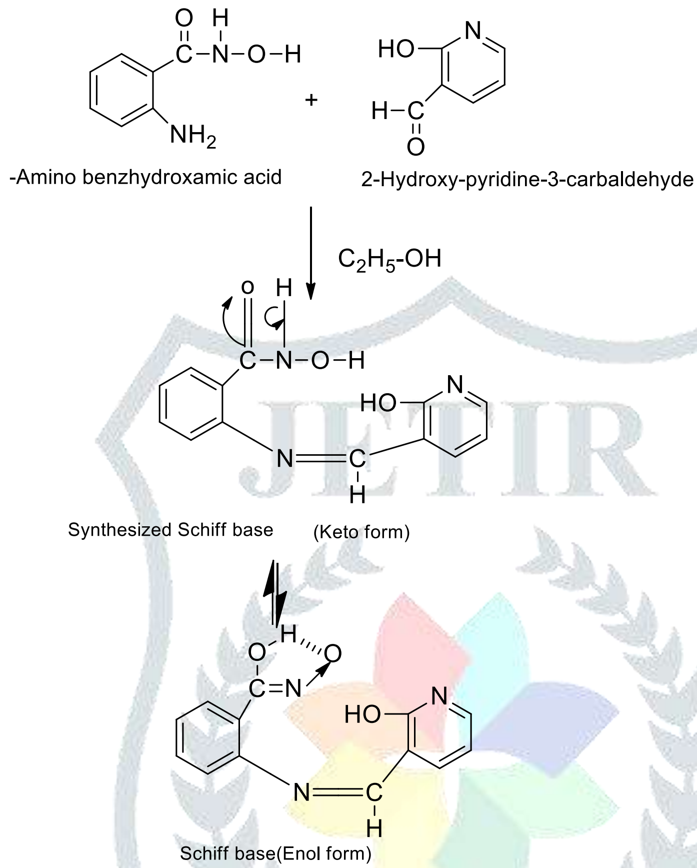
Key words:- Preparation , ligand, tri-dentate, complexes, derivative, condensation, donor site, paramagnetic geometry, filtration etc.

Introduction: Too much research work has been carried out with various Schiff bases [1] containing oxygen , nitrogen and sulphur atoms as their donor sites for the formation of complexes of divalent transition metals in presence of bases containing Oxygen, Nitrogen and Sulphur atoms as their donor sites. But at least work has been done with such Schiff bases derived from 2-amino benzohydroxamic acid[2] and 2-hydroxy pyridine-3-Carbaldehyde. Therefore in this paper I report the complexes of divalent Cobalt and Iron metals formed with 2(2-Hydroxy pyridine-3-carbalidene imino) benzohydroxamic acid.

Preparation of Schiff base ligand: 2(2-hydroxy pyridine-carbalidene imino) benzohydroximic acid

Procedure[3]: 0.1 mole (15.2 grams) of 2-amino benzohydroxamic acid was completely dissolved in minimum volume of ethyl alcohol and 0.1 mole (12.3 gram) of 2-hydroxy pyridine-3-carbaldehyde was dissolved in minimum volume of ethyl alcohol. Both the solutions were mixed together gradually with regular shaking. The resulting solution was filtered and the filtrate was collected in round bottom flask. The filtrate was refluxed for 3 to 4 hours under a condenser fitted with a running water tap. Then solution on cooling under ice bath produced faint brown colour solid. The solid was separated by filtration and the residue was washed with a small amount of acetone. Then the solid was dried over an over at the temperature between 110-112^{0}C. Then the melting point of the compound was recorded and found to be 84-86^{0}C. On the basis of the elemental analysis, the molecular formula of the compound was found to be $C_{13}H_{11}N_3O_3$.

The identification of the compound was further confirmed by (1) Elemental analysis, (2) Test of functional groups and (3) IR spectroscopy.



Preparation of the complexes:

Procedure[4]: 0.001 mole (0.275 gram) of the ligand was completely dissolved in minimum volume of ethyl alcohol and 0.001 mole (0.24 gram) of cobalt (II) chloride hexahydrate was completely dissolved in minimum volume of aqueous ethanolic solution. Both the solutions were mixed together gradually with regular shaking. Than the resulting solution was filtered and the filtarate was collected in small round bottom flask. After that the filtrate was refluxed for two and half an hour. Then a pinkish brown crystalline solid was separated in the solution. The crystalline solid was separated by filtration and the solid was washed with a small amount of acetone followed by ether. Then the product was dried over KOH pellets placed in a desiccator.

The complexes of Iron(II) cations have been prepared with the same ligand in presence of each of bases separately such as water, ammonia, phenyl-isocyanide, quinoline & pyridine. But there are slight variation in the reflux of time and colour of the complexes in each case.

Similar procedure was adopted for the preparation of Iron(II) complexes with the same ligand and the bases with slight variation of time and colour of the complexes in each case.

Precaution: Freshly prepared solution of Ferrous sulphate heptahydrate was taken to avoid the oxidation of Iron(II) into Iron(III) salts. On elemental analysis of the ligand and the complexes, the general molecular formula of the complexes have been found to be [(M(L)(B)$_3$]. Where M= Cobalt(II) and Iron (II) Metals , L=Ligand and B= Bases.

Table No. 1
Elemental analysis of Cobalt (II) & Iron (II) Complexes
Found and (Calculated)

Compounds	Metal	Carbon	Hydrogen	Nitrogen
[Co ($C_{13}H_9N_3O_3$)(H_2O) $_3$]	15.36	41.80	4.60	11.40
	(15.92)	(42.17)	(4.59)	(11.35)
[Co ($C_{13}H_9N_3O_3$)(NH_3) $_3$]	15.66	41.96	5.46	22.96
	(16.05)	(42.51)	(5.45)	(22.89)
Co ($C_{13}H_9N_3O_3$)(C_6H_5NC) $_3$]	9.12	64.64	4.18	13.50
	(9.42)	(65.29)	(4.16)	(13.44)
Co ($C_{13}H_9N_3O_3$)((C_9H_7N)$_3$]	8.12	67.76	4.57	12.00
	(8.83)	(68.28)	(4.55)	(11.95)
[Co ($C_{13}H_9N_3O_3$)(C_5H_5N)$_3$]	10.32	60.16	4.72	15.25
	(10.65)	(60.77)	(4.72)	(15.24)
[Fe($C_{13}H_9N_3O_3$)(H_2O) $_3$]	15.10	42.12	4.65	11.48
	(15.25)	(42.50)	(4.63)	(11.44)
[Fe ($C_{13}H_9N_3O_3$)(NH_3) $_3$]	15.16	42.41	5.50	23.10
	(15.38)	(42.85)	(5.49)	(23.07)
[Fe ($C_{13}H_9N_3O_3$)((C_6H_5NC)$_3$]	8.78	65.10	4.20	13.56
	(9.00)	(65.59)	(4.18)	(13.50)
[Fe ($C_{13}H_9N_3O_3$)(C_9H_7N) $_3$]	7.77	68.10	4.60	12.12
	(8.00)	(68.57)	(4.57)	(12.00)
[Fe ($C_{13}H_9N_3O_3$)(C_5H_5N)$_3$]	10.10	60.70	4.74	15.30
	(10.18)	(61.09)	(4.72)	(15.30)

Chemical required: Cobalt(II) Chloride hexahydrate and Iron(II) sulphate heptahydrate, Dimethylformamide, ethyl alcohol, 2-amino benzohydroxamic acid,2-hydroxy pyridine-3-carbaldehyde, ammonium hydroxide, quinoline, phenyl isocyanide and pyridine. All chemicals obtained either from E.Merk or B.D.H. (A.R.) quality has been used without further purification.

ANALYTICAL METHODS:

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

(i) **Cobalt :-** Coballt has been estimated volumetrically by oxinate method.
(ii**) Iron:-** Iron has been estimated volumetrically as 8-hydroxyquinolinate (oxinate).
(iii) **Hydrogen, Carbon and Nitrogen:**- Hydrogen, Carbon and nitrogen was estimated by semi-macro-duma's method.

CONDUCTIVITY MEASUREMENT:

The measurement of electrical conductivity of the solutions of the complexes has been done by conductivity meter bridge manufactured by Wiss-Techen Wearch Stathen type-LBR-at room temperature. The cell constant has been measured by using N/10 and N/100 KCl solutions. Pure DMF and conductivity water has been used as solvents.

U.V. –VISIBLE SPECTRA PHOTOMETRIC MEASUREMENT:-

Hitachi-320 spectrophotometer has been used to record the electronic absorption spectra of the complexes.

I.R. Spectra:-

Perkin Elemer 577 spectrophotometer has been used to record the infra-red spectra of the complexes and the ligand in nujol mull.

During the course of recording the infrared spectra of the ligand of the complexes in Nujol mull, three peaks has been obtained in the range of 2960 cm^{-1} to 2800 cm^{-1} and at 1460 cm^{-1} to 1380cm^{1} and a small peak at about 700 cm^{-1} has been excluded while recording the I.R. spectra for the determination of structure of the ligand and the complexes.

MAGNETIC SUSCEPTIBILITIES:

The measurement of the magnetic susceptibilities of the complexes has been carried out by Gouy's method using Mercury tetra thiocyanato coballtate, (Hg Co $(SCN)_4$] as celebrant.

Results and Discussion: The values of electrical conductance of Cobalt(II) and Iron(II) complexes have been found in the range of 12-16 mho and 18-24 mho respectively which indicate non-electrolyte nature of the complexes of both the metals.

The values of magnetic moments of Cobalt(II) and Iron(II) complexes have been obtained in the range of 4.84-4.96 BM and 5.86-5.92 BM[5,6] respectively indicating the paramagnetic and spin free (outer orbital) octahedral character of all the complexes.

In our present investigation two bands have been obtained for Cobalt(II) complexes [7]. The first band obtained in range of 14650 to 15100 cm^{-1} is broad and unsymmetrical due to J.T.distortion.The transition takes place between $4T_{1g}$ $^4T_{2g}$ $(^4E_g + {}^4B_{2g}) \rightarrow$ The second band obtained in the range of 22250 to 23550 cm^{-1} is sharp and symmetrical due to $^4T_{1g}$ (F) $^4T_{1g}$ (P) transition which is $\rightarrow$ spin allowed. This electronic transition bands indicate spin free octahedral nature of Cobalt (II) complexes

In case of Iron(II) complexes [8] one broad and unsymmetrical band obtained in the range of 14220- 14950 cm^{-1} due to $^5T_{2g}$ ^5E_g $\rightarrow$ transition indicates distorted octahedral geometry of Iron (II) complexes.

Comparison of I.R. spectra of the ligand and complexes to decide the structure of complexes.

In all the complexes, the positions of bands obtained due to the vibrations of phenolic -OH, azomethine >C=N, oximino (C-N), (N-H) and (N-O) groups present in the ligand molecule have been appreciably changed after complex formation [9-15]. The strong and sharp bands due to the vibrations of (O- H) and (N - H) bonds of the ligand obtained in the range of 3240-3270 cm^{-1} disappear in all the complexes and a new broad and unsymmetrical band has been obtained in the range of 3440-3480 cm^{-1} in the complexes confirming the presence of at least one free (-OH) group even in the complexes. The deprotonation of phenolic(-OH) group attached to Pyridine has been suggested due to the presence of a medium and sharp band obtained in the ligand molecule in the range of

1430-1470 cm^{-1}. This band position of the ligand molecule has been shifted to higher range 1460-1480 cm^{-1} in the complexes. This increase in the band position of phenolic (C-O) group indicates the deprotonation of phenolic -OH group and participation of oxygen atom of phenolic-

OH group in the complex formation. The disappearance of the strong band at 1310-1320 cm^{-1} further suggests the deprotonation of the hydroxy group (-OH) group i.e., (N - OH) proton located at hydroxamic acid moiety. The azomethine band located at 1640-1660 cm^{-1} in the ligand molecule has been shifted to lower range of 1560-1580 cm^{-1} in all the complexes. This shift of (>C=N) band towards lower range in the complexes suggests the coordination of azomethine nitrogen of the ligand in the formation of the complexes. The strong and sharp band due to oximino group of the ligand obtained at 1610-1620 cm^{-1} has been also shifted to higher range between 1540-1560 cm^{-1} in the complexes indicating the coordination of oximino-nitrogen in the complex formation.

The (N-O) band of the ligand located at 1020 cm^{-1} has been also shifted to higher range between 1020-1050 cm^{-1} indicating the participation of oximino nitrogen atom in the bond formation with the metal cation.

Around the nitrogen atom of oximino group, electron density increases on nitrogen atom and it becomes negatively charged thus schiff base ligand 2(2-hydroxy pyridine-3-carbaldene imino) benzohydroxamic acid behaves as bi-anionic tridentate. Thus the one molecule of the ligand satisfied two primary and one secondary coordination sites of the metal cation.

In aquo complexes no separate band has been obtained to indicate the coordination of Oxygen atom of Water molecule and Nitrogen atom of ammonia. A broad and strong band has been obtained in the range of 3360-3390 cm^{-1} due the vibrations of combined (OH + NH) groups. A sharp and medium band has been obtained in the range of 730-760 cm^{-1} in a aqua-complexes due to rocking mode of coordinated water molecule.

I.R. spectra of free phenyl isocyanide molecule has a band obtained at 2170 cm^{-1} has been increased to 2220-2240 cm^{-1} in the complexes. This increase in band position indicates the participation of Nitrogen atom of isocyanide group of phenyl isocyanide in the complex formation.

In quinoline complexes, a band has been obtained at 1370-1410 cm^{-1} is due to the vibration of quinoline ring indicates the participation of nitrogen atom of quinoline in the complex formations.

In pyridine, a number of bands are obtained in finger print and far infra-red region. A band obtained in the range 1050-1080 cm^{-1} due to breathing mode of pyridine ring has been regarded as the characteristic vibrations of the coordinated pyridine.

A sharp and medium band obtained in the range of 540-560 cm^{-1} in the complexes due to the vibration of (M - O) bond further confirms the participation of Oxygen atom in bond formation with the metal cation.

A sharp and medium band obtained in the range of 410-430 cm^{-1} in the complexes due to the vibration of (M - N) bond further confirms the participation of Nitrogen atom in bond formation with the metal cation.

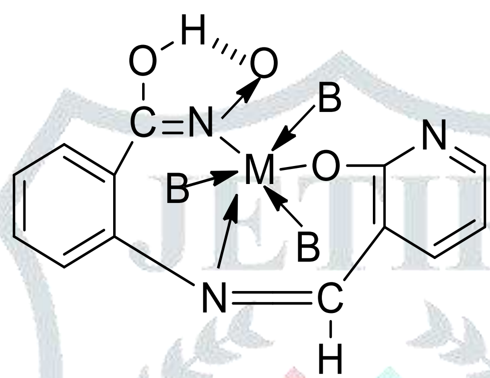
The frequency obtained due to the vibrations of (M-O) bond is greater than that of (M-N) bond because (M-O) bond is more ionic than (M-N) bond.

On the basis of elemental analysis, measurement of electrical conductance, magnetic moment, electronic and I.R. spectra of the ligand and the complexes, octahedral geometry has been suggested for the complexes of Cobalt(II) and Iron(II) cations formed with the Schiff base ligand 2(2-hydroxy pyridine -3-carbalidene imino) benzohydroxamic acid in presence of bases like water, ammonia, phenyl-isocyanide, quinoline, and pyridine.

Conclusion:

Thus from the above discussion, it has been obtained that one nitrogen atom of oximino group of the deprotonated hydroxamic acid part, one nitrogen atom of azomethine group and one oxygen atom of deprotonated phenolic (O-H) group attached to the Pyridine ring are the bonding sites of the Schiff base ligand 2(2-hydroxy pyridine-3-carbalidene imino) benzohydroxamic acid and the probable form of the ligand to form the complexes has been found to be bi -anionic tri-dentate.

The general formula for all the complexes has been suggested to be [M (L)$(B)_3$] as shown below.



Where M = Cobalt(II) and Iron (II) metals
L = 2(2-hydroxy pyridine -3-carbalidene amino) benzohydroxamic acid
B = water , ammonia , quinoline, phenyl -isocyanide , and pyridine.

ACKNOWLEDGMENT:

The author is thankful to Dr. Mithilesh Kumar Singh Principal of Loknayak Jai Prakash Institute of Technology, Chapra for providing available library and laboratory facilities and cordial behaviour during research work. I am also thankful to the Non-teaching members for providing me decorous behavior during the whole research work.

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