

SYNTHESIS AND CHARACTERISATION OF SOME NOVEL COMPLEXES OF CO(II) WITH HYDROXAMIC ACID DERIVATIVE AS LIGAND.

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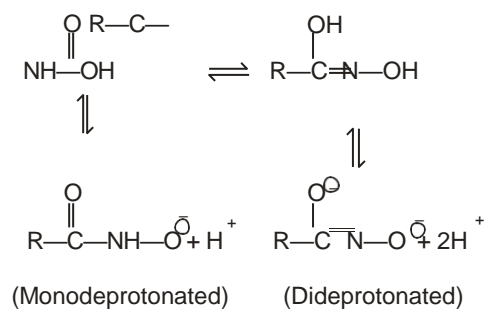
Abstract: Some novel complexes of Co(II) with 2-(o-hydroxybenzophenoneimino) benzohydroxamic acid in presence of bases like water, ammonia, pyridine, phenyl isocyanide, quinoline and α -picoline have been synthesised and characterised on the basis of elemental analyses, molar mass determination, molar conductance and magnetic susceptibility measurements, UV-visible and IR spectroscopic investigations. The complexes have been formulated as $[Co(L)(B)_3]$ where, L=dideprotonated 2-(o-hydroxybenzophenoneimino) benzohydroxamic acid(LH₂) and B=H₂O, NH₃, pyridine, phenyl isocyanide, quinoline and α -picoline. Here, the ligand behaves as dianionic tridentate ligand. The complexes have been found to be paramagnetic and non-electrolytic in nature. All the complexes are found to have octahedral geometry as indicated by the values of magnetic moments and the positions of U.V.-visible spectral bands.

Key words: Hydroxamic acid, chelating ligand, spectral investigation, molar conductance etc.

1. INTRODUCTION

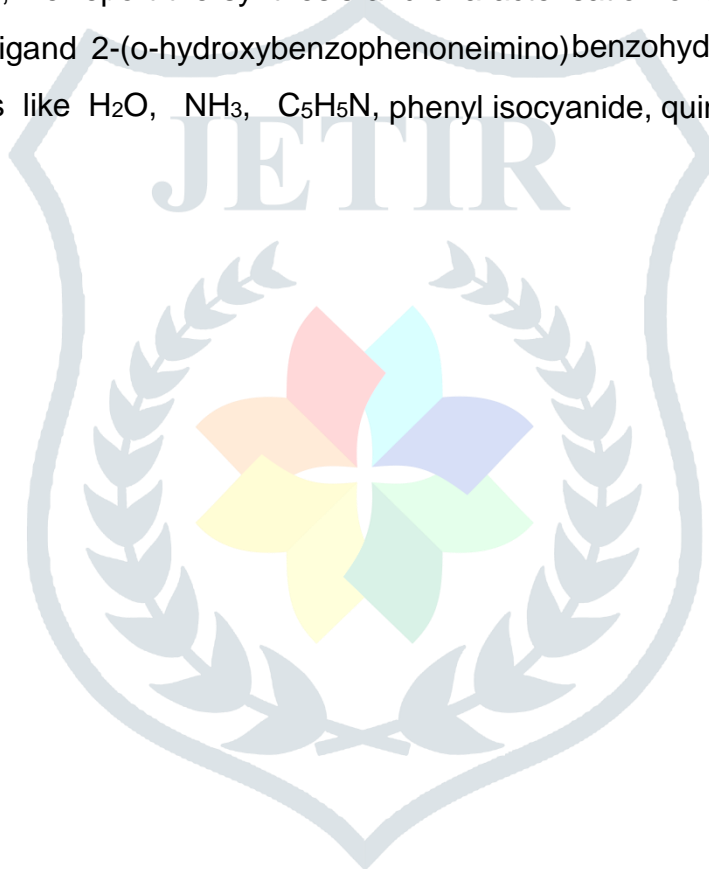
Hydroxamic acids (R-CO-NHOH) and their derivatives have been the domain of research for inorganic and bio-inorganic chemists due to their low toxicity and wide range of biological activities. They exhibit antibacterial [1-3], antifungal [4-5], antitumour [6-8], antituberculous [9] and antimalarial [10] properties. They are also known to inhibit enzymes such as urease [11], peroxidase [12] and metalloproteinase [13]. Numerous hydroxamic acid analogues are known to inhibit DNA synthesis by making the enzyme ribonucleotide reductase inactive [14]. Symptoms of asthma and other obstructive airway diseases are treated with cinnamohydroxamic acids which inhibit 5-lipoxygenase [15]. Hydroxamic acids display antiradical and antioxidant properties [16]. Siderophores, which are involved in the processes of iron transport from environment to living organisms, are complexes of Fe(III) with naturally occurring hydroxamic acids [17-18]. Hydroxamic acids have diverse applications in analytical, industrial and pharmaceutical fields [19-23]. These applications of hydroxamic acids are due to their ability to form stable chelates with transition metal ions whereby their biological

activities are enhanced. Hydroxamic acids are deprotonated in two anionic structures where one of them is mono deprotonated while the other is di deprotonated.



Hydroxamic acids act as (O, O) donor which form five membered chelate rings with metal ions.

In this paper, we report the synthesis and characterisation of some novel complexes of Co(II) with the ligand 2-(o-hydroxybenzophenoneimino)benzohydroxamic acid in the presence of bases like H₂O, NH₃, C₅H₅N, phenyl isocyanide, quinoline and α -picoline.



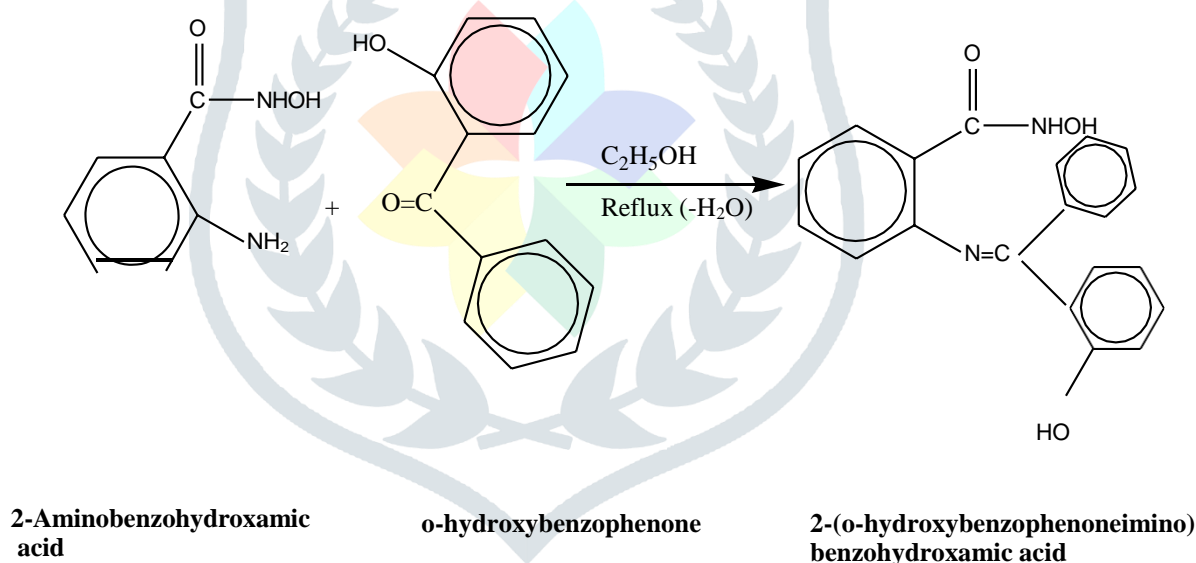
2. EXPERIMENTAL

2.1 Materials and Methods:

All chemicals used were of analytical grade purchased from sigma Aldrich and were used as received without further purification. The microanalysis of C, H and N present in the ligand and complexes was done by elemental analyser EuroEA (Model 3000), the magnetic susceptibility of complexes was determined using vibrating sample magnetometer (Model PAR 155). Molar conductance of complexes was determined using digital conductivity meter (HPG System, G-3001). Metal in complexes was estimated by the standard method [24]. The IR spectra of ligand and complexes were recorded in the range 4000-400 cm^{-1} using Agilent Technologies FT-IR spectrophotometer (Cary 630). Electronic spectra of metal complexes were recorded on Hitachi 300 spectrophotometer. Molar masses of complexes were determined by cryoscopic method.

2.2. Synthesis of the ligand

The ligand 2-(o-hydroxybenzophenoneimino) benzohydroxamic acid was prepared by the condensation of o-hydroxy benzophenone with 2-amino benzohydroxamic acid [25-26].



Procedure: 0.1 mole (15.2 g) of 2-aminobenzohydroxamic acid was dissolved in minimum volume of ethanol. Further, 0.1 mole (19.8 g) of o-hydroxy benzophenone was dissolved in minimum volume of ethanol. The two ethanolic solutions were mixed slowly with constant stirring. The mixture solution was refluxed in a round bottom flask using water condenser for about 4 hours. After cooling the solution, a pale yellow crystalline solid was separated which was filtered and washed with small amount of acetone and then with ether.

C = 72.28%, H = 4.81%., N = 8.43%., Yield = 70%. M.P = 136°C.

2.3 Synthesis of complexes of Co(II) with the ligand 2-(o-hydroxybenzophenoneimino) benzohydroxamic acid in the presence of H₂O, NH₃, pyridine, phenyl isocyanide, quinoline and α -picoline

Procedure: To an ethanolic solution of 0.01 mole (2.4 g) of CoCl₂. 6H₂O was added an ethanolic solution of 0.01 mole (3.32 g) of the ligand (LH₂) slowly with constant stirring. The mixture solution was refluxed with small amount of H₂O / NH₃ / pyridine / phenyl isocyanide / quinoline/ α -picoline in a round bottom flask using water condenser for about 2 hours. After allowing the solution to stand overnight, a coloured crystalline solid was separated which was filtered and washed with small amount of acetone. The solid was dried over KOH pellets kept in a desiccator. Melting point of the solid was then recorded. The complexes were found to be insoluble in common organic solvents such as benzene, toluene, methanol, ethanol, chloroform, carbon tetrachloride and ether. However, they were found to be soluble in DMF and DMSO. The yield was approximately 75%.

3. RESULTS AND DISCUSSION

3.1 Microanalytical data:

From microanalytical data (Table-1), the stoichiometries of the newly synthesised complexes have been established. The experimental molar masses of complexes proved beyond doubt their monomeric nature. The microanalytical data and the observed molar masses of complexes are in good agreement with the proposed molecular formula (Table-1) of respective complexes.

Table-1

Sl. No.	Complex compound	Colour	M.P. (°C)	Molar mass found (Calculated)	%Found (% calculated)			
					C	H	N	Co
1.	[Co(C ₂₀ H ₁₄ N ₂ O ₃)(H ₂ O) ₃]	yellow	178.5	443 (442)	54.18 (54.29)	4.51 (4.52)	6.32 (6.33)	13.29 (13.13)
2.	[Co(C ₂₀ H ₁₄ N ₂ O ₃)(NH ₃) ₃]	yellow	168.2	436 (439)	54.24 (54.66)	5.26 (5.24)	15.96 (15.94)	13.10 (13.21)
3.	[Co(C ₂₀ H ₁₄ N ₂ O ₃)(C ₆ H ₅ NC) ₃]	Light pink	196.8	692 (697)	69.21 (70.58)	4.15 (4.16)	10.05 (10.04)	8.21 (8.32)
4.	[Co(C ₂₀ H ₁₄ N ₂ O ₃)(C ₉ H ₇ N) ₃]	brown	204.3	772 (775)	72.31 (72.77)	4.52 (4.51)	9.16 (9.03)	7.41 (7.48)
5.	[Co(C ₂₀ H ₁₄ N ₂ O ₃)(C ₅ H ₅ N) ₃]	Light pink	184.4	628 (625)	66.66 (67.20)	4.65 (4.64)	11.18 (11.20)	9.18 (9.28)
6.	[Co(C ₂₀ H ₁₄ N ₂ O ₃)(C ₅ H ₄ N.CH ₃) ₃]	Light pink	187.4	663 (667)	67.96 (68.36)	5.26 (5.24)	16.68 (16.79)	8.60 (8.69)

C₂₀H₁₄N₂O₅ = dideprotonated ligand 2-(o-hydroxybenzophenoneimino) benzohydroxamic acid (LH₂).

3.2 Molar conductance

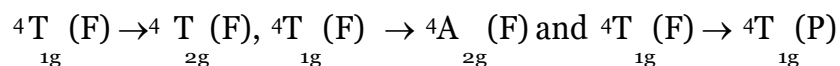
The molar conductance of metal complexes were measured in 10⁻³M DMF solution at room temperature. The molar conductance values of complexes were found in the range of 22-30 ohm⁻¹ cm² mol⁻¹ indicating their non-electrolytic nature [27]. Thus, all the complexes have been reasonably formulated as in Table -1.

3.3 Magnetic susceptibility

The magnetic moment values of Co(II) complexes have been found to be in the range of 4.84 - 4.96 BM. The magnetic moment values are indicative of the octahedral configuration of ligands around the central metal ion.

3.4 Electronic spectra

Electronic spectra of complexes displayed three bands in the region 13400- 13600 cm⁻¹, 16100-16230 cm⁻¹ and 20800 - 20935 cm⁻¹ corresponding to transitions.



respectively indicating octahedral geometry of complexes [28-29].

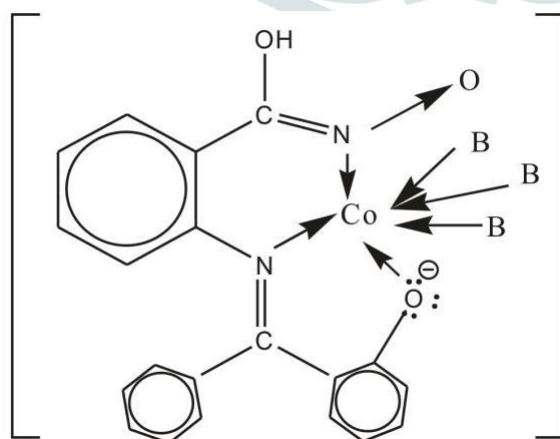
3.5 Infrared Spectra

Comparison of the infrared spectra of the ligand and complexes reveals the following facts-

- (i) The infrared spectrum of the ligand displays a band at 1660 cm^{-1} which may be assigned to $\nu_{C=O}$ mode of vibration of hydroxamic acid moiety [30]. This band remains unaffected in position and intensity in all the complexes indicating non-participation of the oxygen atom of carbonyl group in coordination to the metal ion.
- (ii) The symmetric N — O stretching vibration at 1120 cm^{-1} in IR spectrum of the ligand got shifted to lower frequency region by $10\text{-}15 \text{ cm}^{-1}$ in complexes suggesting the coordination of the ligand through nitrogen atom of the N—O moiety of hydroxamate group [31].
- (iii) The azomethine ($>C=N-$) band located at 1640 cm^{-1} in the spectrum of the ligand got red shifted by $15\text{-}20 \text{ cm}^{-1}$ in the spectra of complexes indicating the coordination of the ligand through nitrogen atom of the azomethine group to the metal ion.
- (iv) The strong and sharp band due to $\nu_{NH} + \nu_{OH}$ modes in the range of $3230\text{-}3250 \text{ cm}^{-1}$ in the spectrum of the ligand disappeared and a new broad and unsymmetrical band appeared in the range $3420\text{-}3460 \text{ cm}^{-1}$ in the spectra of complexes indicating the presence of at least one free —OH group in complexes.
- (v) The band at 1450 cm^{-1} in the spectrum of the ligand due to ν_{C-O} of the phenolic group got shifted to lower frequency region to $1180\text{-}1190 \text{ cm}^{-1}$ in the spectra of complexes indicating the deprotonation of phenolic —OH and participation of its oxygen atom in coordination to the metal ion.
- (vi) In aqua complex, the presence of water molecules in coordination sphere was indicated by the appearance of broad band in the region $3510\text{-}3590 \text{ cm}^{-1}$ and $800\text{-}850 \text{ cm}^{-1}$ due to stretching and deformation modes of vibration respectively of coordinated water molecules.

- (vii) Ammine complex displays a doublet band at 3320 cm^{-1} and 3410 cm^{-1} due to symmetric and antisymmetric modes of ν_{NH} vibrations respectively indicating the presence of ammonia molecules in coordination sphere.
- (viii) Phenyl isocyanide complex displays IR band in the region $2210\text{--}2220\text{ cm}^{-1}$ which may be assigned to $\nu_{\text{C=N}}$ mode of vibration.
- (ix) Appearance of a new band in IR spectrum of quinoline complex due to the vibration of quinoline ring indicating the participation of quinoline molecule in coordination to the metal ion through its nitrogen atom.
- (x) Appearance of a new band at 1483 cm^{-1} in IR spectrum of the pyridine complex assignable to breathing mode of pyridine ring vibration of coordinated pyridine through the nitrogen atom. A similar band is obtained in the IR spectrum of α -picoline complex indicating the presence of α -picoline molecule in coordination sphere.
- (xi) New bands appear in the IR spectra of all the complexes in the region $540\text{--}545\text{ cm}^{-1}$ and $360\text{--}370\text{ cm}^{-1}$ which may be reasonably assigned to $\nu_{\text{Co-O}}$ and $\nu_{\text{Co-N}}$ modes of vibrations respectively [30].

On the basis of the elemental analyses, determination of molar mass, molar conductance and magnetic susceptibility measurements, UV and IR spectral investigations, the following octahedral structure has been established for the newly synthesised complexes:



4. CONCLUSION

The ligand 2-(o-hydroxybenzophenoimino) benzohydroxamic acid (LH₂) undergoes dideprotonation during complex formation behaving as dianionic tridentate chelating ligand. The newly synthesised complexes are found to be monomeric with general molecular formula [Co(L)(B)₃], where L = dideprotonated ligand LH₂ and B=H₂O, NH₃, phenyl isocyanide, quinoline, pyridine and α -picoline. All the complexes are paramagnetic and have octahedral geometry. Complexes are found to be non-electrolytic in nature.

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6. References:

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