

Elucidation of Structures of Cu^{II} Complexes of Dibasic Tetradentate (OO' NO donor) Ligand

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ABSTRACT: The ligand 2-(acetylacetonato)-iminobenzohydroxamic acid and its different mixed ligand novel complexes with Cu^{II} having specific formulae have been synthesized and characterised by elemental analyses, magnetic and conductance measurements, IR and electronic spectral studies. The ligand was found to behave in dibasic tetradentate (OO' NO donor) manner. All the synthesized Cu^{II} complexes were non-electrolyte with magnetic moment ranging from 1.92 to 2.10 BM. The structural assessment of the complexes has been carried out based on electronic, infrared and molar conductivity values. All the complexes were found to be of octahedral geometry.

KEYWORDS: Hydroxamic acids; tetradentate ligand; octahedral complexes; magnetic moment.

INTRODUCTION:

Structural modification of organic molecules has considerable biological relevance. Further, coordination of a biomolecules to the metal ions significantly alters the effectiveness of the biomolecules. There is a correlation between the biological activities with geometry of the complexes. Hydroxamic acids are versatile reagents for organic and inorganic analyses [1, 2]. Their derivatives are biochemically highly active and find applications in medicinal use [3]. The acetylacetonato group containing derivatives of hydroxamic acid have aroused considerable interests over decades [4]. Hydroxamic acids having one or more -CONHOH groups have been extensively studied as a consequence of their biological importance which is related with their ability to form metal ion complexes [5]. These acids are important also due to their pharmacological, toxicological and pathological properties [6-7]. Besides, they have a great number of applications in analytical chemistry. Monohydroxamic acids (such as benzohydroxamic acid, C₆H₅CONHOH = BHA) after deprotonation acts as bidentate ligands forming octahedral complexes with a series of metal ions via co-ordination through the two oxygen atoms of the -CONHO⁻ group. This type of co-ordination has been characterized in previous studies with Ni^{II}, Co^{II} and Zn^{II} ions, which indicated the formation of octahedral complexes both in the solid state and in solution [8].

In continuation [9-13] of our work on the complexes with the hydroxamic acid derivative

ligands we report the Cu^{II} mixed ligand complexes formed by one hydroxamic acid {2-(acetylacetonato)-iminobenzohydroxamic acid [AIBHA-H₂]} [Figure-1] taken as the primary ligand (A) and a secondary ligand (B) represented either by quinoline, pyridine or picolines in this research article. The primary ligand (AIBHA) potentially acts as tetradentate (OO' NO) ligand but all these secondary ligands act as monodentate ligand.

EXPERIMENTAL

Materials:

All the chemicals and reagents used were of AnalaR grade. Anhydrous grade alcohols, DMF, and DMSO were obtained from Fischer scientific. 2-aminobenzhydroxamic acid and acetylacetone (in enolic form) were obtained from Aldrich (USA). The metal chlorides/acetates used were of BDH AR grade in the present investigation. All reactions and experimental manipulations were carried out at appropriate temperature.

Physico chemical measurements:

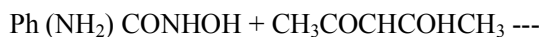
Elemental analysis (C, H & N) of ligand and complexes was carried out in micro analytical laboratory on Carl-Ebra 1106 elemental analyzer. Metal in the complexes was estimated following standard procedure [14]. The molar conductance measurements were carried out for the 10⁻³M solutions of complexes in DMSO

solvent at 300K using a Systronics direct reading digital Conductivity Bridge-304 with a dip type cell. The magnetic measurements of the complexes at 300K were made by Gouy magnetic balance using Hg [Co (NCS)₄] as calibrant. The measured susceptibilities were corrected for diamagnetic susceptibility of the ligand.

The IR spectra of ligand and the complexes as nujal-mull smears were recorded in the region 4000-200 cm⁻¹ on a Perkin-Elmer 577 spectrophotometer. The electronic spectra of the complexes were recorded on Systronics UV-Visible spectrophotometer Type -119 PC based (λ = 200-1000 nm & band width 2 nm) using ethanol as the solvent.

Synthesis of Ligand [AIBHA-H₂]:

0.1 Mole of Na-salt of 2-aminobenzhydroxamic acid dissolved in glacial acetic acid was gradually mixed with 0.1 mole of acetylacetone dissolved in minimum volume of methanol. The whole mixture was shaken well and then refluxed for about 3 hours on water bath at 298K. Then a clear yellowish brown solution was obtained which on cooling gave deep yellow brown crystals of the ligand, AIBHA. The ligand was separated by filtration and then washed with cold water and alcohol and finally recrystallized with methanol.



2-aminobenzhydroxamic acid acetylacetone



(AIBHA-H₂) yellowish brown

Synthesis of Complexes:

The solution of the ligand in methanol was allowed to react with methanolic solution of Cu (II) chloride in equimolar proportion under reflux on water bath for several hours in presence of water, and nitrogen containing bases like pyridine, ammonia, quinoline, phenylisocynide, α , β and γ -picolines. The resulting solution on crystallization gave solids of different colours for different complexes. On the basis of analytical analysis the complexes were found to be monomeric and possess the molecular formula, [Cu(L)(B)₂] where B = water, pyridine, ammonia, quinoline, phenylisocynide, α , β and γ -picolines.



EtOH



RESULTS & DISCUSSION

Physico-chemical characterizations and geometrical configuration of the complexes:

Cu (II) salt reacts with AIBHA ligand in 1:1 molar ratio in alcoholic medium to afford dark reddish/brown complexes. The ligand and its complexes are stable at room temperature and are nonhygroscopic. The ligand is soluble in common polar organic solvents, such as ethanol, methanol, and chloroform but partially soluble in hexane. The complexes are relatively well soluble in DMF and DMSO. The synthesized ligand and its complexes were characterized by elemental analysis, spectra, and molar conductivity measurements. The geometry of the newly synthesized compounds has been elucidated based on their elemental analysis, molar conductivity and spectral data.

Elemental Analysis:

The stoichiometry of the ligand and its complexes were confirmed by their elemental analysis. The metal / ligand ratio was found to be 1:1 has been arrived at by estimating the metal and nitrogen contents of the complexes. Elemental analysis of ligand and its Cu^{II} complexes show good agreement with the proposed structures of the ligand and its complexes (**Table 1**).

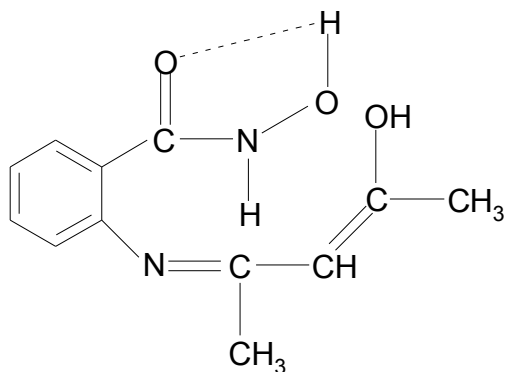
Molar conductance measurements:

The molar conductance values (14-24 ohm⁻¹ cm²mol⁻¹) of the complexes which were determined in DMSO solvent indicate that the complexes under study are non-electrolytic in nature [15-16].

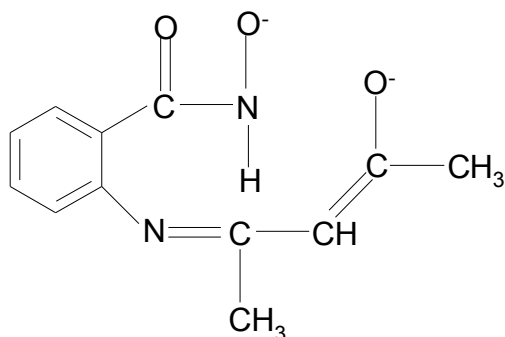
IR Spectral Studies:

The structural possibilities of the complexes depend upon the mode of coordination of the ligands. The IR spectral studies are quite useful on determining the mode coordination of ligands. On critically examining the position and direction of the shifts of the frequencies of the ligands in the complexes, as compared to their positions in the free state, the mode of coordination can be suggested for all the investigated complexes.

The IR spectral studies show that the ligand AIBHA-H₂ acts as a dibasic tetra- dentate in all the synthesized complexes, bonding through the carbonyl oxygen, deprotonated hydroxamic oxygen, deprotonated phenolic oxygen and aldimine nitrogen (C=N) [**Figure-2**]. Since the stretching frequency of the free NH group appears around 3275 cm⁻¹, the decrease for AIBHA, as well as for other hydroxamic acids can be attributed to the formation of hydrogen bonding. This point is also confirmed by observing the vibrational frequencies due to $\nu(\text{CO})$, $\nu(\text{OH})$ (phenolic) and $\nu(\text{OH})$ (hydroxamic). The low frequency of these bands indicates hydrogen bonding [17]. Thus, it is concluded that the structure-I (**Figure-1& 2**) represents the most probable configuration of AIBHA-H₂ and the ligand AIBHA (**Figure-2**):



(Figure-1)

[Hydrogen bonded Structure of ligand-AIBHA-H₂]

(Figure-2)

[Deprotonated Structure of ligand-AIBHA]

The main infrared bands and their assignments are discussed here. The band at 3275 cm^{-1} due to ν (N-H) mode remains intact in complexes indicating the non-participation of N-H group of hydroxamic acid in coordination with the metal ion. The ν (C=O) stretch

shifts to lower in the complexes by $15\text{-}25\text{ cm}^{-1}$, suggesting involvement of carbonyl oxygen in coordination [18]. This is further supported by the appearance of new low intensity bands around $450\text{-}500\text{ cm}^{-1}$ in the spectra complexes due to the ν (M-O) stretch. The ν (O-H) stretch shifted to lower frequency in the complexes by $20\text{-}30\text{ cm}^{-1}$ suggesting coordination of hydroxamic acid group through deprotonated O-H group with metals [19]. The spectrum of the ligand shows two different -C=N bands in the region $1590\text{-}1550\text{ cm}^{-1}$, which is shifted to lower frequencies in the spectra of all the complexes ($1570\text{-}1520\text{ cm}^{-1}$) indicating the involvement of -C=N nitrogen in coordination to the metal ion. Assignment of the proposed coordination sites is further supported by the appearance of medium bands at $450\text{-}400\text{ cm}^{-1}$ which could be attributed to ν (M-N). The medium and sharp band located at 1300 cm^{-1} in the ligand attributed due to the deformation vibration of alcoholic ν (OH) disappears in all the complexes suggesting the deprotonation of the alcoholic OH and coordination of alcoholic O to the metal ion. This is further supported by the appearance of new low intensity bands around $420\text{-}465\text{ cm}^{-1}$ in the spectra complexes due to the ν (M-O) stretch.

In case of aqua-complex the appearance of one more band in the range of $750\text{-}830\text{ cm}^{-1}$ due to rocking and wagging mode of vibrations indicated that water (H_2O) was present in the coordination sphere. In case of ammine complex separate band for (N-H) of coordinated NH_3 was not obtained due to overlapping of ν (N-H) vibration.

The coordination through N donor monodentate ligands, e.g. ammonia, pyridine, phenyl isocyanide and different picolines have been further confirmed by the appearance of ν (M-N) band at $455\text{-}535\text{ cm}^{-1}$.

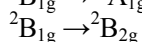
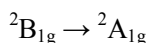
Table -1: Analytical and physical data of the studied Cu-complexes:

Compound	Colour	Mol. Mass	Found %			μ_{eff}	Λ_{M}
			C	N	Cu		
1. $[\text{CuL}(\text{H}_2\text{O})_2]$	deep green	331.54	43.43	08.44	19.16	1.98	22
2. $[\text{CuL}(\text{NH}_3)_2]$	green	329.54	43.69	17.00	19.28	1.90	16
3. $[\text{CuL}(\text{C}_9\text{H}_7\text{N})_2]$	deep green	589.54	61.06	09.49	10.78	1.96	18
4. $[\text{CuL}(\text{C}_6\text{H}_5\text{NC})_2]$	parrot green	501.54	57.42	11.16	12.67	1.96	14
5. $[\text{CuL}(\text{C}_5\text{H}_5\text{N})_2]$	light green	453.54	58.21	12.34	14.01	2.10	15
6. $[\text{CuL}(\alpha\text{C}_5\text{H}_4\text{NCH}_3)_2]$	light green	481.54	59.81	11.63	13.19	2.04	26
7. $[\text{CuL}(\beta\text{C}_5\text{H}_4\text{NCH}_3)_2]$	faint green	481.54	59.81	11.63	13.19	2.00	24
8. $[\text{CuL}(\gamma\text{C}_5\text{H}_4\text{NCH}_3)_2]$	green	481.54	59.81	11.63	13.19	1.94	16

[Mol. Mass is in u, μ_{eff} is in B.M. and Λ_{M} is in $\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$]

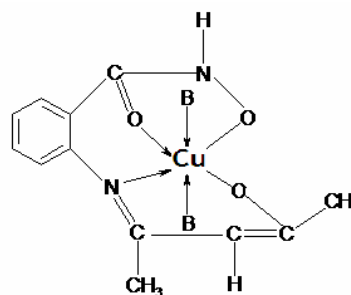
Electronic Spectral Studies:

The study of magnetic and electronic spectra data is quite informative in characterizing the geometry of the complexes. The UV-visible spectrum of the AIBHA ligand and its complexes were recorded in DMSO solution in the range of 200 to 800 nm regions. The absorption spectrum of free ligand consist of an intense bands centered at 366 nm attributed to $n \rightarrow \pi^*$ transitions of the aldimine group. Another intense band in higher energy region of the spectra of the free ligand was related to $\pi \rightarrow \pi^*$ transitions of benzene rings. These transitions are found also in the spectra of the complexes, but they shifted towards lower. Further, the d-d frequencies, confirming the coordination of the ligand to the metallic ions transition of the Cu (II) complexes exhibited two bands at 9900 - 10100, 14500 -15120 and 23500 - 23900 cm^{-1} , assigned to



transitions respectively, which suggesting an approximate distorted octahedral geometry of the ligand around the metal ion in the complexes that was confirmed by the observed magnetic moment value 1.94 to 2.10 B.M. These higher values of magnetic moment than the spin – only value (2.83B.M.) for one unpaired electron and may be ascribed to substantial orbital contribution to the moment [20]. The monomeric nature of the complexes was confirmed by their magnetic moment values.

On the basis of the forgoing evidences, the proposed octahedral geometry or structure for the complexes is presented in figure-3.



(Figure-3)

[Proposed distorted octahedral structure of $[\text{CuLB}_2]$ complexes]

(L= AIBHA & B = Monodentate secondary ligands)

CONCLUSIONS

The ligand AIBHA and its eight complexes with Cu^{2+} ion have been synthesized and characterized. The IR spectral studies revealed that the ligands acted as a dibasic tetradentate ($\text{OO}'\text{NO}$ donor) in all the complexes. The magnetic, conductance and electronic spectral studies revealed that the complexes were paramagnetic with distorted octahedral geometry. All the investigated complexes were non-electrolyte and monomer.

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