



SYNTHESIS AND CHARACTERIZATION OF COPPER COMPLEX

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Abstract: In this study (hydroxyimino) (2-phenyl (1, 2, 3, 4-tetrahydroquinazolin-2-yl) methane was synthesized by reaction of 2-(hydroxyimino)-1-phenylethan-1-one with 2-aminobenzylamine. The ligand is further reacted with copper chloride to get copper complex [CuL(HL)].H₂O. The ligand and complex [CuL(HL)].H₂O were elucidated on the basis of elemental analysis, FT-IR-1H, mass spectra, NMR spectra and TEM.

Keywords: 1, 2, 3, 4 – tetrahydroquinazoline, 2-aminobenzylamine, copper chloride.

INTRODUCTION:

The chelating ligands are polyfunctional molecules which can engage heavy metals in an organic sphere. Many types of Schiff base ligands are known and the properties of their metal chelates have been investigated [1, 2, 3]. Acyclic ligands containing nitrogen, oxygen and sulphur donor atoms in their structures can act as effective chelating agents for transition and non-transition metal ions. The importance of the coordination compounds in biological structure, increasing properties of the application and utilization of these compounds as agents has given rise to an intensification into the investigation of the complexes.

New synthesis methods need to be combined with new techniques in the term to “enabling technologies for organic synthesis” to achieve rapid incorporation into industrial processes. Typical enabling technologies are microwave assistance 3-new solvent systems, continuous flow reactors and immobilization of chemically active species such as reagents and homogenous catalysts^[4]. Oximes, an important class of chelating agents have found numerous applications as highly selective reagents for the separation and determination of a number of metal ions.

The formation of Schiff bases by condensation of amines with aldehydes and ketones have been extensively studied because of their biological and structural importance arising from their specific and selective reactions with metal ions. Many Schiff base derivatives containing substituted oxime have been synthesized, characterized in detail and used for the complexation with transition metal ions in the literature^[5, 6]. α -iminooximes are species like these ligands.

In this study, oxime ligand and its complexes with Cu, was prepared and the compound and its copper complex was characterized by the elemental analysis, mass spectroscopy. FT-IR and NMR size of the ligand is also determined

by TEM. The compounds has also show the secondary bond effects with small size and hence also be called as supramolecular moiety.

MATERIALS AND METHODS:

All chemicals were purchased from Merck and Sigma and used without further purification. Melting points were determined on a BUCHI-B-540 digital melting point apparatus and are uncorrected. ¹H-NMR solution spectra in DMSO-D₆ was recorded at 295.3 K on a Bruker avance II 400 NMR spectrometer with TMS as reference. The IR spectra was recorded on FTIR-8101 A using KBr pallets in the range of 400-4000 cm⁻¹. C, H, N, O elemental analysis was carried out on Eassuperuser elemental analyser system, GmbH, Access, Vario EL super user, NEERI. As well as mass spectroscopy and TEM were also carried out at SAIF, Punjab University, Chandigarh.

Preparation of Ligand:

(Hydroxyimino) (2-phenyl (1, 2, 3, 4-tetrahydroquinazolin-2-yl) methane was prepared by the usual condensation method^[7]. 2-aminobenzylamine (1.222g) was dissolved in 30 ml absolute ethanol and added to solution of 2 (Hydroxyimino)-1-phenylethan-1-one (1.4930 g) in 30 ml absolute ethanol. The reaction mixture was stirred for one and half hour and then left for 48 hrs at room temperature. The crystalline reaction product was filtered and washed with cold ethanol. (Hydroxyimino) (2-phenyl (1, 2, 3, 4-tetrahydroquinazolin-2-yl) methane is soluble in acetone, THF, DMSO, DMF and pyridine and slightly soluble in CHCl₃, EtOH and MeOH.

Yield → 1.87 g and Melting Point → 142°C
(Decomposition point)

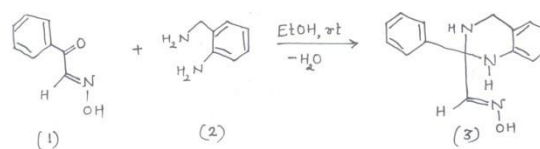


Fig. 1 : Preparation of Ligand

- 1) 2 (Hydroxyimino) -1-phenylethan-1-one
- 2) 2-aminobenzylamine
- 3) (Hydroxyimino) (2-phenyl (1, 2, 3, 4 - tetrahydroquinazolin-2-yl) methane

Synthesis of [CuL(HL)] . H₂O complex

Metal and ligand was taken in the molar ratio 1:2 for the reaction. CuCl₂ was dissolved in minimum quantity of distilled water and ligand was dissolved in minimum quantity of DMF separately. Then the solution was warmed in waterbath. Both the solutions were mixed in warm condition with constant stirring. The mixture was digested for few minutes with constant stirring. Aq. Ammonia (50%) was added drop by drop which formed precipitate at pH 6-7 and the solid complex collected was washed with hot double distilled water to remove excess of metal present in the reaction.

[CuL(HL)] . H₂O is soluble in CHCl₃, DMF, DMSO and slightly soluble in acetone and dioxane. Melting point - 138°C (decomposition point)

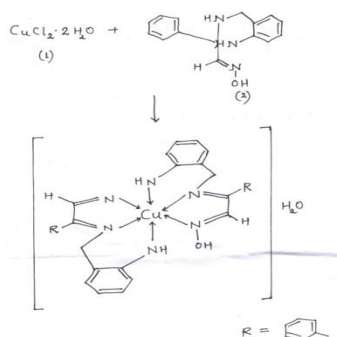


Fig.2: Preparation of Complex [CuL(HL)] . H₂O

- 1) Copper chloride dehydrate
- 2) (Hydroxyimino) (2-phenyl (1, 2, 3, 4 - tetrahydroquinazolin-2-yl)
- 3) [CuL(HL)] . H₂O

RESULT AND DISCUSSIONS:

Table - 1A

Elemental analysis of ligand and copper complex

Compound Molecular formula	Colour	Molecular weight	Found (Calculated)			
			C	H	N	M
H ₂ L C ₁₅ H ₁₅ N ₃ O	Pale yellow	253.31	70.89 (71.12)	6.09 (5.97)	16.56 (16.59)	-
[CuL(HL)] . H ₂ O C ₃₀ H ₂₉ N ₆	Dark Brown	585.16	62.24 (62.24)	4.00 (4.00)	14.04 (14.04)	10.50 (11.00)

O ₃ Cu	wn		70)	92)	40)	40)
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Mass Spectral Studies:

Mass spectra of ligand and complex were determined. An attempt was made to determine the molecular mass of ligand and complex [CuL(HL)].H₂O by means of LC-mass spectral studies. In the ligand, the molecular ion peak was observed at m/e 253.8.

In the spectra of complex [CuL(HL)].H₂O, the strong peaks at m/e 568.2 and 567.2 can be related to [CuL(HL)]⁺ and [CuL(HL)+1]⁺ ions respectively.

Infrared - spectral studies:

IR-spectral bands of H₂L is presented in Table 1B. In this ligand the functional groups >N-H, O-H, C=N and N-O are readily identified from the infrared spectra.

Ligand shows peaks at 3261 cm⁻¹ and 3399 cm⁻¹ attribute to the □ (N-H) vibration. The □ (O-H) band assigned to the stretching hydrogen motions in the intramolecular O-H ... N hydrogen bond appears broadened with a maximum in the range of 2760.34 cm⁻¹, while the bands observed at 1605 cm⁻¹ and 943.50 cm⁻¹ were attributed to the oxime □ (C = N) and □ (N-O) group stretching vibrations respectively. These absorptions are in good agreement with the values reported for similar compound [8, 9, 10].

Table - 1B

Characteristic infrared bands (cm⁻¹) of the ligand and complex (KBr pallets)

Compound Molecular formula	NH/NH ₂	H ₂ O /O-H	C = N			
			Oxime	Imine	N-O	M-N
H ₂ L	3261 m, 3319 m, 3399 sh	(2760-34) b	1605 sh		943.5 sh	-
[CuL(HL)].H ₂ O	3319 m, 3319 b	3057 m, 7 m, sh	1433, s, sh	1613, s, sh	884 m, sh	465 w

W : weak, m : medium, s : strong, b : broad, sh : sharp

In the IR spectrum of copper complex the □ (O-H) bands due to water molecule was assigned at 3057 cm⁻¹. The very broad bands prohibit the appearance of other bands in the region. Complex shows weak and sharp stretching band centered in the 1453-1613

cm⁻¹ range corresponding to the $\nu(\text{C}=\text{N})$ of the azomethine of imine. In IR spectra of ligand, disappearance of this band is further evidence for the tetrahydroquinazoline ring formation. After complexation, the appearance of the new $\nu(\text{C}=\text{N})$ stretching band, the shift of the $\nu(\text{N}-\text{O})$ bands to the upper frequency region and the shift of $\nu(\text{C}=\text{N})$ of oxime bands to the lower frequency region, in the IR spectrum of copper complexes may be attributed to N, N-chelation. These observations indicate the involvement of both the nitrogen atoms of the azomethine (C=N) of imine group and the azomethine (C=N) of oxime group of the coordination with the metal. In addition, the non-ligand bands at 465 cm⁻¹ are tentatively assigned to $\nu(\text{M}-\text{N})$ stretching vibrations.

NMR Analysis and Structure Determination:

The ¹H-NMR spectra (400 MHz) of the ligand is recorded in deuterated dimethylsulfoxide (DMSO) as presented in Table 1C.

The ligand H₂L shows signals corresponding to D₂O exchangeable-NOH (Oxime, 1H)-NH (tetrahydroquinazoline ring nitrogen-3, 1H) protons at δ 10.81–10.91 ppm (s), 6.64–6.71 ppm (s) and 2.50 ppm respectively. For the HC = N proton, a single occurs in the 7.44–7.45 ppm region. The integration of the ¹H-NMR spectrum suggests the presence of a range of proton resonances between 6.45 and 7.57 ppm because of the resonance of 9- phenyl-proton of H₂L.

1, 3-unsaturated tetrahydroquinazolines shows chain-ring-chain tautomeric equilibria containing 1 cyclic form and 2 linear forms. The chain form is easy to differentiate from the ring form based on the proton and carbon signals of SP₂-hybridized C = N carbon and proton attached to it [11, 12]. In addition the ring form can be easily identified from magnetically non-equivalent methylene proton. Tetrahydroquinazoline derivate H₂L has an AB system centre at δ 3.57 ppm, J=17.0 Hz

These signals are in good agreement with values reported for similar compound [13, 14] and more evidence for tetrahydroquinazoline ring formation.

Table-1C

¹H-NMR spectral data (δ ppm) and the coupling constants (Hz) of H₂L in DMSO D₆

Compound Molecular formula	-CH ₂	OH	N H ₂	NHf	Phenyl	H-C=N
(H ₂ L)	3.57 AB syst em	10. 81 S, 1H	-	2.99 - 3.17 b,	6.45 td, J =7.6, 1H	7.4 2s, 1H

	J = 17.0 , 2H			w, 1H 6.60 s, sh, 1H	6.72 t, J=7. 0, 2H 6.90 td, J=7. 2, 1.6, 1H 7.23 t, J=7. 6, 1H; 7.31 t, J=7. 6, 2H 7.57 d, J=7. 2, 2H	
[CuL(HL)]. H ₂ O C ₃₀ H ₂₀ N ₆ O ₃ Cu	3.76 m, 4H	8.1 1 S, 1H	-		7.62 m, 18H	6.9 2s, 2H

(s: Singlet, d : doublet, t : triplet, m : multiplet, b: broad, w: weak, sh: sharp, C : COCL₂ f: D₂O exchange)

Copper complex shows signals corresponding to D₂O, exchangeable-NOH (oxime, 1H), -NH (1H) protons at 7.13–7.41ppm region. The integration of the ¹H-NMR spectrum suggests the presence of a range of proton at 7.61 ppm because of resonance of phenyl proton of H₂L.

CONCLUSION:

The complexes [CuL(HL)].H₂O is brown in colour and is soluble in DMSO and DMF and insoluble in acetone and alcohol. It has decomposition temperature at 138°C. The complex is crystalline in nature. By performing the study of elemental analysis IR spectra, NMR spectra and TEM complexes are found to be have octahedral geometry. Spectral studies also shows secondary bonding in complexes such as hydrogen bonding. TEM shows small size of complex i.e. 120 nm. Hence the ligand and complex are supramolecular complexes. Tetraquinazolines are used as inhibitors of cyclin - dependent kinases. This tetraquinazoline compound also exhibit biological activity.

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