# Part III: Transition Metal Complexes of 2-Pyridyl Amino Derivatives: Synthesis of Copper-Complexes and their Characterization

## III.1: Introduction

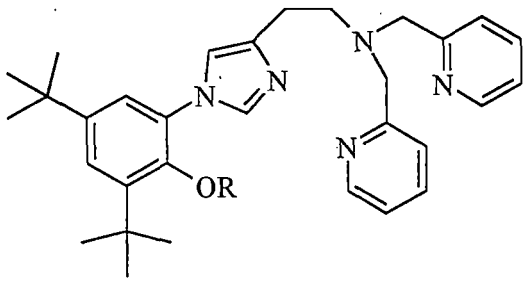
The chemistry of copper (II) carboxylate complexes, especially with *N*-donor ligands, has been extensively studied over the past few decades[1]. Certain complexes have shown properties important for application in diverse areas such as pharmaceuticals, fungicides, catalysts, gas occlusion compounds, and solvent extraction process. Moreover, the attention of, bioinorganic chemists has been directed towards the synthesis and characterization of new copper (II) carboxylates with *N*-donor ligands to model the active sites in metallozymes.[2]

Copper (II) carboxylates containing different ligands originates from the fact that compounds of this type can potentially be used as wood preservatives. Nina Lah *et al.*[3] prepared compounds with increased fungicidal activity.[4]

Cytochrome *c* oxidase is the terminal respiratory enzyme that catalyzes the reduction of dioxygen to water and couples this redox reaction to the membrane translocation of protons for subsequent use in ATP synthesis.[5] The oxygen binding / reduction site is comprised of a heme (heme $a_3$) and a copper ($Cu_B$) in close association. Recent X-ray crystallographic[6] and biochemical[7] studies reveal that one of the copper-bound histidines is covalently linked to a tyrosine through a post-translationally modified cross-link between $C_6$ of Tyr244 and the ε–nitrogen of His240.The His-Tyr moiety is proposed to either function in a structural role[8] or provide an electron and a proton during the $O_2$-reduction cycle.[9] There are a few reports about syntheses and physicochemical investigations of organic models for the imidazole-phenol moiety [10], yet studies of copper complexes of the latter have not been described. Karlin *et al.* [11] reported the first examples of Cu (I) and Cu (II) complexes possessing in imidazole-phenol cross-link, their X-ray structures, and initial chemical insights.

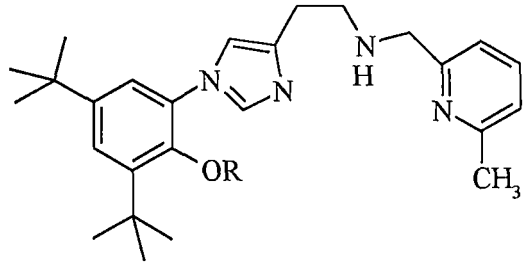
The ligands $L^{N4}OR$ and $L^{N3}OR$ were designed to have an imidazole-phenol (or anisole) cross-link with either a tetra- or a tri-dentate pyridylalkylamine-containing

chelate, as shown, having the advantage that they had previously studied copper-dioxygen chemistry of close analogues.[12] Syntheses of these ligands and various copper complexes had been achieved. In (**1**), the Cu (I) geometry is distorted trigonal pyramidal with three aromatic nitrogens in the basal plane, while the Cu (II) ion in (**4**) is pentacoordinate, having ligation from the three nitrgens of the chelate plus methanol and perchlorate donors.




R=H : $L^{N4}OH$

$[Cu^{I}(L^{N3}OH)]B(C_6F_5)_4$ (**1**)

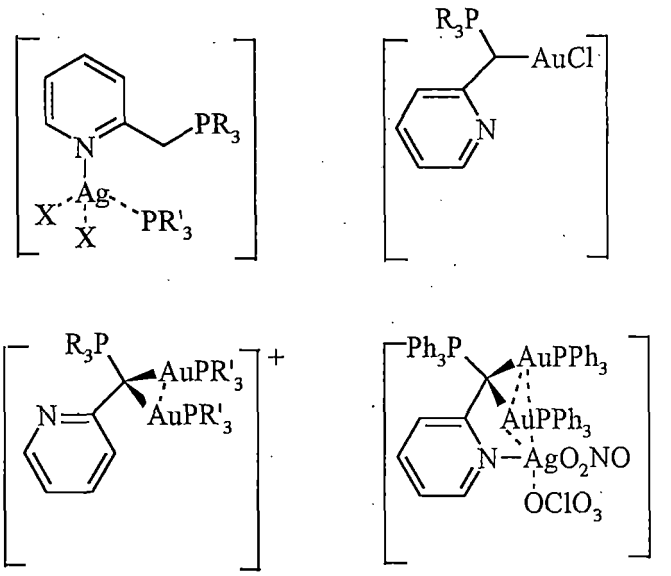



R=H : $L^{N3}OH$

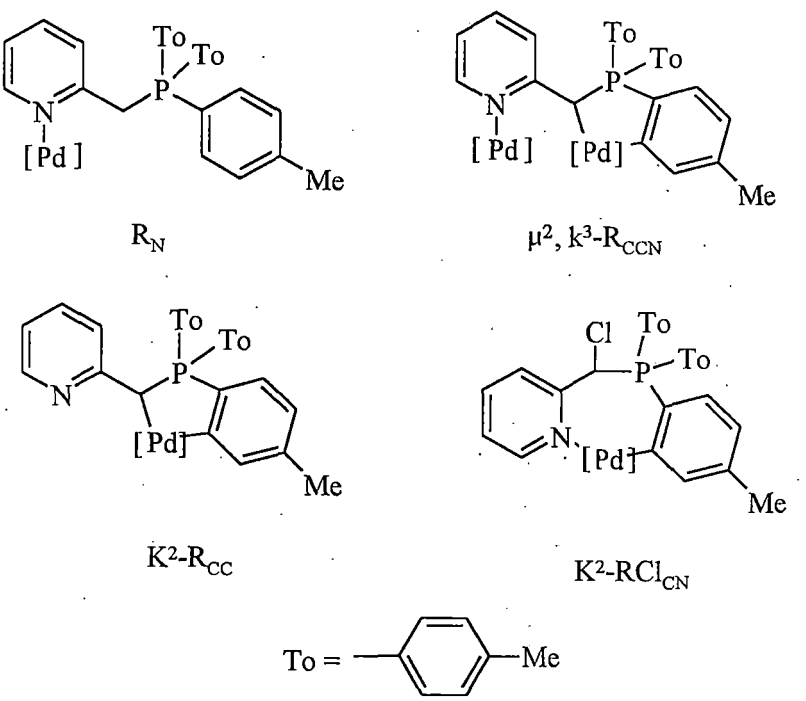
$[Cu^{II}(L^{N3}OH)(MeOH)(OClO_3)]ClO_4$ (**2**)

Vicente *et al.*[13] reported the synthesis and structure of mono-, di-, and tri-, homo- and heteronuclear Au (I), Ag (I), and Cu (I) complexes derived from phosphonium salts $[R_3PCH_2(Py\text{-}2)]X$ [R=Ph, $C_6H_4Me$-4(To), Py =pyridine; X = $ClO_4$, $CF_3SO_3$].[14] These cationic ligands can coordinate through the nitrogen and also, after single or double deprotonation, through the methylene carbon atom. Both donor atoms can bridge up to three metal centers, allowling metal-metal interactions (Scheme 1). The strong tendency of palladium to give *ortho*-metalated complexes and the possibility of preparing Pd (I) and –(IV) complexes move them to extend the study of the coordination ability of these cationic ligands to palladium. They also show that a third coordination mode is also possible after *ortho*-metalation of one of the aryl groups. In (Scheme 2) they represented all modes of coordination found in the palladium complexes reported here, along with the notation used. This notation gives the general symbol R to the skeleton of the phosphonium salt, or RCl to the chlorinated salt, and the atoms appear as subscripts. The k notation is used to indicate the number of coordinated atoms.

**Scheme 1**



**Scheme 2**



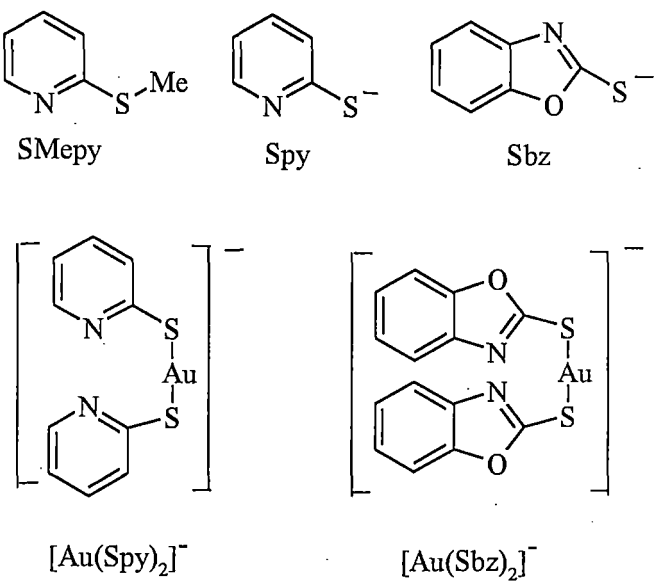

Interest in the study of thiolato complexes is based both on their use as models for the structure, bonding, and reactivity of metallo enzymes and on the structural diversity they display.[15] Heterocyclic thiolato complexes have found interesting applications in analysis, manufacture of polymers, medicine, or industry.[16] In particular, thiolatogold(I) complexes, such as the commercial antiarthritics myocrisin, allochrysine, solganol, auranofin, are among the most important antiarthritic

compounds.[16b, c, g] In addition, solganol has in vitro inhibitory effects on Human inmunodefiency Virus1, which is the etiologic agent of AIDS,[16h] and auranofin was found to be highly cytotoxic to tumour cells[16j] and active against i.p. P388 leukemia.[16j]

Furthermore, 2-pyridinethionato and related ligands can coordinate up to three metal centers at short distances, thus offering the possibility of studying attractive metal-metal interactions, which for $d^{10}$ systems have attracted considerable attention.[17] Vicente *et al.*[17a] found that 2-pyridyl-substituted phosphorous ylides, in which the NCC skeleton is similar to that of the NCS moiety present in the systems can lead to loose $[Au_3]^{3+}$, $[Au_2Ag]^{3+}$, and $[Au_2Cu]^{3+}$ clusters displaying short Au...Au, Au...Ag, or Au...Cu contracts.

Vicente *et al.*[18] reported on the synthsis and charaterization of new mono- and di-nuclear complexes of gold (I), silver (I), and palladium (II) derived from 2-(methyl-thio) pyridine (SMepy), pyridin e-2(1H)-thione(HSpy), benzoxazole-2(3H)-thione (HSbz) (Scheme 3), for which few precedents are known.[19] As far as they were are, only one Rh (I) complexes containing 2-(methylthio)pyridine has been reported, but was not isolated.[20]

**Scheme 3**



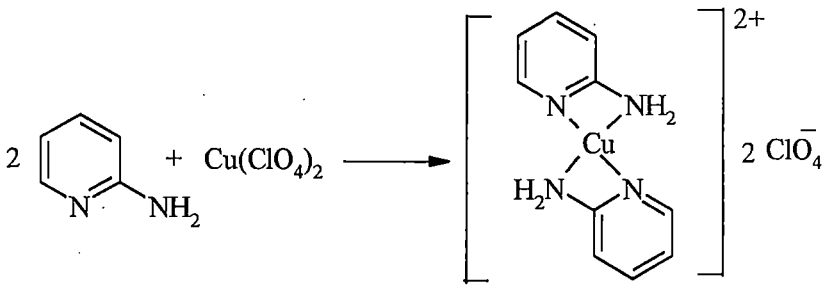
## III.2: Present work: Objectives, Results and Discussion

As mentioned in the introduction of this part that copper (II) carboxylate complexes, especially with *N*-donor ligands have drawn interests from the bioinorganic chemists in view of the synthesis of models of active sites in metalloenzymes. A number of copper (II) carboxylate complexes with 2-amino pyridine ligands have been synthesized and characterized in the recent years. Secondly, analogues of 2-thiolato pyridines have been employed as ligands to prepare gold (Au) and silver (Ag) complexes, which have found interesting applications in medicine and manufacture of polymers. In addition, they are found to be highly cytotoxic to tumors cells.

Considering the importance and versatile applications of aminopyridines and thiolato pyridines as the ligands in forming various metal complexes, we undertook studies on the syntheses and characterization of some copper (Cu) and silver (Ag) complexes with 2-aminopyridine as the ligands. Their synthesis and characterization data along with discussion are presented here. All complexes reported in this part were prepared using acetone as the solvent. The complexes are insoluble in acetone and therefore addition of diethyl ether to precipitate the resulting complexes from solvent was not necessary.[18] The reactions leading to complexes (**1-5**) were carried out using a 1:2 molar ratio of the reagents [$Cu(ClO_4)_2$ : Ligands = 1:2]. Complexes (**1**), (**2**) and (**3**) [Scheme 4, 5 and 6] were obtained in high yields (80%, 90% and 68% respectively). Complexes (**4**) and (**5**) were, however, precipitated out at pH 4-5 of the solution, which was maintained by passing of dry ammonia through the solution of the reaction mixture. The yields of complexes (**4**) and (**5**) was obtained in 33% and 25% respectively. The structures of complexes (**1-5**) have been assigned based on comparison with the reported structures derived from pyridine thiolato compounds [18] and the spectral data obtained so far (IR and UV-Vis spectra). The IR spectra of complexes (**2-5**) show two strong bands in the 1600-1550 $cm^{-1}$ regions, which are assigned to $\nu_{CC}$ and $\nu_{CN}$ of the pyridine ring. Again all complexes show two strong bands around 1100 ($\nu_{ClO}$) and 620 ($\nu_{OClO}$), assignable to perchlorate anion.[18] These IR data support the formation of complexes as proposed. On the other hand, UV spectrum of complexes (**2**), (**3**) show $\nu_{max}$ 297, 308 nm and $\nu_{max}$ 298, 308 nm respectively, corresponding to those shown by their precursors 3,4,5,6-tetrahydro-2H-[1,2,α]-bipyridinyl (297 nm) and 4-Pyridine-2-yl-morpholine (296 nm) respectively.

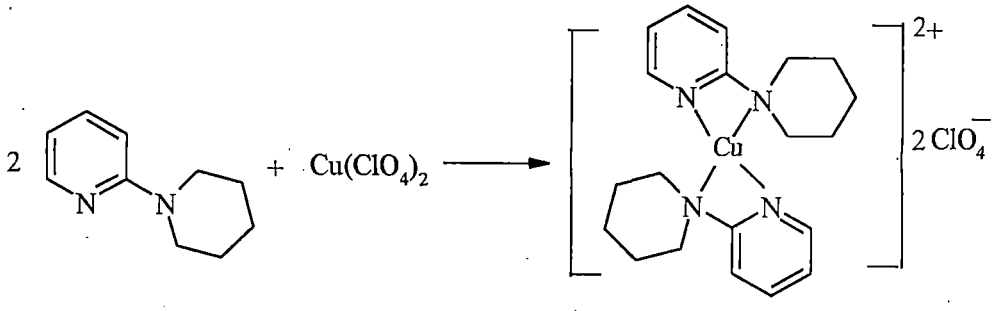
We also attempted preparation of Ag-complexes by using molar ratio of $AgClO_4$ and ligand, but without success.

**Scheme 4**



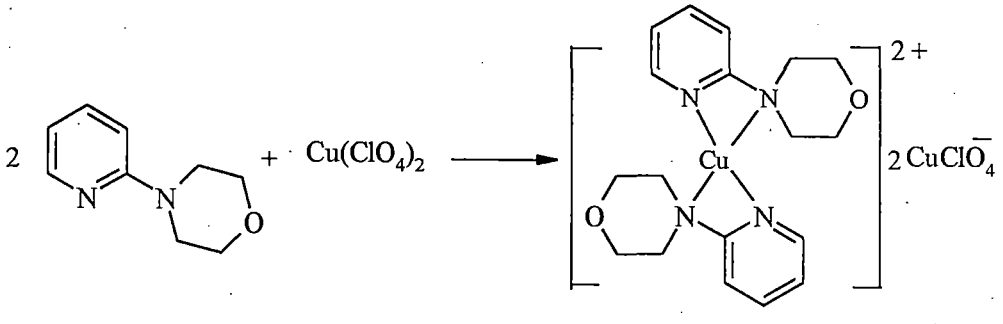
**(1)**

**Scheme 5**



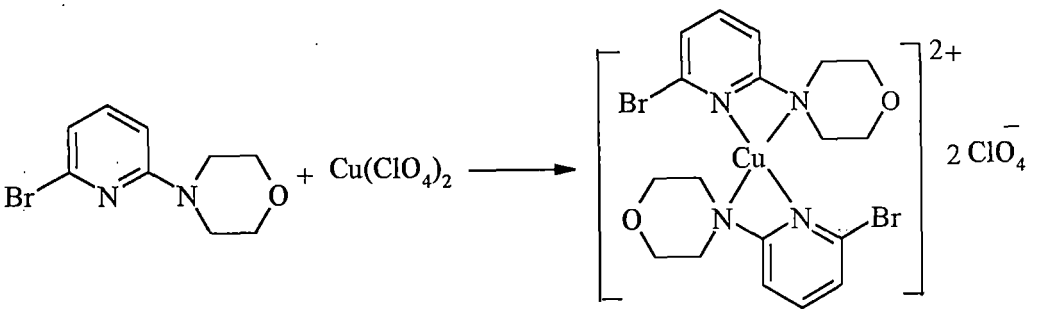
**(2)**

**Scheme 6**



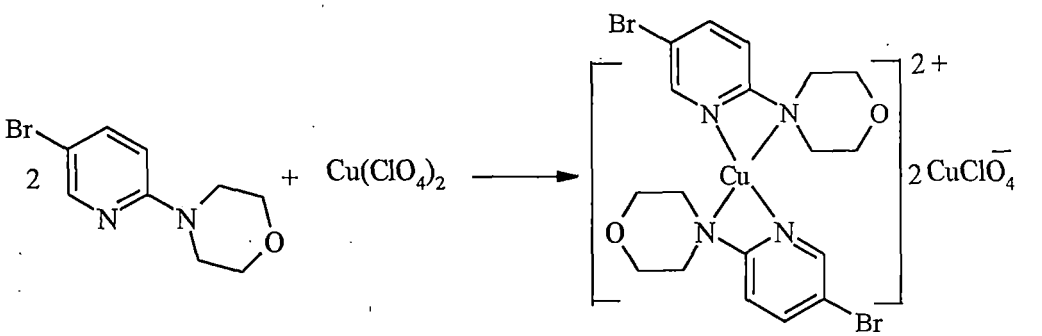
**(3)**

**Scheme 7**



(4)

**Scheme 8**



(5)

In conclusion, an attempt has been made to synthesise some Cu (II) complexes using 2-amino pyridine derivatives as the ligands. The UV-VIS and IR spectra of the solid complexes were consistent with the literature values. Further characterizations are, however, necessary to conclude about their structures. This would be undertaken as a part of future studies.

## III.3: Experimental

### Preparation of copper perchlorate $Cu(ClO_4)_2$

An aqueous solution of basic copper carbonate [$CuCO_3$, $Cu(OH)_2,H_2O$] was neutralized by slow addition of $HClO_4$. Neutralization point was checked by litmus paper. The solution was concentrated by heating and evaporation. The solid residue was then recrystallized to furnish blue crystals, which were collected and kept it for dryness in a desiccator containing anhydrous calcium chloride.

$$CuCO_3, Cu(OH)_2,H_2O + 4HClO_4 = 2Cu(ClO_4)_2 + CO2 + 4H_2O$$

### Preparation of $Ag_2CO_3$

An aqueous solution $AgNO_3$ (2.720 g in 10 ml of water) was added to an aqueous solution of $Na_2CO_3$ (848 mg in 2 ml of water). A yellowish solid precipitate was obtained and filtered off the solution. Pure $Ag_2CO_3$ was collected after washing with water and was dried under vacuum.

$$AgNO_3 + Na_2CO_3 = Ag_2CO_3 + 2NaNO_3$$

### Preparation of $AgClO_4$

An aqueous solution of 2.144 gm. of $Ag_2CO_3$ was neutralized completely by addition of $HClO_4$. Water was removed by azeotropic distillation with benzene. A white solid product is obtained. The silver perchlorate salt was difficult to store as it gradually becomes dark on standing for a day.

$$Ag_2CO_3 + 2\,HClO_4 = AgClO_4 + CO_2 + H_2O$$

### Preparation of copper-2-amino-pyridine complex (1)

To a solution of $Cu(ClO_4)_2$ [131 mg, 0.5 mmol in 5 ml acetone], was added a solution of 2-amino pyridine (94 mg, 1 mmol in 4 ml acetone). A precipitate was settled down momentarily from solution and pH of solution was found 4.34 (by pH meter). After filtration, a solid product was collected.

Yield: 80% (180 mg)

Melting point: 140 °C

UV(MeOH): $\lambda_{max}$ 200, 233, 296.4 nm.

## Preparation of copper complex of 3, 4, 5, 6-Tetrahydro-2H [1, 2'] bipyridinyl (2)

To a solution of $Cu(ClO_4)_2$ in acetone [32 mg, 0.122 mmol in 2.5 ml acetone], a solution of 3, 4, 5, 6-Tetrahydro-2H-[1, 2']-bipyridinyl in acetone (41 mg, 0.25 mmol in 3 ml acetone) was added. A blue precipitate was obtained. The precipitate was filtered and washed with acetone.

Yield: 90% (64 mg)

Melting point: 240 °C (d).

UV (MeOH): $\lambda_{max}$ 204, 237, 297, 308 nm.

IR (Nujol): $\nu_{max}$ 2925.8, 1600.8, 1373.2, 1089.7, 617.2 $cm.^{-1}$

## Preparation of copper complex of 4-pyridin-2-yl-morpholine (3)

To a solution of 4-pyridin-2-yl-morpholine in acetone (65.6 mg, 0.4 mmol in 5 ml acetone), a solution of $Cu(ClO_4)_2$ in acetone (52.5 mg, 0.2 mmol in 3 ml acetone) was added. A greenish precipitate was appeared at pH 5 of the solution. The precipitate was filtered off and washed with little acetone.

Yield: 68% (80 mg).

Melting point: 188 °C.

UV (MeOH): $\lambda_{max}$ 204, 245, 298, 308 nm.

IR (Nujol): $\nu_{max}$ 2925.8, 1577.7, 1373.2, 1083.7, 613.3 $cm.^{-1}$

## Preparation of copper complex of 4-(6-Bromo-pyridin-2-yl)-morpholine (4)

To a solution of $Cu(ClO_4)_2$ in acetone (63 mg, 0.24 mmol in 3 ml acetone), was added a solution of 4-(6-bromo-pyridin-2-yl)-morpholine (116.5 mg, 0.48 mmol in 4 ml acetone) over a period of 30 min. After the addition was complete, dry ammonia was passed into the acetone solution when the pH of the resulting solution was raised. A green precipitate appeared at pH 4. The solid green compound was collected by filtration.

Yield: 33% (59 mg)

Melting point: 160 °C.

UV (MeOH): $\lambda_{max}$ 204, 253, 305 nm.

IR (Nujol): $\nu_{max}$ 2925.8, 1589.2, 1379.2, 1072.7, 607.5 $cm.^{-1}$

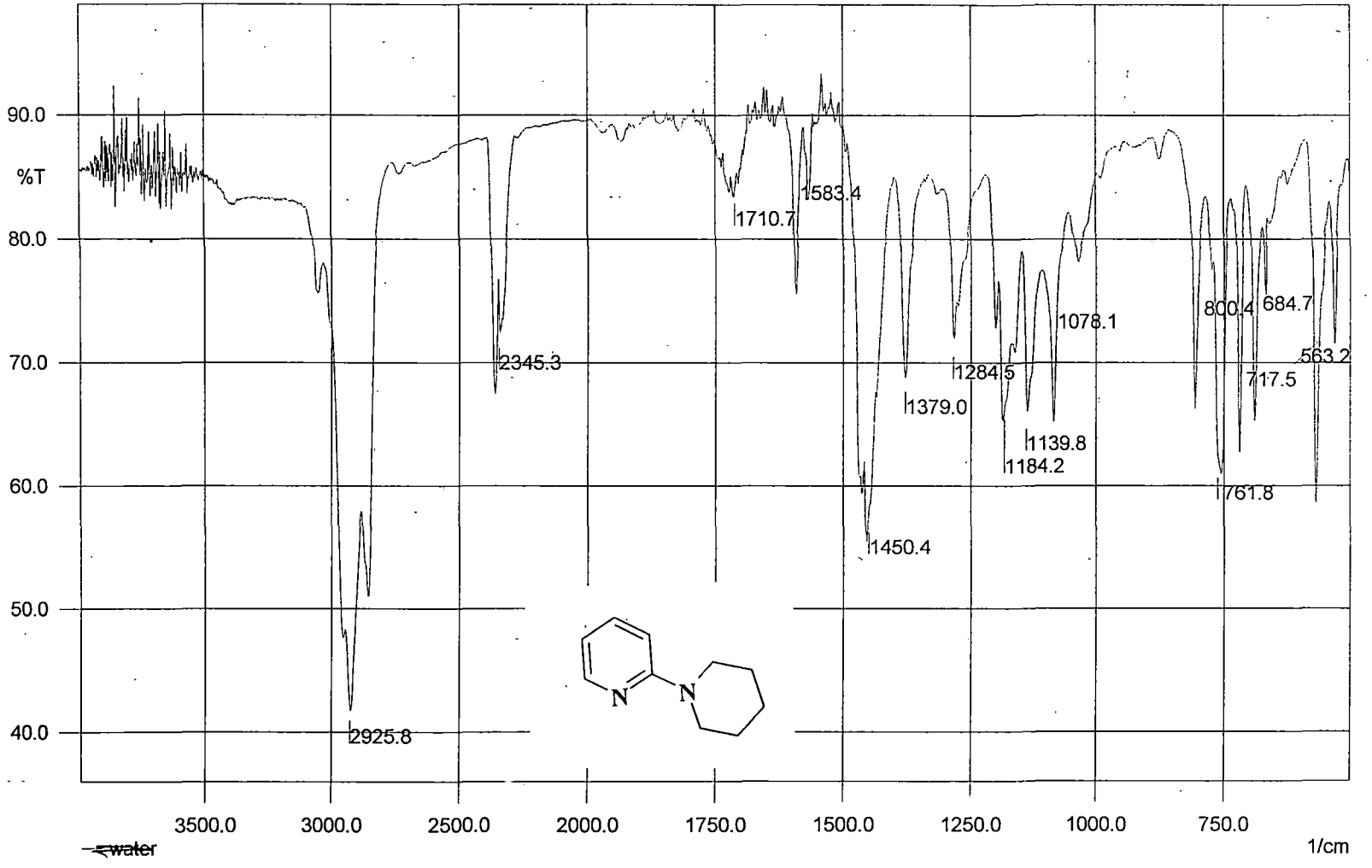
## Preparation of copper complex of 4-(5-Bromo-pyridin-2-yl)-morpholine (5)

To a solution of $Cu(ClO_4)_2$ in acetone (63 mg, 0.24 mmol in 3 ml acetone), was added a solution of 4-(5-bromo-pyridin-2-yl)-morpholine (116.5 mg, 0.48 mmol in 3 ml acetone) over a period of 30 min. After the addition was complete, dry ammonia was passed into the acetone solution when the pH of the resulting solution was raised. A green precipitate appeared at pH 5. The solid green compound was collected by filtration.

Yields: 25% (45 mg)

UV (MeOH): $\lambda_{max}$ 204, 253, 305 nm .

IR (Nujol): $\nu_{max}$ 2925.8, 1588, 1375, 1122.5, 1068, 617.2 $cm.^{-1}$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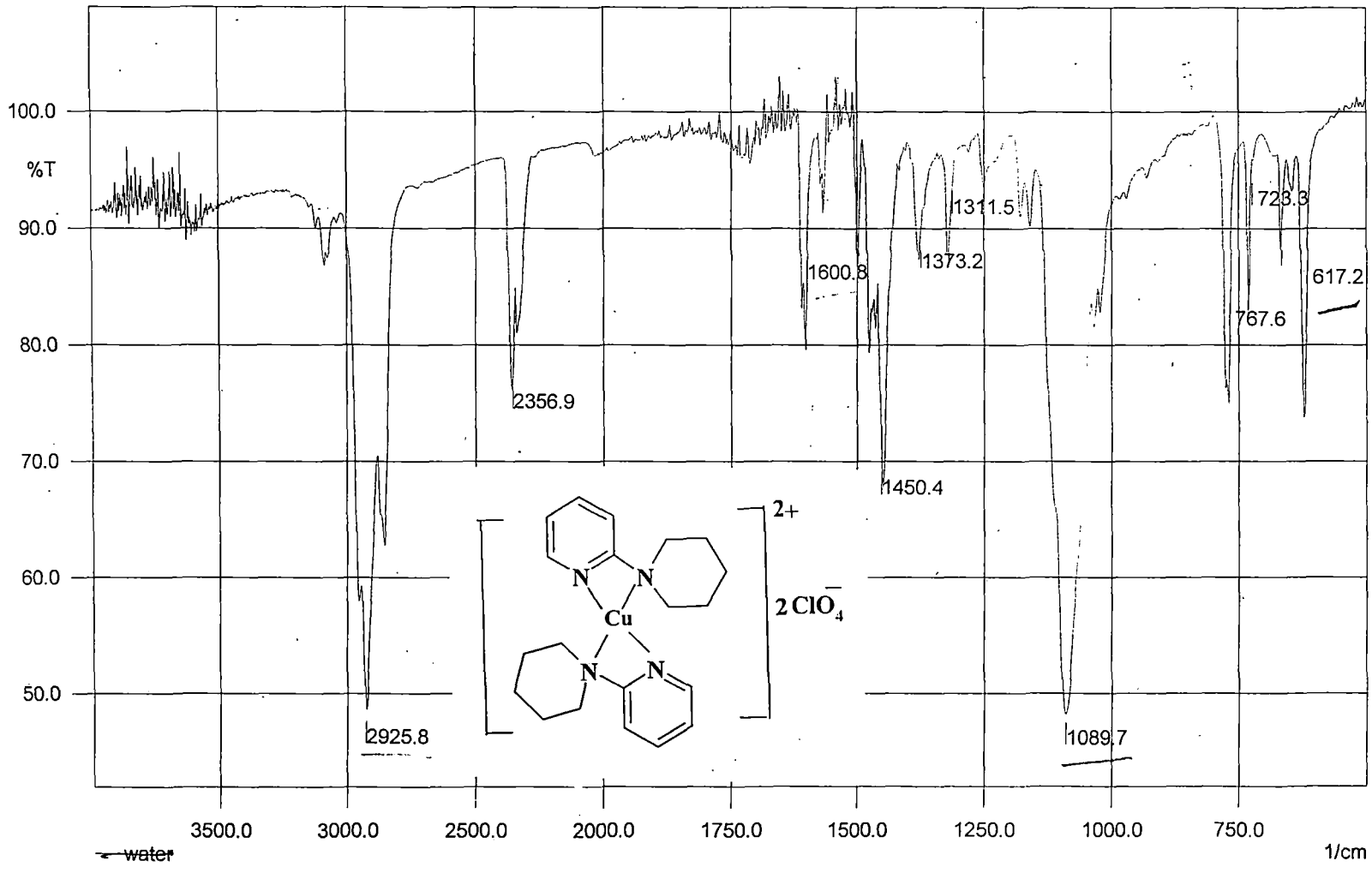
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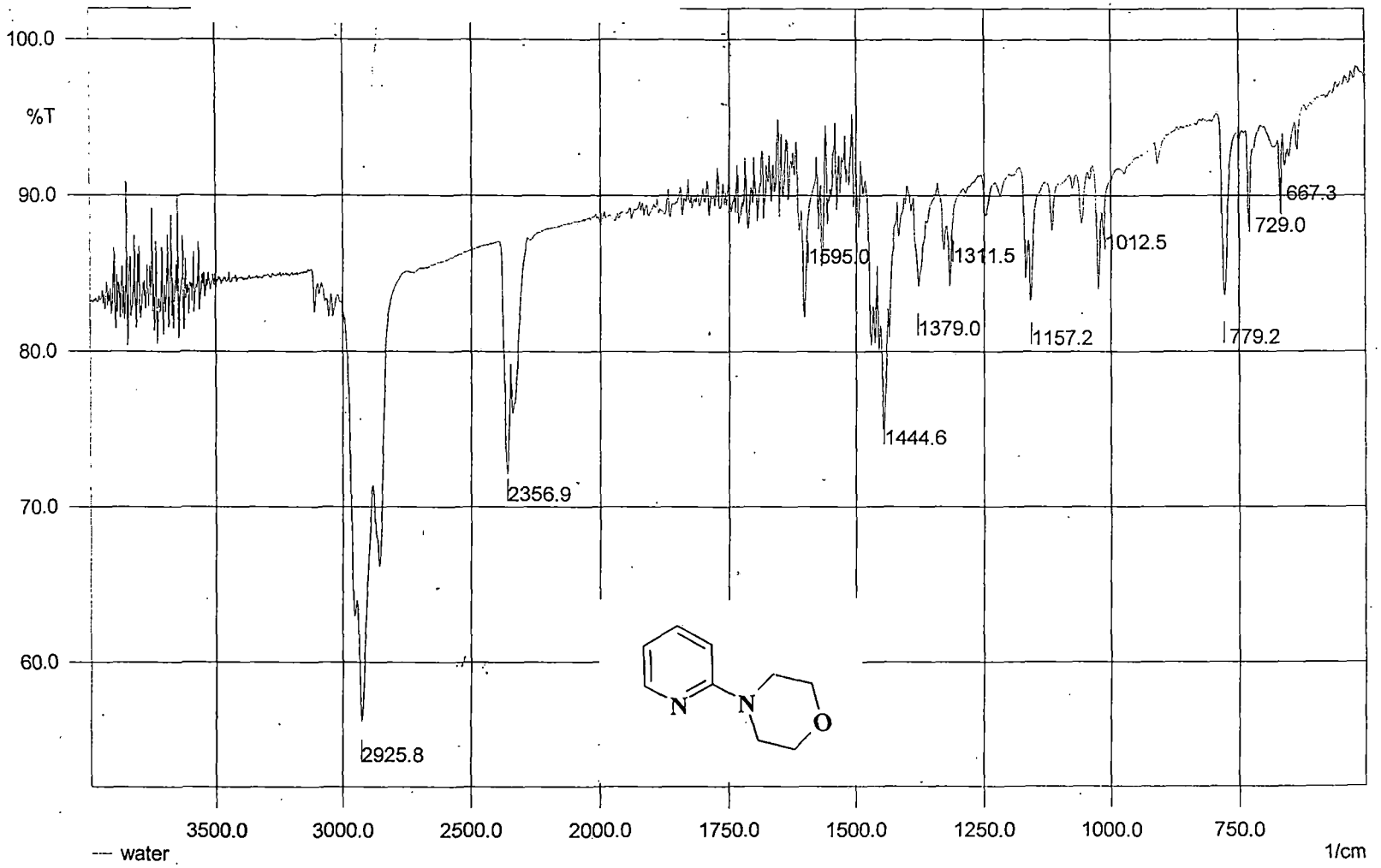
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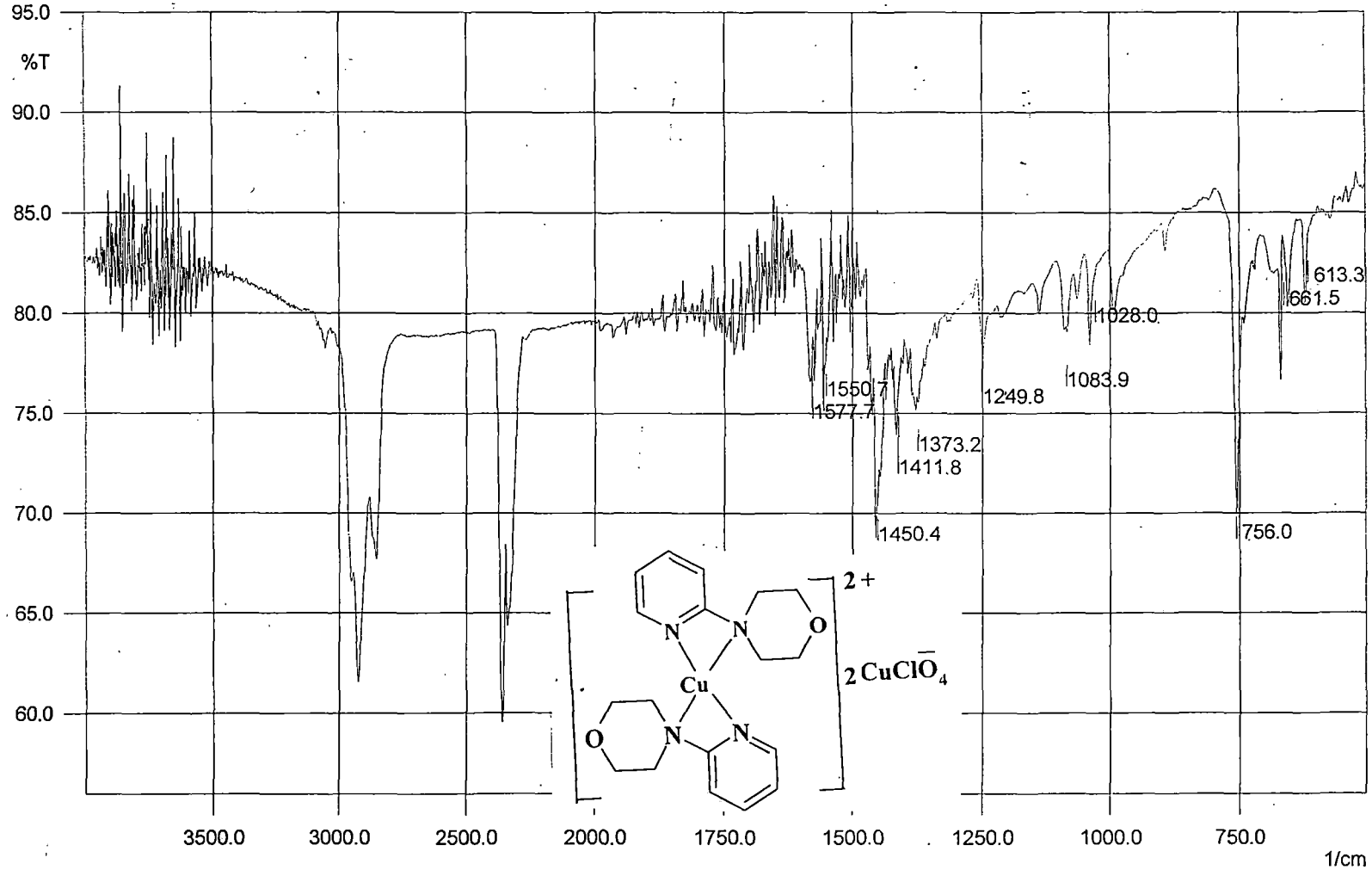
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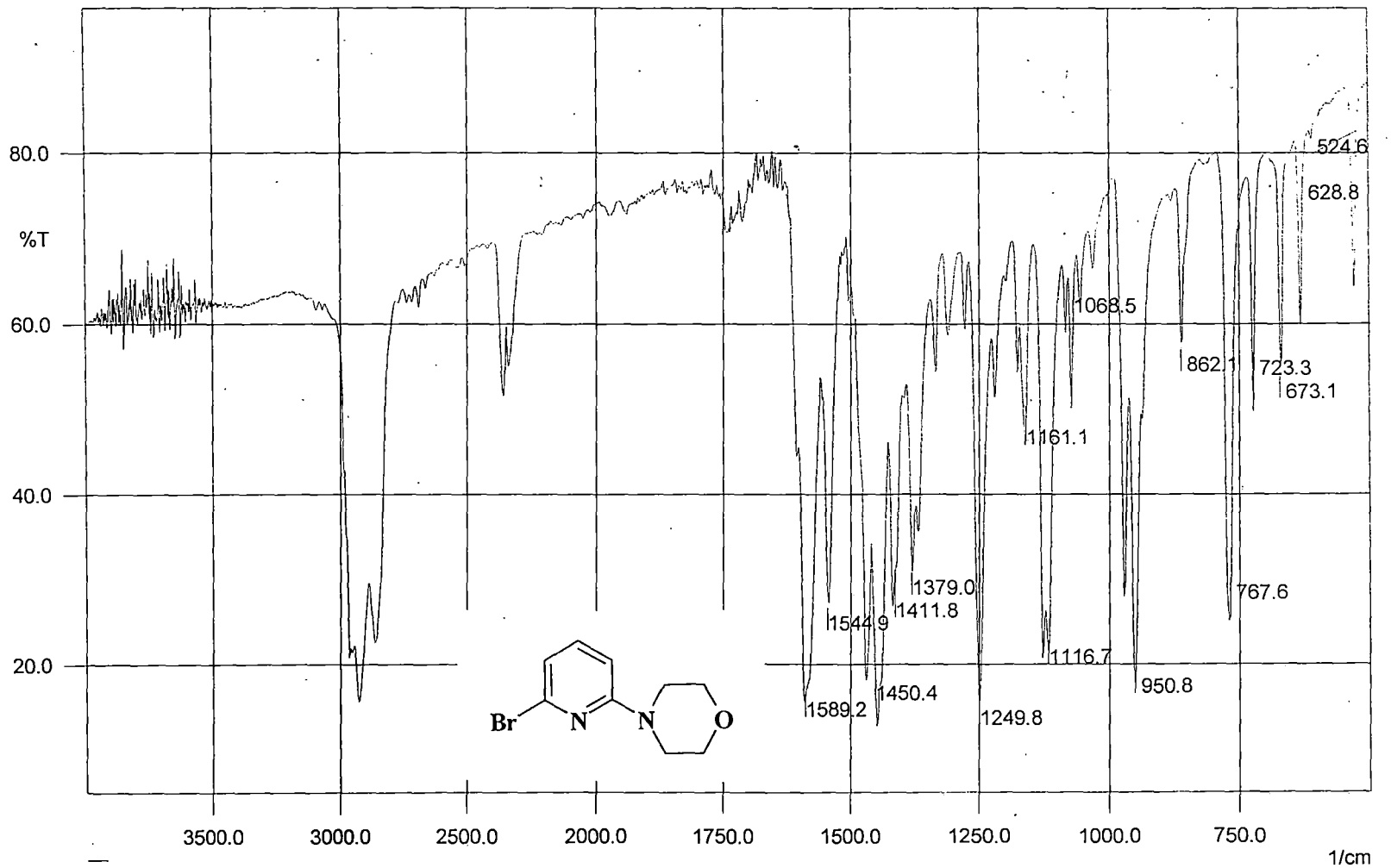
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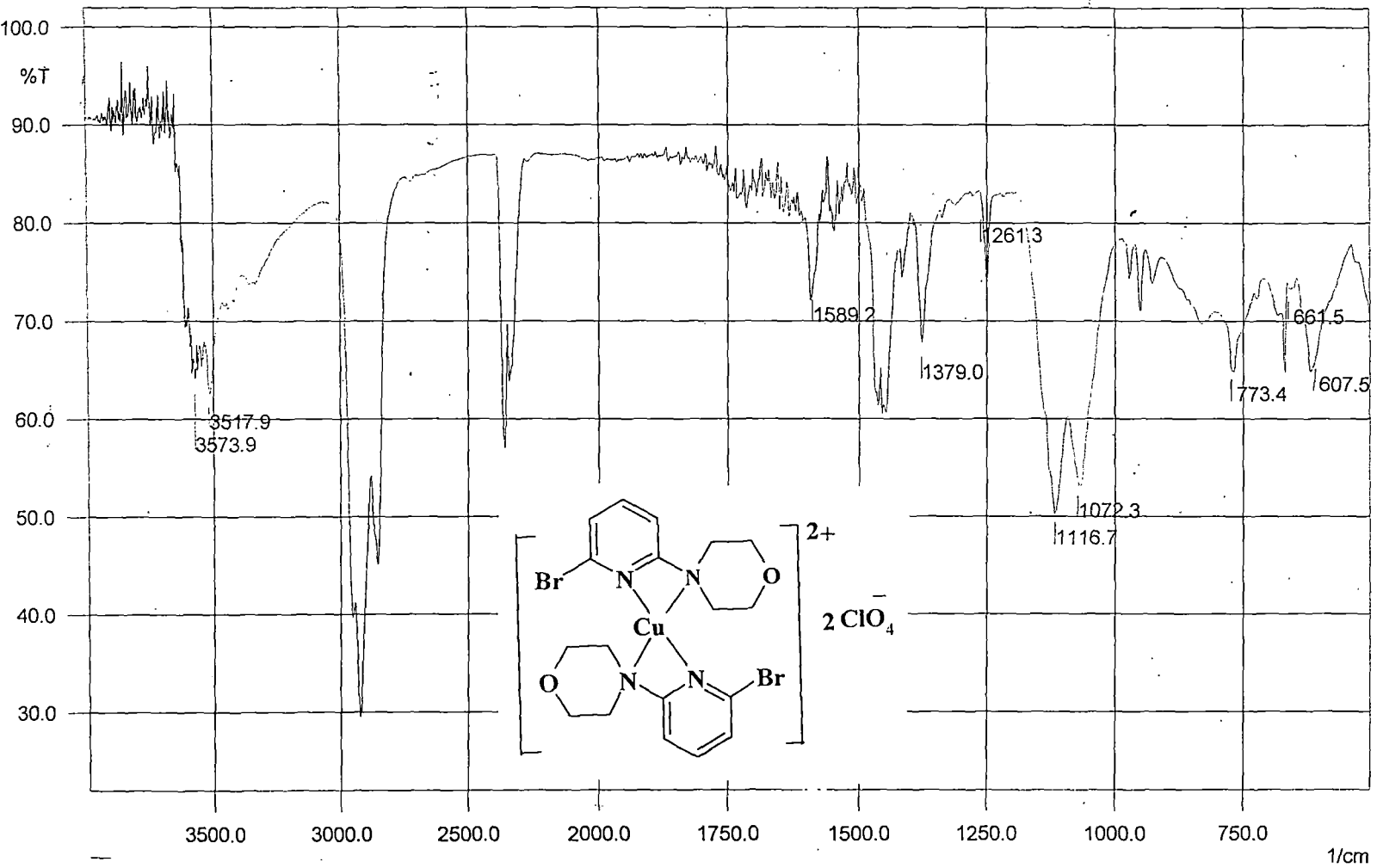
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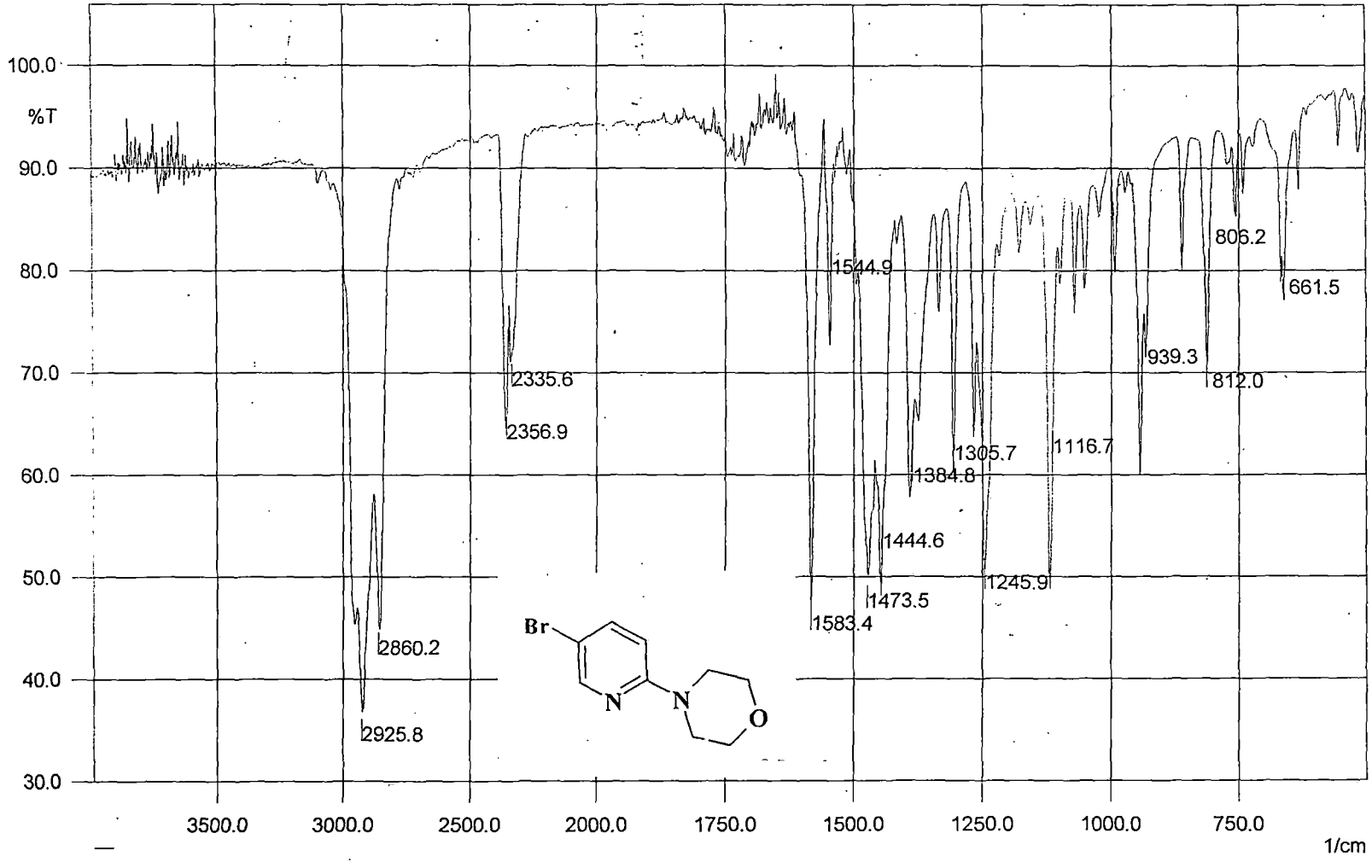
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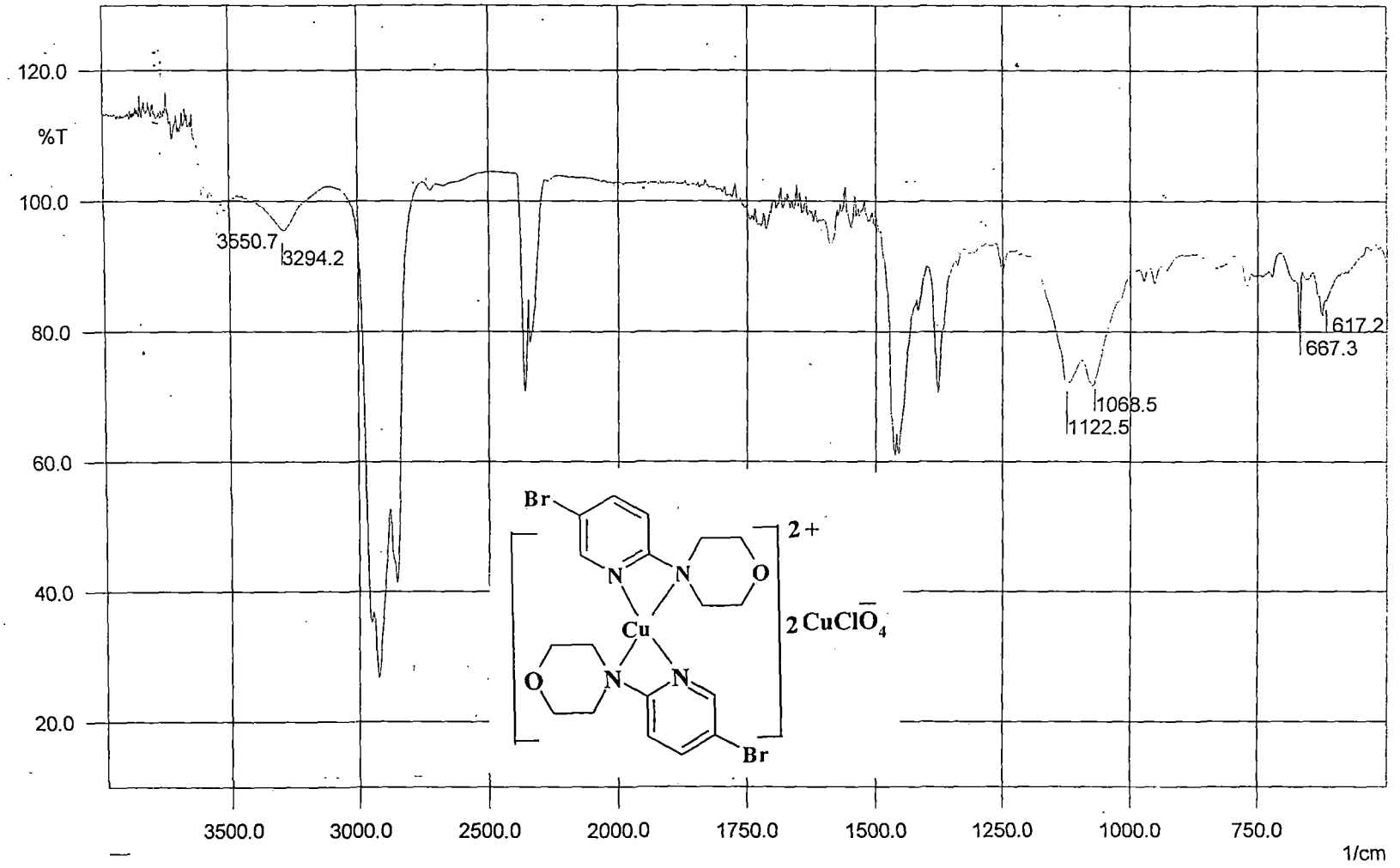
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## III.4: References


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