

# Synthesis, Thermal Study and Biological Activity of Cobalt (II) and Copper (II) Mixed Ligand Complexes Using (*N*-4-Methoxy Phenyl) Amino Phenyl Acetonitrile and Histidine Ligands

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## Abstract:

A mixed ligand complexes derived from histidine (HL<sub>1</sub>) as primary ligand and (*N*-4-methoxy phenyl) amino phenyl acetonitrile (L<sub>2</sub>) as secondary ligand have been prepared and characterized by conventional techniques, including infrared and ultraviolet spectra, molar conductivity and thermal analysis. The infrared spectral data showed that the chelating behavior of the ligand (L<sub>2</sub>) toward transition metal ions is through N-nitrile and N-aniline, whereas the amino acid (HL<sub>1</sub>) coordinates through the carboxylate oxygen, amino nitrogen and imidazole nitrogen as tridentate ligand. The electronic spectral results displayed the existence of d-d electronic transitions beside ligand field transitions and confirmed the mentioned structure. The molar conductivity confirms the non-electrolytic nature of both Co(II) and Cu(II) complexes. The thermo gravimetric analysis data of the complexes displays the existence of lattice water in cobalt complex. Accordingly the suggested formula of cobalt and copper complexes could be [CoCIL<sub>1</sub>L<sub>2</sub>].H<sub>2</sub>O and [CuCIL<sub>1</sub>L<sub>2</sub>] respectively. Anti bacterial activity has been achieved toward two kinds of bacteria (*Staphylococcus aureus* and *Escherichia coli*).

**Keywords** : mixed ligand, histidine, Anti-bacterial activity, thermo gravimetric

## INTRODUCTION

Researchers have been shown significant progress in utilization of mixed ligand transition metal ion complexes as compounds with several activities like antibacterial<sup>(1-4)</sup>, antifungal<sup>(2,5)</sup> and anticancer activities<sup>(5,6)</sup>. Amino acids are well known chelating agents and play an important role in biological process with different equilibrium behavior<sup>(7)</sup>. Ternary complexes of histidine and threonine amino acids are dominant extensively in human serum and are important in transport copper ions in blood<sup>(8)</sup>. Histidine described as a tridentate ligand that has an amino, carboxylate and imidazole groups directed to metal ion binding sites, but only a metal ion with an octahedral coordination sphere can form a tridentate chelate<sup>(9,10)</sup>. Mixed ligand complexes containing amino acid as co-ligand are under investigation to figure out the final geometry<sup>(11,12)</sup> anti microbial activity<sup>(13,14)</sup> anticancer activity<sup>(5)</sup> antiulcer activity<sup>(15)</sup> and potential biomimetic models for metal-protein interaction<sup>(16)</sup>.  $\alpha$ -aminonitrile is an important synthon and there are several methods reported for its preparation; the classical Strecker method<sup>(17)</sup> and its modification using catalysts<sup>(18-20)</sup>. In continuation of the previous work<sup>(21-23)</sup>, this is the first study to introduce an  $\alpha$ -aminonitrile compound in mixed ligand complexes. The present work describe the synthesis of mixed ligand complexes using and taking advantage of histidine as tridentate primary ligand and an  $\alpha$ -aminonitrile ((*N*-4-methoxy phenyl) amino phenyl acetonitrile) as bidentate secondary ligand to achieve the desire mixed ligand complexes.

## EXPERIMENTAL

### Reagents and Chemicals

All the chemicals and solvents were used for the synthesis were of reagent grade and were obtained commercially from British Drug House (BDH) Company with an exception of CoCl<sub>2</sub>.6H<sub>2</sub>O and CuCl<sub>2</sub>.2H<sub>2</sub>O salts were obtained from Fluka company. The prepared ligand (*N*-4-methoxy phenyl) amino phenyl acetonitrile was synthesized and characterized according to published work<sup>(24, 25)</sup>.

### Physical Measurements

Gallen kamp M.F.B. 600.01F apparatus was used to determine the melting points of the ligand and the prepared complexes and were uncorrected. Infrared spectra were recorded using FTIR 8300 Shimadzu as KBr disk in the range (4000 - 600) cm<sup>-1</sup>. Electronic absorption spectra of the prepared compounds were

recorded in the range (200 – 1100) nm on a Shimadzu UV-Vis 160A Ultra-violet spectrophotometer at room temperature using silica cells of 1.0 cm length of freshly prepared 10<sup>-3</sup> M in absolute ethanol. Molar conductivity was used to measure the conductivity of the complexes at room temperature in freshly prepared 10<sup>-3</sup> M in absolute ethanol using by BC3020 Professional Bench top conductivity meter Trans instruments. Thermal analysis TGA was performed with 4000 Perkin-Elmer thermal analyzer maintained at a 20.00 °C min<sup>-1</sup> heating rate.

### Synthesis of mixed ligand complexes<sup>(9,10)</sup>

A solution of histidine (HL<sub>1</sub>) was prepared by dissolving it in equimolar sodium hydroxide. The  $\alpha$ -amino nitrile (*N*-4-methoxy phenyl) amino phenyl acetonitrile (L<sub>2</sub>) was prepared by dissolving it in ethanol. The solutions of metal ions Co(II) and Cu(II) were prepared in one equivalent of hydrochloric acid. To prepare metal complex, the two dissolved ligands HL<sub>1</sub> and L<sub>2</sub> were mixed with 3 ml of 0.1 mol/L metal ion solution in 1:1:1 molar ratio at room temperature and the pH >7 with total volume equal to 10 ml (adding distilled water). The important note is that the mixing started with addition of HL<sub>1</sub> to metal ion solution then followed by the addition of L<sub>2</sub>. The pH of mixture was adjusted by addition of NaOH solution. The color of reaction solution was change and refluxed for 4 hours, the colored precipitate was collected by filtration and washed several times with cold ethanol-water 50% mixture then dried in the oven at 50 °C for one day.

## RESULTS AND DISCUSSION

### Conductivity measurement

The physical properties of the two synthesizes complexes are tabulated in tables 1, and they in a good agreement with the suggested formula of cobalt and copper complexes. The molar conductance of 0.001 M solution of the complexes in absolute ethanol was measured at 25 °C. The conductivity values indicating the non-electrolytic behavior of the complexes.

### Infrared spectral data

Generally amino acid -NH<sub>3</sub><sup>+</sup> group occurs in the range (3130-3030) cm<sup>-1</sup><sup>(26,27)</sup>. In the infrared spectrum of histidine (HL<sub>1</sub>) it appears near 3082 cm<sup>-1</sup> but overlaps with other vibrations such as  $\nu$ NH (imidazole group) and  $\nu$ CH<sub>2</sub> group of heterocyclic near 3016 cm<sup>-1</sup><sup>(26,27)</sup>. Theoretically  $\nu$ NH<sub>3</sub><sup>+</sup> should vanish and disappeared on coordination that it eventually converted to amino group (-NH<sub>2</sub>) in the proper basic medium that normally accurse as two bands in

the region 3300-3500 cm<sup>-1</sup>(27). However, in metal complexes some band appears in the same region near 3300 cm<sup>-1</sup>, which must be arising from other vibrations appearing in this region belong to amino group (-NH-) of  $\alpha$ -amino nitrile (L<sub>2</sub>) as one band. Therefore, the comparison of shifting of histidine amino group was discard and out of our account ,but ,carboxylate group shifting was accounted, that the  $\nu_{asy}COO^-$  and  $\nu_{sy}COO^-$  absorptions appear at 1633 and 1418 cm<sup>-1</sup> respectively(9,10,26,27) which are shifted according coordination to lower frequencies.The coordination with  $\alpha$ -amino nitrile (L<sub>2</sub>) was expected through amine (-NH-) and nitrile (-C≡N ) groups which appeared at the region (3300-3500) cm<sup>-1</sup> and (2100-2270) cm<sup>-1</sup> respectively(26), both vibrations were shifted to lower energy field, which represented the success of bonding with the metal ion as secondary ligand in addition the appearances of other related groups like out of plain deformation. All the mentioned data represented as evidence for the coordination bonding between the reactants. Table 2 shows the related data in addition to some other characteristic bands

**Ultraviolet-visible spectroscopy**

The significant spectral data of electronic absorption bands of the Co(II) complexes recorded in absolute ethanol. The histidine,  $\alpha$ -amino nitrile and the complexes show  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  bands in the region (342-220) nm overall. Charge transfer band accurse on cobalt and copper complexes at 395 nm and 392 nm respectively due to metal to ligand electron movement because of the high electron density of metal ions. The d-d electronic transition bands are observed as two peaks for cobalt complex and one broad peak for copper complex.

The spectrum of Cobalt (II) complex showed two main bands at 961 nm and 590 nm which are assigned to ( $\nu_1$ )  $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$  and ( $\nu_2$ )  $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$  transitions respectively(28). The third transition ( $\nu_3$ )  $^4T_{1g}(F) \rightarrow ^4T_{2g}(P)$  is expected to appear near ultra violet and charge transfer region. Thus it could not be observed. The observed transitions are consistent with an octahedral geometry.

The electronic spectrum of Copper (II) complex showed one broad band. Appeared at 625 nm which ascribed to the (d-d) electronic transition  $^2E_g \rightarrow ^2T_{2g}(F)$  which is more consistent with octahedral geometry(28). Table 3 shows Uv.-Vis. electronic spectral data, assignment, structure and calculated parameters.

**Thermal analysis**

The Thermal behavior of both complexes was studied using thermal gravimetric analysis (TGA) that recorded in helium gas at constant heating rate of 20 °C/min.

The decompositions pattern of cobalt(II) complex in air occurs in two steps of high weight loss, while of copper(II) complex occurs in three steps of low weight loss as shown in figures 1 and 2 respectively. Both compounds decompose upon time starting with dehydration process and gases libration(29, 30). Table 4 shows the thermal decomposition data of both complexes. On the final steps during temperature raise, it was expected to form metal oxides(29-32), but both complexes held out with a part of the ligands in addition to oxide especially copper complex that L<sub>2</sub> held up with the metal.

**Table 1: Physical data of the mixed ligand complexes**

Compound	Yield percentage	Color	melting point	Molar conductivity $\Lambda_m \Omega^{-1} cm^2 mol^{-1}$
[CoCIL <sub>1</sub> L <sub>2</sub> ].H <sub>2</sub> O	68%	Brown	121-123°C	5.81
[CuCIL <sub>1</sub> L <sub>2</sub> ]	77%	Black	112-114°C	11.66

**Table 2: Infrared frequencies of  $\alpha$ -amino nitrile and mixed ligand Co(II) and Cu(II) complexes**

Compound	$\nu$ (O-H) water	$\nu$ (N-H) amine	$\nu$ (C-H) aromatic	$\nu$ (C-H) aliphatic	$\nu$ (C≡N) nitrile	$\nu$ (COO <sup>-</sup> ) asym. , sym.	$\nu$ (C=C) aromatic	$\nu$ (C=N) imidazole	Out of plain	
									Para	mono
L <sub>2</sub>	---	3360m	3040w	2950m 2839m	2210w	---	---	---	850	690,756
[CoCIL <sub>1</sub> L <sub>2</sub> ].H <sub>2</sub> O	3450w broad	3153w 3300w	1031w	2956m 2839m	2175m	1623 , 1390	1508v	1579m	835	688,756
[CuCIL <sub>1</sub> L <sub>2</sub> ]	---	3200w 3296w	3060w	2960m 2839m	2173	1622 , 1330	1508v	1560w	833	690,760

**Table 3: Electronic spectral data in absolute ethanol of mixed ligand Co(II) and Cu(II) complexes.**

Compound	$\lambda$ nm	$\nu$ cm <sup>-1</sup>	Assignments	Suggested Structure
[CoCIL <sub>1</sub> L <sub>2</sub> ].H <sub>2</sub> O	220 289 390 obscured590 961	45454 34602 25641 obscured 16949 10406	$\pi \rightarrow \pi^*$ charge transfer ( $\nu_3$ ) $^4T_{1g}(F) \rightarrow ^4T_{2g}(P)$ ( $\nu_2$ ) $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ ( $\nu_1$ ) $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ $n \rightarrow \pi^*$	Octahedral
[CuCIL <sub>1</sub> L <sub>2</sub> ]	271 317 334 392 635	36900 31545 29940 25510 15748	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ charge transfer $^2E_g \rightarrow ^2T_{2g}(F)$ $n \rightarrow \pi^*$	Octahedral

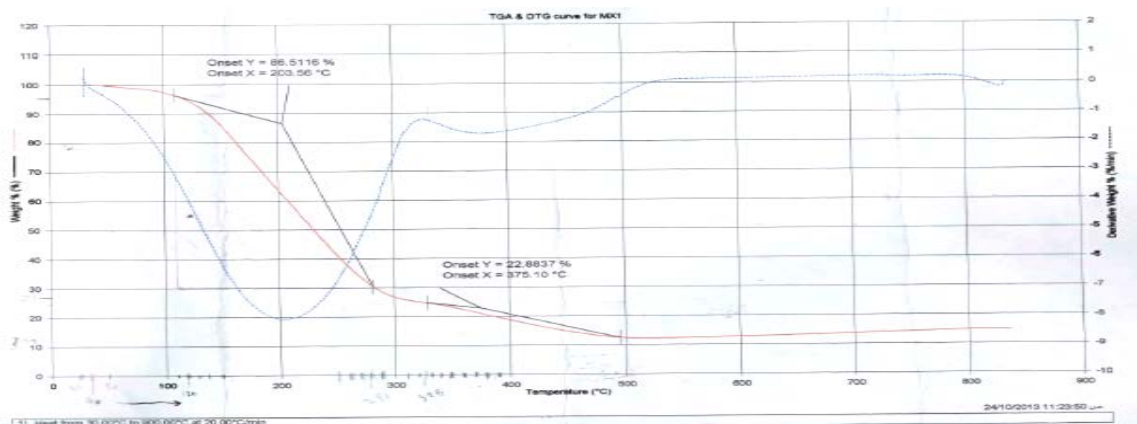


Figure 1: Thermal gravimetric analysis (TGA) of [CoClL<sub>1</sub>L<sub>2</sub>].H<sub>2</sub>O complex.

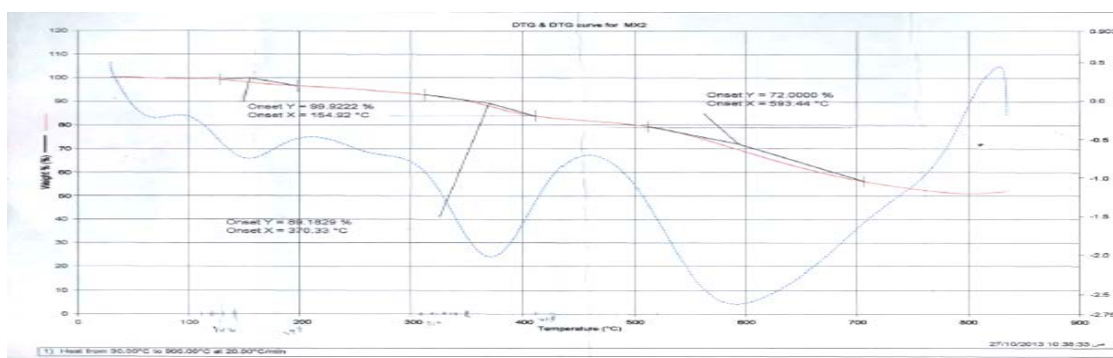


Figure 2: Thermal gravimetric analysis (TGA) of [CuClL<sub>1</sub>L<sub>2</sub>] complex.

Table 4: Thermo analysis data of [CoClL<sub>1</sub>L<sub>2</sub>].H<sub>2</sub>O and [CuClL<sub>1</sub>L<sub>2</sub>] complexes

Complex	Temperature range , °C	Weight loss %		Decomposition product	Librated part
		Found	Calculated		
[CoClL <sub>1</sub> L <sub>2</sub> ].H <sub>2</sub> O	110-280	64.45	60.35	[CoL <sub>1</sub> ]	[H <sub>2</sub> O, HCl, CO, L <sub>2</sub> ]
	325-490	13.06	10.41	[CoO NH <sub>2</sub> C <sub>2</sub> H <sub>3</sub> ]	[imidazolium]
[CuClL <sub>1</sub> L <sub>2</sub> ]	140-195	3.45	2.16	[CuClL <sub>2</sub> (imidazole-C <sub>2</sub> H <sub>3</sub> COO)]	NH <sub>3</sub>
	315-415	7.63	7.69	[CuL <sub>2</sub> (imidazole-C <sub>2</sub> H <sub>2</sub> COO)]	HCl
	520-710	24.93	19.49	[CuOL <sub>2</sub> ]	CO, CH <sub>2</sub> CH <sub>2</sub> -imidazole

Table 5: Anti bacterial activity of tetracycline as standard and mixed ligand Co(II) and Cu(II) complexes in DMSO at MIC against two microorganisms.

Compound	<i>Staphylococcus aureus</i>				<i>Escherichia coli</i>			
	well diffusion method		disk-diffusion method		well diffusion method		disk-diffusion method	
	activity	zone	activity	zone	activity	zone	activity	zone
Tetracycline	++	13	++	11	+++	26	+++	24
[CoClL <sub>1</sub> L <sub>2</sub> ].H <sub>2</sub> O	--	0	--	0	--	0	--	0
[CuClL <sub>1</sub> L <sub>2</sub> ]	++	13	+++	16	--	0	--	0

Key to symbols: -- = No inhibition, += (5-10) mm, ++ = (11-20) mm, +++ > 20 mm.

**Antibacterial Evaluation**

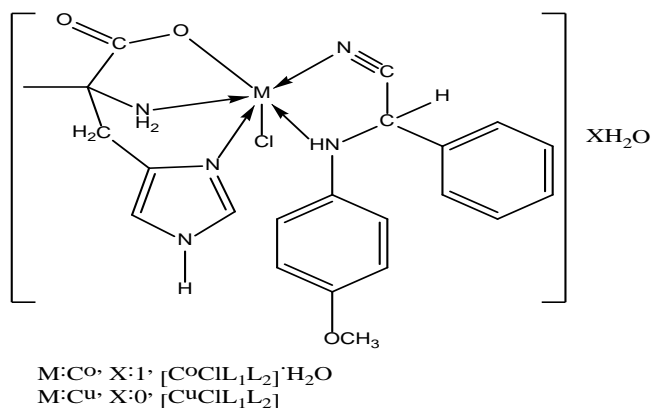
Microorganisms cause different kinds of diseases to human and animals. Discovery of chemotherapeutic agents played a very important role in controlling and preventing such diseases especially those of mixed ligand complexes. Two microorganisms *Staphylococcus aureus* and *Escherichia coli* were isolated and identified, to be used in two *in vitro* techniques at minimal inhibitor concentration (MIC), the first was disk-diffusion method and the second was well diffusion method. Tetracycline anti biotic was used for comparison and dimethyl sulfoxide (DMSO) was used as solvent for all the tested compounds. The anti bacterial

results were not promising. Table 5 shows the results and inhibition zone of the complexes against the two selected bacteria.

**CONCLUSION**

Generally the synthesis of mixed ligand complexes has an accurate method. The presence of primary and secondary ligands in the final product must be followed by the right sequence of addition, that addition of L<sub>2</sub> (bidentate) first and before HL<sub>1</sub> (tridentate) will not achieve the desired product. However, according to the results we conclude that the suggested structure for the prepared complexes could be in octahedral geometry and general formula be [MCIL<sub>1</sub>L<sub>2</sub>].XH<sub>2</sub>O, M: Co or Cu, X: 1 or 0 for cobalt and copper complexes respectively. The ligands interacted

with the metal ion in five and six membered ring pattern beside chloride ions to satisfy the six-coordination number of octahedral as shown in figure 3. Anti bacterial activity was not promising specially cobalt complexes and this could be due to using minimal inhibitor concentration MIC.



**Figure 3: suggested structure of mixed ligand cobalt and copper complexes**

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