

## Preparation and Study Mixed Complexes of Salicylaldehyde Copper (II) and Nickel (II) with Imidazole

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### Abstract

The present paper deals with the synthesis of metal complexes with mixed ligands; we have managed to synthesis several complexes with a primary salicylaldehyde and imidazole molecule as auxiliary ligand. Complexes of Cu (II), Ni(II) were isolated and characterized using several techniques; such as(UV-Visible and IR ) molar conductivity, atomic absorption and magnetic susceptibility. The copper complex and nickel complex is in an octahedral. The intra-molecular hydrogen bonding for salicylaldehyde and its influence on the coordination has been investigated.

**Keywords:** Mixed Complexes; Salicylaldehyde; Imidazole

### Introduction

Mixed-ligand complexes take part in many biological processes, also they have important applications in analytical, and other branches of chemistry [1]. Aldehyde was recognized to function as ligands since quite a long period of time, and Synthesis of transition metal complexes with aldehyde groups are of significant importance; as the aldehyde group can go through different types of chemical reactions [2]. Metal ions, which may regarded as a hard acids would have more tendency to coordinate with aldehyde, as in case of coordination of metal ions such as Ba(II) and Sr(II) with Salicylaldehyde [3]. Salicylaldehyde is very interesting example because it has the hydrogen bonding which exists between the aldehyde and hydroxyl group, will hinder, to certain, via the two groups [4]. It has been well known that salicylaldehyde and also methyl salicylate form strong intra-molecular hydrogen bonds which initiated between the hydroxyl of phenolic group and the oxygen of the carbonyl group [5]. Hydrogen bonding is a very imperative and valuable feature for study and considerate the whole molecular structure for a molecule with the hydrogen atom able to interact with other atoms with high electronegativity; even though the energy of such bonding is quite low [4]. Hydrogen bonding occurred through the, more acidic hydrogen of the hydroxyl group, and more basic carbonyl oxygen, which leads to form six membered ring; in addition to that the distance between the oxygen of the aldehyde group and the hydroxyl hydrogen (2.6 Å) is too long to establish hydrogen bonding [4]. pK<sub>a</sub> of salicylaldehyde and also other chloro derivatives have been determined spectrophotometrically [6]. this would assist to find out the experimental conditions required to synthesis the complexes, in other words acid dissociation constants will be presented in this paper as measures of the relative strengths of proton chelation.). Stability constants of salicylaldehyde and some chloro and nitro derivatives with Cu(II) were determined [2] and it has been found that

the salicylaldehyde complex is more stable than the other derivatives except the 6-chloro salicylaldehyde. The higher acidity of the phenolic group in Salicylaldehyde, so the hydrogen atom of this group will engage in hydrogen bonding with the oxygen atom of the aldehyde group forming a six membered ring.

The low basicity of the oxygen group would not contribute to build relative stable hydrogen bonding. Losing the hydrogen of hydroxyl group will certainly influence the aldehyde group, which will rotate away from the hydroxyl oxygen and preclude the possible coordination [1] various molecular properties of system that has the possibility of an interaction between a hydrogen atom and a more electronegative atom such as F, O and N. intra-molecular hydrogen bonding in particular is very responsible for the molecular conformation and intra-molecular rearrangement of a certain molecule. The free ability of the carbonyl oxygen in the aldehyde or the anion of aldehyde to rotate will affect the coordination with metal. Now, this will be taken over by the extent of how this ligand tend to coordinate with the metal ion, and in the same time depends of the coordination power of the metal ion itself.

## Materials and Methods

### Nickel complex

This complex has been prepared by mixing directly, on the following by the reaction between nickel ion with mixed ligand with mole ration 1:2:2 M: L: L with mole ration 0.01 mole (2.377 gm) of nickel chloride hexa equate which has been already dissolve in water with 0.02 mole (2.68 gm) of salicylaldehyde and 0.02 mole (1.36 gm) imidazole which both have been dissolve d in ethanol Complex has been precipitate and isolated and been washed with ethanol and distill water and dry.

### Copper complex

Copper (II) has been reacted with the salicylaldehyde in ratio 1:2, metal to ligand by the reaction between 0.01 mole of (1.705 gm) of  $NiCl_2 \cdot 2H_2O$  which has been already dissolve in distilled water with 0.02 mole of (2.68 gm) of salicylaldehyde which already been dissolved in ethanol followed by the addition 0.02 mole (1.36) gm of imidazole which dissolved in ethanol. A precipitate was developed and has been isolated and washed by distilled water and ethanol then dried this complex has been synthesized in slightly. Different way, as we are unable to prepare the complex in the same way as in case of nickel. UV-Visible spectra were taken in quartz cell with width 1cm with DMF solvent and the measurement was taken by using Shimadzu (Cary 100). Conductivity measurement were taken with the same solvent (WTW 740) and IR spectra were recorded on shimadzu (FT-IR-8400) spectrophotometer. Atomic absorption measurement was taken by (phoenix-986). Magnetic susceptibility measurement was obtained at 25°C on the solid state applying Faraday's method using Balance Magnetic susceptibility model (MSB-MKI).

TABLE 1: The physical data and atomic absorption of complexes

Compound	Color	MP <sup>o</sup> c	M%	
			Cal	Found
CuL <sub>2</sub> L' <sub>2</sub>	Light Brown	215-220 d <sup>*</sup>	13.44	13.46
Ni L <sub>2</sub> L' <sub>2</sub>	Light Green	310-315 d <sup>*</sup>	14.38	14.74
L= Salicylaldehyde L'= Imidazole d <sup>*</sup> = decompose				

## Result and Discussion

In this present paper, we described the synthesis and characterization of neutral complexes formed from copper (II) and Ni (II) mixed ligands complexes of the type MLL' (L=Salicylaldehyde, the primary ligand, L'= imidazole, the auxiliary

ligand). The reaction of metal ion with 1:1 mixtures of Salicylaldehyde and Imidazole result in the formation of mixed ligands complexes. The resulting complexes are isolated as Green solids. All the complexes are insoluble in most of the organic solvents. The molar conductance of the complexes is very low, indicating their non-ionic nature. In all metal complexes the metal ion appears to be hexa-coordinated and the probable geometry is octahedral. In order to throw more light on the coordination mode in ternary complexes.

We have synthesized two sets of complexes; the first set complexes are the binary complexes, which have been synthesized from the coordination between the metal ion and the primary ligand (Salicylaldehyde) and the proposed complex is  $ML_2$  (M is metal ion Cu (II) and Ni (II) and L is Salicylaldehyde). The IR spectra of the salicylaldehyde shows  $\nu$  (C=O) frequency at  $1720\text{ cm}^{-1}$  the normal absorbance of C=O is  $1725\text{ cm}^{-1}$  (under the influence of conjugation caused by the aromaticity or benzene ring) [7] Shifting towards less frequency is due to hydrogen bonding between the oxygen of the carbonyl and the hydrogen of the hydroxyl group [4]. The  $\nu$  (O-H) frequency in phenol is 3200-3400 ( $14$ ) and this frequency will be shifted down in case of salicylaldehyde to  $3180\text{-}3061\text{ cm}^{-1}$  (the shifting occurs in case of salicylaldehyde is again due to hydrogen bonding as it has been mentioned above. The IR spectra of the Cu (II)-L<sub>2</sub> complex shows  $\nu$  (C=O) frequency at  $1700\text{ cm}^{-1}$  the shifting here is consistent with the coordination of the ligands with the metal ion. Similar shifts to lower wave number have been reported in complexes of transition metals with similar ligands [8] The size of shifting reflects the strength of the coordinated bond in the formed complex between the carbonyl oxygen and the Cu (II) ion; it can be inferred that the coordinated bond is reasonably strong. This is not very expected, if we consider that the oxygen atom is a soft base and the Cu (II) ion is a border line acid [9]. The other link with the salicylaldehyde is through the oxygen of hydroxyl group, which makes the salicylaldehyde ligand bi-dentate. There is no trace of the OH group which confirms the coordination, as the dissociation of the hydrogen ion occurs as a result of coordination [10] The IR spectra of the NiL<sub>2</sub> shows  $\nu$  (C=O) frequency at  $1700\text{ cm}^{-1}$  and as it has been mentioned above, the normal absorbance of C=O is  $1725\text{ cm}^{-1}$  (under the influence of conjugation caused by the aromaticity or benzene ring) [7]. Again shifting towards less frequency is an indication of the complex formation between the ligand and the metal ion. The main aim of this research is to synthesis a mixed ligands complexes; with the Salicylaldehyde as a primer ligand and other mono-dentate ligand (Imidazole) to be added to satisfy the coordination sites of the metal ion. Imidazole ligand has been chosen due to its relative high basicity and with its mono-dentate ability so it would be capable to occupy, through pyridine nitrogen, the axial positions whereby to achieve the octahedral complex. There is no exchange in ligands occurs, this might be due to the similarity in the coordination ability between the salicylaldehyde and the imidazole, so the second ligand (imidazole) L' find its way to settle down within the whole structure of the  $ML_2$ , result in octahedral mixed complex with a structure of  $ML_2L'_2$ . Steric hindrance is not expected to prevent the attachment of imidazole molecules, basically because coordination sites allow to more molecules to be attached. Also it has been found that imidazole would enhance the coordination between of binary Cu (II) complex with ligands having oxygen donor atoms [11]. A possible of intra-hydrogen bonding to occur between the hydrogen of pyrrole nitrogen of imidazole and the oxygen atom of the hydroxyl group on the attached salicylaldehyde molecules. This type of bonding expects to strengthen the whole structure of the complex, and lead to more stability. In the same time the aldehyde group in the coordinated ligand doesn't actually react with the imidazole, as this case has been noticed with other mono-amine used in case of synthesis other mixed ligand complexes [12]. The IR spectra of the ternary Cu(II)-mixed complex ( $CuL_2L'_2$ ) shows the following bands  $1660\text{ cm}^{-1}$  and  $1597\text{ cm}^{-1}$ , the first one assigned for the C=O, absorbance of this group occurs in the same area as in case of the binary complex  $CuL_2$ . This means that the binding

between the salicylaldehyde and the Cu (II) doesn't influenced by the addition of the second ligand this might reflect the strength of the Cu (II)-binding to the primary ligand. The second band is assigned to C=N, as the normal absorbance of this group is in the region 1615 -1700 cm<sup>-1</sup> [7]. and the shifting towards less frequency is due to the contribution of the pyridine nitrogen into the coordination. The IR spectra of the ternary Ni (II)-mixed complex (NiL<sub>2</sub>L'<sub>2</sub>) shows the following bands, 1680 Cm<sup>-1</sup> and 1602 Cm<sup>-1</sup> the first frequency assigned to the C=O group, and the situation in case of Ni (II)-complex is different from the case of Cu(II)-complex and accordingly it can be said the binding in case of the copper ion with the primary ligand is the stronger. The second band assigned to the C=N group, the shifting from the normal value is an indication of the involve of this group in the reaction. Less shifting occurs in the C=N group, and the C=O group in case of Nickel ion complex, and this is an indication of the strength of the binding; this is expected on the light of Irving – William series Other weak bands have been observed in the region (500-550) cm<sup>-1</sup> which are absent in the free ligands, can be assigned to ν (M-O) vibration [2,3] (TABLE 2).

Table 2: IR (νcm<sup>-1</sup>) spectral data of Salicylaldehyde, Imidazole and its complexes

compound	ν (O-H)	ν (C=O)	ν (C=N)	ν (M-O)	ν (M-N)
L=Salicylaldehyde	(3180-3061)	1720	-----	-----	-----
L'= Imidazole	-----	-----	1670	-----	-----
CuL <sub>2</sub> L' <sub>2</sub>	-----	1660	1597	549	426
Ni L <sub>2</sub> L' <sub>2</sub>	-----	1680	1602	522	450

IR spectra reveal the electronic spectra of solution of the complex CuL<sub>2</sub>L'<sub>2</sub> showed several peaks as follows: At 348 nm peak absorbance assigned to the π → π\* which is due to the aromatic system in the ligands. At 368 nm peak absorbance assigned to the n → π\* which is due to the existence of phenolic At 409 nm peak absorbance assigned to the charge transferee At 697 nm assigned to the d-d transition, which is due (FIG. 1) [13-15].

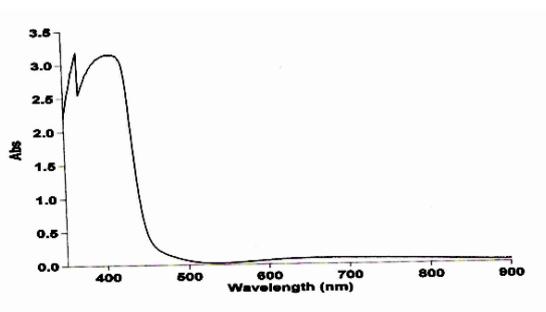
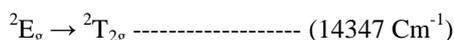


FIG. 1. Electronic Spectrum of Cu-L<sub>2</sub>L'<sub>2</sub>

The electronic spectra of solution of the complex NiL<sub>2</sub>L'<sub>2</sub> showed also several peaks as follows the peak absorbance at 268 nm is (FIG. 2)

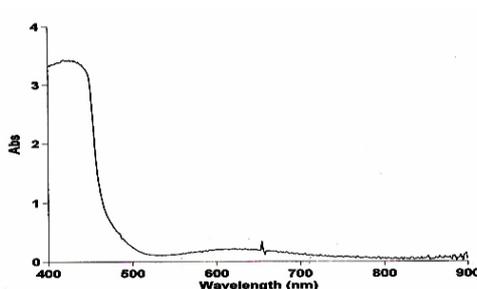


FIG. 2. Electronic Spectrum of Ni-L<sub>2</sub>L'<sub>2</sub>

Assigned to  $\pi \rightarrow \pi^*$  transition, as it is due to the aromatic system in the ligands. The second peak absorbance showed at 326nm, which assigned to then  $n \rightarrow \pi^*$  transition, as it is due to the phenolic oxygen. And the absorbance at 394 nm is assigned to the charge transfer. Nickel (II) ion, in octahedral structure, shows three d-d transitions; two of them positioned in the UV-visible spectrum, which we characterized them as follows: The band (18182-13793  $\text{cm}^{-1}$ ) is assigned to the d-d transition which is due to The Magnetic moment value for  $\text{Cu}^{+2}$  complex was (2.9) BM that's mean its have one singlet electron. But in case of  $\text{Ni}^{+2}$  complexes its appearing has two singular electrons. The conductivity measurement showed that all the solution complexes for both Cu (II) and Ni (II) in DMF solvent ( $10^{-3}$  M) are none electrolyte. From the above measurements it can be concluded and confirmed that the mixed ligand complexes for both ions have molecular formula of  $\text{ML}_2\text{L}'_2$  with geometrical structure of octahedral; and the following scheme shows the structure of the  $\text{ML}_2\text{L}'_2$  complex (TABLE 3, SCHEME 1 and 2) [16,17]

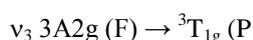
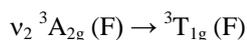
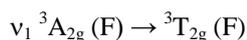
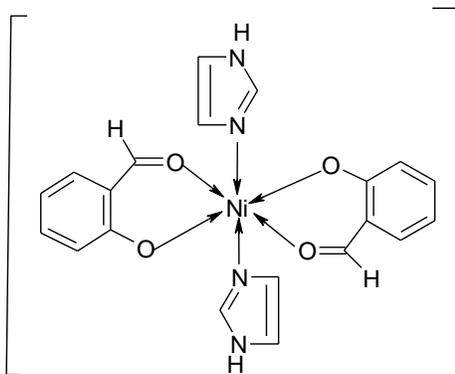


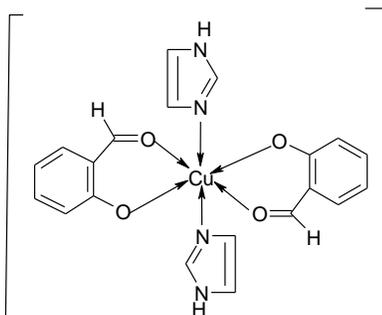
TABLE 3: Electronic transitions .magnetic moments and molar conductivities of prepared compounds

compound	Absorption	Transition	$\mu$	molar	Proposed geometry
	(nm)			(BM)	
Cu- $\text{L}_2\text{L}'_2$	348	$\pi \rightarrow \pi^*$	1.8	15	octahedral
	368	$n \rightarrow p^*$			
	409	C.T			
	697	$^2\text{E}_g \rightarrow ^2\text{T}_{2g}$			
Ni- $\text{L}_2\text{L}'_2$	268	$\pi - \pi^*$	2.9	12	octahedral
	326	$n \rightarrow p^*$			
	394	C.T			
	(550-725)	$^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{2g}(\text{F})$			
		$^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{F})$			
	$^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{P})$				
C.T – Charge Transfer					

(SCHEME 1: Cu-L<sub>2</sub>L'<sub>2</sub>)



SCHEME 2: Ni-L<sub>2</sub>L'<sub>2</sub>



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### REFERENCES

1. Carballo R, Covelo B, Lopez MV, et al. Development of mass detection algorithm based on adaptive thresholding technique in digital mammograms. *Anorg. Allg. Chem.* 2003;629:244-248.
2. Huang Y, Gladysz J. Aldehyde and ketone ligands in organometallic complexes and catalysis. *A. J. Chem. Educ.* 1988;65:298.
3. Saraswat K, Prasad RN, Ratnani R, et al. Synthesis, spectroscopic characterization and structural studies of mixed ligand complexes of Sr(II) and Ba(II) with 2-hydroxybenzophenone and salicylaldehyde, hydroxyaromatic ketones or  $\beta$ -diketones: Crystal structure of 2-HOC<sub>6</sub>H<sub>4</sub>C(O)C<sub>6</sub>H<sub>5</sub>. *Inorganica Chimica Acta.* 2007;29;1291-1295.
4. Chung G, Kwon O, Kwon Y, et al. Theoretical Study on Salicylaldehyde and 2-Mercaptobenzaldehyde: Intramolecular Hydrogen Bonding. *J Phys Chem A.* 1998;102:2381-2387.
5. Pavia LD, Lampman G, Kriz SG, *Introduction to Spectroscopy*, Thomson, USA
6. Postmus Jr, Magnusson BL, Craig C, et al. Coordination in Solutions. IV. Association Constants for 1:1 Complexes of Cu(II), Zn(II), Ca(II), La (III), and Y (III) with Anions of Salicylaldehydes. *Inorg Chem* 1966;5:1154-1157.
7. Huhee JE. *Inorganic Chemistry, Principles of structure and reactivity*, Harper International SI Edition, Cambridge, England.
8. Bellamy IJ, Reece J. The infra-red spectra of chelate compounds. Part I. Systems of keto-enol type. *J Chem Soc* 1954:4487-4490.

9. Boggess KB, Bruce R. Martin Metal ion induced pyrrole ionization in 2-(2'-pyridyl)imidazole. *Inorg. Chem.* 1974;13:1525-1527.
10. Paavo V, Pauli V. Thermodynamics of the Complexation of Imidazole with Divalent Copper, Nickel, Cadmium, Zinc, and Cobalt Ions in Aqueous, Sodium Perchlorate Solutions. *Acta Chem Scand.* 1974;28:1055.
11. Magnusson BL, Postmus C, Craig CA, et al. Coördination in Solutions. I. Acid Strengths of Phenol Derivatives in Water. *J Am Chem Soc.* 1963;85:1711-1715.
12. Jiang Y. Improving breast cancer diagnosis with computer-aided diagnosis. *Acad Radiol.* 1999;6:22-33.
13. Helmut S, Peter H, Rolf G, et al. Ternary complexes in solution IX Stability-increasing effect of the pyridyl and imidazole groups on the formation of mixed-ligand-copper (II)-pyrocatecholate complexes. Horsch K. Classification of breast lesions with multimodality computer-aided diagnosis: observer study results on an independent clinical data set.
14. Nakamoto K, McCarthy Pl, Ruby A., et al. Microwave Absorption and Molecular Structure in Liquids. XXXIX. The Relaxation Times of Some Substituted Phenyl Ethers and Analogous Molecules. *J. Am Chem Soc.* 1961;83:1063-1066.
15. Nakamoto K and Martell AE. Infrared Spectra of Metal Chelate Compounds. VI. A Normal Coordinate Treatment of Oxalato Metal Complexes. *J. Chem Phys.* 1958;32:588.
16. Postmus Jr C, Kaye AI, Craig C, et al. Coordination in Solutions. II. Acid Dissociation Constants in Water and Structural Reassignments of the Isomeric Chlorosalicylaldehydes 1,2. *J Organic Chem.* 1964;29:2693-2698.
17. Tatsuya Y, Nobuhide T, Inoue H. An approach to automated detection of tumors in mammograms. *J Inorg Chem.* 1969;73:477-482.
18. Pavia LD, Lampman G, Kriz SG. *Introduction to Spectroscopy*, Thomson, USA.