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Synthesis and Characterization of Some Co(II), Ni(II) and Cu(II) Mixed Ligand Chelates of 8-Hydroxyquinoline, Anthranilic Acid and *o*-Aminophenol

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The series of mixed ligand chelates of Co(II), Ni(II) and Cu(II) ions with some ligands, such as 8-hydroxyquinoline [L_1], anthranilic acid [L_2] and *o*-aminophenol [L_3] acting as bidentate ligands have been prepared and characterized by various physico-chemical analyses, such as elemental analysis, infrared spectra, molar conductance measurements and electron paramagnetic resonance. Elemental analysis data show the formation of 1 : 1 : 1 [M : L : L′] chelates. The molar conductance measurements of the chelates exhibit the non-electrolytic nature of the chelates. Infrared spectra display that the coordination occurs *via* oxygen and nitrogen atoms. Electron paramagnetic resonance spectra show the presence of paramagnetic phenomena and supported the geometrical structures of the chelates, that indicate the presence of either square-planar, tetrahedral or octahedral geometries.

Key Words: Synthesis, Mixed ligand chelates, Co(II), Ni(II), Cu(II), 8-Hydroxyquinoline, Anthranilic acid, *o*-Aminophenol.

INTRODUCTION

Although mixed ligand chelates of transition metals have long held the interest of the chemists, they remained confined to the category of ligands' capability and reactivities to be exchangeable for a period of time. The ligands' interaction with the metal ions either as monodentate or polydentate led to the development of a variety of procedures using different types of ligands. The chemistry of ligand-ligand exchange has a considerable growth and continues to expand along with the development of a variety of techniques for analysis and identification.

Das[1] reported his results for a study of mixed ligand chelates of Co(II), Ni(II), Cu(II) and Zn(II) with four substituted salicylates. The resulting chelates were chelates through the carboxylic and phenolic hydroxyl groups. The stability sequence for the different metal ions has the order Cu > Ni > Co > Zn.

Purohit and Rao[2] prepared the mixed ligand complexes of copper(II) ions of the type Cu(dtc)(ox) and Cu(β-dik)(ox), where dtc = dithiocarbamate, ox = oxime and β-dik = β-diketone are the ligands used. Such complexes were investigated by different techniques, in particular elemental analysis, molar conductance Infrared, electronic and electron paramagnetic resonance spectra. The resulting complexes have square-planar geometry.

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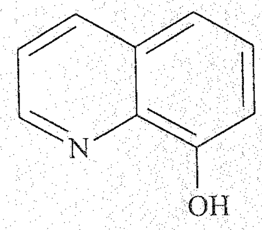
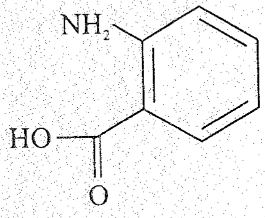
Abou Sekkina *et al.*[3] studied the magnetic moments and electronic spectra of some copper(II) complexes with pyridyl acid amides in correlation with molecular structures. The magnetic moments and the spectral data show the formation of distorted octahedral geometry.

New series of mixed ligand complexes of some divalent transition metals with ligands, such as *o*-phenylenediamine, anthranilic acid, phthalic acid and L-alanine have been prepared and characterized and proved to have octahedral and square-planar geometry[4].

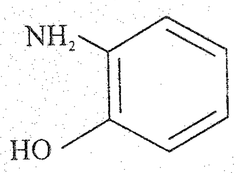
Our studies in this paper concern with the synthesis and physical characterization of some mixed ligand chelates of Co(II), Ni(II) and Cu(II) ions with 8-hydroxyquinoline **[L$_1$]**, anthranilic acid **[L$_2$]** and *o*-aminophenol **[L$_3$]** to establish their geometrical structures.



L$_1$



L$_2$



L$_3$

EXPERIMENTAL

All chemicals were reagent grade and purchased either from BDH or Aldrich as well as the organic solvents which were used in this investigation. Some of the solvents were redistilled. Water was always used as doubly distilled.

Synthesis of the mixed ligand chelates: The mixed ligand chelates were synthesized by stepwise addition of the two ligands to a solution of the metal ion as shown in eqns. (1) and (2).

$$M + L \longrightarrow ML \xrightarrow{L'} MLL' \qquad (1)$$

$$M + L' \longrightarrow ML' \xrightarrow{L} ML'L \qquad (2)$$

The chelates of divalent Co, Ni and Cu ions with mentioned ligands were obtained by mixing equal amounts of hot saturated ethanolic solutions of 0.01 mol of the metal salts [$CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$ and $CuCl_2{\cdot}2H_2O$] (0.01 mol) with saturated ethanolic solution of the first ligand (0.01 mol). The mixture was refluxed for 1 h and then the second ligand was added in the same ratio to the mixture and refluxed for three extra hours. A few drops of dilute ammonia solution were added slowly until pH 6–8 was attained; at this point the chelates were separated. The chelates formed thus were collected and washed several times with hot ethanol to remove traces of unreacted starting material. The chelates were then dried in air and stored in a desiccator over anhydrous $CaCl_2$. The yields of products were in the range of 65–80% and their purity was tested by TLC and elemental analysis.

The prepared chelates were subjected to elemental analysis at the Microanalytical Center, Ras-Lanouf Company, Libya. Infrared spectra were obtained by using KBr disk technique on IFS-25 DPUS/IR spectrometer (Bruker) in the range 4000–500 cm^{-1}. Electron paramagnetic resonance spectra were obtained by using EMX EPR spectrometer (Bruker, 1998). Both analyses were done at the Advanced Laboratory of Chemical Analysis, Al-Fateh University, Tripoli, Libya. Conductivity measurements were carried out in DMF and DMSO using conductivity-meter model CMD 650 digital.

RESULTS AND DISCUSSION

The analytical data of the prepared mixed ligand chelates are shown in Table-1. The metal-ligand interaction gave rise to chelates of the type $[MLL'(H_2O)_x]\cdot nH_2O$, in which M stands for Co(II), Ni(II) and Cu(II) ions, L and L′ represent ligands under investigation and n, x represent the number of water molecules in a way to be equal to 0, 1, 2, 3, etc. depending on the data obtained. The results obtained are in good agreement with those calculated for the proposed tentative formulae. All mixed ligand chelates were coloured, fairly stable under normal atmospheric conditions and soluble in DMSO. The chelates melted and decomposed at relatively high temperature (> 300°C).

The molar conductance values of the synthesized chelate (1×10^{-3} M) solutions in DMSO given in Table-1 display the presence of non-electrolytic chelates in the same solutions[4].

TABLE-1
ELEMENTAL ANALYSIS, MOLAR CONDUCTANCES AND COLOURS OF 8-HYDROXYQUINOLINE. *o*-AMINOBENZOIC ACID AND *o*-AMINOPHENOL WITH METAL ION CHELATES

Ligands/Chelates	m.w.	% Analysis						MC	Colour
		C		H		N			
		Calcd.	Found	Calcd.	Found	Calcd.	Found		
$[CoL_1L_2]\cdot 2H_2O$	375.25	51.21	51.79	4.30	3.92	7.47	7.82	1.00	Pale orange
$[CoL_1L_3]\cdot H_2O$	329.22	54.72	55.30	4.29	4.31	8.51	7.35	1.00	Brownish-orange
$[CoL_2L_3]$	303..18	51.50	51.33	3.99	3.79	9.24	8.42	1.00	Pale brown
$[NiL_1L_2]$	338.97	56.69	56.97	3.57	3.78	8.26	8.21	1.00	Pale green
$[NiL_1L_3]\cdot H_2O$	328.98	54.77	55.10	4.29	4.30	8.52	7.36	1.00	Yellowish-green
$[NiL_2L_3]$	302.94	51.54	51.25	3.99	3.97	9.25	8.40	4.00	Pale brown
$[CuL_1L_2(H_2O)_2]\cdot 3H_2O$	417.91	45.99	45.16	5.31	4.78	6.70	6.14	3.00	Greenish-gray
$[CuL_1L_3(H_2O)_2]\cdot 3H_2O$	405.89	44.39	44.89	5.46	5.21	6.90	6.00	3.00	Brownish-green
$[CuL_2L_3)]\cdot H_2O$	325.81	47.92	47.42	4.33	3.74	8.60	7.67	3.00	Dark Green

MC = molar conductivity ($ohm^{-1}\ cm^2\ mol^{-1}$)

The infrared spectral data of the mixed ligand chelates are presented in Table-2. The data show that the ligands under investigation act as bidentate species and their coordination was through the oxygen atom of hydroxyl or carboxyl group and the nitrogen atom of the amino group. The infrared spectra of the ternary chelates display a broad band in the range 3450–3300 cm^{-1} which is not present in the free ligands due to the existence of ν(OH) of the hydrated and coordinated water[5, 6]. The spectra of these chelates show the absence of δ(OH) and ν(C—OH) bands at 1346–1120 cm^{1} and 850–740 cm^{-1} respectively[7]. The disappearance of these bands and appearance of a new band in the range 650–512 cm^{1} which is attributed to ν(M–O) vibration suggest the involvement of —OH of the phenolic group in coordination with the metal ion[8–10]. The presence of water molecules in the ternary chelates is also supported by elemental analysis data as shown in Table-1 in the ternary chelates of the types $[CoL_1L_2]\cdot 2H_2O$, and $[CuL_1L_2(H_2O)_2]\cdot 3H_2O$, where L_1 represents 8-hydroxyquinoline and L_2 represents anthranilic acid.

TABLE-2
INFRARED SPECTRA AND ELECTRON PARAMAGNETIC RESONANCE OF 8-HYDROXYQUINOLINE, O-AMINOBENZOIC ACID AND O-AMINOPHENOL WITH METAL IONS CHELATES

Ligands/Chelates	IR (cm^{-1})						EPR
	ν(C═N)	ν(C═O)	ν(NH_2)	ν(OH^W)	ν(M—O)	ν(M—N)	(g_{eff})
$[CoL_1L_2]\cdot 2H_2O$	1538	1620	3300	3425	513	428	2.158
$[CoL_1L_3]\cdot H_2O$	1572	–	overlap	3350	650	500	2.158
$[CoL_2L_3]$	–	1600	3300	–	510	413	2.150
$[NiL_1L_2]$	1538	1608	3300	–	513	425	2.013
$[NiL_1L_3]\cdot H_2O$	1572	–	overlap	3325	644	500	2.011
$[NiL_2L_3]$	–	1595	3300	–	524	430	2.011
$[CuL_1L_2(H_2O)_2]\cdot 3H_2O$	1538	1610	3268	3450	513	425	2.123
$[CuL_1L_3(H_2O)_2]\cdot 3H_2O$	1578	–	overlap	3425	620	500	2.110
$[CuL_2L_3)]\cdot H_2O$	–	1596	3275	3425	512	430	2.122

IR = infrared; EPR = Electron Paramagnetic Resonance; ^{W} : of water molecule

The spectra exhibit a band at 1538 cm^{-1}, which is assigned to the ring (C═N) which appeared at 1610 cm^{-1} in the spectrum of the free ligand (L_1). This band is shifted to lower frequency by 72 cm^{-1} suggesting that this group is involved in coordination with the metal ion[10].

In addition, the spectral data of the free ligand (L_2) show a band at 1677 cm^{-1}, which is assigned to the (C═O) of the carboxyl group.[11, 12] and shifted to lower frequency in the spectra of the chelates by 57 cm^{-1}. The band of the bonded OH of the COOH group at 3400–2500 cm^{-1} disappeared on coordination with the metal ion[13].

The infrared spectra of $[CoL_2L_3]$, $[NiL_2L_3]$ and $[CuL_2L_3]$ display a disappearance of OH band of the phenolic group, which appeared at 3300 cm^{-1} in the free ligands indicating the participation of OH group in chelation with the metal ion. With regard to $[CoL_1L_3]\cdot H_2O$, $[NiL_1L_3]\cdot H_2O$ and $[CuL_1L_3(H_2O)_2]\cdot 3H_2O$ complexes, the band which attributed to cyclic (C═N) appeared at 1610 cm^{-1} in the free ligand (L_1) and shifted to lower frequency in the range 1572–1578 cm^{-1} in the infrared spectra of these ternary chelates, also suggesting the involvement of this band in complexation[10].

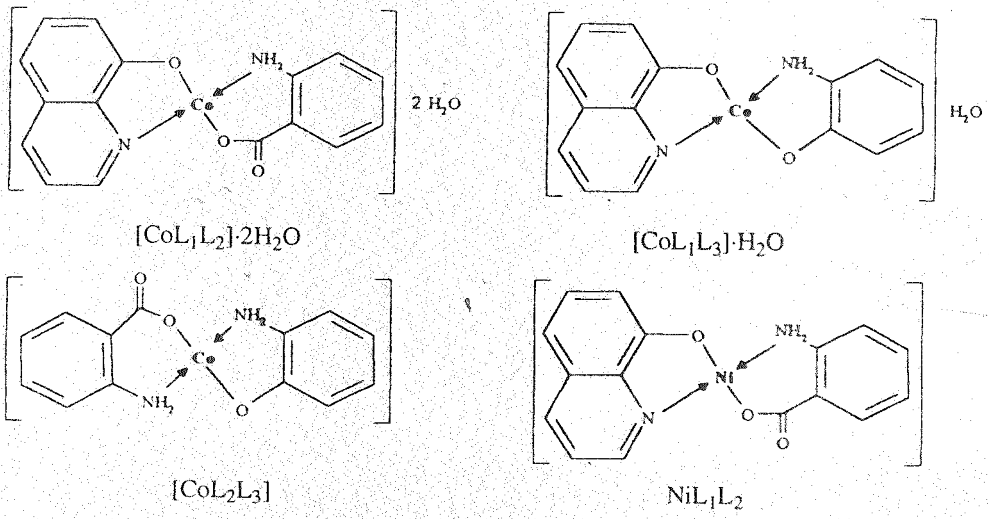
The complexation site that can take part in the chelates of the formulae $[CoL_2L_3]$, $[NiL_2L_3]$ and $[CuL_2L_3]\cdot 2H_2O$ is the COOH group. The strong evidence for the involvement of this group comes from the shift in the frequency of the (C=O) vibration of COOH group in the spectrum of the chelates as compared to the free ligands. The band for —OH of the carboxyl group disappeared on complexation[11–13].

The infrared spectra of most ternary chelates exhibit a band in the range 3300–3268 cm^{-1} that is assigned to the presence of NH_2 group which appeared at 3380 cm^{-1} in the spectra of ligands. This peak is shifted to lower frequency, suggesting that the NH_2 group participated in coordination[14].

On the other hand, the same band of the NH_2 group could not be distinguished in the spectra of the chelates of the formula $[CoL_1L_3]\cdot H_2O$, NiL_2L_3 and $[CuL_1L_3(H_2O)_2]\cdot 3H_2O$ because it coincided with the ν(OH) band of water molecules. It is known that the involvement of NH_2 group in complexation can be supported by the appearance of new band in the range 500–413 cm^{-1} due to ν(M—N) vibration, that is not present in the free ligands.

The electron paramagnetic resonance spectra of the mixed ligand chelates display g_{eff} values in the range of 2.011–2.158. We can notice the increase in these values as compared with the values of the free electron (2.0023) that results from the partial ionic characters of the covalent bond between the metal ions and the ligands. The data have been summarized in Table-2. The obtained information indicates that $[CoL_1L_2]\cdot 2H_2O$ and $[CoL_1L_3]\cdot 2H_2O$ chelates[15] have a tetrahedral geometry and $[NiL_1L_2]$, $[NiL_1L_3]\cdot 2H_2O$, $[NiL_2L_3]$, $[Cu_1L_3]\cdot H_2O$ complexes have a square planar geometry.[16] Meanwhile $[CuL_1L_2(H_2O)_2]\cdot 3H_2O$ and $[CuL_1L_3(H_2O)_2]\cdot 3H_2O$ chelates have an octahedral geometry[15, 16].

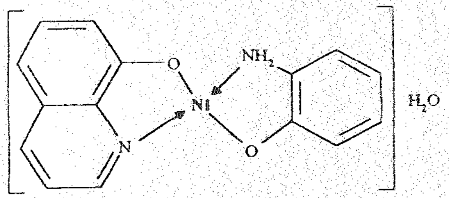
From the above data and their analysis, we may summarize the expected chemical structures for the mixed ligand chelates prepared in this work as shown in Fig. 1.



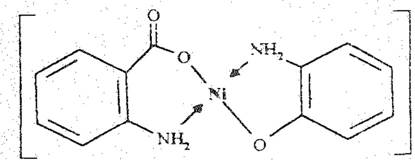
$[CoL_1L_2]\cdot 2H_2O$ $[CoL_1L_3]\cdot H_2O$

$[CoL_2L_3]$ NiL_1L_2

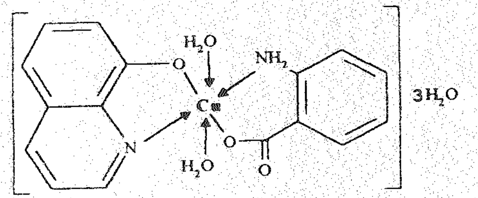
Fig. 1. Proposed structures of metal chelates (*Contd.*)



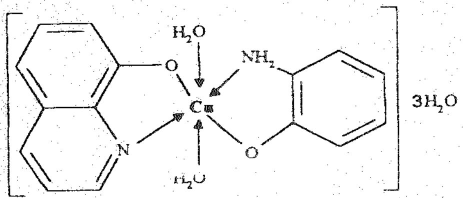
$[NiL_1L_3]\cdot H_2O$



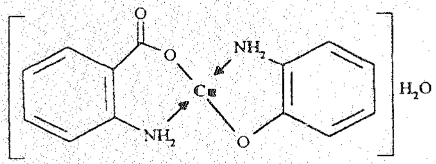
$[NiL_2L_3]$



$[CuL_1L_2(H_2O)_2]\cdot 3H_2O$



$[CuL_1L_3(H_2O)_2]\cdot 3H_2O$



$[CuL_2L_3]\cdot H_2O$

Fig. 1. Proposed structures of metal chelates

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