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Spectroscopic and Thermal Analysis of Mixed Ligand Complexes of Iron(III) and Copper(II) Derived from Catechol and Benzil

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Two new mixed ligand complexes of Fe(III) and Cu(II) with catechol and benzil ligands have been prepared and characterized. The probable structures of the complexes have been elucidated on the basis of elemental analyses, molar conductance, thermogravimetric analysis, magnetic moments, infrared, electron paramagnetic resonance, electronic adsorption and mass spectra. The elemental analysis data reveal the formation of 2:1:1 [M:L^1:L^2] complexes. The molar conductance measurements show the presence of a non-electrolytic nature. The thermogravimetric analysis data of both complexes display the existence of hydrated and coordinated water molecules. The magnetic moments exhibit a paramagnetic resonance spectra of the complexes under investigation show the existence of a paramagnetic phenomena which support their geometrical structures. The infrared spectral data were agreed with the coordination sites of the free ligand with the central metal ion through –OH and C=O groups. The electronic adsorption spectral results display the electronic transitions of the ligand and suggest an octahedral structure for Fe(III) complex and a square planar geometry for Cu(II) complex. The mass spectrum of Fe(III) complex shows the fragmentation process (m/e^+) for this complex.

Key Words: Catechol, Benzil, Mixed ligand complexes, Iron(III), Copper(II).

INTRODUCTION

Some novel mixed ligand complexes of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) ions with salicylaldehyde and catechol have been prepared and investigated by several techniques[1]. The preparation and characterization of mixed ligand complexes of Co(II) and Fe(III) ions with malonic acid and heterocyclic amines are also reported[2]. The binuclear mixed ligand complexes (2,2′-dipyridyl)-(3-methoxysalicylaldiminato) copper(II) perchlorate and (2,2′-dipyridyl)-(4-methoxysalicylaldiminato) copper(II) perchlorate were synthesized and their crystal structures were also determined[3].

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The present paper describes the synthesis, spectral and thermal properties of the mixed ligand complexes of Fe(III) and Cu(II) transition metal ions derived from catechol and benzil, to elucidate their geometrical structures.

EXPERIMENTAL

All chemicals used in the investigation were of AnalaR grade (BDH) *e.g.*, $FeCl_3·6H_2O$, $CuCl_2·2H_2O$, catechol, benzil, NH_4OH, C_2H_5OH, DMF and double distilled water.

The synthesized mixed ligand complexes were subjected to (C and H) elemental analyses using 2400CH elemental analyzer. The molar conductance measurements were carried out in DMF solvent using conductivity meter Model CMD650 digital, were preformed in advanced Laboratory of Physical Chemistry, Garyounis Univeristy, Benghazi, Libya. Thermogravimetric analysis was performed using Shimadzu Thermal Analyzer (Japan). The weight losses were measured from ambient temperature to 1000 ºC in rate of 10 ºC/min. The magnetic moments of the complexes were measured by using magnetic susceptibility balance Sherwood Scientific England. The infrared spectra were obtained by using KBr disk technique on IFS-25 DPUS/Ir spectrometer (Bruker) in the range of 4000-500 cm^{-1}. The electronic adsorption spectra of the complexes were measured in DMF solvent using UV-Vis NIR3101PC Schimadzu (Japan). The electron paramagnetic resonance spectra were recorded by using EMX ESR spectrometer (Bruker) 1998Y. The mas spectra were carried out using Q 1000 EXGC-MS Schimadzu spectrometer at 70 eV and MA energy using a direct insertion probe at temperature 90-110 ºC. All the previous chemical analyses were done at the Micro analytical center, Cairo-University, Egypt.

Preparation of mixed ligand complexes: The present mixed ligand complexes were prepared by mixing equal amounts (0.01 mol) of hot saturated ethanolic solutions of the first ligand (catechol; 1.10 g) with the same ratio of $FeCl_3·6H_2O$ and $CuCl_2·2H_2O$ salts. The mixtures were refluxed for 1 h and then the second ligand (benzil; 2.10 g) was added in the same ratio to the previous mixtures and refluxed again for 3 h. Few drops of ammonia solution were added to adjust the pH at which the complexes even separated. The resulting complexes were washed several times with hot ethanol until the filtrate becomes clear, dried in air and then in vaccum over anhydrous $CaCl_2$. The yield ranged from 70-80 %. The obtained complexes are insoluble in C_2H_5OH but soluble in DMF solvent. All melting points of the prepared mixed ligand complexes were measured and found to be > 360 ºC.

RESULTS AND DISCUSSION

The obtained elemental analysis data of the mixed ligand complexes Table-1 show the formation of 2:1:1 [$M:L^1:L^2$] ratio. It is found that the theoretical values are in a good agreement with the found ones. The purity of the mixed ligand complexes were tested by TLC technique and (C and H) elemental analyses. The molar conductance values of the synthesized mixed ligand complexes with the mentioned metal ions under investigation were determined using 10^{-3} M DMF solvent, as shown in Table-1. These values suggest the presence of a non-electrolytic nature[4]. The thermogram curves of Fe(III) and Cu(II) complexes Table-1 show the weight-losses of 28 and 27 % which are attributed to the presence of various levels of hydration water molecules in the complexes at temperature of 135-180 ºC. Meanwhile, the Fe(III) complexes has a weight-loss at 7 % which is due to the existence of two water molecules of coordination at temperature 210 ºC. The metal oxide residues of these complexes were recorded at 17 and 22 % at temperature of 810-890 ºC.

TABLE-1
SOME PHYSICAL PROPERTIES OF MIXED LIGAND COMPLEXES

Complexes (m.w.)	Elemental analysis %: Found (Calcd.)		Ω_C	μ_{eff} (BM)	Water of hydration weight loss (%)	Water of coordination weight loss(%)
	C	H				
$[Fe_2L^1L^2.4OH.2H_2O]\cdot12H_2O$ (749.69)	32.01 (32.00)	6.13 (6.00)	0.03	6.61	28.18 (28.00)	6.75 (7.00)
$[Cu_2L^1L^2.2OH]\cdot10H_2O$ (659.09)	36.41 (35.50)	5.46 (5.50)	0.20	2.00	27.31 (27.00)	–

Ω_C = ohm^{-1} cm^2 mol^{-1}

The infrared spectra of the present complexes (Table-2) illustrate the main groups of the mixed ligand complexes of $[Fe_2L^1L^2\cdot4OH\cdot 2H_2O]12H_2O$ and $[Cu_2L^1L^2\cdot2OH]10H_2O]$ whereas, the broad bands were recorded at 3400 and 3336 cm^{-1}, respectively, attributed to the presence of water molecules in complexes[5]. The absorption band at 1663 cm^{-1} in the spectrum of the free ligand (benzil) explains the stretching vibration of the carbonyl group of the ligand. The shift of this group to lower region indicates the effect of chelation in this group. New bands at 594 and 671 cm^{-1} due to the appearance of ν(M-O) vibrations[6]. The position of the these bands give a good evidnece for the chelation of oxygen atoms in the ligands under investigation with Fe(III) and Cu(II) ions.

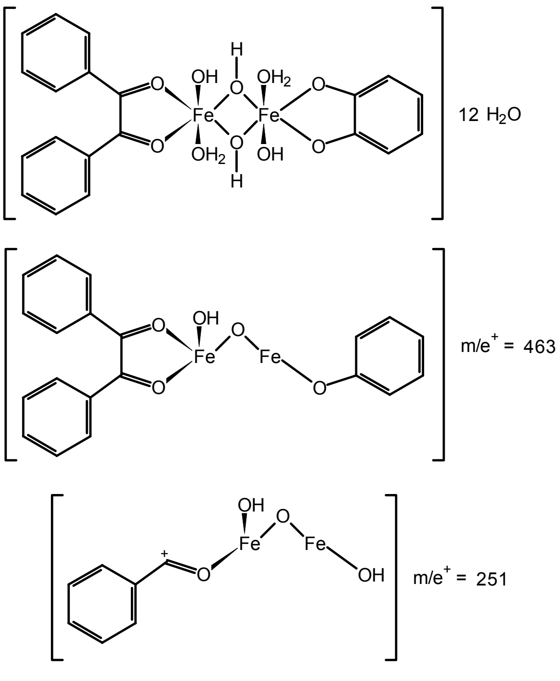
The electronic absorption spectra of the prepared complexes were recorded in DMF solvent (Table-2). The magnetic moment values of the complexes (Table-1) displays the presence of a paramagnetic phenomena for both complexes. The electronic absorption spectrum of the $[Fe_2L^1L^2\cdot4OH\cdot2H_2O]\cdot12H_2O$ complex shows different bands (Table-2) which can be assigned to charge transfer transitions and an octahedral structure was proposed for this complex[7]. For the spectrum of Cu(II) complex, the bands at 736 nm (13587 cm^{-1}), 402 nm (24875 cm^{-1}) and 283 nm (35335 cm^{-1}) are due to charge transfer transitions and based on these data a square planar geometry was proposed[8].

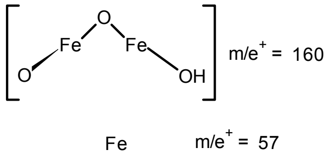
TABLE-2
EPR, IR (cm^{-1}) AND ELECTRONIC SPECTRAL DATA (nm, cm^{-1}) OF THE LIGANDS AND THEIR METAL COMPLEXES

Ligands/complexes	ν(OH) H_2O	ν(C=O) CHO	ν(C=O) Ketone	ν(M-O)	λ_{max}, nm (cm^{-1})	g_{eff}
L^1	-	-	-	-	– (–)	-
L^2	-	-	1663	-	– (–)	-
$[Fe_2L^1L^2.4OH.2H_2O]\cdot 12H_2O$	3400	-	1604	594	278 (35971) 262 (38168)	2.015
$[Cu_2L^1L^2.2OH]\cdot 10H_2O$	3336	-	1602	671	736 (13587) 402 (24875) 283 (35335)	2.135

Electron paramagnetic resonance data of $[Fe_2L^1L^2\cdot 4OH\cdot 2H_2O]\cdot 12H_2O$ and $[Cu_2L^1L^2\cdot 2OH]\cdot 10H_2O$ complexes display g_{eff} values at (2.015 and 2.135). these two values are deviated from the ideal free electron value. The observed deviation is due to the existence of a partial ionic character of covalent bond between the two metal atoms in binuclear complexes, so these values confirm the existence of an octahedral structure for Fe(III) complex and square planar geometry for Cu(II) complex[8,9].

Mass spectra: In Fe(III) complex, the base peak at m/e^+ 463 is corresponding the decomposition of the complex under investigation as shown in the **Scheme-I** and there is a constant weight raising from temperature regarding to the existence of the metallic oxide residue.

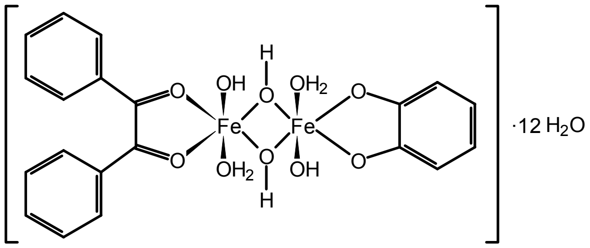


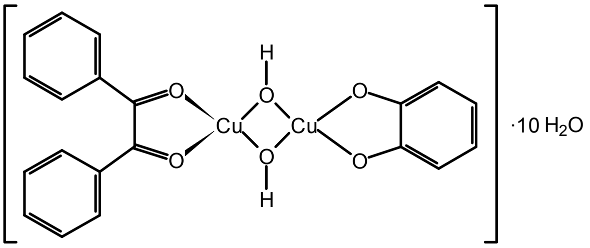


Scheme-I: Mass spectrum of Fe(III) complex

Conclusion

From the reported data, the following chemical structures for the synthesized mixed ligand complexes are proposed.





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