

## Preparation, Characterization and Antibacterial Activity of some Mixed Ligand Chelates

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**Summary:** The Mn(II), Fe(III), Co(II) and Cu(II) mixed ligand chelates derived from catechol (L<sup>1</sup>) and 2-aminobenzothiazole (L<sup>2</sup>) have been prepared and characterized by different techniques, in particular; CHNS elemental analysis, molar conductivity, magnetic moments, infrared and electronic spectra. The CHNS elemental analysis data showed the formation of 1:1:1 and 2:1:1 [M:L<sup>1</sup>:L<sup>2</sup>] chelates. The molar conductance measurements revealed a non-electrolytic nature. The magnetic moment measurements exhibited a paramagnetic phenomenon. The infrared spectral data showed the coordination sites that are via -OH, C=N and NH<sub>2</sub> groups of the mentioned ligands. The electronic spectra exhibited the expected geometrical structures for the chelates. The prepared Cu(II) and Fe(III) chelates were assayed for antibacterial activity against some human pathogenic bacteria: *Staphylococcus aureus*, *Escherichia coli* and *Klebsiella pneumoniae* using the hole diffusion method and placing the chelates on surface at nutrient agar. No effects were recorded. This result suggests the absence of active components or due to the insensitivity of bacteria we assayed.

### Introduction

Catechol and 2-aminobenzothiazole compounds are bidentate ligands and have a good ability to form many transition metal ion chelates [1]. Maihub *et al.* [2] synthesized and investigated some mixed ligand chelates of benzoin and phthalic acid, and their geometrical structures were characterized by several physicochemical techniques. Some mixed ligand chelates of divalent metal ions with salicylaldehyde, phthalic acid and L-alanine were prepared and characterized by using different physical techniques [3]. Mixed ligand chelates of Mn(II) and Co(II) ions with salicylaldehyde and 6-formyl-7-hydroxy-5-methoxy-2-methylchromone have been prepared and characterized by several tools, such as, elemental analysis, molar conductivity and spectroscopic techniques [4].

This investigation aims to prepare and characterize the geometrical structures of some transition metal ion chelates with mixed ligands derived from catechol and 2-aminobenzothiazole. Also to show the biological activity of the ligands and their chelates on some pathogenic bacteria.

### Results and Discussion

#### Microanalysis

The CHNS elemental analysis data of the mixed ligand chelates under investigation (Table-1) display the formation of 1:1 [M:L]ratio. It is found that the theoretical values are in a good agreement

with the found ones. The purity of the mixed ligand chelates were assured by elemental analyses.

#### Molar Conductivity Measurements:

The molar conductivity values of the prepared mixed ligand chelates in 10<sup>-3</sup> M DMF solvent are in the range of 0.13-0.74 Ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> (Table-1). These values exhibit a non- electrolyte nature [5].

#### Infrared Spectra

The infrared band assignments of the Mn(II), Fe(III), Co(II) and Cu(II) mixed ligand chelates are listed in Table-2. The spectra of the chelates exhibit a broad band in the range of 3228-3400 cm<sup>-1</sup> corresponding to the presence of water molecules [6]. Meanwhile, the same spectra display a band in the range of 1577-1618 cm<sup>-1</sup> due to C=N group. The change of this group compared to its original position in the free ligands (1605 cm<sup>-1</sup>) indicating the involvement of C=N group in coordination through nitrogen atom with the metal ions [7]. The disappearance of NH<sub>2</sub> band of the ligand confirming the involvement of this group in chelation. New bands in the range of 466-500 and 598-629 cm<sup>-1</sup> are assigned to the  $\nu$  ( M-N ) and  $\nu$  ( M-O ) vibrations, respectively [8]. The appearance of these bands support the involvement of -C=N, NH<sub>2</sub> and -OH groups via nitrogen and oxygen atoms, Fig. 1.

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Table-1: CHNS elemental analyses and some physical properties of mixed ligand chelates.

Chelates	Mol. Wt	C%	H%	N%	S%	$\Delta$	$\mu$ BM
[MnL <sup>1</sup> L <sup>2</sup> (H <sub>2</sub> O) <sub>2</sub> ].8H <sub>2</sub> O	493	31.64(30.71)	5.68(4.66)	5.67(4.81)	6.49(6.14)	0.13	2.70
[FeL <sup>1</sup> L <sup>2</sup> (OH)(H <sub>2</sub> O)].6H <sub>2</sub> O	457	34.15(33.00)	2.18(3.46)	6.12(4.88)	7.00(5.52)	0.74	--
[Co <sub>2</sub> L <sup>1</sup> L <sup>2</sup> (OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].6H <sub>2</sub> O	590	26.44(25.67)	3.08(3.56)	4.75(5.11)	5.42(5.63)	0.48	2.70
[Cu <sub>2</sub> L <sup>1</sup> L <sup>2</sup> (OH) <sub>2</sub> ].H <sub>2</sub> O	437	35.69(35.51)	2.75(3.91)	6.40(6.08)	7.32(7.44)	0.54	1.00

Table-2: Infrared band assignments (cm<sup>-1</sup>) and electronic spectral data (nm) of the ligands and their mixed ligand chelates.

Chelates	$\nu_{(NH_2)}$	$\nu_{(C-N)}$	$\nu_{(OH)H_2O}$	$\nu_{(M-O)}$	$\nu_{(M-N)}$	UV-Vis (nm)
L <sup>1</sup>	--	--	--	--	--	--
L <sup>2</sup>	3339	1605	--	--	--	--
[MnL <sup>1</sup> L <sup>2</sup> (H <sub>2</sub> O) <sub>2</sub> ].8H <sub>2</sub> O	--	1543	3367	629	500	540 411 390 361
[FeL <sup>1</sup> L <sup>2</sup> (OH)(H <sub>2</sub> O)].6H <sub>2</sub> O	--	1577	3228	598	483	330 438
[Co <sub>2</sub> L <sup>1</sup> L <sup>2</sup> (OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].6H <sub>2</sub> O	--	1550	3400	605	466	305 433 576
[Cu <sub>2</sub> L <sup>1</sup> L <sup>2</sup> (OH) <sub>2</sub> ].H <sub>2</sub> O	--	1618	3400	614	483	519 451 324

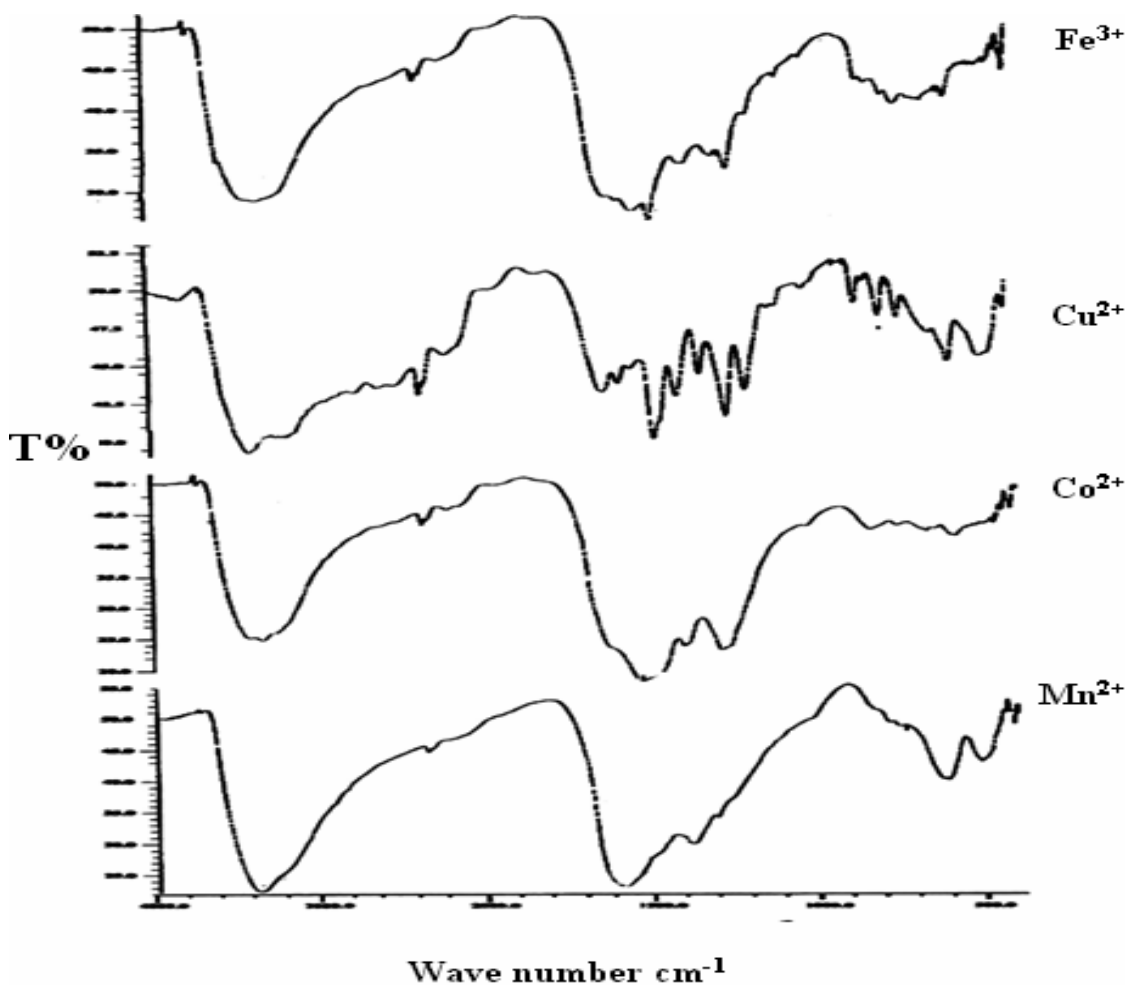


Fig. 1: Infrared Spectra of the Mn(II), Co(II), Cu(II) and Fe(III) mixed Chelates.

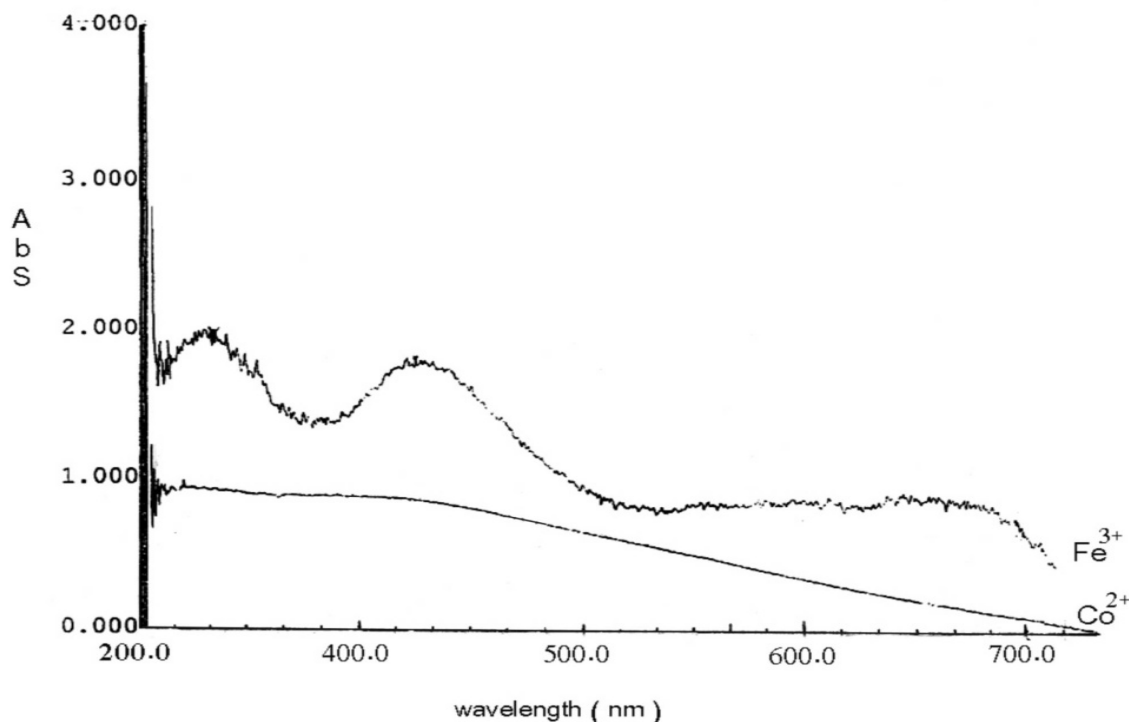


Fig. 2: Electronic Spectra of Co(II) and Fe(III) mixed Ligands chelates.

*Electronic Spectra and Magnetic Moments*

The electronic spectra of the chelates were recorded in DMF solvent and their assignments are listed in Table-2. Their spectra are shown in Fig. 2. The magnetic moment values of the chelates (Table-1) exhibit the presence of paramagnetic phenomena. The electronic spectral data of  $[MnL^1L^2(H_2O)_2]8H_2O$  chelate show four bands (Table-2) suggesting the existence of a charge transfer transition,  ${}^2A_{1g}(I) \rightarrow {}^2A_{2g}(I)$ ,  ${}^2A_{1g}(I) \rightarrow {}^2E_{1g}(I)$  and  ${}^2A_{1g}(I) \rightarrow {}^2T_{1g}(I)$  transitions. An octahedral geometry was proposed for this chelate [9]. The Fe(III) chelate spectrum exhibits two bands at 330nm ( $30303\text{ cm}^{-1}$ ) and 438nm ( $22831\text{ cm}^{-1}$ ) which are due to  $M \rightarrow L$  charge transfer and  ${}^2T_{2g} \rightarrow {}^2E_g$  transitions. An octahedral structure was suggested for the chelate [10]. Meanwhile, the spectral data of  $[Co_2L^1L^2(OH)_2(H_2O)_4]6H_2O$  chelate displays two bands at 305nm ( $32787\text{ cm}^{-1}$ ) and 433 nm ( $23094\text{ cm}^{-1}$ ) assigning to the existence of a charge transfer and  ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$  transitions. The lowering in the magnetic moment value of the Co(II) chelate is due to the presence of Co-Co bond character [11]. Both magnetic moment value and the intensity of the bands suggest an octahedral geometry around Co(II) complex. Also the spectral data of  $[Cu_2L^1L^2(OH)_2]H_2O$  chelate exhibits several bands (Table-2) confirming the existence of a square planar around the chelate [12].

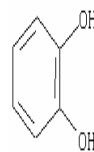
*Antibacterial Activity*

All mixed ligand chelates under investigation found to be inactive against all bacteria tested by two different methods used. These results suggest that the tested bacteria may be unable to utilize the mixed ligand chelates used, or due to the concentration used not enough to inhibit the bacterial growth.

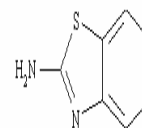
**Experimental**

*Chemicals*

All chemicals were reagent grade (BDH or Aldrich) and all organic solvents used in this study were obtained as pure grade materials from BDH. Doubly distilled water was always used. The ligands under investigation have the following structures:



L<sup>1</sup>



L<sup>2</sup>

### Preparation of Mixed Ligand Chelates

The mixed ligand chelates under investigation were prepared by mixing equal amounts (0.01 mole) of hot ethanolic solutions of the first ligand (Catechol; 0.01 mole) with the same ratio of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  salts. The mixtures were refluxed for one hour, and then the second ligand (2-aminobenzothiazole) was added in the same ratio to the mixtures and refluxed for three extra hours. Few drops of ammonia solution were added to adjust the pH at which the mixed ligand chelates even separated. They were washed several times with hot ethanol until the filtrate becomes colorless. The obtained chelates were dried in desiccators over anhydrous  $\text{CaCl}_2$  and yields 70-85%. All melting points of the obtained mixed ligand chelates were measured and found to be  $>360^\circ\text{C}$ .

### Physical Measurements

The prepared mixed ligand chelates were subjected to (C, H, N and S) elemental analyses using 2400 elemental analyzer, Molar conductivity measurements were carried out in DMF solvent using conductivity meter model CMD650 digital. Magnetic moment measurements of the chelates 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  $400\text{--}500\text{ cm}^{-1}$ . The electronic absorption spectra of the chelates were measured in DMF solvent using UV-Vis-NIR3101PC Shimadzu (Japan). All the previous chemical analyses were done at the Micro analytical center-Cairo University, Giza, Egypt.

### Bacteria Used

Three types of human pathogenic bacteria were used to test the biological effects of the present mixed ligand chelates. All bacteria were obtained and identified from 7<sup>th</sup> October hospital, Benghazi, Libya. The bacteria used were *Escherichia coli*, *staphylococcus aureus* and *Klebsilla pneumonia species*.

### Antibacterial Assay

The antibacterial activity was determined by placing different weights of the prepared mixed ligand chelates on the surface of incubated agar with the tested bacteria and by placing the mixed ligand chelates in the hole of incul method ) [13]. All plates w

at  $37^\circ\text{C}$ . After incubation, the mean of inhibition zone was measured.

### Conclusion

From the previous data [elemental analyses, molar conductivity, magnetic moments, infrared and electronic spectra], we can suggest the following chemical structures for the prepared mixed ligand chelates (Fig. 3).

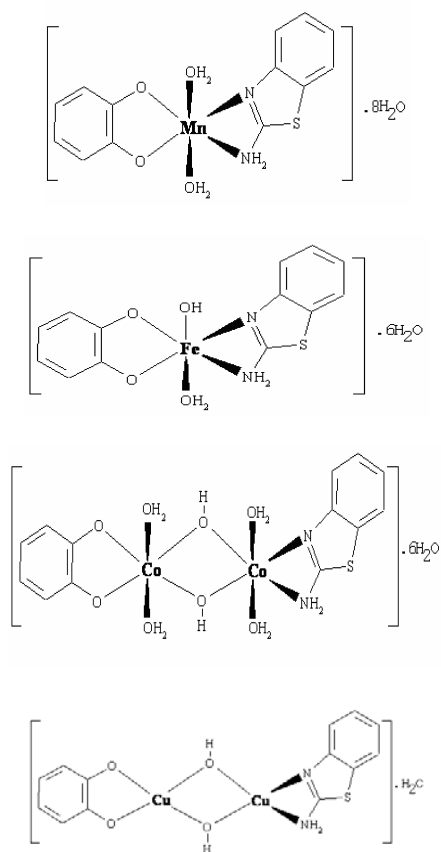


Fig. 3: Chemical structures of mixed ligand chelates.

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