

Studies and Characterization of Mixed Ligands Complexes of VO(IV), Cr(III) and Fe(III)

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Three mixed ligand chelates of V(IV), Cr(III) and Fe(III) metal ions with salicylaldehyde (L^1), catechol (L^2) and benzil (L^3) have been prepared and investigated by elemental analysis, molar conductivity, thermogravimetric analysis, magnetic moments, infrared, electronic and electron paramagnetic resonance spectra. The elemental analysis data show the formation of 1:1:1 [M:L:L'] chelates. The molar conductance measurements reveal the presence of a non-electrolytic nature. The thermogravimetric analysis data display the existence of water molecules in the chelates. The magnetic moment measurements exhibit the presence of paramagnetic phenomena for all chelates. The infrared spectral data show the coordination site *via* -CHO, -OH and C=O groups of salicylaldehyde catechol and benzil moieties. The electronic absorption spectra exhibit the expected geometrical structures for the prepared chelates. The electron paramagnetic resonance spectra show that the chelates that have a paramagnetic character and support the electronic spectra in the determination of the structure.

Key Words: Mixed ligand complexes, VO(IV), Cr(III), Fe(III).

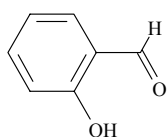
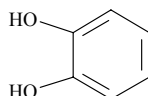
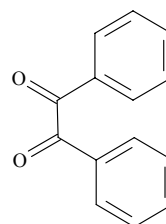
INTRODUCTION

Salicylaldehyde and catechol compounds are bidentate ligand and have a good ability to form many transition metal ion chelates¹. El-Ajaily *et al.*² reported some mixed ligand chelates of divalent metal ions with salicylaldehyde, phenylenediamine, phthalic acid and L-alanine. New mixed ligand complexes of Mn(II) and Co(II) ions with salicylaldehyde and 6-formyl-7-hydroxy-5-methoxy-2-methylchromone have been prepared and characterized by elemental analysis, molar conductivity and spectroscopic techniques³. Maihub *et al.*⁴ synthesized and investigated some mixed ligand complexes of benzoin and phthalic acid, as well the geometrical structures were investigated and characterized. This paper concerned on the synthesis and elucidation of the geometrical structures of the of some mixed ligand complexes of VO(IV), Cr(III) and Fe(III).

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EXPERIMENTAL

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

Salicylaldehyde (L¹)Catechol (L²)Benzil(L³)

Preparation of mixed ligand chelates: The mixed ligand chelates of V(IV), Cr(III) and Fe(III) ions with the ligands under investigation were prepared by mixing equal amounts (0.01 mol) of hot saturated ethanolic solutions of salicylaldehyde (0.01 mol) with the same ratio of $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The mixture refluxed for 1 h and then the second ligand (catechol or benzil) was added in the same ratio to the mixture and refluxed for extra 3 h. Few drops of ammonia solution were added to adjust the pH = 8, at which the mixed ligand chelates even separated. They were washed several times with hot ethanol until the filtrate becomes colourless. The obtained chelates were dried in desiccators over anhydrous CaCl_2 and yields estimated to be 75-85 %.

The prepared mixed ligand chelates were subjected to elemental analysis in the Micro analytical center, Ras-Lanouf Company, Libya. Molar conductivity measurements were carried out in DMF solvent using conductivity meter model CMD650 digital. Thermogravimetric analysis was achieved by using TGA-H50 Shimadzu thermal analyzer (Japan). Magnetic moment measurements of the chelates were measured by using magnetic susceptibility balance Sherwood Scientific England. Infrared spectra were obtained by using KBr disk technique on IFS-25 DPUS/IR spectrometer (Bruker) in the range of $4000\text{-}500\text{ cm}^{-1}$. The electronic absorption spectra of the chelates were measured in chloroform solvent using UV-Vis-NIR 3101 PC Shimadzu (Japan). The electron paramagnetic resonance spectra were carried out EMX ESR spectrometer (Bruker) 1998. The thermo gravimetric analysis, magnetic moments, infrared, electronic and electron paramagnetic resonance spectra were done at Microanalytical center, Cairo University, Giza, Egypt.

RESULTS AND DISCUSSION

The elemental analysis data of the mixed ligand chelates of VO(IV), Cr(III) and Fe(III) ions with the ligands under investigation are given in the Table-1. The data display the formation of 1:1:1 [M: L:L⁻] ratio. It is found that the theoretical values are in a good agreement with the experimental results. The purity of the mixed ligand chelates were assured by elemental analyses and TLC techniques.

The molar conductivity values of the prepared mixed ligand chelates with these metal ions in 10⁻³ M DMF solvent, shown in Table-1, are in the range of 23.70-34.90 ohm⁻¹ cm² mol⁻¹. These values exhibit the presence of a non-electrolytic nature⁵.

The thermogravimetric analysis is a technique opens new possibilities for the characterization of the geometrical structures of the chelates⁶ and to obtain information about the thermal stability of the chelates and decide whether the water molecules are present inside or outside the coordination sphere. For [VOL¹L²(H₂O)]·H₂O, [CrL¹L²(H₂O)₂]·2H₂O, [FeL¹L²(H₂O)₂]·6H₂O, [FeL¹L³(OH)₂]·5H₂O and [CrL¹L³(OH)₂]·2H₂O chelates, the weight losses of 5.45, 11.34, 26.04, 14.07 and 8.01 %, respectively, correspond to the loss of 1, 2, 6 and 5 water molecules of hydration at temperature range of 144-310°C. On the other hand, the weight-losses of 6.55, 11.05 and 11.37 %, respectively, are due to the presence of one or two coordinated water molecules, at 310-341°C. A final product can be observed as metal oxide in the ranging of 425-575°C.

The infrared band assignments of the mixed ligand complexes of VO(IV), Cr(III) and Fe(III) ions exhibit a broad band in the range of 3402-3383 cm⁻¹, corresponding to the presence of water molecules⁷. Meanwhile, same spectra of the chelates display bands in the range of 1662-1609 cm⁻¹, which are assigned to (-C=O) group of the salicylaldehyde and benzil rings moiety. The shifting in the band of the same group to lower region compared to the original position in the free ligands (1690, 1650 cm⁻¹), indicating the involvement in coordination with the metal ions under study⁸. New bands in the range of 640-586 cm⁻¹ are assigned to the ν(M-O) vibration⁹. The appearance of this group supports the involvement of hydroxyl group *via* oxygen atoms.

The electronic spectra of the mixed ligand complexes were recorded in chloroform and their assignments are given in Table-1. The magnetic moment values of the mixed ligand complexes as shown in Table-1 exhibit the presence of paramagnetic phenomena. The electronic spectral data of [VOL¹L²(H₂O)]·H₂O display three bands at 296 nm (33784 cm⁻¹), 326 nm (30675 cm⁻¹) and 387 nm (25840 cm⁻¹) which are attributed to charge transfer transition and ²T_{2g} → ²E_g transition. The data support the presence of an octahedral geometry¹⁰. The absorption spectrum of [CrL¹L²(H₂O)₂]·2H₂O

TABLE-1
 PHYSICAL DATA FOR THE MIXED LIGAND CHELATES OF VO(IV), Cr(III) AND Fe(III) IONS
 WITH SALICYLALDEHYDE, CATECHOL AND BENZYL

Complex	Found (Calcd.) %		Colour	MC	Water of hydration	No ^o of H ₂ O	°C	Water of coordination	No ^o of H ₂ O*	°C*	MO	°C**
	C	H										
[VO(L ¹ L ² (H ₂ O)]·H ₂ O	47.13 (47.10)	3.93 (3.79)	Dark brown	25.30	5.37 (5.45)	1	183	5.68 (6.55)	1	271	25.10 24.37	452
[CrL ¹ L ² (H ₂ O) ₂]·2H ₂ O	44.19 (43.70)	4.81 (4.20)	Black	34.90	10.20 (11.34)	2	144	10.20 (11.05)	2	320	28.30 30.05	425
[FeL ¹ L ² (H ₂ O) ₂]·6H ₂ O	36.90 (37.06)	5.30 (4.90)	Black	23.70	25.00 (26.40)	6	310	11.12 (11.37)	2	341	25.01 26.23	500
[CrL ¹ L ³ (OH) ₂]·2H ₂ O	55.29 (54.10)	4.19 (3.80)	Green	33.00	7.94 (8.01)	2	144	7.94 (8.01)	–	–	22.07 22.00	575
[FeL ¹ L ³ (OH) ₂]·5H ₂ O	49.31 (49.73)	4.90 (3.84)	Dark gray	35.40	14.50 (14.07)	5	185	14.50 (14.07)	–	–	27.37 28.88	540

L¹, L², L³ = Are the ligands (Salicylaldehyde, Catechol and Benzyl)

MC = Molar Conductivity (Ohm⁻¹ Cm² mol⁻¹)

N^o of H₂O = Number of water molecule in the complex

°C = The temperature of water molecule of hydration

N^o of H₂O* = Number of water molecule of hydration

°C* = The temperature of water molecule of coordination

MO = Number of water molecule in the complex

°C** = The temperature of decomposition

TABLE-2
 INFRARED, ELECTRONIC, UV-VIS, ELECTRON PARAMAGNETIC RESONANCE SPECTRAL DATA AND MAGNETIC MOMENTS OF THE MIXED LIGAND CHELATES OF VO(IV), Cr(III) AND Fe(III) IONS WITH SALICYLALDEHYDE, CATECHOL AND BENZYL

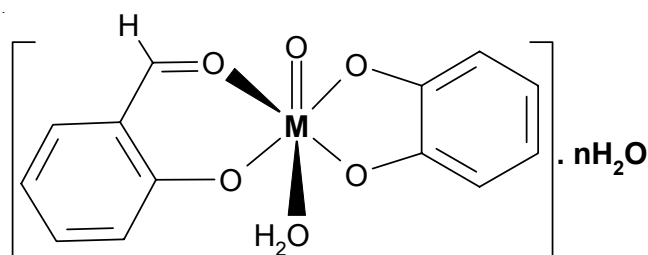
Complex	IR (cm ⁻¹)			v(M-O)	UV-Vis nm (cm ⁻¹)	EPR	μ_{eff} (BM)
	v(OH) _{water}	v(C=O) _{ald}	v(C=O) _{ketone}				
[VO(L ¹ L ² (H ₂ O)]·H ₂ O	3402	1609	–	598	296 (33784), 326 (30675), 387 (25840)	2.0022	1.84
[CrL ¹ L ² (H ₂ O) ₂]·2H ₂ O	3400	1609	–	617	413 (24213)	2.0800	4.40
[FeL ¹ L ² (H ₂ O) ₂]·6H ₂ O	3383	1609	–	586	447 (22371)	2.0045	6.01
[CrL ¹ L ³ (OH) ₂]·2H ₂ O	3402	1593	1659	640	362 (27624), 381 (26274), 406 (24631), 486 (20576), 686 (27473)	2.0880	4.40
[FeL ¹ L ³ (OH) ₂]·5H ₂ O	3395	1593	1662	610	626 (15974), 367 (27473)	1.9705	6.00

complex shows a band at 413 nm (24213 cm^{-1}) suggesting the existence of charge transfer transition, ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition. An octahedral geometry was proposed for this chelate¹¹. The Fe(III) complex spectrum exhibits one band at 447 nm (22371 cm^{-1}) which is due to $M \rightarrow L$ charge transfer transition. An octahedral structure was suggested¹². The electronic spectral data of $[FeL^1L^3(OH)_2] \cdot 5H_2O$ complex show two bands at 364 nm (27473 cm^{-1}) and 626 nm (15974 cm^{-1}) suggesting the presence of a charge transfer transition. Meanwhile the spectrum of $[CrL^1L^3(OH)_2] \cdot 2H_2O$ chelate displays several bands assigning to the existence of a charge transfer transition, ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transitions. An octahedral structure was proposed for both complexes.

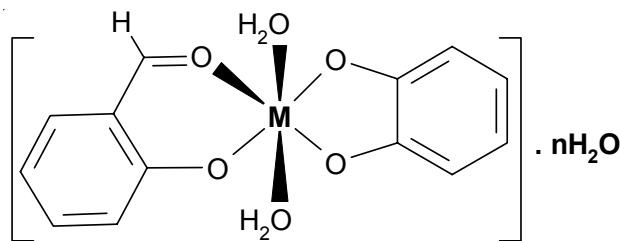
The EPR spectrum of the complex of $[VOL^1L^2(H_2O)] \cdot 2H_2O$, $[CrL^1L^2(H_2O)_2] \cdot 2H_2O$, $[FeL^1L^2(H_2O)_2] \cdot 6H_2O$, $[FeL^1L^2(OH)_2] \cdot 5H_2O$ and $[CrL^1L^3(OH)_2] \cdot 2H_2O$ reveal a g_{eff} values in the range of 1.9705-2.088. The variation of these values compared to the ideal value (2.0023) is due to the presence of partial ionic character of covalent bond of V(IV), Cr(III) and Fe(III) ions with the ligands under investigation. The obtained results support the presence of an octahedral geometry¹³ which confirmed by the previous analyses.

Conclusion

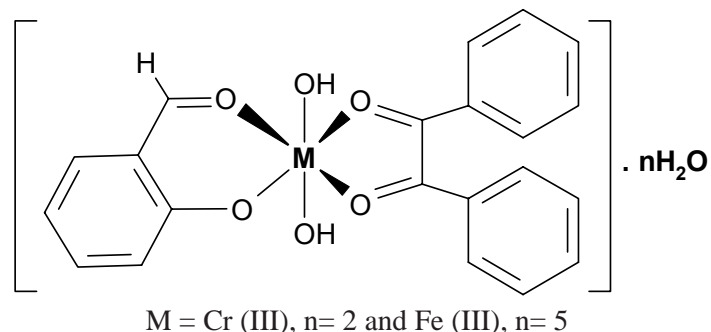
From the previous data; elemental analysis, molar conductivity, thermogravimetric analysis, magnetic moments, infrared, electronic and electron paramagnetic resonance spectra, the following chemical formulae can be suggested for the synthesized mixed ligand chelates.



M = VO(IV), n = 1



M = Cr (III), n = 2 and Fe (III), n = 6



Suggested structures for mixed ligand chelates

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(Received: 11 August 2006;

Accepted: 7 June 2007)

AJC-5680