

Synthesis and spectral characterization of new mixed ligand complexes

Dr. Najla.H.Taher
College of Education for Girls
University of Mosul

Abstract :New mixed ligand complexes of T:(IV), Cr(III) and Fe(III) cations with O-hydroxyacetophenone (hapH) and O-phenely enediamine (PD) have been prepared and characterized by different analysis techniques, such as particular, elemental analysis, molar conductance measurements, infrared and electronic spectra. The elemental analysis data exhibit the formation of M:(hapH):(PD) [1:1:1] ratio. The molar conductance measurements indicate that, the non electrolytic nature of the result complexes at room temperature. The infrared spectra reveal two modes for complexation, through nitrogen atoms of the diamine and oxygen atoms of the carbonyl (C=O) and hydroxyl groups of O-hydroxyacetophenone. The electronic absorption spectra show the existence of the most probable octahedral geometry

Introduction:

There has been growing interest in the formation of mixed ligand complexes involving ligands containing functional groups such as sulfur, nitrogen, hydroxyl and carbonyl groups, and transition or non-transition metals of different oxidation states which can form stable complexes with ligands containing different donation sites^[1-6] due to their important role in biological processes^[7-8], electrochemistry^[9-10], and pharmaceutical synthesis^[11].

In the present work, we report the preparation and characterization of some mixed ligand complexes, formed by the reaction of Ti(IV), Cr(III) or Fe(III) ions with O-hydroxyacetophenone (haph) and O-phenylenediamine (PD).

Experimental:

a. Materials :

CrCl₃.6H₂O, FeCl₃.6H₂O and absolute ethanol from BDH ; TiOSO₄, O-phenylenediamine, O-hydroxyacetophenone and dimethyl formamide (DMF) from Fluka are used as supplied.

b. Elemental analysis and physical measurements :

The contents of C, H and N were estimated by using a Carlo-Erba-Strumentazione 1106 analyzer. Molar conductivities of the complexes, in an electrolytic conductivity measuring set LF-42 using 10^{-3} M solutions of the complexes in dimethylformamide (DMF) were measured at room temperature. The infrared spectra of prepared complexes were recorded by a Tensor-27 spectrophotometer (Bruker) in the range $4000-400\text{ Cm}^{-1}$ using KBr disc . The electronic spectra were recorded on a Shimadzu UV-160 spectrophotometer for 10^{-3} M solution of the complexes in DMF as solvent .

c. Preparation of the mixed ligand complexes :

The mixed ligand complexes of Ti(IV), Cr(III) and Fe(III) cations were prepared by mixing equal amounts (0.01 mol) of each metal and the first ligand (O-hydroxyacetophenone) in hot ethanol. The mixture was refluxed for two hours, and then the second ligand was added in the same ratio to the mixture and refluxed for six extra hours. Few drops of diluted ammonia solution were

added slowly until pH = 6-8 was attained, at this pH range, the mixed ligand complexes were formed, then they were washed several times with distilled water, then with hot ethanol. The complexes were dried in desiccator over anhydrous CaCl₂.

Results and Discussion:

The 1:1:1 molar ratios of metal salts with O-hydroxyacetophenone (hapH) and O-phenylenediamine (PD) result in the formation of mixed ligand complexes. These complexes are insoluble in water and ethanol but soluble in DMF. The characteristics and analysis of the complexes are recorded in table 1. The obtained elemental analysis data are in a good agreement with calculated values. The suggested formulas are [TiO(hapH)(PD)(OH)].2H₂O and [M(hapH)(PD)(OH)₂].nH₂O; where M represent Cr(III) or Fe(III) cation, and n=2 or 3, respectively. The conductances of the complexes are low, indicating their non-electrolytic nature^[12].

The infrared band assignments of the mixed ligand complexes are listed in table 1. The complexes spectra display a broad band in 3391-3418 cm⁻¹ range, indicating

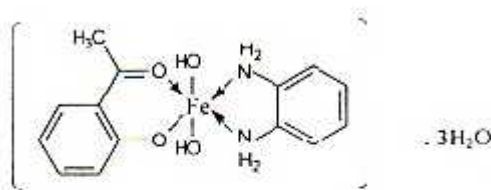
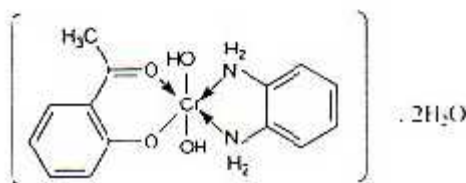
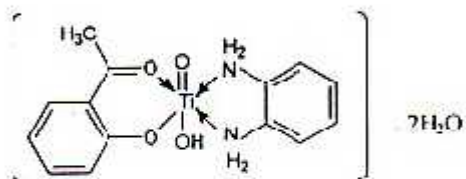
the existence of water molecules^[13]. The spectra exhibit the disappearance of $\delta(\text{OH})$ and $\nu(\text{C-OH})$ bands at 1347 and 841 cm^{-1} , respectively^[14] a result confirmed by microanalyses of these mixed ligand complexes. The infrared spectral data band at 1608-1619 cm^{-1} range are due to carbonyl (C=O) group of O-hydroxyacetophenone moiety. The shifting appeared in this band to lower frequency comparing with the free ligand 1649 cm^{-1} , confirm the participation of this group in complexation^[15]. The complexes spectra show a single band at 457-544 cm^{-1} , assigned to $\nu(\text{M-O})$ vibration^[16], supporting the involvement of oxygen atom of hydroxyl group of (hapH) in chelation. Also the infrared spectra exhibit a band at 503-518 cm^{-1} , which is not present in the free ligand (O-phenylenediamine) attributed to $\nu(\text{M-N})$ vibration^[17].

The octahedral complexes that contain a metal ion of d^0 are diamagnetic, meanwhile, the metal ions of d^3 and d^5 electronic configurations are paramagnetic, which are the case of Ti(IV), Cr(III) and Fe(III) complexes, respectively. The electronic spectral data of the Ti(IV) complex show band at 29850 cm^{-1} , suggesting the octahedral structure^[18] (fig:3). The absorption spectrum of the Cr(III)

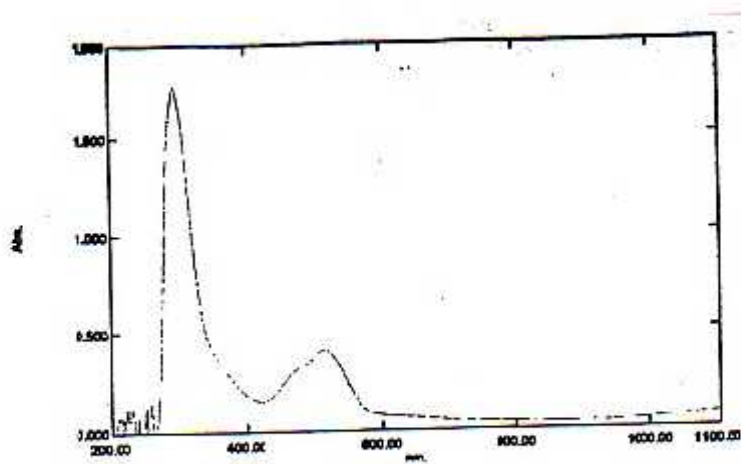
complex displays band at 28901 cm^{-1} , which is due to the ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transition^[19]. The intensity of the band is consistent with octahedral structure. The electronic spectral data of the Fe(III) complex reveal band at 19880 cm^{-1} , which is assigned to the ${}^2A_{2g} \rightarrow {}^2T_{1g}$ transition. Thus, this transition is consistent with octahedral^[20] (fig:2).

Conclusion:

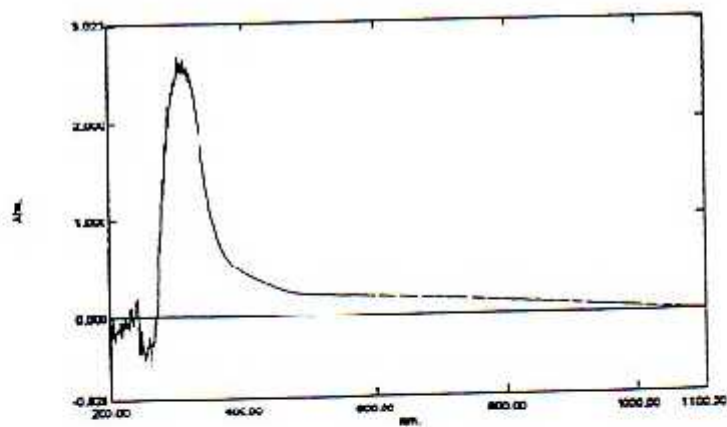
From the previous investigation, the following conclusions can be drawn concerning the properties of the prepared complexes . The elemental analysis data show the agreement of (Calcd.) and (found) of C.H.N values. The molar conductance measurements exhibit that all prepared mixed ligand complexes are non-electrolytic in nature. The infrared spectral data reveal two different modes of complexation, which are through oxygen atoms of carbonyl and hydroxyl groups of O-hydroxyacetophenone and nitrogen atoms of O-phenylenediamine. The electronic absorption spectra display the presence of an octahedral geometry for all mixed ligand complexes. The geometrical structures of these complexes are given (fig : 1) :



(Fig : 1) The proposed structures of complexes



(Fig : 2) The electronic spectra of the Fe³⁺ complex



(Fig : 3) The electronic spectra of the Ti⁴⁺ complex

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تحضير وتشخيص معقدات جديدة ممزوجة النيكاندات

د.نجلة هشام طاهر

كلية التربية للبنات - جامعة الموصل

الخلاصة: يتضمن هذا البحث تحضير بعض معقدات مزيج النيكاند لابونات التيتانيوم الرباعية ، الكروم والحديد الثلاثي باستخدام أورثو-هيدروكسي اسيتو فينون وأورثو فنيولين ثنائي الامين وقد تم تشخيص المعقدات الناتجة بطرق مختلفة مثل التحليل الدقيق للعناصر وقياسات التوصيل المكافئ و أطياف الأشعة تحت الحمراء والاطياف الإلكترونية .

ظهر من خلال التحليل الدقيق للعناصر تكون المعقدات (PD) : (hapH) : M ، بنسبة 1 : 1 : 1 . دلت قياسات التوصيل المكافئ على أن المعقدات ذي طبيعة متعادلة . وضحت اطياف الأشعة تحت الحمراء على أن التناسق لنيكاندات من خلال ذرتي النتروجين في أورثو-فنيولين ثنائي امين وذرتي الاوكسجين في مجموعتي الكاربونيل (C=O) ، والهيدروكسيل لمركب أورثو-هيدروكسي اسيتو فينون . تبين اطياف الامتصاص الإلكترونية بنية شمالي السطوح هي الأكثر احتمالاً لهذه المعقدات.

Table 1. : Elemental analysis, infrared band assignments (cm^{-1}) and molar conductivity ($\text{S cm}^2 \text{mol}^{-1}$) of the mixed ligand complexes

Complexes	% Found (Calcd.)				IR (cm^{-1})				Λ_M $\text{S cm}^2 \text{mol}^{-1}$
	C	H	N	VOH (H_2O)	V C=O	V M-O	V M-N		
[TiO(haPH)(PD)(OH)] \cdot 2H ₂ O	46.92 (46.67)	5.25 (5.55)	7.97 (7.77)	3391	1608	457	503	8	
[Cr(haPH)(PD)(OH)] \cdot 2H ₂ O	45.93 (46.15)	6.03 (5.76)	7.64 (7.69)	3413	1612	542	511	11	
[Fe(haPH)(PD)(OH)] \cdot 3H ₂ O	43.81 (43.54)	6.14 (5.96)	6.99 (7.25)	3418	1619	544	518	9	

