Synthesis , Characterization , and Study of Electrical Properties of Fe(III) and Al(III) Complexes of a Schiff base

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Abstract

A Schiff-base ligand derived from o-aminophenol and salicylaldehyde and its transition metal complexes with the metals Fe(III) and Al(III) have been synthesized. The prepared Schiff-bases and their complexes were identified by IR, UV-Visible and elemental analysis (CHN).These used techniques facilitated to elucidate the chemical structures of the chelates.These techniques show that both transition metals form complexes with Schiff base in the ratio 1:2[M:L]and in Octahedral structures. The electrical properties of Schiff-base and their complexes were studied over temperature range (0 -110 ^{0}C) before and after dopping with iodine. the maximum value of conductivity was 1.81×10^{-4} ohm^{-1} .cm^{-1} . for dopped aluminum complex.

***KeyWord*:Schiff-base , Transition metal complexes, Electrical Properties.**

Introduction

The condensation of carbonyl compounds with primary amines was discovered in 1864 by Hugo Schiff(1). The condensation has been used by many researchers to form both small and large macrocycles, usually templated with transition metals(2) . Schiff-bases have been widely used as ligands because of high stability of the coordination compound,of them and their good solubility in common solvents such ethanol, methanol, chloroform, dimethyl formamide(3). The π-system in a Schiff-base often imposes a geometrical constriction and affects the electronic structure as well(4). Metal complexes of Schiff-base have played a central role in the development of coordination chemistry. The complexes make these compounds effective and stereospecific catalylst for oxidation, reduction and hydrolysis, and they show biological activity and other transformation of organic and inorganic chemistry(5). It is well known that some drugs have higher activity when administered as metal complexes than as free ligand. In addition potential application in many fields such as antibacterial, antiviral, anticancer drugs ,electrochemistry(6,7,8).

In the present study ,Fe(III), and AL(III) complexes of Schiff base were prepared, characterized by IR, UV-visible and elemental analyses and electrical properties were studied.

Experimental

A - Chemicals

Ether, ethanol , methanol, salciyladehyed, o- amino phenol from (Fluka Co), acetic acid, petroleum ether,Iodine, Anhydrous $AlCl_3$, Anhydrous $FeCl_3$ from (Merck Co), were purified before using [9].

B - Instruments

1 – IR- Infrared spectrophotometer from made by (Buck Scientific) Model 500, in the range (4000 – 600) cm^{-1} and form KBr discs in Department of Chemistry / College of Education/ Basrah University.

2– UV–Visible spectrophometer, Model–U-1500- HITACH, Department of Chemistry / College of Education/ Basrah University.

3 – Melting Point, Model – Electro thermal melting point 9300 , Department of Chemistry / College of Education / Basrah University.

4 – Electrical Conductivity apparatus (voltmeter, power supply, Resistance, Temperature Recorded and measured sample cell) were used under vacuum, by using a two probe method at a temperature range (303-373)K, Department of Chemistry / College of Education/ Basrah University.

5 - Elemental analysis (CHN) from Science College – Cairo University .

Method

Synthesis of the Ligand

Schiff base have been synthesized by condensing the methanolic solution of 2-amino phenol (2.18g, 0.02mole) with the methanolic solution of salciyladehyde (2.09ml, 0.02 mole) in equimolar ratio with a few drops of acetic acid as a catalyst. The mixture was refluxed with stirring for 4hours , The condensation product was filtered, washed from ethanol and ether, recrystalised with ethanol, and dried under reduced pressure over anhydrous $CaCl_2$[10]. The resulting red product, 94% yield , m.p. 222-223 ^{0}C. Schiff base have been characterized by elemental analysis and IR , UV spectra.

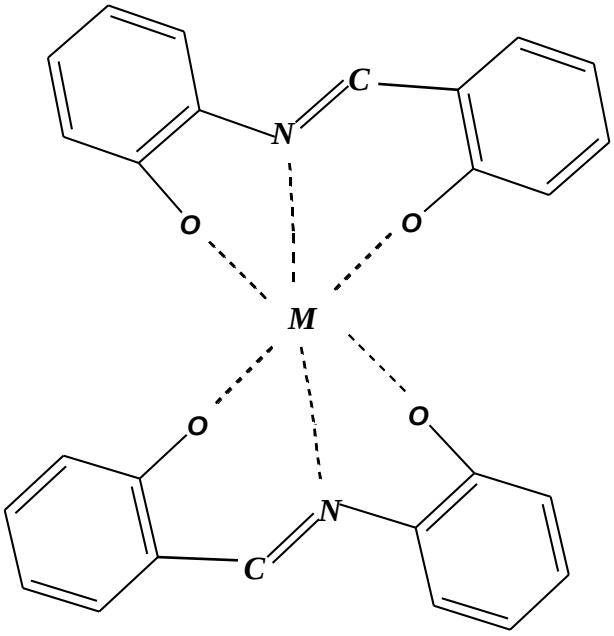
Synthesis of Schiff-base Complexes·

A mixture of the ligand (4.26g, 0.02mole) and (1.33g, 0.01mole) $ALCl_3$ or (1.62g, 0.01mole) $FeCl_3$ in 50ml methanol..The mixture was refluxed for 6h; the volume of the mixture was reduced to one-third by heated. On cooling the crude product was formed, and then filtration and washed several times with mixture (3:1) ethanol water and petroleum ether and dried over anhydrous $CaCl_2$[11], characterized by elemental analysis and IR , UV spectra.

The physical data for the ligand and their complexes are listed in Table (1) .

AL – Complex (brown soild) in 84 % yield . M.p= >300

Fe - Complex (dark black soild) in 86 % yield . M.p= >300



M= Fe(III),AL(III)

Figure(1): Suggested structural of the complexes

Electrical Measurements

The d.c electrical conductivities of dopped and undopped prepared compounds over temperature range (0 – 110 ^{0}C) and under vavuum were measured by using conductivity apparatus which is consisting of (temperature recorder, power supply, voltmeter, resistance and sample cell). The studied samples were as discs covered in two sides by silver paint, .The Schiff-base, Fe(III) and Al(III) complexes were dopped with Iodine by mixing 1g(0.004mole)ligand, 1g(0.0022mole)Al-complex, 1g(0.002mole)Fe-complex with 25ml of iodine solution in CCL_4 (4%, w/v), the mixture was refluxed with stirring for 48 hours, then filtered and dried in the vacuum oven at 50^{0}C . The conductivities at different temperatures were calculated according to Ahrrenious equation as shown below (1). [12, 13] .

$$\sigma = \sigma o * \exp(-\Delta E/2K) \quad \ldots\ldots\ldots\ldots (1)$$

σ = Conductivity ($ohm^{-1}.cm^{-1}$)

σo= Pre – exponential conductivity ($ohm^{-1}.cm^{-1}$)

ΔE = Energy gap (eV)

K = Boltzmann constant (eV)

T = Temperature (Kelvin)

The resistance of the sample and its electrical conductivity is calculated from the equations[14]:

$R_x = (R_s * V_x)/V_s$ and $\sigma = (L/A) * 1/ R_x$

R_s: Standard resistance (ohm).
R_x: Sample resistance (ohm).
V_s: Standard Voltage (volt).
V_x: Sample Voltage (volt).
L: Sample thickness (cm).
A: The painted area of the sample surface (cm^2).

Result and Discussion

Elemental analysis

The structures of the products were confirmed by their elemental analysis, Table(2), which showed that the difference between the found values and calculated values of carbon , hydrogen , and nitrogen elements are situated within the range which confirmed the correctness of the suggested structures of the prepared compounds.

IR Spectra

In the present study, the Schiff-base compounds were identified by IR. spectrophotometer in the as shown in figures (5, 6, 7).

The OH stretching vibration of the ligand was appeared at the range (3450 cm^{-1} – 3330 cm^{-1}), while it disappeared in the IR-spectra of the Schiff-base complexes due to the coordination of the metal ion to the oxygen of the ligand[15].The band at (1648 cm^{-1}) in the free ligand spectra is attributed to ν(C=N) vibration. On the other hand , The absorption band at (1609 cm^{-1}, 1622 cm^{-1}) in Schiff-base complexes spectra due to ν(C=N) vibration. The new bands at the range (749-788 cm^{-1}) and at the range (683-666 cm^{-1}) in the complexes have tentatively been assigned to νM-O and νM-N respectively[16,17]. The all mentioned bands were in Table (3).

UV-Visible Spectra.

The electronic absorption spectra of the Schiff-base ligand and their complexes were recorded at room temperature using DMF as solvent.. The absorption band at (452nm) is observed in the spectrum of the free Schiff-base, suggesting the presence of (π-π*)transition of aromatic rang or azomethine group[18]. For AL(III) complex, and Fe(III) complex, the spectral data display two bands at (540,548nm), (722,740nm) respectively, the first band is due to (π-π*)transition, which can be assigned to electron delocalization over whole molecule on complexation, the second band is attributed to (d-d)transitions[19,20]. The all bands were show in figure (2).

Electrical properties

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The values of electrical conductivities were shown in Table (4). The maximum conductivity value was 1.81×10^{-4} ohm^{-1} $.cm^{-1}$for doped Al(III) complex because of the small size of aluminum atom in compared with iron atom. Also the prepared Schiff-base complexes at different temperatures (303-373)K show the increased of conductivity with increasing of temperatures may be attributed to presence of metals (d-d*) transition[21].

Figures (3-4) show that the conductivities of dopped and undopped compounds increase with increasing of temperatures which is consistent with semiconductors properties[22,23].The dopping compounds have higher conductivities than undopped because Iodine doping lead to oxidation of iodine molecules to form I_3^{-1}, I_5^{-3} and reduction of Schiff base complexes molecules, this effect increase the conductivity by making acceptor bands, and the distance between the energy levels were low[14,24,25].

Table (1) : physical data of the ligand and the complexes

Compound	Color	M.P or dec. temp	U.V/Visible. nm λmax.	Yield (%)
Ligand	**Red**	**222-223**	**452**	**94**
Al-Complex	**Brown**	**>300**	**540, 722**	**٨٤**
Fe-Complex	**Dark black**	**>٣٠٠**	**548, 740**	**٨٦**

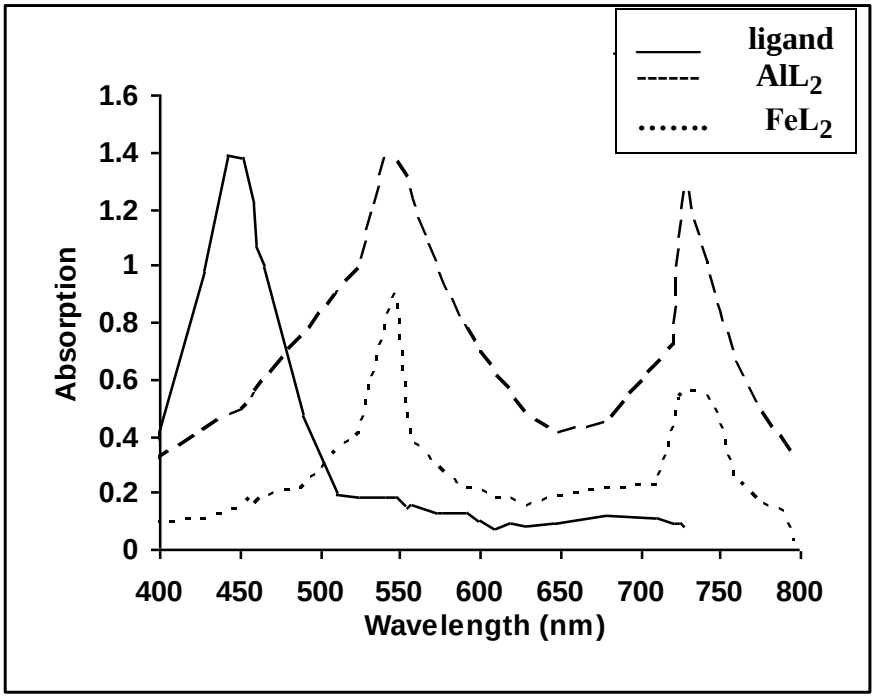
Table (2) , Elemental analysis of the products.

Compound	Molecular Formula	Practical Value %			Theoretical Value %		
		C	H	N	C	H	N
Ligand	$C_{13}H_{11}NO_2$	73.05	5.45	6.12	73.22	5.20	6.56
Complex- Fe	$C_{26}H_{18}N_2O_4Fe$	65.44	2.03	5.96	65.29	3.70	5.85
Complex- AL	$C_{26}H_{18}N_2O_4AL$	69.22	3.97	6.01	69.48	4.03	6.23

Table (3): IR data for prepared compounds

Schiff-base	Wave numbers (cm^{-1})						
	υ O-H br	υ C-H m	υ N=C s	υ C=C m	υ C-O m	υ M-N w	υ M-O w
Ligand	3210-3558 br	3025 m	1648 s	1520 m	1476 m	___	___
Fe-Complex	___	3020 m	1609 s	1533 m	1438 m	664 m	749 m
AL-Complex	___	3040 m	1622 s	1568 m	1411 m	675 m	789 m

Br:broad, s:sharp, m:medium, w:weak

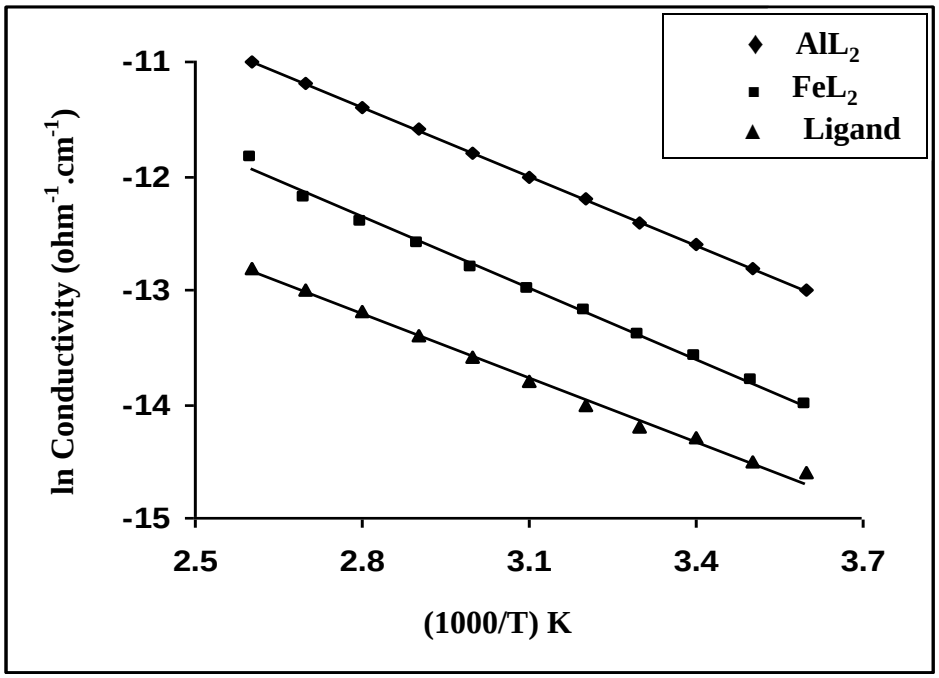


Ligand 1.37 (452nm)
ALL- 1.36 (540), 1.28 (722)
FeL- 0.91 (548), 0.56 (740)

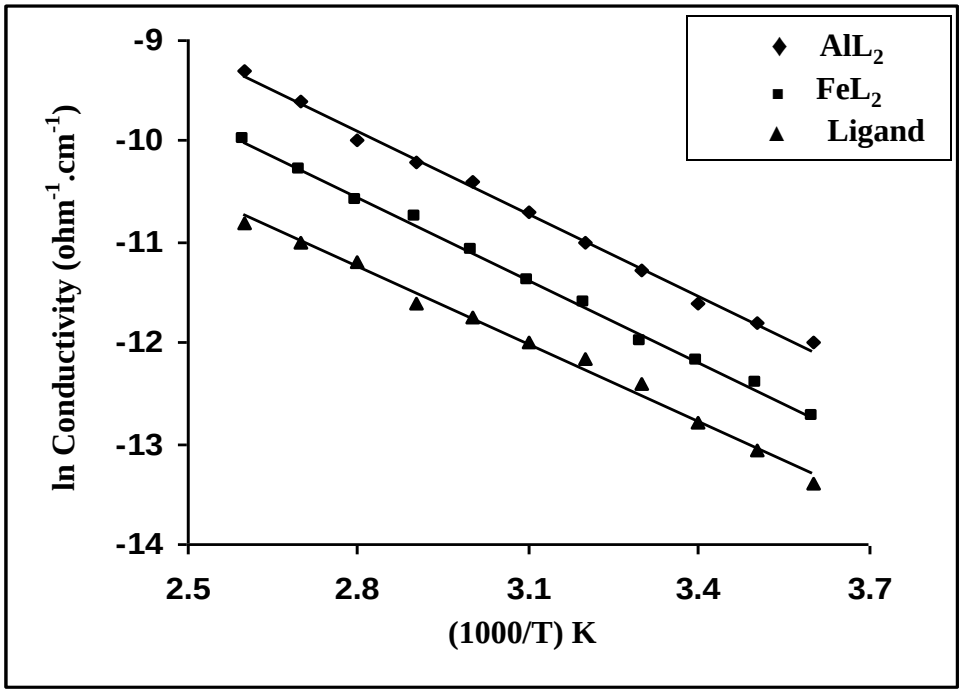
Figure (2): UV-Visible spectra of free ligand , Fe-complex and AL-complex

Table (4): The values of electrical conductivities and ΔE for Schiff-base ligand and metal complexes before and after dopping with Iodine .

Schiff-base	Conductivity ($ohm^{-1}.cm^{-1}$) before doping	ΔE(eV) before doping	Conductivity ($ohm^{-1}.cm^{-1}$) after doping	ΔE(eV) after doping
Ligand	5.13×10^{-6}	0.0438	1.45×10^{-5}	0.0377
AL-Complex	3.11×10^{-5}	0.0315	1.81×10^{-4}	0.0283
Fe-Complex	2.22×10^{-5}	0.0336	1.07×10^{-4}	0.0299



Figure(3):The D.c conductivities of free ligand , Fe-complex and AL-complex before doping



Figure(4):The D.c conductivity of free ligand , Fe-complex and AL-complex after doping

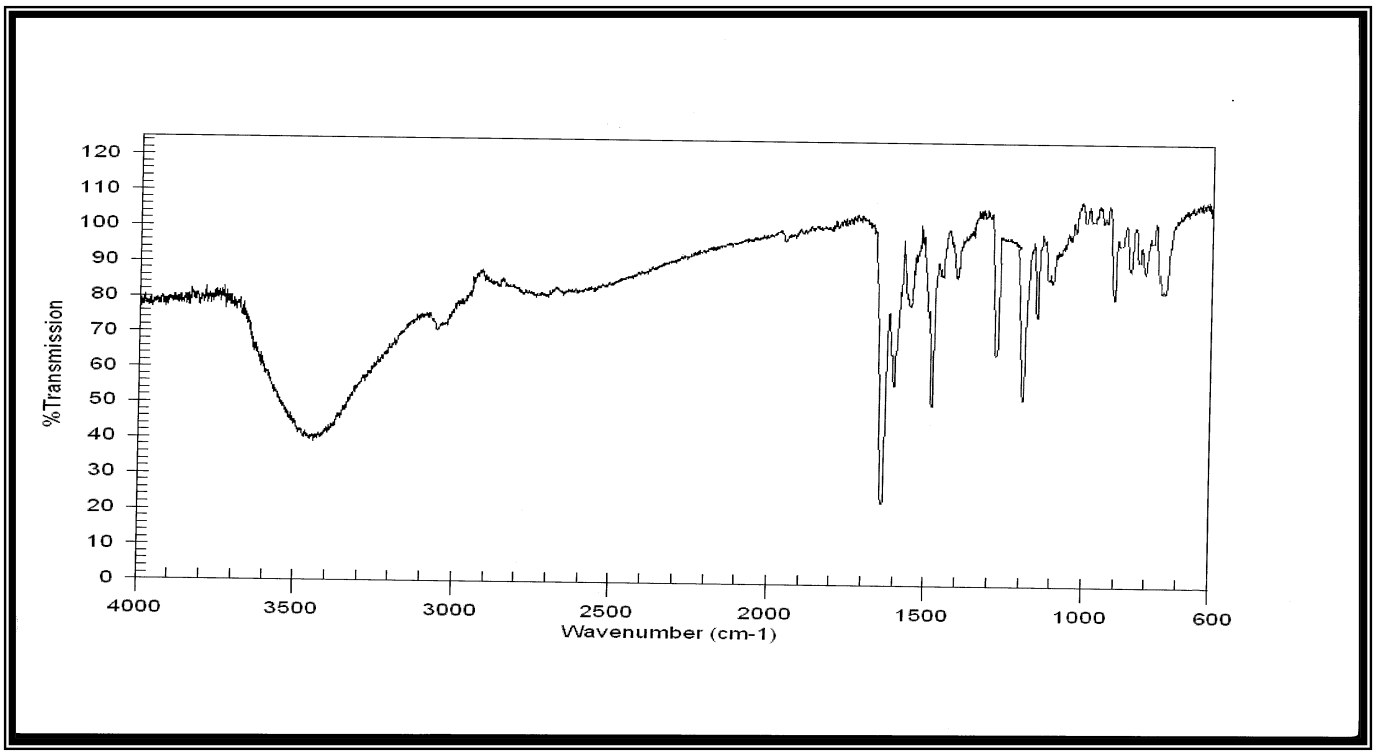


Figure (5) : IR-spectrum of free ligand

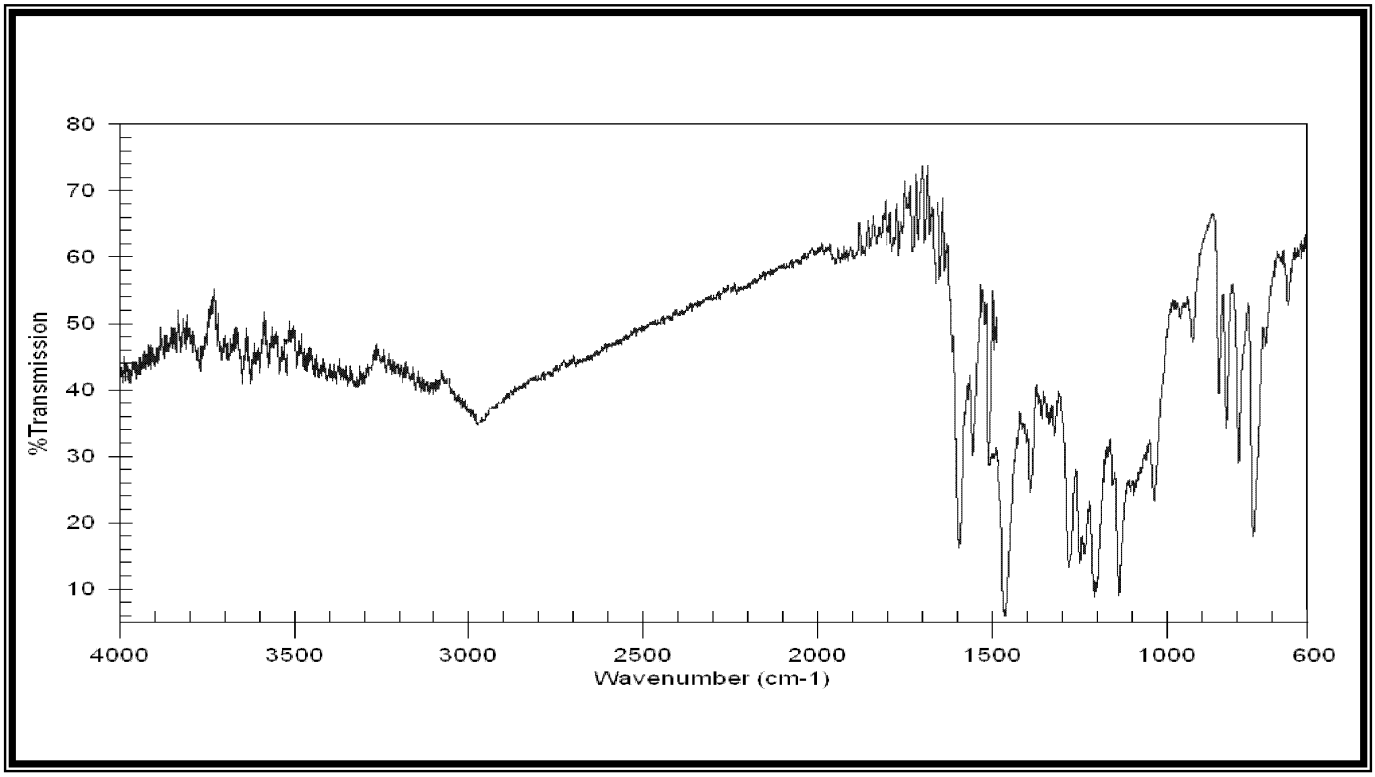
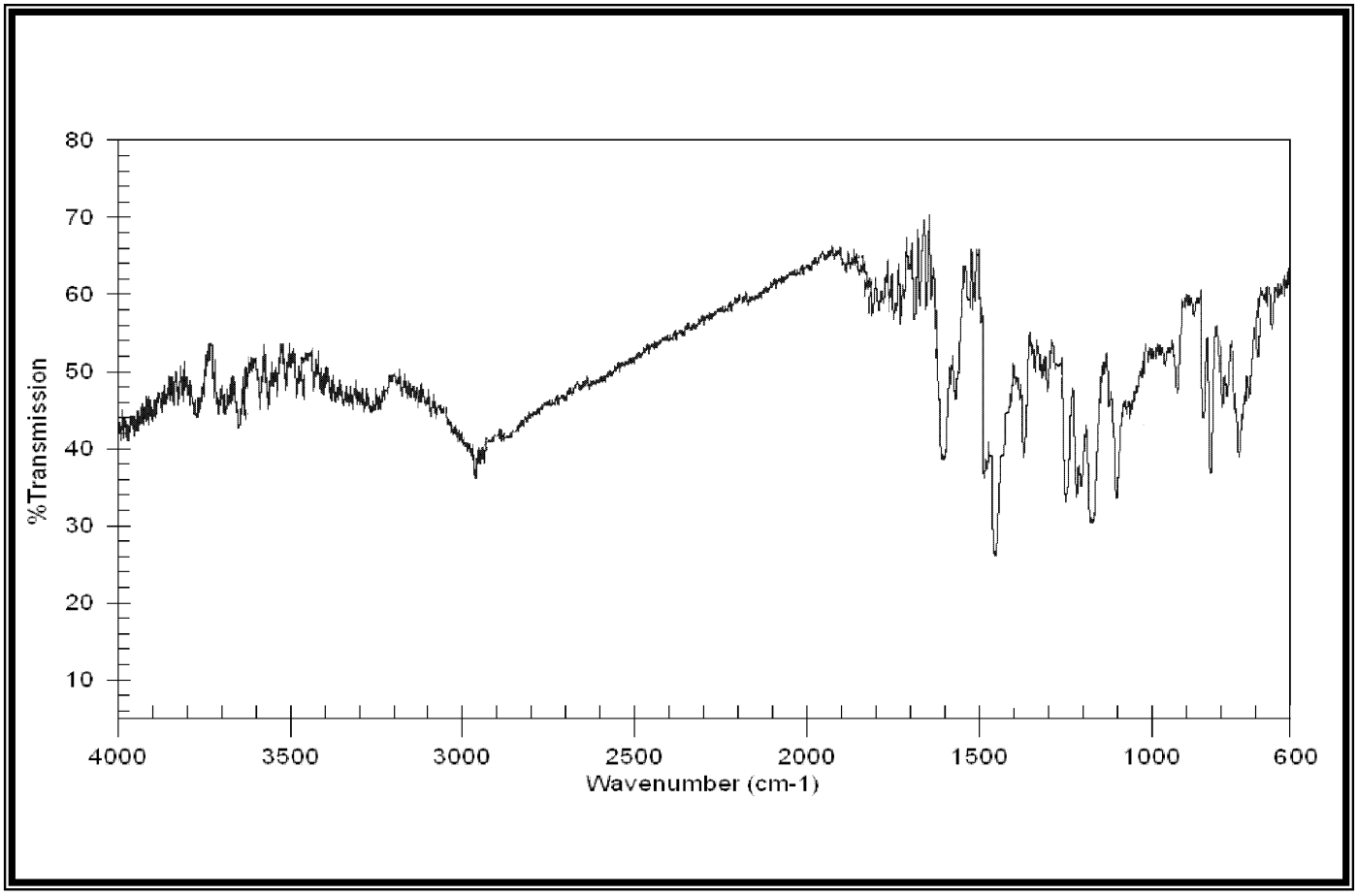


Figure (6): IR-spectrum of Al-Complex



Figure(7): IR-spectrum of Fe-Complex

Conclusions

Schiff bases have been synthesized by condensing o-aminophenol with salicylaldehyde, The1:2[M:L] ratio metal complexes have been prepared by interacting these Schiff base with metal ions viz. AL(III), Fe(III). The complexes are colored and stable in air at room temperature. Based on the experimental evidence thus obtained the complexes were characterized as six – coordinates, via the three bonding siets of the azomethine nitrogen atom , hydroxyl group of the ligand, suggested to possess octahedral structures.The Schiff base and their complexes display electrical properties, and show that the conductivities of dopped and undopped compounds increase with increasing of temperatures which is consistent with semiconductors propertie. The maximum conductivity value was 1.81×10^{-4} ohm^{-1} $.cm^{-1}$for doped Al(III) complex because of the small size of aluminum atom in compared with iron atom.

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المستخلص:

تم تحضيراليكاند المشتق من أورثو – امينوفينو مع ا للسلسالديهايد .وتم تحضير معقدات هدا الليكاند مع الفلزات الانتقالية (الالمنيوم الثلاثي ، الحديد الثلاثي). قواعد شف ومعقداتها المحضرة شخصت باستخدام مطيافية الاشعة تحت الحمراء والاشعة المرئية وفوق البنفسجية وتحاليل العناصر الدقيقة .وهدة التقنيات أستخدمت كوسيلة لتبيين التركيب الكيميائي للتناسق. التقنيات بيينت ان الفلزات الانتقالية تكون معقدات مع القاعدة شف بنسبة (٢:١)(فلز- ليكاند). وان الشكل الهندسي لها هو ثماني السطوح .كما درست الخصائص الكهربائية للقاعدة شف ومعقداتها وبمدى من درجات الحرارة ما بين (٠-١١٠ م) ،قبل وبعد التشويب مع اليود .وأظهرت أعلى قيمة للتوصيلية الكهربائية بحدود(١.٨١×١٠-٤ أوم-١ . سم-١)لمعقد الالمنيوم المشوب.