



## Research Article

### SYNTHESIS AND CHARACTERIZATION OF NEW COMPLEXES FOR

### (1*E*,1'*E*)-*N*, *N'*-(thiobis (4,1-phenylene)) bis(1-phenylmethanimine) SUBSTITUTED LIGANDS WITH Fe<sup>3+</sup>

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#### ABSTRACT

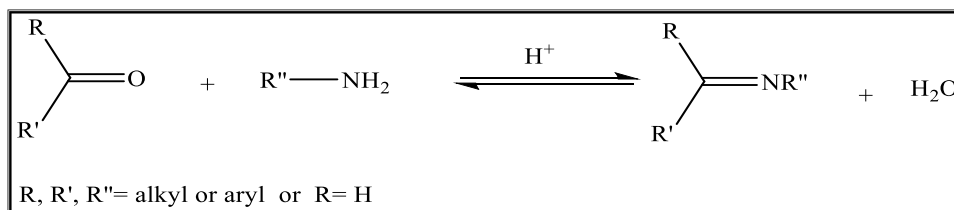
This work include synthesis of two types of aromatic Schiff bases derived by condensation of 4,4'-diaminodiphenyl sulfide with 4-cyanobenzaldehyde and 4-dimethyl amino benzaldehyde. I.R. and U.V-Visible spectroscopy were used to determine metal:ligand ratio and complex formation. The result showed the ligand has an ability to form colored complex with ferric ion at ratio (1:2) M: L, that have  $\lambda_{max}$  575nm of complex 1 and 450 nm complex 2. The optimum complexity was conditions found at pH 6.9 to ligand 1 and ligand 2 with ferric ion at a temperature range (65-70 °C) were identified and the period time of complexity not affected the formation complexes were stable through 24 hours, where the electronic spectrum of the Schiff bases and their complexities were studied using the principle of continues variation method (Job's method), to propose the structural formula of the complex it was (1:2) (metal : Ligand). These ligands and complexes have been identified by using IR, U.V-Visible and melting point measurements.

**Keywords:** Ferric ion, Ligand, 1*E*,1'*E* -*N*, *N'*-(thiobis (4,1-phenylene)) bis 1-phenylmethanimine

#### INTRODUCTION

Schiff bases are regarded as a very important class of organic compounds with a wide range of biological applications <sup>(1,2)</sup>. They include as a functional group azomethine (C= N) and therefore act as an effective ligand. <sup>(3)</sup>.

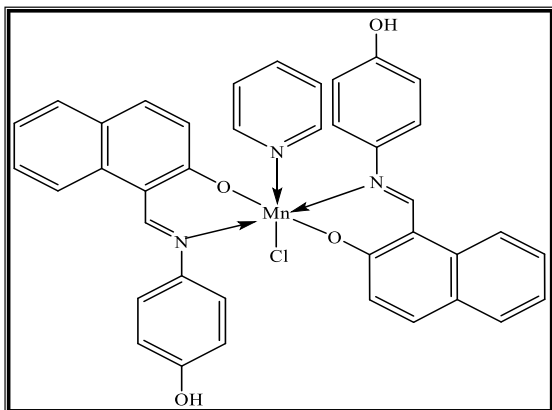
The general structural advantage of these compounds is that the C=N group with a general formula RR'C=N-R". C=N compounds have been widely reportable to possess biological properties like bactericide, antifungal, herbicidal and plant growth regulatory <sup>(4,5)</sup>.



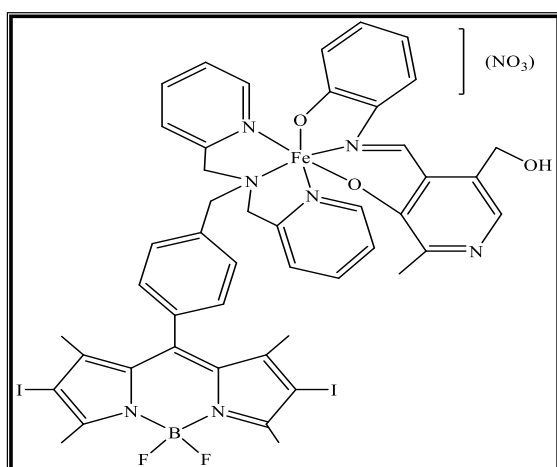
Schiff bases are vital compounds in numerous fields, particularly in medicative and pharmaceutical fields thanks to their wide spectrum of biological activities. <sup>(6)</sup> The bio active of each ligands and metals will result in the synthesis of extremely important active compounds. <sup>(7, 8)</sup>

Schiff base ligands are simply synthesized and kind complexes with the majority metal ions in numerous reaction states. These metal complexes are often employed in chemical process

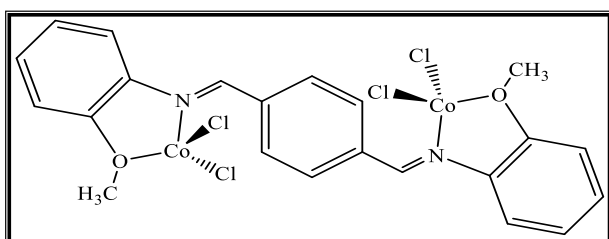
reactions and as models for biological systems <sup>(9, 10)</sup>. This may be associated with their biological activity, together with medicinal drug, antifungal, anticancer, inhibitor, medicinal drug, antiprotozoal drug, antiviral activity further as applications in an exceedingly type of chemical areas like reaction, reduction and reaction chemical change <sup>(11-14)</sup>. Safia et.al. synthesized Mn(III)L2ClPy complicated by reacting between the compounds in the figure. <sup>(15)</sup>



Somarupa et.al. synthesized Iron  $\text{Fe}^{+3}$  metallic compounds of a vit.  $\text{B}_6$  complex azomethine with the compounds <sup>(16)</sup>.



Sahar et.al. synthesized metal (II) Complexes with Schiff Base Ligands Derived from Terephthal organic compound and ortho-substituted anilines with N- propyl- benzo guan amine- $\text{SO}_3\text{H}$ .<sup>(17)</sup>



## Experimental Part

### Materials and instruments

Metal salts- iron (III)-nitrate-nonahydrate (purity 98%) absolute ethanol (purity 99.99%), Benzene (purity 99%), 4-Cyanobenzaldehyde (purity 99%), 4-dimethyl amino benzaldehyde and 4,4'-Diaminodiphenyl sulfide (purity 98%) were purchased from alphabetic character company. The ready matter and its complexes were known by U.V.-visible photometer. FT-IR spectroscopic analyses were recorded on Shimadzu FT-I.R. 8400S mass spectrometer within the vary ( $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ ) victimization KBr pellet.

### Synthesis of 4,4'-((1E,1'E) -((thiobis(4,1-phenylene)) bis(azanylylidene)) bis (methanylylidene)) dibenzonitrile(L1)

The Schiff base ligand was ready by condensation of four,4'-Diaminodiphenyl compound (0.01 mole) with 4-Cyanobenzaldehyde (0.02mol) in fermentation alcohol (30ml) and add three drops of glacial carboxylic acid as a catalyst and also the mixture refluxed for five hours, then cooled to temperature. the merchandise was collected by filtration, washed many times with fermentation alcohol and recrystallized from hot fermentation alcohol and dried during a vacuum desiccator to allow a yellow solid, m.p.= (180-182), 85% yield.

### Synthesis of 4,4'-((1E,1'E) -((thiobis (4,1 phenylene)) bis(azanylylidene)) bis(methanylylidene)) bis(N, N-dimethylaniline) (L2)

The Schiff base ligand was ready by condensation of four,4'-Diaminodiphenyl compound (0.01 mole) with 4-dimethyl amino benzaldehyde (0.02mol) in fermentation alcohol (30ml) and add three drops of glacial carboxylic acid as a catalyst and refluxed the mixture for five hours, then cooled to temperature. the merchandise was collected by filtration, washed many times with fermentation alcohol and recrystallized from hot fermentation alcohol and dried during a vacuum desiccator. to allow light-green yellow solid, m.p.= (220-222°C) 80% yield. <sup>(18)</sup>

### Synthesis of New Iron(III)Complexes

Molar solution(0.01M) of ligand (L1,L2) and (0.01M) Iron(III)-nitrate-nonahydrate were prepared:

**1-** (88mg) (0.19mmole) of L1 dissolved in 20 ml acetone was mixed with (80 mg) (0.19 m mole) of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (dissolved in 75ml of absolute ethanol), the color of the solution is green.

**2-** (95 mg) (0.19mmole) of L2 dissolved in 20 ml acetone was mixed with (80 mg) (0.19mmole) of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (dissolved in 75ml of absolute ethanol), the color of the solution is light orange<sup>(19)</sup>.

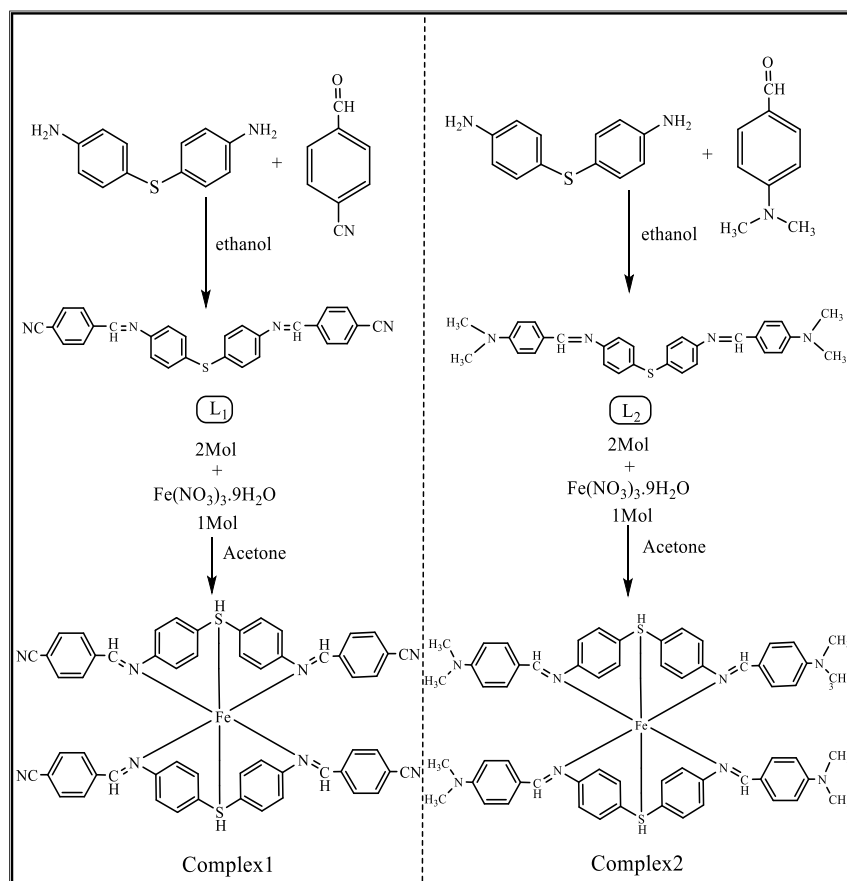


Figure 1: Synthesis of ligands and Iron (III) complexes

## RESULTS AND DISCUSSION

The structures of Schiff base complexes were certain by spectroscopic techniques like UV-vis and IR. The prepared complex has a peak at UV-vis spectrum differ from that of ligands.

### UV-vis spectroscopic study

The UV-vis spectra of the two prepared (ligand L1, ligand L2) in ethanol showed three absorption bands. The first band between (375-380) nm appear ( $n-\pi^*$ ) while the second band (360-365) nm show the ( $\pi-\pi^*$ ) (imino) and the third band (330-335) nm is called (B-band) for phenyl group.<sup>(20)</sup> Table (1).

Generally, in the new prepared complexes these bands appear red shift compared with free ligands and high intensity of the bands indicating the complexes formation<sup>(21, 22)</sup>.

Table 1: U.V- Visible absorption of ligands and amine

Compounds	Band Position (nm)	Assignment
Amine	290	$\pi-\pi^*$ (aromatic)
L1	380	$n-\pi^*$
	365	$\pi-\pi^*$ (imino)
	330	$\pi-\pi^*$ (aromatic)
L2	375	$n-\pi^*$
	360	$\pi-\pi^*$ (imino)
	335	$\pi-\pi^*$ (aromatic)

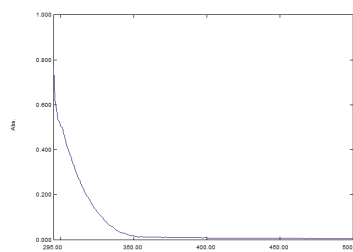


Figure 2: Spectrum of U.V. Absorption for Amine

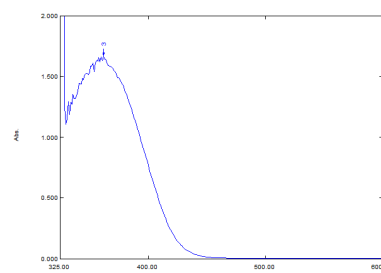


Figure 3: U.V. Absorption for L1

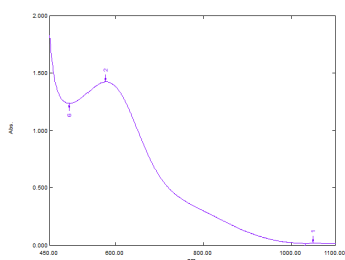


Figure 4: U.V. Absorption for complex (1)

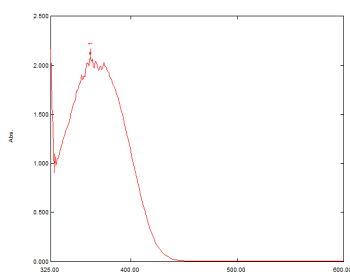


Figure 5: U.V. Absorption from L2

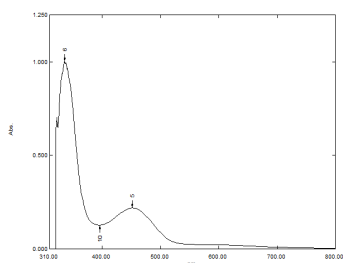


Figure 6: U.V. Absorption for complex (2)

Table 2: FT-IR spectrum for some functional groups of the studied compounds

Functional group	Amine	Ligand1	Complex1	Ligand2	Complex2
$\nu$ -NH <sub>2</sub>	3330,3400	-----	-----	-----	-----
$\nu$ CN	-----	2874	2229	-----	-----
$\nu$ C=N	-----	1623	1596	1604	1602
$\nu$ C-H aromatic	3010	3100	3062	3200	3265
$\nu$ C-H methyl	-----	-----	-----	2804	2827
$\nu$ C= C aromatic	1500	1573	1490	1576	1545
$\nu$ M-N	-----	-----	455	-----	441
$\nu$ M-S	-----	-----	530	-----	541

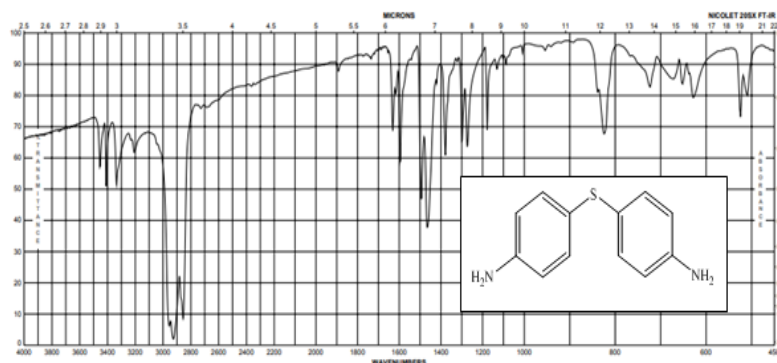


Figure 7: FT-IR of Amine

## Infrared spectrum study

### 1- The FT-IR spectrum of the amine

The amine (4,4'-Diaminodiphenyl sulfide) have two peaks (3330,3400)  $\text{cm}^{-1}$  attributed to stretching vibration of (NH<sub>2</sub>) in amine group, (3010)  $\text{cm}^{-1}$  due to stretching vibration of (C-H) aromatic and (1500)  $\text{cm}^{-1}$  (C= C) aromatic.

### 2- The FT-IR spectra of the ligands

The prepared ligands spectrum shows disappearance of (NH<sub>2</sub>) peak and appearance of peaks at 1666 and 1619  $\text{cm}^{-1}$  in the spectrum of ligand (1) and ligand (2) respectively due to  $\nu$ (C=N) stretching, C-H aromatic appearance at (3147)  $\text{cm}^{-1}$  and (3053)  $\text{cm}^{-1}$  due to (L1) & (L2) and appearance of peak in L1 at (1515)  $\text{cm}^{-1}$  and L2 at (1572)  $\text{cm}^{-1}$  attributed to (C= C aromatic). In the L1 the CN groups appeared at (2229)  $\text{cm}^{-1}$  While in the L2 shows the appearance of CH<sub>3</sub> Alkyl in the position (2879)  $\text{cm}^{-1}$ .<sup>(23)</sup>

### 3- The FT-IR spectra of the complexes

The band at 1666 and 1619  $\text{cm}^{-1}$  in the spectrum of ligand (1) and ligand (2) respectively attributed to  $\nu$ (C=N) stretching vibration which shifted to the lower frequencies in the complexes. The red shift generally in  $\nu$ (C=N) moreover proposition the coordination to metal ions through nitrogen atom of  $\nu$  (-C=N-) Schiff's base of the ligand and on complexation mention commitment of azomethine nitrogen with metal ions. New bands which show at low frequencies in the spectrum of the prepared complexes were perhaps due to (metal- nitrogen) at (455,441)  $\text{cm}^{-1}$  and (metal-Sulphur) at (530,541)  $\text{cm}^{-1}$  bond vibration frequencies. The complexes afford different color from the transition metal salts and the ligands, then this was important significance to coordinate apparition<sup>(24,25)</sup>.

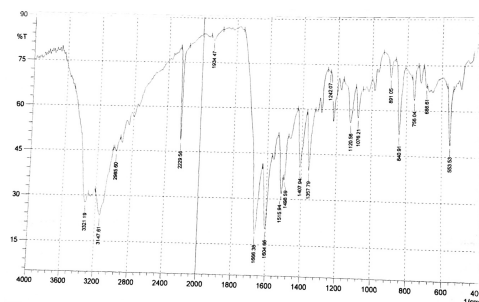


Figure 8: FT-IR of Ligand 1

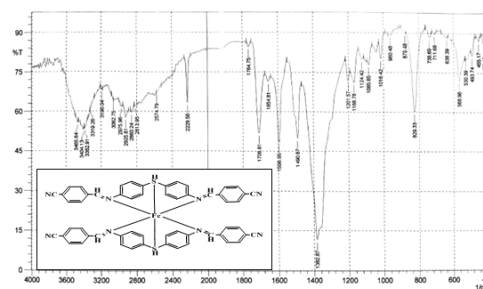


Figure 9: FTIR of Complex 1

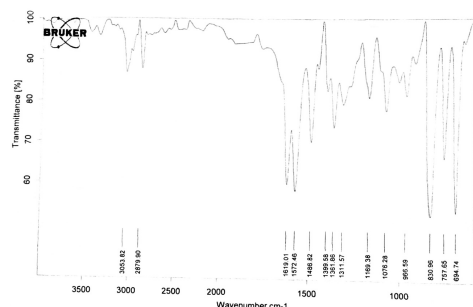


Figure 10: FTIR of Ligand 2

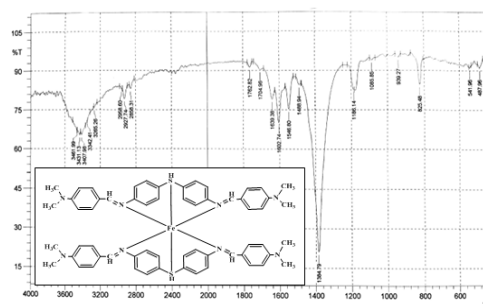


Figure 11: FT-IR of Complex 2

### Optimization of the conditions

1- The Mole Ratio (M: L) by continues variation method (Job's method), shows in Fig 12. From this results show each ligands (L1, L2) formed three coordination bonds by (N, S, N) with metal by determined absorbance of the complex 1 at (575nm) and complex 2 at (450 nm). The results showed that  $\text{Fe}^{+3}$  L1,  $\text{Fe}^{+3}$  L2 were found in (1:2) ratio of (M: L)<sup>(26)</sup>.

VM(mL)	VL(mL)	ABS Com.1at575nm	ABS Com.2 at450nm	VM/(VM+ VL)	VL/(VL+ VM)
10	0	0.0	0.0	1	0.0
9	1	0.23	0.31	0.9	0.1
8	2	0.34	0.45	0.8	0.2
7	3	0.45	0.59	0.7	0.3
6	4	0.53	0.65	0.6	0.4
5	5	0.71	0.79	0.5	0.5
4	6	0.84	0.91	0.4	0.6
3	7	0.42	0.84	0.3	0.7
2	8	0.27	0.53	0.2	0.8
1	9	0.15	0.32	0.1	0.9
0	10	0.0	0	0.0	1

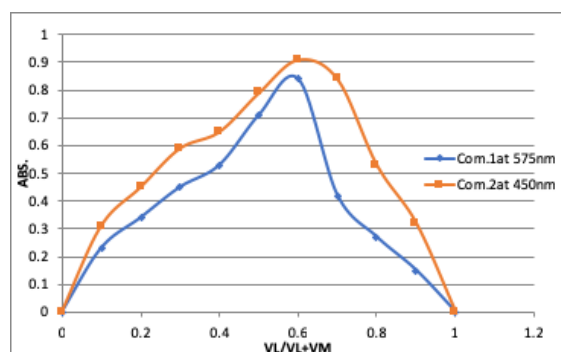


Figure 12: Mole Ratio (M:2L) By Continuous Variation Method (Job's Method)

2- **pH value:** It was found that there is a decrease in absorption value in pH acidic and basic. The absorbance value increase in pH medium because of the effect acid and base on delocalized along the conjugated chain which can protonate the azomethine (Figure 13). The color of the complex varied with pH change, it was found that the optimum pH is 6.9.

Ion	Color				
	Solution	after Ligand addition	acidic	medium	basic
Fe+3	yellow	Green	Green	Gray	Green
Fe+3	yellow	Light Orange	Light Orange	red	Light Orange

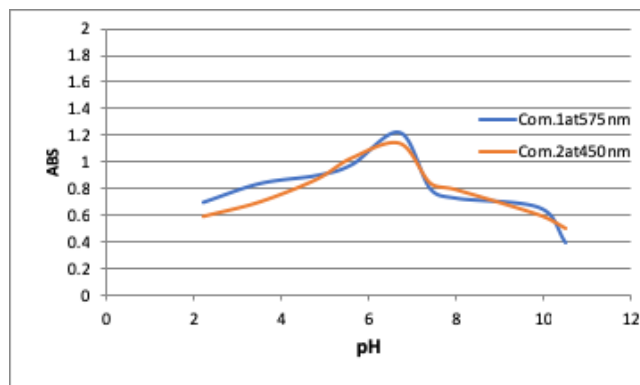


Figure 13: The Effect of pH on ligand - Fe complex formation

**3- Effect of time:** The absorbance of the complex was stable for 24 hours, indicating the high stability. It was found that the maximum absorbance of complex was at ten minutes after reaction and it was the optimum time for reaction completion. (Figure 14) <sup>(27)</sup>.

Ion	Color														
	Solution	after Ligand addition	10	20	30	40	50	60	70	80	90	100	110	120	1440
Fe+3	yellow	Green	No cha	No cha.	No cha.	No cha.	No cha.	No cha.	No cha.	No cha.	No cha.	No cha.	No cha.	No cha.	No cha.
Fe+3	yellow	Light Orange	No cha.	No cha.	No cha.	No cha.	No cha.	No cha.	No cha.	No cha.	No cha.	No cha.	No cha.	No cha.	No cha.

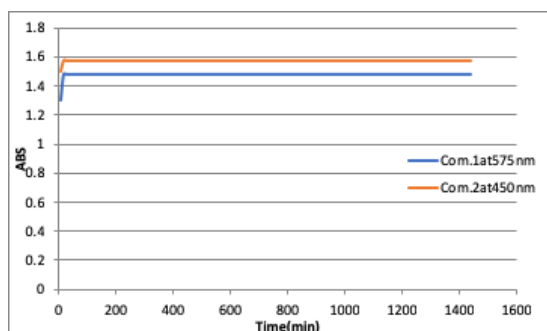


Figure 14: The Effect of time on ligand -Fe complex formation

**4- Effect of temperature:** The absorbance of the complex measured was decreased with increasing in temperature due to complex dissociation. It has found that the optimum absorbance of the complex was at 65 °C (Figure 15).

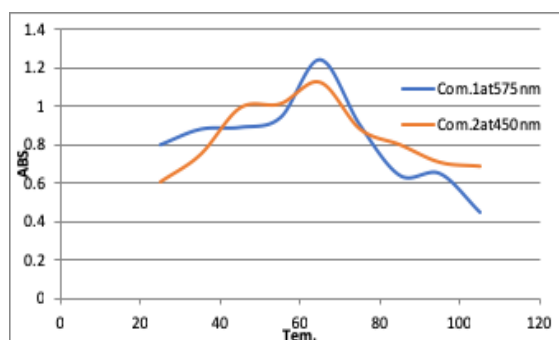


Figure 15: The effect of temperature on ligand- Fe complex formation

## CONCLUSION

It was possible to prepare of New derivatives complexes for (1*E*,1'*E*)-*N*, *N'*-(thiobis (4,1-phenylene))bis(1-phenylmethanimine) Substituted ligands with Fe<sup>3+</sup>. The complexes confer various colors from the ligands and the transitional metal salts, which was important to coordinate the occurrence, therefore these colored complexes appear different characteristic absorption bands. The different results of FT-IR between the Schiff Bases compounds (Ligands) and complexes derivatives showed that the final compounds were the least obstructed in all preparation processes, and because of the complete clarity in infrared beams, this is the basis of organic preparation processes.

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