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Synthesis, Characterization and Thermal Studies of Some Sulfa Drug Schiff Bases and Their Iron III Complexes

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ABSTRACT

A Schiff base ligands was prepared via condensation of o-vanillin with sulfa acetamide sodium and sulfa methoxy pyridazine , also the complexes of these ligands with iron III were prepared . The structure of ligands characterized by IR , 'H NMR , ^{13}C NMR and mass spectrometry , the coordination behavior of ligand towards Fe III ion investigation via IR , elemental analysis , molar conductance and thermal analysis .The thermodynamic parameter (E, ΔH, ΔS and ΔG) are calculated from thermal data using Coats-Redfern method.

Keywords: Sulfa drugs , Coat-Redfern , coordination compounds .

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INTRODUCTION

Schiff base metal complexes have been studied extensively because of their attractive chemical and physical properties and their wide range of application in various fields such as catalytic activity biologically activity , semicondactior , analytical applications [1-3] .The ability of Sulfa drugs allome to formation a complexes , has been widely reported in literature [4, 5], and the resulting complexes formed have active against different disease [4, 5]. Silverdiazine is one of the drugs that are used as a burn cream which prevent the growth of bacteria on the damaged skin.

Experimental

Materials:

Sulfa acetamide sodium and o-vanillin from (Fluka), sulfa methoxy pyridazine (Himedia co.), $FeCl_3$ from (BDH) all solvents are of analytical or reagent grode and used as received.

Instruments:

Melting points were recorded on ThermoFisher and uncorrected . IR spectra were recorded on a shimadzaw FT- IR as KBr disk in wave number region 4000-500 cm^{-1} . The ^{1}HNMR (500MHz) and ^{13}C NMR (125MHz) spectra of ligands were recorded using Brucker (500MHz), DMSO as solvent and TMS as internal reference . The mass spectra of ligands were recorded by EI at 70 eV using Agilent . Elemental analysis for complexes record on Vario EL III(Germany). The molar conductance of complexes was measured in DMF (10^{-3} M) using WTW conductivity meter LBR at 25 - 27 °C .Thermal analysis were carried out in dynamic nitrogen atmosphere (50 mL/min) with a heating rate of 10^oC/min using TGA Q500 V6.7 .

Preparation Methods:

Synthesis of Sodium acetyl (4-(2- hydroxy-3-methoxybenzylideneamion) Phenylsulfonyl) amide (L_1)

4 mmol(0.608 g) of o-vanillin and 4 mmol(0.944 g) of sulfa acetamide sodium in 50mL ethanol and 2 drops of conc. H_2SO_4 in 100 mL R.b.F. was refluxed for 4 hrs. The reaction monitored by TLC . The reaction mixture filtered hot and then lift over night . The solid product obtained was filtered the product was purified by TLC using chloroform : Ethanol (9 : 1) as eluent , yield 67 % . MP: 244 - 245 ^{o}C.

Synthesis of 4-(2-hydroxy-3-methoxybenzylideneamion)-N-(6-methoxypyridazin-3-yl) Benzene sulfonamide (L_2)

10 mmol (1.52 g) of o-vanillin , 10 mmol (2.8 g) of sulfa methoxy pyridazine in 50 mL ethanol , 2 drops of glacial acetic acid in 100 mL R.b.F. was refluxed for 4 hrs the hot solution

was filtered and the filtered lift over night in refrigerator , The solid product which separated recrystalized from ethanol , yield 80 % , m. p. 153 - 155 °C .

Synthesis of metal complexes :

The L_1Fe and L_2Fe complexes were prepared by the addition of warm solution of $FeCl_3$ (1 mmol) in 25 mL ethanol to the hot solutions of ligands (2 mmol) in 25 mL ethanol , the mixture then stirred 3 hrs under reflux where upon the complexes were precipitate , they were collected by filtration , washed several times with diethyl ether , the product collect then dried in desicator over silica gel . each complex is a black powder , L_1Fe m. p. >300 °C , L_2Fe m. p. 140 °C.

RESULT AND DISCUSSION

The structure of the ligands were established from their IR, NMR (proton and ^{13}C) and mass spectrometry. The complexes structure confirmed from elemental analysis , IR , molar conductance and thermal analysis.

I.R : The I.R data of the L_1 and L_2 and their iron III complexes are presented in Table 1.

The I.R spectrum of L_1 exhibited the azomethine stretching at 1625 cm^{-1} in addition the spectrum showed a bands at 1722 cm^{-1} which attributed to C=O stretching , both the bands shifted to lower wave number in the spectrum of L_1Fe indicating the participation of azomethine and carbonyl groups in coordination with metal ion .The OH stretching at 3411 cm^{-1} in Ligand spectrum not effected upon complexation this may be indicated not involument in coordination.

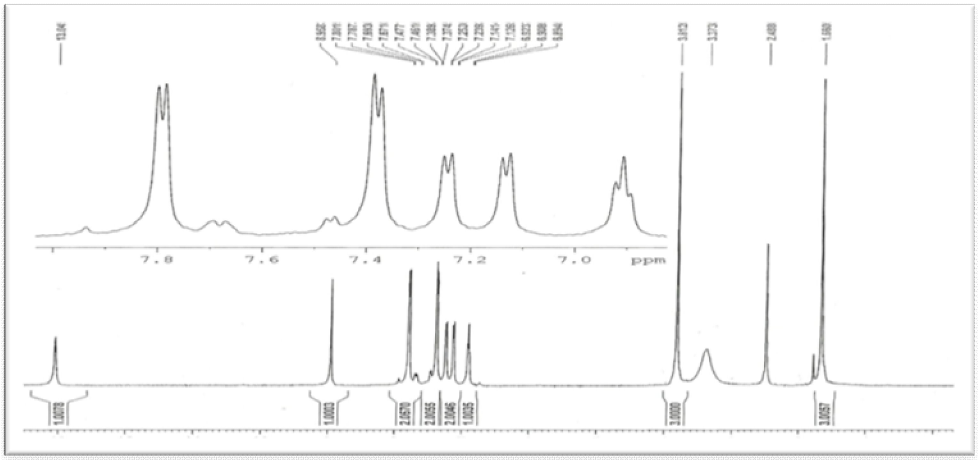
cm^{-1}in the L_2Fe , the increase in wave number upon complexation can be explained by the decrease the planareaty of the complex compared with the Ligand [6] . The disappearance of OH stretching band in the spectrum of the complex indicate the deprotination and complex formed via O^- [7] .

Table 1: IR Spectral Data in Cm^{-1}

Compounds	OH	N-H Sulpha	C-H Alph	-HC=N-	C-O	SO_2 Asym Sym	Other
L_1	3411 phenolic	---------	2929	1625	1257	1369 1137	C=O 1722
L_1Fe	3377 Phenolic	---------	2950	1595	1250	1332 1157	C=O 1710
L_2	3423 phenolic	3251	2943	1622	1259	1301 1141	N=N 1404
L_2Fe	3452 H_2O	3250	2943	1637	1253	1301 1138	N=N 1402

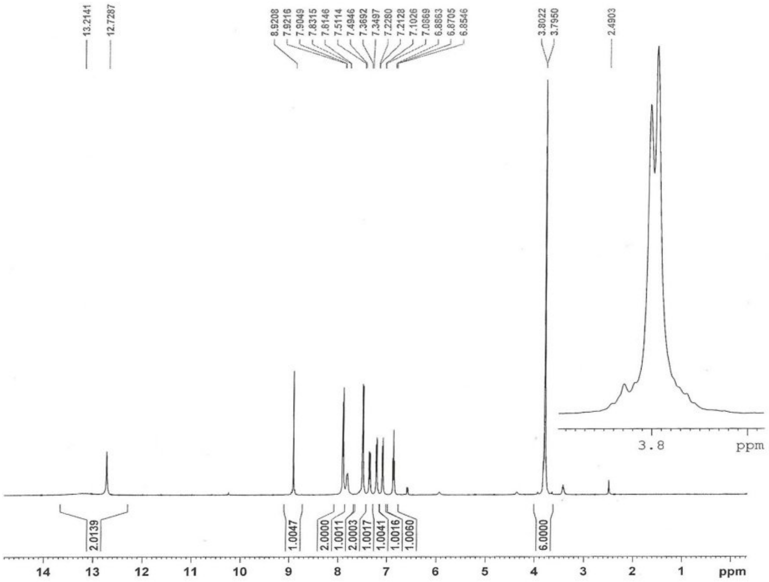
H NMR : The HNMR spectrum of L_1 show the signal of methyl proton at δ 1.66 , the methoxy proton at δ 3.81 , the aromatic protons in the range δ 6.89 – 7.8 , the azomethine proton at δ 8.95[8] and the signal of OH appear at δ 13 as show in Fig 1 .

Figure 1 ^{1}H NMR Spectrum of L_1

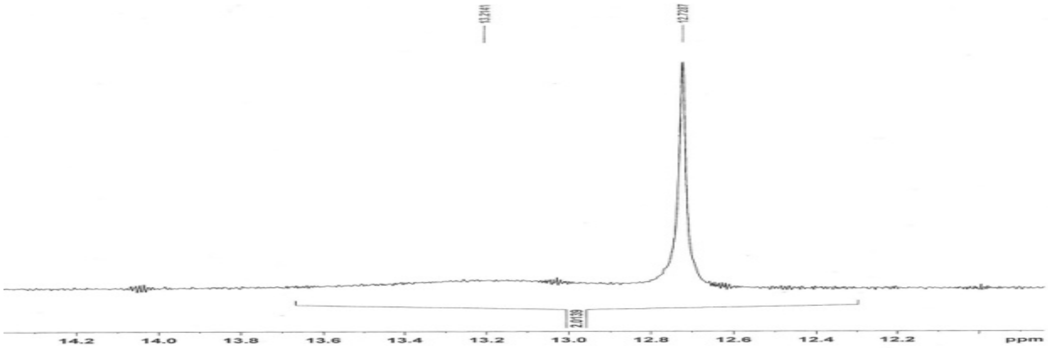


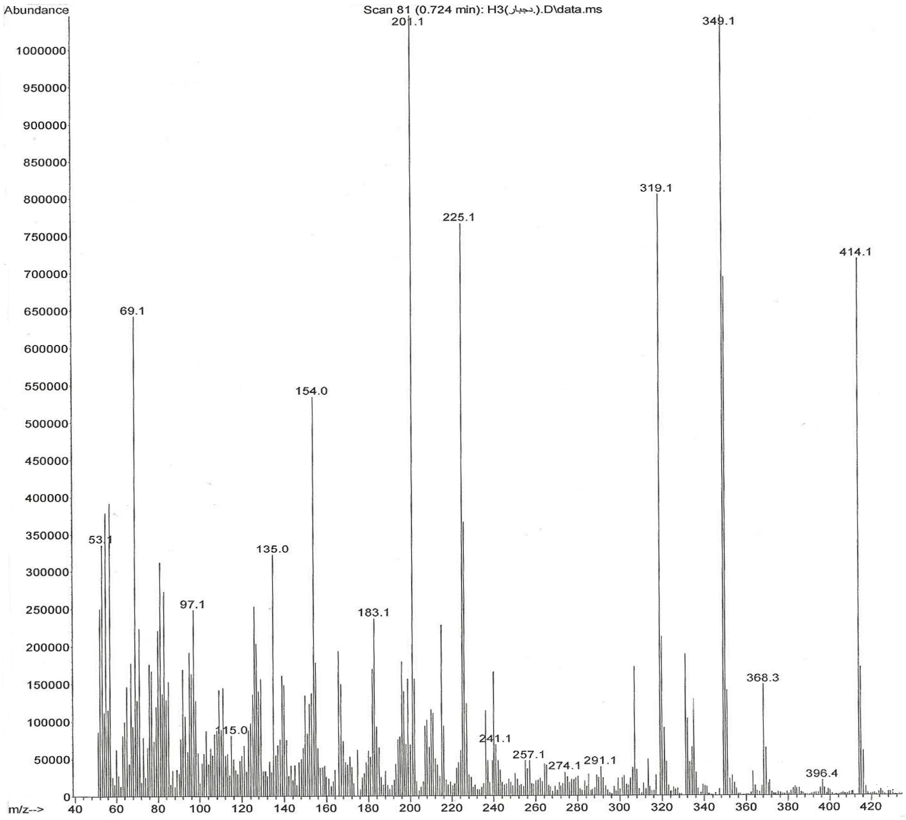
The HNMR spectrum of L_2 show a pair of signals at 3.79 and 3.8 attributed to two methoxy protons. The aromatic protons are observed in the range δ 6.85 – 7.92 , the azomethine proton at δ 8.92 . The NH proton signal appear at 12.72 while the OH proton signal appear as a very broad signal located at 13.21. (Fig 2) .

Figure 2 ^{1}H NMR Spectrum of L_2



Mass spectrometry : The mass spectra of L_1 and L_2 show a peak correspond to M^+ at m/z 370 , 414 respectively . (Fig 3) .





Mass Spectrum of L_2 Figure 3

Characterization of metal complexes : The iron III complexes were prepared by the stoichiometric reaction (1:2) of the $FeCl_3$ with the ligands , The complexes insoluble in common organic solvent but soluble in DMF and DMSO . The elemental analytical data of complexes are very close to the theoretical values as show in Table 2.

Table 2 elemental analysis

Complexes	Analytical Data Calculated (Found) %				$ohm^{-1}\ cm^{2}\ mol^{-1} = {}_{m}\Lambda$
	C	H	N	S	
L_1Fe **$C_{32}H_{30}N_4O_{10}S_2Cl\ Fe$**	48.91 (48.34)	3.82 (4.39)	7.13 (7.00)	8.1 7.76)(	81 electrolytic
L_2Fe **$C_{38}H_{38}N_8O_{12}S_2Cl\ Fe$**	47.84 (47.41)	3.98 (4.03)	11.75 (11.81)	6.71 -------	6.9 non electrolytic

Molar conductance:

The molar conductance value of L_1Fe (81 Ω^{-1}. cm^2. mol^{-1}) indicate the electrolytic nature of the complex furthermore the chloride ion is located outside the coordination sphere [9] .While the molar conductance of L_2Fe (6.9 Ω^{-1}. cm^2. mol^{-1}) indicating the non electrolyte nature and the chloride ion is located inside the coordination sphere and is directly involved in coordination with the Fe center . Table 2.

Thermal stability and kinetic parameter:

The complexes are subjected to a TG analysis from 25 - 900°C under nitrogen atmosphere, (50 mL / min) with heating rate 10 °C/min the data are collected in Table 3. L_1Fe is thermally stable up to about 180 °C. (Fig 4) indicated the totally absence of hydrated or coordinated water molecules [10]. The first stage of decomposition starts at 185 °C and end 235 °C (DTG $_{max}$ 192 °C) involves a mass loss of about 4.4 % (theoretical 4.5 %) which correspond to loss of chloride as HCl [11]. The second stage starts at 240 °C and ends 550 °C (DTG $_{max}$ 275 °C) involves a mass loss of about 31.65 % (theoretical 32.3 %) which involves the decomposition of the ligand moiety and loss $C_4H_6O_6N_2S_2$ [12].

Step I $[Fe(L)_2].Cl \xrightarrow{185\text{-}235°C} [Fe(L)_2] + HCl$

The TG curve of L_2Fe (Fig 5) show four stages of decomposition . The first stage starts at 80 °C and ends at 105 °C (DTG $_{max}$ 90 °C) with mass loss 1.86 % (theoretical 1.88 %) which represent a loss one lattice water molecule [11]. The second stage starts at 110 °C and ends 170 °C (DTG $_{max}$ 143 °C) with mass loss 1.95 % (theoretical 1.92 %) which represent a loss of one coordinated water molecule . The third stage starts at 175 °C and end at 215 °C (DTG $_{max}$ 195 °C) with mass loss 3.8 % (theoretical 3.9 %) which represent a loss of HCl. The final stage starts at 230 °C and end at 640 °C (DTG $_{max}$ 290 °C) with mass loss 42.2 % (theoretical 42.6 %) which involves the decomposition of the ligand moiety and loss $C_{10}H_{12}O_6N_6S_2$.

Step I $[Fe(L)_2(H_2O)Cl].H_2O \xrightarrow{110\text{-}170°C} [Fe(L)_2(H_2O)Cl] + H_2O$

$H_2O + [Fe(L)_2Cl] \xrightarrow{80\text{-}105°C}$ Step II $[Fe(L)_2(H_2O)Cl]$

$\xrightarrow{175\text{-}215°C}$

Step III [Fe $(L)_2$ Cl] [Fe $(L)_2$] + HCl

Table 3 Thermal decomposition data of the complexes

complex	stage	TG range °C	DTG_{max} °C	Mass loss %		Assignment
				Found	Calcu.	
L_1Fe	I	185-235	192	4.4	4.5	HCl
	II	240-550	275	31.65	32.30	$C_4H_6O_6N_2S_2$
L_2Fe	I	80-105	90	1.86	1.88	H_2O
	II	110-170	143	1.95	1.92	H_2O
	III	175-215	195	3.8	3.9	HCl
	IV	230-640	290	42.2	42.6	$C_{10}H_{12}O_6N_6S_2$

Figure 4
TG and DTG Curve of complex L_1Fe

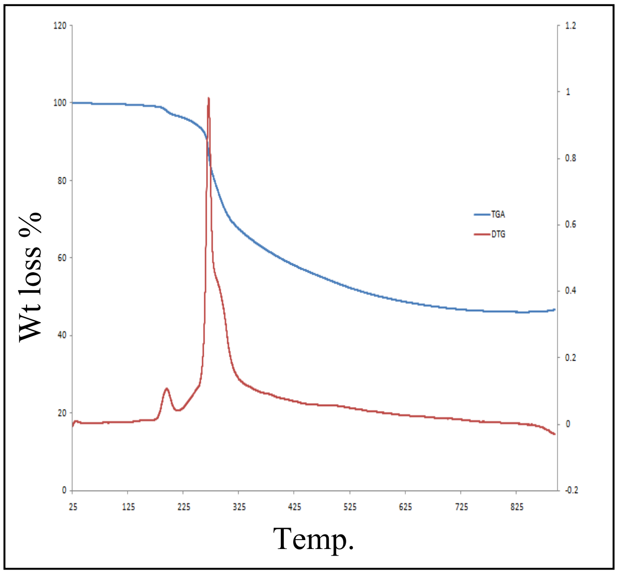
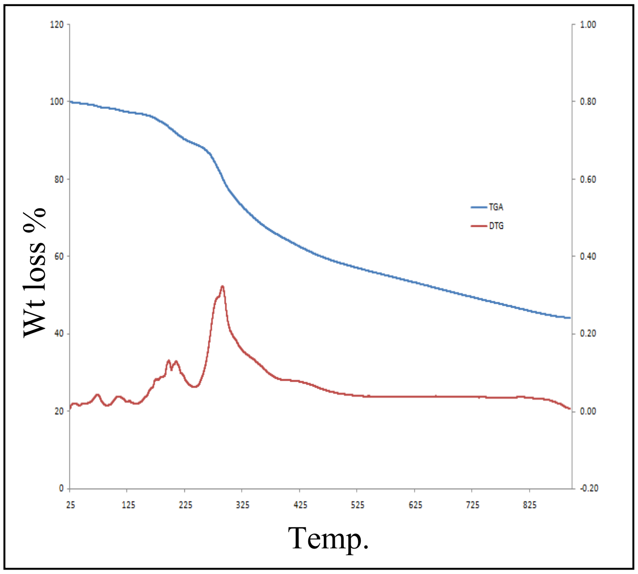


Figure 5
TG and DTG Curve of complex L_2Fe



The kinetic parameters namely E , ΔH, ΔS and ΔG where calculating from TG and DTG data using Coats - Redfern method [13 - 16] .

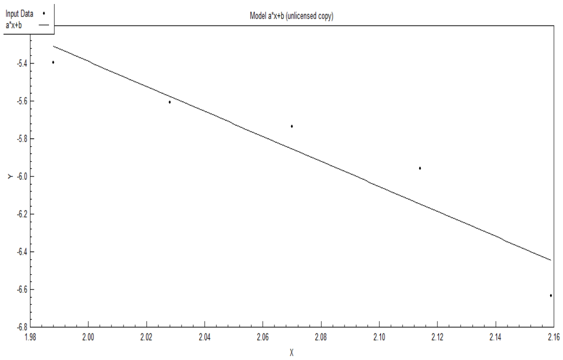
$$\log\left[\frac{\log\frac{Wf}{Wf-Wt}}{T^2}\right]=\log\left[\frac{AR}{\theta E}\left(1-\frac{2RT}{E}\right)-\frac{E}{2.303RT}\right]$$

where **Wf :**the weight loss at the end of stage, **Wt:** the weight loss at temp. **A:** Arrhenius factor (S^{-1})

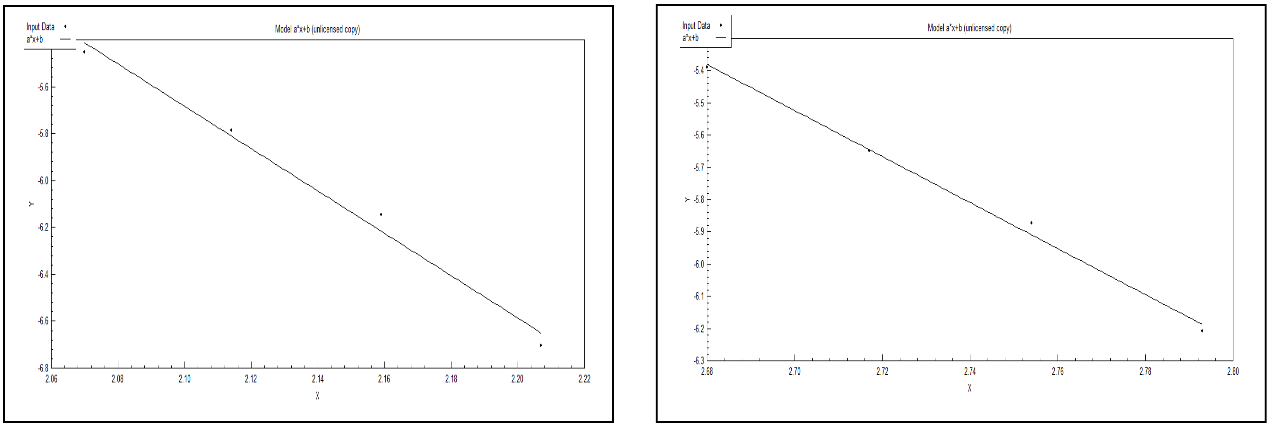
R : gas constant , **θ :** heating rate C^o/m , **E:** activation energy KJ/mol

When plot the left side of equation against $\frac{1}{T}$ a straight line obtained (Fig 6) . The activation energy E in KJ/mole are calculated from the slope , the high value of E (79.5 − 179.4 KJ /mole) indicated to the stability of the complexes .

L_1Fe…Step I



L_2Fe…Step I **L_2Fe…Step III**



$X = 1000/T$, $Y = \log\left[\frac{\log\left(\frac{Wf}{Wf-Wt}\right)}{T^2}\right]$

Figure 6 Coats - Redfern plot of complexes

The ΔH calculated from the relation $\Delta H = E - RT$. All values of ΔH are positive (endothermic process).

$$\Delta S = R\ln\left(\frac{A\,h}{K_B\,T_s}\right)$$

The value of ΔS are calculate by using the relation Where A calculate from the intercept K_B Boltzmann constant 1.3806×10^{-23}

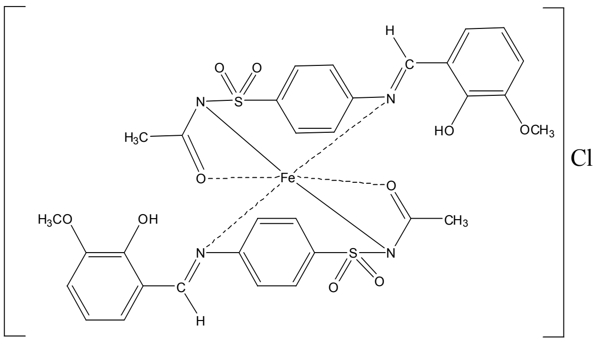
The low or negative values of ΔS indicate that the decomposition occur at very low rate.

The ΔG for each Step are calculated from Gibbs relation (ΔG = ΔH−TΔS) all Values of ΔG obtained ranging from (105.8 − 170.6 KJ/mole) , indicate that all steps are non spontaneous.

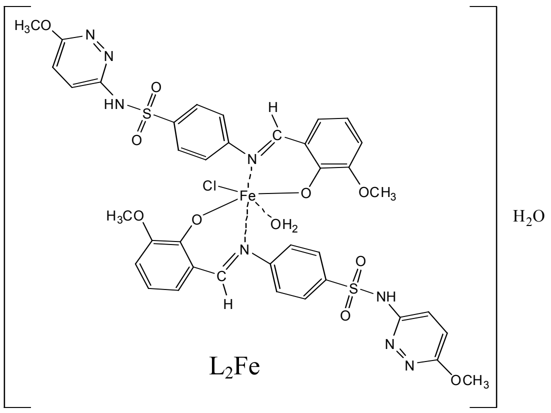
Table 4 Kinetic parameter of the complexes calculated from Coat - Redfern method

Comp.	stage	A (s^{-1})	E (KJmol^{-1})	HΔ (KJmol^{-1})	SΔ(KJmol^{-1}K^{-1})	GΔ(KJmol^{-1})
L_1Fe	I	1.92×10^{11}	127.02	123.1	-0.032	138.2
	II	2.1×10^{5}	91.5	86.9	-0.148	168
L_2Fe	I	1.5×10^{17}	136.6	133.5	0.082	105.8
	II	2.22×10^{7}	79.5	76.04	-0.107	120.5
	III	2.19×10^{17}	179.4	175.5	0.083	136.5
	IV	2.63×10^{5}	93.2	88.5	-0.146	170.6

Based on the above thermal data , physiochemical properties (□$_{m}$ and IR) and elemental analysis , the following structure are proposed for complexes .



L_1Fe



L_2Fe

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