Synthesis, characterization and thermal studies of 4-(2-hydroxy-3-methoxybenzylidene amino) - N-(pyridine -2-yl) Benzene Sulphonamide and their complexes

Hanadi M. Jarallah   and   *Jabbar S. Hadi

Departement of Chemistry , College of Education , University of Basrah
Basrah – Iraq
*Email :jshalkabi@yahoo.com

Abstract

A Schiff base ligand was prepared via condensation of o-vanillin with sulphapyridine in order to be used as ligand for complexation with Ni(II) , Cu(II) and Fe(III) ions. The structure of ligand characterized by IR , 'H NMR , ^{13}C NMR and mass spectroscopy , the coordination behavior of ligand towards metal ions 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 : Sulphapyridine , o-vanillin , thermodynamic parameter.

1- Introduction

Sulpha drugs are well known for their biological activity .The condensation of sulpha drugs with aldehyde gives also biologically active Schiff bases [1,2] . In addition sulpha drugs alone have ability to coordinate with different metal ions [3] , and the resulting complexes formed have biologically active against differ disease like malaria[4] . The Schiff bases derived from sulpha ligand having multi dentate site , C=N , SO2 , NH , OH and salin type Schiff bases and the heterocyclic moiety in some sulpha drug like sulphapyridine , sulphamethaxazole , etc.[5,6].

2- Experimental

2.1 Materials: sulpha pyridine (Himedia co.) ,o-vanillin (Fluka), $FeCl_3$,Copper Chloride and Nickel Chloride hexahydrate (BDH) .

2.2 Instruments: melting points were recorded on ThermoFisher , IR spectra were recorded on a shimadzw FT-IR as KBr disk in wave number region 4000-500 cm^{-1} . The molar conductance of complexes was measured in DMF (10^{-3} M) using WTW conductivity meter LBR at 25-27C^o ^{1}HNMR (500MHz) and ^{13}C NMR   (125MHz) spectra of ligand were recorded using Brucker 500MHz, DMSO as solvent and TMS as internal reference . The mass spectrum of ligand was recorded by EI technique at 70ev using Agilent , thermal analysis (TG and DTG) were carried out in dynamic nitrogen atmosphere (50 ml/min) with a heating

rate of 10°C/min using TGA Q500 V6.7.Elemental analysis for complexes record on Vario EL III(Germany) .

2.3 Preparation Methods :

2.3.1 Synthesis of Ligand: 10 mmol(1.52 g) of o-vanillin in 25ml ethanol was added to 10 mmol(2.49 g) of hot ethanolic solution of sulphpyridine , two drops of conc. H_2SO_4 was added and the resulting solution was refluxed for 4 h and then lift over night in refrigerator , the solid product obtained was filtered and washed with petroleum-ether and the final product was purified by 20x20cm TLC using chloroform : Ethanol 9 : 1 as eluent , m. p. 197-199°C yield 85% orange crystal.

2.3.2 Synthesis of metal complexes: The Ni(II), Cu(II) and Fe(III) complexes (HNi , HCu and HFe) were prepared by the addition of warm solutions of metal salts (1 mmol) in an ethanol 25ml to the hot solution of ligand (2 mmol) in ethanol 25ml, a few drops of 1N KOH were added to the mixture then stirred 3h under reflux where upon the complexes were precipitate they were collected by filtration , washed several times with diethylether the product collect then dried. The physical properties are shown in Table 1.

Table 1   Physical Data and elemental analysis

Comp.	Physical state	Yield %	M.Wt g/mole	M.p ℃	C% Found(cal.)	H% Found(cal.)	N% Found(cal.)	S% Found(cal.)	Λ m Ω^{-1}Cm^{2}mol^{-1}
Ligand H	Orange Crystal	85	383	197-199	(59.5)	(4.43)	(10.96)	(8.35)	——
H Ni	Pall green powder	84	894	>300	51.32 (51)	4.38 (4.47)	9.7 (9.39)	(7.15)	17.2
H Cu	Brown powder	79	881	>300	51.31 (51.75)	4.41 (4.31)	9.82 (9.53)	(7.26)	21.5
H Fe	Crystal Black	80	909	>300	50.67 (50.16)	4.04 (4.18)	9.44 (9.24)	(7.04)	115

3- Result and discussion

The structure of the ligand was established from their IR , ^{1}H NMR , ^{13}C NMR and mass spectrometry . The IR spectrum exhibited the azomethine stretching at 1622cm^{-1} in addition the spectrum showed a bands resulting from the OH and NH str. at 3423and 3246 cm^{-1} respectively also the asymmetric and sym. Str. of SO_2 group appear at 1386 and 1139 cm^{-1} respectively.

The mass spectrum (Fig 1) show the moleculer ion at m/z 383.2 with relative abundance 6% which indicating the condensation . The important peaks and their relative intensities shown in scheme 1 .

The proton NMR spectrum of the ligand show the signal of methoxy protons of o-vanillin moiety at 3.79 ppm . The signal attributed to azomethine proton appear as singlet at 8.93 ppm [1-3] , the signal of OH appear at 12.6 ppm ,will the signal of NH proton as appear a very broad signal at 12 ppm the other aromatic proton appear as multiple signals at 6.8-8.0 ppm region as shown in Fig 2 .

The ^{13}C NMR spectrum show (Fig 3) the isomethine carbon signal appear at 165 ppm[1-3],The methoxy carbon appear at 56ppm, The carbon attached to hydroxyl group appear at150ppm,TheC$_{15}$ appear at153 aromatic Carbon Signals Cited as follow . Based on above spectral data the following structure is proposed for the ligand .

C_1 165 , C_2 119.5 , C_3 124 , C_4 116 , C_5 115 , C_6 149 , C_7 150 , C_8 56 , C_9 155 , C_{10} 122 ,

C_{11} 128 , C_{12} 138 , C_{13} 128 , C_{14} 122 , C_{15} 153 , C_{16} 110 , C_{17} 138 , C_{18} 118 , C_{19}

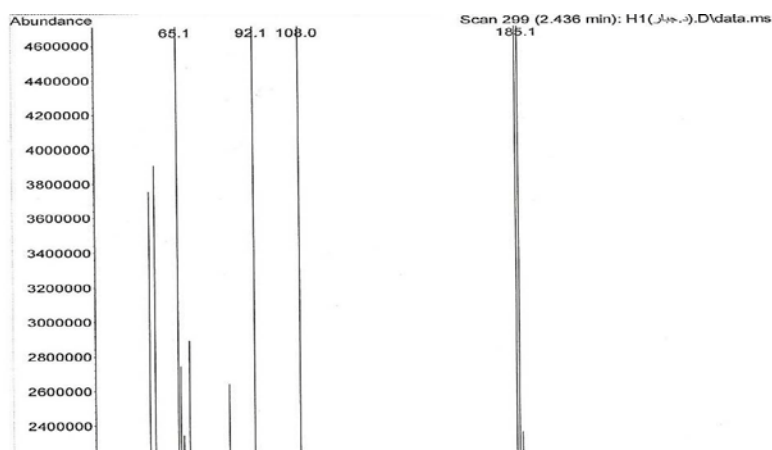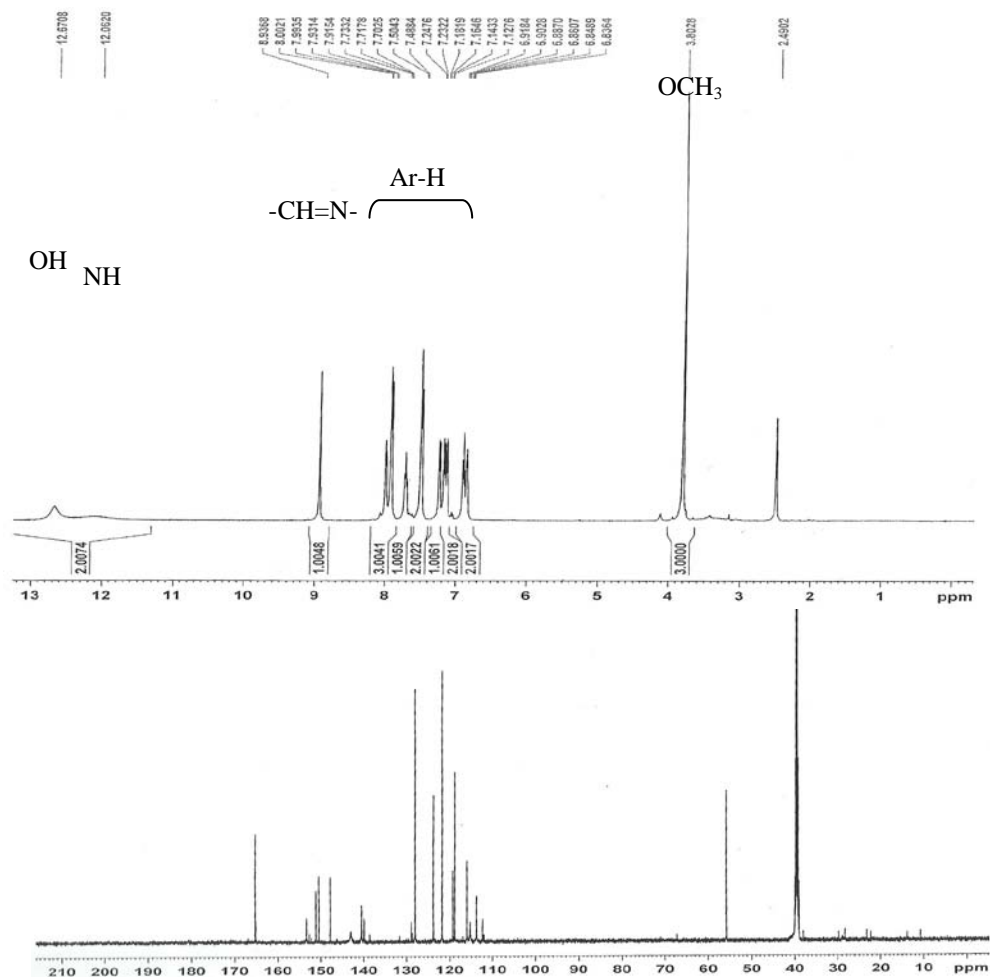**Scheme 1 Mass fragmentation pattern of Ligand H**

Figure 1   Mass Spectrum of Ligand H

3.1 Characterization of metal complexes : all metal complexes were prepared by the stoichiometric reaction of the corresponding $FeCl_3$, $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$ with ligand in the , insoluble in common organic solvent but soluble in DMF and DMSO . The results of elemental analysis are in good agreement with these required by the proposed formula.

3.2 IR of Complexes : the comparison of IR spectrum of ligand and their complexes showed that the ligand were principally bidentate coordinated through azomethine nitrogen and oxygen of the ionized phenolic hydroxyl group , where the band appearing at 1622 cm^{-1} due to azomethine is shifted to higher or lower frequency [7,8] , and the disappearance of OH band in metal complexes spectra . The IR spectral data are listed in table 2 .

Table 2   IR Spectral Data in Cm^{-1}

Comp.	OH str.	NH str.	C=N str.	O=S=O Asy. Sym.	C-O
Ligand H	3446 phenolic	3246	1622	1386 1139	1263
H Ni	3415 H_2O	3245	1614	1388 1132	1242
H Cu	3448 H_2O	3245	1627	1384 1137	1267
H Fe	3448 H_2O	3245	1627	1384 1137	1251

3.3 Molar conductance : the molar conductance of the complex ($\square_m$) calculated by using the relation $\square_m$=**k/c** (c = 10^{-3} M) and k/ specific conductance which determine from the relation K=G.A

The molar conductance values for **HNi** 17.2 Ω^{-1}.cm^2. mol^{-1} and for **HCu** 21.5 Ω^{-1}.cm^2. mol^{-1} these value indicate these complexes are non-electrolyte [9,10]. The molar conductance of **HFe** 115 Ω^{-1}.cm^2. mol^{-1} indicating the ionic nature of this complex , furthermore it indicate the presence of chloride ion out of coordination sphere [11] .

4- Thermal stability and kinetic parameter

The complexes are subjected to a TG analysis from 25-900℃ under nitrogen atmosphere, 50ml/min with heating rate 10 C^o/min the data are collected in table 3 and 4.

The **HNi** undergoes decomposition in three steps the first step in range 30-110 ℃ accord to loss two H_2O lattice molecules [12,13] (Theoretical 4.02% found 4.16%). The second step at 115-240 ℃   (Theoretical 4.19% found 4.3%) correspond to loss of two H_2O molecules and this result indicate these two molecules are more tightly bonded to the Ni(II) ion . The third step began at 250 ℃ which represent the decomposition of Ligand parts.

The **HCu** complex undergoes decomposition in three steps the first step in the rang 30-70 ℃ (DTG $_{max}$ 50℃) which represent a loss one lattice water molecule , (theoretical 2%, found 2.2%) . The second step at 120-235 ℃ (DTG $_{max}$ 190℃) correspond to the loss two coordinated water molecule (Theoretical 4.1% found 4.0%). The third step began at 240-550 ℃ (DTG $_{max}$ 310℃) with present loss 37.7 (theoretical 37.9%) which may be attributed to loss $C_{10}H_{10}O_4N_4S_2$ [14]. The final weight 25% at 900 ℃ indicate that the final product of decomposition not metal oxide but may be a part of ligand remain with metal or the final product polluted with carbon atoms [15] .The **HFe** complex undergoes decomposition in four steps , the first step in the rang 40-80 ℃ (DTG $_{max}$ 50℃) represent loss one water lattice

molecule (Theoretical 1.98% found 2.0%) (DTG $_{max}$ 145℃). The second step at 125-220 ℃ represent the loss of two coordinated water molecules. The third step at 225-255 ℃ correspond to loss of Cl as HCl [14], (theoretical 4.21%, found 4.18%). The fourth step from 255-450 ℃ (DTG $_{max}$ 275℃) with mass loss present 38% theoretical 38.2% , attributed to degradation of the organic part where $C_{10}H_{10}O_4N_4S_2$ loss .
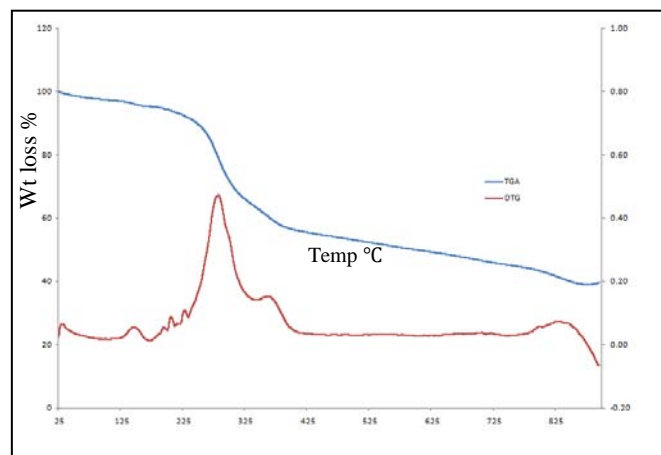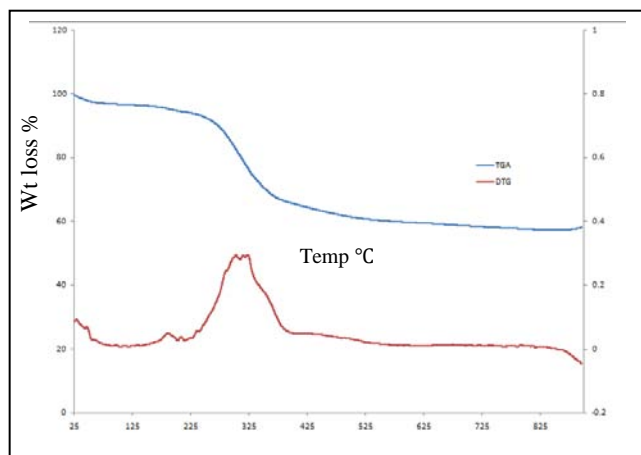

Table 3 Thermal decomposition data of the complexes

complex	stage	TG range ℃	DTG$_{max}$ ℃	Mass loss %		Assignment
				Found	Calcu.	
H Ni	I	30-110	90	4.16	4.02	$2 H_2O$
	II	115-240	165	4.3	4.19	$2 H_2O$
	III	250-650	410	38.21	38.19	$C_{10}H_{10}O_4N_4S_2$
H Cu	I	30-70	50	2.2	2	H_2O
	II	80-235	190	4	4.1	$2 H_2O$
	III	240-550	310	37.7	37.9	$C_{10}H_{10}O_4N_4S_2$
H Fe	I	40-80	50	2	1.98	H_2O
	II	125-220	145	4.1	4	$2 H_2O$
	III	225-255	235	4.18	4.21	HCl
	IV	255-450	275	38	38.2	$C_{10}H_{10}O_4N_4S_2$

Based on the above thermal data, physiochemical properties ($\square_m$ and IR) and elemental analysis , the following structure are proposed for complexes .

**HFe**   **HCu**

HNi

The kinetic parameters namely E , ΔH, ΔS and ΔG where calculating from TG and DTG data using Coats-Redfern method [12,16] .

$$\log\left[\frac{\log\frac{Wf}{Wf-Wt}}{T^2}\right] = \log\left[\frac{AR}{\theta E}\left(1 - \mathbf{152}\right)\frac{E}{2.303\,RT}\right]$$

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) . The activation energy E in KJ/mole are calculated from the slope , the high value of e (36-189 KJ /mole) indicated to the stability of the complexes .

Step I HNi

Step II HNi
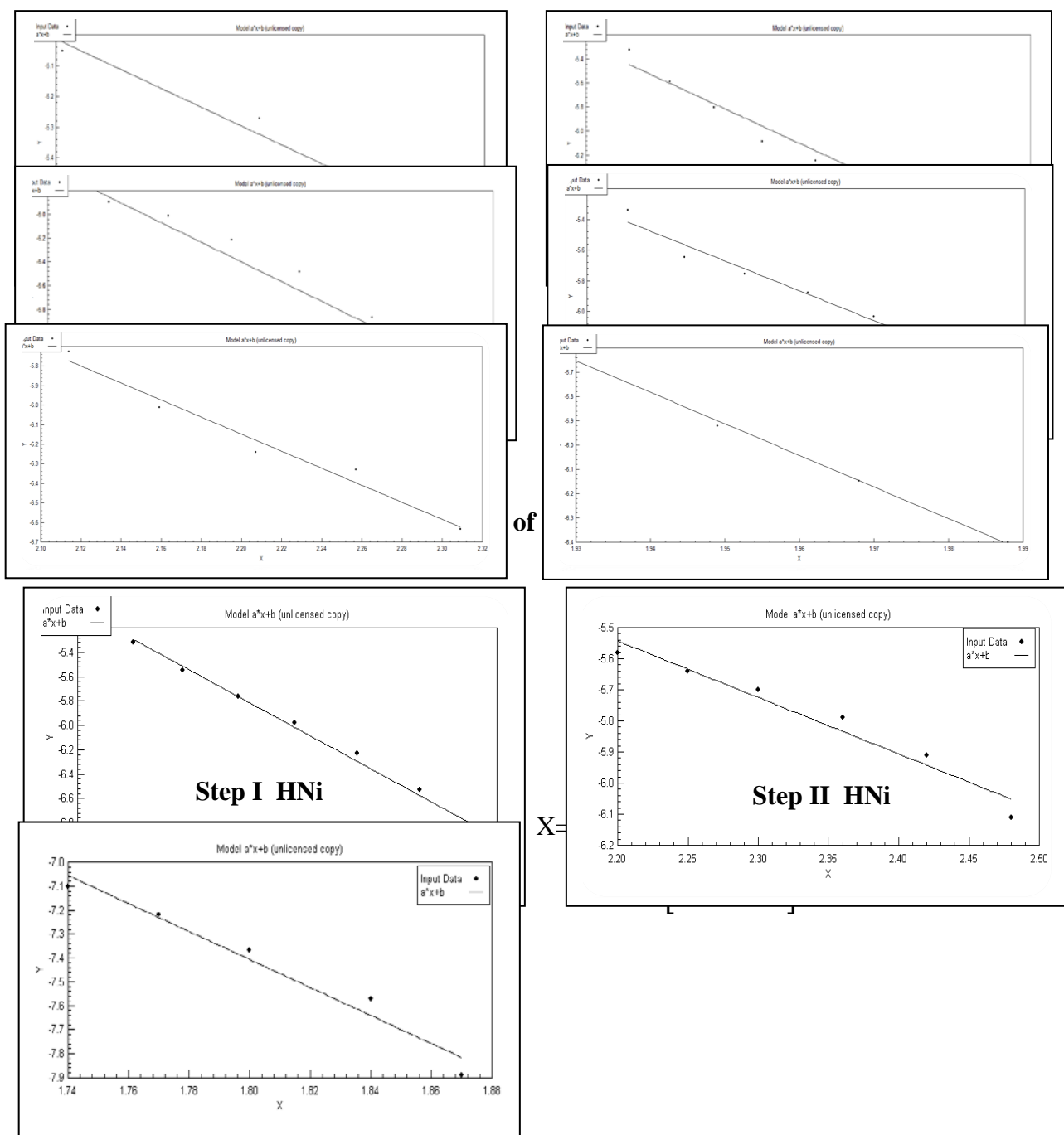
Coats-Redfern plot of complex

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

The value of ΔS are calculate by using the relation $\Delta S = R \ln \left(\dfrac{A\,h}{K_B\,T_s} \right)$

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 ($\Delta G = \Delta H - T\Delta S$) all Values of ΔG obtained ranging from ($90.2 - 199.1$ 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})	ΔH (KJmol^{-1})	ΔS (KJmol^{-1} K^{-1})	ΔG (KJmol^{-1})
H Ni	I	1.44×10^{6}	59.8	56.7	-0.128	103.1
	II	1.59×10^{3}	49.4	45.7	-0.186	127.2
	III	3.62×10^{4}	92.7	87.1	-0.164	199.1
H Cu	I	7.98×10^{7}	62.6	59.9	-0.094	90.2
	II	1.53×10	36.4	32.6	-0.225	136.7
	III	6.08×10^{4}	88.1	83.3	-0.158	175.9
H Fe	I	4.36×10^{3}	48.5	45.1	-0.177	115.8
	II	4.64×10^{6}	83.4	79.7	-0.120	133.8
	III	8.82×10^{16}	189	184	0.075	145.87
	IV	1.42×10^{5}	89.76	85.2	-0.151	168.1

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References

[1] A. Emandi ; A. Nicolace ; M. Badea and R. olar , Analele university , din Bucuresti-chimi , Anul XIII
     (serienoua) , Vol. I-II , pp 167-172. **(2004)** .

[2] A. C. Talla and J. A. Obalexe , Vol. 2, No 1 , pp 11-26 , **(2010)** .

[3] M. K. Hassan ; R. M. Hassan and M. A. Abd-Alla , Monatshelfte fur chemie , 122, pp 829-839 **(1991)** .

[4] J.A. Obaleye ; S. A. Amolegbe and G. O. Gbotoso , proceeding of the second conference on science and
     national development, 10-13, **(2006) .**

[5] B. B. Subudhi ; P. K. Panda and S. Sahoo , Iranian j. of pharmaceutical science , 3 , No 4 , pp 245-250,
     (2007) .

[6] V. Uma, S. Joshi and V. Pawer ; International J. of pharm and Bio Science ,Vol.2 ,No.1 ,pp 170-178
     (2011) .

[7] H. M. Abd El – Fattah, A. L. El – Ansary and N. S. Abd El – Kader ; J. Therm. Anal. Calorim,
     Vol. 96, PP. 961 − 969, **(2009)** .

[8] V. Pawar, S. Joshi and V. Uma ; Int. J. ChemTech Res., Vol. 2, No. 4, PP. 2169– 2172, **(2010)** .

[9] P.Jayaseelan,S.Prasad, S. Vedanayaki and R. Rajavel ; International J. of Chemical, Environmental and
     Pharmaceutical Research Vol.1 ,No. 2 ,pp 80-88,**(2010)** .

[10] M.S.Sureshand, and V. Prakash ; International of the physical science ,Vol.5 ,No. 9 ,pp 1443-1449
     (2010) .

[11] A. A. M. Aly ,A. H. Osman, M. A. El. Mottaleb and G. A. H. Gouda ; J .Chil.Chem.Soc.,54 No.4
     pp 349−353**, (2009)** .

[12] S.A.Abdel-Latif ,H.B.Hassib and Y.M.Issa:Spectro Chimica Acta part A 67,pp 950-957 **(2007)**

[13] M.M.Mashaly ,Z. H. Abd-El-wahab and A. A. Faheim ; J. of the Chinese Chem .Soc. ,Vol. 51, No. 5A
     PP 901-915 **(2004) .**

[14] P.Jelaja ; ph. D. thesis ,Cochin University of Science and Technology Kochi-682022 ,KERAIA **(2003) .**

[15] M.S.Refat ,S. A. El-Korashy ,D. N. Kumar and A. S. Ahmad ; Specrtrochimica Acta part A70 , pp898-
     906 **(2008) .**

[16] Chon Shin Jou ; M.Sc. thesis ,Texas Technology University **(1986) .**

تخليق وتشخيص ودراسة حرارية لـ
4-(2-hydroxy-3-methoxybenzylidene amino)-N-(pyridine -2-yl) Benzene Sulphonamide
ـ ومعقـــداتـه

هنـادي مهـــدي جار الله و جبار صالح هــادي
قسم الكيمياء ــ كلية التربية ــ جامعة البصرة
البصرة - العراق

المستخلص

حضر في هذه الدراسة قاعدة شف مشتقة من اورثو فانلين مع السلفا بريدين لغرض استخدامها كليكاند في تحضير معقدات النيكل الثنائي والنحاس الثنائي والحديد الثلاثي . شخص الليكاند باستخدام مطيافية تحت الحمراء والرنين النووي المغناطيسي وطيف الكتلة . وقد شخص طبيعة الارتباط بين اليكاندات والذرة المركزية بواسطة تحت الحمراء والتوصيلية المولارية وتحليل العناصر والتحاليل الحرارية . حسبت الدوال الثرموديناميكية , طاقة التنشيط والتغيير في الانثاليبية والتغير في الانتروبي والتغير في الطاقة الحرة باستخدام طريقة Coats-Redfern .