PAPER • OPEN ACCESS

Synthesis, Characterization and Thermal Studies of Fe(II), Co(II), Ni(II) and Cu(II) Complexes with bis-(4-benzylidenamino-phenyl)-methane Schiff base ligand

To cite this article: Atared F. Hassan *et al* 2021 *J. Phys.: Conf. Ser.* **2063** 012004

View the article online for updates and enhancements.

Synthesis , Characterization and Thermal Studies of Fe(II) , Co(II) , Ni(II) and Cu(II) Complexes with bis-(4-benzylidenamino-phenyl)-methane Schiff base ligand

Atared F. Hassan , Hiba H. Sabah and Afaq A. Turki

Department of chemistry, College of Science, University of Basrah

Atared.hassan@uobasrah.edu.iq , heba.hani@uobasrah.edu.iq,

afaq.turki@uobasrah.edu.iq

Abstract. A new series of Co(II), Fe(II) , Cu(II) and Ni(II) complexes of Bis –(4-benzylidenamino-phenyl)-methane (L) have been prepared and characterized . The complexes conform to general formula $[CoL(H_2O)_3] Cl_2$, $[FeL(H_2O)_5]SO_4.2H_2O$, $[CuL(H_2O)_5] NO_3$ and $[NiL(H_2O)_3Cl_2]$, Infra red spectra and elemental analysis reveal uni-dentate coordination of Schiff base to metal ions. Molar conductivity measurements show that complexes (I , III) behave as 2:1 electrolyte while complex (II) behave as 1:1 electrolyte. The thermal studies for complexes shows that the complexes are thermal stable.

1. Introduction

Schiff bases are an important organic compounds which carrying imin or azomethane group . Schiff bases are versatile compounds in many fields including biological , analytical , medical and pharmaceutical such as Anti tubercular [1,2] , Anti depressant [3] , Anticonvulsant [4,5] and anti-inflammatory [6]. Schiff bases easily formed high thermal stability complexes with almost all metal ions were useful for uses as catalysis in highly temperature for both homogeneous and heterogeneous reaction such as polymerization [7,8] , For reduction of thionyl chloride [9] and oxidation of organic compounds [10].

These organometallic compounds exhibit larger biological activity than free Schiff base themselves such as anti bacterial [11] , Anti fungal [12-14], Anti cancer [15-17] and antiviral activity [18].

The aim of this work , the preparation , spectroscopic studies of Fe(II) ,Co(II) ,Ni(II) and Cu(II) complexes with mono-dentate bis-(4-benzylidenamino-phenyl)-methane ligand and we have study thermal behaviors of these complexes .

2. Material and methods

All chemicals and solvents used in this study were supplied (Merck and Fluka) company . The ^{1}H NMR spectra were recorded with (Bruker DPX-300)Spectrometer(Iran) . The elemental analysis was done by using (CE-440)Elemental analyzer(Iran) . FT-Infrared spectra were recorded as KBr pellets with (FT-IP 8400S) Shimadzu instrument(Univercity of BAsrah) . Melting point of complexes were determined on (Gallnkamp melting point apparatus). Thermal analysis were carried out under (N_2) atmosphere using α -Al$_2$O$_3$ as reference(Iran) . The ionic conductivity was measured by using (Konduktoskop E 365B Metrohm Herisau) conductivity instrument at room temperature.

2.1. Synthesis:

2.1.2. Preparation of Schiff base complexes:

To a hot solution of CoCl$_2$.6H$_2$O , FeSO$_4$.7H$_2$O , Cu(NO$_3$)$_2$.3H$_2$O ,and NiCl$_2$.6H$_2$O in (15 ml)ethyl alcohol (2.5mmol)was added (2.5mmol) solution of Schiff base (L) are mentioned in literature [19] in 25ml ethyl alcohol drop wise with continues stirring and gentle heating for 1hr. The volume of solution reduced to half, colored solid compound was formed were filtered off , washed several times with hot deionized water and then with ethyl alcohol and dried under vacuum.

2.2. Computational methods

The theoretical study in work was performed using the computationals method by hyper chem. 8.02. Geometry optimization of the studied , compounds by performing the semi-empirical molecular orbital theory at the level PM3[20].

Result and discussion

The C.H.N , molar conductunce data and physical characteristic of new complexes are listed in table (1).

Table(1). Physical properties , molar conductivity and C.H.N data of prepared complexes.

No.	Empirical formula	Ω^{-1} cm^2 mol^{-1}	%	Color	m.p ^{o}C	Elemental analysis found(calc)			
						C	H	N	S
I	[CoL(H$_2$O)$_3$] Cl$_2$	243.7	%60	Dark green	> 320	58.61(57.97)	5.39(5.04)	5.11(5.01)	
II	[FeL(H$_2$O)$_5$]SO$_4$.2H$_2$O	108.6	%70	Golden yellow	126-128	48.89(49.70)	5,23(5.56)	4.20(4.29)	4.33(4.90)
III	[CuL(H$_2$O)$_5$] NO$_3$. H$_2$O	226	%65	Dark brown	260-262	48.33(48.29)	4.80(5.01)	9.01(8.36)	
IV	[NiL(H$_2$O)$_3$Cl$_2$]	-	%62	Green	233-235	60.60(60.15)	5.71(4.67)	5.73(5.19)	

The assignment bands of(IR) spectra of Schiff base ligand and their metal complexes are listed in table(2).

In The Infrared spectra of Schiff base ligand (L) , The vC=N stretching frequency for azomethane group is observed at 1625 cm^{-1} . The value of these band was shifted to lower wave number in the spectra of all metal complexes in the range (1589-1618)cm^{-1} which due to coordination the nitrogen of azomethane with the central metal ions [21,22]. On the other hand all complexes exhibit a broad bands at (3315-3454) and bands at (910 -960)cm^{-1} which due to stretching modes of O-H group and rocking mode of coordinated water to metal ion respectively [23,24]. The v(C-N) stretching modes appeared around(1172-1244) cm^{-1} and the v(C=C)stretching frequency of aromatic ring appears a round(1508-1591) cm^{-1}, While the bands in the (3020-3059) cm^{-1} and (2860-2924) cm^{-1} attributed to v(C-H) stretching of aromatic rings and v(C-H) aliphatic respectivily. The new bands appears in the spectral of all metal complexes a round (509-580) and (428-518)cm^{-1}due to Metal-Oxigen(M-O) and Metal-Nitrogen(M-N)stretching mode[25]

Table2. The assignment IR bands of schiff base ligand and their complexes:

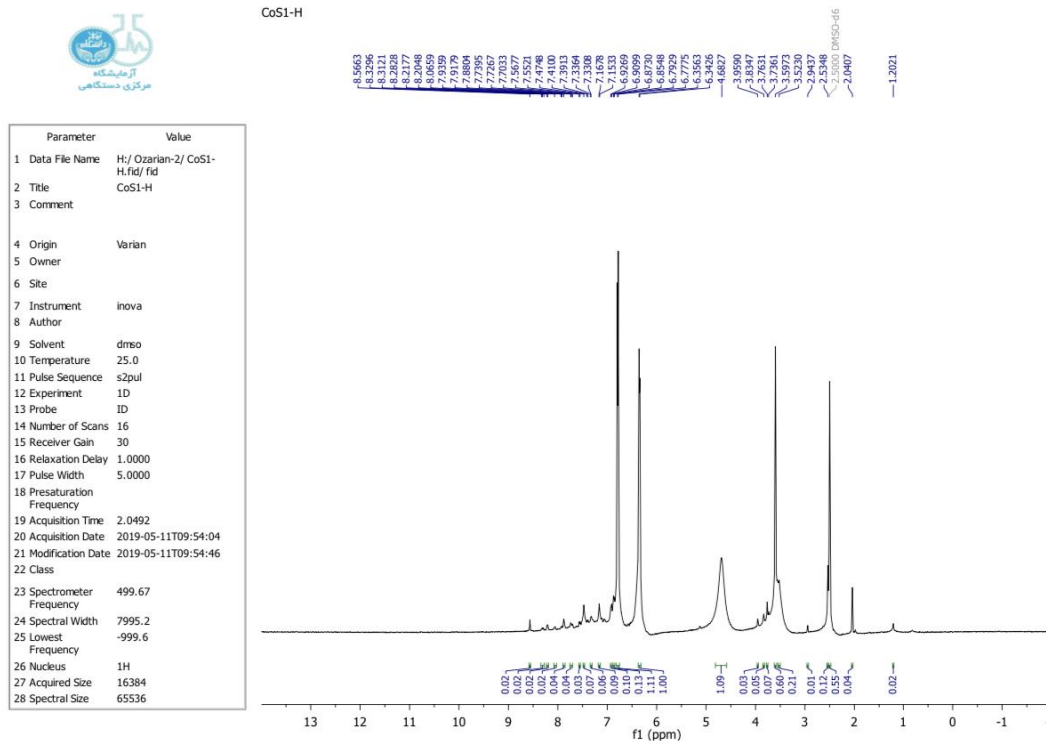| Com	vC=N (cm^{-1})	vO-H (cm^{-1})	vC-H aro. (cm^{-1})	vC-H ali. (cm^{-1})	vC-N (cm^{-1})	vM-N (cm^{-1})	vM-O (cm^{-1})
L	1625		3030	2950	1192		
Co(II)	1589	(3348-3444)	3036	2924	1222	428	516
Fe(II)	1599	(3358-3454)	3020	2916	1244	456	520
Cu(II)	1600	(3352-3444)	3059	2920	1172	432	509
Ni(ii)	1618	(3315-3446)	3030	2860	1234	518	580

Figures 1 and 2 show the typical ^{1}H NMR spectrum of compound(I) and (III) respectively , The   N M R data for all complexes are summarized in the table(3). All the ^{1}H NMR spectrum of new complexes were studied [26,27] by the presence of singlet signals in the range (7.73-8.56) ppm which due to proton of azomethane group in (1) position. The aromatic protons showed multiplet signals in the range (6.18-8.22) ppm due to the protons in (4,5,6,7 and 8) positions in the aromatic rings. While the aliphatic proton of CH$_2$ group (proton in 2 position) showed singlet signals within the range (1.19-2.08) ppm . The OH protons showed singlet signal in the region (3.81-4.68) ppm which appeared to coordinated water with metals. While the peak of solvent (DMSO) showed singlet signal within the range 2.50 ppm and 3.30 ppm

Table (3). The ^{1}H NMR spectral data of new complexes

Complex	δ ppm CH=N	δ ppm aromatic protons	δ ppm -CH$_2$-	δ ppm O-H
Co(II)	8.56	(6.35-6.92)	2.04	4.68
Fe(II)	7.73	(7.01-7.20)	2.08	3.81
Cu(II)	8.23	(6.25-7.52)	1.20	4.14
Ni(IV)	8.56	(6.87-8.22)	1.19	3.92

X = Cl in Co S1 and Ni S1 compounds
X = OH_2 in FeS1 and Cu S1 compounds
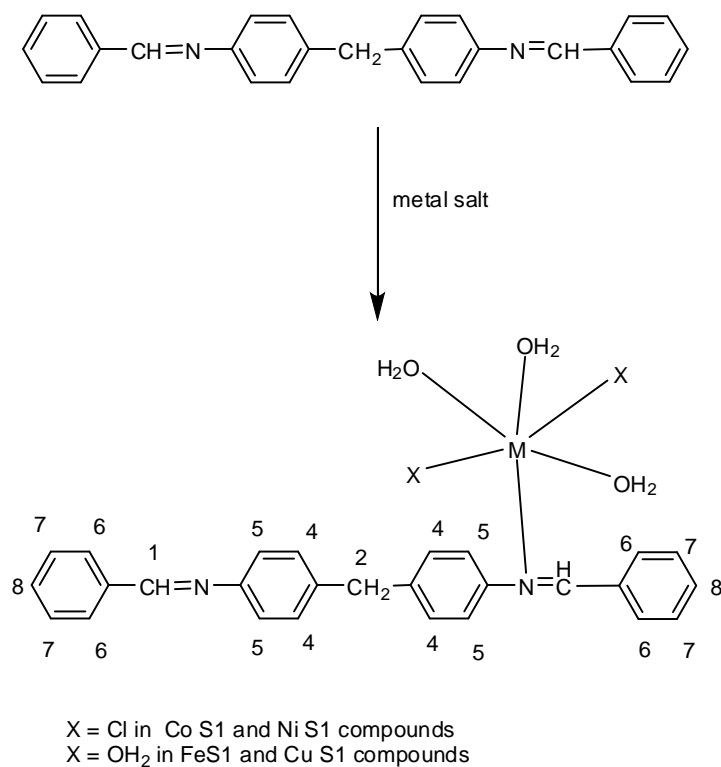
Scheme (1)

Figure (1) ^{1}HNMR spectrum of (I)

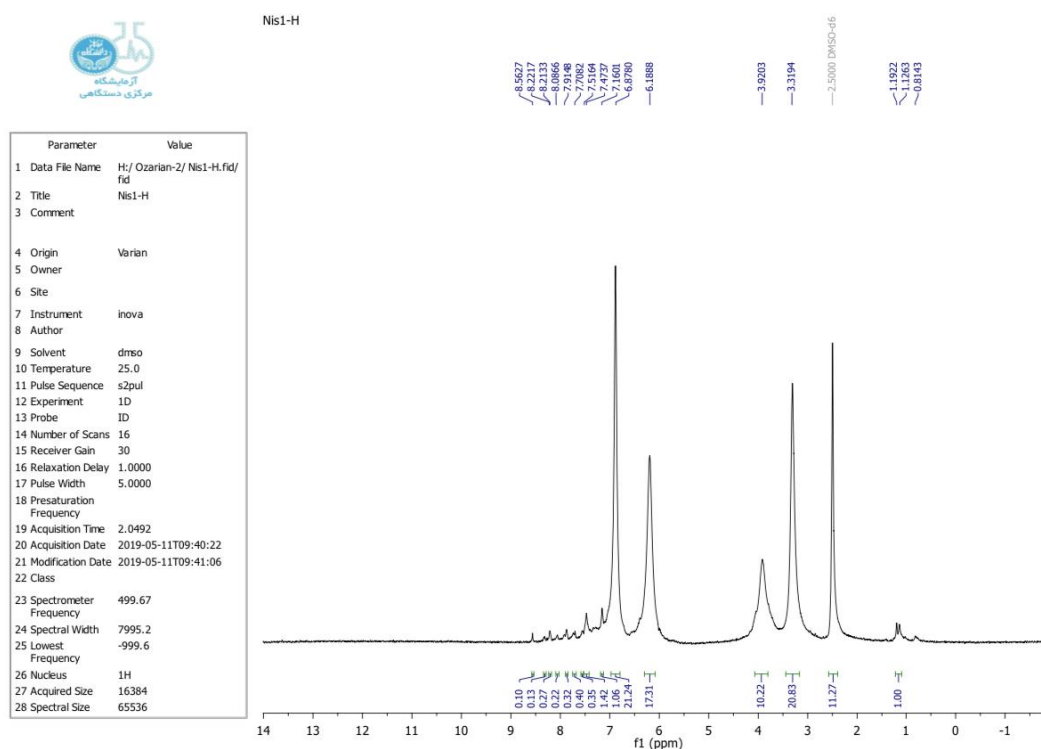**Figure (2)** ^{1}HNMR spectrum of (III)

TG/DTA analysis of synthesized complexes was done from ambient temperature to 817 °C under (N$_2$) atmosphere. The TG/DTA data for prepared complexes are listed in table (4), and the thermo grams are given in figurs (3-6). The TG/DTA curve of Co(II) complex (I) exhibit one exothermic decomposition step occur in the range 334-360 °C with weight loss 36.17% calc.(36.60 21% found) indicate to removal the three coordinated water ,chlorine and non-coordinated ligand moiety [29-30].The mass residue at 801°C is 29.12%(30.44%) may be attributed to formation C$_7$H$_6$NCo.

The TG/DTA curve of Fe (II) complex (II) exhibit three exothermic decomposition step . The first step occur in the range 116-140 °C with mass loss of 5.517%(5.14%) due to removal the two crystalline water molecules. A small peak at 126°C indicate to melting point .The second step occur between 280 -340 °C with weight loss of 20.23%(20.23%) due to removal sulfate ions . In the third step which occur in the range 480-510 °C a peak exhibit at 498°C with mass loss of 54.88% (54.31%) attributed to loss the five coordinated water and non-coordinated part of Schiff base ligand[29,30]. The mass residue at 750°C is 35.48% (35.51%) may be attributed to formation Fe$_3$O$_4$.

The TG/DTA curve of Cu(II) complex(II) exhibit three endothermic decomposition step .The mass loss 2.69% (2.63%) in the first step occur at 100°C due to loss crystalline water molecules . The second step between 165-260 °C with mass loss of 16.12% (16.12%) attributed to loss coordinated water molecules. In the third stage which occur in the range 430-500 °C with mass loss of 34.62% (34. 63%) due to loss tow nitrate ions .At 817°C the mass loss 46.128% (46.52%) due to loss the non-coordinated part of Schiff base ligand .

In the TG/DTA curve of Ni(II) complex (IV)exhibit two exothermic decomposition step . The first step consist of two peaks at 128 and 198°C with mass loss of 3.33% (3.35%) due to elimination of one water molecule . A small peak at 235 °C indicate to its melting point . Next stage occur in the

range 341 to 428 °C with mass loss of 54.82% (54.42) attributed to loss coordinated water , two chloride ions and non-coordinated ligand moiety .

Table(4). TG/DTA of synthesis complexes:

| Complex | Step | Type of molecule loss | Temp. of TGA (^{O}C) | Temp. of DTA^{O}C | Mass residue% | | Mass loss% | Temp. of 50% Mass loss^{O}C |
					Calc.	Found		
Co (II)	I	$3H_2O+2Cl^-$	334-	344			36.17	
	Last	$+C_6H_5$ Formation C_7H_6NCo	360	801	29.3	30.44	36.21	387
Fe (II)	I	$2H_2O$	116-140	119			5.547	
	m.p			126			5.136	489
	II	SO_4^{2-}	280-340	298				
	III	$5H_2O +$	480-510	498			20.23	
	Last	$2C_6H_5$ Formation of F_3O_4		750	35.48	35.51	19.24 54.88 54.31	
Cu (II)	I	H_2O		100			2.69	>
	II	$5H_2O$	165-260	255			2.63	700
	III	$2NO_3^{-1}$	430-500	450			16.12	
	Last	C_6H_5		817			16.12 34.62 34.63 46.128 46.52	
Ni (II)	I	H_2O	123-265	128,198			3.22	
	m.p			235			3.35	403
	II	$2H_2O +2Cl^-$ $+C_{13}H_{11}N$	341-428	411			54.82 54.42	

Concerning the computational Study, All optimised structure of this study molecules are shown in Figures (7) and (8). The (PM3) geometry optimizations yields planar structure for the new compounds. The generals geometry of molecules all this compounds are very similar. The [the dipole moment, μ (in Debyes), highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO, respectively) energies, total energy, and the energy band gap (LUMO–HOMO energy difference) and for the studied molecules are given in Table (5)]. The dipole moment calculated indicates the molecules are pole. This means that these molecules may, especially other polar molecules.The spatial distributions of(HOMO LUMO) are shown in Figure. (9). In general the all molecules gave similar (HOMO) and (LUMO) orbitals.

Conclusion:

Co(II), Fe(II) ,Cu(II) and Ni(II) complexes with bis-(4-benzyllidenamino-phenyl)-methane have been prepared and characterized by different physical and chemical methods. The analysis confirmed the

structures of complexes . All synthesized complexes are thermally stable Based on the thermal studies and most of the complexes in this studies shows similar behaviors and the Cu(II) complexes are more stable . Molar conductrivity measurements show that complexes (I , III) behave as 2:1 electrolyte while complex (II) behave as 1:1 electrolyte.

Table(5). The Total energy, MO energy of the lowest, highest, (HOMO) , (LUMO) , levels, and the dipole moment, μ (in Debyes) for the studied molecules

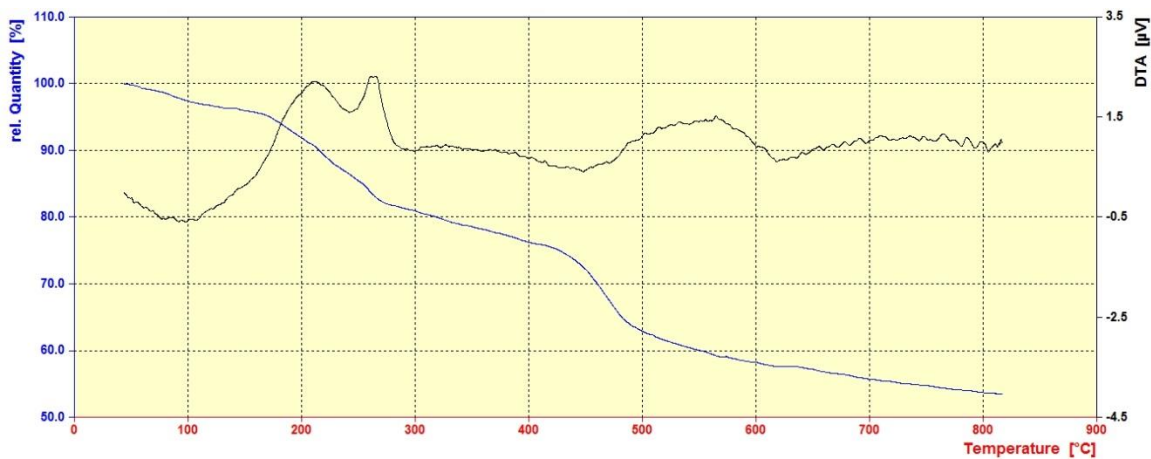| Mol.	Method	Total energy (Kcal/mol)	HOMO (ev)	LUMO (ev)	μ (D)
II	PM3	-1.38871	-6.503585	-0.4283036	6.287
IV	PM3	-1.50249	-9.076046	-1.378737	8.481
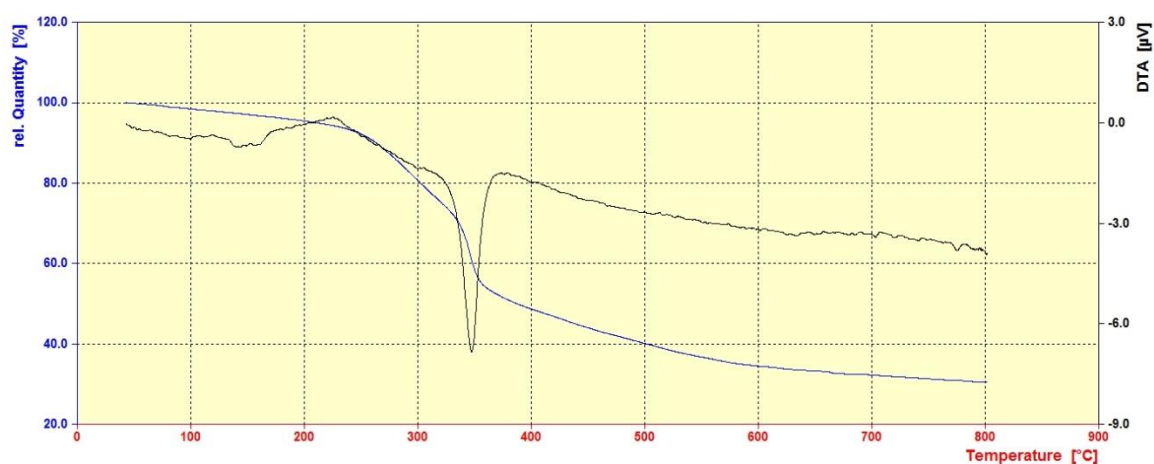
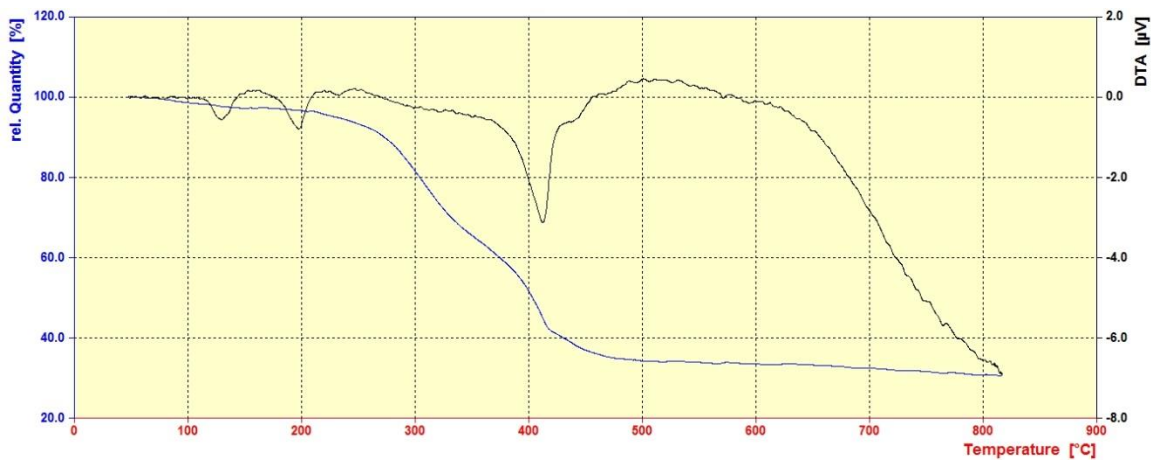**Figure (3) TG Curve of (I)**
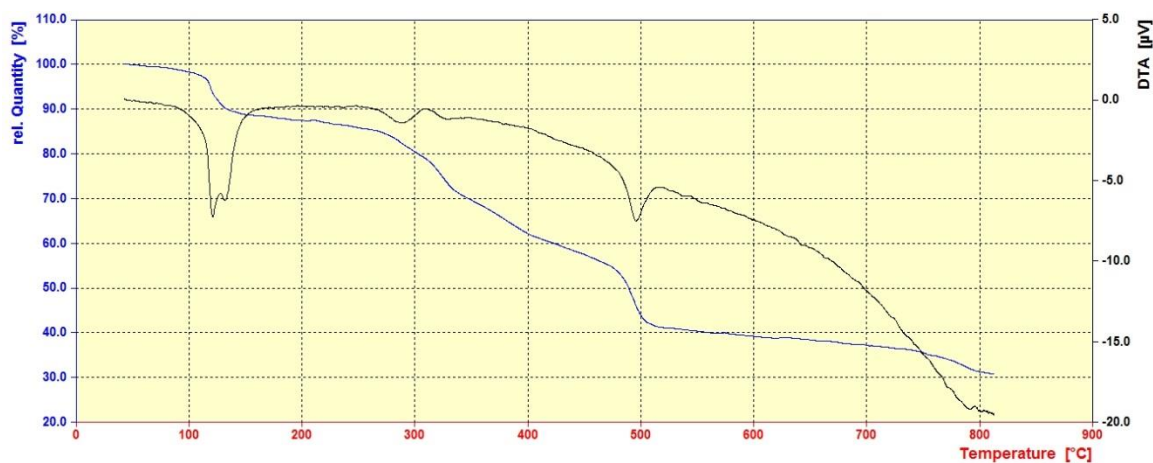
Figure (4) TG curve of (II)
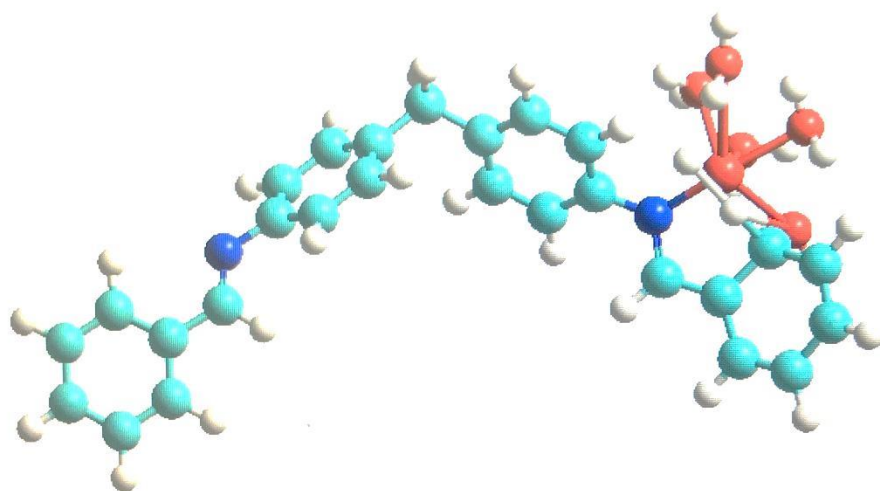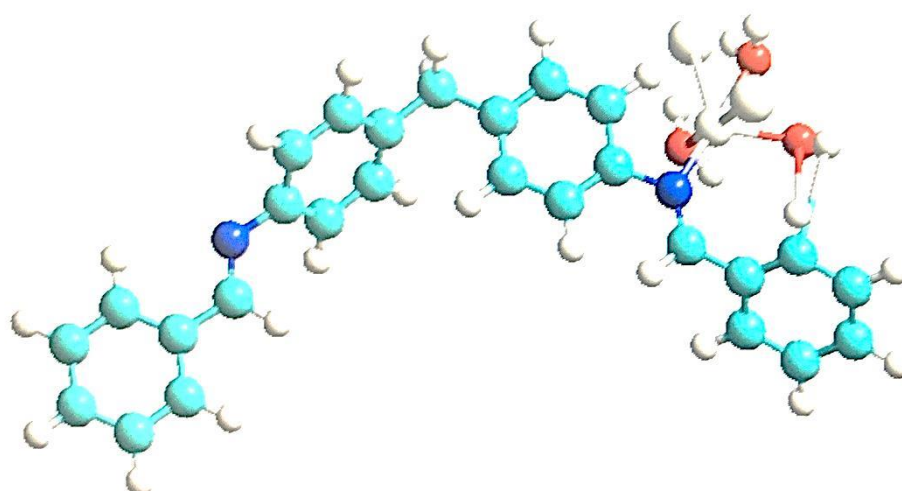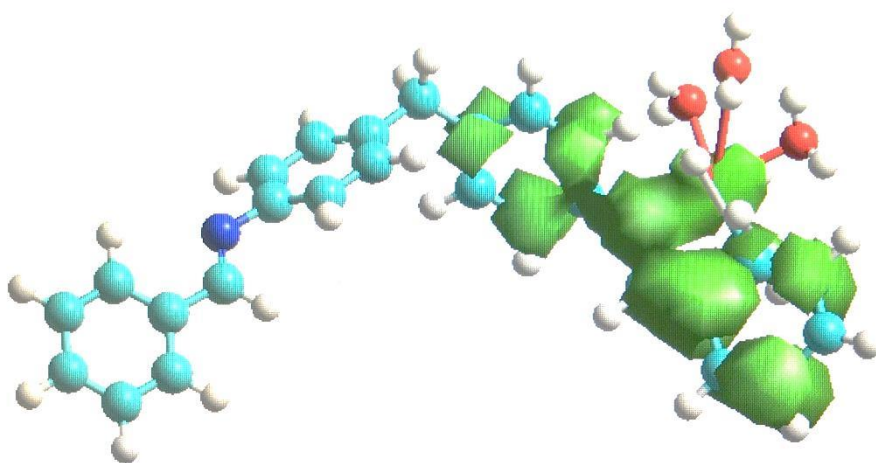
Figure (5) TG curve of (III)

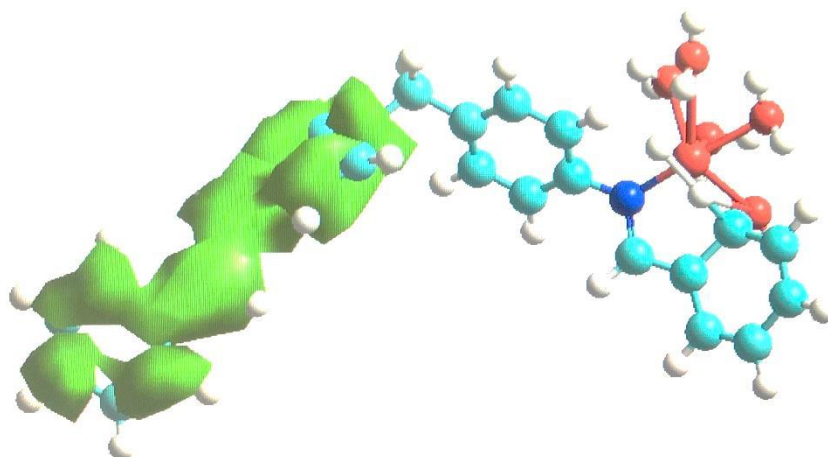**Figure (6) TG curve of (IV)**

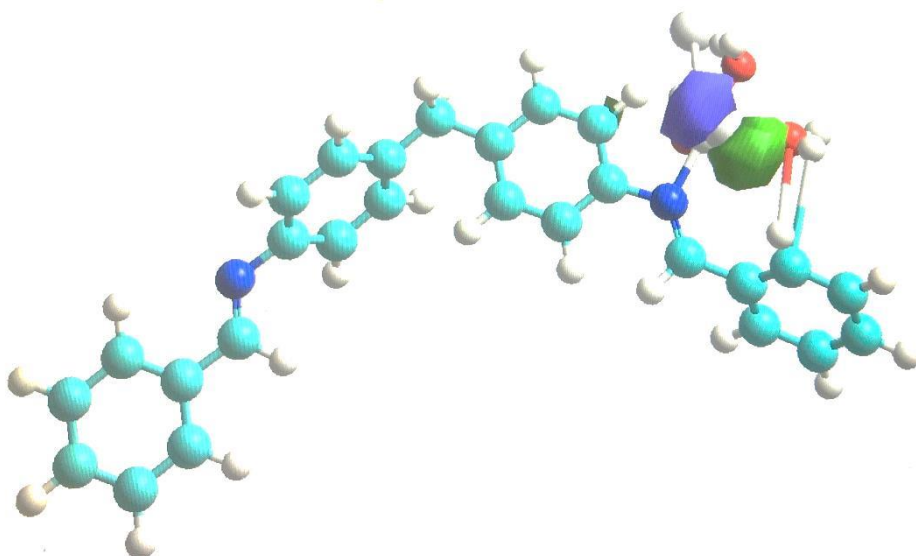**Figure (7)** Balls and cylinders model of (II)

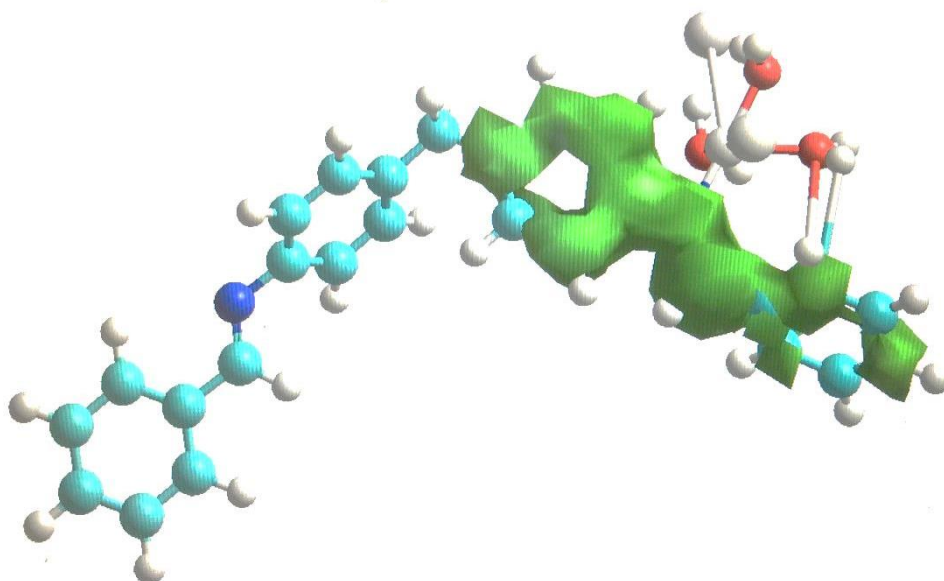**Figure (8)** Balls and cylinders model of (IV)

HOMO (II)

LUMO(II)

HOMO (IV)

LUMO (IV)

Figure (9) The optimized structure of the studied molecules optimization has been performed by PM3 method.

References:

[1] T. Aboul-Fadl , F A S Bin-Jubair and O. Aboul-Wafa 2010 *European Journal of Medicinal Chemistry*. **45** 4578-4586 .

[2] M D I Ferreira , T R A Vasconcelos and E M. de Carvalho 2009 *Carbohydrate Research*. **334** 2042-2047.

[3] A B Thomas , R K Nanda , L P Kothapalli and S C Hamane 2011 *Arabian Journal of Chemistry* .

[4] M A Bhat and M A Al-Omar 2011 *Acta Poloniac pharmaceutica* **68** 375-380 .

[5] A A Kulkarni , S B Wankhede , N D Dhawale , P B Yadav , V V Deore and I D Gonjar 2012 *Arabian Journal of Chemistry* .

[6] Nithinchandra, B Kalluraya, S Aamir , and A R Shabaraya 2012 *European Journal of Medicinal Chemistry* **54** 597-604.

[7] Gupta K G ,Sutar AK 2008 *Gatalytic activity of Schiff base complexes coord. Chem. Rev* **25a** 1420-1450.

[8] M S Alam , J Choi and D Lee 2012 *Bioorganic Medical Chemistry* **20** 4103-4108.

[9] Lin Che T ,Chang Gao Q , She zhao J and Zhang G 2008 *Chin. Journal Cem* **26** 1079-1084 .

[10] MM Tamizh, K Mereiter, K Kurchner and R Karvembu 2012 *J Organomet Chem* **700** 194-201.

[11] AS Gaballa , MS Asker , AS Barakat and SM Teleb 2007 *J Spectrochim Acta* **67** A 114-121.

[12] N Raman, A Kulandaisamy , A Shanmugasundaram and K Jeyasubramanian 2001 *J Trans Met Chem* **26** .

[13] Y Prashanthi, K Kiranmai , Subhashini NJP and Shivaraj S 2008 *J Spectrochim Acta* **70** A 30-35.

[14] S. Santhi and CG. Radhakrishnan Namboori 2013 *Int J Chem Tech Res* **4** 1750-1755 .

[15] M. Hajrezaie, M. Paydar , SZ. Moghadamtous, P. Hassan Darvish and M. Zahedifard 2014 *Sci World J* **1**.

[16] Li YF , Liu ZQ 2011 *Eur J Pharm Sci* **44** 158-163.

[17] TS. Kamatchi , N. Chitrapriya , H. Lee, CF. Fronczek , FR. Fronczek and K. Natrajan 2012 *Dalton Trans J* 2066-2077.

[18] KS. Kumar , S. Gangly, R. Veerasamy and E. De Clercq 2010 *Eur J Med Chem col*. **45** 5474-5479.

[19] H. Heba -Sabah 2014 *J .Derpharma chemical*, **6** 38-41.

[20] M. Yoko, M. Mai , T. Yuriko , S. Mitsuaki , W. Hidetsugu and T. Hiroyuki 2010 *J Tetrahydron,* **66** 605-611.

[21] D. Fatih , U. Mahmut , F. Omar and Ozturk 2009 *J Therm Anal Calorim* **98** 785-792 .

[22] P. Yokeswari Nithya , P. Ananthi and D. Shanmuga priya 2019 *International J of Advanced Scientific Research and Management* , *Special ISSU* **4** 77-81.

[23] W.J Geary 1971 *The use of conductivity measurements inorganic solvent for the characterization of coordination compound Coot. Chem. Rev.* **7** 81.

[24] Atared F Hassan , H. Hayat Abass and A. Nadhim Abul-Hussein 2016 *International Research Journal of Natural Sciences* **4** .

[25] JR. Ferraro (1971) *Loww Frequency Vibrations of inorganic and coordination compounds* 2nd. Edn..(Wiley , New York).

[26] R M Silverstien, F X Webster and D J Kiemle 2005 *Spectrometric Identification of Organic Compounds* 6th ed (John Wiley and Sons, New Yourk, USA).

[27] R L Shriner and C K Hermann 2004 *Spectroscopic Techniques for Organic Chemistry* (John Wiley and Sons, New Yourk, USA).

[28] J.W. Cooper   1980 *Spectroscopic Techniques for Organic Chemistry* (John Wiley and Sons, New Yourk, USA).

[29] N Kavitha , P V Anatha Lakshmi 2017 *Journal of Saudi chemical Society* **21** S456-S466.

[30] S M. Abdalah , MA. Zayed and G. Gehad 2010 *Arabian J Chem.* **3** 103-113 .