Some metal Complexes of Schiff- Base Derived from Dithiooxamide and 2, 4, 5-Trimethoxeybenzaldehyde

Dr.Ayad Hamza Jassim
Chemistery, College
University Of Al-Nhreen

Dr.Bassim Ibrahem Mehdi
Chemistery,College
University Of Baghdad

M.Sc Hayder Haimed Mihsen
Chemistery, College
University Of Kerbala

Abstract

A new Schiff base (LH_1) derived from Dithiooximide and 2,4,5-Trimethoxybenz-aldehyde and its transition metal complexes with Ni(II),Pd(II) and Pt(IV) have been prepared and characterized by vibrational and electronic spectroscopy ,in addition to thermal analysis (TG-DTG),magnetic and conductivity measurement .The M:L ratio was 1:2 in all cases .The structural formula for the new complexes were proposed.

Introduction

The field of Schiff base complexes is fast developing on occount of the wide variety of structures possible for the ligands depending upon the aldehydes and amines (1-4). During the past two decades ,considerable attention has been raid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donor(5,6).This may be attributed to their stability ,biological activity and potential applications in many fields such as oxidation catalysis, electrochemistry(7). In this study the synthesis and characterization of Ni(II),Pd(II) and Pt(IV) complexes with new Schiff base ligand (LH) which obtained from condensation 2,4,5-trimethoxybenzaldehyde and dithiooxamide, as possible antibacterial and antitumour agents .

Experimental

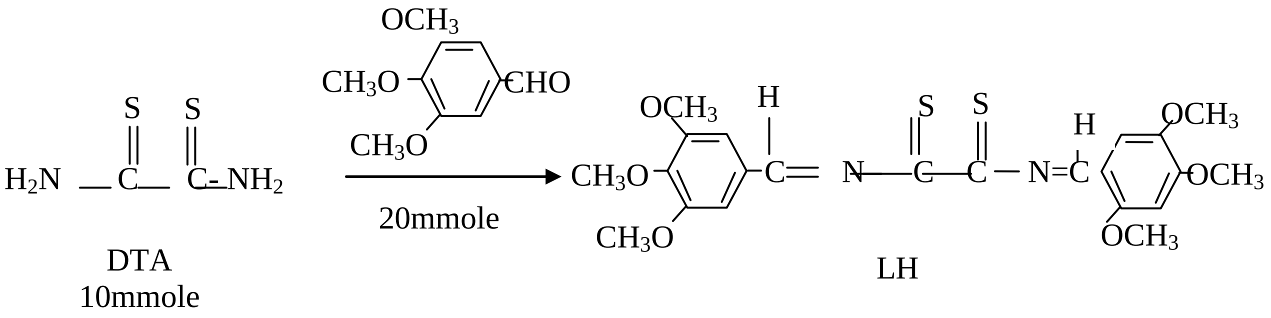
Chemicals: Ethanol(absolute),dichloromethane (98%),diethyl ether(99%) ,dimethylformamide (pure) and petroleum ether (40-60C) were of Fluka .Dithioox-amide (>99%) ,piperidine (99%) were of Fluka and 2,4,5-trimethoxybenzaldehyde (95%) was of Pract Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2.6H2O$),palladium (II) chloride $PdCl_2$ were Fluka,Platinum (IV) chloride $H_2PtCl_6.6H_2O$ was of BDH.

$PdCl_2(PhCN)_2$ was prepared by the method reported by Rochow(8),$K_2PtCl_6.6H_2O$ was prepared by the method reported by Chall and Seale(9).

The electronic spectra were recorded using (Shimadzu UV-Vis 160A) ultraviolet spectrophotometer. The I.R spectra of CsI discs were recorded using (Shimadzu FT.IR 3800 spectrophotometer). Magnetic susceptibility measurements were obtained at room temperature using: Bruker B.M.6 Instrument. The melting points of the prepared compounds were obtained using: Gallenkamp Melting Point Apparatus. The conductivity values of the prepared complexes were measured using: Dist wp3 conductivity / TDS meters at concentration 1×10^{-3}M and temperature 25° C.These complexes dissolved in DMF.

Preparation of the ligand(LH)

- Trimethoxybenzaldehyde (20mmole) and The ligand scheme(1) was prepared by mixing 2, 4, 5Dithiooxamide (10mmole) in (10 ml) absolute ethanol followed by (2-3) drops of piperidine.The mixture was stirred and refluxed for one hour. Orange colored product is obtained ; it's filtered; washed with cold ethanol several times and dried. The prepared crude product was recrystallized from dichloromethane and dried in vacuum over anhydrous $CaCl_2$. Color, melting point and yield % are given in table (I).



Scheme (1): Preparation of the ligands LH

Preparation of Ni (II) and Pd (II) complexes .

To a ligand solution (20mmole in 10 ml CH_2CL_2),(lo mmole) of the metal salt dissolved in (5 ml) acetone was added drop wise. The mixture was refluxed for one hour , then the resultant complex was precipitated by the addition of light petroleum ether (40-60) ^{0}C and washed by ethanol several times .Table(I) shows the color ,melting points and yield % of the products.

Preparation of Pt (IV) complex:

To a ligand solution (20 mmole in 30ml CH_2CL_2/Ethanol),(10mmole) of the $K_2PtCl_6 .6H_2O$ dissolved in (30 ml) absolute ethanol was added drop wise .the mixture was refluxed for (10) hours , then the volum of the solution was reduced to about (5ml) and complex was precipitated by addition of petroleum ether (40-60) ^{0}C and washed with diethyl ether several times . The physical properties of prepared complexes are given in table(I).

Table (I): The physical properties and yield% of LH and its metal complexes

Compound	**Colour**	**Melting point**	**Yield %**	**Empirical formula**
LH	Orange	218 - 222	78	$C_{22}H_{24}N_2S_2O_6$
$[Ni(LH)_2]C_2H_6O.H_2O$	Brown	283 – 285	76	$C_{47}H_{58}N_6S_4O_{21}Ni$
$[Pd(LH)_2Cl]Cl.H_2O.1.5CH_2Cl_2$	Deep brown	250 >dec.	65	$C_{45.5}H_{53}N_4S_4O_{13}Cl_5Pd$
$[Pt(LH)_2]Cl_2.H_2O.Eth.OH$	Brown	270 – 272	52	$C_{46}H_{56}N_4S_4O_{14}Cl_4Pt$

Result and discusstion

Infrared spectra

LH fig.(1) has two important groups, these are azomethine and thiocarbonyl (C=S).In general azomothine group (C==N) absorption occurs in the region (1690-1570) Cm^{-1}depending on nature of group linked to it (10,11) .The I.R spectrum of LH,table(II), showed the azomethine stretching band at 1589 cm^{-1}, the stretching the C=S group appeared at1213 cm^{-1}.The nickel-complex spectrum the azomethine stretching frequency shifts from 1589 to 1606 cm^{-1} ,this shift indicates complexation via azomethine nitrogen(12,13),Furthermore ,new bands appeared such as υ (Ni-N) in 526 cm^{-1} (14) ,the spectrum also displayed the peaks characteristic to monodentate NO_3^{-1} ion (14,15)as shown in table (II).The frequency of azometine groups shifted to 1614cm^{-1} in Pd LH_1,indicating the coordination of azometine nitrogen with palladium ion (16).Furthermore, new bands have been absorbed around 310 and 540 cm^{-1} which can be attributed to be υ (Pd-Cl) (14),and υ (Pd-N) (17) .The mostgnificant difference between the I,R spectrum of the ligand LH and its platinum complex fig.(2) was region by the shift of (C==N) stretching frequency to higher 29 cm^{-1} due to metal –ligand coordination (16) ,New bands have been absorbed around

318 and 524 cm^{-1} were attributed to υ (Pt-Cl) (14) and υ (Pt-N) (17),as shown in table (II).

Table (II); The most characteristic I.R. frequency of LH and its metal complexes.

Compound	υ(C==N)	υ(C==S)	υ(M-N)	υ(M-Cl)	υ NO_3^-
LH	1589	1213	_	_	_
Ni($LH)_2$	1606	1213	526	_	1026 780
Pd$(LH)_2$	1614	1215	540	310	_
Pt$(LH)_2$	1608	1217	524	318	_

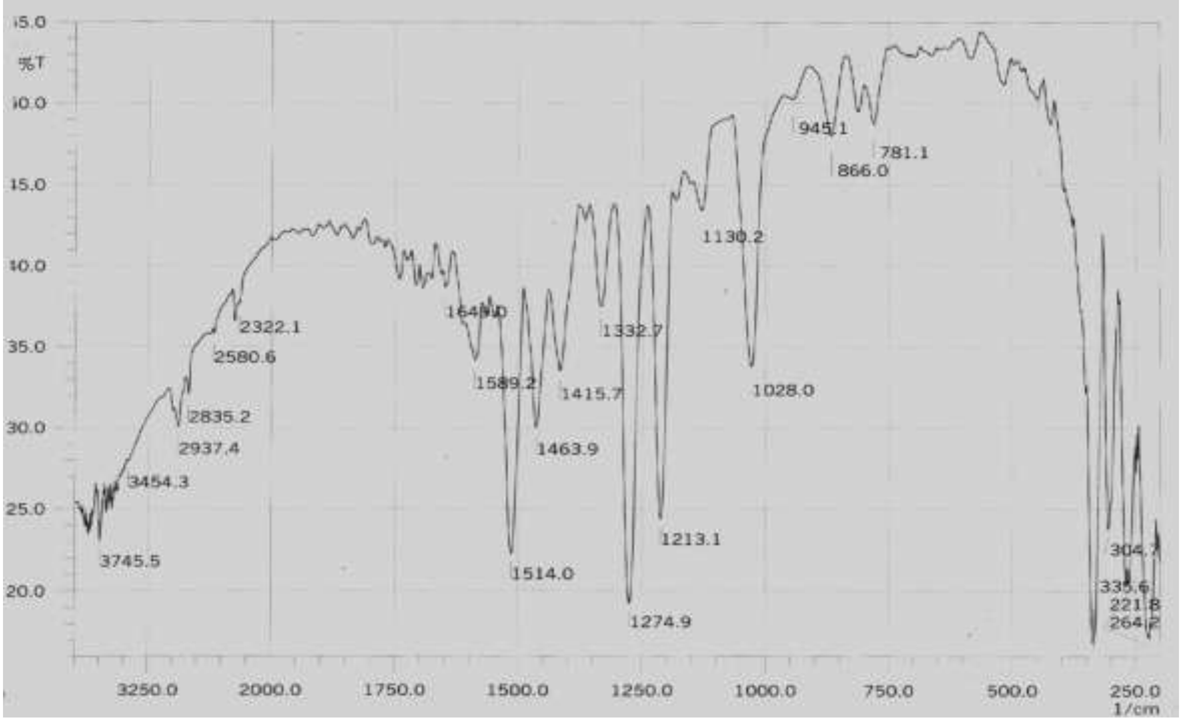


Fig.(1) FT-IR of LH

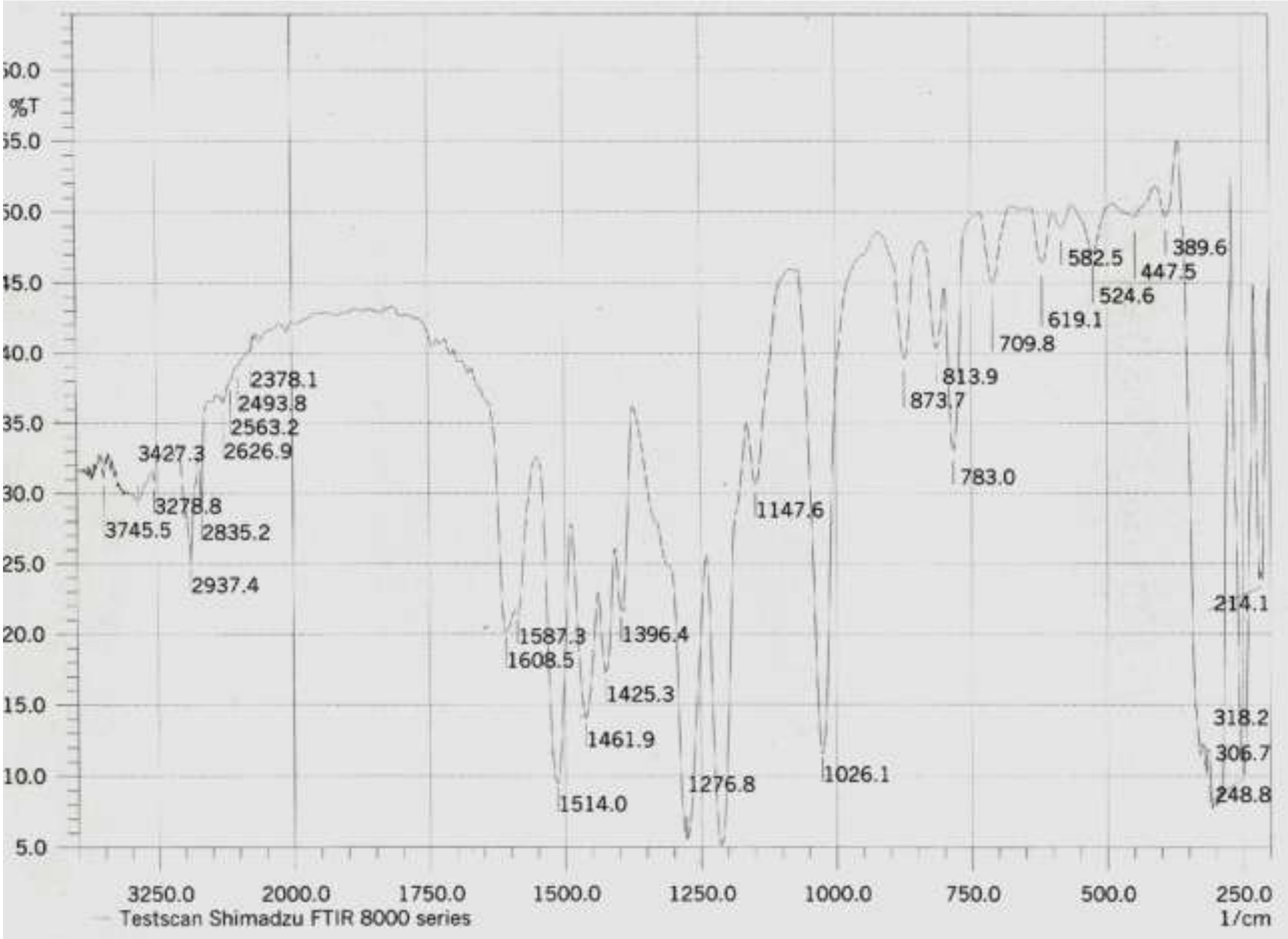
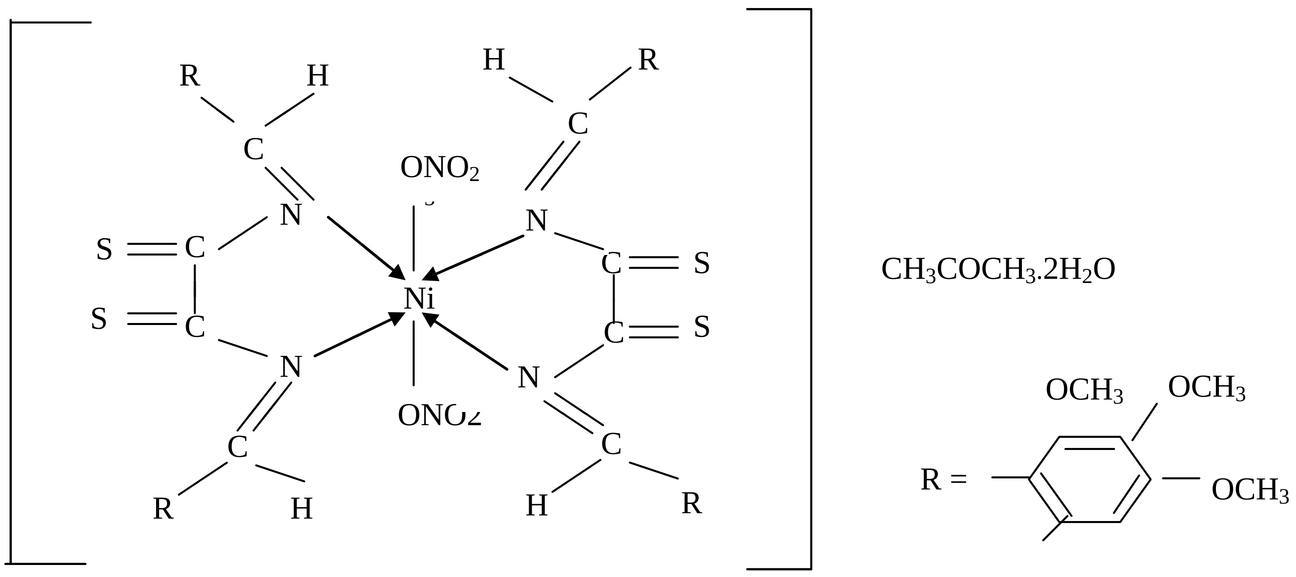


Fig.(2) FT-IR of complex Pt(LH)$_2$

Electronic spectra

spectrum of the ligand fig.(3) showed the first absorbed band at 239 nm (41841cm^{-1}) which can be attributed to(π-π^*) transition for the aromatic nucleus .The second band which appeared at 437 nm (22883cm^{-1})was attributed to (n-π^*) transition in imino group (C==N) (17).Electronic spectrum of the Ni LH$_1$ complex showed an absorption band as a shoulder at 650nm (15384cm^{-1}) due to $^3A_2g \rightarrow {}^3T_1g$ (F) υ_2 transition and another band at 442nm (22624cm^{-1})due to$^3A_2g \rightarrow {}^3T_1g$(P) υ_3 transition in octahedral field(18),from υ_3/υ_2 ratio and using (Tanabe –Sugano) diagram for d^8 configuration, υ_1 was calculated and found to be (9134 cm$^{-1)}$,this which refers to the value of 10 Dq $^{(19)}$ .The racah interelectronic repulsion parameter $\beta^{\backslash}$ was calculated following the equation$15\beta^{\backslash} = \upsilon_3+\upsilon_2-\upsilon_1$,and found to be 707 cm^{-1}.Taking the value of B for the free nickel (II) ion of 1030 cm^{-1}, the nephelauxetic factor $\beta = B^{\backslash} \backslash B$ was calculated and found to be 0.687.This value refers to appreciable covalent character in the(Ni-N) bond of the Complex $^{(14)}$ .The magnetic susceptibility (3.08 B.M) and molar conductivity measurement indicated that the complex is paramagnetic and no electrolyte.

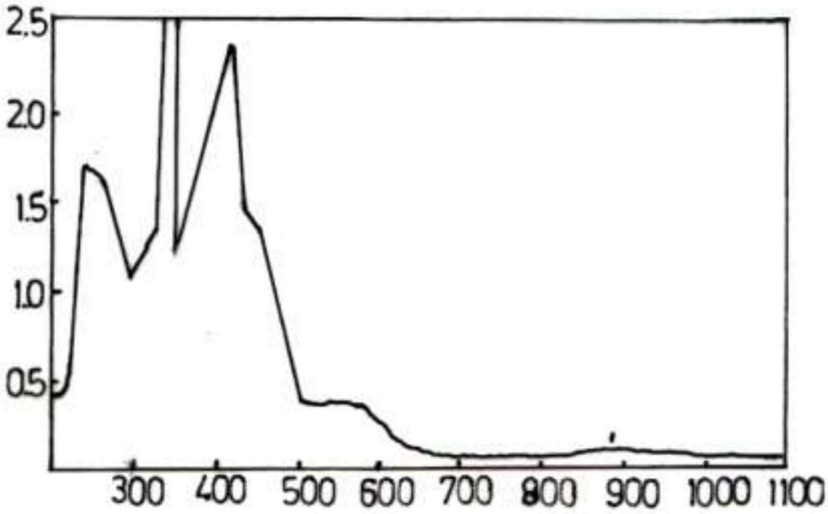
According to these results and those obtained from IR study and thermal analysis data, an octahedral geometry around Ni (II) ion can be suggested, as Follows:



The electronic spectrum of the palladium complex showed absorption band a shoulder at 486 nm (20576 cm^{-1}) due to $'A'_1 \rightarrow {}'E''$transition .These bands indicated a trigonal bipyrimidal geometry around palladium ion $^{(18)}$.The magnetic susceptibility and molar conductivity measurement (61µs(cm^{-1})) indicated that the complex has diamagnetic property and behaves as an electrolyte.

Electronic spectrum of the platinum (IV) complex fig.(4) showed absorption band at 553nm (18083 cm^{-1}) due to $^1A_1g \rightarrow {}^3T_1g$ υ_1 transition and a second band at a shoulder at 456 nm (21930 cm^{-1}) due to $^1A_1g \rightarrow {}^3T_1g$ υ_3 spin forbidden transition to an octahedral field in platinum complexes $^{(20)}$. The magnetic susceptibility and molar conductivity measurement (145µs(cm^{-1})) indicates that the complex as a diamagnetic and electrolytic

Fig.(3) Electronic spectrum of LH



Thermal Analysis

The result from thermal analysis of LH fig.(5) and its metal complexes by(TG) and (DTG) techniques within the rang (30-800)^{0}C at a heating rate of 20 ^{0}C/min under nitrogen atmosphere are described in table (III)

Steps of thermal decomposition at maximum of(DTG) are recorded together with weight loss percent .The following points can be concluded:

1-Lattice water and organic solvents that are not directly coordinated to the metal ion were found to be lost at earlier stages of lower temperatures (21).

2- Stages of decomposition reflect the nature of bonding between the metal and ligand atoms and the stability of the complexes (22).

3- In the case of Pd and Pt fig.(6) complexes, the free elements were left at higher temperatures, which reflect the relative instability of their complexes compared to the nickel complex.

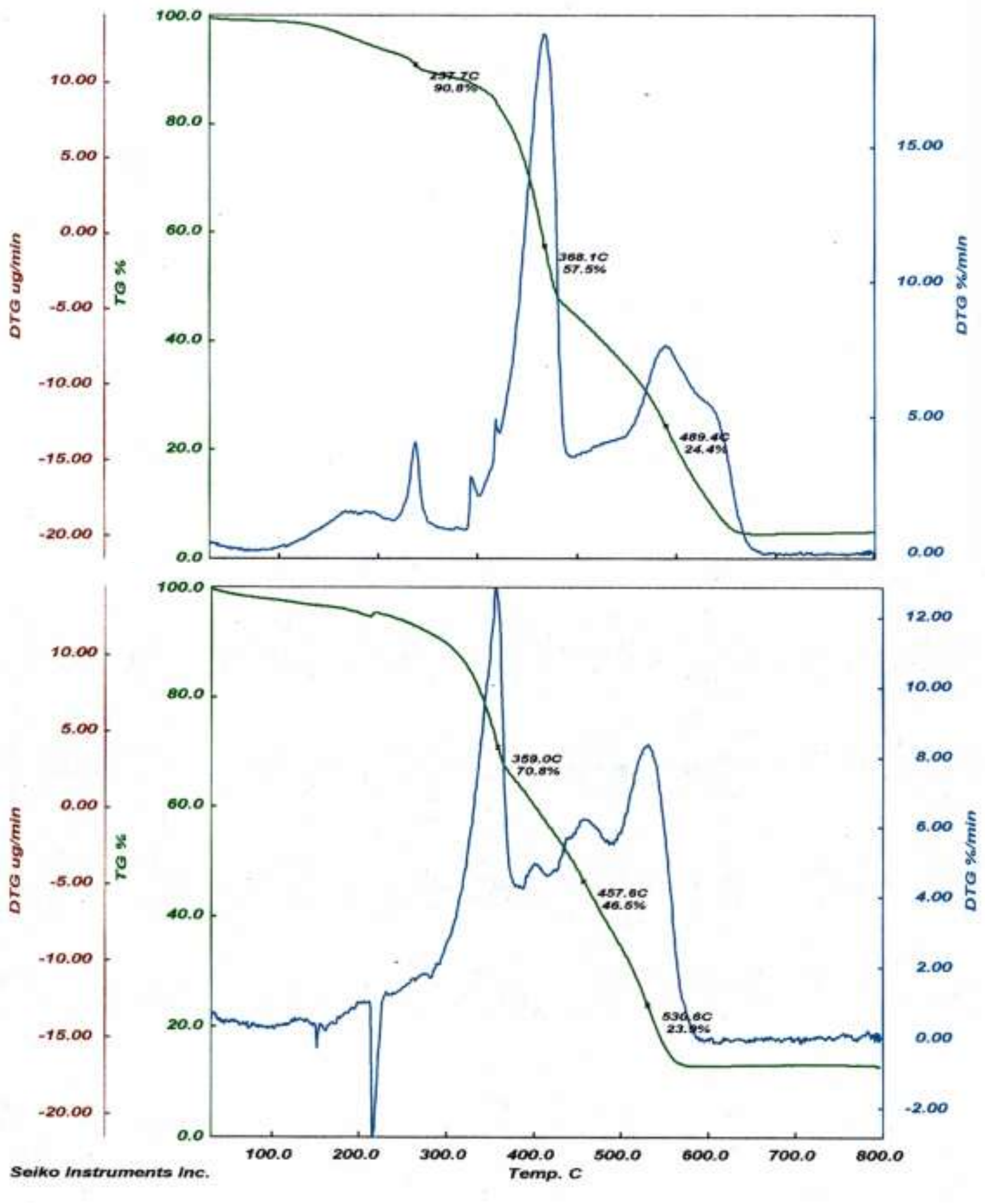

DTG ug/min
TG %
DTG %/min
100.0
80.0
60.0
40.0
20.0
0.0
10.00
5.00
0.00
-5.00
-10.00
-15.00
-20.00
15.00
10.00
5.00
0.00
237.7C
90.8%
368.1C
57.5%
489.4C
24.4%
12.00
8.00
6.00
4.00
2.00
-2.00
359.0C
70.8%
457.6C
46.5%
530.6C
23.9%
100.0
200.0
300.0
400.0
500.0
600.0
700.0
800.0
Temp. C
Seiko Instruments Inc.

Table (III) Thermal decomposition of compound (LH), Ni $(LH)_2$, Pd $(LH)_2$ and $Pt(LH)_2$

Stable phase of LH	**Temp.range of decomp. at DTG(C)**	**Peak temp. at DTG(C)**	**Weight loss% found(calc.)**
-2 OCH_3	100-285	240	12.77(13.01)
-4 OCH_3	285-465	369	56.38(57.07)
-2 Ph			
2 CS	465-585	489	30.82(29.8)
2 CHN			
Stable phase of $Ni(LH)_2$			
- Acetone			
	26-100	66	4.61(4.72)
-2 H_2O			
	100-220	200	3.07(2.29)
-8 OCH_3			
	220-371	377	29.99(30.27)
-4 Ph			
-4 CHN			
-4 CS	371-557	433	47.68(47.20)
$Ni(NO_3)_2$			
Stable phase of$Pd(LH)_2$	-		14.61(14.86)
- H_2O			
- Cl			
-1.5 CH_2Cl_2			
	44-161	125	14.2(14.7)
-12 OCH_3			
-4 Ph	161-377	337	28.56(29.14)
-4 CHN			
-4 CS			
- Cl	377-500	439	50.37(48.18)
Pd			
Stable phase of $Pt(LH)_2$			
-Eth,OH	-		6.76(8.3)
-H_2O			
-2 Cl	50-210	-	5.25(4.72)
-12 OCH_3			
-4 Ph			
-4 CHN	210-483	359	54.84(54.56)
-4 CS		451	
-2 Cl			
Pt			
	483-590	530	26.29(26.21)
	-	-	13.52(14.40)

References

1- T.D.Thangadurai and K.Natarajan,Trans. Metal Chem. ***26***,717(2001)
2- D.M.Boghaei and sajjad Mohebi,J. of Molec. Cat. A:Chemical ***179***,45(2002)
3- B.A Jani and P.K.Bhattacharga,J.,Indian Chem.Soc.,***LVIII*** 207(1981)
4- T.D. Thangadurai and K.Natarajan, Trans. Metal Chem.,***26***,500(2001)
5- P.Bhattacharyya,J.Parr,A.T.Ross,J.Chem.Soc.Dalton,3149(1998).
6- L.He,S.H.Qou,Q.F.Shi, J,Chem.Crystallogr. ***29***,207-210(1999).
7-X.Tai,X.Yin,Q.Chen,and M.Tan.Molecular,***8***,439(2003).
8 E.G.Rochow , Inorg . Synth. , ***4***, 218 (1960).
9 J.Chall and M.L.Seale , Inorg. Synth. , ***5***, 210(1957).
10.S.Dagagi and Y. Degani,"TheChemistry of Carbon-Nitrogen Double Bond",S.Patai,Johan Wiley and Sons Inter Science, New York,64(1970)
11.R.m.Silverstein,G.C.Bassler and T.G.Marrill,66 Sectrometeric
12.R.Dadmaja Shukla and M.A.Jaiswal,J.Indian Chem.Soc.,***LX***,1014(1983) .
13.O.D.Arora and N.S Misra J.Indian Chem.Soc. ***LIX***, 32(1982).
14.K.Nakamoto,"Infrared and Raman Spectra of Inorganic and Coordination Compounds" Johan Wiley and Sons, Inc, (1978).
15.G.A.A.Al-Safar M.Sc.Thesis,University of Baghdad(1998).

16.N.M Al-Abidy.M.Sc.Thesis,University of Baghdad(1997).
17.R.A.M.Al-Araji, M.Sc.Thesis,University of Baghdad(2000).
18.A.B.P,Lever,"Inorganic Electronic Spectroscopy",Elesevier Publishing Company Amsterdam-London- New York (1968).
19.M,N.Al-Zikom."Transition Elements Chemistry"Arabic Version,Basrah,University Press(1986)

20.N.N.Greenwood and A.Earnshaw,;;Chemistry of Elements",Pergamon Press(1984).
21.A.Seminara,S.Gurriert,G.SracusaandA.Gassol,Thermoch. Acta,***12***,173(1975)
22.D.Czakis-Sulikowska,A.Malinowska and J.Radwanska-Doczekalska. Polish J.Chem.Soc.,***74***,607(2000).

بعض المعقدات الفلزية لقاعدة شيف المشتقة من الثنائي ثايو كساميد مع, -2, 4, 5 ثلاثي ميثوكسي بنزالديهايد

الباحثون: أ.د. أياد حمزة جاسم جامعة النهرين–كليه العلوم–قسم الكيمياء
م.د.باسم إبراهيم مهدي جامعة بغداد––كليه العلوم–قسم الكيمياء
م.م. حيدر حميد الحميداوي جامعة كربلاء––كليه العلوم–قسم الكيمياء

المستخلص

تم تحضير قاعدة شيف جديدة(LH) مشتقه من الثنائي ثايو كساميد مع 2, 4, 5- ثلاثي ميثوكسي بنزالديهايد ومن هذه القاعدة تم تحضير المعقدات الفلزية العائدة للأيونات(Ni(II)و Pd(II)و Pt(IV).
شخصت المركبات المحضرة بواسطة تقنيات(I.R)و(UV-Vis) والتحاليل الحرارية(TG-DTG) أضافه الى قياسات التوصيلية والحساسية المغناطيسية للمعقدات المحضرة.
نسبه الفلز إلى الليكاند كانت 2:1 في جميع المعقدات المحضرة, ومن جميع هذه القياسات والنتائج اقترحت الصيغ التركيبية للمعقدات المحضرة.

مفاتيح الكلمات: قاعدة شيف – الثنائي ثايو كساميد–المقدات الفلزية