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Synthesis, Characterization and Analytical Studies of Schiff Base, their Transition Metal Complexes and Their Polymers

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Abstract

A novel bidentate Schiff bases has been prepared from the condensation of 1,4-bis-(aminomethyl)cyclohexan with 2,4-dihydroxyacetophenon and 2,4-dihydroxybenzaldehyde. Schiff base A and B and their metal complexes were characterized via UV-Visible, FTIR and NMR. The metal complexes are expected to be octahedral in geometry based on physicochemical and spectroscopic analyses. New resins PoA and PoB were prepared by mixing schiff base A and B respectively with MDI, thermogravimetric analysis of resins proved that the PoA and PoB were thermally stable up to 209^{o}C and 291^{o}C respectively , and the study of loading capacity of resins towards transition metals showed that the PoA and PoB had high selectivity (more than 90%) toward lead and zinc respectively.

Keywords: Cobalt Complex, Nickel Complex , Thermal stability , Loading capacity

الخلاصة :

تضمنت الدراسة الحالية تحضير وتشخيص قاعدتي شف A و B من خلال تفاعل 1,4-bis-(aminomethyl)cyclohexan مع كل من 2,4-dihydroxyacetophenon و 2,4-dihydroxybenzaldehyde على التوالي ، وكذلك تم تحضير معقد قاعدة شف A مع عنصر الكوبلت وكذلك تحضير معقد قاعدة شف B مع عنصر النيكل كما تم بلمرة قاعدتي شف المحضرة

للحصول على PoA و PoB على التوالي ، وتم تشخيص الليكندات المحضرة و معقداتها بيتقنيد الاشعة المرئية وفوق البنفسجية وتقنية الاشعة الحمراء وتقنية الرنين النووي المغناطيسي ، بالاضافة الى ذلك تم حساب الاستقرارية الحرارية للبوليمرين المحضرين فوجد انها تكون مستقرة حراريا لغاية ٢٩١ درجة مؤية و ٢٠٩ درجة مؤية على التوالي ، كما تمت دراسة كفاءة البوليمرات تجاه ايونات العناصر بالاعتماد على طريقة الوجبة ووجد انها ذات كفاءة عالية (اعلى من ٩٠ %) تجاه عنصري الرصاص والخارصين على التوالي.

Introduction:

When an aldehyde or a ketone is condensed with a primary amine, a Schiff base syntheses , a compound containing imine or azomethine group ($R - C = N -$)[1].The common structural feature of these compounds is the azomethine group with a general formula RHC=N-R1, where R and R1 are alkyl, aryl, cycloalkyl or heterocyclic groups which may be differently substituted. Schiff bases were known since 1864 when Hugo Schiff discovered the condensation of primary amines with carbonyl compounds[2]. There has been an increasing growth in the preparation, reactivity and structure of the Schiff bases because of their wide and potential applications in catalysis, ligand modeling, material chemistry and biological activity [3,4].

The chemistry of Schiff base metal complex is undergoing rapid development due to their essential roles in biological systems and chemical industries. Schiff base ligands are excellent coordinating molecules and can exhibit variety in the structure of their metal complexes[5] because the Schiff base ligands which usually contain oxygen and nitrogen donor atoms have played an important role in coordination chemistry [6,7] . Several studies showed that the presence of a lone pair of electrons in sp^2 hybridized orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance [8] .

Although transition metal complexes of chiral Schiff base ligands (CSBLs) concisely fascinated in asymmetric organic transformations, recently there is emerging curiosity in the field of biochemical responses of inorganic metal complexes. As a result many research groups have focused their attention towards the bio-manifestations of chiral metal complexes [9-13].

Materials and Methods:

Chemicals used in this research are: 1,4-bis(aminomethyl)cyclohexan (Aldrich), 2,4-dihydroxyl acetophenon (Aldrich), 2,4-dihydroxyl benzaldehyde (Aldrich), ethanol (Scharlau), glicirail acetic acid (Sigma Aldrich), nickle(II) nitrate (Alpha), copper(II) nitrate (Fluka), Cobalt(II) nitrate (H&W), triethyl amine (Fluka) and (Sigma Aldrich). All chemicals were of analytical grade and were used as supplied without any further purification.

Physical Measurements:

The infrared spectra of the prepared compounds were recorded using Shimadzu FTIR-8400S-JAPAN, in the wave length range of (4000-400) cm^{-1}. Carbon, hydrogen, nitrogen and sulfur analyses were carried out using a Leco CHNS-923 (Made In USA). The electronic spectra obtained using (UV-Vis-160A) Shimadzu Spectrophotometer, in the range of wave-length (200-1100 nm). Melting point apparatus of Gallen kamp M.F.B 600.01 was used to measure the melting points of all prepared compounds. Analyses conducted ^{1}HNMR for the prepared Schiff Base (A,B) and some of the complexes prepared (A-Co , B-Ni) for the purpose of enhancing the diagnosis of these compounds by Bruker٥٠٠ MHZ. Thermal gravimetric analysis is performed for polymers prepared (PoA, PoB) using the device of the TGA type Q50-USA .

Batch System[14] had been studied to determine the analytical efficiency of polymers PoA and PoB towards metal ions (Ga^{3+}, In^{3+}, Co^{3+}, Al^{3+}, Cr^{3+}, Cd^{2+}, Cu^{2+}, Zn^{2+} , Fe^{2+}, Pb^{2+}, Ni^{2+}) by using Shimadzu A.630,12, and GBC901 flame atomic absorption spectroscopy (AAS).

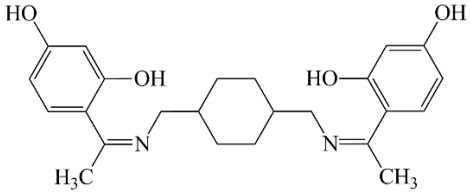
Preparation of Schiff base (A) and (B):

Schiff base (A) and (B) were prepared by dissolving of 3 mmole (0.408gm) of 1,4-bis(aminomethyl)cyclohexan in 20 mL of hot absolute ethanol, to this an ethanolic solution 6 mmol (0.912 gm) of ethanolic solution of 2,4-dihydroxyl acetophenon and 6 mmol (0.828 gm) of 2,4-dihydroxyl benzaldehyde respectively was add drop wise with constant stirring.

The solution was acidified by glacial acetic acid and then the mixture was refluxed for three hours, the orange solid product that formed after cooling was filtered, washed with hot

water and recrystallized from water – ethanol (1:1) and dried in an oven at 70°C. Table (1) shows the physical and chemical properties for products.

Schiff base (A)



Schiff base (B)

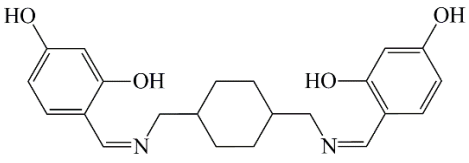


Table (1) : Physical and Chemical Properties of Schiff Base (A) and (B).

	Schiff Base (A)	Schiff Base (B)
Ketone or Aldehyde	2,4-dihydroxyacetophenon (6mmole)(0.912g)	2,4-dihydroxybenzaldehyde (6mmole)(0.828g)
Amine	1,4-bis(aminomethyl)cyclohexan (3mmole)(0.408g)	1,4-bis(aminomethyl)cyclohexan (3mmole)(0.408g)
Temp.	90°C	70°C
M.P	285-290 °C	119-125 °C
Phys. Properties	Yellow Powder	Yellow Powder
RF / TLC	0.88	0.82
Yield %	71%	85%

Preparation of Metal Complexes:

Metal complexes (A-Co) and (B-Ni) were prepared by addition of ethanolic solution of the Co(II) and Ni(II) metal nitrate to the ligand A and B respectively dissolved in the solvent in 1:1 (metal : ligand) molar ratios. After reflexing with stirring at least for 30 min, colored precipitates formed at room temperature, the rustling solids were filtered off, washed with 5 mL hot 50 vol. % ethanol to remove any traces of the unreacted starting materials air dried, and recrystallized from ethanol and dried in the oven at 80°C for several hrs.

The Table (2) shows the reaction conditions for synthesis metals complexes (A-Co and B-Ni) and physical and chemical properties for products.

Table (2): Reaction Conditions for Synthesis Metals Complexes (A-Co and B-Ni) , Physical and Chemical Properties for Products .

	Complex (A-Co)	Complex (B-Ni)
Schiff Base	Schiff Base (A) (1mmole)(0.402g)	Schiff Base (B) (1mmole)(0.404g)
Metal	$Co(NO_3)_2.6H_2O$ (1mmole)(2.910gm)	$Ni(NO_3)_2.6H_2O$ (1mmole)(2.900gm)
M.P	$205C^0$	$195C^0$
Phys. Properties	Blue powder	Light Brown Powder
RF/TLC	0.85	0.71
Yield %	65%	75%

Polymerization of Schiff Base (A) and (B) :

Polymers of prepared schiff bases (Po-A) and (Po-B) were prepared by mixing of (0.500g) of compound A and B respectively with (1.500g) of methylene diphenyl isocynate MDI in the presence of (1%) of TEA as catalyst , the resulting mixtures were left for curing at room

temperature for 24 hours the heated at 70°C for 2-3 hours to complete the curing and finally at 120°C for an hour for post curing, table (3) shows physical properties of polymers formed.

Table (3): Physical Properties of Polymers (PoA,PoB).

Phys. Properties	M.P	polymers
Light brown powder	310°C	PoA
Yellow Powder	170°C	PoB

Results and Discussion

Elemental Analysis

Table 4 shows percentage of carbon, hydrogen and nitrogen of the schiff bases A and B and their complexes.

Table (4): The percentage of carbon, hydrogen and nitrogen of the compounds.

Compound	%C		%H		%N	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
Schiff Base (A)	69.43	69.66	7.51	7.73	8.20	8.12
Schiff Base (B)	68.72	68.55	6.41	6.88	8.28	8.69
Complex (A-Co)	51.84	51.75	5.33	5.85	7.89	6.96
Complex (B-Ni)	52.33	52.13	4.00	4.97	5.49	5.53

FTIR Spectroscopy

The results of interpreted data from the spectrum of Fourier Transform Infrared Spectroscopy (FTIR) are as shown in Table 4. In Schiff bases (A and B) There are peak at *ca*(1585.49 cm^{-1},

1631.78 cm^{-1}) which attribute to C=N, from this observation, it is concluded that the schiff bases are formed via condensation reaction in which the primary amine reacted with the carbonyl group to yield the respective product. In the Schiff base (A) there is a peak assigned to C-H str., asym. 2922.16 and C-H str., sym. 2848.86 it's indicating that the Schiff base appear in keton form. But in the Schiff base (B) there is no peak assigned to C-H it's indicating that the Schiff bases appear in aldehyde form.

For complexes of cobalt and nickel, there are peak assigned at *ca.*,(420 (N-Co), 480 (O-Co)cm^{-1} and 497,63 (N-Ni),460 to 490 (O-Ni) cm^{-1} bending) , which indicating that the ligands were bending to form complexes .In Schiff base C=N showed at peak (1585.49 cm^{-1}, 1631.78 cm^{-1}) but as we can see that in the metal complexes, it is shift to the frequency to (1614.49 cm^{-1}, 1631.78-1616.35cm^{-1}) this indicating that the metal bonded through azomethine nitrogen atom, ν (N-N) was also shifted to lower due to complexation with central metal ion[15,16,17].

Table (5): Spectroscopy (FTIR) for Schiff bases and metal complexes.

Compound	OH st. cm^{-1}	OH (bend) *out of plane* cm^{-1}	OH (bend) *in plane* cm^{-1}	C-O *aromatic* cm^{-1}	C=C *aromatic st.* cm^{-1}	C=N cm^{-1}	Specific bands cm^{-1}
Schiff Base (A)	3425.85	680	1384.89	1265.30	1471.69	1585.49	C-H str., asym. 2922.16 C-H str., sym. 2848.86
Schiff Base (B)	3128.54	634.58	1394.53	1230.58	1498.96	1631.78	-
Complex (A-Co)	3338.78-3305.99	620	1384.89	1261.45	1544.98	1614.49	C-H str., *asym.* 2926.06 C-H str., *sym.* 2854.65 N-Co 420 O-Co 480
Complex (B-Ni)	3132.40-3101.54	634.58	1384.89	1230.58	1496.76	1631.78-1616.35	N-Co 497.63 O-Co 460-490

Diagnosed of the polymers (Po-A and Po-B) by the infrared spectra as diagnostic results and a common packages showed. Table (6) shows the Infrared spectra of polymers .

Table (6) : Spectroscopy (FTIR) of the polymers Po-A and Po-B

Bands (cm^{-1})	PoA	PoB
-OH *str*. + -N-H- *str*.	3390.86 (*broad*)	3331.07 (*broad*)
-OH *bend out of plane*	628.7	609.51
-OH *bend in plane*	1311.50	1315.81
C-O (Ar-OH)	1234.44	1242.16
C=C *aromatic str.*	1506.40	1452.40
C=N	1589.34	1600.92
-C=O *(amide)*	1760.00	1776.44
N-C *(amide)*	1650.00	1650.00
Specific band	C-H *str. Asymm.* 2918.30 C-H *str. Symm.* 2848.66	-

NMR Spectroscopic Analyses

For the NMR analysis, the products were dissolved in dimethyl sulphoxide. proton NMR was done. The result are shown in units of parts per million. Based on the ^{1}H assignment of the

structure of (A,B,A-Co and B-Ni) compounds the peaks are satisfied with expected results. There are some peak does not appear in the spectrum because there were some overlapping due to the symmetrical structure.[17,18,19] . Table 5 shows ^{1}H assignment in the ligands (A and B) and their complexes.

Table 7: ^{1}H assignment in the ligands (A and B) and their complexes.

Compound	H-Hexan	Ar-H	O-H	$-CH_2-$	DMSO	Specific
Schiff Base (A)	1.55	6.08-7.43	9.75	3.40	1.09	(=C-CH_3) 1.85
Schiff Base (B)	1.52	6.31-6.38	10.62-10.89	3.38	2.50	-
Complex (A-Co)	1.55	6.10-7.41	10.23-10.45	3.48	1.85	(=C-CH_3) 1.83
Complex (B-Ni)	1.52	6.31-6.81	9.93	3.47	1.45	-

UV / Visible Analyses

The prepared solution from the compounds were run at UV/Vis bands in the region 200-1000 nm. The compounds were dissolved in absolute ethanol . In the Russell –Saunders states, the electronic states were splitting in the presence of crystal fields, The rise to the electronic absorption bands in the UV/Vis spectra of the complexes are the results from the transition electrons between the levels.As we see from Table 8 below, the Schiff base ligands show the absorption on n-π* and π- π* which give band around (≈295 nm - 320 nm) the electronic spectra region which are attribute to charge transfer. While for cobalt (II) and nickel,(II) complexes, mostly gave bands at 404 nm and 407 nm respectively which attribute to d-d transition [20-21] .

Table 8. The UV-Vis spectral data of the Schiff base ligand and its metal complexes

Compound	λ (nm)	Type of trans.
Schiff Base (A)	246,306,366	$(\pi- \pi^*),(n- \pi^*)$
Schiff Base (B)	295,320,375	$(\pi- \pi^*),(n- \pi^*)$
Complex (A-Co)	322,326,404	$(\pi- \pi^*),(n- \pi^*),$(M-L)
Complex (B-Ni)	340,350,407	$(\pi- \pi^*),(n- \pi^*),$(M-L)

Chelating behavior of the polymers toward Metal ions:

a- Effect of treatment time on the loading capacity

Figure 1 and figure 2 show the effect of treatment time on the loading capacity for Po-A and Po-B toward lead and zinc ions respectively. These figures show that the loading capacity increasing with time of shaking until 6 hrs, after that there is no effect of increasing of time on the loading capacity for all pH studied. Therefore, the best treatment time is 6 hrs which can be explained as the treatment tine of the resin with Pb^{2+} and Zn^{2+} ions the ability of resin to make more chelating bonds with ions until 6 hrs of treatment.

b- Effect of pH on the loading capacity

The loading capacity for Pb^{2+} and Zn^{2+} ions were studied in different pH , (2,4 and 6) for lead and (3 and 5) for zinc . The maximum loading capacity in all studied the time was in pH=6 and pH=5 for Pb^{2+} and Zn^{2+} respectively , as shown in figure 3 and figure 4. In this pH, the polymers were more powerful to withdraw ions from the solution.

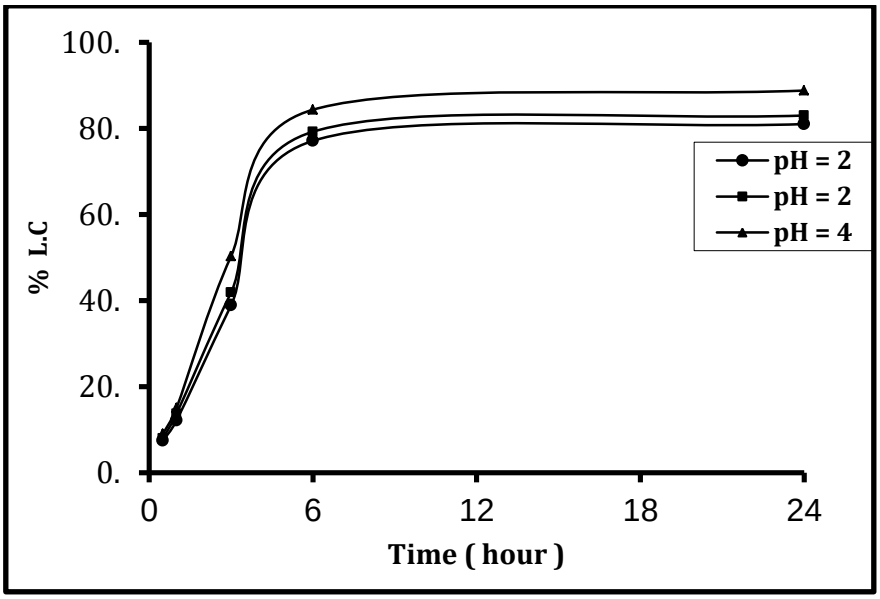
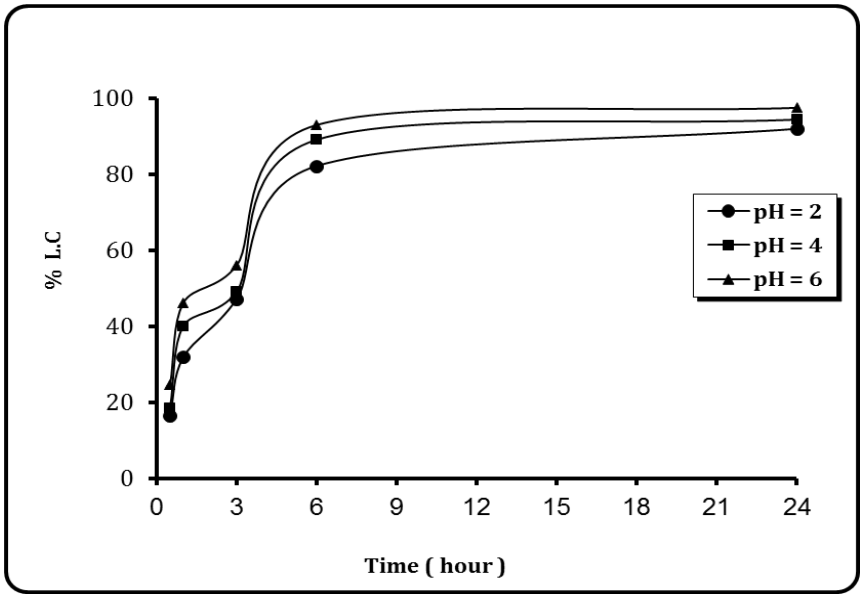


Figure (1): The effect of treatment time and shaking on the loading capacity of the polymer PoA withdrawing lead ion at different pH.



Figure(3): The effect of treatment time and shaking on the loading capacity of the polymer Po-B withdrawing zinc ion at different pH.

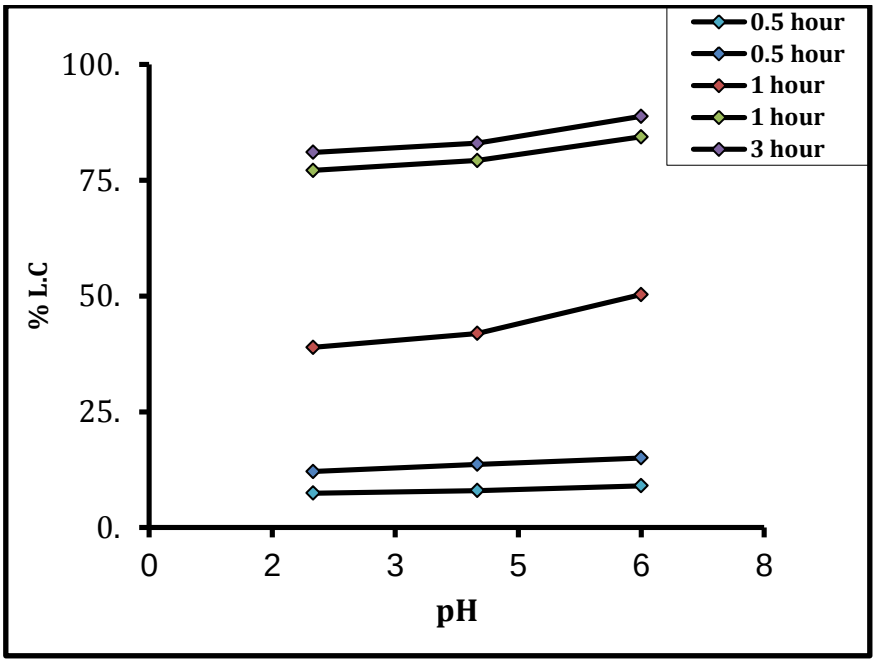
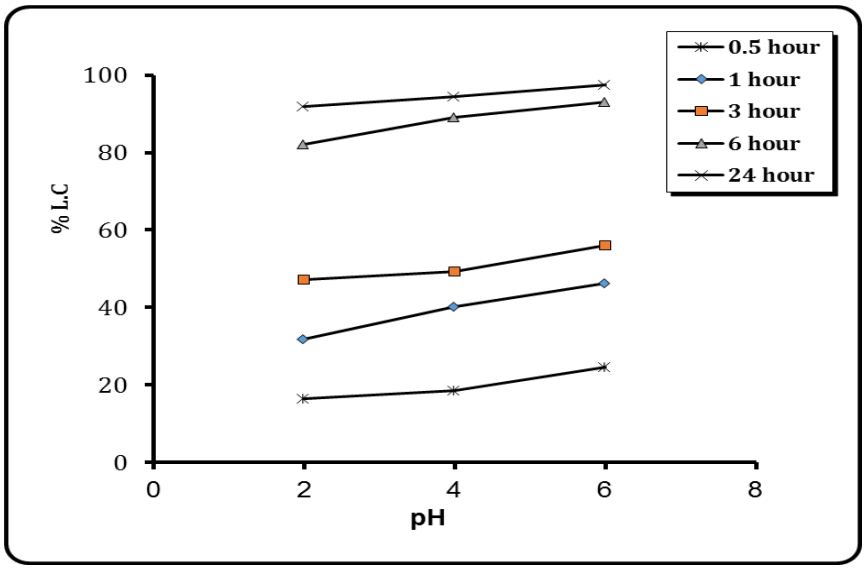


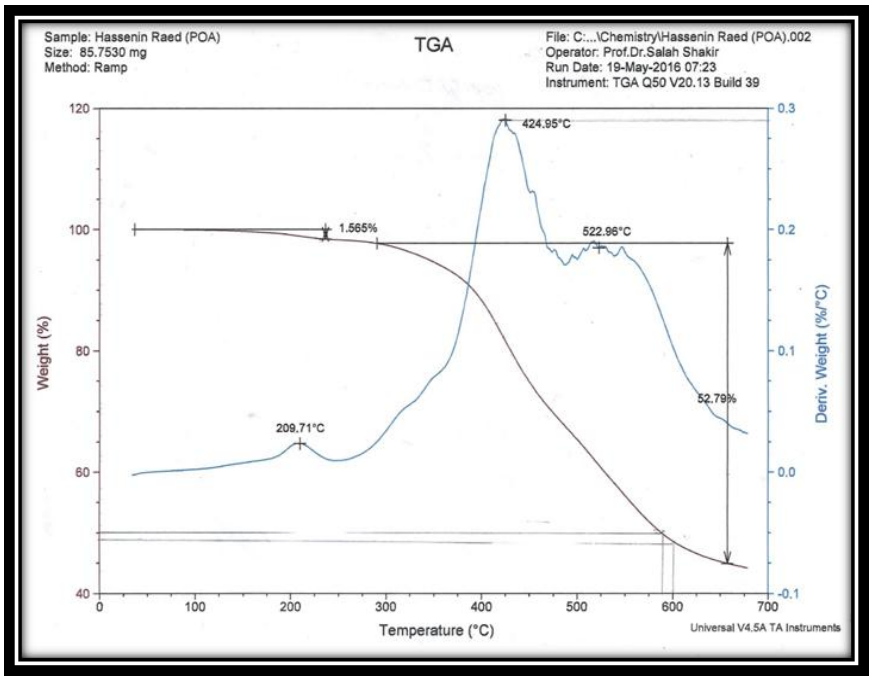
Figure (2) : Change the loading capacity of the polymer Po-A direction of the lead ion with pH when different treatment times.



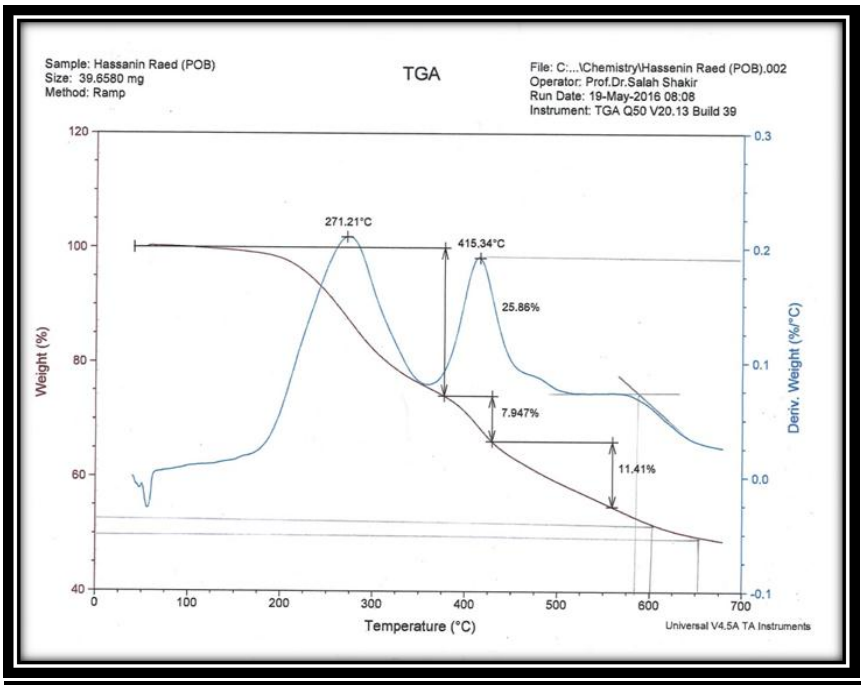
Figure(4): Change the loading capacity of the polymer PoB direction of the zinc ion with pH when different treatment times.

Thermo Gravimetric Analysis (TGA)

Analysis is performed thermal gravimetric polymers prepared (PoB, PoA) by Q50 type-USA TGA where it is studying this technique, weighing changes to the models when exposed to different degrees of heat, figures (5) - (6) curves represent the thermal gravimetric analysis of polymers prepared.



Figure(5):The curve Thermal gravimetric analysis of the polymer PoA



Figure(6):The curve Thermal gravimetric analysis of the polymer PoC

By observing the previous figures we have become a clear vision of how the thermal stability polymers PoA and PoB. Table (9) shows Some thermodynamic functions derived from the curves of the thermal gravimetric analyzes of the polymers (PoA, PoB).

Table (9): Some Thermodynamic Functions Derived from the Curves of the Thermal Gravimetric Analyzes of the Polymers (PoA, PoB).

No.	Compound	Opt. Decomp.Temp. C^0		
		T_i	$T_{op.}$	T_f
1	PoA	209	424	522
2	PoB	271	415	580

When exposed to heat polymers suffer fragmented thermally within the polymer chains. As it has been the activation energy expense (Activation Energy) to the process of disintegration by calculating the slope of the thermal curves and through chart log. rapid disintegration rate (In K) with an inverted temperature scale absolute (1 / T0K) was obtained straight tendency line represents (E / R) where R represents a hard year for gases, (E) activation energy for the process of disintegration based on the Arrhenius equation[22] :

$$In\ K = In\ A - K^{RT}$$

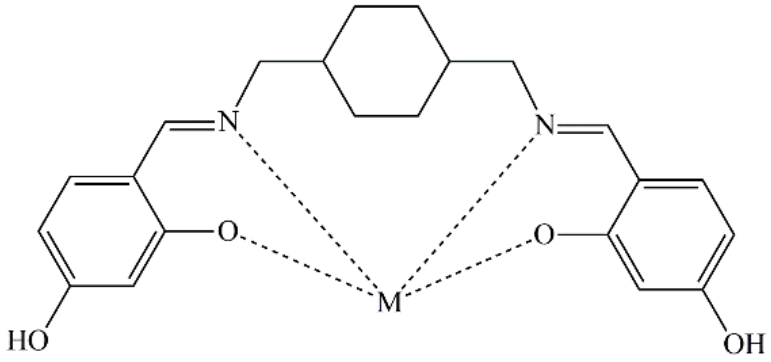
Table (10) shows the activation energy of polymers prepared.

Table (10) : Activation Energy of Prepared Polymers.

Code	Decomposition Stage	Rate of Decomp.% wt/min	Activation Energy kJ.mol^{-1}	Temp.Range for Activation Energy (C^0)
PoA	1$^{st.}$Decomp.	0.173	0.0011	300-380
PoB	1$^{st.}$Decomp.	0.128	0.00013	180-230
	2$^{nd.}$Decomp.	0.15	0.0095	380-398
	3$^{rd.}$Decomp.	0.089	0.004	430-460

Conclusions

On the basis of the analytical data and spectral studies, it has been observed that the ligands coordinate to the metal atom in a N2O2 manner as shown below. Analytical study shoed that the behavior of schiff base toward transition metals different from the behavior of their polymers, thus the loading capacities of polymers increased with time and pH increasing, thermal study showed that the polymers were thermally stable.



Conflict of interests :

The authors declare that there is no conflict of interests regarding the publication of this paper.

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