



Synthesis and Characterization of Schiff Base Derived From Chitosan and Its Complexes With (Co^{+2} , Ni^{+2} and Cu^{+2})

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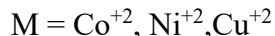
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Received in: 25/ May/2015, Accepted in :10/June/2015

Abstract

In this research, new Schiff base is derived from chitosan O-nitrobenzyldehyde and its complexes were synthesized. All compounds were characterized by FT-IR, UV-Visible, TGA, DTA, TG and molar conductivity with melting point.

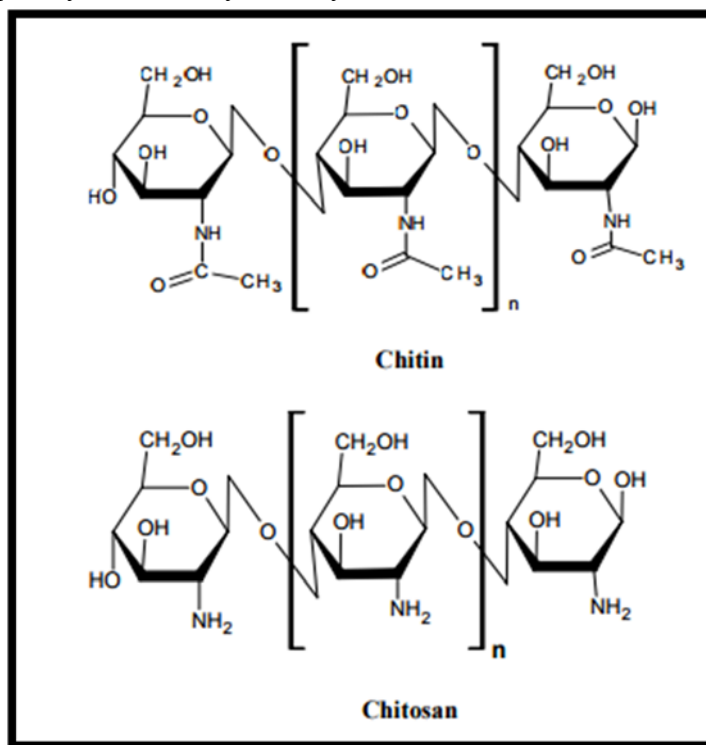
The results showed that Schiff base was coordinated via nitrogen atom azomethine with the center metal ions Co^{+2} , Ni^{+2} and Cu^{+2} behaving monodentate ligand and forming complexes with molecular formula $[\text{M}(\text{L})\text{Cl}_2\text{H}_2\text{O}]$ The tetrahedral geometrical was suggested for all prepared complexes based on the characterization data for all techniques.



Key words: chitin, chitosan, schiff base, complexes.

Introduction

Chitosan is typically obtained by deacetylation of chitin under alkaline conditions [1].



Chitosan displays interesting properties such as biocompatibility, biodegradability [2,3] and its degradation products are non-toxic, non-immunogenic and non-carcinogenic[4,5]. Therefore, chitosan has prospective applications in many fields such as biomedicine, waste water treatment.

Recently, there has been a growing interest in the chemical modification of chitosan in order to improve its properties and widen its application [6,7]. Schiff base containing imine groups can be prepared from reaction between active carbonyl groups and amino groups[8]. Schiff bases and their metal complexes have received a great deal of attention during the last decade in order to prepare new sets of these bases and their transition metal complexes [9]. These complexes have proved that it is antitumor and has carcinostatic activities [10]. In this study we report the grafting modification of chitosan with O-nitrobenzaldehyde. The complexes were synthesized from modified chitosan and (Co^{+2} , Ni^{+2} and Cu^{+2}) metals ions.

Experimental

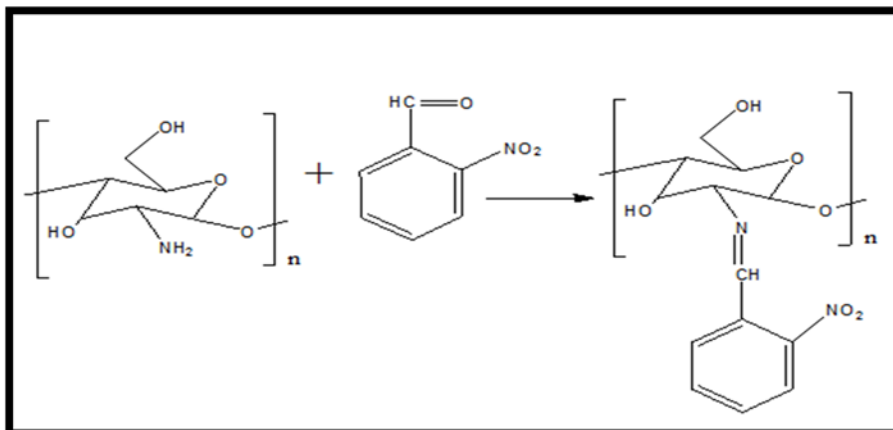
Polymer and reagents

Chitosan with 85% degree of deacetylation was obtained from J&K Iran and all reagents and solvents were obtained from BDH and used without further purification.

Synthesis of chitosan Schiff base (CSB) [11]

0.5 gm Chitosan was dissolved in a mixed 10 ml of methanol with 5 drops of acetic acid and stirred at room temperature for 30 min. Then, 0.015gm o-nitrobenzaldehyde was added to the mixture. The mixture was stirred and heated at 60°C for 12 h under water bath heating.

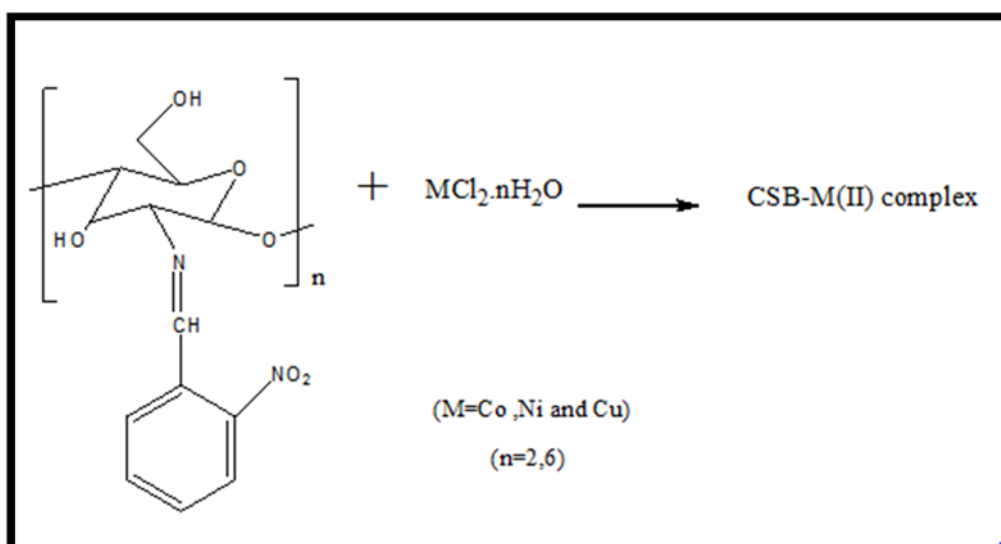
After cooling, the crude product was washed with Methanol to the point of colorless filtrate. The product was dried at 60°C in vacuum for 24 h. The synthetic route of target compounds is shown in scheme.



Scheme synthesis of chitosan schiff base (L)

Preparation of chitosan schiff base of (Co^{+2} , Ni^{+2} and Cu^{+2}) complexes

0.2 gm of Schiff base ligand mixed with 0.2 gm of ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$,) were dissolved in DMSO, and stirred and heated at 60°C for 12 h under water bath heating. After cooling, the crude complex was washed with DMSO, subsequently washed to colourlessness by excess amounts of water, and then dried at 60°C in vacuum for 24 h. The synthetic route of target compounds is shown in scheme .



Scheme (1)

Instruments

FTIR spectrophotometer of shimadzu company as KBr disc in the wavelength range f (4000-400) cm^{-1} were recorded using IR prestige – 21, single beam path laser.

Electrical conductivity measurement of the complexes was recorded at (25C⁰) with 0.001M, all complexes were dissolved in DMSO.

The electronic spectra were measured in the range of 200- 1100 nm for 10⁻³ by usig DMSO solvent by using UV-Visible spectrophotometer type shimadzu UV-160A using quartz cell of (1.0 cm) length.

TG-DSC were carried out by STA PT-1000 (Linseis) instrument.

Results and discussion

Firstly chitosan and the target productions were characterized by FTIR, UV-Visible spectroscopy and Thermal analysis. The yellow ligand were formed and soluble in DMSO solvent.

Table (1) shows physical behavior of the ligand and its complexes with metal ions (Co⁺², Ni⁺² and Cu⁺²).

FTIR – characterization of chitosan Schiff –base ligands and their metal complexes

The FTIR spectra for prepared ligand and its (Co⁺², Ni⁺² and Cu⁺²) complexes are shown in Figure [(1) and (2)]. The assignment of the characteristic band are summarized in Table (2).

The (FT-IR) spectrum for the ligand (L), Figure (1) shows bands at (3037) cm^{-1} , (1022) cm^{-1} , (2885) cm^{-1} and (3105) cm^{-1} due to stretching frequency $\nu(\text{O—H})$, $\nu(\text{C—O—H})$, $\nu(\text{C—H})$ aldehydic and $\nu(\text{C—H})$ aromatic. The new band at (1643) cm^{-1} was due to $\nu(\text{C=N})$ group of the azomethine stretching frequency of the ligand (L3), this refers to formation of Schiff base compound [12,13].

The IR spectra of all prepared complexes exhibited broad band at range (3379 – 3444) cm^{-1} , that may be attributed to (O-H) due to starting material (polymer), and the band ant range (3670- 3750) cm^{-1} , that may be attributed to $\nu(\text{O-H})$ water molecules in molecular formula of all complexes [14,15] the stretching frequency of azomethine group $\nu(\text{C= N})$ of the free ligand was shifted to lower or high frequency at range (+8 to -4) cm^{-1} with ligand complexes, this shift to lower or high frequency may be due to involved nitrogen atom of azomethine group in coordination with metal ions and delocalization of metal electronic density to the ligands (π –system)[16,17],(HOMO→ LUMO), where:
HOMO = Highest Occupied Molecular Orbital

LUMO = Lowest unoccupied Molecular Orbital

Assignment of proposed coordination sites is further supported by the appearance of medium bands at range (432-459) cm^{-1} which could be attributed to $\nu(\text{M—N})$ [18].

The IR spectra of ligand and all prepared complexes, suggested that the ligand behaves as monodentate ligand via N atom of azomethine group.

Electronic spectra of the ligand and its metal complexes

The UV-Vis. Spectrum of ligand, Figure (3), displayed one absorption peak, the peak at [(262nm,38167 cm^{-1})] were attributed to ($\pi \rightarrow \pi^*$) electronic transition [19].

The electronic spectra of Co⁺² complex figure (4) showed three additional absorption peaks. The first peak at range (496nm-20408 cm^{-1}) the second peak at [(569 nm,17574 cm^{-1}), (859

nm,11641cm⁻¹) and (569nm,17574cm⁻¹), were attributed to (d-d) spin –allowed electronic transition type ⁴T_{2F}→⁴T_{1P}, ⁴A_{2F}→⁴T_{1F} and ⁴A_{2F}→⁴T_{1F}, respectively, characteristic tetrahedral geometry around Co⁺²[20,21].

The UV-Vis spectra of Ni⁺² complexes with all, Figures (5) display two additional absorption peaks. The first peak at [(601nm,16638cm⁻¹)] and the second peak at [(846nm,11820cm⁻¹)] respectively, were due to (d-d) spin-allowed electronic transition type ³T_{1F}→¹T₂ and ³T_{1F}→³T_{1P} respectively, which was a good agreement for tetrahedral geometry of Ni⁺² complex [22,23].The UV-Vis spectra of Cu⁺² complexes with ligand display one additional absorption peak (750nm, 13333 cm⁻¹) for ligand complexes,were attributed to (d-d) spin-allowed electronic transition type (²T₂→²E), confirming tetrahedral geometry about Cu⁺²[24].

The electronic spectra for ligand complexes are summarized in Table (3) together with electronic transition and suggested geomotrics.

3-3Molar Conductance

The molar conductance values, Table (3) of the soluble complexes in DMSO solvent in (10⁻³M) solution at room temperature refers to non-electrolytic nature [25].

Thermal analysis

The TG-DTA curves of chitosan ,modified chitosan, Their complexes were obtained at the heating rate of 10C⁰ min⁻¹ under nitrogen, figures from [(6) to (8)]and the detailed data are shown in Table (4).

The TG and DTG curves Figure (6) of chitosan show relatively rapid decomposition in the first (29.3-99.3⁰C) and second (215.8-3395⁰C) steps with T_{DTG} peaks at 67⁰C and 270⁰C. The very large and strongly sharp T_{DTG} peak observed for the first step at 67⁰C is preceded by a sharp endothermic peak (T_{dta}) in DTA curve at 70.7⁰C 1.97% and 46.46% mass losses in the first and second steps correspond to the release of (2H₂O)and (CO₂+C₂H₃NN) fragments[cal.2.10% and 45.8%] respectively.

The TG and DTG curves of modified chitosan (ligand) curves figure (7) show the DTG peak (T_{DTG}) of the first (28.1-130⁰C) and second (245-349.8⁰C)steps at 60.8⁰C and 249⁰C. The strongly sharp exothermic peak (T_{dta}) observed for the first-step at 60.8⁰C was due to a rapid release of (H₂O) fragment (found 1.14%,cal. 1.18%). 91.6% mass loss of the second (245-349.8⁰C)step with T_{DTG} peak at 249⁰C and T_{dta} at 248.5⁰C is to the (C_qH₈N₂O+CO₂)fragment (cal. 90.96%).

The TG thermogram of Co-Ligand complex was characterized by two decomposition steps in the range [(35-197) and (197-349) C⁰].

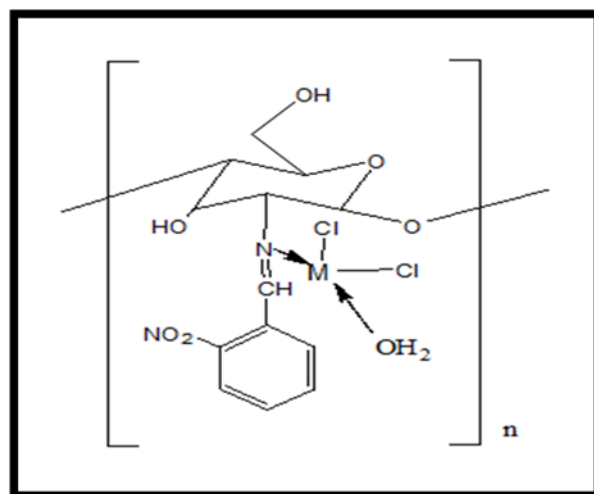
The first steps at T_{DTG} of (130⁰C) ill-defined are consistent with the evolution of (Cl₂) only with one coordinated water molecule [(Cal.24.15, found 23.38%)].The final ill-defined residue are [(C₈H₇N₂O₂)] fragments [(Cal.63.03%, found 63.23% respectively].

The TG thermogram of Ni- ligand complex Figure (8) is characterized by two decomposition steps in the range [(60-160) and (160-320)⁰C]. The first steps at T_{DTG} of (115⁰C), ill-defined are consistent with the evolution of (CO₂+ClC₂HO) only with two coordinated water molecule (Cal 38.01%, found 37.95%) and their overlapping peaks. The final ill-defined residue is(C₁₀H₈N₂ONiCl) fragments [(Cal.61.77, found 61.61%) respectively].

The TG thermogram of Cu-Ligand was characterized by one decomposition steps in the range [47-146⁰C] . The first steps at T_{DTG} of (74.5⁰C) respectively, ill-defined are consistent with the evolution of [(CO₂+C₆H₆N₂Cl₂)] only with one coordinated water molecule (Cal 75.15%, found 74.5%).

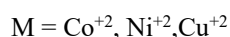
The broad endothermic peaks at 134⁰C of Cu-L, , which do not due to correspond to any weight losses in the TG curve, may be due to some rearrangement in the structure of the complexes [26].

According to the above - mentioned analysis, the suggested structures for the prepared complexes are illustrated below



O-Nitrobenzyldehyde chitosan complex

Suggested structure of prepared complexes [M(L)Cl₂H₂O]



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Table (1): Shows physical behavior of the ligand with metal ions (Co^{+2} , Ni^{+2} and Cu^{+2}).

Symbol	Colors	Melting point
Chitosan	Off white	284
NBC(L)	Yellow	250
CoL	Light Red	266
NiL	Light Green	232
CuL	Olive Green	210

Table (2) :Infrared spectral data (cm^{-1}) for the ligands and complexes

Comp.	OH_{ROH}	H_2O	C-H-O	$\text{C}\equiv\text{N}$	$\text{C-H}_{\text{ald.}}$	$\text{C-H}_{\text{arom.}}$	M-N	Figs.
NBC(L)	3437	-----	1022	1643	2885	3105	----	3-5
CoL	3417	3720 3750	1026	1643	2916 2881	3090	432	3-6
NiL	3444	3680 3740	1022	1647	2916	3008	451	3-7
CuL	3394	3750	1026	1651	2916	3005	459	3-8

Table (3) Electronic spectral data of ligand and its complexes and molar conductance for all complexes

Compound	λ (nm)	ν - cm^{-1}	ABS	Assignment	$\Delta\text{ohm}^{-1}\text{cm}^2.\text{mol}^{-1}$	Suggested structure	Fig.
NBC(L)	262	38167	1.727	$\pi \rightarrow \pi^*$	-----	-----	3-5
CoL	260	38461	1.220	$\pi \rightarrow \pi^*$	9.70	Tetrahedral	3-6
	342	29239	1.310	C.T			
	490	20408	0.062	${}^4T_{2F} \rightarrow {}^4T_{2p}$			
	569	17574	0.146	${}^4A_{2F} \rightarrow {}^4T_{1F}$			
	859	11641	0.140	${}^4A_{2F} \rightarrow {}^4T_{1F}$			
NiL	274	36496	1.509	$\pi \rightarrow \pi^*$	4.09	Tetrahedral	3-7
	325	30769	1.701	C.T			
	601	16638	0.231	${}^3T_{1F} \rightarrow {}^1T_2$			
	846	11820	0.211	${}^3T_{1F} \rightarrow {}^3T_{1p}$			
CuL	272	36764	1.680	$\pi \rightarrow \pi^*$	9.66	Tetrahedral	3-8
	750	13333	0.196	${}^2T_2 \rightarrow {}^2E$			

Table (4) Characterization parameter of thermal decomposition (10^0min^{-1}) for compound

Comp.	Step	TGA				DTA		Reaction	Total mass %loss	Figures
		T _i /°C	T _f /°C	T _{DTGmax}	Weight mass %loss	T _{dta}	ΔH			
Chitosan	Stage1	29.3	99.3	67	1.27(2.10)	70.7	end	-2(H ₂ O)	47.73(47.9)	3-9
	Stage2	215.8	339.5	270	46.46(45.8)	283.8	exo	-(CO ₂)+C ₂ H ₃ N		
NBC(L)	Stage1	28.1	130	60.8	1.14(1.18)	60	end	-H ₂ O	92.74(92.14)	3-10
	Stage2	245	349.8	249	91.6(90.96)	248.5	exo	-C ₉ H ₈ N ₂ +CO ₂		
[Co L]	Stage1	35	197	130	23.38(24.15)	55	end	-H ₂ O+Cl ₂	86.61(87.18)	3-11
	Stage2	197	349	259.6	63.23(63.03)	261	exo	-C ₈ H ₇ N ₂ O ₂		
[Ni L]	Stage1	60	160	115	37.95(38.01)	120	end	-2H ₂ O+CO ₂ + C ₂ HOCl	99.56(99.8)	3-12
	Stage2	160	320	221.8	61.61(61.77)	232	exo	C ₁₀ H ₈ N ₂ ONiCl		
[Cu L]	Stage1	47	146	130	74.5(75.15)	89	end	H ₂ O+CO ₂ +Cl ₂ + C ₆ H ₆ N ₂	74.5(75.15)	3-13
						134	end	Rearrangement to complex		
							205.1	exo		

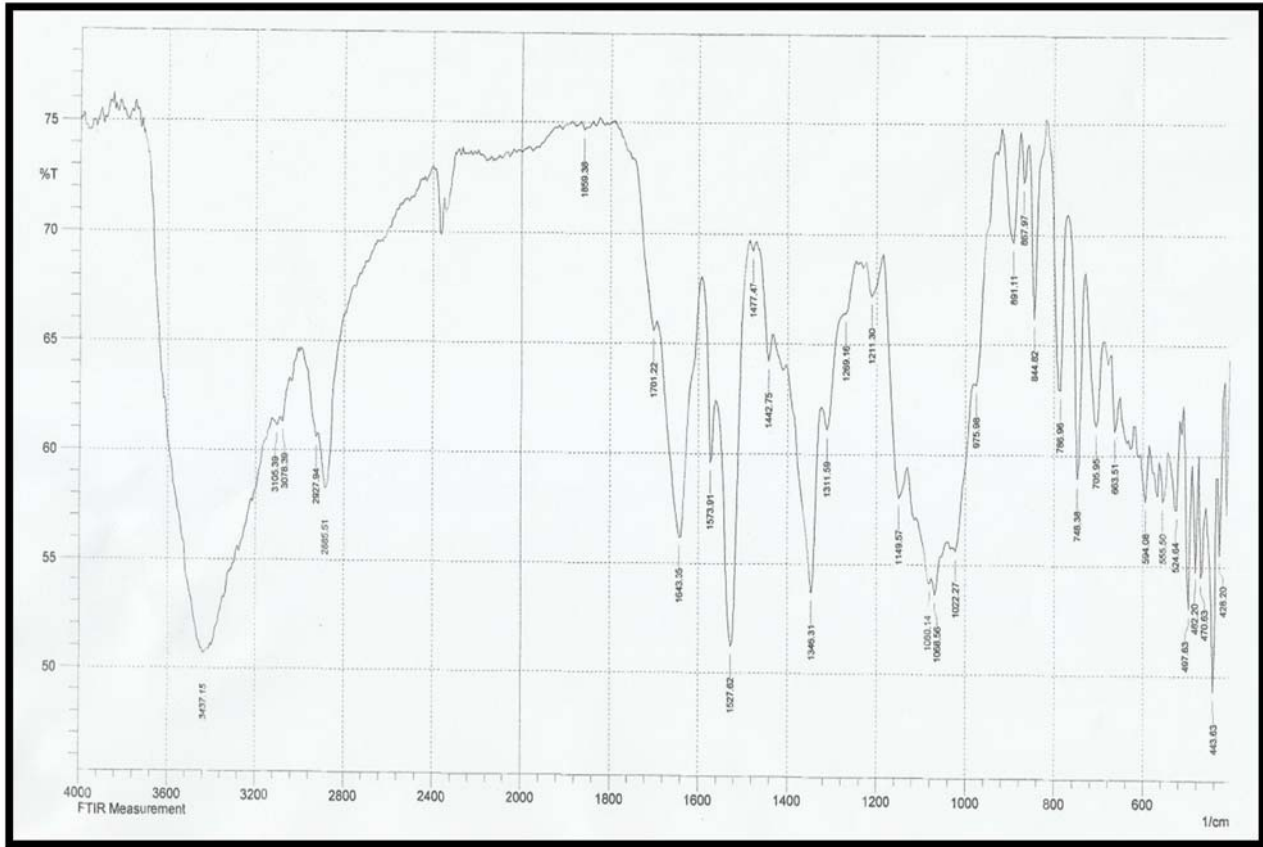


Figure (1): FTIR spectrum of NBC (L)

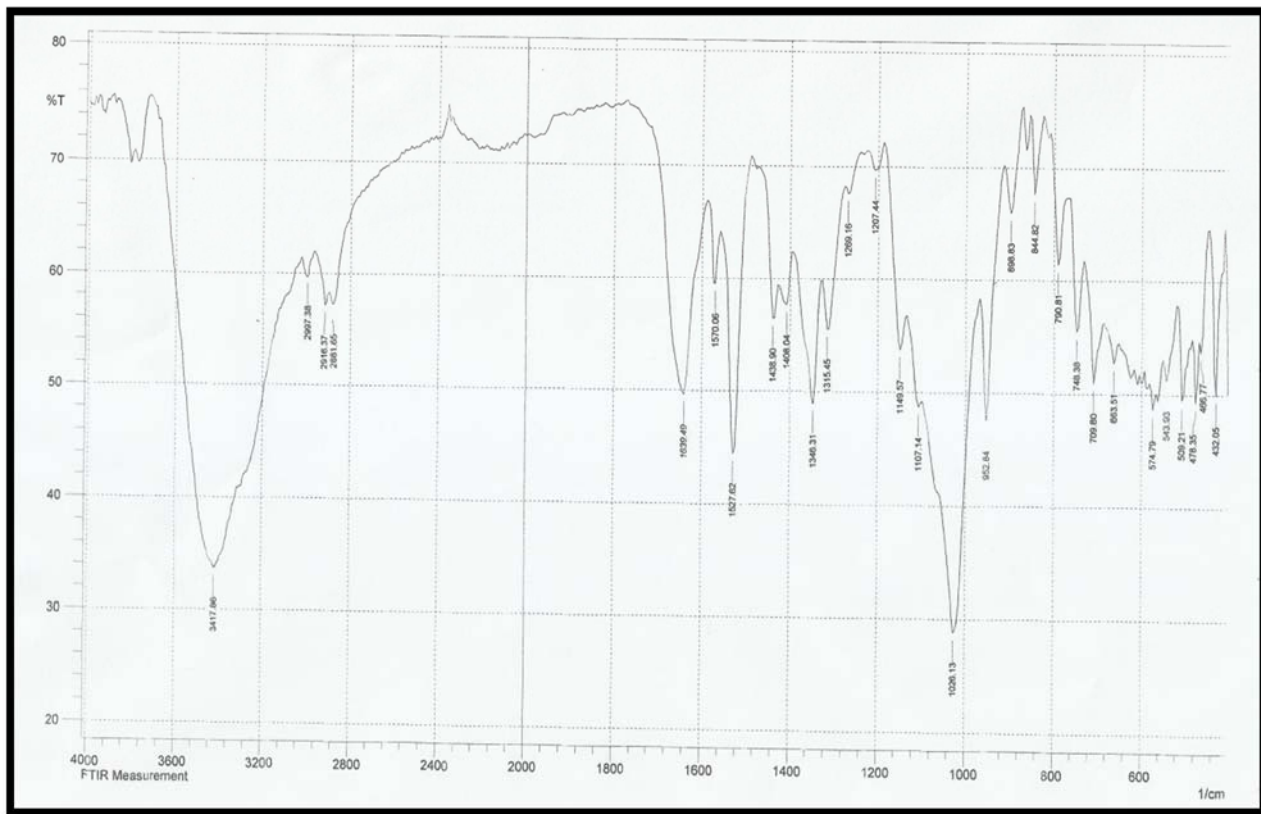


Figure (2): FTIR spectrum of CoL complex

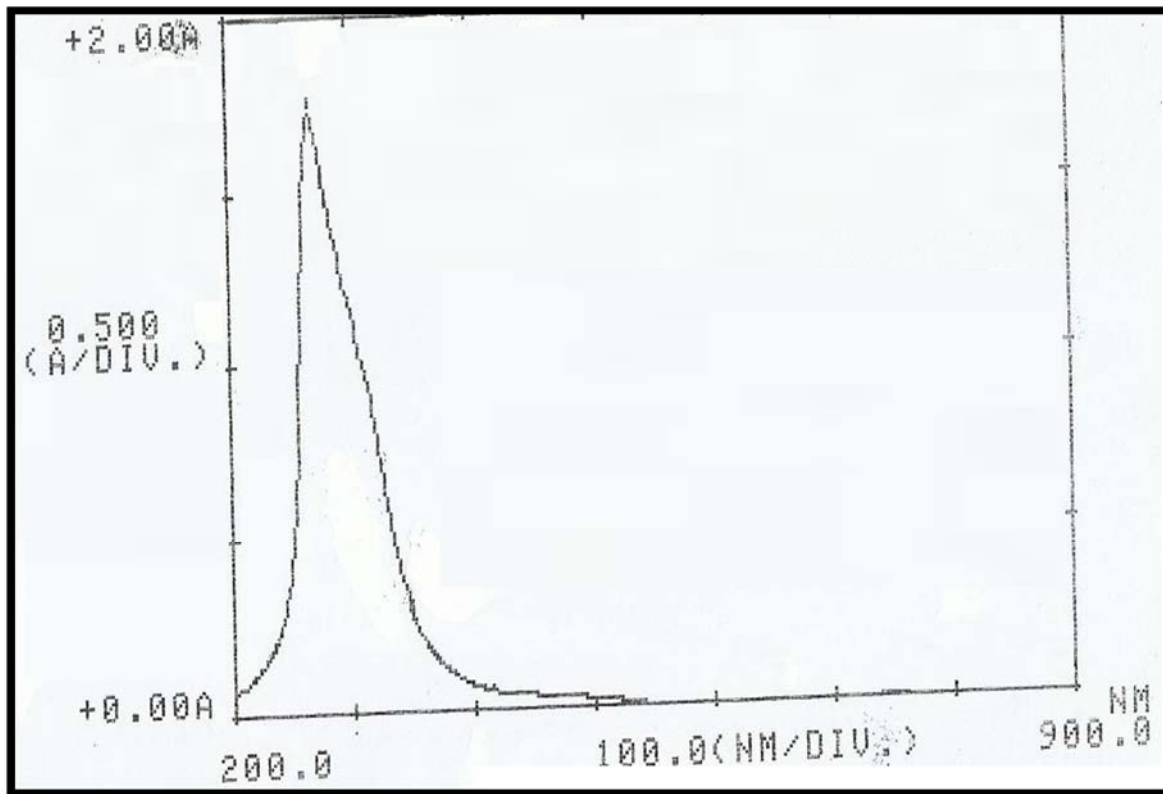


Figure (3): Electronic spectrum of NBC (L)

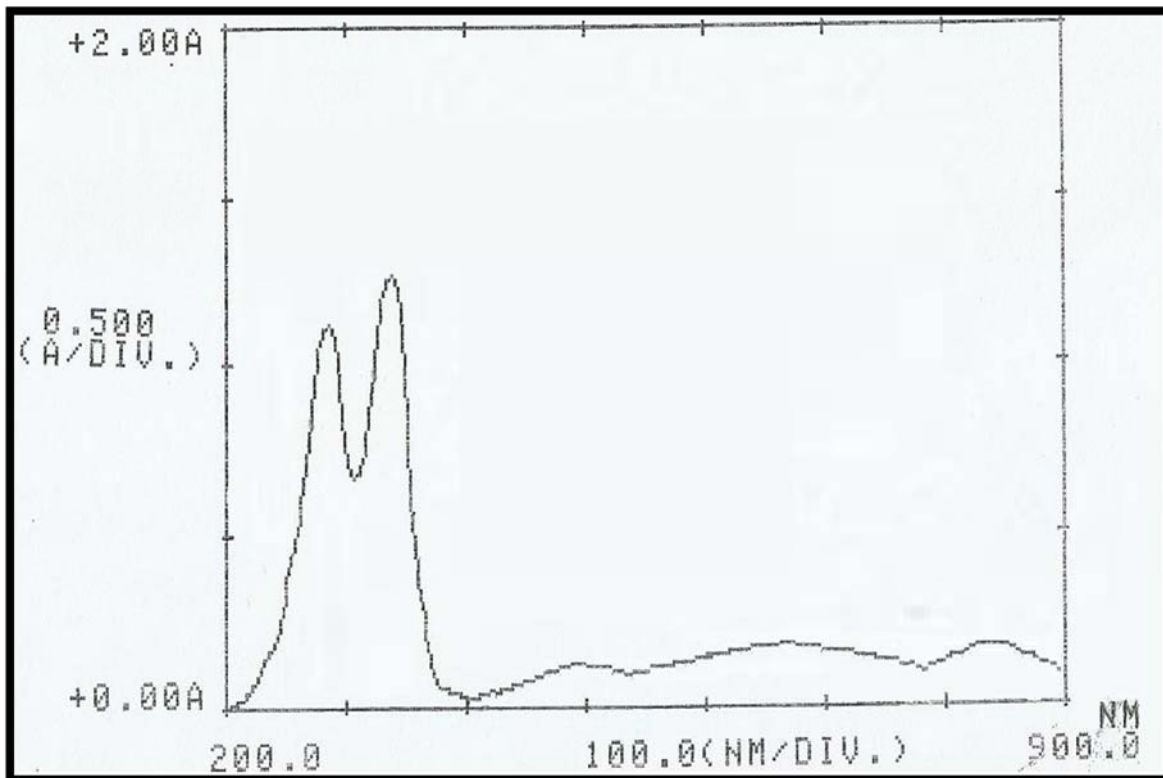


Figure (4): Electronic spectrum of CoL

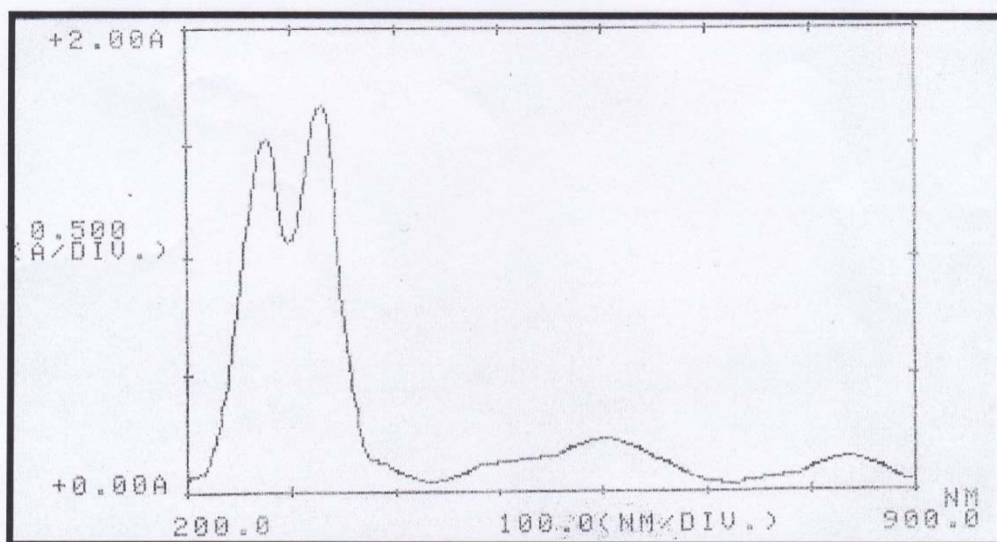


Figure (5) Electronic spectrum of NiL

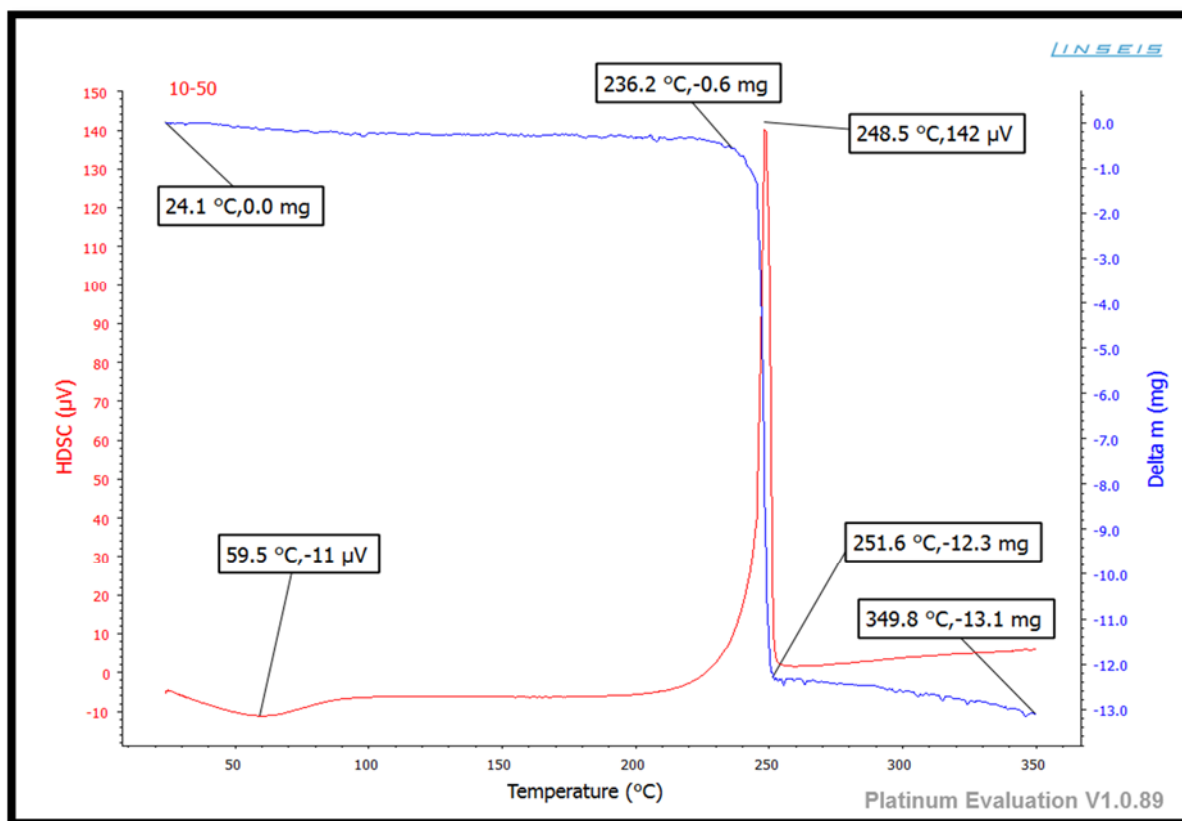


Figure (6): Thermal analysis of chitosan

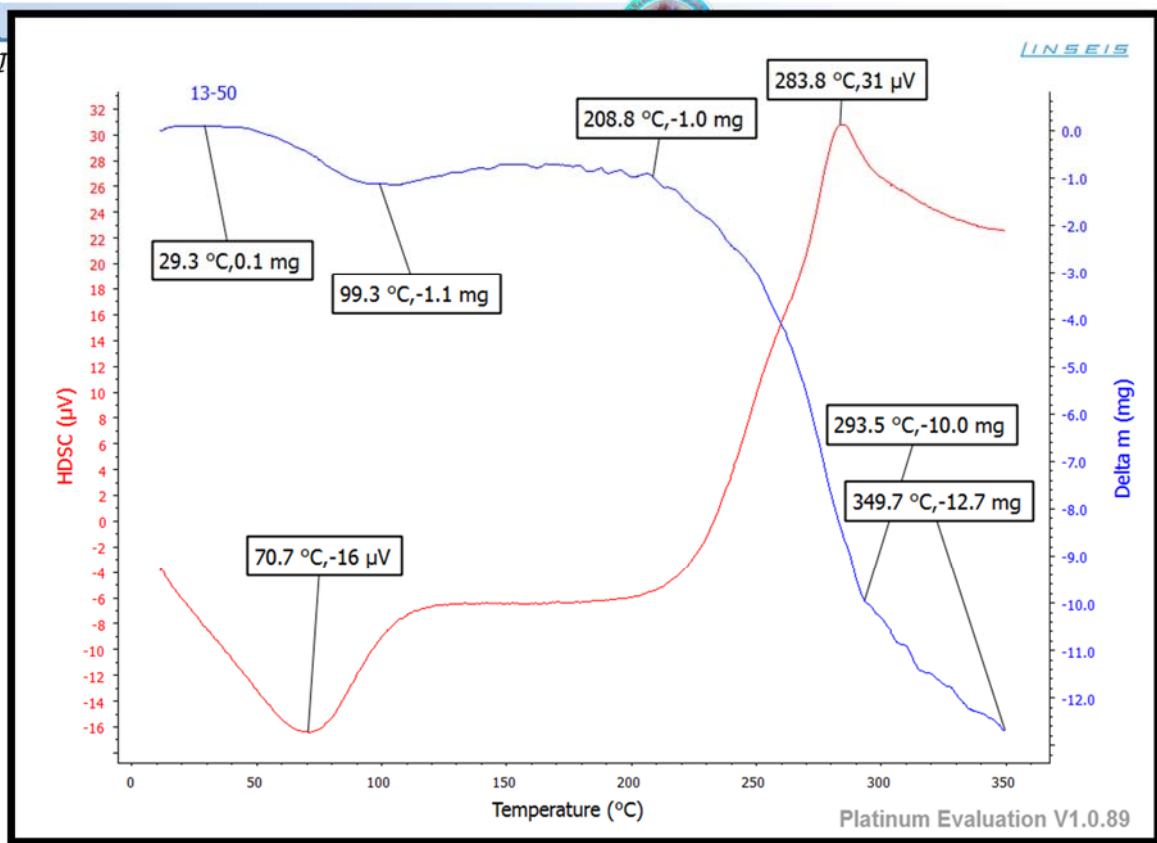
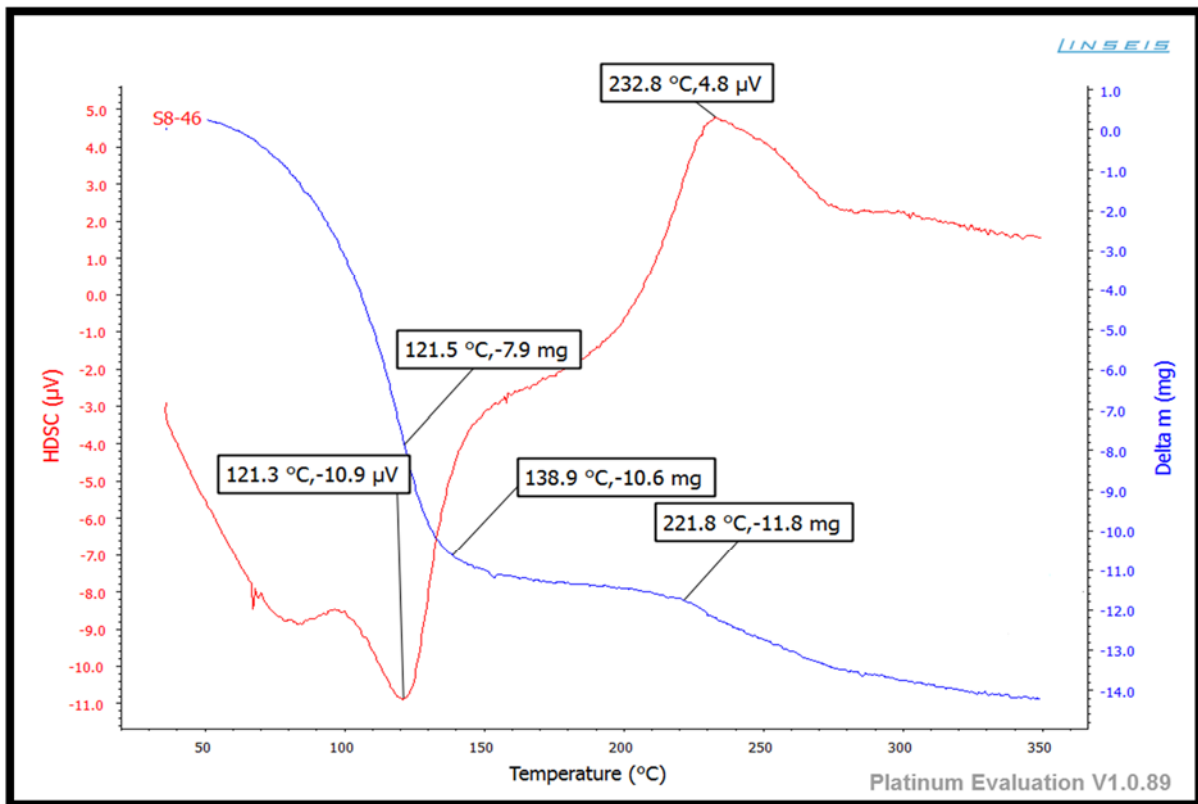


Figure (7): Thermal analysis of NBC(L)



Figure(8): Thermal analysis of Ni

تحضير وتشخيص قاعده شيف مشتقه من كيتوسان ومعقداته مع الايونات Co^{+2} , Ni^{+2} and Cu^{+2}

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قسم الكيمياء / كلية العلوم للبنات / جامعه بغداد

فاضل سليم متي

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استلم في: 25/أيار/2015 ، قبل في: 10/حزيران/2015

الخلاصة

تضمنت الرسالة تحضير قواعد شيف بتفاعل التكثيف من الكيتوسان و اورثو نايترو بنزليديهايد وكذلك تحضير معقدات هذه الليكنادات تحت تأثير لظروف التفاعل مثل درجة الحرارة .
شخصت مركبات الكيتوسان قواعد شيف ومعقداتها المحضرة بوساطة طيف الاشعة تحت الحمراء (FTIR) وطيف الاشعة فوق البنفسجية والمرئية (UV-Visible) والتوصيلية المولارية وظهرت النتائج بأن الليكند أحادي المخلب من خلال تناسق ذره النتروجين الازوميثين مع ايونات الفلزات Co^{+2} , Ni^{+2} , Cu^{+2} ووفقا لطرائق التشخيص المشار اليها اعلاه فأن الشكل الهندسي المقترح لمعقدات الكيتوسان قواعد شيف مع ايونات Co^{+2} , Ni^{+2} , Cu^{+2} رباعي السطوح .
وتم دراسة الاستقرارية الحرارية لكيتوسان والكيتونات المحور لقواعد شيف والمعقدات وجد هناك اختلاف في الاستقرارية الحرارية لهذه المركبات بسبب اختلاف التركيب.
الكلمات المفتاحية: كايوتين- كيتوسان- قواعد شيف -معقدات.