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Synthesis, Characterization and Thermal Studies of New Chelating Fulven Monomers, Polymers and Their Metal Complexes

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The monomer exo-7-isopropylidenebicyclo[2,2,1]hept-2-ene-5,6-dicarboxylic acid anhydride (**I**) undergoes smooth ring-opening metathesis polymerization (ROMP) using the $WCl_6/(CH_3)_4Sn$ based catalyst to give the anhydride polymer (PI). Aiming to synthesize a chelating polymers, the monomer (I) was treated with potential complexing agent thiocarbohydrazide or oxalyldithiosemicarbazide to give exo-7 isopropylidenebicyclo[2,2,1]hept-2-ene-5,6-dicarboxylic acid amidothiocarbohydrazone and exo-7-isopropyli denebicyclo[2,2,1]-hept-2-ene-5,6-dicarboxylic acid amido-oxalylthiosemicarbazone monomers (**II**) and (**III**), respectively. Unfortunately these two monomers are relatively inactive toward metathesis ring-opening polymerization using the $WCl_6/(CH_3)_4Sn$ based catalyst. It is already reported that the complex formation between chelating group namely S-methylhydrazinecarbodithioate and the WCl_6 initiator completely inhibited the ROMP process. Therefore the synthesis of the desired chelating polymers (PII) and (PIII) were achieved by treating the anhydride precursor polymer (PI) with thiocarbohydrazide or oxalyldithiosemicarbazide, respectively. The current work also presents the synthesis and characterization of the metal complexes derived from monomers (II and III) and polymers (PII and PIII) with $Cu(OAc)_2.H_2O$, $Co(OAc)_2.4H_2O$ and $Ni(OAc)_2.2H_2O$. The thermal analysis of the monomers, polymers and their metal complexes were studied by means of thermogravimetric analysis. The isolated complexes were formulated as $[M_2(II)(H_2O)_n].nH_2O$, $[M_2(III)(H_2O)_n]$, $[M_2(PII)(H_2O)_n].nH_2O$ and $[M_2(PIII)(H_2O)_n]$ where M = Cu(II), Co(II) or Ni(II), n = 0-4 and (II), (III), (PII) and (PIII) are the chelating monomers and polymers used. The structures of polynuclear monomeric and polymeric thiosemicarbazones complexes are $[Ni_4(III)(OAcO)_2(H_2O)_8].2H_2O$ and $[Cu_4(PIII)(H_2O)_8].4H_2O$.

Key Words: Synthesis, Fluven, Monomers, Polymers, Metal complexes.

INTRODUCTION

Recently, there has been an increasing interest in chelating polymers that have a selective properties towards some toxic metals ions[1]. We and other workers have synthesized and examined several kinds of binuclear polymer complexes which contains a different coordinating atoms capable of holding two metal ions in close proximity[2]. Homobinuclear polymer complexes are of interest in the field of bioinorganic chemistry[3]. Thiocarbohydrazide, thiosemicarbazide, thiosemicarbazones and their metal complexes have attracted interest from their industrial applications[4,5] and biomedical response[6,7]. They drawn particular interest due to their antibacterial effectivenes, antiviral against viruses[8,9], protozoa, small pox and certain types of tumours[10,11]. The aim of the present study is to incorporate an excellent chelating groups namely thiocarbohydrazide or oxalyldithiosemicarbazide into monomer (**I**), exo-7-isopropylidenebicyclo-[2,2,1]hept-2-ene-5,6-dicarboxylic acid anhydride[12,13] and its established ring opening metathesis polymer (PI) to form monomoers (II) and (III), and polymers (PII) and (PIII) as shown in schemes (I and II). However, the chelating monomers (II), (III), polymers (PII) and (PIII) reacts with the metal acetate in 1:2 and 1:4 repeating units : to metal molar ratios giving polynuclear polymer complexes.

EXPERIMENTAL

Preparation of monomers and polymers

Preparation of monomer (II): Exo-7-isopropylidenebicyclo [2,2,1]-hept-2-ene-5,6-dicarboxylic acid anhydride (I) was obtained from the Diels-Alder reaction between dimethyl fulvene and maleic anhydride following the same procedure described before[12-14]. A hot clear solution of thiocarbohydrazide (1.2 g, 1.1 mol) was added to a hot solution of monomer (I), (5 g, 2.5 mol), in dry DMF (40 mL). The reaction mixture was heated on an oil bath at 95°C for 4 h; the authentic sample of the dimer was obtained as a white microcrystallized material. The product was recrystallized from ethanol to give the difunctional monomer (II) as a white solid product. It was recovered by filtration and dried under vacuum (5.7 g, 1.27 mol, 52%, m.p. 212°C).

Preparation of monomer (III): This monomer was prepared following the same procedure as described above except using oxalyldithiosemicarbazide instead of thiocarbohydrazide. The product was recovered as a white crystalline material (99.9%, m.p.= 235°C).

Preparation of polymer (PII): The exo adduct of monomer (I) was polymerized to (PI) using an activated catalyst system $WC_6/(CH_3)_4Sn$ in chlorobenzene at 70°C[14]. A clear solution of the anhydride polymer (PI) (0.2 mol) in dry DMF (10 mL) was treated with thiocarbohydrazide (0.1 mol). The reaction mixture was heated on an oil bath at 85°C for 2 h; the mixture became very viscous and produced a gel like material, where, the anhydride polymer was occurred to give polymer (PII). The polymer was formed as an insoluble gel. After removal of the solvent by decantation, the precipitated network polymer was recovered by filtration, washed thoroughly with DMF, then dried under vacuum with heat at 50°C for 24 h, (87%), (**Scheme-II**).

Preparation of polymer (PIII): This polymer was prepared following the same procedure described above except using oxalyldithiosemicarbazide as chelating group. The precipitated material was dried for 24 h under vacuum with heat at 50°C (yield= 68%).

Prepration of monomeric metal complexes

Preparation of monomeric metal complex (IV): A hot clear solution of metal acetate monohydrate (0.01 mol) in ethanol (30 mL) was added dropwise with constant stirring to a hot solution of monomer (II) (0.02 mol) in ethanol (30 mL). The bluish green solution of the acetate disappeared instantaneously. The colourless solution was refluxed for 0.5 h, during this time a white precipitate was deposited, which was recovered by filtration of the hot mixture and washed with hot ethanol. The title compound was dried under vacuum.

Preparation of monomeric metal complex (V): This complex was prepared using the same procedure described above except using monomer (III) instead of monomer (II). The precipitated complex (V) was recovered by filtration, washed thoroughly with hot ethanol, dried for 24 h under vacuum.

Preparation of polymeric metal complexes

Preparation of polymeric metal complexes (PIV) of the general formula $[M_2(PII)(H_2O)_4]_n$, where M=Co(II), Ni(II) or Cu(II): Polymer (PII) was difficult to dissolve in any of a common organic solvents. Therefore the polymeric metal complexes of the general formula $[M_2(PII).(H_2O)_4]_n$ (**Scheme-II**), was prepared by treating the reaction mixture of a diluted solution of the anhydride polymer (PI), (0.2 mol) and thiocarbohydrazide (0.1 mol) in dry DMF (30 mL) with the desired metal acetate. A coloured complex (PIV) was precipitated instantaneously. The precipitated complex was recovered by filtration, washed thoroughly with hot ethanol and then ether and dried under vacuum for 6 h.

Preparation of polymeric metal complexes (PV) of the general formula $[M_2(PIII)(X)]$, where M=Co(II) or Cu(II): The polymeric metal complex (PV) was prepared by treating the reaction mixture of a diluted solution of the anhydride precursor polymer (PI), (0.2 mol) and oxalylthiosemicarbazide (0.1 mol) in dry DMF (30 mL) with the desired metal acetate. A coloured polymeric complex was precipitated instantaneously. The solution was refluxed for an additional 1 h. The precipitated complex was recovered by filtration, washed thoroughly with hot ethanol and ether then dried under vacuum for 6 h.

Physical measurements

Infrared spectra in the region 4000 - 400 cm^{-1} were recorded by Perkin Elmer FTIR 1605 using KBr pellets. ^1H NMR spectra for monomers (II) and (III) made using fourier transfer nuclear magnetic resonance spectrometer model NR/100 with an electromagnetic field 100 MHz attached with aspect 3000 computer. Elemental analysis for carbon, hydrogen and nitrogen were analyzed by the microanalytical center, Cairo University, Egypt. Thermal gravimetric analysis for the compounds are carried out using a Perkin Elmer TGA7 computerized thermal analysis system. The rate of heating of the samples was kept at 5°C/min. Nitrogen gas was allowed to pass at flow rate of 20 cc/min. during measurements. $CuSO_4.5H_2O$ was used as the calibrating standard material.

RESULTS AND DISCUSSION

Characterization of the isolated compounds

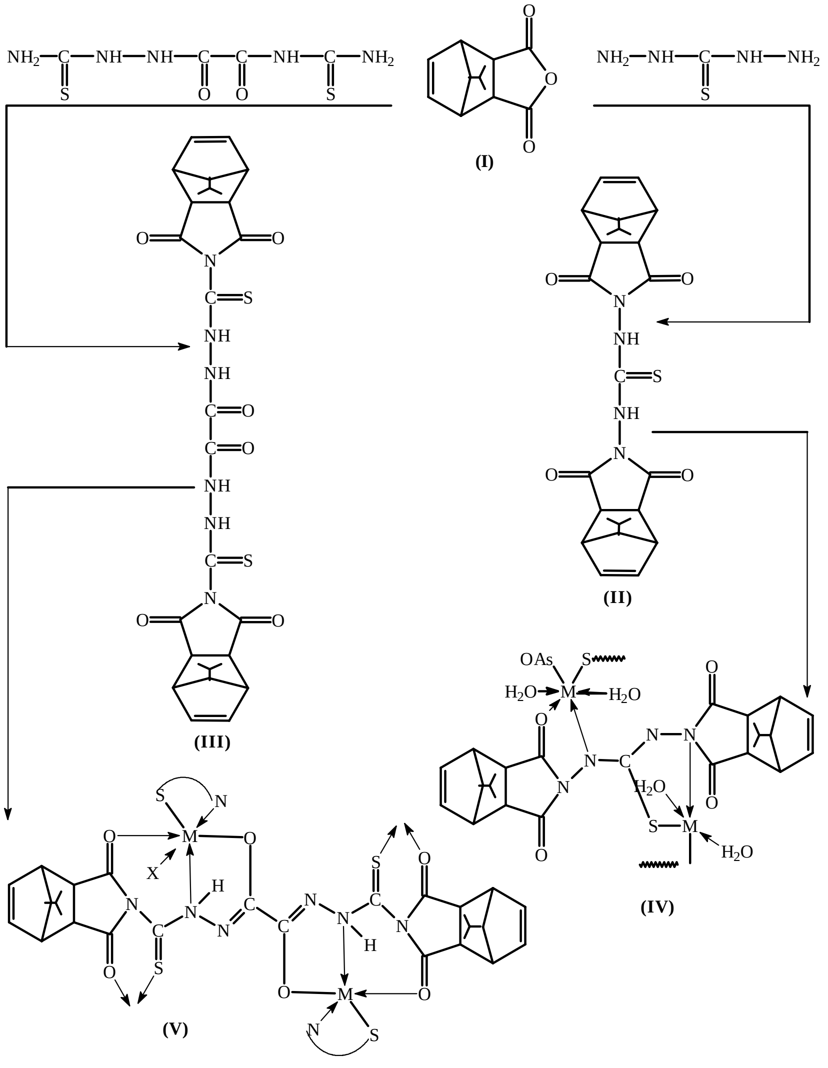
The monomers exo-7-isopropylidenebicyclo[2,2,1]hept-2-ene-5,6-dicarboxylic acid amidothiocarbohydrazone (II) and exo-7-isopropylidene - bicyclo[2,2,1]hept-2-ene-5,6-dicarboxylic acid amidooxalylthiosemicarbazone (III) were prepared by reaction of monomer (I) with thiocarbohydrazide and oxalylthiosemicarbazide in dry DMF, respectively. Monomers (II) and (III), were recovered as a white crystalline solids with correct elemental analysis (Table-1). As it has been known that the complex formation between these two kind of monomer and the WCl_6 initiator completely inhibited the the ROMP process[2]. However, the synthesis of the desired polymers (PII) and (PIII) were carried out by the condensation of thiocarbohydrazide and oxalylthiosemicarbazide with the anhydride precursor polymer (PI). Monomers (II), (III), polymers (PII) and (PIII) were synthesized according to **Scheme I** and **II**. The synthesis and ring opening polymerization of monomer (I) to give linear polymer containing unsaturated carbon - carbon double bond linkages (PI) using the classical initiator $WCl_6/(CH_3)_4Sn$ is already established process[2,12]. Polymer (PI) was easily soluble in DMF when the solution of thiocarbohydrazide was added in 1:2 molar ratio of the polymer, the mixture became viscous after a few min. The resulting viscous mass was taken as an indication that the product undergoes cross-linking to polymer (PII) using the same procedure described. Polymer (PI) was used to prepare polymer (PIII) using oxalylthiosemicarbazide as a chelating group in 1:2 molar ratio of the polymer. The isolated polymers were obtained as a hard material. In practice it proved impossible to incorporate metal into the chelating groups carried by polymer (PII) or (PIII) to prepare the new metal complexes of polymer (PIV) and (PV), respectively as shown in (**Scheme-II**). The precipitated chelating polymers (PII) and (PIII) were creamy in colour, but nevertheless it could not be redissolved in any of a range of organic solvents. The reason for this insolubility is not too surprising, since the polymer products undergoes crosslinking. Therefore, the synthesis of the desired metal complexes of polymers (PIV) and (PV) were carried out by adding a hot clear solution of the metal acetate in ethanol to the refluxed mixture solution of the anhydride precursor polymer (PI) and the chelating group used in dry DMF, the experimental procedure adopted is described in the experemental part. The isolated monomers, polymers and their metal complexes were

TABLE-1
ANALYTICAL DATA FOR MONOMERS (II) AND (III) AND POLYMERS (PII) and P(III) AND THEIR METAL COMPLEXES

Compound	Colour	Calcd. (Found) %			X (%)
		C	H	N	
$[C_{25}H_{26}N_4O_4S]$,(II)	White	62.60 (62.60)	5.40 (4.10)	11.70 (10.70)	6.70[a] (6.90)
$[Cu_2(II)(H_2O)_4(OAc)].2H_2O$	Dark-green	40.24 (40.20)	4.70 (3.70)	6.90 (5.80)	-
$[Co(II)(H_2O)_2]$	Dark-brown	51.03 (51.10)	4.20 (3.30)	9.50 (8.80)	-
$[Ni_2(II)(H_2O)_4].4H_2O$	Dark-brown	37.30 (37.80)	4.70 (5.30)	6.90 (5.80)	24.10[b] (24.50)
$[C_{25}H_{26}N_4O_4S]_n$,P(II)	Cream	62.60 (62.50)	5.40 (6.40)	11.60 (12.40)	6.70[a] (7.00)
$[Cu_2(PII)(H_2O)_4].3H_2O$	Dark-green	42.10 (41.80)	4.70 (4.40)	7.80 (7.60)	-
$[Co_2(PII)(H_2O)_4].4H_2O$	Dark-brown	40.70 (40.90)	4.70 (4.40)	7.80 (7.60)	-
$[Ni_2(PII)(H_2O)_4].4H_2O$	Dark-brown	37.00 (36.40)	3.50 (3.60)	8.70 (9.10)	18.60[b] (18.10)
$[C_{28}H_{28}N_6O_6S_2]$,(III)	White	55.26 (55.60)	4.60 (5.30)	13.80 (13.50)	9.53[a] (8.50)
$[Cu_2(II)(DMSO)_2]$	Green	43.20 (43.50)	4.30 (4.10)	9.50 (10.50)	-
$[Ni_4(III)(OAc)_2(H_2O)_8].2H_2O]$	Brown	32.60 (32.70)	4.50 (5.30)	-	25.00[b] (24.50)
$[C_{25}H_{26}N_4O_4S]_n$,P(III)	Cream	55.26 (55.70)	4.60 (5.00)	13.80 (12.30)	10.50[a] (10.60)
$[Cu_4(PIII)(H_2O)_8].4H_2O$	Dark Green	31.17 (31.10)	-	10.30 (10.70)	29.50[b] (28.50)
$[Co_2(PIII).2(H_2O)]$	Dark-brown	44.20 (44.60)	4.20 (4.50)	11.00 (10.00)	19.70[b] (20.10)
$[Ni_2(PIII).4(H_2O)]$	Dark-brown	42.10 (42.10)	4.50 (4.70)	10.50 (10.20)	18.90[b] (19.20)

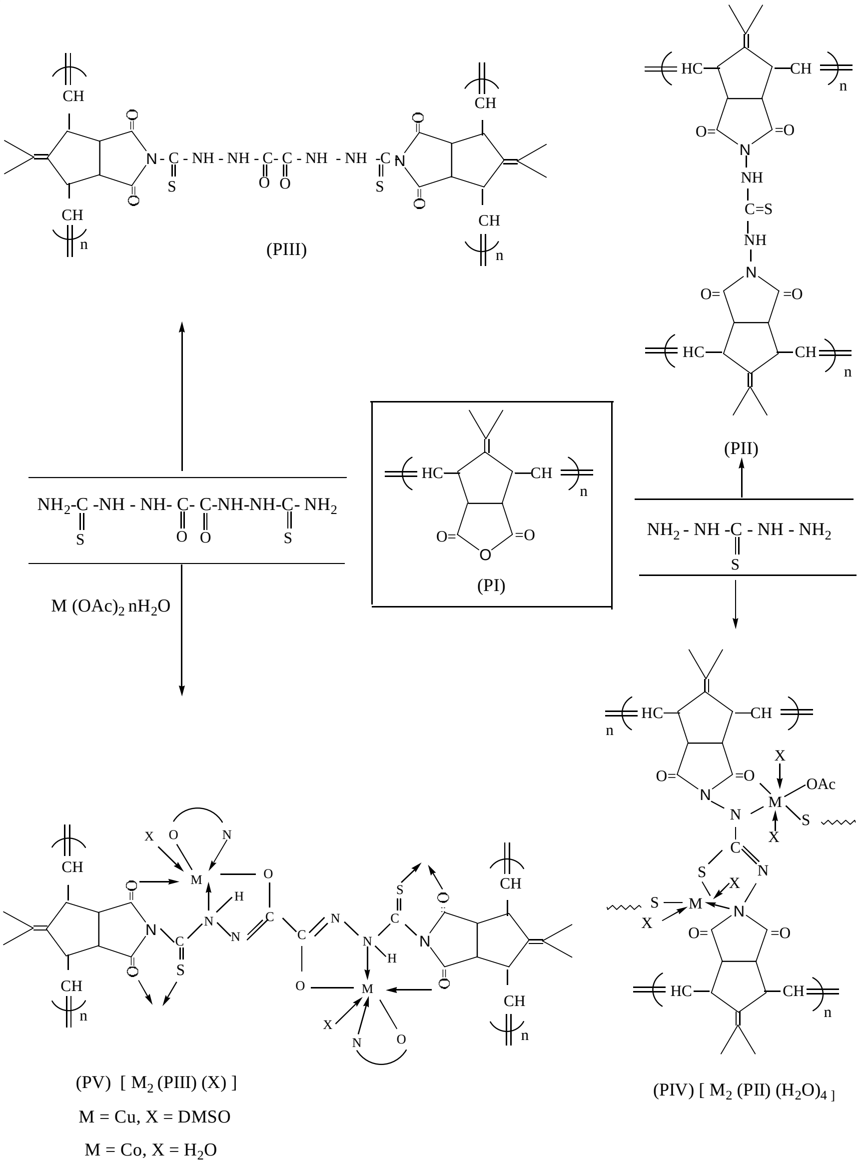
X = [a]sulpher, [b]metal oxide

characterized by elemental analysis, IR, TG and DTG measurements. The result of elemental analysis of all the isolated materials are in reasonably good agreement with the calculated values (Table-1). The proposed structure of the collected complexes were listed in **Schemes I-III**.



(Scheme-1)

Infrared spectral analysis for monomers and polymers: Infrared spectra of the monomers (II), (III), polymers (PII) and (PIII) are recorded which indicated that the four infrared spectra have common features. They show the expected frequencies consistent with the proposed structure. The spectra show the expected C-H vinylic absorptions above 3000 cm^{-1} and the unsaturated aliphatic C-H absorptions in the region between 2900 and 2800 cm^{-1}. The IR spectrum of monomer (II) exhibited ν(N-H) absorption bands at 3172 and 3228 cm^{-1} and strong absorption bands at 1736 and 1700 cm^{-1} due to the ν(C=O) vibrations. The bands at 1197 and 800 cm^{-1} may be assigned to thioamide ν(C=S) vibrations[4,9]. In the polymers spectra there are a broad bands in the 2931 and 3448 cm^{-1} region which were probably due to ν(C-H) and ν(N-H) vibrations, respectively. The C-H out of plane vinylic C-H bending modes occur at 980 (*trans*) and *ca.* 640 cm^{-1} (*cis*)[12].



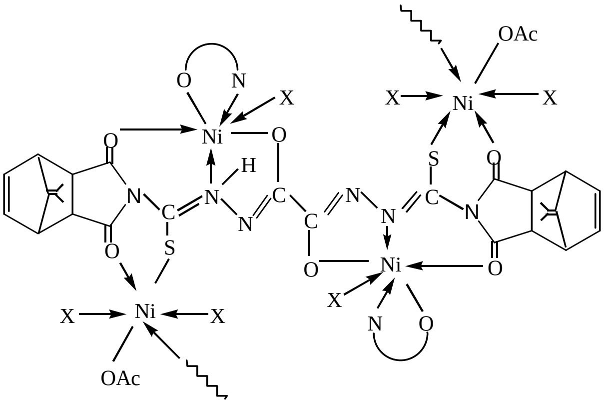
(PIV) [M_2 (PII) $(H_2O)_4$]

(PV) [M_2 (PIII) (X)]

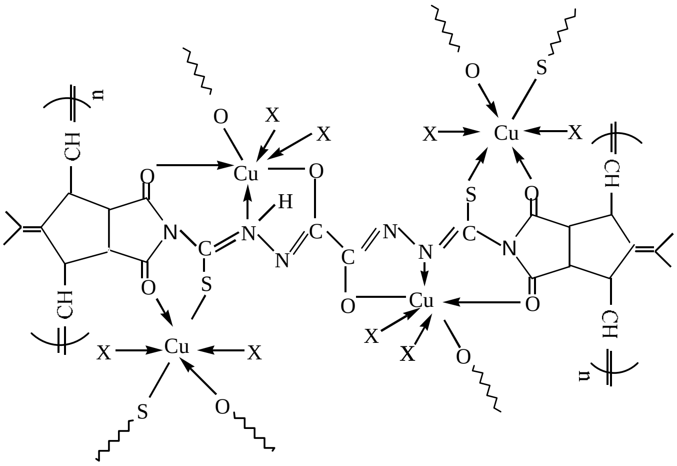
M = Cu, X = DMSO

M = Co, X = H_2O

Scheme-II



[Ni_4(III) $(AcO)_2$ $(H_2O)_6$].$2H_2O$; X=H_2O



[Cu_4(PIII) $(H_2O)_8$].$4H_2O$; X=H_2O

(Scheme-III)

Proton and carbon nuclear magnetic resonance: ^{1}H NMR spectra of monomer (II) and (III) were in agreement with the structures proposed and showed a generally similar pattern of chemical shifts and intensities as reported earlier[2,12,13]. The ^{1}H-NMR chemical shifts of monomers (II) and (III) are recorded in Table-3. An examination of the ^{1}H NMR spectrum of monomer(II) showed resonance at 2.12 ppm due to the methyl protons, at 4.35 ppm due to the four methine protons adjacent to the olefinic groups, the other four methine protons adjacent to (C=O) appear at 4.79 ppm. The vinylic signal appears as a doublet at 7.70 and 8.10 ppm and another signal at 9.9 ppm may be due to the (N-H) protons. ^{1}H NMR spectrum of monomer(III) is similar to the spectrum of monomer(II). Monomer(III) has one extra band due to the NH protons adjacent to the (C=O) group at 6.40

ppm, this proton has resonance interaction with the adjacent carbonyl group. The chemical shifts and assignments based on ^{13}C NMR spectra of compound (III) are recorded in Table-4. The spectra showed signals at 19 ppm assigned to the methyl carbons, signals at 44.68 and 45.64 ppm were assigned to the methine carbons C1, C4 and C5, C6, respectively, lower intensity signals in the low field region at 117.59, 139.97 and 181.19 ppm. were assigned to the two quaternary carbons C7, C8 and the thiocarbonyl carbon C11, respectively[2]. The carbonyl carbon C10 in the low field region appears at 174.12 ppm. No NMR spectra of insoluble polymers (PII), (PIII) and their metal complexes were obtained.

TABLE-2
INFRARED BANDS (cm^{-1}) AND ASSIGNMENTS FOR MONOMERS, POLYMERS AND THEIR METAL COMPLEXES

Compound	ν(C=O)	ν(C=S)	ν(S-C=N)	ν(N-N)	ν(C-S)	ν(M-S)	ν(M-N)
$C_{25}H_{26}N_4O_4S$ (II)	1735	705	-	1000	-	-	-
$[Cu_2(II)(H_2O)_4(OAc)].2H_2O$	1718	-	1618	1034	629	468	433
$[Co(II)(H_2O)_2]$	1716	-	1613	1039	638	463	449
$[Ni_2(II)\ ((H_2O)_4].4H_2O$	1716	-	1615	1031	637	464	453
$[C_{25}H_{26}N_4O_4S]_n$ (PII)	1738	708	-	995	-	-	-
$[Cu_2(II)(H_2O)_4].3H_2O$	1715	-	1619	1029	637	470	433
$[Co_2(II)(H_2O)_4].4H_2O$	1716	-	1618	1031	639	469	445
$[Ni_2(II)(H_2O)_4].4H_2O$	1716	-	1620	1028	636	465	448

TABLE-3
^1H NMR SHIFTS FOR COMPOUNDS (II) AND (III) MEASURED 100 MH$_z$ RELATIVE TO INTERNAL TMS IN DMSO

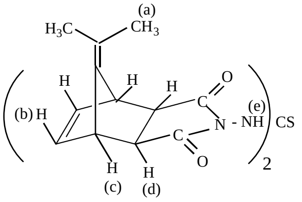
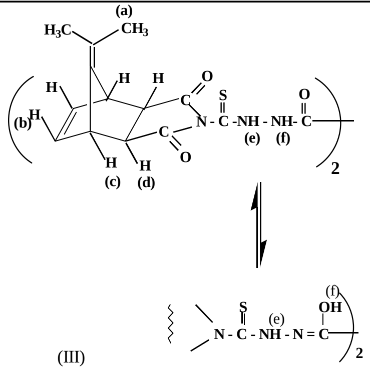
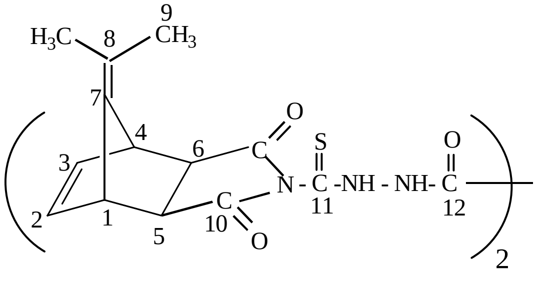
Compound	Shift (multiplicity)	Integral	Assignment
 (II)	2.12 (s)	12	H(a)
	4.35 (s)	4	H(c)
	4.79 (s)	4	H(d)
	7.90 (d)	4	H(b)
	9.93 (s)	2	H(e)
 (III)	1.50 (s)	12	H(a)
	2.70 (s)	4	H(c)
	3.59 (s)	4	H(d)
	6.40 (t)	2	H(f)
	7.98 (d)	4	H(b)
	10.12 (s)	2	H(e)

TABLE-4

^{13}C NMR SPECTRUM RECORDED AT 400 MHz IN DMSO OF MONOMER (III)

Compound	Shift	Assignment
	19.06	C 9
	44.68	C 1,4
	45.64	C 5,6
	117.59	C 8
	137.19	C 2,3
	139.97	C 7
	174.12	C 10,12
(III)	181.19	C 11

Infrared for the isolated monomer and polymer complexes: The spectral data show that monomer(II) and polymer(PII) are coordinated to the metal ions *via* the nitrogen atom and the thioenol sulfur atom (=C-SH) with the displacement of the hydrogen ion from the latter group forming a five membered ring. This mode of chelation (Table-2) is supported by the following evidence: (i) the disappearance of ν(C=S) with the appearance of new bands in the 1618 and 1615 cm^{-1} regions assigned to ν(S-C=N)[15,16] and ν(C-S)[17,18], respectively; (ii) ν(N-N) shifts to a higher wave number from 1000 to 1039 cm^{-1}; (iii) the appearance of a new bands in the regions 500-460 and 450-440 cm^{-1} assigned to ν(M-S) and ν(M-N)[19]. The principle characteristic infrared bands for this polymer (PIII) appears at 3320 cm^{-1} due to ν(NH) absorption, CH stretches at 2978 and 2925 cm^{-1} and at 1758 and 1730 cm^{-1} attributed to the carbonyl vibrations. The spectrum also shows two bands at 715 and 1250 cm^{-1} assignable to ν(C=S) vibrations band (I) and thioamide band (II)[20]. The other thioamide band, [ν(C-N) + ν(C=S)] (III), are observed at 930 cm^{-1}. The keto-enol and thioketo-thioenol forms are a possible tautomeric forms for the polymer structure[21].The chelating polymer (PIII) reacts with metal(II) acetates to give a polynuclear 4:1 metal to ligand molar ratio of repeating unit giving a neutral polymer complexes of the general formula $[Cu_4(PIII)(H_2O)_8].4H_2O$. In this complex, the polymer acts as a tetrabasic acid links to four copper(II) ions and another polymer molecules to neutralized the charges of the copper(II) ions forming a cross linking[22-28]. The octahedral structures completed with a water molecules inside the coordination sphere. The polymer ligand material coordinates via the oxygen of the carbonyl group and the sulfur atom (OS) donors forming a stable one six membered ring and *via* the oxygen of enolic carbonyl group and the nitrogen of the azo methine group (ON) donors systems forming two five-membered rings with the formation of a conjugated system as shown in (**Scheme-III**). The complexes formed are very stable at room temperature and do not show any decomposition after a long period of standing.

Thermal analysis: The thermal analysis of the prepared, monomers (II), (III), polymers (PII) and (PIII) and their metal complexes Cu(II), Co(II) and Ni(II) were studied using TG and DTG techniques as shown in Figs. 1-4. The thermal diagram of Ni(II) complex of P(II), $[Ni_2P(II)(H_2O)_4].4H_2O$ show exothermic peaks at 99, 186, 319 and 494°C corresponding to hydrated, coordinated water, decomposition of the organic material and final formation of metal oxide, respectively, described as follows. The thermograms of $[Ni_2P(II)(H_2O)_4].4H_2O$ shows a weight loss at 99 and 189°C, (calcd.: 17.98; found; 19.1 %) corresponding to loss of hydrated and coordinated water form the polymer complex unit[23-26]. The anhydrous polymer complex begins to decompose above 190°C, a process continuing up to 494°C and corresponding to the decomposition of the organic part (calcd.; 61.9; found 62.4 %). Above 500°C, a stable steady state was observed. The remaining masses of (PII) metal acetate polymer complexes, which can be considered as metal oxides, are in good agreement with those calculated, (NiO calcd.: 18.6; found; 18.1 %). A similar behaviour for other thermograms were observed where the remaining masses of the polymer complexes considered as metal oxides are in good agreement with the calculated values. All the evidence gathered from elemental analysis, IR and thermal studies suggest the general formula $[M_2(II)(H_2O)_4].nH_2O$ and $[M_2(PII)(H_2O)_4].nH_2O$ for the monomer and polymer complexes, respectively. The TG curves of monomers, polymers and their metal complexes (Figs. 1-4) indicate that the polymer complexes are more stable than the uncoordinated polymers. This higher stabilities of the polymer complexes may be due to the formation of stable five and six membered ring structures in the polymer complexes[25,26].

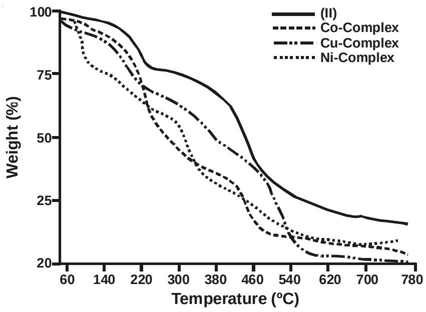


Fig. 1. The TG Thermogram of monomer (II) and its metal complexes

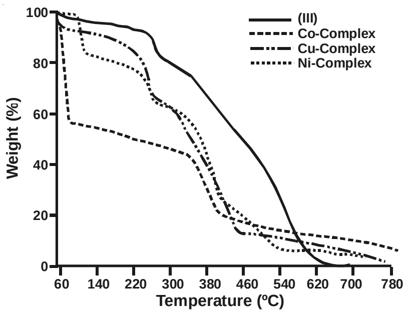


Fig. 2. The TG Thermogram of monomer (III) and its metal complexes

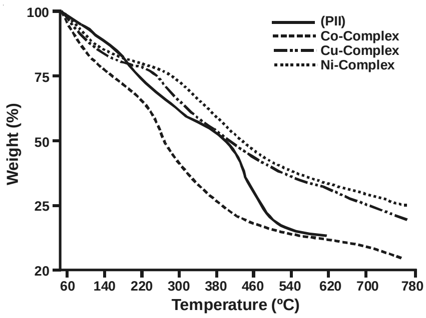


Fig. 3. The TG Thermogram of monomer (PII) and its metal complexes

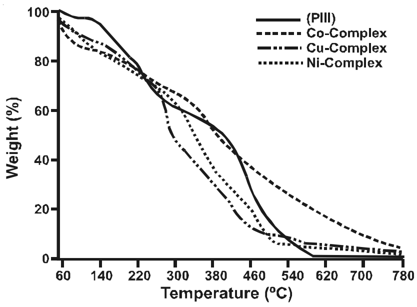


Fig. 4. The TG Thermogram of monomer (PIII) and its metal complexes

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