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Polymer Complexes. LVI. Supramolecular Architectures Consolidated by Hydrogen Bonding and p-p Interaction.

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Polymer complexes. LVI. Supramolecular Architectures Consolidated by Hydrogen Bonding and π - π Interaction

التركيب البنائي لبعض مترابطات البوليمرات المدعومة بروابط هيدروجين (روابط باي - باي)

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الملخص العربي

تمت دراسة مترابطات البوليمرات المدعومة بروابط هيدروجين وخصوصاً كيميائية التركيب البنائي وقياس الثبات الحراري لها. وقد تم تحضير وإثبات التركيب البنائي لمترابطات بوليمرات ن - اكريلويل هيدرازين. تم تعيين طاقة التنشيط للتكسير الحراري للهوموبوليمر ومترابطته ووجد أنها تزداد بنفس رتبة الثبات الحراري.

Abstract

In this study, amidation of aliphatic amine with acryloyl chloride in the dry benzene as solvent has been prepared. Moreover, the polymer complexes have been prepared. All compounds have been characterized by the analytical, spectroscopic (IR, UV, NMR, ESR) and thermal methods. Addition, the magnetic susceptibility and molar conductance measurements have been made. Acryloylhydrazin (AH) has been shown to behave as a bidentate ligand *via* its nitrogen (of the NH_2 of hydrazine group) and C-O/C=O (of the acryloyl group) in polymer complexes, all of which exhibit supramolecular architectures assembled through weak interaction including hydrogen bonding and π - π stacking. The magnetic and spectral data indicate a square planar geometry for Cu^{2+} complex and an octahedral geometry for Co(II) and $\text{UO}_2(\text{II})$. The ESR spectral data of the Cu(II) complexes showed that the metal-ligand bonds have considerable covalent character. The thermal stability was investigated using thermogravimetric analysis. The results showed that the polymer complexes are more stable than the homopolymer.

Keywords: Poly(acryloylhydrazin) homopolymer, supramolecular polymer complexes; and thermal analysis.

1. Introduction

Polymer-metal complexes are currently attracting considerable attention for a variety of application [1-7], like development in nuclear chemistry, organic synthesis, waste water treatment, pollution control, hydrometallurgy, polymer drug grafts, preconcentration and recovery of trace metal ions. In addition, they are also used as mechanochemical systems and as models of bio-inorganic systems. A number of polymer-bound chelating ligands, including polydentate amines, crown ethers and porphyrins, have been reported [8,9]. The free radical polymerization of metal complex with Schiff's base/monomers ligand containing the vinyl group and radical polymerization of methacrylate monomers coordinated to transition metal have been studied [10-14]. The preparation of functional polymers by chemical modification is an important technique, which has been used extensively both industrially to modify the properties of the polymers for various technological application and in the area of polymer-supported chemistry to prepare chemically reactive polymers [15-17].

Coordination polymers are useful as engineering materials [18] and find an important

place in material chemistry [19-21]. The coordination chemistry of metals are vast to its ability to form complexes with different coordination numbers [22-25]. The preparation of functional polymers by chemical modification is an important technique, which has been used extensively both industrially to modify the properties of the polymers for various technological applications and in the area of polymer-supported chemistry to prepare chemically reactive polymers. The reaction of metal ions with polymeric ligands containing pendant functional groups which act as chelating groups in binding polyvalent metal ions, produces coordinated systems with enhanced thermal stability and thereby improved chemical resistance [26,27].

In the laboratories of Diab and El-Sonbati, the coordinating behaviour, chemical equilibria and thermal analysis of mixed-ligand homopolymer, novel mixed-valence-ligand homopolymer and novel mixed-metal-ligand homopolymer complexes have been investigated in depth [28-30]. In this work, the characterization and thermal stability of poly(acryloyl hydrazine) and its complexes have been studied.

2. Experimental

2.1 Materials

Acryloyl chloride (AC), 2,2'-azobisisobutyronitrile (AIBN) (Estman Kodak) was used as initiator for all polymerizations. It was purified by dissolving in hot ethanol and filtering [31]. Hydrazine (BDH Chemical Ltd.) was used without further purification. Copper(II), cobalt(II), nickel(II), cadmium(II) and uranyl salts (BDH Chemical Ltd.) were purified by drying under vacuum, any previously absorbed water being condensed in a liquid nitrogen trap, and stored in a desiccator over P_2O_5 . All other chemicals and solvents were purified by standard procedures.

2.2 Preparation of acryloyl hydrazine (AH) monomer and poly(acryloyl hydrazine) (PAH)

AH monomer was performed by the reaction of equimolar amounts of AC and hydrazine in the presence of hydroquinone as inhibitor and dry benzene as solvent.

PAH homopolymer was prepared by refluxing the monomer with dimethylformamide (DMF) as solvent and 0.1 w/v % AIBN as initiator for 6 h. The polymer product was precipitated by pouring in distilled water. The precipitated polymer was filtered, washed several times with ether and dried under vacuum for several days.

2.3 Preparation of polymer complexes

Polymer complexes were prepared by dissolving equimolar amounts of AH and the metal salts in DMF as a solvent. Complexes were precipitated by pouring it into a large excess of distilled water containing dilute hydrochloric acid to remove all the metal salts incorporated in the polymer complexes. The precipitated polymer complexes were filtered, washed several times with ether and dried under vacuum for several days with 0.1% w/v AIBN as initiator. The mixture was refluxed for ~ 6 h and the resulting polymer.

2.4 Measurements

C, H, and N microanalyses were carried out at the Cairo University Analytical Center, Egypt. The metal content in the polymer complexes was estimated by standard methods. The metal content in the polymer complexes was estimated by standard methods [10-15].

The 1H -NMR spectrum was obtained with a Jeol FX90 Fourier transform spectrometer with DMSO- d_6 as the solvent and TMS as an internal reference. Infrared spectra were recorded using Perkin-Elmer 1340 spectrophotometer. Ultraviolet-Visible (UV-Vis) spectra of the polymer were recorded in nuzol solution using Unicam SP 8800 spectrophotometer.

The magnetic moment of the prepared solid complexes was determined at room temperature using the Gouy's method. Mercury(II) (tetrathiocyanato)cobalt(II), $[Hg\{Co(SCN)_4\}]$, was used for the calibration of the Gouy tubes. Diamagnetic corrections were calculated from the values given by Selwood [32] and Pascal's constants. Magnetic moments were calculated using the equation, $\mu_{eff} = 2.84 [T\chi_M^{corr}]^{1/2}$. EPR measurements of powdered samples were recorded at room temperature (Tanta University, Egypt) using an X-band spectrometer utilizing a 100 KHz magnetic field modulation with diphenylpicrylhydrazyle (DPPH) as a reference material. TG measurements were made using a Du Pont 950 thermobalance. Ten milligram samples were heated at a rate of 10 °C/min in a dynamic nitrogen atmosphere (70 ml/min); the sample holder was boat-shaped, 10 x 5 x 2.5 mm deep; the temperature measuring thermocouple was placed within 1 mm of the holder. The halogen content was determined by combustion of the solid complex (30 mg) in an oxygen flask in the presence of a KOH- H_2O_2 mixture. The halide content was then determined by titration with a standard $Hg(NO_3)_2$ solution using diphenyl carbazone indicator.

3. Results and Discussion

The novel M(II)/(III) polymer complexes were synthesized from bidentate ligand acryloylhydrazine (AH). The IR spectrum of ligand does not show band at 3500 cm^{-1} corresponding to OH group. This indicates that the ligand exist in ketonic form in solid state. However the 1H NMR spectrum of ligand shows a singlet at 10.2 ppm corresponding to OH group which suggest the existence of ligand in enolic form in solution. (Fig. 1). The molar conductivities in DMF solution indicate that the polymer complexes are in the range expected for non-electrolytes [19]. All of the polymer complexes are stable at room temperature and do not undergo any decomposition for a long time, and remarkably soluble in DMSO and DMF. The value of magnetic moments calculated with the help of measured value of magnetic susceptibility indicates that the polymer complexes are paramagnetic in nature except Cd(II) and $UO_2(II)$ polymer complexes. Analytical data of the ligand and their polymer complexes are given in Table 1 and are in well agreement with the expected values. [see Fig. 2].

The 1H NMR spectrum of PAH homopolymer exhibit three broad signals centered

at NH_2 (5.3), OH (10.2 and imino protons (11.7) ppm assigned for hydrogen bonded OH or NH protons (Fig. 1). This signals were disappeared in the presence of D_2O . The spectrum exhibit also a singlet at δ 2.2 and δ 1.9 ppm correspond to methylene and methane protons, respectively, are in agreement with the presence of AH in its enolic form in solution.

The NMR spectrum of AH monomer showed the expected peaks and pattern of the vinyl group ($\text{CH}_2=\text{CH}$), i.e. $\delta(\text{DMSO}-d_6)$ 6.25 ppm (dd, $J=17, 11$ Hz) for the vinyl CH proton and proton δ 5.12 ppm (AM part of AMX system dd, $J = 17, 1$ Hz) for the vinyl CH_2 protons, respectively. These peaks disappeared on polymerization while a triplet at δ 1.86 ppm (t, $J=7$ Hz) and a doublet at 1.80 ppm (d, $J=7$ Hz) appeared. This indicates that the polymerization of AH monomer occurs on the vinyl group [22,23]. It is worth noting that the rest of the proton spectrum of the monomer and polymer remain almost without change.

3.1 Magnetic and electronic spectral studies

3.1.1 Copper(II) polymer complexes

The room temperature magnetic moments for copper(II) polymer complexes (Table 2) are 1.85 and 1.79 B.M. for polymer complexes, (2) (structure I, Fig. 2) and (3) (structure III, Fig. 2), respectively, characteristic of one unpaired electron. This indicates the presence of low-lying excited term, which mixes some of its orbital angular momentum with the spin angular momentum of the ground state via spin orbital coupling [33]. This mixing is quit common for copper(II) complexes with distorted ligand fields [33].

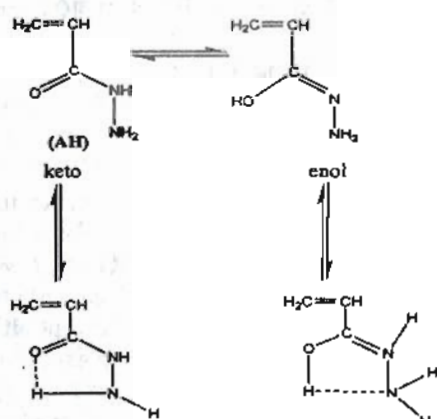


Fig.1. Synthesized monomer AH in tautomeric form

The electronic spectra of both polymer complexes are similar and display bands at 16400, 15300 cm^{-1} (${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$) for chloro complex (structure I, Fig. 2) and at 16550, 15050 cm^{-1}

(${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$) transitions, for the acetate complex (structure III, Fig.2) (Table 2), in D_{4h} symmetry. These bands are due to d-d transitions and consistent with that reported for copper(II) ions in square planar ligand fields [34] with a bidentate and/tridentate ligands. In square planar field three possible transitions are expected. The third band due to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ could not be identified but it may be responsible for the asymmetric nature of the lower energy band.

3.1.2 ESR spectra

The spectra of the copper(II) polymer complexes (2 & 3) show typical axial behaviour with slightly different g_{\parallel} and g_{\perp} values. In these Cu(II) polymer complexes tensor values of $g_{\parallel} > g_{\perp} > g_e$ (2.0023), are consistent with a $d_{x^2-y^2}$ ground state [13]. The geometric parameter G , which is a measure of the exchange interaction between the copper centers in the polycrystalline compound, is calculated using the equation reported by others [13]. If $G > 4$, exchange interaction is negligible (2 & 3), but if $G < 4$, considerable exchange interaction is indicated in the solid complex.

The various Hamiltonian parameters have been calculated for polymer complexes [$g_{\parallel} = 2.321$, $g_{\perp} = 2.078$, $A_{\parallel} = 145$ for (2) and $g_{\parallel} = 2.330$, $g_{\perp} = 2.071$, $A_{\parallel} = 145$ for (3)]. It has been reported that g_{\parallel} values of copper(II) complexes can be used as a measure of the covalent character of the metal-ligand bond. If the value is more than 2.3, the metal-ligand bond is essentially ionic and the value less than 2.3 is indicative of covalent character [13]. A part from this, the covalency parameter (α^2) has been calculated using Kivelson and Neiman equation [35]. The covalency parameter [$\alpha^2 = 0.795$ for (2) and 0.803 for (3)] indicates considerable covalent character for the metal-ligand bond [13]. Also, The trend $g_{\parallel} > g_{\perp} > g_e$ observed for this complexes indicated that the unpaired electron is most likely in the $d_{x^2-y^2}$ orbital. The empirical ratio $g_{\parallel}/A_{\parallel}$ is frequently used to evaluated distortions in tetracoordinated copper(II) complexes [36]. The values of the $g_{\parallel}/A_{\parallel}$ ratio for polymer complexes (2 & 3) (ca. 160) indicate nearly square planar, environments. Based on this observation, a square planar geometry is proposed for the polymer complexes. The ESR study of the copper(II) polymer complexes has provided supportive evidence to the conclusion obtained on the basis of electronic spectra and magnetic moment values.

3.1.3 Cobalt(II) polymer complexes

Co(II) polymer complex (4) (Structure II, Fig. 2) (Table 2) exhibits a typical spectrum for octahedral

species in the solid state [34,37]. Two main bands (ν_2 and ν_3) transitions are observed, the band ν_1 , due to transition ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ which is usually under 10000 cm^{-1} , as ligand field parameters, $10Dq$, B and β were calculated using the following equations the following equations:

$$10Dq = 1/3(2\nu_2 - \nu_3) + 5B$$

$$B = 1/510[7(\nu_2 - 2\nu_3) \pm 3\{81\nu_3^2 - 16\nu_2(\nu_2 - \nu_3)\}^{1/2}]$$

$$10Dq = \nu_2 - \nu_1$$

$$340Dq^2 - 18(\nu_2 + \nu_3)Dq + \nu_2\nu_3 = 0$$

$$B = 1/15(\nu_3 + \nu_2 - 30Dq)$$

$$\beta = B/B^0$$

The calculated values of the ligand field parameters are in good agreement with the predicted values for octahedral polymer complexes of Co(II) [38]. The nephelauxetic ratio β for the polymer complex (4) suggesting an ionic character of cobalt(II)-ligand bonds [39]. The room temperature magnetic moment value, 5.23 B.M. demonstrates that the Co(II) polymer complex is paramagnetic and has a high-spin octahedral configuration.

3.1.4 Nickel(II) polymer complex

The electronic spectrum of AH-NiCl₂ polymer complex (5) (Table 2) shows bands at 17100 and 27700 cm^{-1} characteristic of a distorted octahedral structure. They may be assigned to the ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition, respectively. There is also a band at 22720 cm^{-1} similar to the one reported for square planar Ni(II) complexes and may be assigned to a ${}^3A_{1g} \rightarrow {}^1B_{2g}$ transition (40). Although such transition is expected to be forbidden according to the selection rules, some intensity comes to this band from the near stronger one (34). The magnetic moment of the AH-NiCl₂ polymer complex as represented in Table 2 was found to be 1.89 BM, suggesting that the complex forms a mixture of octahedral and square planar structures.

3.1.5 Iron(III) polymer complex

The spectrum of AH-FeCl₃ (6) (structure V, Fig. 2) (Table 2) display bands at 15680, 19980 and 22720 cm^{-1} . The room temperature magnetic moment of 2.2 B.M. indicates a low spin octahedral iron(III) complex [41]. In an octahedral ligand field around iron(III), the in the 16000-21000 cm^{-1} range are commonly due to $L \rightarrow M$ CT transition [34]. Also, in this iron polymer complex, the shoulder at 15680 and the band at 19980 cm^{-1} are due to ${}^2T_2 \rightarrow {}^4A_2$ and $\pi-t_{2g}$ transitions.

The spectrum of the Cd(II) polymer complex (7) (structure I, Fig. 2) exhibited bands assigned to ligand $\pi-\pi^*$ and $L \rightarrow M$ charge transfer [34]. This polymer complex is diamagnetic as expected. The metal normally prefer tetrahedral coordination.

3.2 IR spectra

The IR spectrum of ligand exhibits bands at 3350 (w), 3280 (w); 1650 (s); 810 (s), 515 (m) and 495 (m) cm^{-1} [42], due to different modes of vibrations of NH₂ group, namely ν , δ , γ , and ρ . These bands are affected in position and shape on complexation with metal ions. So, the NH₂ group (exocyclic NH₂ nitrogen) is coordinated to the metal ion in polymer complexes [40]. The shift of band (NH₂) at 672 cm^{-1} on complexation indicated that the NH₂ is involved in chelation [43]. In the IR spectra of the polymer complexes (except 3, 6 and 8) the $\nu_{C=O}$ (1661 cm^{-1}) stretching vibration corresponding to the free ligand are not observed. This fact, along with the presence of a medium intensity band in 1385-1395 cm^{-1} range, assignable to ν_{C-O} , indicates that the deprotonated ligand is predominantly in the enolate in the polymer complexes (see Fig. 1). These observations support the formation of M-O bonds via deprotonation. So, the H-bond-OH group has been replaced by the metal ion. On complex formation, there is also a characteristic band at $\sim 1635\text{ cm}^{-1}$ due to C=N group.

The IR spectra of copper and uranyl acetate polymer complexes show downward shift in $\nu(C=O)$ and $\nu(NH_2)$ in comparison with the free ligand. This is indicating coordination through oxygen and nitrogen, respectively [42]. Hence, it may be concluded that in these polymer complexes, the ligand is behaving as neutral bidentate ON donor through the exocyclic oxygen and the terminal nitrogen of hydrazine. The bands corresponding to $\nu(M-N)$ and $\nu(M-O)$ are observed in the range 343-464 cm^{-1} and 450-550 cm^{-1} [44].

The dioxouranium(VI) compound (7) exhibits $\nu_{sym}(O=U=O)$ and $\nu_{asym}(O=U=O)$ at 794 and 916 cm^{-1} , respectively, the usual range for such complex [13,27] being ν_{asym} 870-950 and ν_{sym} 780-855 cm^{-1} . The force constant (F_{U-O}) value is 6.78 mdynes/\AA , which agree well with the force constant values of similar dioxouranium(VI) complexes [13,27]. The U-O bond distance calculated from the equation,

$$R_{U-O} = 1.17 + 1.08 f^{1/3}$$

is 1.73 \AA , well within the usual range (1.60-1.9 \AA) observed for dioxouranium(VI) complexes [13,27]. The dioxouranium complex exhibits a new band at 24690-24510 cm^{-1} , which is assigned to the ${}^1\Sigma_{gu} \rightarrow {}^3\pi_u$ transition, typical of OUO for the symmetric stretching frequency for the first excited state.

The elemental analysis, IR, and the electronic spectra data indicate that AH reacts with $\text{CuCl}_2/(\text{OAc})_2$, FeCl_3 and CdCl_2 in a 1:1 ratio (structure I, III & V, Fig. 2))

and with CoCl_2 and $\text{UO}_2(\text{OAc})_2$ in 2:1 molar ratios (structures II & IV, Fig. 2). The AH- NiCl_2 polymer complex is a mixture of both structures (I and II).

3.2.1 Vibration modes of the inorganic co-ligand

The acetate polymeric complexes display bands at 1642-1638 and 1355-1348 cm^{-1} due to the symmetric and asymmetric stretching vibrations of the acetate group [7] with $\Delta\nu = 290 \text{ cm}^{-1}$ characteristic for monodentate nature of this group [7]. The Fe(III) polymer complex show (Fe-Cl) frequencies that seem too low for terminal Fe-Cl bonds and corresponding to bridging chlorine ($\sim 236 \text{ cm}^{-1}$) groups. However, bands in the region 355-385 cm^{-1} may be attributed to terminal Fe-Cl groups, to which there are no corresponding ligand bands. These assignments are in good agreement with the assignment given by Woodward and Taylor [45] and El-Sonbati [28]. The chloro polymeric complexes exhibit new bands at 275-305 cm^{-1} characteristic of terminally coordinated chloride ions. The IR spectra of polymer complexes 2, 4 and 7 show broad troughs in the region 3650-3350 cm^{-1} indicative of $\nu(\text{OH})$ of coordinated water [6,7,13] as confirmed by thermal analysis. The rocking mode of coordinated water is also observed in the range 985-905 cm^{-1} [6,7,13]. The non-ligand bands in the range of 520-280 cm^{-1} are due to $\nu(\text{M-N})$, $\nu(\text{M-O})$ and $\nu(\text{M-Cl})$ vibrations [6,7,13,42].

We have recently reported seven polymer complexes of acryloylhydrazin (AH) generated with CuCl_2 , $\text{Cu}(\text{OAc})_2$, NiCl_2 , CoCl_2 , CdCl_2 , FeCl_3 and $\text{UO}_2(\text{OAc})_2$, all of which exhibit an infinite chain structure with AH acting as the bridging ligand [7,44]. The Supramolecular assembly in these polymer complexes via weak interactions such as hydrogen bonding and π - π stacking interaction is worthy of note.

Fig 2. shows the coordination environment of the metal centers in the polymer complexes. The metal atoms in structures (II, IV & V) both adopt octahedral coordination geometry; in II, it is coordinated to two pairs of trans-related ligands, namely aqua ligands, monodentate; in IV it is surrounded by a four pairs of chloro groups and two AH ligands in trans positions. The Cu(II) atom in III exhibits a square planar coordination geometry, binding to a two pairs of acetate groups and on AH ligand in cis-positions.

In our previously reported metal polymer complexes of acryloylhydrazin, the nitrogen atom (of NH_2 of the hydrazine group) and the carbonyl group (of the acryloyl group) in an individual ligand AH are consistently cis-related, while in polymer

complexes (structure II, IV & V), they are trans-related as shown in Fig. 2.

The IR spectra of these polymer complexes show significant differences in the vibrational modes of ligand AH.

3.3 Thermal methods of analysis:

DTA traces of PAH homopolymer and AH with CuCl_2 , CoCl_2 , NiCl_2 and CdCl_2 polymer complexes are illustrated in Figure 3. Two endothermic peaks are clearly visible. Their relative importance being dependent upon the type of polymer complexes. The T_{max} for each peak is shown on the traces, which are comparable to those of the corresponding polymers.

TG curves of PAH homopolymer and polymer complexes of AH with CuCl_2 , CoCl_2 , NiCl_2 and CdCl_2 are shown in Figure 4. PAH homopolymer degrades in two stages. The first starts at $\sim 112 \text{ }^\circ\text{C}$ with a weight loss of 47% and the second at $\sim 235 \text{ }^\circ\text{C}$ with a weight loss of 45 %. In the AH- CuCl_2 , AH- CoCl_2 , AH- NiCl_2 and AH- CdCl_2 polymer complexes, there are three degradation steps. The first stage at 130, 127, 128 and 132 $^\circ\text{C}$, respectively due to coordinated water molecules. Table 3 lists the percentage of weight losses for each polymer complex and the maximum rate of weight loss shown by the derivative equipment associated with the TG apparatus. The final weight of residues, which can be considered as metal oxide, are in good agreement with those calculated from the metal content using EDTA.

The polymer complexes are more stable than PAH homopolymer. This is similar to the results obtained by Diab et al. [47,48] with polymer complexes derived from 5-vinylsalicylaldehyde and 5-vinylsalicylidene anthranilic acid with some transition metal salts. The stabilities of the polymer complexes of AH increase in the order AH- CdCl_2 > AH- CuCl_2 > AH- NiCl_2 > AH- CoCl_2 > PAH-homopolymer. The greater stabilities of the polymer complexes compared with PAH homopolymer may be due to the formation of 5-membered ring structures.

The effective activation energies for the thermal degradation of PAH and AH-metal salt polymer complexes were determined from the temperature dependence of the chain rupture rate. The rate constant of the thermal degradation was plotted according Arrhenius relationship (Figure 5). Table 4 lists the activation energy of PAH homopolymer and AH-metal salt polymer complexes. The activation energy of the homopolymer is smaller than that of the polymer complexes. Therefore PAH homopolymer will undergo decomposition more readily than the polymer complexes.

4. Conclusion

Acryloylhydrazin (AH) has been shown to behave as a monobasic/neutral bidentate ligand via its C-O/C=O (of the acryloyl group) and N atom (of the NH₂ of hydrazine group) in seven new metal(II)/(III) polymer complexes, all of which exhibit supramolecular architectures assembled through weak interactions including hydrogen bonding and π - π stacking. The present report, together with our previous work, indicates that the structure of polymer complexes of AH can be turned by variation of the inorganic co-ligands.

UO₂(II), Co(II) and Fe(III) ions are six coordinated in an elongated octahedral fashion. The center metal ion is coordinated equatorially by a nitrogen atom (of hydrazine group) and an oxygen atom (of acryloyl group) and oxygen atom of each acetato group, and also, the oxygen atoms of two water molecules and two chloro molecules with axial/bridge positions, respectively.

The significant change in the PAH bands upon complexation is the decrease in $\nu(\text{C}=\text{N})$ group indicating the involvement of the adjacent oxygen in the coordination. The antisymmetric and symmetric (NH₂) stretching frequencies appear in the region 3450-3100 cm⁻¹ in the homopolymer. These frequencies have been considerably higher in the polymer complexes and this fact, along with changes in deformation, wagging and rocking (NH₂) vibration suggest that the metals are coordinated through the nitrogen atom of amine group.

The ESR study of the copper(II) polymer complexes has provided supportive evidence to the conclusion obtained on the basis of electronic spectra and magnetic moment values.

The thermogravimetric analysis confirm the presence of coordinated water molecules in polymer complexes 2,4 and 7.

Scientific motivation. The purpose for the synthesizing AH polymeric complexes was a model for the active site of the enzyme and also a good model for the physical properties of protein active sites. These polymer complexes are used in some chemical processes as catalyst and also as biological models in understanding the structure of biomolecules and biological processes. Polymer complexes exhibit supramolecular architectures assembled through weak interactions including hydrogen bonding and π - π stacking.

Table 1.

Elemental analysis^a, residual weights and magnetic moments of the PAH homopolymer and polymer complexes (for molecular structures see Fig.2)^b.

Polymer	Analysis, % (Calc. / Found)				
	C	H	N	M	MO*
PAH 1	41.86 (41.81)	6.98 (6.93)	32.56 (32.58)	-	-
AH-CuCl ₂ 2	17.82 (17.61)	3.47 (3.55)	13.86 (13.72)	31.44 (31.82)	39.55 (40.12)
AH- Cu(OAc) ₂ 3	27.18 (27.23)	5.29 (5.33)	21.14 (21.08)	22.23 (22.52)	-
AH-CoCl ₂ 4	27.18 (27.23)	5.29 (5.33)	21.14 (21.08)	22.23 (22.52)	29.68 (29.92)
AH- NiCl ₂ 5	18.26 & 27.21 (23.74)	3.55 & 5.29 (4.65)	14.21 & 21.16 (18.22)	29.73 & 22.5 (26.21)	39.85 & 29.69 (35.21)
AH-FeCl ₃ 6	14.49 (14.27)	2.42 (2.21)	11.27 (10.89)	22.50 (22.09)	-
AH-CdCl ₂ 7	14.35 (14.31)	2.78 (2.69)	11.16 (11.32)	44.80 (45.35)	-
AH- UO ₂ (OAc) ₂ 8	17.91 (18.10)	3.36 (3.28)	10.45 (10.00)	44.40 (43.80)	-

MO*: Residual weight of the polymer complexes at 1000 °C., dia: diamagnetic

^aMicroanalytical data as well as metal estimations are in good agreement with the stoichiometry of the proposed complexes.

^bThe excellent agreement between calculated and found data supports the assignment suggested in the present work.

Table 2.

Electronic spectral bands and magnetic moments of the polymer complexes (for molecular structures see Fig. 2).

Comp ^a	Spectral bands (cm ⁻¹)	Assignments	$\mu_{\text{eff.}}^b$ (BM)
2	16400, 15300	² B _{1g} → ² E _g	1.85
3	16550, 15050	² B _{1g} → ² B _{2g}	1.79
4	13550 18365	⁴ T _{1g} (F) → ⁴ A _{2g} (F) (ν_2) ⁴ T _{1g} (F) → ⁴ T _{1g} (P) (ν_3) 10Dq = 7261 cm ⁻¹ , B = 867 cm ⁻¹ , $\beta = 0.88$	5.23
5	17100 27700 22720	³ A _{1g} → ³ T _{2g} (F) ³ A _{2g} → ³ T _{1g} (P) ³ A _{1g} → ¹ B _{2g}	1.89
6	15680 19980 16000- 21000	² T ₂ → ⁴ A ₂ π -t _{2g} L → M and CT	2.10
8	~ 24690	¹ Σ_{gu} → ³ π_u	dia.

^a See footnote Table 1.

^b Measured at room temperature.

Table 4. Activation energies of the thermal degradation of PAH homopolymer and AH-metal chloride polymer complexes.

Polymer	E_a (KJ mol ⁻¹)
PAH	15.2
AH-CuCl ₂	25.3
AH-CoCl ₂	21.7
AH-NiCl ₂	23.0
AH-CdCl ₂	27.2

Table 3. Weight loss percentage for the homopolymer of PAH and AH-metal chloride polymer complexes.

Polym.	Volat Temp °C	First stage		Second stage		Third stage		Wt., % rem. at 000 °C
		T _{max} , °C	Wt. loss, %	T _{max} , °C	Wt. loss, %	T _{max} , °C	Wt. loss, %	
PAH	112	207	47	233	45	-	-	8
AH- CuCl ₂	130	155	11	253	30	363	26	33
AH- CoCl ₂	127	151	14	248	32	359	29	25
AH- NiCl ₂	128	156	12	250	32	360	28	28
AH- CdCl ₂	132	158	9	258	24	371	21	46

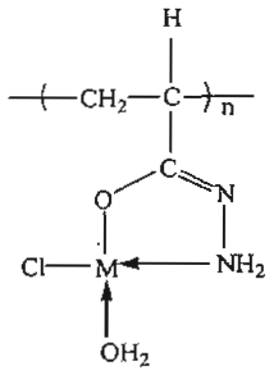
Volat. = Volatilization

Rem. = remaining

References

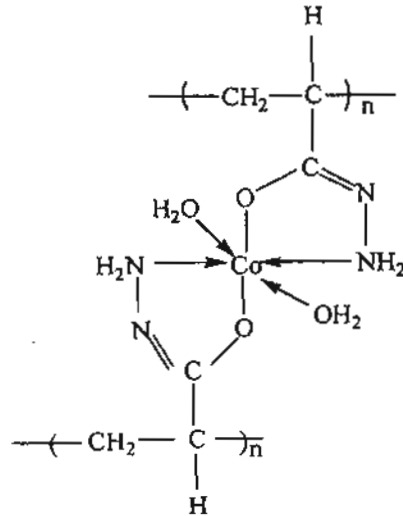
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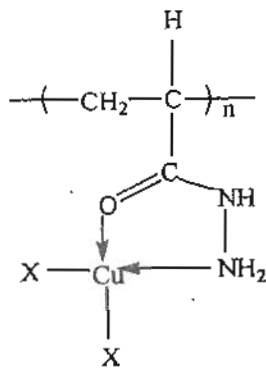


M= Cu(II) and Cd(II)

structure I

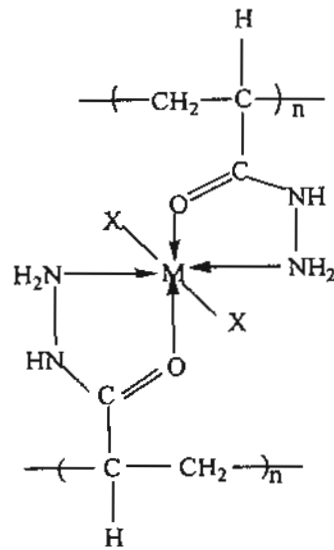


structure II



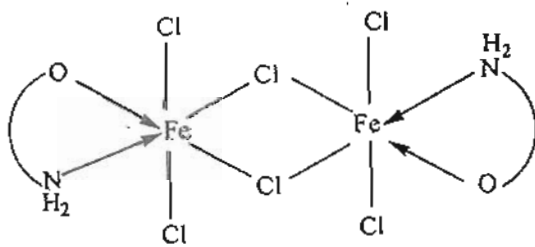
X= OAC

structure III



X= OAC, M= UO2

structure IV



structure V

Fig. 2. Proposed structure of polymer complexes

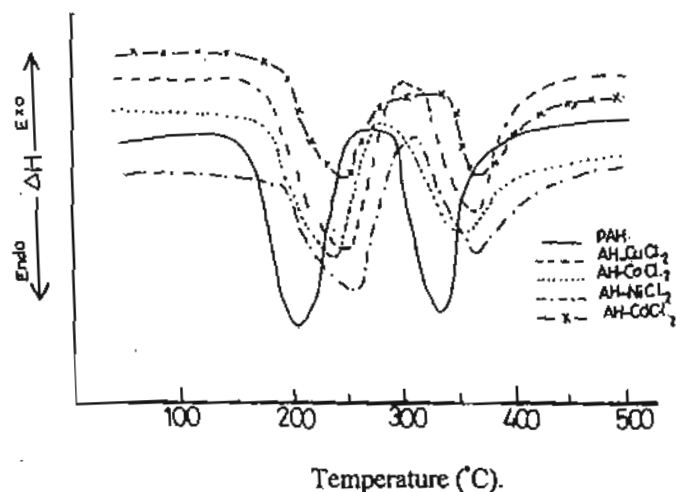


Fig. 3. DTA traces of PAH homopolymer and AH-metal chloride polymer complexes.

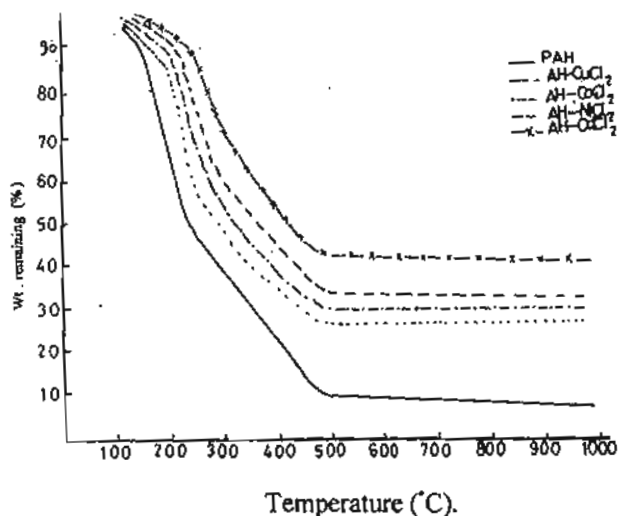


Fig. 4. TG curves of PAH homopolymer and AH-metal chloride polymer complexes.

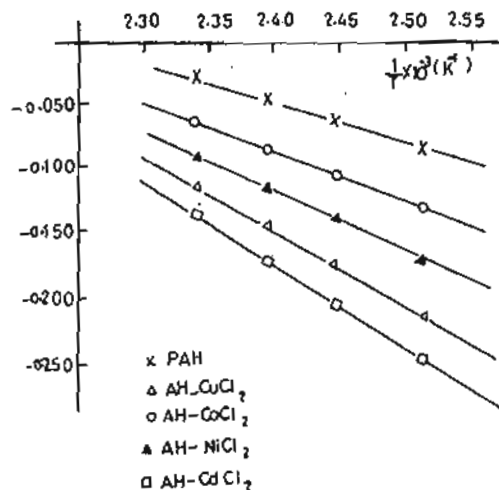


Fig. 5. Arrhenius plots for the degradation of PAH homopolymer and AH-metal chloride polymer complexes.