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# Polymer complexes. LXVI, thermal, spectroscopic studies and supramolecular structure of N-[ $\beta$ -(ethylamino)] acrylamide polymer complexes



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# ABSTRACT

Novel polymeric complexes with a potentially bidentate ligand N-[ $\beta$ -(ethylamino)] acrylamide (EA), formed by amidation of 1,2-diaminoethane with acryloyl chloride were synthesized and characterized on the basis of elemental analyses, IR, <sup>1</sup>H NMR, UV–Vis, magnetic susceptibility measurements, ESR, molar conductance and thermal analysis. Molecular docking was used to predict the binding between EA ligand (keto and enol forms) and the receptor of prostate cancer mutant 2q7k-hormone and the receptor of breast cancer mutant 3hb5-oxidoreductase. The molecular and electronic structures of the different forms of the ligand are optimized theoretically and the quantum chemical parameters are calculated. The molar conductance data reveal that all the polymer complexes are non-electrolytes. Ligand (EA) has been shown to behave as neutral bidentate *via* its nitrogen atom of NH<sub>2</sub> group and nitrogen atom of NH group in polymer complexes. On the basis of electronic spectral data and magnetic susceptibility measurements, suitable geometry has been proposed for each polymeric complex. The ESR spectral data of the Cu(II) complex showed that the metal-ligand bonds have considerable covalent character. The activation energies of the degradation of the polymer complexes were calculated.

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# 1. Introduction

Acrylamide polymers have been important applications as flocculants in the treatment of acid-leached uranium ores and oil-well stimulation, and friction reduction but acrylamide polymers continue to enjoy substantial markets as paper additives to increase dry strength and in mineral processing [1]. Acrylamide polymers were considered important class of water-soluble polymers. Acry1amide is a crystalline, relatively stable monomer that is soluble in water and many organic solvents. It readily undergoes polymerization by conventional freeradical methods, but can also be polymerized photochemically, in the solid state with ionizing radiation and anionically [2]. Chelating compounds derived from acryloyl monomers are being utilized as suitable ligands. They enable the formation of rigid coordination polymers. Ghoneim et al. [3], were discussed preparation and structurally characterization the acryloyl polymer complexes by different methods.

The relative stabilities of copper(II) and calcium(II) ions with the polyampholytes containing ethylenediamine-*N*,*N*'-diacetic acid residues were discussed [4]. The free and two cross-linked polymers have been studied by potentiometry and solution calorimetry. Copper(II) is completely coordinated and the ligand acts as a sequestering agent.

\* Corresponding author. *E-mail address:* elsonbatisch@yahoo.com (A.Z. El-Sonbati). Arshady et al. [5] were directed their attention towards polyamide supports for which solvation compatibility with attached peptides could be readily envisaged. They were synthesized monomers (dimethyl acrylamide, bis(acry1amido) ethane and N-(N-t-butoxycarbonyl- $\beta$ alany1)-N'-acryloylhexamethylenediamine) provide directly a stable cross-linked polymer appropriately functionalized for use in peptide synthesis without further major modification [6].

In this paper, we will prepare polymer based on the reaction of 1,2diaminoethane (EDA) with acryloyl chloride (AC) to produce new acrylamide polymers, which having promising applications. Study ESR spectral data of the Cu(II) complex and the thermal behavior of chelates the polymer complexes. The molecular docking binding between EA ligand (Fig. 1) and the receptors (2q7k-hormone and 3hb5-oxidoreductase) are studied. Moreover, the molecular structures of the EA ligand are studied and quantum chemical parameters are calculated.

# 2. Experimental

## 2.1. Materials

1,2-Diaminoethane (EDA) (BDH Chemical Ltd.) and acryloyl chloride (AC) (Aldrich Chemical Co. Inc.) were used without further purification. 2,2'-Azobisisobutyronitrile (AIBN) (Aldrich Chemical Co. Inc.) was purified by dissolving in hot ethanol and filtering [7]. The solution was left to cool. The pure material was collected by filtration and dried.



Fig. 1. Synthesized monomer EA and PEA.



Fig. 2. <sup>1</sup>H NMR spectrum of EA monomer.

# 2.2. Preparation of N-[ $\beta$ -(ethylamino)] acrylamide (EA) monomer

N-[ $\beta$ -(ethylamino)] acrylamide (EA) monomer was prepared by the reaction of equimolar amounts of acryloyl chloride (AC) (0.01 mol) 1,2diaminoethane (EDA) (0.01 mol) in dry benzene (25 mL) until the evolution of hydrogen chloride ceased forming white powder of monomer. The EA monomer has been characterized by IR and <sup>1</sup>H NMR spectra (Fig. 2).

#### 2.3. Preparation of poly N-[\(\beta-(ethylamino))\) acrylamide (PEA) homopolymer

PEA homopolymer was prepared by free radical initiation of EA (0.5 mol) using 0.1 w/v % AIBN as initiator and DMF (50 mL) as solvent

for 6 h. The polymer product was precipitated by pouring in distilled water and dried in a vacuum oven for several days at 40 °C. The PEA homopolymer has been characterized by IR and <sup>1</sup>H NMR spectra (Fig. 3).

# 2.4. Preparation of the polymer complexes

Polymer complexes were prepared by refluxing anhydrous Cu(II), Ni(II), Co(II), Cd(II) chlorides and UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·5H<sub>2</sub>O (0.001 mol) with the corresponding ligand (EA) (0.001 and/or 0.002 mol) in 20 mL DMF as a solvent and 0.1% (w/v) AIBN as initiator. The resulting mixture was heated at reflux for ~8 h. The hot solution was precipitated by pouring in a large excess of distilled water containing dilute



Fig. 3. <sup>1</sup>H NMR spectrum of PEA homopolymer.

#### Table 1

Elemental analyses a of EA monomer and polymer complexes (for molecular structures, see Figs. 1 and  $13)^{\rm b}$ .

Compound	Exp. (calcd.) (%)				
	С	Н	Ν	М	
EA	52.44 (52.63)	8.63 (8.77)	24.21 (24.56)	-	
EA-CuCl <sub>2</sub> (1)	24.00 (24.14)	3.89 (4.02)	10.88 (11.27)	25.35 (25.57)	
EA-CoCl <sub>2</sub> (2)	24.45 (24.60)	3.98 (4.10)	11.16 (11.48)	23.87 (24.16)	
$EA-CdCl_2$ (3)	19.79 (20.17)	3.21 (3.36)	9.23 (9.42)	37.66 (37.80)	
EA-NiCl <sub>2</sub> (4)	33.34 (33.55)	5.34 (5.59)	15.45 (15.66)	16.23 (16.41)	
EA-uranyl nitrate (5)	19.03 (19.29)	3.10 (3.22)	8.75 (9.00)	38.01 (38.27)	

<sup>a</sup> Microanalytical data as well as metal estimations are in good agreement with the stoichiometry of the proposed complexes.

<sup>b</sup> The excellent agreement between calculated and found data supports the assignment suggest in the present work.

hydrochloric acid, to remove the metal salts that incorporated into the polymer complexes. The polymer complexes were filtered, washed with water, and dried in a vacuum oven at 40 °C for several days. The polymer complexes were determined after decomposition by aquaregia, by complexometric titration using EDTA [8].

#### 2.5. Measurements

Elemental microanalyses of the separated solid chelates for C, H and N were performed in the Microanalytical Center. <sup>1</sup>H NMR spectrum was obtained with a Joel FX90 Fourier transform spectrometer with DMSO-d<sub>6</sub> as a solvent. Infrared spectra were recorded using Perkin-Elmer 1340 spectrophotometer and the spectra were recorded as KBr discs. Ultraviolet-Visible (UV-vis) spectra of the polymer were recorded in Nujol mull using a Unicom 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)<sub>4</sub>}], was used for the calibration of the Gouy tubes. Diamagnetic corrections were calculated from the values given by Selwood [9] and Pascal's constants. Magnetic moments were calculated using the equation,  $\mu_{eff.} = 2.84 [T\chi_M^{COr}]^{1/2}$ . 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,  $10 \times 5 \times 2.5$  mm deep; the temperature measuring thermocouple was placed within 1 mm of the holder. ESR measurements of powdered samples were recorded at room temperature using an X-band spectrometer utilizing a 100 kHz magnetic field modulation with diphenyl picrylhydrazyle (DPPH) as a reference material. This study simulates the actual docking process in which the ligandprotein interaction energies are calculated using a Docking Server [10]. The MMFF94 Force field was used for energy minimization of ligand molecule using Docking Server. Gasteiger partial charges were added to the ligand atoms. Non-polar hydrogen atoms were merged, and rotatable bonds were defined. Docking calculations were carried out on EA ligand protein models. Essential hydrogen atoms, Kollman united atom type charges, and solvation parameters were added with the aid of AutoDock tools [11]. Affinity (grid) maps of 0.375 Å spacing were generated using the Autogrid program [12]. Auto Dock parameter set- and distancedependent dielectric functions were used in the calculation of the van der Waals and the electrostatic terms, respectively. The molecular structures of the ligand were optimized by HF method with 3-21G basis set. The molecules were built with the Perkin Elmer ChemBio Draw and optimized using Perkin Elmer ChemBio3D software [13,14]. Quantum chemical parameters such as the highest occupied molecular orbital energy  $(E_{HOMO})$ , the lowest unoccupied molecular orbital energy  $(E_{IUMO})$  and HOMO-LUMO energy gap ( $\Delta E$ ) for the investigated molecules were calculated.

#### 3. Results and discussion

#### 3.1. General

The 1:1 amidation of 1,2-diaminoethane and acryloyl chloride under certain condition yielded the N-[ $\beta$ -(ethylamino)] acrylamide (EA) monomer. Elemental analyses of the synthesized compounds are summarized in Table 1. The analytical data agree well with the proposed formula of the compounds. The synthetic mechanism of the principal ligand is shown in Fig. 1. The ligand can exist either in the keto forms **I** 



Fig. 4. Tautomerism of EA monomer and PEA homopolymer.

Table 2	
Energy values obtained in docking calculations of ligand (EA) with of prostate cancer mutant 2q7k and breast cancer mu	tant 3hb5 receptors.

Receptor	Ligand	Est. free energy of binding (kcal/mol)	Est. inhibition constant $(K_i) \ (\mu M)$	vdW + bond + desolve energy (kcal/mol)	Electrostatic energy (kcal/mol)	Total intercooled energy (kcal/mol)	Interact surface
2q7k	Keto form	-3.96	1.25	-4.59	-0.51	-5.10	304.346
	Enol form	-3.98	1.21	-4.28	-0.53	-4.81	300.208
3hb5	Keto form	-4.26	759.29	-4.94	-0.46	-5.40	297.089
	Enol form	-3.39	3.27	-4.85	-0.03	-4.88	376.244

and **III** or enol forms **II** and **IV** (Fig. 4). However, the IR and <sup>1</sup>H NMR spectra of the ligand (EA) indicate that in the solid state it exists in keto form. The molecular structure of the ligand is depicted in Fig. 4. The physical analyses results indicate that the complexes synthesized under the common solvent reaction have a 1:1/1:2 metal to ligand stoichiometry, in which the ligand (EA) converts to the enol form and function as a neutral bidentate chelating agent coordinated to the metal ion,

(A)







Fig. 5. The ligand (keto and enol forms) (green in (A) and blue in (B)) in interaction with prostate cancer mutant 2q7k receptor. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1. The results obtained are in good agreement with those calculated for the suggested formula indicating the purity of the prepared ligand.

#### 3.2. Molecular docking

The docking study showed a favorable interaction between ligand (keto and enol forms) and the prostate cancer (2q7k) and the breast cancer (3hb5) receptors. The calculated energy is listed in Table 2 and Figs. 5 and 6 for 2q7k and 3hb5 receptors, respectively. According to the results obtained in this study, HB plot curve indicated that, the ligand binds to the two proteins hydrogen bond and decomposed interactions energies in kcal/mol were existed between the ligand with 2q7k and 3hb5 receptors as shown in Figs. 7 and 8. The calculated efficiency is favorable where K<sub>i</sub> values estimated by AutoDock were compared with experimental K<sub>i</sub> values, when available, and the Gibbs free energy is negative [15,16]. Also, based on this data, it can propose that interaction between the 2q7k and 3hb5 receptors and the ligand is possible. 2D plot curves of docking with ligand are shown in Figs. 9 and 10. It was found that the enol form of EA ligand shows best interaction with 2q7k receptor other than 3hb5 receptor.

# 3.3. Molecular structures

The optimized structures of the ligand (keto and enol forms) are given in Fig. 11. The selected geometrical structures of ligand were calculated. Selected geometric parameters bond lengths and bond angles of ligand are tabulated in Tables 3 and 4.

The HOMO and LUMO of ligand (keto and enol forms) is shown in Fig. 12. The enol form is more stable than the keto form as reflected from energy gap values (Table 5). The HOMO–LUMO energy gap,  $\Delta E$ , which is an important stability index, is applied to develop theoretical models for explaining the structure and conformation barriers in many molecular systems [16]. The calculated quantum chemical parameters are given in Table 5. Additional parameters such as  $\Delta E$ , absolute electronegativities,  $\chi$ , chemical potentials, Pi, absolute hardness,  $\eta$ , absolute softness,  $\sigma$ , global electrophilicity,  $\omega$ , global softness, S, and additional electronic charge,  $\Delta N_{max}$ , have been calculated according to the following equations [15,17]:



(1)



Fig. 6. The ligand (keto and enol forms) (green in (A1) and blue in (B1)) in interaction with breast cancer mutant 3hb5 receptor. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. HB plot of interaction between ligand (a) keto form and (b) enol form with receptor of prostate cancer mutant 2q7k.



Fig. 8. HB plot of interaction between ligand (a) keto form and (b) enol form with receptor of breast cancer mutant 3hb5.



Fig. 9. 2D plot of interaction between ligand (a) keto form and (b) enol form with receptor of prostate cancer mutant 2q7k.

(a) Keto form

Key

Thr 140 X

Val 113/X

Ligand bond

Non-ligand bond

Hydrogen bond and its length

Val 139XX



Con \$9733

Non-listand residues involved in other

where if all

Les 162(X)

$$\sigma = \frac{1}{\eta} \tag{4}$$

$$\mathrm{Pi} = -\chi \tag{5}$$

$$S = \frac{1}{2\eta}$$
(6)

$$\omega = \frac{\mathrm{Pi}^2}{2\mathrm{n}} \tag{7}$$

$$\Delta N_{max} = -\frac{Pi}{\eta}.$$
(8)

# 3.4. Elemental analyses of the polymer complexes

Reaction of the ligand with Cu(II), Co(II), Ni(II), Cd(II) and UO<sub>2</sub>(II) ions, in the molar ratio 1:1/1:2 M:L), yielded polymer complexes a part from the molar ratio. The prepared polymer complexes are stable at room temperature, colored, non-hygroscopic and insoluble in water and common organic solvents, but soluble in solvents such as DMF and DMSO.

The results of elemental analyses (Table 1) are in good agreement with those required by the proposed formulae. The formation of these polymer complexes proceeds according to the following equations:

**Fig. 10.** 2D plot of interaction between ligand (a) keto form and (b) enol form with receptor of breast cancer mutant 3hb5.

$$\chi = \frac{-(E_{\text{HOMO}} + E_{\text{LUMO}})}{2} \tag{2}$$

$$\eta = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2} \tag{3}$$

$$\begin{split} \text{MCl}_2 \cdot n\text{H}_2\text{O} + \text{EA} & \xrightarrow{\text{AIBN}} & [\text{M}(\text{EA})\text{Cl}_2]_n \ \text{M} = \text{Cu}(\text{II}) \ (1), \text{Co}(\text{II}) \ (2) \text{ or } \ \text{Cd}(\text{II}) \ (3) \\ \\ \text{NiCl}_2 \cdot n\text{H}_2\text{O} + \text{EA} & \xrightarrow{\text{AIBN}} & \left[\text{Ni}(\text{EA})_2(\text{Cl})_2\right]_n \ (4) \end{split}$$

$$UO_2(NO_3)_2 \cdot 5H_2O + EA \xrightarrow{\text{AIBN}} [UO_2(EA)_2(ONO_2)_2]_n(5).$$

# 3.5. Molar conductance of the polymer complexes

The molar conductance of  $10^{-3}$  M of solutions of the polymer complexes in DMSO is calculated as  $25 \pm 2$  °C. It is concluded from the results that Cu(II), Co(II), Ni(II), Cd(II) and UO<sub>2</sub>(II) chelates with EA ligand under investigation had molar conductance values in the range from 2.35 to  $12.60 \ \Omega^{-1} \ mol^{-1} \ cm^2$  indicating their non-electrolytic nature [18]. Hence the two chlorides in copper(II), cobalt(II), nickel(II) and cadmium(II) polymer complexes are in the coordination sphere.

#### 3.6. <sup>1</sup>H NMR spectrum

The <sup>1</sup>H NMR spectra of EA, PEA and its diamagnetic Cd(II) polymer complex were recorded in d<sub>6</sub>-dimethylsulphoxide (DMSO-d<sub>6</sub>) solution using tetramethylsilane (TMS) as internal standard. The <sup>1</sup>H NMR spectrum of EA monomer (Fig. 2) showed the expected peaks and pattern of the vinyl group (CH<sub>2</sub> = CH)  $\delta$  6.25 ppm (dd, J = 17, 11 Hz) for the vinyl CH proton and proton  $\delta$  5.12 ppm (AM part of AMX system dd, I = 17, 1 Hz) for the vinyl CH<sub>2</sub> protons, respectively. These peaks disappeared on polymerization while a triplet at  $\delta$  1.86 ppm (t, J = 7 Hz) and a doublet at 1.80 ppm (d, J = 7 Hz) appeared, indicating that the polymerization of EA monomer occurs on the vinyl group [20]. The peaks at 2.9-3.1 ppm of EA monomer are due to the methylene groups of 1,2diaminoethane. The <sup>1</sup>H NMR spectrum of PEA (Fig. 3) includes four resonances at 11.85, 5.55, 2.2 and 1.9 ppm relative to TMS which may be tively [19]. There is a weak peak at 10.25 ppm due to the enolic —OH proton indicating that the ligand exist in enol form (Fig. 3), upon addition of D<sub>2</sub>O the intensities of both NH/OH, and NH<sub>2</sub> protons significantly decrease. The peaks at 10.30/11.75 ppm, which is due to the exchangeable hydrogen-bonded hydroxyl/aminly (OH/NH) proton (Fig. 4). It disappears upon exchange with  $D_2O$ .



Fig. 11. The calculated molecular structures of ligand (a) keto form and (b) enol form.

#### 3.7. IR spectra and mode of bonding

The IR spectra of the complexes are compared with those of the free ligand in order to determine the coordination sites that may involve in chelation. There are some guide peaks, in the spectrum of the ligand, which are of good help for achieving this goal. These peaks are expected to be involved in chelation such as NH<sub>2</sub>, CO and NH. The position and/or the intensities of these peaks are expected to be changed upon chelation. New peaks are also guide peaks in chelation. Upon comparison it is found that:

The antisymmetric and symmetric (NH and NH<sub>2</sub>) stretching frequencies appear in the region ~3425–3315 and 3480–3390 cm<sup>-1</sup> in the ligand, these frequencies have been considerable higher in the complexes and this fact, along with changes in deformation, wagging and rocking (NH<sub>2</sub>) vibrations suggest that the metals are coordinated *via* N atom of the amino group. The participation of the NH<sub>2</sub> group is further confirmed by clarifying the effect of chelation on the in-plane bending,  $\delta$ (NH<sub>2</sub>) vibration. The shift of this band, from 1565 cm<sup>-1</sup> in the free ligand to 1545–1585 cm<sup>-1</sup> in the complexes indicates the participation of the NH<sub>2</sub> group in complexes formation [21].

- The very sharp absorption band appeared in the free ligand at  $\simeq$  1650 cm<sup>-1</sup> is assigned to v(C=0) group.
- IR spectrum of the ligand showed the absence of the bands due to carbonyl v(C=0) and amino v(NH) stretching vibration and instead a

Table 3 The selected geometri	c parameters for	keto form ligand.	
Bond lengths (Å)		Bond angles (°)	
C(8)-H(18)	1.1	H(15)N(6)H(14)	104.988
C(8)-H(17)	1.102	H(15)-N(6)-C(5)	110.756
C(7)-H(16)	1.101	H(14)N(6)C(5)	110.365
N(6)-H(15)	1.035	H(13)-C(5)-H(12)	107.633
N(6)-H(14)	1.035	H(13)-C(5)-N(6)	108.868
C(5)-H(13)	1.114	H(13)-C(5)-C(4)	111.034
C(5)-H(12)	1.116	H(12)-C(5)-N(6)	108.873
C(4)-H(11)	1.112	H(12)-C(5)-C(4)	109.984
C(4)-H(10)	1.116	N(6)-C(5)-C(4)	110.378
N(2)-H(9)	1.019	H(11)-C(4)-H(10)	105.411
C(7) - C(8)	1.343	H(11)-C(4)-C(5)	112.445
C(1)-C(7)	1.36	H(11)-C(4)-N(2)	112.1
C(5)-N(6)	1.472	H(10)-C(4)-C(5)	108.659
C(4) - C(5)	1.534	H(10)-C(4)-N(2)	107.179
N(2) - C(4)	1.465	C(5)-C(4)-N(2)	110.714
C(1)-O(3)	1.208	H(9)N(2)C(4)	118.84
C(1) - N(2)	1.366	H(9) - N(2) - C(1)	114.611
		C(4) - N(2) - C(1)	126.353
		H(18)-C(8)-H(17)	116.227
		H(18)-C(8)-C(7)	123.242
		H(17)-C(8)-C(7)	120.531
		H(16)-C(7)-C(8)	115.287

new band assigned to azomethine (C==N) and (OH) linkage appeared at  $\approx 1605 \text{ cm}^{-1}$  and  $\approx 3090 \text{ cm}^{-1}$ , respectively, in all polymer complexes, indicating its participation in coordination [22]. This coordination is more likely than that of the other nitrogen because the basicity is believed to decrease by inductive effect of the (C==N) group. The position of the band due to (OH) is unchanged, indicating non-involvement of this group in complexation.

H(16)-C(7)-C(1)

C(8) - C(7) - C(1)

C(7) - C(1) - O(3)

C(7)-C(1)-N(2)

O(3) - C(1) - N(2)

• New bands that appear in the polymer complexes at 425, 410, 440 and 445 cm<sup>-1</sup> are attributed to v(Cu-N), v(Co-N), v(Ni-N) and v(Cd-N) vibrations [23–25], respectively. The band at 280–340 cm<sup>-1</sup> is assigned to the v(M-Cl) vibration.

Table 4					
The selected g	geometric	parameters	for eno	l form	ligand.

Bond lengths (Å)		Bond angles (°)	
C(8)-H(18)	1.099	H(15)N(6)H(14)	105.15
C(8)-H(17)	1.102	H(15)N(6)C(5)	110.503
C(7)-H(16)	1.105	H(14)N(6)C(5)	110.27
N(6)-H(15)	1.035	H(13)-C(5)-H(12)	107.798
N(6)-H(14)	1.035	H(13)-C(5)-N(6)	108.509
C(5)-H(13)	1.115	H(13)C(5)C(4)	109.931
C(5)-H(12)	1.114	H(12)-C(5)-N(6)	108.967
C(4)-H(11)	1.114	H(12)-C(5)-C(4)	110.925
C(4)-H(10)	1.117	N(6)-C(5)-C(4)	110.631
O(3)-H(9)	0.97	H(18)-C(8)-H(17)	116.286
C(7)-C(8)	1.342	H(18)-C(8)-C(7)	123.324
C(1) - C(7)	1.346	H(17)-C(8)-C(7)	120.39
C(5)-N(6)	1.472	H(11)-C(4)-H(10)	105.39
C(4) - C(5)	1.534	H(11)-C(4)-C(5)	110.964
N(2)-C(4)	1.482	H(11)-C(4)-N(2)	112.164
C(1)O(3)	1.363	H(10)-C(4)-C(5)	108.669
C(1)-N(2)	1.269	H(10)-C(4)-N(2)	107.381
		C(5)-C(4)-N(2)	111.934
		H(16)-C(7)-C(8)	116.713
		H(16) - C(7) - C(1)	119.066
		C(8)-C(7)-C(1)	124.221
		H(9)O(3)C(1)	110.173
		C(4)-N(2)-C(1)	118.123
		C(7)-C(1)-O(3)	121.854
		C(7)-C(1)-N(2)	116.823
		O(3)-C(1)-N(2)	121.323

121.386

123.327

122.925

120 455

116.618



Fig. 12. The Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) of ligand (a) keto form and (b) enol form.

• The dioxouranium (VI) polymer complex (5) exhibits  $\upsilon_{sym}(O = U = O)$  and  $\upsilon_{asym}(O = U = O)$  at 794 and 919 cm<sup>-1</sup>, respectively, the usual range for such complex [25,26] being  $\upsilon_{asym}$  870-950 and  $\upsilon_{asym}$  870-950 and  $\upsilon_{sym}$  780-955 cm<sup>-1</sup>. The force constant (F<sub>U-O</sub>) value is 6.8  $\times$  10<sup>-8</sup> N/Å which agree well with the force constant values of similar dioxouranium(VI) complexes [26]. The U-O bond distance calculated from the equation, R<sub>U-O</sub> = 1.17 + 1.08  $^{f-1/3}$  is in the usual range (1.60-1.92 Å) observed for dioxouranium(VI) complexes [25-27]. In the polymer complex (5), the appearance of two new bands in 1415 ( $\upsilon_5$ ) and 1370 cm<sup>-1</sup> ( $\upsilon_1$ ) confirmed the monodentate nature of the coordinated ONO<sub>2</sub>- group. The dioxouranium polymer complex exhibits a new band at ~ 24820-24680 cm<sup>-1</sup>, which is assigned to the  $^1\sum_g ^u \to ^3\pi_u$  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 EA reacts with CuCl<sub>2</sub>, CoCl<sub>2</sub>, and CdCl<sub>2</sub> in a 1:1 ratio; and with NiCl<sub>2</sub> and UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> in 2:1 molar ratio (Fig. 13). In the present investigation, it is well established that uranyl ion possess planar hexagonal structure with nitrogen and oxygen atoms in the axial position. Two ligands units and two NO<sub>3</sub><sup>---</sup> molecules remain in the trans-position. The UO<sub>2</sub>(II) and Cd(II) polymer complexes are found to be diamagnetic as expected. The geometry of Cd(II) complex is square planar.

# 3.8. Magnetic susceptibility and electronic spectra measurements

Electronic spectrum of the ligand and their polymer complexes have been measured in Nujol mull. All the polymer complexes show an intense band in the 31,000–32,780 cm<sup>-1</sup> range which is assigned to a  $\pi$ - $\pi$ \* transition associated with the azomethine linkage [28]. The spectra of the polymer complexes show intense bands in the high-energy region in the 20,800–28,160 cm<sup>-1</sup> range which can be assigned to charge transfer L  $\rightarrow$  M bands [29]. The bands observed in the 20,620–27,900 cm<sup>-1</sup> region can be attributed to d-d transitions of the metal ions.

The electronic spectrum of Cu(II) polymer complex shows a broad band at 14,295 cm<sup>-1</sup>. This is in agreement with those generally observed for square planar Cu(II) complexes and can be due to  ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$  transition. The magnetic moment value of complex is 1.68 B.M., corresponding to the spin value (1.73 B.M.), indicating the monomeric nature [30]. Electronic spectrum of EA-NiCl<sub>2</sub> polymer complex shows three bands at 9900 to 10,100, 16,500 and 23,810 to 24,400 cm<sup>-1</sup> assigned to  ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$  (F) ( $\upsilon_1$ )  $\rightarrow {}^{3}T_{1g}$ (F) ( $\upsilon_2$ )  $\rightarrow {}^{3}T_{1g}$ (P) ( $\upsilon_3$ ) transitions, respectively. The ligand field parameters [B = 645,  $\beta$  = 0.62, Dq = 1010 cm<sup>-1</sup> and  $\upsilon_2/$  $\upsilon_1$  = 1.62 cm<sup>-1</sup>] in the same range reported for an octahedral structure around Ni(II) [31]. The value of magnetic moment (3.15 B.M.) is an additional for an octahedral structure. However, the spectrum of Co(II) polymer complex shows two bands ( $\upsilon_3$ )  ${}^{4}T_2 \rightarrow {}^{4}T_1$ (P) (14,715 cm<sup>-1</sup>) and

Table 5				
The calculated quar	ntum chemical param	eters for ligand (	keto and end	l forms).

Compound	E <sub>HOMO</sub> (eV)	E <sub>LUMO</sub> (eV)	$\Delta E (eV)$	χ (eV)	η (eV)	$\sigma(\text{eV})^{-1}$	Pi (eV)	$S (eV)^{-1}$	$\omega \; (eV)$	$\Delta N_{\rm max} ({\rm eV})$
Keto form	-11.58	-3.454	8.128	7.518	4.064	0.246	- 7.518	0.123	6.954	1.849
Enol form	-11.13	-3.043	8.087	7.087	4.044	0.247	-7.087	0.124	6.209	1.753



Fig. 13. The structures of M(II) complexes.

 $(\upsilon_2)$  <sup>4</sup>A<sub>2</sub>  $\rightarrow$  <sup>4</sup>T<sub>1</sub>(F) (8300 cm<sup>-1</sup>) in the visible and near ir regions. The values of 10Dq and B parameters calculated from the positions of  $\upsilon_3$  and  $\upsilon_2$  bands. These values are of the same order of magnitude as those reported previously for the tetrahedral Co(II) complexes [32–34]. The racah parameter value (B)(635 cm<sup>-1</sup>) of the free ion value (967 cm<sup>-1</sup>), suggesting considerable orbital overlap [35]. The observed 10 Dq value (4265 cm<sup>-1</sup>) shows that the N atoms of the ligand make effective contribution to the ligand field in the complex. The magnetic moment value (4.4 B.M.) indicative of tetrahedral geometry of the Co(II) complex.

#### 3.9. ESR spectrum

The solid state ESR spectra of some complexes exhibit axially symmetric g-tensor parameters with  $g_e < g_\perp > 2.0023$  indicating that the copper site has a  $d_{x2} - _{y2}$  ground state characteristic of tetrahedral, square planer or octahedral stereochemistry [36]. Kivelson and Neiman [37] have reported the  $g_{II}$  value <2.3 for covalent character of the metalligand bond and >2.3 for ionic character. Applying the criterion the covalent character of the metalligand bond in the complex under study can be predicted. The trend  $g_{II} > g_{\perp} > g_e$  (2.0023) observed for this complex shows that the unpaired electron is localized in  $d_{x2} - _{y2}$  orbital [38] of the Cu(II) ion and the spectral features are characteristics of the axial symmetry [39]. The complex under may have four coordinate square geometry.

In square planar complex, the unpaired electron lies in the  $d_{x2} - _{y2}$  orbital giving  ${}^{2}B_{1g}$  as the ground state with  $g_{11} > g_{\perp} > g_{e}$ , while the unpaired electron lies in the  $d_{z2}$  orbital giving  ${}^{2}A_{1g}$  as the ground state



Weight loss percentage for PEA homopolymer and EA-metal chloride polymer complexes<sup>a</sup>.

Polymer	Volatilization	First st	tage	Second	l stage	Third s	stage	Wt.%
	temp., °C	T <sub>max</sub> ., °C	Wt. loss,%	T <sub>max</sub> ., °C	Wt. loss,%	T <sub>max</sub> ., °C	Wt. loss,%	remaining at 1000 °C
PEA	120	170	35	273	57	-	-	8
(1)	115	152	27	241	27	273	17	39
(2)	110	150	28	232	40	271	22	26
(3)	117	155	14	242	23	275	12	51
(4)	105	141	16	227	38	265	28	27

<sup>a</sup> Numbers as given in Table 1.

with  $g_{\perp} > g_{II} > g_e$ . For the present Cu(II) complex, the observed g-values are  $g_{II}$  (2.32)  $> g_{\perp}$  (2.09)  $> g_e$  (2.0023), which suggest that the unpaired electron lies in the  $d_{x2} - {}_{y2}$  [40] orbital. In the axial spectra, the g-values are related with exchange interaction coupling constant (G) by the following equation:

$$\mathbf{G} = \mathbf{g}_{\mathrm{ll}} - 2/\mathbf{g}_{\perp} - 2.$$

According to Hathaway and Billing [41], If G > 4, the exchange interaction between Cu(II) centers in the solid state is negligible. If G < 4, considerable exchange interaction is indicated in the solid complex. The observed value for the exchange interaction parameter for the copper complex (G = 3.6) suggests that significant exchange coupling is present and the misalignment is appreciable, and the unpaired electron is present in the d<sub>x2</sub> – y<sub>2</sub> orbital. This result also indicates that the exchange coupling effects are not operative in the present complex. It is usual to determine the bonding parameters for Cu(II) ion in various ligand field environments. The in-plane  $\sigma$ -bonding parameter,  $\alpha^2$  is related to g<sub>II</sub> and g<sub>⊥</sub> by the following equation [40,42]:

$$\alpha^2 = A_{II}/0.036 + (g_{II} - 2.0023) + 3/7(g_{I} - 2.0023) + 0.04.$$

The  $\alpha^2$  value of 0.72 indicates complete covalent bonding, while that 1.0 suggests complete ionic bonding. The observed value (0.72)



Fig. 14. TGA curves of PEA homopolymer and EA-metal chloride polymer complexes.

indicates that the metal complexes are predominantly ionic in character. The out-of-plane  $\pi$ -bonding ( $\gamma^2$ ) and in-plane  $\pi$ -bonding ( $\beta^2$ ) parameters are calculated using the following eqs.:

$$\beta^2 = (g_{11} - 2.0023)E/-8\lambda\alpha^2,$$
  
 $\gamma^2 = (g_1 - 2.0023)E/-2\lambda\alpha^2.$ 

Here,  $\lambda = -828~{\rm cm}^{-1}$  for free Cu(II) ion and E is the electronic energy for  $^2B_{1g} \rightarrow ^2A_{1g}$  transition. The observed  $\beta^2$  value (0.95) and  $\gamma^2$  value (1.05) indicate that there is interaction in the out-of-plane  $\pi$ -bonding, whereas the in-plane  $\pi$ -bonding is predominantly ionic. This is also confirmed by orbital reduction factors K, which can be estimated from the simple relation [43]:

$$K_{ll} = \alpha^2 \beta^2$$

$$K_{\perp}=\alpha^2\gamma^2$$

Significant information about the nature of bonding in the Cu(II) complex can be derived from the relative magnitude of K<sub>II</sub> and K<sub>⊥</sub>. In the case of pure  $\sigma$ -bonding, K<sub>II</sub>  $\approx$  K<sub>⊥</sub> = 0.77, whereas K<sub>II</sub> < K<sub>⊥</sub> implies considerable in-plane  $\pi$ -bonding, while for out-of-plane  $\pi$ -bonding K<sub>II</sub> > K<sub>⊥</sub>. For the present complex, the observed order K<sub>⊥</sub>(0.76) > K<sub>II</sub> (0.68) implies a greater contribution from in-plane  $\pi$ -bonding than for out-of-plane  $\pi$ -bonding in metal-ligand  $\pi$ -bonding. Thus, the ESR study of the copper complex has provided supporting evidence for the optical results.

#### 3.10. Thermal analyses

TG curves of PAH homopolymer and polymer complexes of EA with CuCl<sub>2</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub> and CdCl<sub>2</sub> are shown in Fig. 14. PEA homopolymer degrades in two stages. The first starts at ~120 °C with a weight loss of 35% and the second at ~190 °C with a weight loss of 57%. There are three TG degradation stages for all the polymer complexes. The first stage is due to the loss of chlorine molecules. Table 6 lists the percentage of weight loss shown by the derivative equipment associated with the TG apparatus. Their relative importance being dependent upon the



Fig. 15. Arrhenius plots for the degradation of PEA homopolymer and EA-metal chloride polymer complexes.

#### Table 7

Activation energies of the thermal degradation of PEA homopolymer and EA-matal chloride polymer complexes<sup>a</sup>.

Polymer	E <sub>a</sub> (kJ/mol)
PEA	13.7
(1)	12.2
(2)	11.7
(3)	12.9
(4)	11.2

<sup>a</sup> Numbers as given in Table 1.

type of polymer complexes. The final weight residues, which can be considered as metal oxide, are in good agreement with those calculated from the metal content using EDTA. Table 6 shows the residual weight percentage at 1000  $^{\circ}$ C.

The effective activation energies for the thermal degradation of PEA and EA-metal salt polymer complexes were determined from the temperature dependence of the chain rupture rate [44,45]. The rate constant of the thermal degradation was plotted according Arrhenius relationship (Fig. 15). Table 7 lists the activation energy of the thermal degradation ( $E_a$ ) of PEA homopolymer and EA-metal salt polymer complexes. The activation energy of the homopolymer is higher than that of the polymer complexes. It is clear that the activation energies are in the same order of the stabilities.

From the values of the activation energy of the thermal degradation  $(E_a)$  of PEA homopolymer and complexes (1-4), it is observed that the complexes (1-4) are less stable than the PEA homopolymer. These results are inconsistent with our previous results [13]. As shown in Fig. 16, the activation energy  $(E_a)$  of the complexes is expected to increase with the increasing thermal stability of complexes. Therefore, the  $E_a$  value for the complex (1) is higher compared to the other complexes (2 and 4), due to the higher atomic number which indicate that the complex (1) is more stable than other complexes (2 and 4).

# 4. Conclusion

The ligand of *N*-[ $\beta$ -(ethylamino)] acrylamide (EA) behaves as a neutral bidentate *via* its nitrogen atom of NH<sub>2</sub> group and nitrogen atom of NH group in polymer complexes. The polymer complexes characterized on the basis of elemental analyses, IR, <sup>1</sup>H NMR, UV–Vis spectra, magnetic susceptibility measurements, ESR, molar conductance and thermal analysis. Molecular docking and binding energy calculations of ligand with prostate cancer mutant 2q7k-hormone and breast cancer mutant 3hb5-oxidoreductase receptors indicated that the ligand is efficient inhibitor of 3hb5-oxidoreductase and 2q7k-hormone receptors. It was



Fig. 16. The relation between activation energy of the thermal degradation  $(E_a)$  and atomic number of metal complexes (1, 2 and 4).

found that the enol form of EA ligand shows best interaction with 2q7k receptor other than 3hb5 receptor. From molecular and electronic structures of the ligand (keto and enol forms), it was found that the enol form is more stable than keto form as reflected from energy gap values. It was found that the activation energy of the thermal degradation ( $E_a$ ) of the homopolymer is higher than that of the polymer complexes. It is clear that the activation energies are in the same order of the stabilities.

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