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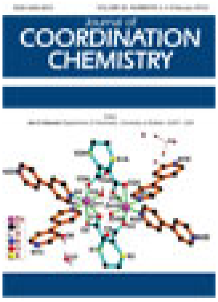

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Polymer complexes. LV. Spectroscopic, thermal studies, and coordination of metal ions N-[3-(5-amino-1,2,4-triazolo)] acrylamide polymer complexes

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Polymer complexes. LV. Spectroscopic, thermal studies, and coordination of metal ions *N*-[3-(5-amino-1,2,4-triazolo)] acrylamide polymer complexes

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Novel polymeric complexes with a potentially bidentate ligand formed by amidation of 3,5-diamino-1,2,4-triazole with acryloyl chloride were synthesized and characterized on the basis of elemental analyses, IR, ^{1}H-NMR, UV-Vis, magnetic susceptibility measurements, molar conductance, and thermal analyses. The molar conductance data reveal that all the polymer complexes are non-electrolytes. Spectral studies reveal that the free ligand coordinates bidentate to the metal ion through the oxygen of the carbonyl and azomethine of the heterocyclic ring. Elemental analyses of the polychelates indicate the metal to ligand ratio of 1 : 1/1 : 2. On the basis of electronic spectral data and magnetic susceptibility measurements, suitable geometry has been proposed for each polymeric complex. The electron spin resonance spectral data of the Cu(II) complex showed that the metal–ligand bonds have considerable covalent character. The thermal behavior of these chelates shows that the polymer complexes lose coordinated water in the first step immediately followed by decomposition of the anions and ligand molecules in a subsequent step.

Keywords: *N*-[3-(5-Amino-1,2,4-triazolo)] acrylamide; Polymer complexes; Spectroscopic; Thermal studies

1. Introduction

There has been growing interest in the design and synthesis of polymer–metal complexes due to their special properties and potential applications in sorption, waste water treatment, organic synthesis, hydrometallurgy, catalysis, and recovery of trace metal elements [1–4]. Polymer metal complexes are in general polymers containing one or more electron donors such as N, S, O, and P that can form coordinate bonds with toxic heavy metals. A polymeric ligand is usually used to selectively bind a specific metal ion in a mixture to isolate important metal ions from waste water and aqueous media. One type that has been extensively used in the separation and preconcentration of metal ions is chelating ion exchange resin with specific chelating groups attached to the polymer [5–7]. Among polymers, those containing nitrogen donors have been

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synthesized and used in complexation of transition metal cations. Various nitrogen containing ligands such as salicylaldiminate derivatives [8], oligoethyleneimine [9], vinyl amine [10], and quinoline [11, 12] have been used in the preparation of resins.

In our laboratory, the coordination behavior and chemical equilibria of some aliphatic [13–15] and aromatic [16–18] polymer complexes have been investigated. However, no structural chemistry and coordination studies have been reported for homopolymer containing amino heterocyclic functional groups. The major interests of this article are: (i) the synthesis of *N*-[3-(5-amino-1,2,4-triazolo)]acrylamide (ATA), (ii) the synthesis of some transition metal salt polymer complexes derived from this homopolymer, (iii) assigning the stereochemistry of the polymer complexes based on electronic studies.

Our interest is focused on coordination chemistry of transition metals with acrylamide-based ligands [12–15, 18]. To gain more information about the structure and stereochemistry of such polymer complexes, a detailed investigation on new mono- and binuclear metal(II) polymer complexes with ligands involving imine nitrogen and carbonyl oxygen as donors has been initiated [18].

This study describes the chelation behavior of ligands derived from amidation of 3,5-diamino-1,2,4-triazole with acryloyl chloride toward some transition elements, which may help to clarify the mode of chelation of ATA toward metals. The structure of the studied polymer complexes is elucidated using elemental analyses, infrared (IR), solid reflectance, electron spin resonance (ESR), magnetic moment, molar conductance, and thermal analyses.

2. Experimental

2.1. *Materials*

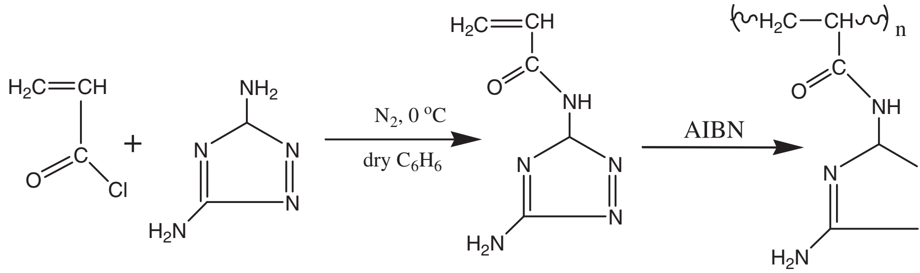
3,5-Diamino-1,2,4-triazole and acryloyl chloride (AC) (Aldrich Chemical Co. Inc.) were used without purification. 2,2′-Azobisisobutyronitrile (AIBN) (Aldrich Chemical Co. Inc.) was purified by dissolving in hot ethanol and filtering [19]. The solution was left to cool, pure material was then collected by filtration and dried.

2.2. *Preparation of the N-[3-(5-amino-1,2,4-triazolo)] acrylamide (ATA) monomer*

The ATA monomer was prepared by the reaction of equimolar amounts of AC (0.9 g, 0.01 mol) and 3,5-diamino-1,2,4-triazole (0.84 g, 0.01 mol) in dry benzene (25 mL) until the evolution of hydrogen chloride ceased, forming a yellow powder of monomer (0.82 g, ~60%). Microanalysis for $C_5H_7N_5O$: Found (%): C, 39.27; H, 4.48; N, 45.57; Calcd (%): C, 39.22; H, 4.58; N, 45.75.

2.3. *Preparation of poly{N-[3-(5-amino-1,2,4-triazolo)]}acrylamide homopolymer*

The poly{*N*-[3-(5-amino-1,2,4-triazolo)]}acrylamide (PATA) homopolymer was prepared by free radical initiation of ATA (0.7 g, 0.5 mol) using 0.1 w/v % AIBN as initiator and DMF (50 mL) as solvent for 6 h. The polymer product (0.6 g, ~86%) was precipitated by pouring in distilled water and dried in a vacuum oven for several days at 40°C. The PATA homopolymer was characterized by IR and ^{1}H-NMR spectroscopy.



ATA PATA

2.4. *Preparation of the polymer complexes*

Polymer complexes were prepared by refluxing anhydrous Cu(II), Ni(II), Co(II), and Cd(II) chlorides and $UO_2(CH_3COO)_2 \cdot 2H_2O$ (0.001 mol) with the corresponding ligand (ATA) (0.001 and/or 0.002 mol) in 20 mL DMF, and 0.1% (w/v) AIBN as initiator. The resulting mixture was heated under reflux for ~8 h. The hot solution was precipitated by pouring in large excesses of distilled water containing dilute hydrochloric acid to remove the metal salts that were incorporated into the polymer complexes. The polymer complexes (**2**–**6**, see table 1) were filtered, washed with water, and dried in a vacuum oven at 40°C for several days. The polymer complexes were determined by complexometric titration using EDTA [20] after decomposition by *aqua-regia*.

2.5. *Measurements*

Elemental microanalyses (C, H, and N) of the solid chelates were performed in the Microanalytical Center, Cairo University, Egypt. The analyses were repeated twice to check the accuracy of the analyzed data. The ^{1}H-NMR spectrum was obtained with a Joel FX90 Fourier transform spectrometer with DMSO-d_6. IR spectra were recorded using a Perkin-Elmer 1340 spectrophotometer as KBr pellets. Ultraviolet-Visible (UV-Vis) spectra of the polymer were recorded in Nujol mull using a Unicom SP 8800 spectrophotometer. The magnetic moments of the prepared solid complexes were determined at room temperature using Gouy's method. Mercury(II) (tetrathiocyanato)cobalt(II), [Hg{Co(SCN)$_4$}], was used for calibration of the Gouy tubes. Diamagnetic corrections were calculated from the values given by Selwood [21] and Pascal's constants. Magnetic moments were calculated using the equation $\mu_{\mathrm{eff}} = 2.84\ [T_{\mathrm{CM}}^{\mathrm{coor}}]^{1/2}$. Thermogravimetric (TG) measurements were made using a Du Pont 950 thermobalance. Ten milligram samples were heated at $10^\circ\mathrm{C\,min^{-1}}$ in a dynamic nitrogen atmosphere ($70\,\mathrm{mL\,min^{-1}}$); the sample holder was boat-shaped, $10 \times 5 \times 2.5\,\mathrm{mm}^3$ deep; the temperature measuring thermocouple was placed within 1 mm of the holder. ESR 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 diphenyl picrylhydrazyl (DPPH) as a

Table 1. Microanalysis and magnetic moment data of PATA homopolymer and ATA–metal salt polymer complexes.*

	Analysis, Calcd (found) %						
Polymer complexes[a]	C	H	N	Cl	M	MO*	$\mu_{eff.}$[b] (BM)
PATA (**1**)	39.22 (39.27)	4.58 (4.48)	45.75 (45.57)	–	–	–	–
P[Cu(ATA)Cl_2] (**2**)	20.87 (20.81	2.43 (2.41)	24.34 (24.72)	24.69 (24.52)	22.10 (22.31)	27.57 (27.82)	1.81
P[Co(ATA)$(OH_2)_2Cl_2$] (**3**)	18.81 (18.93)	3.45 (3.23)	21.95 (21.85)	22.26 (22.17)	18.47 (18.31)	23.83 (23.77)	5.21
P[Ni(ATA)$(OH_2)_2Cl_2$] (**4**)	18.83 (18.71)	3.45 (3.51)	21.97 (22.03)	22.28 (22.37)	18.39 (18.42)	23.42 (23.21)	3.00
P[Cd(ATA)Cl_2] (**5**)	17.84 (17.63)	2.08 (2.17)	20.81 (20.71)	21.11 (21.07)	33.41 (33.72)	38.25 (38.51)	dia.
P[$UO_2(ATA)_2(OAc)_2$] (**6**)	24.21 (24.29)	2.88 (3.31)	20.17 (20.37)	–	34.29 (34.48)	–	dia.

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

*Microanalytical data as well as metal estimations are in good agreement with the stoichiometry of proposed complexes. The excellent agreement between calculated and experimental data supports the assignment suggested in this work.

[a] ATA is the ligand; air-stable; no-hygroscopic; insoluble in water; soluble in coordinating solvents, such as DMF and DMSO.

[b] The magnetic moments (as B.M.) of the polymer complexes were measured at room temperature.

reference material. 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. The conductance measurement was achieved using a Sargent Welch Scientific Co., Skokie, IL, USA instrument.

3. Results and discussion

The ligand was prepared as described in section 2, dried under vacuum and subjected to elemental analyses, ^{1}H-NMR and IR spectral analysis. The results of the elemental analyses (C, H, and N) with molecular formula are presented in table 1 and are in good agreement with those calculated for the suggested formula, indicating the purity of the prepared ligand.

3.1. *Composition and structure of ligand and polymer complexes*

ATA monomer was not previously prepared and no studies concerning metal polymer complexes reported. Hence, these polymer complexes are prepared and completely characterized by various physico-chemical techniques, namely elemental analyses (C, H, and N, metal content), IR, solid reflectance, magnetic studies, ESR, molar conductance, and thermal analyses.

3.2. *Elemental analyses of the polymer complexes*

The polymer complexes were prepared according to the following equations:

$$\mathrm{MCl_2 + ATA \xrightarrow{AIBN} [M(ATA)Cl_2]_{\mathit{n}}} \quad \mathrm{M = Cu(II)\ or\ Cd(II)}$$

$$\mathrm{MCl_2 + ATA \xrightarrow{AIBN} \left[M(ATA)(OH_2)_2Cl_2\right]_{\mathit{n}}} \quad \mathrm{M = Co(II)\ or\ Ni(II)}$$

$$\mathrm{UO_2(OAc)_2 + ATA \xrightarrow{AIBN} \left[UO_2(ATA)_2(OAc)_2\right]_{\mathit{n}}}.$$

The resulting polymer complexes of Cu(II), Co(II), Ni(II), Cd(II), and UO_2(II) with the ligand are colored, air stable, and soluble in DMF and DMSO but insoluble in common organic solvents. The composition, coordination mode, and geometry of the polymer complexes were established on the basis of spectral analyses, thermal analysis, conductivity measurements, and magnetic properties.

3.3. *Molar conductance of the polymer complexes*

The molar conductances of $10^{-3}\,\mathrm{mol\,L^{-1}}$ of solutions of the polymer complexes are determined in DMSO at $25 \pm 2°\mathrm{C}$ to be in the range from 2.52 to $12.65\,\Omega^{-1}\,\mathrm{mol^{-1}\,cm^2}$, indicating non-electrolytes [22]. Conductivity values for a non-electrolyte are below $50\,\Omega^{-1}\,\mathrm{mol^{-1}\,cm^2}$ in DMSO [22]. Hence the chloride and acetate ions in the metal–polymer complexes are in the coordination sphere [23].

Table 2. Important IR frequencies (cm^{-1}) of PATA homopolymer and polymer complexes of ATA–metal chloride.

	Wavenumber (cm^{-1})						
Polymer complex[a]	ν(C–N=N)	Ring breathing mode	Ring deformation mode	ν(C=O)	ν(M–Cl)	ν(M–N)	Coordinated H_2O molecules
1	2100	972	827,780	1630	–	–	–
2	2075	965	831,794	1615	340	430	–
3	2085	970	836,792	1620	300	310	3400,890,625
4	2085	960	835,792	1620	290	320	3400,870,600
5	2090	965	831,795	1613	310	340	–

[a]Numbers as given in table 1.

3.4. *^{1}H-NMR spectrum*

^{1}H-NMR spectrum of PATA was recorded in DMSO-d_6 solution using tetramethylsilane (TMS) as internal standard. There are five peaks at 11.3, 5.2, 3.1, 2.2, and 1.8 ppm due to –NH, –NH_2, –CH of triazole ring, –CH and –CH_2 protons, respectively. The ligand does not show any peak attributed to enolic –OH protons, indicating that the ligand exists in the keto form; upon addition of D_2O the intensities of both NH and NH_2 protons significantly decrease, supporting the assignments.

The ^{1}H-NMR spectrum of the ATA monomer showed the expected peaks and pattern of the vinyl group ($CH_2=CH$), δ 6.25 ppm (dd, $J=17$, 11 Hz) for the vinyl CH and δ 5.12 ppm (AM part of AMX system dd, $J=17$, 11 Hz) for CH_2. These peaks disappear 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, indicating that polymerization of ATA monomer occurs on the vinyl group [24]. The rest of the proton spectrum of the monomer and polymer remain almost without change.

3.5. *IR spectra and mode of bonding*

Important spectral bands of the synthesized ligand as well as the polymer complexes are compared in table 2 to determine the coordination sites involved in chelation. Peaks such as C=O and lone pair of azomethine nitrogen of the heterocyclic ring are expected to be involved in chelation [25]. The ligand exists in the keto-enol form in the solid state [11, 13, 18].

The IR spectrum of PATA homopolymer shows three medium broad bands at 3325, 3290, and 3450 cm^{-1} of overlapping ν_{sym}(N–H) and ν_{asym}(NH and NH_2 group). The band at 1630 cm^{-1} is assigned to carbonyl [13, 18] and bands at 2100, 1450, 972, and 820 cm^{-1} are due to triazole N–C=N ring breathing and ring deformation modes. Table 2 lists some characteristic IR bands of PATA homopolymer, suggesting that the polymer exists mainly in the keto form. The triazole ring increases the electron density of the neighboring –NH. Significant change in PATA bands upon complexation is the decrease in ν(C=O) by 10–15 cm^{-1}, indicating involvement of carbonyl in coordination. The IR spectrum of ATA displayed characteristic bands due to ν(NH), ν(CO) and ν(C=N) at 3325, 1750, and 1670 cm^{-1}, respectively. The band due to azomethine ν(C=N) shifted to higher wavenumber (15–25 cm^{-1}) in the IR spectrum of the polymer complex, indicating its participation in coordination [12, 26, 27]. This coordination is more likely than that of the other nitrogen because the basicity is believed to decrease by inductive effect of the N=N group. The position of the bands at 3450–3290 $\mathrm{cm^{-1}}$ assigned to asymmetric and symmetric modes of NH_2 are unchanged, indicating non-involvement of this group in complexation. In the ATA–$CoCl_2$ and ATA–$NiCl_2$ polymer complexes, there is a strong broad band at 3400 $\mathrm{cm^{-1}}$, together with bands at 1145, 870, and 600–625 $\mathrm{cm^{-1}}$ that have been reported to be due to coordinated water [13, 16, 28]. New bands that appear in the polymer complexes at 430, 310, 320, and 340 $\mathrm{cm^{-1}}$ are attributed to ν(Cu–N), ν(Co–N), ν(Ni–N), and ν(Cd–N) vibrations [15, 18, 24], respectively. The band at 290–340 $\mathrm{cm^{-1}}$ is assigned to the ν(M–Cl) vibration. Table 2 represents some characteristic IR bands of the polymer complexes.

IR bands due to the uranyl group of the ATA–uranyl acetate polymer complexes appear at 918 $\mathrm{cm^{-1}}$ [ν_{asym}(U–O)], 793 $\mathrm{cm^{-1}}$ [ν_{sym}(U–O)], and 246 $\mathrm{cm^{-1}}$ [O–U–O bend] [16]. The force constant (F_{UO}) was calculated following the method given by McGlynn *et al.* [29] as 6.88 mdynes/Å, which agrees well with the force constant values of similar dioxouranium(VI) complexes [16, 30–32]. The UO bond distance is in the usual range (1.60–1.92 Å) observed for dioxouranium(VI) complexes [16, 30–32]. The uranyl polymeric complex displays bands at 1638 and 1348 $\mathrm{cm^{-1}}$ due to symmetric and asymmetric stretching vibrations of the acetate group [15] with $\Delta\nu = 290\,\mathrm{cm^{-1}}$ characteristic for monodentate acetate. The electronic spectrum of the ATA–uranyl acetate polymer complex shows bands in the 34,980 $\mathrm{cm^{-1}}$ and 23,000 $\mathrm{cm^{-1}}$ regions which may be assigned to carbonyl $n-\pi^*$ transition and UO_2 moiety [31, 33]. The dioxouranium complex exhibits a new band at ~23,960 $\mathrm{cm^{-1}}$, which is assigned to $^1\Sigma_g^u \rightarrow {}^3\pi_u$ transition typical for the symmetric stretching frequency for the first excited state. In the present investigation, uranyl possesses an elongated octahedral structure with nitrogen and oxygen atoms in axial positions. Two ligand units and two OAc molecules remain in *trans* positions. The UO_2(II) and Cd(II) polymer complexes were diamagnetic as expected.

It is clear from these results that elemental analyses and IR spectral measurements are in agreement with each other.

3.6. *Magnetic susceptibility and electronic spectra measurements*

The 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 $\mathrm{cm^{-1}}$ range, which is assigned to a π–π^* transition associated with the azomethine linkage [34]. The spectra of the polymer complexes show intense bands in the high-energy region in the 20,800–28,160 $\mathrm{cm^{-1}}$ range which can be assigned to charge transfer L → M bands [35]. Bands observed at 20,620–27,900 $\mathrm{cm^{-1}}$ can be attributed to d–d transitions of the metal ions. Magnetic and spectroscopic studies are discussed in detail in the following section.

3.7. *Copper(II) spectrum*

The ATA–$CuCl_2$ polymer complex has a magnetic value of 1.81 BM, indicative of Cu^{2+}. Four-coordinate copper(II) polymer complexes may possess either tetrahedral or square-planar structures. In the spectrum of the Cu(II) polymer complex, the d–d transitions are observed in the 16,000–16,400 cm^{-1} range. These values are of particular importance since they are highly dependent on the geometry of the molecule. Transition from a square-planar structure to a deformed tetrahedral structure leads to a red shift of absorption in the electronic spectrum [36]. Thus, the smaller value of the wavelength of the band corresponding to the transition resembles a geometry of the complex between tetrahedral and square planar. Ferrer *et al.* [37] reported copper(II) complexes derived from 1,2,4-triazole ligands contain a pyramidal structure formed by the *N*,*N*-bridging triazolato groups. The copper atoms are five-coordinate with a distorted square-pyramidal geometry. In our case, Cu(II) coordinates bidentate through oxygen of carbonyl and azomethine nitrogen of the triazole ring.

3.7.1. ESR spectrum. The ESR spectrum of Cu(II) complex was as polycrystalline sample recorded at room temperature. The $g_{\parallel}$ and g values were computed from the spectrum using DPPH free radical as the "g" marker. In square planar geometry, the unpaired electron lies in the $d_{x^2-y^2}$ orbital giving $^2B_{1g}$ as the ground state with $g_{\parallel} > g$. The observed g value was characteristic of a square planar. Kivelson and Neiman [38] have reported the $g_{\parallel} < 2.3$ for covalent character of the metal ligand band and $g_{\parallel} > 2.3$ for ionic character. Appling this criterion the covalent character of the metal ligand bond in the complex under study can be predicted. The g_{iso} (2.149) value and the geometric parameter G (2.3), i.e., the measurement of exchange interaction between the copper centers were evaluated by using the expressions:

$$
\begin{aligned}
g_{\mathrm{iso}} &= (g_{\parallel} + 2g)/3,\\
G &= (g_{\parallel} - 2.0023)/(g - 2.0023).
\end{aligned}
$$

The evaluated value of g tensor parameter show the order as $g_{\parallel}$ (2.204)>g (2.092)>g_e (2.0023) which is typical of axially symmetric d^9 Cu(II) having one unpaired electron $d_{x^2-y^2}$ orbital [39]. The complex in the present study show the value of $G<4$ which indicate the effective interaction between the copper centers [40]. The odd electron is present in the $^2B_{1g}$ anti-bonding orbital.

3.8. *Cobalt(II) spectrum*

The electronic spectrum of the ATA–$\mathrm{CoCl_2}$ polymer complex shows two main bands at 18,900 cm^{-1} [$^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)$] ($\nu_3$) and 16,540 cm^{-1} [$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$] ($\nu_2$), suggesting that there is an octahedral geometry around Co(II) [41]. The ligand field parameters were calculated using the following equations:

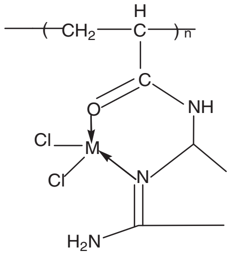
$$
\begin{aligned}
10D_q &= (2\nu_2 - \nu_3) + 15B,\\
B &= 1/510[7(\nu_3 - 2\nu_2) \pm 3\{81\nu_3^2 - 16\nu_2(\nu_2 - \nu_3)\}^{1/2}],\\
10D_q &= \nu_2 - \nu_{1,}\\
340D_q^2 &= 18(\nu_2 + \nu_3)D_q + \nu_2\nu_3 = 0,\\
B &= 1/15\left(\nu_3 + \nu_2 - 30D_q\right),\\
\beta &= B/B^{\circ}.
\end{aligned}
$$

From the position of the bands and the calculated Racah parameters, the complex is octahedral with largely covalent bonds between the ligand and Co(II) [42]. The room temperature magnetic moment, 5.21 B.M., demonstrates a high-spin octahedral configuration with $^4T_{1g}(F)$ ground state [36, 43].

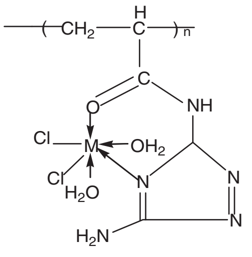
3.9. *Nickel(II) spectrum*

The electronic spectrum of the ATA–$NiCl_2$ polymer exhibits three bands at 10,100, 16,500 and 23,810 to 24,400 cm^{-1} due to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2), and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3), respectively. The calculated values of $Dq = 1010\,cm^{-1}$, $B = 644\,cm^{-1}$, $\beta = 0.62$, and $\nu_2/\nu_1 = 1.63$ lie in the same range reported for an octahedral Ni(II) [42]. The value of the magnetic moment (3.00 B.M.) is an additional evidence for an octahedral structure.

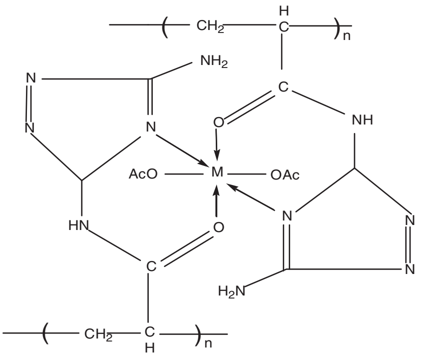
According to IR and electronic spectra and elemental analyses, ATA reacts with Cu(II), Co(II), Ni(II), and Cd(II) in a 1 : 1 molar ratio and UO_2(II) in a 2 : 1 molar ratio of monomer unit as follows:



M = Cu(II) or Cd(II)



M = Co(II) or Ni(II)



M = UO_2(II)

3.10. *Thermal methods of analysis*

In order to give more insight into the structure of the polymer complexes, thermal studies of the polymer complexes have been carried out using TG techniques.

TG curves of PATA homopolymer and of polymer complexes of ATA with Cu(II), Co(II), Ni(II), and Cd(II) chlorides are shown in figure 1. The polymer complexes are more stable than the PATA homopolymer. This is similar to the results obtained by Desai and Suthar [44] with polychelates from poly(m-*N*-acryloyl-aminobenzoic acid). The stabilities of the polymer complexes increase in the order ATA–$CdCl_2$ > ATA–$CuCl_2$ > ATA–$CoCl_2$ > ATA–$NiCl_2$ > PATA homopolymer.

There are three TG degradation stages for ATA–Co(II) and ATA–Ni(II) chloride polymer complexes. The first at ~130°C is attributed to loss of water. There are only two TG degradation stages for ATA with Cu(II) and Cd(II) chloride polymer complexes and PATA homopolymer, due to the absence of water in these polymer complexes.

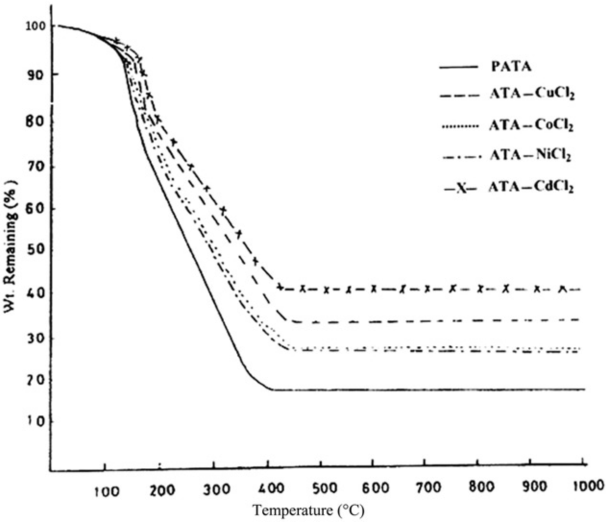


Figure 1. TG curves of PATA homopolymer and polymer complex of ATA with $CuCl_2$, $CoCl_2$, $NiCl_2$, and $CdCl_2$.

Table 3. Weight loss percentage for PATA homopolymer and ATA–metal chloride polymer complexes.

		First stage		Second stage		Third stage		
Polymer complex[a]	Volatilization temperature (°C)	$T_{max.}$ (°C)	Wt loss (%)	$T_{max.}$ (°C)	Wt loss (%)	$T_{max.}$ (°C)	Wt loss (%)	Wt (%) remaining after 1000°C
1	123	175	24	293	59	–	–	17
2	140	205	22	314	43	–	–	35
3	133	141	12	200	24	305	35	29
4	130	139	13	198	23	302	36	28
5	145	209	22	316	36	–	–	42

[a]Numbers as given in table 1.

The remaining weights of the polymer complexes which can be considered as metal oxide are in good agreement with those calculated by determination of the metal with EDTA. Table 3 represents the remaining weights of the polymer complexes as compared to the homopolymer, which may be due to formation of stable six-membered ring structures in the polymer complexes.

4. Conclusion

ATA behaves as a chelating bidentate neutral ligand, bonding through azomethine N and carbonyl O (of acryloyl group). ATA was characterized by analytical and spectral methods before using it for the preparation of polymer complexes.

Co(II) and Ni(II) ions are six-coordinate octahedral, coordinated equatorially by nitrogen (of azomethine), an oxygen (of acryloyl) and oxygen atoms of two water molecules, while Cu(II) or Cd(II) in these complexes is four-coordinate (square-planar structure), coordinated equatorially by a nitrogen (of azomethine), an oxygen (of acryloyl), and two chlorides. UO_2(II) is eight coordinate through a nitrogen of azomethine, an oxygen of acryloyl, and oxygen of each acetate. Thermal analyses of Co(II)/Ni(II) polymer complexes show that the weight loss is equivalent to two moles of coordinated water.

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