DOI: 10.17344/acsi.2019.5566 *Acta Chim. Slov.* **2020,** *67,* 551–559

Scientific paper

Synthesis and Characterization of Cross Linked Acetoguanamine Polymer Complexes: Investigation of their Thermal and Magnetic Properties

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Received: 09-12-2019

Abstract

In this study, 2,4-diamino-6-methyl-1,3,5-triazine (acetoguanamine) was used as the starting material. 2,4-diamino-6-methyl-1,3,5-triazine was boiled under reflux with glutaraldehyde and terephthaldehyde in acetonitrile. And, s-triazine-containing polymer ligands (IV and V) were obtained by these condensation reactions. These target s-triazin containing polymer ligands we obtained were analyzed by ^{1}H-NMR, FT-IR and elemental analysis. Then, polymeric metal (Co^{2+}, Ni^{2+} and Cu^{2+}) complexes of the polymeric ligands (VI-XI) were obtained from the interaction with $CoCl_2·6H_2O$, $NiCl_2·6H_2O$ and $CuCl_2·2H_2O$ at 60 °C in ethyl alcohol. The structures of these complexes were also illuminated and elucidated using FT-IR, elemental analysis and magnetic susceptibility analysis. The polymerization degrees of the polymeric ligands were determined by the molecular weight determination study with the viscometer.

Keywords: Acetoguanamine; s-triazine; Schiff bases; cross-linked polymeric complexes; thermal decomposition; magnetic properties.

1. Introduction

In recent years, an important class of compounds consisting of substituted s-triazine derivatives has been a growing interest in the using of s-triazine derivatives in different fields.[1,2] The remarkable reactivity and unique structure of the s-triazine moiety attracted the researchers to utilize it in the modification and construction of new materials.[3] s-Triazine based polymers have a high transparency and an enormous thermal and mechanical stability.[4,5] They have been widely used as matrixes for advanced composites or as resins in their own right for structural applications, especially for automotive, aerospace and microelectronic utilities.[6] Acetoguanamine (2,4-diamino-6-methyl-1,3,5-triazine) is one of the most widely used s-triazine derivatives, because it is a commercially available, inexpensive material and it has an excellent ability to undergoes nucleophilic substitution reaction under controlled temperature,[7,8] which allow it to be useful in many material and pharmaceutical,[9,10] and industrial applications.[11–13]

The design and synthesis of supramolecular polynuclear metal complexes have been an area of rapid growth for the past 20 years.[14] During the last decade, a remarkable development in the preparation of self-assembled architecture through metal ion coordination has been observed.[8] The motivation behind much of the studies related with polynuclear metal complexes has been provided by the prospect of producing a wide range of purpose-built materials with predetermined structures and potential applications in separation, gas storage, molecular recognition, and catalysis.[8,14,15] The preparation of polymetallic complexes can be achieved using rationally designed polydentate ligands.[16] On the other hand, it has been demonstrated that the 1,3,5-triazine ring is a suitable structural element to be incorporated into thermotropic liquid crystals.[17]

Schiff base chemistry, formed by the reversible condensation of amines and aldehydes has been made available in biomedicine as a result of its high efficiency and inoffensive by-product (only water).[18–20] The Schiff-base cross-linked injectable hydrogels were reported to have tunable gelation kinetics, biodegradability, and self-repair functions.[21–23]

We now report the synthesis and characterization of polymeric Schiff base including two imin groups as new templates. The condensation reaction of acetoguanamine (2,4-diamino-6-methyl-1,3,5-triazine) with glutaraldehyde and terephthaldehyde in acetonitrile gave the desired polynuclear metal complexes moieties in a single step.[24] The NH_2 groups were then modified with dimeric acetoguanamine (2,4-diamino-6-methyl-1,3,5-triazine) as a single-directional linker,[6–10] followed by treatment with Co(II), Ni(II) and Cu(II)[11–20] to give the mentioned new cross linked polymeric Schiff bases metal complexes IV and V.

2. Experimental

2. 1. Reagents and Solvents

Both of solvents (acetonitrile and ethanol), acetoguanamine (**1**), glutaraldehyde, tereftaldehyde and *o*-phenylenediamine, acetic acid, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ and sodium hydroxide were bought from Sigma and they were used without further purification. The ^1H NMR spectra of the polymers were taken with an Agilent NMR VNMRS spectrometer at 400 MHz, through their dimethyl sulfoxide (DMSO-d_6) solutions. The internal standard of the NMR measurements was tetramethylsilane (TMS). FT-IR spectra were taken by Perkin Elmer 1600 Spectrum 100 ATR Polarization (4000–440 cm^{-1}). Thermogravimetric Analysis (TGA) were performed using Hitachi STA7300 instrument. Elemental analyses were realized on a Leco 932 CHNS device where the results were in good harmony with the theoretical values. The metal contents of each complex were defined on a Varian, Vista AX CCD Simultaneous model ICP-AES. The pH values of all solutions were measured from a Milwaukee Mi 150 pH meter. Magnetic moment values of the metal complexes were determined with a Sherwood Scientific MX Gouy magnetic susceptibility apparatus using the Gouy method with $Hg[Co(SCN)_4]$ as calibrant. The effective magnetic moments per metal atom, μ_{eff}, were calculated using the well-known formula $\mu_{eff} = 2.84\sqrt{X_M T}$ B.M., where χ_M is the molar susceptibility.

2. 2. Synthesis of Polymeric Ligands

2. 2. 1. Synthesis of IV

Acetoguanamine (0.125 g, 1.00 mmol) was solved in 25 mL acetonitrile under reflux for an hour. Equivalent amount of glutaraldehyde solution (%2) was added to this solution drop by drop. Then, 5-6 drops of acetic acid were dropped as catalyst. This mixture was boiled under reflux for 3 hrs. The resulting precipitate was filtered off and dried under vacuum at 60 °C.

^1H NMR (ppm) data for IV: 7.50 (2H, triplet), 2.40 (3H, singlet), 2.20–2.05 (6H, multiplet); FT-IR (cm^{-1}) data for **IV** = 2926, 2854 ($CH_{aliphatic}$), 1655 (CH=N), 1537 ($CH=N_{triazine}$).

2. 2. 2. Synthesis of V

Acetoguanamine (0.125 g, 1.00 mmol) was solved in 25 mL acetonitrile under reflux for an hour. Then, teraftaaldehyde (0,134 g, 1.00 mmol) was added to this solution portionwise. And then, 2 mL of acetic acid were dropped as catalyst. This mixture was boiled under reflux for 2 hrs. The resulting precipitate was filtered off and dried under vacuum at 60 °C.

^1H NMR (ppm) data for **V**: 8.80 (2H, singlet), 8.05–7.70 (4H, multiplet), 2.40 (3H, singlet); FT-IR (cm^{-1}) data for **V**: 1633 (CH=N), 1556 (CH=N triazine).

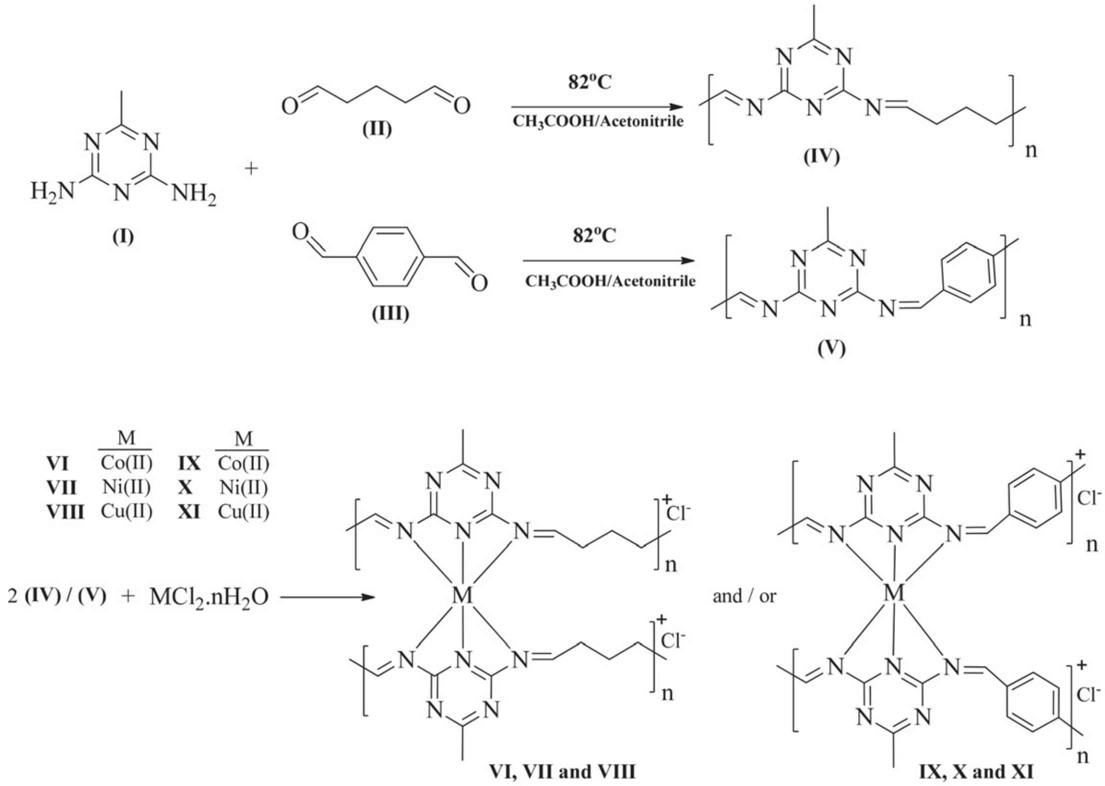
2. 3. Synthesis of Cross-Linked Polymeric Complexes (VI–XI)

IV or **V** (0.44 g or 0.51 g, 1.00 mmol) were solved in 50 mL of 0.1 M HCl solution. Then, equivalent amount of 0.001 M $CoCl_2·6H_2O$, $NiCl_2·6H_2O$, $CuCl_2·2H_2O$ in ethanol were added to these solutions drop by drop. These mixtures were heated under reflux at 60 °C. Finally, the pH of the system was adjusted to around 6.00 with NaOH 5%. The resulting precipitate (the Co(II), Ni(II), Cu(II) cross-linked polymeric complexes of AGGA and AGTA) were filtered off and dried under vacuum at 60 °C.

FT-IR (cm^{-1}) data for **VI**: 2926, 2854 ($CH_{alifatic}$), 1662 (CH=N), 1545 ($CH=N_{triazine}$), 540 (Co-N); FT-IR (cm^{-1}) data for **VII**: 2926, 2854 ($CH_{alifatic}$), 1662 (CH=N), 1545 ($CH=N_{triazine}$), 541 (Ni-N); FT-IR (cm^{-1}) data for **VIII**: 2926, 2854 ($CH_{alifatic}$), 1662 (CH=N), 1545 ($CH=N\text{-}_{triazine}$), 540 (Cu-N); FT-IR (cm^{-1}) data for **IX**: 1648 (CH=N), 1568 (CH=N triazine), 545 (Co-N); FT-IR (cm^{-1}) data for **X**: 1648 (CH=N), 1568 (CH=N triazine), 546 (Ni-N); FT-IR (cm^{-1}) data for **XI**: 1648 (CH=N), 1568 (CH=N triazine), 545 (Cu-N).

2. 4. Determination of The Average Molecular Weight of IV and V by Measuring Intrinsic Viscosity

In order to determine the average molecular weights of the IV and V polymers we synthesized here, we measured their solution viscosity using the Ostwald viscometer. The average molecular weight of polymeric ligands **IV** and **V** was then determined from the Mark Houwink's relation ($[\eta] = KM^{\alpha}$, where M is the molecular weight and $[\eta]$ is the intrinsic viscosity). The value of $[\eta]$ was determined by using the Huggins relationship $\eta_{sp} = [\eta]c + k'[\eta]^2c^2 +$ (or $\eta_{sp}/c = [\eta] + k'[\eta]^2c$), where c is the concentration, η_{sp} is the specific viscosity η_{sp} $(= \eta_{rel} - 1 = (\eta - \eta_0)/\eta_0)$, and η_{rel} $(= \eta/\eta_0 = t/t_0)$ is the relative viscosity that was obtained from the measured viscosities of solvent (η_0) and polymer solution (η); t and t_0 are flow times of the solution and the solvent. The specific viscosity is affected by the solution concentration and its dependence on c is given by the Huggins relation. The intrinsic viscosity $[\eta]$ is determined by extrapolation of η_{sp}/c to $c = 0$. According to this, dilute solutions of IV and V were prepared at different concentrations in toluene at 30 °C. Intrinsic viscosity values obtained are $[\eta] = 1.494$ kg s m–^{1} (for **IV**), $\eta = 1.985$ kg s m^{-1} (for **V**).



Scheme 1: The synthetic route of polymeric ligands and their cross linked polymeric complexes.

Table 1. The elemental analysis data and physical properties of all ligands and complexes.

[Empirical Formula] (Compound Codes)	**μeff (B.M.) 296 K**	**M.P °C**	**Color**	**[Mw]**	**Yield %**	**Contents (%)** Calculated/**Found**			
						C	**H**	**N**	**M****
$C_9H_{11}N_5$ (IV)	Dia	106	White	$[189]_n$	68	57.14	5.82	37.04	–
						56.70	**5.75**	**36.91**	
$C_{12}H_9N_5$ (V)	Dia	108	Yellow	$[223]_n$	65	64.57	4.04	31.39	–
						64.15	**3.85**	**29.13**	
$C_{18}H_{22}N_{10}CoCl_2$ (VI)	3.76	>400*	Orange	$[507.93]_n$	58	42.53	4.31	27.56	11.60
						41.78	**3.85**	**26.82**	**10.98**
$C_{18}H_{22}N_{10}NiCl_2$ (VII)	2.81	>400*	Brown	$[507.69]_n$	60	42.55	4.33	27.56	11.56
						41.90	**3.98**	**27.18**	**11.17**
$C_{18}H_{22}N_{10}CuCl_2$ (VIII)	1.76	>400*	Claret Red	$[512.55]_n$	55	42.14	4.29	27.31	12.40
						41.78	**3.82**	**27.06**	**12.02**
$C_{24}H_{18}N_{10}CoCl_2$ (IX)	3.75	>400*	Violet	$[575.93]_n$	62	50.01	3.13	24.31	10.23
						49.73	**2.97**	**24.11**	**10.01**
$C_{24}H_{18}N_{10}NiCl_2$ (X)	2.79	>400*	Dark Green	$[575.69]_n$	65	50.02	3.13	24.32	10.19
						49.55	**3.12**	**23.77**	**09.38**
$C_{24}H_{18}N_{10}CuCl_2$ (XI)	1.75	>400*	Light Green	$[580.55]_n$	67	49.61	3.10	24.12	10.95
						49.08	**3.04**	**24.01**	**10.16**

* Decomposition point, ** M = Co(II), Ni(II) ve Cu(II), μ_{eff} = Effective magnetic moment

3. Results and Discussions

In this study, 2,4-diamino-6-methyl-1,3,5-triazine (acetoguanamine) was used as the starting material. 2,4-diamino-6-methyl-1,3,5-triazine was boiled under reflux with glutaraldehyde and terephthaldehyde in acetonitrile using acetic acid as catalyst. And, s-triazine-containing polymer ligands codded as IV and V were obtained by these condensation reactions. These target s-triazin containing polymer ligands obtained were analyzed by ^{1}H NMR, FT-IR, TGA and elemental analysis. Then, polymeric metal (Co^{2+}, Ni^{2+} and Cu^{2+}) complexes of the polymeric ligands codded as (**VI**–**XI**) were obtained from the interaction with $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ at 60 °C in ethyl alcohol. The structures of these complexes were also illuminated and elucidated using FT-IR, elemental analysis, thermogravimetric analysis and magnetic susceptibility analysis. The polymerization degrees of the polymeric ligands were determined by the molecular weight determination study with the viscometer. Based on the elemental analysis, spectral studies and the coordination geometry has been assigned and is shown in Scheme 1 and Table 1.

3. 1. Interpretation of ^{1}H NMR Spectra

In the ^{1}H-NMR spectrum of the resulting s-triazine-containing polymer **IV**, the triplet for two protons at 7.50 ppm, the singlet for three protons at 2.40 ppm and the multiplet for six protons in the range of 2.20–2.05 ppm were observed and attributed to CH=N group, CH_3 group on triazine and aliphatic CH/CH_2 groups, respectively. As for the polymer **V**, the singlet for two protons at 8.80 ppm, the multiplet for four protons in the range of 8.05–7.70 ppm and the singlet for three protons at 2.40 ppm were observed and attributed to CH=N group, aromatic CH and CH_3 group on triazine, respectively. These peaks observed in the ^{1}H NMR spectra proved that both structures were successfully obtained.[25–28]

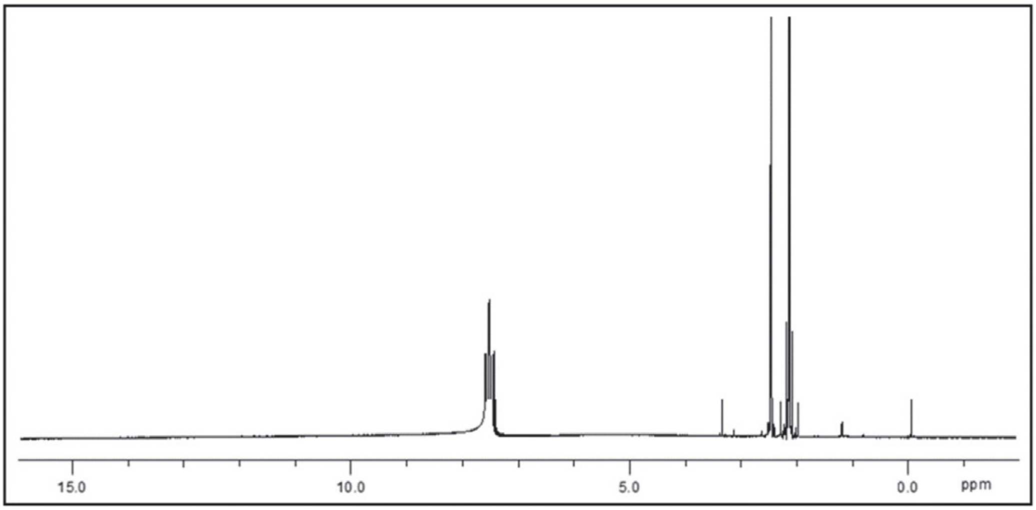


Figure 1. ^{1}H NMR spectrum of **IV**.

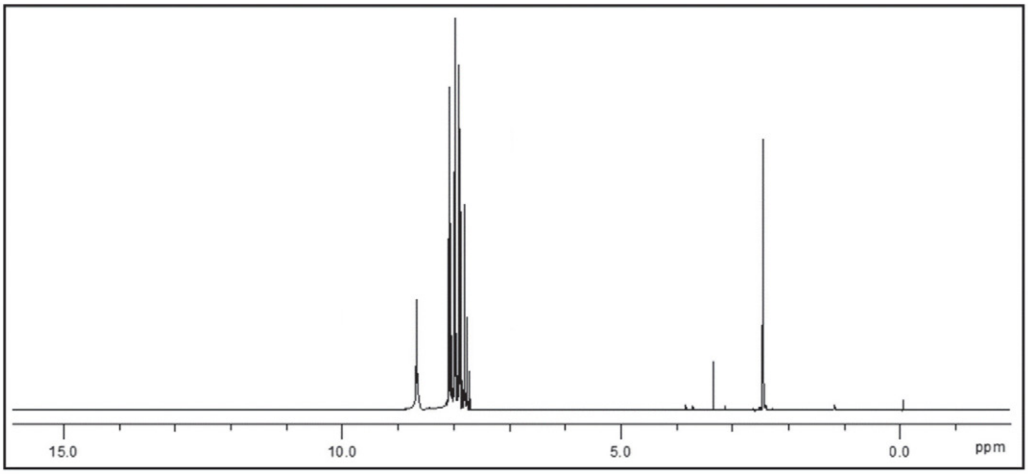


Figure 2. ^{1}H NMR spectrum of **V**.

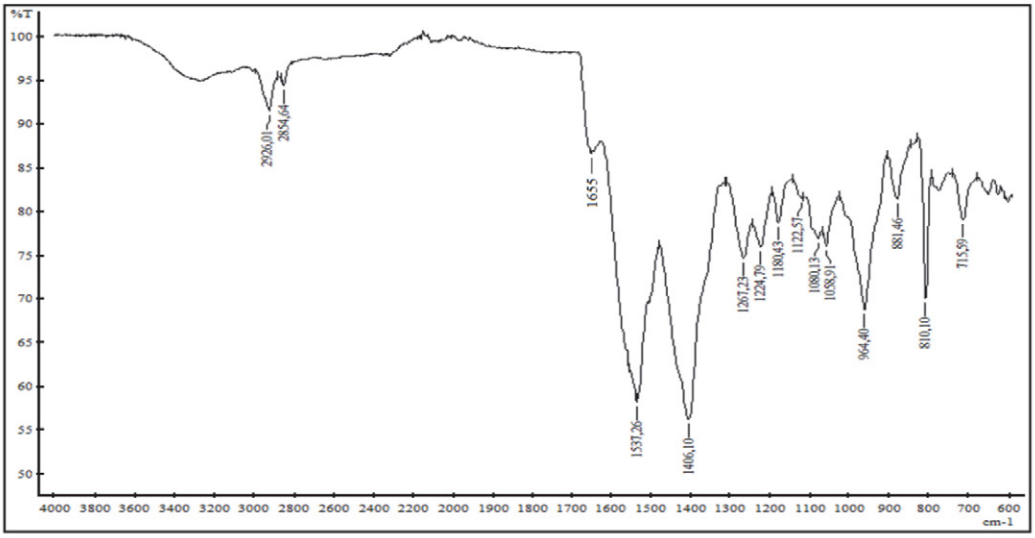


Figure 3: FT-IR spectrum of **IV**.

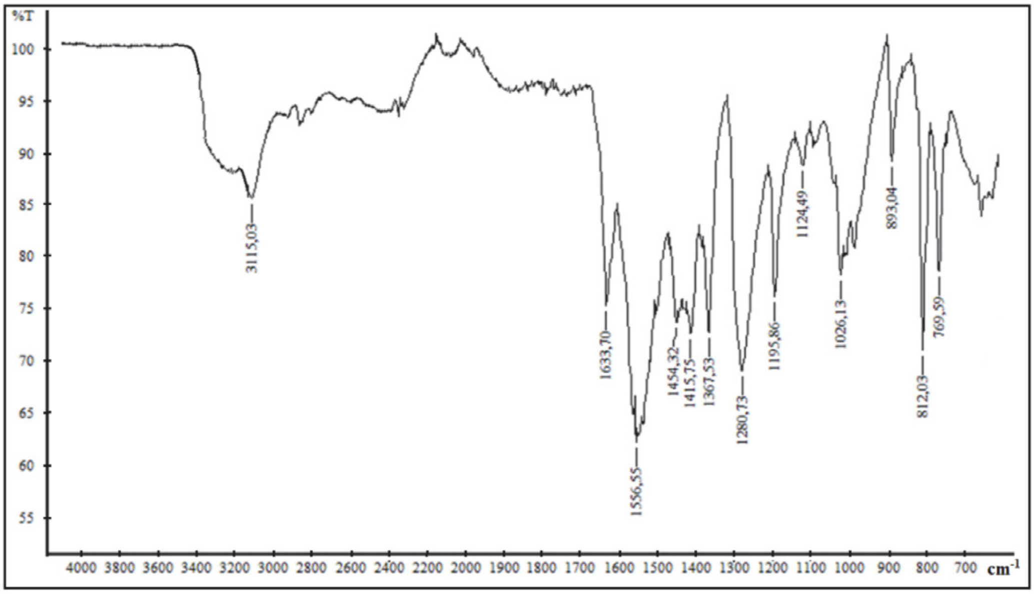


Figure 4: FT-IR spectrum of **V**.

3. 2. Interpretation of FT-IR Spectra

The FT-IR spectra of the polymer ligands and their complexes we synthesized were recorded and the bands we observed were summarized in the experimental section. Firstly, when we look at the FT-IR spectra of the polymer ligands we synthesized, C=N bands from the central s-triazine groups were observed at 1537 cm^{-1} and 1556 cm^{-1} for **IV** and **V**, respectively. Disappearance of N–H bending band at 3391 cm^{-1} and N-H bending band at 1510 cm^{-1} for acetoguanamine and instead, appearance of C=N stretching bands at 1655 cm^{-1} and 1633 cm^{-1} for **IV** and **V**, respectively, aliphatic C–H stretching bands at 2926 cm^{-1} and 2854 cm^{-1} for **IV** proves that glutaraldehyde and terefitalaldehyde linked to the s-triazine ring of acetoguanamine.[5,29,30]

Schiff base polymeric complexes were obtained from the reaction of polymer Schiff base ligands (**IV** and **V**) with metal salts of $CoCl_2·6H_2O$, $NiCl_2·6H_2O$ and $CuCl_2·$ $2H_2O$ under reflux in ethanol. In order to study the binding mode of the ligand to the metal in complexes, the FT-IR spectrum of the free ligand was compared with the spectra of the metal(II) complexes. In the FT-IR spectra of the obtained complexes, bands of C=N Schiff base and s-triazine C=N groups were observed to shift to 12–15 cm^{-1} higher wave number after complex formation. The FT-IR spectra of the ligands show strong bands at 1537 cm^{-1} and 1556 cm^{-1} for **IV** and **V**, respectively assigned to C=N group of s-triazine. These bands are shifted to higher wave number in the spectra of all the complexes indicate the coordination of triazine ring nitrogen to the metal. In addition, M–N stretching bands

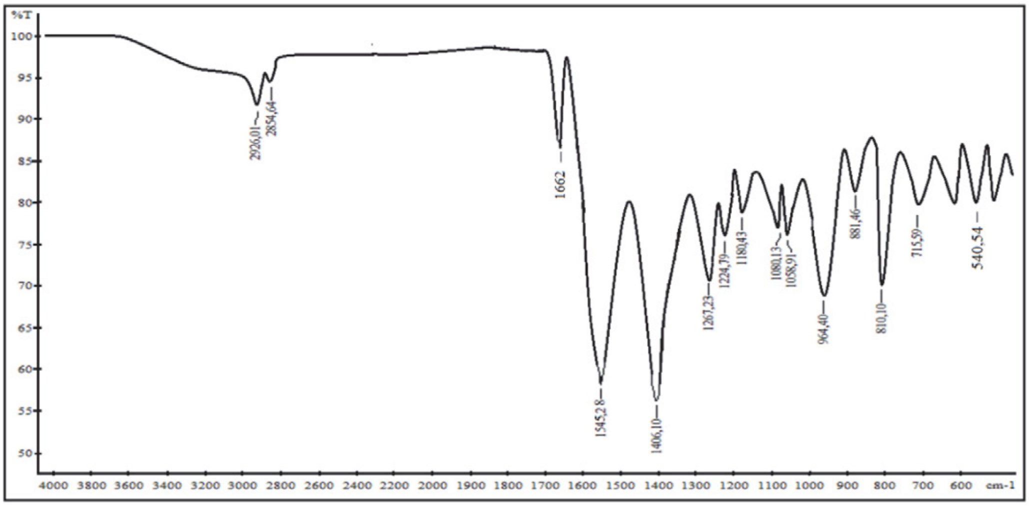


Figure 5. FT-IR spectrum of Co(II) cross polymer complex of **IV**.

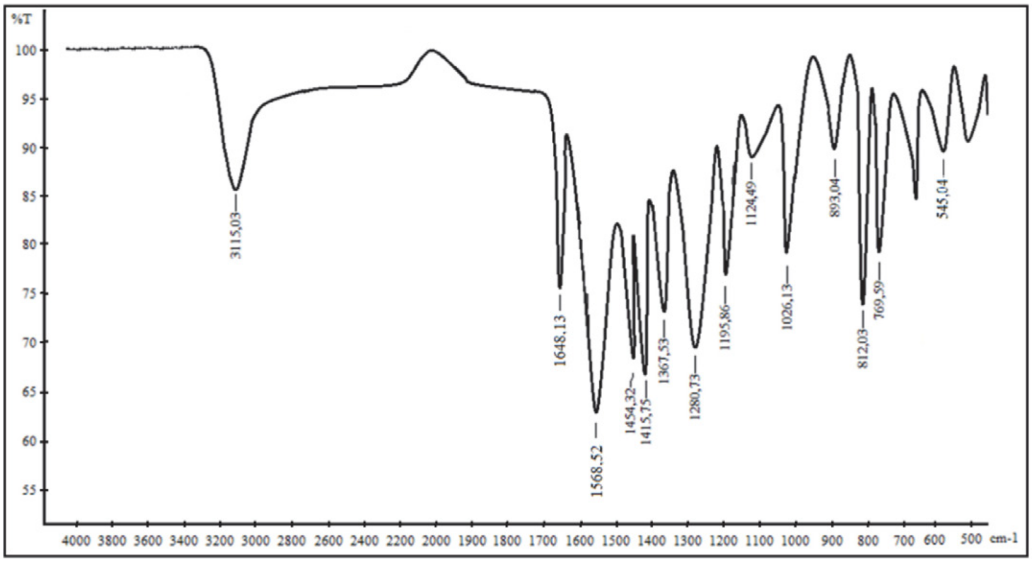


Figure 6: FT-IR spectrum of Co(II) cross polymer complex of **V**.

were observed at 540 cm^{-1} and 545 cm^{-1}, respectively.[5,28,29,31–34]

3. 3. Interpretation of Magnetic Data

In order to obtain information about the magnetic characters and geometries of s-triazine-containing polymeric complexes, effective magnetic moment (μ_{eff}) values were measured at 25 °C. μ_{eff} values of all complexes are given in Table 1. All polymeric complexes were determined as paramagnetic with d^7, d^7, d^8, d^8, d^9 and d^9 metal ions electron arrangement for VI-XI, respectively. Their effective magnetic moment (μ_{eff}) values were determined as follows: 3.76, 3.75, 2.81, 2.79, 1.76 and 1.75 B.M for each Co(II), Ni(II) and Cu(II) ions in $[(b_{2g})^2(e_g)^3(b_{1g})^1(a_{1g})^1]$, $[(b_{2g})^2(e_g)^4(b_{1g})^1(a_{1g})^1]$ and $[(b_{2g})^2(e_g)^4(b_{1g})^2(a_{1g})^1]$ electronic arrangement, respectively. The magnetic moments of the complexes are lower than the theoretical spin-only values for three, two and one unpaired electrons, respectively. According to our results, it was concluded that these complexes have distorted octahedral geometry (flat tetragonal distortion).[5,32,35–39] These results also support the proposed geometry. In other words, the fact that the s-triazine ring acts as a three-dentate ligand has forced geometry into distorted (flat tetragonal distortion) octahedral geometry. There are some examples in the literature supporting this geometry.[40,41]

3. 4. Interpretation of Thermal Analyses Curves

In order to determine the thermal behavior of the ligands and complexes we obtained, the ligands and complexes were heated in a nitrogen atmosphere at a temper-

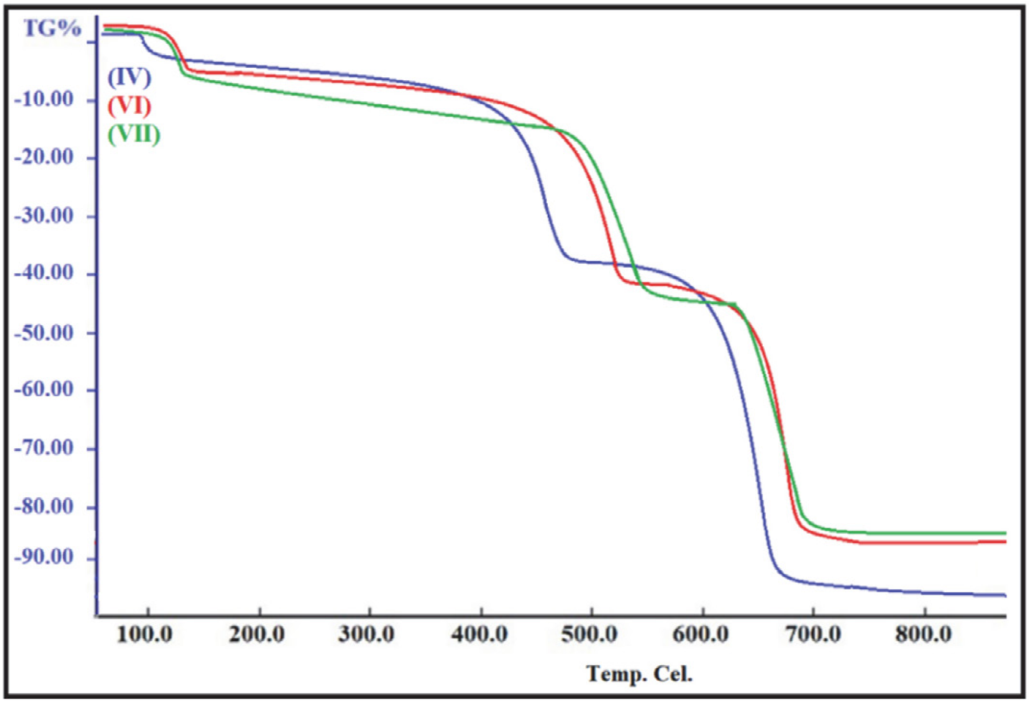


Figure 7. TGA curves of **IV**, **VI** and **VII**

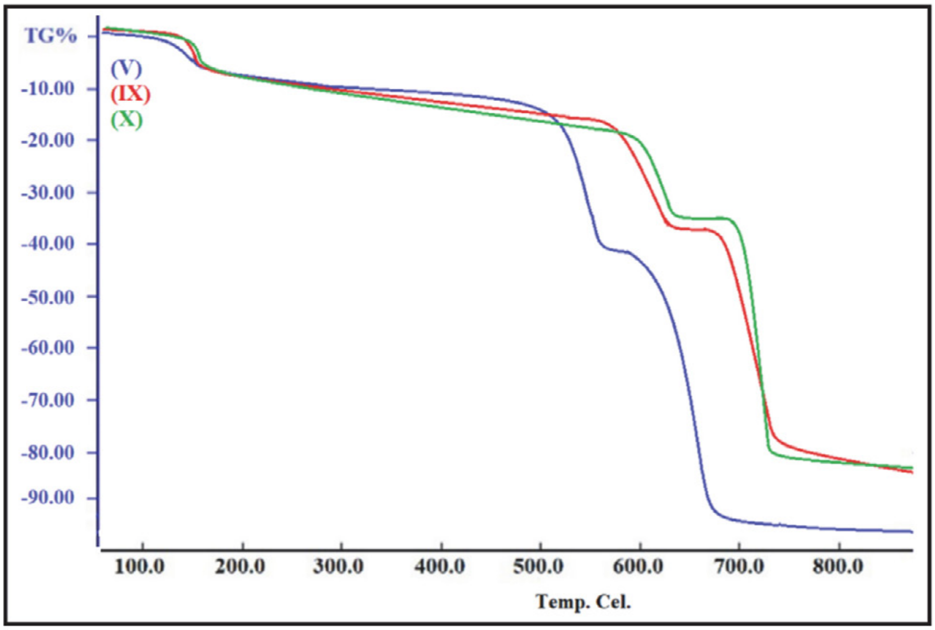


Figure 8. TGA curves of **V**, **IX** and **X**

ature of 50–1000 °C at a rate of 10 °C/min. When we interpret the TGA graphs obtained as a result of thermal analysis, we observed that the ligands and complexes decompose in two steps. However, we observed that the ligand **V** begins to decompose at a temperature of about 65 °C higher than the ligand **IV** that the main skeleton is degraded immediately after both ligands begin to decompose. The experimentally observed mass loss corresponds approximately to the mass of glutaraldehyde for the ligand **IV** and tereftaldehyde for the ligand **V**. After 5.5% moisture loss of the ligand **IV** in the temperature range of 90–105 °C, the weight loss in the first step began at 480 °C and was completed at 485 °C. The weight loss in this step is about 33%. After 4.5% moisture loss of the ligand **V** in the temperature range of 90–105 °C, the weight loss in the first step began at 545 °C and was completed at 550 °C. The weight loss in this step is about 40%. It was calculated that the weight losses in the last steps observed around

650 °C were equal to the mass of the remaining s-triazine ring.[5,42]

When we examined the TGA curves of the Co(II), Ni(II) and Cu(II) complexes of these ligands, we observed that the decomposition temperature shifted to about 40 °C higher. When we look at the rate of decomposition, we observed that there is not much difference compared to ligands. That is, while these polymeric complexes using metal ions as crosslinkers decompose, the 5-membered aliphatic chain from glutaraldehyde, and the aromatic ring from terephthaldehyde, which are the polymerizing groups, appear to decompose, firstly. It was calculated that the weight losses in the last steps observed in the temperature range of 680–720 °C were equal to the mass of the remaining s-triazine ring. The metal halide salts remain in the complexes without decomposition.[5,42]

3. 5. Interpretation of Average Molecular Weight of Polymer Ligands

The average molecular weights of the polymers **IV** and **V** were determined from the measured intrinsic viscosities: $\eta = 1.494$ kg s m^{-1} (for IV), $\eta = 1.985$ kg s m^{-1} (for V). Using the equation $\eta = KM\alpha$ (with polystyrene as standard,[5] $K = 1.7 \times 10^{-4}$ and $\alpha = 0.78$), the average molecular weights of these polymers are 9800 g/mol (IV) and 14200 g/mol (V). Using these data, it is concluded that these polymers consist of an average of 48 and 56 monomer units, respectively.[5,43,44] Because of the usage of polystyrene as standard, the actual molecular weight values might be slightly higher than observed. The reason of the detected values to be lower is the fact that the polymers have a spherical type structure, also supported by other studies.[5]

4. Conclusion

In this work, we synthesized two novel s-triazine-cored Schiff base polymeric ligands including acetoguanamine group and their six-novel cross-linked polynuclear complexes. These complexes are the first examples of these s-triazine-cored Schiff base polymeric complexes coordinated by imine groups to the Co(II), Ni(II) or Cu(II) centers. The magnetic data for the complexes show good harmony with the d^7 (S = 3/2) (for Co(II) complexes), the d^8 (S = 1) (for Ni(II) complexes) and d^9 (S = 1/2) (for both Cu(II) complexes) metal ion in distorted octahedral geometry (flat tetragonal distortion). When we interpret the TGA graphs obtained as a result of thermal analysis, we observed that the ligands and complexes decompose in two steps. It has been observed that these polymeric complexes are thermally stable complexes until 480 °C. According to the results of viscosity measurement, it can be concluded that polymeric ligands (**IV** and **V**) have average 48 and 56 monomer units, respectively.

Conflict of Interest

The authors declare that there is no conflict of interest related to this work.

5. Acknowledgement

We acknowledge that this study was financially supported by the Karabuk University Scientific Research Projects Coordinatorship (Project No: KBÜBAP-17-YL-036).

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Povzetek

2,4-diamino-6-metil-1,3,5-triazin (acetogvanamin) smo uporabili kot izhodno spojino. 2,4-diamino-6-metil-1,3,5-triazin smo refluktirali z glutaraldehidom in tereftalaldehidom v acetonitrilu. S to kondenzacijsko reakcijo smo pripravili polimerne ligande, ki vsebujejo s-triazin (**IV** in **V**). Te polimere smo analizirali z ^{1}H NMR, FT-IR in elementno analizo. V naslednji stopnji smo pripravili polimerne kovinske komplekse (Co^{2+}, Ni^{2+} in Cu^{2+}) (**VI**–**XI**) z reakcijo z $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ in $CuCl_2 \cdot 2H_2O$ pri 60 °C v etanolu. Strukture teh polimerov smo določili z uporabo FT-IR, elementne analize in analize magnetne susceptibilnosti. Stopnjo polimerizacije polimernih ligandov smo določili z molekulsko maso določeno z viskozimetrijo.