

New Complexes of Polyurea with Copper (II), Manganese (II) and Chromium (III) (Synthesis and Characterization)

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Abstract

New coordination polymers of the transition metal ions Cu(II), Mn(II) and Cr(III) with six polyurea ligands were prepared. The polyurea ligands were synthesized by the condensation of urea with the corresponding diamine. These ligands were:

- Poly (N,N'-1,4-phenylene diamine) urea (PPU)
- Poly (N,N'-1,3-phenylene diamine) urea (PMU)
- Poly (N,N'-1,2-phenylene diamine) urea (POU)
- Poly (N,N'-2,4-Toluidene diamine) urea (PTU)
- Poly (N,N'-Benzidene) urea (PBU)
- Poly (N,N'-ethylene diamine) urea (PEU)

The prepared compounds were characterized by elemental analysis, UV, IR and ^1H NMR spectroscopy and magnetic susceptibility measurements. Moreover, thermal stability were investigated by thermogravimetric analysis (TGA). For polyureas it was found that increasing aromaticity enhances thermal stability as follows:



On the other hand, the higher thermal stability was observed for Mn(II) followed by Cr(III) then Cu(II) complexes. The structure of the complexes was suggested on the basis of the physicochemical measurements obtained. The ligand

acts as mono or bidentate with copper and manganese complexes with tetracoordination while the chromium complexes are hexadentate.

	:		
(PPU)	(-4,1-N` N)	-
(PMU)	(-3,1-N` N)	-
(POU)	(-2,1-N` N)	-
(PTU)	(-4,2-N` N)	-
(PBU)	(-N` N)	-
(PEU)	(-N` N)	-

(TGA)

PBU > PPU > PMU ≈ PTU > POU > PEU

Introduction

Coordination polymers with various channels or cavities have useful properties applicable to catalysis, conductivity luminescence, magnetism, adsorption and gas storage, and therefore, they are currently under intensive study⁽¹⁻³⁾.

For the preparation of these polymers, multifunctional linking ligands such as pyridyls and carboxylate with strongly coordinating

hard oxygen – or nitrogen donor atoms are typically used⁽⁴⁻⁶⁾.

The use of metal atoms in coordination polymers offers several possible advantages over purely organic chains, grids or frameworks which are organized by non-covalent interactions, covalent metal ligand bonds are stronger than hydrogen bonds. Metal ligand bonds have more directionality than other weak interaction such as π - π stacking⁽⁷⁾.

Mn-content of polystyrene beads obtained by radical cross-linking suspensions copolymerization of chiral, dendritically styryl-substituted salens with styrene and loading with Mn(OAc)₂/LiCl to give polymer-bond Mn-salen complexes⁽⁸⁾.

Polyurea due to their excellent mechanical properties and outstanding resistance to hydrolysis find limited uses⁽⁹⁾, However, Polyurea containing other functional group in the main chain like poly-(amide-urea)⁽¹⁰⁾, poly(sulphonamide-urea)⁽¹¹⁾, polyurethane-urea⁽¹²⁾ have recognized to have better properties.

In view of these interesting results and as a continuation of our study on transition metal complexes with substituted polyurea ligands⁽¹³⁾ we have prepared a coordination polymers of chromium (III) manganese (II) and copper (II) with the above polyurea ligands and study their thermal stabilities.

Experimental

General

IR spectra were recorded on Perkin-Elmer 580B IR spectrophotometer in the (4000-200 cm⁻¹) range using CsI discs. Elemental analysis were carried out on a CHN analyzer type 1106 Carlo Erba. The

metal content was estimated spectrophotometrically using Shimadzu AA670. Conductivity measurements were made on 10⁻³M solution of the complexes in dimethylsulfoxide (DMSO) solvent at room temperature using conductivity meter model 4070 Jenway. Electronic spectra were recorded on Shimadzu UV/Vis spectrophotometer UV-160 for 10⁻³M solutions of the complexes in DMSO using 1 cm quartz cell. The magnetic measurements were carried out at 25°C on the solid state by Faradays method using Bruker BM6 instrument. The effective magnetic moment (μ_{eff}) was calculated from the formula:

$$\mu_{\text{eff}} = 2.828\sqrt{\chi_A \cdot T}$$

where T = absolute temperature

χ_A = susceptibility per gram atom corrected for the presence of diamagnetic compounds⁽¹⁴⁾.

Materials

The metal salts were used as supplied by Fluka. All chemicals were reagent grade. The synthesis of polyurea ligands were prepared according to previous literature^(13, 15).

Preparation of complexes

A clear solution of CrCl₃.6H₂O, MnCl₂.4H₂O or CuCl₂.2H₂O (1mmol) in ethanol (10 ml) was added to a

solution of ligand (1mmol) of the type POU, PMU, PTU and PEU in DMSO (15 ml), and for PBU and PPU (2 mmol) in DMSO (15 ml). The mixture was refluxed for 6-8h. The isolated solid was filtered, washed several times with hot ethanol, followed by ether then dried at 60°C. The products yield was ranged between 70-90%.

Results and Discussion

Ligands characterization

Table 1 shows the chemical structure and some physical properties of polyurea ligands. The IR spectra of the ligands shows broad band of the ureid (-NHCONH-) which is secondary amide groups. Their stretching are observed around 3330-3390 cm^{-1} . The $\nu(\text{C}=\text{O})$ frequency of the amide carbonyl was seen at about 1640-1690 cm^{-1} .

Complexes characterization

The coordination complexes of Cu(II), Mn(II) and Cr(III) with the prementioned polyurea ligands are vary in color from green, brown to black (Table 2).

Elemental analysis

The main unit ($\text{C}_7\text{H}_6\text{N}_2\text{O}$) for the ligands PPU, PMU and POU proposed in Table 1. As well as, the unit ($\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}$) for PBU, ($\text{C}_8\text{H}_8\text{N}_2\text{O}$) for PTU and ($\text{C}_5\text{H}_6\text{N}_2\text{O}$) for PEU, which

upon chelation coordinates with the central metal atom at two sites. Therefore, the general molecular formula of the resulting coordination complexes are given by: $[\text{MLCl} \cdot \text{H}_2\text{O}]_n\text{Cl}$ and $[\text{Cr}(\text{L})\text{Cl}_2 \cdot (\text{H}_2\text{O})_n]\text{Cl}$ where L=PMU, POU, PTU, PEU and M=metal ions, $[\text{M}(\text{L})_2\text{Cl} \cdot \text{H}_2\text{O}]_n\text{Cl}$ and $[\text{Cr}(\text{L})_2\text{Cl}_3 \cdot \text{H}_2\text{O}]_n$, where L=PPU and PBU. These structures have been confirmed by the results of elemental analyses of all complexes. The CHN data reported in Table 2 are in agreement with the calculated C,H and N values based on the above mentioned formulas of the ligands and the coordination complexes.

Table 1: Physical properties of polyurea ligands

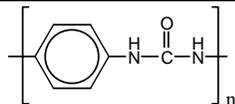
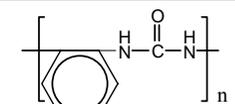
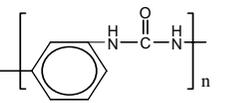
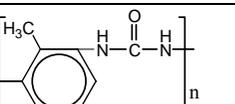
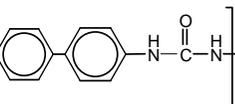
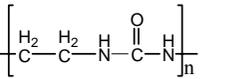
No.	Polyurea ligand	Sign	Color	Softening Pt. (°c)	CHN Analysis (calcd) %			IR (cm ⁻¹)	
					C	H	N	v(NH)	v(C=O)
1	 Poly (N,N'-1,4-Phenylene diamin Urea)	PPU	Violet	280	62.23 (62.68)	4.21 (4.47)	20.56 (20.89)	3380 (s)	1658 (s)
2	 Poly (N,N'-1,2-Phenylene diamin Urea)	POU	Pale Yellow	220	62.41 (62.68)	4.19 (4.47)	20.61 (20.89)	3390 (s)	1660 (s)
3	 Poly (N,N'-1,3-Phenylene diamin Urea)	PMU	Black	270	62.37 (62.68)	4.41 (4.47)	20.71 (20.89)	3330 (s)	1675 (s)
4	 Poly (N,N'-2,4-Tolidine diamin Urea)	PTU	Pale Brown	263	64.21 (64.86)	3.21 (3.37)	18.60 (18.91)	3365 (m)	1641 (m)
5	 Poly (N,N'-2,4-Benzidene Urea)	PBU	Pale Yellow	300	74.11 (74.28)	4.23 (4.76)	13.21 (12.33)	3550 (m)	1640 (m)
6	 Poly (N,N'-Ethylene diamin Urea)	PEU	White	190	41.41 (41.86)	6.56 (6.99)	32.45 (32.55)	3360 (m)	1690 (m)

Table 2: Physical properties, magnetic moments and molar conductance of polycomplexes

Seq.	Complex	Color	Softening point (°c)	C (%)		H (%)		N (%)		M (%)		μ_{eff} (B.M.)	Λ ohm ⁻¹ .mol ⁻¹ . cm ²
				Found	Cal.	Found	Cal.	Found	Cal.	Found	Cal.		
1	Cu(PPU)	Dark-green	300	40.98	41.74	2.76	2.98	13.50	13.91	14.63	15.79	1.91	-
2	Cu(PMU)	Black	260	20.01	29.32	2.51	2.79	9.31	9.77	21.99	22.18	1.20	46.1
3	Cu(POU)	Pale-brown	280	29.10	29.32	2.80	2.79	9.63	9.77	21.63	22.18	1.10	-
4	Cu(PTU)	Brown	250	31.99	32.27	2.29	2.35	9.23	9.41	21.11	21.36	1.4	29.0
5	Cu(PBU)	Brown	300	55.98	56.27	3.33	3.60	9.91	10.10	10.99	11.46	2.1	-
6	Cu(PEU)	Brown	2050	15.81	16.33	2.41	2.72	12.43	12.70	27.90	28.82	1.03	40.0
7	Mn(PPU)	Pale-brown	380	40.98	42.65	3.33	3.55	14.03	14.21	13.21	13.44	5.32	-
8	Mn(PMU)	Dark-brown	386	29.46	29.69	2.10	2.12	9.52	9.89	21.34	21.19	5.43	40.0
9	Mn(POU)	Pale-yellow	315	30.10	30.23	2.49	2.87	10.01	10.09	19.41	19.77	5.61	-
10	Mn(PTU)	Red-brown	390	33.53	33.73	2.40	2.42	9.58	9.69	18.97	19.02	5.41	37.2
11	Mn(PBU)	Red-brown	400	52.96	53.62	3.32	3.43	9.43	9.62	9.34	9.44	5.51	-
12	Mn(PEU)	Brown	376	14.43	14.52	3.96	4.03	11.11	11.29	22.56	22.16	5.42	20.6
13	Cr(PPU)	Red-brown	350	37.59	37.80	3.56	3.60	6.21	6.30	11.51	11.70	3.45	-
14	Cr(PMU)	Dark-brown	310	29.70	30.55	2.71	2.91	9.99	10.18	8.53	8.91	3.66	46.9
15	Cr(POU)	Green	305	25.33	25.58	3.01	3.04	8.32	8.52	15.56	15.80	3.42	-
16	Cr(PTU)	Dark-brown	330	28.01	28.28	2.39	2.56	8.06	8.25	14.10	15.32	3.57	43.2
17	Cr(PBU)	Pale-green	350	49.01	49.33	3.27	3.47	8.56	8.85	7.96	8.22	3.75	-
18	Cr(PEU)	Brown	300	14.16	14.26	3.03	3.04	10.46	10.67	19.53	19.82	3.71	23.2

Infrared analyses

The characteristic IR spectra of coordination complexes are listed in Table 3. The comparison of the ligands spectra from Table 1 with their coordination complexes (Table 3) revealed characteristic differences. One of the significant differences is the shift of the bands at $3330-3390\text{ cm}^{-1}$ (νNH of the ligands) to a lower frequencies by $100-150\text{ cm}^{-1}$ (νNH of the complexes). This indicates that the (NH) group was shared in coordination with the metal ion⁽¹⁶⁾. The $\nu(\text{C}=\text{O})$ amide carbonyl which occurred between $1640-1690\text{ cm}^{-1}$ is another noticeable difference which also shifted to lower frequency due to metal-oxygen bonds formation. The bands at 3500 & $800-880\text{ cm}^{-1}$ are attributed to $\nu(\text{OH})$ stretching, $\nu(\text{OH}_2)$

vibrations⁽¹⁷⁾. Another support for the coordination of the ligands with ion, provided by the appearance of new bands at about $610-650\text{ cm}^{-1}$, $405-550\text{ cm}^{-1}$ and $280-340\text{ cm}^{-1}$ which are assigned to $\nu(\text{M}-\text{O})$, $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{Cl})$ respectively⁽¹⁸⁾.

Table 3: IR spectral assignment and electronic spectra of polymer complexes

Seq.	complex	Band Maxima (cm ⁻¹)	Selected IR bands (cm ⁻¹)					
			$\nu(\text{NH})$	$\nu(\text{C=O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{M-Cl})$	$\nu(\text{M-O})\text{H}_2\text{O}$
1	Cu(PPU)	Insoluble	3280 (w)	1632 (m)	610 (w)	-	348 (w)	831 (w)
2	Cu(PMU)	13800	3215 (w)	1661 (m)	-	430 (w)	325 (w)	885 (w)
3	Cu(POU)	Insoluble	3275 (w)	1632 (m)	630 (w)	434 (w)	282 (w)	853 (w)
4	Cu(PTU)	13600	3280 (w)	1630 (m)	645 (w)	465 (w)	340 (w)	840 (w)
5	Cu(PBU)	Insoluble	3330 (w)	1625 (m)	600 (w)	-	333 (w)	-
6	Cu(PEU)	13900	3118 (w)	1690 (B)	-	468 (w)	349 (w)	861 (w)
7	Mn(PPU)	Insoluble	3239 (w)	1624 (s)	-	343 (w)	329 (w)	-
8	Mn(PMU)	Insoluble	3210 (w)	1662 (m)	-	550 (w)	310 (w)	887 (w)
9	Mn(POU)	27932	3261 (w)	1630 (m)	634 (w)	431 (w)	340 (w)	885 (w)
10	Mn(PTU)	34602	3215 (w)	1626 (B)	650 (w)	487 (w)	346 (w)	830 (w)
11	Mn(PBU)	30321	3225 (m)	1625 (m)	625 (w)	410 (w)	325 (w)	735 (w)
12	Mn(PEU)	31113	3154 (B)	1690 (B)	-	517 (w)	315 (w)	809 (w)
13	Cr(PPU)	Insoluble	3330 (w)	1632 (m)	-	428 (w)	339 (w)	846 (w)
14	Cr(PMU)	Insoluble	3160 (w)	1662 (m)	-	405 (w)	290 (w)	825 (w)
15	Cr(POU)	27700, 15873	3278 (w)	1643 (s)	615 (w)	443 (w)	336 (w)	807 (w)
16	Cr(PTU)	27027, 16400	3297 (w)	1625 (m)	650 (w)	465 (w)	330 (w)	840 (w)
17	Cr(PBU)	Insoluble	3268 (w)	1640 (m)	-	418 (w)	344 (w)	836 (w)
18	Cr(PEU)	27932, 16000	3152 (w)	1676 (B)	-	424 (w)	294 (w)	827 (w)

Magnetic properties

The Cr(III) polychelates shows magnetic moments of 3.42-3.75 BM, which are in the range required for an octahedral structure⁽¹⁹⁾. The Mn(II) polychelates have magnetic moment of 5.32-5.61 BM, which is slightly lower than the spin only value, but still in the range of tetrahedral structure⁽²⁰⁾. The Cu(II) polychelates shows a magnetic moments of 1.03-2.10 BM, these values are lower than those expected for tetrahedral complexes, this is due to the interaction of the secondary magnetic moments of the Cu ions⁽²¹⁾.

Electronic spectra

The ligands show a broad band at 320-293 nm. these bands may be due to $n-\pi^*$ or $\pi-\pi^*$ transitions.

The electronic spectra of Cr(III) polychelate shows two bands at 370-358 and 630-609 nm which may be assigned to ${}^4A_{2g} \rightarrow {}^4T_{1g} (v_2)$ and ${}^4A_{2g} \rightarrow {}^4T_{2g} (v_1)$ in octahedral geometry⁽²²⁾. The Mn(II) complexes doesn't show any transition because it is forbidden due to (laport rule)⁽¹⁴⁾.

The electronic spectra of Cu(II) polychelate consist of one band at 735-719nm which may be assigned to ${}^2T_2 \rightarrow {}^2E$ transition in tetrahedral environment⁽²³⁾.

Thermogravimetric analysis

Thermal stability of polyurea and its metal complexes with Cu, Mn and Cr was estimated by dynamic TGA as shown in figures 1-4. The important regions in TGA thermograms are mentioned in table 4 where:

IDT: initial decomposition temperature

MDT: medium decomposition temperature

CDT: complete decomposition temperature

In general, the table shows that the complexes posses higher degradation temperatures than the polyurea ligands alone. The aromatic ligands show thermal stability (IDT) between (260-330°c), while the aliphatic ligand (PEU) start decomposition at much lower temperature (190°c) which coincides with the literature information⁽²⁴⁾ where the aliphatic ethylene bridge are thermally sensitive. As well as, the chemical structure of the diamine shifts IDT of the polyurea ligands in the following order:

PBU > PPU > PMU > POU > PTU > PEU

The maximum thermal stability was observed in PBU ligands where the polymer containing two adjacent aromatic rings. As well as, the char

yield (%) at 500°C shows that polyurea ligands decomposes completely when the temperature exceeds 400°C⁽²⁵⁾. Comparison of IDT values of the complexes with those of the ligands indicates that complexes required higher temperatures for their degradation. Chelation of the polyurea ligands leads to stiffer chains may be the reason for such behaviour. The CDT of Mn and Cr complexes exceeds 500°C, as well as, high weight percent at 500°C reveals the high stability of these complexes.

The decomposition temperature of activation is calculated by the equation⁽²⁶⁾:

$$E = RT_i^2 / w(dw/dt)$$

Where: e: energy of activation
 T_i: initial decomposition
 temp. (IDT)

W_i: weight percent at T_i

R: gas constant

Dw/dt: tangent at (IDT) point

The energy of activation values listed in table 5 shows that the energy of the complexes are much higher than those for the free ligands.

Table 4: Decomposition temperatures of polyurea-metal complexes

Seq.	Ligands & complexes	IDT (°c)	MDT (°c)	CDT (°c)	(%) weight 500°c
1	(PPU)	260	330	415	8
2	(PMU)	240	310	460	13
3	(POU)	215	260	340	4
4	(PTU)	250	310	420	6
5	(PBU)	330	370	420	7
6	(PEU)	190	300	460	9
7	Cu(PPU)	320	350	450	15
8	Cu(PMU)	298	330	475	20
9	Cu(POU)	320	360	410	16
10	Cu(PTU)	300	335	420	15
11	Cu(PBU)	340	420	460	17
12	Cu(PEU)	242	340	450	10
13	Mn(PPU)	420	450	>500	18
14	Mn(PMU)	430	460	>500	32
15	Mn(POU)	370	358	425	20
16	Mn(PTU)	420	440	>500	20
17	Mn(PBU)	460	480	>500	20
18	Mn(PEU)	395	400	490	15
19	Cr(PPU)	380	400	>500	15
20	Cr(PMU)	370	440	>500	30
21	Cr(POU)	340	385	470	20
22	Cr(PTU)	380	460	>500	30
23	Cr(PBU)	400	425	460	12
24	Cr(PEU)	350	420	500	22

Such high thermal stability of the complexes may be due to the crosslinked structures formed as a result of coordination with metal ions. The stable ring structures formed hindered the molecular rotation. As well as, the considerable increase in

the molecular weight due to coordination. We believe that these factors together play an important role for increasing stiffness and thermal stability of the polymer-metal ion complexes.

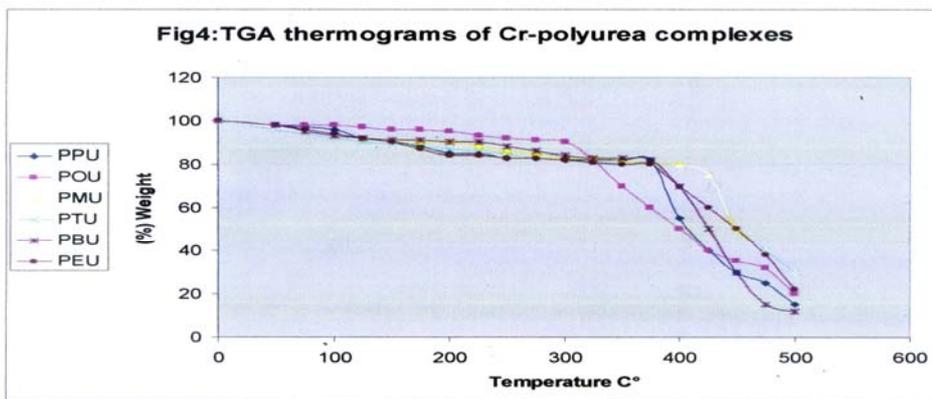
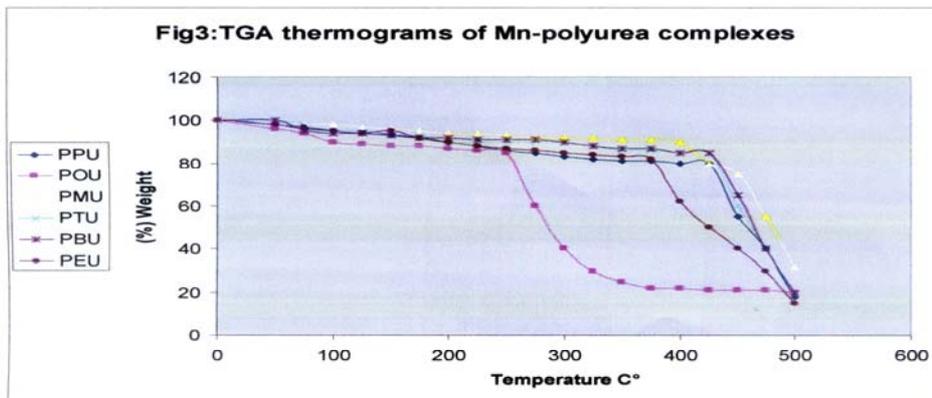
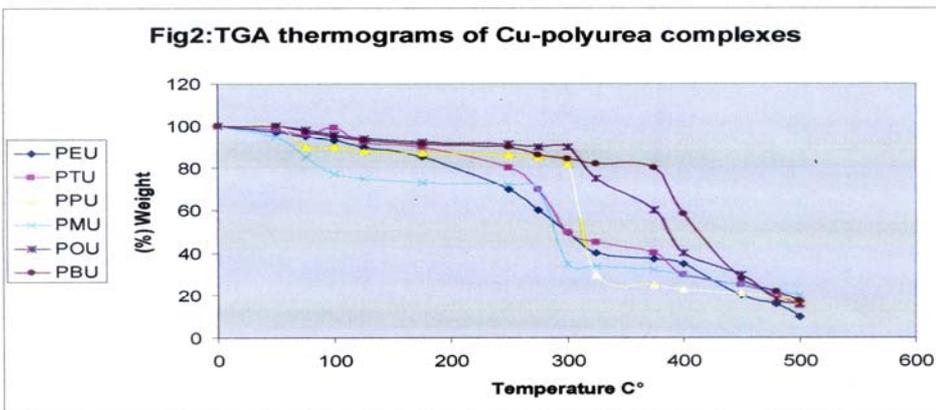
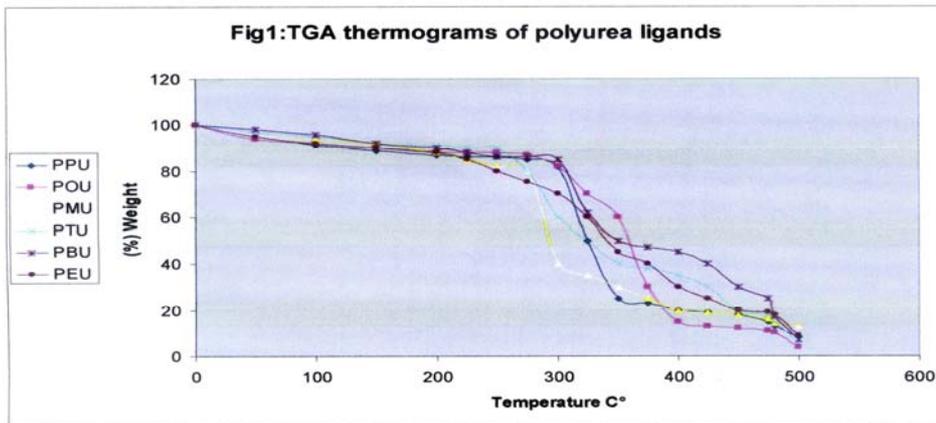
Table 5: Activation energies (Kj/mol) for decomposition of Cu, Mn and Cr polyurea complexes

Ligand Metal	PEU	PBU	PPU	PMU	POU	PTU
-	8.04	14.30	12.40	13.83	12.39	12.49
Cu	18.10	25.52	14.19	16.26	22.51	18.06
Mn	30.72	35.48	31.87	34.06	33.44	23.41
Cr	28.36	27.02	20.06	28.73	24.25	29.40

Conclusion

From the listed information, it may be concluded that the suggested chemical structures of the prepared coordination polymer are as follows:

1. The ligands PEU, POU, PMU and PTU (in which N atoms are close to each other) show tetrahedral structure with Cu(II) and Mn(II) and octahedral geometry with Cr (III) as shown in Fig. 5.
2. The ligands PBU and PPU (in which N atoms are faraway from each other) show a square planer geometry with Cu(II) and Mn(II) and an octahedral structure with Cr(III) as shown in Fig. 6.



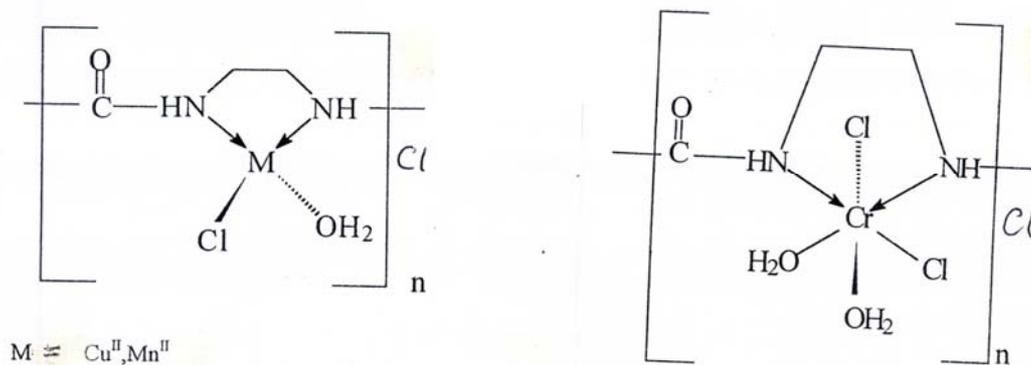


Fig. 5: Coordination polymers of PEU, POU, PMU and PTU ligands with Cu(II), Mn(II) and Cr(III)

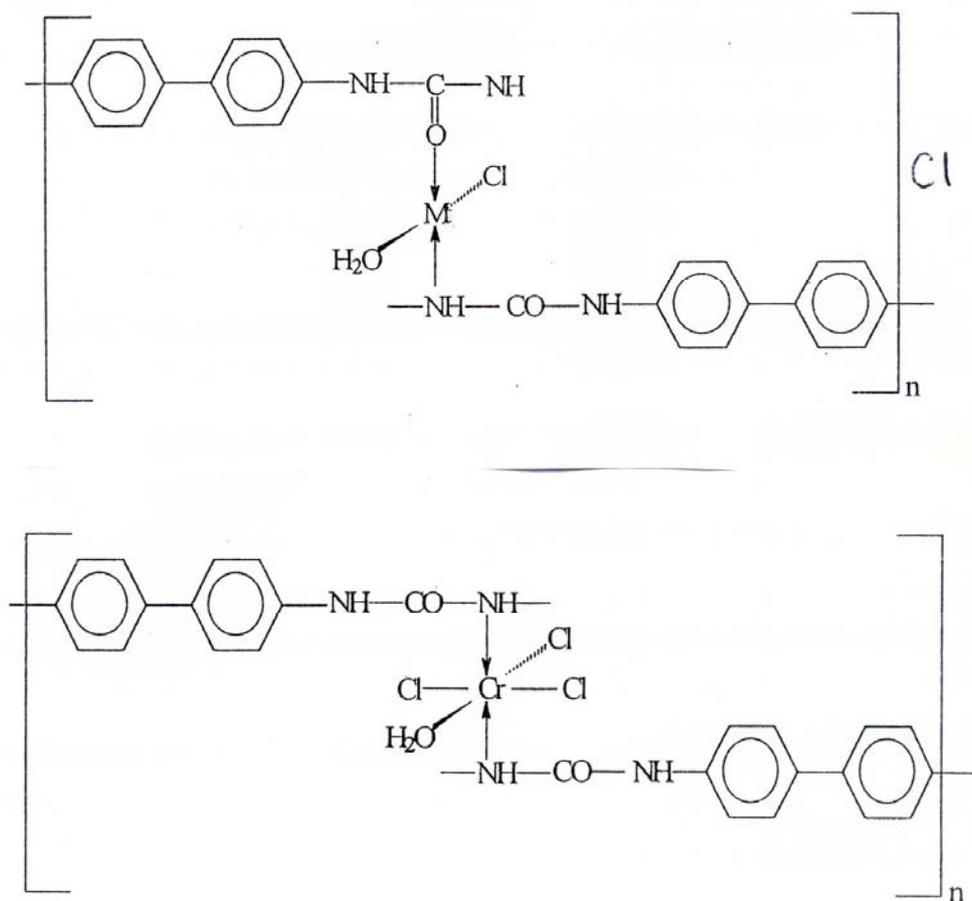


Fig. 6: Coordination polymers of PBU and PPU ligands with Cu(II), Mn(II) and Cr(III)

References

1. Robin A.Y. and Fromm, K.M.; *Coord. Chem. Rev.*, 2006, **250**, 2127.
2. Ockwing N.W., Friedrichs, O.D., Keeffe, M. and Yaghi, O.M.; *Acc. Chem. Res.*, 2005, **38**, 176.
3. Zaworotko, M.J.; *Chem. Rev.*, 2001, **101**, 1629.
4. Roger D.L., Watson, R.P., Gradinier J.R., and Smith M.D.; *Inorg. Chem.*, 2004, **43**, 6609.
5. Kitagawa, S., Kitaura, R. and Noro, S. I.; *Angew. Chem. Int. Ed.*, 2004, **43**, 2334.
6. Lu, J.Y.; *Coord. Chem. Rev.*, 2003, **246**, 327.
7. Janiak C.; *Dalton Trans*, 2003, 2781.
8. Sellner, H., Hamether, K., Günther, D. and Seebach, D., *J. Catal.*, 215, 87, (2003).
9. Reddys T.A. and Srinivasan, M., *J. Polym. Sci.*, 1989, **Part A**, 2805.
10. Gopal, J. and Srinivasan; *J. polym. Sci. Chem.*, 1985, **23**, 2719.
11. Iwakura, Y., Hayashi, K. and Langaki K.; *Makromol. Chem.*, 1967, **100**, 22.
12. Lehamann, W. and Ronke H., *U.S.*, 1988, **Part 2**, 852, 494.
13. Mohammed A.A., Buttrus N.H., and Yunis M.K.; *National J. Chem.*, 2003, **12**, 533.
14. Al-Mukhtar S.E. and Mustafa I.A., "Inorganic and Coordination Chemistry", (Arabic Version) Mosul Univ. (1988).
15. Sanders, S.R., and Karo, W., "Polymer synthesis" 8th ed., Academic press (1974).
16. Al-Alaf, T.A., Buttrus, N.H. and Hitchcock P.B., *Assian J. Chem.*, 1997, **9**, 187.
17. Gano, I., *Bull. Chem. Soc.*, Japan 1962, **34**, 760.
18. Hyams, I.J. and Lippincott, E.R., *Spectrochim. Acta*, 1969, **25A**, 1845.
19. Karampurwala, A.M., Patel, R.P. and Shan, J.R., *J. Macromol. Sci-Chem.*, 1981, **A15(3)**, 341.
20. Cotton, F.A., Wilkinson, J. "Advanced Inorganic Chemistry", 5th Ed., Interscience, N.Y. (1986).
21. Gosh, S., Bandyopadhyay, T.K., *J. Ind. Chem. Soc.*, 1980, **57**, 433.
22. Dahr, M.L., Singh, O., Gupta, V.K. and Raina, R., *J. Iraqi Chem. Soc.*, 1986, **11**.1.41.
23. Rana, A.K. and Shah, J.R., *J. Ind. Chem. Soc.*, 1986, **LXIII**, 281.

24. Periadi, D.M.A., Adam, G.A.,
Macromolecules (Arabic version)
(1980), 225.
25. Mohamed, A.A., Buttrus, N.H.
and Younis, M.K., *Nat. J. of
Chem.*, 2003, **12**, 533-545.
26. Fuoss, R., Salyer, I. and Wilson,
H., *Polym. Sci.*, 1964, **A2**, 3147.