

# Some Polyamidoxime Derivatives and Their Metal Complexes

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Received 23.09.2002

In this paper the synthesis of six polyamidoximes from their corresponding diamines with 4,4'-methylenebis (phenylglyoxylohydroximoyl chloride) and 4,4'-methylenebis(chlorophenylgly-oxime) is presented. The average molecular weights of these organic polymers were determined. In addition, the complexes of 4,4'-methylenebis(phenylglyoxylohydroximoyl chloride) with Ni(II), Co(II) and Cu(II) salts were prepared. The structures of these compounds were identified by IR or <sup>1</sup>H NMR spectral data, elemental analyses, magnetic measurements and thermal analysis.

## Introduction

The present interest in inorganic polymers stems from the growing need for materials which have thermal stability or good mechanical properties under conditions in which polymers based on carbon are unsatisfactory. One group of such compounds which has only recently come under investigation is that of the metal chelate polymers, in which metal ions are linked by di- or poly-functional organic ligands to form polymer chains. Metal chelate polymers thus occupy an intermediate position between organic and purely inorganic compounds.

One way of avoiding the difficulties arising from the insolubility of coordination compounds of high molecular weight is to synthesise an organic polymer by standard methods and then to introduce metal ions. The introduction can be used either to reinforce an existing linear polymer, or, alternatively, to effect cross-linking<sup>1,2</sup>.

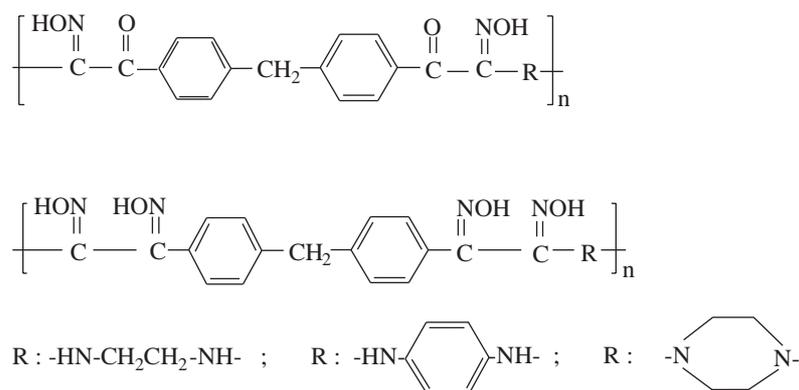
There are several standard methods of organic polymer synthesis. One of them, the linking of polydentate ligands by metal ions, was used before<sup>3-6</sup>. In these studies, the incorporation of metal ions into an existing polymer is used.

The synthesis of 4,4'-methylenebis(phenylglyoxylohydroximoyl chloride) and 4,4'-methylenebis(chlorophenylglyoxime) and their various derivatives has been the subject of previous research. The literature contains no information concerning the molecular weight and other properties of these polymers and their metal complexes, but there are some reports of related organic polymer formation<sup>7-10</sup> and complex formation<sup>7</sup>.

We report the synthesis of six new polyamidoximes, shown in Figure 1. Then metal complexes polymeric in nature were isolated and their molecular structures were described.

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**Figure 1.** Bis(keto oxime) and bis(glyoxime) polymers.

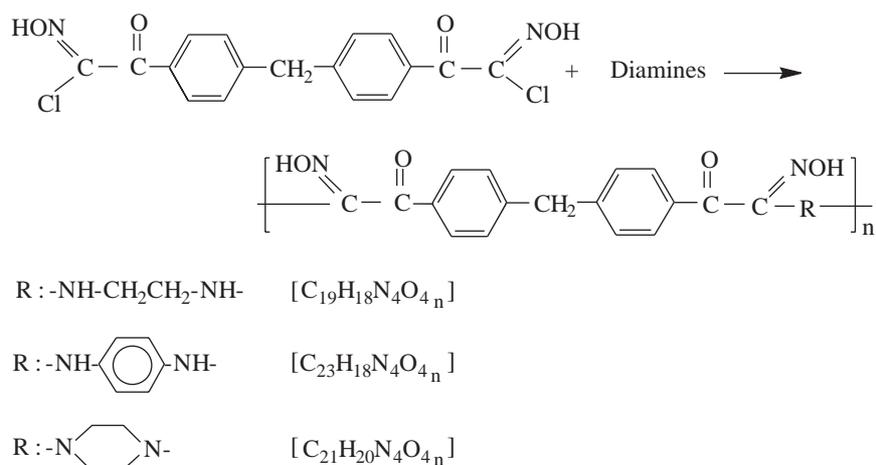
## Experimental

### Materials and Measurements

All chemicals were purchased from Merck and Fluka, and used without further purification. The <sup>1</sup>H NMR spectra and elemental analyses for carbon, hydrogen and nitrogen were carried out by the Laboratories of the Scientific and Technical Research Council of Turkey (TUBITAK). Thermogravimetric analyses (TGA) were performed at 50-850 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. Infrared spectra were recorded on a Perkin Elmer Model 1605 FT-IR spectrophotometer as KBr pellets in the region of 500-4000 cm<sup>-1</sup>. The metal contents of the compounds were determined on a Unicam 929 AA spectrometer. The magnetic moments of the complexes were measured using a Sherwood Scientific model MX1 Gouy magnetic susceptibility balance at room temperature. Average molecular weights were determined on a Knauer Model Vapour Pressure Osmometer.

In this study, 4,4'-bis(chloroacetyl)diphenylmethane<sup>11-14</sup>, 4,4'-methylenebis(phenylgly- oxylohydrox- imoyl chloride)<sup>13-15</sup> and 4,4'-methylenebis(chlorophenylglyoxime)<sup>13</sup> were synthesised by methods described in the literature.

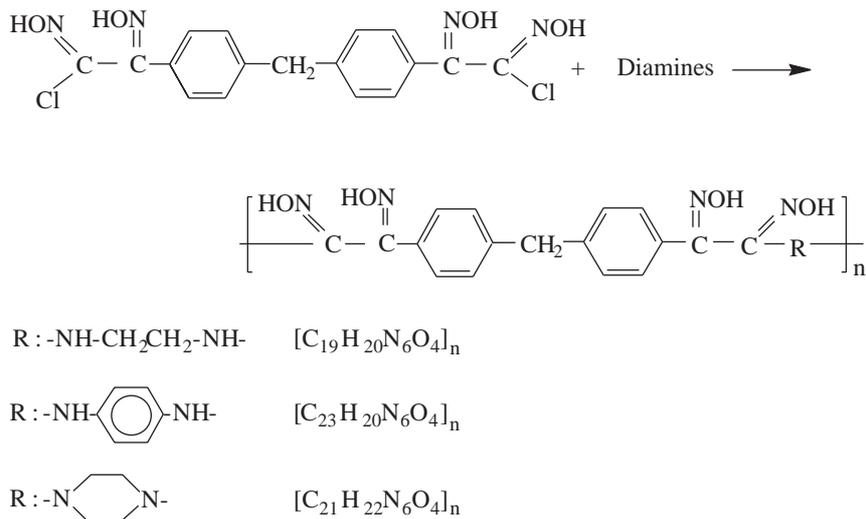
### Synthesis of keto oxime polymers



**Figure 2.** The structure of polyoxoamidoximes.

4,4'-Methylenebis(phenylglyoxylohydroximoyl chloride) (1.9 g, 5 mmol) was dissolved in 30 mL of dioxane. To this solution was added a solution of 5 mmol of diamine (0.33 mL of ethylenediamine, 0.54 g of 1,4-phenylenediamine and 0.43 g of piperazine) and 10 mmol (1.38 mL) of triethylamine in 30 mL of dioxane. The mixture was stirred for about 4 h. The precipitate was filtered off, washed with 1% NaHCO<sub>3</sub>, water and ethanol, in that order, and dried.

### Synthesis of glyoxime polymers



**Figure 3.** The structure of polyglyamidoximes.

4,4'-Methylenebis(chlorophenylglyoxime) (2.0 g, 5 mmol) was suspended in 30 mL of dioxane. To this solution was added a solution of 5 mmol of diamine (0.33 mL of ethylenediamine, 0.54 g of 1,4-phenylenediamine and 0.43 g of piperazine) and 10 mmol (1.38 mL) of triethylamine in 30 mL of dioxane. The mixture was stirred for about 4 h. The precipitate was filtered, washed with 1% NaHCO<sub>3</sub>, water and ethanol, in that order and dried <sup>7,16</sup>.

### Synthesis of Ni(II), Co(II) and Cu(II) complexes of keto oxime polymers

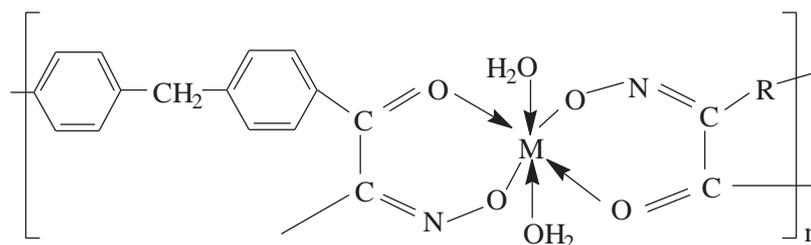
0.5 mmol polymeric keto oxime was dissolved in 10 mL of hot DMF. An equivalent amount of solution of Cu(CH<sub>3</sub>COO)<sub>2</sub>.H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O or Co(CH<sub>3</sub>COO)<sub>2</sub>.4H<sub>2</sub>O in 20 mL of ethanol (95%) was added dropwise with stirring to each polymer solution. The colour of the solution changed immediately, and the pH of the solution was then adjusted to 5.5-6.0 by adding 1% KOH in ethanol. The complex was kept on a water bath at 60 °C for about 1 h in order to complete precipitation of the complex. The precipitate was filtered, washed with water, ethanol and ether, and dried. The polymeric metal complexes thus obtained were almost completely insoluble.

## Results and Discussion

All polyamidoximes in this work were originally prepared by the polycondensation of keto oxime and dioxime with diamines.

The melting points, and the fact that their intervals are not large and they are completely soluble in solvents such as DMSO and DMF show that the molecular weights of these polymers are not very large and their molecular weight distributions are uniform. The average molecular weights of the synthesised organic polymeric ligands were determined with an osmometer. Their average molecular weights are 1040-1720 g.mol<sup>-1</sup>. Based on the obtained values, we have concluded that the synthesised polyamidoximes were formed from 3-4 mer units<sup>7</sup>.

The Cu(II), Ni(II) and Co(II) complexes of the keto oxime polymers were obtained in ethanol by the addition of sufficient 1% KOH to increase the pH to 5.5-6.0. The structures of the complexes are shown in Figure 3; their colours, melting points, results of elemental analysis are given in Table 1 and FT-IR data and magnetic measurements are given in Table 2. The structures of the complexes were characterised by IR, elemental analyses and magnetic measurements. Since the synthesised polymeric metal complexes were not sufficiently soluble in any solvents, we were not able to study their <sup>1</sup>H NMR properties. Thus, the spectral studies, limited only to the IR spectroscopy, and elemental analyses, were considered to provide sufficient evidence.



**Figure 4.** Suggested octahedral structures of the metal complexes of keto oxime polymers.

In the <sup>1</sup>H NMR spectra of 4,4'-methylenebis(chlorophenylglyoxime) and its polymers, two peaks are present for the O-H protons (10.67-11.60 ppm and 9.39-10.35 ppm), while the OH protons of 4,4'-methylenebis(phenylglyoxylohydroximoyl chloride) and its polymers appear as a single peak (10.50-11.49 ppm). The NH protons adjacent to oxime groups were observed at 6.30 and 8.40 ppm, the aromatic C-H protons at 6.29-7.86 ppm, and CH<sub>2</sub> protons at 2.10-4.12 ppm. These values are in good agreement with those of *vic*-dioximes<sup>17,18</sup> (Table 3).

In the FT-IR spectra of bis(keto oxime)-diamine ligands (as KBr pellets), bands at 3366-3312, 3377-3115, 1671-1654, 1603-1600, and 1018-982 cm<sup>-1</sup> were assigned to NH, OH, C=O, C=N, and N-O stretching vibrations, respectively. C=N stretching vibrations appearing at about 1600 cm<sup>-1</sup> in the polymeric ligands appeared at the same place in the metal complexes of these ligands, indicating coordination through the O-atoms. In the complexes of these ligands, the band attributed to the C=O group became weaker. This indicated coordination through the C=O group. Bands appearing at 2359-2360 cm<sup>-1</sup> in the ligands indicate that there are intramolecular H-bridges. In the IR spectra of the complexes, this vibration was not observed. The OH vibration of oxime appearing at 3115-3328 cm<sup>-1</sup> in the polymeric ligands disappeared completely in the metal complexes. However, the OH vibration of the H-bridge and coordinated H<sub>2</sub>O appeared in the keto oxime-piperazine ligand and its complexes.

In the FT-IR spectra of tetra oxime-diamine ligands (as KBr pellets), bands at 3285-3361, 2361-2365, 1612-1631 and 1013-943 cm<sup>-1</sup> were assigned to NH, H-bridge, C=N and N-O stretching vibrations, respectively. These absorption data are in agreement with those previously reported for substituted *vic*-dioximes.

**Table 1.** Some physical properties and elemental analyses of the polymeric ligands and complexes.

Compounds	Formula Weight	Colour	M.p. (°C)	Yield (%)	Calc.(Found) %			
					C	H	N	Metals
[C <sub>17</sub> H <sub>12</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> ]	379	Cream	171 172	76	53.83 (54.41)	3.17 (3.29)	7.39 (6.95)	-
[C <sub>17</sub> H <sub>14</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>4</sub> ]	409	Colourless	228	45	49.88 (50.64)	3.42 (3.75)	13.69 (13.13)	-
[C <sub>19</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> ] <sub>n</sub>	366	Pale yellow	208	58	62.3 (62.12)	4.92 (5.05)	15.3 (14.78)	-
[C <sub>19</sub> H <sub>16</sub> N <sub>4</sub> O <sub>4</sub> Co.2H <sub>2</sub> O] <sub>n</sub>	458.9	Green-brown	>300	78	49.68 (49.19)	4.36 (4.86)	12.2 (11.94)	12.84 (12.45)
[C <sub>19</sub> H <sub>16</sub> N <sub>4</sub> O <sub>4</sub> Ni.2H <sub>2</sub> O] <sub>n</sub>	458.7	Green	>300	81	49.71 (49.55)	4.36 (4.72v)	12.21 (11.86)	12.8 (11.98)
[C <sub>19</sub> H <sub>16</sub> N <sub>4</sub> O <sub>4</sub> Cu.2H <sub>2</sub> O] <sub>n</sub>	463.5	Green	>300	71	49.19 (48.84)	4.31 (4.51)	12.08 (12.55)	13.7 (12.96)
[C <sub>23</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> ] <sub>n</sub>	414	Pale yellow	220	68	66.67 (66.25)	4.35 (4.14)	13.53 (13.47)	-
[C <sub>23</sub> H <sub>16</sub> N <sub>4</sub> O <sub>4</sub> Co.2H <sub>2</sub> O] <sub>n</sub>	506.9	Dark brown	>300	72	54.45 (54.22)	3.95 (4.15)	11.05 (10.43)	11.62 (11.24)
[C <sub>23</sub> H <sub>16</sub> N <sub>4</sub> O <sub>4</sub> Ni.2H <sub>2</sub> O] <sub>n</sub>	506.7	Dark green	>300	73	54.47 (54.29)	3.95 (4.39)	11.05 (10.18)	11.58 (11.07)
[C <sub>23</sub> H <sub>16</sub> N <sub>4</sub> O <sub>4</sub> Cu.2H <sub>2</sub> O] <sub>n</sub>	511.5	Dark green	>300	76	53.96 (53.89)	3.91 (4.25)	10.95 (10.19)	12.41 (11.86)
[C <sub>21</sub> H <sub>20</sub> N <sub>4</sub> O <sub>4</sub> ] <sub>n</sub>	392	Cream	206	62	64.29 (63.6)	5.1 (5.65)	14.29 (13.92)	-
[C <sub>21</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> Co.2H <sub>2</sub> O] <sub>n</sub>	484.9	Light brown	>300	75	51.97 (51.56)	4.54 (4.82)	11.55 (11.14)	12.15 (11.79)
[C <sub>21</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> Ni.2H <sub>2</sub> O] <sub>n</sub>	484.7	Yellow-green	>300	76	51.99 (51.46)	4.54 (4.27)	11.55 (10.98)	12.11 (11.74)
[C <sub>21</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> Cu.2H <sub>2</sub> O] <sub>n</sub>	489.5	Green	>300	80	51.48 (51.59)	4.49 (4.26)	11.44 (11.7)	12.97 (11.41)
[C <sub>19</sub> H <sub>20</sub> N <sub>6</sub> O <sub>4</sub> ] <sub>n</sub>	396	Yellow	184	55	57.58 (56.98)	5.05 (4.84)	21.21 (21.06)	-
[C <sub>23</sub> H <sub>20</sub> N <sub>6</sub> O <sub>4</sub> ] <sub>n</sub>	444	Cream	240	57	62.16 (62.79)	4.5 (4.43)	18.92 (18.63)	-
[C <sub>21</sub> H <sub>22</sub> N <sub>6</sub> O <sub>4</sub> ] <sub>n</sub>	422	Yellow-orange	206	61	59.72 (59.47)	5.21 (5.73)	19.91 (19.5)	-

When the elemental analyses and metal analyses of the complexes were investigated, the metal-ligand ratios were found to be 1:1 in the polymeric metal complexes of the bis(keto oxime)-diamine polymeric ligands. The molecular weights of polymeric metal complexes could not be determined due to their insolubility in organic solvents. According to the FT-IR data, elemental analyses and magnetic susceptibility measurements, the Cu(II), Ni(II) and Co(II) complexes have an octahedral structure<sup>19,20</sup>. Magnetic susceptibility measurements of the complexes provide information regarding their structures and are shown in Table 2. Cu(II), Co(II) and Ni(II) complexes are paramagnetic with magnetic susceptibility values of 0.78-1.23, 2.14-3.21 and 1.49-2.13 B.M., respectively. The room temperature magnetic moments of the complexes are well below the calculated values, indicating spin-exchange interaction between metal ions<sup>21</sup>.

**Table 2.** Magnetic measurements and characteristic IR bands ( $\text{cm}^{-1}$ ) of the polymeric ligands and their complexes as KBr pellets.

Compounds	$\mu_{eff}$ (B.M.)	N-H	$\nu$ (O-H)	$\nu$ (O-H H)	C=O	$\nu$ (C=N)	$\nu$ (N-O)
$[\text{C}_{17}\text{H}_{12}\text{Cl}_2\text{N}_4\text{O}_4]$	-	-	3261 m	-	1654 s	1600 s	1010 s
$[\text{C}_{17}\text{H}_{14}\text{Cl}_2\text{N}_4\text{O}_4]$	-	-	3252 m	2361 w	-	1605 s	986 s
$[\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_4]_n$	-	3364 m	3261 w	2360 w	1654 s	1602 s	1018 m
$[\text{C}_{19}\text{H}_{16}\text{N}_4\text{O}_4\text{Co}.2\text{H}_2\text{O}]_n$	2.14	3356 m	-	-	1654 m	1603 s	1018 w
$[\text{C}_{19}\text{H}_{16}\text{N}_4\text{O}_4\text{Ni}.2\text{H}_2\text{O}]_n$	1.94	3312 m	-	-	1654 m	1602 s	1017 w
$[\text{C}_{19}\text{H}_{16}\text{N}_4\text{O}_4\text{Cu}.2\text{H}_2\text{O}]_n$	0.78	3366 m	-	-	1657 m	1602 s	1018 w
$[\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_4]_n$	-	3328 m	3115 w	2359 w	1671 s	1600 s	991 m
$[\text{C}_{23}\text{H}_{16}\text{N}_4\text{O}_4\text{Co}.2\text{H}_2\text{O}]_n$	3.21	3357 m	-	-	1654 m	1601s	990 w
$[\text{C}_{23}\text{H}_{16}\text{N}_4\text{O}_4\text{Ni}.2\text{H}_2\text{O}]_n$	1.49	3342 m	-	-	1670 m	1601 s	989 w
$[\text{C}_{23}\text{H}_{16}\text{N}_4\text{O}_4\text{Cu}.2\text{H}_2\text{O}]_n$	1.23	3362 m	-	-	1666 m	1601 s	992 w
$[\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_4]_n$	-	-	3328 w	2360 m	1670 s	1600s	988 m
$[\text{C}_{21}\text{H}_{18}\text{N}_4\text{O}_4\text{Co}.2\text{H}_2\text{O}]_n$	3.21	-	3367 w	-	1670 m	1602 s	986 w
$[\text{C}_{21}\text{H}_{18}\text{N}_4\text{O}_4\text{Ni}.2\text{H}_2\text{O}]_n$	2.13	-	3362 w	-	1654 m	1602 s	982 w
$[\text{C}_{21}\text{H}_{18}\text{N}_4\text{O}_4\text{Cu}.2\text{H}_2\text{O}]_n$	1.02	-	3377 w	-	1654 m	1602 s	984 w
$[\text{C}_{19}\text{H}_{20}\text{N}_6\text{O}_4]_n$	-	3285 m	-	2363 w	-	1631 s	1013 m
$[\text{C}_{23}\text{H}_{20}\text{N}_6\text{O}_4]_n$	-	3361 m	-	2361 w	-	1625 s	943 m
$[\text{C}_{21}\text{H}_{22}\text{N}_6\text{O}_4]_n$	-	-	3254 w	2365 w	-	1612 s	986 m

s, strong; m, medium; w, weak

**Table 3.**  $^1\text{H}$  NMR spectra of the polymeric ligands in  $\text{DMSO-d}^6$ , ( $\delta$  ppm).

Compounds	O-H <sup>a</sup>	O-H <sup>b</sup>	C-H (arom)	C-H (aliph)	N-H	Others
$[\text{C}_{17}\text{H}_{12}\text{Cl}_2\text{N}_2\text{O}_4]$	13.2 (s, 2H)	-	6.90-7.40 (d, J = 8.20 Hz, 8H)	3.7 (s, 2H)	-	-
$[\text{C}_{17}\text{H}_{14}\text{Cl}_2\text{N}_4\text{O}_4]$	12.5 (s, 2H)	12.04 (s, 2H)	7.03-7.57 (dd, J=8.13 Hz, 8H)	3.96 (s, 2H)	-	-
$[\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_4]_n$	-	10.5 (s, 2H)	7.70-7.52 (m, 8H)	4.2-2.50 (m, 6H)	6.3 (t, J = 6.95 Hz, 2H)	-
$[\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_4]_n$	-	11.02 (s, 2H)	7.86-7.38 (m, 12H)	4.09 (s, 2H)	8.4 (s, 2H)	-
$[\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_4]_n$	-	11.49 (s, 2H)	7.70-7.21 (m, 8H)	3.99 (s, 2H)	-	2.57-2.50 (ring)(m, 8H)
$[\text{C}_{19}\text{H}_{20}\text{N}_6\text{O}_4]_n$	11.6 (s, 2H)	9.8 (s, 2H)	7.52-7.22 (m, 8H)	3.93-2.1 (m, 6H)	6.67 (s, 2H)	3.56-2.12 (-C <sub>2</sub> H <sub>4</sub> -)(m,4H)
$[\text{C}_{23}\text{H}_{20}\text{N}_6\text{O}_4]_n$	11.48 (s, 2H)	10.35 (s, 2H)	7.39-6.29 (m, 12H)	3.86 (s, 2H)	7.6 (s, 2H)	-
$[\text{C}_{21}\text{H}_{22}\text{N}_6\text{O}_4]_n$	10.67 (s, 2H)	9.39 (s, 2H)	7.8-7.4 (m, 8H)	4.12 (s, 2H)	-	3.57-2.51 (ring) (s, 8H)

a: the oxime protons adjacent to amine groups, b: the oxime protons adjacent to amine groups

s: singlet, d: doublet, t: triplet, m: multiplet, dd: doublet of doublet

The Cu(II), Ni(II) and Co(II) complexes of the tetra oxime polymers were not obtained. These complexes are stable in solution, but give a tough coating on metals when the solvent is evaporated by air-drying or heating. This is a cross-linking effect<sup>1,2</sup>.

The thermal behaviour of some synthesised polymeric ligands was studied by DTA and TG. Bis(keto oxime)-phenylenediamine polymer melts at 220 °C with simultaneous decomposition. This decomposition was observed at 408 °C in the TG profile with a 36.13% mass loss (Theo: 33.33%) and the end products are phenylenediamine and diphenylmethane. We did not observe any peak after that temperature in the DTA curve, but mass loss was going on in the TG curve.

As seen from the TG curve, bis(keto oxime)-piperazine polymer decomposes in two stages over the temperature range 168-486 °C. The first decomposition occurs between 168 and 312 °C with a mass loss of 19.79% (Theo: 21.94%) and the second decomposition starts at 312 °C and end at 486 °C with a 26.24% mass loss (Theo: 28.10%); this stage corresponds to the mass of piperazine. The end product is probably diphenylmethane at that temperature and mass loss is going on.

The DTA curves of the bis(glyoxime)-ethylenediamine polymer showed a exothermic peak at 185 °C which corresponds to melting and decomposition. The sample decomposes with a mass loss of 44.33% (Theo: 42.42%). We did not observe any peak after that temperature in the DTA curve, but mass loss was going on.

From the TG curve of bis(glyoxime)-piperazine polymer, it appeared that the sample decomposes over the temperature range 189-231 °C with a mass loss of 39.09% (Theo: 39.81%). The end products are probably diphenylmethane and piperazine at that temperature, and mass loss is going on.

It was concluded from TG and DTA studies that organic polymers decompose in one or two stages and compounds melt with simultaneous decomposition. The theoretical and experimental percentage mass losses obtained from these decomposition stages are in good agreement.

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