

Synthesis of melamine based polymer complexes and their thermal degradations and magnetic properties

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Received: 6 May 2011 / Accepted: 5 June 2012 / Published online: 23 June 2012
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Abstract In this study, new polymer Fe(III) and Cr(III) complexes were synthesized. These polymer complexes were characterized by using elemental analysis, FT-IR spectroscopy, MS, thermal analyses and magnetic susceptibility measurement technics. Their thermal degradations were investigated, and co-polymerization was compared to aliphatic polymerization by using 1,2-dibromomethylbenzene and *o*-phenylenedialdehyde. Finally, metal ratios of the complexes were determined by using atomic absorption spectroscopy. The complexes are distorted octahedral low-spin ($S = 1/2$) Fe(III) and distorted octahedral ($S = 3/2$) Cr(III) bridged by COO^- and catechol groups.

Keywords Melamine · Salen · Salophen · Schiff bases · Co-polymers · Polymer complexes

Introduction

Melamine resins have been used in many applications including the manufacture of plastic dishes under the trade name Melmac. Melamine based co-polymers have interesting applications in material science because of their optical, electrical, and optoelectronic properties. Melamine resins have a high transparency and an enormous thermal and mechanical stability [1] which make them interesting as potential candidates in optical applications, like the fabrication of optical waveguide devices or holographic data stores [1, 2]. 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. However, the synthesis of thermally stable high-molecular weight s-triazine-containing ring-chain polymers is relatively unusual. The aromatic s-triazine-containing polymers derived from either aromatic nitriles or cyano-containing oligomers are often of low molecular weight [3].

The reaction of $[\text{Fe}(\text{salen})_2\text{O}]$ with carboxylic acids has been described by Wollmann and Hendrickson [4]. They used trichloroacetic acid, trifluoroacetic acid, salicylic acid and picric acid, and characterized the prepared complexes as dimers of composition $[\text{Fe}(\text{salen})\text{X}]$, where X is mono-anion of the appropriate acid. Koc and Ucan [5] have reported the synthesis and characterization of 1,3,5-tricarboxylato bridges with $[\text{Salen}$ or $\text{SalophenFe(III)}]$. We have previously reported the synthesis and characterization of monocarboxylato [6], monocatechol [6], 1,3,5-tricarboxylato [7], 1,3,5-tricatechols [8], and polymeric-carboxylato/chatechol [9] bridges with $[\text{Salen}$ or $\text{SalophenFe(III)/Cr(III)}]$. Uysal and Koc [10, 11] have reported the synthesis and characterization of dendrimeric-multi-carboxylato bridges with $[\text{Salen}$ or $\text{SalophenFe(III)/Cr(III)}]$.

The aim of the present study is to synthesize new polymer systems and to present their effects on magnetic behaviour of $[\text{salen}$ or $\text{salophenFe(III)/Cr(III)}]$ capped complexes and to investigate their thermal degradation and to compare co-polymerization with aliphatic polymerization by using 1,2-dibromomethylbenzene and *o*-phenylenedialdehyde. The reaction of melamine ($\text{C}_3\text{N}_6\text{H}_6$) with an equiv of 4-carboxybenzaldehyde or an equiv of 3,4-dihydroxybenzaldehyde in benzene produced the desired iminocarboxylic acid and iminocatechol in a single step at room temperature, coded to be L^1 and L^2 [6]. Then, $[\text{salen}$ or $\text{salophenFe(III)/Cr(III)}]$ capped complexes of L^1 and L^2 were obtained with reflux of the reactants [6]. Finally,

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[salen or salophenFe(III)/Cr(III)] capped polymer complexes were obtained from the reaction with 1,2-dibromomethylbenzene or 1,2-phthalaldehyde and the products. Their structures were characterized by using FT-IR, LC-MS, TGA and magnetic susceptibility. By using atomic absorption spectrophotometer (AAS), the metal ratios of the prepared complexes were determined.

Experimental

Materials

Melamine, 4-carboxybenzaldehyde, 3,4-dihydroxybenzaldehyde, 1,2-dibromomethylbenzene, *o*-phenylenedialdehyde, diisopropylethylamine (DIPEA) and all other reagents were purchased from Merck and used without further purification. 2-(4-carboxybenzimidino)-4,6-diamino-1,3,5-triazine **L¹** (**2**) [6], 2-(3,4-dihydroxybenzimidino)-4,6-diamino-1,3,5-triazine **L²** (**3**) [6] and their monomer complexes [L¹FeSalen (**4**), L¹FeSalophen (**5**), L¹CrSalen (**6**) and L¹CrSalophen (**7**), L²FeSalen (**8**), L²FeSalophen (**9**), L²CrSalen (**10**) and L²CrSalophen (**11**)] [6], [Fe/Cr(salen)]₂O, [Fe/Cr(salophen)]₂O [10–15] were synthesized according to previously reported methods. All characterization data for these complexes were given in related literatures [6].

Instruments

FT-IR spectra on a Perkin-Elmer Spectrum 100 with Universal ATR Polarization Accessory. Elemental analyses were carried out using a Hewlett-Packard 185 analyzer. Metal contents in complexes were determined by using Unicam 929 AAS spectrometer. Mass spectra of the compounds were obtained on Varian MAT 711 spectrometer. pH values were measured on a WTW pH, 537 pH meter. Magnetic susceptibilities of metal complexes were determined using a Sheerwood Scientific MX Gouy magnetic susceptibility apparatus carried out using the Gouy method with Hg[Co(SCN)₄] as calibrant. The effective magnetic moments, μ_{eff} per metal atom were calculated from the expression: $\mu_{\text{eff}} = 2.84\sqrt{\chi_M T}$ B.M., where χ_M is the molar susceptibility.

Preparation of [(L¹FeSalen)DBMB]_n (**12**), [(L¹FeSalophen)DBMB]_n (**13**), [(L¹CrSalen)DBMB]_n (**14**), [(L¹CrSalophen)DBMB]_n (**15**), [(L²FeSalen)DBMB]_n (**16**), [(L²FeSalophen)DBMB]_n (**17**), [(L²CrSalen)DBMB]_n (**18**) and [(L²CrSalophen)DBMB]_n (**19**) complexes

Solutions of L¹FeSalen (**4**), L¹FeSalophen (**5**), L¹CrSalen (**6**) and L¹CrSalophen (**7**), L²FeSalen (**8**), L²FeSalophen (**9**), L²CrSalen (**10**) and L²CrSalophen (**11**) complexes

(1.0 mmol) and 1,2-dibromomethylbenzene (1.0 mmol) in 100 mL of absolute ethanol with DIPEA (0.26 g, 0.35 mL, 2 mmol) were refluxed for 48 h. The mixture was allowed to cool to room temperature. Then the mixture was filtered, washed with methanol and dried in vacuum. The IR data and yield for **12–19** are given in Table 1 and 2.

Preparation of [(L¹FeSalen)OPHDA]_n (**20**), [(L¹FeSalophen)OPHDA]_n (**21**), [(L¹CrSalen)OPHDA]_n (**22**), [(L¹CrSalophen)OPHDA]_n (**23**), [(L²FeSalen)OPHDA]_n (**24**), [(L²FeSalophen)OPHDA]_n (**25**), [(L²CrSalen)OPHDA]_n (**26**) and [(L²CrSalophen)OPHDA]_n (**27**) complexes

Solutions of L¹FeSalen (**4**), L¹FeSalophen (**5**), L¹CrSalen (**6**) and L¹CrSalophen (**7**), L²FeSalen (**8**), L²FeSalophen (**9**), L²CrSalen (**10**) and L²CrSalophen (**11**) complexes (1.0 mmol) and *o*-phenylenedialdehyde (1.0 mmol) in 100 mL of acetonitrile were refluxed for 48 h. The mixture was allowed to cool to room temperature. Then the mixture was filtered, washed with methanol and dried in vacuum. The IR data and yield for **20–27** are given in Table 1 and 2.

Results and discussion

The all characterization data of the monomer ligands and complexes were discussed in our previously reported manuscript [6].

Polymer synthesis and characterization

All mononuclear complexes were polymerized with 1,2-dibromomethylbenzene or *o*-phenylenedialdehyde in ethanol by refluxing. Verified structural data of the polymer complexes (Scheme 1) by using elemental analyses, FT-IR, thermal analysis and mass spectral data were given in Fig. 1 and Table 1 and 2 [5–11, 16]. The results of all these analyses are in a good harmony with the structures suggested for the ligands and their polymer complexes. The results exhibit that all complexes are polymer [6, 11, 17]. After polymerization of complex **4–11** with 1,2-dibromomethylbenzene, ir bands at 3,468–3,421 cm⁻¹ for complex **4–11** were seen as weak bands at the same point for polymer complexes **12–19**. And, these bands were assigned to NH stretching vibrations. Some broad bands were seen at 1,618–1,644 cm⁻¹ for complex **12–19** and assigned to C=N (b) stretching vibrations, which have evidenced 1,2-dibromomethylbenzene has polymerized the mononuclear complexes. Bands at 1,573–1,609 and 1,588–1,596 cm⁻¹ were assigned to C=N (a) (triazine ring) and C=N (c) stretching vibrations for complexes **12–19**, respectively, whereas C=N (c) stretching vibration bands were found at 1,560–1,567 cm⁻¹ for [(salen or salophen)Fe(III)/Cr(III)]₂O

Table 1 Some physical properties, molecular weight (g/mol) data and elemental analyses, AAS analyses of the ligands and complexes

Compounds	μ_B	M.p. (°C)	Yield (%)	Color	M_W (g/mol)	Found calculated % of				
						C	H	N	Fe	Cr
$[C_{35}H_{29}N_8O_4Fe]_n$	12	1.69	278 ^a	68	Brown	61.98	3.94	16.15	8.01	–
$[(L^1FeSalen)DBMB]_n$					(681.50) _n	62.63	4.26	16.43	8.22	
$[C_{39}H_{29}N_8O_4Fe]_n$	13	1.65	276 ^a	65	Red	64.03	3.73	15.20	7.55	–
$[(L^1FeSalophen)DBMB]_n$					(729.55) _n	64.15	3.98	15.35	7.68	
$[C_{35}H_{29}N_8O_4Cr]_n$	14	2.95	272 ^a	60	Green	61.48	3.10	16.40	–	7.42
$[(L^1CrSalen)DBMB]_n$					(677.65) _n	61.98	4.28	16.53		7.67
$[C_{39}H_{29}N_8O_4Cr]_n$	15	2.90	270 ^a	55	Green	64.23	3.85	15.29	–	7.05
$[(L^1CrSalophen)DBMB]_n$					(725.70) _n	64.49	4.00	15.43		7.17
$[C_{34}H_{29}N_8O_4Fe]_n$	16	1.66	305 ^a	70	D. Brown	60.76	3.97	16.60	8.31	–
$[(L^2FeSalen)DBMB]_n$					(669.48) _n	60.94	4.33	16.73	8.36	
$[C_{38}H_{29}N_8O_4Fe]_n$	17	1.64	301 ^a	72	Brown	63.37	3.90	15.41	7.51	–
$[(L^2FeSalophen)DBMB]_n$					(717.54) _n	63.55	4.04	15.61	7.80	
$[C_{34}H_{29}N_8O_4Cr]_n$	18	2.85	296 ^a	60	D. Green	61.13	4.00	16.61	–	7.74
$[(L^2CrSalen)DBMB]_n$					(665.63) _n	61.30	4.36	16.83		7.81
$[C_{38}H_{29}N_8O_4Cr]_n$	19	2.86	294 ^a	60	Green	63.71	3.88	15.35	–	7.11
$[(L^2CrSalophen)DBMB]_n$					(713.69) _n	63.89	4.06	15.69		7.29
$[C_{35}H_{25}N_8O_4Fe]_n$	20	1.62	261 ^a	75	Brown	61.90	3.64	16.45	8.16	–
$[(L^1FeSalen)OPHDA]_n$					(677.50) _n	61.99	3.69	16.53	8.24	
$[C_{39}H_{25}N_8O_4Fe]_n$	21	1.60	269 ^a	75	Brown	64.41	3.38	15.36	7.61	–
$[(L^1FeSalophen)OPHDA]_n$					(725.55) _n	64.50	3.45	15.44	7.70	
$[C_{35}H_{25}N_8O_4Cr]_n$	22	2.79	256 ^a	58	Green	62.29	3.65	16.55	–	7.68
$[(L^1CrSalen)OPHDA]_n$					(673.65) _n	62.35	3.71	16.63		7.72
$[C_{39}H_{25}N_8O_4Cr]_n$	23	2.75	258 ^a	55	Green	64.77	3.41	15.45	–	7.15
$[(L^1CrSalophen)OPHDA]_n$					(721.70) _n	64.85	3.46	15.52		7.20
$[C_{34}H_{25}N_8O_4Fe]_n$	24	1.63	276 ^a	70	D. Brown	61.24	3.72	16.77	8.35	–
$[(L^2FeSalen)OPHDA]_n$					(665.48) _n	61.31	3.77	16.83	8.39	
$[C_{38}H_{25}N_8O_4Fe]_n$	25	1.64	272 ^a	75	Brown	63.85	3.47	15.63	7.80	–
$[(L^2FeSalophen)OPHDA]_n$					(713.54) _n	63.91	3.50	15.70	7.83	
$[C_{34}H_{25}N_8O_4Cr]_n$	26	2.77	265 ^a	60	D. Green	61.64	3.75	16.90	–	7.82
$[(L^2CrSalen)OPHDA]_n$					(661.63) _n	61.67	3.78	16.93		7.86
$[C_{38}H_{25}N_8O_4Cr]_n$	27	2.75	268 ^a	62	Green	64.20	3.49	15.71	–	7.30
$[(L^2CrSalophen)OPHDA]_n$					(709.69) _n	64.25	3.52	15.78		7.33

^a Decomposition

complexes [5, 11, 18–22]. Bands at 1,690–1,696 cm^{-1} for complexes **12–15** and **20–23** were assigned to C=O groups due to the coordination of (salen or salophen)Fe(III)/Cr(III) to COO groups. We suggest that both O-atoms for complexes **12–15** and **20–23** of carboxylate groups are chelated to the metal centers.

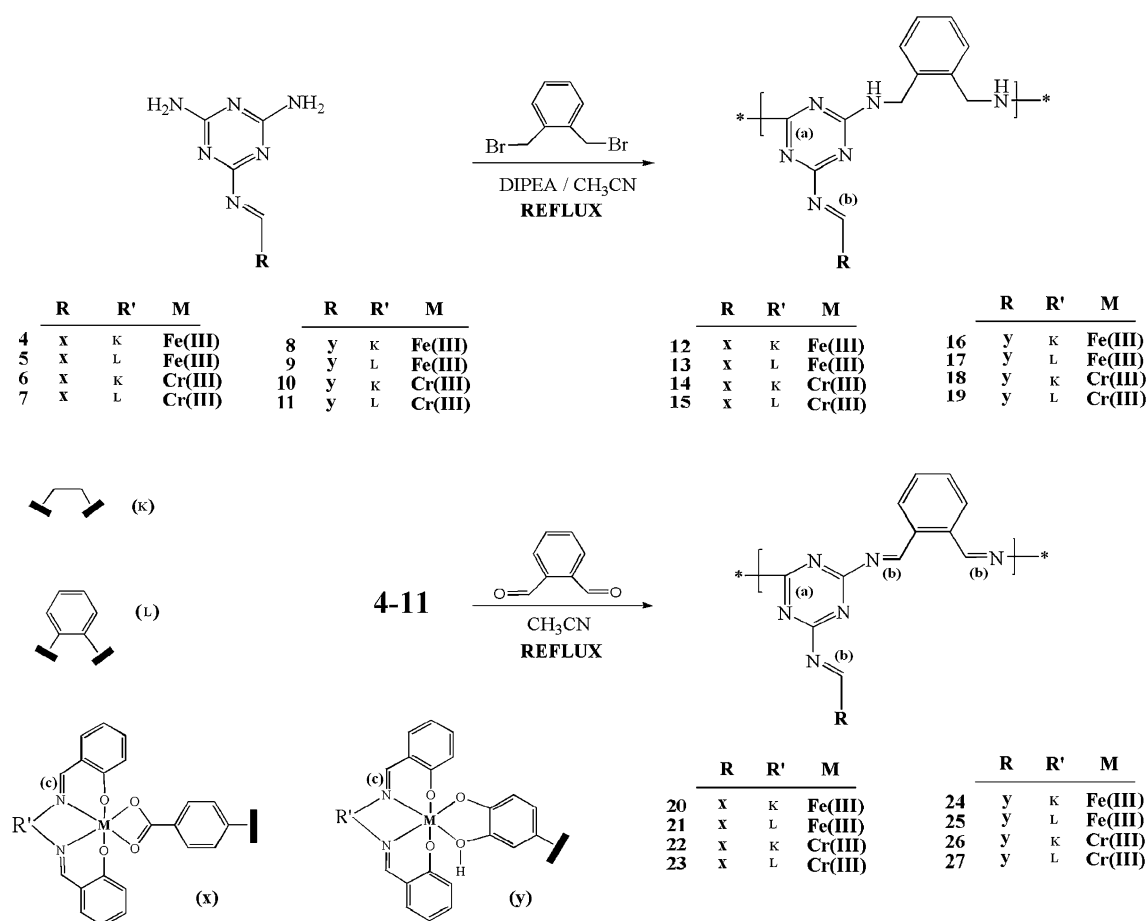
These bands from 1,405 to 1,369 cm^{-1} may be assigned to carboxylate bending vibrations [5, 11, 13, 21]; and, bands at 1,382–1,389 cm^{-1} are attributed to the COO-bending vibrations of the acetate groups. The bands at 1,382–1,389 cm^{-1} for complexes **12–15** and **20–23** indicate that the carboxylate groups are chelating to the metal centers [23–25]. Bands in

FTIR spectrum of all polymer complexes was seen as comparatively broad then those of monomer complexes. Additionally, after polymerization, the bands seen at 674 cm^{-1} for 1,2-bis(bromomethyl)benzene have completely disappeared. Similarly, bands at 3,469–3,418 cm^{-1} assigned to NH_2 vibrations disappeared after addition of *o*-phenylenedialdehyde for polymer complexes **20–27**. And, bands at 1,632–1,645 cm^{-1} appeared. It was assigned to C=N (imin) vibrations. It has been assigned to polymerization. In the polymer complexes, the bands in the 552–536 and 464–489 cm^{-1} ranges can be attributed to the M–N and M–O stretching modes (Fig. 1) [5–11, 20, 21, 26].

Table 2 Characteristic FT-IR bands (cm^{-1}) of complexes

Compounds		C=N	C–N	C–C _{ar}	N–H	C–H	C=O	COO	C–O _{ph}	OH _{ph}
[C ₃₅ H ₂₉ N ₈ O ₄ Fe] _n	12	1,625 ^a	1,124	1,441	3,465	3,125 _{ar}	1,696	1,383	1,301	–
[(L ¹ FeSalen)DBMB] _n		1,618 ^b		1,465	3,424	2,875 _{al}			1,336	
		1,592 ^c								
[C ₃₉ H ₂₉ N ₈ O ₄ Fe] _n	13	1,608 ^a	1,125	1,484	3,466	3,125 _{ar}	1,692	1,380	1,301	–
[(L ¹ FeSalophen)DBMB] _n		1,636 ^b		1,462	3,425	2,914 _{al}			1,335	
		1,591 ^c		1,440						
[C ₃₅ H ₂₉ N ₈ O ₄ Cr] _n	14	1,606 ^a	1,122	1,485	3,469	3,125 _{ar}	1,690	1,385	1,298	–
[(L ¹ CrSalen)DBMB] _n		1,645 ^b		1,468	3,427	2,870 _{al}			1,332	
		1,590 ^c		1,437						
[C ₃₉ H ₂₉ N ₈ O ₄ Cr] _n	15	1,606 ^a	1,123	1,486	3,464	3,125 _{ar}	1,694	1,382	1,298	–
[(L ¹ CrSalophen)DBMB] _n		1,640 ^b		1,465	3,421	2,912 _{al}			1,329	
		1,593 ^c		1,435						
[C ₃₄ H ₂₉ N ₈ O ₄ Fe] _n	16	1,608 ^a	1,124	1,485	3,469	3,125 _{ar}	–	–	1,302	3,328
[(L ² FeSalen)DBMB] _n		1,633 ^b		1,461	3,420	2,875 _{al}			1,290	
		1,596 ^c		1,437						
[C ₃₈ H ₂₉ N ₈ O ₄ Fe] _n	17	1,573 ^c	1,125	1,482	3,469	3,127 _{ar}	–	–	1,304	3,328
[(L ² FeSalophen)DBMB] _n		1,648 ^b		1,460	3,418	2,826 _{al}			1,285	
		1,607 ^a		1,434						
[C ₃₄ H ₂₉ N ₈ O ₄ Cr] _n	18	1,601 ^a	1,124	1,485	3,467	3,125 _{ar}	–	–	1,303	3,328
[(L ² CrSalen)DBMB] _n		1,644 ^b		1,465	3,421	2,875 _{al}			1,296	
		1,588 ^c		1,436						
[C ₃₈ H ₂₉ N ₈ O ₄ Cr] _n	19	1,609 ^a	1,128	1,483	3,466	3,125 _{ar}	–	–	1,286	3,328
[(L ² CrSalophen)DBMB] _n		1,642 ^b		1,462	3,425	2,926 _{al}			1,308	
		1,589 ^c		1,438		2,845 _{al}				
[C ₃₅ H ₂₅ N ₈ O ₄ Fe] _n	20	1,596 ^a	1,130	1,484	–	3,125 _{ar}	1,694	1,387	1,310	–
[(L ¹ FeSalen)OPHDA] _n		1,628, 1,635 ^b		1,466					1,337	
		1,541 ^c		1,445		2,875 _{al}				
[C ₃₉ H ₂₅ N ₈ O ₄ Fe] _n	21	1,591 ^a	1,125	1,486	–	3,125 _{ar}	1,692	1,389	1,308	–
[(L ¹ FeSalophen)OPHDA] _n		1,625, 1,644 ^b		1,465		2,875 _{al}			1,332	
		1,568 ^c		1,446					1,279	
[C ₃₅ H ₂₅ N ₈ O ₄ Cr] _n	22	1,594 ^a	1,128	1,443	–	3,125 _{ar}	1,694	1,387	1,308	–
[(L ¹ CrSalen)OPHDA] _n		1,625–1,632 ^b		1,465		2,875 _{al}			1,336	
		1,570 ^c							1,280	
[C ₃₉ H ₂₅ N ₈ O ₄ Cr] _n	23	1,593 ^a	1,122	1,446	–	3,125 _{ar}	1,692	1,384	1,315	–
[(L ¹ CrSalophen)OPHDA] _n		1,620–1,642 ^b		1,463		2,912 _{al}			1,337	
		1,572 ^c							1,280	
[C ₃₄ H ₂₅ N ₈ O ₄ Fe] _n	24	1,595 ^a	1,114	1,442	–	3,125 _{ar}	–	–	1,316	3,326
[(L ² FeSalen)OPHDA] _n		1,625, 1,634 ^b		1,462		2,875 _{al}			1,330	
		1,566 ^c							1,282	
[C ₃₈ H ₂₅ N ₈ O ₄ Fe] _n	25	1,572 ^c	1,115	1,432	–	3,133 _{ar}	–	–	1,278	3,325
[(L ² FeSalophen)OPHDA] _n		1,651, 1,635 ^b		1,461		2,738 _{al}				
		1,603 ^a		1,478		2,826 _{al}				
[C ₃₄ H ₂₅ N ₈ O ₄ Cr] _n	26	1,595 ^a	1,116	1,435	–	3,125 _{ar}	–	–	1,334	3,325
[(L ² CrSalen)OPHDA] _n		1,624, 1,641 ^b							1,315	
		1,578 ^c		1,465		2,875 _{al}			1,280	
[C ₃₈ H ₂₅ N ₈ O ₄ Cr] _n	27	1,596 ^a	1,114	1,436	–	3,125 _{ar}	–	–	1,334	3,326
[(L ² CrSalophen)OPHDA] _n		1,622, 1,645 ^b		1,463		2,875 _{al}			1,318	
		1,568 ^c							1,279	

^a, ^b, ^c were defined in Scheme 1



Scheme 1 Synthetic route for the preparation of polymer complexes

The magnetic behaviors of all polymer complexes

The magnetic moments of the polymer complexes were measured at room temperature. The values are given in Table 1. The results indicate that the Cr(III) and Fe(III) complexes have polymer structures in which the cations have an octahedral environment. It must be stressed that the magnetic behavior of the Cr(III) and Fe(III) complexes is consistent with the proposed polymer structures. For Fe(III) complexes such as (salen or salophen)Fe(III), the magnetic moments depend greatly upon the axial ligands. Many reports state that Fe(III) exhibits high spin ($S = 5/2$), if only one oxygen donor coordinates to salen- or salophen-Fe(III) [12, 27]. We report here that when COO^- ion coordinates to salen- or salophen-Fe(III) through both oxygens, Fe(III) exhibits low spin ($S = 1/2$) [5–11]. The magnetic behaviours of all polymer complexes are in good harmony with the proposed polymer structures [11, 28]. While the magnetic moment of the monomer complexes exhibit paramagnetic properties with a magnetic susceptibility value per atom: 1.89–1.86 and 3.61–3.41 B.M., respectively [1], the magnetic moment polymer complexes

exhibit paramagnetic property with a magnetic susceptibility value per atom: 1.69–1.63 and 2.95–2.75 B.M., respectively. These values are consistent with the presence of one unpaired electrons per Fe(III)-ion. According to these results, the $[\text{Fe}(\text{salen})_2\text{O}]$, $[\text{Fe}(\text{salophen})_2\text{O}]$, $[\text{Cr}(\text{salen})_2\text{O}]$ and $[\text{Cr}(\text{salophen})_2\text{O}]$ containing polymers are preferred to the electronic structure of $t_{2g}^5e_g^0$ and $t_{2g}^3e_g^0$. The magnetic data for these polymer complexes are in compliance with the low spin d^5 ($S = 1/2$) and high spin d^3 ($S = 3/2$) metal ion in an octahedral structure. It was seen that magnetic results of polymer complexes reported in this paper are similar to magnetic results of polymer complexes reported by us [9].

The thermal behaviors of the selected polymer complexes

The thermal properties [TG, DTA diagram (Fig. 2a–d)] of $[\text{Fe}(\text{Salen/salophen})]$ capped polymer complexes (**12**, **17**, **20** and **25**) were investigated and discussed. The decompositions of **12**, **17**, **20** and **25** occur in three steps. The first weight losses of **12** and **20**, 8.00 % and 7.67(calcd. 6.46

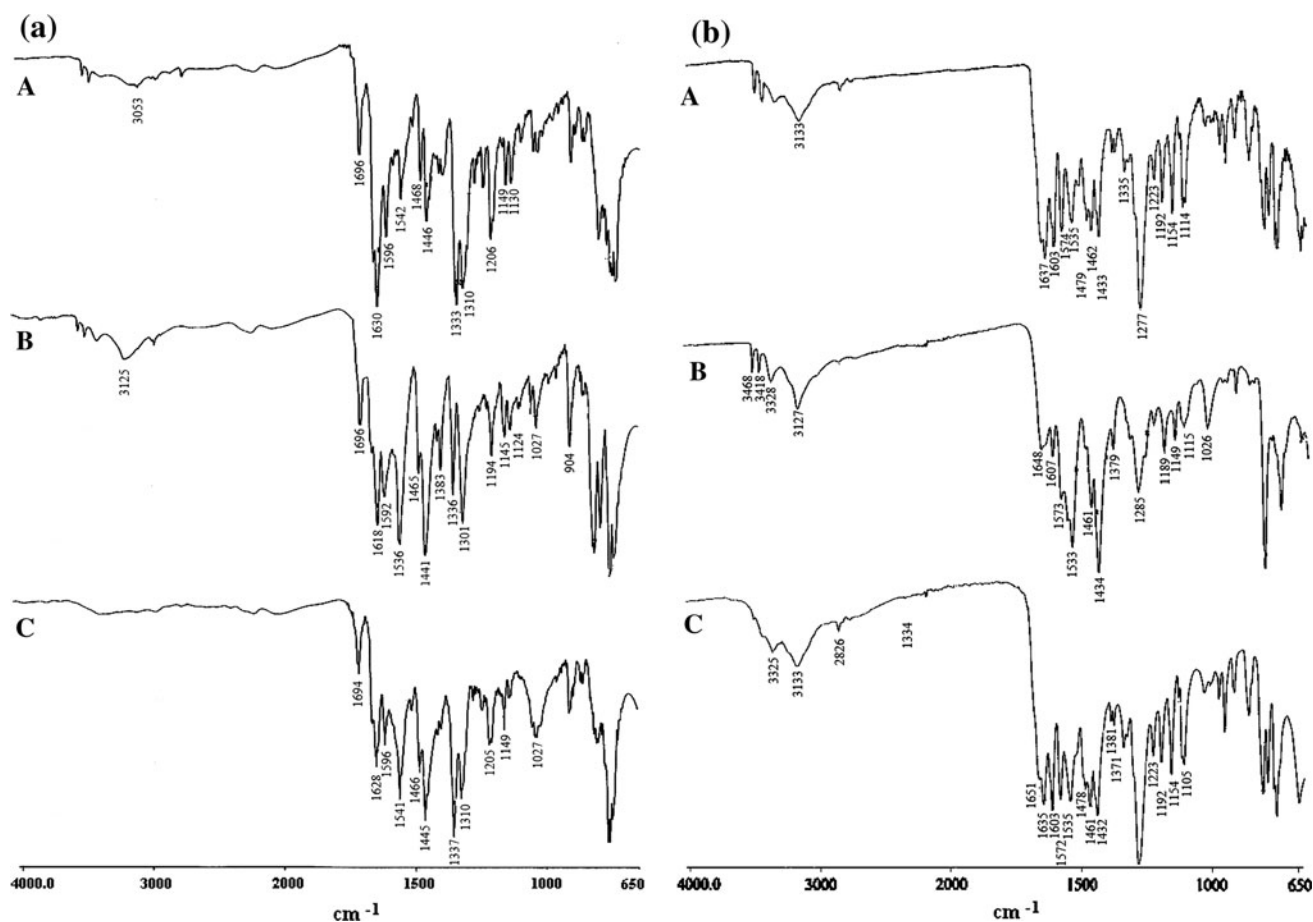


Fig. 1 a: FTIR spectra of $[L^1\text{FeSalen}]$ (**4**) (A), $[L^1\text{FeSalenDBMB}]_n$ (**12**) (B) and $[L^1\text{FeSalenOPHDA}]_n$ (**20**) (C), b: FTIR spectra of $[L^2\text{FeSalophen}]$ (**9**) (A), $[L^2\text{FeSalophenDBMB}]_n$ (**17**) (B) and $[L^2\text{FeSalophenOPHDA}]_n$ (**25**) (C)

and 6.49 %), occurs at 278 and 261 °C and corresponds to the decomposition of the carboxylate groups of the complex. While CO_2 and H_2O gases left the medium, $[\text{Fe}(\text{salen})]$ groups also left the main structure. Second weight losses, 30.23 and 35.08 % (calcd. 34.63 and 34.83 %), occurs at 397 and 472 °C are. The final weight losses occur at 633 and 612 °C, and total weight losses were 74.02 and 73.85 % (calcd. 76.82 and 76.68 %). The first weight losses of **17** and **25**, 21.07 and 20.01 % (calcd. 18.81 and 18.92 %), occurs at 301 and 272 °C and corresponds to the decomposition of the catechol groups of the complex. While H_2O and C_6H_6 gases left the medium, $[\text{Fe}(\text{salen})]$ groups also left the main structure. Second weight losses, 41.65 and 41.20 % (calcd. 39.58 and 39.80 %), occurs at 554 and 569 °C are. The final weight losses occur at 670 and 723 °C, and total weight losses were 73.26 and 72.97 % (calcd. 77.98 and 77.86 %). The last two steps of all complexes correspond to the decomposition of the aromatic groups and the residual ligand, respectively. The remain products as a result of degradations were C_3N_3 and Fe_2O_3 [6, 11]. When this polymer complexes were compared with other previously reported polymer complexes of

which decompositions started from 142 to 172 °C [9], it was understood that thermal stabilities of this polymer complexes of which decompositions started from 261 to 301 °C are more. When the decomposition points of all polymer complexes are compared, it is observed that thermal stabilities of polymer complexes coordinated to metal centers with COO groups are lower than those of catechol groups; i.e., decomposition points of polymer complexes of L^1 are lower than those of L^2 . Additionally, it was observed that decomposition points of all polymer complexes of Cr(III) were lower than those of Fe(III) [5–11, 25, 27].

Molecular weight calculations and LC–MS spectrum evaluations of polymer complexes

Inherent viscosities (η) of four polymer complexes (**14**, **19**, **22** and **26**) selected in all polymer complexes were measured as 0.18, 0.14, 0.15 and 0.14 for complexes 14, 19, 22 and 26, respectively by using an Ostwald viscosimeter. Molecular weight values were calculated from the expression: $\eta = k\mu^z$, where μ is the molecular weight. The

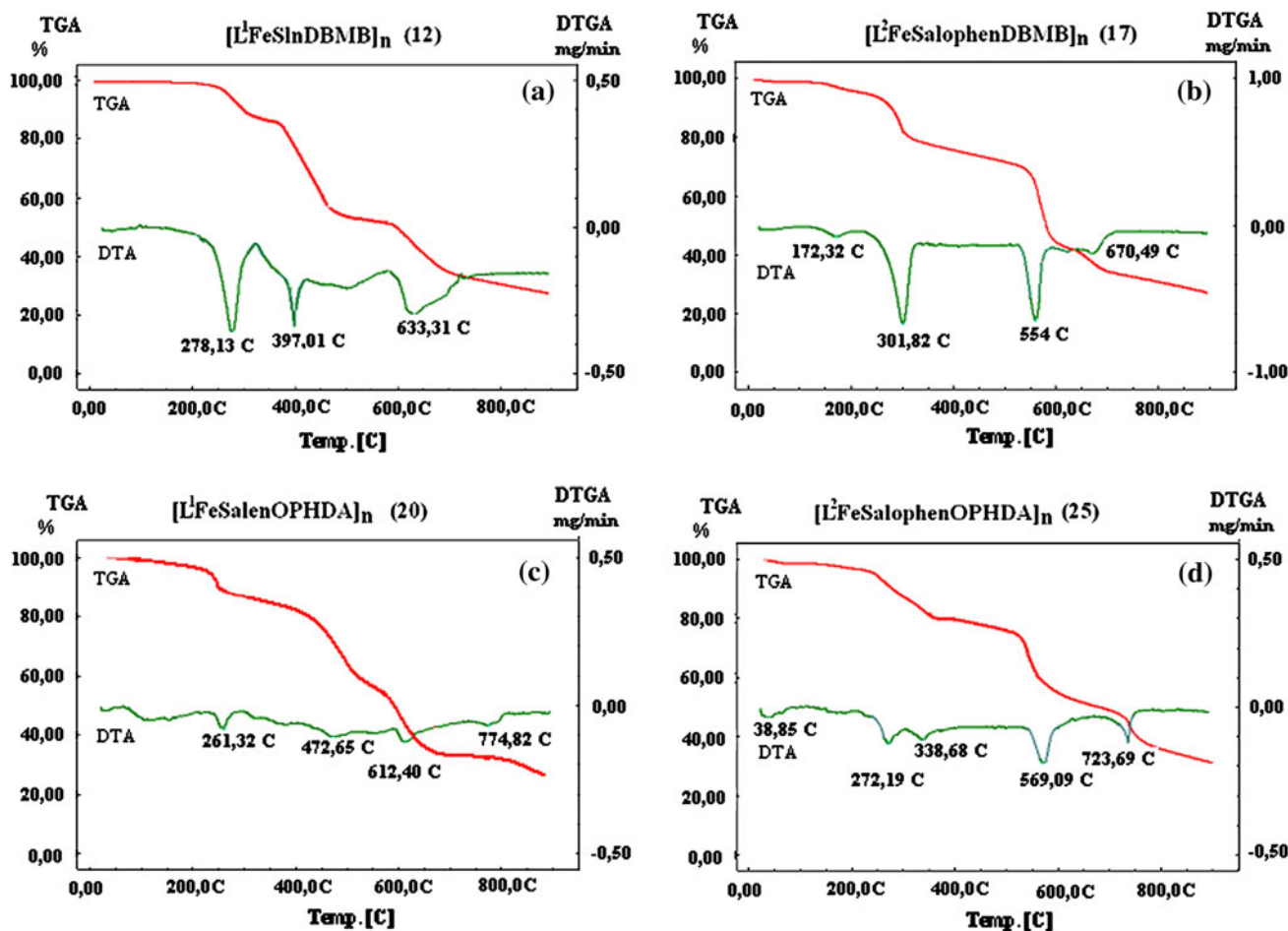


Fig. 2 TGA-DTA diagrams of some polymer complexes

molecular weights of polymer complexes were determined using linear polystyrene as the standard, so the exact value may be little higher than the observed value [29], and (k and α) constants were considered as 1.7×10^{-4} and 0.78 according to previously reported studies [29, 30]. Molecular weight values were found to be relatively low. These relatively low molecular weights may be due to globular type structure as supported by other reports [29, 30]. The determination of molecular weight of the polymer complexes confirmed that it is not a chemical compound rather low molecular weight polymer. The average molecular weight of polymer complexes are 7,413, 5,495, 6,025, 5,495 g/mole for complexes **14**, **19**, **22** and **26**, respectively.

Some complexes were selected in all complexes, and their MS (ESI^+) spectrum was investigated. MS (ESI^+) $m/z = 677$ [100 %, **14**], $m/z = 713$ [100 %, **19**], $m/z = 673$ [100 %, **22**], $m/z = 661$ [100 %, **26**]. The calculated molecular weights of all ligands and complexes have been given in (Table 1). Molecular peaks of the cations are observed with the same isotope distribution as the calculated ones, theoretically. On the basis of MS (ESI^+) spectral

evidence, it has been observed that the values of the peaks are seven to twelve times their monomer complexes (i.e., $n = 8-12$). That is, from the investigation of MS spectra of the compounds, it has been seen that molecular weights of ligands and complexes are in good harmony with the intensity of the observed values in MS spectra.

Conclusions

New polymer and melamine based Schiff bases complexes were synthesized. We have chosen $[\text{Fe}/\text{Cr}(\text{salen or saloph})]_2\text{O}$ as “ligand complexes”. These complexes are the examples of polymer complexes bridged by carboxylate anions and catechol groups to the iron and chromium centers. Their structures were characterized by means of elemental analysis, MS, thermal analyses and magnetic susceptibility measurements. The magnetic data for the polymer complexes show good harmony with the low spin d^5 ($S = 1/2$) and high spin d^3 ($S = 3/2$) metal ion in an octahedral structure. Thermal stabilities of polymer

complexes reported here are higher than previously reported polymer complexes (in Ref. [9]) of which decompositions started from 142 to 172 °C.

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