

# The synthesis and characterization of single substitute melamine cored Schiff bases and their [Fe(III) and Cr(III)] complexes

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**Abstract** In this study, firstly, two single substitute novel ligands have been synthesized by reacting melamine with 3,4,-dihydroxybenzaldehyde or 4-carboxybenzaldehyde. Then, eight new mono nuclear single substitute [Salen/Salophen Fe(III) and Cr(III)] complexes have been synthesized by reacting the ligands [2-(3,4-dihydroxybenzimidino)-4,6-diamino-1,3,5-triazine and 2-(4-carboxybenzimidino)-4,6-diamino-1,3,5-triazine] with tetradentate Schiff bases *N,N'*-bis(salicylidene)ethylenediamine-(salenH<sub>2</sub>) or bis(salicylidene)-*o*-phenylenediamine-(salophen H<sub>2</sub>). And then, all ligands and complexes have been characterized by means of elemental analysis, FT-IR spectroscopy, <sup>1</sup>H NMR, LC-MS, thermal analyses and magnetic susceptibility measurements. Finally, metal ratios of the prepared complexes were determined using AAS. The complexes have also been characterized as distorted octahedral low-spin Fe(III) and Cr(III) bridged by catechol and COO<sup>-</sup> groups.

**Keywords** Melamine · Salen · Salophen · Schiff bases · Catechol

## Introduction

Melamine (2,4,6-triamino-1,3,5-triazine) resins have been used in many applications. 1,3,5-Triazine derivatives are widely used as herbicides [1], drugs [2] or polymers [3] like melamineformaldehyde that has excellent thermal and

electrical properties [4]. Phenolic melamine is a good non-flammable resin owing to its nitrogen content in the chemical structure [5].

The magnetochemical properties of the  $\mu$ -oxo-bridged complexes and their X-ray studies have widely been presented in the literature [6–13]. The reaction of [Fe(salen)<sub>2</sub>O] with carboxylic acids has been described by Wollmann and Hendrickson [14]. Koç and Uçan [15] have reported the synthesis and characterization of 1,3,5-tricarboxylato bridges with [SalenFe(III)] and [SalophenFe(III)]. In our previous studies, we also reported the synthesis and characterization of 1,3,5-tricarboxylato and 1,3,5-tris(catechol) bridges with [SalenFe(III)], [SalophenFe(III)], [SalenCr(III)] and [SalophenCr(III)] [16, 17].

The anion of the Schiff base *N,N'*-ethylene-bis-(salicylideneiminato) (Salen) or 'Salen-type' ligands and their complexes have been considered as interesting species in many fields of chemical research because of some specific properties. Fe(Salen) complexes have been extensively studied in the solid state and in solution. Barone et al. [18] show a catalytic activity toward the blend oxidation of hydrocarbons and undergo electron transfer reactions, mimicking the catalytic functions of peroxidases. Getachew et al. synthesized a water soluble Fe(III)-salen complex and studied its biochemical effects on DNA in vitro and on cultured human cells. They showed that Fe(III)-salen produces free radicals in the presence of the reducing agent, dithiothreitol (DTT), and induces DNA damage in vitro. Their results demonstrated that Fe(III)-salen not only damages DNA in vitro, but also induces apoptosis in human cells via a mitochondrial pathway [19].

We have especially preferred chromium complexes because chromium is a unique transition metal ion, which has been established to be biologically significant at all the levels of living organisms [20]. Out of the two stable

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oxidation states of chromium, -VI and -III, trivalent chromium has been shown to play a positive role in controlling carbohydrate and lipid metabolism [21]. Chromium(III) Schiff base complexes (especially  $[\text{Cr}(\text{salen})(\text{OH}_2)_2]^+$ ) have been found to enhance insulin activity, and similarly insulin derivatives have been found to exhibit higher activity in glucose metabolism in animal models when compared to both free insulin and other derivatives [22, 23]. A broad range of asymmetric catalytic reactions have been described including oxidations, additions and reductions such as the epoxidation of olefins, epoxide ring opening [24–28]. Various metal-Salen complexes such as manganese(III) [29], chromium(III) [30] and nickel(II)-Salen [31] have been used for the epoxidation of olefins [32].

The aim of the present study is to synthesize novel single substitute mononuclear systems and to present their effects on magnetic behaviour of [salen/salophenFe(III)] and [salen/salophenCr(III)] capped complexes. We are thinking of synthesizing polymer systems out of the single substitute mononuclear systems in near future.

## Experimental

### Materials and methods

Melamine, 3,4-dihydroxybenzaldehyde, 4-carboxybenzaldehyde and all other reagents were purchased from Merck and used without further purification.  $[\text{Fe}(\text{salen})_2\text{O}$ ,  $[\text{Fe}(\text{salophen})_2\text{O}$ ,  $[\text{Cr}(\text{salen})_2\text{O}$  and  $[\text{Cr}(\text{salophen})_2\text{O}$  were prepared according to previously published methods [31–33].  $\text{L}^1\text{FeSalen(IV)}$ ,  $\text{L}^1\text{FeSalophen(V)}$ ,  $\text{L}^1\text{CrSalen(VI)}$ ,  $\text{L}^1\text{CrSalophen(VII)}$ ,  $\text{L}^2\text{FeSalen(VIII)}$ ,  $\text{L}^2\text{FeSalophen(IX)}$ ,  $\text{L}^2\text{CrSalen(X)}$  and  $\text{L}^2\text{CrSalophen(XI)}$  complexes were synthesized according to the following methods.  $^1\text{H-NMR}$  spectra were taken using a Varian-Mercury 200 NMR spectrometer. The chemical shifts for NMR spectra are ascribed in relation to the external standard of TMS. IR spectra were recorded using a Perkin-Elmer 1600 FT-IR spectrometer and through KBr pellets. Elemental analyses were carried out using a Hewlett-Packard 185 analyzer. Metal contents in complexes were determined using Unicam 929 AAS spectrometer. Mass spectra of the compounds were obtained through Varian MAT 711 spectrometer. pH values were measured through a WTW pH, 537 pH meter. The purification of the products obtained at the end of the reaction was carried out using Combi Flash Chromatography. Magnetic susceptibilities of metal complexes were determined using a Sheerwood Scientific MX Gouy magnetic susceptibility apparatus using the Gouy method with  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as calibrant. The effective magnetic moments,  $\mu_{\text{eff}}$ , per metal atom were

calculated from the expression:  $\mu_{\text{eff}} = 2.84\sqrt{\chi_M T}$  B.M., where  $\chi_M$  is the molar susceptibility.

### Preparation of ligand complexes

$[\text{Fe}(\text{salen})_2\text{O}$ ,  $[\text{Fe}(\text{salophen})_2\text{O}$ ,  $[\text{Cr}(\text{salen})_2\text{O}$  and  $[\text{Cr}(\text{salophen})_2\text{O}$  were prepared by adding concentrated ammonia solution (26% w/w) till alkaline to hot EtOH solutions of  $[\text{Fe}(\text{salen})]\text{Cl}$ ,  $[\text{Fe}(\text{salophen})]\text{Cl}$ ,  $[\text{Cr}(\text{salen})]\text{Cl}$  and  $[\text{Cr}(\text{salophen})]\text{Cl}$ , respectively [33–35].

### Synthesis of 2-(3,4-dihydroxybenzimidino)-4,6-diamino-1,3,5-triazine $\text{L}^1$ (II)

A suspension of melamine (6.30 g, 50 mmol) in 200 mL dry benzene was stirred at room temperature for 1 h. An equivalent amount of 3,4-dihydroxybenzaldehyde (6.90 g, 50 mmol) was added to suspension portion by portion. The mixture was stirred for 48 h. The white product was collected by filtration and then dried in vacuo. The obtained mixture was purified using Combi Flash Chromatography and using 1:1 acetone/chloroform mixture as eluent. The product was recrystallized from a mixture of methanol and water (1:1). Yield: 90% (11.07 g). The characterization data for **II** are given in Tables 1, 2 and 3.

### The synthesis of 2-(4-carboxybenzimidino)-4,6-diamino-1,3,5-triazine $\text{L}^2$ (III)

A suspension of melamine (6.30 g, 50 mmol) in 200 mL of dry benzene was stirred at room temperature for 1 h. An equivalent amount of 4-carboxybenzaldehyde (7.50 g, 50 mmol) was added to suspension portion by portion. The mixture was stirred for 48 h. The white product was collected by filtration and then dried in vacuo. The obtained mixture was purified using Combi Flash Chromatography and using 1:1 acetone/chloroform mixture as eluent. The product was recrystallized from a mixture of methanol and water (1:1). Yield: 92% (11.88 g). The characterization data for **III** are also given in Tables 1, 2 and 3.

### Preparation of $\text{L}^1\text{FeSalen(IV)}$ , $\text{L}^1\text{FeSalophen(V)}$ , $\text{L}^1\text{CrSalen(VI)}$ and $\text{L}^1\text{CrSalophen(VII)}$ complexes

A solution of  $\text{L}^1$  (0.49 g, 2.0 mmol) and  $[\text{Fe}(\text{salen})_2\text{O}$  or  $[\text{Fe}(\text{salophen})_2\text{O}$  or  $[\text{Cr}(\text{salen})_2\text{O}$  or  $[\text{Cr}(\text{salophen})_2\text{O}$  (1.0 mmol) in 100 mL of absolute ethanol were refluxed for 3 h. The mixture was allowed to cool down to room temperature. Then, the mixture was filtered and dried in vacuum. Yield: 80% (0.90 g), 81% (1.00 g), 64% (0.85 g), 60% (0.73 g) for **IV**, **V**, **VI** and **VII**, respectively. The characterization data for **IV**, **V**, **VI** and **VII** are given in Tables 2–3.

**Table 1** The  $^1\text{H-NMR}$  data of ligands in  $\text{DMSO-d}^6$ 

| Compounds  | $\text{NH}_2$ | $\text{NH}_3^+$ | C–H <sub>arom.</sub>   | HC=N–         |
|--|---------------|-----------------|--|---------------|
| $\text{C}_{10}\text{H}_{10}\text{N}_6\text{O}_2$<br>$\text{L}^1$ (II)                                    | –             | 6.06 (6H, s)    | 6.89–6.92 (1H, d)<br>7.23–7.26 (1H, dd)<br>7.28–7.29 (1H, d) | 9.70 (1H, s)  |
| $\text{C}_{10}\text{H}_{10}\text{N}_6\text{O}_2$<br>$\text{L}^1$ (II), $\text{D}_2\text{O}_{\text{ex}}$  | 3.91 (4H, s)  | –               | 6.89–6.92 (1H, d)<br>7.23 (1H, dd)<br>7.29–7.30 (1H, d)      | 9.66 (1H, s)  |
| $\text{C}_{11}\text{H}_{10}\text{N}_6\text{O}_2$<br>$\text{L}^2$ (III)                                   | –             | 6.36 (6H, s)    | 7.98–8.02 (2H, dd)<br>8.12–8.16 (2H, d)                      | 10.10 (1H, s) |
| $\text{C}_{11}\text{H}_{10}\text{N}_6\text{O}_2$<br>$\text{L}^2$ (III), $\text{D}_2\text{O}_{\text{ex}}$ | 3.76 (4H, s)  | –               | 7.97–8.00 (2H, d)<br>8.01–8.13 (2H, d)                       | 10.06 (1H, s) |

**Table 2** Some physical properties, molecular weight (g/mol) data and elemental analyses, AAS analyses of the ligands and complexes

| No   | Compounds  | $\mu_{\text{B}}$ | M.p. ( $^{\circ}\text{C}$ ) | Color $M_{\text{W}}$ (g/mol) | Found calculated % of |       |      |      |      |
|------|--|------------------|-----------------------------|------------------------------|-----------------------|-------|------|------|------|
|      |  |                  |                             |                              | C                     | N     | H    | Fe   | Cr   |
| II   | $\text{C}_{10}\text{H}_{10}\text{N}_6\text{O}_2$<br>$\text{L}^1$                           | –                | 158 <sup>a</sup>            | White [246.2]                | 48.69                 | 34.08 | 4.04 | –    | –    |
|      |  |                  |                             |                              | 48.73                 | 34.11 | 4.06 | –    | –    |
| III  | $\text{C}_{11}\text{H}_{10}\text{N}_6\text{O}_2$<br>$\text{L}^2$                           | –                | 220                         | White [258.2]                | 51.07                 | 32.50 | 3.85 | –    | –    |
|      |  |                  |                             |                              | 51.12                 | 32.53 | 3.87 | –    | –    |
| IV   | $\text{C}_{26}\text{H}_{23}\text{N}_8\text{O}_4\text{Fe}$<br>$\text{L}^1\text{FeSalen}$    | 1.88             | 220 <sup>a</sup>            | D. brown [567.3]             | 54.92                 | 19.71 | 4.04 | 9.84 | –    |
|      |  |                  |                             |                              | 54.99                 | 19.74 | 4.05 | 9.84 | –    |
| V    | $\text{C}_{30}\text{H}_{23}\text{N}_8\text{O}_4\text{Fe}$<br>$\text{L}^1\text{FeSalophen}$ | 1.85             | 290 <sup>a</sup>            | Red [615.4]                  | 58.44                 | 18.15 | 3.73 | 9.06 | –    |
|      |  |                  |                             |                              | 58.50                 | 18.20 | 3.74 | 9.07 | –    |
| VI   | $\text{C}_{26}\text{H}_{23}\text{N}_8\text{O}_4\text{Cr}$<br>$\text{L}^1\text{CrSalen}$    | 3.45             | 291 <sup>a</sup>            | D. green [663.5]             | 47.00                 | 16.84 | 3.44 | –    | 7.81 |
|      |  |                  |                             |                              | 47.02                 | 16.88 | 3.47 | –    | 7.84 |
| VII  | $\text{C}_{30}\text{H}_{23}\text{N}_8\text{O}_4\text{Cr}$<br>$\text{L}^1\text{CrSalophen}$ | 3.52             | 291 <sup>a</sup>            | Brown-green [611.6]          | 58.81                 | 18.29 | 3.74 | –    | 8.48 |
|      |  |                  |                             |                              | 58.86                 | 18.31 | 3.76 | –    | 8.50 |
| VIII | $\text{C}_{27}\text{H}_{23}\text{N}_8\text{O}_4\text{Fe}$<br>$\text{L}^2\text{FeSalen}$    | 1.89             | 252 <sup>a</sup>            | D. brown [579.4]             | 55.88                 | 19.29 | 3.96 | 9.62 | –    |
|      |  |                  |                             |                              | 55.92                 | 19.33 | 3.97 | 9.64 | –    |
| IX   | $\text{C}_{31}\text{H}_{23}\text{N}_8\text{O}_4\text{Fe}$<br>$\text{L}^2\text{FeSalophen}$ | 1.86             | 337 <sup>a</sup>            | Red [627.4]                  | 59.24                 | 17.81 | 3.64 | 8.88 | –    |
|      |  |                  |                             |                              | 59.29                 | 17.85 | 3.67 | 8.90 | –    |
| X    | $\text{C}_{27}\text{H}_{23}\text{N}_8\text{O}_4\text{Cr}$<br>$\text{L}^2\text{CrSalen}$    | 3.61             | 330 <sup>a</sup>            | Green [575.5]                | 56.25                 | 19.41 | 3.98 | –    | 9.01 |
|      |  |                  |                             |                              | 56.29                 | 19.46 | 4.00 | –    | 9.03 |
| XI   | $\text{C}_{31}\text{H}_{23}\text{N}_8\text{O}_4\text{Cr}$<br>$\text{L}^2\text{CrSalophen}$ | 3.41             | 304 <sup>a</sup>            | D. green [623.5]             | 59.61                 | 17.92 | 3.66 | –    | 8.32 |
|      |  |                  |                             |                              | 59.65                 | 17.96 | 3.69 | –    | 8.34 |

<sup>a</sup> Decomposition

#### Preparation of $\text{L}^2\text{FeSalen}$ (VIII), $\text{L}^2\text{FeSalophen}$ (IX), $\text{L}^2\text{CrSalen}$ (X) and $\text{L}^2\text{CrSalophen}$ (XI) complexes

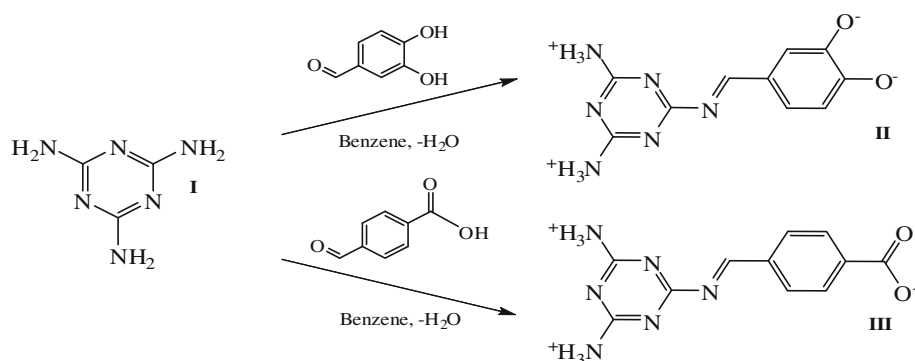
A solution of  $\text{L}^2$  (0.52 g, 2.0 mmol) and  $[\text{Fe}(\text{salen})]_2\text{O}$  or  $[\text{Fe}(\text{salophen})]_2\text{O}$  or  $[\text{Cr}(\text{salen})]_2\text{O}$  or  $[\text{Cr}(\text{salophen})]_2\text{O}$  in 100 mL of absolute ethanol were refluxed for 3 h. The mixture was allowed to cool down to room temperature. Then, the mixture was filtered and dried in vacuum. Yield: 81% (0.94 g), 80% (1.00 g), 65% (0.75 g), 62% (0.78 g) for **VIII**, **IX**, **X** and **XI**, respectively. The characterization data for **VIII**, **IX**, **X** and **XI** are given in Tables 2 and 3.

#### Results and discussion

The target ligands were synthesized in one step from melamine. The conversion of melamine into mono-substituted-melamine derivatives was accomplished in more than 70% yield. The characterization of both of the ligands 2-(3,4-dihydroxybenzimidino)-4,6-diamino-1,3,5-triazine  $\text{L}^1$  (II) and 2-(4-carboxybenzimidino)-4,6-diamino-1,3,5-triazine  $\text{L}^2$  (III) was accomplished by elemental analyses,  $^1\text{H}$  NMR, FT-IR and mass spectral data [36] (Scheme 1; Tables 1, 2, 3). Both of the ligands are soluble in common organic

**Table 3** Characteristic FT-IR bands ( $\text{cm}^{-1}$ ) of complexes in KBr pellets

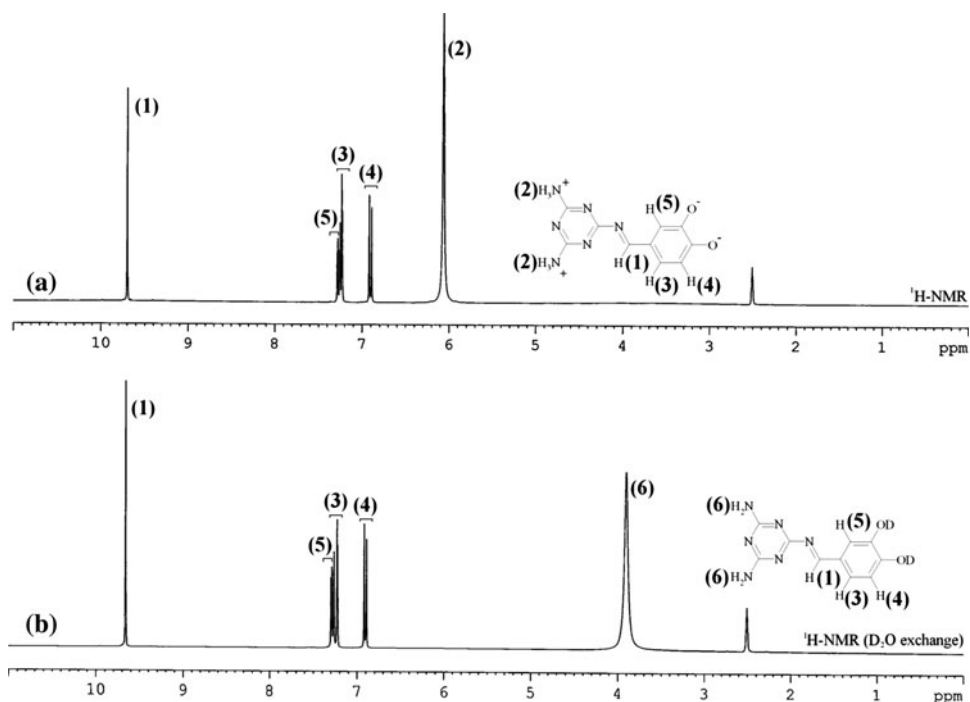
| No   | Compounds  | C=N                    | C–N  | C–H <sub>ar</sub> | C–H <sub>al</sub> | O–H   | CO <sub>ph</sub> | C=O  | COO  | N–H <sub>st</sub> |
|------|--|------------------------|------|-------------------|-------------------|-------|------------------|------|------|-------------------|
| II   | C <sub>10</sub> H <sub>10</sub> N <sub>6</sub> O <sub>2</sub>    | 1588 <sup>a</sup>      | 1119 | 3130              | 2825              | 1386w | 1277             | –    | –    | 3333              |
|      | L <sup>1</sup>   | 1654 <sup>b</sup>      |      |                   |                   | 3470s |                  |      |      | 3419              |
| III  | C <sub>11</sub> H <sub>10</sub> N <sub>6</sub> O <sub>2</sub>    | 1607 <sup>a</sup>      | 1128 | 3128              | 2858              | –     | –                | 1654 | 1394 | 3344              |
|      | L <sup>2</sup>   | 1654 <sup>b</sup>      |      |                   |                   |       |                  |      |      | 3427              |
| IV   | C <sub>26</sub> H <sub>23</sub> N <sub>8</sub> O <sub>4</sub> Fe | 1580 <sup>a</sup>      | 1122 | 3131              | 2940              | 1380w | 1254             | –    | –    | 3420              |
|      | L <sup>1</sup> FeSalen   | 1670–1619 <sup>b</sup> |      |                   | 2972              | 3326s | 1288             |      |      | 3468              |
|      |  | 1542 <sup>c</sup>      |      |                   |                   |       |                  |      |      |                   |
| V    | C <sub>30</sub> H <sub>23</sub> N <sub>8</sub> O <sub>4</sub> Fe | 1579 <sup>a</sup>      | 1115 | 3130              | 2828              | 1371w | 1281             | –    | –    | 3420              |
|      | L <sup>1</sup> FeSalophen  | 1605–1657 <sup>b</sup> |      |                   |                   | 3404s | 1300             |      |      |                   |
|      |  | 1537 <sup>c</sup>      |      |                   |                   |       |                  |      |      |                   |
| VI   | C <sub>26</sub> H <sub>23</sub> N <sub>8</sub> O <sub>4</sub> Cr | 1571 <sup>a</sup>      | 1118 | 3131              | 2938              | 3219  | 1289             | –    | –    | 3420              |
|      | L <sup>1</sup> CrSalen   | 1647 <sup>b</sup>      |      |                   | 2976              | 3344  |                  |      |      |                   |
|      |  | 1543 <sup>c</sup>      |      |                   |                   |       |                  |      |      |                   |
| VII  | C <sub>30</sub> H <sub>23</sub> N <sub>8</sub> O <sub>4</sub> Cr | 1607 <sup>a</sup>      | 1114 | 3120              | 2828              | 1397w | 1286             | –    | –    | 3337              |
|      | L <sup>1</sup> CrSalophen  | 1651 <sup>b</sup>      |      |                   |                   |       |                  |      |      | 3419              |
|      |  | 1549 <sup>c</sup>      |      |                   |                   |       |                  |      |      |                   |
| VIII | C <sub>27</sub> H <sub>23</sub> N <sub>8</sub> O <sub>4</sub> Fe | 1599 <sup>a</sup>      | 1207 | 3130              | 2857              | –     | –                | 1698 | 1386 | 3344              |
|      | L <sup>2</sup> FeSalen   | 1646–1631 <sup>b</sup> |      |                   | 2935              |       |                  |      |      |                   |
|      |  | 1543 <sup>c</sup>      |      |                   |                   |       |                  |      |      |                   |
| IX   | C <sub>31</sub> H <sub>23</sub> N <sub>8</sub> O <sub>4</sub> Fe | 1580 <sup>a</sup>      | 1125 | 3132              | 2859              | –     | –                | 1695 | 1379 | 3378              |
|      | L <sup>2</sup> FeSalophen  | 1607–1653 <sup>b</sup> |      |                   |                   |       |                  |      |      |                   |
|      |  | 1535 <sup>c</sup>      |      |                   |                   |       |                  |      |      |                   |
| X    | C <sub>27</sub> H <sub>23</sub> N <sub>8</sub> O <sub>4</sub> Cr | 1636 <sup>a,b</sup>    | 1117 | 3131              | 2813              | –     | –                | 1684 | 1372 | 3343              |
|      | L <sup>2</sup> CrSalen   | 1542 <sup>c</sup>      |      |                   | 2931              |       |                  |      |      |                   |
| XI   | C <sub>31</sub> H <sub>23</sub> N <sub>8</sub> O <sub>4</sub> Cr | 1595 <sup>a</sup>      | 1128 | 3120              | 2857              | –     | –                | 1695 | 1378 | 3335              |
|      | L <sup>2</sup> CrSalophen  | 1618 <sup>b</sup>      |      |                   |                   |       |                  |      |      | 3420              |
|      |  | 1547 <sup>c</sup>      |      |                   |                   |       |                  |      |      |                   |

**Scheme 1** Synthetic routes for the preparation of ligands **II** and **III**

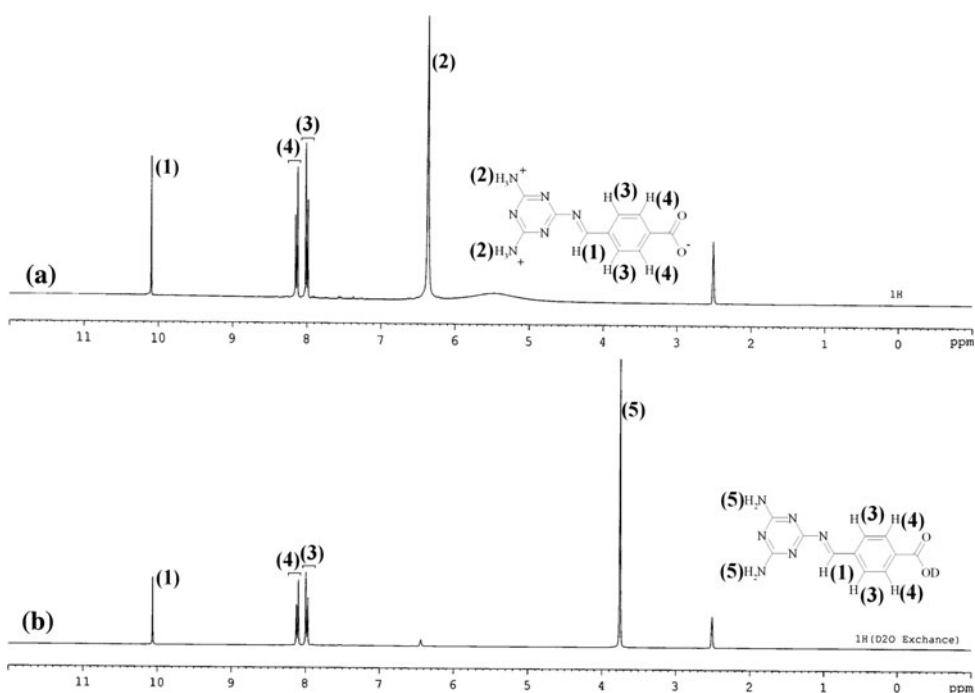
solvents. Synthetic strategy was adopted in preparing a single substitute mononuclear iminocatechol and/or iminocarboxylate that could be used in a complex formation as a “ligand” and contain a potential donor group capable of coordinating with another ligand. Previously, we chose [Fe(salen)]<sub>2</sub>O, [Fe(salophen)]<sub>2</sub>O, [Cr(salen)]<sub>2</sub>O and [Cr(salophen)]<sub>2</sub>O as “ligand complex” [37]. These

complexes are the first examples of single substitute mononuclear complexes bridged to the iron/chromium centers by carboxylate anions and catechol group. Other examples of complexes bridged to the iron centers by catechol group were published in 2008 by Uysal et al. [38]. Other examples of complexes bridged to the iron/chromium centers by carboxylate [16] and catechol [17] groups were

**Fig. 1** The  $^1\text{H-NMR}$  spectra of 2-(3,4-dihydroxybenzimidino)-4,6-diamino-1,3,5-triazine (a), the  $^1\text{H-NMR}$  spectra ( $\text{D}_2\text{O}$  exchange) of 2-(3,4-dihydroxybenzimidino)-4,6-diamino-1,3,5-triazine (b)



**Fig. 2** The  $^1\text{H-NMR}$  spectra of 2-(4-carboxy benzimidino)-4,6-diamino-1,3,5-triazine (a), the  $^1\text{H-NMR}$  spectra  $\text{D}_2\text{O}$  exchange of 2-(4-carboxybenzimidino)-4,6-diamino-1,3,5-triazine (b)

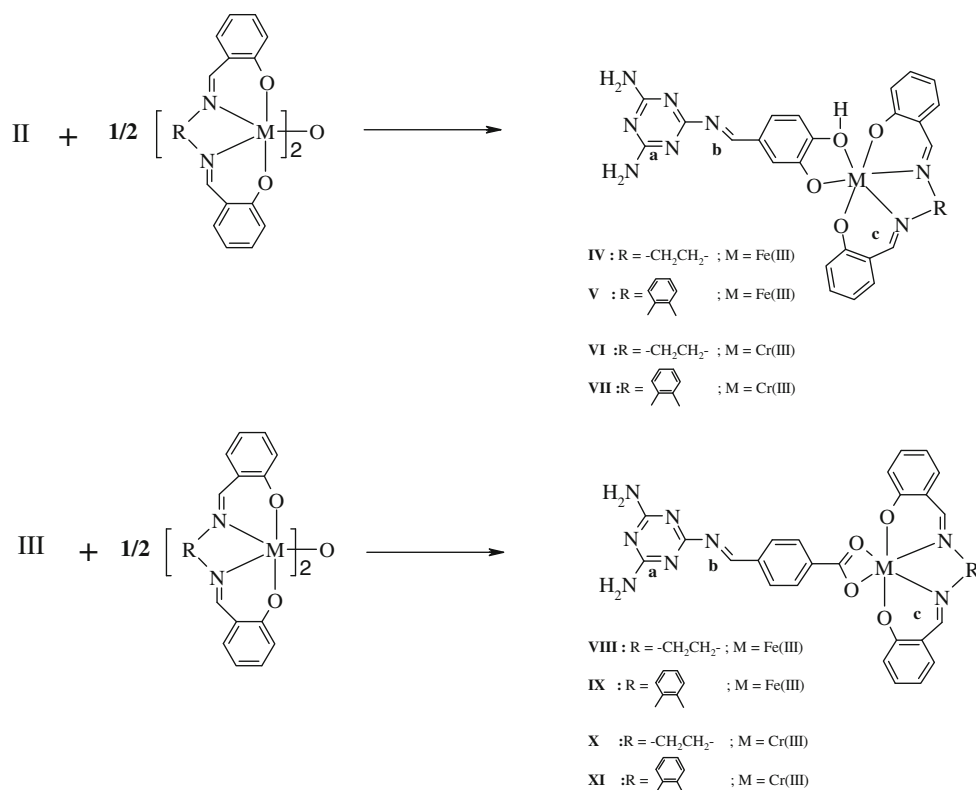


published in 2009 by Uysal and Uçan. All compounds are stable at room temperature in the solid state. They are insoluble in water but, soluble in organic solvents such as ethylacetate, DMSO and DMF. The results of the elemental analyses, given in Table 2 are in a good harmony with the structures suggested for the ligands and their complexes. The results show that all complexes are mononuclear.

In order to identify the structure of **II** and **III**, the  $^1\text{H-NMR}$  spectra were recorded in  $\text{DMSO-d}_6$ .  $^1\text{H-NMR}$

spectra (Figs. 1a, 2a) of both ligands also confirmed their structures by showing a singlet for a single proton which corresponds to  $-\text{N}=\text{CH}-$  groups at 9.70 and 10.10 ppm for **II** and **III** respectively [16, 17, 39]. Besides this, in case of **II** monosubstitution could be visualized through a singlet at 6.06 and 6.36 ppm for two  $-\text{NH}_3^+$  groups in the  $^1\text{H-NMR}$  spectra of **II** and **III** respectively. This was supported by the deuterium-exchanged  $^1\text{H-NMR}$  spectra showing the disappearance of signals at 6.06 and 6.36 ppm for two

**Fig. 3** The single substitute [Fe(salen/salophen)] and [Cr(salen/salophen)] complexes of  $L^1$  and  $L^2$



$-\text{NH}_3^+$  and appearance of new peaks at 3.90 and 3.76 ppm for  $-\text{NH}_2$  groups of both the ligands respectively (Fig. 1b, 2b). Because the deuterium-exchangeable protons of phenolic-OH groups could migrate to  $-\text{NH}_2$  groups, forming two equivalent  $-\text{NH}_3^+$  groups after the intramolecular conversion, the signals disappeared at 3.90 ppm for  $-\text{NH}_2$  and reappeared at 6.06 ppm for  $-\text{NH}_3^+$  in the  $^1\text{H-NMR}$  spectra of **II** (Fig. 1a). Likewise, because the deuterium-exchangeable protons of carboxylic-OH groups could migrate to  $-\text{NH}_2$  groups forming  $-\text{NH}_3^+$  groups after the intramolecular conversion, the signals disappeared at 3.76 ppm for  $-\text{NH}_2$  and reappeared at 6.36 ppm for  $-\text{NH}_3^+$  in the  $^1\text{H-NMR}$  spectra of **III** (Fig. 2a). If the linkage had come true as three substitutes, the phenolic-OH protons couldn't have migrated (Fig. 3).

IR bands at  $1,579\text{--}1,636\text{ cm}^{-1}$  were assigned to triazine ring C=N (a) stretching vibrations for complexes **IV–XI**. Bands at  $1,653\text{--}1,605\text{ cm}^{-1}$  for complex **IV–XI** were assigned to C=N (b) stretching vibrations, and bands at  $1,535\text{--}1,549\text{ cm}^{-1}$  were assigned to C=N (c) stretching vibrations for complexes **IV–XI**, respectively, whereas C=N (c) stretching vibration bands were found at  $1,560\text{--}1,567\text{ cm}^{-1}$  for  $[\text{Fe}(\text{salen})]_2\text{O}$ ,  $[\text{Fe}(\text{salophen})]_2\text{O}$ ,  $[\text{Cr}(\text{salen})]_2\text{O}$  and  $[\text{Cr}(\text{salophen})]_2\text{O}$  complexes [15–17, 38, 40, 41]. Aromatic stretching vibrations are between  $1,481$  and  $1,433\text{ cm}^{-1}$  for **IV–VII**. Phenolic C–O stretching vibrations at  $1,254\text{--}1,300\text{ cm}^{-1}$  have clearly been observed at

the IR spectra of **IV–VII**, whereas they had been observed at  $1,277\text{ cm}^{-1}$  for  $L^1$ . It has been interpreted that a downward shift of  $12\text{--}10\text{ cm}^{-1}$  for phenolic C–O stretching vibration in the complexes indicates coordination through the oxygen atoms. A downward shift from  $1,560\text{--}1,567\text{ cm}^{-1}$  for C=N (c) to  $1,543\text{--}1,537\text{ cm}^{-1}$  also indicated that capped coordination was formed [15–17, 34, 38–42]. The FT-IR spectra of **IV–VII** bands observed between  $3,468$  and  $3,337\text{ cm}^{-1}$  was obviously assigned to the presence of the two  $\text{NH}_2$  groups on the main structure. The bands at  $1,698\text{--}1,684\text{ cm}^{-1}$  for complexes **VIII–XI** were assigned to C=O groups due to the coordination of Fe(salen), Fe(salophen), Cr(salen) and Cr(salophen) to COO group. Furthermore, the bands at  $1,386\text{--}1,372\text{ cm}^{-1}$  were assigned to  $\text{COO}^-$  ions of those complexes [15, 16, 34]. In the FT-IR spectra of complexes **VIII–XI**, two bands were obviously observed between  $3,420$  and  $3,335\text{ cm}^{-1}$  assigned to the presence of the two  $\text{NH}_2$  groups on the main structure. In the single substitute mononuclear complexes, the bands in the  $558\text{--}532$  and  $466\text{--}483\text{ cm}^{-1}$  ranges can be attributed to the M–N and M–O stretching modes [39].

The magnetic moments of the complexes given in Table 2 were measured at room temperature. On the basis of spectral evidence, the Fe(III) and Cr(III) complexes have mononuclear structures, in which the Fe(III) and Cr(III) cations have an approximately octahedral environment. The magnetic behaviour of Fe(III) and Cr(III) complexes is

in accord with the proposed mononuclear structures. The magnetic moment of mononuclear complexes which were composed of  $[\text{Fe}(\text{salen})]_2\text{O}$ ,  $[\text{Fe}(\text{salophen})]_2\text{O}$ ,  $[\text{Cr}(\text{salen})]_2\text{O}$  and  $[\text{Cr}(\text{salophen})]_2\text{O}$  of (**L<sup>1</sup>** and **L<sup>2</sup>**) shows paramagnetic properties with a magnetic susceptibility value: The magnetic moments of all Fe(III) complexes are between 1.85 and 1.89 B.M., and all Cr(III) complexes are between 3.41 and 3.61 B.M. [15–17, 35, 38, 42, 43]. It is seen that the Fe(salen), Fe(salophen), Cr(salen) and Cr(salophen) containing compounds are represented by the electronic structure of  $t_{2g}^5e_g^0$  and  $t_{2g}^3e_g^0$ . The magnetic data for the FeSalen, FeSalophen, CrSalen and CrSalophen capped complexes of **L<sup>1</sup>** and **L<sup>2</sup>** show good harmony with the  $d^5$  and  $d^3$  metal ions in an octahedral structure. This result is supported by the results of the elemental analyses, suggesting that these mononuclear complexes have also an octahedral structure [15–17, 33, 35, 38, 42, 43].

Samples (**VI**, **VIII** and **XI**) chosen from all the complexes were thermally investigated. It is well known that there is a strong relation between temperature range for the dehydration process and the binding mode of the water molecules to the respective metal complexes [44]. That the elimination of water took place in a single-step process attributed to the release of the hydrated water molecules (in the range of 60–120 °C) [15–17, 38, 42, 45]. Thermal decomposition of the anhydrous  $[\text{Fe}/\text{Cr}(\text{salen})]$  and  $[\text{Fe}/\text{Cr}(\text{salophen})]$  complexes left the ligands **L<sup>1</sup>** and **L<sup>2</sup>** started in the range of 290–392 °C and completed in the range of 565–650 °C. The final decomposition products were metal oxides and triazine ring. The observed weight losses for complexes were in good harmony with the calculated values.

In TGA-DTA diagram (Fig. 4) of  $[\text{Cr}(\text{salen})]$  capped complexes of 2-(3,4-dihydroxybenzimidino)-4,6-diamino-1,3,5-triazine (**VI**), decomposition of  $[\text{Cr}(\text{salen})]$  capped complexes of **L<sup>1</sup>** was determined in two steps. At the thermal decomposition steps,  $\text{H}_2\text{O}$  firstly left the main structure at 90.75 °C and weight loss was theoretically calculated to

be 5.65% and measured experimentally to be 7.46%. When the sample was heated up to 290.79 °C, it was calculated theoretically and measured experimentally that the weight loss was 43.29 and 35.35%, respectively.

In TGA-DTA diagram (Fig. 5) of  $[\text{Fe}(\text{salen})]$  capped complexes of 2-(4-carboxybenzimidino)-4,6-diamino-1,3,5-triazine (**VIII**), the first decomposition step was started at 251.99 °C. Although the weight loss was theoretically calculated to be 9.64%, it was experimentally observed to be 8.01%. While  $\text{CO}_2$  gases left the medium,  $[\text{Fe}(\text{salen})]$  group also left the main structure. At the second decomposition step,  $\text{C}_2\text{H}_2$  and  $\text{N}_2$  gasses went away from the main structure at 392 °C. Although the weight loss was theoretically calculated to be 11.86%, it was experimentally observed to be 13.44%. At the third decomposition step,  $\text{C}_6\text{H}_6$  left the main structure at 565 °C. Although the weight loss was theoretically calculated to be 27.9%, it was experimentally observed to be 35.1%.

In TGA-DTA diagram (Fig. 6) of  $[\text{Cr}(\text{salophen})]$  capped complexes of 2-(4-carboxybenzimidino)-4,6-diamino-1,3,5-triazine (**XI**), while  $\text{CO}_2$  gases left the medium,

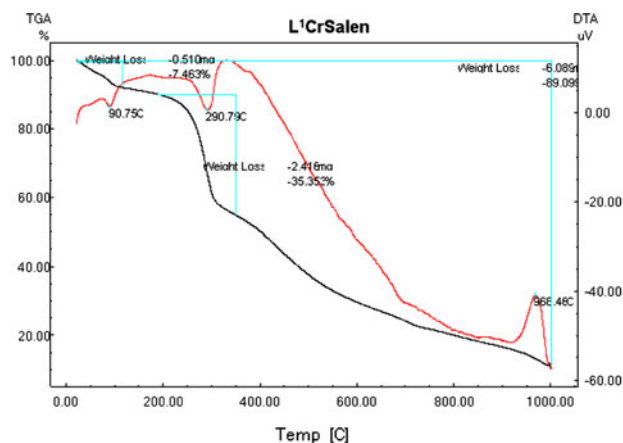


Fig. 4 Thermal decomposition diagram of **L<sup>1</sup>**CrSalen (**VI**)

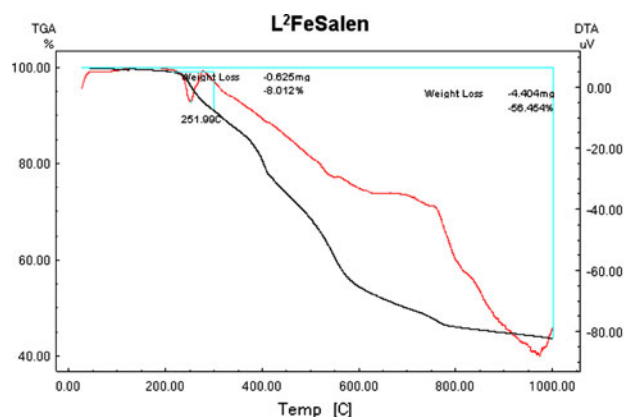


Fig. 5 Thermal decomposition diagram of **L<sup>2</sup>**FeSalen (**VIII**)

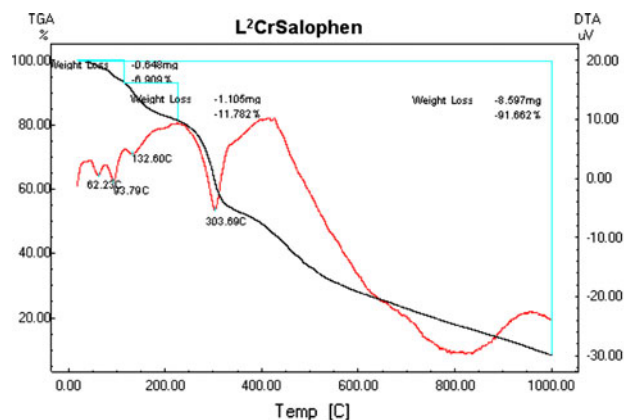


Fig. 6 Thermal decomposition diagram of **L<sup>2</sup>**CrSalophen (**XI**)

[Cr(salophen)] the group was also left the main structure at 93.7 °C. At first decomposition when CO<sub>2</sub> was leaving, weight loss was both theoretically calculated and experimentally observed to be 7.0%. The decomposition of the [Cr(salophen)] group also occurred at 303 °C at the second step, and the weight loss was theoretically calculated to be 53.6% and experimentally measured to be 56.0%. The third decomposition was completed at around 650 °C. It was theoretically obtained 14.0% and experimentally 12.0%, indicating the loss of C<sub>6</sub>H<sub>6</sub> and N<sub>2</sub> gasses from the medium.

From the investigation of LC–MS spectra of all compounds, it was seen that the molecular weights of ligands and complexes were in good harmony with the intensively observed values in LC–MS spectras (Table 2).

## Conclusion

In this study, novel single substitute and melamine cored Schiff bases “2-(3,4-dihydroxybenzimidino)-4,6-diamino-1,3,5-triazine and 2-(4-carboxybenzimidino)-4,6-diamino-1,3,5-triazine” were synthesized. Synthetic strategy for preparing mononuclear complexes uses a complex as a “ligand” that contains a potential donor group capable of coordinating with the other ligand. We have chosen [Fe(salen)]<sub>2</sub>O, [Fe(salophen)]<sub>2</sub>O, [Cr(salen)]<sub>2</sub>O and [Cr(salophen)]<sub>2</sub>O as “ligand complexes” because they can coordinate with the other ligand. These complexes are the examples of single substitute mononuclear complexes bridged by carboxylate anions and catechol group to iron and chromium centers. Their structures were characterized by elemental analysis, <sup>1</sup>H NMR, FT-IR spectroscopy, LC–MS, thermal analyses and magnetic susceptibility measurements. The magnetic data for the single substitute mononuclear melamine complexes show good harmony with the d<sup>5</sup> and d<sup>3</sup> metal ions in an octahedral structure.

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