



Synthesis and characterization of dendrimeric melamine cored [salen/salophFe(III)] and [salen/salophCr(III)] capped complexes and their magnetic behaviors

Şaban Uysal*, Ziya Erdem Koç

Department of Chemistry, Faculty of Science, Selcuk University, Campus of Alaaddin Keykubat, 42075 Selcuklu, Konya, Turkey

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ABSTRACT

2,4,6-Tris(4-hydroxybenzimidino)-1,3,5-triazine [1] **2** has been synthesized from the reaction of 1 equiv. melamine (2,4,6-triamino-1,3,5-triazine) and 3 equiv. 4-hydroxybenzaldehyde. Then, 2,4,6-tris(4-(4,6-dichloro-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine **3** has been synthesized from the reaction of 1 equiv. **2** and 3 equiv. cyanuric chloride. And then, two new triazine centered dendrimeric ligands 2,4,6-tris(4-(4,6-bis(4-carboxyphenoxy)-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine **4** and 2,4,6-tris(4-(4,6-bis(3,5-dicarboxyphenoxy)-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine **5** have been synthesized from the reaction of 1 equiv. **3** and 6 equiv. 4-hydroxybenzoic acid or 5-hydroxyisophthalic acid. Finally, eight new multinuclear Fe(III) and Cr(III) complexes involving tetradenta Schiff bases N,N'-bis(salicylidene)ethylenediamine-(salenH₂) or bis(salicylidene)-o-phenylene diamine-(salophH₂) with **4** or **5** have been synthesized and characterized by means of elemental analysis, ¹H NMR, FT-IR spectroscopy, thermal analyses and magnetic susceptibility measurements. The complexes can also be characterized as low-spin distorted octahedral Fe(III) and Cr(III) bridged by carboxylic acids.

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1. Introduction

An important class of compounds having anticancer, antitumor, antiviral and antifungal activity consists of substituted s-triazine derivatives. These compounds have been used in the treatment of depression and hence gained considerable significance. These are valuable bases for estrogen receptor modulators [2] and also used as bridging agents to synthesize herbicides and in the production of drugs or polymers [3].

Melamine resins have been used in many applications including the manufacture of plastic dishes under the trade name Melmac. 1,3,5-Triazine derivatives are widely used as herbicides [4], drugs [5] or polymers [6], like melamineformaldehyde that has excellent thermal and electrical properties [7]. Phenolic melamine has a good non-flammability owing to containing nitrogen in its chemical structure [8].

We have reported here that dendrimeric Schiff bases including hexacarboxylic and dodecarboxylic groups have been synthesized to be a new template. The reaction of melamine (C₃N₆H₆) with 3 equiv. of 4-hydroxybenzaldehyde in benzene has given the desired triazomethine groups and triphenolic groups in a single step. Phenolic-OH groups [9,10] were then reacted to trimeric

cyanuric chloride (C₃N₃Cl₃) as single directional at 0–5 °C. Then, the obtained product was reacted under reflux with 6 equiv. 4-hydroxybenzoic acid and 6 equiv. 5-hydroxyisophthalic acid [11–15]. It may be useful to stress at the point that the new products mentioned above are the main output of this work. These are the first in the literature and we call them “oxy-Schiff Bases” due to literature [9,10].

The magnetochemical properties of the μ-oxo-bridged complexes [{Fe(salen)}₂O] [(salenH₂ = N,N'-bis(salicylidene)ethylene diamine)] and [{Fe(saloph)}₂O] [(salophH₂ = bis(salicylidene)-2-phenylenediamine)] and their X-ray studies have widely been presented in the literature [16–19]. The reaction of [{Fe(salen)}₂O] with carboxylic acids have been given by Wollmann and Hendrickson [20].

Chromium is a unique transition metal ion, which has been established to be biologically significant at all the levels of living organisms [21]. Out of the two stable oxidation states of chromium, -VI and -III, trivalent chromium has been shown to play a positive role in controlling carbohydrate and lipid metabolism [22]. A Schiff base complex of chromium(III), [Cr(salen)(OH)₂]⁺, was found to enhance insulin activity, and insulin derived with the same was found to exhibit higher activity in glucose metabolism in animal models when compared with either free insulin or other derivatives [23,24]. Their asymmetric catalytic reactions have been described including oxidations, additions and reductions such as epoxidation of olefins, epoxide ring

* Corresponding author. Tel.: +90 532 303 30 35.

E-mail addresses: uysal77@hotmail.com, suysal@selcuk.edu.tr (Ş. Uysal).

opening [25–29]. Various metal–Salen complexes in the homogeneous phase such as manganese(III) [30], chromium(III) [31] and nickel(II) [32] Salen have been used for the epoxidation of olefins [33].

Therefore, in the present study, we have aimed to synthesize other dendrimeric multicarboxylato bridges and to present their certain influences on the magnetic behavior of the prepared complexes. We are also interested in dendrimeric multinuclear systems formed by the carboxylato bridges because of some satisfactory work concerning this bridge and associated data have appeared in the literature [34–38].

2. Experimental

2.1. Materials and methods

Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. The IR spectra were recorded using KBr discs (4000–440 cm^{-1}) on a Perkin Elmer 1600 series FT-IR spectrophotometer. The ^1H NMR spectra in CDCl_3 , d_6 -DMSO was obtained using a Bruker 200 MHz spectrometer. MMM-Medcenter, Einrichtungen GmbH VacuCell 22 was used as Vacuum Cabinets. Melting points were measured using a Buchi SMP-20 melting point apparatus. Metal contents in complexes were determined using Unicam 929 AAS spectrometer. Mass spectra of the compounds were obtained on Varian MAT 711 spectrometer. The purification of the products obtained at the end of the reaction was carried out using Combi Flash Chromatography. The thermal analyses were performed on Shimadzu DTA 50 and TG 50 H models using 10 mg samples. The DTA and TG curves were obtained at a heating rate of $10^\circ\text{C min}^{-1}$. In all cases, the 22–750 $^\circ\text{C}$ temperature range was studied under a dry nitrogen atmosphere. All the other chemicals were purchased from Aldrich. Magnetic susceptibilities of metal samples were determined using a Sheerwood Scientific MX Gouy magnetic susceptibility apparatus and magnetic measurements were carried out using the Gouy method with $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. The effective magnetic moments, μ_{eff} , per metal atom were calculated from the equation: $\mu_{\text{eff}} = 2.84\sqrt{\chi_{\text{M}}T}$ B.M., where χ_{M} is the molar susceptibility.

2.1.1. Preparation of ligand complexes

$[\text{Fe}(\text{salen})]_2\text{O}$, $[\text{Fe}(\text{saloph})]_2\text{O}$, $[\text{Cr}(\text{salen})]_2\text{O}$ and $[\text{Cr}(\text{saloph})]_2\text{O}$ were prepared by adding concentrated ammonia solution to stirred hot EtOH solutions of $[\text{Fe}(\text{salen})\text{Cl}]$, $[\text{Fe}(\text{saloph})\text{Cl}]$, $[\text{Cr}(\text{salen})]$ and $[\text{Cr}(\text{saloph})\text{Cl}]$, respectively, until it became alkaline [16,39–41].

2.1.2. The synthesis procedure for 2,4,6-tris(4-hydroxybenzimidino)-1,3,5-triazine **2**

Previously, this compound was synthesized by a method [1], but we synthesized this compound by following method. Melamine (5 mmol, 0.63 g) was suspended in benzene (10 mL) and a suspension of 4-hydroxybenzaldehyde (1.83 g, 15 mmol) in benzene (25 mL) was added by stirring. The reaction mixture was boiled under reflux for 5 h, and the pink powder formed was dried under vacuum [37,38]. The obtained mixtures were purified using Combi Flash Chromatography and using 1:4 ethylacetate/n-hexane mixture as eluent. Characterization data for **2**: LC–MS data for **2** m/z : 438 \pm 2. FT-IR (cm^{-1}) 3338 (OH), 2842 (CH), 1615 (CH=N), 1565 (C=N triazine). ^1H NMR (d_6 -DMSO) δ 9.77 (s, 3H), 7.76–7.73 (d, 6H, $j = 2.8$ Hz), 6.93–6.90 (d, 6H, $j = 2.8$ Hz), 6.08 (s, 3H).

2.1.3. The synthesis procedure for 2,4,6-tris(4-(4,6-dichloro-1,3,5-triazine-2-yloxy) benzimidino)-1,3,5-triazine **3**

To stirred cyanuric chloride (2.76 g, 15 mmol), dissolved in acetone (100 mL), was added dropwise in a solution of **2** (2.19 g, 5 mmol) and NaOH (0.6 g, 15 mmol) in H_2O (50 mL) at 0–5 $^\circ\text{C}$. The

reaction mixture was stirred vigorously for 3 h at 0–5 $^\circ\text{C}$ and for 2 h at 15–20 $^\circ\text{C}$. At these stages the Fujiwara Test [12] for dichlorotriazine was positive. The temperature was allowed to increase to 25 $^\circ\text{C}$ and maintained for 25–30 $^\circ\text{C}$. The pale white solid was filtered, washed with cold water, then with ethyl alcohol. The obtained mixture was purified using Combi Flash Chromatography and using 1:4 ethylacetate/n-hexane mixture as eluent, and recrystallized from acetone. Characterization data for **3**: LC–MS data for **3** m/z : 882 \pm 2. FT-IR (cm^{-1}) 2847 (CH), 1618 (CH=N), 1574 (C=N triazine), 1366 (C–O–C), 845 (C–Cl). ^1H NMR (d_6 -DMSO) δ 10.03 (s, 3H), 8.05–8.01 (d, 6H, $j = 4.2$ Hz), 7.56–7.52 (d, 6H, $j = 4.2$ Hz).

2.1.4. The synthesis procedure for 2,4,6-tris(4-(4,6-bis(4-carboxyphenyloxy)-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine **4** or 2,4,6-tris(4-(4,6-bis(3,5-dicarboxyphenyloxy)-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine **5**

A solution of **3** (0.88 g, 1 mmol) in acetone (50 mL) was added dropwise to deionised (100 mL) water in a 250 mL flask cooled in an ice bath (0–5 $^\circ\text{C}$) under vigorous stirring. This was followed by the addition of 4-hydroxybenzoic acid (0.83 g, 6 mmol) or 5-hydroxyisophthalic acid (1.09 g, 6 mmol) and sodium carbonate (0.636 g, 6 mmol) in deionised saturated water, respectively. The mixture was stirred for 3 h while being cooled in the ice bath. The reaction mixture was boiled under reflux for 10 h, and the dirty white or grey powder formed was dried under vacuum. These obtained mixtures were purified using Combi Flash Chromatography and using 1:4 ethylacetate/n-hexane mixture as eluent. Characterization data for **4**: LC–MS data for **4** m/z : 1492 \pm 2. FT-IR (cm^{-1}) 3263 (OH), 2843 (CH), 1688 (C=O), 1612 (CH=N), 1572 (C=N triazine), 1408 (COO⁻), 1364 (COC). ^1H NMR (CDCl_3) δ 14.05 (s, 6H), 9.08 (s, 3H), 8.06–8.02 (d, 18H), 7.96–7.91 (d, 12H), 7.55–7.51 (d, 6H). Characterization data for **5**: LC–MS data for **5** m/z : 1756 \pm 2. FT-IR (cm^{-1}) 3244 (OH), 2846 (CH), 1694 (C=O), 1618 (CH=N), 1579 (C=N triazine), 1407 (COO⁻), 1375 (COC). ^1H NMR (d_6 -DMSO) δ 14.10 (s, 6H), 9.17 (s, 3H), 8.66–8.62 (d, 6H), 8.04–8.01 (d, 12H), 7.54–7.51 (d, 6H), 6.93–6.91 (d, 6H).

2.1.5. $[\{\text{Fe}(\text{salen})/(\text{saloph})\}_6(2,4,6\text{-tris}(4\text{-}(4,6\text{-bis}(4\text{-carboxyphenyloxy})\text{-}1,3,5\text{-triazine-}2\text{-yloxy)benzimidino})\text{-}1,3,5\text{-triazine})]$ **6x**, **6y** or $[\{\text{Cr}(\text{salen})/(\text{saloph})\}_6(2,4,6\text{-tris}(4\text{-}(4,6\text{-bis}(4\text{-carboxyphenyloxy})\text{-}1,3,5\text{-triazine-}2\text{-yloxy)benzimidino})\text{-}1,3,5\text{-triazine})]$ **6'x**, **6'y** complexes

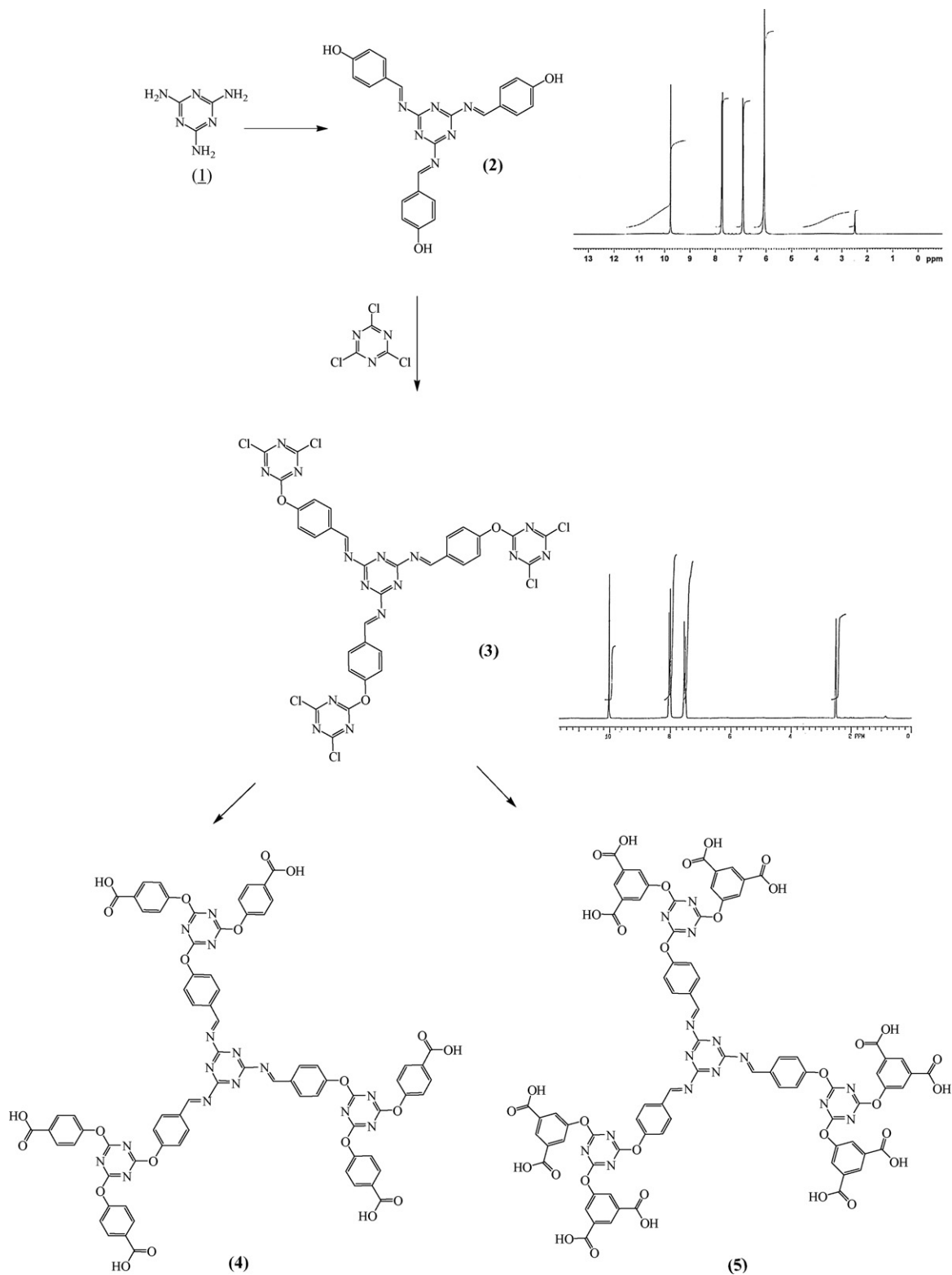
$[\{\text{Fe}(\text{salen})/(\text{saloph})\}_2\text{O}]$ (1.98 g, 3 mmol/2.27 g, 3 mmol) or $[\{\text{Cr}(\text{salen})/(\text{saloph})\}_2\text{O}]$ (1.96 g, 3 mmol/2.25 g, 3 mmol) were suspended in hot EtOH (50 mL) and a solution of **4** (1.49 g, 1 mmol) in EtOH was added by stirring. The reaction mixture was boiled under reflux for 4 h, and the solid formed was dried under vacuum. These obtained mixtures were purified using Combi Flash Chromatography and using 1:4 methanol/n-hexane mixture as eluent. Characterization data for **6x**, **6'x**: LC–MS data for **6x** m/z : 3431 \pm 2. LC–MS data for **6'x** m/z : 3408 \pm 2. FT-IR (cm^{-1}) 2894 (CH₂), 3145 (CH_{ar}), 1699–1697 (C=O), 1544–1620 (CH=N), 1575 (C=N triazine), 1386 (COO⁻), 1366 (COC), 535 (M–N), 466 (M–O). Characterization data for **6y**, **6'y**: LC–MS data for **6y** m/z : 3719 \pm 2. LC–MS data for **6'y** m/z : 3696 \pm 2. FT-IR (cm^{-1}) 3143 (CH_{ar}), 1698–1696 (C=O), 1546–1628 (CH=N), 1579 (C=N triazine), 1385 (COO⁻), 1365 (COC), 542 (M–N), 476 (M–O).

2.1.6. $[\{\text{Fe}(\text{salen})/(\text{saloph})\}_{12}(2,4,6\text{-tris}(4\text{-}(4,6\text{-bis}(3,5\text{-dicarboxyphenyloxy})\text{-}1,3,5\text{-triazine-}2\text{-yloxy)benzimidino})\text{-}1,3,5\text{-triazine})]$ **7x**, **7y** or $[\{\text{Cr}(\text{salen})/(\text{saloph})\}_{12}(2,4,6\text{-tris}(4\text{-}(4,6\text{-bis}(3,5\text{-dicarboxyphenyloxy})\text{-}1,3,5\text{-triazine-}2\text{-yloxy)benzimidino})\text{-}1,3,5\text{-triazine})]$ **7'x**, **7'y** complexes

$[\{\text{Fe}(\text{salen})/(\text{saloph})\}_2\text{O}]$ (3.96 g, 6 mmol/4.54 g, 6 mmol) or $[\{\text{Cr}(\text{salen})/(\text{saloph})\}_2\text{O}]$ (3.92 g, 6 mmol/4.49 g, 6 mmol) were suspended in hot EtOH (100 mL) and a solution of **5** (1.76 g, 1 mmol)

in EtOH was added by stirring. The reaction mixture was boiled under reflux for 4 h, and the solid formed was dried under vacuum. These obtained mixtures were purified using Combi Flash Chromatography and using 1:4 methanol/*n*-hexane mixture as eluent. Characterization data for **7x**, **7'x**: LC-MS data for **7x** m/z : 5634 \pm 2. LC-MS data for **7'x** m/z : 5588 \pm 2. FT-IR (cm^{-1}) 2891 (CH_2), 3147

(CH_{ar}), 1699–1698 ($\text{C}=\text{O}$), 1542–1621 ($\text{CH}=\text{N}$), 1572 ($\text{C}=\text{N}$ triazine), 1386 (COO^-), 1363 (COC), 534 ($\text{M}-\text{N}$), 469 ($\text{M}-\text{O}$). Characterization data for **7y**, **7'y**: LC-MS data for **7y** m/z : 6210 \pm 2. LC-MS data for **7'y** m/z : 6164 \pm 2. FT-IR (cm^{-1}) 3136 (CH_{ar}), 1698–1697 ($\text{C}=\text{O}$), 1543–1619 ($\text{CH}=\text{N}$), 1575 ($\text{C}=\text{N}$ triazine), 1384 (COO^-), 1365 (COC), 537 ($\text{M}-\text{N}$), 475 ($\text{M}-\text{O}$).



Scheme 1. Proposed structures of the tripodal oxy-Schiff base.

3. Results and discussion

2,4,6-Tris(4-hydroxybenzimidino)-1,3,5-triazine **2** was prepared through the reaction of melamine and 4-hydroxybenzaldehyde (Scheme 1). Afterwards, cyanuric chloride was added to **2**, and the structural formula of the 2,4,6-tris(4-(4,6-dichloro-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine **3** was verified by elemental analyses, ^1H NMR and FT-IR [9] (Scheme 1). 2,4,6-Tris(4-(4,6-dichloro-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine **3** with 4-hydroxybenzoic acid or 5-hydroxyisophthalic acid was readily furnished, and as a result of this reaction, “dendrimeric oxy-Schiff bases” have been obtained. Obtained tripodal oxy-Schiff bases were characterized by their elemental analyses, thermal analyses, ^1H NMR, and FT-IR, AAS and mass spectral data.

3.1. FT-IR spectra interpretations of the ligands and complexes

We have chosen $[\text{Fe}(\text{salen})]_2\text{O}$, $[\text{Fe}(\text{saloph})]_2\text{O}$, $[\text{Cr}(\text{salen})]_2\text{O}$ and $[\text{Cr}(\text{saloph})]_2\text{O}$ as “ligand complex” because it can coordinate with another ligand [34–39]. These complexes are the examples of tripodal multinuclear complexes bridged by carboxylate anions to the iron and chromium centers (Scheme 2). All compounds are stable at room temperature in solid state. The results of the some physical properties, given in Table 1, are in a good harmony with the structures suggested for the ligands and their complexes. The results show that all complexes are multinuclear, all complexes are also stable at room temperature and they are only soluble in organic solvents such as DMSO, DMF and insoluble in water.

When cyanuric chloride was added to tripodal Schiff base ligand **2**, phenolic OH band disappeared. The vibrations of the azomethine C=N, triazine C=N and C–O–C of the free ligands were observed at 1618–1605, 1574–1560 and 1375–1359 cm^{-1} range, respectively [34–38,42,43]. In the complexes, the fact that these bands were shifted to lower frequencies has indicated that oxygen atoms of the dendrimeric oxy-Schiff base ligands are coordinated with the ligand complexes. In the ligands 2,4,6-tris(4-(4,6-bis(4-carboxyphenyloxy)-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine **4** or 2,4,6-tris(4-(4,6-bis(3,5-dicarboxyphenyloxy)-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine **5** the band at 3263–3244 cm^{-1} can be assigned to the carboxylate OH group vibrations [10,34–38]. Bands at 1699–1697 cm^{-1} for all complexes were assigned to C=O groups due to the coordination of $[\text{Fe}(\text{salen})]$, $[\text{Fe}(\text{saloph})]$, $[\text{Cr}(\text{salen})]$ and $[\text{Cr}(\text{saloph})]$ with COO groups. Furthermore, bands at 1386–1384 cm^{-1} were assigned to COO[−] ions of those complexes. On the other hand, these bands for C=O and COO groups were at 1688–1694 cm^{-1} and 1408–1407 cm^{-1} before the coordination, respectively. In the dendrimeric-multinuclear complexes, that these bands at 3263–3244 cm^{-1} for carboxylate OH group vibrations disappeared can also be attributed to the coordination of COO groups with the metal. The bands in the 534–542 and 466–476 cm^{-1} ranges can be attributed to the M–N and M–O stretching modes [34–38,44].

3.2. ^1H NMR spectra interpretations of the ligands

In order to identify the structure of **2**, the ^1H NMR spectra were recorded in DMSO- d_6 [45,46]. ^1H NMR spectra also confirmed the structure of the synthesized compound. The signals in ^1H NMR spectrum of **2** at singlet $\delta=9.77$ ppm correspond to three $-\text{N}=\text{CH}-$ groups and at singlet $\delta=6.08$ ppm for three phenolic OH groups. The values have also showed that a three directional linkage to melamine had occurred. The “oxy-Schiff bases” prepared in this way have been obtained in nearly quantitative

yields (Scheme 1). In addition, 3 equiv. of cyanuric chloride was added to **2**. When cyanuric chloride was added to **2**, phenolic OH band at 6.08 ppm disappeared. When elemental analyses, ^1H NMR, FT-IR and mass spectral data were investigated, Cyanuric chloride was seen to be linked to OH groups of **2** as single directional. Fujiwara test of **3** has also evidenced that cyanuric chloride was linked to OH groups of **2** as single directional [12]. In addition to this, 6 equiv. of 4-hydroxybenzoic acid or 5-hydroxyisophthalic acid was added to **3**. When 4-hydroxybenzoic acid or 5-hydroxyisophthalic acid was added to **3**, the phenolic OH signals at 10.2 ppm for the former and at 10.3 ppm for the latter disappeared, and the acidic OH signals at 14.05 ppm for **4** and 14.10 ppm for **5** appeared. At ^1H NMR spectra of **4** and **5**, the acidic OH signals at 12.4 ppm for 4-hydroxybenzoic acid and 13.2 ppm for 5-hydroxyisophthalic acid have shifted downward. As a result, these data have evidenced that the compounds **4** and **5** have been successfully obtained. All the ligands are soluble in common organic solvents. Synthetic strategy for preparing dendrimeric multinuclear compounds uses a complex as a “ligand” that contains a potential donor group capable of coordinating with another ligand.

3.3. Magnetic moment interpretations of the complexes

The magnetic moments of the complexes given in Table 1 were measured at room temperature. On the basis of spectral evidence, the dendrimeric low spin Fe(III) and Cr(III) complexes have hexanuclear and dodecanuclear structures in which the low spin Fe(III) and Cr(III) cations have an approximately octahedral environment. The magnetic behavior of low spin Fe(III) and Cr(III) complexes is in accord with proposed hexanuclear and dodecanuclear structures. The magnetic moment per hexanuclear and dodecanuclear complexes which were constructed from $[\text{Fe}(\text{salen})]_2\text{O}$, $[\text{Fe}(\text{saloph})]_2\text{O}$, $[\text{Cr}(\text{salen})]_2\text{O}$ and $[\text{Cr}(\text{saloph})]_2\text{O}$ either of 2,4,6-tris(4-(4,6-bis(4-carboxyphenyloxy)-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine **4** or 2,4,6-tris(4-(4,6-bis(3,5-dicarboxyphenyloxy)-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine **5** shows paramagnetic property with a magnetic susceptibility value per atom: 1.59–1.70 and 3.70–3.90 μ_B , respectively. It is seen that the $[\text{Fe}(\text{salen})]_2\text{O}$, $[\text{Fe}(\text{saloph})]_2\text{O}$, $[\text{Cr}(\text{salen})]_2\text{O}$ and $[\text{Cr}(\text{saloph})]_2\text{O}$ containing compounds are represented by the electronic structure of $t_2g^5eg^0$ and $t_2g^3eg^0$. The magnetic data for the $[\text{Fe}(\text{salen})]_2\text{O}$, $[\text{Fe}(\text{saloph})]_2\text{O}$, $[\text{Cr}(\text{salen})]_2\text{O}$ and $[\text{Cr}(\text{saloph})]_2\text{O}$ dendrimeric complexes show good harmony with the low spin d^5 and d^3 metal ion in an octahedral structure. This conclusion is supported by the results of the elemental analyses suggesting that these dendrimeric complexes also have an octahedral structure [16,34–38].

3.4. Thermal analysis interpretations of the chosen ligands and complexes

The chosen ligands and complexes have also been thermally investigated and their plausible degradation schemes are presented in Table 2 [47,48]. Thermal decomposition of the anhydrous $[\text{Fe}(\text{salen})]$, $[\text{Fe}(\text{saloph})]$, $[\text{Cr}(\text{salen})]$ and $[\text{Cr}(\text{saloph})]$ complexes left from the ligands **4** and **5** have started in the range of the first step 135–292, the second step 272–367 and the final step 348–507 °C and completed in the range 565–650 °C. The final decomposition products were metals and triazine ring. The observed weight losses for all ligands and complexes are in good harmony with the calculated values.

From the investigation of LC–MS spectra of all compounds, it has been seen that molecular weights of ligands and complexes are in good harmony with the values observed in the area of intensity in LC–MS spectra (Table 1).

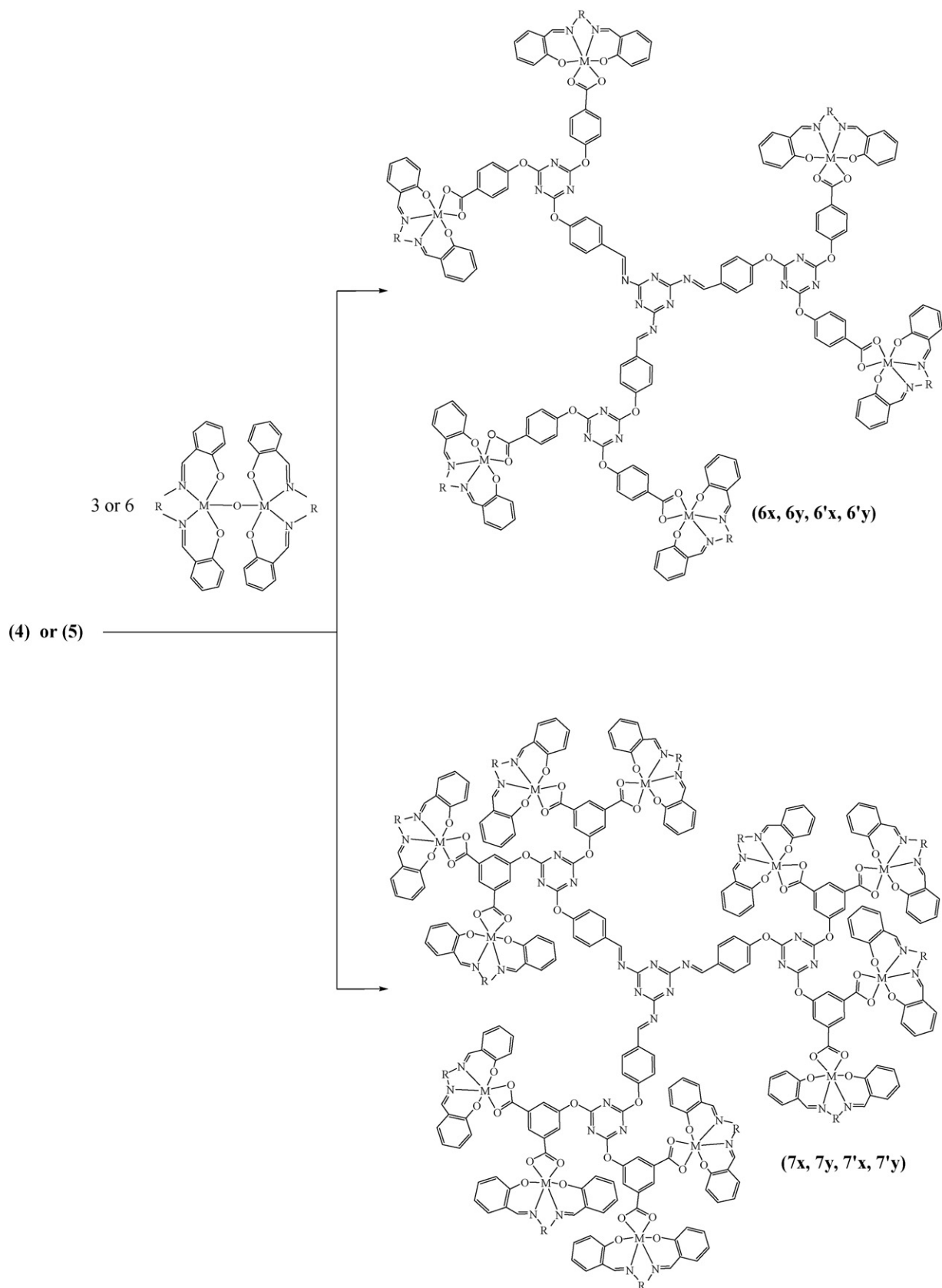






Table 1
Some physical properties, molecular weight (g/mol) data and elemental analyses, AAS analyses of the ligands and complexes.

Compounds	R	M	$\mu_{\text{eff}} (\mu_B)$ (296 K)	M.p. ($^{\circ}\text{C}$)	Yield (%)	Color [M_w (g/mol)]	Found calculated (%)				
							C	H	N	Fe	Cr
$\text{C}_{24}\text{H}_{18}\text{N}_6\text{O}_3$ (2)	–	–	–	142	72	Pink [438.45]	65.67 (65.75)	4.12 (4.14)	19.15 19.17	–	–
$\text{C}_{33}\text{H}_{15}\text{N}_{15}\text{O}_3\text{Cl}_6$ (3)	–	–	–	278	80	Pale white [882.30]	42.88 (42.92)	1.67 (1.71)	23.77 (23.81)	–	–
$\text{C}_{75}\text{H}_{45}\text{N}_{15}\text{O}_{21}$ (4)	–	–	–	277	66	White [1492.28]	60.34 (60.37)	3.03 (3.04)	14.06 (14.08)	–	–
$\text{C}_{81}\text{H}_{45}\text{N}_{15}\text{O}_{33}$ (5)	–	–	–	289	63	Pale white [1756.34]	55.32 (55.39)	2.55 (2.58)	11.95 (11.96)	–	–
$\text{C}_{171}\text{H}_{135}\text{N}_{27}\text{O}_{33}\text{Fe}_6$ (6x)	–CH ₂ –H ₂ –	Fe ³⁺	1.60	280 ^a	69	Brown [3431.23]	59.81 (59.86)	3.96 (3.97)	11.00 (11.02)	9.74 (9.77)	–
$\text{C}_{195}\text{H}_{135}\text{N}_{27}\text{O}_{33}\text{Fe}_6$ (6y)		Fe ³⁺	1.68	270 ^a	61	Brown [3719.49]	62.89 (62.97)	3.65 (3.66)	10.14 (10.17)	8.97 (9.01)	–
$\text{C}_{171}\text{H}_{135}\text{N}_{27}\text{O}_{33}\text{Cr}_6$ (6x)	–CH ₂ –H ₂ –	Cr ³⁺	3.73	275 ^a	58	Orange [3408.12]	60.23 (60.27)	3.97 (3.99)	11.07 (11.10)	–	9.11 (9.15)
$\text{C}_{195}\text{H}_{135}\text{N}_{27}\text{O}_{33}\text{Cr}_6$ (6y)		Cr ³⁺	3.86	265 ^a	54	Orange [3696.39]	63.28 (63.36)	3.63 (3.68)	10.20 (10.23)	–	8.42 (8.44)
$\text{C}_{273}\text{H}_{225}\text{N}_{39}\text{O}_{57}\text{Fe}_{12}$ (7x)	–CH ₂ –H ₂ –	Fe ³⁺	1.59	288 ^a	66	Dark brown [5634.23]	58.16 (58.20)	4.00 (4.03)	9.67 (9.70)	11.82 (11.89)	–
$\text{C}_{321}\text{H}_{225}\text{N}_{39}\text{O}_{57}\text{Fe}_{12}$ (7y)		Fe ³⁺	1.70	292 ^a	77	Dark brown [6210.76]	62.03 (62.08)	3.62 (3.65)	8.76 (8.80)	10.75 (10.79)	–
$\text{C}_{273}\text{H}_{225}\text{N}_{39}\text{O}_{57}\text{Cr}_{12}$ (7x)	–CH ₂ –H ₂ –	Cr ³⁺	3.70	283 ^a	65	Green [5588.02]	58.65 (58.68)	4.02 (4.06)	9.75 (9.78)	–	11.15 (11.17)
$\text{C}_{321}\text{H}_{225}\text{N}_{39}\text{O}_{57}\text{Cr}_{12}$ (7y)		Cr ³⁺	3.90	273 ^a	64	Dark green [6164.55]	62.50 (62.54)	3.64 (3.68)	8.83 (8.86)	–	10.08 (10.12)

^a Decomposition.

Table 2

Decomposition steps with the temperature range and weight loss for ligand and complexes.

Compound	Step no.	Temperature range (°C)	Weight loss found/Calcd. (%)
C ₇₅ H ₄₅ N ₁₅ O ₂₁ (4)	I	153–294	55.60/57.90
	II	297–395	28.87/30.42
C ₈₁ H ₄₅ N ₁₅ O ₃₃ (5)	I	193–317	60.65/63.93
	II	320–445	16.50/17.61
C ₁₇₁ H ₁₃₅ N ₂₇ O ₃₃ Fe ₆ (6x)	I	145–280	23.87/24.98
	II	285–359	45.24/46.68
	III	362–498	8.87/9.03
C ₁₉₅ H ₁₃₅ N ₂₇ O ₃₃ Cr ₆ (6iy)	I	135–265	21.62/23.15
	II	272–354	49.98/51.18
	III	358–493	8.13/8.39
C ₃₂₁ H ₂₂₅ N ₃₉ O ₅₇ Fe ₁₂ (7y)	I	163–292	16.87/17.95
	II	295–367	59.72/60.94
	III	372–507	4.97/5.00
C ₂₇₃ H ₂₂₅ N ₃₉ O ₅₇ Cr ₁₂ (7x)	I	138–283	18.34/19.24
	II	287–342	56.02/57.55
	III	348–436	5.88/6.25

The final thermal decomposition products are metals and triazine rings.

4. Conclusions

In this study, novel tri-directional melamine and cyanuric chloride based Schiff bases “2,4,6-tris(4-hydroxybenzimidino)-1,3,5-triazine, 2,4,6-tris(4-(4,6-dichloro-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine, 2,4,6-tris(4-(4,6-bis(4-carboxyphenyloxy)-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine and 2,4,6-tris(4-(4,6-bis(3,5-dicarboxyphenyloxy)-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine” were synthesized. Synthetic strategy for preparing multinuclear compounds uses a complex as a “ligand” that contains a potential donor group capable of coordinating with the other ligand. We have chosen [Fe(salen)]₂O, [Fe(saloph)]₂O, [Cr(salen)]₂O and [Cr(saloph)]₂O as “ligand complexes” because they can coordinate with the other ligand. These complexes are the examples of multinuclear complexes bridged by carboxylate anions to the iron and chromium centers. Their structures were characterized by means of elemental analysis, ¹H NMR, FT-IR spectroscopy, thermal analyses and magnetic susceptibility measurements. The magnetic data for the multinuclear complexes show good harmony with the d⁵ and d³ metal ion in an octahedral structure.

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