



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

ARTICLE INFO

Article history:

Received 10 August 2009

Received in revised form 2 October 2009

Accepted 13 October 2009

Available online 20 October 2009

Keywords:

s-Triazine

Melamine

Cyanuric chloride

Salen

Saloph

Schiff bases

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 a 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. $[\{\text{Fe}(\text{salen})/(\text{saloph})\}_6(2,4,6\text{-tris(4-(4,6-bis(4-carboxyphenyloxy)-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine})]$ **6x**, **6y** or $[\{\text{Cr}(\text{salen})/(\text{saloph})\}_6(2,4,6\text{-tris(4-(4,6-bis(4-carboxyphenyloxy)-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine})]$ **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. $[\{\text{Fe}(\text{salen})/(\text{saloph})\}_{12}(2,4,6\text{-tris(4-(4,6-bis(3,5-dicarboxyphenyloxy)-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine})]$ **7x**, **7y** or $[\{\text{Cr}(\text{salen})/(\text{saloph})\}_{12}(2,4,6\text{-tris(4-(4,6-bis(3,5-dicarboxyphenyloxy)-1,3,5-triazine-2-yloxy)benzimidino)-1,3,5-triazine})]$ **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)

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