



The (salophen)-bridged Fe/Cr (III) capped complexes with triphenylene core: Synthesis and characterization

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ABSTRACT

This article describes synthesis of the difference carboxylic acid derivatives of triphenylene and its complexation properties with Fe/Cr (III)–salophen. For this purpose, the carboxylic acid derivatives of 2,3,6,7,10,11-hexahydroxytriphenylene were synthesized and then reacted with four new Fe(III) and Cr(III) complexes involving tetradenta Schiff bases bis(salicylidene)-*o*-phenylenediamine-(salophenH₂). The prepared compounds were characterized by means of elemental analysis carrying out infrared spectroscopy (IR), thermogravimetric analysis (TG), nuclear magnetic resonance (¹H NMR), elemental analysis and magnetic susceptibility measurement. 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

Investigation on metal organic complexes represents one of the most active areas of material science and chemical research. Major advances have been made in these materials due to their interesting properties and potential in various applications, e.g., electrical conductivity, magnetism, host guest chemistry, ion exchange, catalysis, nonlinear optics, etc. [1–3]. Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. They show interesting properties, e.g., their ability to reversibly bind oxygen [4], catalytic activity in hydrogenation of olefins [5], transfer of an amino group [6], photochromic properties [7] and complexing ability toward toxic metals [8].

Schiff base ligands are considered “privileged ligands” because they are easily prepared by the condensation between aldehydes and imines. The Schiff base ligands with nitrogen, oxygen and sulfur donor atoms in their structures act as good chelating agents for the transition and non-transition metal ions [9,10]. As is known, transition metal complexes of Schiff bases are compounds which are becoming increasingly important in the pharmaceutical, dye and plastic industries as well as for liquid-crystal technology and mechanistic investigations of the drugs used in pharmacology, biochemistry and physiology [11,12]. Schiff bases a class of chelators capable of forming coordinate bonds with many of metal ions through both azomethine and phenolic groups [13–16].

Condensation of salicylaldehydes or salicylaldehyde derivatives with 1,2-diamines leads to the formation of one extremely important class of ligands, generally known as “Salens” (accordingly with *o*-phenylenediamine, Salophen). Salen-type and Salophen-type ligands with N and O donor atoms are important since their metal complexes find widespread applications as homogeneous and heterogeneous catalysts in various organic transformation reactions [17]. The bridged complexes of salen–salophen are especially attractive by latest studies in inorganic chemistry [18–20].

Triphenylene with a disc structure was first described in 1935 [21]. Chandrasekhar et al. [22] reported that a disc-shaped molecule is able to organize into a liquid-crystalline structure. Now, triphenylene derivatives, especially symmetrically substituted hexaethers, have developed into an important class of discotic liquid-crystalline structures. These fascinating discogens may find commercial applications in quasi-one-dimensional conductors [23,24], photoconductors [25], and light-emitting diodes [26]. Many efforts have been directed toward triphenylene-related areas during the past two decades [27,28].

In the present study, we synthesized the carboxylic acid derivatives of triphenylene as ligand and their Fe/Cr(III) salophen capped complexes. In addition, the characteristic properties, FT-IR and TG/dTG results of these complexes were presented and evaluated in this study.

2. Results and discussion

In order to evaluate the complexation with [{Fe/Cr(salophen)}₂O] of the carboxylic acid derivatives of triphenylene as ligand, firstly we

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have synthesized compounds **3**, **4** and **5** using ethyl bromoacetate, methyl 5-bromovalerate or methyl (4-bromomethyl) benzoate in presence of K_2CO_3 (Fig. 1). After then, the prepared ester derivatives of triphenylene was converted to the carboxylic acid derivatives (**5**, **6** and **7**) with NaOH in ethanol media (Fig. 1). These compounds were characterized with 1H NMR, FT-IR and elemental analysis. The 1H

NMR values of the synthesized compounds was given in experimental part. In addition to this, the 1H NMR spectrums of compound **2** and **5** were presented in Figs. 2 and 3. The formation of **2** (2,3,4,6,7,10,11-Hexakis(ethoxycarbonylmethoxy)triphenylene) was confirmed by the disappearance of the phenolic–OH at 9.26 ppm in HHTP and the appearance of the $-OCH_2$ and $-CH_3$ protons at 4.33

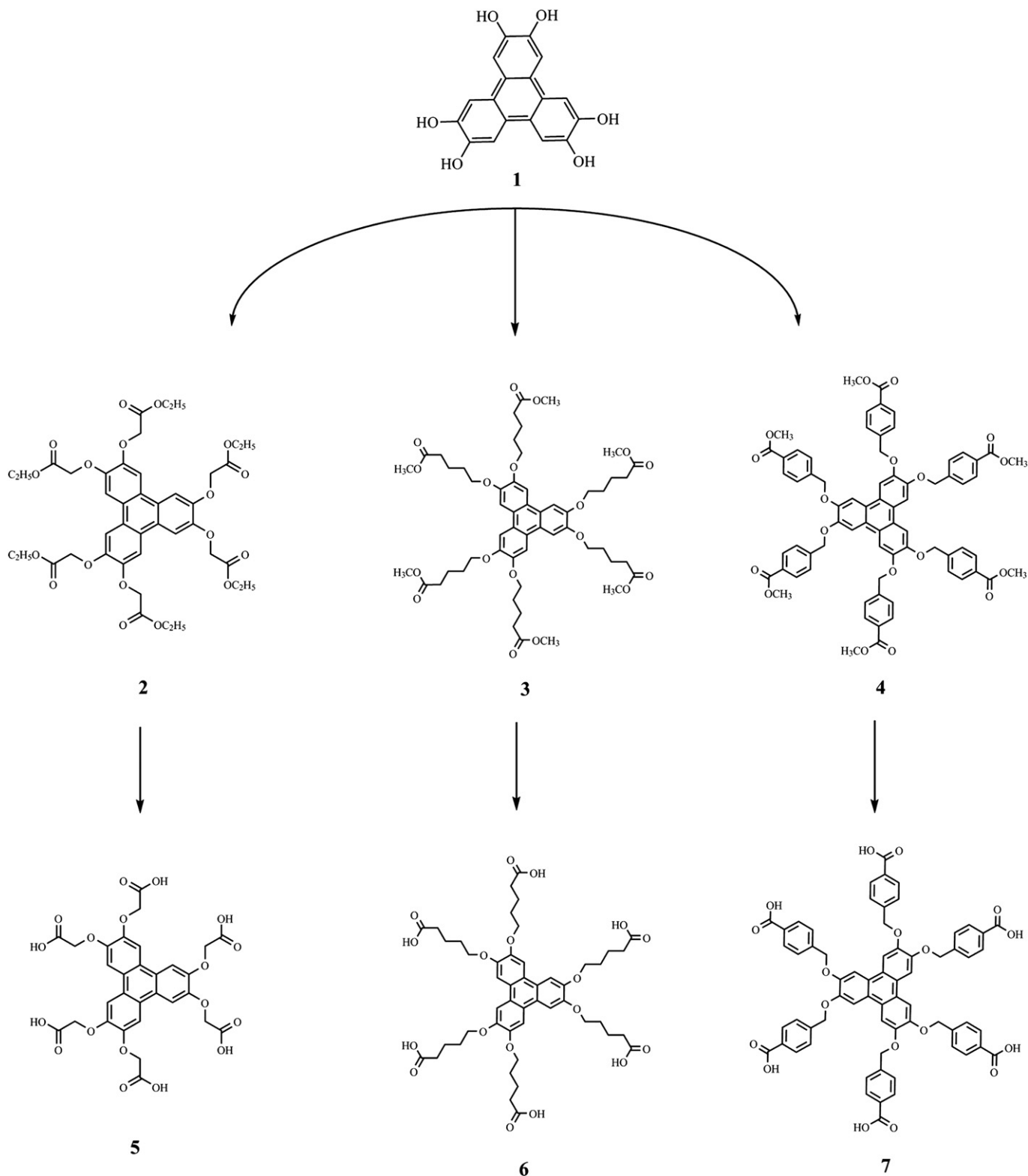


Fig. 1. Synthesis of the carboxylic acid derivatives of triphenylene.

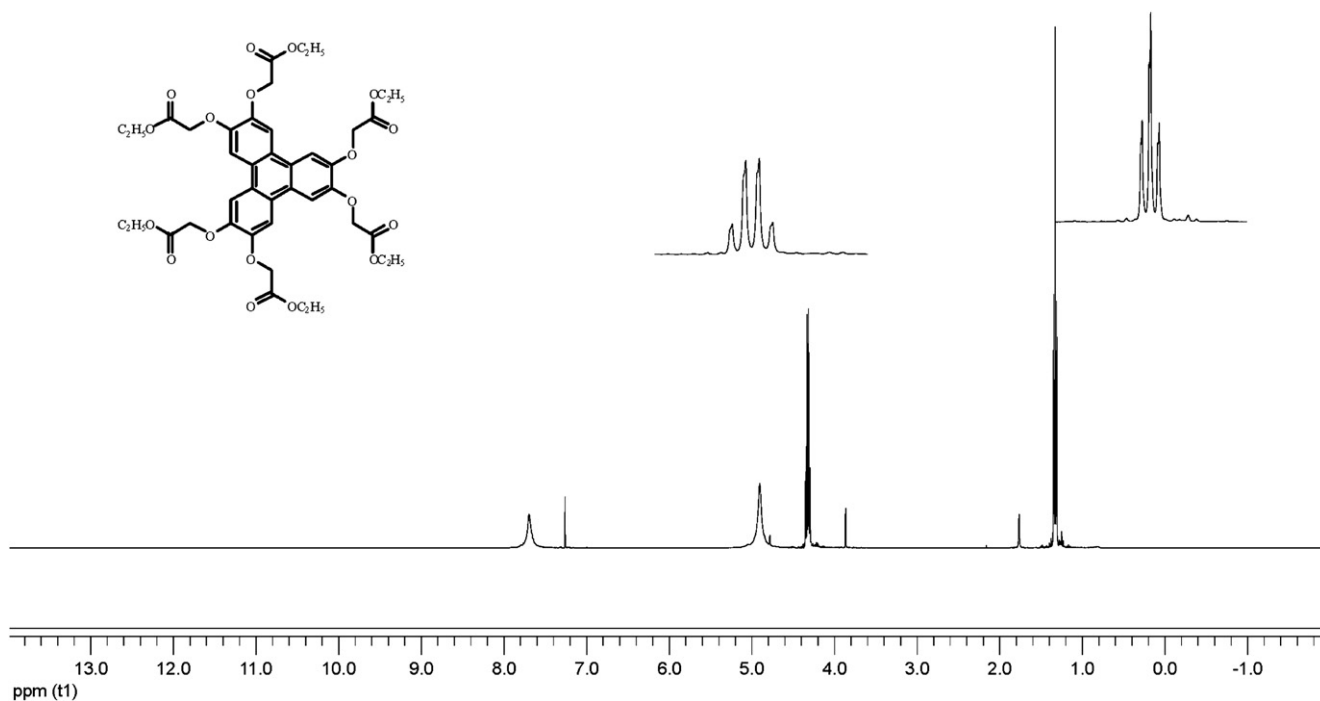


Fig. 2. The ^1H NMR spectrum of compound 2.

and 1.32 ppm in **2**, respectively (Fig. 2). As seen Fig. 3, the synthesis of **5** was confirmed by the disappearance of $-\text{OCH}_2$ and $-\text{CH}_3$ protons belong to compound **2**. All of compounds prepared in the way have been obtained in nearly quantitative yield and high purity. The obtained carboxylic acid derivatives were converted to complexes

bridged by carboxylate anions to the chromium and iron center with $[\{\text{Fe}/\text{Cr}(\text{salophen})\}_2\text{O}]$ as “ligand complex”. We have chosen $[\{\text{Fe}/\text{Cr}(\text{salophen})\}_2\text{O}]$ as “ligand complex” because it can coordinate to another ligand [29]. These complexes are the first examples of complexes bridged by carboxylate anions to the iron and chromium

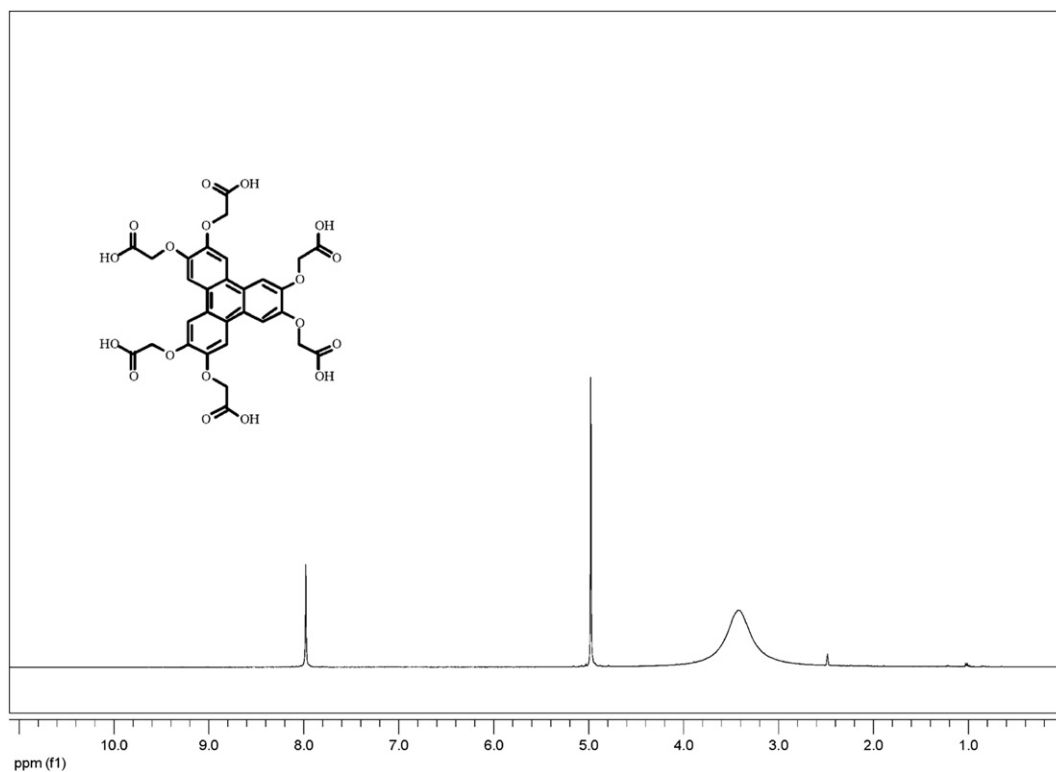


Fig. 3. The ^1H NMR spectrum of compound 5.

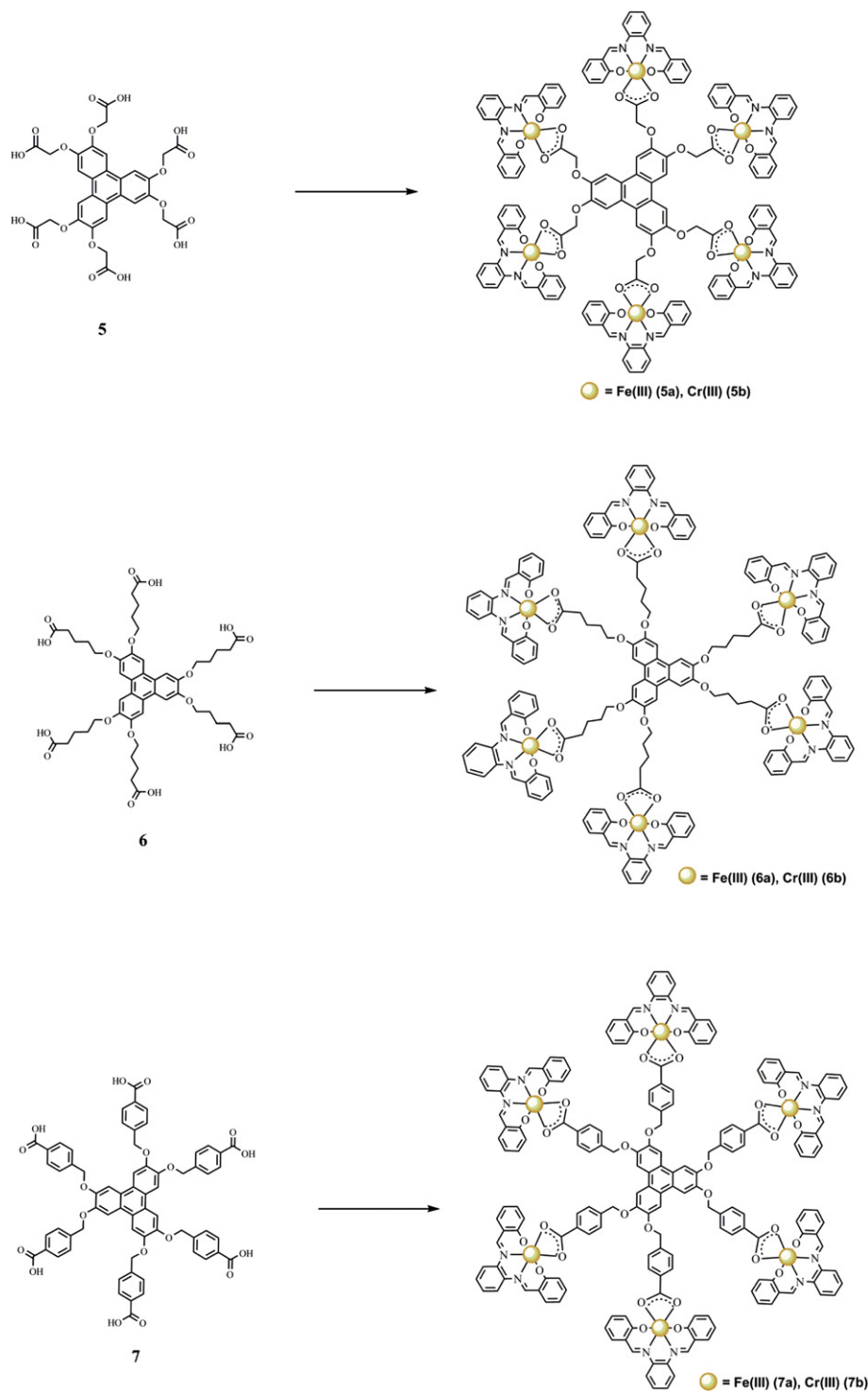


Fig. 4. Synthetic routes for complexation between Fe/Cr(III)–salophen and compound **5**, **6** or **7**.

centers (Fig. 4). All compounds are stable at room temperature in the solid state. The results of the elemental analyses, given in Table 1, are in a good agreement with the structures suggested for the ligands and their complexes. In addition, the synthesized Fe/Cr–salophen capped complexes were characterized with elemental analysis, thermal gravimetric analysis, magnetic susceptibility and FT-IR.

The magnetic moments of the complexes presented in Table 1 were measured at room temperature. The results shows that the

Fe(III) and Cr(III) complexes have hexanuclear structures in which the Fe(III) and Cr(III) cations have an approximately octahedral environment. The magnetic behavior of Fe(III) and Cr(III) complexes is in accord with proposed hexanuclear structures. The magnetic moment per hexanuclear complexes which were constructed from $[\{\text{Fe}(\text{salophen})\}_2\text{O}]$ and $[\{\text{Cr}(\text{salophen})\}_2\text{O}]$ either of **5**, **6** and **7** indicates paramagnetic property with a magnetic susceptibility value per atom: 1.98, 3.42 B.M. for **5**, 1.79, 3.42 B.M. for **6** and 1.85,

Table 1
Elemental analysis, magnetic and physical properties of the compounds.

Complex	Color	μ_{eff} (B.M.) 298 °C	m.p (°C)	Yield (%)	Found (Calcd.) (%)			
					C	N	H	M
5a	Orange	1.98	312	80	62.26 (62.20)	5.81 (6.85)	3.76 (3.74)	11.58 (11.55)
5b	Brown-green	3.42	387 ^a	65	62.76 (62.71)	5.86 (5.80)	3.79 (3.75)	10.87 (10.80)
6a	Tile red	1.79	350 ^a	64	64.14 (61.10)	5.34 (5.31)	4.61 (4.64)	10.65 (10.60)
6b	Red-green	3.42	>400	61	64.61 (64.59)	5.38 (5.34)	4.65 (4.69)	9.99 (9.93)
7a	Tile red	1.85	279	78	66.68 (66.60)	5.02 (4.98)	3.97 (3.95)	10.00 (9.90)
7b	Brown-green	3.52	394	67	67.15 (67.20)	5.05 (5.00)	4.00 (4.05)	9.38 (9.34)

^a Decomposition.

Table 2
Characteristic FT-IR bands (cm^{-1}) of the prepared Fe/Cr–salophen complexes.

Compounds	OH	C=O	C–N	C–C _{ar}	C–H _{aliph}
5a	3438	1738	1607	1584	3076
5b	3392	1715	1623	1605	3056
6a	3446	1723	1623	1615	3069
6b	3430	1730	1628	1600	3046
7a	3430	1750	1623	1605	3053
7b	3407	1753	1630	1600	3069

3.52 B.M. for **7**. It is seen that the $[\{\text{Fe}(\text{salophen})\}_2\text{O}]$ and $[\{\text{Cr}(\text{salophen})\}_2\text{O}]$ containing compounds are represented by the electronic structure of $t_2g^5eg^0$ and $t_2g^3eg^0$. The magnetic data for the $[\{\text{Fe}(\text{salophen})\}_2\text{O}]$ and $[\{\text{Cr}(\text{salophen})\}_2\text{O}]$ complexes demonstrate well agreement with the d^5 and d^3 metal ion in an octahedral structure. This consequence is supported by the results of the elemental analyses suggesting that these complexes have also an octahedral structure [30,31].

The characteristic FT-IR bands for the prepared Fe/Cr(III)–salophen complexes (**5a–5b**, **6a–6b** and **7a–7b**) were given Table 2.

The FT-IR spectra of the complexes have different absorption bands, compared with that of the ligands. The vibrations of the carboxylic acid $\text{C}=\text{O}$ of **5**, **6** and **7** ligands have been observed at 1735, 1740 and 1707 cm^{-1} , respectively. In the complexes, these bands are, however, shifted to lower or higher frequencies indicating that the oxygen atoms of **5**, **6** and **7** are coordinated to the ligand complexes. The $\text{C}=\text{O}$ band in complexes **5a**, **5b**, **6a**, **6b**, **7a** and **7b** shift to 1738, 1715, 1723, 1730, 1750 and 1753 cm^{-1} depending on the electron density of the $\text{C}=\text{O}$ group, respectively. Also, in the FT-IR analysis of the complexes, the bands in the $556\text{--}533$ and $465\text{--}478\text{ cm}^{-1}$ range can be attributed to the M–N and M–O stretching modes [31].

The thermal stability of the prepared complexes was evaluated by thermal gravimetric analysis (TG). TG curve of complex **5b** was depicted in Fig. 5. It was found that **5b** undergoes a three-step thermal degradation. The first step ($50\text{--}200\text{ °C}$) is due to the loss of moisture. At the second and third decomposition step, CO_2 and C_6H_6 groups left from the main structure at $250\text{--}450\text{ °C}$ and $450\text{--}850\text{ °C}$, respectively [32]. Although the total weight lost was theoretically calculated to be 42.33%, it was observed experimentally to be 37.11%. Moreover, the thermal behaviors of the obtained other complexes are summarized in Table 3.

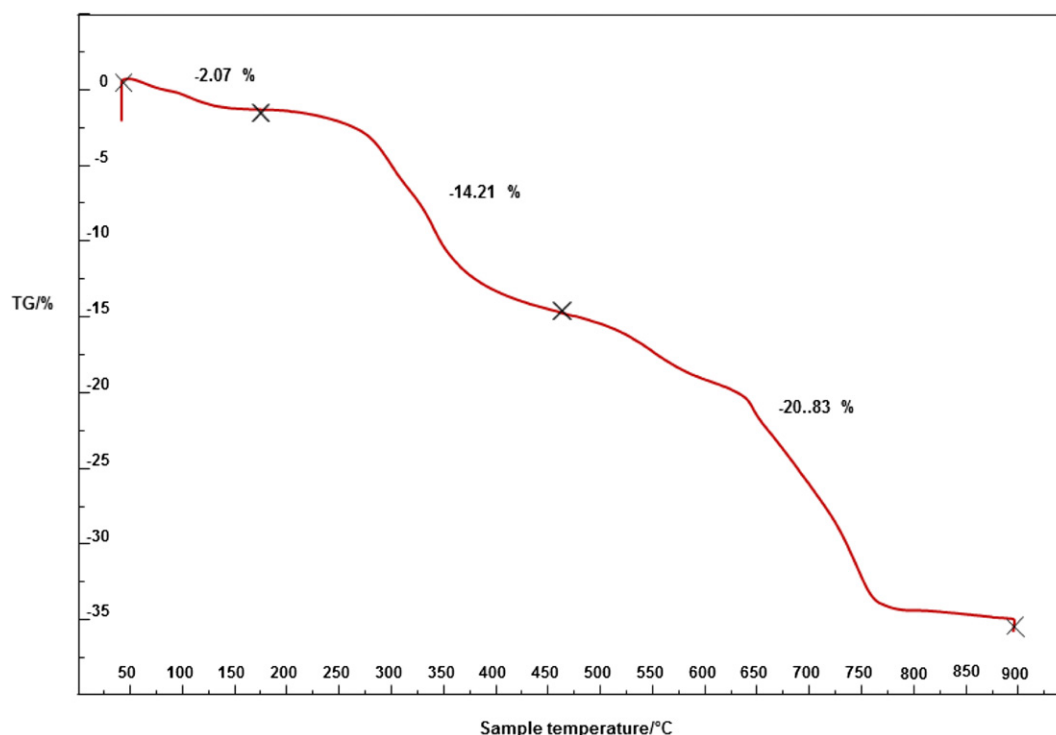


Fig. 5. TG curve of compound **5b**.

Table 3

Thermal analysis of the prepared Fe/Cr–salophen complexes.

Complexes	TG range (°C)	Fragments	Weight loss found (Calcd.) (%)
5a	50–100 °C	Moisture	45.58 (42.34) (%)
	200–425 °C	CO ₂	
	500–875 °C	C ₆ H ₆ groups	
5b	50–200 °C	Moisture	42.33 (37.11) (%)
	250–450 °C	CO ₂	
	450–850 °C	C ₆ H ₆ groups	
6a	50–150 °C	Moisture	32.03 (35.67) (%)
	200–450 °C	H ₂ , CO ₂	
	575–800 °C	C ₂ H ₄ , C ₆ H ₆ , CN	
6b	50–150 °C	Moisture	29.75 (32.17) (%)
	250–475 °C	H ₂ , CO ₂	
	600–700 °C	C ₂ H ₄	
	750–850 °C	CN, C ₆ H ₆ groups	
	850–1000 °C	Moisture	
7a	50–150 °C	Moisture	41.75 (45.13) (%)
	250–375 °C	CO ₂	
	400–700 °C	CN, C ₆ H ₆	
7b	50–140 °C	Moisture	40.62 (45.43) (%)
	200–425 °C	CO ₂	
	450–750 °C	CN, C ₆ H ₆	

3. Conclusion

The design and synthesis of novel the carboxylic acid derivatives of triphenylene as ligand and their Fe/Cr(III)–salophen complexes have been demonstrated in this report. These complexes are the examples of 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 analysis and magnetic susceptibility measurements. The magnetic data for the complexes show well agreement with the d⁵ and d³ metal ion in an octahedral structure. It may be possible to try to test these triphenylene based Fe/Cr–salophen complexes as antibacterial, antitubercular, antifungal and anticoagulant activity. In other words, further studies on the complexation reactions and catalytic activity of the prepared complexes on model reactions will be carried out soon.

4. Experimental

4.1. Materials and methods

All starting materials and reagents used were of standard analytical grade from Fluka, Merck as well as from Aldrich and used without further purification. [{Fe(salophen)}₂O] and [{Cr(salophen)}₂O] were prepared according to previously published methods [30,33]. Melting points were measured using a Buchi B-540 melting point apparatus. ¹H NMR spectra were recorded on a Varian 400 MHz spectrometer at room temperature. Thermal gravimetric analysis (TG) was carried out with Seteram thermogravimetric analyzer. The sample weight was 15–16 mg. Analysis was performed from room temperature to 900 °C at heating rate of 15 °C/min in argon atmosphere with a gas flow rate of 20 mL/min. The elemental analysis for the ligand and the bridged complexes were carried out at on a Hewlett–Packard 185 analyzer. FT-IR spectra were recorded using a Mattson-1000 FT-IR using KBr pellets. 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 was calculated from the expression: $\mu_{\text{eff}} = 2.84 \cdot (\chi_M)^{1/2}$, where χ_M is the molar susceptibility.

4.2. Synthesis of compounds 2, 3 and 4

2,3,6,7,10,11-hexahydroxytriphenylene **1** (HHTP) was prepared according to the reported procedure [34]. To give compounds **2**, **3** and **4**, the mixture of HHTP (1 mmol) and K₂CO₃ (8 mmol) in 50.0 mL of dry acetone was refluxed for 1 h. Then, ethyl bromoacetate, methyl 5-bromovalerate or methyl (4-bromomethyl) benzoate (8 mmol) upon this solution were added and refluxed for 24 h. The reaction was monitored by TLC. The resulting solution was allowed to warm up to room temperature. At the end of the reaction, the reaction mixture was filtered and the organic layer was removed under reduced pressure. The observed solid product was dissolved in CHCl₃ and washed twice with 0.2 N HCl and water. The combined organic phase was dried over Na₂SO₄ filtered, and concentrated under reduced pressure to afford the desired pure product (**2**, **3** and **4**).

Compound 2; Yield 75%; mp: 154 °C; FT-IR: 1750 (C=O) cm⁻¹; ¹H NMR (CDCl₃): δ 1.32 (t, 18H, –CH₂CH₃), 4.33 (q, 12H, –CH₂CH₃), 4.91 (s, 12H, OCH₂), 7.69 (s, 6H, Ar–H). Anal. Calcd for C₄₂H₄₈O₁₈: C, 59.99%; H, 5.75%. Found: C, 60.10%; H, 5.62%.

Compound 3; Yield 60% (oil); FT-IR: 1755 (C=O) cm⁻¹; ¹H NMR (CDCl₃): δ 1.65–1.75 (m, 12H, –CH₂), 1.88–2.02 (m, 12H, –CH₂), 2.49 (t, 12H, CH₂CO), 3.68 (s, 18H, OCH₃), 4.25 (t, 12H, OCH₂), 7.81 (s, 6H, Ar–H). Anal. Calcd for C₅₄H₇₂O₁₈: C, 64.27%; H, 7.19%. Found: C, 63.02%; H, 7.12%.

Compound 4; Yield 72%; mp: 105 °C; FT-IR: 1723 (C=O) cm⁻¹; ¹H NMR (CDCl₃): δ 3.94 (s, 18H, –OCH₃), 5.43 (s, 12H, O–CH₂), 7.52 (d, 12H, Ar–H), 8.09 (d, 12H, Ar–H), 8.10 (s, 6H, Ar–H). Anal. calcd. for C₇₂H₆₀O₁₈: C, 71.28%; H, 4.98%. Found: C, 72.02%; H, 4.82%.

4.3. Synthesis of compound 5, 6 and 7

A mixture of compounds **2**, **3** or **4** (1.0 mmol) and 15% aqueous sodium hydroxide (13 mL, 6 mmol) in ethanol (50 mL) was refluxed for 24 h. Ethanol was distilled off and the residue was diluted with water (50 mL). HCl (3 mol L⁻¹) was added to the resulting suspension until pH 1 was reached. The solid was filtered off and dissolved in chloroform (50 mL). This solution was washed with HCl (3 mol L⁻¹, 30 mL) and brine (30 mL). The organic layer was dried over MgSO₄ and concentrated to afford compounds **5**, **6** or **7**.

Compound 5; Yield 85%; mp: 255 °C; FT-IR: 1735 (C=O) cm⁻¹; ¹H NMR (DMSO): δ 5.01 (s, 12H, OCH₂), 8.00 (s, 6H, Ar–H). Anal. Calcd for C₃₀H₂₄O₁₈: C, 53.58%; H, 3.60%. Found: C, 54.10%; H, 3.62%.

Compound 6; Yield 50% (oil); FT-IR: 1740 (C=O) cm⁻¹; ¹H NMR (DMSO): δ 1.72–1.84 (m, 24H, –CH₂), 2.34 (t, 12H, CH₂CO), 4.23 (t, 12H, OCH₂), 7.95 (s, 6H, Ar–H). Anal. Calcd for C₄₈H₆₀O₁₈: C, 62.33%; H, 6.54%. Found: C, 62.12%; H, 6.23%.

Compound 7; Yield 60%; mp: 340 °C (decomp.); FT-IR: 1707 (C=O) cm⁻¹; ¹H NMR (DMSO): δ 5.47 (s, 12H, O–CH₂), 7.66–7.73 (m, 12H, Ar–H), 7.94 (s, 6H, Ar–H), 7.91–7.98 (m, 12H, Ar–H). Anal. Calcd for C₆₆H₄₈O₁₈: C, 70.21%; H, 4.29%. Found: C, 70.02%; H, 4.31%.

4.4. Preparation of the (salophen)-bridged Fe/Cr (III) capped complexes (5a,5b, 6a,6b, 7a,7b)

A solution of compounds **5**, **6** or **7** (1 mmol) and [{Fe/Cr(salophen)}₂O] (3.0 mmol) in 80 mL of absolute ethanol were refluxed for 4 h. The mixture was allowed to cool to room temperature. Then the mixture was filtered off, washed with ethanol and dried in vacuum. Elemental analysis, magnetic and physical properties of the synthesized complexes are given in Table 1.

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