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A novel Schiff base bearing dopamine groups with tripodal structure. Synthesis and its salen/salophen-bridged Fe/Cr(III) capped complexes

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HIGHLIGHTS

- ▶ A novel Schiff base bearing dopamine groups with tripodal structure have been synthesized.
- ▶ The Fe/Cr(III)-salen/salophen complexes of this Schiff base have been prepared.
- ▶ These complexes are the examples of trinuclear complexes.
- ▶ The magnetic data for the complexes show well agreement with the d^3 and d^5 metal ion in an octahedral structure.
- ▶ All of the complexes were characterized by means of magnetic susceptibility and other techniques.

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ABSTRACT

This work presents the synthesis of a novel Schiff base and its complexation properties with Fe(III) and Cr(III). A Schiff base bearing dopamine (TRDPA) was synthesized using dopamine hydrochloride and 1,3,5-tris (formylphenoxymethyl)benzene in methanol media. The prepared TRDPA was then reacted with four new trinuclear Fe(III) and Cr(III) complexes involving tetradenta Schiff bases N,N-bis(salicylidene)ethylenediamine-(salenH_2) or bis(salicylidene)-o-phenylenediamine-(salophenH_2). The structures of these compounds were characterized through ^1H NMR, ^{13}C NMR, FT-IR, thermal analysis (TG), elemental analysis, and magnetic susceptibility measurements. The complexes were also characterized as low-spin distorted octahedral Fe(III) and Cr(III) bridged by a catechol group.

1. Introduction

The investigation of metal organic complexes is one of the most active areas of material science and chemical research. Major advances have been made with these materials due to their interesting properties and potential uses various applications, e.g., electrical conductivity, magnetism, host–guest chemistry, ion exchange, catalysis, nonlinear optics, etc. [1–3]. Many recent investigations have aimed to synthesize new Schiff bases and their metal complexes.

Schiff base ligands are considered "privileged ligands" because they are easily prepared by a simple one-pot condensation of an aldehyde and primary amines. The Schiff base ligands with nitrogen, oxygen and sulfur donor atoms in their structures act as good chelating agents for transition and non-transition metal ions [4,5]. Transition metal complexes of Schiff bases are becoming increasingly important in the pharmaceutical, dye, and plastic industries as well as in liquid-crystal technology and mechanistic investigations of drugs used in pharmacology, biochemistry and physiology [6,7]. Schiff bases are a class of chelators capable of forming coordinate bonds with many metal ions through both azomethine and phenolic groups [8–11]. Condensation of salicylaldehyde 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 [12]. The bridged complexes of salen–salophen are especially attractive, according to recent studies in inorganic chemistry [13,14].

Tripodal ligands have also long been used in both coordination and bioinorganic chemistry [15,16]; typical examples include the tripodal ligands, tripyridylalkylamine, triazine, and polypyridylamine [17,18].

We report here that a tris aldehyde and its Schiff base derivative have been synthesized to become a new template. The reaction of

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trimeric 1,3,5-tris(bromomethyl)benzene ($C_9H_9Br_3$) with 3 equiv of 4-hydroxybenzaldehyde in acetonitrile media has given the desired tris aldehyde in a single step, coded as TRIPOD. Tris aldehyde [20,21] was then converted to a novel Schiff base (TRDPA) with dopamine. It may be useful to stress at this point that the new products mentioned above are the main results of this work.

2. Experimental

2.1. Materials and methods

All starting materials and reagents used were of standard analytical grade from Fluka, Merck, and Aldrich, and used without further purification. [{Fe(salen)$_2$}O], [{Fe(salophen)$_2$}O], [{Cr(salen)$_2$}O] and Cr(salophen)$_2$}O] were prepared according to previously published methods [22,23]. Melting points were measured using a Buchi B-540 melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Varian 400 MHz spectrometer in $CDCl_3$. Thermal analysis (TG) was carried out with a Seteram thermogravimetric analyzer. The sample weight was 15–17 mg. Analysis was performed from room temperature to 900 °C at a heating rate of 10 °C/min in an argon atmosphere with a gas flow rate of 20 mL/min. Elemental analyses of the ligand and its complexes were carried out on a Hewlett-Packard 185 analyzer. FT-IR spectra were recorded using a Perkin Elmer Spectrum 100. Magnetic susceptibilities of metal complexes were determined using a Sheerwood Scientific MX Gouy magnetic susceptibility apparatus, and carried out using the Gouy method with Hg[Co(SCN)$_4$] as a calibrant. The effective magnetic moments, μ_{eff}, per metal atom was calculated from the expression: $\mu_{eff} = 2.84.(\chi_M)^{1/2}$, where χ_M is the molar susceptibility.

2.2. Synthesis

1,3,5-Tris(formylphenoxymethyl)benzene (**1**,TRIPOD) as starting material was obtained from the reaction of trimeric 1,3,5-tris(bromomethyl)benzene ($C_9H_9Br_3$) with 3 equiv of 4-hydroxybenzaldehyde, in our previous study [19]. For compound **1**, ^{1}H NMR ($CDCl_3$): $\delta = 5.20$ (s, 6H, Ar—CH$_2$—O), 7.07 (d, 6H, Ar—H, $J = 8.8$ Hz), 7.50 (s, 3H, Ar—H), 7.84 (d, 6H, Ar—H, $J = 8.8$ Hz), and 9.89 (s, 3H, CHO).

2.2.1. Schiff base containing dopamine (2, TRDPA)

The suspension of 1,3,5-Tris(formylphenoxymethyl)benzene (TRIPOD) (0.48 g, 1 mmol) and K_2CO_3 (1.55 g, 9 mmol) in methanol (20 mL) was refluxed for 1 h. Next, a solution of dopamine hydrochloride (0.59 g, 3.1 mmol) in methanol (30 mL) and a catalytic amount of triethylamine were added dropwise to the above solution. The mixture was refluxed for 36 h. The reaction mixture was then allowed to cool to room temperature, and filtered. The precipitate was washed with cool ethanol. Yield: 80%, FT-IR (KBr): 1665 cm^{-1} (C═N), 3373 cm^{-1} (OH), ^{1}H NMR (DMSO): δ 2.80 (m, 6H, C*H$_2$*CHN), 3.00 (m, 6H, PhC*H$_2$*), 4.93 (s, 3H, ArOH), 5.11 (br s, 9H, CH$_2$O, ArOH), 6.00 (s, 3H, ArH), 6.48 (s, 3H, ArH), 6.92–7.01 (m, 9H, ArH), 7.15-7.18 (m, 6H, ArH), 7.50 (m, 6H, CHN, ArH). ^{13}C NMR (DMSO): δ 162.50, 155,68, 154,94, 144,21, 135,67, 131,27, 128,60, 126,89, 117.87, 115.92, 111.77, 110.54, 108.35, 73.22, 63.93, 42.50.

2.2.2. Preparation of [TRDPA-{Fe(III)(Salen/Salophen) (**3**,**4**)}] and [TRDPA-{Cr(III)(Salen/Salophen) (**5**,**6**)}] complexes

A solution of TRDPA (1.72 g, 2 mmol) and [{Fe/Cr(salen)}$_2$O] or [{Fe/Cr(salophen)}$_2$O] (3.1 mmol) in 80 mL of absolute ethanol was refluxed for 4 h. The mixture was allowed to cool to room temperature. The precipitate obtained was filtered and dried under vacuum. The elemental analysis results, magnetic and physical properties of the synthesized complexes are given in Table 1.

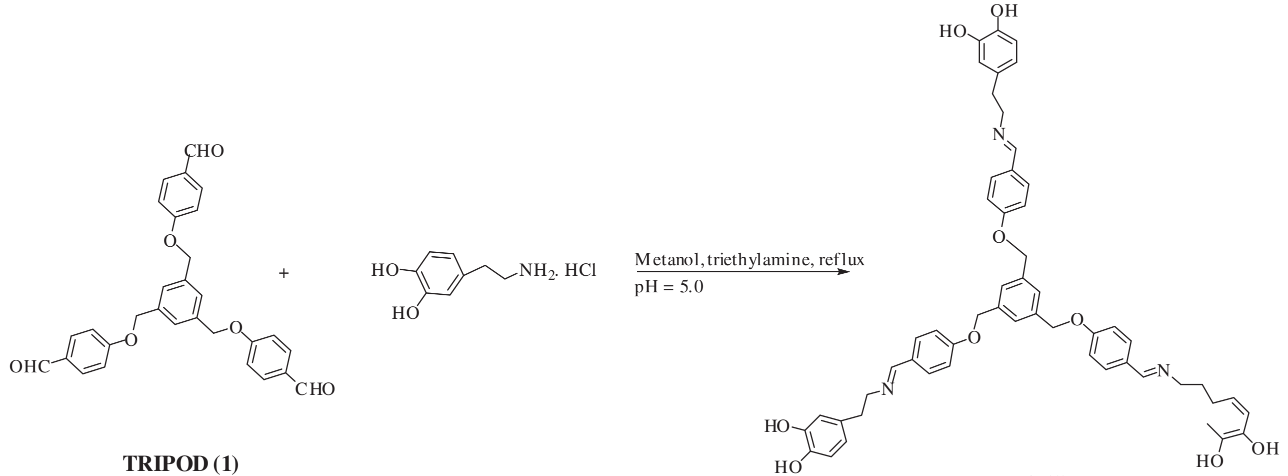
3. Results and discussion

We will describe the synthesis of a novel tripodal Schiff base bearing dopamine (TRDPA) and its complexation properties with [{Fe/Cr(salen)}$_2$O] and [{Fe/Cr(salophen)}$_2$O]. The synthesis of TRDPA depicted in Fig. 1 was carried out as follows: Firstly, TRIPOD (**1**) was synthesized using 1,3,5-trisbromomethylbenzene and 4-hydroxybenzaldehyde in the presence of K_2CO_3 according to the literature [19]. Then, the tripodal Schiff base (TRDPA, **2**) was synthesized using TRIPOD (**1**) and dopamine hydrochloride and a catalytic amount of triethylamine in methanol (Fig. 1). The synthesized compounds were characterized with ^{1}H NMR, ^{13}C NMR, FT-IR, and elemental analysis. The ^{1}H NMR spectra of TRDPA (**2**) is depicted in Fig. 2. As can be seen in Fig. 2, the synthesis of TRDPA (**2**) with new a Schiff base was confirmed by the disappearance of aldehyde protons (9.89 ppm) in TRIPOD and the appearance of the imine protons belong to a TRDPA compound (CH═N) at 7.50 ppm. TRDPA prepared in this way has been obtained in nearly quantitative yield and high purity. Synthetic strategy for preparing Tripodal–Trinuclear uses a complex as a “ligand” that contains a potential donor group capable of coordinating to another ligand. [{Fe(salen)}$_2$O] and [{Fe(salophen)}$_2$O] have been chosen as “ligand complex” because they can coordinate to another ligand [24]. These complexes are the first examples of tripodal–trinuclear complexes bridged by catechol groups to the iron and chromium centers (Figs. 3 and 4). All compounds are stable at room

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

Compound	Formula	Color	μ_{eff} (BM)	m.p (°C)	Yield (%)	Found (Calcd.) (%)			
						C	N	H	M
1	$C_{30}H_{24}O_{16}$	Cream	–	155	85	74.99 (74.95)	– –	5.03 (5.02)	– –
2	$C_{54}H_{51}N_3O_9$	Brown	–	205	80	73.31 (73.20)	4.82 (4.74)	5.89 (5.80)	– –
3	$C_{102}H_{90}N_9O_{15}Fe_3$	Red Brown	1.51	312[a]	70	66.70 (66.24)	6.99 (6.82)	5.12 (4.91)	9.29 (9.06)
4	$C_{102}H_{90}N_9O_{15}Cr_3$	Dark Green	3.62	310[a]	75	66.73 (66.66)	7.03 (6.86)	5.05 (4.94)	8.60 (8.49)
5	$C_{114}H_{90}N_9O_{15}Fe_3$	Brown	1.73	305[a]	65	68.82 (68.68)	6.47 (6.32)	4.69 (4.55)	8.60 (8.40)
6	$C_{114}H_{90}N_9O_{15}Cr_3$	Dark green	3.55	360[a]	75	69.23 (69.08)	6.51 (6.36)	4.72 (4.58)	8.15 (8.08)

[a] Decomposition.



TRIPOD (1)

TRDPA (2)

Fig. 1. Synthesis of a novel Schiff base containing dopamine (TRDPA).

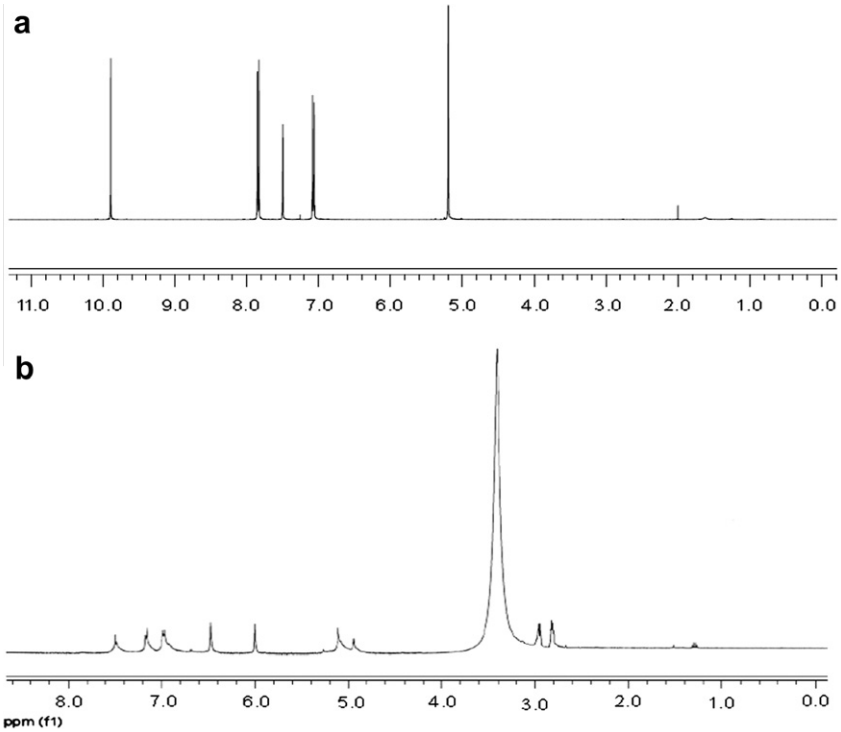


Fig. 2. The ^{1}H NMR spectra of TRIPOD (a) and TRDPA (b).

temperature in the solid state. The results of the elemental analyses presented in Table 1 are in a close agreement with the structures suggested for the ligand and its complexes. In addition, the prepared salen and salophen capped complexes were characterized through elemental analysis, thermal analysis, magnetic susceptibility and FT-IR techniques.

The magnetic moments of the complexes presented in Table 1 were measured at room temperature. On the basis of spectral evidence, the Fe(III) and Cr(III) complexes have trinuclear structures in which the Fe(III) and Cr(III) cations have an approximately octahedral structure. The magnetic behaviour of Fe(III) and Cr(III) complexes is in accord with proposed trinuclear structures. The magnetic moments of the trinuclear complexes indicate paramagnetic properties with magnetic susceptibility values per atom of 1.51, 1.73, 3.62 and 3.55 B.M., respectively. The [{Fe(salen)}$_2$O], [{Fe(salophen)}$_2$O], [{Cr(salen)}$_2$O] and [{Cr(salophen)}$_2$O] containing compounds appear to be represented by the electronic structures of $t_2g^5eg^0$ and $t_2g^3eg^0$. The magnetic data for the [{Fe(salen)}$_2$O], [{Fe(salophen)}$_2$O], [{Cr(salen)}$_2$O] and [{Cr(salophen)}$_2$O] tripodal complexes demonstrate strong agreement with the d^5 and d^3 metal ion in an octahedral structure. This finding is supported by the results of the elemental analyses also suggesting that these trinuclear complexes have an octahedral structure [19,22,23].

A FT-IR spectrum is one of the most suitable techniques to give enough information to elucidate the nature of bonding of the ligand to the metal ion. The FT-IR spectra of the free ligand and metal complexes were carried out in the range 4000–400 cm^{-1}. The characteristic FT-IR bands for compound **2** (TRDPA) and its Fe/Cr(III)-salen/salophen complexes (**3**, **4**, **5** and **6**) are given in Table 2.

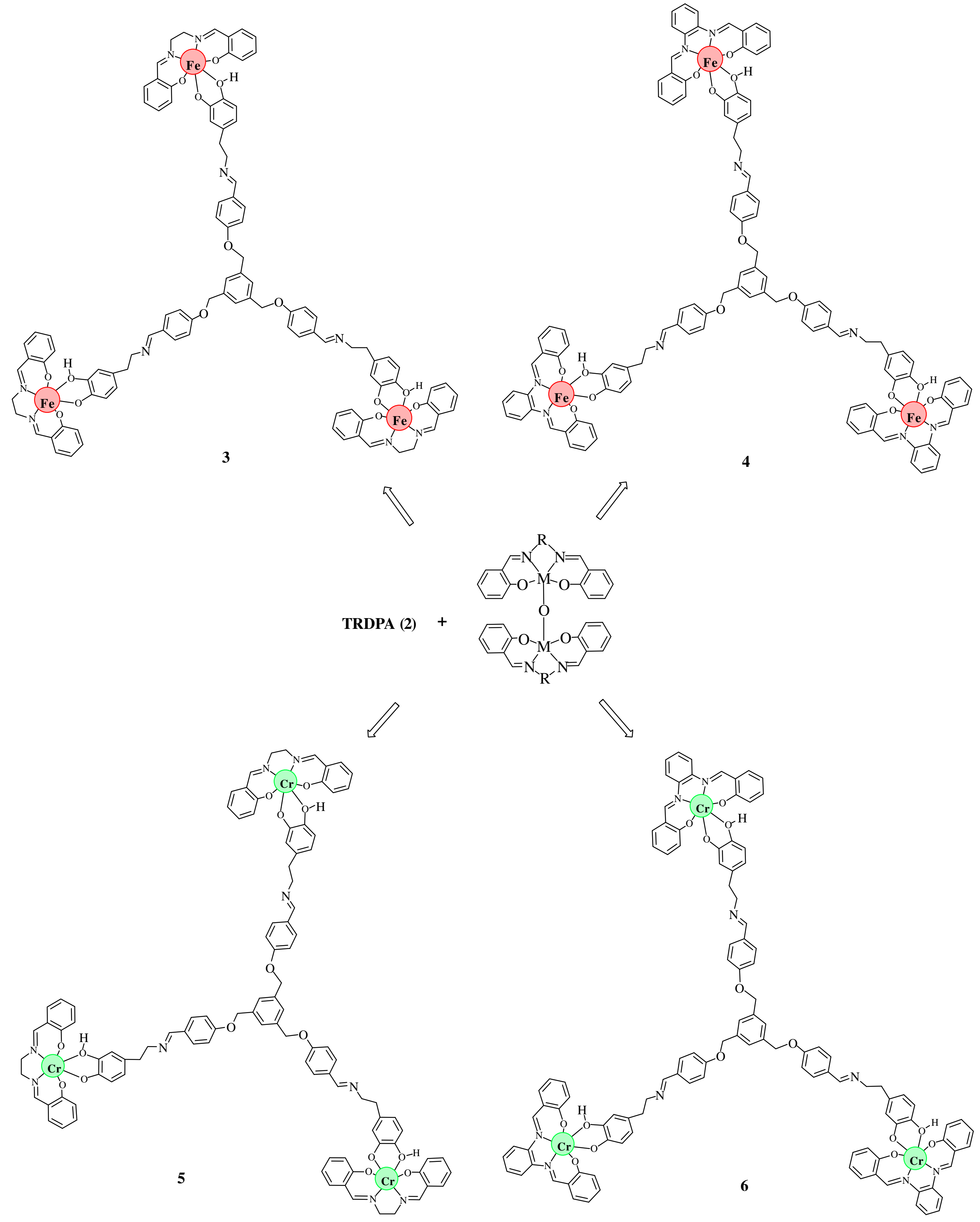


Fig. 3. Synthetic routes for complexation between TRDPA and Fe(III)–Cr(III).

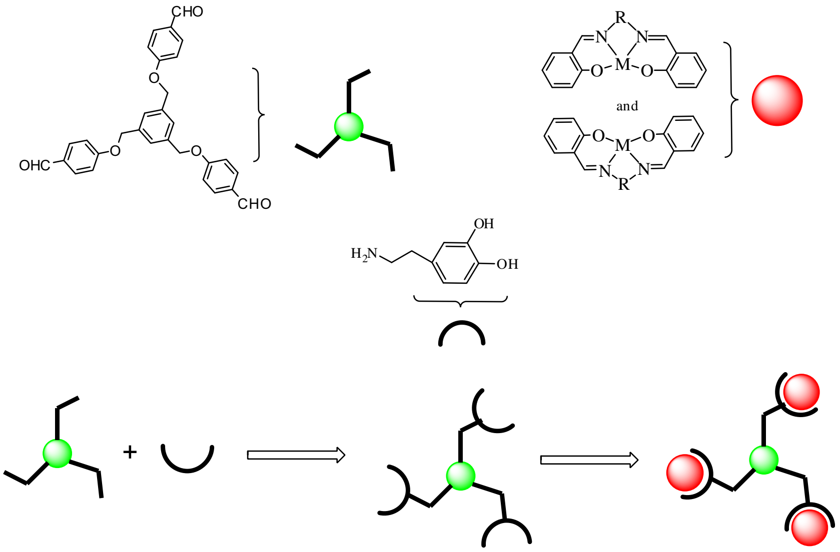


Fig. 4. Proposed models of Tripodal Oxy-Schiff base ligand and Tripodal–Trinuclear complexes.

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

Compounds	C=N	O—H	C—N	C—C_{ar}	C—H_{aliph}	C—O_{ph}
2	1665 *s*	3373 *b*	1125 *s*	1570 *m*	2936 *w*	1281 *s*
3	1655 *m*	3380 *b*	1129 *m*	1565 *m*	2928 *w*	1272 *m*
4	1648 *m*	3358 *b*	1108 *m*	1546 *m*	2924 *w*	1272 *m*
5	1668 *m*	3340 *b*	1121 *m*	1571 *m*	2930 *w*	1273 *m*
6	1661 *m*	3395 *b*	1101 *m*	1525 *m*	2933 *w*	1271 *m*

s, strong; *m*, medium; *w*, weak; *b*, broad.

For exemplary, the FT-IR spectra of **2** and complex **6** were also depicted in Fig. 5. The FT-IR spectra of the complexes have different absorption peaks, compared with that of the ligand. As can be seen in Table 2, the imine C=N and phenolic OH stretching vibrations for **2** were observed at 1665 and 3373 cm^{-1}, respectively. In the complexes, however, these bands are shifted to lower or higher frequencies, indicating that the nitrogen and oxygen atoms of compound **2** are coordinated to the ligand complexes [25]. The C=N bands in complexes **3**, **4**, **5** and **6** shift from 1665 to 1655, 1648, 1668, and 1661 cm^{-1}, respectively. The phenolic OH bands in complexes **3**, **4**, **5** and **6** also shift from 3373 to 3380, 3358, 3340, and 3395 cm^{-1}, respectively. Phenolic C—O stretching vibrations at 1272, 1272, 1273 and 1271 cm^{-1} have also been observed at the FT-IR spectra of **3**, **4**, **5** and **6**, respectively, whereas they had been observed at 1281 cm^{-1} for **2**. It has been interpreted that a downward shifts of 8–10 cm^{-1} for phenolic C—O stretching vibration in the complexes indicates coordination through the oxygen atoms. In the FT-IR analysis of the complexes (**3**, **4**, **5** and **6**), the bands in the 554–535 and 467–475 cm^{-1} range can be attributed to the M—N and M—O stretching modes [5].

The thermal stability of prepared complex **4** was evaluated by thermal gravimetric analysis (TG) and recorded in an argon atmosphere from 40 °C to 900 °C. It was found that complex **4** undergoes a four-step thermal degradation (Fig. 6). The first step (40–150 °C) is due to the loss of moisture. The decompositions within the 250–575 °C and 575–750 °C temperature ranges are due to the loss of coordinated water, N_2, C_2H_4, salen groups, and C_6H_6 from the main structure. Although the total weight lost was

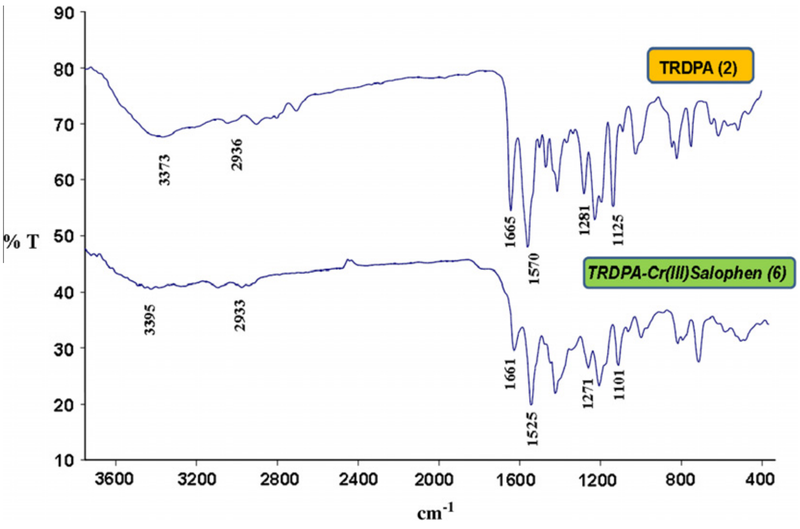


Fig. 5. FT-IR spectra of TRDPA (**2**) and TRDPA-Cr(III)/Salophen (**6**).

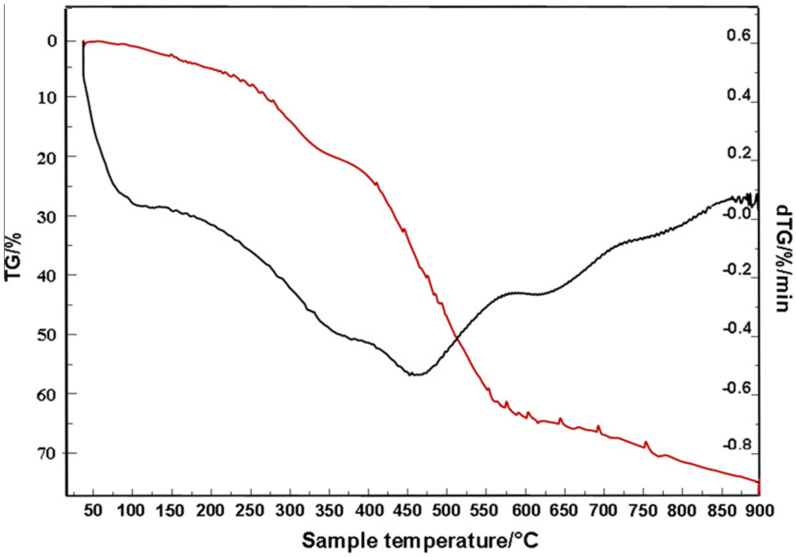


Fig. 6. TG and dTG curve of complex 4.

theoretically calculated to be 73.71%, it was observed experimentally to be 75.55%.

4. Conclusion

In the present study, a new Tripodal Oxy-Schiff base containing dopamine was synthesized and its complexes were prepared. Synthetic strategy for preparing Tripodal–Trinuclear uses a complex as a "ligand" that contains a potential donor group capable of coordinating to the other ligand. We have chosen [{Fe(salen/salophen)}$_2$-O] and [{Cr(salen/salophen)}$_2$O] as "ligand complexes" because they can coordinate to the other ligands. The prepared complexes are examples of tripodal–trinuclear complexes bridged by catechol groups to the iron and chromium centers. Their structures were characterized by means of elemental analysis, ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopy, thermal analyses, and magnetic susceptibility measurements. The magnetic data for the tripodal–trinuclear complexes show strong agreement with the d^5 and d^3 metal ions in an octahedral structure.

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