

Synthesis of 1,3,5-tris(4-(4-nitrophenyliminomethyl)phenoxy)methyl)benzene as a new Schiff base and its complexation properties with the (salen and salophen)-bridged Fe/Cr(III)

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Abstract In the present study, we discussed to synthesis of a new Schiff base with nitro groups and its complexation properties with Fe/Cr(III) salen/salophen capped complexes. For this, 1,3,5-tris (formylphenoxy)methyl)benzene (**1**, TRIPOD) involving aldehyde groups was converted to the Schiff base derivative (**2**, TNPIM-TRIPOD) using 4-nitroaniline. The synthesized compound **2** were reacted with four new trinuclear Fe(III) and Cr(III) complexes involving tetradenta Schiff bases *N,N*-bis(salicylidene) ethylenediamine-(salenH₂) or bis(salicylidene)-*o*-phenylenediamine-(salophenH₂). Characterization of all compounds was made with elemental analysis, infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), nuclear magnetic resonance (¹H-NMR), and magnetic susceptibility measurement. The complexes can also be characterized as low-spin distorted octahedral Fe(III) and Cr(III) bridged by nitro groups.

Keywords Synthesis · Trisaldehyde · Schiff base · 4-Nitroaniline

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, non-linear optics, etc. [1–3]. Synthesis of new Schiff bases and their metal complexes still the aim of many recent investigations.

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] and transfer of an amino group [6], photochromic properties [7], and complexing ability towards toxic metals [8].

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). Schiff base complexes of either salen or salophen type ligands with transition and main groups metal ions have been attracting increasing attention because of their importance in different fields, such as catalysis and material chemistry. The bridged complexes of salen–salophen are especially attractive by latest studies in inorganic chemistry [9–11]. The role of the metal center in determining the characteristics of these complexes is manifold. For example, it has been shown that catalytic and fluorescent properties of complexes are strictly related to the coordinated metal [12–15].

Salen/salophen ligands can be used to achieve this coordination number for soluble, stable, and higher-coordinate main group compounds [16]. For example, some five-coordinate compounds of aluminum [17–21], gallium [22, 23], indium [24] have been reported. Some of these can act as precursors to six-coordinate cations [25, 26]. Beyond their fundamental interest and novelty, these high

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coordinate Salen-main group compounds are finding applications in catalysis [27–30]. For example, the asymmetric addition of diorgano-H-phosphonates to carbonyls (the phospho-aldol reaction) has been found to be catalyzed by chiral complexes of aluminum containing the salycen ligand framework, [(R,R)-Salcyen]AlX (X^{1/4}Me, OSi-Me₂tBu) [31].

Tripodal ligands have long been used in both coordination and organometallic chemistry [32, 33]. Tripodal ligands have also long been used in both coordination and bioinorganic chemistry; typical examples include the tripodal ligands, tripyridylalkylamine, triazine and polypyridylamine [34–36].

The aim of the present study is to synthesis of new Tripodal-Trinuclear systems formed by the 1,3,5-tri nitro bridges and to present their effects on magnetic behaviour of Fe/Cr(III) salen/salophen capped complexes.

Experimental

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(salen)₂}O], [{Fe(salophen)₂}O], [{Cr(salen)₂}O] and [{Cr(salophen)₂}O] were prepared according to previously published methods [37, 38]. 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 (TGA) 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.

Synthesis

1,3,5-Tris(formylphenoxyethyl)benzene (1,TRIPOD) used in this study was synthesized in previously our study [39].

1,3,5-Tris(4-(4-nitrophenyliminomethyl)phenoxyethyl)benzene (2, TNPIM-TRIPOD)

The solution of 1,3,5-Tris(formylphenoxyethyl)benzene (1.0 mmol, 0.48 g) in methanol was added drop by drop upon the solution of 4-aminonitrobenzene (3.0 mmol, 0.51 g) in 50 mL methanol. The mixture was refluxed 24 h. Then, the mixture was precipitated with 1.0 N HCl solution and the residue was filtered. The crude product was extracted with ethyl acetate/water mixture (1:1) (3 × 30 mL). The organic phase was separated and dried with Na₂SO₄. The solvent was removed in a rotary evaporator. The resulting solid was dried in 70 °C. For C₄₈H₃₆N₆O₉, Yield; 63%, FT-IR (KBr); 1,684 cm⁻¹ (C=N), ¹H-NMR (CDCl₃): δ = 5.20 (s, 6H, CH₂-O), 6.61 (d, 6H, Ar-H, *J* = 8.6 Hz), 7.21–7.24 (m, 6H, Ar-H), 7.83 (s, 3H, Ar-H), 7.85–7.89 (m, 6H, Ar-H), 8.06 (d, 6H, Ar-H, *J* = 8.6 Hz), 8.35 (s, 3H, CH=N).

Preparation of [TNPIM-TRIPOD-Fe(III)(salen/salophen)(3,4)] and [TNPIM-TRIPOD-Cr(III)(salen/salophen)(5,6)] complexes

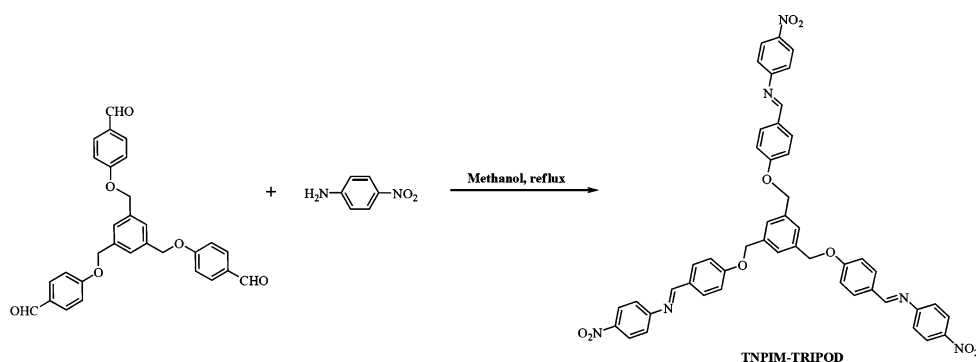
A solution of TNPIM-TRIPOD (0.84 g, 1 mmol) and [{Fe/Cr(salen)₂}O] (1.03 g, 1.5 mmol) or [{Fe/Cr(salophen)₂}O] (1.02 g, 1.5 mmol) in 20 mL of absolute ethanol were refluxed for 3 h. The mixture was allowed to cool to room temperature. Then the mixture was filtered and dried in vacuum. Elemental analysis, magnetic and physical properties of the synthesized complexes are given in Table 1. Molecule formulas of complex 3,4,5 and 6 are Fe₃C₁₀₂H₈₇N₁₂O₁₅Cl₃·3H₂O, Fe₃C₁₁₄H₈₇N₁₂O₁₅Cl₃·3H₂O, Cr₃C₁₀₂H₈₇N₁₂O₁₅Cl₃·3H₂O and Cr₃C₁₁₄H₈₇N₁₂O₁₅Cl₃·3H₂O respectively.

Results and discussion

The complexation with [{Fe/Cr(salen)₂}O] and [{Fe/Cr(salophen)₂}O] of TNPIM-TRIPOD ligand was observed in this manuscript. For this, we have synthesized to TRIPOD (1) using 1,3,5-trisbromomethylbenzene and 4-hydroxybenzaldehyde in presence of K₂CO₃ according to literature [10]. Then, the Tripodal Schiff base (TNPIM-TRIPOD, 2) was synthesized using TRIPOD (1) and 4-aminonitrobenzene in methanol media (Scheme 1). The synthesized compounds were characterized with ¹H-NMR, FT-IR and elemental analysis. The synthesis of TNPIM-TRIPOD (2) as new a Schiff base was confirmed by the disappearance of aldehyde protons (9.89 ppm) in TRIPOD and the appearance of imine protons (CH=N) at 8.35 ppm belong to

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

Compound	Colour	μ_{eff} (B.M.) 298 °C	M.p. (°C)	Yield (%)	Found (Calcd.) (%)			
					C	N	H	M
TRIPOD	Cream	–	155	85	74.99 (74.95)	–	5.03 (5.02)	–
TNPIM-TRIPOD	Yellow	–	100	63	68.56 (68.60)	9.99 (9.94)	4.32 (4.30)	–
[{Fe(salen)} ₃ (TNPIM-TRIPOD)] Cl ₃ ·3H ₂ O	Tile red	1.66	310	60	63.80 (63.76)	9.30 (9.27)	4.35 (4.32)	9.27 (6.58)
[{Cr(salen)} ₃ (TNPIM-TRIPOD)] Cl ₃ ·3H ₂ O	Light green	3.40	298	65	64.21 (64.16)	9.36 (9.37)	4.38 (4.32)	8.69 (8.62)
[{Fe(salophen)} ₃ (TNPIM-TRIPOD)]Cl ₃ ·3H ₂ O	Brick red	1.70	325	70	66.47 (66.39)	8.61 (8.64)	4.03 (4.00)	8.59 (8.55)
[{Cr(salophen)} ₃ (TNPIM-TRIPOD)]Cl ₃ ·3H ₂ O	Dark green	3.52	>400	65	66.87 (66.80)	8.66 (8.63)	4.05 (4.01)	8.04 (8.00)

Scheme 1 Synthesis of TNPIM-TRIPOD (2)

TNPIM-TRIPOD compound. The TNPIM-TRIPOD prepared in the way have 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. The [{Fe(salen)}₂O] and [{Fe(salophen)}₂O] as “ligand complex” have been chosen because it can coordinate to another ligand [40]. These complexes are the first examples of Tripodal-Trinuclear complexes bridged by nitro groups to the iron and chromium centers (Scheme 2). The complexation with ligand of salen or salophen complexes does not occur with CH=N-system, because CH=N region of ligand has steric hindrance for salen or salophen groups and six-coordination is more stable than five-coordination for Fe(III) and Cr(III) complexes. Therefore, salen or salophen groups prefers to complexation with nitro groups instead of CH=N-system. Prepared complexes are stable at room temperature in the solid state. The results of the elemental analyses presented in Table 1 are in a good agreement with the structures suggested for the ligand and their complexes. In addition, the prepared salen and salophen based capped complexes were characterized with elemental analysis, thermal gravimetric analysis, magnetic susceptibility and FT-IR.

The magnetic moments of the prepared all complexes were measured at room temperature (Table 1). On the basis

of spectral evidence, the Tripodal Fe(III) and Cr(III) complexes have trinuclear 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 trinuclear structures [41]. The magnetic moment per trinuclear complexes which were constructed from [{Fe(salen)}₂O], [{Fe(salophen)}₂O], [{Cr(salen)}₂O] and [{Cr(salophen)}₂O] either of 1,3,5-Tris(4-(4-nitrophenyliminomethyl)phenoxy)methyl benzene (TNPIM-TRIPOD) shows paramagnetic property with a magnetic susceptibility value per atom: 1.66–1.70 B.M. and 3.40–3.52 B.M., respectively. It is seen that the [{Fe(salen)}₂O], [{Fe(salophen)}₂O], [{Cr(salen)}₂O] and [{Cr(salophen)}₂O] 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 [{Fe(salen)}₂O], [{Fe(salophen)}₂O], [{Cr(salen)}₂O] and [{Cr(salophen)}₂O] tripodal complexes indicate good agreement with the d^5 and d^3 metal ion in an octahedral structure. This magnetic data are supported by the results of the elemental analyses suggesting that these Tripodal complexes have also an octahedral structure [37].

The FT-IR spectrums of the ligand and salen and salophen based capped complexes were presented in Figs. 1 and 2. The Fig. 1 shows TRIPOD, TNPIM-TRIPOD,

Scheme 2 Complexation between TNPIM-TRIPOD and Fe(III)–Cr(III) salen/salophen groups

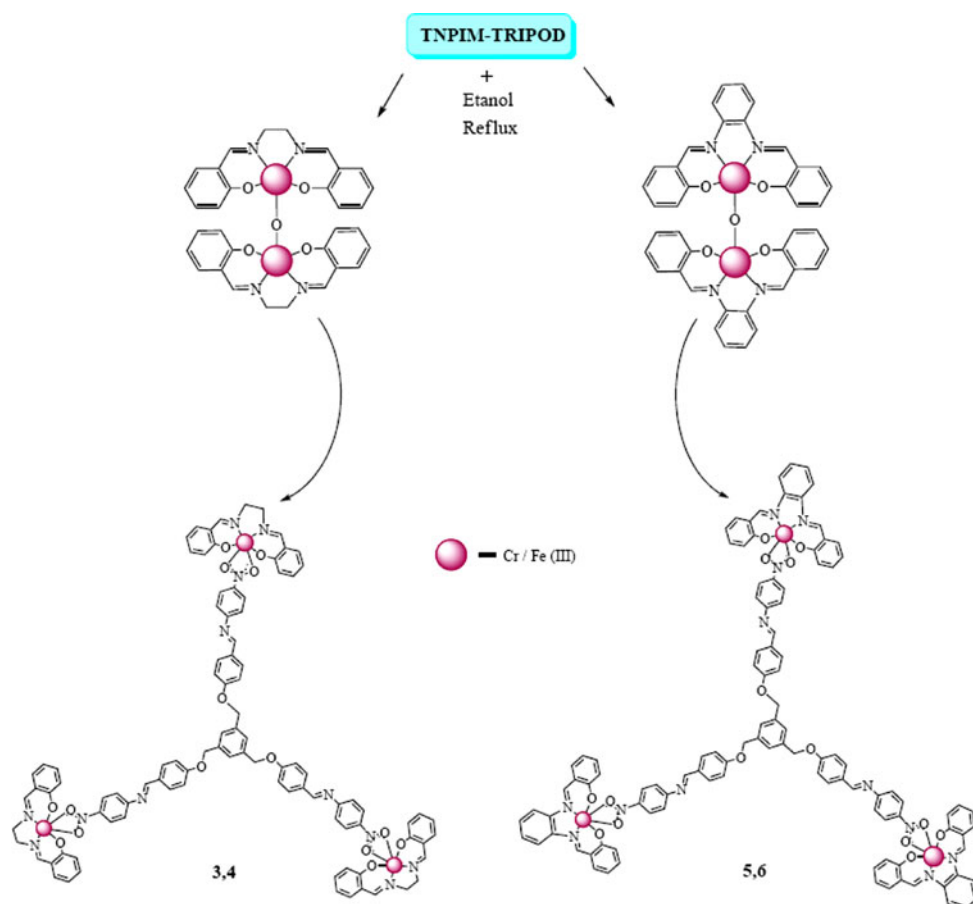
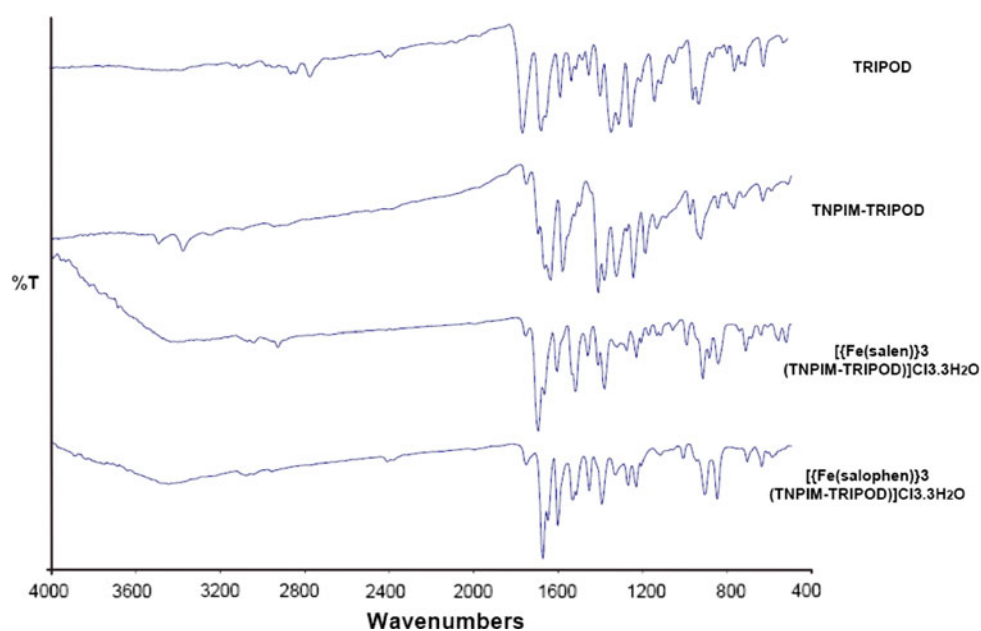


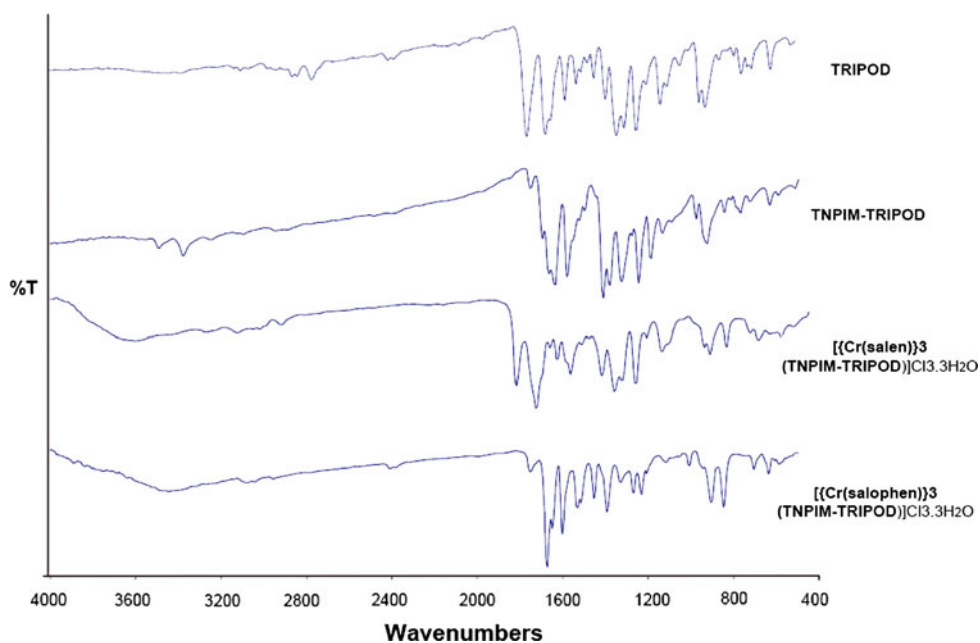
Fig. 1 The FT-IR spectra of TRIPOD, TNPIM-TRIPOD, $[\{\text{Fe}(\text{salen})\}_3(\text{TNPIM-TRIPOD})]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ and $[\{\text{Fe}(\text{salophen})\}_3(\text{TNPIM-TRIPOD})]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$



$[\{\text{Fe}(\text{salen})\}_3(\text{TNPIM-TRIPOD})]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ and $[\{\text{Fe}(\text{salophen})\}_3(\text{TNPIM-TRIPOD})]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$. The Fig. 2 shows TRIPOD, TCPIM-TRIPOD, $[\{\text{Cr}(\text{salen})\}_3(\text{TCPIM-TRIPOD})]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ and $[\{\text{Cr}(\text{salophen})\}_3(\text{TCPIM-TRIPOD})]$

$\text{Cl}_3 \cdot 3\text{H}_2\text{O}$. The vibrations of the aldehyde $\text{C}=\text{O}$ of TRIPOD, $\text{N}=\text{O}$ and imine $\text{C}=\text{N}$ of TNPIM-TRIPOD have been observed at 1707, 1570 and 1684 cm^{-1} respectively. In the complexes, although the $\text{C}=\text{N}$ bands shifted to higher

Fig. 2 The FT-IR spectra of TRIPOD, TNPIM-TRIPOD, $[\{\text{Cr}(\text{salen})\}_3(\text{TNPIM-TRIPOD})]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ and $[\{\text{Cr}(\text{salophen})\}_3(\text{TNPIM-TRIPOD})]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$



frequencies ($1,692\text{ cm}^{-1}$ for **3,4** and $1690, 1684\text{ cm}^{-1}$ for **5,6**), the N=O bands shifted to lower frequencies ($1538, 1539\text{ cm}^{-1}$ for **3,4** and $1514, 1540\text{ cm}^{-1}$ for **5,6**), and reduced intensity of these bands. These results indicate that the nitrogen and oxygen atoms of the Tripodal Schiff base ligands are coordinated to the ligand complexes [41]. In the Tripodal-Trinuclear complexes, the bands in the $540\text{--}550$ and $470\text{--}488\text{ cm}^{-1}$ range can be attributed to the M-N and M-O stretching modes.

The thermal stability of prepared some complexes ($[\{\text{Cr}(\text{salen})\}_3(\text{TNPIM-TRIPOD})]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$) and ($[\{\text{Fe}(\text{salophen})\}_3(\text{TNPIM-TRIPOD})]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$) was evaluated by thermal gravimetric analysis (TGA). It was found that $[\{\text{Cr}(\text{salen})\}_3(\text{TNPIM-TRIPOD})]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ undergoes a three-step thermal degradation (Fig. 3). At $50\text{--}350\text{ }^\circ\text{C}$, decomposition is due to the loss of crystal water and NO_2 from main structure. Also, the C_6H_6 , C_2H_4 , CN and CO groups leaves from structure at $350\text{--}700\text{ }^\circ\text{C}$. Although the

Fig. 3 TG and its 1st derivatives (dTG) of $[\{\text{Cr}(\text{salen})\}_3(\text{TNPIM-TRIPOD})]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$

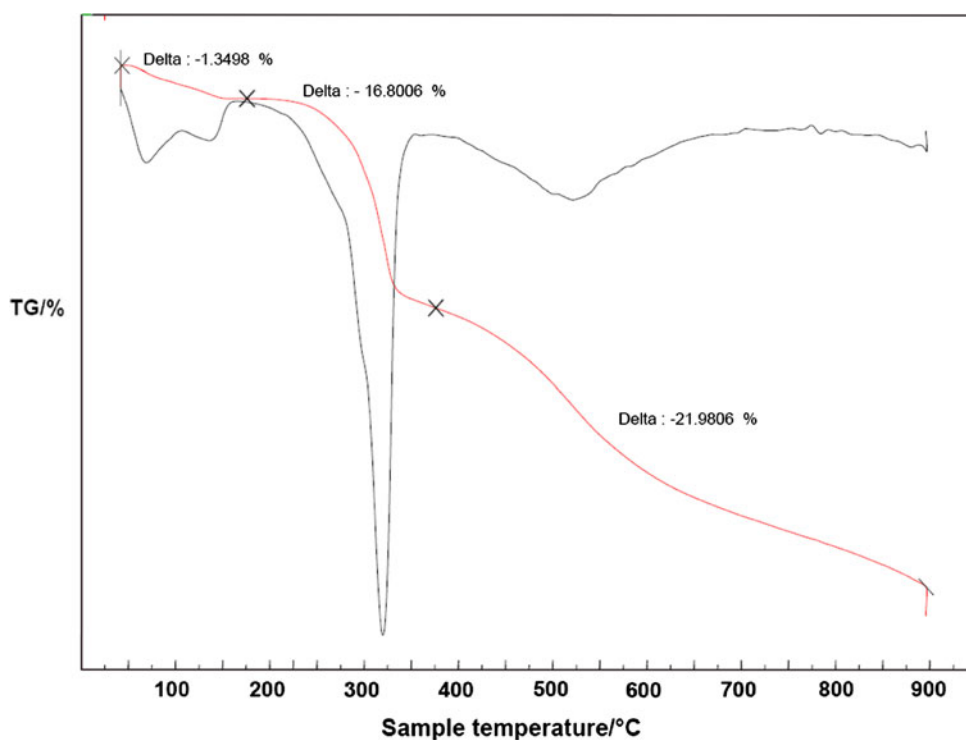
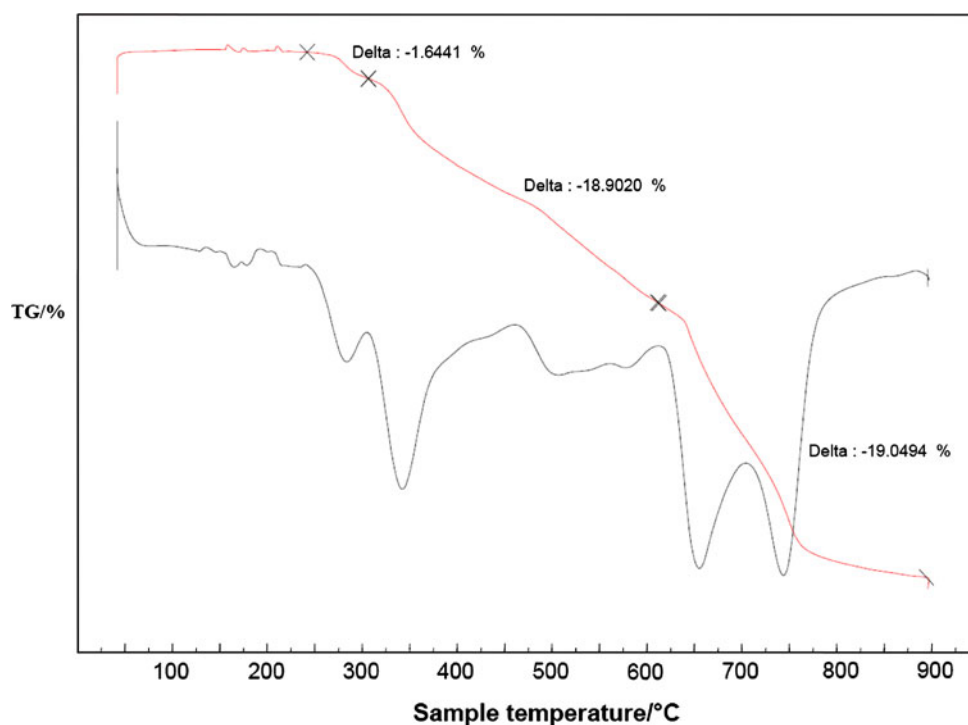


Fig. 4 TG and its 1st derivatives (dTG) of $[\{\text{Fe}(\text{salophen})\}_3(\text{TNPIM-TRIPOD})]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$



total weigh lost was theoretically calculated to be 36.05%, it was observed experimentally to be 40.15%. Besides, Fig. 4 shows thermal stability of $[\{\text{Fe}(\text{salophen})\}_3(\text{TNPIM-TRIPOD})]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex. At 50–300 °C, leaves crystal water and NO_2 from main structure. At the other a step (300–605 °C), C_6H_6 and CN left from the residue structure. As finally step, at 605–800 °C, leaves C_6H_6 , C_2H_4 and CO groups. For this complex, although the total weigh lost was theoretically calculated to be 34.97%, it was observed experimentally to be 39.60%.

Conclusion

We synthesized the 1,3,5-Tris(4-(4-nitrophenyliminoethyl)phenoxy)methyl)benzene as novel a Tripodal Schiff base and prepared its Fe/Cr(III) salen/salophen complexes in this study. These complexes are the examples of Tripodal-Trinuclear complexes bridged by nitro group to the iron and chromium centers. Their structures were characterized by means of elemental analysis, $^1\text{H-NMR}$, FT-IR spectroscopy, thermal analyses and magnetic susceptibility measurements. The magnetic data for Tripodal-Trinuclear complexes show well agreement with the d^5 and d^3 metal ion in an octahedral structure.

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References

- Gatteschi, D., Kahn, O., Miller, J. (eds.): *Molecular Magnetic Materials*, Nato ASI Series E198. Kluwer, Dordrecht, The Netherlands (1991)
- Yaghi, O.M., Li, G., Li, H.: Selective binding and removal of guests in microporous metal-organic framework. *Nature*. **378**(6558), 703–706 (1995)
- Chen, C.T., Suslick, K.S.: One-dimensional coordination polymers-applications to material science. *Coord. Chem. Rev.* **128**(1–2), 293–322 (1993)
- Jones, R.D., Summerville, D.A., Basolo, F.: Synthetic oxygen carriers related to biological systems. *Chem. Rev.* **79**(2), 139–179 (1979)
- Henrici-Olive, G., Olive, S.: *The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide*, p. 152. Springer, Berlin (1984)
- Dugas, H., Penney, V.: *Bioorganic Chemistry*. Springer, New York (1981)
- Margerum, J.D., Miller, L.J.: *Photochromism*. Interscience, Wiley, New York (1971)
- Sawodny, W.J., Riederer, M.: Addition compounds with polymeric chromium(II)–Schiff base complexes. *Angew. Chem. Int. Ed. Engl.* **16**(12), 859–860 (1977)
- Koc, Z.E., Ucan, H.I.: Complexes of iron(III) and chrom(III) salen and salophen Schiff bases with bridging 2, 4, 6-tris(4-nitrophenylimino-4'-formylphenoxy)-1, 3, 5 triazine. *J. Macromol. Sci. Part A Pure Appl. Chem.* **45**, 1072–1077 (2008)
- Silva, A.R., Freire, C., Castro, B.: Modulation of the catalytic activity of manganese (III) salen complexes in the epoxidation of styrene: influence of the oxygen source. *New J. Chem.* **28**, 253–260 (2004)
- Wang, S.H., Li, Y.T., Yan, C.W.: Synthesis, characterization and antiferromagnetic interaction in oxalato-bridged chromium(III)–chromium(III) binuclear complexes. *Pol. J. Chem.* **80**, 865–872 (2006)

12. Sabater, M.J., Alvaro, M., Garcia, H., Palomares, E., Scaiano, J.C.: Laser flash photolysis study of Jacobsen catalyst and related manganese(III) salen complexes. Relevance to catalysis. *J. Am. Chem. Soc.* **123**, 7074–7080 (2001)
13. Canali, L., Sherrington, D.C.: Utilisation of homogeneous and supported chiral metal(salen) complexes in asymmetric catalysis. *Chem. Soc. Rev.* **28**, 85–93 (1999)
14. Cozzi, P.G., Dolci, L.S., Garelli, A., Montalti, M., Prodi, L., Zaccheroni, N.: Photophysical properties of Schiff-base metal complexes. *New J. Chem.* **27**, 692–697 (2003)
15. Briggs, M.S.J., Fossey, J.S., Richards, C.J., Scott, B., Whateley, J.: Towards novel biolabels: synthesis of a tagged highly fluorescent Schiff-base aluminium complex. *Tetrahedron Lett.* **43**, 5169–5171 (2002)
16. Harvey, M.J., Atwood, D.A.: Group 13 compounds incorporating salen ligands. *Chem. Rev.* **101**, 37–52 (2001)
17. Dzugan, S.J., Goedken, V.L.: Factors affecting Al–C bond reactivity of tetradentate Schiff-base organoaluminum complexes. *Inorg. Chem.* **25**, 2858–2864 (1986)
18. Leung, W.H., Chan, E.Y.Y., Chow, E.K.F., Williams, I.D., Peng, S.M.: Metal complexes of a chiral quadridentate Schiff base. *J. Chem. Soc., Dalton Trans.* **7**, 1229–1236 (1996)
19. Rutherford, D., Atwood, D.: Five-coordinate aluminum amides. *Organometallics*, **15**, 4417–4422 (1996)
20. Gurian, P.L., Cheatham, L.K., Ziller, J.W., Barron, A.R.: Aluminum complexes of *N,N'* ethylenebis (salicylideneimine). *J. Chem. Soc., Dalton Trans.* **6**, 1449–1456 (1991)
21. Atwood, D.A., Hill, M.S., Jegier, J.A., Rutherford, D.: The use of five-coordinate aluminum alkyls to prepare molecules containing a single Al–O–Si linkage. *Organometallics*, **16**, 2659–2664 (1997)
22. Chong, K.S., Rettig, S.J., Storr, A., Trotter, J.: *N, N*-ethylenebis(salicylideneimine) derivatives of gallium trimethyl: crystal and molecular structure of *N, N*-ethylenebis(salicylideneiminato) bis(dimethylgallium). *Can. J. Chem.* **55**, 2540–2546 (1977)
23. Hill, M.S., Atwood, D.A.: Formation and reactivity of five-coordinate gallium supported by salen ligands. *Eur. J. Inorg. Chem.* **1**, 67–72 (1998)
24. Atwood, D.A., Jegier, J.A., Rutherford, D.: The first structurally characterized salen-indium complexes. *Bull. Chem. Soc. Jpn.* **70**, 2093–2100 (1997)
25. Davidson, M.G., Lambert, C., Lopez-Solera, I., Raithby, P.R., Snaith, R.: Aggregation of metalated organics by hydrogen-bonding—synthesis and crystal-structures of 2-aminophenoxy-aluminum and salen-aluminum ligand-separated ion-pairs. *Inorg. Chem.* **34**, 3765–3779 (1995)
26. Atwood, D.A., Jegier, J.A., Rutherford, D.: A new class of aluminum cations based upon tetradentate (N₂O₂) chelating ligands. *Inorg. Chem.* **35**, 63–70 (1996)
27. Munoz-Hernandez, M.-A., Keizer, T.S., Yearwood, B., Atwood, D.A.: Six-coordinate aluminium cations: characterization, catalysis, and theory. *J. Chem. Soc. Dalton Trans.* **3**, 410–414 (2002)
28. Ovitt, R.M., Coates, G.W.: Stereoselective ring-opening polymerization of meso-lactide: synthesis of syndiotactic poly(lactic acid). *J. Am. Chem. Soc.* **121**, 4072–4073 (1999)
29. Radano, P.C., Baker, G.L., Smith, M.R.: Stereoselective polymerization of a racemic monomer with a racemic catalyst: direct preparation of the polylactic acid stereocomplex from racemic lactide. *J. Am. Chem. Soc.* **122**(7), 1552–1553 (2000)
30. Duxbury, J.P., Warne, J.N.D., Mushtaq, R., Ward, C., Thornton-Pett, M., Jiang, M., Greatrex, R., Kee, T.P.: Phospho-aldol catalysis via chiral Schiff base complexes of aluminum. *Organometallics* **19**, 4445–4457 (2000)
31. Wang, Y.Z., Bhandari, S., Parkin, S., Atwood, D.A.: Five-coordinate organoaluminum acetylides and crystal structure of the hydrosylate, [salophen(tBu)Al]₂O. *J. Organomet. Chem.* **689**, 759–765 (2004)
32. Etienne, M.: Hydridotris(pyrazolyl)borato complexes of the group 5 metals: inorganic and organometallic chemistry. *Coord. Chem. Rev.* **156**, 201–236 (1996)
33. Lisa, F.S., Withamb, L.M., Takeuchi, K.J.: Tris(2-pyridyl) tripod ligands. *Coord. Chem. Rev.* **174**, 5–32 (1998)
34. Schatz, M., Becker, M., Thaler, F., Hampe, F., Schindler, S., Jacobson, R.R., Tyeklar, Z., Murthy, N.N., Phalguni, G., Chen, Q., Zubieta, J., Karlin, K.D.: Copper(I) complexes, copper(I)/O₂ reactivity, and copper(II) complex adducts, with a series of tetradentate tripyridylalkylamine tripodal ligands. *Inorg. Chem.* **40**, 2312–2322 (2001)
35. Tahmassebi, D.C., Sasaki, T.: Synthesis of a new trialdehyde template for molecular imprinting. *J. Org. Chem.* **59**, 679 (1994)
36. Jitsukawa, K., Harataa, M., Ariia, H., Sakuraib, H., Masudaa, H.: SOD activities of the copper complexes with tripodal polypyridylamine ligands having a hydrogen bonding site. *Inorg. Chim. Acta* **324**, 108–116 (2001)
37. Kopel, P., Sindelar, Z., Klicka, R.: Complexes of iron(III) salen and salophen Schiff bases with bridging dicarboxylic and tricarboxylic acids. *Transit. Met. Chem.* **23**, 139–142 (1998)
38. Gembicky, M., Boca, R., Renz, F.: A heptanuclear Fe(II)–Fe(III)₆ system with twelve unpaired electrons. *Inorg. Chem. Commun.* **3**, 662–665 (2000)
39. Kocyigit, O., Guler, E.: The investigation of complexation properties and synthesis of the (salen and salophen)-bridged Fe/Cr(III) capped complexes of novel Schiff bases. *J. Incl. Phenom. Macrocycl. Chem.* (in press) (2009)
40. Dorfman, J.R., Girerd, J.J., Simhon, E.D., Stack, T.D.P., Holm, R.H.: Synthesis, structure, and electronic features of (.mu.-sulfido)bis[(*N, N'*-ethylenebis(salicylaldiminato))iron(III)], [Fe(salen)]₂S, containing the only authenticated example of the iron(III)–sulfur–iron(III) single bridge. *Inorg. Chem.* **23**, 4407–4412 (1984)
41. Dotson, D.L.: PhD. Dissertation, Virginia Polytechnic Institute and State University, Virginia (1996)