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ORIGINAL ARTICLE

The investigation of complexation properties and synthesis of the (salen and salophen)-bridged Fe/Cr(III) capped complexes of novel Schiff bases

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Abstract This article describes synthesis of novel Schiff base and its complexation properties with Fe(III) and Cr(III). Firstly 1,3,5-tris (formylphenoxymethyl)benzene (**1**, TRIPOD) with tris aldehyde groups were synthesized using the 1,3,5-trisbromomethylbenzene and 4-hydroxybezaldehyde. The compound **1** was converted to the Schiff base derivative (**2**, TCPIM-TRIPOD) with *p*-aminobenzoic acid. The prepared TCPIM-TRIPOD were 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$_2$) and characterized by means of elemental analysis carrying out infrared spectroscopy (IR), thermogravimetric analysis (TG), nuclear magnetic resonance (^{1}H-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. The tricarboxylic acids play a role as bridges for weak antiferromagnetic intramolecular exchange.

Keywords Complexation · Trisaldehyde · Schiff base · Trisbromomethylbenzene

Introduction

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 sulphur donor atoms in their structures act as good chelating agents for the transition and non-transition metal ions [1, 2]. 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 [3, 4]. Schiff bases a class of chelators capable of forming coordinate bonds with many of metal ions through both azomethine and phenolic groups [5–8]. 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). 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 [9]. The bridged complexes of salen–salophen are especially attractive by latest studies in inorganic chemistry [10–12].

Schiff bases of iron(III) have been known since 1938. The magnetochemical properties of the l-oxobridgedcomplexes [{Fe(salen)$_2$O] [(salenH$_2$ = *N*,*N*^{1}-bis(salicylidene) ethylene diamine)] and [{Fe(salophen)$_2$O] [(salophen H$_2$ = bis(salicylidene)-2-phenylenediamine)] and their X-ray studies have widely been presented in the literature [13–17]. Kessel and Hendrickson [18] have studied Schiff base complexes of iron(III) incorporating p-quinone bridges. The reactions of [{Fe(salen)$_2$O] with carboxylic acids have been given by Wollmann and Hendrickson [19]. They used trichloroacetic, trifluoroacetic, salicylic and picric acids, and characterized the prepared complexes as dimers of composition [Fe(salen)X]$_2$, where X is the monoanion of the appropriate acid. The complexes

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[{Fe(salen)$_2$L]and [{Fe(salophen)$_2$L] (where L = terephthalate, fumarate, oxalate and succinate dianion) have been prepared. The crystal and molecular structure of [{Fe(salen)$_2$ter] (H_2ter = terephthalic acid) have been reported [20]. Other complexes of composition [{Fe(salen)$_2$L] (where L = glutarate, adipate, pimelate, suberate and dithiooxamidedianion) were prepared by Smekal et al. [21]. Therefore, in this work, we have intended to make other 1,3,5-tricarboxylato bridges and to present their certain influences on the magnetic behaviour of the prepared complexes. We are also interested in Tripodal–Trinuclear systems formed by the 1,3,5-tricarboxylato bridges because no satisfactory work dealing with this bridge and associated data have appeared in the literature.

Tripodal ligands have long been used in both coordination and organometallic chemistry [22, 23]. Tripodal ligands have also long been used in both coordination and bioinorganic chemistry; typical examples include the tripodal ligands, tripyridylalkylamine, triazine and polypyridylamine [24–26].

We have reported here that a trialdehyde and its Schiff bases have been synthesized to become a new template. The reaction of trimeric 1,3,5-tris(bromomethyl)benzene ($C_9H_9Br_3$) with 3 equiv of 4-hydroxybenzaldehyde in acetonitrile has given the desired trialdehyde in a single step, coded to be TRIPOD. Trialdehyde [27, 28] was then converted to 1,3,5-Tris(4-(4-carboxyphenyliminomethyl) phenoxymethyl)benzene (TCPIM-TRIPOD) with 4-aminobenzoic acid. It may be useful to stress at this point that the new products mentioned above are the main result of this work.

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 [13, 29, 30]. Melting points were measured using a Buchi B-540 melting point apparatus. ^{1}H-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 15–17 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(formylphenoxymethyl)benzene (**1**,TRIPOD)*

1,3,5-trisbromomethylbenzene (0.35 g, 1.0 mmol), 4-hydroxybenzaldehyde (0.38 g, 3.2 mmol) and equivalent amount of K_2CO_3 were refluxed in 100 mL acetonitrile. Reaction was monitored with TLC. After the substrate was consumed, the reaction was terminated. Reaction mixture was filtered and organic phase was evaporated. The residue was solved with CH_2Cl_2 and extracted with 2.5 N NaOH (2 × 25 mL). Then the organic phase was seperated and dried with Na_2SO_4. The CH_2Cl_2 was removed in a rotary evaporator and dried in vacuo at 70 °C. Yield; 85%, FT-IR (KBr); 1,707 cm^{-1} (CHO), ^{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), 9.89 (s, 3H, CHO) (Fig. 1).

*1,3,5-Tris(4-(4-carboxyphenyliminomethyl)phenoxymethyl) benzene (**2**,TCPIM-TRIPOD)*

K_2CO_3 (9 mmol, 1.55 g) was added to a solution 4-aminobenzoic acid (3 mmol, 0.51 g) in 20 mL metanol and stirred. After then, the suspension of 1,3,5-Tris(formylphenoxymethyl)benzene (TRIPOD) (0.48 g, 1 mmol) in 20 methanol was added dropwise to above solution. The mixture was refluxed 36 h. The reaction solution was left stirring overnight. 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 pahase was seperated and dried with Na_2SO_4. The solvent was removed in a rotary evaporator. The resulting solid was dried in a vacuo and stored in a desiccator over $CaCl_2$. Yield; 60%, FT-IR (KBr); 1,700 cm^{-1} (C=O, COOH), 3,150 cm^{-1} (OH), ^{1}H-NMR (DMSO): $\delta = 5.26$ (s, 6H, CH_2–O), 6.52 (d, 6H, Ar–H, $J = 8.8$ Hz), 7.18 (d, 6H, Ar–H, $J = 8.8$), 7.54 (s, 3H, Ar–H), 7.59 (d, 6H, Ar–H, $J = 8.9$ Hz), 7.84 (d, 6H, Ar–H, $J = 8.6$), 8.53 (s, 3H, CH = N), 12.08 (s, broad, 3H, COOH) (Fig. 2), ^{13}C-NMR (DMSO): $\delta = 69.9$, 113.3, 115.9, 117.5, 130.4, 131.8, 132.4, 153.7, 163.8, 168.2, 180.3.

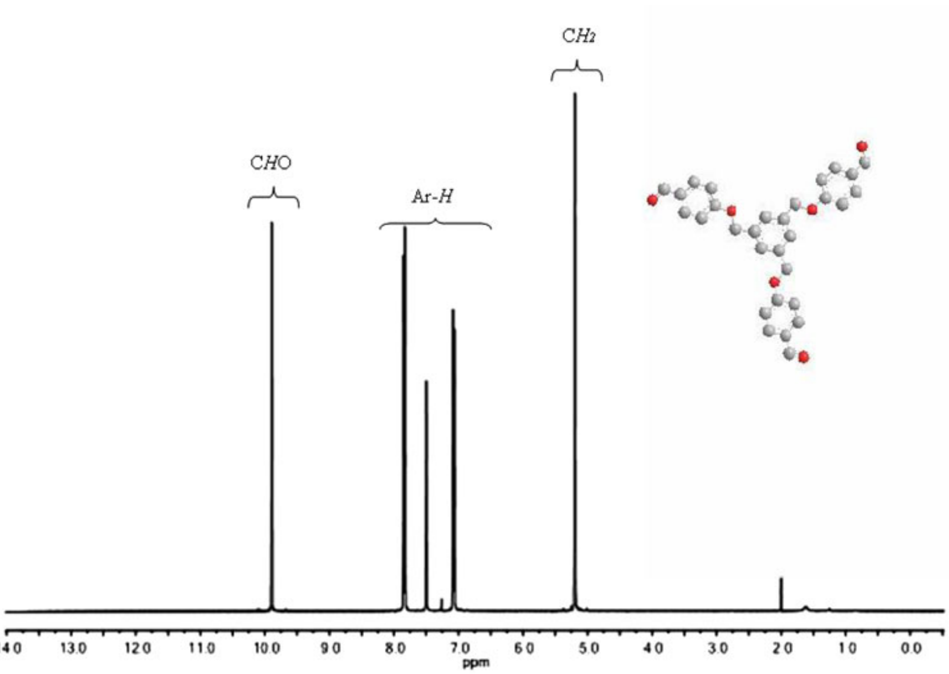


Fig. 1 ^{1}H-NMR spectrum of TRIPOD (**1**)

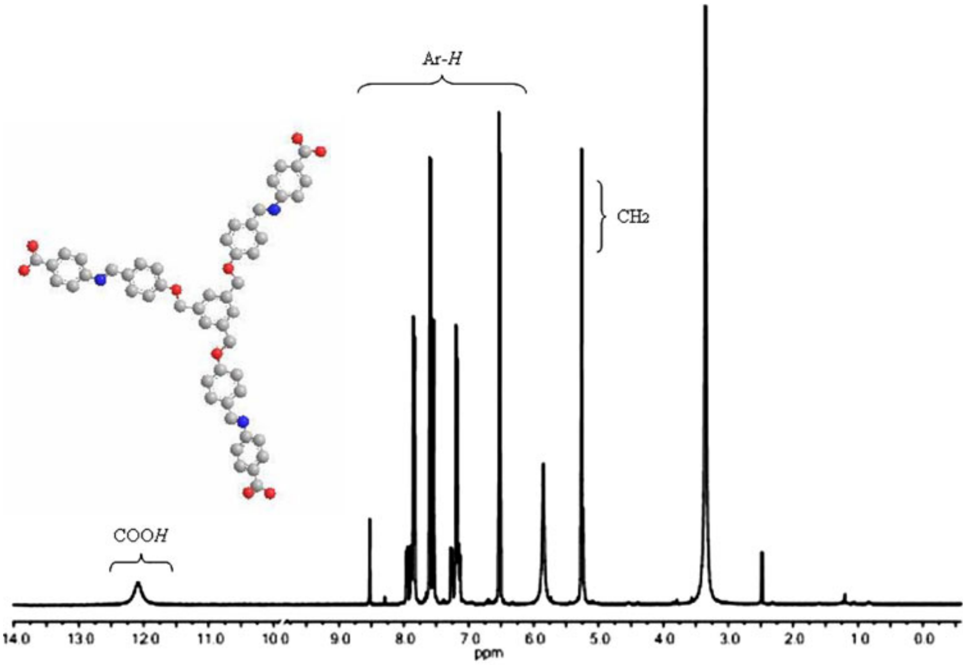


Fig. 2 ^{1}H-NMR spectrum of TCPIM-TRIPOD (**2**)

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

A solution of TCPIM-TRIPOD (1.72 g, 2 mmol) and [{Fe/Cr(salen)}$_2$O] (3.0 mmol) or [{Fe/Cr(salophen)}$_2$O] (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 and dried in vacuum. Elemental analysis, magnetic and physical properties of the synthesized complexes are given in Table 1.

Results and discussion

In order to evaluate the complexation with [{Fe/Cr(salen)}$_2$O] and [{Fe/Cr(salophen)}$_2$O] of TCPIM-TRIPOD ligand, Firstly, we have synthesized to TRIPOD (**1**) using

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

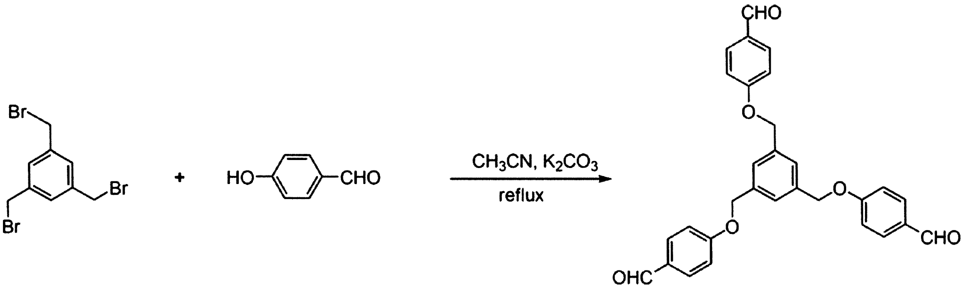
Compound	Colour	μ_{eff} (B.M.) 298 °C	M.p. (°C)	Yield (%)	Found (Calcd.) (%)			
					C	N	H	M
TRIPOD	Cream	–	155	85	74.99 (74.95)	–	5.03 (5.02)	–
TCPIM-TRIPOD	Light yellow	–	245	60	73.11 (73.07)	5.02 (5.04)	4.69 (4.65)	–
TCPIM-TRIPOD[(Salen)Fe]$_3$	Tile red	1.55	270	75	65.90 (65.86)	6.99 (6.96)	4.52 (4.48)	9.29 (6.58)
TCPIM-TRIPOD[(Salen)Cr]$_3$	Red-green	3.60	310[a]	70	66.33 (66.28)	7.03 (7.00)	4.55 (4.51)	8.70 (8.68)
TCPIM-TRIPOD[(Salophen)Fe]$_3$	Orange	1.78	305	65	68.42 (68.39)	6.47 (7.48)	4.19 (4.16)	8.60 (6.58)
TCPIM-TRIPOD[(Salophen)Cr]$_3$	Green	3.52	360[a]	75	68.83 (68.80)	6.51 (6.54)	4.22 (4.19)	8.05 (8.08)

[a] Decomposition

1,3,5-trisbromomethylbenzene and 4-hydroxybenzaldehyde in presence of K_2CO_3 (Scheme 1). After then, the TRIPOD was converted to Tripodal Schiff base (TCPIM-TRIPOD, **2**) with 4-aminobenzoic acid in methanol media (Scheme 2). These compounds were charecterized with ^{1}H-NMR, FT-IR and elemental analysis. Figures 1 and 2 show ^{1}H-NMR spectrums of TRIPOD and TCPIM-TRIPOD, respectively. The formation of TRIPOD was confirmed by the disappearance of the phenolic-*OH* in 4-hydroxybenzaldehyde and the appearance of the aldehyde protons at 9.89 ppm (Fig. 1). In addition, the synthesis of TCPIM-TRIPOD was confirmed by the disappearance of aldehyde protons (9.89 ppm) in TRIPOD and the appearance of imine protons (CH=N) at 8.53 ppm belong to TCPIM-TRIPOD compound (Fig. 2). The TCPIM-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 the another ligand (Fig. 3). We have chosen [{Fe(salen)}$_2$O] and [{Fe(salophen)}$_2$O] as "ligand complex" because it can coordinate to another ligand [15]. These complexes are the first examples of Tripodal–Trinuclear complexes bridged by carboxylate anions to the iron and chromium centres (Scheme 3, 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 salen and salophen based capped complexes were charecterized with elemental analysis, TGA, magnetic susceptibility and FT-IR. All complexes are also stable at room temperature.

The magnetic moments of the complexes presented in Table 1 were measured at room temperature. On the basis of

Scheme 1 Synthesis of TRIPOD (**1**)



Scheme 2 Synthesis of TCPIM-TRIPOD (**2**)

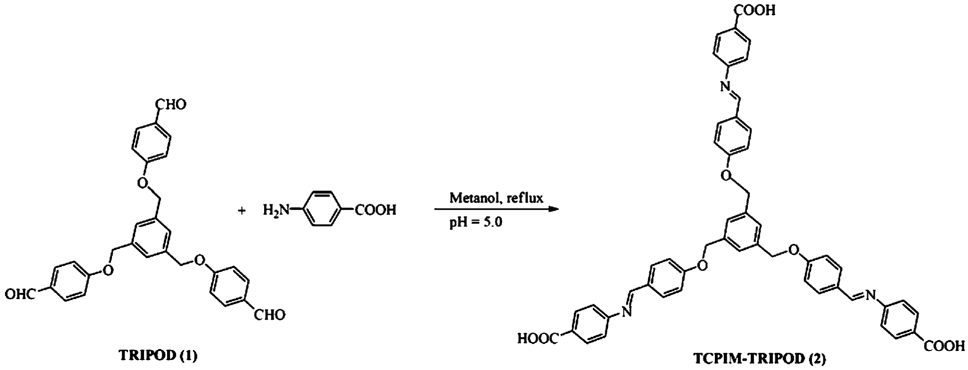
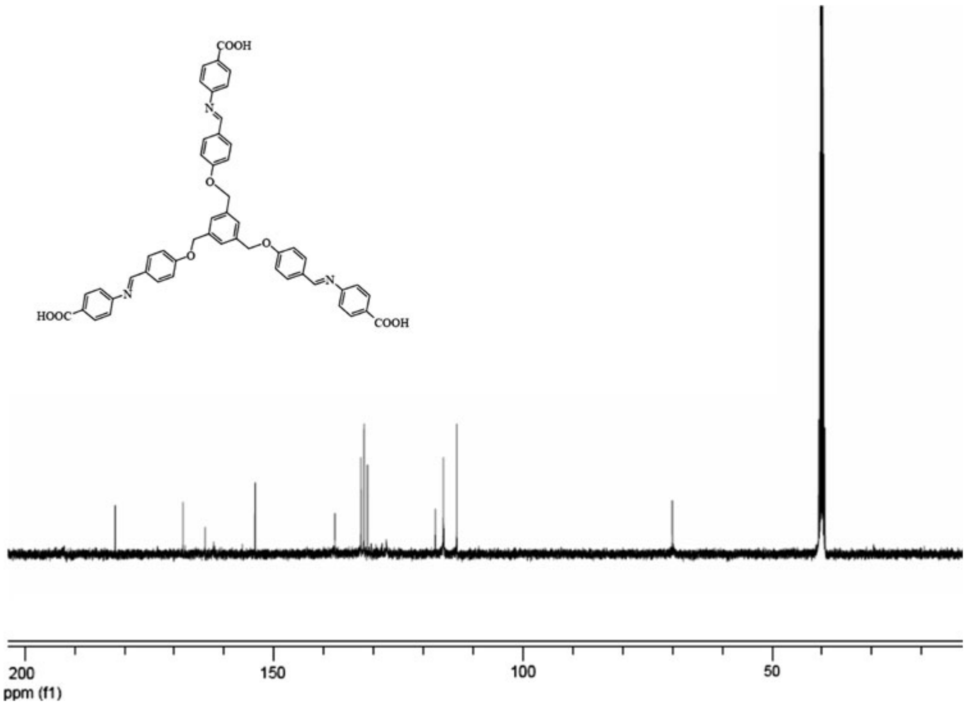


Fig. 3 ^{13}C-NMR spectrum of TCPIM-TRIPOD (2)



Scheme 3 Synthetic routes for complexation between TCPIM-TRIPOD and Fe(III)–Cr(III)

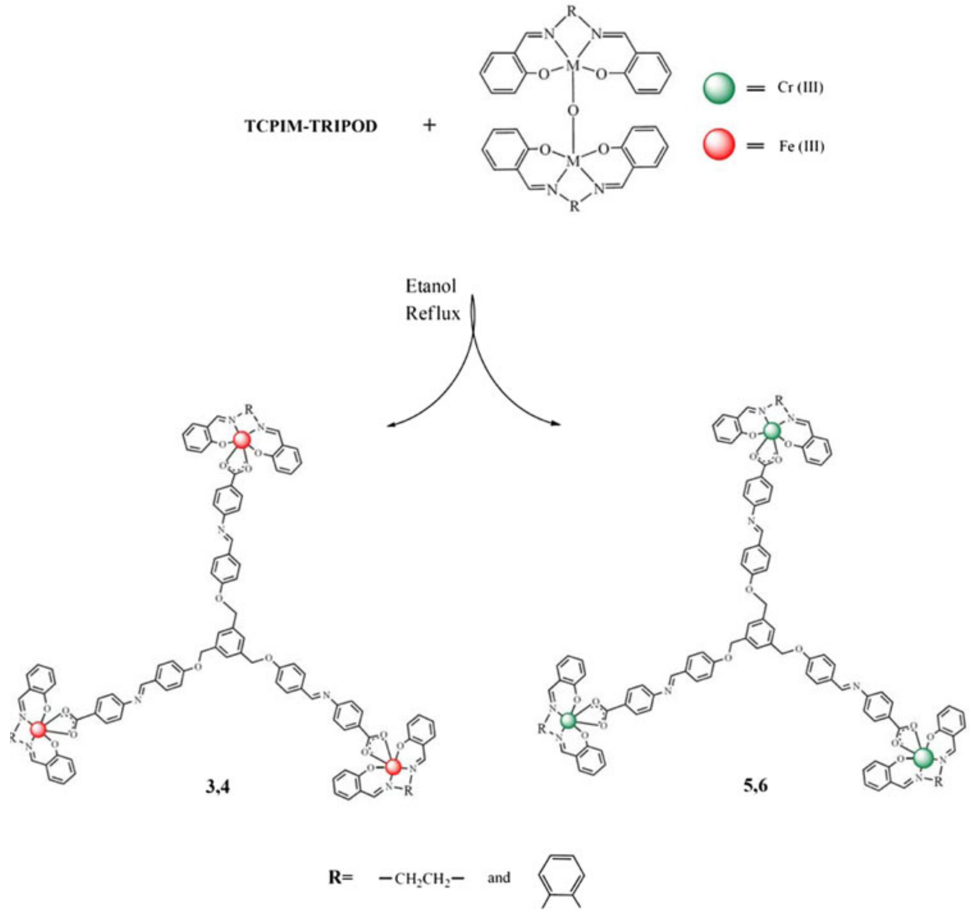
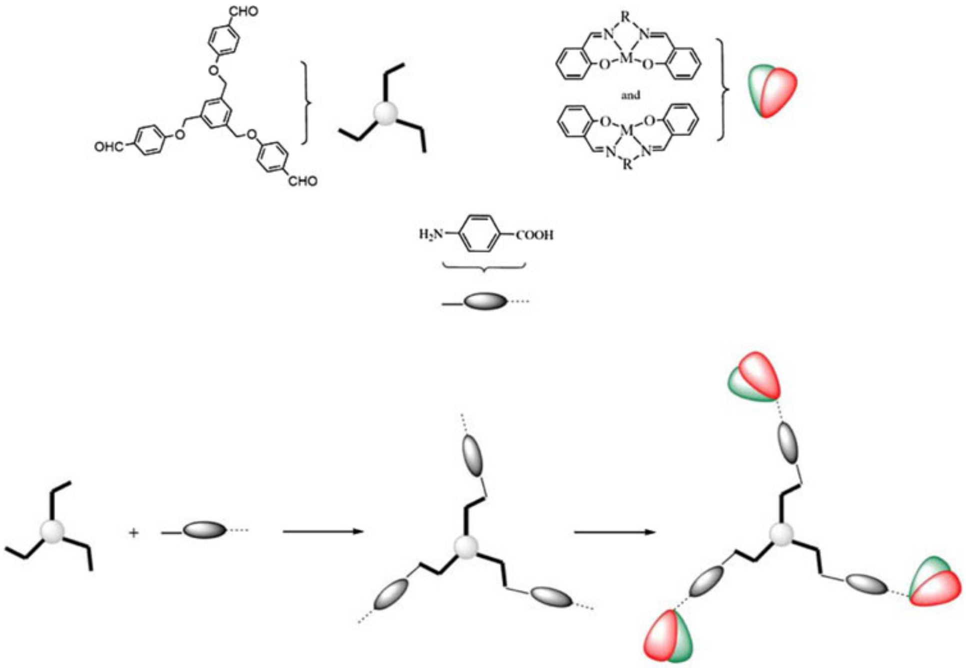
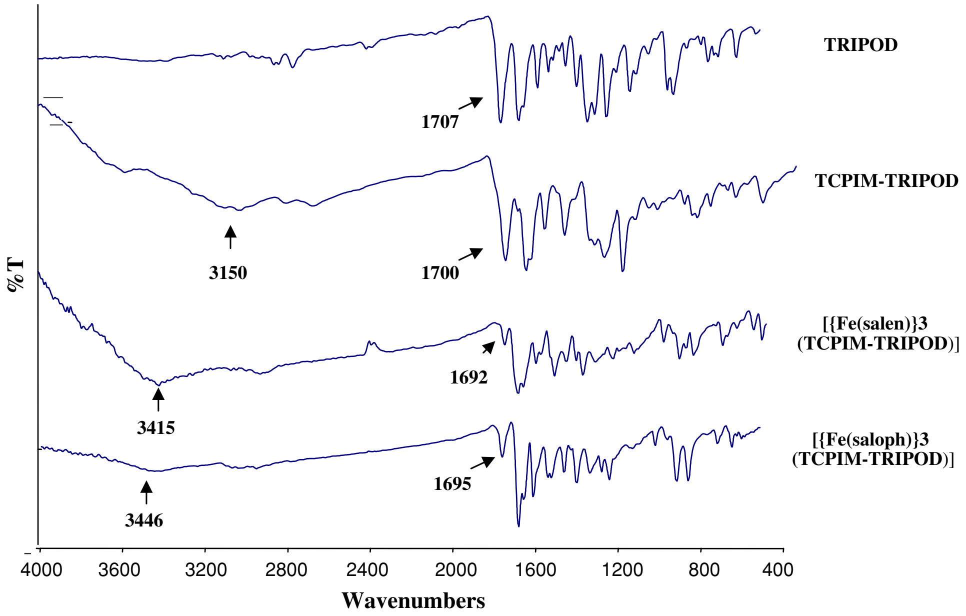


Fig. 4 Proposed models of Tripodal oxy-Schiff base ligand and Tripodal–Trinuclear complexes



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 environment. The magnetic behaviour of Fe(III) and Cr(III) complexes is in accord with proposed trinuclear structures. The magnetic moment per trinuclear complexes which were constructed from [{Fe(salen)}$_2$O], [{Fe(salophen)}$_2$O], [{Cr(salen)}$_2$O] and [{Cr(salophen)}$_2$O] either of 1,3,5-Tris(4-(4-carboxypheny liminomethyl)phenoxymethyl)benzene (TCPIM-TRIPOD) indicates paramagnetic property with a magnetic susceptibility value per atom: 1.55, 1.78 and 3.60, 3.52 B.M., respectively. It is seen that the [{Fe(salen)}$_2$O], [{Fe(salophen)}$_2$O], [{Cr(salen)}$_2$O] and [{Cr(salophen)}$_2$O] containing compounds are represented by the electronic structure 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 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 Trinuclear complexes have also an octahedral structure [13, 25, 30, 31].

Fig. 5 The FT-IR spectra of TRIPOD, TCPIM-TRIPOD, [{Fe(salen)}$_3$ (TCPIM-TRIPOD)] and [{Fe(salophen)}$_3$ (TCPIM-TRIPOD)]



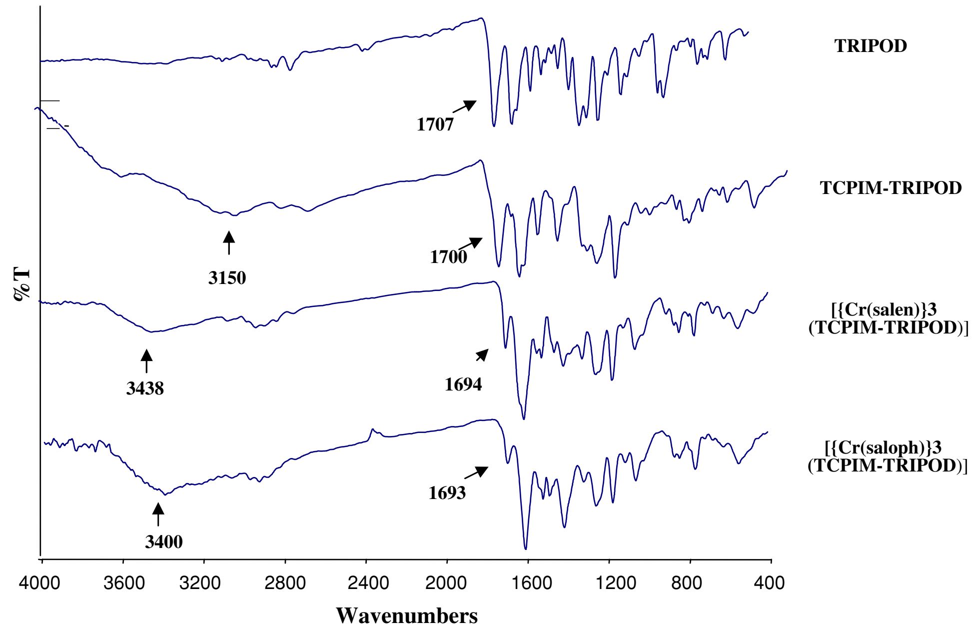


Fig. 6 The FT-IR spectra of TRIPOD, TCPIM-TRIPOD, $[\{Cr(salen)\}_3$ (TCPIM-TRIPOD)] and $[\{Cr(salophen)\}_3$ (TCPIM-TRIPOD)]

FT-IR spectrums of the ligand and salen and salophen based capped complexes were presented in Figs. 5 and 6. Figure 5 shows TRIPOD, TCPIM-TRIPOD, $[\{Fe(salen)\}_3$ (TCPIM-TRIPOD)] and $[\{Fe(salophen)\}_3$ (TCPIM-TRIPOD)]. Figure 6 shows TRIPOD, TCPIM-TRIPOD, $[\{Cr(salen)\}_3$ (TCPIM-TRIPOD)] and $[\{Cr(salophen)\}_3$ (TCPIM-TRIPOD)]. The vibrations of the aldehyde C=O of TRIPOD, carboxylic acid C=O and imine C=N of TCPIM-TRIPOD have been observed at 1,707, 1,700 and 1,680 cm^{-1}, respectively. In the complexes, these bands are, however, shifted to lower frequencies (1,692, 1,695 cm^{-1} for **3**,**4** and 1,694, 1,693 cm^{-1} for **5**,**6**) and reduced intensity of these bands, indicating that the nitrogen and oxygen atoms of the Tripodal Schiff base ligands are coordinated to the ligand complexes [25]. Tripodal–Trinuclear complexes, the bands in the 556–533 and 465–478 cm^{-1} ranges can be attributed to the M–N and M–O stretching modes [2].

The thermal stability of $[\{Cr(salen)\}_3$ (TCPIM-TRIPOD)] complex was evaluated by TGA. It was found that $[\{Cr(salen)\}_3$(TCPIM-TRIPOD)] undergoes a two-step thermal degradation (Fig. 7). The first step (50–350 °C) is due to the loss of moisture, CO_2, N_2 and C_2H_4 from main structure. At the second decomposition step, C_6H_6 left from the main structure at 350–600 °C [31]. Although the total weigh lost was theoretically calculated to be 47.93%, it was observed experimentally to be 48.15%. In addition, Fig. 8 shows thermal stability of $[\{Fe(salophen)\}_3$ (TCPIM-TRIPOD)] complex. This complex decomposed at three-

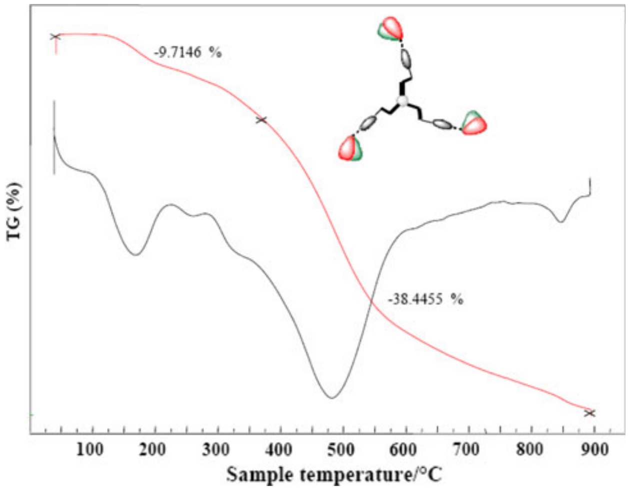


Fig. 7 TG and their first derivatives (dTG) of $[\{Cr(salen)\}_3$ (TCPIM-TRIPOD)]

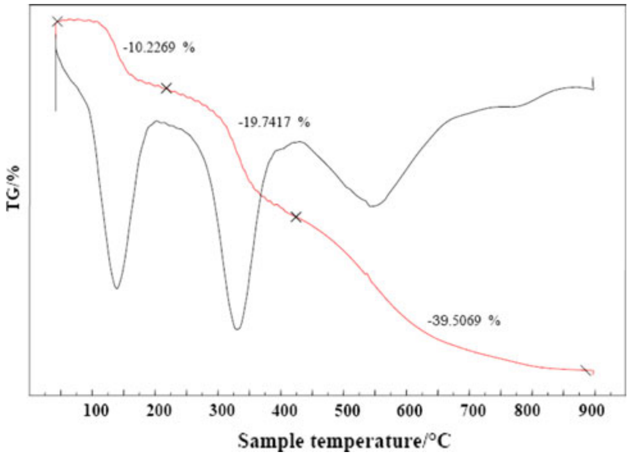


Fig. 8 TG and its first derivatives (dTG) of $[\{Fe(salophen)\}_3$ (TCPIM-TRIPOD)]

step thermal degradation. At 40–200 °C, leaves moisture, and CO_2 from main structure. At the second decomposition step, C_6H_6 and CN left from the residue structure at 250–400 °C. As finally decomposition step, at 400–700 °C, leaves C_6H_6, C_2H_4 and CO groups. For this complex, although the total weigh lost was theoretically calculated to be 65.93%, it was observed experimentally to be 69.45%.

Conclusion

In this study, new Tripodal Schiff base "1,3,5-Tris(4-(4-carboxyphenyliminomethyl)phenoxymethyl)benzene" were synthesized. 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 $[\{Fe(salen/salophen)\}_2O]$ and $[\{Cr(salen/Salophen)\}_2O]$ as "ligand complexes" because they can coordinate to the other ligand. These complexes are the examples of Tripodal–Trinuclear complexes bridged by carboxylate anions to the iron and chromium centers. Their structures were characterized by means of elemental analysis, ^{1}H-NMR, FT-IR spectroscopy, thermal analyses and magnetic susceptibility measurements. The magnetic data for the Tripodal–Trinuclear complexes show well agreement with the d^5 and d^3 metal ion in an octahedral structure.

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References

1. Mishra, A.K., Manav, N., Kaushik, N.K.: Organotin(IV) complexes of thiohydrazones: synthesis, characterization and antifungal study. Spectrochim. Acta Part A **61**, 3097–3101 (2005)
2. Guler, E., Kocyigit, O.: Synthesis and characterization of Ni(II) and Co(II) complexes of Schiff bases derived from 3,4-dimethyl-Delta(3)-tetrahydrobenzaldehyde and 4,6-dimethyl-Delta(3)-tetrahydrobenzaldehyde and glycene. Russ. J. Coord. Chem. **33**, 607–610 (2007)
3. Shamspur, T., Mashhadizadeh, M.H., Sheikhshoaie, I.: Flame atomic absorption spectrometric determination of silver ion after preconcentration on octadecyl silica membrane disk modified with bis[5-((4-nitrophenyl)azosalicylaldehyde)] as a new Schiff base ligand. J. Anal. At. Spectrom. **18**, 7–1410 (2003)
4. Hankare, P.P., Gavali, L.V., Bhuse, V.M., Delekar, S.D., Rokade, R.S.: Synthesis and characterization of tridentate Schiff's base derived from 5-(2′-thiazolylazo)salicylaldehyde and *p*-methoxy aniline and their Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes. Ind. J. Chem. Sect. A **43**, 2578–2581 (2004)
5. Guler, E., Sevindir, H.C., Kurbanov, S., Mirzaoglu, R.: Synthesis and characterization of copper(II) and nickel(II) complexes of the Schiff bases derived from Delta(3)-tetrahydrobenzaldehyde and 2-methyl-Delta(3)-tetrahydrobenzaldehyde and glycine. Synth. React. Inorg. Met. Org. Chem. **28**, 296–301 (1998)
6. Prabhakaran, R., Geetha, A., Thilagavathi, M., Karvembu, R., Krishnan, V., Bertagnolli, H., Natarajan, K.: Synthesis, characterization, EXAFS investigation and antibacterial activities of new ruthenium(III) complexes containing tetradentate Schiff base. J. Inorg. Biochem. **98**, 2131–2140 (2004)
7. Balasubramanian, K.P., Karvembu, R., Prabhakaran, R., Chinnusamy, V., Natarajan, K.: Synthesis, spectral, catalytic and antimicrobial studies of PPh3/AsPh3 complexes of Ru(II) with dibasic tridentate O, N, S donor ligands. Spectrochim. Acta Part A **68**, 50–54 (2007)
8. Guler, E., Ertul, S., Okudan, A., Kocyigit, O.: Synthesis and characterization of nickel(II) and copper(II) complexes of the Schiff bases derived from 4-/6-methyl-Delta(3)-tetrahydrobenzaldehyde and glycine. Asian J. Chem. **20**, 1533–1538 (2008)
9. Adam, W., Saha-Moeller, C.R., Ganeshpure, P.A.: A convenient synthesis of nickel(II) and cobalt(II) complexes of unsymmetrical salen-type ligands and their application as catalysts for the oxidation of 2,6-dimethylphenol and 1,5-dihydroxynaphthalene by molecular oxygen. Ind. J. Chem. **43A**, 56–62 (2004)
10. 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 **45**, 1072–1077 (2008)
11. 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)
12. 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)
13. 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)
14. Ashmawy, F.M., Ujaimi, A.R.: A facile synthesis of [(Fe(Salphen))2O] (Salphenh2 = N, N′-*O*-phenylenebis(salicylidineimine)) and the X-ray crystal-structure of [(Fe(Salphen))2O]. DMSO. Inorg. Chim. Acta **187**, 155–158 (1991)
15. 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)
16. Elmali, A., Atakol, O., Svoboda, I., Fuess, H.: Crystal-structure of mu-(*N*,*N*′-1,3-propyl-dısalıcyl-aldımınato)-bıs(*N*,*N*-1,3-propyl-dısalıcylaldımınato)-di-Iron(III) ethanol solvate, (OC6H4CHN)2C3H6(Fe(OC6H4CHN)2C3H6)2(C2H5OH). Z. Kristallogr. **203**, 271–273 (1993)
17. Kamenicek, J., Travnicek, Z., Sindelar, Z., Walla, J.: Redetermination of the structure of mu-oxo-bis[*N*,*N*′-*o*-phenylene-bis (salicylaldiminato)iron(III)]dimethyl sulfoxide solvate. J. Pol. J. Chem. **70**, 854 (1996)
18. Kessel, S.L., Hendrickson, D.N.: Magnetic exchange interactions in binuclear transition-metal complexes. 16. Binuclear ferric complexes from the reaction of iron(II)(salen) with *p*-quinones. Inorg. Chem. **17**(9), 2630–2636 (1978)
19. Wollmann, R.G., Hendrickson, D.N.: Reaction of. mu.-oxo-bridged iron(III) complexes with organic acids: a characterization of the products. Inorg. Chem. **17**(4), 926–930 (1978)
20. Sindelar, Z.: PhD Dissertation, Palacky University, Olomouc (1987)
21. Smekal, Z., Brezina, F., Sindelar, Z., Klicka, R.: Binuclear iron(III)–iron(III) complexes with the tetradentate Schiff base *N*,*N*0-bis(salicylidene)ethylenediamine and dicarboxylic acids or

dithiooxamide as bridging ligands. Transit. Metal. Chem. **21**, 49–51 (1996)

22. Etienne, M.: Hydridotris(pyrazolyl)borato complexes of the group 5 metals: inorganic and organometallic chemistry. Coord. Chem. Rev. **156**, 201–236 (1996)
23. Lisa, F.S., Withamb, L.M., Takeuchi, K.J.: Tris(2-pyridyl) tripod ligands. Coord. Chem. Rev. **174**, 5–32 (1998)
24. Schatz, M., Becker, M., Thaler, F., Hampe, Frank., Schindler, S., Jacobson, R.R., Tyeklár, Z., Murthy, N.N., Phalguni, G., Chen, Q., Zubieta, J., Karlin, K.D.: Copper(I) complexes, copper(I)/O_2 reactivity, and copper(II) complex adducts, with a series of tetradentate tripyridylalkylamine tripodal ligands. Inorg. Chem. **40**, 2312–2322 (2001)
25. Koc, Z.E., Ucan, H.I.: Complexes of iron(III) salen and salophen Schiff bases with bridging 2,4,6-tris(2,5 dicarboxyphenylimino-4-formylphenoxy)-1,3,5-triazine and 2,4,6-tris(4-carboxyphenylimino-4′-formylphenoxy)-1,3,5-triazine. Transit. Metal Chem. **32**, 597–602 (2007)
26. 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)
27. Dillip, K.C., Parimal, K.B.: Synthesis of designed hetero-polytopic cryptands through Schiff base condensation. Tetrahedron **53**, 10517–10522 (1997)
28. Rajakumar, P., Srisailas, M.: Synthesis of bicyclic cyclophanes with chiral cages by sixfold coupling. Tetrahedron Lett. **43**, 1909–1913 (2002)
29. Kopel, P., Sindelar, Z., Biler, M., Klicka, R.: Complexes of iron(III) salen and salophen Schiff bases bridged by dicarboxylic-acids. Pol. J. Chem. **72**(9), 2060–2066 (1998)
30. 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)
31. Uysal, S., Ucan, H.I.: The synthesis and characterization of melamine based Schiff bases and its trinuclear [salen/salophenFe(III)] and [salen/salophenCr(III)] capped complexes. J. Incl. Phenom. Macrocycl. Chem. in press (2009)