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Syntheses, characterization and X-ray crystal structures of hexa-coordinated monomeric and oxo-bridged dimeric Fe(III) compounds with salen-type Schiff bases

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ABSTRACT

Five Fe(III) compounds, [Fe(salophen)(N_3)(MeOH)] (**1**) [Fe(salophen)(NCS)(MeOH)] (**2**), [Fe(vanophen)$(HIm)_2$]ClO_4 (**3**), [(μ-O){Fe(vanophen)}$_2$]·$2H_2O$ (**4**) and [(μ-O){Fe(naphophen)}$_2$]·$2CH_2Cl_2$ (**5**) where, H_2salophen = *N*,*N*′-bis(salicylidene)phenylediamine, H_2vanophen = *N*,*N*′-(1,2-phenylene)-bis(3-methoxysalicylideneimine) and H_2naphophen = *N*,*N*′-bis(2-hydroxy-1-naphthaldehyde)-1,2-phenylenediimine, have been prepared and characterized by elemental analysis, IR and UV–Vis spectroscopy and single-crystal X-ray diffraction studies. In compounds **1**, **2** and **3**, Fe(III) has six-coordinated pseudo-octahedral geometry in which the O(1), O(2), N(1) and N(2) atoms of the deprotonated di-Schiff base constitute the equatorial plane. Both in compounds **1** and **2**, methanol molecules are present in the fifth coordination sites in apical positions. The sixth coordination sites are occupied by one N atom of an azide in compound **1** and an N atom of thiocyanate in compound **2**. In compound **3**, both axial positions are occupied by nitrogen atoms from two different imidazole molecules. In both compounds **4** and **5**, Fe(III) has a five-coordinated square pyramidal geometry with bridging oxygen atoms in the axial positions.

1. Introduction

Organic molecules containing imine groups, commonly known as Schiff bases, are of interest to inorganic chemists as these are widely used in designing molecular ferromagnets, in catalysis, in biological modeling applications and in preparing liquid crystals [1–7]. Schiff bases also play a key role as chelating ligands in main group metal and transition metal coordination chemistry, due to their ease of synthesis, stability under a variety of oxidative and reductive conditions, and their structural versatility which is associated with their diverse applications [8–13]. Undoubtedly, salen type ligands are receiving the most attention among all the Schiff bases. Ligands categorized under this class consist of two imine nitrogen and two phenolic oxygen donors that usually coordinate in the basal plane of the metal ion. They are readily prepared from the condensation of a diamine with salicylaldehyde, 3-methoxy salicylaldehyde, 2-hydroxy-1-naphthaldehyde etc. Salen-type ligands are significant because of the ability of the phenoxo oxygen atoms to form μ^2-bridges, thus affording high-nuclearity compounds [14–16], which could act as promising candidates to offer valuable insight into various natural electron-transfer events [17–19]. Polynuclear compounds achieved by these types of ligands, along with other appropriate co-ligands, provide tractable examples to rationalize the magnetic exchange phenomena [20–24] emerging from the temperature-dependent interactions between the spin states of individual magnetic centers. Fe(III)–salen compounds are known to show various catalytic activities by using vacant or labile axial sites, especially in solution [25]. There has also been huge interest in synthesizing oxo-bridged Fe(III) dimeric systems due to their relevance to important metalloproteins and metallo-enzymes, including hemerythrin, methane monooxygenase (MMO), ribonucleotide reductase and purple acid phosphatases, where the di-iron motif in these enzymes is crucial to their function [26–28]. Several compounds of this type have been synthesized and characterized by magnetic susceptibility measurements [29,30] and Mossbauer spectra [29]. Infrared frequencies associated with the oxo-bridging unit have been identified [31]. Dimeric ferriporphyrins, containing the Fe–O–Fe structural unit, have also been characterized [32]. Although, X-ray structures have also been obtained in certain cases [30], there are rather fewer studies concerning the solid state properties of these Schiff base compounds compared to those of solution chemistry.

In this paper, we describe the preparation of some new Schiff base compounds of Fe(III). Our attempts with H_2salophen {*N*,*N*′-bis(salicylidene)phenylediamine} as a representative of the quadridentate bis(salicylidene)-type Schiff-base ligand family,

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furnished two hexa-coordinated Fe(III) species, whereas the ligand, H_2naphophen {*N*,*N*′-bis(2-hydroxy-1 naphthaldehyde)-1,2-phenylenediimine} afforded penta-coordinated dimeric Fe(III) species and H_2vanophen {*N*,*N*′-(1,2-phenylene)-bis(3-methoxysalicylideneimine)} formed both mono- and di-nuclear Fe(III) compounds. Hexa-coordinated Fe(III) compounds with H_2Salophen and H_2vanophen are relatively scarce, and to the best to our knowledge [33] only three such compounds of Fe(III) with these ligands are reported in the literature [34–36]. Herein, we report the synthesis, spectroscopic characterization and electrochemical studies of five Fe(III) compounds. X-ray crystal structure determinations have established their structures.

2. Experimental

2.1. Materials

All chemicals were of reagent grade and were used without further purification.

Caution! Azide compounds of metal perchlorates are potentially explosive. Although no problem was encountered in the present study, only small amounts of the materials should be prepared and they must be handled with great care.

2.2. Synthesis

2.2.1. Synthesis of the ligands N,N′-(1,2-phenylene)-bis(salicylideneimine) (H_2salophen), N,N′-(1,2-phenylene)-bis(3-methoxysalicylideneimine) (H_2vanophen) and N,N′-bis(2-hydroxy-1-naphthaldehyde)-1,2-phenylenediimine (H_2naphophen)

The Schiff base ligands H_2salophen, H_2vanophen and H_2naphophen were synthesized in a similar method by refluxing *o*-phenylenediamine (10 mmol, 1.08 g) with salicylaldehyde (20 mmol, 2.10 ml), 3-methoxy salicylaldehyde (commonly known as *o*-vaniline) (20 mmol, 3.04 g) and 2-hydroxy-1-naphthaldehyde (20 mmol,3.44 g) respectively in methanol solution (20 ml) for ca. 1 h. The ligands were isolated as crystalline solids, which were collected by filtration after cooling.

2.2.2. Synthesis of [Fe(salophen)(N_3)(MeOH)] (**1**)

A methanol solution (20 ml) of Fe(III) perchlorate (1 mmol, 0.354 g) was added to a hot methanol solution (30 ml) of H_2salophen (1 mmol, 0.314 g). A solution of sodium azide (1 mmol, 0.065 g) in methanol was added to it and refluxed for 1.5 h. The resulting solution was then filtered hot. Diffraction quality single crystals were obtained after a few days by slow evaporation of the dark red filtrate in a refrigerator.

Yield: 0.27 g (61%). *Anal.* Calc. for $C_{21}H_{18}FeN_5O_3$ (444.25): C, 56.78; H, 4.08; N, 15.76. Found: C, 56.8; H, 4.1; N, 15.6%; IR (KBr, cm^{-1}): 1602 ($\nu_{C{=}N}$), 2059 (ν_{N3}); UV–Vis, λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) (CH_3CN): 292 (3969), 376 (1684).

2.2.3. Synthesis of [Fe(salophen)(NCS)(MeOH)] (**2**)

This was prepared in a similar method to that of compound **1**, except that sodium thiocyanate (1 mmol, 0.081 g) was added instead sodium azide. Diffraction quality single crystals were obtained after a few days by slow evaporation of the dark red filtrate in the open atmosphere.

Yield: 0.25 g (54%). *Anal.* Calc. for $C_{22}H_{18}FeN_3O_3S$ (460.31): C, 57.40; H, 3.94; N, 9.13. Found: C, 57.3; H, 4.1; N, 9.2%; IR (KBr, cm^{-1}): 1602 ($\nu_{C{=}N}$), 2059 (ν_{SCN}); UV–Vis, λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) (CH_3CN): 293 (4093), 378 (2186).

2.2.4. Synthesis of [Fe(vanophen)$(HIm)_2$]ClO_4 (**3**)

A methanol solution (20 ml) of Fe(III) perchlorate (1 mmol, 0.354 g) was added to a mixture of H_2vanophen (1 mmol, 0.376 g) and imidazole (2 mmol, 0.136 g) in methanol (30 ml). The resulting mixture was then refluxed for ca. 15 min and filtered hot. Diffraction quality single crystals were obtained after one day by slow evaporation of the dark green filtrate in a refrigerator.

Yield: 0.34 g (51%). *Anal.* Calc. for $C_{28}H_{26}FeN_6O_8Cl$ (665.85): C, 50.51; H, 3.94; N, 12.62. Found: C, 51.1; H, 3.9; N, 12.6%; IR (KBr, cm^{-1}): 1602 ($\nu_{C{=}N}$), 1090 (ν_{ClO4}); UV–Vis, λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) (CH_3CN): 332 (2728), 451 (2500), 650 (796).

2.2.5. Synthesis of [(μ-O){Fe(vanophen)}$_2$]·$2H_2O$ (**4**)

A methanol solution of (10 ml) of Fe(III) perchlorate (1 mmol, 0.354 g) was added dropwise to a stirred solution (30 ml) of

Table 1
Crystal data and refinement details of compounds **1**–**5**.

Compound	**1**	**2**	**3**	**4**	**5**
Formula	$C_{21}H_{18}FeN_5O_3$	$C_{22}H_{18}FeN_3O_3S$	$C_{28}H_{26}FeN_6O_8Cl$	$C_{44}H_{40}Fe_2N_4O_{11}$	$C_{58}H_{40}Cl_4Fe_2N_4O_5$
Formula weight	444.25	460.31	665.85	912.47	1126.44
Crystal size (mm)	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.40	0.11 × 0.13 × 0.14	0.11 × 0.12 × 0.13	0.20 × 0.20 × 0.20
T (K)	293	293	293	293	293
Crystal system	triclinic	monoclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	C_2/c	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions					
a (Å)	7.9235(3)	15.1233(4)	10.1262(5)	12.7078(14)	12.328(5)
b (Å)	9.9603(3)	9.8765(4)	10.5504(4)	13.5823(16)	13.821(5)
c (Å)	12.2561(4)	27.5475(8)	15.5460(9)	14.5019(17)	14.695(5)
α (°)	97.172(2)	90	101.472(4)	72.657(8)	92.420(5)
β (°)	91.274(2)	92.515(3)	104.265(4)	78.002(8)	97.555(5)
γ (°)	92.600(2)	90	105.984(3)	65.441(8)	91.342(5)
Z	2	8	2	2	2
D_{calc} (g cm^{-3})	1.540	1.488	1.492	1.346	1.509
μ (mm^{-1})	0.822	0.865	0.659	0.729	0.857
F (000)	458	1896	686.0	904	1152
Total reflections	15557	15052	15098	17411	21456
Unique reflections	5130	1730	5445	7584	4872
Observed data [$I > 2\sigma(I)$]	4258	1542	2919	3278	3803
No. of parameters	275	275	399	536	658
R_{int}	0.020	0.041	0.041	0.0791	0.057
R_1, wR_2 (all data)	0.0407, 0.0975	0.0456, 0.1278	0.1323, 0.2347	0.1410, 0.1649	0.0776, 0.1946
R_1, wR_2 [$I > 2\sigma(I)$]	0.0330, 0.0928	0.0386, 0.1098	0.0841, 0.2085	0.0791, 0.1490	0.0610, 0.1686

H_2vanophen (1 mmol, 0.376 g). Then a few drops of water were added to it. The resulting solution was stirred for 3 h to obtain a brown precipitate which was filtrated and washed with methanol. Diffraction quality single crystals were obtained after a few days by slow evaporation of a DMF solution in the open atmosphere.

Yield: 0.44 g (48%). *Anal.* Calc. for $C_{44}H_{40}Fe_2N_4O_{11}$ (912.47): C, 57.91; H, 4.42; N, 6.14. Found: C, 58.1; H, 4.3; N, 6.2%; IR (KBr, cm^{-1}): 1604 ($\nu_{C=N}$), 854 ($\nu_{Fe-O-Fe}$); UV–Vis, λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) (CH_3CN): 234 (4380), 302 (4756), 411 (1264).

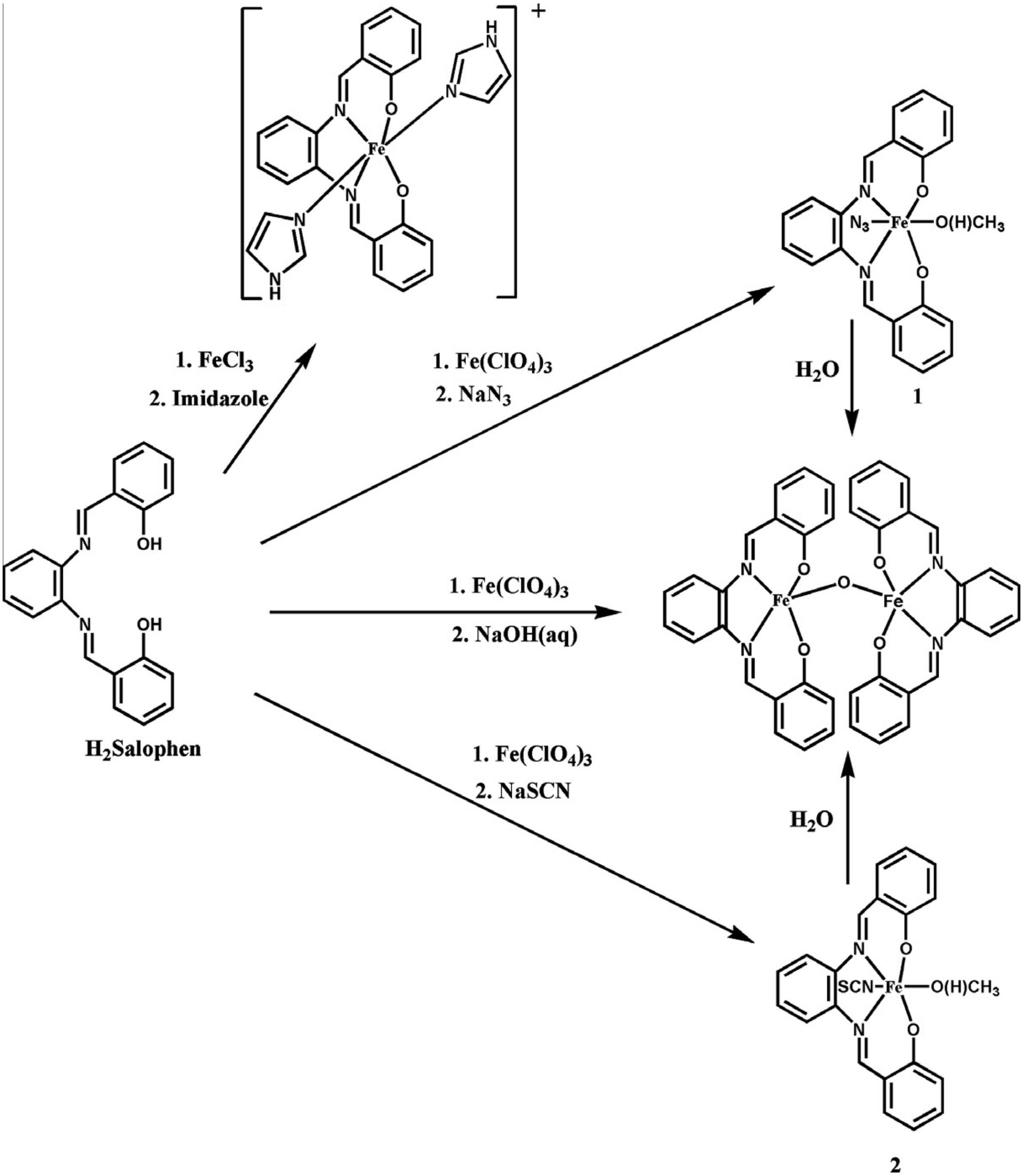
2.2.6. Synthesis of $[(\mu\text{-}O)\{Fe(naphophen)\}_2]\cdot 2CH_2Cl_2$ (**5**)

A methanol solution (10 ml) of Fe(III) perchlorate (1 mmol, 0.354 g) was added to a methanol solution (30 ml) of H_2naphophen (1 mmol, 0.416 g) with constant stirring. A few drops of water were added to it. Then the mixture was stirred for ca. 2 h. A black precipitate was formed, which was collected by filtration. Diffraction quality single crystals were obtained after a few days by slow evaporation of a 1:1 acetonitrile/dichloromethane solution in a refrigerator.

Yield: 0.55 g (49%). *Anal.* Calc. for $C_{58}H_{40}Cl_4Fe_2N_4O_5$ (1126.44): C, 61.84; H, 3.58; N, 4.97. Found: C, 61.2; H, 3.4; N, 5.1%; IR (KBr, cm^{-1}): 1599 ($\nu_{C=N}$), 829 ($\nu_{Fe-O-Fe}$); UV–Vis, λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) (CH_3CN): 228 (1640), 337 (745), 402 (40).

2.3. Physical measurements

Elemental analysis (carbon, hydrogen and nitrogen) was performed using a Perkin–Elmer 240 C elemental analyzer. IR spectra



Scheme 1. Synthetic scheme to produce **1**, **2** and the other reported compounds.

in KBr (4000–400 cm^{-1}) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. Electronic spectra in acetonitrile (1000–200 nm) were recorded in a Perkin Elmer Lambda-25 UV–Vis spectrometer at 298 K. Electrochemical measurements were performed in DMF solution under a dry nitrogen atmosphere in a conventional three-electrode configuration using a Pt disk working electrode, Pt auxiliary electrode and Ag/AgCl reference electrode, with tetrabutylammonium perchlorate as the supporting electrolyte in the potential range from −2 to 2 V, and were uncorrected for junction contributions. The value for the Fc–Fc^+ couple under our conditions is 0.4 V.

2.4. X-ray crystallography

Single crystals of the compounds, having suitable dimensions, were used for data collection using a 'Bruker SMART APEX II' diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The molecular structure was solved by direct methods and refinement by full-matrix least squares on

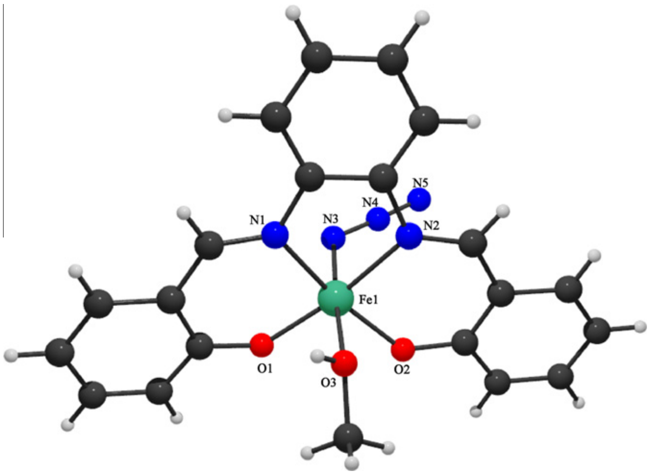
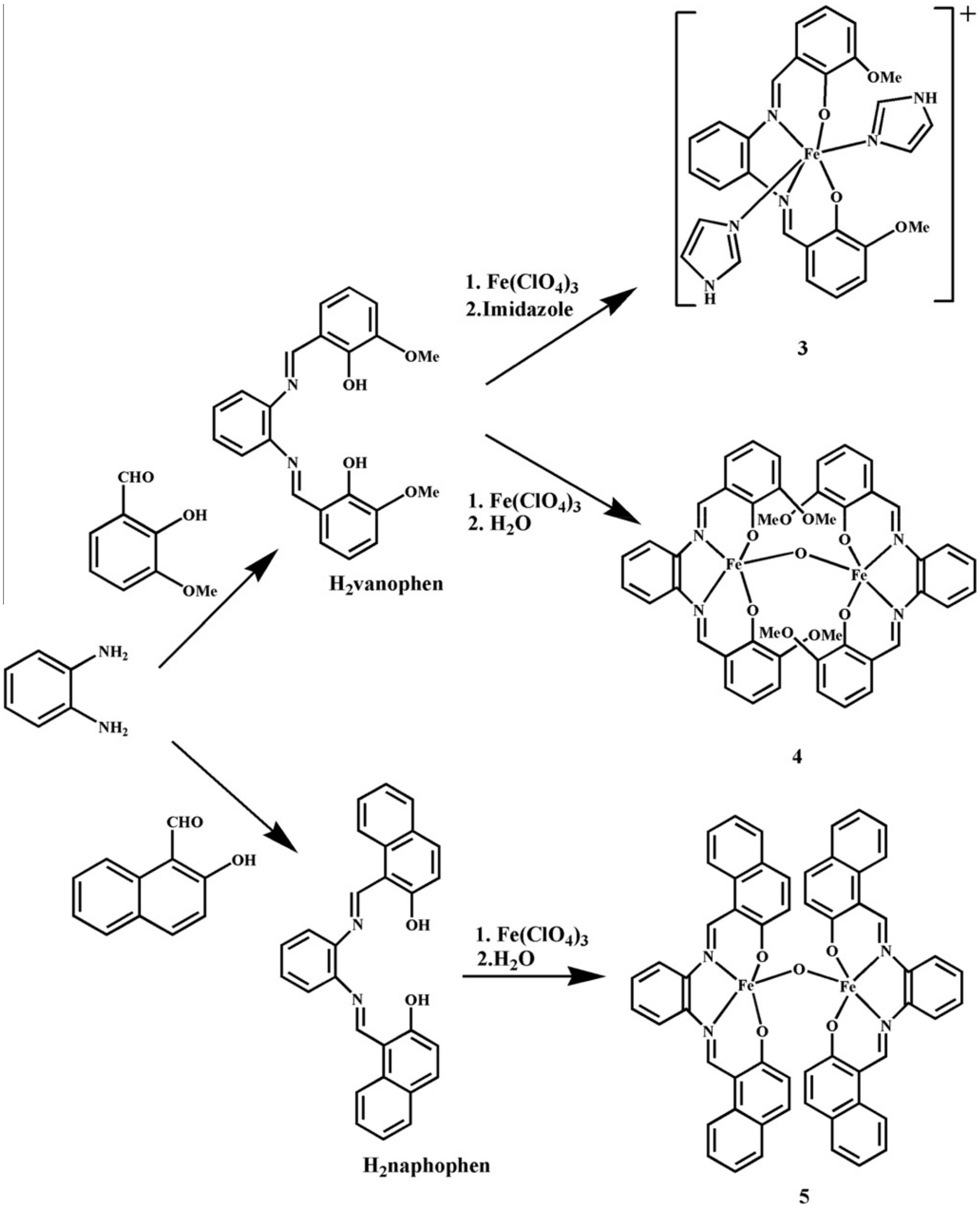


Fig. 1. Perspective view of compound **1** along with the atom numbering of all non-carbon and non-hydrogen atoms.



Scheme 2. Synthesis of the compounds **3**, **4** and **5**.

Table 2
Selected bond lengths (Å) and bond angles (°) for compounds **1**, **2** and **3**.

Compound	**1**	**2**	**3**
Fe(1)–O(1)	1.8818(13)	1.932(3)	1.907(4)
Fe(1)–O(2)	1.9017(13)	1.873(4)	1.881(4)
Fe(1)–O(3)	2.2373(16)	2.125(5)	–
Fe(1)–N(1)	2.1127(13)	2.111(6)	2.108(4)
Fe(1)–N(2)	2.1254(14)	2.107(5)	2.125(4)
Fe(1)–N(3)	2.0487(16)	2.037(6)	2.112(4)
Fe(1)–N(4)	–	–	2.139(6)
O(1)–Fe(1)–O(2)	103.22(5)	105.27(17)	103.74(18)
O(1)–Fe(1)–O(3)	88.25(6)	83.59(15)	–
O(1)–Fe(1)–N(1)	89.04(5)	88.46(18)	89.21(17)
O(1)–Fe(1)–N(2)	165.04(5)	163.53(18)	166.54(18)
O(1)–Fe(1)–N(3)	97.42(6)	93.80(18)	91.36 (17)
O(1)–Fe(1)–N(4)	–	–	89.65(19)
O(2)–Fe(1)–O(3)	86.29(6)	89.85(17)	–
O(2)–Fe(1)–N(1)	163.34(6)	165.73(19)	166.64(18)
O(2)–Fe(1)–N(2)	89.24(5)	89.2(2)	89.66(18)
O(2)–Fe(1)–N(3)	96.33(6)	93.8(2)	93.01(18)
O(2)–Fe(1)–N(4)	–	–	91.4(2)
O(3)–Fe(1)–N(1)	82.81(5)	87.81(17)	–
O(3)–Fe(1)–N(2)	84.28(6)	88.76(17)	–
O(3)–Fe(1)–N(3)	173.01(6)	176.0(2)	–
N(1)–Fe(1)–N(2)	77.20(5)	76.7(2)	77.34(17)
N(1)–Fe(1)–N(3)	93.16(6)	89.1(2)	89.91(17)
N(1)–Fe(1)–N(4)	–	–	85.28(19)
N(2)–Fe(1)–N(3)	89.27(6)	93.0(2)	89.26(17)
N(2)–Fe(1)–N(4)	–	–	88.64(19)
N(3)–Fe(1)–N(4)	–	–	175.07(19)

F^2 using the SHELX-97 package [37]. Non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms of the hydroxyl groups of the methanol molecules in **1** and **2** were located from difference Fourier maps and were kept fixed. Other hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Multi-scan absorption corrections were applied to the data using the program SADABS [38]. A summary of the crystallographic data are given in Table 1.

The crystal structure of compound **4** is somewhat problematic. The unit cell includes some highly disordered solvent molecules, which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent molecules and thereby produce a set of solvent-free diffraction intensities. Details about the SQUEEZE procedure are given in the CIF file. The SQUEEZE technique was also employed to produce a set of solvent-free diffraction intensities for compound **3**.

Table 3
Hydrogen bond distances (Å) and angles (°) for compounds **1, 2** and **3**.

Compound	D–H···A	D–H	D···A	H···A	∠D–H···A	
1	O(3)–H(3A)···N(5)$^{\#}$	0.85(3)	2.824(2)	1.99(3)	167(2)	# = −1 + *x*, *y*, *z*
2	O(3)–H(3A)···O(1)*	0.86(5)	2.689(5)	1.84(5)	175(7)	* = 1 − *x*, *y*, 3/2 − *z*
3	N(5)–H(5A)···O(3)$^{\$}$	0.8800	3.030(9)	2.18	161	$ = 1 − *x*, −*y*, 1 − *z*
	N(6)–H(6A)···O(7)$^{@}$	0.8800	2.908(9)	2.06	161	@ = 2 − *x*, 1 − *y*, 1 − *z*

D, donor; H, hydrogen; A, acceptor.

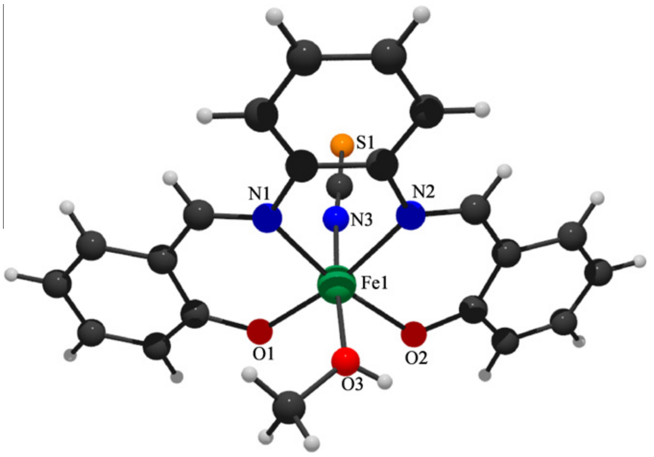


Fig. 3. Perspective view of compound **2** along with the atom numbering of all non-carbon and non-hydrogen atoms.

3. Results and discussion

3.1. Synthesis

The ligand (H_2salophen) was prepared by the 1:2 condensation of *o*-phenylenediamine with salicyldehyde in methanol following the literature method [39]. A methanol solution of Fe(III) perchlorate was then added to the methanol solution of the ligand, followed by the addition of a methanol solution of sodium azide or sodium thiocyanate under reflux to prepare compounds **1** and **2** respectively. Initially, a red crystalline compound started to

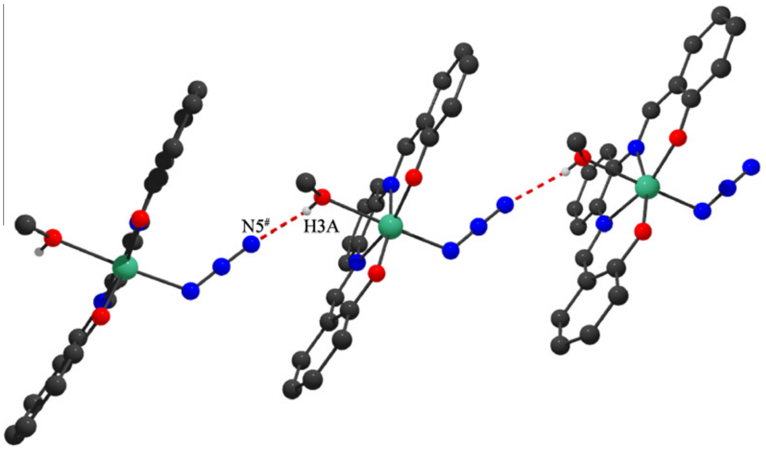


Fig. 2. H-bonded chain of compound **1**. Hydrogen atoms (except methanol hydrogen) have been omitted for clarity (# = −1 + *x*, *y*, *z*).

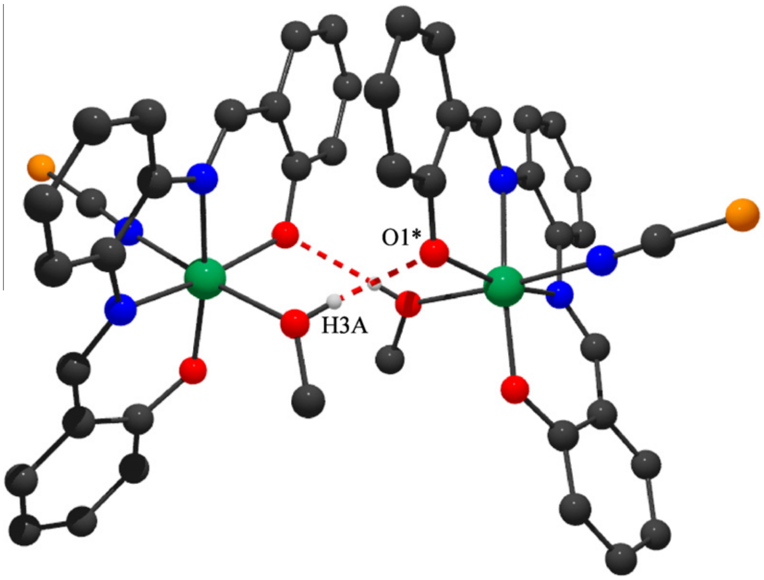


Fig. 4. H-bonded dimer of compound **2**. Hydrogen atoms (except methanol hydrogen) have been omitted for clarity ($* = 1 - x, y, 3/2 - z$).

precipitate, which was identified as (μ-O){Fe(salophen)$_2$} by C,H,N analysis and mass spectrometry. The amount of this product increased with an increase in the amount of water in the methanol solution of sodium azide or sodium thiocyanate. The compound could be better prepared by refluxing Fe(III) perchlorate with H_2salophen and KOH solution. The structure of this species was reported elsewhere [40–42]. It is worth mentioning that when a methanol solution of Fe(III) perchlorate with H_2salophen was refluxed with NaNCO, the sole product was (μ-O){Fe(salophen)$_2$}, as confirmed by C,H,N analysis and mass spectrometry and an X-ray diffraction study. The weaker cyanate nucleophile might fail to prepare [Fe(salophen)(NCO)], even after prolonged refluxing, however when (μ-O){Fe(salophen)$_2$} was refluxed with acetic acid, [Fe(salophen)OAc] was formed [43]. Use of Fe(III) chloride, instead of Fe(III) perchlorate, produced [Fe(salophen)Cl], the structure of which was reported by a different group [44]. Surprisingly, sodium azide/sodium thiocyanate could not replace the chloride by azide/thiocyanate, whereas imidazole could easily replace chloride on heating the solution at 60 °C for 10 min to form the hexa-coordinated [Fe(salophen)(HIm)$_2$]$^+$ [35]. The preparations of all these compounds are shown in Scheme 1.

Table 4
Selected bond lengths (Å) and bond angles (°) for compounds **4** and **5**.

	4	5
Fe(1)–O(1)	1.925(4)	1.941(4)
Fe(1)–O(2)	1.928(4)	1.933(4)
Fe(1)–O(3)	1.760(3)	1.775(5)
Fe(1)–N(1)	2.068(5)	2.091(5)
Fe(1)–N(2)	2.091(6)	2.111(6)
Fe(2)–O(3)	1.779(3)	1.778(4)
Fe(2)–O(4)	1.884(4)	1.930(4)
Fe(2)–O(5)	1.936(6)	1.928(5)
Fe(2)–N(3)	2.089(6)	2.086(5)
Fe(2)–N(4)	2.074(5)	2.104(6)
O(1)–Fe(1)–O(2)	91.82(18)	92.51(19)
O(1)–Fe(1)–O(3)	109.36(18)	109.72(19)
O(1)–Fe(1)–N(1)	141.00(18)	85.6(2)
O(1)–Fe(1)–N(2)	86.97(19)	142.52(18)
O(2)–Fe(1)–O(3)	109.62(19)	107.24(18)
O(2)–Fe(1)–N(1)	88.2(2)	147.11(18)
O(2)–Fe(1)–N(2)	153.48(18)	85.51(18)
O(3)–Fe(1)–N(1)	107.29(18)	104.26(18)
O(3)–Fe(1)–N(2)	95.69(18)	106.56(18)
N(1)–Fe(1)–N(2)	76.5(2)	76.6(2)
O(3)–Fe(2)–O(4)	110.57(18)	112.53(19)
O(3)–Fe(2)–O(5)	109.68(19)	109.05(19)
O(3)–Fe(2)–N(3)	94.6(2)	104.4(2)
O(3)–Fe(2)–N(4)	104.45(17)	103.10(18)
O(4)–Fe(2)–O(5)	93.1(2)	91.05(18)
O(4)–Fe(2)–N(3)	87.5(2)	85.70(19)
O(4)–Fe(2)–N(4)	142.31(17)	143.24(18)
O(5)–Fe(2)–N(3)	153.7(2)	144.9(2)
O(5)–Fe(2)–N(4)	87.8(2)	85.55(19)
N(3)–Fe(2)–N(4)	76.1(2)	76.8(2)
Fe(1)–O(3)–Fe(2)	154.3(2)	153.1(3)

H_2vanophen was prepared by a similar method, by refluxing a methanol solution of *o*-phenylenediamine and 3-methoxysalicyldehyde in a 1:2 ratio [45]. The ligand was then made to react with a methanol solution of imidazole, followed by a methanol solution of Fe(III) perchlorate to prepare compound **3**. In the absence of imidazole, a green crystalline compound started to precipitate, which was identified as (μ-O){Fe(vanophen)$_2$} (**4**) by C,H,N analysis and mass spectrometry. The amount of this product increased when a measured excess of water was added to the reaction medium. Suitable single crystals of compound **4** could be grown from DMF solution.

H_2naphophen was prepared similarly by refluxing a methanol solution of *o*-phenylenediamine and 2-hydroxy-1-naphthaldehyde in a 1:2 ratio. Reaction of H_2naphophen, with Fe(III) perchlorate produces (μ-O){Fe(naphophen)$_2$} (**5**). In the presence of azide, thiocyanate or imidazole, compound **5** is produced as the sole product. We have tried several times to prepare hexa-coordinated Fe(III) compounds with H_2naphophen, but none of the attempts yielded any fruitful results, even after increasing the concentration of azide/thiocyanate/imidazole to ~5 times the metal concentration. Single crystals of compound **5**, suitable for X-ray diffraction, were grown from a 1:1 acetonitrile/dichloromethane solution. The formation of compounds **3**, **4** and **5** are shown in Scheme 2.

3.2. IR and electronic spectra

In the IR spectra of all the compounds, distinct bands due to the azomethine (C=N) group were observed around 1600 cm^{-1}. The presence and the coordination mode of azide to a transition metal can be detected by the intense IR band due to $\nu_{as}(N_3)$ that usually appears within 2000–2055 cm^{-1} for a terminal azide ligand [46]. In

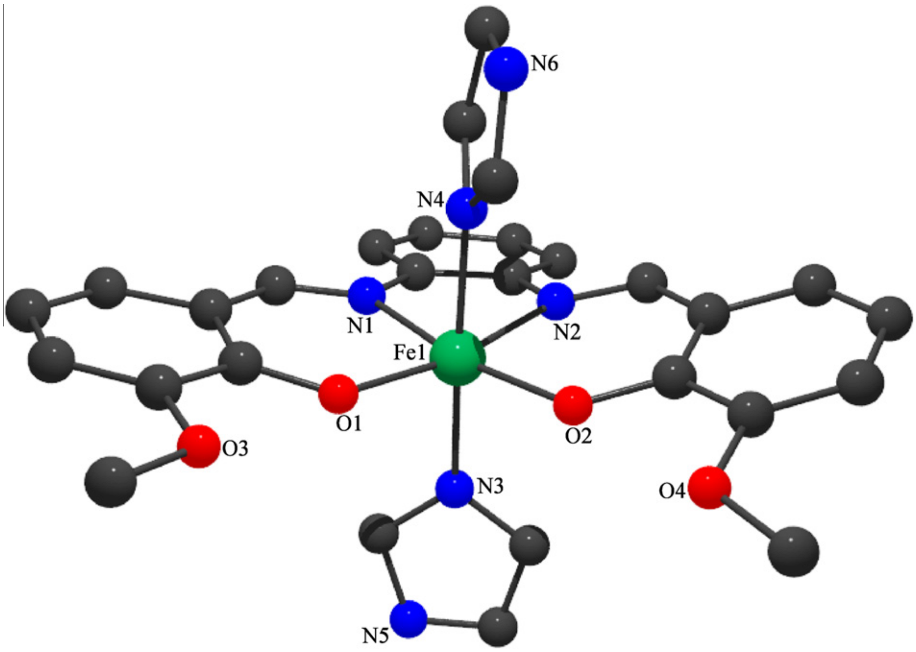


Fig. 5. Perspective view of compound **3**. Hydrogen atoms and the perchlorate ion have been omitted for clarity.

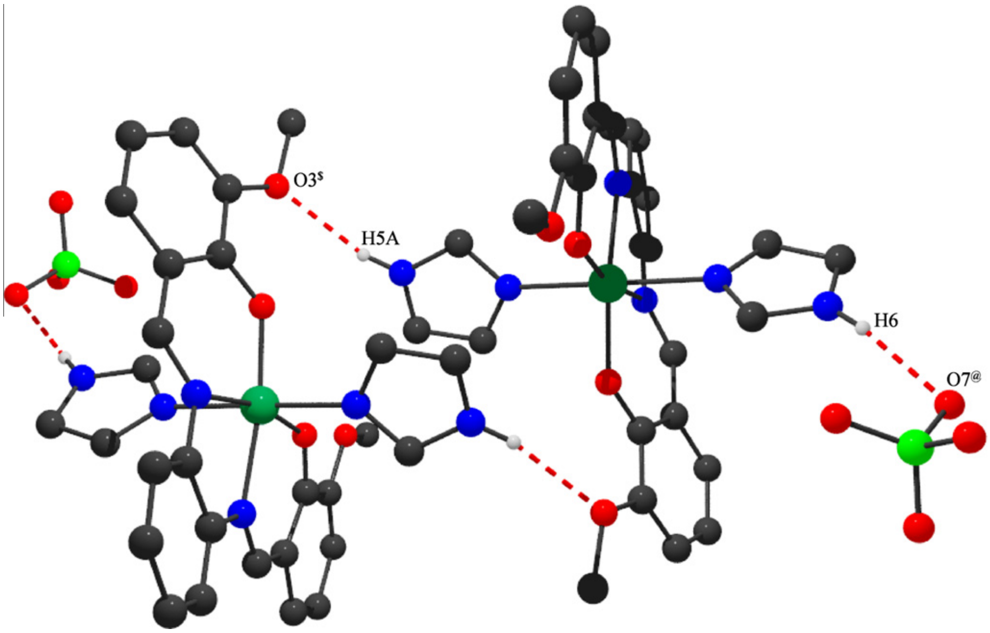


Fig. 6. H-bonded dimer of compound **3**. Hydrogen atoms (except imidazole N–H) have been omitted for clarity ($ = 1 − x, −y, 1 − z, @ = 2 − x, 1 − y, 1 − z).

the IR spectrum of **1**, the appearance of a strong band at 2059 cm^{-1} indicates the presence of a monodentate azide. Similarly, a band at 2059 cm^{-1} in the IR spectrum of compound **2** is indicative of the presence of the *N*-coordinated thiocyanate. In the IR spectrum of compound **3**, a broad band at 1096 cm^{-1} is observed, which is devoid of any splitting and is consistent with the IR active normal mode for perchlorate [47]. In compounds **4** and **5**, weak bands at 854 and 829 cm^{-1} respectively are observed due to the antisymmetric stretching of the Fe–O–Fe unit [48].

The electronic spectra of all the compounds in acetonitrile were recorded in the range 200–1000 nm. The intense absorption bands at short wavelengths, around 300 nm, may be assigned to Schiff base to metal ion charge transfer bands (LMCT) [49]. The absorptions around 400–600 nm may be assigned to *d–d* transitions.

3.3. Description of the structures

3.3.1. [Fe(salophen)(N_3)(MeOH)] (1)

Compound **1** crystallizes in the triclinic space group $P\bar{1}$. The structural representation of **1** is shown in Fig. 1, and important bond lengths and angles are listed in Table 2. The compound shows a distorted octahedral geometry involving N_2O_2 donors as the basal plane {N(1), N(2), O(1) and O(2)}. One oxygen atom, O(3), from a methanol and one nitrogen atom, N(3), from an azide are attached to the metal atom to fill its two axial sites. The Fe(1)–O(1), Fe(1)–O(2), Fe(1)–N(1) and Fe(1)–N(2) distances are 1.8818(13), 1.9017(13), 2.1127(13) and 2.1254(14) Å respectively, and the Fe(1)–O(3) and Fe(1)–N(3) distances are 2.2373(15) and 2.0487(16) Å respectively, which fall within the ranges observed

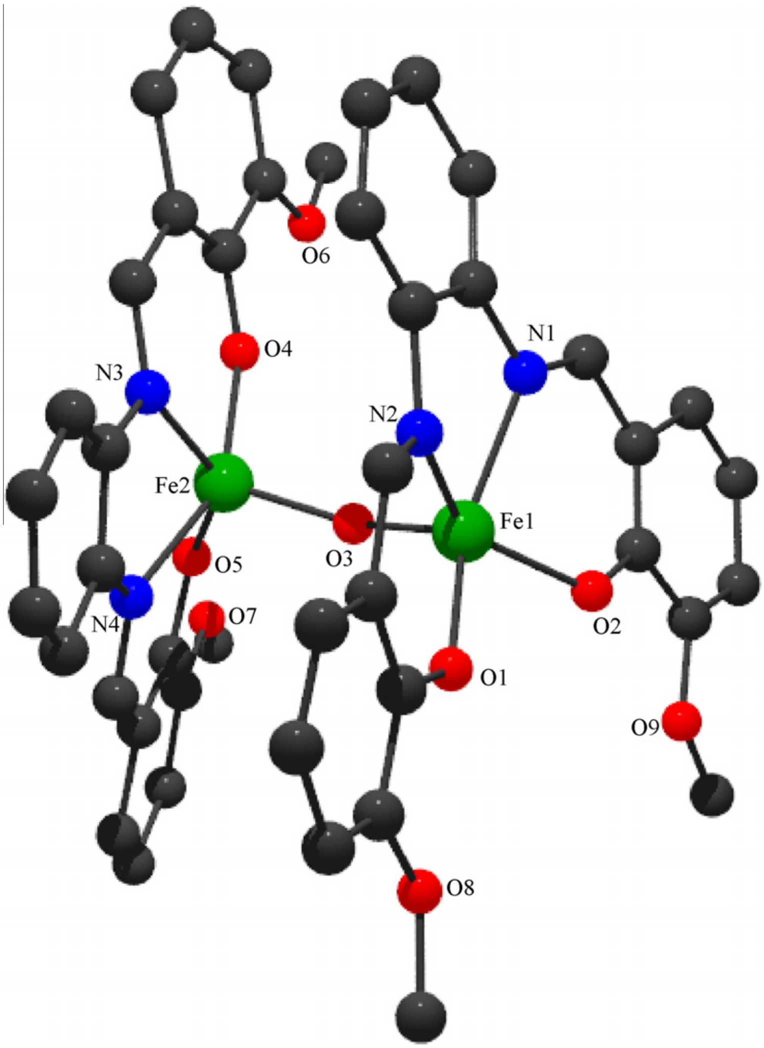


Fig. 7. Perspective view of compound **4**. Hydrogen atoms have been omitted for clarity.

for structurally characterized Fe(III) compounds [34–36]. The basal bond angles are all close to 90° [O(1)–Fe(1)–O(2), O(1)–Fe(1)–N(1), N(1)–Fe(1)–N(2) and O(2)–Fe(1)–N(2) are 103.22(5), 89.04(5), 77.20(5), and 89.24(5)° respectively]. The deviation of all the coordinating atoms in the basal plane O(1), O(2), N(1) and N(2) from the mean plane passing through them are 0.028, 0.028, −0.032 and 0.031 Å, and that of Fe(1) from the same plane is −0.152 Å.

The H atom, H(3A), attached to O(3) of the coordinated methanol, forms a strong hydrogen bond with a symmetry-related (−1 + *x*, *y*, *z*) nitrogen atom, N(5), of an azide to form a chain (Fig. 2). Details of the H-bonding are given in Table 3.

3.3.2. [Fe(salophen)(NCS)(MeOH)] (**2**)

Compound **2** crystallizes in the monoclinic space group C_2/c. It is a mononuclear Fe(III) compound in which Fe(1) has a six-coordinate pseudo-octahedral geometry where the O(1), O(2), N(1) and N(2) atoms of the deprotonated di-Schiff base {(salophen)$^{2-}$} constitute the equatorial plane. In the apical position, the Fe(III) center is coordinated by one NCS$^-$ ion and one methanol molecule as terminal ligands, finishing its distorted octahedral coordination sphere (Fig. 3). In the equatorial plane, the Fe(1)–O(1), Fe(1)–O(2), Fe(1)–N(1) and Fe(1)–N(2) bond lengths are 1.932(3), 1.873(4), 2.111(6) and 2.107(5) Å, respectively, which are close to those in other related Fe(III) compounds [34–36]. The bond distances in the axial positions are Fe(1)–N(3), 2.037(6) Å and Fe(1)–O(3), 2.125(5) Å. The deviation of all the coordinating atoms in the basal plane O(1), O(2), N(1) and N(2) from the mean plane passing through them are −0.036, 0.037, 0.042 and −0.042 Å, and that of Fe(1) from the same plane, is 0.090 Å. Selected bond lengths and bond angles of compound **2** are given in Table 2.

Each mononuclear Fe(III) species is connected to a neighbor through intermolecular interactions creating well-isolated supramolecular dimers (Fig. 4). In forming this, the hydrogen atom H(3A), attached to O(3) of the coordinated methanol molecule, is engaged in hydrogen bond formation with the symmetry related (1 − *x*, 1 − *y*, 1 − *z*) O(2) atom. Details of the H-bonding are given in Table 4.

3.3.3. 3[Fe(vanophen)(HIm)$_2$]ClO$_4$ (**3**)

Compound **3** is a mononuclear Fe(III) compound. It is crystallizes in the triclinic space group $P\bar{1}$. The Fe(III) center has six coordinated pseudo-octahedral geometry in which two nitrogen atoms from the imidazole (HIm) coordinate in the axial positions, whereas the N_2O_2 donors from the deprotonated Schiff-base ligand {(vanophen)$^{2-}$} coordinate in the basal plane. A perspective view of the compound is shown in Fig. 5. The axial bond lengths of Fe(1)–N(3) and Fe(1)–N(4) are 2.112(4) and 2.139(6) Å respectively. The bond lengths in the equatorial plane, Fe(1)–O(1), Fe(1)–O(2), Fe(1)–N(1) and Fe(1)–N(2), are 1.907(4), 1.881(4), 2.108(4) and 2.125(4) Å respectively. The axial N(3)–Fe(1)–N(4) angle is

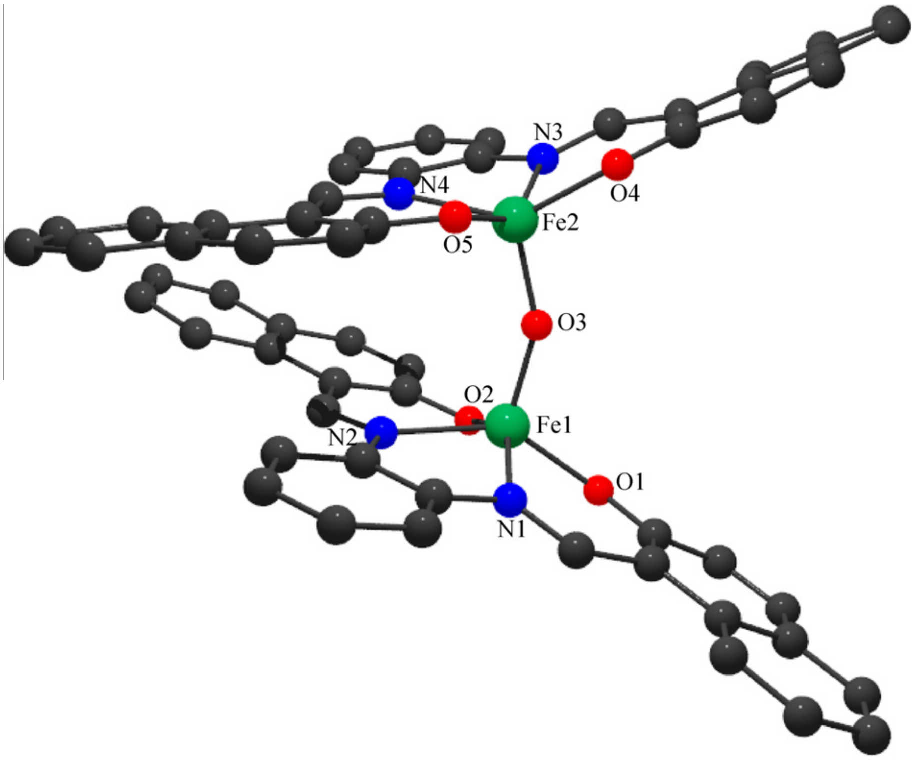


Fig. 8. Perspective view of compound **5**. Hydrogen atoms and dichloromethane molecules have been omitted for clarity.

175.07(19)° and the two imidazole rings are almost orthogonal to each other. The deviations of all the coordinating atoms in the basal plane, O(1), O(2), N(1) and N(2), from the mean plane passing through them are 0.018, −0.018, 0.020 and −0.020 Å respectively, and that of Fe(1) from the same plane is 0.036 Å. Selected bond lengths and bond angles of compound **3** are given in Table 2.

The compound forms two symmetry related hydrogen bonds, one between the H(5A) atom attached to N(5) and the (1 − *x*, −*y*, 1 − *z*) O(3) atom and another between the H(6A) atom attached to N(6) and the (2 − *x*, 1 − *y*, 1 − *z*) O(7) atom to form a H-bonded supramolecular dimer (Fig. 6). Details of the H-bonding are given in Table 4.

3.3.4. [(μ-O){Fe(vanophen)}$_2$]·2H$_2$O (**4**)

Compound **4** is an oxo-bridged dinuclear Fe(III) compound. It crystallizes in the triclinic space group $P\bar{1}$. Each Fe(III) center has a five coordinated square pyramidal geometry. The basal plane of the square pyramid is formed by N_2O_2 donors from the {(vanophen)$^{2-}$} ligand and the axial position is occupied by a bridging oxygen atom (Fig. 7). It is worth mentioning here that H$_2$vanophen is a compartmental, potentially hexadentate N_2O_4 ligand. In the present compound, only the N_2O_2 compartment is occupied by Fe(III), keeping the O_4 compartment vacant. The axial Fe(1)–O(3) and Fe(2)–O(3) bond lengths are 1.760(3) and 1.779(3) Å respectively. The Fe(1)–O(3)–Fe(2) angle is 154.3(2)°. The trigonality indices, $\tau = (\alpha - \beta)/60$ (where α and β are the two largest L–M–L angles of the coordination sphere) [50], have been calculated for the two pentagonal Fe(III) sites. $\tau = 0.21$ for Fe(1) and $\tau = 0.19$ for the Fe(2) center, confirming the square pyramidal character of both sites ($\tau = 0$ infers a perfect square pyramid and $\tau = 1$, a perfect trigonal bipyramid). The Fe–Fe distance is 3.448 Å in the μ-oxo dimer. The deviations of the coordinating atoms O(1), O(2), N(1) and N(2) from the mean basal plane passing through them are 0.100, −0.100, −0.107 and 0.108 Å respectively, and that of Fe(1) from the same plane is 0.544 Å. Similarly, the deviations of the coordinating atoms O(4), O(5), N(3) and N(4) from the mean basal plane passing through them are −0.090, 0.091, 0.098 and −0.098 Å respectively, and that of Fe(2) from the same plane is 0.523 Å. The bond lengths and bond angles are given in Table 3.

Table 5
Electrochemical data of the iron(III) centers of the compounds.

Compound	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	ΔE_p (V)
1	−1.31	−1.07	−1.185	0.24
2	−1.27	−1.01	−1.14	0.26
3	−0.35	−0.15	−0.20	0.20
4	−1.10	−0.58	−0.84	0.52
5	−1.14	−0.57	−0.85	0.57

$E_{1/2}$ is calculated as the average of the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials; $\Delta E_p = (E_{pa} - E_{pc})$.

3.3.5. [(μ-O){Fe(naphophen)}$_2$]. 2CH$_2$Cl$_2$ (**5**)

Compound **5** is a dinuclear Fe(III) molecule. It crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit contains two CH_2Cl_2 molecules in the crystal lattice. Both the Fe(III) centers have a five coordinated square-pyramidal geometry, in which N_2O_2 donors from the {(naphophen)$^{2-}$} ligand form the basal plane and the axial position is coordinated by a bridging O atom (Fig. 8). The Fe(1) center is equatorially coordinated by the O(1), O(2), N(1) and N(2) atoms and axially by the O(3) atom. Similarly, the Fe(2) center equatorially coordinated by the O(4), O(5), N(3) and N(4) atoms and axially by the O(3) atom. The τ value for the Fe(1) and Fe(2) centers are 0.07 and 0.04 respectively, confirming the square pyramidal character of both sites. The Fe–Fe distance is 3.455 Å in μ-oxo dimer. The mean Fe–O (naphophen) bond distance is around 1.933 Å. The mean Fe–O (bridge) distance is 1.776 Å, which is shorter than the mean Fe–O (naphophen) distance. The Fe(1)–O(3)–Fe(2) angle is 153.1(3)°. The deviations of the coordinating atoms O(1), O(2), N(1) and N(2) from the mean basal plane passing through them are 0.041, −0.041, −0.044 and 0.044 Å and those of O(4), O(5), N(3) and N(4) from the mean basal plane passing through them are −0.016, 0.016, 0.017 and 0.016 Å. The Fe(1) and Fe(2) centers are about 0.590 and 0.604 Å respectively above the plane of the N_2O_2 ligands. Selected bond lengths and bond angles are given in Table 3.

4. Cyclic voltammetry studies

The redox properties of all five Fe(III) compounds exhibit grossly similar features, consisting of a quasi-reversible Fe^{III}/Fe^{II} reduction. The criteria of reversibility were checked by observing the constancy of the peak–peak separation ($\Delta E_p = E_{pa} - E_{pc}$) and the ratio of peak heights ($i_{pa}/i_{pc} \sim 1$) with variation of scan rates [51]. The single-electron nature of the voltammograms has been confirmed by a comparison of the current heights for the compounds and that of a simple $[Fe(bipy)_3]^{2+}$ compound under identical conditions [52]. It has been observed that no well defined oxidative or reductive responses could be observed on running further to positive or negative potential. The $E_{1/2}$ and ΔE_p values for these redox couples are given in Table 5. All the redox signals remain virtually invariant under different scan rates (0.01–1.0 V s^{-1}) in the temperature range 300–280 K. Solvent dependent shifts and changes in electrochemical reversibility of the redox couples are not noteworthy.

5. Conclusion

In summary, three six-coordinated monomeric and two five-coordinated oxo-bridged dimeric Fe(III) compounds with salen-type Schiff bases have been synthesized and characterized. Fe(III) Schiff base compounds have a common tendency to form μ-oxo dimers in the presence of H_2O (pH > 7). In absence of azide, thiocyanate or imidazole etc., a μ-oxo dimer is formed as the major product. The presence of a measured excess of azide, thiocyanate or imidazole reagent favors the formation of hexa-coordinated monomeric compounds **1**, **2** and **3**. Two oxo-bridged dimers, **4** and **5**, are also reported in this paper. On the other hand, the percentage yield of the μ-oxo dimer increases when NaOH solution is used to increase the pH of the medium. Details of a systematic study of the synthesis of oxo-bridged dimeric and hexa-coordinated monomeric Fe(III) compounds with salen type Schiff bases has also not been carried out before the present work. Thus this work opens up a new outlook in tilting the balance between hexa-coordinated monomeric and oxo-bridged dimeric Fe(III) compounds with salen type Schiff bases.

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Appendix A. Supplementary data

CCDC 838744 (for **1**), 838745 (for **2**), 870309 (for **3**), 870310 (for **4**) and 870311 (for **5**) contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.08.085.

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