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Iron carbonyl complexes from 2-[2,3-diaza-4-(2-thienyl)buta-1,3-dienyl]thiophene: N–N bond cleavage and cyclometalation

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Abstract

When thienyl Schiff base **1**, derived from 2-formylthiophene and hydrazine, reacted with $Fe_2(CO)_9$ in *n*-hexane, three major complexes were obtained: (1) a diironhexacarbonyl complex with two 2-thienylmethylideneamido bridging ligands **2**, which resulted from the =N–N= bond cleavage of ligand **1**; (2) a doubly cyclometalated di-μ-di-(η^1:η^2-thienyl; η^1:η^1(*N*))bis(hexacarbonyldiiron) complex (**3**); and (3) a cyclometalated (μ-η^1:η^2-thienyl; η^1:η^1(*N*))hexacarbonyldiiron complex (**4**). Molecular structures of compounds **1a**, **1c**, and **2a** have been determined by single-crystal X-ray diffraction.

Keywords: Iron carbonyl complexes; Conjugated diimine; Cyclometalation; N–N Bond activation

1. Introduction

In the past decades, transition-metal mediated activation of C–H bond remains one of the most prominent challenges in organometallic chemistry. Cyclometalation is one of the classical ways used to activate C–H bond in hetero-substituted organic molecules [1]. It is well known that N-donor ligands have a strong tendency to give five-membered metallacycle [2] and Schiff base ligands are the compound of choice to study cyclometalation reactions due to their strong tendency to give *endo* cyclometalated derivatives [3].

The study of reactivity of organic molecules linked to binuclear transition-metal (e.g. diiron) complexes has received a great deal of attention during past years. With the possibility of donating from two to eight electrons, via the N lone-pairs, the C=N π-electrons, conjugated diimine ligands are known to behave a very versatile coordination property to the bonded metal center [4].

We report here the preparation and characterization of hexacarbonyldiiron complexes to which the ligand bridges the diiron (Fe–Fe) unit(s) through thienyl imine group(s) or imine nitrogen groups. The original ligand is a Schiff base derived from 2-formylthiophene and hydrazine, which undergoes nitrogen–nitrogen bond cleavage, cyclometalation, and double cyclometalation during the course of reaction with $Fe_2(CO)_9$. The choice of heterocyclic Schiff base stems from our interest in the synthesis and finding the reactivity of newly synthesized diiron complexes as well as their biological aspects [5]. The (μ-η^1:η^2-thienyl; η^1:η^1(*N*))hexacarbonyldiiron complexes and di-μ-di-(η^1:η^2-thienyl; η^1:η^1(*N*))bis(hexacarbonyldiiron) complexes show a unique binding mode to which the β-carbon and a C=C π bond of the bridging thiophene(s) and the imine nitrogen atom(s) all are coordinated to the diiron (Fe–Fe) unit(s).

Furthermore, the N–N bond activation in various types of organic ligands is important for its relevance especially to catalysis and organic synthesis in general. However, the metal-mediated N–N bond cleavage reactions are not so many [6]. Products resulting from the metal-mediated C–H activation and N–N activation in the reactions were observed and reported herein.

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Table 1
Crystal and data collection parameters for compounds **1a**, **1c**, and **2a**

Compound	**1a**	**1c**	**2a**
Empirical formula	$C_{10}H_8N_2S_2$	$C_{12}H_{12}N_2S_2$	$C_{16}H_8Fe_2N_2O_6S_2(C_3H_6O)_{0.4}$
Formula weight	220.31	248.36	523.29
Temperature (K)	296	298	298
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)
Unit cell dimensions			
a (Å)	9.762(2)	7.7009(9)	20.380(4)
b (Å)	11.376(1)	7.5963(6)	8.070(1)
c (Å)	9.830(1)	11.0835(6)	26.771(4)
β (°)	100.82(1)	93.909(6)	95.73(1)
V (Å^3)	1072.2(3)	646.86(9)	4381(1)
Z	4	2	8
D_{calc} (g cm^{-3})	1.365	1.275	1.587
F_{000}	456.00	260.00	2102.40
Crystal size (mm)	$0.28 \times 0.36 \times 0.72$	$0.60 \times 0.80 \times 0.90$	$0.40 \times 0.70 \times 0.80$
$2\theta_{max}$ (°)	50.5	50.0	55.1
Scan type	ω–2θ	ω–2θ	ω–2θ
No. of reflns meads: total, unique	2113, 1992	1327, 1233	5578, 5420
No. of obsd reflns ($I > 3.00\sigma(I)$)	1057	968	3782
No. of variables	127	73	261
μ (Mo–K$_\alpha$) (cm^{-1})	4.65	3.70	15.50
R	0.080	0.035	0.034
Rw	0.060	0.026	0.029

2. Results and discussion

The thienyl Schiff bases **1a**, **1b**, and **1c** were prepared by condensation of 2-formylthiophene derivatives with hydrazine in anhydrous methanol. These compounds were fully characterized as described in the Section 2. The structures of compounds **1a** and **1c** were further confirmed by single-crystal X-ray analysis. Crystal and data collection parameters are shown in Table 1. Their crystal structures are shown in Figs. 1 and 2, respectively. Selected bond distances and angles are tabulated in Table 2. The geometries of both **1a** and **1c** are well planar and packed in pair in their unit cells. However, the corresponding bond lengths and angles between two **1a** molecules in the pair are different.

The thienyl Schiff base 2-[2,3-diaza-4-(2-thienyl)buta-1,3-dienyl]thiophene (**1a**), reacts with diiron nonacarbonyl in *n*-hexane to give three iron carbonyl complexes, which we formulated as **2a**, **3a**, and **4a**, respectively, as the major products (Scheme 1).

The product **2a** is a reddish orange solid. Its ^{1}H-NMR spectrum shows four sets of signal with the same pattern as that of ligand **1a**, indicating that two thienyl rings as well as two imines in the complex are in the

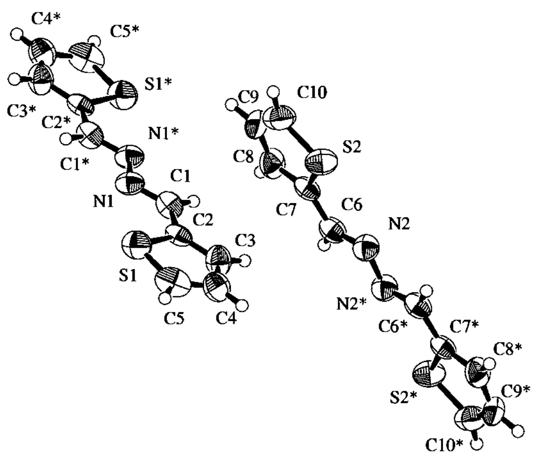


Fig. 1. ORTEP diagram of compound **1a** at the 30% probability level.

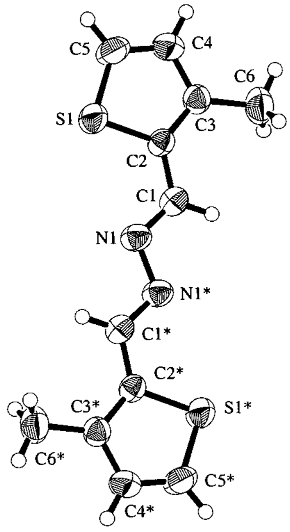


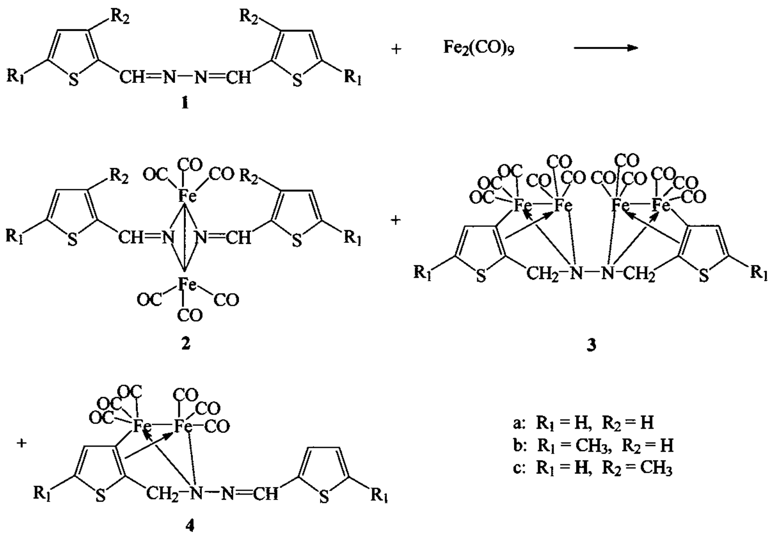
Fig. 2. ORTEP diagram of compound **1c** at the 30% probability level.

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

Compound	1a	1c	2a
Bond lengths			
N(1)–N(1*)–N(2)–N(2*)	1.44(1)–1.40(1)	1.412(3)	N(1)···N(2) 2.395
N(1)–C(1)–N(2)–C(6)	1.286(10)–1.27(1)	1.277(2)	1.262(4)–1.267(4)
C(1)–C(2)–C(6)–C(7)	1.44(1)–1.44(1)	1.430(2)	1.456(4)–1.450(4)
Fe(1)–Fe(2)			2.4349(6)
Fe(1)–N(1)–Fe(2)–N(1)			1.925(2)–1.922(2)
Fe(1)–N(2)–Fe(2)–N(2)			1.915(3)–1.917(2)
Fe(1)–C(11)–Fe(2)–C(14)			1.792(4)–1.804(4)
Fe(1)–C(12)–Fe(2)–C(15)			1.801(4)–1.803(4)
Fe(1)–C(13)–Fe(2)–C(16)			1.807(4)–1.794(4)
Bond angles			
N(1*)–N(1)–C(1)–N(2*)–N(2)–C(6)	110.5(9)–110.8(9)	112.1(2)	
N(1)–C(1)–C(2)–N(2)–C(6)–C(7)	121.9(8)–122.8(8)	121.7(2)	128.1(3)–128.1(3)
Fe(1)–N(1)–Fe(2)–Fe(1)–N(2)–Fe(2)			78.55(9)–78.9(1)
Fe(2)–Fe(1)–N(1)–Fe(2)–Fe(1)–N(2)			50.67(7)–50.59(7)
Fe(1)–Fe(2)–N(1)–Fe(1)–Fe(2)–N(2)			50.79(7)–50.52(8)
N(1)–Fe(1)–N(2)–N(1)–Fe(1)–N(2)			77.2(1)–77.2(1)
Fe(1)–N(1)–C(1)–Fe(2)–N(2)–C(6)			136.4(2)–135.3(2)
Fe(2)–N(1)–C(1)–Fe(1)–N(2)–C(6)			145.0(2)–145.8(2)

same chemical environment. Although three sets of thienyl protons show a little shift, the signal corresponding to the imine proton down field shifts from δ 8.80 to 9.26 ppm (ligand **1a**). In its IR spectrum, while the C=N stretching shifted from 1608 to 1614 cm^{-1} in **1a**, there are three sharp and intense C=O stretches appearing at 2067, 2029, and 1984 cm^{-1}. The fragmentation pattern of its mass spectrum shows no evidence of peak with m/e value of 220, corresponding to ligand **1a**. However, peaks at m/e 110 and 111 were observed accompany with the presence of a molecular ion peak at m/e 500 and six peaks corresponding to sequential CO loss products, in accordance with the formulated structure.

The structure of **2a** was further confirmed by the single crystal X-ray analysis. Its crystal and data collection parameters are shown in Table 1. The structure of **2a**, in two stereo views, is shown in Fig. 3 [7]. Selected bond distances and angles are tabulated in Table 2. The structure, as shown in the figure, contains two 2-thienylmethylideneamido groups which bridge two $Fe(CO)_3$ units through nitrogen atoms. From this it is clear that the N–N bond in ligand **1a** had been cleaved during the coordination reaction and the nonbonded N···N distance is 2.395 Å. The configuration of the individual molecule has idealized two-fold symmetry. The tricarbonyl groups are eclipsed. The nitrogen and iron atoms form a tetrahedron. The central position of



Scheme 1.

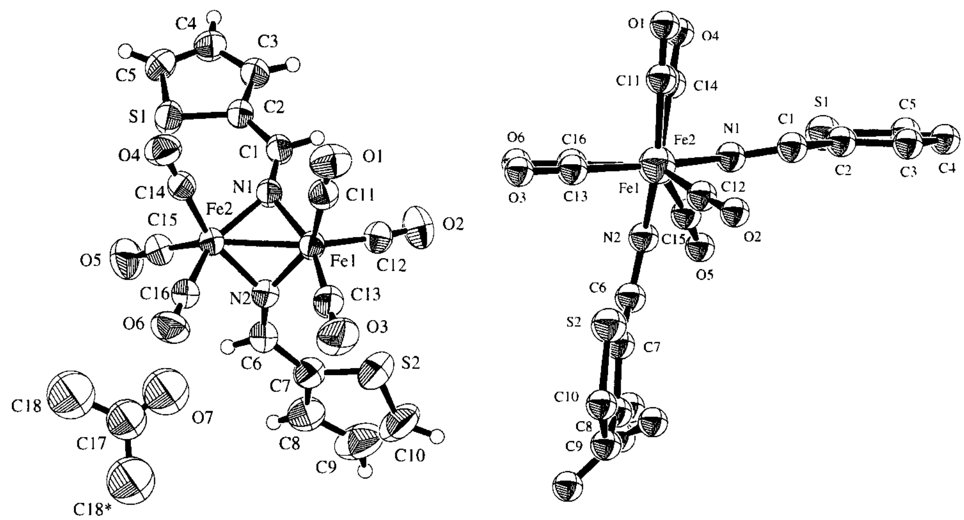


Fig. 3. ORTEP diagrams of compound **2a** in two stereo-views at the 30% probability level.

the molecule is thus similar in shape to that of $Co_2(CO)_8$. Plane calculations show that all pairs of atoms are equidistant from opposite side to the C_2 axis, which perpendicular to the mid-point of the Fe–Fe bond. Each iron center is coordinated by two nitrogen atoms and three carbonyls located at the corner of a distorted octahedron. The Fe–Fe distance is only 2.4349(6) Å which is shorter than usual for diiron complexes (2.5–2.7 Å) [8], but can be compared with the value found in some nitrogen-bridged diiron complexes [6e,9], and can be attributed to a distinct 'bent' iron–iron bond [10]. The bond distances between iron and bridging nitrogen are Fe(1)–N(1) 1.925(2) Å, Fe(1)–N(2) 1.915(3) Å, Fe(2)–N(1) 1.922(2) Å, and Fe(2)–N(2) 1.917(2) Å, respectively, which are shorter than those reported nitrogen bridged diiron complexes [6e, 8e–g, 9]. The significantly shorter averaged Fe–N bond distance of 1.92 Å in this complex can be ascribed to the structure possessing two three-coordinated trigonal-like, instead of four-coordinated tetrahedral-like, bridging nitrogen atoms, and the nitrogen atoms of the complex can be considered as sp^2 hybridized [11]. The bond distances between C(1) and N(1) as well as C(2) and N(2) are 1.262(4) and 1.267(4) Å, respectively, which are shorter than the C=N bond distance in **1a** (1.27(1)–1.286(10) Å), and yet are still in the range of usual bond length of imine double bond. In the central Fe_2N_2 system, the averaged Fe–N–Fe bond angle is 78.7° and the averaged N–Fe–Fe bond angle is 50.64°. The dihedral angle between the two planes each formed by the two iron atoms and one bridging nitrogen atom is 107.58°. The bond angles of Fe(1)–N(1)–C(1), Fe(2)–N(1)–C(1), Fe(1)–N(2)–C(6), and Fe(2)–N(2)–C(6) are 136.4(2), 145.0(2), 145.8(2), and 135.3(2)°, respectively. These large angles are associated with the short Fe–Fe bond length and the sp^2 hybridization of nitrogen atoms.

The cleavage of the N–N bond during the course of ligand coordination to form bridges through three-electron-donor nitrogen atoms might decrease the electron density on the methine group that explains why there is a 0.46 ppm down field chemical shift of the imine protons in its ^{1}H-NMR spectrum. On the other hand, relative to the highly conjugated ligand, the bond order of the imine group in the complex might increase due to the rupture of the N–N bond and the formation of the iminato-bridged complex that decreases the degree of conjugation on the iminato ligand. The IR stretching absorption of the C=N group is 1608 cm^{-1} in ligand **1a** which is higher energy shifted to 1614 cm^{-1} in iminato-bridged complex and is confirmed by the shortening of the C=N bond length.

The orange product **3a** is a novel doubly cyclometalated tetrairon complex. The ^{1}H-NMR spectrum of **3a** shows the absence of the methine proton (resonance at δ 8.80 ppm in **1a**) and has three sets of signal with a ratio of 1:1:2. In the aromatic region, two doublet signals appear at δ 7.67 and 7.42 ppm with a coupling constant $J_{H-H} = 5.1$ Hz, indicating only the protons on the α′- and β′-carbon of the thienyl ring are left. The most significant feature for this complex is the resonance representing the methylene group that is formed during the reaction and is observed at δ 4.21 ppm in its ^{1}H-NMR and at δ 64.9 ppm in its ^{13}C-NMR spectrum. The singlet signal of the methylene protons indicates that two protons are equivalent [8f, 8g, 8i, 9f, 9h–k, 12]. In its IR spectrum, while the C=N stretching is absent, there are three sharp and intense C=O stretches appearing at 2068, 2042, and 1972 cm^{-1}. This result presumably is due to the coordination of each imine nitrogen of the thienyl Schiff base to one of the iron centers of each of two diiron carbonyl moieties, cyclometalation occurs at the β-carbon site of each thienyl ring and followed by the 1,3-hydrogen shift, and each methine carbon becomes a methylene by accepting the hydride that was removed from the β-carbon. The mass spectrum of the product contains a signal for the molecular ion at $m/e = 780$ and 12 peaks corresponding to the fragments with sequential loss of CO from this molecular ion, in accordance with the formulated structure. A signal for the symmetrically N–N bond cleaved ion at m/e 390 and six peaks corresponding to the stepwise loss of six CO groups from the N–N bond cleaved ion are also found in the same spectrum. In complex **3a**, each of two thienyl rings in the organic ligand serves as a three-electron donor and bridges to two iron centers of each diiron carbonyl moieties to furnish a μ-η^1:η^2-thienyl mode of coordination. Each nitrogen atom also serves as another three-electron donor and bridges to two iron centers of each diiron carbonyl moieties.

The ^{1}H-NMR spectrum of the red product **4a** shows one methine proton at δ 8.25 ppm and two methylene protons at δ 4.54 ppm in addition to the five sets of thienyl protons in the range of δ 7.77–7.11 ppm. Among the five sets of thienyl protons, three are doublet with a coupling constant $J_{H-H} = 5.1$ Hz, one is a doublet with a coupling constant $J_{H-H} = 3.6$ Hz, and another set is a doublet of doublet with coupling constants $J_{H-H} =$ 5.1 and 3.6 Hz, respectively. This result indicates that a β-proton on one of the thienyl rings disappeared and an extra proton added to one of the methine carbon to make it become a methylene group during the course of ligand coordination. The IR spectrum of the complex shows a characteristic C=N stretching at 1597 cm^{-1} and three sharp and intense C=O stretches at 2067, 2028, and 1986 cm^{-1}. The mass spectrum of **4a** shows the molecular ion peak and the complete loss of six CO ligands in a sequential manner, in accordance with the formulated structure. In contrast to complex **3a**, complex **4a** is a diiron hexacarbonyl complex with cyclometalation occurring only on one of the two thienylmethylidene moieties.

A similar result was found from the reaction of 5-methyl-2-[2,3-diaza-4-(5-methyl-2-thienyl)buta-1,3-dienyl]thiophene (**1b**), with diiron nonacarbonyl under exactly the same reaction condition as that of **1a**. An iron carbonyl complex with N–N bond cleaved ligand **2b**, and two cyclometalated complexes **3b** and **4b**, were isolated as shown in Scheme 1. Complexes **2b**, **3b**, and **4b** were characterized to be spectrally and structurally similar to that of complexes **2a**, **3a**, and **4a**, respectively. While the yield of **4b** is much lower than that of **4a**, the yields of **2b** and **3b** are higher than that of **2a** and **3a**. The product yield of **2b** is twice as much as that of **2a**. Obviously, the inductive effect of the methyl substituents on the α′-carbon of the thienyl rings encouraged the rupture of the =N–N= bond during the course of reaction. The formation of product **3b** also gets benefit from the same effect.

The reaction of 3-methyl-2-[2,3-diaza-4-(3-methyl-2-thienyl)buta-1,3-dienyl]thiophene (**1c**), in which the β-positions of thienyl rings are blocked with methyl substituents, with diiron nonacarbonyl gives only the N–N bond cleaved iron carbonyl complex **2c**. The product yield of **2c** is lower than that of **2a** and **2b** and might be attributed to the steric hindrance of the methyl substituents on the β-position of the thienyl rings.

3. Experimental

Diiron nonacarbonyl was prepared by photolysis of iron pentacarbonyl (Aldrich) in glacial acetic acid [13]. Solvents were dried (sodium–benzophenone, P_4O_{10}) and distilled under nitrogen prior to use. 2-Formylthiophene (Aldrich), 5-methyl-2-formylthiophene and 3-methyl-2-formylthiophene (Acres) were distilled by a Kugelrohr distillation apparatus under reduced pressure (0.1 mmHg) prior to use. All other chemicals were reagent grade and without further purification. The NMR spectra were recorded on a Varian VXR-300 NMR spectrometer (^{1}H, 299.95 MHz; ^{13}C, 75.43 MHz). Chemical shifts were referenced to TMS and deuterated acetone (Janssen) was used as a solvent and as a secondary reference. Mass spectra were obtained from a VG-Biotech Quattro 5022 spectrometer. IR spectra were recorded from a Bio-Rad FTS-40 spectrometer. Elemental analyses were performed using a Heraeus CHNO rapid analyzer. Crystals for X-ray diffraction were obtained from acetonitrile (**1a** and **1c**) or from acetone–dichloromethane mixed solution (**2a**). A single crystal was mounted on a glass fiber and the X-ray diffraction intensity data were measured on a Rigaku AFC7S diffractometer at room temperature.

*3.1. Synthesis of thienyl Schiff bases 2-[2,3-diaza-4-(2-thienyl)buta-1,3-dienyl]-thiophene (**1a**), 2-[2,3-diaza-4-(5-methyl-2-thienyl)buta-1,3-dienyl]-5-methylthiophene (**1b**), and 2-[2,3-diaza-4-(3-methyl-2-thienyl)buta-1,3-dienyl]-3-methylthiophene (**1c**)*

The synthesis of Schiff base employed the usual approach of condensation in alcohol solution [14]. 2-Formylthiophene, 5-methyl-2-formylthiophene, or 3-methyl-2-formylthiophene (40 mmol) and $N_2H_4 \cdot H_2O$ (Acros, 20 mmol) were heated at reflux in 95% ethanol (E. Merck, 100 ml) for 24 h. The solvent was removed by filtration. The precipitate was washed with several portions of ether to give pure yellow product.

*3.1.1. Compound **1a***

96% yield. m.p. 148–149 °C. ^{1}H-NMR: δ 8.80 (s, 2H), 7.69 (d, $J_{H-H} = 5.1$ Hz, 2H), 7.60 (d, $J_{H-H} = 3.6$

Hz, 2H), 7.20 (dd, $J_{H–H}$ = 3.6, 5.1 Hz, 2H). ^{13}C-NMR: δ 156.6, 140.1, 134.0, 131.2, 128.9. IR (KBr film) $\nu_{C=N}$: 1608 cm^{-1}. MS (FAB): *m/e* 220 (M^+). Anal. Calc. for $C_{10}H_8N_2S_2$: C, 54.55; H, 3.64; N, 12.73; S, 29.10. Found: C, 54.54; H, 3.70; N, 12.72; S, 29.12%.

3.1.2. Compound **1b**

97% yield. m.p. 138–139 °C. ^{1}H-NMR: δ 8.60 (s, 2H), 7.30 (d, $J_{H–H}$ = 3.6 Hz, 2H), 6.84 (d, $J_{H–H}$ = 3.6 Hz, 2H), 2.51 (s, 6H). ^{13}C-NMR: δ 155.0, 145.3, 136.5, 133.2, 126.3, 14.5. IR (KBr film) $\nu_{C=N}$: 1606 cm^{-1}. MS (FAB): *m/e* 248 (M^+). Anal. Calc. for $C_{12}H_{12}N_2S_2$: C, 58.06; H, 4.84; N, 11.29; S, 25.81. Found: C, 58.02; H, 4.88; N, 11.22; S, 25.78%.

3.1.3. Compound **1c**

95% yield. m.p. 148–150 °C. ^{1}H-NMR: δ 8.80 (s, 2H), 7.56 (d, $J_{H–H}$ = 5.1 Hz, 2H), 7.00 (d, $J_{H–H}$ = 5.1 Hz, 2H), 2.45 (s, 6H). ^{13}C-NMR: δ 154.9, 143.7, 133.7, 132.0, 130.2, 14.1. IR (KBr film) $\nu_{C=N}$: 1600 cm^{-1}. MS (FAB): *m/e* 248 (M^+). Anal. Calc. for $C_{12}H_{12}N_2S_2$: C, 58.06; H, 3.84; N, 11.29; S, 25.81. Found: C, 58.07; H, 4.85; N, 11.26; S, 25.80%.

3.2. Reaction of Schiff base **1** with $Fe_2(CO)_9$ in n-hexane

In a typical reaction, 8.0 mmol of compound **1** in 30 ml of anhydrous *n*-hexane was added gradually to a 70 ml of anhydrous *n*-hexane solution containing 30.0 mmol of $Fe_2(CO)_9$ in the dark under nitrogen and the reaction mixture was refluxed for 6 h. The reaction mixture was filtered through Celite 545 and the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column with *n*-hexane as eluent to separate the reddish orange product **2**, orange product **3**, and red product **4**. Substantial amount of $Fe_3(CO)_{12}$ was also collected.

3.2.1. Reaction of **1a** with $Fe_2(CO)_9$ to give di-μ-(2-thienylmethylideneamido)bis(tricarbonyliron) (**2a**), [di-μ-N,N′-1,2-bis((((2,3-η^1:η^2)-2-thienyl)methyl)-η^1:η^1(N))-diaza]bis(hexacarbonyldiiron) (**3a**), and (μ-N-(((2,3-η^1:η^2)-2-thienyl)methyl)-η^1:η^1(N)-2-thienylmethylidenehydrazonato]hexacarbonyldiiron (**4a**)

Complex **2a**: 21.5% yield; m.p. 124–125 °C. ^{1}H-NMR: δ 9.26 (s, 2H), 7.79 (d, $J_{H–H}$ = 4.8 Hz, 2H), 7.45 (d, $J_{H–H}$ = 3.6 Hz, 2H), 7.23 (d, $J_{H–H}$ = 3.6, 4.8 Hz, 2H). ^{13}C-NMR: δ 212.0, 167.2, 141.8, 132.1, 130.5, 128.8. IR ($CHCl_3$) $\nu_{C=N}$: 1608 cm^{-1}, $\nu_{C=O}$: 2067, 2029, 1984 cm^{-1}. MS (FAB): *m/e* 500 (M^+), 472 (M^+ − CO), 444 (M^+ − 2CO), 416 (M^+ − 3CO), 388 (M^+ − 4CO), 360 (M^+ − 5CO), 332 (M^+ − 6CO), 276 (M^+ − 6CO − Fe), 110 (L^+/2). Anal. Calc. for $Fe_2C_{16}H_8N_2O_6S_2$: C, 38.40; H, 1.60; N, 5.60; S, 12.80. Found: C, 38.36; H, 1.63; N, 5.62; S, 12.83%. Complex **3a**: 10.8% yield; m.p. 61 − 62 °C. ^{1}H-NMR: δ 7.69 (d, $J_{H–H}$ = 5.1 Hz, 2H), 7.42 (d, $J_{H–H}$ = 5.1 Hz, 2H), 4.21 (s, 4H). ^{13}C-NMR: δ 211.8, 154.8, 140.5, 132.2, 115.6, 64.9. IR ($CHCl_3$) $\nu_{C=O}$: 2068, 2024, 1972 cm^{-1}. MS (FAB): *m/e* 780 (M^+), 752 (M^+ − CO), 724 (M^+ − 2CO), 696 (M^+ − 3CO), 668 (M^+ − 4CO), 640 (M^+ − 5CO), 612 (M^+ − 6CO), 584 (M^+ − 7CO), 556 (M^+ − 8CO), 528 (M^+ − 9CO), 500 (M^+ − 10CO), 472 (M^+ − 11CO), 444 (M^+ − 12CO), 388 (M^+ − 12CO − Fe), 332 (M^+ − 12CO − 2Fe), 276 (M^+ − 12CO − 3Fe), 220 (L^+), 390 (M^+/2), 362 (M^+/2 − CO), 334 (M^+/2 − 2CO), 306 (M^+/2 − 3CO), 278 (M^+/2 − 4CO), 250 (M^+/2 − 5CO), 222 (M^+/2 − 6CO), 166 (M^+/2 − 6CO − Fe), 110 (L^+/2). Anal. Calc. for $Fe_4C_{22}H_8N_2O_{12}S_2$: C, 33.85; H, 1.03; N, 3.59; S, 8.21. Found: C, 33.82; H, 1.06; N, 3.61; S, 8.26%. Complex **4a**: 18.5% yield; m.p. 89 − 90 °C. ^{1}H-NMR: δ 8.25 (s, 1H), 7.77 (d, $J_{H–H}$ = 5.1 Hz, 1H), 7.58 (d, $J_{H–H}$ = 5.1 Hz, 1H), 7.45 (d, $J_{H–H}$ = 5.1 Hz, 1H), 7.42 (d, $J_{H–H}$ = 3.6 Hz, 1H), 7.11 (d, $J_{H–H}$ = 3.6, 5.1 Hz, 1H), 4.54 (s, 2H). ^{13}C-NMR: δ 211.2, 154.3, 145.3, 140.6, 139.7, 132.8, 131.9, 130.2, 128.7, 117.0, 68.7. IR ($CHCl_3$) $\nu_{C=N}$: 1597 cm^{-1}, $\nu_{C=O}$: 2066, 2026, 1981 cm^{-1}. MS (FAB): *m/e* 500 (M^+), 472 (M^+ − CO), 444 (M^+ − 2CO), 416 (M^+ − 3CO), 388 (M^+ − 4CO), 360 (M^+ − 5CO), 332 (M^+ − 6CO), 276 (M^+ − 6CO − Fe), 220 (L^+). Anal. Calc. for $Fe_2C_{16}H_8N_2O_6S_2$: C, 38.40; H, 1.60; N, 5.60; S, 12.80. Found: C, 38.41; H, 1.62; N, 5.63; S, 12.76%.

3.2.2. Reaction of **1b** with $Fe_2(CO)_9$ to give di-μ-(5-methyl-2-thienylmethylideneamido)bis(tricarbonyliron) (**2b**), [di-μ-N,N′-1,2-bis((((2,3-η^1:η^2)-5-methyl-2-thienyl)methyl)-η^1:η^1(N))-diaza]bis(hexacarbonyldiiron) (**3b**), and [μ-N-(((2,3-η^1:η^2)-5-methyl-2-thienyl)methyl)-η^1:η^1(N)-5-methyl-2-thienylmethylidenehydrazonato]hexacarbonyldiiron (**4b**)

Complex **2b**: 44.7% yield; m.p. 140 °C (dec.). ^{1}H-NMR: δ 9.10 (s, 2H), 7.22 (d, $J_{H–H}$ = 3.6 Hz, 2H), 6.90 (d, $J_{H–H}$ = 3.6 HZ, 2H), 2.57 (s, 6H). ^{13}C-NMR: δ 211.7, 166.5, 145.0, 139.2, 132.0, 126.5, 15.2. IR ($CHCl_3$) $\nu_{C=N}$: 1614 cm^{-1}, $\nu_{C=O}$: 2065, 2027, 1982 cm^{-1}. MS (FAB): *m/e* 528 (M^+), 500 (M^+ − CO), 472 (M^+ − 2CO), 444 (M^+ − 3CO), 316 (M^+ − 4CO), 388 (M^+ − 5CO), 360 (M^+ − 6CO), 304 (M^+ − 6CO − Fe), 124 (L^+/2). Anal. Calc. for $Fe_2C_{18}H_{12}N_2O_6S_2$: C, 40.91; H, 2.27; N, 5.30; S, 12.12. Found: C, 40.89; H, 2.30; N, 5.31; S, 12.16%. Complex **3b**: 14.6% yield. ^{1}H-NMR: δ 7.07 (s, 2H), 4.11 (s, 4H), 2.45 (s, 6H). ^{13}C-NMR: δ 211.9, 158.7, 147.3, 137.6, 119.3, 65.3, 15.9. IR ($CHCl_3$) $\nu_{C=O}$: 2065, 2022, 1978 cm^{-1}. MS (FAB): *m/e* 808 (M^+), 780 (M^+ − CO), 752 (M^+ − 2CO), 724 (M^+ − 3CO), 696 (M^+ − 4CO), 668 (M^+ − 5CO), 640 (M^+ − 6CO), 612 (M^+ − 7CO), 584 (M^+ − 8CO), 556 (M^+ − 9CO), 528 (M^+ − 10CO), 500 (M^+ − 11CO), 472 (M^+ − 12CO), 416 (M^+ − 12CO − Fe), 360 (M^+ − 12CO − 2Fe), 304 (M^+ − 12CO − 3Fe), 248 (L^+), 404 (M^+/2), 366 ($M^+/2-CO$), 348 ($M^+/2-2CO$), 320 ($M^+/2-3CO$), 292 ($M^+/2-4CO$), 264 ($M^+/2-5CO$), 236 ($M^+/2-6CO$), 180 ($M^+/2-6CO-Fe$), 124 ($L^+/2$). Anal. Calc. for $Fe_4C_{24}H_{12}N_2O_{12}S_2$: C, 35.64; H, 1.49; N, 3.47; S, 7.92. Found: C, 35.58; H, 1.52; N, 3.50; S, 7.94%. Complex **4b**: 6.8% yield. ^{1}H-NMR: δ 8.09 (s, 1H), 7.20 (d, $J_{H–H}=3.6$ Hz, 1H), 7.09 (s, 1H), 6.79 (d, $J_{H–H}=3.6$ Hz, 1H), 4.42 (s, 2H), 2.49 (s, 3H), 2.46 (s, 3H). ^{13}C-NMR: δ 211.3, 158.6, 147.9, 145.3, 137.8, 137.4, 132.4, 127.7, 127.2, 113.5, 69.3, 15.8, 15.7. IR ($CHCl_3$) $\nu_{C=N}$: 1596 cm^{-1}, $\nu_{C=O}$: 2065, 2025, 1983 cm^{-1}. MS (FAB): m/e 528 (M^+), 550 (M^+-CO), 472 (M^+-2CO), 444 (M^+-3CO), 416 (M^+-4CO), 388 (M^+-5CO), 360 (M^+-6CO), 304 ($M^+-6CO-Fe$), 248 (L^+). Anal. Calc. for $Fe_2C_{18}H_{12}N_2O_6S_2$: C, 40.91; H, 2.27; N, 5.30; S, 12.12. Found: C, 40.95; H, 2.29; N, 5.29; S, 12.10%.

*3.2.3. Reaction of **1c** with $Fe_2(CO)_9$ to give di-μ-(3-methyl-2-thienylmethylideneamido)-bis(tricarbonyliron) (**2c**)*

Complex **2c**: 8.4% yield. ^{1}H-NMR: δ 9.27 (s, 2H), 7.68 (d, $J_{H–H}=5.1$ Hz, 2H), 7.03 (d, $J_{H–H}=5.1$ Hz, 2H), 2.37 (s, 6H). ^{13}C-NMR: δ 212.5, 165.8, 141.1, 135.0, 131.9, 129.5, 14.0. IR ($CHCl_3$) $\nu_{C=N}$: 1607 cm^{-1}, $\nu_{C=O}$: 2062, 2023, 1980 cm^{-1}. MS (FAB): m/e 528 (M^+), 500 (M^+-CO), 472 (M^+-2CO), 444 (M^+-3CO), 316 (M^+-4CO), 388 (M^+-5CO), 360 (M^+-6CO), 304 ($M^+-6CO-Fe$), 124 ($L^+/2$). Anal. Calc. for $Fe_2C_{18}H_{12}N_2O_6S_2$: C, 40.91; H, 2.27; N, 5.30; S, 12.12. Found: C, 40.92; H, 2.29; N, 5.32; S, 12.09%.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 163161 for compound **1a**, 163162 for compound **1c**, and 163163 for complex **2a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[7] The asymmetric unit cell contains one diiron complex and roughly 0.4 acetone molecule. The acetone molecule sits on a two-fold axis passing through O(7)–C(17) (the carbonyl group of acetone molecule). The H atoms on acetone molecule were not located and hence not put in for the final cycle of calculation. The site occupancy factor (s.o.f = 0.4) of acetone molecule was assigned to obtain reasonable temperature factors for the atoms in acetone molecule.
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