

# Novel iron carbonyl complexes from thiophene-2-carboxaldehyde thiosemicarbazone

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Received 13 August 2003; accepted 14 October 2003

## Abstract

The reaction of thiophene-2-carboxaldehyde thiosemicarbazone (2-C<sub>4</sub>H<sub>3</sub>SCHNNHC(S)NH<sub>2</sub>) (**1**) with diiron nonacarbonyl under mild conditions in anhydrous benzene yields three iron carbonyl organometallic clusters: (i) Fe<sub>2</sub>S<sub>2</sub> square-base pyramidal cluster **2** ([Fe(CO)<sub>3</sub>]<sub>3</sub>(μ<sub>3</sub>-S)<sub>2</sub>), (ii) Fe<sub>2</sub>S<sub>2</sub> square-base pyramidal metal carbene cluster **3** ([Fe(CO)<sub>3</sub>]<sub>2</sub>Fe(CO)<sub>2</sub>(μ<sub>3</sub>-S)<sub>2</sub>(C(NH<sub>2</sub>)NHNCH(2-C<sub>4</sub>H<sub>3</sub>S))), and (iii) double butterfly cluster **4** ([Fe(CO)<sub>3</sub>]<sub>3</sub>Fe(CO)<sub>2</sub>(μ<sub>4</sub>-S)(C,N; C(NH<sub>2</sub>)NHNCH(2-C<sub>4</sub>H<sub>3</sub>S)) (μ<sub>2</sub>-S, N; SC(NH<sub>2</sub>)NNCH(2-C<sub>4</sub>H<sub>3</sub>S))), and an octahedral complex **5** (Fe(CO)<sub>2</sub>(S, N; SC(NH<sub>2</sub>)NNCH(2-C<sub>4</sub>H<sub>3</sub>S))<sub>2</sub>). These products were fully characterized spectrally. The molecular structures of **1**, **3**, **4**, and **5** have been determined by single-crystal X-ray diffraction. © 2003 Elsevier B.V. All rights reserved.

## 1. Introduction

Metal complexes of thiosemicarbazones have been extensively investigated in last decades because of their structural feature and biological activity [1,2]. These complexes usually contain either main group metal or transition metal ion with various valancies, and the thiosemicarbazones usually bind to metal ion(s), either in the neutral thione form or in the anionic thiolate form, as N,S-donor or N,N-donor bidentate ligands forming five- or four-membered chelate rings. However, no metal carbonyl complex derived from thiosemicarbazones has ever been explored.

In the present work, which has emerged from our continued interest in the synthesis and characterization of cyclometallated iron carbonyl complexes from thiophene contained Schiff bases [3], we report the preparation and characterization of mono-, tri-, and tetra-iron carbonyl complexes derived from thiophene-2-carboxaldehyde thiosemicarbazone. In these complexes the original ligand either (i) coordinates to an iron metal as a bidentate N,S-donor ligand, (ii) bridges to a diiron (Fe–Fe) unit via

(N,μ<sub>2</sub>-S) binding mode, (iii) undergoes C=S activation and coordinates to an iron as a carbene ligand; or (iv) undergoes C=S activation and bridges to a diiron (Fe–Fe) unit via (N,<sub>2</sub>C) bridging mode. No cyclometallation on the thienyl ring has been observed during the course of the reaction.

## 2. Results and discussion

### 2.1. Synthesis and structures

The thienyl Schiff base thiophene-2-carboxaldehyde thiosemicarbazone (**1**) was prepared by condensation of thiophene-2-carboxaldehyde with thiosemicarbazide in ethanol. It was fully characterized as described in Section 3 and its structure was further confirmed by the single-crystal X-ray analysis as shown in Fig. 1. Its crystal and collection parameters are shown in Table 1, and selected bond distances and angles are tabulated in Table 2. The geometry of compound **1** is well planar and packed in pair in its unit cell. The bond distances between C(5) and N(1) is 1.275(3) Å, which is in the range of typical bond length of imine double bond. The bond distance of 1.687(3) Å for the thiocarbonyl group

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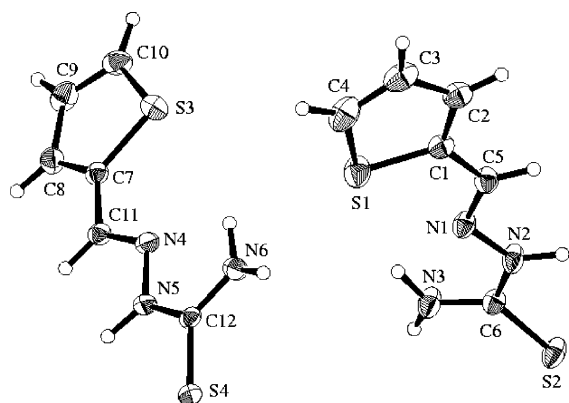


Fig. 1. ORTEP diagram of **1** with thermal ellipsoids at 30% probability.

(S(2)–C(6)) is about the average value of the typical C=S double bond (1.56 Å) and C–S single bond (1.82 Å), showing a partial double bond character in feature.

The partial double bond character also appears between N(2) and C(6) as well as N(3) and C(6), which show the distance of 1.344(3) and 1.307(3) Å, respectively. A distance of 2.30 Å between a proton on the thioamide nitrogen N(3) and the azomethine nitrogen N(1), showing the existence of a hydrogen bonding [2].

The reaction of thienyl Schiff base **1** with diiron nonacarbonyl in benzene yields three polynuclear iron carbonyl clusters and a mononuclear iron carbonyl complex, which we formulated as **2**, **3**, **4**, and **5**, respectively, as the major products (Scheme 1). These products were characterized spectrally and their structures were further confirmed by the single-crystal X-ray analyses. The ORTEP plots of **3**, **4**, and **5** are shown in Figs. 2–4, respectively. Their crystal and collection parameters are summarized in Table 1 and selected bond lengths and bond angles are tabulated in Tables 3–5.

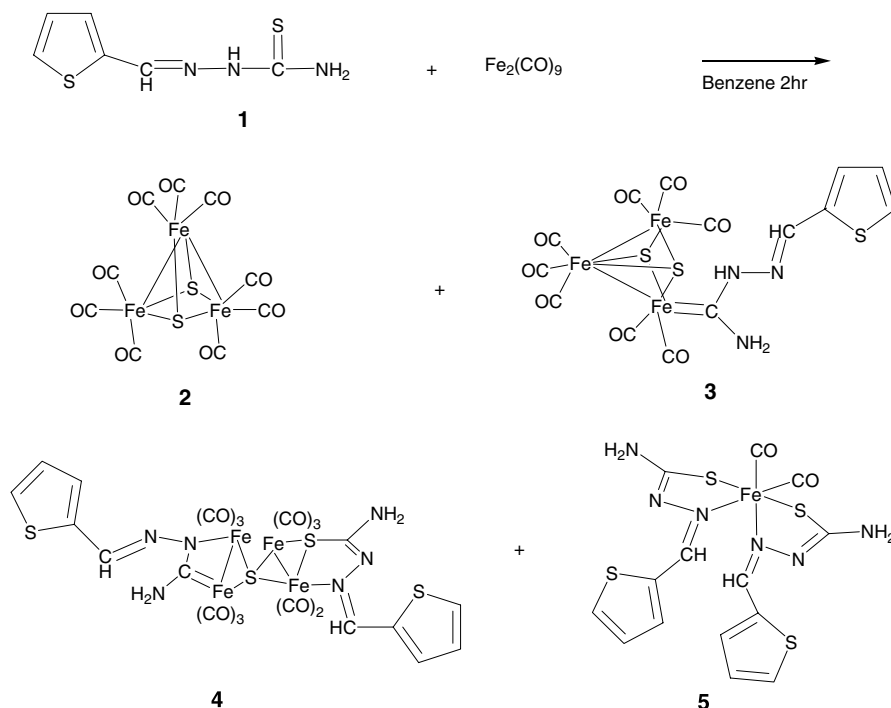
The product **2** is a red tetranuclear iron carbonyl cluster with a distorted square base pyramidal geometry.

Table 1  
Crystal and data collection parameters for compounds **1**, **3**, **4**, and **5**

Compound	<b>1</b>	<b>3</b>	<b>4</b>	<b>5</b>
Formula	C <sub>6</sub> H <sub>7</sub> N <sub>3</sub> S <sub>2</sub>	C <sub>14</sub> H <sub>7</sub> Fe <sub>3</sub> N <sub>3</sub> O <sub>8</sub> S <sub>3</sub>	C <sub>30</sub> H <sub>29</sub> Fe <sub>4</sub> N <sub>6</sub> O <sub>12</sub> S <sub>4</sub>	C <sub>14</sub> H <sub>12</sub> FeN <sub>6</sub> O <sub>2</sub> S <sub>4</sub>
Formula weight	185.26	608.95	1017.22	480.37
Cryst. system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	13.593(4)	9.050(2)	9.52(1)	9.072(2)
<i>b</i> (Å)	5.8311(9)	11.044(4)	12.70(1)	9.468(2)
<i>c</i> (Å)	21.402(7)	13.102(4)	18.82(1)	12.179(1)
$\alpha$ (°)		109.97(3)	102.78(6)	87.11(2)
$\beta$ (°)	96.51(3)	109.15(2)	94.70(7)	87.83(1)
$\gamma$ (°)		103.04(2)	107.24(8)	68.51(1)
Volume (Å <sup>3</sup> )	1685.3(7)	1075.4(9)	2092(4)	972.0(3)
<i>Z</i>	8	2	2	2
<i>D</i> <sub>calc.</sub> (g/cm <sup>3</sup> )	1.460	1.880	1.615	1.641
Cryst. size (mm)	0.60 × 0.60 × 0.90	0.20 × 0.22 × 0.26	0.20 × 0.20 × 0.60	0.20 × 0.22 × 0.48
Temperature (K)	298.0	298.0	298.0	298.0
2 $\theta$ <sub>max</sub> (°)	50.5	50.0	55.0	50.1
Scan type	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
No. of refln. meads				
Total, unique	3428, 3285	4003, 3786	8670, 8629	4060, 3816
No. of obsd. reflns ( <i>I</i> > 3.00 $\sigma$ ( <i>I</i> ))	2612	2470	2836	2682
No. of variables	199	280	475	292
<i>F</i> <sub>000</sub>	768.00	604.00	1030.00	488.00
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	5.68	23.32	16.20	12.27
<i>R</i>	0.031	0.039	0.082	0.032
<i>R</i> <sub>w</sub>	0.040	0.039	0.092	0.044

Table 2  
Selected bond lengths (Å) and angles (°) for **1**

C(1)–C(5)	1.437(3)	N(2)–C(6)	1.344(3)
N(1)–C(5)	1.275(3)	S(2)–C(6)	1.693(2)
N(1)–N(2)	1.378(2)	N(3)–C(6)	1.307(3)
C(1)–C(5)–N(1)	121.0(2)	C(5)–N(1)–N(2)	115.8(2)
N(1)–N(2)–C(6)	119.9(2)	N(2)–C(6)–N(3)	117.7(2)
S(2)–C(6)–N(2)	118.9(2)	S(2)–C(6)–N(3)	123.4(2)

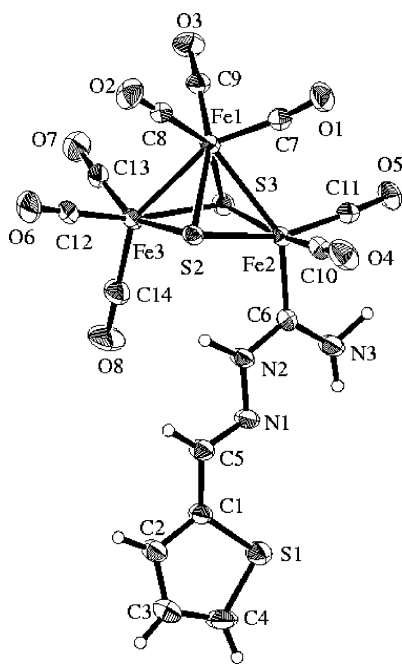
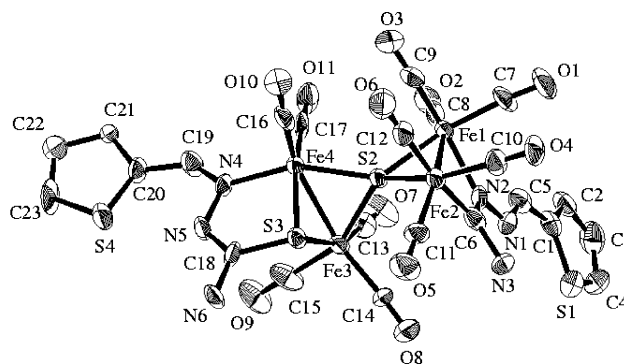


Scheme 1.

Each of the two sulfur atoms on the square base triply bridges to the two basal tricarbonyliron units on the same base and the third tricarbonyliron group at the apex of the pyramid. The same cluster had been obtained, from the reaction of organic sulfide with  $\text{Fe}_3(\text{CO})_{12}$  [4] and from the reaction of thione with

$\text{Fe}_2(\text{CO})_9$  [5] as well, and its molecular structure had been confirmed [6].

The red product **3**, as seen from Fig. 2, is also a tetranuclear iron carbonyl cluster with a distorted square base pyramidal geometry as product **2**. However, the axial carbonyl ligand on one of the iron centers on the square base has been substituted with a carbene moiety, which is resulted from the C=S activation of the original ligand **1**. The geometric parameter of the carbene moiety in **3** remains almost the same as that of its mother ligand **1**. The distance of 1.929(6) Å for the metal–carbene bond, Fe(2)–C(6), indicating a double bond character is comparable to that of reported iron carbonyl carbene complexes [7]. The distances of 1.345(7) and 1.311(8) Å for C(6)–N(2) and C(6)–N(3) bonds showing the partial

Fig. 2. ORTEP diagram of **3** with thermal ellipsoids at 30% probability.Fig. 3. ORTEP diagram of **4** with thermal ellipsoids at 30% probability.

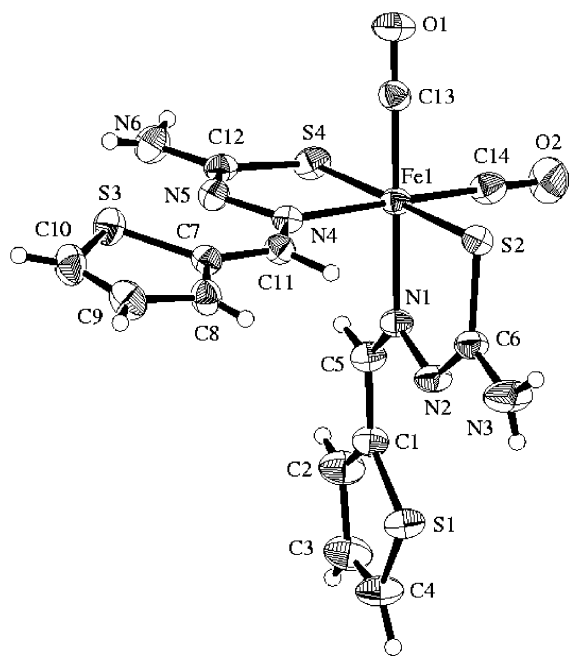


Fig. 4. ORTEP diagram of **5** with thermal ellipsoids at 30% probability.

double bond character in these two bonds. This supports the fact that  $\pi$  bonding in this Fischer type complex are delocalized over Fe(2), C(6), N(2), and N(3) atoms. The bond angles around the  $sp^2$  C(6) center are  $119.9(5)^\circ$ ,  $126.5(5)^\circ$ , and  $113.7(6)^\circ$  for Fe(2)–C(6)–N(2), Fe(2)–C(6)–N(3), and N(2)–C(6)–N(3), respectively. The geometry of the carbene ligand is kept in well planar and about perpendicular to the  $Fe_2S_2$  basal plane.

The product **4** is a novel chiral double cluster complex which consists of the two different butterfly

subcluster cores Fe(1)Fe(2)S(2)C(6)N(2) and Fe(3)Fe(4)S(2)S(3) jointed to a spiro type of  $\mu_4$ -S, i.e., the S(2) atom, as shown in Fig. 3. There are two organic ligands that are involved in the cluster **4**. In the left subcluster core of **4**, the thiophene-2-carboxaldehyde thiosemicarbazone ligand (**1**) bridges to Fe(3)–Fe(4) unit via  $\mu_2$ -S(3) atom and at the same time the azomethine nitrogen N(4) atom of the ligand attaches to Fe(4) center to substitute a carbonyl ligand to form an equatorial five-membered chelate ring. In addition, it can be seen that each of the two COs that attached to Fe(4) and the three COs that attached to Fe(3) is terminal. In the right subcluster core, a carbene moiety, which is resulted from the C=S activation of **1**, acts as a bidentate ligand and bridges to Fe(1)–Fe(2) iron pair via its carbene carbon C(6) and the deprotonated hydrazine nitrogen N(2) to form an axial four-membered ring. It can also be seen that two tricarbonyl groups on Fe(1) and Fe(2) are eclipsed and all COs are terminal. Selected bond lengths and bond angles for complex **4** are tabulated in Table 4. It is noteworthy that the corresponding bond lengths and angles related to the two subcluster cores are different. While the Fe(3)–Fe(4) bond length of  $2.530(4)$  Å and the Fe(3)–S(2) bond length of  $2.248(5)$  Å are comparable to that in other  $\mu_4$ -S- $Fe_4$  clusters [8], the Fe(1)–Fe(2) bond length is shown to be longer ( $2.601(4)$  Å) and the Fe(1)–S(2), Fe(2)–S(2), and Fe(4)–S(2) bond lengths ( $2.223(5)$ ,  $2.228(5)$ , and  $2.215(5)$  Å, respectively) are found to be shorter. The dihedral angle between S(2)Fe(1)Fe(2) plane and S(2)Fe(3)Fe(4) plane is  $86.13^\circ$ . The bond angles Fe(1)–S(2)–Fe(2) and Fe(3)–S(2)–Fe(4) are  $71.5(2)^\circ$  and  $69.1(2)^\circ$ , respectively. In the left subcluster core, the five-membered chelate ring is planar in geometry and has a dihedral angle of  $73.94^\circ$  with the S(3)Fe(3)Fe(4)

Table 3

Selected bond lengths (Å) and angles ( $^\circ$ ) for **3**

Fe(1)–Fe(2)	2.613(1)	Fe(1)–Fe(3)	2.558(1)
Fe(1)–S(2)	2.260(2)	Fe(1)–S(3)	2.266(2)
Fe(2)–S(2)	2.242(2)	Fe(2)–S(3)	2.226(2)
Fe(3)–S(2)	2.257(2)	Fe(3)–S(3)	2.253(2)
Fe(2)–C(6)	1.929(6)	C(1)–C(5)	1.436(8)
N(1)–C(5)	1.282(7)	N(1)–N(2)	1.395(6)
N(2)–C(6)	1.345(7)	C(6)–N(3)	1.311(8)
Fe(2)–Fe(1)–Fe(3)	82.75(4)	Fe(1)–Fe(2)–S(2)	55.84(5)
Fe(2)–Fe(1)–S(2)	54.21(3)	Fe(1)–Fe(2)–S(3)	55.16(5)
Fe(2)–Fe(1)–S(3)	53.72(5)	S(2)–Fe(2)–S(3)	80.36(7)
Fe(3)–Fe(1)–S(2)	55.44(5)	Fe(1)–Fe(3)–S(2)	55.56(5)
Fe(2)–Fe(1)–S(3)	55.28(5)	Fe(1)–Fe(3)–S(3)	55.77(5)
S(2)–Fe(1)–S(3)	79.13(6)	S(2)–Fe(3)–S(3)	79.48(7)
Fe(1)–S(2)–Fe(2)	70.96(5)	Fe(1)–S(2)–Fe(3)	69.00(5)
Fe(1)–S(3)–Fe(2)	71.12(6)	Fe(1)–S(3)–Fe(3)	68.94(6)
Fe(2)–S(2)–Fe(3)	98.90(7)	Fe(2)–S(3)–Fe(3)	99.49(7)
Fe(1)–Fe(2)–C(6)	144.8(2)	S(2)–Fe(2)–C(6)	101.2(2)
S(3)–Fe(2)–C(6)	99.4(2)	Fe(2)–C(6)–N(2)	119.9(5)
Fe(2)–C(6)–N(3)	126.5(5)	N(1)–C(5)–C(1)	121.5(6)
N(2)–N(1)–C(5)	114.6(5)	N(1)–N(2)–C(6)	121.1(5)
N(2)–C(6)–N(3)	113.7(6)		

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

Fe(1)–Fe(2)	2.601(4)	Fe(3)–Fe(4)	2.530(4)
Fe(1)–S(2)	2.223(5)	Fe(2)–S(2)	2.228(5)
Fe(3)–S(2)	2.248(5)	Fe(4)–S(2)	2.215(5)
Fe(3)–S(3)	2.320(5)	Fe(4)–S(3)	2.232(5)
Fe(1)–N(2)	2.01(1)	Fe(4)–N(4)	1.98(1)
Fe(2)–C(6)	1.91(2)	C(1)–C(5)	1.41(2)
N(1)–C(5)	1.27(2)	C(19)–C(20)	1.46(3)
N(1)–N(2)	1.40(2)	N(4)–C(19)	1.29(2)
N(4)–N(5)	1.40(2)	N(2)–C(6)	1.34(2)
N(5)–C(18)	1.28(2)	S(2)–C(6)	1.76(2)
N(3)–C(6)	1.40(2)	N(6)–C(18)	1.35(2)
Fe(1)–S(2)–Fe(2)	71.5(2)	Fe(2)–S(2)–Fe(3)	128.4(2)
Fe(1)–S(2)–Fe(3)	133.1(2)	Fe(2)–S(2)–Fe(4)	134.1(2)
Fe(1)–S(2)–Fe(4)	132.1(2)	Fe(3)–S(2)–Fe(4)	69.1(2)
Fe(1)–N(2)–C(6)	105(1)	Fe(1)–N(2)–N(1)	136(1)
Fe(2)–C(6)–N(2)	112(1)	Fe(2)–C(6)–N(3)	132(1)
Fe(3)–S(3)–Fe(4)	67.5(2)	Fe(3)–S(3)–C(18)	109.8(7)
Fe(4)–S(3)–C(18)	97.4(6)	Fe(4)–N(4)–C(19)	128(1)
Fe(4)–N(4)–N(5)	121(1)	S(2)–Fe(1)–N(2)	82.9(4)
S(2)–Fe(2)–C(6)	84.1(5)	S(2)–Fe(3)–S(3)	77.7(2)
S(2)–Fe(4)–S(3)	80.3(2)	S(2)–Fe(4)–N(4)	154.9(4)
S(3)–Fe(4)–N(4)	84.0(4)	N(1)–N(2)–C(6)	119(2)
N(1)–C(5)–C(1)	124(2)	N(2)–N(1)–C(5)	121(2)
N(2)–C(6)–N(3)	115(2)	N(4)–C(19)–C(20)	133(2)
N(4)–N(5)–C(18)	115(2)	N(5)–C(18)–N(6)	119(2)
N(5)–N(4)–C(19)	111(2)	S(3)–C(18)–N(5)	112(2)
S(3)–C(18)–N(6)	119(1)	N(2)–Fe(1)–Fe(2)	71.1(4)
C(6)–Fe(2)–Fe(1)	71.2(5)	S(2)–Fe(1)–Fe(2)	54.3(1)
S(2)–Fe(2)–Fe(1)	54.1(1)	S(2)–Fe(3)–Fe(4)	54.9(1)
S(2)–Fe(4)–Fe(3)	56.1(1)	S(3)–Fe(3)–Fe(4)	54.6(1)
S(3)–Fe(4)–Fe(3)	57.9(1)		

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

Fe(1)–S(2)	2.2796(9)	Fe(1)–S(4)	2.2718(9)
Fe(1)–N(2)	2.023(2)	Fe(1)–N(4)	2.029(1)
N(1)–C(5)	1.291(4)	N(1)–N(2)	1.385(3)
N(2)–C(6)	1.293(4)	N(3)–C(6)	1.347(4)
S(2)–C(6)	1.732(3)	C(1)–C(5)	1.431(4)
S(2)–Fe(1)–S(4)	178.83(3)	N(1)–Fe(1)–C(13)	178.0(1)
N(4)–Fe(1)–C(14)	177.0(1)	S(2)–Fe(1)–N(4)	95.42(7)
S(2)–Fe(1)–N(1)	84.00(7)	N(1)–Fe(1)–S(4)	95.87(7)
S(4)–Fe(1)–N(4)	83.41(7)	N(1)–Fe(1)–N(4)	88.2(1)
Fe(1)–N(1)–N(2)	119.9(2)	Fe(1)–S(2)–C(6)	95.4(1)
N(1)–N(2)–C(6)	114.5(2)	Fe(1)–N(1)–C(5)	126.4(2)
N(2)–C(6)–N(3)	117.0(3)	N(1)–C(5)–C(1)	129.2(3)
N(2)–N(1)–C(5)	113.7(3)		

plane, which in turn has a dihedral angle of 100.48° with the S(2)Fe(3)Fe(4) plane. The four bridging angles S(2)–Fe(4)–Fe(3), S(2)–Fe(3)–Fe(4), S(3)–Fe(4)–Fe(3), and S(3)–Fe(3)–Fe(4) are 54.9(1)°, 56.1(1)°, 54.6(1)°, and 57.9(1)°, respectively, and the bond angle Fe(3)–S(3)–Fe(4) is 67.5(2)°. The distances from the bridging S(3) atom to Fe(3) and Fe(4) atoms are 2.320(5) and 2.232(5) Å, respectively. In the five-membered chelate ring, the Fe(4)–N(4) bond distance is 1.98(1) Å. While the S(3)–C(18) and N(4)–N(5) bond distances are elongated from 1.693(2) and 1.378(2) Å (that in the free ligand **1**) to

1.76(2) and 1.40(2) Å, the bond length N(5)–C(18) is shortened from 1.344(3) to 1.28(2) Å, a distance representing a typical imine double bond. The variation of these bond lengths indicates that the thiosemicarbazone bridges to Fe(3)–Fe(4) unit in its anionic thiol form instead of the usual neutral thione form, that restricts the delocalization of the  $\pi$  electrons within the range of S(3)–C(18)–N(5) atoms. This result also causes the extension of the C(18)–N(6) distance to a value of 1.35(2) Å. The five inner angles of the five-membered chelate ring S(3)–Fe(4)–N(4), Fe(4)–N(4)–N(5), N(4)–N(5)–

C(18), N(5)–C(18)–S(3), and C(18)–S(3)–Fe(4) are 84.0(4)°, 121.1(1)°, 115(2)°, 112(2)°, and 97.4(6)°, respectively. The C(19)–N(4) bond distance of 1.29(2) Å showing a typical imine double bond character in feature. In the right subcluster core, the two bridging angles S(2)–Fe(1)–Fe(2) and S(2)–Fe(2)–Fe(1) are about the same (54.3(1)° vs. 54.1(1)°). The four inner angles of the four-membered ring are 71.1(4)°, 71.2(5)°, 105(1)°, and 112(1)° for N(2)–Fe(1)–Fe(2), C(6)–Fe(2)–Fe(2), C(6)–N(2)–Fe(1), and N(2)–C(6)–Fe(2), respectively. The Fe(1)–N(2) bond length is 2.01(1) Å and is longer than that of Fe(4)–N(4). The bond distances of 1.91(2) and 1.34(2) Å for Fe(2)–C(6) and C(6)–N(2) are close to that in cluster **3**, indicating a typical metal–carbene feature of the coordination. The four-membered chelate ring and the whole carbene ligand are kept in a well planar geometry and has a dihedral angle of 84.53° with the Fe(1)Fe(2)S(2) plane. The C(5)–N(1) bond distance of 1.27(2) also showing the remaining of an imine double bond character. The structure and bonding feature of this organic moiety is quite similar to that in cluster **3** except the additional coordination of the deprotonated hydrazine nitrogen N(2) to the Fe(1) center. As to the chiral property of compound **4**, the solid state crystal structure, as shown in Fig. 3, does show the chirality in feature. However, in its solution state, it seems that this compound is kinetically labile with respect to racemisation. The CD/ORD spectrum of this compound does not show any evidence of optical activity.

The product **5** is a mononuclear octahedral iron complex with two bidentate thiosemicarbazone ligands and two carbonyl ligands, as shown in Fig. 4. The bond angles S(2)–Fe(1)–S(4), N(1)–Fe(1)–C(13), and N(4)–Fe(1)–C(14) are 178.83(3)°, 178.0(1)°, and 177.0(1)°, respectively. The bite angles S(2)–Fe(1)–N(1) and S(4)–Fe(1)–N(4) are 84.00(7)° and 83.41(7)°. The S(2)–Fe(1)–N(4), S(4)–Fe(1)–N(1), and N(1)–Fe(1)–N(4) bond angles are 95.42(7)°, 95.87(7)°, and 88.2(1)°, respectively. In the five-membered chelate ring, while the Fe(1)–S(2) (2.2796(9) Å) and Fe(1)–N(2) (2.203(2) Å) bond distances are longer than that of the corresponding distances in **4**, the N(1)–N(2) (1.385(3) Å) and S(2)–C(6) (1.732(3) Å) bond lengths are found to be relatively shorter and N(2)–C(6) bond length is kept about the same. This phenomenon indicates that the thiosemicarbazone coordinates to the iron center also in its anionic thiol form as that in **4**, but the degree of  $\pi$ -electrons delocalization in this case is better than that in cluster **4**.

## 2.2. $^1\text{H}$ NMR spectroscopy

The  $^1\text{H}$  NMR data of the free ligand **1** and iron carbonyl products **3**, **4**, and **5** are summarized in Table 6. The imine proton and each thienyl proton in each compound can be easily assigned according to its spe-

cific position and the characteristic coupling constant(s). The  $^1\text{H}$  NMR spectrum of **4** shows two sets of signals for the thienyl protons and imine proton as well, indicating that two thienyl imine moieties are involved in different environments.

## 2.3. IR spectroscopy

The IR  $\nu(\text{CO})$  frequencies of terminal carbonyls on iron center that appear in the range of 2070–1962  $\text{cm}^{-1}$  are characteristic for complexes **2**, **3**, **4**, and **5** as shown in Table 6. Complexes **3**, **4**, and **5** also show the characteristic C=N stretching absorption in the range of 1623–1598  $\text{cm}^{-1}$ , which is comparable to that of free ligand **1** (1611  $\text{cm}^{-1}$ ) due to the long conjugate chain of ligand [9].

## 2.4. Mass spectrometry

The molecular formula of each complex has been confirmed by the observation of a signal for the molecular ion peak ( $m/e = M^+$ ) and absorption peaks corresponding to the fragments with sequential loss of COs from the molecule as shown in Table 6.

## 2.5. Proposed mechanisms for the formation of cluster **2**, **3**, and **4**

The carbonyl sulfide iron cluster **2** has been known to be obtained from the reaction of organic sulfide with  $\text{Fe}_3(\text{CO})_{12}$  or from the reaction of thione with  $\text{Fe}_2(\text{CO})_9$  [4,5]. In all cases, the carbon–sulfur bond activation plays the key role and directs to the formation of cluster **2**. The cluster thus formed might be further attacked by the carbene moiety, which is another fragment resulting from the C=S bond cleavage of the ligand **1**, and the substitution of a carbonyl ligand on one of the basal  $\text{Fe}(\text{CO})_3$  group by the carbene leads to the formation of cluster **3**.

The spiro type double butterfly cluster **4** might be tentatively considered to be a product from the coupling of two precursors **A** and **B**, as shown in Scheme 2. **A** is resulted from the activation of the C=S bond of the ligand **1** and followed by an oxidative addition on the diiron centers and the coordination of hydrazine nitrogen. On the other hand, **B** is derived from the direct coordination of the deprotonated thiosemicarbazone, in which the ligand is in its thiol form and acts as a bidentate chelate via its mercapto sulfur atom and azomethine nitrogen atom [2], toward one of the diiron centers, and at the same time the sulfur atom bridges to another iron center. The bridging sulfur atom of **A** might further substitute the bridging carbonyl ligand of **B** and bridges to its diiron centers and end up with the formation of cluster **4** [8e].

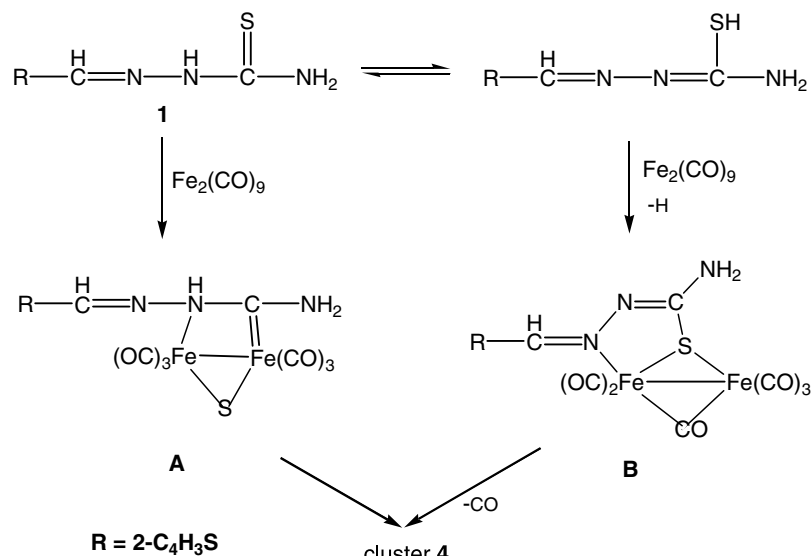
Table 6  
<sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, and MS data for compounds 1, 3, 4, and 5

	1	3	4	5
<sup>1</sup> H NMR (δ, ppm)				
Thienyl proton	7.56 (d) <sup>a</sup> , H <sub>5</sub>	7.57 (d) <sup>a</sup> , H <sub>5</sub>	7.74/7.54 (d) <sup>a</sup> , H <sub>5</sub> /H <sub>5</sub> ,	7.67 (d) <sup>a</sup> , H <sub>5</sub>
Thienyl proton	7.43 (d) <sup>b</sup> , H <sub>3</sub>	7.47 (d) <sup>b</sup> , H <sub>3</sub>	7.69/7.52 (d) <sup>b</sup> , H <sub>3</sub> /H <sub>3</sub>	7.48 (d) <sup>b</sup> , H <sub>3</sub>
Thienyl proton	7.12 (dd) <sup>c</sup> , H <sub>4</sub>	7.13 (dd) <sup>c</sup> , H <sub>4</sub>	7.12/7.08 (dd) <sup>c</sup> , H <sub>4</sub> /H <sub>4</sub>	7.08 (dd) <sup>c</sup> , H <sub>4</sub>
-C(H)=N-	8.36 (s)	8.31 (s)	8.53 (s), 7.92 (s)	8.56 (s)
<sup>13</sup> C NMR (δ, ppm)	179.4, 139.1, 137.6, 130.6, 128.5, 127.8	218.5, 144.3, 142.5, 137.9, 132.6, 130.0, 128.0	211.3, 154.6, 140.5, 138.3, 136.2, 135.7, 135.0, 133.8, 130.6, 128.2, 127.8, 126.7, 110.4	212.1, 177.3, 144.2, 135.6, 133.9, 132.7, 126.4
IR (KBr) ν (cm <sup>-1</sup> )				
CO		2070, 2016, 2006, 1962	2069, 2028, 2004, 1978	2044, 1993
C=N	1611	1607	1623, 1619	1598
N-H	3414, 3402	3515, 3442, 3338	3500, 3443, 3433, 3409, 3386	3458, 3336
MS (FAB) <i>m/e</i>	185 (M <sup>+</sup> )	609 (M <sup>+</sup> ) 581 (M <sup>+</sup> - CO) 553 (M <sup>+</sup> - 2CO) 525 (M <sup>+</sup> - 3CO) 497 (M <sup>+</sup> - 4CO) 469 (M <sup>+</sup> - 5CO) 441 (M <sup>+</sup> - 6CO) 413 (M <sup>+</sup> - 7CO) 385 (M <sup>+</sup> - 8CO) 176 (Fe <sub>2</sub> S <sub>2</sub> )	902 (M <sup>+</sup> ), 874 (M <sup>+</sup> - CO) 846 (M <sup>+</sup> - 2CO), 818 (M <sup>+</sup> - 3CO) 790 (M <sup>+</sup> - 4CO), 761 (M <sup>+</sup> - 5CO) 734 (M <sup>+</sup> - 6CO), 706 (M <sup>+</sup> - 7CO) 678 (M <sup>+</sup> - 8CO), 650 (M <sup>+</sup> - 9CO) 622 (M <sup>+</sup> - 10CO), 594 (M <sup>+</sup> - 11CO) 288 (Fe <sub>4</sub> S <sub>2</sub> ), 153 (L - S)	481 (M <sup>+</sup> ) 453 (M <sup>+</sup> - CO) 425 (M <sup>+</sup> - 2CO) 240 (M <sup>+</sup> - 2CO - Fe) 185 (L) 153 (L - S)

<sup>a</sup> *J*<sub>H-H</sub> = 5.1 Hz.

<sup>b</sup> *J*<sub>H-H</sub> = 3.6 Hz.

<sup>c</sup> *J*<sub>H-H</sub> = 5.1, 3.6 Hz.



Scheme 2.

### 3. Experimental

#### 3.1. General

Diiron nonacarbonyl was prepared by photolysis of iron pentacarbonyl (Aldrich) in glacial acetic acid [10]. Solvents were dried (sodium/benzophenone,  $P_4O_{10}$ ) and distilled under nitrogen prior to use. Thiophene-2-carboxaldehyde (Aldrich) was distilled by a Kugelrohr distillation apparatus under reduced pressure (0.1 mm Hg) prior to use. All other chemicals were reagent grade and used without further purification. The NMR spectra were recorded on a Bruker DX-300 NMR spectrometer ( $^1H$ , 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 Micromass Platform II spectrometer. IR spectra were recorded from a Mattson Genesis FTIR spectrophotometer. Elemental analyses were performed using a Perkin–Elmer 2400, 2400II elemental analyzer. Crystals for X-ray diffraction were obtained from acetone (ligand **1**) or from ether/hexane (1:4) mixed solution (complexes **2**, **3**, **4**, and **5**). A single crystal was mounted on a glass fiber and the X-ray diffraction intensity data were measured on a Rigaku AFC7S diffractometer with graphite monochromated Mo  $K\alpha$  radiation at room temperature.

#### 3.2. Synthesis of thiophene-2-carboxaldehyde thiosemicarbazone (**1**)

The synthesis of Schiff base **1** employed the usual approach of condensation in alcohol solution [11]. Thiophene-2-carboxaldehyde (1.40 g, 12.5 mmol) and thiosemicarbazide (0.91 g, 10 mmol) were refluxed in ethanol (Merck, 20 ml) for 1 h. The solvent was removed by filtration. The yellow precipitate was washed with several portions of ether to give pure product **1** (1.40 g, 75%). m.p. 176.6–177.0 °C. Anal.

Calc. for  $C_6H_7N_3S_2$ : C, 38.97; H, 3.95; N, 22.98; S, 35.11. Found: C, 38.89; H, 3.78; N, 22.78; S, 34.84%.

#### 3.3. Reaction of **1** with $Fe_2(CO)_9$ in benzene to give complexes **2**, **3**, **4**, and **5**

About 0.347 g (1.88 mmol) of compound **1** in 30 ml of anhydrous benzene was added gradually to a 70 ml of anhydrous benzene solution containing 3.63 g (10.0 mmol) of  $Fe_2(CO)_9$  in the dark under nitrogen and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was then filtered and the solvent removed under reduced pressure. The residue was separated by 3.5 cm diameter and 40 cm height column (230–400 mesh ASTM silica gel (Merck)) with dichloromethane/*n*-hexane (3:5) as eluent. The purple band produced complex **2** (38 mg, 8.4%). m.p. 108–

109 °C. IR (KBr film)  $\nu(CO)$ : 2041, 2014, 1993  $cm^{-1}$ . The dark red band produced complex **3** (276 mg, 24.1%). m.p. 131–132 °C. Anal. Calc. for  $Fe_2C_{14}H_7N_3S_3$ : C, 27.79; H, 1.65; N, 6.83; S, 15.52. Found: C, 27.70; H, 1.48; N, 6.89; S, 15.62%. The brown band produced complex **4** (154 mg, 18.2%). m.p. 108–109 °C. Anal. Calc. for  $Fe_4C_{23}H_{12}N_6O_{11}S_4$ : C, 30.67; H, 1.33; N, 9.33; S, 14.22. Found: C, 30.58; H, 1.39; N, 9.30; S, 14.24%. The orange band produced complex **5** (136 mg, 30.1%). m.p. 79–80 °C. Anal. Calc. for  $FeC_{14}H_{12}N_6O_2S_4$ : C, 34.97; H, 2.50; N, 17.49; S, 26.65. Found: C, 35.01; H, 2.44; N, 17.42; S, 25.53%. Substantial amount of iron cluster,  $Fe_3(CO)_{12}$ , was also collected.

$^1H$  NMR,  $^{13}C$  NMR, IR, and MS spectral data for **1**, **3**, **4**, and **5** are tabulated in Table 6.

### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 216502 (**1**), 216503–216505 (**3–5**). 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 <http://www.ccdc.cam.ac.uk>).

### Acknowledgements

The authors express their appreciation to the National Science Council (Taiwan, ROC) and National Dong Hwa University for providing the financial support necessary to carry out this study.

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