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Syntheses and structures of iron carbonyl complexes derived from *N*-(5-methyl-2-thienylmethylidene)-2-thiolethylamine and *N*-(6-methyl-2-pyridylmethylidene)-2-thiolethylamine

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Abstract

The reaction of *N*-(5-methyl-2-thienylmethylidene)-2-thiolethylamine (**1**) with $Fe_2(CO)_9$ in refluxing acetonitrile yielded di-(μ_3-thia)nonacarbonyltriiron (**2**), μ-[*N*-(5-methyl-2-thienylmethyl)-η^1:η^1(N);η^1:η^1(S)-2-thiolatoethylamido]hexacarbonyldiiron (**3**), and *N*-(5-methyl-2-thienylmethylidene)amine (**4**). If the reaction was carried out at 45 °C, di-μ-[*N*-(5-methyl-2-thienylmethylidene)-η^1(N);η^1(S)-2-thiolethylamino]-μ-carbonyl-tetracarbonyldiiron (**5**) and trace amount of **4** were obtained. Stirring **5** in refluxing acetonitrile led to the thermal decomposition of **5**, and ligand **1** was recovered quantitatively. However, in the presence of excess amount of $Fe_2(CO)_9$ in refluxing acetonitrile, complex **5** was converted into **2**–**4**. On the other hand, the reaction of *N*-(6-methyl-2-pyridylmethylidene)-2-thiolethylamine (**6**) with $Fe_2(CO)_9$ in refluxing acetonitrile produced **2**, μ-[*N*-(6-methyl-2-pyridylmethyl)-η^1(N_{py});η^1:η^1(N); η^1:η^1(S)-2-thiolatoethylamido]pentacarbonyldiiron (**7**), and μ-[*N*-(6-methyl-2-pyridylmethylidene)-η^2(C,N); η^1:η^1(S)-2- thiolethylamino]hexacarbonyldiiron (**8**). Reactions of both complex **7** and **8** with $NOBF_4$ gave μ-[(6-methyl-2-pyridylmethyl)-η^1(N_{py});η^1:η^1(N);η^1:η^1(S)-2-thiolatoethylamido](acetonitrile)tricarbonylnitrosyldiiron (**9**). These reaction products were well characterized spectrally. The molecular structures of complexes **3**, **7**–**9** have been determined by means of X-ray diffraction. Intramolecular 1,5-hydrogen shift from the thiol to the methine carbon was observed in complexes **3**, **7**, and **9**.

Keywords: Iron carbonyl complex; *N*-(5-methyl-2-thienylmethylidene)-2-thiolethylamine; *N*-(6-methyl-2-pyridylmethylidene)-2-thiolethylamine; Imine π-coordination

1. Introduction

Sulfur ligands are widespread among coordination compounds [1] and are important components of biological transition metal complexes [2]. Research on Fe–S complexes has flourished as a result of the discovery that they are present in electron-transfer and nitrogen fixing enzymes [3]. Metal complexes with sulfur containing unsaturated ligands are also of great interest in inorganic and organometallic chemistry, especially due to their potential with novel electrical and magnetic properties [4].

The study of the reactivity of various types of heteroaromatic containing Schiff bases linked to metal complexes has received a great deal of attention during the past decades. With the possibility of donating two to four electrons via the N lone-pair and/or C=N π-system, heteroaromatic containing Schiff bases are known to show very versatile coordination property to the bonded metal center(s) [5].

In the present work, which has emerged from our continued interest in the studies of iron carbonyl complexes from thiophene containing Schiff bases [5h,6], we incorporate a thiol functional group in the thienyl/pyridyl Schiff bases and study their coordination to the iron–iron binuclear centers. It is interesting to find that the original ligand bridges to the diiron (Fe–Fe) centers

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either: (i) via μ-($\eta^1\eta^1$(S);$\eta^1\eta^1$(N)) binding mode; (ii) via μ-(η^1(S);η^1(N)) binding mode; (iii) via μ-($\eta^1\eta^1$(S); $\eta^1\eta^1$(N)) binding mode with the N_{py} donor bonded to one of the diiron centers at the same time; or (iv) via μ-($\eta^1\eta^1$(S);η^2 (C=N)) binding mode. Neither cyclometallation [5h,6] on the thienyl/pyridyl ring nor the complex resulting from the C–S activation of the original ligand [6f] has been observed during the course of complexes formation.

2. Results and discussion

2.1. Syntheses of ligands

The thienyl and pyridyl Schiff bases *N*-(5-methyl-2-thienylmethylidene)-2-thiolethylamine (**1**) and *N*-(6-methyl-2-pyridylmethylidene)-2-thiolethylamine (**6**) ligands were prepared by condensation of 5-methyl-2-thiophenecarboxaldhyde and 5-methyl-2-pyridinecarboxaldehyde with 2-aminoethanethiol in ethanol. These two ligands were fully characterized spectrally as described in Section 3.

2.2. Reaction of ligand *1* with $Fe_2(CO)_9$

The thienyl Schiff base **1** reacted with $Fe_2(CO)_9$ in refluxing acetonitrile to give off iron carbonyl complexes **2** and **3,** and an organic product **4** as the major products (Scheme 1). If the reaction was conducted at 50 °C, an iron carbonyl complex **5** and trace amount of organic compound **4** were obtained. No cyclometallation as expected for other previously studied thienyl Schiff bases [6] was observed in this reaction.

Complex **5** undergoes thermal decomposition at elevated temperature. Further reaction of complex **5** with $Fe_2(CO)_9$ in refluxing acetonitrile led to the formation of **2**–**4** products as shown in Scheme 1. However, in the absence of $Fe_2(CO)_9$, complex **5** decomposed quickly in refluxing acetonitrile and ligand **1** was recovered quantitatively.

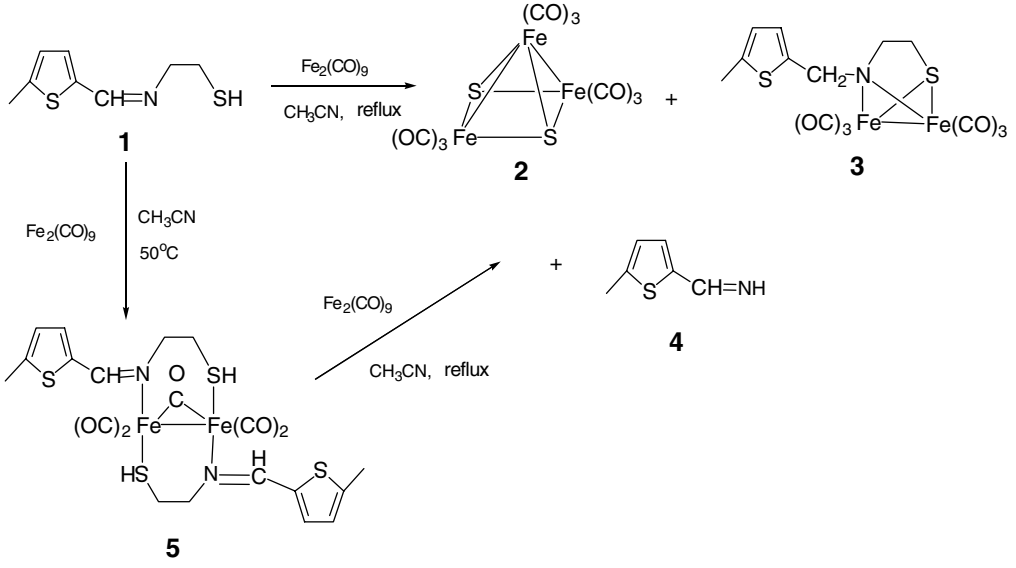
2.3. Reaction of ligand *6* with $Fe_2(CO)_9$

The reaction of pyridyl Schiff base **6** with $Fe_2(CO)_9$ in refluxing acetonitrile produced **2** and another two iron carbonyl complexes, which we formulate as **7** and **8**, as the major products (Scheme 2).

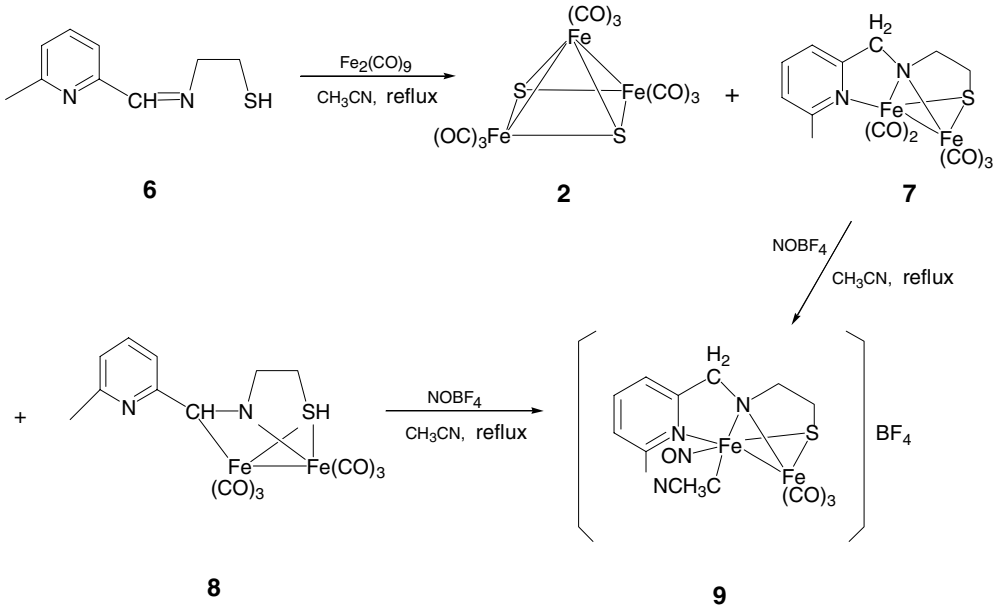
2.4. Spectral characterization

The product **2** is a red trinuclear iron carbonyl cluster with a distorted square base pyramidal geometry. Each of the two sulfur atoms on the square base triply bridges to the two basal $Fe(CO)_3$ units on the same base and the third $Fe(CO)_3$ unit at the apex of the pyramid. The same cluster had been obtained from the reaction of organic sulfide with $Fe_3(CO)_{12}$ [7] and from the reaction of thione with $Fe_2(CO)_9$ [8] as well, and its molecular structure had been confirmed [9].

The product **3** is a hexacarbonyldiiron complex. The ^{1}H NMR spectrum of **3** shows the absence of methine proton, which appears at δ 8.26 ppm in free ligand **1**, and a new singlet methylene signal appears at δ 4.44 ppm in addition to the two up-field shifted triplet signals, δ 3.62 and 2.36 ppm, for the two adjacent methylene groups, indicating a hydrogen transferred through an intramolecular 1,5-hydrogen shift from the thiol



Scheme 1.



6 2 7 8 9

Scheme 2.

toward the methine carbon, thus producing a new methylene group. In its IR spectrum, while the C=N stretching is absent, there are sharp and intense CO stretches appearing at 2067, 2027, 1993, and 1967 cm^{-1}, indicating the presence of terminal carbonyl-iron moiety. The mass spectrum of **3** shows the molecular ion peak at *m/e* 465 (M^+) and six fragments corresponding to the sequential loss of six COs, in accordance with the formulated structure.

The ^1H NMR spectrum of **4** shows only a pair of doublet signals at δ 7.78 and 6.80 ppm with a coupling constant of 15.6 Hz, and another pair of doublet signals at δ 7.30 and 6.84 ppm with a coupling constant of 3.6 Hz. While the latter pair of signals represent two protons on the β- and β′-carbon of the thienyl ring, the former pair of signals can be assigned as two adjacent protons on the azomethine carbon and nitrogen. In its IR spectrum, the C=N stretching absorption appears at 1600 cm^{-1}. The spectral data indicates that the compound **4** is an organic species and the ethanthiol group had been cleaved from the original ligand **1** during the course of reaction. The molecular ion peak at *m/e* 125 (M^+) in the mass spectrum of **4** is also consistent with the formulated structure.

Although complex **5** is unstable, we were able to deduce its structure, as shown in Scheme 1, from its ^1H NMR, IR, and mass spectra. In its IR spectrum, while the three sharp and intense absorptions at 2068, 2031, and 1983 cm^{-1} indicate the existence of terminal metal-carbonyl moiety, a stretching frequency of 1732 cm^{-1} represents the presence of bridging carbonyl in the complex. Besides, a C=N stretching absorption appears at 1600 cm^{-1}. The mass spectrum shows the complete loss of five COs successively, and the molecular ion peak at *m/z* 622 suggests that two organic ligands **1** are incorporated. The simplicity of the ^1H NMR spectrum suggests that two organic ligands are arranged more or less symmetrically.

The product **7** is a pentacarbonyldiiron complex. When compared to the spectrum of free ligand **6**, the ^1H NMR spectrum of **7** shows the disappearance of methine proton and the appearance of two sets of doublet signals at δ 5.07 and 4.97 ppm with a coupling constant of 18.6 Hz. The latter correspond to the two protons of the newly formed methylene group and indicate a hydrogen transferred through an intramolecular 1,5-hydrogen shift from the thiol toward the methine carbon during the course of ligand coordination, and the formation of a new metallacyclic ring. The two original methylene groups were also found up-field shifted and appear at δ 3.62 and 2.36 ppm. In its IR spectrum, while the C=N stretching is absent, there are sharp and intense CO stretches appearing at 2024, 1966, 1945, and 1909 cm^{-1}. The mass spectrum of **7** shows the molecular ion peak at *m/e* 432 (M^+) and five fragments corresponding to the sequential loss of five COs, in accordance with the formulated structure.

The way the pyridyl Schiff base **6** coordinates to the Fe–Fe diiron unit, via the thiol sulfur atom and the azomethine C=N π-system, in the complex **8** is quite a novel bonding mode. In its ^1H NMR spectrum, the signal for the methine proton greatly up-field shifted from δ 8.33 ppm (in free ligand **6**) to δ 3.67 ppm, indicating a complete conversion of a sp^2 carbon to a sp^3 carbon configuration. There are four sharp and intense terminal CO stretches appearing at 2061, 2014, 1973, and 1931 cm^{-1} in its IR spectrum, but no absorption corresponding to the C=N group is observed. The mass

spectrum of complex **8** shows the molecular ion peak at *m/e* 460 (M^+) and six fragments corresponding to the sequential loss of six COs, in accordance with the formulated structure.

2.5. Reactions of diiron carbonyl complexes *3*, *7*, and *8*

Chemical oxidations of diiron carbonyl complexes **3**, **7**, and **8** with ferric chloride or ceric ammonium nitrate lead to the decomposition of these complexes. So does nitosonium tetrafluoroborate when added to the complex **3**. However, reactions of both complex **7** and **8** with nitosonium tetrafluoroborate resulted in the formation of complex **9**. The structure of cationic complex of **9** is geometrically similar to that of complex **7** except that the two carbonyl ligands of the $Fe(CO)_2$ moiety in **7** have been displaced by a nitrosyl and an acetonitrile ligands. In addition to the terminal carbonyl stretches at 2045, 2031, and 1004 cm^{-1}, the IR spectrum of **9** shows two extra characteristic absorption bands at 2247 and 1815 cm^{-1}, which may be assigned due to the CN and NO stretching absorption, respectively, In its mass spectrum, the molecular ion peak at *m/e* 534, peaks corresponding to the loss of MeCN, COs, and NO ligands, and the free ligand peak, appear, consistent with the formulated structure.

2.6. Molecular structures of *3*, *7–9*

The molecular structures of complexes **3**, **7–9**, as determined by means of single-crystal X-ray diffraction analysis, are shown in Figs. 1–4, respectively. Their

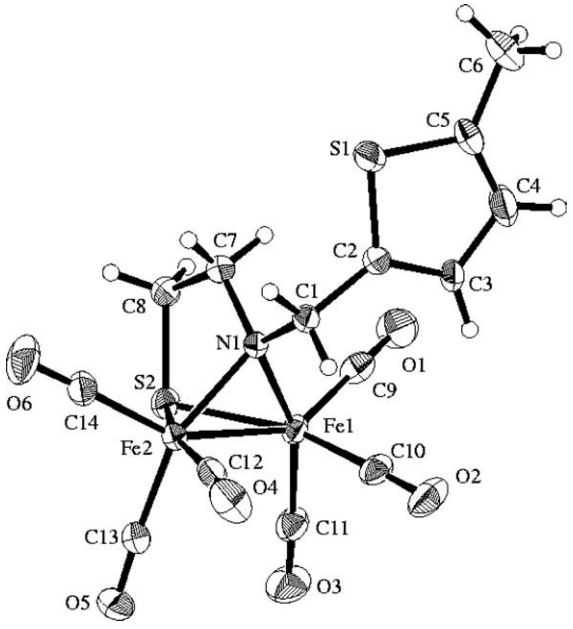


Fig. 1. ORTEP diagram of complex **3** with thermal ellipsoids at 30% probability.

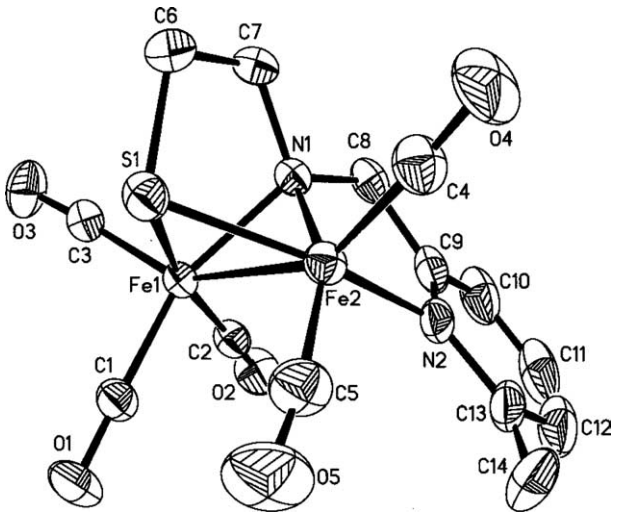


Fig. 2. ORTEP diagram of complex **7** with thermal ellipsoids at 30% probability.

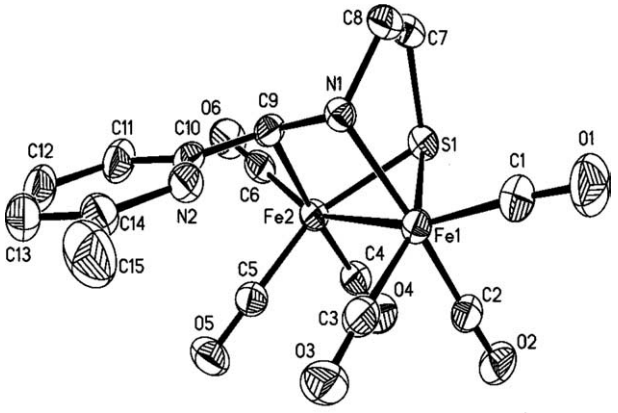


Fig. 3. ORTEP diagram of complex **8** with thermal ellipsoids at 30% probability.

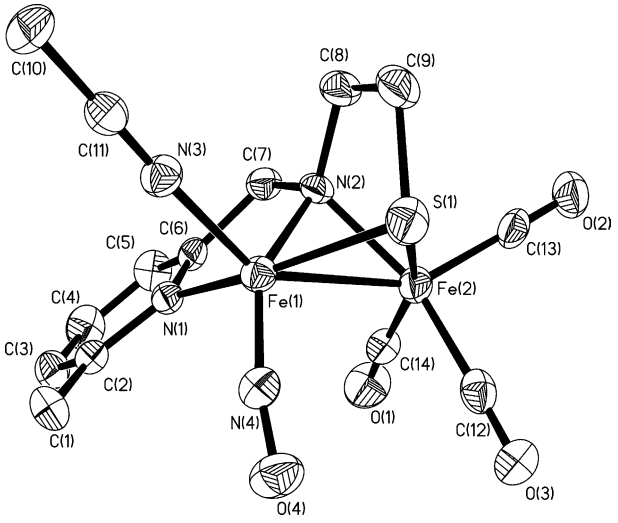


Fig. 4. ORTEP diagram of cationic complex of **9** with thermal ellipsoids at 30% probability.

Table 1
Crystal and data collection parameters for compounds **3**, **7**–**9**

Compound	**3**	**7**	**8**	**9**
Formula	$C_{14}H_{11}Fe_2NO_6S_2$	$C_{14}H_{12}Fe_2N_2O_5S$	$C_{15}H_{11}Fe_2N_2O_6S$	$C_{14}H_{15}BF_4Fe_2N_4O_4S$
Formula weight	465.06	432.02	459.02	533.87
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$	$P2_1/n$
a (Å)	8.889(2)	14.3200(2)	15.5940(1)	12.1025(8)
b (Å)	9.140(1)	10.5090(2)	11.1490(1)	12.9382(9)
c (Å)	11.948(3)	22.8380(3)	21.7270(2)	14.1981(10)
α (°)	95.34(2)			
β (°)	110.58(2)	98.230(1)	105.037(1)	113.747(1)
γ (°)	93.86(2)			
Volume (Å^3)	899.6(4)	3401.47(9)	3648.06(5)	2035.0(2)
Z	2	8	8	4
$D_{calc.}$ (g/cm^3)	1.717	1.687	1.672	1.743
Crystal size (mm)	$0.62 \times 0.40 \times 0.32$	$0.20 \times 0.15 \times 0.10$	$0.25 \times 0.20 \times 0.15$	$0.23 \times 0.20 \times 0.10$
Temperature (K)	298.2	295(2)	295(2)	150(2)
θ (°)	2.25–25.00	1.80–27.48	1.45–27.49	2.22–27.52
No. of reflection meads: total, unique	3385, 3166	3909, 3895	8352, 8312	4672, 3816
No. of observed reflections	2736 ($I > 3.00\sigma(I)$)	3229 ($I > 2.00\sigma(I)$)	5988 ($I > 2.00\sigma(I)$)	2637 ($I > 2.00\sigma(I)$)
No. of variables	226	218	470	273
F_{000}	468	1744	1848	1072
μ (Mo Kα) (cm^{-1})	18.72	23.32	17.38	15.93
R	0.048	0.044	0.046	0.040
R_w	0.056	0.108	0.109	0.050

crystal and data collection parameters are tabulated in Table 1 and selected bond lengths and bond angles are summarized in Table 2.

2.6.1. $Fe_2(CO)_6(MeC_4H_2SCH_2NCH_2CH_2S)$ (**3**)

Regarding complex **3**, it is evident in Fig. 1 that the thiolatoethylamido moiety is bonded to the diiron centers via the amido nitrogen, N(1), and thiolato sulfur, S(1), atoms. Each of these two donor atoms acts as a 3-electron donor and symmetrically bridges the two iron tricarbonyl fragments with an equal bond distance (1.986(9) Å for N–Fe bonds and 2.245 Å for S–Fe bonds). The Fe(1)–N(1)–Fe(2) and Fe(1)–S(1)–Fe(2) bond angles are 75.7(1) and 65.77(4)°, respectively, and the dihedral angle between two bridging planes is 77.1°. The ethylene moiety of the ligand is perpendicular to the iron–iron axis. The iron centers are in distorted octahedral environment. It can also be seen that two tricarbonyl groups on Fe(1) and Fe(2) are eclipsed and all COs are terminal. An iron–iron distance of 2.4378(9) Å is shorter than usual for diiron complexes and sulfur bridged diiron complexes [10] but is in accordance with that of other nitrogen bridged diiron complexes [6,11]. The distance from C(1) to N(1) is lengthened, from its former C=N double bond, to an extent of 1.487(6) Å, which is in the typical single bond range and is comparable to that of N(1)–C(6) single bond distance (1.488(6) Å).

2.6.2. $Fe_2(CO)_5(MeC_5H_3NCH_2NCH_2CH_2S)$ (**7**)

The way the thiolatoethylamido moiety coordinates to the diiron centers in complex **7**, as shown in Fig. 2, is the same as that in complex **3**. However, in complex **7**, the pyridine group displaces one of carbonyl ligands on the Fe(2) center via its basic nitrogen N(2) to form a new 5-membered chelating ring. While the distances from Fe(1) to N(1) and S(1) (1.995(2) and 2.2492(8) Å) as well as the dihedral angle between two bridging plane (77.2°) are kept about the same as those in complex **3**, the bond distances of Fe(2)–N(1) and Fe(2)–S(1) are found to be shortened to 1.927(2) and 2.189(8) Å, respectively, and the Fe(1)–N(1)–Fe(2) and Fe(1)–S(1)–Fe(2) bond angles are enlarged a little bit to the values of 77.56(5)° and 66.73(2)°. The adjustment of these bond distances may be attributed to the displacement of a carbonyl ligand with a weaker π-acceptor pyridine ligand. The N(2)–Fe(2) bond distance, 2.021(2) Å, is the longest one among the three Fe–N bonds in the complex. The N(1)–Fe(2)–N(2), S(1)–Fe(2)–N(2), and N(2)–Fe(2)–Fe(1) bond angles are 83.30(10), 154.55(7), and 97.82(7)°, respectively. An iron–iron distance of 2.4574(5) Å is longer than that in complex **3**. The C(8)–N(1) distance of 1.458(3) Å and the N(2)–C(8)–C(9) bond angle of 110.0(2)° also indicates the conversion of the original sp^2 methine carbon to a sp^3 methylene carbon, consistent with the appearance of new set of methylene protons (two doublet signals due to the two non-equivalent methylene protons) in its ^{1}H NNR spectrum and the disappearance of the C=N stretching absorption in its IR spectrum.

2.6.3. $Fe_2(CO)_6(MeC_5H_3NCHNCH_2CH_2SH)$ (**8**)

The coordination of the organic ligand in complex **8**, as shown in Fig. 3, is quite a novel mode. The thiol

Table 2
Selected bond lengths (Å) and bond angles (°) for complexes **3**, **7**–**9**.

Complex **3**			
Fe(1)–Fe(2)	2.4378(9)	Fe(1)–N(1)	1.984(4)
Fe(1)–S(2)	2.245(1)	Fe(2)–N(1)	1.987(9)
Fe(2)–S(2)	2.245(1)	C(1)–N(1)	1.487(6)
N(1)–Fe(1)–Fe(2)	52.2(1)	S(2)–Fe(1)–Fe(2)	57.10(4)
N(1)–Fe(1)–S(2)	77.1(1)	N(1)–Fe(2)–Fe(1)	52.1(1)
S(2)–Fe(2)–Fe(1)	57.13(4)	N(1)–Fe(2)–S(2)	77.1(1)
Fe(1)–N(1)–Fe(2)	75.7(1)	Fe(1)–S(2)–Fe(2)	65.77(4)
C(7)–N(1)–Fe(1)	114.3(3)	C(7)–N(1)–Fe(2)	113.4(3)
C(8)–S(2)–Fe(1)	98.9(2)	C(8)–S(2)–Fe(2)	98.0(2)
C(1)–N(1)–C(7)	108.2(3)	C(2)–C(1)–N(1)	115.9(4)
Complex **7**			
Fe(1)–Fe(2)	2.4574(5)	Fe(1)–N(1)	1.995(2)
Fe(1)–S(1)	2.2492(8)	Fe(2)–N(1)	1.927(2)
Fe(2)–S(1)	2.2189(8)	Fe(2)–N(2)	2.021(2)
C(8)–N(1)	1.458(3)		
N(1)–Fe(1)–Fe(2)	49.99(6)	S(1)–Fe(1)–Fe(2)	56.05(2)
N(1)–Fe(1)–S(1)	77.19(6)	N(1)–Fe(2)–Fe(1)	52.45(6)
S(1)–Fe(2)–Fe(1)	57.22(2)	N(1)–Fe(2)–S(1)	77.21(7)
N(2)–Fe(2)–Fe(1)	97.82(7)	N(1)–Fe(2)–N(2)	83.30(10)
N(2)–Fe(2)–S(1)	154.55(7)	Fe(1)–S(1)–Fe(2)	66.73(2)
Fe(1)–N(1)–Fe(2)	77.56(8)	C(8)–N(1)–Fe(1)	112.5(2)
C(6)–S(1)–Fe(1)	98.10(12)	C(6)–S(1)–Fe(2)	98.73(11)
C(7)–N(1)–Fe(1)	112.7(2)	C(7)–N(1)–Fe(2)	116.9(2)
Complex **8**			
Fe(1)–Fe(2)	2.5543(6)	Fe(1)–N(1)	2.030(2)
Fe(1)–S(1)	2.2473(9)	Fe(2)–S(1)	2.2602(9)
Fe(2)–C(9)	2.088(3)	C(9)–N(1)	1.489(4)
N(1)–Fe(1)–Fe(2)	76.12(7)	S(1)–Fe(1)–Fe(2)	55.72(2)
N(1)–Fe(1)–S(1)	80.83(8)	C(9)–Fe(2)–Fe(1)	77.74(8)
S(1)–Fe(2)–Fe(1)	55.24(2)	C(9)–Fe(2)–S(1)	86.87(9)
C(8)–N(1)–Fe(1)	110.2(2)	C(9)–N(1)–Fe(1)	103.2(2)
C(8)–N(1)–C(9)	111.3(2)	Fe(1)–S(1)–Fe(2)	69.04(3)
N(1)–C(9)–Fe(2)	104.7(2)	N(1)–C(9)–C(10)	110.2(3)
Complex **9**			
Fe(1)–Fe(2)	2.4220(6)	Fe(2)–N(2)	1.952(2)
Fe(2)–S(1)	2.2422(10)	Fe(1)–N(2)	1.937(2)
Fe(1)–S(1)	2.2675(9)	Fe(1)–N(1)	2.015(2)
Fe(1)–N(3)	1.996(3)	Fe(1)–N(4)	1.637(3)
C(7)–N(2)	1.480(3)	C(11)–N(3)	1.135(3)
N(4)–O(4)	1.180(3)		
N(2)–Fe(2)–Fe(1)	51.22(7)	S(1)–Fe(2)–Fe(1)	58.02(3)
N(2)–Fe(2)–S(1)	76.68(8)	N(2)–Fe(1)–Fe(2)	51.57(7)
S(1)–Fe(1)–Fe(2)	57.01(3)	N(2)–Fe(1)–S(1)	76.34(7)
N(1)–Fe(1)–Fe(2)	105.02(7)	N(1)–Fe(1)–N(2)	83.40(10)
N(1)–Fe(1)–S(1)	158.77(8)	Fe(1)–S(1)–Fe(2)	64.96(3)
Fe(1)–N(2)–Fe(2)	77.03(9)	Fe(1)–N(1)–C(2)	126.9(2)
C(7)–N(2)–C(8)	109.4(7)	Fe(1)–N(4)–O(4)	168.1(2)
Fe(1)–N(3)–C(11)	176.6(3)		

sulfur, i.e., S(1), serves as a 4-electron donor atom and bridges two iron centers. While the S(1)–Fe(1) bond distance, 2.2473(9) Å, is close to that in complexes **3** and **7**, the S(1)–Fe(2) bond distance is extended to 2.2602(9) Å. The Fe(1)–S(1)–Fe(2) bond angle is enlarged to a value of 69.04(3)°. The second bridge comes from the azomethine group, which coordinates to two iron centers via its π-electron system to form a 4-membered metallacycle with a Fe(1)–N(1)–C(9)–Fe(2) torsion angle of 10.12°. The C(9)–Fe(2) and N(1)–Fe(1) bond distances are 2.088(3) and 2.030(2) Å, and the bond angles for N(1)–Fe(1)–S(1) and C(9)–Fe(2)–S(1) are 80.83(8) and 86.87(9)°, respectively. The C(9)–N(1) bond distance is also found to be lengthened to a single bond value of 1.489(4) Å. This explains why the former imine proton signal is found to have substantially upfield shifted to δ 3.67 ppm in its ^{1}H NMR spectrum and the iron–iron distance in this case is extended to 2.5543(6) Å. The four inner angles N(1)–Fe(1)–Fe(2), C(9)–Fe(2)–Fe(1), C(9)–N(1)–Fe(1), and N(1)–C(9)–Fe(2) for the 4-membered metallacycle are 76.12(7), 77.74(8), 103.2(2), and 104.7(2)°, respectively. The iron centers are in distorted octahedral environment. It can also be seen that two tricarbonyl groups on Fe(1) and Fe(2) are eclipsed and all COs are terminal.

2.6.4. $[Fe_2(CO)_3(MeC_5H_3NCH_2NCH_2CH_2S)(NO)(MeCH_3)]BF_4$ (**9**)

The structure of cationic complex of **9**, as shown in Fig. 4, is similar to that of complex **7** geometrically. However, a nitrosyl and an acetonitrile ligands instead of two carbonyl ligands are linearly coordinated [12], with Fe(1)–N(4)–O(4) bond angle 168.1(2)° and Fe(1)–N(3)–C(11) bond angle 176.6(3)°, to the Fe(1) metal center. The strong π-backbonding nitrosyl ligand makes the Fe(1)–N(4) bond distance to be the shortest one (1.637(3) Å) among the five Fe–N bonds in the complex. The other four bonds are Fe(1)–N(1) 2.015(2), Fe(1)–N(3) 1.996(3), Fe(2)–N(2) 1.952(2), and Fe(1)–N(2) 1.937(2) Å, respectively. The presence of nitrosyl and acetonitrile ligands adjust the Fe(1)–S(1) bond distance from 2.2189(8) in complex **7** to 2.2675(9) Å and shorten the Fe(1)–Fe(2) bond distance to a value of a 2.4220(6) Å.

3. Experimental

Diiron nonacarbonyl was prepared through the 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. 5-Methyl-2-thiophenecarboxaldehyde (Fluka), 6-methyl-2-pyridincarboxaldehyde (ACROS), and 2-aminoethanethiol hydrochloride (Aldrich) were 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 (^{1}H, 299.95 MHz; ^{13}C, 75.43 MHz). Chemical shifts were referenced to TMS and deuterated chloroform or 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 employing 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 *n*-hexane (**3**), methanol/*n*-hexane (**7**), dichloromethane/*n*-hexane (**8**), and acetonitrile (**9**). A single crystal was mounted on a glass fiber and the X-ray diffraction intensity data were measured on a Rigaku AFC7S diffractometer (**3**) or a Bruker Smart 1000 CCD XRD (**7, 8**, and **9**).

*3.1. Synthesis of thienyl Schiff bases N-(5-methyl-2-thienylmethylidene)-2-thiolethylamine (**1**) and N-(6-methyl-2-pyridylmethylidene)-2-thiolethylamine (**6**)*

The synthesis of Schiff base employed the usual approach of condensation in ethanol solution [14]. 37 mmol of 2-aminoethanethiol hydrochloride was stirred with 50 mmol of sodium hydroxide in 50 ml distilled water for 4 h. 2-Aminoethanethiol was extracted with dichloromethane five times. After the concentration, the extracted 2-aminoethanethiol was mixed with 40 mmol of 5-methyl-2-thiophenecarboxaldehyde or 6-methyl-2-pyridinecarboxaldehyde in 50 ml 95% ethanol and the reaction mixture was heated at reflux for 20 h. The reaction mixture was then filtered and the solvent as well as unreacted starting material were removed in vacuo over night to yield pure oily yellow product **1** (29 mmol, 78% yield) or **6** (30 mmol, 81% yield).

Compound **1**. ^{1}H NMR ($CDCl_3$): δ 8.26 (s, 1H), 7.09 (d, J_{H-H} = 3.5 Hz, 1H), 6.71 (d, J_{H-H} = 3.5 Hz, 1H), 3.82 (t, J_{H-H} = 6.8 Hz, 2H), 3.00 (t, J_{H-H} = 6.8 Hz, 2H), 2.47 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$): δ 156.1, 144.5, 140.0, 131.4, 125.9, 59.9, 39.6, 15.9 ppm. IR (KBr film) ν_{max} (CN) 1631 cm^{-1}. MS (FAB): *m/z* 185 (M^+). Anal. Calc. for $C_8H_{11}NS_2$: C, 51.89; H, 5.95; N, 7.57; S, 34.59. Found: C, 51.76; H, 5.63; N, 7.75; S, 35.05%.

Compound **6**. ^{1}H NMR (CD_3COCD_3): δ 8.33 (s, 1H), 7.85 (d, J_{H-H} = 7.8 Hz, 1H), 7.70 (t, J_{H-H} = 7.8 Hz, 1H), 7.25 (d, J_{H-H} = 7.8 Hz, 1H), 3.97 (t, J_{H-H} = 6.6 Hz, 2H), 3.13 (t, J_{H-H} = 6.6 Hz, 2H), 2.51 (s, 3H) ppm. ^{13}C NMR (CD_3COCD_3): δ 163.7, 158.0, 154.1, 136.6, 124.1, 117.6, 59.5, 39.3, 23.4 ppm. IR (KBr film) ν_{max} (CN) 1631 cm^{-1}. MS (FAB): *m/z* 180 (M^+). Anal. Calc. for $C_9H_{12}N_2S$: C, 60.23; H, 6.40; N, 14.25; S, 14.53. Found: C, 60.25; H, 6.59; N, 14.23; S, 14.51%.

*3.2. Reaction of **1** with $Fe_2(CO)_9$ in refluxing acetonitrile to yield di-(μ_3-thia)nonacarbonyltriiron (**2**), μ-[N-(5-methyl-2-thienylmethyl)-η^1:η^1(N);η^1:η^1(S)-2-thiolatoethylamido]hexacarbonyldiiron (**3**), and N-(5-methyl-2-thienylmethylidene)amine (**4**)*

3.20 mmol of ligand **1** and 10.0 mmol of $Fe_2(CO)_9$ were heated at reflux in a 60 ml of anhydrous acetonitrile in the dark under nitrogen for 4 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 resulting red product **2** and yellow product **3**. The column was further treated with *n*-hexane/ethyl acetate (5/1) as eluent to obtain another yellow product **4**.

Compound **2**: 0.37 mmol, 23% yield; m.p. 108.6–109.0 °C. IR ($CHCl_3$) ν_{max} (CO) 2041, 2014, 1993 cm^{-1}. Anal. Calc. for $C_9Fe_3O_9S_2$: C, 22.31; S, 13.22. Found: C, 22.53; S, 13.06%.

Compound **3**: 0.45 mmol, 14% yield; m.p. 101.5–102.0 °C. ^{1}H NMR ($CDCl_3$): δ 6.78 (d, J_{H-H} = 3.3 Hz, 1H), 6.59 (d, J_{H-H} = 3.3 Hz, 1H), 4.44 (s, 2H), 2.62 (t, J_{H-H} = 6.3 Hz, 2H), 2.47 (s, 3H), 2.36 (t, J_{H-H} = 6.3 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 207.4, 140.5, 138.9, 128.2, 124.4, 69.5, 62.4, 33.6, 15.5 ppm. IR (KBr film) ν_{max} (CN) 1631 cm^{-1}; (CO) 2067, 2027, 1993, 1967 cm^{-1}. MS (FAB): *m/z* 465 (M^+), 437 (M^+–CO), 409 (M^+–2CO), 381 (M^+–3CO), 353 (M^+–4CO), 325 (M^+–5CO), 297 (M^+–6CO), 241 (M^+–6CO–Fe), 185 (L^+). Anal. Calc. for $C_{14}H_{11}Fe_2NO_6S_2$: C, 36.16; H, 2.37; N, 3.01; S, 13.79. Found: C, 36.18; H, 2.21; N, 2.99; S, 13.63%.

Compound **4**: 0.74 mmol, 23% yield; ^{1}H NMR ($CDCl_3$): δ 7.78 (d, J_{H-H} = 15.6 Hz, 1H), 7.30 (d, J_{H-H} = 3.6 Hz, 1H), 6.84 (d, J_{H-H} = 3.6 Hz, 1H), 6.80 (d, J_{H-H} = 15.6 Hz, 1H), 2.51 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$): δ 145.1, 136.0, 132.7, 126.9, 123.4, 16.0 ppm. IR ($CHCl_3$) ν_{max} (CN) 1600 cm^{-1}. MS (FAB): *m/z* 125 (M^+). Anal. Calc. for C_6H_7NS: C, 57.56; H, 5.64; N, 11.20; S, 25.63. Found: C, 57.78; H, 5.82; N, 11.16; S, 25.37%.

*3.3. Reaction of **1** with $Fe_2(CO)_9$ in acetonitrile at 45 °C to yield N-(5-methyl-2-thienylmethyliden)amine (**4**), and di-μ-[N-(5-methyl-2-thienylmethylidene)-η^1(N);η^1(S)-2-thiolethylamino]-μ-carbonyl-tetracarbonyldiiron (**5**)*

If the above mentioned reaction (Section 3.2) was carried out at 45 °C, after an aluminum oxide (neutral) column separation with *n*-hexane as eluent, only reddish orange complex **5** and trace amount of **4** were produced.

Compound **5**: 0.76 mmol, 48% yield; ^{1}H NMR (CD_3CN): δ 8.29 (s, 2H), 7.15 (d, J_{H-H} = 3.3 Hz, 2H), 6.77 (d, J_{H-H} = 3.3 Hz, 2H), 3.70 (t, J_{H-H} = 6.3 Hz, 4H), 2.73 (t, J_{H-H} = 6.3 Hz, 4H), 2.47 (s, 6H) ppm. IR (CH_3CN) ν_{max} (CO) 2068, 2031, 1983, 1732 cm^{-1}; (CN) 1609 cm^{-1}. MS (FAB): *m/z* 622 (M^+), 594 (M^+–CO), 566 (M^+–2CO), 538 (M^+–3CO), 510 (M^+–4CO), 482 (M^+–5CO), 297 (M^+–5CO–L), 241 (M^+–5CO–Fe–L), 185 (L^+). Anal. Calc. for $C_{21}H_{22}Fe_2N_2O_5S_4$: C, 40.53; H, 3.56; N, 4.50; S, 20.61. Found: C, 40.68; H, 3.70; N, 4.55; S, 20.52%.

3.4. Reaction of **5** with $Fe_2(CO)_9$ in refluxing acetonitrile to yield **2**–**4**

Stirring **5** in refluxing acetonitrile for 3 h led to the thermal decomposition of **5**, and ligand **1** was recovered quantitatively. However, in the presence of excess amount of $Fe_2(CO)_9$ in refluxing acetonitrile, complex **5** was converted into **2**–**4** with the similar % yields to that in Section 2.2 after 4 h of reaction.

3.5. Reaction of ligand **6** with $Fe_2(CO)_9$ in refluxing acetonitrile to yield di-(μ_3-thia)nonacarbonyltriiron (**2**), μ-[*N*-(6-methyl-2-pyridylmethyl)-$\eta^1(N_{py})$;η^1:$\eta^1(N)$;η^1:$\eta^1(S)$-2-thiolatoethylamido]pentacarbonyldiiron (**7**), and μ-[*N*-(6-methyl-2-pyridylmethylidene)-$\eta^2(C,N)$;η^1:η^1-(*S*)-2-thiolethylamino]hexacarbonyldiiron (**8**)

3.00 mmol of ligand **6** and 10.0 mmol of $Fe_2(CO)_9$ were heated at reflux in a 60 ml of anhydrous acetonitrile solution in the dark under nitrogen for 4 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 resulting red product **2** (0.14 mmol, 9.3% yield). The column was further treated with *n*-hexane/ethyl acetate (10/1) as eluent to obtain deep red product **7** and yellow product **8**.

Compound **7**: 1.08 mmol, 36% yield; m.p. 116.0–117.0 °C. ^{1}H NMR (CD_3COCD_3): δ 7.63 (t, $J_{H-H} = 7.8$ Hz, 1H), 7.27 (d, $J_{H-H} = 7.8$ Hz, 1H), 7.22 (d, $J_{H-H} = 7.8$ Hz, 1H), 5.07 (d, $J_{H-H} = 18.6$ Hz, 1H), 4.94 (d, $J_{H-H} = 18.6$ Hz, 1H), 3.42 (td, $J_{H-H} = 6.0$, 20.4 Hz, 2H), 2.93 (s, 3H), 2.35 (t, $J_{H-H} = 6.0$ Hz, 2H) ppm. ^{13}C NMR (CD_3COCD_3): δ 219.2, 211.9, 166.6, 162.7, 136.5, 123.9, 117.5, 72.8, 65.1, 36.0, 28.2 ppm. IR (KBr film) ν_{max} (CO) 2024, 1966, 1945, 1909 cm^{-1}. MS (FAB): *m*/*z* 432 (M^+), 404 (M^+–CO), 376 (M^+–2CO), 348 (M^+–3CO), 320 (M^+–4CO), 292 (M^+–5CO), 180 (L^+). Anal. Calc. for $C_{14}H_{12}Fe_2N_2O_5S$: C, 38.92; H, 2.80; N, 6.49; S, 7.42. Found: C, 39.06; H, 2.91; N, 6.42; S, 7.36%.

Compound **8**: 0.31 mmol, 10% yield; m.p. 122.5 – 123.0 °C. ^{1}H NMR (CD_3COCD_3): δ 7.52 (t, $J_{H-H} = 7.8$ Hz, 1H), 6.87 (d, $J_{H-H} = 7.8$ Hz, 1H), 6.83 (d, $J_{H-H} = 7.8$ Hz, 1H), 5.38 (s, 1H), 3.67(s, 1H), 3.37 (td, $J_{H-H} = 6.6$, 19.8 Hz, 1H), 3.05 (td, $J_{H-H} = 6.6$, 19.8 Hz, 1H), 2.76 (m, 2H), 2.50 (s, 3H) ppm. ^{13}C NMR (CD_3COCD_3): δ 208.0, 167.1, 156.0, 136.6, 129.4, 118.0, 116.9, 59.4, 51.2, 27.3, 23.0 ppm. IR (KBr film) ν_{max} (CO) 2061, 2014, 1973, 1931 cm^{-1}. MS (FAB): *m*/*z* 460 (M^+), 432 (M^+–CO), 404 (M^+–2CO), 376 (M^+–3CO), 348 (M^+–4CO), 320 (M^+–5CO), 292 (M^+–6CO), 180 (L^+). Anal. Calc. for $C_{15}H_{12}Fe_2N_2O_6S$: C, 39.16; H, 2.63; N, 6.09; S, 6.97. Found: C, 39.31; H, 2.81; N, 6.13; S, 6.92%.

3.6. Reactions of complexes **7** and **8** with $NOBF_4$ to give μ-[*N*-(6-methyl-2-pyridylmethyl)-$\eta^1(N_{py})$;η^1:$\eta^1(N)$;η^1:$\eta^1(S)$-2-thiolatoethylamido](acetonitrile)tricarbonylnitrosyldiiron (**9**)

0.22 mmol of complex **7**/**8** and 0.26 mmol of $NOBF_4$ in 50 ml of anhydrous acetonitrile was stirred at room temperature for 72 h. The red precipitate thus formed was filtered, washed with several portions of acetonitrile, and dried under vacuum to give 0.068 mmol (31%)/0.014 mmol (6%) of complex **9**. IR (KBr film) ν_{max} (CN) 2247 cm^{-1}; (CO) 2048, 2031, 2004 cm^{-1}; (NO) 1815 cm^{-1}. MS (FAB): *m*/*z* 447 (M^+), 406 (M^+–MeCN), 378 (M^+–MeCN–CO), 350 (M^+–MeCN–2CO), 292 (M^+–MeCN–3CO–NO), 180 (L^+). Anal. Calc. for $C_{14}H_{15}BF_4Fe_2N_4O_4S$: C, 31.50; H, 2.83; N, 10.49; S, 6.01. Found: C, 31.62; H, 3.01; N, 10.77; S, 6.24%.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 220746 (**3**), 220747-220749 (**7**–**9**). 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).

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