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Synthesis and characterization of new acyclic polyethers and macrocyclic crown ethers containing double-butterfly Fe_4S_3 cluster cores. Crystal structures of $\{[Fe_2(CO)_6]_2(\mu_4\text{-}S)\}_2[\mu\text{-}SCH_2(CH_2OCH_2)_2CH_2S\text{-}\mu_2]$ and $\{[Fe_2(CO)_6]_2(\mu_4\text{-}S)\}_2[\mu\text{-}SCH_2(CH_2OCH_2)_2CH_2S\text{-}\mu][\mu\text{-}SCH_2(CH_2OCH_2)_3CH_2S\text{-}\mu]$

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Abstract

The $[Et_3NH]^+$ salts of dianions $\{[(\mu\text{-}CO)Fe_2(CO)_6]_2(\mu\text{-}SZS\text{-}\mu)\}^{2-}$, prepared from $Fe_3(CO)_{12}$, dithiol HSZSH and Et_3N, with $(\mu\text{-}S_2)Fe_2(CO)_6$ followed by treatment with monohalides $ClCH_2CO_2Et$, PhHgCl and PhC(Cl)=NPh to give acyclic polyether clusters $\{(\mu\text{-}RS)[Fe_2(CO)_6]_2(\mu_4\text{-}S)\}_2(\mu\text{-}SZS\text{-}\mu)$ [**1**–**5**: R = CH_2CO_2Et, PhHg, PhC=NPh; Z = $CH_2(CH_2OCH_2)_{2-4}CH_2$], while they reacted with $(\mu\text{-}S_2)Fe_2(CO)_6$ and subsequent treatment with dihalides $BrCH_2(CH_2OCH_2)_{2-4}CH_2Br$ under similar conditions to afford macrocyclic crown ether clusters $\{[Fe_2(CO)_6]_2(\mu_4\text{-}S)\}_2(\mu\text{-}SZS\text{-}\mu)(\mu\text{-}SYS\text{-}\mu)$ [**6**–**11**: Z, Y = $CH_2(CH_2OCH_2)_{2-4}CH_2$]. Clusters **1**–**11** are new, and have been characterized by elemental analysis and spectroscopy, as well as for **6** [Z = Y = $CH_2(CH_2OCH_2)_2CH_2$] and **9** [Z = $CH_2(CH_2OCH_2)_2CH_2$, Y = $CH_2(CH_2OCH_2)_3CH_2$] by X-ray diffraction techniques.

Keywords: Fe_4S_3 Clusters; Crown ethers; Synthesis; Crystal structure

1. Introduction

In recent years, the acyclic polyethers and macrocyclic crown ethers, have drawn growing interest, primarily because of their unique structures, novel properties and the important applications in numerous fields, such as catalytic organic synthesis, molecular and ion recognition, and chemical sensor technology [1–5]. Among such ethers we are particularly interested in those containing transition-metal cluster cores, since the affinity of the crown ether or its acyclic analog subunit toward metal complexation could be controlled by the oxidation state of the redox-active metal centers in the cluster cores. So far, we have reported some acyclic polyethers and macrocyclic crown ethers, such as those with the redox-active tetrahedral MCoFeS and M_2FeS (M = Mo, W) cluster cores [6–9]. Herein we describe the synthesis and structural characterization of some other new acyclic polyethers and macrocyclic crown ethers containing the double-butterfly Fe_4S_3 cluster cores, which were prepared by reactions of the CO-bridged dianions $\{[(\mu\text{-}CO)Fe_2(CO)_6]_2(\mu\text{-}SZS\text{-}\mu)\}^{2-}$ with a series of electrophiles, such as $ClCH_2CO_2Et$, PhHgCl, PhC(Cl)=NPh and $BrCH_2(CH_2OCH_2)_nCH_2Br$ (n = 2–4).

2. Results and discussion

2.1. Synthesis and spectroscopic characterization of $\{(\mu\text{-}RS)[Fe_2(CO)_6]_2(\mu_4\text{-}S)\}_2(\mu\text{-}SZS\text{-}\mu)$ (**1**–**5**) and $\{[Fe_2(CO)_6]_2(\mu_4\text{-}S)\}_2(\mu\text{-}SZS\text{-}\mu)(\mu\text{-}SYS\text{-}\mu)$ (**6**–**11**)

The $[Et_3NH]^+$ salts of dianions $\{[(\mu\text{-}CO)Fe_2(CO)_6]_2(\mu\text{-}SZS\text{-}\mu)\}^{2-}$ (**m**) [Z = $CH_2(CH_2OCH_2)_{2-4}CH_2$] were

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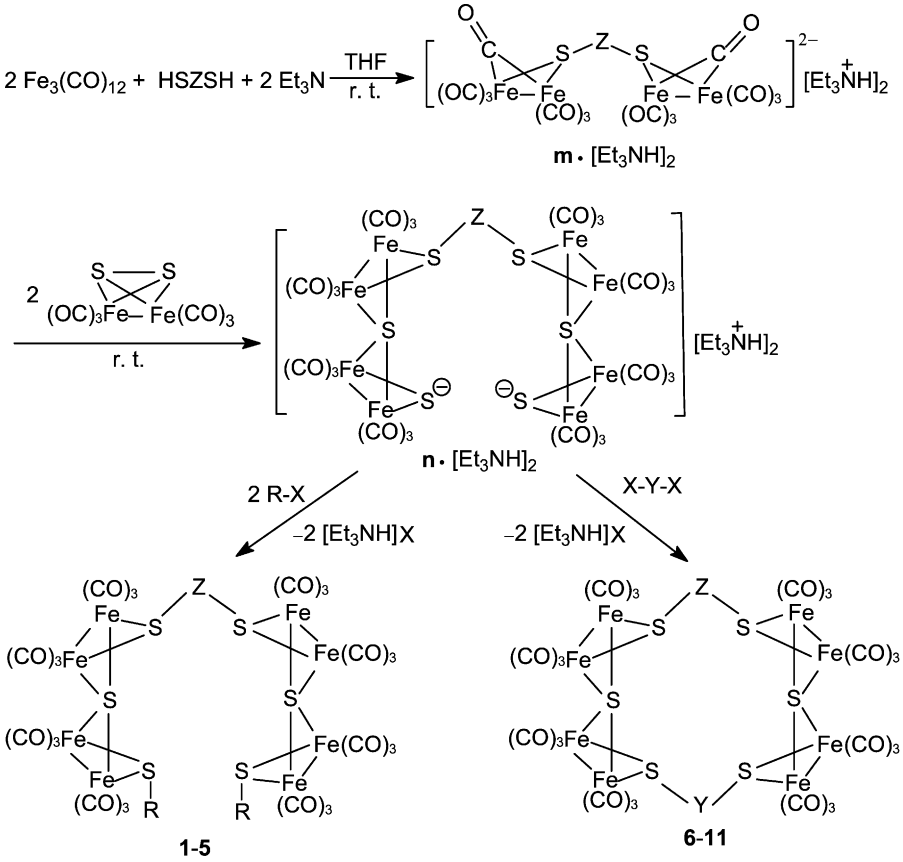
prepared from $Fe_3(CO)_{12}$, dithiol HSZSH and Et_3N, which showed an absorption band at ca. $\nu = 1744\ cm^{-1}$, characteristic of their μ-CO ligands [10]. These salts reacted in situ with an equivalent of $(\mu\text{-}S_2)Fe_2(CO)_6$ to give the $[Et_3NH]^+$ salts of the S-centered dianions $\{(\mu\text{-}S^-)[Fe_2(CO)_6]_2(\mu_4\text{-}S)\}_2(\mu\text{-}SZS\text{-}\mu)$ (**n**) [10]. Further treatment of the $[Et_3NH]^+$ salts of dianions **n** with an equivalent or an excess of mono- and dihalides afforded a series of the corresponding acyclic polyether clusters **1**–**5** and macrocyclic crown ether clusters **6**–**11**, respectively (Scheme 1).

These products, particularly the macrocyclic crown ethers containing multiple iron metal centers, **6**–**11**, are of great interest, since they might like pentaoxaferrocenophane [11], an organometallic crown ether with single iron metal center, to have the electrochemically switched cation-binding ability. Products **1**–**11** are air-stable solids, which have been characterized by elemental analysis, and IR and ^1H NMR spectroscopy. The IR spectra of **1**–**11** showed one absorption band in the range 1102–1124 cm^{-1} for their C–O–C ether chains and several absorption bands in the region 1981–2090 cm^{-1} for their terminal carbonyls. In addition, the IR spectra of **1** and **2** displayed one absorption band at 1738 and 1737 cm^{-1} for their ester's carbonyls, whereas **5** exhibited absorption band at 1613 cm^{-1} for its C=N double bond. It is worth pointing out that the ^1H NMR spectra of **1**–**11** showed only one set of signals for their μ_2-SCH_2 groups at above 2 ppm, which implies that the R, Z and Y groups are attached to the bridged μ_2-S atoms by an equatorial type of bond [12], in order to avoid the strong repulsions between the axially bonded R, Z and Y groups with the adjacent butterfly Fe_2S_2 subcluster cores [13]. Fortunately, this has been confirmed by X-ray crystallographic studies of **6** and **9** (vide infra).



	Z	R
1	$CH_2(CH_2OCH_2)_2CH_2$	CH_2CO_2Et
2	$CH_2(CH_2OCH_2)_3CH_2$	CH_2CO_2Et
3	$CH_2(CH_2OCH_2)_2CH_2$	PhHg
4	$CH_2(CH_2OCH_2)_3CH_2$	PhHg
5	$CH_2(CH_2OCH_2)_3CH_2$	PhC=NPh

	Z	Y
6	$CH_2(CH_2OCH_2)_2CH_2$	$CH_2(CH_2OCH_2)_2CH_2$
7	$CH_2(CH_2OCH_2)_3CH_2$	$CH_2(CH_2OCH_2)_3CH_2$
8	$CH_2(CH_2OCH_2)_4CH_2$	$CH_2(CH_2OCH_2)_4CH_2$
9	$CH_2(CH_2OCH_2)_2CH_2$	$CH_2(CH_2OCH_2)_3CH_2$
10	$CH_2(CH_2OCH_2)_2CH_2$	$CH_2(CH_2OCH_2)_4CH_2$
11	$CH_2(CH_2OCH_2)_3CH_2$	$CH_2(CH_2OCH_2)_4CH_2$

Scheme 1.

2.2. Crystal structures of **6** and **9**

The molecular structures of **6** and **9** were confirmed by X-ray crystallography. While Figs. 1 and 2 show the structures of **6** and **9**, Tables 1 and 2 list their selected bond lengths and angles, respectively. As can be seen in Fig. 1, cluster **6** consists of two double-butterfly Fe_4S_3 cluster cores and the two μ_4-S atoms, S(2) and S(5), are coordinated, respectively, to the four corresponding iron atoms. In addition, the two μ_2-S atoms, S(1) and S(6), are bonded to C(31) and C(36) of one ether chain $CH_2(CH_2OCH_2)_2CH_2$, and the other two μ_2-S atoms, S(3) and S(4), are bound to C(25) and C(30) of another ether chain $CH_2(CH_2OCH_2)_2CH_2$ to form a 26-membered macrocycle. The two identical ether chains are indeed attached to the double-butterfly Fe_4S_3 clusters by an equatorial type of bond [12], which is necessary to avoid the strong axial–axial repulsions of one ether chain with the axially bonded subclusters Fe(3)Fe(4)S(2)S(3) and Fe(7)Fe(8) S(4)S(5) or another ether chain with the axially bound subclusters Fe(1)Fe(2)S(1)S(2) and Fe(5)Fe(6)S(5)S(6) [13].

The structure of **9**, as shown in Fig. 2, is very similar to that of **6**. However, it is different from **6** that complex **9** contains two different ether chains, $CH_2(CH_2OCH_2)_2CH_2$ and $CH_2(CH_2OCH_2)_3CH_2$; thus, **9** is a 29-membered macrocyclic cluster crown ether and has slightly different magnitude of the corresponding geometric parameters, as compared to those of **6**. For example, as seen in Table 3, the selected geometric parameters of **6** is slightly larger than the corresponding those of **9**. Finally, it should be noted that each unit cell of **6** contains two molecules of **6** and two molecules of CH_2Cl_2, whereas that of **9** has two molecules of **9** and three molecules of MeOH, apparently the solvent molecules CH_2Cl_2 and MeOH being derived from the crystal growing processes.

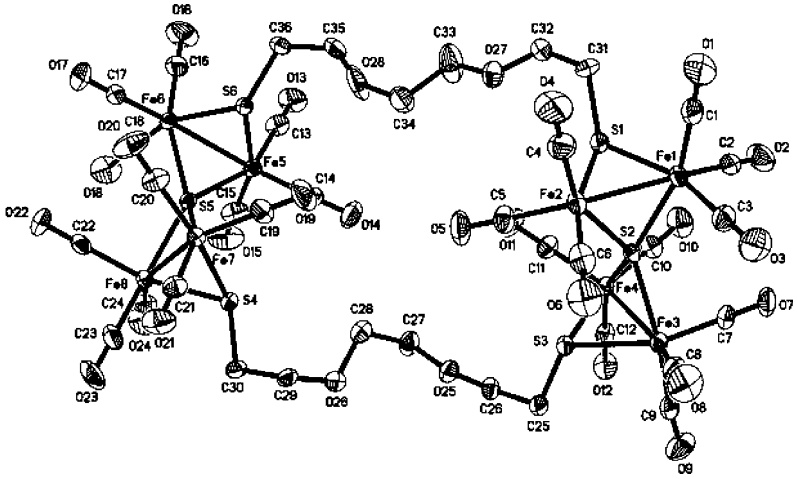


Fig. 1. ORTEP plot of **6** with the atom labeling scheme.

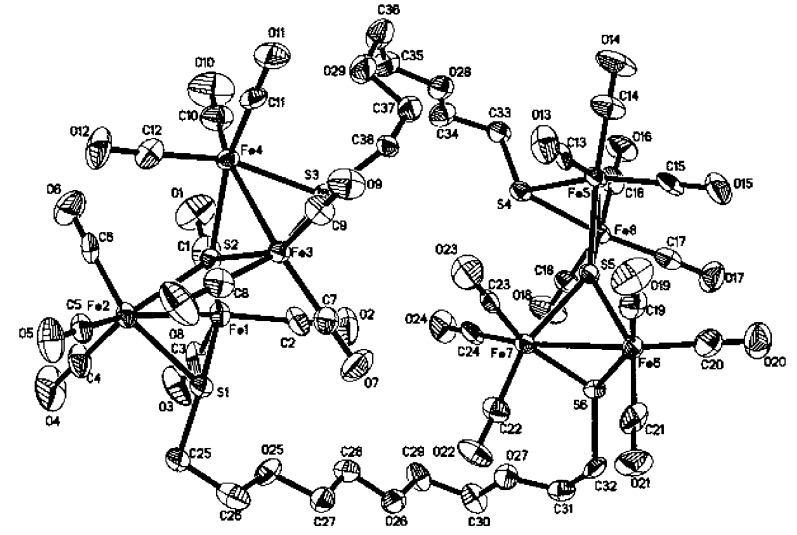


Fig. 2. ORTEP plot of **9** with the atom labeling scheme.

Table 1
Selected bond lengths (Å) and angles (deg) for **6**

Fe(1)–S(2)	2.235(2)	Fe(3)–S(3)	2.276(2)
Fe(1)–S(1)	2.269(3)	Fe(3)–Fe(4)	2.5445(19)
Fe(1)–Fe(2)	2.556(2)	Fe(3)–S(2)	2.245(3)
Fe(2)–S(2)	2.236(3)	Fe(4)–S(2)	2.247(2)
Fe(2)–S(1)	2.290(3)	Fe(4)–S(3)	2.290(3)
S(2)–Fe(1)–S(1)	76.80(9)	S(2)–Fe(2)–Fe(1)	55.12(7)
S(2)–Fe(1)–Fe(2)	55.15(7)	Fe(1)–S(1)–Fe(2)	68.19(9)
S(1)–Fe(1)–Fe(2)	56.28(8)	Fe(1)–S(2)–Fe(2)	69.72(8)
S(2)–Fe(2)–S(1)	76.37(9)	S(2)–Fe(3)–S(3)	76.77(8)
S(1)–Fe(2)–Fe(1)	55.53(7)	S(2)–Fe(3)–Fe(4)	55.54(7)

Table 2
Selected bond lengths (Å) and angles (deg) for **9**

Fe(1)–S(2)	2.239(3)	Fe(3)–S(3)	2.253(4)
Fe(1)–S(1)	2.253(4)	Fe(3)–Fe(4)	2.532(2)
Fe(1)–Fe(2)	2.511(3)	Fe(3)–S(2)	2.239(3)
Fe(2)–S(2)	2.244(3)	Fe(4)–S(2)	2.238(3)
Fe(2)–S(1)	2.250(4)	Fe(4)–S(3)	2.255(3)
S(2)–Fe(1)–S(1)	76.73(12)	S(2)–Fe(2)–Fe(1)	55.85(9)
S(2)–Fe(1)–Fe(2)	56.04(10)	S(2)–Fe(3)–S(3)	77.79(12)
S(1)–Fe(1)–Fe(2)	56.06(10)	S(2)–Fe(4)–S(3)	77.77(12)
S(2)–Fe(2)–S(1)	76.70(12)	S(2)–Fe(4)–Fe(3)	55.58(9)
Fe(2)–S(1)–Fe(1)	67.76(11)	S(3)–Fe(4)–Fe(3)	55.79(9)

Table 3
A comparison between some geometric parameters (average bond length (Å) or average bond angle (°)) of **6** and **9**

	6	**9**
Fe–Fe	2.547	2.526
Fe–(μ_2-S)	2.274	2.260
Fe–(μ_4-S)	2.246	2.238
Fe–(μ_2-S)–Fe	68.12	67.98
Fe–(μ_4-S)–Fe	69.07	68.74

3. Experimental

All reactions were carried out under an atmosphere of prepurified nitrogen using standard Schlenk and vacuum-line techniques. Tetrahydrofuran (THF) was distilled from Na/benzophenone ketyl under nitrogen. (μ-S_2)$Fe_2(CO)_6$ [12], $Fe_3(CO)_{12}$ [14], $HSCH_2(CH_2OCH_2)_nCH_2SH$ ($n = 2$–4) [15], $BrCH_2(CH_2OCH_2)_n$-CH_2Br ($n = 2$–4) [16], PhHgCl [17] and PhC (Cl)=NPh [18] were prepared according to the literature. Et_3N and $ClCH_2CO_2Et$ were of commercial origin and used without further purification. Preparative TLC was carried out on glass plates ($26 \times 20 \times 0.25$ cm) coated with silica gel H (10–40 μm). IR spectra were recorded on a Bio-Rad FTS 135 infrared spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AC-P 200 NMR spectrometer. Elemental analysis was performed on an elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus and were uncorrected.

3.1. Standard in situ preparation of the intermediate salts {[(μ-CO)$Fe_2(CO)_6$]$_2$(μ-SZS-μ)}[Et_3NH]$_2$ (**m**·[Et_3NH]$_2$)

A 100 ml three-necked flask equipped with a magnetic stir-bar, a rubber septum and a nitrogen inlet tube was charged with 1.00 g (1.98 mmol) of $Fe_3(CO)_{12}$, 30 ml of THF, 1.0 mmol of HSZSH [$Z = CH_2(CH_2OCH_2)_nCH_2$ ($n = 2$–4)] and 0.28 ml (2.0 mmol) of Et_3N. The mixture was stirred at room temperature for 45 min to give a brown-red solution of the intermediate salts **m**·[Et_3NH]$_2$, which were employed immediately in the following preparations.

3.2. Preparation of {(μ-SCH_2CO_2Et)[$Fe_2(CO)_6$]$_2$(μ$_4$-S)}$_2$[μ-$SCH_2(CH_2OCH_2)_2$ CH_2S-μ] (**1**)

To the above prepared solution of **m**·[Et_3NH]$_2$ [$Z = CH_2(CH_2OCH_2)_2CH_2$] was added 0.688 g (2.0 mmol) of (μ-S_2)$Fe_2(CO)_6$ and the mixture was stirred at room temperature for ca. 2 h. To this mixture was added 0.245 g (2.0 mmol) of $ClCH_2CO_2Et$ and the new mixture was stirred at room temperature for 24 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 2:1) as eluent. From the main red band 0.315 g (20%) of **1** was obtained as a red solid; m.p. 54–56 °C. Anal. Found: C, 28.70; H, 1.81.Calc. for $C_{38}H_{26}Fe_8O_{30}S_6$: C, 28.49; H, 1.64%. IR (KBr disk): $\nu_{C\equiv O}$ 2085 s, 2039 vs, 1993 vs; $\nu_{C=O}$ 1738 s; ν_{C-O-C} 1117 m cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.29 (br s, 6H, $2CH_3$), 2.65 (br s, 4H, $2CH_2S$), 3.16 (br.s, 4H, $2SCH_2CO_2$), 3.69 (br s, 8H, $4CH_2O$), 4.23 (br s, 4H, $CO_2CH_2CH_3$) ppm.

3.3. Preparation of {(μ-SCH_2CO_2Et)[$Fe_2(CO)_6$]$_2$(μ$_4$-S)}$_2$ [μ-$SCH_2(CH_2OCH_2)_3CH_2S$-μ] (**2**)

The same procedure as that for **1** was followed, but **m**·[Et_3NH]$_2$ [$Z = CH_2(CH_2OCH_2)_3CH_2$] was used. From the main red band 0.460 g (28%) of **2** was obtained as a red solid; m.p. 58–60 °C. Anal. Found: C, 29.30; H, 2.01. Calc. for $C_{40}H_{30}Fe_8O_{31}S_6$: C, 29.19; H, 1.84%. IR (KBr disk): $\nu_{C\equiv O}$ 2085 s, 2040 vs, 1993 vs; $\nu_{C=O}$ 1737s; ν_{C-O-C} 1117m cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.30 (br s, 6H, $2CH_3$), 2.66 (br s, 4H, $2CH_2S$), 3.17 (br s, 4H, $2SCH_2CO_2$), 3.68 (br s, 12H, $6CH_2O$), 4.23 (br s, 4H, $CO_2CH_2CH_3$) ppm.

3.4. Preparation of {(μ-$SHgPh$)[$Fe_2(CO)_6$]$_2$(μ$_4$-S)}$_2$ [μ-$SCH_2(CH_2OCH_2)_2CH_2S$-μ] (**3**)

The same procedure as that for **1** was followed, but 1.252 g (4.0 mmol) of PhHgCl was used instead of $ClCH_2CO_2Et$. From the main red band 0.596 g (30%) of **3** was obtained as a red solid; m.p. 116 °C (dec). Anal. Found: C, 25.41; H, 1.13. Calc. for $C_{42}H_{22}Fe_8Hg_2O_{26}S_6$:

C, 25.44; H, 1.12%. IR (KBr disk): $\nu_{C\equiv O}$ 2067 s, 2030 vs, 1986 vs; ν_{C-O-C} 1124 m cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 2.68 (br s, 4H, $2CH_2S$), 3.69 (br s, 8H, $4CH_2O$), 7.20–7.40 (m, 10H, $2C_6H_5$) ppm.

3.5. Preparation of {(μ-SHgPh)[Fe$_2$(CO)$_6$]$_2$(μ$_4$-S)}$_2$[μ-SCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$S-μ] (4)

The same procedure as that for **1** was followed, but $\mathbf{m}\cdot[Et_3NH]_2$ [$Z = CH_2(CH_2OCH_2)_3CH_2$] and 1.252 g (4.0 mmol) of PhHgCl were used. From the main red band 0.636 g (31%) of **4** was obtained as a red solid; m.p. 118 °C (dec). Anal. Found: C, 26.05; H, 1.16. Calc. for $C_{44}H_{26}Fe_8Hg_2O_{27}S_6$: C, 26.07; H, 1.29%. IR (KBr disk): $\nu_{C\equiv O}$ 2079 s, 2033 vs, 1986 vs; ν_{C-O-C} 1113 m cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 2.68 (br s, 4H, $2CH_2S$), 3.69 (br s, 12H, $6CH_2O$), 7.19–7.41(m, 10H, $2C_6H_5$) ppm.

3.6. Preparation of {[μ-SC(Ph)=NPh][Fe$_2$(CO)$_6$]$_2$(μ$_4$-S)}$_2$[μ-SCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$S-μ] (5)

The same procedure as that for **1** was followed, but $\mathbf{m}\cdot[Et_3NH]_2$ [$Z = CH_2(CH_2OCH_2)_3CH_2$] and 0.864 g (4.0 mmol) of PhC(Cl)=NPh were used. From the main red band 0.946 g (52%) of **5** was obtained as a red solid; m.p. 95–97 °C. Anal. Found: C, 37.98; H, 1.97, N, 1.54. Calc. for $C_{58}H_{36}Fe_8N_2O_{27}S_6$: C, 38.02; H, 1.98, N, 1.53%. IR (KBr disk): $\nu_{C\equiv O}$ 2084 s, 2040 vs, 1996 vs; $\nu_{C=N}$ 1613 m, 1591 m; ν_{C-O-C} 1116 m cm^{-1}.^1H NMR (200 MHz, $CDCl_3$): δ 2.67 (t, 4H, $J = 3.6$ Hz, $2CH_2S$), 3.68–3.76 (m, 12H, $6CH_2O$), 6.52–8.19 (m, 20H, $4C_6H_5$) ppm.

3.7. Preparation of {[Fe$_2$(CO)$_6$]$_2$(μ$_4$-S)}$_2$[μ-SCH$_2$(CH$_2$OCH$_2$)$_2$CH$_2$S-μ]$_2$ (6)

To the above prepared solution of $\mathbf{m}\cdot[Et_3NH]_2$ [$Z = CH_2(CH_2OCH_2)_2CH_2$] was added 0.688 g (2.0 mmol) of (μ-S_2)$Fe_2(CO)_6$ and the mixture was stirred at room temperature for ca. 2 h. To this mixture was added 0.276 g (1.0 mmol) of $BrCH_2(CH_2OCH_2)_2CH_2Br$ and the new mixture was stirred at room temperature for 24 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 2:1) as eluent. From the main red band 0.362 g (23%) of **6** was obtained as a red solid; m.p. 175 °C (dec). Anal. Found: C, 27.90; H, 1.58. Calc. for $C_{36}H_{24}Fe_8O_{28}S_6$: C, 28.01; H, 1.57%. IR (KBr disk): $\nu_{C\equiv O}$ 2090 m, 2050 vs, 1981 vs; ν_{C-O-C} 1113 w cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 2.50–2.75 (m, 8H, $4CH_2S$), 3.68–3.73 (m, 16H, $8CH_2O$) ppm.

3.8. Preparation of {[Fe$_2$(CO)$_6$]$_2$(μ$_4$-S)}$_2$[μ-SCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$S-μ]$_2$ (7)

The same procedure as that for **6** was followed, but $\mathbf{m}\cdot[Et_3NH]_2$ [$Z = CH_2(CH_2OCH_2)_3CH_2$] and 0.320 g (1.0 mmol) of $BrCH_2(CH_2OCH_2)_3CH_2Br$ were used. From the main red band 0.218 g (14%) of **7** was obtained as a red solid; m.p. 176 °C (dec). Anal. Found: C, 30.66; H, 2.07. Calc. for $C_{40}H_{32}Fe_8O_{30}S_6$: C, 30.65; H, 2.06. IR (KBr disk): $\nu_{C\equiv O}$ 2090 s, 2034 vs, 1985 vs; ν_{C-O-C} 1117s cm^{-1}.^1H NMR (200 MHz, $CDCl_3$): δ 2.66 (br s, 8H, $4CH_2S$), 3.72 (br s, 24H, $12CH_2O$) ppm.

3.9. Preparation of {[Fe$_2$(CO)$_6$]$_2$(μ$_4$-S)}$_2$[μ-SCH$_2$(CH$_2$OCH$_2$)$_4$CH$_2$S-μ]$_2$ (8)

The same procedure as that for **6** was followed, but $\mathbf{m}\cdot[Et_3NH]_2$ [$Z = CH_2(CH_2OCH_2)_4CH_2$] and 0.364 g (1.0 mmol) of $BrCH_2(CH_2OCH_2)_4CH_2Br$ were used. From the main red band 0.337 g (20%) of **8** was obtained as a red solid; m.p. 185 °C (dec). Anal. Found: C, 30.78; H, 2.46. Calc. for $C_{44}H_{40}Fe_8O_{32}S_6$: C, 30.72; H, 2.35%. IR (KBr disk): $\nu_{C\equiv O}$ 2081 s, 2053 vs, 2036 vs, 1993 vs; ν_{C-O-C} 1102 m cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 2.50–2.75 (m, 8H, $4CH_2S$), 3.67–3.81 (m, 32H, $16CH_2O$) ppm.

3.10. Preparation of {[Fe$_2$(CO)$_6$]$_2$(μ$_4$-S)}$_2$[μ-SCH$_2$(CH$_2$OCH$_2$)$_2$CH$_2$S-μ] [μ-SCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$S-μ] (9)

The same procedure as that for **6** was followed, but 0.320 g (1.0 mmol) of $BrCH_2(CH_2OCH_2)_3CH_2Br$ was used. From the main red band 0.303 g (19%) of **9** was obtained as a red solid; m.p. 125 °C (dec). Anal. Found: C, 28.81; H, 1.80. Calc. for $C_{38}H_{28}Fe_8O_{29}S_6$: C, 28.75; H, 1.78%. IR (KBr disk): $\nu_{C\equiv O}$ 2090 s, 2050 vs, 1989 vs; ν_{C-O-C} 1117m cm^{-1}.^1H NMR (200 MHz, $CDCl_3$): δ 2.69 (br s, 8H, $4CH_2S$), 3.73 (br s, 20H, $10CH_2O$) ppm.

3.11. Preparation of {[Fe$_2$(CO)$_6$]$_2$(μ$_4$-S)}$_2$[μ-SCH$_2$(CH$_2$OCH$_2$)$_2$CH$_2$S-μ] [μ-SCH$_2$(CH$_2$OCH$_2$)$_4$CH$_2$S-μ] (10)

The same procedure as that for **6** was followed, but 0.364 g (1.0 mmol) of $BrCH_2(CH_2OCH_2)_4CH_2Br$ was used. From the main red band 0.220 g (14%) of **10** was obtained as a red solid; m.p. 113 °C (dec). Anal. Found: C, 29.60; H, 2.05. Calc. for $C_{40}H_{32}Fe_8O_{30}S_6$: C, 29.44; H, 1.98%. IR (KBr disk): $\nu_{C\equiv O}$ 2082 s, 2057 s, 2036 vs, 1991 vs; ν_{C-O} 1107 s cm^{-1}.^1H NMR (200 MHz, $CDCl_3$): δ 2.55 –2.67 (m, 8H, $4CH_2S$), 3.62–3.78 (m, 24H, $12CH_2O$) ppm.

3.12. Preparation of {[Fe$_2$(CO)$_6$]$_2$(μ$_4$-S)}$_2$[μ-SCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$S-μ] [μ-SCH$_2$(CH$_2$OCH$_2$)$_4$CH$_2$S-μ] (11)

The same procedure as that for **6** was followed, but $\mathbf{m}\cdot[Et_3NH]_2$ [$Z = CH_2(CH_2OCH_2)_3CH_2$] and 0.364 g (1.0 mmol) of $BrCH_2(CH_2OCH_2)_4CH_2Br$ were used.

Table 4
Crystal data and structural refinements details for **6** and **9**

	6	**9**
Formula	$C_{36}H_{24}Fe_8O_{28}S_6 \cdot CH_2Cl_2$	$C_{38}H_{28}Fe_8O_{29}S_6 \cdot 1.5CH_3OH$
Formula wt.	1628.64	1635.83
Crystal syst.	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.078(4)	12.511(3)
b (Å)	15.889(6)	14.514(4)
c (Å)	21.945(8)	18.673(5)
α (°)	73.971(7)	90.802(5)
β (°)	89.548(7)	108.565(5)
γ (°)	83.921(8)	97.540(5)
V (Å^3)	3024(2)	3181.1(14)
Z	2	2
D_c (g cm^{-3})	1.788	1.708
$F(000)$	1620	1638
μ(Mo Kα) (mm^{-1})	2.236	2.048
Temp. (K)	293(2)	293(2)
Scan type	ω–2θ	ω–2θ
$2\theta_{max}$ (°)	50	50.06
Data/restraints/ parameters	10526/0/742	11141/3/754
R	0.0801	0.0648
Rw	0.1949	0.1477
Goodness of fit	1.101	1.025
Largest diff. peak and hole (e Å^{-3})	0.953 and −0.877	0.915 and −0.502

From the main red band 0.283 g (17%) of **11** was obtained as a red solid; m.p. 172 °C (dec). Anal. Found: C, 30.18; H, 2.15. Calc. for $C_{42}H_{36}Fe_8O_{31}S_6$: C, 30.10; H, 2.17%. IR (KBr disk): $\nu_{C\equiv O}$ 2081 vs, 2055 vs, 2035 vs, 1993 vs; ν_{C-O} 1119 s cm^{-1}.^{1}H NMR (200 MHz, $CDCl_3$): δ 2.64 (br s, 8H, 4CH_2S), 3.55–3.79 (m, 28H, 14CH_2O) ppm.

3.13. X-ray structure determinations of 6 and 9

The single-crystals suitable for X-ray diffraction analyses were grown by slow evaporation of the CH_2Cl_2/hexane solution for **6** and the CH_2Cl_2/MeOH solution for **9** at about 4 °C. Each crystal was mounted on a Bruker SMART 1000 automated diffractometer equipped with a graphite monochromator with Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and expanded by Fourier techniques. The final refinements were accomplished by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. The calculations for **6** and **9** were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation. Details of the crystal data, data collection, and structure refinements are summarized in Table 4.

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 222979 and 222980. 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; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] G.W. Gokel, Crown Ethers and Cryptands, Monographs in Supramolecular Chemistry, Royal Society of Chemistry, Cambridge, UK, 1991.
[2] F. Vögtle, Supramolecular Chemistry, An Introduction, Wiley, Chichester, UK, 1991.
[3] J.-M. Lehn, Supramolecular Chemistry, Concepts and Perspectives, VCH, Weinheim, 1995.
[4] P.D. Beer, Adv. Inorg. Chem. 39 (1992) 79.
[5] F.C.J.M. Van Veggel, W. Verboom, D.N. Reinhoudt, Chem. Rev. 94 (1994) 279.
[6] L.-C. Song, D.-S. Guo, Q.-M. Hu, X.-Y. Huang, Organometallics 19 (2000) 960.
[7] L.-C. Song, D.-S. Guo, Q.-M. Hu, J. Sun, J. Organomet. Chem. 616 (2000) 140.
[8] L.-C. Song, D.-S. Guo, Q.-M. Hu, F.-H. Su, J. Sun, X.-Y. Huang, J. Organomet. Chem. 622 (2001) 210.
[9] L.-C. Song, D.-S. Guo, Q.-M. Hu, J. Chem. Res. (S) (1999) 516.
[10] (a) L.-C. Song, H.-T. Fan, Q.-M. Hu, J. Am. Chem. Soc. 124 (2002) 4566;
(b) L.-C. Song, H.-T. Fan, Q.-M. Hu, Z.-Y. Yang, Y. Sun, F.-H. Gong, Chem. Eur. J. 9 (2003) 170.
[11] T. Saji, Chem. Lett. (1986) 275.
[12] D. Seyferth, R.S. Henderson, L.-C. Song, Organometallics 1 (1982) 125.
[13] L.-C. Song, X.-D. Qin, Q.-M. Hu, X.-Y. Huang, Organometallics 17 (1998) 5437.
[14] R.B. King, Organometallic Syntheses, vol. 1, Transition-metal Compounds, Academic Press, New York, 1965, p. 95.
[15] (a) D.J. Martin, C.C. Greco, J. Org. Chem. 33 (1968) 1275;
(b) C.J. Pedersen, J. Am. Chem. Soc. 89 (1967) 7017.
[16] J.R. Dann, P.P. Chiesa, J.W. Gates Jr., J. Org. Chem. 26 (1961) 1991.
[17] D. Seyferth, J.M. Burlitch, J. Organomet. Chem. 4 (1965) 127.
[18] W.R. Vaughan, R.D. Carlson, J. Am. Chem. Soc. 84 (1962) 769.