

## 两个大环二茂铁环蕃的合成与晶体结构

张 鑫<sup>1</sup> 秦言智<sup>1</sup> 肖 飞<sup>1</sup> 景 苏<sup>\*,1,2</sup> 吉 玮<sup>1</sup>

(<sup>1</sup>南京工业大学理学院, 南京 210009)

(<sup>2</sup>南京大学配位化学重点实验室, 南京 210008)

**摘要:** 本文合成了 2 个大环硒杂二茂铁环蕃, 1,9-二硒杂-5-硫杂[9]二茂铁环蕃(**1**)和 1,9,21,29-四硒杂-5,25-二硫杂[9.9]二茂铁环蕃(**2**), 并应用核磁、质谱、单晶 X-射线衍射进行了表征。循环伏安法测得二茂铁的氧化还原半波电位分别为 -30 (81) mV (**1**)和 42(67) mV (**2**)。

**关键词:** 二茂铁环蕃; 晶体结构; 电化学

中图分类号: O614.81<sup>†</sup>

文献标识码: A

文章编号: 1001-4861(2012)05-1015-04

## Synthesis and Crystal Structures of Two Macrocyclic Ferrocenophanes

ZHANG Xin<sup>1</sup> QIN Yan-Zhi<sup>1</sup> XIAO Fei<sup>1</sup> JING Su<sup>\*,1,2</sup> JI Wei<sup>1</sup>

(<sup>1</sup>College of Sciences, Nanjing University of Technology, Nanjing 210009, China)

(<sup>2</sup>State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210008, China)

**Abstract:** Two macrocyclic ferrocenophanes, 1,9-diselena-5-sulfur-[9]ferrocenophane (**1**) and 1,9,21,29-tetraselena-5,25-disulfur-[9.9]ferrocenophane (**2**), have been prepared. The new compounds have been characterized by <sup>1</sup>H NMR spectroscopy, X-ray crystallography and electrochemistry. The CV of **1** and **2** showed one clearly reversible oxidation process with  $E_{1/2}$  value of -30(81) mV and 42(67) mV respectively. CCDC: 849326, **1**; 849327, **2**.

**Key words:** ferrocenophane; crystal structure; electrochemistry

The design and study of polyselenaferrocenophanes is an exciting challenge because of their unique chemical properties resulting from the functionality of the side arm and the possibility working as highly sensitive electrochemical sensors for the soft metal cations. In light of this, we have successfully obtained several macrocyclic polyselenaferrocenophanes<sup>[1-4]</sup>. The nature of donor atoms is one of most important parameters that define the coordination properties of macrocyclic ligands<sup>[5-6]</sup>. We report herein the synthesis, characterization and crystallographic study of two novel macrocyclic ferrocenophane with mixed donor atoms, 1,9-diselena-5-sulfur-[9]ferrocenophane (**1**) and 1,9,21,29

-tetraselena-5,25-disulfur-[9.9]ferrocenophane (**2**).

### 1 Experimental

#### 1.1 Materials, general procedures and physical measurements

All the reactions were carried out under nitrogen using standard Schlenk techniques. Mass spectra were recorded using positive ion electrospray (ES);  $m/z$  values have been rounded to the nearest integer or half-integer. Assignments are based on isotopomers containing <sup>1</sup>H, <sup>12</sup>C, <sup>56</sup>Fe, <sup>80</sup>Se. Cyclic voltammetry (CV) was performed at room temperature in a dry MeCN solution containing 0.1 mol · L<sup>-1</sup> [NBu<sub>4</sub>]PF<sub>6</sub> electrolyte

收稿日期: 2011-10-31。收修改稿日期: 2012-01-11。

国家自然科学基金(No.21171092)资助项目。

\*通讯联系人。E-mail: sjing@njut.edu.cn

using an Autolab PGSTAT30 potentiostat system. The sweep rate was  $100 \text{ mV} \cdot \text{s}^{-1}$  (CV). A three-electrode arrangement was used with a Pt working electrode, a Pt wire counter electrode and a  $\text{Ag}/\text{Ag}^+$  ( $0.01 \text{ mol} \cdot \text{L}^{-1}$   $\text{AgNO}_3$  in MeCN) reference electrode. All the E values listed below are with respect to  $\text{FcH}/[\text{FcH}]^+$ , the separation of  $E_a$  and  $E_c$  is given in brackets.

## 1.2 Synthesis

$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  (0.721 g, 3 mmol) was added to EtOH (150 mL), 1,1'-bis (3-bromopropylseleno)ferrocene (0.587 g, 1 mmol) in tetrahydrofuran (5 mL) was then added. The mixture left to stir for 8 h at  $80^\circ \text{C}$ . The solvent was removed by evaporation under reduced pressure. The residue was treated with water (25 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 25 \text{ mL}$ ). The extract was dried over  $\text{MgSO}_4$ , evaporated to dryness, the residue was chromatographed on silica gel. The target products, 1,9-diselena-5-sulfur-[9]ferrocenophane (**1**), a yellow solid (0.223 g, 49%), was obtained by elution with hexane/toluene (2:1); and 1,9,21,29-tetraselena-5,25-disulfur-[9.9]ferrocenophane (**2**), a yellow solid (0.044 g, 9%), was then obtained by elution with toluene.

**1:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$ : 4.23 ( $\text{C}_5\text{H}_4$ ,  $\text{H}_{2+5}$ , s, 4H),

4.22 ( $\text{C}_5\text{H}_4$ ,  $\text{H}_{3+4}$ , s, 4H), 3.07 ( $\text{fcSeCH}_2$ , m, 4H), 2.81 ( $\text{CH}_2\text{SeCH}_2$ , m, 4H), 2.21 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ , m, 4H). ES MS: 458 ( $[\text{M}]^+$ ).

**2:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$ : 4.36 ( $\text{C}_5\text{H}_4$ ,  $\text{H}_{2+5}$ , m, 8H), 4.28 ( $\text{C}_5\text{H}_4$ ,  $\text{H}_{3+4}$ , m, 8H), 2.72 ( $\text{fcSeCH}_2$ , m, 8H), 2.59 ( $\text{CH}_2\text{SeCH}_2$ , m, 8H), 1.89 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ , m, 8H). EI/CI MS: 918 ( $[\text{M}]^+$ ).

## 1.3 Single crystal structure determination

X-ray quality crystals of the complex were obtained by slow evaporation of a mixed solution (*n*-hexane:methylene chloride=3:1, V/V). The yellow crystals of two compounds with dimensions of  $0.20 \text{ mm} \times 0.10 \text{ mm} \times 0.10 \text{ mm}$  were selected for structure analysis. Data collection used an Enraf-Nonius CAD4 diffractometer, and graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda=0.071\,069 \text{ nm}$ ). The structure was solved by the Patterson method with SHELXS-97<sup>[7]</sup> and refined on  $F^2$  by full-matrix least-squares method using the SHELXL-97 program<sup>[8]</sup>. Crystal data, data collection parameters and analysis statistics are summarized in Table 1. Selected bond angles and distances are listed in Tables 2.

CCDC: 849326, **1**; 849327, **2**.

Table 1 Crystal data and structure refinement for **1** and **2**

	<b>1</b>	<b>2</b>
Empirical formula	$\text{C}_{16}\text{H}_{20}\text{FeSSe}_2$	$\text{C}_{32}\text{H}_{40}\text{Fe}_2\text{S}_2\text{Se}_4$
Formula weight	458.15	916.30
$T / \text{K}$	293(2)	293(2)
Wavelength / nm	0.071 073	0.071 073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
$a / \text{nm}$	0.600 6(1)	1.461 0(3)
$b / \text{nm}$	2.709 6(5)	0.598 7(1)
$c / \text{nm}$	1.004 7(2)	1.842 4(4)
$\beta / (^\circ)$	90.79(3)	99.86(3)
Volume / $\text{nm}^3$	1.634 9(6)	1 587.7(5)
$Z$	4	4
Calculated density / ( $\text{g} \cdot \text{cm}^{-3}$ )	1.861	1.917
Absorption coefficient / $\text{mm}^{-1}$	5.490	5.653
$F(000)$	904	904
Crystal size / mm	$0.20 \times 0.10 \times 0.10$	$0.20 \times 0.10 \times 0.10$
$\theta$ range for data collection / ( $^\circ$ )	1.50~25.27	1.65~25.28
Limiting indices	$0 \leq h \leq 7, 0 \leq k \leq 32, -12 \leq l \leq 12$	$0 \leq h \leq 17, 0 \leq k \leq 7, -22 \leq l \leq 22$
Reflections collected	3 253	2 988

Continued Table 1

Independent reflections ( $R_{int}$ )	2 960 (0.055 5)	2 870 (0.044 7)
Observed reflections ( $I > 2\sigma(I)$ )	1835	1853
Data / restraints / parameters	2 960 / 0 / 181	2 870 / 0 / 181
Goodness-of-fit on $F^2$	1.001	1.009
Final $R$ indices ( $I > 2\sigma(I)$ )	$R_1=0.051\ 6$ , $wR_2=0.094\ 5$	$R_1=0.050\ 2$ , $wR_2=0.120\ 8$
$R$ indices (all data)	$R_1=0.099\ 0$ , $wR_2=0.105\ 8$	$R_1=0.092\ 5$ , $wR_2=0.149\ 6$
Largest diff. peak and hole / ( $e \cdot nm^{-3}$ )	544, -740	600, -648

Table 2 Selected bond lengths (nm), bond angles ( $^\circ$ ) and dihedral angles ( $^\circ$ ) for **1** and **2**

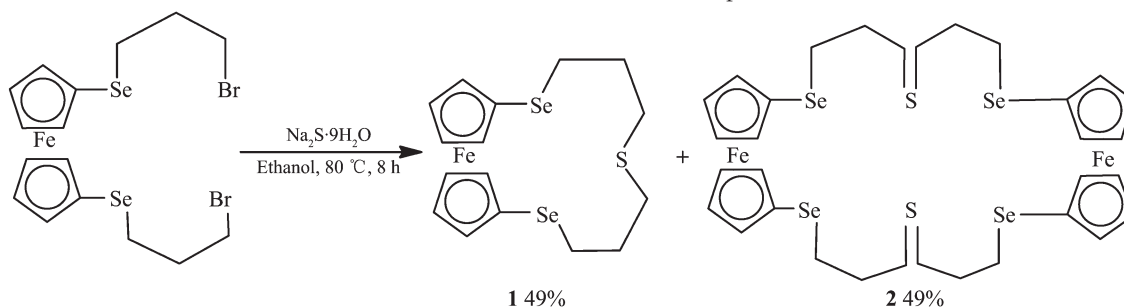
1					
Se1-C1	0.192 3(7)	Se1-C11	0.197 1(8)	Se2-C6	0.189 4(7)
S-C13	0.179 2(8)	S-C14	0.180 0(8)	Se2-C16	0.199 6(7)
C1-Se1-C11	101.8(3)	C6-Se2-C16	101.7(3)	C13-S-C14	100.4(4)
C1-Se1-C11-C12	111.8(6)	C6-Se2-C16-C15	121.3(6)	C13-S-C14-C15	-70.6(6)
2					
Se1-C1	0.191 4(7)	Se1-C16	0.195 4(8)	Se2-C6	0.189 8(7)
S-C13	0.181 4(8)	S-C14	0.180 1(8)	Se2-C11	0.195 9(8)
C1-Se1-C16	100.3(3)	C6-Se2-C16	97.2(3)	C13-S-C14	102.4(4)
C1-Se1-C16-C15	82.5(7)	C6-Se2-C11-C12	-69.3(6)	C14-S-C13-C12	-97.4(7)

## 2 Results and discussion

### 2.1 Synthesis and characterization

**1** and **2** were synthesized as shown in Scheme 1. Reaction of  $Na_2S$  with one equivalent of 1,1'-bis(3-

bromopropylseleno)ferrocene in an ethanol solution gave, **1** (49%) with [1+1] cyclisation process and **2** (9%) with [2+2] cyclisation process. It is worth noting that the two macrocycles are formed in significant amounts without template effect.

Scheme 1 Synthetic route to **1** and **2**

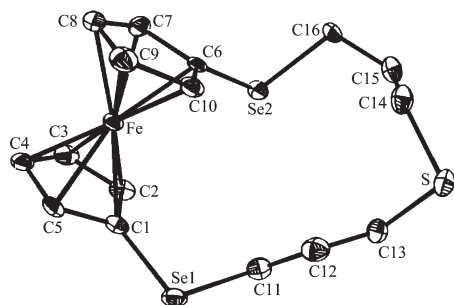
In the  $^1H$  NMR spectrum, the protons of the Cp rings in **1** appeared as two well separated broad singlets at  $\delta=4.23$  and  $4.22$  ppm (4:4), which suggest a nearly parallel conformation of the two rings in solution. And the protons of the Cp rings in **2** appeared as two virtual-triplets at  $\delta=4.36$  and  $4.28$  ppm (8:8), which suggest a staggered conformation. Same phenomena were

observed in selenium analogues.

### 2.2 Single crystal structure determination

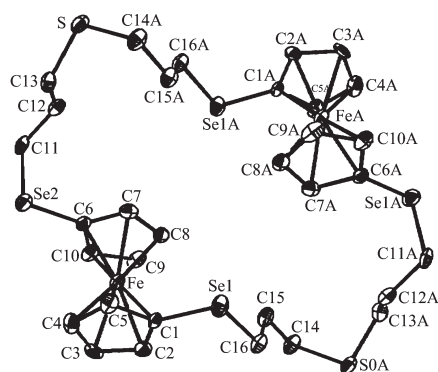
Crystals of **1** and **2** were obtained as orange blocks from  $CH_2Cl_2$ /hexanes. Fig.1 and 2 depicts a view of **1** and **2** molecules along with the atomic numbering respectively. The molecules of **1** and **2** all adopt an exo conformation with the Se and S atoms pointing out of

the cyclic cavity. **1** adopts “synclinal eclipsed” conformation with the torsion angle  $C1\cdots X1\cdots X2\cdots C6$   $65.48^\circ$  ( $X1$  and  $X2$  are the centroids of the two Cp rings). **2** adopts nearly anticlinal conformation of Se-CH<sub>2</sub> substituents<sup>[9]</sup>. While Se-CH<sub>2</sub> substituents in the analogue 1,5,9,21,25,29-hexaselena-[9.9]ferrocenophane is antiperiplanar<sup>[9]</sup>. The torsion angle  $C1\cdots X1\cdots X2\cdots C6$  in **2** is  $126.23^\circ$ , much smaller than that in 1,5,9,21,25,29-hexaselena-[9.9]ferrocenophane ( $163.67^\circ$ ).



Hydrogen atoms are omitted for clarity

Fig.1 View of the structure of **1** with the atom-numbering scheme adopted with thermal ellipsoids drawn at 30% probability level



Hydrogen atoms are omitted for clarity; Symmetry code: A:  $0.5-x, 0.5+y, 0.5-z$

Fig.2 View of the structure of **2** with the atom-numbering scheme adopted with thermal ellipsoids drawn at the 30% probability level

The structure of **2** contains a single conformer with twofold rotational symmetry around an axis perpendicular to the molecular plane. The molecule is [4848] quadrangle with four corner positions occupied by sulfur and selenium<sup>[10-12]</sup>.

### 2.3 Electrochemical study

The cyclic voltammograms (CV) of **1** and **2** all showed one clearly reversible oxidation process

corresponding to ferrocene oxidation. The  $E_{1/2}$  value in **1** is  $-30(81)$  mV, which is more negative than that of 1,2,3-triselena[3]ferrocenophane ( $E_{1/2}=213$  mV)<sup>[13]</sup> and 1,5,9-triselena[9]ferrocenophane ( $E_{1/2}=-13$  mV)<sup>[2]</sup>. The observation shows that ferrocene unit in **1** becomes much easier to oxidize, meaning the decrease of the ring strain and the interaction between the middle sulfur atom in the bridge and the iron. The  $E_{1/2}$  value of **2** is  $42(67)$  mV, which is more positive than that of **1**, and similar as that of 1,5,9,21,25,29-hexaselena-[9.9]ferrocenophane ( $E_{1/2}=46$  mV). The through-bond distance between the iron atoms of **2** is obviously out the threshold for communication. The staggered conformation of cyclopentadienyl rings or through-space communication between two iron centres in **2** may have an effect on the half-wave potential of the 1,1'-ferrocenylene group.

**Acknowledgements:** We gratefully acknowledge financial support from the National Natural Science Foundation of China (Grant No. 21171092).

### References:

- [1] Li Z W, Jing S, Morley C P, et al. *Inorg. Chem. Commun.*, **2009**, *12*:440-443
- [2] Jing S, Gu C Y, Ji W, et al. *Inorg. Chem. Commun.*, **2009**, *12*: 846-848
- [3] Gu C Y, Jing S, Ji W, et al. *Inorg. Chim. Acta*, **2010**, *363*:1604-1606
- [4] Jing S, Morley C P, Gu C Y, et al. *Dalton Trans.*, **2010**, *39*: 8812-8819
- [5] Lindoy L F. *The Chemistry of Macrocyclic Ligand Complexes*. Cambridge: Cambridge University Press, **1989**.
- [6] Tamayo A, Casabó J, Escriche L, et al. *Inorg. Chem.*, **2006**, *45*: 1140-1149
- [7] Sheldrick G M. *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, **1997**.
- [8] Sheldrick G M. *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, **1997**.
- [9] Togni A, Hayashi T. *Ferrocenes: Homogeneous Catalysis-organic Synthesis-Materials Science*. Weinheim: VCH, Germany, **1995**.
- [10] Dale J. *J. Chem. Soc.*, **1963**:93-111
- [11] Dale J. *Top Stereochem.*, **1976**, *9*:199-270
- [12] Batchelor R J, Einstein F W B, Gay I D, et al. *J. Am. Chem. Soc.*, **1989**, *111*:6582-6591
- [13] Ushijima H, Akiyama T, Kajitani M, et al. *Chem. Lett.*, **1987**: 2197-2200