



基于 1,5,9-三硒杂[9]二茂铁环蕃的一维链状汞(II) 配位聚合物的合成与晶体结构

顾诚云¹ 景 苏^{*,1,2} 杨 波¹ 魏 烨¹ 张 文¹ 吉 玮¹

(¹ 南京工业大学理学院, 南京 210009)

(² 南京大学配位化学重点实验室, 南京 210008)

关键词: 汞(II); 1,5,9-三硒杂[9]二茂铁环蕃; 配位聚合物

中图分类号: O613.52; O614.24+3; O614.81+1 文献标识码: A 文章编号: 1001-4861(2010)02-0339-04

Synthesis and Crystallographic Study of 1D Mercury(II) Coordination Polymer of 1,5,9-Triseleno[9]ferrocenophane

GU Cheng-Yun¹ JING Su^{*,1,2} YANG Bo¹ WEI Ye¹ ZHANG Wen¹ JI Wei¹

(¹ School of Science, Nanjing University of Technology, Nanjing 210009)

(² State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210008)

Abstract: A mercury(II) coordination polymer with 1,5,9-triseleno[9]ferrocenophane (L), $[\text{HgI}_2\text{L} \cdot 0.5\text{C}_4\text{H}_4\text{O} \cdot 0.5\text{CH}_3\text{OH}]_n$, has been synthesized and characterized. The X-ray crystal structure shows that bridging by the ligand L causes compound to form one-dimensional chain. The half-wave potential of 1,1'-ferrocenylene group is more negative than that of the "free" ligand, which reveals no through-space interaction $\text{Hg} \cdots \text{Fe}$ in the coordination polymers. CCDC: 742585.

Key words: Mercury(II); 1,5,9-Triseleno[9]ferrocenophane; coordination polymer

Metal coordination polymers have attracted considerable attentions due to their potential applications in many fields, such as catalysis, molecular adsorption, magnetism, nonlinear optics, luminescence and molecular adsorption^[1]. The ferrocenyl compounds have been extensively incorporated into the frameworks, which provide a good opportunity of preparing new functional materials with unique features. Up to now, almost all of those studies use ferrocenyl ligands with hard donor atoms, O^[2-4] and N^[5-7]. As softer donor ligands, polyselenaferrocenophanes are expected to have a rich chem-

istry, especially with the post-transition metals^[8]. We are now prompting the study of the metal coordination polymers incorporating polyselenaferrocenophanes.

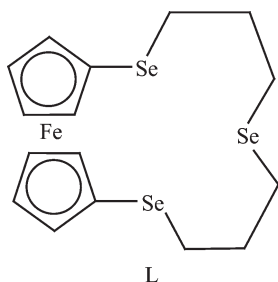
Mercury complexes have been the focus of many recent studies^[9]. To investigate the influence of the nature of multidentate polyselenaferrocenophane ligands on the construction of mercury(II) polymers, the conformationally flexible tridentate ligand 1,5,9-triseleno[9]ferrocenophane (L) was first employed. In the present communication, we report the crystal structure along with the electrochemical property of a novel 1D

收稿日期: 2009-07-30。收修改稿日期: 2009-12-13。

江苏省高校自然科学基金(No.08kjb150008), 教育部留学回国人员启动基金。

*通讯联系人。E-mail: sjing@njut.edu.cn

第一作者: 顾诚云, 女, 24 岁, 硕士研究生; 研究方向: 配位化学。



mercury(II) coordination polymer $[\text{HgI}_2\text{L}]_n$.

1 Experimental

1.1 Materials, general procedures and physical measurements

All the reactions were carried out under nitrogen using standard Schlenk techniques. 1,5,9-Triseleno[9]ferrocenophane was prepared following the previously reported method^[10]. 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 ^1H , ^{12}C , ^{56}Fe , ^{80}Se , and ^{200}Hg . Cyclic voltammetry (CV) was performed at room temperature in a dry MeCN solution containing $0.1 \text{ mol} \cdot \text{L}^{-1}$ $[\text{NBu}_4]\text{PF}_6$ electrolyte 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 Ag/Ag^+ ($0.01 \text{ mol} \cdot \text{L}^{-1}$ AgNO_3 in MeCN) reference electrode.

1.2 Synthesis of $[\text{HgI}_2\text{L}]_n$

A THF solution of L (0.051 g, 0.1 mmol) was

added dropwise to a THF solution of HgI_2 (0.045 g, 0.1 mmol), and the mixture was left to stir at room temperature for 20 h. The solvent was removed by evaporation under reduced pressure, the residue was washed by diethyl ether, then drying the residue produced the target product as a red solid powder, yield 0.050 g, (52%). ES MS: 354 ($[\text{M}-2\text{I}]^{2+}$). Anal. calc. for $\text{C}_{16}\text{H}_{20}\text{FeHgI}_2\text{Se}_3$: C 20.03. H 2.10; Found: C 20.06. H 2.14%.

1.3 Single crystal structure determination

X-ray quality crystals of the complex was obtained by slow evaporation from a mixed THF- CH_3OH -MeCN solution of $[\text{HgI}_2\text{L}]_n$. The dark-red crystal with dimensions of $0.10 \text{ mm} \times 0.10 \text{ mm} \times 0.10 \text{ mm}$ was selected for structure analysis. Data collection used an Enraf-Nonius CAD4 diffractometer, and graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.071\,069 \text{ nm}$). The structure was solved by the Patterson method with SHELXS-97^[11] and refined on F^2 by full-matrix least-squares method using the SHELXL-97 program^[12]. Crystal data, data collection parameters and analysis statistics are summarized in Tables 1. Selected bond angles and distances are listed in Tables 2. Crystallographic data (excluding structure factors) for the structure has been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk), and is available on request quoting the deposition number CCDC: 742585.

Table 1 Crystal data and structure refinement for $[\text{HgI}_2\text{L} \cdot 0.5\text{C}_4\text{H}_4\text{O} \cdot 0.5\text{CH}_3\text{OH}]_n$

Empirical formula	$\text{C}_{18.50}\text{H}_{24}\text{FeHgI}_2\text{OSe}_3$	Calculated density / ($\text{Mg} \cdot \text{m}^{-3}$)	2.293
Formula weight	1 009.5	Absorption coefficient / mm^{-1}	11.591
T / K	293(2)	$F(000)$	914
Wavelength / nm	0.071 073	Crystal size / mm	$0.10 \times 0.10 \times 0.10$
Crystal system	Triclinic	θ range for data collection / ($^\circ$)	1.66–25.27
Space group	$P\bar{1}$	Limiting indices	$0 \leq h \leq 10, -15 \leq k \leq 16, -16 \leq l \leq 16$
a / nm	0.911 4(2)	Reflections collected	5 668
b / nm	1.351 0(2)	Independent reflections (R_{int})	5 303 (0.035 3)
c / nm	1.369 0(2)	Observed reflections [$I > 2\sigma(I)$]	3 065
$\alpha / (^\circ)$	63.68(2)	Data / restraints / parameters	5 303 / 40 / 253
$\beta / (^\circ)$	85.51(2)	Goodness-of-fit on F^2	1.022
$\gamma / (^\circ)$	75.56(2)	Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.077\,1, wR_2 = 0.098\,8$
Volume / nm^3	1.462 2(4)	R indices (all data)	$R_1 = 0.047\,1, wR_2 = 0.088\,9$
Z	2	Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	166, –983

Table 2 Selected bond lengths (nm) and bond angles ($^{\circ}$) for $[\text{HgI}_2\text{L} \cdot 0.5\text{C}_4\text{H}_4\text{O} \cdot 0.5\text{CH}_3\text{OH}]_n^a$

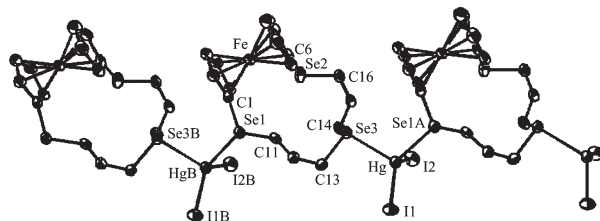
Hg-Se1A	0.280 9(1)	Hg-Se3	0.272 9(1)	Hg-I1	0.269 5(1)
Hg-I2	0.269 7(1)	Fe-C1	0.203 5(9)	Fe-C6	0.203 9(9)
Se1-C1	0.191 8(9)	Se1-C11	0.196 8(8)	Se2-C6	0.190 2(11)
Se2-C16	0.197 1(9)	Se3-C13	0.196 0(9)	Se3-C14	0.199 2(9)
Se1-HgB-Se3B	102.24(4)	I1-Hg-I2	128.17(3)	Se1A-Hg-I1	105.38(3)
Se1A-Hg-I2	102.67(3)	Se3-Hg-I1	107.92(4)	Se3-Hg-I2	107.48(4)

^a Symmetry code: A: $x+1, y, z$; B: $x-1, y, z$.

2 Results and discussions

The reaction of L with HgI_2 in dry and degassed THF at room temperature afforded $[\text{HgI}_2\text{L}]_n$. The electrospray mass spectra showed molecular ion peaks with the correct isotopic pattern.

The title molecular crystallizes in the triclinic space group $P\bar{1}$. The crystal structure reveals that the complex is a one-dimensional infinite chain structure consisting of $[\text{HgI}_2\text{L} \cdot 0.5\text{C}_4\text{H}_4\text{O} \cdot 0.5\text{CH}_3\text{OH}]$ entities (Fig.1). Each Hg(II) ion adopts a distorted tetrahedral environment, and binds to Se1 and Se3 from two different Ls. All the Hg ions are linked by bridging L to form one-dimensional chain running along the a -axis, with the ferrocene fragments are located along the same side of the one-dimensional chains. The Se-Hg-Se angle is $102.24(4)^{\circ}$, which is larger than that of the mononuclear mercury complex of the chelating ferrocenophane ligand, 1,5-diselena [5]ferrocenophane ($87.63(4)^{\circ}$ and $90.20(5)^{\circ}$)^[10]. This can be ascribed that L adopts unusual monodentate coordination mode.



Hydrogen atoms and solvates are omitted for clarity, symmetry code: A: $x+1, y, z$; B: $x-1, y, z$

Fig.1 One dimensional chain of $[\text{HgI}_2\text{L} \cdot 0.5\text{C}_4\text{H}_4\text{O} \cdot 0.5\text{CH}_3\text{OH}]_n$, with the atomic numbering scheme adopted

In the structural unit, L adopts an exo conformation with the Se atoms pointing out of the cyclic cavity. The intramolecular Se \cdots Se distance

becomes larger on complexation (0.5145 nm) than that of free ligand (0.4902 nm). The cyclopentadienyl rings adopt a slightly staggered conformation and the angle between the two ring planes is 2.82° .

The packing diagram shows that the chain structure extends along the a -axis, and the distance between the Hg ions along the chain is 0.9114 nm . It is noted that a relatively short Se3 \cdots I1 distance (0.3747 nm) is found between two adjacent chains, so the structure can be regarded as a double-chain one. The weak Se3 \cdots I1 interactions in adjacent chains may play the role of orienting the ferrocene moieties. The spaces between the two double-chains are occupied by the uncoordinated solvent molecules, THF and CH_3OH .

One reversible wave, ($E_{1/2} = -21\text{ mV}$, $|E_{\text{pa}} - E_{\text{pc}}| = 73\text{ mV}$) was observed in the cyclic voltammogram of $[\text{HgI}_2\text{L}]_n$, corresponding to ferrocene oxidation. The half-wave potential is a little more negative than that of the “free” ligand L ($E_{1/2} = -13\text{ mV}$, $|E_{\text{pa}} - E_{\text{pc}}| = 62\text{ mV}$). This negative shift mirrors that there is no through-space interaction $\text{Hg} \cdots \text{Fe}$.

References:

- [1] Janiak C. *Dalton Trans.*, **2003**:2781-2804
- [2] Kühnert J, Rüffer T, Ecorchard P, et al. *Dalton Trans.*, **2009**: 4499-4508
- [3] Li L K, Song Y L, Hou H W, et al. *Eur. J. Inorg. Chem.*, **2005**: 3238-3249
- [4] Zhang E P, Hou H W, Meng X R, et al. *Cryst. Growth & Des.*, **2009**, **9**:903-913
- [5] Barranco E M, Crespo O, Gimeno M C, et al. *J. Chem. Soc., Dalton Trans.*, **2001**:2523-2529
- [6] Horikoshi R, Mochida T, Moriyama H. *Inorg. Chem.*, **2002**, **41**:

- 3017-3024
- [7] Horikoshi R, Okazawa K, Mochida T. *J. Organomet. Chem.*, **2005**, **690**:1793-1799
- [8] Li Z W, Jing S, Morley C P, et al. *Inorg. Chem. Commun.*, **2009**, **12**:440-443
- [9] Morsali A, Masoomi M Y. *Coord. Chem. Rev.*, **2009**, **253**:1882-1905
- [10] Jing S, Gu C Y, Ji W, et al. *Inorg. Chem. Commun.*, **2009**, **12**:846-848
- [11] Sheldrick G M. *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, **1997**.
- [12] Sheldrick G M. *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, **1997**.