

过渡金属配合物为模板合成两个新的硫代锡酸盐

付明来^{1,2} 郭国聪^{*1} 刘 冰¹ 吴阿清¹ 黄锦顺¹

(¹ 结构化学国家重点实验室, 中国科学院福建物质结构研究所, 福州 350002)

(² 中国科学院研究生院, 北京 100039)

摘要: 利用溶剂热方法在温和的条件下合成了二个新的硫代锡酸盐 $[\text{Mn}(\text{en})_3]_2\text{Sn}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$ ($\text{en}=\text{H}_2\text{NC}_2\text{H}_4\text{NH}_2$) (**1**) 和 $[\text{Mn}(\text{dien})_2]_2\text{Sn}_2\text{S}_6$ ($\text{dien}=\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2$) (**2**), 通过 X-射线衍射分析表征其晶体结构。化合物 **1** 的晶体学参数: $\text{C}_{12}\text{H}_{48}\text{Mn}_2\text{N}_{12}\text{S}_6\text{Sn}_2 \cdot 2\text{H}_2\text{O}$, $M_r=936.28$, 单斜晶系, $P2_1/c$, $a=1.012\ 9(3)$, $b=1.574\ 6(4)$, $c=1.152\ 4(3)$ nm, $\beta=102.36(1)^\circ$, $V=1.795\ 5(8)$ nm³, $Z=2$, $D_c=1.732$ g·cm⁻³, $\mu(\text{MoK}\alpha)=2.442$ mm⁻¹, $F(000)=940$, $R=0.063\ 3$, $wR=0.081\ 4$; 化合物 **2** 的晶体学参数: $\text{C}_{16}\text{H}_{32}\text{Mn}_2\text{N}_{12}\text{S}_6\text{Sn}_2$, $M_r=952.32$, 单斜晶系, $P2_1/c$, $a=1.248\ 12(3)$, $b=0.937\ 60(4)$, $c=1.776\ 17(7)$ nm, $\beta=121.752(2)^\circ$, $V=1.767\ 5(1)$ nm³, $Z=2$, $D_c=1.789$ g·cm⁻³, $\mu(\text{MoK}\alpha)=2.479$ mm⁻¹, $F(000)=956$, $R=0.057\ 9$, $wR=0.137\ 4$ 。在两个化合物中存在的 $[\text{Sn}_2\text{S}_6]^{4-}$ 阴离子均由共边的两个 SnS_4 四面体构成。在 **1** 中, 锰离子螯合 3 个乙二胺做为阳离子模板, 而在 **2** 中锰离子螯合 2 个二乙烯三胺做为阳离子模板。金属配合物作为模板对阴离子 $[\text{Sn}_2\text{S}_6]^{4-}$ 在晶体结构中的排列产生重要的影响。

关键词: 水热合成; 硫代锡酸盐; 晶体结构

中图分类号: O614.43²

文献标识码: A

文章编号: 1001-4861(2005)01-0025-05

Two New Thiostannates Templated by Transition Metal Complexes

FU Ming-Lai^{1,2} GUO Guo-Cong^{*1} LIU Bing¹ WU A-Qing¹ HUANG Jin-Shun¹

(¹State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the
Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002)

(²Graduate School of Chinese Academy of Sciences, Beijing 100039)

Abstract: Two new thiostannates $[\text{Mn}(\text{en})_3]_2\text{Sn}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$ ($\text{en}=\text{ethylenediamine}$) (**1**) and $[\text{Mn}(\text{dien})_2]_2\text{Sn}_2\text{S}_6$ ($\text{dien}=\text{diethylenetriamine}$) (**2**) have been prepared under mild solvothermal conditions and structurally characterized by X-ray crystallography. Crystallographic data for **1**: $[\text{Mn}(\text{en})_3]_2\text{Sn}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$, $M_r=936.28$, monoclinic $P2_1/c$, $a=1.012\ 9(3)$, $b=1.574\ 6(4)$, $c=1.152\ 4(3)$ nm, $\beta=102.36(1)^\circ$, $V=1.795\ 5(8)$ nm³, $Z=2$, $D_c=1.732$ g·cm⁻³, $\mu(\text{MoK}\alpha)=2.442$ mm⁻¹, $F(000)=940$, $R=0.063\ 3$, $wR=0.081\ 4$; and for **2**: $[\text{Mn}(\text{dien})_2]_2\text{Sn}_2\text{S}_6$, $M_r=952.32$, monoclinic $P2_1/c$, $a=1.248\ 12(3)$, $b=0.937\ 60(4)$, $c=1.776\ 17(7)$ nm, $\beta=121.752(2)^\circ$, $V=1.767\ 5(1)$ nm³, $Z=2$, $D_c=1.789$ g·cm⁻³, $\mu(\text{MoK}\alpha)=2.479$ mm⁻¹, $F(000)=956$, $R=0.057\ 9$, $wR=0.137\ 4$. In each complex $[\text{Sn}_2\text{S}_6]^{4-}$ anions is composed of two SnS_4 tetrahedra sharing a common edge. In the complex **1** the transition metal Mn cations are coordinated each by three en ligands, while in complex **2** the Mn cations are coordinated each by two dien ligands. The metal complex templates make a significant influence on the arrangement of $[\text{Sn}_2\text{S}_6]^{4-}$ anions in their crystal structures. CCDC: 246260, 246261.

Key words: solvothermal synthesis; thiostannates; crystal structures

收稿日期: 2004-04-12. 收修改稿日期: 2004-08-26.

国家自然科学基金资助项目(No.2000F006, 2003I031), 福建省自然科学基金资助项目(2000F006, 2003I031).

*通讯联系人. E-mail: gcguo@ms.fjirsm.ac.cn

第一作者: 付明来, 男, 32 岁, 博士生, 研究方向: 有机无机杂化材料的合成与表征。

0 Introduction

During the past years the syntheses of new chalcogenide solids such as thiogermanates and thiostannates have received much attention^[1-8]. Various synthetic routes have successfully been employed to crystallize thiostannates. The starting phases are either molten salts as in the case of $\text{Na}_6\text{Sn}_2\text{S}_7$ ^[1] and $\text{Na}_4\text{Sn}_3\text{S}_8$ ^[2], aqueous solutions for $\text{Na}_4\text{Sn}_2\text{S}_6 \cdot 14\text{H}_2\text{O}$ ^[3] and $\text{Na}_4\text{Sn}_4 \cdot 14\text{H}_2\text{O}$ ^[4], or organic solvent solutions as in the case of $(\text{Et}_4\text{N})_2[\text{Sn}(\text{S}_4)_3]_{0.4}[\text{Sn}(\text{S}_4)_2(\text{S}_6)]_{0.6}$ (Et_4N =tetraethylammonium)^[5]. Solvothermal syntheses employed for the preparation of chalcogenides have seen a dramatic evolution in the past few years. The low temperature environment and the dedicated use of suitable solvents are thought to retain complex building units and facilitate their controlled linkage. In practice, the result of a solvothermal synthesis is barely predictable and obviously strongly influence of counterpart. On the other hand, thiostannates containing a variety of anions like isolated $[\text{Sn}_2\text{S}_6]^{4-}$ dimmers^[3,6], $[\text{Sn}_2\text{S}_6]^{4-}$ sheets^[1], $[\text{Sn}_3\text{S}_7]^{2-}$ sheets^[7], and $[\text{Sn}_2\text{S}_5]^{2-}$ frameworks^[8] exhibit a rich structure diversity based on tin sulfide.

Normally solvothermal syntheses are performed using organic molecules as structure-director. The $[\text{Sn}_2\text{S}_6]^{4-}$ compounds with transition-metal complex cations acting as “template” are less explored^[9]. Bensch et al. reported very recently four new compounds of $[\text{Ni}(\text{en})_3]_2\text{Sn}_2\text{S}_6$, $[\text{Ni}(\text{dap})_3]_2\text{Sn}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$ (dap=1,2-diaminopropane), $[\text{Co}(\text{tren})_3]_2\text{Sn}_2\text{S}_6$ and $[\text{Ni}(\text{tren})_3]_2\text{Sn}_2\text{S}_6$ (tren=tris (2-aminoethyl)amine)^[10]. For an insight into the general structural chemistry of the thiostannates new compounds must be synthesized and characterized. In this paper, the syntheses and structures of two new complexes $[\text{Mn}(\text{en})_3]_2 \cdot \text{Sn}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Mn}(\text{dien})_2]_2 \cdot \text{Sn}_2\text{S}_6$ (**2**) are reported, both of which contain isolated anion of Sn_2S_6 dimers and are templated by Mn complex cations.

1 Experimental

1.1 Syntheses

Complex 1: The complex was prepared under solvothermal conditions by reacting manganese (0.055 g, 1 mmol), tin (0.119 g, 1 mmol) and sulfur (0.096 g, 3 mmol). The reactants were loaded into a Teflon-lined steel autoclave and 3 mL of 80% en aqueous

solution was added. The reaction took place at 453 K for 5 d. The product was filtered and washed with acetone. The title compound $[\text{Mn}(\text{en})_3]_2 \cdot \text{Sn}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$ is unstable in air, and must be stored under nitrogen atmosphere. Found (%): C, 15.45; H, 5.78; N, 18.01; O, 3.37. Calcd. for **1** (%): C, 15.39; H, 5.60; N, 17.95; O, 3.42.

Complex 2: The complex was prepared by the similar procedure except 3 mL of 30% dien aqueous solution was used instead and the reaction took place at 423 K for 10 d. The product was filtered and washed with acetone. Unlike to **1**, **2** is stable in air. Found (%): C, 20.31; H, 5.63; N, 17.68. Calcd. for **2** (%): C, 20.18; H, 5.50; N, 17.65.

1.2 Crystal structure determination

A colorless block crystal with dimension of 0.09 mm × 0.10 mm × 0.12 mm of **1** and a colorless platelet crystal with dimensions of 0.06 mm × 0.18 mm × 0.30 mm of **2** were respectively sealed into glass capillary and used for measurement of precise cell constant and intensity data collection. Diffraction data were collected on a Rigaku Mercury CCD diffractometer for **1** and on a Siemens Smart CCD diffractometer for **2** with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) by using ω scan technique at 293 K. 11 962 reflections were measured in the range of 3.28° to 25.02° for **1** and 4 887 reflections were measured in the range of 2.35° to 24.98° for **2**. Crystal Clear software¹¹ was used for data reduction of **1** and Siemens SAINT12 software was used for data reduction of **2**. Empirical absorption corrections SAD-BAS13 for **2** based on measurements of equivalent reflections were applied. For **1**, 2 343 reflections with $I>2\sigma(I)$ out of 3 148 unique reflections ($R_{\text{int}}=0.066\ 8$) were considered as observed. For **2**, 2 072 reflections with $I>2\sigma(I)$ out of 3 038 unique reflections ($R_{\text{int}}=0.050\ 8$) were considered as observed. The structures were solved by the direct method using the Siemens SHELXTLTM Version 5 package of crystallographic software^[14]. The difference Fourier maps based on these atomic positions yield the other non-hydrogen atoms. Hydrogen atoms of en and dien in the present complexes were added according to the theoretical models. Hydrogen atoms of water molecules in **1** were located from the difference Fourier syntheses and refined isotropically with the O-H distances fixing at

0.095 nm. The structures were refined using a full-matrix least-squares refinement on F^2 . All non-hydrogen atoms were refined anisotropically. For **1**, the final $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.063\ 3$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / (\sum w(F_o^2)^2)]^{1/2} = 0.081\ 4$ with 171 parameters, $w = 1/[\sigma^2(F_o^2) + (0.020\ 7P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$, $S = 1.071$, $(\Delta/\sigma)_{\max} = 0.001$, maximum and minimum peaks in final difference map: 584 and $-817\ \text{e} \cdot \text{nm}^{-3}$. For **2**, the final $R_1 = 0.057\ 9$, $wR_2 = 0.137\ 4$ with 172 parameters, $w = 1/[\sigma^2(F_o^2) + (0.090\ 0P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$, $S = 0.982$, $(\Delta/\sigma)_{\max} = 0.001$, maximum and minimum peaks in final difference map: 729 and $-763\ \text{e} \cdot \text{nm}^{-3}$.

CCDC: 246260, 246261.

2 Results and discussion

The selected bond lengths and bond angles are

Table 1 Selected bond lengths (nm) and bond Angles ($^\circ$) of complex **1**

Sn(1)-S(1)	0.245 1(1)	Mn(1)-N(11)	0.227 1(2)	Mn(1)-N(15)	0.222 3(2)
Sn(1)-S(2)	0.234 7(1)	Mn(1)-N(12)	0.229 4(3)	Mn(1)-N(16)	0.231 2(2)
Sn(1)-S(3)	0.234 1(1)	Mn(1)-N(13)	0.225 9(2)		
Sn(1)-S(1) ^a	0.244 6(1)	Mn(1)-N(14)	0.230 1(3)		
S(1)-Sn(1)-S(2)	112.1(1)	N(11)-Mn(1)-N(13)	166.7(1)	N(13)-Mn(1)-N(14)	76.0(1)
S(1)-Sn(1)-S(3)	113.1(1)	N(11)-Mn(1)-N(14)	91.6(1)	N(13)-Mn(1)-N(15)	95.2(1)
S(2)-Sn(1)-S(3)	113.8(1)	N(11)-Mn(1)-N(15)	90.4(1)	N(13)-Mn(1)-N(16)	90.6(1)
S(1)a-Sn(1)-S(1)	92.6(1)	N(11)-Mn(1)-N(16)	102.4(1)	N(14)-Mn(1)-N(15)	94.8(1)
S(1)a-Sn(1)-S(2)	112.3(1)	N(12)-Mn(1)-N(13)	99.4(1)	N(14)-Mn(1)-N(16)	163.5(1)
S(1)a-Sn(1)-S(3)	111.1(1)	N(12)-Mn(1)-N(14)	97.5(1)	N(15)-Mn(1)-N(16)	76.7(1)
Sn(1)a-S(1)-Sn(1)	87.4(1)	N(12)-Mn(1)-N(15)	162.8(1)		
N(11)-Mn(1)-N(12)	77.3(1)	N(12)-Mn(1)-N(16)	94.0(1)		

Symmetry transformations used to generate equivalent atoms: ^a $-x+2, -y, -z+1$.

Table 2 Selected bond lengths (nm) and bond angles ($^\circ$) of complex **2**

Sn(1)-S(1)	0.247 9(1)	Mn(1)-N(11)	0.228 7(2)	Mn(1)-N(22)	0.238 4(3)
Sn(1)-S(2)	0.234 8(1)	Mn(1)-N(12)	0.234 9(3)	Mn(1)-N(24)	0.224 6(2)
Sn(1)-S(3)	0.234 0(1)	Mn(1)-N(14)	0.227 1(3)		
Sn(1)-S(1) ^a	0.249 2(1)	Mn(1)-N(21)	0.228 5(3)		
S(1)-Sn(1)-S(2)	111.8(1)	N(11)-Mn(1)-N(14)	100.2(1)	N(14)-Mn(1)-N(21)	96.7(1)
S(1)-Sn(1)-S(3)	111.8(1)	N(11)-Mn(1)-N(21)	91.0(1)	N(14)-Mn(1)-N(22)	164.0(1)
S(2)-Sn(1)-S(3)	114.8(1)	N(11)-Mn(1)-N(22)	94.0(1)	N(14)-Mn(1)-N(24)	92.3(1)
S(1)-Sn(1)-S(1) ^a	90.4(1)	N(11)-Mn(1)-N(24)	158.2(1)	N(21)-Mn(1)-N(22)	75.6(1)
S(2)-Sn(1)-S(1) ^a	112.1(1)	N(12)-Mn(1)-N(14)	77.5(1)	N(21)-Mn(1)-N(24)	105.3(1)
S(3)-Sn(1)-S(1) ^a	113.6(1)	N(12)-Mn(1)-N(21)	163.8(1)	N(22)-Mn(1)-N(24)	76.6(1)
Sn(1)-S(1)-Sn(1) ^a	89.6(1)	N(12)-Mn(1)-N(22)	113.5(1)		
N(11)-Mn(1)-N(12)	75.5(1)	N(12)-Mn(1)-N(24)	90.1(1)		

Symmetry transformations used to generate equivalent atoms: ^a $-x, -y, -z$.

listed in Tables 1 and 2 for **1** and **2**, respectively.

X-ray crystallography reveals that **1** consists of two template $[\text{Mn}(\text{en})_3]^{2+}$ cations, discrete $[\text{Sn}_2\text{S}_6]^{4-}$ anions, and two lattice water molecules, as shown in Fig.1. The crystal structure of **2** contains two template $[\text{Mn}(\text{dien})_2]^{2+}$ cations and discrete $[\text{Sn}_2\text{S}_6]^{4-}$ anions, as shown in Fig.2. In both complexes the cations occupy general positions whereas the anions are located at a crystallographic inversion center.

In **1**, the Mn atom is surrounded by six N atoms from three crystallographically independent neutral en ligands, which function as bidentate ligands to form five-membered chelate rings, with the Mn-N bond lengths ranging from 0.222 3(2) to 0.231 2(2) nm to give a distorted octahedral environment. The significant distortion of the Mn octahedron in **1** is reflected

in the axial *trans*-N-Mn-N angles with the range of $162.8(1)^\circ \sim 166.7(1)^\circ$. The configuration of the en rings in $[\text{Mn}(\text{en})_3]^{2+}$ is $\Lambda(\delta\delta\delta)$ or $\Delta(\lambda\lambda\lambda)$ according to Saito's description^[15]. However, in **2**, the Mn atom is coordinated by six N atoms from two crystallographically independent dien ligands with the Mn-N bond lengths between 0.224 6(2) and 0.238 4(3) nm. The severe distortion of the Mn octahedral environment in **2** is also manifested by the axial *trans*-N-Mn-N angles varying from $158.2(1)^\circ$ to $164.0(1)^\circ$. Hexacoordinated $[\text{M}(\text{dien})_2]^{2+}$ (M=transition metal) cations have been known for a long time^[16,17], and three possible geometric isomers of the cations (*mer*, *s-fac*, and *u-fac*) were intensively studied^[16,18-23]. However, the single crystal structural characterization of complexes $[\text{M}(\text{dien})_2]$

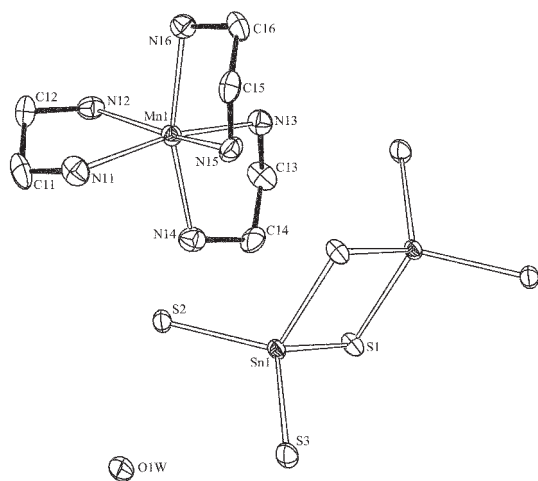


Fig.1 ORTEP drawing of complex **1** with ellipsoids drawn with 30 % probability level
Hydrogen atoms are omitted for clarity.

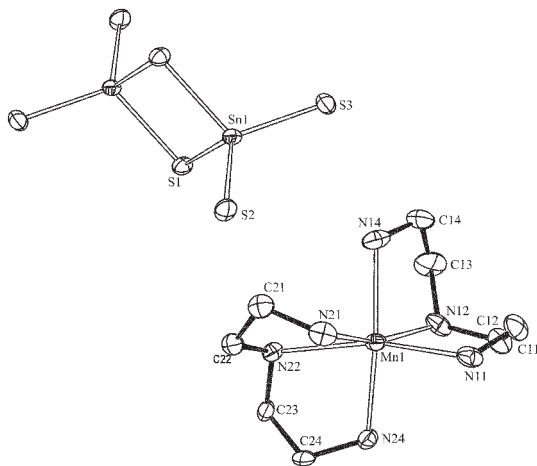


Fig.2 ORTEP drawing of complex **2** with ellipsoids drawn with 30% probability level
Hydrogen atoms are omitted for clarity.

$[\text{MoS}_4]$ and $[\text{M}(\text{dien})_2]\text{Mo}_2\text{O}_2\text{S}_6$ containing $[\text{Mn}(\text{dien})_2]^{2+}$ with three forms has been recently reported^[24]. The $[\text{Mn}(\text{dien})_2]^{2+}$ cation in **2** shows the unsymmetrical facial (*u-fac*) geometry. The Mn-N bond distances of $[\text{Mn}(\text{en})_3]^{2+}$ in **1** and $[\text{Mn}(\text{dien})_2]^{2+}$ in **2** are in the normal range as found in the literature^[24-26].

The $[\text{Sn}_2\text{S}_6]^{4-}$ anions in **1** and **2** are formed by two edge-sharing SnS_4 tetrahedra (Fig.3). The terminal Sn-St distances, ranging from 0.234 1(1) nm to 0.234 7(1) nm in **1** and 0.234 0(1) nm to 0.234 8(1) nm in **2**, are obviously shorter than the bridging Sn-Sb bond lengths which are in the range 0.244 6(1)~0.245 1(1) nm in **1** and 0.247 9(1)~0.249 2(1) nm in **2**. The St-Sn-St angle is $113.79(3)^\circ$ in **1** and $114.78(3)^\circ$ in **2**, while the Sb-Sn-Sb angle is $92.62(3)^\circ$ in **1** and $90.41(3)^\circ$ in **2**, which deviate significantly from the ideal value of 109.5° . As a result the two SnS_4 tetrahedra forming $[\text{Sn}_2\text{S}_6]^{4-}$ anions are seriously deformed. The Sn-S distances and Sb-Sn-Sb angles found in the title compounds match well with other compounds containing $[\text{Sn}_2\text{S}_6]^{4-}$ anions^[10,27-30]. In all examples of dimer $[\text{M}_2\text{Q}_6]^{n-}$ with M being a main group metal and Q=S, Se and Te, the terminal M-Q_t distances are shorter than the M-Q_b bridging bond^[31]. In addition, the Q_b-M-Q_b and the Q_t-M-Q_t angles show a significant deviation from 109.5° .

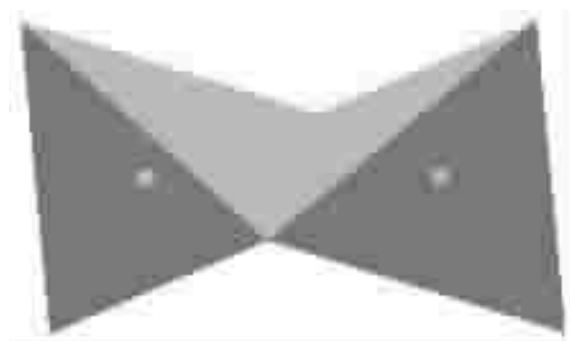


Fig.3 Polyhedral diagram of $[\text{Sn}_2\text{S}_6]^{4-}$

Unlike $[\text{Ni}(\text{en})_3]\text{Sn}_2\text{S}_6$ ^[10], which crystallizes in the orthorhombic centrosymmetric space group *Pbca*, both **1** and **2** crystallize in the monoclinic crystal system with space group *P2₁/c*. In both complexes the $[\text{Sn}_2\text{S}_6]^{4-}$ anions are located in the midpoint of the b axis and c axis with different direction. In **1** the $[\text{Mn}(\text{en})_3]^{2+}$ cations and water molecules are located between the anions. The sulfur atoms S2 and S3 of $[\text{Sn}_2\text{S}_6]^{4-}$ anion acts as hydrogen acceptor to form intermolecular hydrogen bond with O atom of H_2O molecule (Table 3).

Table 3 Hydrogen bond distances (nm) and bond angles (°) of complex 1

Atom involved	Distance / (nm)		Angles / (°)	
	O1w-H	H···S	O1w···S	O1w-H···S
O1W-H1W···S2	0.094 7(6)	0.227 0(5)	0.319 0(2)	163.7(1)
O1W-H2W···S3	0.094 9(6)	0.224 7(6)	0.317 4(2)	164.9(2)

In **2** the $[\text{Mn}(\text{dien})_2]^{2+}$ cations are located between the anions and no hydrogen bonds exist. It is obvious that the arrangement of $[\text{Sn}_2\text{S}_6]^{4-}$ anions is caused by the influence of the cations as well as by the interactions between cationic and anionic species.

References:

- [1] Krebs B, Schiwy W Z. *Anorg. Allg. Chem.*, **1973**,**398**:63~71
- [2] Jumas J C, Philippet E, Maurin M. *J. Solid State Chem.*, **1975**, **14**:152~159
- [3] Krebs B, Pohl S, Schiwy W. *Z. Anorg. Allg. Chem.*, **1972**,**393**: 241~252
- [4] Schiwy W., Pohl S., Krebs B. *Z. Anorg. Allg. Chem.*, **1972**, **402**,77~86
- [5] Müller A, Schimanski J, Römer M, et al. *Chimica*, **1985**,**39**: 25~27
- [6] Jiang T, Ozin G A, Bedard R L. *Adv. Mater.*, **1994**,**6**:860~865
- [7] Jiang T, Ozin G A, Bedard R L. *Adv. Mater.*, **1995**,**7**:166~170
- [8] Liao J H, Varotsis C, Kanatzidis M G. *Inorg. Chem.*, **1993**,**32**: 2453~2462
- [9] Jing L, Chen Z, Wang R J, et al. *Coord. Chem. Rev.*, **1999**, **190~192**:707~735
- [10] Behrens M, Scherb S, Näther C et al. *Z. Anorg. Allg. Chem.*, **2003**,**629**:1367~1373
- [11] Rigaku, CrystalStructure Version 3.10, Rigaku Corporation and Rigaku/MS, **2002**.
- [12] Siemens, SAINT Software Reference Manual, Siemens Energy & Automation Inc., Madison, Wisconsin, USA, **1994**.
- [13] Sheldrick G M. *SADABS, Absorption Correction Program*, University of Goettingen, German, **1996**.
- [14] Siemens, *SHELXTLTM Version 5 Reference Manual*, Siemens Energy & Automation Inc., Madison, Wisconsin, USA, **1994**.
- [15] Saito Y. *Inorganic Molecular Dissymmetry*, Springer-Verlag: Berlin, **1979**:56~59
- [16] Searle G H, Lincoln S F, Keene F R et al. *Aust. J. Chem.*, **1977**,**30**:1221~1228
- [17] Mann F G. *J. Chem. Soc.*, **1934**:466~474
- [18] Keene F R, Searle G H. *Inorg. Chem.*, **1972**,**11**:148~156
- [19] Yoshikawa Y, Yamasaki K. *Bull. Chem. Soc. Jpn.*, **1972**,**45**: 179~184
- [20] Searle G H, House D A. *Aust. J. Chem.*, **1987**,**40**:361~374
- [21] Mukherjee A K, Korner S, Ghosh A, et al. *J. Chem. Soc., Dalton Trans.*, **1994**:2367~2371
- [22] Stephens F S. *J. Chem. Soc.*, **1969**:883~890; Stephens F S. *J. Chem. Soc.*, **1969**:2233~2239
- [23] Harada K. *Bull. Chem. Soc. Jpn.*, **1993**,**66**:2889~2899
- [24] Ellermeier J, Bensch W. *Monatsh. Chem.*, **2002**,**133**:945~957
- [25] Chen Z, Wang R J. *Wuli Huaxue Xuebao(Acta Phys. -Chim. Sin.)*, **1999**,**15**:1070~1075
- [26] Li J, Chen Z, Emge T J, Yuen T, Proserpio D M. *Inorg. Chim. Acta*, **1998**,**273**:310~315
- [27] Löken S, Tremel W Z. *Anorg. Allg. Chem.*, **1998**,**624**:1588~1594
- [28] Liao J H, Kanatzidis M G. *Chem. Mater.*, **1993**,**5**:1561~
- [29] Li J, Marler B, Kessler H, Soulard M, Kallus S *Inorg. Chem.*, **1997**,**36**:4697~4701
- [30] Krebs B, Pohl S, Schiwy W. *Angew. Chem.*, **1970**,**9**:897~898
- [31] Eulenberger G. *Monatsh. Chem.*, **1982**,**113**:859~867