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无机–有机杂化硫属化合物[Mn(1,2-dap)$_2$(H$_2$O)]$_2$(μ-Sn$_2$Q$_6$)(Q=S、Se)和[Mn(tren)]$_2$(μ-Sn$_2$S$_6$)的合成、晶体结构与性能

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摘要:采用溶剂热方法合成了 3 个多元硫属化合物[Mn(1,2-dap)$_2$(H$_2$O)]$_2$(μ-Sn$_2$Q$_6$)(Q=S (**1**)和 Se (**2**))和[Mn(tren)]$_2$(μ-Sn$_2$S$_6$) (**3**),用 X-射线单晶衍射测定了化合物的结构,并通过红外光谱、紫外–可见漫反射光谱对其进行了表征。单晶结构解析表明,化合物 **1** 和 **2** 都属于正交晶系,*Pccn* 空间群(No.56),晶体结构是由[Mn(1,2-dap)$_2$(H$_2$O)]$^{2+}$配合物阳离子和[Sn$_2$Q$_6$]$^{4-}$二聚体通过 Mn-Q 键连接而成的[Mn(1,2-dap)$_2$(H$_2$O)]$_2$(μ-Sn$_2$Q$_6$)低聚体,相邻的低聚体之间通过氢键相连形成三维结构。化合物 **3** 属于三斜晶系,晶体结构是由[Mn(tren)]$_2$(μ-Sn$_2$S$_6$)单元通过氢键连接而成的二维结构。紫外–可见漫反射光谱结果显示化合物 **1**,**2** 和 **3** 的带隙分别为 2.5,2.1,2.4 eV,属于半导体材料。

关键词:硫属化合物;溶剂热合成;晶体结构
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Solvothermal Syntheses, Crystal Structures and Properties of [Mn(1,2-dap)$_2$(H$_2$O)]$_2$(μ-Sn$_2$Q$_6$) (Q=S, Se) and [Mn(tren)]$_2$(μ-Sn$_2$S$_6$)

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Abstract: Three thiostannates(Ⅳ) and selenidostannate(Ⅳ), namely, [Mn(1,2-dap)$_2$(H$_2$O)]$_2$(μ-Sn$_2$Q$_6$) (1,2-dap=1,2-diaminopropane, Q=S (**1**) and Se (**2**)) and [Mn(tren)]$_2$(μ-Sn$_2$S$_6$) (tren=tris(2-aminoethyl)amine; **3**), have been solvothermally synthesized and structurally characterized. Their crystal structures were established by single-crystal X-ray diffraction, IR and UV-Vis spectra. The compounds **1** and **2** crystallize in the orthorhombic system, space group *Pccn* (No.56). In their structures, [Mn(1,2-dap)$_2$(H$_2$O)]$^{2+}$ complex cation and [Sn$_2$Q$_6$]$^{4-}$ dimer are interconnected via Mn-Q covalent bonds to form oligomer, which are further interlinked via hydrogen bonds to form 3D H-bonding network structure. Compound **3** crystallizes in the triclinic system, space group $P\bar{1}$ (No.2), and features 2D H-bonding network structure based on [Mn(tren)]$_2$(μ-Sn$_2$S$_6$) units. The optical absorption spectra indicate that compounds **1**, **2** and **3** are semiconductors with estimated band gaps of 2.5, 2.1 and 2.4 eV, respectively. CCDC: 1024637, **1**; 1024638, **2**; 1024636, **3**.

Key words: chalcogenometalate; solvothermal reaction; crystal structure

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0 Introduction

Metal chalcogenides are investigated intensively in the past several decades because of their fascinating structural diversity and topologies, and potential applications in many areas such as fast-ion conductivity, photocatalysis, electro-optic and chemical sensor[1-5]. Traditional chalcogenide materials always were produced by solid state reaction or flux method at high temperature, such as $SnGa_4Q_7$ (Q=S, Se)[6].

Since the cobalt thioantimonate of $[Co(en)_3][CoSb_4S_8]$ was prepared in ethylenediamine under mild solvothermal condition in 1996, solvothermal reaction in polyamine solution has become a versatile route to synthesis the inorganic-organic hybrid chalcogenides[7]. In the solvothermal reaction, the chelating amine is not only an excellent solvent for solvothermal synthesis and reducing agent reacting with chalcogen elements, but also perform as protonated cations or in situ chelate transitional metal ions forming large $[TM(amine)_x]^{n+}$ complex counterions to stabilize chalcogenide anionic frameworks[8-10]. Moreover, the optical and magnetic properties of the transition metal complexes may integrate with the inorganic chalcogenide network, which can be expected to give rise to multi-functional physical properties[11-15]. Now, the transitional metal complex has been widely used as structure-directing reagent or counterion in the syntheses of inorganic-organic hybrid chalcogenides.

In general, the transitional metals trend to form saturated $[TM(en)_3]^{2+}$, $[TM(1,2\text{-dap})_3]^{2+}$ or $[TM(dien)_2]^{2+}$ complexes in the bi- or tridentate chelate amine solvent (en, 1,2-dap and dien, etc) due to their strong stabilities, and there are only a few reports on unsaturated $[TM(en)_2]^{2+}$, $[TM(1,2\text{-dap})_2]^{2+}$ or $[TM(dien)]^{2+}$ units[16]. Here, we present two organic-inorganic hybrid thiostannate and selenidostannate, $[Mn(1,2\text{-dap})_2(H_2O)]_2(\mu\text{-}Sn_2Q_6)$ (Q=S and Se), which is formed by unsaturated $[Mn(1,2\text{-dap})_2]^{2+}$ complex cations and Sn_2Q_6 dimers via Mn-Q bonds. Using tren ligand instead of 1,2-dap leads to one similar thiostannate of $[Mn(tren)]_2(\mu\text{-}Sn_2S_6)$ built from the unsaturated $[Mn(tren)]^{2+}$ complex cation and Sn_2S_6 dimer. Herein, we report their syntheses, crystal structures and optical properties.

1 Experimental

All analytical grade chemicals were obtained commercially and used without further purification. Elemental analyses (C, H, and N) were performed using a PE2400 Ⅱ elemental analyzer. Semi-quantitative elemental analyses for Mn, Ge and S were performed on a JSM-6700F scanning electron microscope (SEM) equipped with an energy dispersive spectroscope (EDS) detector. The UV-Vis spectra were measured at room temperature using a computer-controlled Perkin-Elmer Lambda 900 UV/Vis spectrometer in the wavelength range of 200~800 nm.

1.1 Preparation of $[Mn(1,2\text{-dap})_2(H_2O)]_2(\mu\text{-}Sn_2S_6)$ (1)

A mixture of $Mn(CH_3COO)_2\cdot 4H_2O$ (0.5 mmol), Sn powder (0.5 mmol), S powder (1.8 mmol) was added in the 4 mL of 1,2-diaminopropane aqueous solution (20%). After continuously stirring for 20 minutes, the mixture was sealed in a stainless steel reactor with a Teflon liner (15 mL), and then heated at 140 ℃ for 5 days and slowly cooled to room temperature at a rate of 0.1 ℃·min^{-1}. The mixture was filtered and the residue was dried in air. The product consists of light yellow block crystals of **1** and indefinite dark powders. The block crystals suitable for single crystal X-ray analysis were collected by hand under microscope. The crystals of **1** were selected by hand and washed with distilled water and ethanol (Yield: 15 mg, 7% based on Sn). The crystals are stable in air and insoluble in common solvents. Microprobe elemental analyses on clean surfaces of several single crystals of **1** gave molar ratio n_{Mn}:n_{Sn}:n_S of 1.00(5):1.21(5):3.04(7), which was in good agreement with that determined by single crystal X-ray diffraction study. Anal. for $C_6N_4H_{22}MnSnS_3O$ (%), Calcd.: C 16.52, H 5.08, N 12.85; Found: C 16.60, H 5.10, N 12.72. IR (cm^{-1}): 3 270 (s), 3 250 (s), 2 930 (w), 2 870 (w), 1 630 (m), 1 580 (m), 1 450 (w), 1 320 (w), 1 020 (s), 650 (m), 520 (m).

1.2 Preparation of $[Mn(1,2\text{-dap})_2(H_2O)]_2(\mu\text{-}Sn_2Se_6)$ (2)

The compound **2** was prepared in a manner analogous to that of **1** except that Se powder was used instead of S powder. Orange block crystals of **2** were filtered, washed by ethanol and air-dried (Yield: 25 mg, 9% on the basis of Sn). Microprobe elemental analyses on clean surfaces of several single crystals of compound **2** gave molar ratio n_{Mn}:n_{Sn}:n_S of 1.00(4):0.98(1):3.14(6), which was in good agreement with that determined by single crystal X-ray diffraction study. Elemental analysis for $C_6N_4H_{22}MnSnSe_3O$(%), Calcd.: C 12.49, H 3.84, N 9.71; Found: C 12.40, H 3.72, N 9.81. IR (cm^{-1}): 3 260 (s), 3 240 (s), 2 920 (w), 2 850 (w), 1 620 (m), 1 570 (m), 1 460 (w), 1 330 (w), 1 010 (s), 660 (w), 510 (w).

1.3 Preparation of $[Mn(tren)]_2(\mu\text{-}Sn_2S_6)$ (3)

The reagents of $Mn(CH_3COO)_2\cdot 4H_2O$ (0.5 mmol), Sn (0.5 mmol), S powder (1.8 mmol), triethylenetetramine (teta, 4 mL) and H_2O (1 mL) were mixed and stired for 20 minutes. Then, the mixture was sealed in a stainless steel reactor with a Teflon liner (15 mL), which was heated at 140 ℃ for 5 days and slowly cooled to room temperature at a rate of 0.1 ℃·min^{-1}. The mixture was filtered and the residue was dried in air. The products contain a small amount of yellow block shaped crystals, subsequently determined as $[Mn(tren)]_2Sn_2S_6$, and a large amount of unknown black powder. In the reaction, tren, which has the same chemical formula and different structure as teta, was formed by the rearrangement of teta in the solvothermal condition[18]. The crystals were selected by hand and washed with distilled water and ethanol. The yield of the crystal of **3** is 0.016 g (8%) based on Sn metal. Microprobe elemental analyses on clean surfaces of several single crystals of compound **3** gave molar ratio n_{Mn}:n_{Sn}:n_S of 1.00(2):0.93(8):3.18(5), which was in good agreement with that determined by single crystal X-ray diffraction study. Elemental analysis for For $C_6N_4H_{18}MnSnS_3$ (%), Calcd.: C 17.32, H 4.36, N 13.46; Found: C 17.27, H 4.30, N 13.58. IR (cm^{-1}): 3 510 (m), 3 220 (s), 2 850 (s), 1 560 (s), 1 470 (m), 1 070 (s), 640 (m).

1.3 Structure determination

Single-crystal X-ray diffraction data of the title compounds were recorded on a Bruker SMART CCD-based diffractometer (Mo $K\alpha$ radiation, λ=0.071 073 nm, graphite monochromator) at 293(2) K. Absorption corrections were applied using multi-scan technique. All the data sets were corrected for Lorentz factor, polarization, air absorption and absorption because of variations in the path length through the detector faceplate.

All the structures were solved using direct methods and refined by full-matrix least squares with atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms using the SHELXL-97 program[17]. Both the space groups of the compounds **1** and **2** were determined to be $Pccn$ (No.56), and **3** belongs to $P\bar{1}$ (No.2) based on the systematic absences, E-value statistics and satisfactory refinements. The hydrogen atoms attached to C and N atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters. Site occupancy refinements for these compounds indicated all sites were fully occupied. For compounds **1** and **2**, the final R=0.034 8 and 0.037 1, wR=0.095 8 and 0.089 5 for 3 532 and 3 865 observed reflections ($I>2\sigma(I)$) with 151 parameters, respectively. For compound **3**, the final R=0.058 3, wR=0.148 5 for 2 912 observed reflections ($I>2\sigma(I)$) with 136 parameters. Final difference Fourier maps showed featureless residual peaks of 1 866 e·nm^{-3} (0.07 nm from the H(3B) atom) and −588 e·nm^{-3} (0.086 nm form the O(1) atom) for **1**; 1 593 e·nm^{-3} (0.068 nm from the H(2A) atom) and −1 131 e·nm^{-3} (0.074 nm from the Se(1) atom) for **2**; and 3 560 e·nm^{-3} (0.129 nm from the S(1) atom) and −1 120 e·nm^{-3} (0.067 nm from the O(1) atom) for **3**, respectively. Relevant crystal and collection data parameters and refinement results can be found in Table 1. Selected bond lengths for the title compounds are listed in Table 2.

CCDC: 1024637, **1**; 1024638, **2**; 1024636, **3**.

Table 1　Crystal and structure refinement data for compounds 1~3

Complex	1	2	3
Empirical formula	$C_{12}N_8H_{44}Mn_2Sn_2S_6O_2$	$C_{12}N_8H_{44}Mn_2Sn_2Se_6O_2$	$C_6N_4H_{18}MnSnS_3$
Formula weight	436.09	576.79	416.05
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Temperature / K	293(2)	293(2)	293(2)
Space group	*Pccn* (No.56)	*Pccn* (No.56)	$P\bar{1}$ (No.2)
a / nm	1.609 4(2)	1.643 7(2)	0.763 5(7)
b / nm	1.657 78(17)	1.686 2(2)	0.808 4(8)
c / nm	1.166 0 (7)	1.200 5(6)	1.214 8(12)
α / (°)			97.306(11)
β / (°)			104.012(11)
γ / (°)			108.831(10)
Volume / nm^3	3.111 1(5)	3.327 5(7)	0.671 1(11)
Z	4	4	2
D_c / (g·cm^{-3})	1.862	2.303	2.059
μ / mm^{-1}	2.808	8.812	3.244
F(000)	1 736	2 168	410
Crystal size / mm	0.10×0.09×0.08	0.10×0.05×0.05	0.09×0.08×0.07
θ range for data collection / (°)	3.27 to 27.44	1.73 to 27.68	2.90 to 27.09
Limiting indices	$-20 \leqslant h \leqslant 20$, $-21 \leqslant k \leqslant 21$, $-14 \leqslant l \leqslant 14$	$-21 \leqslant h \leqslant 21$, $-21 \leqslant k \leqslant 22$, $-15 \leqslant l \leqslant 15$	$-9 \leqslant h \leqslant 9$, $-10 \leqslant k \leqslant 10$, $-15 \leqslant l \leqslant 15$
Reflections collected	34 065	36 694	7 505
Independent reflections (R_{int})	3 532 (0.042 0)	3 865 (0.042 1)	2 912 (0.046 7)
Observed reflections ($I>2\sigma(I)$)	2 719	2 822	2 263
Final GooF	1.035	1.026	1.013
R_1, wR_2 ($I>2\sigma(I)$)	0.034 8, 0.095 8	0.037 1, 0.089 5	0.058 3, 0.148 5
R_1, wR_2 (all data)	0.051 2, 0.105 5	0.058 7, 0.098 8	0.075 7, 0.160 2
Largest different peak and hole / (e·nm^{-3})	1 866 and −588	1 593 and −1 131	3 560 and −1 120

Table 2 Selected bond lengths (nm) for compounds 1~3

		1			
Sn(1)-S(3)	0.232 50(13)	Sn(1)-S(2)^i	0.244 08(12)	Sn(1)-S(1)	0.235 82(13)
Sn(1)-S(2)	0.245 17(13)	Mn(1)-N(1)	0.225 6(5)	Mn(1)-N(3)	0.228 7(4)
Mn(1)-N(4)	0.225 6(4)	Mn(1)-O(1)	0.229 7(7)	Mn(1)-N(2)	0.228 4(4)
Mn(1)-S(1)	0.256 03(15)				
		2			
Sn(1)-Se(2)	0.244 98(7)	Sn(1)-Se(3)^i	0.256 59(7)	Sn(1)-Se(1)	0.247 98(7)
Sn(1)-Se(3)	0.257 61(8)	Mn(1)-N(2)	0.224 8(6)	Mn(1)-N(3)	0.227 8(5)
Mn(1)-N(1)	0.225 1(5)	Mn(1)-O(1)	0.232 2(11)	Mn(1)-N(4)	0.226 2(6)
Mn(1)-Se(1)	0.270 46(11)				
		3			
Sn(1)-S(2)	0.231 2(3)	Sn(1)-S(1)^i	0.245 1(3)	Sn(1)-S(3)	0.235 6(3)
Sn(1)-S(1)	0.246 9(3)	Mn(1)-N(2)	0.222 9(7)	Mn(1)-N(4)	0.235 6(7)
Mn(1)-N(1)	0.223 0(7)	Mn(1)-S(3)	0.249 0(3)	Mn(1)-N(3)	0.227 1(8)

Symmetry codes: ^{i} $-x$, $-y+1$, $-z+1$ for **1**; ^{i} $-x$, $-y+1$, $-z+1$ for **2**; ^{i} $-x$, $-y+1$, $-z$ for **3**.

2 Results and discussion

2.1 Crystal structure

The compounds **1** and **2** are isostructural phases and crystallize in the orthorhombic system *Pccn* (No. 56) space group with four formulas in the unit cell. Their structures contain $[Mn(1,2\text{-dap})_2(H_2O)]_2(\mu\text{-}Sn_2Q_6)$ oligomer built form the $[Mn(1,2\text{-dap})_2(H_2O)]^{2+}$ complex cation and $[Sn_2Q_6]^{4-}$ dimer linked via Mn-Q covalent bonds. In the follow discussion, only the structure of **1** will be discussed as represent.

The asymmetric unit of compound **1** contains one crystallographically independent Sn^{4+} center, one Mn^{2+} ion, one H_2O and three S^{2-} ions. As shown in Fig.1, the Sn^{4+} ion is surrounded by four S^{2-} ions with a slightly distorted tetrahedral geometry with Sn-S bond lengths of 0.232 50(13)~0.245 17(13) nm and S-Sn-S angles of 93.22(4)° ~114.77(5)°, which are consistent with the corresponding values of SnS_4 tetrahedron observed in the thiostannates(Ⅳ), such as $[Ni(en)_3]_2Sn_2S_6$, $[Ni(dien)_3]_2Sn_2S_6$, $[Mn(phen)]_2SnS_4$, etc[19-21]. Two neighboring SnS_4 tetrahedra are condensed via edge-sharing to form a Sn_2S_6 dimer, which has been reported in many thiostannates(Ⅳ). The Mn^{2+} ion is coordinated by four nitrogen donors from two 1,2-dap ligands and one oxygen from H_2O molecule as well as one terminal S^{2-} ion of Sn_2S_6 dimer with distorted octahedral environment. Such coordination mode of Mn^{2+} ion is similar to that of $[Mn(dach)_2(H_2O)]Sn_2S_6$ (dach =1,2-diaminocyclohexane)[22]. The Mn-N, Mn-O and Mn-S bond distances are of 0.225 6(4)~0.228 7(4) nm, 0.229 7(7) nm, 0.256 03(15) nm, respectively, which belong to the normal values.

Each Sn_2S_6 dimer is attached by two $[Mn(1,2\text{-dap})_2(H_2O)]$ complexes via Mn-S bonds to form a $[Mn(1,2\text{-dap})_2(H_2O)]_2(\mu\text{-}Sn_2S_6)$ oligomer. The neighboring $[Mn(1,2\text{-dap})_2(H_2O)]_2(\mu\text{-}Sn_2S_6)$ oligomers feature parallel arrangement along the *a*-axis and *c*-axis, which are interconnected via N–H⋯S and O–H⋯O hydrogen bonding interactions to form a 3D H-bonding network with two different types of 1D tunnels (Fig.2). The N⋯S distances (0.347 6(5)~0.373 6(5) nm) and N–H⋯S angles (142.0°~172.2°) are comparable with those of metal chalcogenidogermanates[8-10].

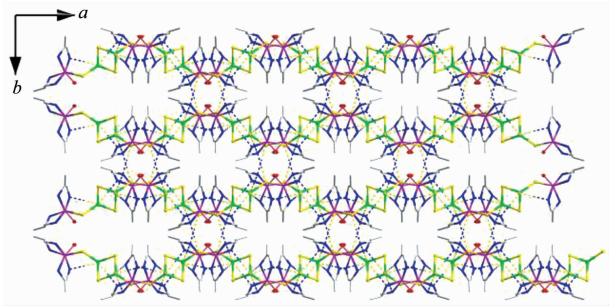
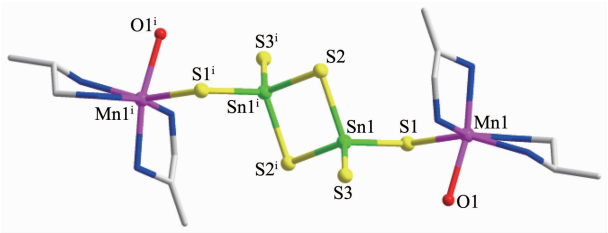


Fig.2 3D H-bonding network structure of the compound **1**

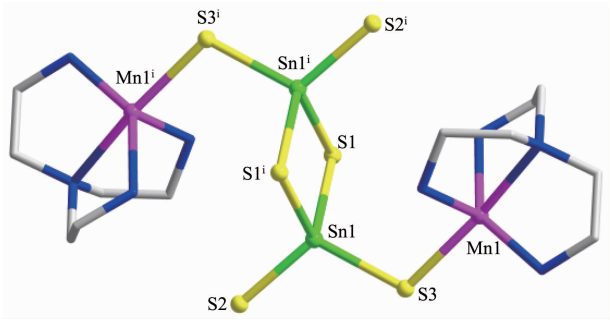
Compound **3** belongs to the triclinic system $P\bar{1}$ (No.2), and its structure is consisted of $[Mn(tren)]_2(\mu\text{-}Sn_2S_6)$ unit based on $[Mn(tren)]^{2+}$ complex cation and Sn_2S_6 dimer. The asymmetric unit of compound **3** contains one crystallographically independent Sn^{4+} center, one Mn^{2+} ion and three S^{2-} ions.

As shown in Fig.3, the Sn(1) atom is coordinated by four S^{2-} ions with distorted tetrahedral coordination, and two SnS_4 tetrahedra are condensed via edge-sharing to form a Sn_2S_6 dimer. The Sn-S bond distances are close to those of compound **1**. The Mn(1) atom is surrounded by four nitrogen donors from one tren ligands and one S atom of Sn_2S_6 dimer with a distorted trigonal biyramidal coordination environment,



Symmetry codes: ⁱ −*x*, −*y*+1, −*z*+1

Fig.1 View of the structure of the $[Mn(1,2\text{-dap})_2(H_2O)]_2(\mu\text{-}Sn_2S_6)$ oligomer



Symmetry codes: ⁱ −*x*, −*y*+1, −*z*

Fig.3 Detailed view of the structure of $[Mn(tren)]_2(\mu\text{-}Sn_2S_6)$ unit in compound **3**

which is similar to that of [Mn(tren)]HgSb$_2$S$_5$[10]. Each Sn$_2$S$_6$ dimer is attached by two [Mn(tren)]$^{2+}$ complexes via Mn-S bonds to form a [Mn(tren)]$_2$(μ-Sn$_2$S$_6$) unit.

The neighboring [Mn(tren)]$_2$(μ-Sn$_2$S$_6$) units are interconnected via Mn(1)-S(3) secondary bonding interactions (0.290 5 nm) along the *b*-axis into 1D [Mn(tren)]$_2$(μ-Sn$_2$S$_6$) chains, which are further interlinked via N-H…S hydrogen bonds to form 2D layer within ab-plane (Fig.4). These 2D layers feature parallel packing via van der Waals forces according to A…A…A order along the c-axis (Fig.5). The N…S distances (0.341 9(8)~0.375 9(8) nm) and N-H…S angles (143.1°~172.0°) are comparable with those of compound **1**.

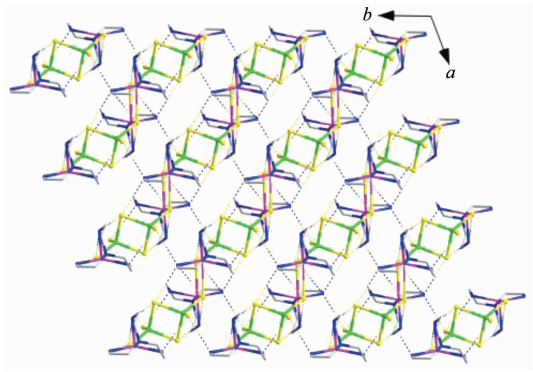


Fig.4　View of the 2D H-boning layer in compound **3**

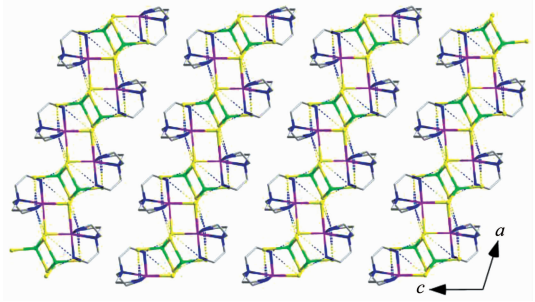


Fig.5　Packing structure of compound **3**

It is very interesting to compare the structures of [Mn(tren)]$_2$(μ-Sn$_2$S$_6$) with [Co(tren)]$_2$(μ-Sn$_2$S$_6$) and [Ni(tren)]$_2$(μ-Sn$_2$S$_6$)[23]. Despite of the similar chemical composition and structural units, these compounds feature different space groups and connecting manners. [Mn(tren)]$_2$(μ-Sn$_2$S$_6$) crystallizes in the triclinic system $P\bar{1}$, whereas [Co(tren)]$_2$(μ-Sn$_2$S$_6$) and [Ni(tren)]$_2$(μ-Sn$_2$S$_6$) belong to the monoclinic system *C*2/*c*. In [Co(tren)]$_2$(μ-Sn$_2$S$_6$), each Sn$_2$S$_6$ dimer is terminally attached by two [Co(tren)]$^{2+}$ complexes via Co-S bonds to form isolated [Co(tren)]$_2$(μ-Sn$_2$S$_6$) unit. [Mn(tren)]$_2$(μ-Sn$_2$S$_6$) also contains similar [Mn(tren)]$_2$(μ-Sn$_2$S$_6$) unit, differently, the neighboring [Mn(tren)]$_2$(μ-Sn$_2$S$_6$) units are further interlinked via Mn-S secondary bonding interactions to form 1D chain. Such 1D zigzag-like chain is very similar to that of [Ni(tren)]$_2$(μ-Sn$_2$S$_6$), in which each neighboring Sn$_2$S$_6$ dimer is bridged by a pair of [Ni(tren)]$^{2+}$ complexes to form a 1D zigzag-like [Ni(tren)]$_2$(μ-Sn$_2$S$_6$) chain.

2.2　Optical properties

The solid-state optical diffuse reflection spectra of the compounds **1~3** were measured at room temperature as represent. The optical absorption spectra indicate that these compounds are semiconductors. As shown in Fig.6, the optical band gaps obtained by extrapolation of the linear portion of the absorption edge is estimated as 2.5, 2.1 and 2.4 eV, respectively, which is in accordance with the distinction between their colors (yellow for compounds **1** and **3**, and orange for **2**). These band gaps were close to those of other thiostannates(Ⅳ) and selenidostannate(Ⅳ), such as [Fe(tepa)]$_2$Sn$_2$S$_6$ (2.3 eV), [Ni(tepa)]$_2$Sn$_2$S$_6$ (2.8 eV) and [Mn(tepa)]Sn$_3$Se$_7$ (2.2 eV), etc[24-25].

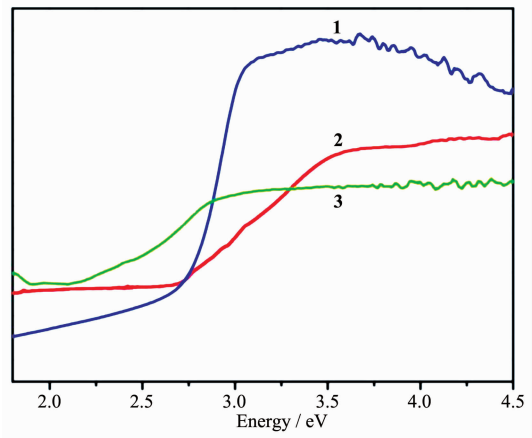


Fig.6　Solid-state optical absorption spectra of compounds **1~3**

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