Supporting Information

Co-Assembly of a Three-Dimensional Open Framework Sulfide with a Novel Linkage between Oxygen-Encapsulated T3 Cluster and Supertetrahedral T2 Cluster

Xiaohui Han,[ab‡] Zhenqing Wang,[‡] Dan Liu,[a] Jin Xu,[a] Yongxin Liu[a,b] and Cheng Wang *[a]

[a] State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, P. R. China. Fax: (+86) 431-85698041

[b] The University of Chinese Academy of Sciences, Beijing 100049, P. R.China.

E-mail: cwang@ciac.ac.cn (C.W.)

1. Single-crystal structure determination

Intensity data collections were carried out with the Bruker APEX-II diffractometer and equipped with a CCD two-dimensional detector using the graphite monochromatized wavelength λ(Mo-$K\alpha$)=0.71073 Å at 185(2) K. The structure was solved with direct methods using *SHELXS-97* [1], and structure refinement was performed by full matrix least-squares on F^2 using the *SHELXL-97* crystallographic software package [2]. All atoms except those in disordered organic amine were refined with anisotropic displacement parameters. For compound **1** with large clusters/cavities and extensive disorder of organic species, the "Squeeze" routine, which corrects the effects due to disorder of organic amine, was applied. Relevant crystallographic data and refinement details for open framework of compound **1** are summarized in Table S1. Selected bond lengths and angles are listed in Table S2 and Table S3, respectively.

Table S1. The crystallographic data for compound **1**.

	1
Formula	$C_{86.4}H_{201.6}N_{14.4}Ga_{6.4}Sn_{21.6}S_{52}O_{22.4}$
Formula weight	6478.75
Crystal size (mm)	0.15×0.10×0.07
Temperature (K)	185(2)
Wavelength (Å)	0.71073
Crystal system	Tetragonal
Space group	*P-42c*
a (Å)	14.6663(3)
b (Å)	14.6663(3)
c (Å)	24.9609(11)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	5369.1(3)
Z	8
D_c (g cm^{-3})	2.004
μ (mm^{-1})	3.800
F (000)	3110

θ range (°)	1.39-24.99
hkl range	-17, 13; -17,17; -22,29
Reflections	26534
Data/restraints/parameters	4739/7/104
R_{int}	0.0536
GOF	1.087
R_1, ωR_2 [I>2$\sigma(I)$] [a]	0.0516, 0.1517
R_1, ωR_2 (all data) [a]	0.0612, 0.1586
Largest diff. peak and hole(e	0.772, -1.046

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma |F_o|$, $\omega R_2 = \{\Sigma[\omega(F_o^2 - F_c^2)^2]/\Sigma[\omega(F_o^2)^2]\}^{1/2}$

Table S2. Selected bond lengths (Å) for compound **1**[a].

Sn(1)-O(1)#1	2.087(8)	Sn(1)-O(1)#2	2.120(8)
Sn(1)-S(1)	2.591(3)	Sn(1)-S(1)#1	2.581(3)
Sn(1)-S(3)	2.403(3)	Sn(1)-S(6)#3	2.431(3)
Sn(2)-O(1)	2.090(8)	Sn(2)-O(1)#2	2.090(8)
Sn(2)-S(1)	2.570(3)	Sn(2)-S(1)#2	2.570(3)
Sn(2)-S(5)	2.445(3)	Sn(2)-S(5)#2	2.445(3)
Sn(3)-O(1)#2	2.511(8)	Sn(3)-S(3)	2.375(4)
Sn(3)-S(4)	2.386(3)	Sn(3)-S(6)	2.387(3)
Sn(3)-S(5)	2.388(3)	Ga(1)-S(2)	2.299(4)
Ga(1)-S(4)	2.222(4)	Ga(1)-S(7)	2.326(3)
Ga(1)-S(8)	2.339(3)		

[a] Symmetry transformations used to generate equivalent atoms: #1 y-2,-x+1,-z+2; #2 -x-1,-y+3,z; #3 -y+1,x+2,-z+2; #4 x,-y+2,-z+5/2; #5 -x-1,y,-z+5/2; #6 -x-1,-y+2,z.

Table S3. Selected bond angles (°) for compound **1**[a].

O(1)#1-Sn(1)-O(1)#2	91.9(5)	O(1)#1-Sn(1)-S(1)	78.2(2)
O(1)#1-Sn(1)-S(3)	177.7(2)	O(1)#1-Sn(1)-S(1)#1	77.8(2)
O(1)#1-Sn(1)-S(6)#3	85.3(2)	O(1)#2-Sn(1)-S(1)	76.7(2)
O(1)#2-Sn(1)-S(3)	85.9(3)	O(1)#2-Sn(1)-S(1)#1	77.9(2)
O(1)#2-Sn(1)-S(6)#3	177.2(3)	S(3)-Sn(1)-S(1)	100.38(12)

S(1)#1-Sn(1)-S(1)	144.21(14)	S(6)#3-Sn(1)-S(1)	102.99(12)
S(3)-Sn(1)-S(1)#1	102.58(12)	S(3)-Sn(1)-S(6)#3	96.79(12)
S(6)#3-Sn(1)-S(1)#1	101.14(12)	O(1)-Sn(2)-O(1)#2	92.1(5)
O(1)-Sn(2)-S(1)	78.0(2)	O(1)-Sn(2)-S(5)	177.7(3)
O(1)-Sn(2)-S(1)#2	77.7(2)	O(1)-Sn(2)-S(5)#2	85.7(2)
O(1)#2-Sn(2)-S(1)	77.7(2)	O(1)#2-Sn(2)-S(5)	85.7(2)
O(1)#2-Sn(2)-S(1)#2	78.0(2)	O(1)#2-Sn(2)-S(5)#2	177.7(3)
S(5)-Sn(2)-S(1)	100.94(12)	S(1)#2-Sn(2)-S(1)	144.73(15)
S(5)#2-Sn(2)-S(1)	102.31(12)	S(5)-Sn(2)-S(1)#2	102.31(12)
S(5)#2-Sn(2)-S(5)	96.63(16)	S(5)#2-Sn(2)-S(1)#2	100.94(12)
S(3)-Sn(3)-O(1)#2	78.4(2)	S(4)-Sn(3)-O(1)#2	176.0(2)
S(6)-Sn(3)-O(1)#2	77.65(19)	S(5)-Sn(3)-O(1)#2	78.27(19)
S(3)-Sn(3)-S(4)	97.70(13)	S(3)-Sn(3)-S(5)	116.75(13)
S(3)-Sn(3)-S(6)	117.49(13)	S(4)-Sn(3)-S(5)	104.52(12)
S(4)-Sn(3)-S(6)	103.55(12)	S(6)-Sn(3)-S(5)	113.37(14)
S(4)-Ga(1)-S(2)	101.13(15)	S(2)-Ga(1)-S(7)	111.64(8)
S(2)-Ga(1)-S(8)	112.43(8)	S(4)-Ga(1)-S(7)	108.85(14)
S(4)-Ga(1)-S(8)	109.06(14)	S(7)-Ga(1)-S(8)	113.00(7)

[a] Symmetry transformations used to generate equivalent atoms: #1 y-2,-x+1,-z+2; #2 -x-1,-y+3,z; #3 -y+1,x+2,-z+2; #4 x,-y+2,-z+5/2; #5 -x-1,y,-z+5/2; #6 -x-1,-y+2,z.

2. Supplementary structural figures of compound 1

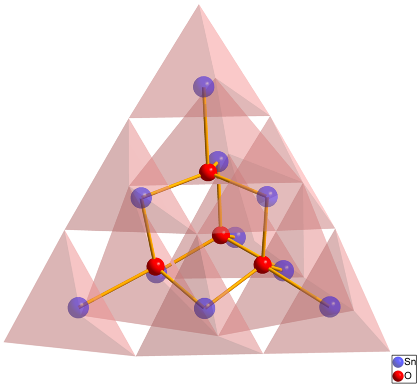

Fig. S1 The coordination environment of oxygen atom in [Sn$_{10}$S$_{20}$O$_4$]$^{8-}$ anion.

Red ball stands for O, purple for Sn.

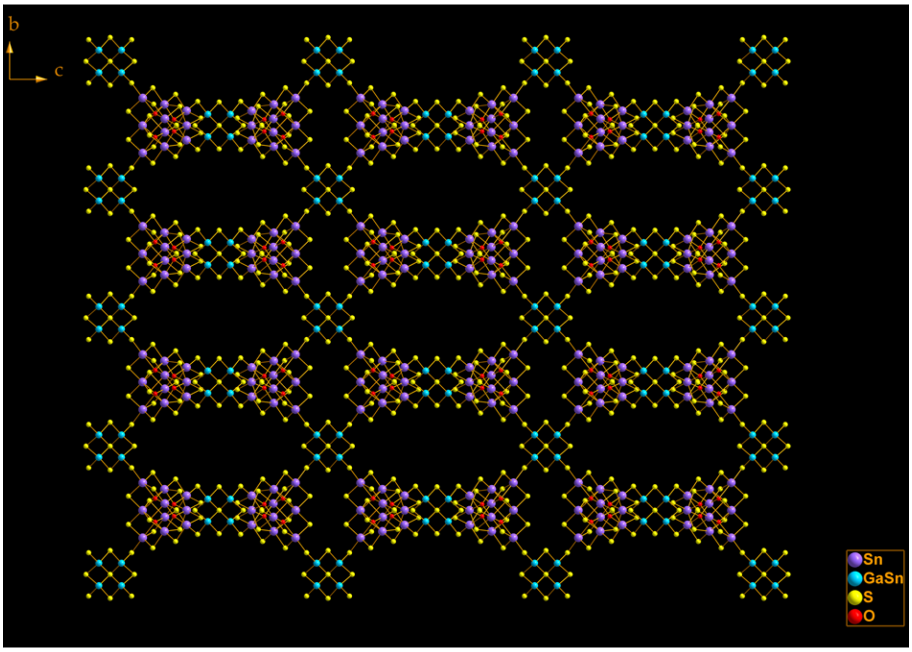

Fig. S2 A view of the 3D framework of compound **1** projected down along a-axis. Red ball stands for O, yellow for S, cyan for Ga/Sn mixed sites, purple for Sn.

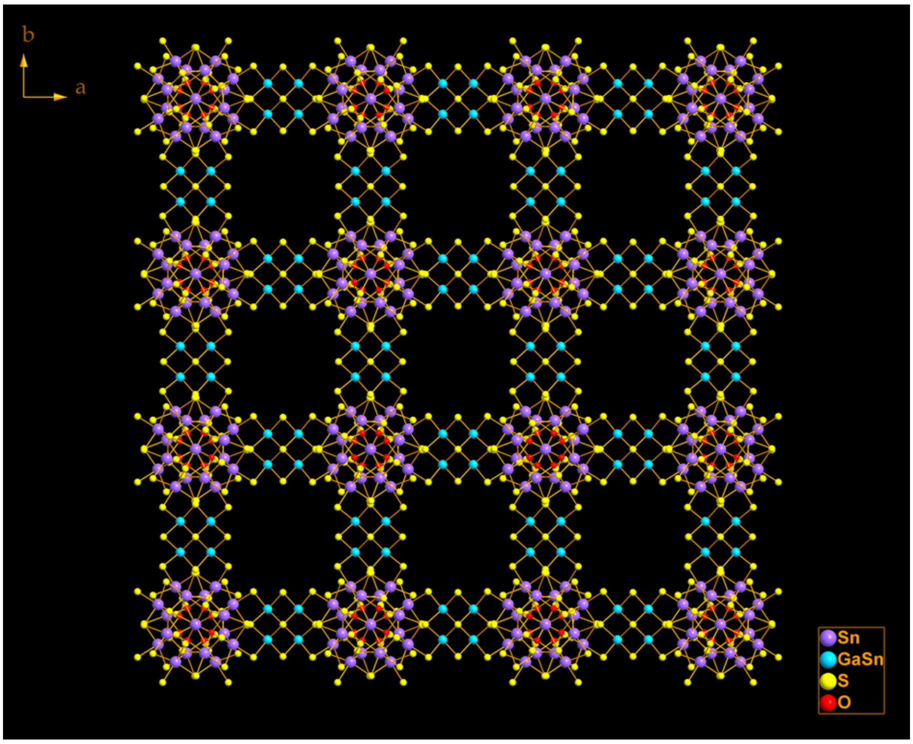

Fig. S3 A view of the 3D framework of **1** projected down along c-axis. Red ball stands for O, yellow for S, cyan for Ga/Sn mixed sites, purple for Sn.

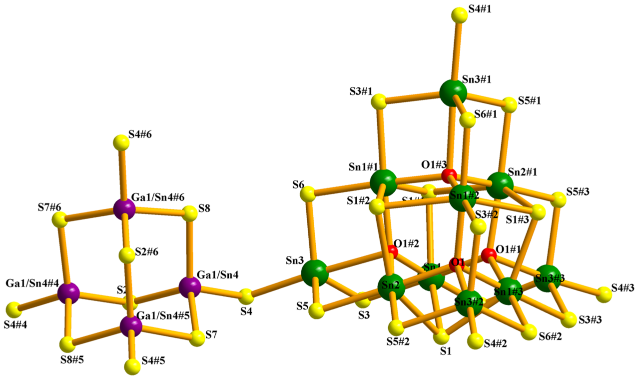

Fig. S4 A view of the anionic clusters of **1**. Red ball stands for O, yellow for S, purple for Ga/Sn mixed sites; green for Sn. Symmetry transformations used to generate equivalent atoms: #1 y-2,-x+1,-z+2; #2 -x-1,-y+3,z; #3 -y+1,x+2,-z+2; #4 x,-y+2,-z+5/2; #5 -x-1,y,-z+5/2; #6 -x-1,-y+2,z.

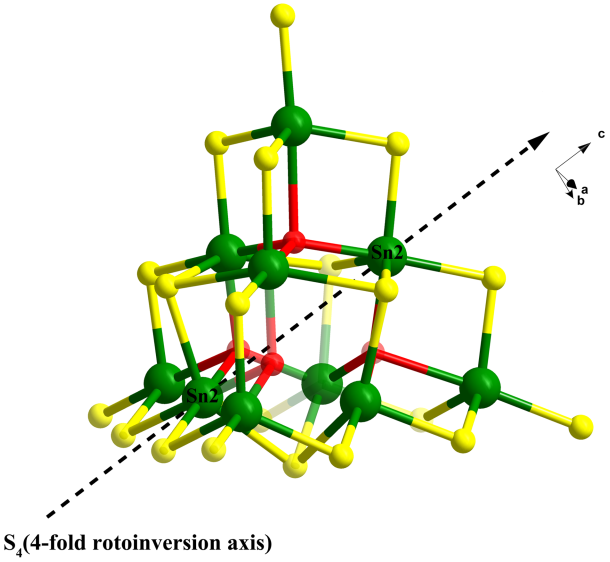

Fig. S5 Diagrammatic presentationof the 4-fold rotoinversion axis in *P-42c* space group. Sn2 atoms in T3 cluster lay on the 4-fold rotoinversion axis (*c* direction).

3. Experimental section

All chemicals were reagent grade and used as received without further purification. Distilled water was used throughout.

3.1 Synthesis of compound 1

Compound **1** was synthesized by mixing 139.4 mg Ga (2 mmol), 296.8 mg Sn (2.5 mmol), 128 mg S (4 mmol), 0.5 ml H_2O and 2 ml *cis*-2,6-dimethylmorpholine (DMMP) in a 23 ml Teflon-lined stainless steel autoclave and stirred for 1 h. The vessel was then sealed and heated at 180°C for 12 days without being disturbed. After cooling to room temperature slowly, the reaction mixture was filtered, washed with ethanol and water, and dried in air at room temperature. The yellow diamond crystals were obtained via handpicking under a microscope (yield 25%, based on Sn).

3.2 Discussion of the preparation

Title crystal could only be obtained with the existence of H_2O. If using *cis*-2, 6-dimethylmorpholine (DMMP) as solvent separately, only T2 cluster with mixed Ga/Sn sites could be isolated from the reaction system. It exhibits that the auxiliary H_2O provides O^{2-} source and assists the growth of oxygen-encapsulated T3 cluster simultaneously. It may preferentially select on forming oxygen-encapsulated T3 cluster $[Sn_{10}S_{20}O_4]^{8-}$ than normal T3 cluster $[Ga_{10}S_{20}]^{10-}$, and take an important role in forming the final structure of **1**.

3.3 Details of the structure refinement

Semi-quantitative energy dispersive X-ray (EDS) analysis confirmed the presence of all constituent heavy elements in compound **1** and the quantitative elemental analysis, inductively Coupled Plasma Optical Emission Spectrometry analysis Spectrometry (ICP-OES), gave a Ga/Sn/S mole ratio of 1.0/3.375/8.125. This ratio is in accordance with the results of single-crystal structure refinement based on significant difference in terms of atomic scattering power between Ga and Sn elements. Extra-framework species (protonated organic amine molecules) in structure could not be located in the final structural refinement due to their disorder. Even data collected at lower temperatures could not improve the ordering of these molecules. The final protonated organic amines in molecular formula were given from CHN analysis. Calcd: C 16.02, H 3.14, N 3.11; found: C 16.08, H 3.09, N 3.17. %

3.4 Results of elemental analysis (in wt. %) by the ICP-OES

Element	S	Ga	Sn
wt. (%)	22.924	6.135	35.253

4. Physical measurements

Powder X-ray diffraction (XRD) measurement was performed by a Bruker D8

Focus diffractometer with Cu-Kα radiation (λ=1.5406 Å) and a Lynx Eye detector in the 2θ range of 4-40° at 298 K. Optical diffuse reflectance spectrum was measured with a Hitachi U-4100 UV/Vis spectrophotometer by using $BaSO_4$ powder as the 100% reflectance reference. The absorption data was calculated from the reflectance using the Kubelka-Munk function [3]. Thermal analysis was conducted on a Pyris Diamond thermal analyzer under a flowing nitrogen atmosphere with a heating rate of 10°C/min in the range of 50-800℃. Semi-quantitative energy dispersive X-ray analysis (EDS) for heavier elements was performed on Bruker Quantax 200 attached to Hitachi S-4800 field emission scanning electron microscopy. CHN Analysis was obtained on Vario EL. Inductively Coupled Plasma Optical Emission Spectrometry analysis (ICP-OES) was performed on Thermo Scientific iCAP 6000 ICP spectrometer.

4.1 Powder X-ray diffraction (XRD) pattern

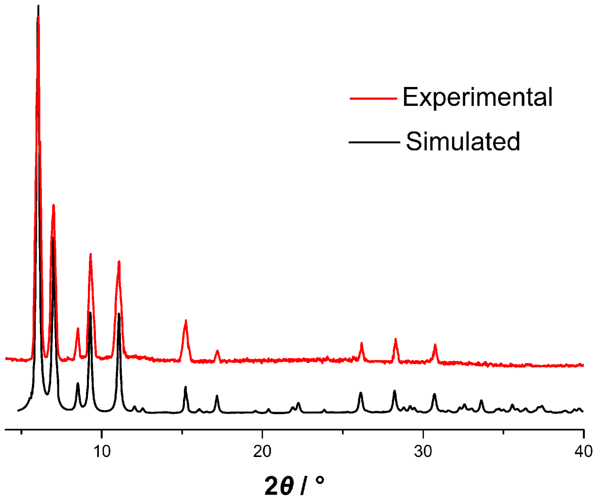

Fig. S6 The PXRD pattern of **1** (top) is comparable with its simulated from the single crystal X-ray data (bottom).

4.2 Solid-state UV/Vis spectra

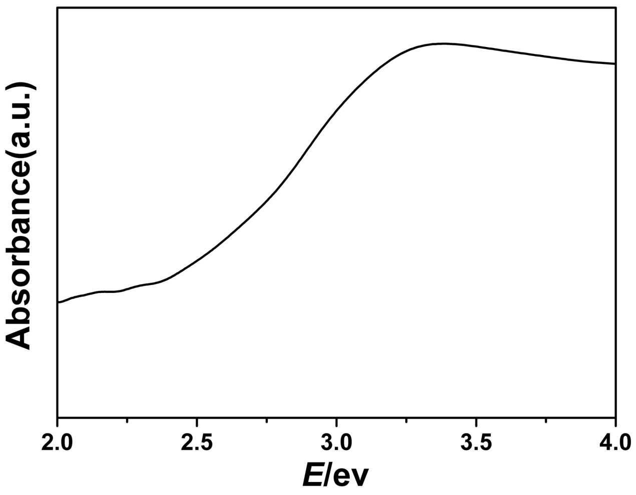

Fig. S7 Solid-state optical absorption spectra of **1**.

4.3 TGA

The thermal stability of compound **1** was determined by TGA under a nitrogen atmosphere. In the case of compound **1**, two stags of weight loss are observed over the temperature range 50-800℃. The initial weight loss between 50-314℃ could be attributed to loss of part solvent molecules trapped in the pore or adsorbed on the surface. The following weight loss between 314-755 ℃ corresponds to the decomposition of the remainder organic molecules together with the collapse of framework.

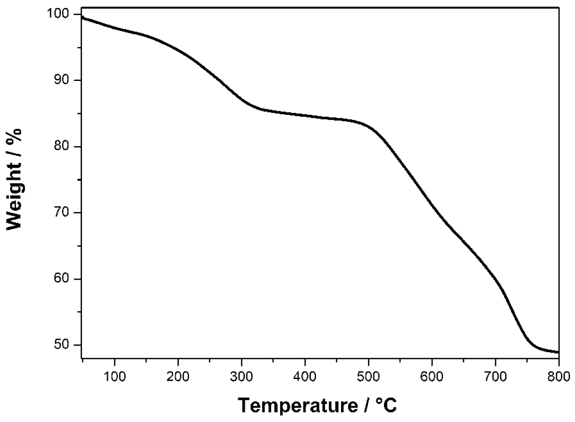

Fig. S8 TGA curve of **1** under N_2 atmosphere.

4.4 The energy dispersive X-ray spectra (EDS)

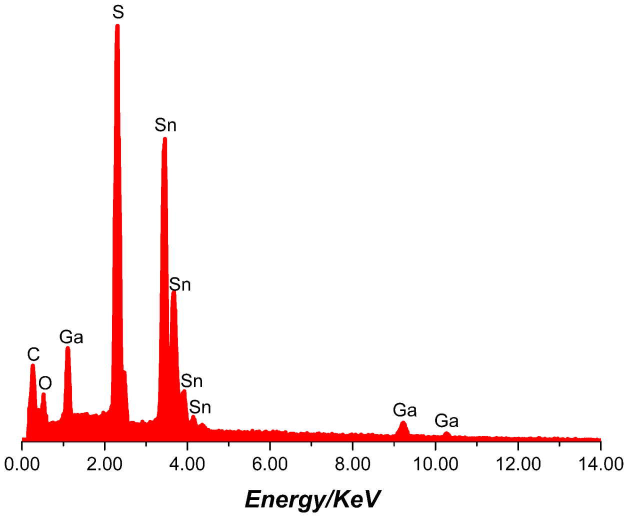

Fig. S9 The energy dispersive X-ray spectra of **1**.

Reference

[1] G. M. Sheldrick, *SHELXS97*, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.

[2] G. M. Sheldrick, *SHELXS97*, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1997.

[3] W. W. Wendlandt and H. G. Hecht, Reflectance Spectroscopy, Interscience Publishers, New York, 1966.