

Supporting Information for

Crown-like heterometallic unit as building block for 3D In-Ge-S framework

Xiaohui Han, ^{ab} Zhenqing Wang, ^a Jin Xu, ^a Dan Liu^a and Cheng Wang^{a*}

^a State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, P. R. China.

Tel: +86-431-85262770

^b University of Chinese Academy of Sciences, Beijing 100039, P. R. China.

E-mail: cwang@ciac.ac.cn

1. Single-crystal structure determination

Single-crystal X-ray diffraction data of compound **1** were collected on a Bruker APEX-II CCD diffractometer equipped with a graphite-monochromatized Mo- $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation source at 153(2) K. The structure of **1** was solved by direct method and refined by full matrix least-squares on F^2 using the *SHELXL-2014/7* program package^[1].

All framework atoms were unambiguously determined, and they were refined with anisotropic thermal parameters. While, extra-framework molecules could not be located from Fourier maps owing to their disorder. This is similar to those found of other chalcogenide open frameworks^[2]. In order to eliminate all the disordered molecules, SQUEEZE process in the PLATON^[3] software package was applied. The final guest molecules in molecular formula were calculated from TGA combined with elemental analysis data. Relevant crystallographic data and structure refinement details are summarized in Table S1, selected bond lengths and angles are listed in Table S2. .

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

| | |
|------------------------------|--|
| Formula | $\text{C}_{24}\text{H}_{59}\text{N}_4\text{O}_{5.50}\text{In}_6\text{Ge}_3\text{S}_{17}$ |
| Formula weight | 1943.46 |
| Temperature (K) | 153(2) K |
| Wavelength (\AA) | 0.71073 |
| Crystal system | Cubic |
| Space group | $I2(1)3$ |
| a (\AA) | 18.6836(9) |
| b (\AA) | 18.6836(9) |
| c (\AA) | 18.6836(9) |
| α ($^\circ$) | 90 |
| β ($^\circ$) | 90 |
| γ ($^\circ$) | 90 |
| V (\AA^3) | 6522.0(9) |
| Z | 4 |
| D_c (g cm^{-3}) | 1.979 |
| μ (mm^{-1}) | 4.019 |
| $F(000)$ | 3748 |

| | |
|---|---------------------------|
| θ range (°) | 1.54-26.02 |
| hkl range | -13, 23; -23, 21; -21, 23 |
| Reflections | 17606 |
| Data/restraints/parameters | 2155 / 0 / 42 |
| R_{int} | 0.0899 |
| GOF | 0.948 |
| $R_1, \omega R_2 [I > 2\sigma(I)]$ ^[a] | 0.0320, 0.0509 |
| $R_1, \omega R_2$ (all data) ^[a] | 0.0415, 0.0530 |
| Largest diff. peak and hole (e Å ⁻³) | 0.383, -0.341 |

$$^{\text{[a]}} R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \omega R_2 = \left\{ \frac{\sum [\omega(F_o^2 - F_c^2)^2]}{\sum [\omega(F_o^2)^2]} \right\}^{1/2}$$

Table S2. Selected bond lengths (Å) and bond angles (°) for compound **1^a**

| | | | |
|---------------------|------------|-------------------|------------|
| In(1)-S(1) | 2.466(2) | In(1)-S(2) | 2.4932(8) |
| In(1)-S(3) | 2.416(2) | In(1)-S(4)#1 | 2.455(2) |
| In(1)#2-S(3) | 2.416(2) | In(1)#3-S(2) | 2.4932(8) |
| In(1)#4-S(2) | 2.4932(8) | In(1)#5-S(4) | 2.455(2) |
| Ge(2)-S(1) | 2.192(2) | Ge(2)-S(1)#2 | 2.192(2) |
| Ge(2)-S(4) | 2.204(2) | Ge(2)-S(4)#2 | 2.204(2) |
| | | | |
| S(1)-In(1)-S(2) | 111.59(7) | S(3)-In(1)-S(1) | 108.80(8) |
| S(3)-In(1)-S(2) | 109.08(9) | S(3)-In(1)-S(4)#1 | 116.30(8) |
| S(4)#1-In(1)-S(1) | 97.06(8) | S(4)#1-In(1)-S(2) | 113.42(8) |
| S(1)-Ge(2)-S(1)#2 | 113.22(13) | S(1)-Ge(2)-S(4) | 105.98(8) |
| S(1)#2-Ge(2)-S(4)#2 | 105.98(8) | S(1)#2-Ge(2)-S(4) | 111.78(9) |
| S(1)-Ge(2)-S(4)#2 | 111.78 (9) | S(4)-Ge(2)-S(4)#2 | 108.08(13) |

^a Symmetry transformations used to generate equivalent atoms: #1 $z-1/2, x+1/2, y+1/2$, #2 $x+0, -y+1, -z+3/2$, #3 $-z+1, x+1/2, -y+3/2$, #4 $y-1/2, -z+3/2, -x+1$, #5 $y-1/2, z-1/2, x+1/2$.

2. Supplementary structural figures of compound 1

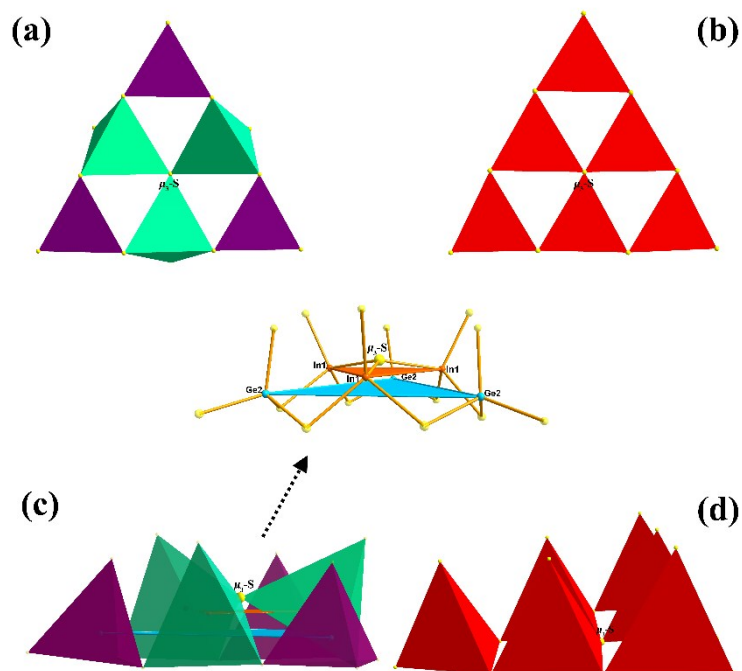


Fig. S1 Views of the crown-like unit in **1** (a, c) and one of the four faces in T3 cluster (b,d) in different directions.

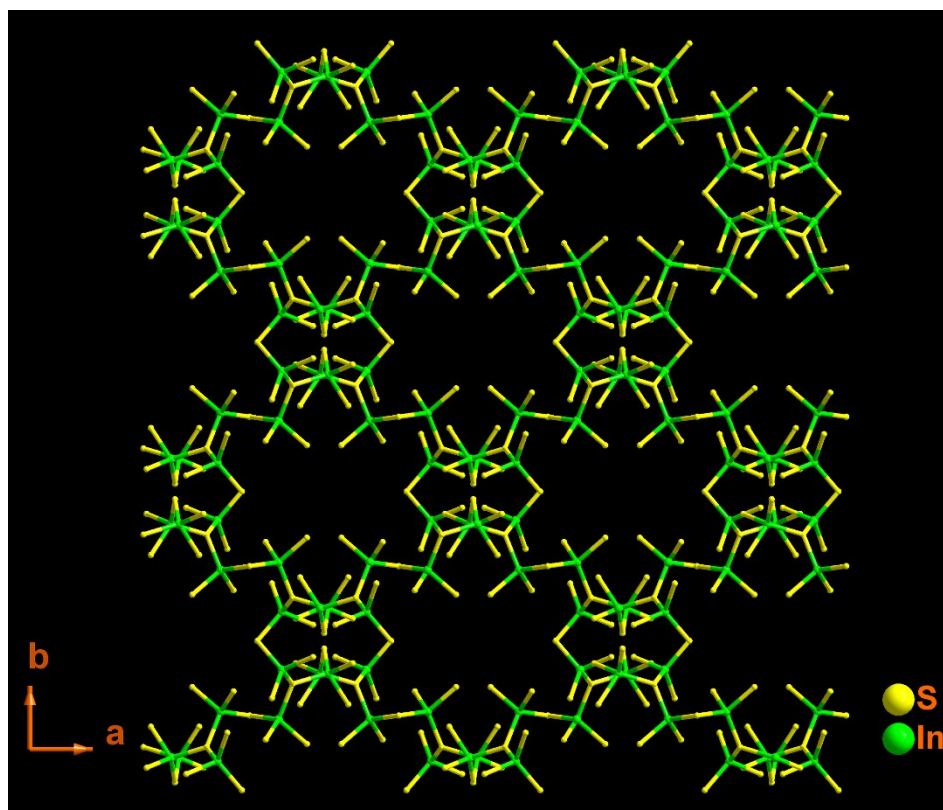


Fig. S2 View of the 3D anionic framework of compound **1** along the c axis

dislodging “decorative” Ge atoms.

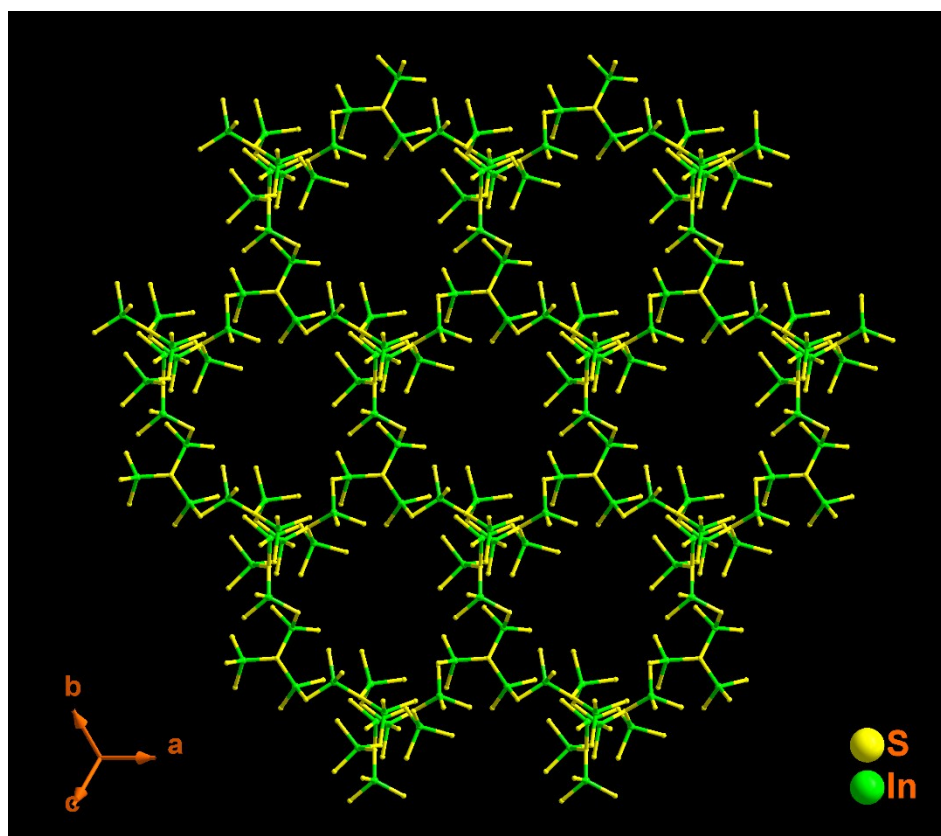


Fig. S3 View of the 3D anionic framework of compound **1** along the [1 1 1] projection dislodging “decorative” Ge atoms.

3. Experimental section

All chemicals were analytical grade and used as received without further purification.

3.1 Synthesis of compound 1

Typical synthesis of compound **1**: InCl₃ (2 mmol, 442.4 mg), Ge (0.5 mmol, 36.32 mg), S (3 mmol, 96.2 mg) and *cis*-2,6-dimethylmorpholine (DMMP, 2.5 mL) were mixed together in a 23 ml Teflon-lined stainless steel autoclave. The mixture was stirred for 15 min and then the autoclave was heated at 200 °C for 7 days without being disturbed. After cooling to room temperature very slowly, pale-yellow diamond crystals were collected by hand, washed with ethanol, and dried in air (yield 25%, based on Ge). Calcd: C, 14.83; H, 3.06; N, 2.88. Found: C, 14.52; H, 3.30; N, 2.93. FT-IR (cm⁻¹): 3382 (m), 3220 (w), 2933 (m), 2859 (w), 2756 (m), 1568 (s), 1452 (s), 1379 (s), 1321 (m), 1176 (s), 1101 (s), 1031(s), 958 (s), 862 (s), 588 (m).

3.2 Details of the structure refinement

All framework atoms were unambiguously determined, semi-quantitative energy dispersive X-ray (EDS) analysis confirms the presence of all constituent heavy elements in compound **1** and a quantitative mole ratio of 1.000/2.010/5.687 for Ge/In/S is given by Inductively Coupled Plasma Optical Emission Spectrometry analysis Spectrometry (ICP-OES). It is in good agreement with results from single-crystal structure refinement. Extra-framework guest molecules could not be located from Fourier maps owing to their disorder. The final guest molecules in molecular formula were calculated from TGA combined with elemental analysis data.

4. Physical measurements

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. Inductively Coupled Plasma Optical Emission Spectrometry analysis (ICP-OES) was performed on Thermo Scientific iCAP 6000 ICP spectrometer. CHN Analysis was obtained on Vario EL. The Fourier transform infrared (FT-IR) spectroscopy was recorded on a Perkin-Elmer FT-IR spectrophotometer in the range 4000-400 cm^{-1} . Powder X-ray diffraction (PXRD) measurement was performed on a Bruker D8 Focus diffractometer with Cu- $K\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$) and a Lynx Eye detector with the operating angle 2θ ranging from 5° to 40° at 298 K. Thermogravimetric analysis (TGA) was conducted on a Pyris Diamond thermal analyzer under a flowing nitrogen atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$ in the range of $25\text{-}800^\circ\text{C}$. Optical diffuse reflectance spectrum was measured at room temperature on a Hitachi U-4100 UV/Vis spectrophotometer using BaSO_4 powder as standard (100% reflectance). The absorption data was calculated from the reflectance using the Kubelka-Munk [4] function.

4.1 The energy dispersive X-ray spectroscopy (EDS)

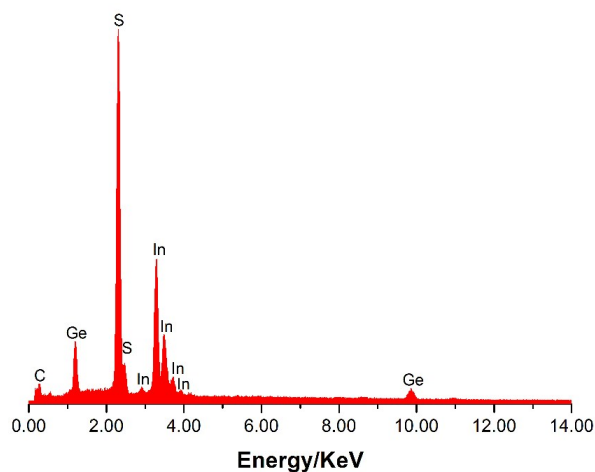


Fig. S4 The energy dispersive X-ray spectra of **1**.

4.2 Powder X-ray diffraction (PXRD) pattern

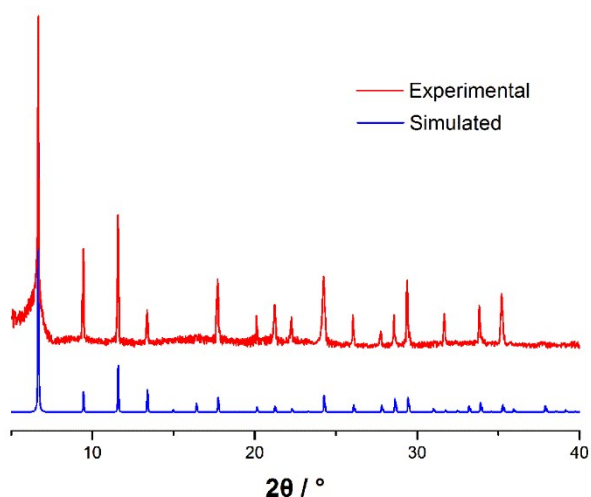


Fig. S5 The PXRD pattern of **1** (top) is comparable with its simulated from the single crystal X-ray data (bottom).

4.3 Thermal Analysis

The thermal stability of compound **1** was determined by TGA under a nitrogen atmosphere. As the TG curve exhibited in Figure S6, the initial weight loss of ca. 1.29% could be attributed to loss of water molecules. On further heating, another abrupt weight loss of 23.58% occurs between 247-382°C, which could be correspond to the decomposition of the charge-balancing organic molecules. Then the following third gradual weight loss may account for the collapse of framework together with the removal of partial sulfur atoms.

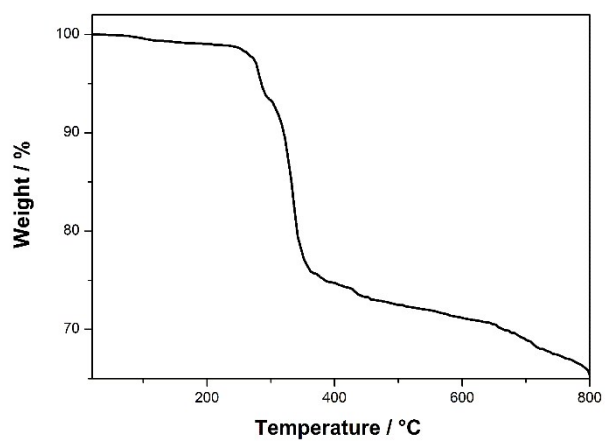


Fig. S6 TGA curve of **1** under N₂ atmosphere.

4.4 Solid-state UV/Vis spectroscopy

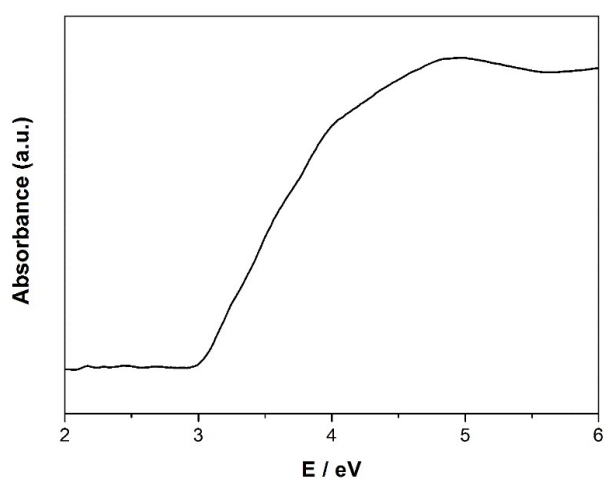


Fig. S7 Solid-state optical absorption spectra of **1**.

Reference

- [1] (a) G. M. Sheldrick, *SHELXS97*, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXS97*, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1997; (c) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, **64**, 112.
- [2] (a) L. Wang, T. Wu, F. Zuo, X. Zhao, X. Bu, J. Wu and P. Feng, *J. Am. Chem. Soc.*, 2010, **132**, 3283; (b) C. Wang, X. Bu, Na. Zheng and P. Feng, *Chem. Commun.*, 2002, 1344.
- [3] A. L. Spek, *Acta Crystallogr. Sect. D*, 2009, **65**, 148.
- [4] W. W. Wendlandt and H. G. Hecht, *Reflectance Spectroscopy*, Interscience Publishers, New York, 1966.