Synthesis and characterization of (H$_2$dab)$_2$Cu$_8$Ge$_4$S$_{14}$·2H$_2$O: An expanded framework based on icosahedral Cu$_8$S$_{12}$ cluster

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ABSTRACT

A new three-dimensional framework copper-thiogermanate, (H$_2$dab)$_2$Cu$_8$Ge$_4$S$_{14}$·2H$_2$O (**1**), was prepared under solvothermal condition and characterized by elemental analysis, single-crystal and powder X-ray diffraction, thermogravimetric analysis and UV–vis diffuse reflectance spectroscopy. Compound **1** crystallizes in the monoclinic space group $P2(1)/c$, $a=11.444(4)$ Å, $b=12.984(4)$ Å, $c=12.455(6)$ Å, $\beta=91.527(1)°$, $V=1850.2(3)$ Å^3, $Z=2$. It contains a new three-dimensional Cu–Ge–S framework constructed from icosahedral [Cu$_8$S$_{12}$]$^{16-}$ clusters linked by [GeS$_4$]$^{4-}$ and dimeric [Ge$_2$S$_6$]$^{4-}$ units, with diprotonated 1,4-dab (1,4-diaminobutane) and H$_2$O molecules located in the intersecting channels. UV–vis reflectance spectroscopy reveals the band gap of compound **1** is 2.5 eV.

1. Introduction

Microporous metal chalcogenides and chalcogenometallates are promising multifunctional materials because they are capable of integrating porosity with semiconductivity and find potential applications in fast-ion conductivity, selective ion exchange and efficient visible-light photocatalysis [1–8].

Recently, one promising approach for construction of porous chalcogenides is assembly of large chalcogenides clusters or building units into three-dimensional (3-D) framework [9–13]. Considerable efforts have been devoted to the synthesis of 3-D framework chalcogenides from large tetrahedral clusters, such as T$_n$, P$_n$ and C$_n$ series clusters [9–30]. These tetrahedral clusters with various sizes and tunable components can decorate 4-connected sites to form diamond topology or zeolite-type frameworks with large cavities and channels. For example, ASU-31 has a sodalite net decorated by T$_3$ unit, and contains cavities up to 25.6 Å in diameter [20]. However, relatively less progress has been made in other cluster and framework types [31–40]. Transition metal M^I(M=Cu, Ag) ions are readily incorporated into the inorganic chalcogenide framework, and possess diverse coordination modes (2, 3, 4) with chalcogen Q^{2-}(Q=S, Se) anions [41–58]. Interestingly, corner or edge-sharing linkage between these primary $M^I Q_x$ units can form novel M–Q secondary building units (SBUs) to construct polynary framework in high M^I-

containing chalcogenometallates [50–58]. Among these SBUs, the high symmetrical Cu–S clusters, such as icosahedral [Cu$_8$S$_{12}$]$^{16-}$ [53–55,57], [Cu$_8$S$_{13}$]$^{17-}$ [50] and hetereometallic [Cu$_7$SnS$_{12}$]$^{15-}$ clusters [57], are of particular interest due to their octahedral connectivity. In contrast to large tetrahedral clusters, these Cu–S clusters can decorate 6-connected sites and may be employed as octahedral SBUs to design new porous chalcogenides [50,53–55,57]. In this paper, we report the synthesis, crystal structure and optical property of a new 3-D framework copper-thiogermanate, (H$_2$dab)$_2$Cu$_8$Ge$_4$S$_{14}$·2H$_2$O, built up from icosahedral [Cu$_8$S$_{12}$]$^{16-}$ clusters interconnected with [GeS$_4$]$^{4-}$ and dimeric [Ge$_2$S$_6$]$^{4-}$ units.

2. Materials and methods

2.1. Materials and physical measurements

All reagents were purchased from commercial sources and were used without further purification. Energy dispersive spectroscopy (EDS) was made on a JEOL JSM-5600LV scanning electronic microscope. Elemental analysis (C, H, N and S) was carried out on a Vario EL III elemental analyzer. Thermogravimetric analysis (TGA) of the compound **1** was carried out using Mettler Toledo Star under a flow of nitrogen (40 mL/min) from 25 to 550 °C at heating rate of 10 °C/min. Powder X-ray diffraction (XRD) data were obtained using a Shimadzu XRD-6000 diffractometer with CuKα radiation (λ=1.5418 Å). The data were collected at room temperature with a step size of 0.02° and the

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operating power was 40 kV/20 mA. The UV–vis spectra were measured at room temperature using JASCO V-570UV/VIS/NIR double-beam, double monochromator spectrophotometer, and wavelength range from 200 nm to 800 nm.

2.2. Synthesis of $(H_2dab)_2Cu_8Ge_4S_{14} \cdot 2H_2O$ (1)

Cu powder (0.047 mmol, 3.0 mg), GeO_2 powder (0.067 mmol, 7.0 mg) and S (1.03 mmol, 33 mg) were placed into a Pyrex-glass tube (about 10 ml in volume), then about 280 mg 1,4-diaminobutane and 200 mg $CH_3OH:H_2O$ ($V_{CH_3OH} : V_{H_2O} = 1 : 1$) were added as solvent. After the mixture being stirred thoroughly, the glass tube was sealed (reagents filled about 10% volume of the tube) under air atmosphere, placed in a stainless-steel autoclave, into which water as a media for heat transferring was added to 80% filling, and heated at 165 °C for 7 days, and then cooled to room temperature naturally. The products were washed with ethylenediamine and ethanol several times, respectively. Pale yellow block crystals were obtained in 62% yield (5.3 mg) based on Cu. Addition of small amount of Li_2CO_3 (7.0 mg) can promote growth of large crystals. EDS analysis on several crystals gave an average composition of $Cu_{8.1}Ge_{3.9}S_{14.0}$. Elemental analysis (%) calc. for **1** ($C_8H_{32}O_2N_4Cu_8Ge_4S_{14}$): C, 6.56; H, 2.19; N, 3.83; S, 30.63. Found: C, 6.80; H, 2.20; N, 3.80; S, 30.52.

2.3. Crystallographic studies

A suitable single crystal of **1** with the dimensions of about $0.15 \times 0.15 \times 0.15$ mm³ was carefully selected under an optical microscope and glued to thin glass fiber with epoxy resin. The intensities of the crystal data were collected on Bruker Smart APEX II diffractometer equipped with graphite monochromitized MoKα radiation ($\lambda = 0.71073$ Å) at room temperature. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 [59]. All non-hydrogen atomic positions were located in Fourier maps and refined anisotropically based on F^2 using SHELXL-97 [60]. SIMU restraint was used to rationalize the thermal ellipsoids of adjacent C(2) and C(1) atoms. The hydrogen atoms of organic amine were positioned with idealized geometry and refined isotropically, while the hydrogen atoms of water molecule were not added in the model, which were also taken into considerations when calculating the cell contents. Crystallographic data are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2 (Supporting Information). Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre with CCDC no. 805465. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the monoclinic space group $P2(1)/c$ and contains a unique 3-D anionic framework, $[Cu_8Ge_4S_{14}]^{4-}$, with H_2dab^{2+} and H_2O molecules located in the channels. As depicted in Fig. 1, the asymmetric unit of **1** consists of four crystallographically independent Cu^+ ions, two Ge^{4+} ions, seven S^{2-} ions, one H_2O and one 1,4-dab molecule. Each Cu^+ ion adopts planar trigonal geometry and coordinates to three S^{2-} ions with the Cu–S bond length ranging from 2.252(4) to 2.297(4) Å and the S–Cu–S angle between 112.1(2)° and 126.7(9)°, each Ge^{4+} ion is tetrahedrally coordinated by four S^{2-} ions with the Ge–S bond length ranging from 2.198(4) to 2.275(4) Å and the S–Ge–S angle between 94.4(2)° and 115.2(2)°. These geometric

Table 1
Crystallographic data of **1**.

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Formula	$C_8H_{32}Cu_8Ge_4N_4O_2S_{14}$
Formula weight	1463.90
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions	$a = 11.444(4)$ Å
	$b = 12.984(4)$ Å
	$c = 12.455(6)$ Å
	$\beta = 91.527(1)°$
Volume	1850.2(3) Å³
Z	2
Calculated density	2.628 Mg m⁻³
Absorption coefficient	8.501 mm⁻¹
$F(0\,0\,0)$	1416
θ range for data collection	2.27–25.00
Limiting indices	$-12 \le h \le 13, -13 \le k \le 15, -14 \le l \le 14$
Reflections numbers	8360
Unique data	3225
Observed data ($I > 3\sigma(I)$)	1882
Largest diff. peak and hole	$-2.043/2.242$ e Å⁻³
Goodness-of-fit on F^2	1.014
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0870$, w$R_2 = 0.2083$
R indices (all data)	$R_1 = 0.1354$, w$R_2 = 0.2254$
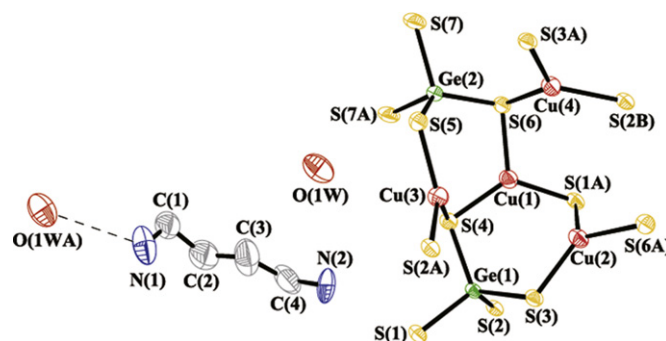
Fig. 1. Thermal ellipsoid plot (50% probability) and atomic labeling scheme for the asymmetric unit of **1**. Atom labels with "A" or "B" refer to symmetry-generated atoms. Hydrogen atoms of the 1,4-diaminobutane are omitted for clarity.

parameters are in good agreement with reported values [53–55,57,61–67]. Sulfide ions show two different bridging modes: μ_3 and μ_2. Each μ_3-S^{2-}(S(1)–S(6)) bridges one Ge^{4+} and two Cu^+ ions, and each μ_2-S^{2-}(S(7)) bridges two Ge^{4+} ions.

The SBU of the 3-D framework is a $[Cu_8S_{12}]^{16-}$ cluster, which consists of a cubic array of 8 Cu^+ ions bridged by S^{2-} ions, and has an icosahedral shape defined by the 12 bridging S^{2-} ions (Fig. 2). Such a cluster is comparable to icosahedral $[Cu_8S_{12}]^{16-}$ clusters found in recently reported high copper-containing thiometallates [53–55,57], except having lower symmetry C_i. It adopts octahedral coordination geometry with adjacent six Ge^{4+} ions, and displays octahedral connectivity in the framework, as shown in Fig. 2. Similar SBUs such as $[Cu_8S_{13}]^{17-}$ [50], $[Cu_7SnS_{12}]^{15-}$ clusters [57], closely related In_4S^{10+} and Ga_4S^{10+} building units also show octahedral connectivity [34,68].

To form 3-D framework, the icosahedral $[Cu_8S_{12}]^{16-}$ clusters serving as octahedral nodes are linked together in six directions via two types of Ge–S units: mononuclear $[GeS_4]^{4-}$ units along the [0 1 1], [0 –1 1], [0 1 –1] and [0 –1 –1] directions (Fig. 3), and dimeric $[Ge_2S_6]^{4-}$ units, each of which is constructed by edge-sharing of two GeS$_4$ tetrahedra, along [1 0 0] and [–1 0 0] directions (Fig. 4). The extended Cu–Ge–S framework exhibits 3-D intersecting channels, in which 1,4-dab (1,4-diaminobutane) and H_2O molecules are located. To balance the negative charge of the framework, the 1,4-dab molecules are diprotonated. However, the
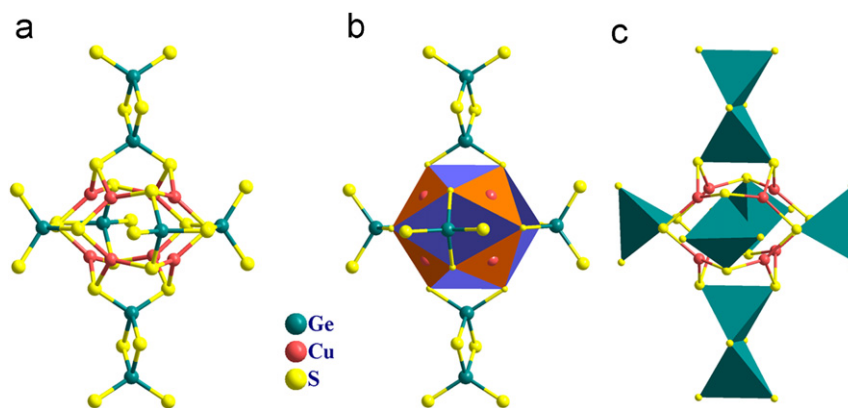
Fig. 2. Icosahedral $[Cu_8S_{12}]^{16-}$ cluster and its octahedral connection with monomeric $[GeS_4]^{4-}$ and dimeric $[Ge_2S_6]^{4-}$ units by sharing common S atoms: (a) ball and stick modes; (b) polyhedral mode of the icosahedral $[Cu_8S_{12}]^{16-}$ cluster; and (c) polyhedral mode of monomeric $[GeS_4]^{4-}$ and dimeric $[Ge_2S_6]^{4-}$ units.
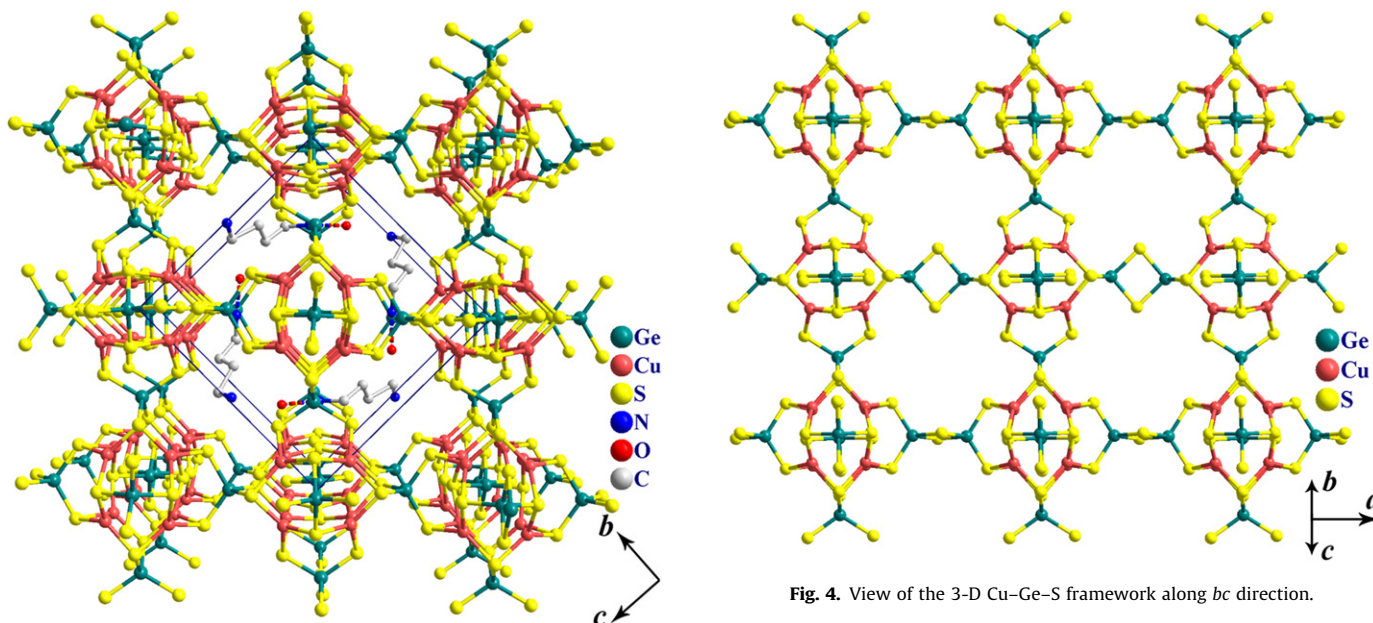

Fig. 3. View of the 3-D Cu–Ge–S framework along a direction.

Fig. 4. View of the 3-D Cu–Ge–S framework along bc direction.

molecule geometry of 1,4-dab is seriously distorted arising from the rotation of C(1)–C(2) bond with the torsion angle of 70.5° between C(3)–C(2) and C(1)–N(1) bonds. The short intermolecular N⋯O contact (2.950 Å) (Fig. 1) suggests obvious hydrogen bond interactions existing between each diprotonated 1,4-dab and its adjacent H_2O molecule. The solvent-accessible volume excluding the diprotonated 1,4-dab cations and H_2O molecules is 45.6%, as calculated with the program PLATON [69].

Interestingly, compound **1** is a expanded structure of our recently reported $A_4Cu_8Ge_3S_{12}$ (A=K$^+$ or Rb$^+$) [55]. The latter contains a 3D copper-rich framework built up from icosahedral $[Cu_8S_{12}]^{16-}$ clusters linked by mononuclear $[GeS_4]^{4-}$ units in six directions, with alkaline metal cations located in the cavities. While in compound **1**, the framework is expanded due to the long links of dimeric $[Ge_2S_6]^{4-}$ units in two of the six directions. It is worth noting that the expansion of a framework is rarely realized in construction of porous chalcogenides [31,37,70], though that is very common in MOFs and porous coordination polymers [71–74]. Since the framework is expanded, the solvent-accessible volume of a unit cell excluding extra-framework species increases from 36% to 45.6%. In comparison to $A_4Cu_8Ge_3S_{12}$, in which four K$^+$ or Rb$^+$ ions are statistically distributed over six equivalent positions in each cavity, **1** contains long chain organic amines 1,4-dab and solvent H_2O in the relatively large cavities and

channels. Additionally, compound **1** is structurally related to $[Cu_8Ge_5S_{16}] \cdot x$(solvent) [53], recently reported by Feng et al. 3-D $[Cu_8Ge_5S_{16}]^{4-}$ framework is also built up from icosahedral $[Cu_8S_{12}]^{16-}$ clusters interconnected with mixed Ge–S units, but contains a more expanded framework than framework of **1**, because the icosahedral $[Cu_8S_{12}]^{16-}$ clusters are linked by mononuclear $[GeS_4]^{4-}$ units in two directions, and dimeric $[Ge_2S_6]^{4-}$ units in rest four directions. In these structures, icosahedral $[Cu_8S_{12}]^{16-}$ clusters serve as invariable octahedral nodes, and exhibit flexible linkage with different Ge–S units either monomer $[GeS_4]^{4-}$ or dimeric $[Ge_2S_6]^{4-}$. This phenomenon confirms the good integrity of the icosahedral $[Cu_8S_{12}]^{16-}$ cluster and its variety in linkage [55]. Particularly, these three Cu–Ge–S frameworks reveal an interesting trend that the framework can preserve the same topology, while be gradually expanded with increasing length of the bridging units by controlling the condensation degree of tetrahedral GeS$_4$ units [53,55]. It also shows a promise that the framework can be expanded further if the $[Cu_8S_{12}]^{16-}$ clusters could copolymerize with dimeric $[M_2^{IV}S_6]^{4-}$ units [66] in six directions or longer bridging units, such as $[M_3^{IV}S_8]^{4-}$ [75], under specific conditions.

Thermogravimetric analysis of Compound **1** reveals two steps of weight loss (Fig. S2). The first weight loss 2.8% between room temperature and 140 °C is corresponding to the removal of the H_2O molecule (2.5%) residing in the channels. The second weight loss 16.2% is in good agreement of the removal of 1,4-diaminobutane and
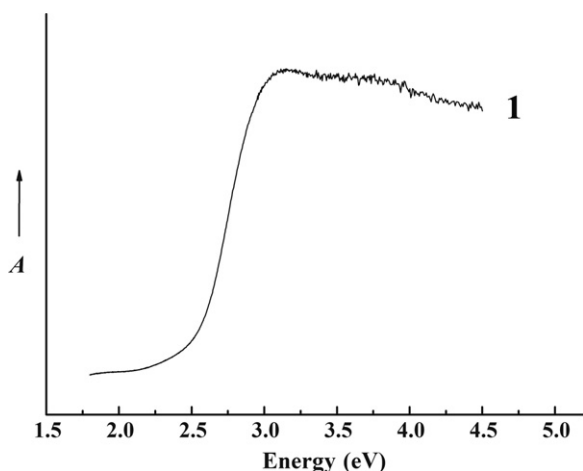
Fig. 5. UV–visible spectrum of the compound **1**.

H_2S (16.7%). The products are free of organic component and show formation of Cu_2GeS_3, as identified by powder XRD data. UV–vis reflectance spectrum of compound **1** (Fig. 5) reveals that **1** is a semiconductor with the band gap of 2.5 eV. This value is slightly larger than that of $K_4Cu_8Ge_3S_{12}$ and $Rb_4Cu_8Ge_3S_{12}$ [55], while is comparable to $[Cu_8Ge_5S_{16}] \cdot x$(solvent) which shows efficient visible-light photovoltaic activity [53].

4. Conclusions

In summary, we have synthesized a new 3-D Cu–Ge–S framework copper-thiogermanate based on icosahedral $[Cu_8S_{12}]^{16-}$ cluster, whereas possesses an expanded framework of $[Cu_8Ge_3S_{12}]^{4-}$ due to the incorporation of dimeric $[Ge_2S_6]^{4-}$ units as long links in two of the six directions. Particularly, the icosahedral $[Cu_8S_{12}]^{16-}$ clusters serving as stable octahedral SBUs can bear some extent distortion for flexible linkage with different Ge–S units, this provides a new strategy to expand octahedral SBUs-based frameworks by increasing the length of bridging units via tuning the condensation degree of tetrahedral $M^{IV}S_4$ units.

Supporting Information available

Crystallographic data (CIF), selected bond lengths and angles, powder XRD patterns and TGA curve are provided as supplementary materials. This material is available free of charge via the Internet at http://pubs.

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.11.030.

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