

pH-induced solvothermal synthesis and characterization of two novel thioarsenate compounds: three-dimensional $(1,2\text{-pdaH}_2)_{0.5}\text{As}_5\text{S}_8$ containing $\psi\text{-As(III)S}_4$ and two-dimensional $(\text{NH}_4)_2\text{As}_8\text{S}_{13}$

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1. Synthesis

The optimal reaction for **1** is described as follows. A mixture of As_4S_4 powder (0.107g, 0.25 mmol), S powder (0.096 g, 3 mmol), NH_4Cl powder (0.080 g, 1.5 mmol), 0.2 mL 1,2-pda and 6 mL CH_3OH was sealed in a stainless steel reactor with a 28 mL Teflon liner and kept at 150 °C for 6 days, and then cooled to room temperature. Brown octahedral crystals of **1** along with yellow powder were obtained by filtration and washed with ethanol and air-dried. The crystals were selected by hand (stable in the air) in 37% yield (0.245 g) based on As_4S_4 . Anal. Calcd. for **1**: C 2.69%, H 0.90%, N 2.09%; found: C 2.68%, H 0.62%, N 2.16%.

The optimal reaction for synthesizing **2** was similar to that for **1**. The only difference is that the NH_4Cl for **1** was replaced by the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ for **2**. Black sheet-like crystals of **2** along with yellow powder were obtained by filtration and washed with ethanol and air-dried. The crystals were selected by hand (stable in the air) in 21% yield (0.224 g) based on As_4S_4 . Anal. Calcd. for **2**: C 0, H 0.77%, N 2.66%; found: C <0.3%, H 0.77%, N 2.66%.

2. More structural details

The intensity data were collected on a Rigaku Saturn 724 CCD diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 123 K. An empirical absorption correction was applied using the multiscan method. The structure was solved by direct methods and refined by full-matrix least-squares cycles in SHELX-97.¹ The 1,2-pdaH₂ cation in **1** is highly disordered over symmetrically related positions therefore the site occupancies of the N, C, and H

atoms were set to be 0.25, corresponding to quarter of a 1,2-pdaH₂ cation per asymmetry unit. The empirical formulae for **1** and **2** were confirmed by thermogravimetric analyses and elemental analyses. Selected hydrogen-bonding data of **1** and **2** are listed in Tables S1 and S2, respectively..

Table S1. Selected hydrogen bond data for compound **1**.

D-H...A	<i>d</i> (D-H) (Å)	<i>d</i> (H...A) (Å)	<i>d</i> (D...A) (Å)	D-H...A (°)
N(1)-H(1A)...S(4)	0.90	2.44	3.19(3)	141.2
N(1)-H(1A)...S(2)#3	0.90	2.86	3.57(2)	136.5
N(1)-H(1B)...S(1)#3	0.90	2.38	3.11(2)	138.2
N(2)-H(2A)...S(1)#10	0.90	2.49	3.341(9)	158.2
N(2)-H(2B)...S(4)#8	0.90	2.71	3.320(2)	126.5
N(2)-H(2C)...S(4)#7	0.90	2.57	3.320(2)	140.7

Symmetry transformations used to generate equivalent atoms: #1 $x+1/4, y+1/4, -z+1$; #2 $-x+1/4, -y+5/4, z$; #3 $x-1/4, -y+1, z-1/4$; #4 $-x+1/2, y+1/4, z-1/4$; #5 $x+1/4, -y+1, z+1/4$; #6 $x-1/4, y-1/4, -z+1$; #7 $-x+3/4, -y+3/4, z$; #8 $-x+3/4, y, -z+3/4$; #9 $x, -y+3/4, -z+3/4$; #10 $-x+1, y-1/4, z-1/4$.

Table S2. Selected hydrogen bond data for compound **2**.

D-H...A	<i>d</i> (D-H) (Å)	<i>d</i> (H...A) (Å)	<i>d</i> (D...A) (Å)	D-H...A (°)
N(1)-H(1)...S(13)	0.89	2.46	3.300(7)	157.9
N(1)-H(2)...S(2)#5	0.89	2.79	3.675(7)	171.2
N(1)-H(3)...S(9)#6	0.89	2.96	3.678(6)	138.9
N(1)-H(4)...S(6)#5	0.89	2.86	3.394(6)	119.7
N(1)-H(4)...S(11)#7	0.89	2.93	3.742(6)	153.0
N(1)-H(4)...S(4)#5	0.89	3.01	3.573(7)	123.3
N(2)-H(5)...S(6)#4	0.89	2.64	3.391(7)	143.4
N(2)-H(5)...S(7)#6	0.89	2.93	3.545(8)	127.3
N(2)-H(6)...S(8)#8	0.89	2.96	3.518(7)	122.1
N(2)-H(7)...S(8)	0.89	2.60	3.449(7)	160.3
N(2)-H(8)...S(3)	0.89	2.65	3.534(8)	171.9

Symmetry transformations used to generate equivalent atoms: #1 $x, -y, z+1/2$; #2 $x, y+1, z$; #3 $x, y-1, z$; #4 $x, -y, z-1/2$; #5 $x-1/2, y+1/2, -z+1/2$; #6 $-x+1, y, -z+1/2$; #7 $-x+1, -y+1, -z$; #8 $-x+3/2, y-1/2, z$.

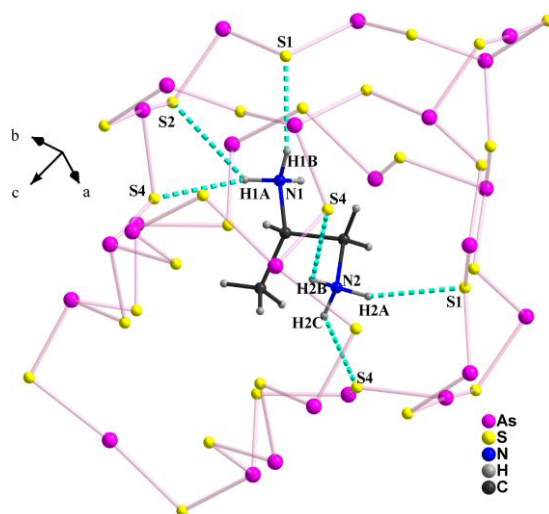


Fig. S1 A fragment of **1** showing the H-bonds between the cation and anionic 3D framework.

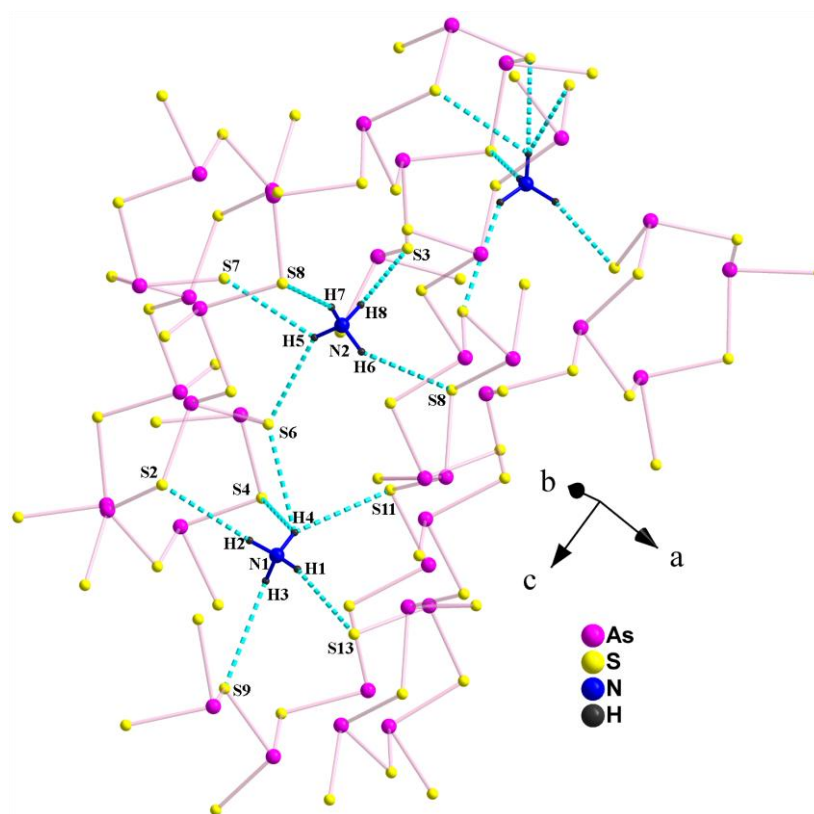


Fig. S2 A fragment of **2** showing the H-bonding between the cations and anionic layers.

3. Physical measurements

All chemicals were used as purchased without further purification. Element analyses of C, H and N were performed on a German Elementar Vario EL III instrument. The infrared spectrum was taken on a Magna 750 FTIR spectrometer with sample as KBr pellet in the range of 4000-400 cm^{-1} . Powder X-ray diffraction (PXRD) patterns were recorded on a Miniflex II diffractometer at 30 kV and 15 mA using $\text{CuK}\alpha$ (1.54178 Å), with a scan speed of 1°/min at room temperature. The simulated PXRD pattern from single crystal data was produced using the PowderCell program. Simultaneous thermoanalysis (TG–DSC) was carried out with a NETZSCH STA449C unit, at a heating rate of 5 °C/min under a nitrogen atmosphere. Optical diffuse reflectance spectrum was measured at room temperature with a Perkin-Elmer Lambda 900 UV/Vis spectrophotometer by using BaSO_4 powder as 100% reflectance and the room-temperature optical absorption spectrum of the title compound was obtained from diffuse reflectance experiment.²

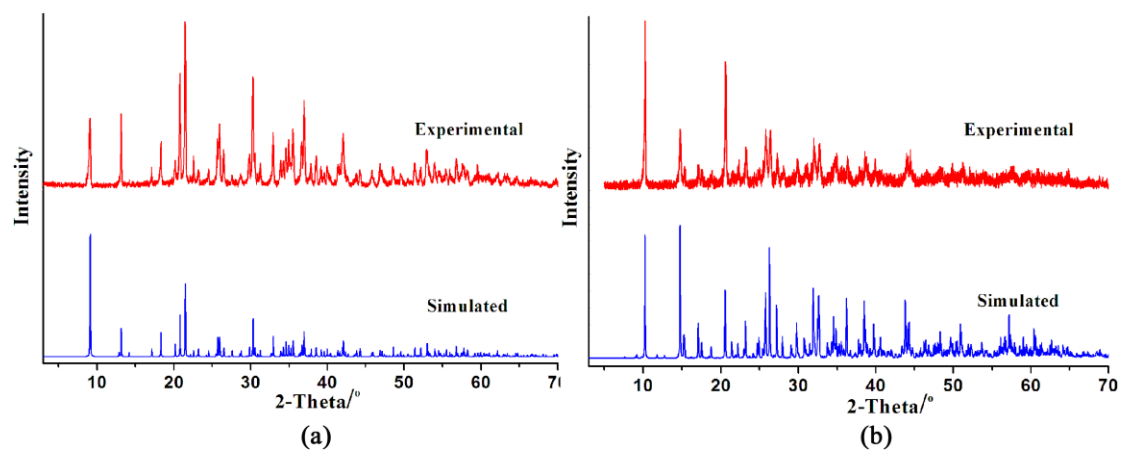


Figure S3 The PXRD patterns (red) are in good agreement with the simulated PXRD patterns (blue) for compounds **1** (a) and **2** (b).

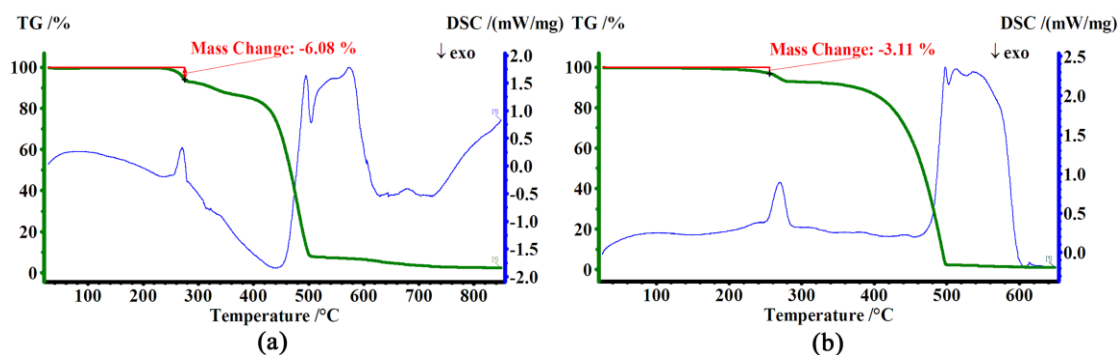


Figure S4 DSC-TG curves for compounds **1** (a) and **2** (b).

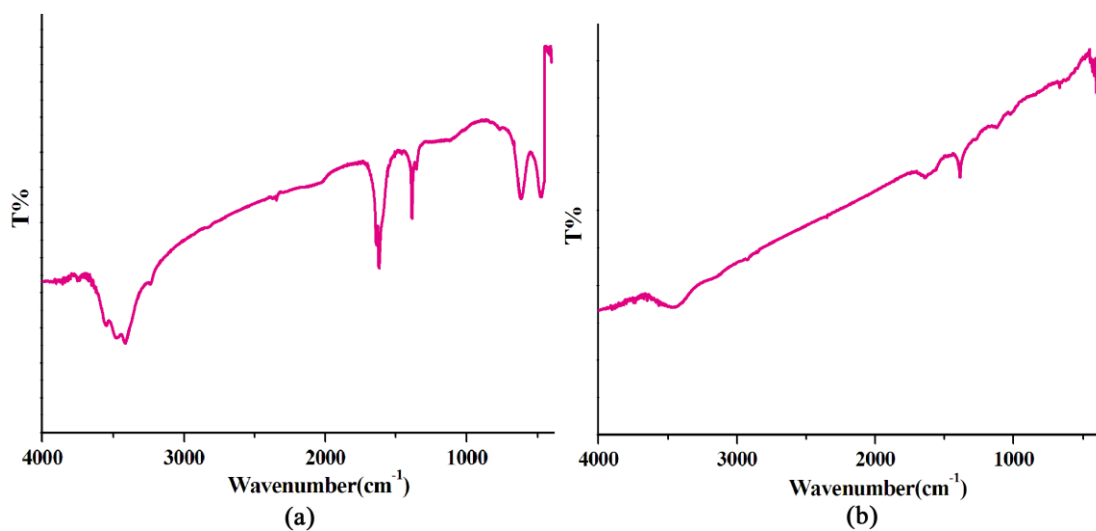


Figure S5 IR spectra of compounds **1** (a) and **2** (b).

References

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2. (a) Li, J.; Chen, Z.; Wang, X.-X.; Proserpio, D. M. *J. Alloy. Compd.* 1997, **262**, 28-33; (b) Wendlandt, W. W.; Hecht, H. G., *Reflectance spectroscopy*. Interscience Publishers: New York, 1966.