

(enH₂)_{4.5}[In(As^VS₄)₃][As₂^{III}(μ-S₂)S₃]Cl and (enH₂)MnAs^{III}As^VS₆: Two thioarsenates(III, V) with mixed-valent optical properties

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1. Synthesis

Compound **1** was obtained from a mixture of In (0.116 g, 1.01 mmol), As₂S₃ (0.248 g, 1.00 mmol), S (0.099 g, 3.09 mmol), and NH₄Cl (0.080 g, 1.50 mmol), 0.2 mL ethanediamine, and 6 mL CH₃OH, which was sealed in a stainless steel reactor with a 20 mL Teflon liner and heated to 150 °C within 4h. After 6d at 150 °C, the reactor was cooled down to room temperature at the rate of 1 °C/h. The product consisted of dark green crystals of **1** and a small amount of yellow powder after washed by ethanol and ether. The crystals were selected by hand (stable in the air) in 16.3% yield based on S (0.040 g). Elemental analysis, calcd. (%) of **1**: C 8.01, H 3.36, N 9.34; found: C 8.12, H 3.37, N 9.25.

Compound **2** was obtained from a mixture of LaCl₃·7H₂O (0.182 g, 0.49 mmol), As₂S₂ (0.106 g, 0.50 mmol), S (0.081 g, 2.53 mmol), Mn (0.063 g, 1.14 mmol) and NH₄Cl (0.047 g, 0.88 mmol), 0.1 mL ethanediamine, and 3 mL H₂O, which was sealed in a stainless steel reactor with a 28 mL Teflon liner and heated to 130 °C within 2h. After 3.5d at 130 °C, the reactor was cooled down to room temperature at the rate of 2 °C/h. The product consisted of dark red crystals of **2** and a small amount of black powder after washed by ethanol and ether. The crystals were selected by hand (stable in the air) in 20.9% yield based on As₂S₂ (0.048 g). Elemental analysis, calcd. (%) of **2**: C 5.23, H 2.19, N 6.10; found: C 5.35, H 2.28, N 6.07. Although the LaCl₃·7H₂O hasn't entered the crystal structure, it was essential for the synthesis of compound **2**, as we could not obtain the

compound **2** in the absence of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$. Since $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ is a Lewis acid, it may influence the pH of the reaction system which is the key to synthesizing thioarsenates.¹

2. Crystal Structure

The intensity data were collected on an Oxford Xcalibur Eos CCD diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The data were corrected for Lorentz and Polarization effects as well as for absorption. The structure was solved by direct methods and refined by full-matrix least-squares cycles in SHELX-97 and SHELX 2013.² The empirical formulae were confirmed by thermogravimetric analyses (TGA) and element analyses (EA) results. Selected hydrogen-bonding data of compound **1** and **2** are listed in Table S1 and Table S2, respectively.

CCDC-958717 and 958716 contain the supplementary crystallographic data of the crystals **1** and **2**, respectively. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK.

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

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	<(DHA)
N(1)–H(1C)...S(11)#2	0.89	2.30	3.174(4)	165.9
N(1)–H(1D)...Cl(1)	0.89	2.27	3.151(4)	171.2
N(1)–H(1E)...S(17)#3	0.89	2.57	3.273(4)	136.2
N(2)–H(2C)...S(17)#4	0.89	2.38	3.252(4)	165.0
N(2)–H(2D)...S(8)#2	0.89	2.39	3.215(4)	154.5
N(2)–H(2E)...S(7)#5	0.89	2.49	3.347(4)	161.2
C(1)–H(1B)...S(7)#5	0.97	2.82	3.657(4)	144.8
N(3)–H(3C)...Cl(1)	0.89	2.29	3.162(4)	166.6
N(3)–H(3D)...S(4)#6	0.89	2.59	3.400(4)	152.0
N(3)–H(3E)...S(16)	0.89	2.41	3.295(4)	172.6
N(4)–H(4C)...S(3)	0.89	2.67	3.341(4)	133.2
N(4)–H(4D)...S(12)#2	0.89	2.41	3.247(4)	156.4
N(4)–H(4E)...S(16)	0.89	2.40	3.270(4)	165.3
N(5)–H(5C)...Cl(1)#2	0.89	2.23	3.115(4)	170.6
N(5)–H(5D)...S(5)	0.89	2.70	3.338(4)	129.4
N(5)–H(5D)...S(16)#2	0.89	2.75	3.389(4)	130.3
N(5)–H(5E)...S(8)	0.89	2.34	3.214(3)	168.4
N(6)–H(6C)...S(2)#7	0.89	2.55	3.252(4)	136.4
N(6)–H(6D)...S(7)#7	0.89	2.31	3.181(4)	166.2
N(6)–H(6E)...Cl(1)#8	0.89	2.23	3.113(4)	169.8
C(5)–H(5A)...S(14)#2	0.97	2.87	3.782(4)	157.4
N(7)–H(7C)...S(1)	0.89	2.71	3.519(3)	151.1
N(7)–H(7D)...S(12)	0.89	2.50	3.282(4)	146.3
N(7)–H(7E)...S(11)#9	0.89	2.43	3.324(4)	177.9

N(8)–H(8C)...S(7)#10	0.89	2.77	3.403(4)	129.3
N(8)–H(8C)...S(8)#10	0.89	2.67	3.414(4)	141.4
N(8)–H(8D)...S(4)#2	0.89	2.51	3.367(4)	162.5
N(8)–H(8E)...S(16)	0.89	2.62	3.492(4)	165.4
N(9)–H(9C)...S(2)	0.89	2.85	3.504(4)	131.4
N(9)–H(9C)...S(3)	0.89	2.60	3.392(4)	148.4
N(9)–H(9D)...S(11)#9	0.89	2.59	3.296(3)	137.2
N(9)–H(9D)...S(12)#9	0.89	2.72	3.449(4)	139.9
N(9)–H(9E)...S(17)#1	0.89	2.44	3.320(3)	170.9

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

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

D–H...A	$d(D-H)$	$d(H...A)$	$d(D...A)$	$\angle(DHA)$
N(1)–H(1C)...S(1)#4	0.89	2.84	3.388(7)	121.2
N(1)–H(1C)...S(3)#4	0.89	2.52	3.273(7)	142.1
N(1)–H(1D)...S(3)	0.89	2.46	3.330(7)	166.6
N(1)–H(1E)...S(6)#1	0.89	2.64	3.471(8)	156.6
N(2)–H(2C)...S(6)#5	0.89	2.81	3.489(8)	133.8
N(2)–H(2D)...S(3)	0.89	2.55	3.430(7)	171.4
N(2)–H(2E)...S(3)#6	0.89	2.46	3.231(7)	145.0
N(2)–H(2E)...S(4)#6	0.89	2.84	3.456(7)	128.1
C(2)–H(2B)...S(4)#7	0.97	2.80	3.723(9)	158.6

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

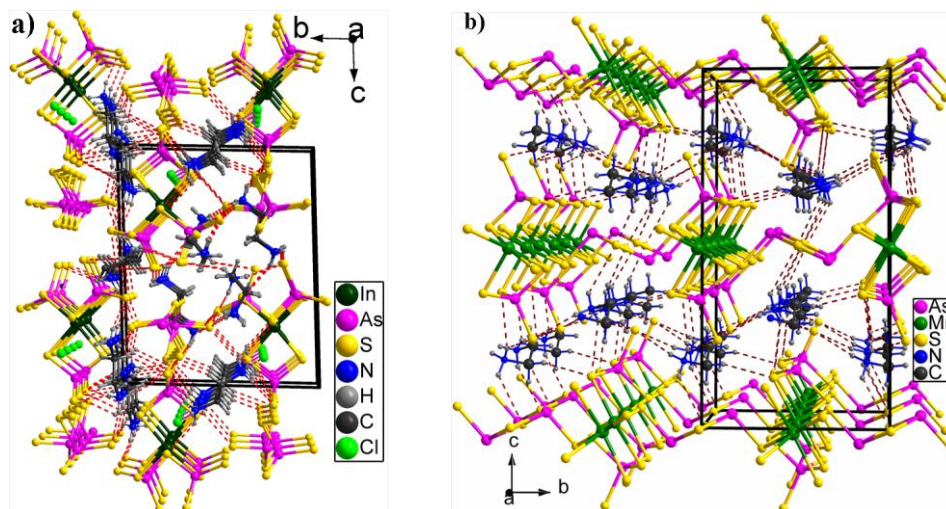


Figure S1. The H-bond networks of **1** (a) and **2** (b).

3. Theoretical Calculations

The density functional calculations were performed by the CASTEP package. The generalized gradient approximation (GGA) Perdew-Burke-Ernzerhof³ was used in calculating the total energy

and band structure. For **1**, a plane wave cut off energy of 300 eV was set. The DOS calculations were performed in a $2 \times 2 \times 1$ Monkhorst-Pack k-point grid within the Brillouin zone. The calculated band structure of **1** along high symmetry points (G(0,0,0), F(0,0.5,0), Q(0, 0.5,0), Z(0,0,0.5)), is plotted in Figure S2a. For **2**, a plane wave cut off energy of 280 eV was set. And we used a $3 \times 2 \times 1$ Monkhorst-Pack k-point grid within the Brillouin zone in the DOS calculations. The calculated band structure of **2** along high symmetry points (G(0,0,0), Y(0,0.5,0), Z(0,0,0.5), B(-0.5,0,0), D(-0.5,0,0.5), E(-0.5,0.5,0.5), C(0,0.5,0.5), A(-0.5, 0.5,0)), is plotted in Figure S2b. Because of the unpaired electrons of Mn 3d in the compound **2**, the spin polarized and LDA+U method with initial spin of 5 and $U = 2.5$ eV were employed.

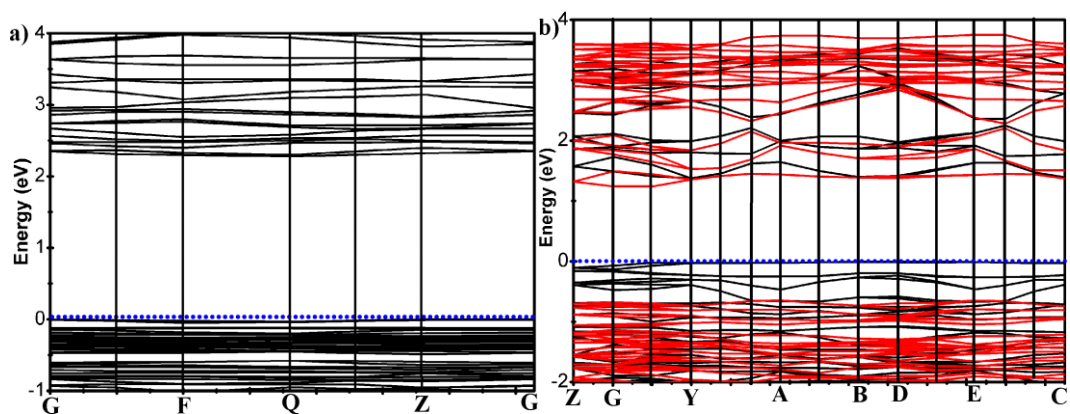


Figure S2. The band structures of **1** (a) and **2** (b). Fermi level is set at 0 eV(dot line). Black curve is spin up and red curve is spin down.

4. 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 $1^\circ/\text{min}$ 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 $5^\circ\text{C}/\text{min}$ under a nitrogen atmosphere.

Thermogravimetric analyses (TGA) for **1** (8.925 mg) and **2** (5.198 mg) were performed on the pure powder samples in a N_2 atmosphere. **1** had little weight loss until 145°C , and then decomposed with a weight loss of 75.68% from 145°C to 800°C gradually (Figure S4a). The In_2S_3

could be identified in the X-ray powder pattern of the residue (Figure S5a). Whereas **2** was stable up to 160 °C, and then decomposed with a weight loss of 78.91% from 160 °C to 800 °C gradually (Figure S4b). The X-ray powder pattern suggested the main component of the residue is MnS (Figure S5b).

Optical diffuse reflectance spectrum was measured at room temperature with a Perkin-Elmer Lambda 900 UV/Vis spectrophotometer by using BaSO₄ powder as 100% reflectance and the room-temperature optical absorption spectrum of the title compound was obtained from diffuse reflectance experiment.⁴ The variable-temperature magnetic susceptibilities (2~300k) were measured with a Quantum Design PPMS 6000 magnetometer under an applied field of 1000 Oe with the crystalline powder samples kept in a capsule for weighing.

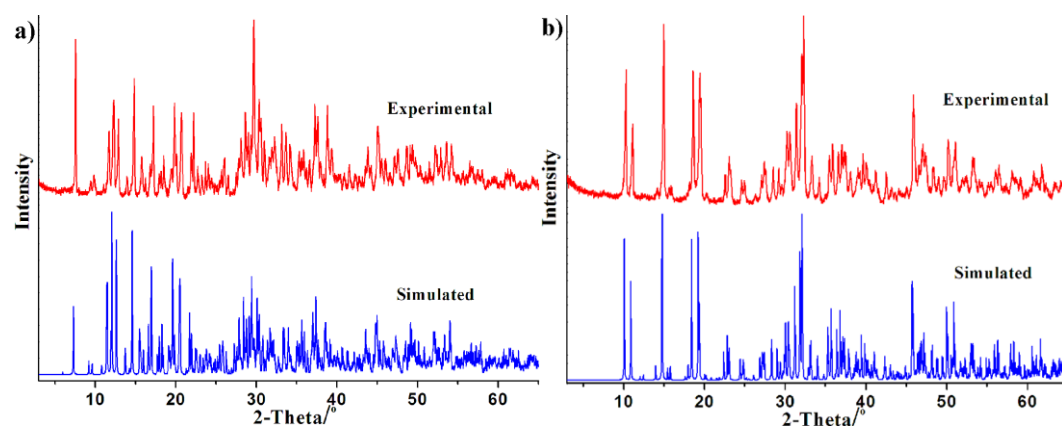


Figure S3 The PXRD patterns of **1** (a) and **2** (b) (red) is in good agreement with that simulated from the single crystal X-ray data (blue).

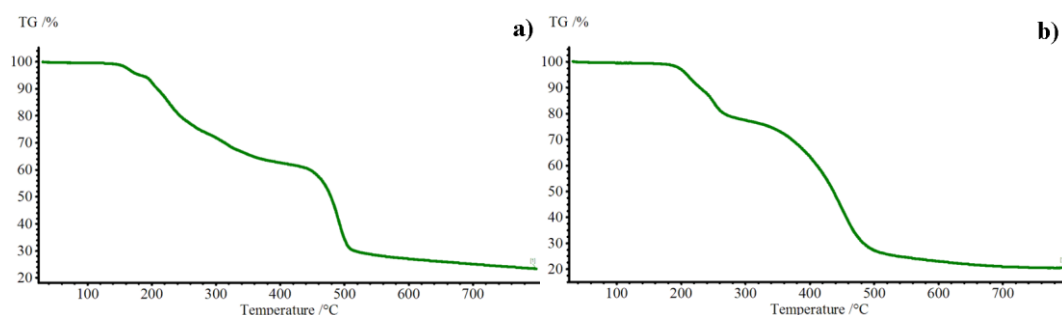


Figure S4 TG curves for compounds **1** (a) and **2** (b).

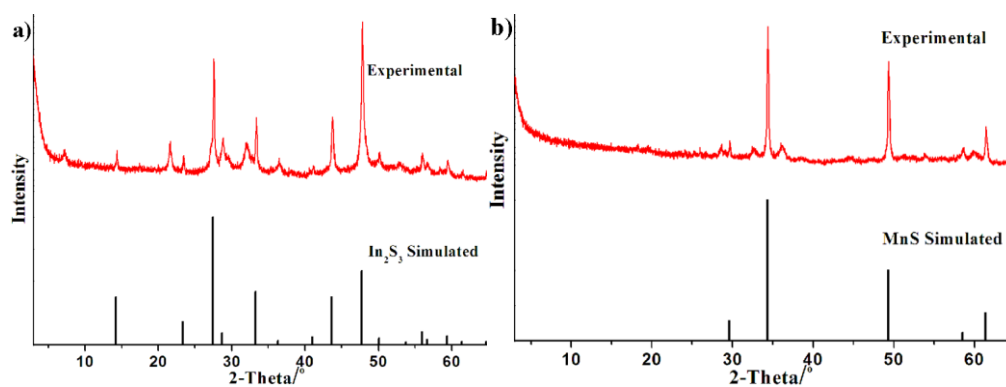


Figure S5 The PXRD patterns of the residues of **1** (a) and **2** (b) after 800°C

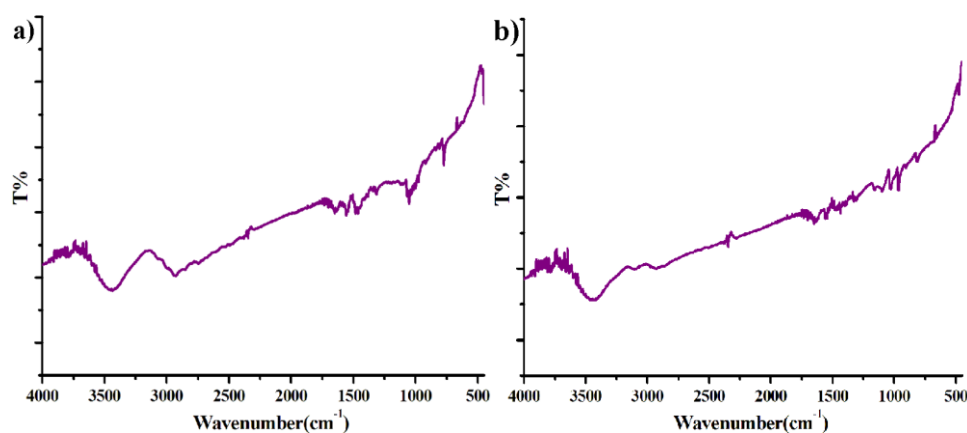


Figure S6 IR Spectra of compounds **1** and **2**.

References

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