Solid-state synthesis and crystal structure of a novel quaternary metal chalcogenide

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An unprecedented quaternary metal chalcogenide $Hg_3Zn_2S_4I_2$ (**1**) has been obtained by solid-state reaction and structurally characterised by X-ray diffraction. Compound **1** crystallises in the space group $C222_1$ of the orthorhombic system with four formula units in a cell: a = 12.571(4), b = 7.258(3), c = 10.742(4) Å, V = 980.1(6) Å^3, $Hg_3I_2S_4Zn_2$, M_r = 1114.55, D_c = 7.553 g cm^{-3}, T = 123.15 K, F(000) = 1880 and $R1/wR2$ = 0.0636/0.1658 for 542 observed reflections ($I > 2\sigma(I)$) and 572 unique reflections. Compound **1** is characterised by a novel 3-D framework motif.

Keywords: chalcogenide, halide, mercury, sulfur, zinc

The transition and main group metal chalcogenides show rich structural chemistry and useful physical and chemical properties for potential applications in solar energy conversion[1] and ferroelectrics.[2] As a branch of metal chalcogenides, many ternary metal chalcogenides have been prepared and widely used in military areas, such as $CuInSe_2$ and $Hg_{1-x}Cd_xTe$, whose primary applications are found in photovoltaic devices for IR detection.[1,3]

Among the known ternary metal chalcogenides, many are A–M–Q (A = alkali metal or alkaline-earth metal; M = p-block metal; Q = chalcogen = S, Se, Te) systems, while group 12–Q–X (12 = Zn, Cd, Hg; X = F, Cl, Br, I) systems are relatively rare. Moreover, quaternary 12–Q–X compounds (only containing 12, Q and X elements) are much more rare, although many other quaternary metal chalcogenides such as $Cd_{13}P_4S_{22}I_2$[4] and CuHgSeCl,[5] have been documented. Our efforts in synthesising novel 12-based compounds have focused largely on the systems containing both chalcogenide and halide anions. Here we describe the synthesis and characterisation of a novel quaternary metal chalcogenide $Hg_3Zn_2S_4I_2$ (**1**) (see Fig. 1).

Experimental

Materials and instrumentation: All reactants of A.R. grade were obtained commercially and used without further purification.

Synthesis of $Hg_3Zn_2S_4I_2$ (**1**): Prepared by the reaction of HgI_2 (3 mmol, 1365 mg), ZnI_2 (2 mmol, 640 mg) and S (4 mmol, 128 mg). The starting materials were loaded into a silica tube, which was flame-sealed under a 10^{-3} Torr atmosphere and subsequently placed into a furnace. The tube was heated to 200 °C in 6 h from room temperature and kept for 24 h, then heated to 450 °C in 6 h and kept for 15 days, followed by cooling to 100 °C at a rate of 5 °C /h to promote crystal growth, then cooled to 35 °C during 5 h. Yield: 56%.

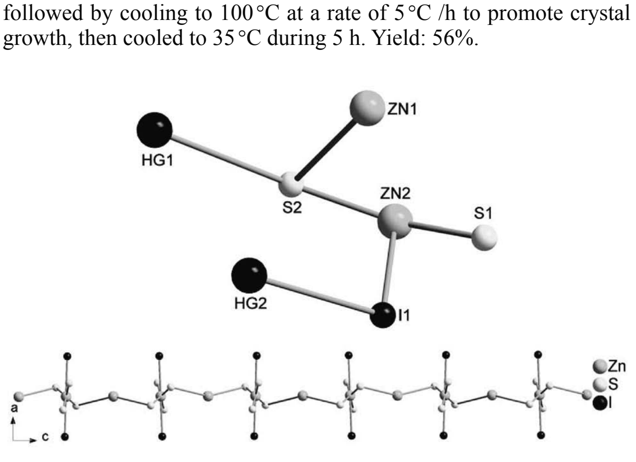

Fig. 1 The molecular structure of **1**.

X-ray structure determination: X-ray diffraction data were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) using a ω scan technique. CrystalClear software was used for data reduction and empirical absorption correction. The structure was solved by the direct methods using the Siemens SHELXTL™ Version 5 package of crystallographic software. The difference Fourier maps based on the atomic positions yielded all atoms. The structure was refined using a full-matrix least-squares refinement on F^2. All atoms were refined anisotropically. The summary of crystallographic data and structure analysis is given in Table 1. The selected bond lengths and bond angles are listed in Table 2.

Crystallographic data in CIF format have been deposited with FIZ Karlsruhe with the following CSD number: 420768. The data can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (Fax: (49) 7247-808-666; E-mail: crysdata@fiz.karlsruhe.de).

Table 1 Summary of crystallographic data and structure analysis for **1**

Formula	$Hg_3I_2S_4Zn_2$
Formula weight	1114.55
Colour	Yellow
Crystal size/mm^3	0.07, 0.05, 0.04
Crystal system	Orthorhombic
Space group	$C222_1$
a (Å)	12.571(4)
b (Å)	7.258(3)
c (Å)	10.742(4)
V (Å^3)	980.1(6)
Z	4
$2\theta_{max}$ (°)	50
Index ranges	$-14 \le h \le 14$, $-7 \le k \le 8$, $-12 \le l \le 12$
Reflections collected	1989
Independent, observed reflections (R_{int})	572, 542 (0.1059)
$d_{calcd.}$ (g cm^{-3})	7.553
μ (mm^{-1})	58.732
T (K)	123.15
F(000)	1880
$R1$, $wR2$	0.0636, 0.1658
S 1.011	
Largest, mean Δ/σ	0, 0
$\Delta\rho$(max, min) (e Å^{-3})	1.962, –1.091

Table 2 Selected bond lengths (Å) and bond angles (°)

Bond	Distance	Bond	Distance
Hg(1)–S(2)#1	2.860(6)	Zn(2)–S(1)	1.800(4)
Hg(1)–S(2)#2	2.860(6)	Zn(2)–S(1)#1	1.800(4)
Hg(2)–I(1)#3	2.893(2)	Zn(2)–S(2)	1.864(4)
Hg(2)–I(1)	3.043(2)	Zn(2)–S(2)#1	1.864(4)
Zn(1)–S(2)#4	2.822(6)	Zn(2)–I(1)#1	2.279(3)
Zn(1)–S(2)	2.822(6)	Zn(2)–I(1)	2.279(3)

Symmetry codes: #1 $-x + 1$, y, $-z-1/2$; #2 $-x + 1$, $-y$, $z-1/2$; #3 $-x + 1/2$, $y-1/2$, $-z-1/2$; #4 x, $-y-1$, $-z$.

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Results and discussion

X-ray diffraction analysis reveals that the title compound is characteristic of a 3-D framework structure. Each Hg1 atom is coordinated by two sulfur atoms with the bond lengths of Hg1–S2 being of 2.860(6) Å, while each Hg2 atom is bound to two iodine atoms with the bond lengths of Hg2–I1 being of 2.893(2) and 3.043(2) Å, respectively (see Table 2). The Zn1 atom also links to two sulfur atoms with the bond lengths of Zn1–S2 being of 2.822(6) Å. Differently, each Zn2 atom coordinates to four sulfur atoms and two iodine atoms with the bond lengths of Zn2–S1, Zn2–S2 and Zn2–I1 being of 1.800(4), 1.864(4) and 2.279(3) Å, respectively, yielding a ZnS_4I_2 moiety, as shown in Fig. 2. Such ZnS_4I_2 moieties interlink together *via* Zn1 atoms to give a one-dimensional chain-like structure running along the *c* axis. These one-dimensional chains are further interconnected through Hg1 atoms to form a two-dimensional layer extending along the *bc* plane, as shown in Fig. 3. The two-dimensional layers connect to each other through the Hg2 atoms to construct a three-dimensional framework, as shown in Fig. 4. It is noteworthy that in the title compound there are 12-membered $Hg_4Zn_2I_6$ rings. These rings interlink to six neighbouring ones through edge-sharing to complete a honeycomb-like three-dimensional framework. To our best knowledge, compound **1** is the first example of quaternary 12–Q–X metal chalcogenide.

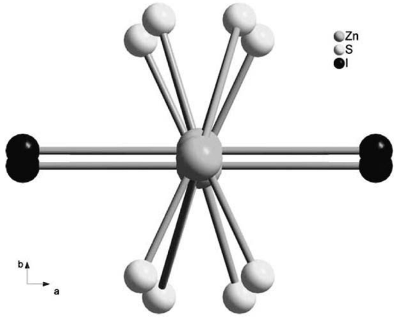

Fig. 2 The chain-like structure viewed down along different directions.

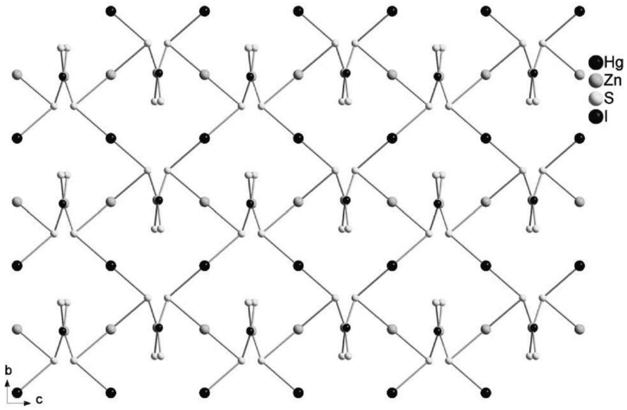

Fig. 3 A view of **1** showing a 2-D layer.

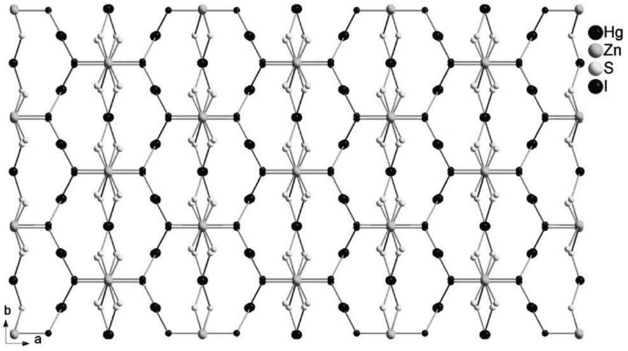

Fig. 4 The three-dimensional framework of **1** viewed along the *c* axis.In summary, a novel quaternary metal sulfochloride $Hg_3Zn_2S_4I_2$ has been synthesised via solid-state reactions. The crystal structure of the title compound is characterised by a 3-D framework structure. The title compound is the first example of quaternary 12–Q–X metal chalcogenides.

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