



Solid-State Preparation and Single-Crystal Structure of Hg₄I₂Cl₄S

HAN-MAO KUANG, HUA-LONG CHEN and WEN-TONG CHEN*

School of Chemistry and Chemical Engineering, Jiangxi Province Key Laboratory of Coordination Chemistry, Institute of Applied Chemistry, Jingtangshan University, 343009, Ji'an, Jiangxi, P.R. China

*Corresponding author: E-mail: wtchen_2000@yahoo.cn

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A new quaternary metal chalcogenide Hg₄I₂Cl₄S (**1**) was obtained through a solid-state reaction and characterized by a single-crystal X-ray diffraction. Compound **1** crystallizes in the space group P2₁/c of the monoclinic system with two formula units in a cell: a = 6.660(7) Å, b = 5.198(6) Å, c = 13.582(5) Å, β = 97.936(13)°, V = 465.6(7) Å³, Cl₄Hg₄I₂S, M_r = 1230.02, D_c = 8.773 g/cm³, S = 0.869, μ(MoKα) = 73.663 mm⁻¹, F(000) = 1020, R = 0.0678 and wR = 0.1349. Compound **1** features a 2-D layered structure with the iodine ions locating between the layers.

Key Words: Chalcogenide, Crystal structure, MCT analog, Solid-state reaction.

INTRODUCTION

Metal chalcogenides show a rich structural chemistry and abundant properties that allow them can be used in many areas such as chemical absorption^{1,2}, thermal electrics^{3,4}, solar energy conversion⁵, optical storage^{6,7}, ferroelectrics⁸, ion-exchange^{9,10}, second harmonic generation¹¹, nonlinear optics^{12,13} and so forth. Therefore, metal chalcogenides have attracted more and more attentions. As an important part of metal chalcogenides, many ternary metal chalcogenides have been found and applied to military and civil areas, representative examples like Hg_{1-x}Cd_xTe (MCT) and CuInSe₂, which have been put to use in photovoltaic devices and infrared detectors¹⁴. However, ternary metal chalcogenides are so far basically A-M-Q (A = alkaline-earth metals or alkali metals; M = p-block metals; Q = chalcogen = S, Se, Te) modes, while other types are infrequent¹⁵⁻¹⁷, especially quaternary IIB-Q-X chalcogenides (IIB = Zn, Cd, Hg; X = F, Cl, Br, I)¹⁶⁻¹⁸. To get new materials bearing novel structures and properties, our efforts in synthesizing new chalcogenides are mainly aimed at the analogs of MCT. We report herein the synthesis and structure of a new quaternary chalcogenide-Hg₄I₂Cl₄S (**1**).

EXPERIMENTAL

Synthesis of Hg₄I₂Cl₄S (1**):** All reactants of analytical reagent grade were commercially obtained and used without further purification. The compound Hg₄I₂Cl₄S was prepared *via* a reaction of HgCl₂ (2 mmol, 0.544 g), HgI₂ (1 mmol, 0.455 g) and S (5 mmol, 0.160 g). The starting reagents were mixed

and ground, followed by loading into a glass tube, which was flame-sealed under a 10⁻³ Torr atmosphere and then put into a computer-controlled furnace. The tubes were heated to 300 °C in 10 h from room temperature and hold there for 15 days, followed by cooling to 35 °C at a rate of 6 °C/h to promote crystal growth, then power off. Yield: 12 % (based on mercury).

X-ray structure determination: X-ray diffraction data were measured on a Rigaku Mercury CCD X-ray diffractometer with graphite monochromated MoK_α radiation (λ = 0.71073 Å) using a ω scan technique. Crystal clear 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 yield all the atoms. The structure was refined using a full-matrix least-squares refinement on F². All atoms were refined anisotropically. The summary of crystallographic data and structure analysis is listed in Table-1. The selected bond lengths and bond angles are given in Table-2.

Crystallographic data in CIF format have been deposited with FIZ Karlsruhe with the following CSD number: 422546. The data can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de).

RESULTS AND DISCUSSION

Single-crystal X-ray diffraction analysis exhibits that Hg₄I₂Cl₄S compound is characterized by a 2-D layered motif.

S(1) atom is in a special position, while other crystallographically independent atoms are in general sites. Hg(1) atom coordinate to three chlorine atoms to give a triangle pyramid of HgCl_3 , as shown in Fig. 1. The bond angles of Cl-Hg(1)-Cl are between $77.5(4)^\circ$ and $95.4(2)^\circ$. Differently, Hg(2) atom is surrounded by one sulfur atom and three chlorine atoms to form a distorted square pyramid of HgSCl_3 . The bond length of Hg-Cl is in the range of $1.993(10)$ Å- $2.414(10)$ Å with an average value of $2.135(10)$ Å, comparable with the counterpart documented^{16,17}. The HgCl_3 triangle pyramid edge-shares with HgSCl_3 square pyramid in an up-and-down arrangement mode (Fig. 1). The HgCl_3 triangle pyramids and HgSCl_3 square pyramids interconnect to each other to construct a two-dimensional layer, running along the bc plane (Fig. 2). The layers parallelly stack along the a axis with the iodine ions locating between the layers, yielding a sandwich-like structure (Fig. 3).

structurally characterized by a single-crystal X-ray diffraction. The crystal structure of the title compound is characteristic of a 2-D layered structure.

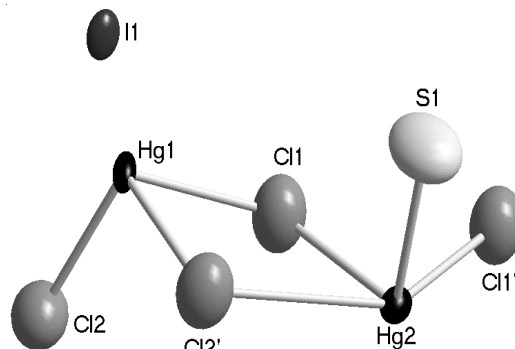


Fig. 1. ORTEP drawing of 1 with 30 % thermal ellipsoids

TABLE-1 SUMMARY OF CRYSTALLOGRAPHIC DATA AND STRUCTURE ANALYSIS	
Empirical formula	$\text{Cl}_4\text{Hg}_4\text{I}_2\text{S}$
Formula weight	1230.02
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 6.660(7)$ Å $b = 5.198(6)$ Å $c = 13.582(5)$ Å $\beta = 97.936(13)^\circ$
Z	2
V	$465.6(7)$ Å ³
D_c	8.773 Mg/m ³
Absorption coefficient	73.663 mm ⁻¹
Crystal size	$0.05 \times 0.04 \times 0.04$ mm
No. of reflections collected/unique	2271/789 [$R_{\text{int}} = 0.0834$]
Goodness-of-fit on F^2	0.869
Final R indices	$R_1 = 0.0678$, $wR_2 = 0.1349$
R indices (all data)	$R_1 = 0.0737$, $wR_2 = 0.1388$
Index ranges	$-7 \leq h \leq 7$, $-6 \leq k \leq 5$, $-16 \leq l \leq 16$
$(\Delta/\sigma)_{\text{max}}$	0

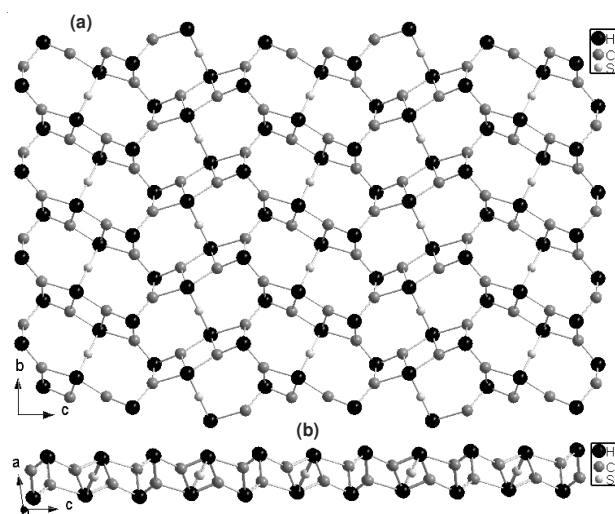


Fig. 2. A 2-D layer viewed down along: (a) a axis and (b) b axis

TABLE-2 SELECTED BOND LENGTHS (Å) AND BOND ANGLES ($^\circ$)			
Bond lengths (Å)		Bond angles ($^\circ$)	
Hg(1)-Cl(1)	2.027(9)	Cl(2)-Hg(1)-Cl(1)	94.2(4)
Hg(1)-Cl(2)	1.993(10)	Cl(2)-Hg(1)-Cl(2)#1	95.4(2)
Hg(1)-Cl(2)#1	2.095(10)	Cl(1)-Hg(1)-Cl(2)#1	77.5(4)
Hg(1)-Hg(2)	3.435(3)	S(1)-Hg(2)-Cl(1)	92.7(3)
Hg(2)-S(1)	1.9218(17)	S(1)-Hg(2)-Cl(1)#2	88.3(3)
Hg(2)-Cl(1)	2.099(10)	Cl(1)-Hg(2)-Cl(1)#2	72.3(4)
Hg(2)-Cl(1)#2	2.183(9)	S(1)-Hg(2)-Cl(2)#1	84.3(3)
Hg(2)-Cl(2)#1	2.414(10)	Cl(1)-Hg(2)-Cl(2)#1	69.4(3)
		Cl(1)#2-Hg(2)-Cl(2)#1	140.5(4)
Symmetry codes: #1 -x, y+1/2, -z+1/2; #2 -x, -y, -z+1			

It should be pointed out that the closest distance between two neighboring mercury atoms is $3.435(3)$ Å, which locates in the range of the sum of the van der Waals radii (3.4 - 4.0 Å)¹⁹ and comparable with that in other mercury compounds,^{16, 17, 20-23} suggesting the existence of a weak Hg...Hg interaction. The weak Hg...Hg interaction can solidify the structure of 1.

In summary, a new quaternary metal chalcogenide $\text{Hg}_4\text{I}_2\text{Cl}_4\text{S}$ has been synthesized from a solid-state reaction and

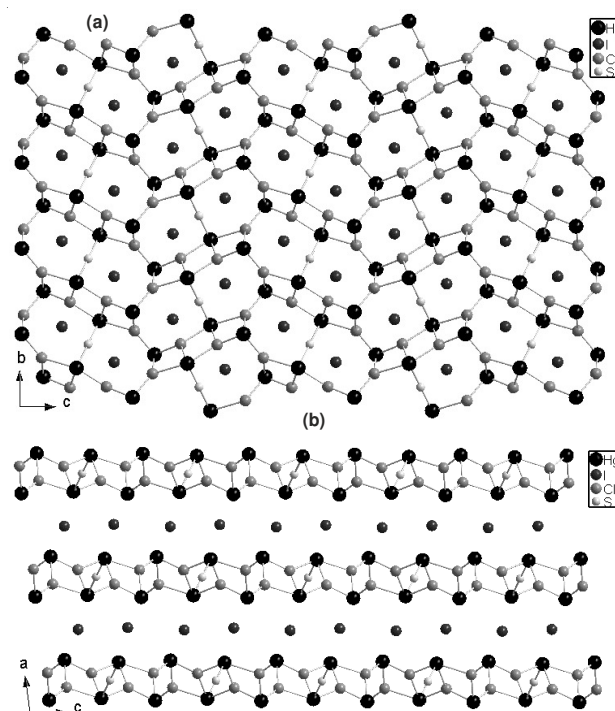


Fig. 3. Packing diagram of 1: (a) viewed along a axis and (b) viewed along b axis

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