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NOTE

A Novel Quaternary Metal Chalcogenide $HgZn_2I_4Cl_2$: Solid-State Synthesis and Structure

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An unprecedented quaternary metal chalcogenide $HgZn_2I_4Cl_2$ (**1**) was synthesized by a solid-state reaction and structurally characterized by single crystal X-ray diffraction. Compound **1** is characterized by a one-dimensional (1-D) infinite chain-like structure, which is constructed from the interconnected 9-membered $HgZn_2I_4Cl_2$ quadrangles.

Key Words: Chalcogenide, $HgZn_2I_4Cl_2$, Synthesis, Structure.

Metal chalcogenides usually exhibit abundant structural chemistry and interesting physical or chemical properties for potential applications in different fields such as ferroelectrics[1], solar energy conversion[2], *etc*. To our best of knowledge, a lot of ternary metal chalcogenides - as a branch of metal chalcogenides, have been synthesized and broadly used in military areas. Among which, the most famous is probably $Hg_{1-x}Cd_xTe$ (MCT) and $CuInSe_2$, whose important application is found in photoelectric devices of infrared detection[2,3]. Up to date, most of the ternary metal chalcogenides are A-M-Q (A = alkali/alkaline-earth metals, M = *p*-block metals, Q = chalcogen = S/Se/Te) compounds, while IIB-Q-X (IIB = Zn/Cd/Hg, X = F/Cl/Br/I) compounds are still relatively rare. Furthermore, quaternary IIB-Q-X metal chalcogenides (only containing IIB, Q and X) are much more scarce, although lots of other quaternary metal chalcogenides (not only containing IIB, Q and X) like CuHgSeCl[4] and $Cd_{13}P_4S_{22}I_2$[5], have been reported. Our recent efforts in preparing novel IIB-based compounds are mainly focusing on the systems containing both chalcogenide and halide elements. We herein report the solid-state synthesis and crystal structure of a novel quaternary metal chalcogenide $HgZn_2I_4Cl_2$ (**1**) with an infinite chain-like structure.

Synthesis: The chalcogenide $HgZn_2I_4Cl_2$ was synthesized from the reaction of $HgCl_2$ (1 mmol, 272 mg) and ZnI_2 (2 mmol, 638 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 523 K in 6 h from room temperature and kept there for 2 days, then heated to 723 K in 12 h and kept for 15 days, followed by cooling to 373 K at a rate of 5 K/h to promote crystal growth, then cooled down to room temperature and power off. Yield: 29 %.

Single-crystal X-ray diffraction experiment: X-Ray diffraction data set was collected on a Rigaku Mercury CCD X-ray diffractometer with graphite monochromated MoK_α radiation (λ = 0.71073 Å) using an 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 SHELXTLTM Version 5 package of crystallographic software. The difference Fourier maps based on the atomic positions yield 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.

Compound **1** was obtained from the reaction of $HgCl_2$ and ZnI_2 by solid-state reactions at an intermediate temperature. X-Ray diffraction analyses reveal that compound **1** is characteristic of a 1-D infinite chain-like structure. An ORTEP diagram of **1** together with the atomic numbering scheme is shown in Fig. 1. The Hg(II) ion coordinates to four iodine ions with the bond distances of Hg-I being of 2.661(2) and 2.8069(19) Å, as shown in Fig. 2 and Table-2. The bond lengths of Hg-I are normal and comparable with the counterparts documented previously[6]. The Zn(II) ion binds to two iodine ions with the bond lengths of Zn-I being of 2.666(3) and 2.775(3) Å, respectively, which are normal and comparable with those reported in the literature[7]. Additionally, each zinc ion connects to a neighboring one with the Zn···Zn distance being of

TABLE-1
CRYSTAL DATA OF **1**

Empirical formula	$Cl_2HgI_4Zn_2$
Formula weight	909.83
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 9.798(3) Å, b = 14.779(5) Å, c = 12.318(4) Å, β = 110.556(4)°
Z	4
V	1670.1(10) $Å^3$
D_c	3.618 Mg/m^3
Absorption coefficient	19.686 mm^{-1}
Crystal size	0.08 mm × 0.06 mm × 0.05 mm
No. of reflections collected/unique	2888/945 [$R_{(int)}$ = 0.0270]
Goodness-of-fit on F^2	0.932
Final R indices	R_1 = 0.0891, wR_2 = 0.2032
R indices (all data)	R_1 = 0.1258, wR_2 = 0.2388
$(\Delta/\sigma)_{max}$	0.001

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

Hg(1)-I(1)#1	2.661(2)	I(1)-Hg(1)-I(2)	90.21(6)
Hg(1)-I(1)	2.661(2)	I(1)#1-Hg(1)-I(1)	177.90(8)
Hg(1)-I(2)	2.8069(19)	I(1)#1-Hg(1)-I(2)	89.75(6)
Hg(1)-I(2)#1	2.8069(19)	I(1)#1-Hg(1)-I(2)#1	90.21(6)
Zn(1)-I(1)#1	2.775(3)	I(1)-Hg(1)-I(2)#1	89.75(6)
Zn(1)-I(2)	2.666(3)	I(2)-Zn(1)-I(1)#1	90.35(10)
Zn(1)-Zn(1)#2	2.452(6)	I(2)-Hg(1)-I(2)#1	177.84(7)

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

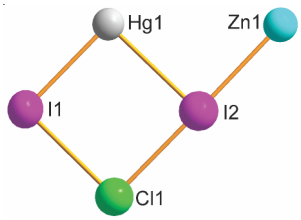

Fig. 1. An ORTEP drawing of **1** with 50 % thermal ellipsoids

2.452(6) Å which is comparable with those documented before[8]. One mercury, two zinc, two chlorine and four iodine atoms interconnect together to form a 9-membered $HgZn_2I_4Cl_2$ quadrangle. The $HgZn_2I_4Cl_2$ quadrangles interlink together *via* zinc atoms to give a 1-D infinite chain-like structure running along the a axis, as shown in Fig. 2. The 1-D infinite chains stack together to give a crystal packing motif, as shown in Fig. 3.

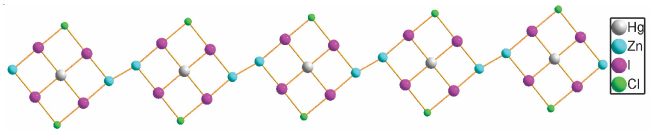

Fig. 2. A chain-like structure of **1** running along the a axis

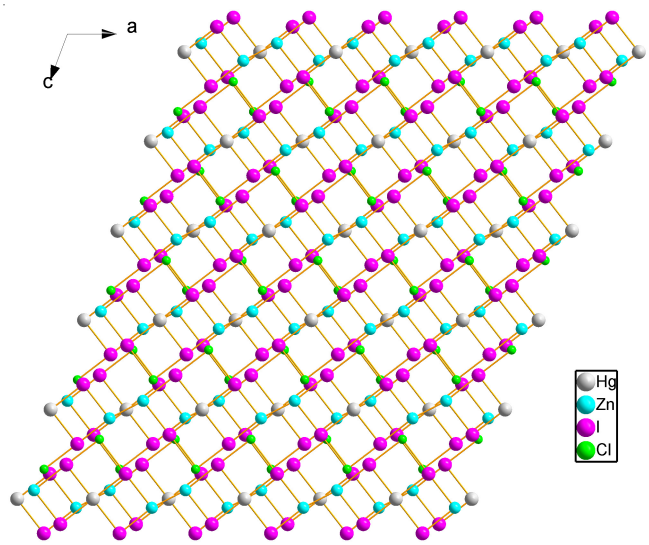

Fig. 3. Packing diagram of **1** viewed down along the b axis

In summary, a novel quaternary metal chalcogenide $HgZn_2I_4Cl_2$ has been obtained *via* a solid-state reaction. Its crystal structure is characteristic of a one-dimensional infinite chain-like structure, which is constructed from the interconnected 9-membered $HgZn_2I_4Cl_2$ quadrangles.

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