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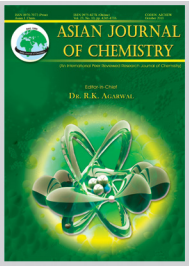

Molten Salt Synthesis and Crystal Structure of a Novel Quinary Metal Chalcogenide

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An unprecedented quinary metal chalcogenide $HgZnCl_{15}Se_3S_3$ (**1**) has been prepared *via* a molten salt synthesis method and structurally characterized by X-ray diffractions. Compound **1** crystallizes in the space group $P_{3}c_1$ of the hexagonal system with two formula units in a cell: a = b = 9.3909(3), c = 10.3540(6) Å, V = 790.78(6) Å^3, $Cl_{15}HgS_3Se_3Zn$, Mr = 1130.77, D_c = 4.749 g/cm^3, T = 293(2) K, F(000) = 1030 and R1/wR2 = 0.0500/0.1422 for 3383 observed reflections ($I > 2\sigma(I)$) and 925 unique reflections. Compound **1** features a novel three-dimensional (3-D) framework structure.

Key Words: Chalcogenide, Halide, Mercury, Selenium, Zinc.

INTRODUCTION

Metal chalcogenides have attracted more and more attention due to their rich structural motifs and properties for potential applications in solar energy conversion[1], optical storage[2], nonlinear optics[3], thermal electrics[4], second harmonic generation[5] and ferroelectrics[6]. Lots of ternary metal chalcogenides have so far been synthesized and widely used in military and civil areas, such as $CuInSe_2$ (CIS) and $Hg_{1-x}Cd_xTe$ (MCT), whose primary applications are found in photovoltaic devices for infrared detection and solar energy conversion[1,7]. Comparing with ternary metal chalcogenides, quaternary IIB-Q-X (IIB = Zn, Cd, Hg; Q = chalcogen = S, Se, Te; X = F, Cl, Br, I) metal chalcogenides are rare[8], although many other quaternary metal chalcogenides (containing none IIB, Q and X elements) such as $Mo_{0.5}W_{0.5}S_xSe_{2-x}(0 \le x \le 2)$[9], $Cd_{13}P_4S_{22}I_2$[10], $In_{0.2}Sn_6Bi_{1.8}Se_9$[11], $La_4MnCu_6S_{10}$[12] and CuHgSeCl[13] have been documented. To our best of knowledge, quinary metal chalcogenides are much rarer. Therefore, the structures and functions of quinary metal chalcogenides have yet to be explored. Our efforts in synthesizing novel IIB-based compounds have focused largely on the systems containing both chalcogenide and halide anions[14-16]. We report herein the synthesis and characterization of a novel quinary metal chalcogenide $HgZnCl_{15}Se_3S_3$ (**1**).

EXPERIMENTAL

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

Synthesis of $HgZnCl_{15}Se_3S_3$ (1): This compound was synthesized from the molten salt reaction of $HgCl_2$ (3 mmol, 816 mg), ZnS (1 mmol, 97 mg) and Se (3 mmol, 237 mg). The starting materials were loaded into a silica tube, which was flame-sealed under a 10^{-3} Torr atmosphere and subsequently put into a computer controlled furnace. The tube was heated to 400 ºC in 12 h from room temperature and kept for 24 h, then heated to 700 ºC in 12 h and kept for 15 days, followed by cooling to 100 ºC at a rate of 5 ºC/h to promote crystal growth, then cooled to 35 ºC in 5 h and power off. Yield: 12 % (based on zinc).

X-ray structure determination: 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 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 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 are 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: 422642. 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	$Cl_{15}HgS_3Se_3Zn$
Formula weight	1130.77
Colour	Colourless
Crystal (size/mm^3)	0.07 0.06 0.04
Crystal system	Hexagonal
Space group	P_3c_1
a (Å)	9.3909(3)
c (Å)	10.3540(6)
V (Å^3)	790.78(6)
Z	2
$2\theta_{max}$ (º)	50
Index ranges	$-10 \le h \le 11$, $-10 \le k \le 9$, $-12 \le l \le 12$
Reflections collected	3383
Independent, observed reflections (R_{int})	925, 908 (0. 0.0213)
$d_{calcd.}$ (g/cm^3)	4.749
μ (mm^{-1})	21.032
T (K)	293(2)
F(000)	1030
R1, wR2	0.0500, 0.1422
S	1.129
Largest and mean Δ/σ	0, 0
Δρ (max, min) (e/Å^3)	1.982, -1.954

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

Bond	Dist.	Bond	Dist.
Hg(1)-Cl(3)	2.125(3)	Zn(1)-Cl(4)#4	2.387(3)
Hg(1)-Cl(3)#1	2.125(3)	Zn(1)-Cl(4)#5	2.387(3)
Hg(1)-Cl(3)#2	2.125(3)	Zn(1)-Cl(2)#6	2.421(3)
Hg(1)-Cl(5)#2	2.145(3)	Zn(1)-Cl(2)#7	2.421(3)
Hg(1)-Cl(5)	2.145(3)	Zn(1)-Cl(2)	2.421(3)
Hg(1)-Cl(5)#1	2.145(3)	Cl(1)-Cl(5)	1.466(5)
Se(1)-Cl(4)	1.448(3)	Cl(1)-S(1)	1.519(6)
Se(1)-Cl(2)	1.453(3)	Cl(2)-Cl(3)	2.422(4)
Se(1)-Cl(3)	1.482(3)	Cl(2)-Cl(4)	2.451(3)
Se(1)-S(1)	1.776(3)	Cl(3)-Cl(4)	2.404(4)
Zn(1)-Cl(4)#3	2.387(3)	Cl(5)-S(1)	2.505(5)

Symmetry codes: #1 -y+1, x-y+1, z; #2 -x+y, -x+1, z; #3 -y+1, -x+1, z+1/2; #4 x, x-y+2, z+1/2; #5 -x+y-1, y, z+1/2; #6 -x+y-1, -x+1, z; #7 -y+1, x-y+2, z.

RESULTS AND DISCUSSION

In recent years, reactive flux method techniques or high-temperature molten salt synthesis have been widely used as a powerful method for access to a great number of new binary, ternary and quaternary chalcogenides[17,18]. As for the preparation of the title compound, we choose a top temperature of 700 ºC because $HgCl_2$ (m.p. = 276, b.p. = 302 ºC) and Se (m.p. = 217, b.p. = 685 ºC) are melted under this temperature, which makes the reaction similar to molten salt or reactive flux method synthesis. Therefore, it is proposed that this method may promote the reactions.

X-ray diffraction analysis displays that compound **1** features a 3-D framework motif. All of the crystallographically independent atoms, except for Hg1 and Zn1, are on general positions (Fig. 1). Each Hg1 atom is coordinated by six bridging chlorine atoms with the bond lengths of Hg-Cl being of 2.125(3) and 2.145(3) Å (Table-2), yielding a slightly distorted octahedron (Fig. 2). The bond lengths of Hg-Cl are normal and comparable with the counterpart documented[19]. The Zn1 atom also links to six bridging chlorine atoms with the bond lengths of Zn-Cl being of 2.387(3) and 2.421(3) Å (Fig. 2), which is similar to those reported[20,21]. The coordination environment of Zn1 atom can be described as a severely distorted octahedron (Fig. 2). By *virtue* of the connection of selenium, each Hg-centred octahedron connects to three neighboring Zn-centred octahedra and *vice versa*, forming a ring comprising of three Hg-centred octahedra and three Zn-centred octahedra. The rings interconnect together to construct a 3-D framework (Fig. 3). To our best of knowledge, compound **1** is the first example of quinary IIB-Q-X metal chalcogenides so far.

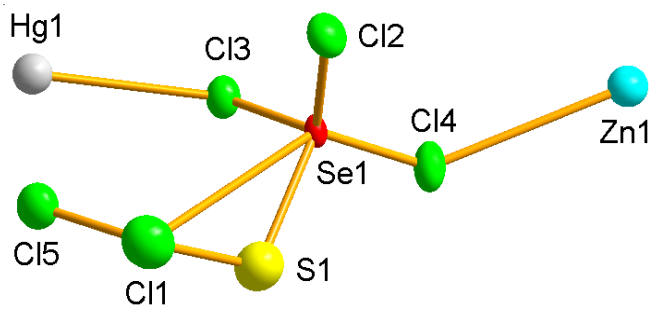

Fig. 1. Molecular structure of **1**

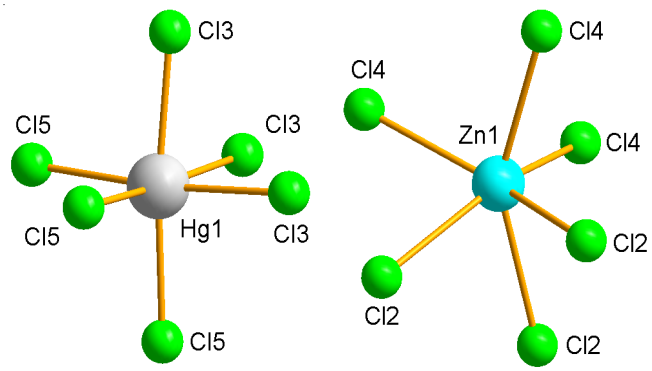

Fig. 2. Coordination environments of Hg1 and Zn1 atoms

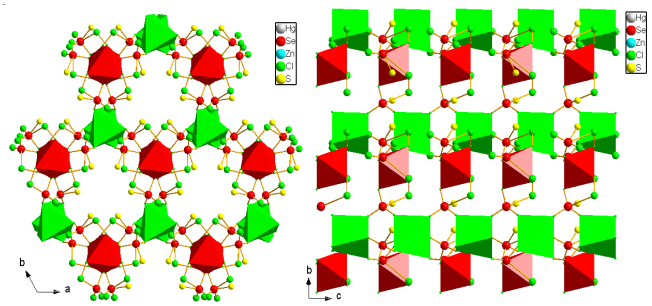

Fig. 3. Three-dimensional framework of **1** viewed along the c (left) and a (right) axis

In summary, a novel quinary metal chalcogenide $HgZnCl_{15}Se_3S_3$ has been synthesized *via* a molten salt synthesis method and structurally characterized by X-ray diffractions. The crystal structure of the title compound is characteristic of a 3-D framework structure. The title compound is the first example of quinary IIB-Q-X metal chalcogenides.

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