Synthesis, structure and property of a metal sulfochloride–$Hg_3S_2Cl_2$

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The compound [$Hg_3S_2Cl_2$] has been obtained by solid-state reactions. It crystallises in the acentric space group R_3 of the rhombohedral system with six formula units in a cell [$a = b = 12.654(3)$, $c = 7.753(4)$ Å, $V = 1075.1(6)$ Å^3, $Cl_2Hg_3S_2$, $M_r = 736.79$, $D_c = 6.828$ g cm^{-3}, $S = 0.987$, $\mu(\mathrm{Mo}K\alpha) = 65.308$ mm^{-1}, $F(000) = 1836$, $R = 0.0631$ and $wR = 0.1443$] and is characterised by a 3-D framework structure, which is composed of interconnected right-handed helices formed by tetrahedral Hg atoms. Optical absorption spectra reveal the presence of an optical bandgap of 2.51 eV and the composition $Hg_3S_2Cl_2$ is confirmed by semiquantitative microscope analysis.

Keywords: chalcogenide, halide, mercury, SEM/EDS, sulfur

The transition and main group metal chalcogenides show rich structural chemistry and useful physical and chemical properties for potential applications in nonlinear optics,[1] optical storage,[2] solar energy conversion,[3] thermal electrics,[4] ion-exchange,[5] second harmonic generation,[6] chemical absorption,[7] ferroelectrics,[8] and so on. As an important branch of metal chalcogenides, many ternary metal chalcogenides have been synthesised and some of them have been widely used in military and civil areas, famous examples including $CuInSe_2$ (CIS) and $Hg_{1-x}Cd_xTe$ (MCT), whose primary applications are found in photovoltaic devices for solar energy conversion and infrared detection.[3,9]

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, to our knowledge, amounting to 14 compounds in four stoichiometric ratio types of 3:2:2, 3:1:4, 2:1:3, and 2:2:2, namely $Hg_3S_2F_2$, $Hg_3S_2Br_2$, $Hg_3S_2I_2$, $Hg_3Se_2Cl_2$, $Hg_3Se_2Br_2$, $Hg_3Se_2I_2$, $Hg_3Te_2Cl_2$, $Hg_3Te_2Br_2$, $Hg_3Te_2I_2$, Hg_3TeCl_4, Hg_3TeBr_4, Hg_2TeBr_3, $Hg_2Te_2Br_2$ and $Hg_2Te_2I_2$.[10-18] To obtain new materials which maybe possess excellent photovoltaic and optical properties, our recent efforts in synthesising novel Group 12-based compounds have focused largely on the systems containing both chalcogenide and halide anions. Herein we describe the synthesis and characterisation of a metal sulfochloride $Hg_3S_2Cl_2$ (**1**), which was obtained by solid-state reaction at intermediate temperatures ($150 < T < 500$ °C).

Experimental

Materials and instrumentation

All reactants of A.R. grade were obtained commercially and used without further purification. The UV-vis spectra were recorded at room temperature on a computer-controlled PE Lambda 900 UV-vis spectrometer equipped with an integrating sphere in the wavelength range 190–2500 nm. A $BaSO_4$ plate was used as a reference (100% reflectance), on which the finely ground powder samples were coated. The absorption spectra were calculated from reflection spectra by the Kubelka–Munk function:[19] $\alpha/S = (1-R)^2/2R$, (α is the absorption coefficient, S is the scattering coefficient and R is the reflectance), which is practically wavelength independent when the particle size is larger than 5 μm. Semiquantitive microscope analysis was performed on a field emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy dispersive X-ray spectroscope (EDS).

Synthesis of $Hg_3S_2Cl_2$ (**1**): Prepared from the reaction of $HgCl_2$ (1 mmol, 272 mg), $CdCl_2$ (1 mmol, 183 mg) and sulfur (2 mmol, 64 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 290 °C in 6 h and kept for 6 days, followed by cooling to 100 °C at a rate of 5 °C /h to promote crystal growth, then cooled to 35 °C in 5 h with power off. Yield: 23% (based on mercury). Analyses of the crystals with SEM/EDS showed only the presence of Hg, S and Cl in a ratio of 2.9:2.1:2.0, which is close to the chemical formula of $Hg_3S_2Cl_2$ established by the X-ray diffraction analysis. The product is very stable in air and water.

X-ray structure determination: X-ray diffraction data were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) using an ω scan technique. CrystalClear software was used for data reduction and empirical absorption correction. The structure was solved by direct methods using the Siemens SHELXTL^{TM} 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.

Results and discussion

In recent years, hydro(solvo)thermal and high-temperature molten salt synthesis or reactive flux method techniques have proved to be a powerful method for access to a huge number of new binary, ternary, and quaternary chalcogenide compounds.[20,21] Differently, we adopted intermediate-temperature ($150 < T < 500$ °C) solid-state reactions to prepare new chalcogenides. Considering the melting and boiling points of $HgCl_2$ (m.p. = 276, b.p. = 302 °C), we decided to exploit a heating temperature of 290 °C. At this temperature, $HgCl_2$ is molten, which makes the reaction similar to molten salt or reactive flux method synthesis. Therefore, we considered that this method might promote the reactions.

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

Empirical formula	$Hg_3S_2Cl_2$
Formula weight	736.79
X-rays	Mo$K\alpha$
Crystal system	monoclinic
Space group	R_3
Unit cell dimensions	$a = 12.654(3)$ Å $b = 12.654(3)$ Å $c = 7.753(4)$ Å $\gamma = 120°$
Z	6
V	1075.1(6) Å^3
D_x	6.828 Mg/m^3
Absorption coefficient	65.308 mm^{-1}
Crystal size	0.06 × 0.05 × 0.05 mm
No. of reflections collected/ unique	1404/684 [$R_{(int)} = 0.0892$]
Refinement	full matrix least squares on F^2
Goodness-of-fit on F^2	0.987
Final R indices	$R_1 = 0.0631$, $wR_2 = 0.1443$
R indices (all data)	$R_1 = 0.0669$, $wR_2 = 0.1454$
Index ranges	$-14 \le h \le 14$, $-14 \le k \le 14$, $-9 \le l \le 9$
Measurement	Rigaku Mercury CCD diffractometer
Monochromator	graphite
Structure determination	Siemens SHELXTL
$(\Delta/\sigma)_{max}$	0

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Table 2 Selected bond lengths and bond angles of 1

Bond	Distance	Bond	Distance
Hg(1)–S(2)	2.402(4)	Hg(2)–Cl(1)	2.419(4)
Hg(1)–S(2)#1	2.429(5)	Hg(2)–S(2)	2.433(5)
Hg(1)–S(1)	2.863(2)	Hg(2)–Cl(2)	2.850(5)
Hg(1)–Cl(2)#2	2.870(7)	Hg(2)–Cl(2)#3	2.879(7)
Angle	**(°)**	**Angle**	**(°)**
S(2)–Hg(1)–S(2)#1	165.4(2)	Cl(1)–Hg(2)–S(2)	164.6(2)
S(2)–Hg(1)–S(1)	96.2(2)	Cl(1)–Hg(2)–Cl(2)	95.6(1)
S(2)#1–Hg(1)–S(1)	93.0(1)	S(2)–Hg(2)–Cl(2)	93.3(2)
S(2)–Hg(1)–Cl(2)#2	92.5(2)	Cl(1)–Hg(2)–Cl(2)#3	93.2(2)
S(2)#1–Hg(1)–Cl(2)#2	95.5(2)	S(2)–Hg(2)–Cl(2)#3	96.0(2)
S(1)–Hg(1)–Cl(2)#2	108.1(2)	Cl(2)–Hg(2)–Cl(2)#3	108.0(2)

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

Compound 1 was obtained from the reaction of $HgCl_2$, $CdCl_2$ and S by solid-state reactions. Notably, the title compound cannot be obtained without $CdCl_2$ in the starting reaction mixture, although the title compound does not contain cadmium. Therefore, it is proposed that the $CdCl_2$ may be a catalyst in the formation of the title compound. X-ray diffraction analysis reveals that compound 1 features a 3-D framework structure. The two crystallographically different mercury atoms are in general positions and have different coordination spheres (Fig. 1). Atoms S2 and Cl2 are also in general positions but S1 and Cl1 are in special positions. The Hg1 atom is tetrahedrally coordinated by one chlorine atom and three sulfur atoms with the bond lengths of Hg1–Cl2($-x+y-1/3$, $-x+1/3$, $z-2/3$), Hg1–S1, Hg1–S2 and Hg1–S2($-x+y+1/3$, $-x+2/3$, $z-1/3$) being of 2.870(7), 2.863(2), 2.402(4) and 2.429(5) Å, respectively, and the bond angles of S(2)–Hg(1)-S(2)($-x+y+1/3$, $-x+2/3$, $z-1/3$), S(2)–Hg(1)–S(1), S(2)#1–Hg(1)–S(1), S(2)–Hg(1)–Cl(2)($-x+y-1/3$, $-x+1/3$, $z-2/3$), S(2)($-x+y+1/3$, $-x+2/3$, $z-1/3$)–Hg(1)–Cl(2)($-x+y-1/3$, $-x+1/3$, $z-2/3$) and S(1)–Hg(1)–Cl(2)($-x+y-1/3$, $-x+1/3$, $z-2/3$) being 165.4(2), 96.2(2), 93.0(1), 92.5(2), 95.5(2) and 108.1(2)°, respectively. The Hg2 atom also has a tetrahedral geometry but the coordination environment is different, coordinating with one sulfur atom and two chlorine atoms with the bond lengths of Hg2–S2, Hg2–Cl1, Hg2–Cl2 and Hg2–Cl2($-x+y-1/3$, $-x+1/3$, $z+1/3$) of 2.433(5), 2.419(4), 2.850(5) and 2.879(7) Å, respectively, and the bond angles of Cl(1)–Hg(2)–S(2), Cl(1)–Hg(2)–Cl(2), S(2)–Hg(2)–Cl(2), Cl(1)–Hg(2)–Cl(2)($-x+y-1/3$, $-x+1/3$, $z+1/3$), S(2)–Hg(2)–Cl(2)($-x+y-1/3$, $-x+1/3$, $z+1/3$), and Cl(2)–Hg(2)–Cl(2)($-x+y-1/3$, $-x+1/3$, $z+1/3$) being of 164.6(2), 95.6(1), 93.3(2), 93.2(2), 96.0(2) and 108.0(2)°, respectively. Two Hg1– and Hg2–tetrahedron corner-share to each other via one S2 atom, forming a dimer of Hg-tetrahedra (Fig. 1). Such dimers corner-share to each other via the S2 atoms to yield a right-handed helix (Fig. 2), to our knowledge, this right-handed helix is the first example in the metal chalcogenides. The helices are interconnected to each other by corner sharing to complete a 3-D framework (Fig. 3).

Notably, the shortest Hg…Hg distance is of 3.543(4) Å, which is in the range of the sum of the van der Waals radii (3.4–4.0 Å)[22] and comparable with those of other mercury compounds,[23,24] indicating the existence of the weak Hg…Hg interaction. The weak Hg…Hg interactions may solidify the structure of the title compound.

For the structure of 1, a Flack × parameter of –0.0(3) was calculated, indicating a correct absolute structure.[25] Results of bond valence calculations indicate that all the mercury atoms are in the + 2 oxidation state (Hg1: 1.97, Hg2: 1.89).[26]

Optical absorption spectra of 1 reveal the presence of a sharp optical gap of 2.51 eV (Fig. 4), which suggests that this material may be a potential semiconductor. The steep slope of the optical absorption edge is indicative of the existence of a direct transition.[27] The energy band gap of 1 is larger than those of CdTe (1.5 eV), GaAs (1.4 eV) and $CuInS_2$ (1.55 eV), all of which are highly efficient photovoltaic materials.[28,29]

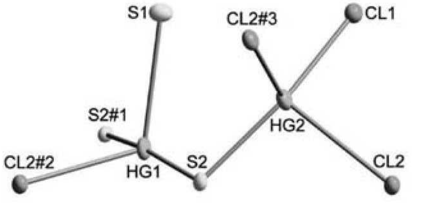

Fig. 1 ORTEP drawing of 1 with 40% thermal ellipsoids.

Fig. 2 Polyhedral perspective of 1 shows one right-handed helix.

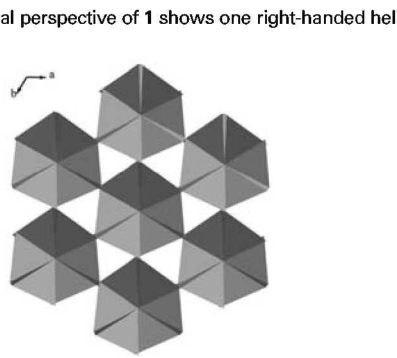

Fig. 3 A polyhedral representation of the 3-D framework of 1.

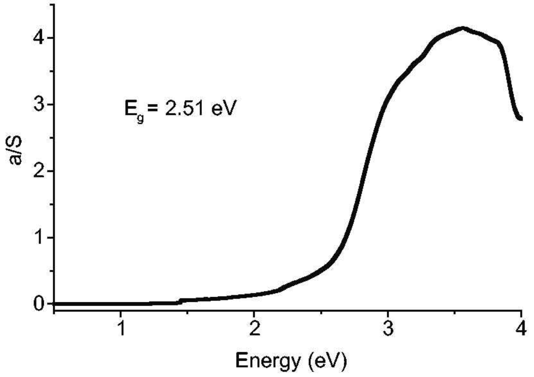

Fig. 4 The solid-state diffuse reflectance spectra for 1.

In summary, a metal sulfochloride $Hg_3S_2Cl_2$ has been synthesised *via* solid-state reactions. The crystal structure is characterised by a 3-D framework structure, comprising interconnected right-handed helices. The optical absorption spectrum shows that the title compound may be a potential photoelectric material. The transparent and acentric nature of **1** suggests that it may have nonlinear optical properties. Future investigations on the relationship between the crystal structure and the photoelectric or NLO properties in this field are in progress in our laboratory.

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