Short Communications

(HgBr$_2$)$_3$(As$_4$S$_4$)$_2$: An Adduct of HgBr$_2$ Molecules and Undistorted As$_4$S$_4$ Cages

Michael F. Bräu and Arno Pfitzner*

Regensburg, Universität, Institut für Anorganische Chemie

Abstract. (HgBr$_2$)$_3$(As$_4$S$_4$)$_2$ is obtained by high temperature reaction of stoichiometric amounts of HgBr$_2$ and As$_4$S$_4$. It crystallizes in the monoclinic space group $P2_1/c$ with the lattice constants a = 9.593(5) Å, b = 11.395(5) Å, c = 13.402(5) Å, β = 107.27(3)°, V = 1399(1) Å^3, and Z = 2. The crystal structure consists of molecular units built from two undistorted As$_4$S$_4$ cages which are coordinated weakly by three almost linear HgBr$_2$ units. Raman spectra clearly indicate minor bonding interactions between HgBr$_2$ and As$_4$S$_4$.

Keywords: Mercury halides; Molecular adducts; Arsenic sulfides; Crystal structures; Raman spectroscopy

Copper(I) halides are well established as a preparative tool to obtain new molecular or polymeric compounds of group 15 and 16 elements [1]. Inspired by early investigations of *Rabenau* et al. [2], and *Möller* and *Jeitschko* [3] many molecules or polymers of phosphorus [4], phosphorus chalcogenides [5], and heteroatomic chalcogen polymers [6] were synthesized. Extraction of CuI from the adducts (CuI)$_8$P$_{12}$ and (CuI)$_3$P$_{12}$ leaves the pure phosphorus polymers behind [7]. Even mixed arsenic-phosphorus polymers are accessible using this experimental approach [8]. A reason for the stability of these compounds is the structural flexibility of the copper halide framework, which is obviously able to host various molecules. In addition, the d^{10} ion Cu$^+$ seems to form strong bonds to phosphorus and thus helps to stabilize the embedded main group molecules.

Extending this approach, the next goal is to get access to adduct compounds of binary cage molecules or polymers of arsenic and sulfur or selenium. The reaction of copper(I) halides with arsenic and sulfur reveals Cu$_3$AsS$_4$, known as the mineral *enargite*, CuAsS, known as the mineral *lautite*, and other binary phases. Obviously, these are the preferred products in high temperature syntheses. In low temperature syntheses a reaction of As$_4$S$_4$ or As$_4$Se$_4$ cages with transition metals ends in fragmentation of the cages [9].

Recently, a molecular adduct of linear HgI$_2$ moieties and As$_4$S$_4$ cages was described [10]. This shows that the d^{10} ion Hg^{2+} is also able to form adducts with main group element cages. The structure consists of mercury iodide molecules with the mercury atoms are weakly coordinated to the sulfur atoms of As$_4$S$_4$ cages. In case of HgI$_2$ and As$_4$S$_4$, dimeric units (HgI$_2$)$_2$(As$_4$S$_4$)$_2$ are formed.

A wide spectrum of these compounds forming polycationic networks of mercury and chalcogen atoms is known in the compounds HgQ_2X_2 (Q = S, Se, Te; X = F, Cl, Br, I) and Hg$_3$AsQ_4X (Q = S, Se, X = Cl, Br, I) [11]. Also, a whole family of mercury chalcogenometalate halides is described in the literature [12]. These materials are usually prepared by high temperature syntheses from stoichiometric amounts of the corresponding mercury halide and the chalcogens, respectively. They can be described as polycationic frameworks of QHg$_3$ pyramids (Q = S, Se) which are linked to one-, two- or three dimensional networks. The anions occupy layers in between the cationic networks. Bonding between mercury and chalcogen atoms is assumed to be mainly covalent with distances d(Hg-S) ≈ 2.4 Å and d(Hg-Se) ≈ 2.55 Å. These compounds are very stable and some of them are known as minerals. However, during the synthesis of (HgI$_2$)$_2$(As$_4$S$_4$)$_2$ from HgI$_2$, arsenic and sulfur none of these compounds were observed. In contrast, almost linear HgI$_2$ molecules and As$_4$S$_4$ cages remain and form the dimeric molecular adduct [10]. Herein, we report about the mercury bromide adduct (HgBr$_2$)$_3$(As$_4$S$_4$)$_2$.

Experimental Details

(HgBr$_2$)$_3$(As$_4$S$_4$)$_2$ is obtained by melting a mixture of HgBr$_2$, As and S at 400 °C in evacuated silica ampoules and subsequent annealing at 190 °C for two weeks. The main products of this reaction are Hg$_3$S$_2$Br$_2$ and As$_4$S$_4$. Besides these small amounts of (HgBr$_2$)$_3$(As$_4$S$_4$)$_2$ are obtained as well shaped single crystals by this high temperature route. Higher yields are obtained by reaction of a mixture of HgBr$_2$ and As$_4$S$_4$ in CS$_2$ at 160 °C for two weeks. This solvothermal route results in (HgBr$_2$)$_3$(As$_4$S$_4$)$_2$ as the major product. The main byproduct again is Hg$_3$S$_2$Br$_2$.

Single crystals of (HgBr$_2$)$_3$(As$_4$S$_4$)$_2$ were selected under a microscope, mounted on a glass fiber and checked for their quality by Weissenberg photographs. Diffraction data were collected on a Stoe IPDS at room temperature applying Mo$K\alpha$ radiation. Cell constants were determined from powder patterns of the pure product (STOE STADI P, Cu$K\alpha_1$, Ge(111) monochromator).

Raman spectra were recorded on a Bruker RFS100/S FT spectrometer equipped with a Nd:YAG laser (λ = 1064 nm) and Ge-detector cooled by liquid nitrogen.

* Prof. Dr. Arno Pfitzner
Universität Regensburg
Institut für Anorganische Chemie
Universitätsstraße 31
D-93040 Regensburg /Germany
Fax: (+49)941/943 4983
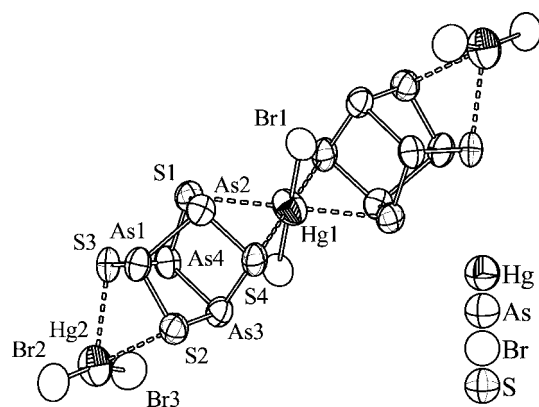E-mail: arno.pfitzner@chemie.uni-regensburg.de

Fig. 1 In $(HgBr_2)_3(As_4S_4)_2$ As_4S_4 cages are connected by $HgBr_2$ units. Ellipsoids are drawn at the 70 % probability level. Selected interatomic distances in Å:

Hg1-Br1: 2.457(2), Hg2-Br2: 2.410(2), Hg2-Br3: 2.515(2), Hg1-S1: 3.15(3), Hg1-S4: 3.12(2), Hg2-S2: 3.19(6), Hg2-S3: 3.07(1), As1-As2: 2.552(2), As3-As4: 2.572(2), As1-S2: 2.250(3), As1-S3: 2.245(3), As2-S1: 2.244(3), As2-S4: 2.247(3), As3-S2: 2.239(3), As3-S4: 2.244(4), As4-S1: 2.241(3), As4-S3: 2.249(3).

Results and Discussion

$(HgBr_2)_3(As_4S_4)_2$ is a reaction product of $HgBr_2$ and As_4S_4, forming yellow transparent crystals of irregular shape. The crystal structure was determined from single crystal diffraction data. Data were corrected numerically for absorption after refining the description of the shape of the crystal with *X-SHAPE* [13] using 500 independent reflections selected within *X-RED* [14]. Extinction conditions allowed the space groups $P2_1/c$, $P2_1$ and Pc. A reasonable solution and refinement of the crystal structure was possible in $P2_1/c$. The refinement converged to final *R*-values $R1 = 0.0525$ and $wR2 = 0.0863$ for all data [15]. The structure consists of adducts of three $HgBr_2$ units with two As_4S_4 cages. Figure 1 shows the arrangement of the $HgBr_2$ and As_4S_4 molecules with Hg and Br atoms forming more or less linear units. Mercury atoms are additionally coordinating sulfur atoms in comparably long distances. Thus, one exactly linear $HgBr_2$ in the centre of the adduct and two slightly bent $HgBr_2$ molecules (;wk(Br2-Hg2-Br3) = 162.5°) at both ends result. The distance $d(Hg1-Br1) = 2.457(2)$ Å of the central $HgBr_2$ unit corresponds to binary $HgBr_2$, $d(Hg-Br) = 2.445(3)$ Å, whereas the terminating $HgBr_2$ units differ slightly with $d(Hg2-Br2) = 2.410(2)$ Å and $d(Hg2-Br3) = 2.515(2)$ Å, respectively. The distances $d(Hg2-S2) = 3.19(2)$ Å and $d(Hg2-S3) = 3.07(1)$ Å (terminal) and $d(Hg1-S1) = 3.15(3)$ Å and $d(Hg1-S4) = 3.12(2)$ Å (center) of the molecule are all in the same range, but vary significantly. The distances and angles in the As_4S_4 cage correspond to those in $(HgI_2)_2(As_4S_4)_2$ and the isostructural cage in the mineral Realgar. The shape of the As_4S_4 cage is not restricted by the space group symmetry. Nevertheless, it has nearly the ideal symmetry of the point group D_{4d} within the standard deviations.

The arrangement of the resulting adduct molecules $(HgBr_2)_3(As_4S_4)_2$ is displayed in Figure 2. The As_4S_4 cages are arranged in stacks along the *c*-axis with $HgBr_2$ molecules located between these stacks.

In order to get some more insight in the bonding situation between Hg and S, and As and S, respectively, we recorded Raman spectra of $(HgBr_2)_3(As_4S_4)_2$. Table 1 shows that most of the frequencies
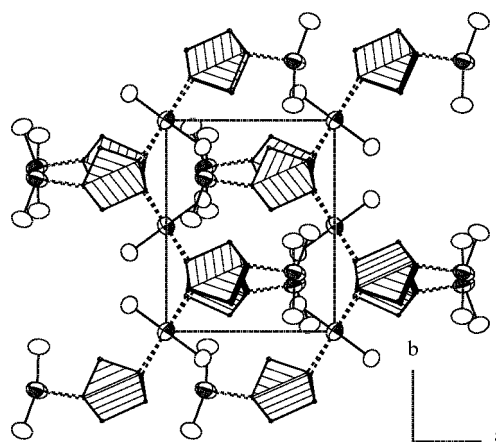

Fig. 2 Section of the crystal structure of $(HgBr_2)_3(As_4S_4)_2$. The As_4S_4 cages (shown as polyhedra) are arranged in columns along [0 0 1]. Ellipsoids are drawn at the 70 % probability level.

Table 1 Vibrational frequencies in cm^{-1} for $(HgBr_2)_3(As_4S_4)_2$ and a tentative assignment. Most of the frequencies correspond to the cages in binary As_4S_4.

Assignment	Intensity	$(HgBr_2)_3(As_4S_4)_2$	As_4S_4 [17]
As-S stretch	very weak	374	376
As-S stretch	very strong	359	355
As-S stretch	very weak	344	345
–	very weak	279	–
–	very weak	248	–
As-S wag	very strong	225	222
As-S-As bend	very strong	198	196
–	strong	191	–
As-As stretch	strong	183	184
As-S-As wag	weak	164	167
As-S-As bend	weak	148	144

can be assigned to the As_4S_4 cage in binary As_4S_4. Since the shifts of the frequencies are within two times the experimental resolution it can be assumed that the bonds within the coordinated cage are very similar to the non-coordinated cage in binary As_4S_4. The question whether the weak bands, cf. Table 1, have to be assigned to Hg-Br vibrational modes or to weak vibrations of the slightly distorted cages is subject of further investigations. The vibrational modes of the $HgBr_2$ molecule depend on the angle Br-Hg-Br and the chemical environment. Thus, in solid $HgBr_2$ containing molecular units with an angle $\sphericalangle(Br1-Hg-Br2) = 179.9(1)°$ only one Raman resonance at $\nu_1 = 184\ cm^{-1}$ is observed. In molten $HgBr_2$ this line shifts to $\nu_1 = 195\ cm^{-1}$ and an additional line appears at $\nu_3 = 271\ cm^{-1}$ [18]. These frequencies are in the same range as the not assigned frequencies observed for $(HgBr_2)_3(As_4S_4)_2$. Especially the finding that all vibrational frequencies of the cage molecules remain unchanged shows that the bonding interactions between mercury and the As_4S_4 cages are extremely small. Otherwise one would find significant shifts for these frequencies.

$(HgBr_2)_3(As_4S_4)_2$ is the second example for an adduct compound of a d^{10} ion and a main group cage molecule with the d^{10} ion being Hg^{2+}. Obviously, this family of compounds contains examples for the coinage metals Cu and Ag and now also for the group 12 cation Hg^{2+}. However, the arrangement of the "ionic part" of the compounds, i.e. the *MX* or the MX_2 part (M = metal, X = halide) and also the composition and the structures of the main group elemen-
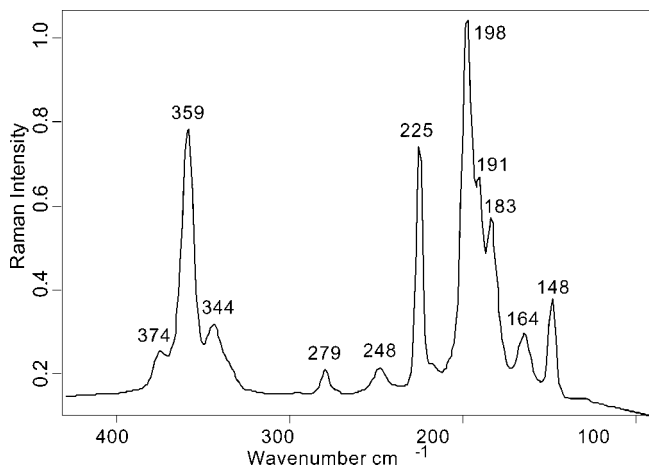
Fig. 3 Raman spectrum of (HgBr$_2$)$_3$(As$_4$S$_4$)$_2$ recorded at room temperature with a resolution of 2 cm^{-1}.

tal part differ significantly in dependence of the given combination of elements. So we did not yet observe any molecular species ZnX$_2$ or CdX$_2$ in similar systems. In case of ZnI$_2$ and CdI$_2$ boracite type structures (Zn$_7$I$_{12}$Q$_2$)(P$_4$Q$_4$) (Q = S, Se) [19] and (Cd$_7$I$_{12}$S$_2$)(As$_4$S$_4$) are found.

[1] A. Pfitzner, *Chem. Eur. J.* **2000**, *6*, 1891.

[2] W. Milius, *Z. Anorg. Allg. Chem.* **1990**, *586*, 175; J. Fenner, *Acta Crystallogr.* **1976**, *B 32*, 3084; W. Milius, A. Rabenau, *Mater. Res. Bull.* **1987**, *22*, 1493.

[3] M. H. Möller, W. J. Jeitschko, *Solid State Chem.* **1986**, *65*, 178.

[4] A. Pfitzner, E. Freudenthaler, *Z. Kristallogr.* **1995**, *210*, 59; A. Pfitzner, E. Freudenthaler, *Angew. Chem.* **1995**, *107*, 1784; *Angew. Chem. Int. Ed. Eng.* **1995**, *34*, 1647; E. Freudenthaler, A. Pfitzner, *Z. Kristallogr.* **1997**, *212*, 103; A. Pfitzner, E. Freudenthaler, *Z. Naturforsch.* **1997**, *52b*, 199; E. Freudenthaler, A. Pfitzner, *Solid State Ionics* **1997**, *101−103*, 1053.

[5] A. Pfitzner, S. Reiser, *Inorg. Chem.* **1999**, *38*, 2451; A. Pfitzner, S. Reiser, H.-J. Deiseroth, *Z. Anorg. Allg. Chem.* **1999**, *625*, 2196; A. Pfitzner, S. Reiser, T. Nilges, *Angew. Chem.* **2000**, *112*, 4328; *Angew. Chem. Intl. Ed. Engl.* **2000**, *39*, 4160; S. Reiser, G. Brunklaus, J. H. Hong, J. C. C. Chan, H. Eckert, A. Pfitzner, *Chem. Eur. J.* **2002**, *8*, 4228; T. Nilges, S. Reiser, A. Pfitzner, *Z. Anorg. Allg. Chem.* **2003**, *629*, 563; G. Brunklaus, J. C. C. Chan, H. Eckert, S. Reiser, T. Nilges, A. Pfitzner, *Phys.*

[6] *Chem. Chem. Phys.* **2003**, *5*, 3768; S. Nilges, T. Nilges, H. Haeuseler, A. Pfitzner, *J. Mol. Struc.* **2004**, *706/1-3*, 89.

A. Pfitzner, S. Zimmerer, *Z. Anorg. Allg. Chem.* **1995**, *621*, 969; A. Pfitzner, S. Zimmerer, *Z. Anorg. Allg. Chem.* **1996**, *622*, 853; A. Pfitzner, S. Zimmerer, *Z. Kristallogr.* **1997**, *212*, 203; A. Pfitzner, S. Zimmerer, *Angew. Chem.* **1997**, *109*, 1031; *Angew. Chem. Int. Ed. Eng.* **1997**, *36*, 982; A. Pfitzner, F. Baumann, W. Kaim, *Angew. Chem.* **1998**, *110*, 2057; *Angew. Chem. Intl. Ed. Engl.* **1998**, *37*, 1955; J. Stanek, P. Fornal, S. S. Hafner, A. Pfitzner, *Acta Phys. Polon.* **A 2001**, *100(5)*, 807, T. Nilges, S. Zimmerer, D. Kurowski, A. Pfitzner, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2809.

[7] A. Pfitzner, M. F. Bräu, J. Zweck, G. Brunklaus, H. Eckert, *Angew. Chem.* **2004**, *116*, 4324; *Angew. Chem. Int. Ed.* **2004**, *43*, 4324.

[8] B. Jayasekera, K. Somaskandan, S. L. Brock, *Inorg. Chem.* **2004**, *43*, 6902; B. Jayasekera, S. L. Brock, A. Y. H. Lo, R. W. Schurko, G. Nazri, *Chem. Eur. J.* **2005**, *11*, 3762.

[9] J. Wachter, *Angew. Chem.* **1998**, *110*, 782; *Angew. Chem. Int. Ed.* **1998**, *37*, 750.

[10] A. Pfitzner, M. F. Bräu, *Angew. Chem.* **2006**, *118*, 4576; *Angew. Chem. Int. Ed.* **2006**, *45*, 4464.

[11] Yu. Minets, Yu. Voroshilov, V. Panko, *J. Alloys. Compd.* **2004**, *367*, 109; J. Beck, S. Hedderich, K. Köllisch, *Inorg. Chem.* **2000**, *39*, 5847. J.-P. Zou, G.-C. Guo, W.-T. Chen, X. Liu, M.-L. Fu, Z.-J. Zhang, J.-S. Huang, *Inorg. Chem.* **2006**, *45*, 6365.

[12] A. Shevel'kov, E. Dikarev, B. Popovkin, *J. Solid State Chem.* **1996**, *126*, 324.

[13] *X-SHAPE*, Crystal Optimization for Numerical Absorption Correction STOE, Darmstadt, **1999**.

[14] *X-RED*, STOE, Darmstadt, **1999**.

[15] Crystal data for (HgBr$_2$)$_3$(As$_4$S$_4$)$_2$: M = 1937.1 g/mol, monoclinic, space group P2$_1$/c, lattice constants (refined from X-ray powder diffraction data):, a = 9.593(5) Å, b = 11.395(5) Å, c = 13.402(5) Å, β = 107.27(3)°, V = 1399(1) Å^3, Z = 2, μ = 35.0 cm^{-1}, θ-range = 2.22-25.03°; reflections collected: 14504, reflections independent: 2470, R$_{int}$: 0.0632, R$_\sigma$: 0.0423, parameters: 115, Goof: 0.949, R_1(all data) = 0.0525, wR_2(all data) = 0.0863, largest residual peaks: 1.358 and −1.070 eÅ^{-3}. Refinement on F^2 with SHELX97 [16]. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-417625.

[16] G. M. Sheldrick, *SHELX*97 Program for the solution and refinement of crystal structures, University of Göttingen, Germany, **1997**.

[17] A. Banerjee, J. O. Jensen, J. L. Jensen, *J. Mol. Struct.* **2002**, *626*, 63.

[18] G. J. Janz, D. W. James, *J. Chem. Phys.* **1963**, *38*, 902.

[19] J. H. Hong, PhD thesis, University of Regensburg **2004**.