Solid-State Structures

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$HgI_2 \cdot As_4S_4$: An Adduct from HgI_2 Molecules and Undistorted As_4S_4 Cages**

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Dedicated to Professor Herbert Jacobs on the occasion of his 70th birthday

Copper(I) halides have been successfully established as a preparative tool for the synthesis of neutral and low-charge molecules of the fifth and sixth main-group elements. Inspired by publications of Rabenau et al.[1–3] as well as Möller and Jeitschko,[4] a whole series of phosphorus,[5] phosphorus chalcogenide,[6] and heteroatomic chalcogen molecules[7] were obtained in a copper halide matrix. Mixed phosphorus–arsenic polymers can also be obtained in this way.[8] The catalytic influence of Cu^+ ions and the structural flexibility of the copper halide are the major reasons for the success of this approach. A possible stabilizing influence of the matrix on the embedded molecules must also be taken into account. Thus,

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the heteroatomic chains $^1_\infty$[SeTe] and $^1_\infty$[STe] decompose and release elemental tellurium upon separation from the copper halide. In contrast, the phosphorus polymers $^1_\infty$[P8]P4(4)[and $^1_\infty$[P10]P2[can be obtained from their adducts $(CuI)_8P_{12}$ and $(CuI)_3P_{12}$, respectively, by separation of the copper halide matrix.[9] The isostructural arsenic-bearing polymers can be obtained in the same way.[8]

After the successful synthesis of a number of otherwise unknown or inaccessible phosphorus chalcogenides in a matrix of copper halides,[6] the next challenging task was the synthesis of binary cages As_4Q_4 (Q = S, Se) that are coordinated as neutral ligands to a transition metal. To date, these molecules, which are also known as minerals, could not be built into complex structures without fragmentation.[10] Reaction of the cage molecules with transition-metal compounds typically leads to cleavage of the As–As bond or further fragmentation. For this kind of reaction, d^{10} ions should be preferable according to the present state of knowledge. A larger number of such adducts are known, especially with Cu^+ ions. However, a few phosphorus chalcogenide adducts are also known with d^0 ions.[11] In order to suppress the formation of pnicogen–halogen bonds, the metals should be used in the form of metal iodides. Herein, we present our first results for the HgI_2/As_4S_4 system.

Mercury forms halides of the composition Hg_2X_2 and HgX_2, which exist in molecular form as the linear molecules X–Hg–Hg–X and X–Hg–X, respectively. At room temperature, these molecules are stable in the solid state only for X = Cl and Br. In contrast, HgI_2 exists in a yellow high-temperature form that is composed of such molecules as well as in two futher modifications that consist of layers of corner-sharing HgI_4 tetrahedra.[12] The red modification is stable at room temperature. With increasing temperature, it is transformed into an orange modification, and ultimately into the yellow form at even higher temperature. In the ternary mercury/arsenic/halogen system, the family of mercury pnicogen halides is known and forms compounds of different compositions and structures.[13] The ternary compounds $Hg_3Q_2X_2$ (Q = S, Se, Te; X = F, Cl, Br, I) are built of Hg_3Q pyramids, sharing common corners to result in one-, two-, or three-dimensional networks.[14] The vacancies in these cationic networks are occupied by the halide counterions. The quaternary compounds Hg_3AsQ_4X (Q = S, Se; X = Cl, Br, I) are built of Hg_3Q pyramids and AsQ_3 units that are connected to cationic layers, between which the halide counterions are embedded.[15] In each of these compounds, covalent bonds are observed exclusively between the mercury and chalcogen atoms, but no contacts between the mercury and halide atoms are formed. Adducts of mercury halides and molecular arsenic chalcogenides have not yet been reported.

The crystal structure of $HgI_2{\cdot}As_4S_4$ was determined from single-crystal X-ray diffraction data. In the crystal, nearly linear HgI_2 molecules and As_4S_4 cages are observed. The coordination sphere of mercury consists of two iodide ions, as well as two sulfur atoms of an As_4S_4 cage with Hg–S distances of 2.984 and 3.236 Å. These adducts form centrosymmetric dimers, in which the mercury atoms coordinate to one sulfur atom of a second cage with a Hg–S distance of 3.596 Å (Figure 1). Because of this irregular environment of mercury,

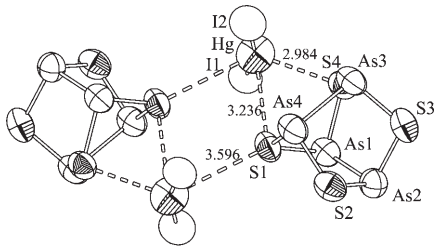

Figure 1. Coordination of mercury atoms by I and As_4S_4 cages in $HgI_2{\cdot}As_4S_4$. Two linear molecules of HgI_2 and the two coordinating As_4S_4 cage molecules are shown. Broken lines show d(Hg–S) in Å. Ellipsoids are set at 80% probability.

the HgI_2 molecules are more significantly bent (I-Hg-I 165.92°) than in yellow mercury iodide (178.3°). Figure 2 shows the three-dimensional arrangement of the dimeric units in the crystal structure. The centers of the dimers form the motif of a distorted cubic close packing. The shortest distances between the dimers are observed between the sulfur atoms and are greater than 3.7 Å.

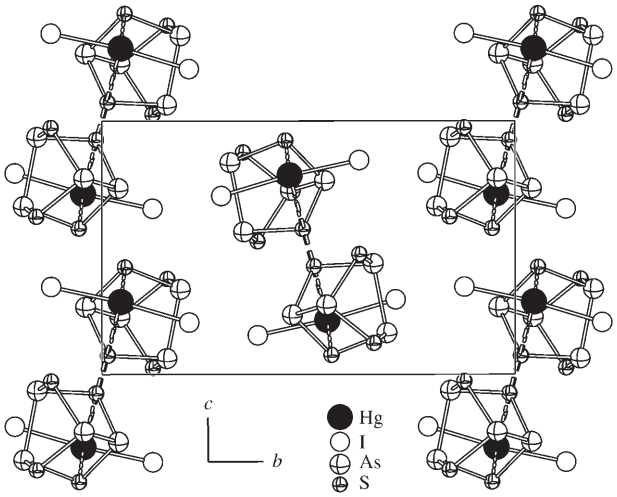

Figure 2. Excerpt of the crystal structure of $HgI_2{\cdot}As_4S_4$. The centers of the dimers shown in Figure 1 form the motif of a distorted cubic close packing.

A question arises about the bonds between the HgI_2 molecules and the As_4S_4 cages, and initial insights can be derived from the crystal structure. In this solid state, all atoms occupy the general position 4*e* in the space group $P2_1/c$. Hence, the ideal symmetry of the As_4S_4 cage is not determined by the space-group symmetry. The point group D_{4d} of the free molecule is nearly preserved in the adduct $HgI_2{\cdot}As_4S_4$. The intramolecular distances show only minor influences from the coordination of the sulfur atoms to the mercury centers. Thus, the bond lengths d(S–As) for the sulfur atoms S1 and S4 are elongated only by 0.02 Å as compared to those of the noncoordinating atoms S2 and S3. The elongation of the bond lengths for S4 is slightly more pronounced than for S1, which might be a result of the shorter Hg–S4 distance (2.984 Å) as compared to Hg–S1 (3.236 Å). If

the decuple of the standard deviation is used as a criterion for significance, the distances d(S–As) are not significantly different. The same observation holds true for the distances d(As–As), for which the differences are also minimal. The Hg–I bond lengths (ca. 2.60 Å) are not significantly different from those in yellow HgI_2 when the higher temperature for the crystal structure determination of yellow HgI_2 is taken into account. As mentioned above, the I-Hg-I angle (165.92°) is, however, distinctly smaller.

As interatomic distance is no real criterion for the strength of a bond, further insight into the influence of the coordination of the As_4S_4 cage to mercury can be obtained by Raman spectroscopy. Earlier investigations showed that vibrational frequencies of such embedded molecular units are quite sensitive to bonding interactions with the environment.[16] The Raman spectrum of $HgI_2{\cdot}As_4S_4$ is shown in Figure 3, and Table 1 gives the assignment of the observed

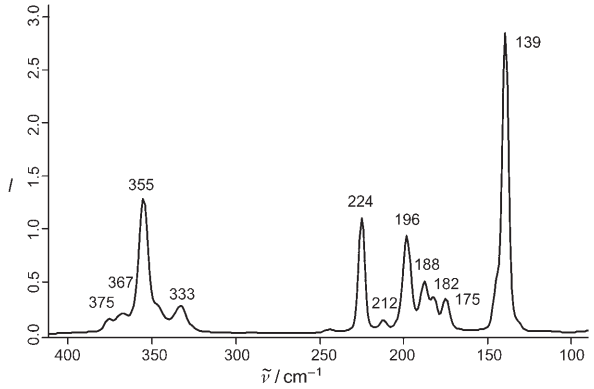

Figure 3. Raman spectrum of $HgI_2{\cdot}As_4S_4$, resolution = 2 cm^{-1}, T = 25 °C. The peaks correspond to As_4S_4 and yellow HgI_2.

Table 1: Comparison of the Raman frequencies for $HgI_2{\cdot}As_4S_4$ and realgar (all frequencies in cm^{-1}).

Assignment	Intensity	$HgI_2As_4S_4$	Realgar[17]
ν(As-S)	very weak	375	376
ν(As-S)	very weak	367	370
ν(As-S)	strong	355	355
ν(As-S)	weak	333	330
ω(As-S)	strong	225	222
δ(As-S)	very weak	212	212
δ(As-S-As)	strong	196	196
ν(As-As)	weak	188	184
–	very weak	182	–
ν(As-As)	weak	175	173
ν(HgI_2)	very strong	139	–

peaks. The linear stretching vibration of the HgI_2 unit (139 cm^{-1}) differs only slightly from the one observed in yellow HgI_2 (133 cm^{-1}), and the different temperatures of the measurements have to be taken into account. The vibrational frequencies of the As_4S_4 cage in $HgI_2{\cdot}As_4S_4$ and the free As_4S_4 cage agree within the experimental errors.[18] Thus, the Raman spectrum of the adduct compound can be interpreted as a combination of the spectra of yellow HgI_2 and realgar (arsenic sulfide). Vibrational spectroscopy demonstrates that the molecular units in this compound show only very weak interactions, in agreement with the structural data.

Finally the question remains as to why no cationic network of mercury and sulfur atoms is formed in $HgI_2{\cdot}As_4S_4$ and why molecular units are favored in contrast to all known compounds in this system. As based on available data for compounds in the ternary and quaternary systems $Hg_3Q_2X_2$ and Hg_3AsQ_4X, one might expect preferential formation of Hg–S bonds and of a polycationic network that incorporates arsenic. Obviously the total energy of the system, which is supposed to be the crucial factor for thermodynamically controlled reactions, is optimum when linear HgI_2 molecules, which are usually unstable at room temperature, are weakly coordinated by As_4S_4 cages. Structural and spectroscopic investigations show that the interactions between the molecular units are very weak. Thus, it is possible to preserve the As_4S_4 cage for the first time in an undistorted manner.

Experimental Section

$HgI_2{\cdot}As_4S_4$ was obtained by heating HgI_2 (Merck, 99.9%), gray arsenic (Merck, 99.999%), and sulfur (Merck, 99.9995%) in the molar ratio 1:4:4 in evacuated quartz ampoules. The reactants were molten at 400 °C and then annealed at 200 °C for two weeks. $HgI_2{\cdot}As_4S_4$ was obtained in good yield as orange crystals along with red HgI_2 and As_4S_4. $HgI_2{\cdot}As_4S_4$ decomposes peritectically at 212 °C and cannot be obtained directly from the melt.

X-ray structure analysis and crystallographic data: $HgI_2As_4S_4$, M_r = 882.31 g mol^{-1}, monoclinic, space group $P2_1/c$, a = 9.433(3), b = 14.986(9), c = 11.624(5) Å, β = 127.72(2)°, V = 1299(1) Å^3 (lattice constants from powder data, transmission geometry, STOE STADI P), Z = 4, ρ_{calcd} = 4.509 g cm^{-3}, $F(000)$ = 1528, T = 293 K, $\lambda(Mo_{K\alpha})$ = 0.71073 Å. Single-crystal diffraction data were collected on a STOE IPDS I: 16111 measured reflections, 2244 independent reflections (R_{int} = 0.0616). Absorption correction with X-Red[19] after optimizing the shape of the crystal with X-Shape,[20] structure solution with SIR92,[21] refinement with SHELX-97,[22] 100 parameters, $R1(I \geq 2\sigma(I))$ = 0.0380, $wR2(I \geq 2\sigma(I))$ = 0.0861, $R1$(all) = 0.0479, $wR2$(all) = 0.0899, GooF = 1.073, residual electron density = 1.675/–1.051 Å^{-1}. 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-416258.

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

Thermal analyses were performed on a Setaram TG-DTA in evacuated quartz ampoules with a heating rate of 2 °C min^{-1}.

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