$(AgI)_2Te_6$ and $(AgI)_2Se_6$: New Composite Materials with Cyclic Te_6 and Se_6 Molecules Stabilized in the “Solid Solvent” AgI

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Dedicated to Prof. Dr. H. Oppermann on the occasion of his 70th birthday

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The new deeply colored solids $(AgI)_2Te_6$ and $(AgI)_2Se_6$ are obtained under hydrothermal conditions in hydroiodic acid. They contain molecules of cyclic hexatellurium and hexaselenium (Te_6, Se_6, respectively, both chair conformations) stabilized in a matrix of AgI. Whereas Se_6 molecules are well known as isolated species in rhombohedral selenium, Te_6 molecules are not known to exist in any modification of that element. They can be stabilized only in an appropriate "solid solvent" like AgI. To date, the new compound $(AgI)_2Te_6$ is the second example only of a composite material containing cyclic Te_6 molecules [the first example is $Re_6Te_{10}Cl_6(Te_6)$].

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Introduction

The stabilization of unusual molecules of group 15 and 16 elements in composite materials based on a matrix of solid CuI has been generally known for about 30 years.[1] In particular, those molecules that do not exist as free molecules in one of the known element modifications of the respective group 15 or 16 element have attracted great attention in the past (for example see ref.[2]). Among others, the scientific interest in the field of those materials is focused on the chemical bonding nature in “nonexistent” molecules of, for example, phosphorus[3] as potential candidates for a suitable stabilizing matrix. The possibility of isolating the molecules from the solid composite by either dissolving the CuI matrix in a suitable liquid or vice versa is another area of interest.[4] The only known example in which AgI serves as a “solid solvent” instead of CuI is AgITe[5] with a Te_∞ screw.

In the course of a sequence of hydrothermal syntheses under strongly acidic conditions (concentrated hydroiodic acid) aiming to form new argyrodites (argyrodite: Ag_8GeS_6) with improved silver ionic conduction by systematic substitution of S with Se/Te and/or halides,[6] we repeatedly obtained deeply colored by-products of initially unknown chemical character. Analytical scanning electron microscopy, in combination with X-ray investigations, revealed the unexpected formation of the two new compounds $(AgI)_2Te_6$ (= $AgITe_3$) and $(AgI)_2Se_6$ (= $AgISe_3$) with cyclic Te_6 and Se_6 molecules (chair conformation) that are embedded in a matrix of AgI. Although we have not been able to produce the title compounds without any contaminants, we decided to publish our preliminary results. The reason for this is that it was explicitly stated in ref.[7] that $(AgI)_2Ch_6$ (Ch: Se, Te) should not exist. Furthermore, to the best of our knowledge, $(AgI)_2Te_6$ is only the second literature example of cyclic Te_6, which, in contrast to Se_6, is *not* known to exist in one of the elemental modifications of tellurium.

Results and Discussion

Both title compounds crystallize isotypically to $CuBrSe_3$[8] but *not* to $CuISe_3$,[9] although the latter was claimed to be more likely in a former paper.[10] The difference between $CuBrSe_3$ and $CuISe_3$ is related to the stacking and coordination of the cyclic Se_6 molecules only, but not to the molecular structure of Se_6.

To date, $(AgI)_2Te_6$ and $(AgI)_2Se_6$ can only be obtained as components of hydrothermal reaction products containing at least two phases. Because of the characteristic color and morphology of the crystalline samples, it is possible to separate them mechanically under the light microscope. Typically single crystals of the tellurium compound show a significantly better quality for structure determinations than those of the selenium compound. The latter crystals are unfortunately characterized by extended intergrowth. On the other hand, an excellent X-ray powder diagram can only be obtained for the selenium compound (Figure 1). It is for

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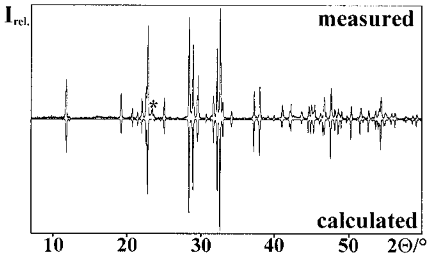

Figure 1. X-ray powder diagram for $(AgI)_2Se_6$ (Cu-$K_{\alpha1}$, Siemens D5000) relative to a calculated pattern based on single crystal data (*: α-Se)

this reason that we restrict the subsequent structure discussion involving structural details of $(AgI)_2Se_6$ (e.g. bond lengths) to reasonably rounded values. Table 1 contains a summary of all relevant X-ray data for $(AgI)_2Te_6$ and $(AgI)_2Se_6$, whereas in Table 2 and 3 the atomic coordinates and relevant interatomic distances are given.

Table 2. Atomic coordinates, Wyckoff notations and equivalent isotropic displacement parameters U_{eq} /10^4 pm^2 for $AgISe_3$ and $AgITe_3$ (second line); U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} *tensor; s.o.f. = 1*

Atom	Wyckoff	x	y	z	U_{eq}
Ag	4*g*	0.75	0.75015(5)	0.25	0.0420(5)
		0.75	0.7057(3)	0.25	0.0333(2)
Se1	4*h*	0.5	0.6023(5)	0.2401(2)	0.0291(5)
Te1		0.5	0.6324(2)	0.21725(6)	0.0218(2)
Se2	8*i*	0.61862(8)	0.3710(3)	0.3749(3)	0.0275(4)
Te2		0.62483(2)	0.35589(8)	0.36338(5)	0.0176(2)
I	4*e*	0.66265(8)	1	0	0.0338(4)
		0.67345(3)	1	0	0.0228(2)

Table 3. Selected interatomic distances *d* [pm] for $AgICh_3$

		$AgISe_3$	$AgITe_3$
Ag	Se/Te2 (2 ×)	268.6(2)	279.7(1)
	I (2 ×)	279.9(1)	288.9(1)
Se/Te1	Se/Te2	234.6(2)	272.9(1)
Se/Te2	Se/Te2	238.1(2)	276.0(1)

The structure projection of $(AgI)_2Te_6$ (Figure 2), which is representative for $(AgI)_2Se_6$ also, clearly shows the composite character of this material with respect to the Te_6/Se_6 units embedded in a matrix of AgI. The silver and iodine atoms form zigzag chains along [001] that are separated by Te_6 units. In addition to the two iodine atoms, each silver atom is coordinated by two tellurium/selenium atoms from different Te_6/Se_6 units that are stacked along [010], such that each Ag has a total coordination number of four. Only four of the six Te/Se atoms of each Te_6/Se_6 unit coordinate

Table 1. Summary of data collection and refinement details for $AgICh_3$ (Ch = Se, Te)

Name	Silver triseleniumiodide	Silver tritelluriumiodide
Chemical formula	$AgISe_3$	$AgITe_3$
Molecular mass [g·mol^{-1}]	471.65	617.57
Temperature [K]	293(2)	
Wavelength [pm]	Mo-K_α, $\lambda = 71.073$	
Crystal system, space group	orthorhombic, *Pmna* (No. 53)	
Cell dimensions [pm]	$a = 1493.5(3)$, $b = 458.9(1)$, $c = 825.4(2)$	$a = 1623.0(3)$, $b = 469.6(1)$, $c = 880.5(2)$
Volume [10^6 pm^3]	565.7(2)	671.1(2)
Z, X-ray crystal density [Mg·m^{-3}]	4, 5.538	4, 6.113
Absorption coefficient [mm^{-1}]	28.156	20.248
$F(000)$	808	1024
Diffractometer	IPDS (Stoe), oriented graphite monochromator	
Scan type	φ	
Crystal size [mm]	0.26 × 0.06 × 0.03	0.31 × 0.01 × 0.01
Measured range (Θ) [°]	2.82−30.52	2.63−30.33
Index ranges	$-21 \le h \le 17$, $-6 \le k \le 6$, $-11 \le l \le 11$	$-23 \le h \le 22$, $-5 \le k \le 6$, $-11 \le l \le 12$
Measured reflections; unique; significant	1991; 748; 442	5406; 1048; 853
$R_{int.}$, R_σ	0.1294, 0.0961	0.0835, 0.0440
Completeness to Θ = 30.33°	82.6%	99.3%
$T_{min.}$, $T_{max.}$	0.1576, 0.8258	0.1576, 0.8258
Structure solution	Direct methods[a]	
Structure refinement	Full-matrix least-squares on F^2[b]	
Data/restraints/parameter	748 / 0 / 27	1048 / 0 / 27
$S(F^2)$	0.901	0.995
Absorption correction	numerical[c]	
R_1, $wR2$ [$1 > 2\sigma(I)$]	0.0518, 0.1437	0.0285, 0.0694
R_1, $wR2$ (all data)	0.0879, 0.1581	0.0388, 0.0726
Extinction coefficient	0.005(2)	0.0005(2)
$\rho_{min.}$, $\rho_{max.}$ [10^{-6}e·pm^{-3}]	−2.0(5), 1.6(5)	−1.8(4), 2.5(4)

[a] G. M. Sheldrick, SHELXS-97, Program for the solution of Crystal Structures, Universität Göttingen, **1997**. [b] G. M. Sheldrick, SHELXL-97, Program for Structure Refinement, Universität Göttingen, Germany, **1997**. [c] STOE & CIE, X-SHAPE 1.06, − Crystal Optimisation for Darmstadt, **1999**.

directly to a silver atom. This feature is consistent with the corresponding coordination for the cyclic Se_6 units in $(CuBr)_2Se_6$ and $(CuI)_2Se_6$, and indicates a bonding interaction between Ag and Te/Se (see below).

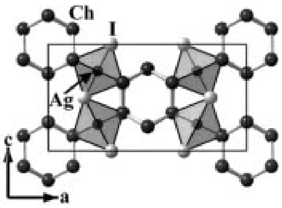

Figure 2. Crystal structure of $(AgI)_2Ch_6$ (Ch: Se, Te) projected along [010]; the coordination of Ag (2 × Ch, 2 × I) is emphasized by a shaded polyhedral representation; the distance between neighboring Ch_6 molecules along [010] corresponds to the lattice constant *b*

In further compounds with cyclic Se_6 molecules, for example $(PdCl_2)Se_6$ and $Rb_3AsSe_4(Se_6)_2$ (see ref.[11,12] and papers cited therein), *differences* in the coordination of the Se_6 units with respect to the matrix are found relative to the title compounds [e.g. in $(PdCl_2)Se_6$ only *two* of the six Se atoms are coordinated to Pd].

However, in the cluster compound $Re_6Te_{16}Cl_6$ [13] [= $Re_6Te_{10}Cl_6(Te_6)$], the analogous Te_6 molecules are *similar* to those in $(AgI)_2Te_6$ as *four* of the six Te atoms are coordinated directly to surrounding Re_6 clusters. The comparison with $(AgI)_2Te_6/Se_6$ has to be restricted to the cyclic Te_6 molecules only, because $Re_6Te_{16}Cl_6$ is a unique cluster compound with a completely different structural chemistry.

A closer inspection of the bond lengths (Table 3 and Figure 3) shows that the average Te−Te distance for Te_6 in $(AgI)_2Te_6$ ($d_{av(Te-Te)} = 273.9$ pm) is slightly shorter than for the infinite helices in α-Te[14] ($d_{Te-Te} = 283.4$ pm) and for Te_6 in $Re_6Te_{10}Cl_6(Te_6)$ ($d_{av} = 281$ pm). Interestingly, the $d_{av(Se-Se)}$ value of 237 pm for Se_6 in $(AgI)_2Se_6$ is closer to, for example, Se_6 in $(CuBr)_2Se_6$ ($d_{av(Se-Se)} = 237$ pm), Se_6 in $(PdCl_2)Se_6$ ($d_{av(Se-Se)} = 236$ pm) and Se_6 in rhombohedral selenium[15] ($d_{av} = 235.6$ pm]. For a more detailed discussion of the geometry see ref.[6]

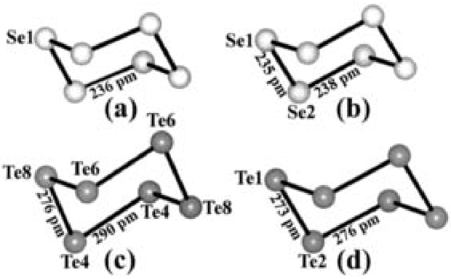

Figure 3. Cyclic Ch_6 molecules (chair conformation) in rhombohedral selenium (a), $(AgI)_2Se_6$ (b), $Re_6Te_{10}Cl_6(Te_6)$ (c), and $(AgI)_2(Te_6)$ (d)

In addition, the bond length $d_{Ag-I} = 288$ pm in $(AgI)_2Te_6$ [280 pm in $(AgI)_2Se_6$] compares well with $d_{Ag-I} = 281.7$ pm in β-AgI.[16]

The bond lengths $d_{Ag-Te/Se}$ are somewhat puzzling because the values $d_{Ag-Te} = 279.6$ pm and $d_{Ag-Se} = 269$ pm are in the range expected for covalent interactions $d_{Ag-Te/Se}$ (sum of atomic radii for Ag^0 and Te^0/ Se^0: 288/261 pm) in a variety of compounds (for an overview concerning the range of experimental d_{Ag-Te} see ref.[17]). This finding does not seem to be consistent with the conventional formulation $Ag^{1+}I^{1-}(Te_6)^{\pm 0}$ and $Ag^{1+}I^{1-}(Se_6)^{\pm 0}$, and suggests a van der Waals interaction between Ag and Te (Se) rather than a covalent one, and thus emphasizes the special bonding character in composite materials such as the title compounds. A similar ambiguity was found and discussed in the context of those materials that contain copper halides as a stabilizing matrix instead of silver iodide.[2]

Calculations of densities of states, crystal orbital Hamilton populations (COHP) and ELF representations (ELF: electron localization function,[18] Figure 4) based on the TB-LMTO-ASA formalism[6,19] clearly show significant differences between the Te (Se) atoms that are coordinated directly to Ag (Te2, Se2) and those that are not (Te1, Se1). From Figure 4 it is evident that, in contrast to Te1 (Se1), *one lone pair* of each Te2 (Se2) is involved in a bonding interaction with neighboring Ag atoms, resulting in a charge transfer from Te2 (Se2) to Ag. Further, it is interesting to note that the COHP values for the electronic states that are dominated by the cyclic Te_6 (Se_6) indicate that these electronic states are exclusively bonding below the Fermi energy (E_F) with an unusual steep transition to antibonding states immediately above E_F. This finding might be one of the keys to a deeper understanding of why Te_6 is stabilized in appropriate matrices like AgI only and is not known as a free molecule in an elemental Te modification. Raman and IR spectroscopic measurements, together with more detailed calculations of the electronic structure, are currently under progress.

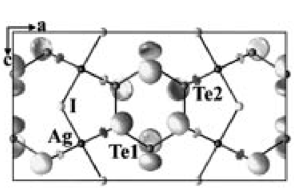

Figure 4. Projection of the crystal structure of $(AgI)_2Te_6$ with a superimposed ELF pattern (0.9-localization domain); the polarizing interaction between Ag^+ and *one* lone pair at each of the four Te2 is indicated by a significant reduction in the effective volume of the interacting lone pair relative to those of the noninteracting lone pairs

Experimental Section

$AgISe_3$ was repeatedly obtained as major component of a hydrothermal reaction product. A stoichiometric mixture of the roughly homogenized elements [silver powder (Degussa), selenium metal grey (Fluka AG- 99.995%, typical weight sum: 0.5 g)] was placed in a quartz tube ($l \approx 8$ cm, $ø = 8$ mm, $V \approx 4$ cm^3), together with about 0.5 mL of concentrated HI (Merck- 57%). Subsequently, the glass tube was sealed and transferred to a steel autoclave (Berghof BAR 845, internal volume: approximately 240 cm^3). The pressure

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balance inside the autoclave was achieved with water as counter pressure medium. The autoclave was then heated up to 220 °C and kept at this temperature for 5 days. Finally, the temperature was lowered at a rate of 2 °C/h down to room temperature. Red transparent hexagonal crystals of $(AgI)_2Se_6$, characterized by strong intergrowth were separated mechanically from the other products under the light microscope. $(AgI)_2Se_6$ is not significantly air sensitive. Crystals of the grey-metallic-black $(AgI)_2Te_6$ were obtained by a similar procedure [tellurium powder (Johnson Matthey GmbH, 99.5%)] with traces of GeO_2 as "mineralizer". The chemical composition of the selected crystals was checked by EDX analyses prior to X-ray structure determination. Further details of the crystal-structure investigation of $(AgI)_2Se_6$ and $(AgI)_2Te_6$ may be obtained from the Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-414116 and -414117.

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