Polychalcogenoaurates(I) with pseudo-onedimensional structures: Preparation and crystal structure of Cs₂Au₂Se₃

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ABSTRACT. Cs₂Au₂Se₃ was obtained as red platelike crystals by reacting a stoichiometric mixture of Cs₂Se, Au and Se at 670K. It crystallizes in space group C2/c, Z = 4 with a = 9.769(5) Å, b = 13.44(1) Å, c = 7.178(3) Å, β = 90.69(1)°. The crystal structure was determined from single crystal data and refined to a conventional R of 0.042 for 674 Fo's and 34 variables. The characteristic structural feature of this new selenoaurate is the formation of infinite helical anionic chains, $\frac{1}{\infty}$ -[AuSeAuSe₂]²⁻ which run parallel to [001] and are separated by the alkali cations. The average Au-Se bond length is 2.402 Å, the bond length in the Se₂-unit is 2.436 Å. Au...Au contacts of 3.200 Å are formed within the anionic chains. The cesium atoms are coordinated to seven Se in an irregular configuration.

INTRODUCTION

The propensity of gold metal to react in mixtures with alkalipolychalcogenides [1] has led to the detection of a still increasing number of alkali chalcogenoaurates in the last decade. With the exception of the Au(III) compounds NaAuSe₂ [2], KAuSe₂ [2], Na₅AuSe₁₂ [3],

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K₃AuSe₁₃ [4] and Na₃AuSe₈ [5] the predominating oxidation state of gold in these compounds is +1. The d¹⁰ ion Au(I) has an unparalleled tendency to adopt a linear twofold coordination which has been explained by the small energy difference between the 5d and the 7s orbital energies [6]. This and the often observed short Au-Au distances which are ascribed to attractive d¹⁰-d¹⁰ interactions [7] make synthetic and structural studies in this field rewarding. The complex anions found in the ternary compounds show a puzzling diversity ranging from discrete moieties like the linear [O-Au-Ol³⁻ anions of Na₃AuS₂ [8], K₃AuSe₂ [9] or Na₃AuSe₂ [3], the [Au₄Se₄]⁴ rings of NaAuSe [10] or the cage type $[Au_6S_5]^{4-}$ anions of $A_4Au_6S_5$ (A = K, Rb) [11,12] to infinite nets like in AAu_3Q_2 (A = Rb,Cs, Q = S,Se) [13] or Cs₄Au₆S₅ [12]. The majority of the chalcogenoaurates, however, are characterized by infinite anionic chains where both, Au and the chalcogen atoms are in twofold coordinations. Linear zig-zag chains are the characteristic groups of the equiatomic ternary compounds AAuQ (A = K,Rb,Cs; Q = S, Se) [14-16], RbAuTe and CsAuTe [15]. Conformationally different [AuQ]⁻ chains are found in Na₇Au₅S₆ [17]. Infinite chains may also be formed with polychalcogenide ligands ranging from Se₃ in CsAuSe₃ [2] or Se₅ in KAuSe₅ [4] to Se₄ and Se₈ in the complex $[Se_4AuSe_8Au]^{2-}$ chains which are an independent species of the anionic partial structure in mixed valent chalcogenoaurate Rb₆Au₆Se₄₆ [18].

EXPERIMENTAL

Starting materials for the preparation of the title compound were the high purity elements (Cs 99.98%, Se 99.5%, Alfa Ventron, Au: 99.98%; Demetron). In a first step of the synthesis the binary alkali chalcogenide Cs₂Se was prepared by reacting the elements in liquid ammonia allowing a 5% excess of the alkali metal. The reaction product was dried under vacuum and annealed at 250°C in order to remove the free alkali metal. Homogeneity of the reaction product was checked through their powder diffraction diagram. 0.3723 g Cs₂Se, 0.4253 g Au and 0.1705 g Se were mixed in an Argon glove box and sealed into a silica tube under a vacuum of 10^{-2} Pa. The sample was gradually heated to 670 K, held at this

103

temperature for one week and finally cooled to ambient temperature at a controlled rate of $2Kh^{-1}$. The reaction product was obtained as an ingot, which after crushing, yielded red thin platelets of the title compound which were sensitive to moisture and air and had hence to be handled under inert conditions. According to its Guinier diagram (CuK α_1 -radiation) the reaction product was nearly pure Cs₂Au₂Se₃, interfering diffraction lines were identified as due to minor amounts of CsAuSe₃[2].

Preliminary roentgenographic investigations were performed with Weissenberg techniques (CuK α -radiation) which revealed Laue symmetry 2/m. The systematic extinctions $hk\ell$: $h+k \neq 2n$ and $h0\ell$: $\ell \neq 2n$ led to C2/c or Cc as possible space groups. For the determination of the crystal structure a crystal of the dimensions $0.05 \times 0.05 \times 0.03$ mm³ was sealed into a thin walled glass capillary and mounted on a four circle diffractometer (Enraf Nonius CAD4) operated with graphite monochromated MoK α -radiation ($\lambda = 0.71073$ Å). Reflection intensities were collected at 294K over one quadrant of the reflection sphere up to 2θ = 54° applying ω -2 θ scans mode (scan-width 1.2°+0.35°tan θ , maximum scan time 120s). Three periodically determined control reflections showed only statistical variations. Cell dimensions were refined from the angular values of 25 reflections ($28^\circ \le 2\theta \le 35^\circ$) carefully centred on the diffractometer.

The crystal structure was solved in space group C2/c using direct methods (MULTAN-82) [19]. The E-syntheses calculated from 196 $E \ge 1.234$ phased through 3031 triplet relations, revealed all atomic positions. Isotropic least squares refinements (F-refinement) converged rapidly at a conventional R-value of 0.052. The final refinements, allowing anisotropic atomic displacements and assigning weights according to the counting statistics led to R = 0.042 (R_w = 0.039). No physically significant peaks were found in the final difference Fourier synthesis. Crystal data and further details on the structure refinement are listed in Table I. All calculations were performed with programs of the MolEN crystallographic software package [20]. Atomic scattering factors for the neutral atoms and coefficients for the anomalous dispersion correction were taken from the

International Tables [21]. Absorption effects were accounted for by an empirical correction [22].

The final atomic positions and anisotropic temperature factors are listed in Table II: Selected interatomic distances and bond angles are compiled in Table III. Lists of observed and calculated structure factors have been deposited with the Fachinformationszentrum Karlsruhe, Eggenstein-Leopoldshafen, D-76344 Karlsruhe under CSD-no.407749.

Compound	Cs ₂ Au ₂ Se ₃			
Pearson Symbol	mC28			
Space Group	C2/c			
Z	4			
a (Å)	9.769(5)			
b (Å)	13.44(1)			
c (Å)	7.178(3)			
β (°)	90.69(1)°			
V (Å ³)	942.4			
d_x (gcm ⁻³)	6.32			
M _r	896.62			
$\mu_{(MoK\alpha)} (cm^{-1})$	500.08			
hkl-range	$-12 \le h \le 12, -1 \le k \le 17, 0 \le \ell \le 9$			
Measured reflections	1235			
Unique reflections:	1011			
R _{int}	0.024			
absorption correction (min., max.)	0.810, 1.213			
Observed reflections $> 3\sigma(Fo^2)$	674			
Variables	34			
$\mathbf{R} = \sum \mathbf{F}_{\mathbf{o}} - \mathbf{F}_{\mathbf{c}} / \sum \mathbf{F}_{\mathbf{o}} $	0.042			
$R_{w} = \left[\sum w F_{o} - F_{c} ^{2} / \sum w F_{o} ^{2}\right]^{\frac{1}{2}}$	0.039			
$\mathbf{w} = \left[\sum (F_0^2)^2 + 0.01 \ (F_0^2)^2\right]^{-\frac{1}{2}}$				
residual electron density (eÅ-3)	2.15 /-2.58			

Table I: Crystallographic Data for Cs₂Au₂Se₃

104

Atom	WP	x	у	Z	B _{eq}
Cs	8f	0.2355(2)	0.1050(1)	0.1384(2)	2.49(3)
Au	8f	0.0639(1)	0.29075(8)	0.4563(1)	2.18(2)
Se(1)	4e	0.000	0.4240(3)	0.250	2.83(8)
Se(2)	8f	0.3917(3)	0.3443(2)	0.3319(4)	2.62(5)

Table II: Positional parameters and temperature factors for Cs₂Au₂Se₃

$$B_{eq} = \frac{8\pi^2}{3} \sum_{i} \sum_{j} U_{ij} \mathbf{a}_i^* \mathbf{a}_j^* \mathbf{a}_i \mathbf{a}_j$$

Table III: Interatomic Distances (Å) and Bond Angles for Cs₂Au₂Se₃

Coordination of the Cs^+ -cation

Cs	Se(1)	3.631(3)	Cs	Au	3.750(2)
Cs	Se(2)	3.647(3)	Cs	Au	3.759(2)
Cs	Se(2)	3.724(3)	Cs	Au	3.788(2)
Cs	Se(2)	3.815(3)	Cs	Au	3.899(2)
Cs	Se(1)	3.844(2)			
Cs	Se(2)	4.051(3)			
Cs	Se(2)	4.072(3)			

Geometry of the $\frac{1}{\infty} [Au_2Se_3]^{2-}$ anion

Au	Se(1)	2.401(3)	∠Se(1)	Au	Se(2)	175.4(1)°
Au	Se(2)	2.404(3)	∠Au	Se(1)	Au	83.6(1)°
Au	Au	3.200(2)	∠Au	Se(2)	Se(2)	98.8(1)°
Au	Se(2)	3.412(3)				
Au	Se(2)	3.674(3)				
Se(2)	Se(2)	2.434(6)				

Shortest interanionic contacts

Au	Au	3.843(2)	Se(1)	Se(2)	4.010(3)
			Se(1)	Se(1)	4.130(4) 2 ×

RESULTS AND DISCUSSION

The polyselenoaurate(I) Cs₂Au₂Se₃ crystallizes with a new structure whose outstanding feature is the formation of infinite helical chains, $\frac{1}{m}$ - $[Au_2Se_3]^2$. These chains run through the structure along [001]. As can be seen from Fig.1 the chains are arranged in slabs parallel to (100) which are separated from each other by layers of alkali cations. In contrast to the pseudo-onedimensional chalcogenoaurates(I) AAuSe (A = K [14], Rb [16], Cs [15]), CsAuSe₃ [2] and KAuSe₅ [2,4] the anionic chains of Cs₂Au₂Se₃ contain two different chalcogen species, Se and Se₂, which are coordinated to the gold atoms according to the sequence ... AuSe₂AuSe... (Fig. 2). The gold atoms are in an almost linear coordination through Se. The two crystallographically independent Au-Se-bond lengths (2.401(3) Å and 2.404(3) Å) are identical within experimental error and compare well with the Au-Se bonds found in other alkali selenoaurates(I) while the Se-Se bond in the diselenide group $(d_{Se(2)-Se(2)} = 2.434(6) \text{ Å})$ is significantly larger than in trigonal Se (2.373 Å) [23]. The reason for this difference may be due to matrix effects of the packing. A comparison with other selenoaurates containing polyselenide groups shows, that the bonds from the ligand Seatom to its homonuclear neighbour are in the narrow range of 2.343 Å in K₃AuSe₁₃ [4] and Na₅AuSe₁₂ [3] to 2.385 Å in CsAuSe₃ [2]. The elongation of the bond lengths of diselenide groups - due to intramolecular strain - has, however, been observed in the selenoaurate rings of $(Ph_4P)_2[Au_2(Se_2)(Se_3)]$ $(d_{Se-Se} = 2.402(5) \text{ Å})$ and $(Ph_4P)_2[Au_2(Se_2)(Se_4)] (d_{Se-Se} = 2.46(1) \text{ Å}) [24].$

The bond angles on the selenium atoms differ appreciably from each other. While the angle \angle .Au-Se(2)-Se(2) of 98.8(1)° corresponds well with the bond angle on the ligand Se-atom in CsAuSe₃ (\angle Au-Se-Se = 98.4(1)°)[2] the \angle Au-Se(1)-Au is considerably smaller (83.6(1)°). Acute bond angles on the chalcogen atoms are a characteristic structural feature of the anionic zig-zag chains $\frac{1}{\infty}$ -[AuQ]⁻ of the equiatomic chalcogenoaurates AAuQ. They allow the formation of relatively short Au-Au contacts which range from 2.968 Å in RbAuTe to 3.431 Å in CsAuSe [15] indicating attractive d¹⁰-d¹⁰ interactions between the gold atoms. In contrast to AAuQ where these interactions extend infinitely along the chain direction and

CsAuSe₃, which lacks short Au-Au-distances, the [AuSeAuSe₂]-chain of Cs₂Au₂Se₃ is unique since it allows the formation of discrete Au-Au pairs (Fig. 2) with a distance d_{Au-Au} of 3.200(2) Å. The next nearest Au-Au contact is an interchain contact of 3.843(2) Å. Though this value rules out any significant aurophilic interactions it is nevertheless the shortest contact between the anionic chains. Interanionic Se-Se-contacts are found with distinctly larger distances of 4.010(3) Å and 4.130(4) Å, respectively.



Fig. 1: The crystal structure of Cs₂Au₂Se₃ in perspective projection along [001], (Cs-, Au- and Se-atoms are represented by shaded, full and open circles, resp.)

The cesium atoms which are arranged in almost planar layers occupy the nodes of a distorted 6^3 -net. They are coordinated to seven selenium atoms in the distance range from 3.63 Å to 4.07 Å, a relatively low coordination for Cs⁺. The coordination polyhedron is irregular and can be conceived as a distorted octahedron with one of the apical atoms replaced through a diselenide group side-on coordinated to the central atom. The coordination of Cs⁺ is completed by four gold atoms at distances between 3.75 Å to 3.90 Å. Similar distances - which appear rather short with respect to the sum of the van der Waals radii of the two atoms - have also been observed in CsAuSe₃.



Fig. 2: Clinographic view of the $^{1}_{\infty}$ -[Au₂Se₃]²⁻ chains. Short Au-Au contacts are indicated by shaded lines.

The $\frac{1}{\infty}$ -[Au₂Se₃]²⁻ anion may be considered as the final product obtained through oxidative polymerisation of discrete V-shaped [SeAuSeAuSe]⁴⁻ anions. Though anions of this type have so far not been observed in the alkali chalcogenoaurates known so far, they might well be present in cation rich compounds of the sections A_{2x}Au_{2-x}Q. Anionic groups have recently been found in the chemically related thiocuprate Na₄Cu₂S₃ [25]. Our present investigations in the A-Au-Q systems (A = Na, K, Rb, Cs; Q = S, Se, Te) give indications on the formation of a number of cation rich alkali chalcogenoaurates(I); their structures, however, have so far not been elucidated.

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UR. J. SOLID STATE INORG. CHEM.

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