NaAuSe—A selenoaurate with cyclic anions

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Abstract

Transparent deep orange crystals of NaAuSe were obtained by fusing together stoichiometric amounts of Na_2Se, Au and Se at 730 °C, followed by slow cooling of the melt. NaAuSe is tetragonal, $tI48$, space group $I4_1/amd$ (No. 141), $Z = 16$ with $a = 9.772(2)$ Å, $c = 11.469(2)$ Å. The crystal structure was determined from single crystal diffractometer data and refined to a conventional R of 0.030 (276 F_o values, 20 variables). An outstanding feature of the crystal structure is the formation of discrete anions, which consist of V-shaped eight-membered rings, $[Au_4Se_4]^{4-}$. Au is in an almost linear coordination by Se ($\angle$Se–Au–Se: 168.31°, d_{Au-Se}: 2.457(2) Å); the bond angle on Se is only 82.9(1)°. The crystal structure is based on a c.c.p.-packing of the chalcogen atoms.

Keywords: Crystal structure; Chalcogenides; Selenium; Gold; Sodium

1. Introduction

The ternary alkali gold chalcogenides, which can easily be prepared by fusion reactions, constitute a small but nevertheless structurally interesting group of compounds. Thus, the crystal structure of Na_3AuS_2 [1] and $Na_7Au_5S_6$ [2] are extraordinary in being based on a filled up b.c.c.-packing of the sulfur atoms. $K_4Au_6S_5$ [3] is remarkable since it contains discrete tricyclic anionic cages.

A number of novel alkali gold selenides and polyselenides with unusual structural features, $NaAuSe_2$, $KAuSe_2$, Na_3AuSe_8 and K_3AuSe_{13}, has been prepared from polyselenide melts [4]. They merit particular interest since they are the first examples for this class of compounds which contain gold in the +III oxidation state.

Thanks to a recent systematic study [5], all equiatomic alkali gold chalcogenides AAuX (A = K, Rb, Cs; X = S, Se, Te) are now structurally characterized. With the exception of KAuTe [6] and NaAuTe [5], which adopt a ternary variant of the Ni_2In structure type, they are characterized by infinite anionic zig-zag chains, $-[AuX]^-$, with linearly coordinated gold atoms, as first described for KAuS and KAuSe [7]. Apart from NaAuTe no equiatomic gold chalcogenides of the lighter alkali metals have been reported.

NaAuSe, which was obtained during investigation of the Na–Au–Se system, crystallizes with a new structure containing discrete anions. Its structural features will be presented below.

2. Experimental

2.1. Synthesis

High purity elements (Na rods, 99.9%; Au flake, 99.999% Se pellets, 99.999%) were used as starting materials. The synthesis was performed in two steps. In the first, the binary compound Na_2Se was prepared by reacting the elements (in the molar ratio 2.05:1) in carefully dried liquid ammonia using a modified Föppl apparatus [8]. The reaction product was annealed at 350 °C under high vacuum in order to remove traces of ammonia and Na metal. A white colored product without impurities due to polyselenides was obtained by this method. For the preparation of the ternary compound, stoichiometric amounts of Na_2Se, Au and Se were intimately mixed in an argon-dry box and sealed into an evacuated silica ampoule. The mixture was allowed to react at 750 °C for two days, the thermal treatment was followed by a controlled cooling to ambient temperature (cooling rate 2 °C h^{-1}).

The microscopic investigation of the crushed reac-

tion product showed that the gold metal had reacted completely. The sample was of heterogeneous appearance, its major component was a deep orange crystalline phase which was identified as NaAuSe in the course of the structure determination. In order to keep absorption effects low, a very small crystal with uniform dimensions (approximately $0.06 \times 0.06 \times 0.07$ mm^3) was isolated and sealed into a thin walled glass capillary. Owing to the air sensitivity of the reaction product, all operations were carried out under inert conditions.

2.2. Structure determination

Preliminary crystallographic investigations were performed by Weissenberg and precession techniques. They revealed a tetragonal unit cell, Laue symmetry $4/mmm$. From the serial extinctions hkl: $h + k + l \neq 2n$, $hk0$: $h \neq 2n$ and hhl: $2h + l \neq 4n$ the space group was uniquely determined as $I4_1/amd$ (No. 141). The intensity data collection was performed on a CAD4-diffractometer (Enraf-Nonius). Graphite monochromated Mo Kα ($\lambda = 0.71069$ Å) from a sealed tube operated at 50 kV, 32 mA was used as radiation. The intensities were determined by conventional BPB scans over one octant of the reflection sphere ($2° < 2\theta < 56°$; ω–2θ scan mode, scan width $0.8° + 0.35°$ tan θ) allowing a maximum scan time of 180 s per reflection. The intensities of three control reflections showed only statistical fluctuations during the period of the data collection, indicating a good crystal and electronic stability. A total of 766 reflections was determined. Precise lattice dimensional parameters (Table 1) were calculated from the positions of 24 high

Table 1
Crystallographic data for NaAuSe

Pearson symbol $tI48$
  $a = 9.772(2)$ Å
  $c = 11.469(2)$ Å
Space group $I4_1/amd$ (No. 141)
  $Z = 16$
  V (Å^3) = 1095.1
  d_x (g cm^{-3}) = 8.28
  $M_r = 298.92$
  μ(Mo Kα) (cm^{-1}) = 759.75
  $F(000) = 2263$

Structural refinement
Unique reflections	369
Observed reflections	276
Cut-off	3.0 $\sigma(F_o)$
Variables	20
$R = \Sigma \|F_o\| - \|F_c\|/\Sigma^\circ\|F_o\|^\circ$	0.030
$R_w = [\Sigma w(\|F_o^\circ\| - F_c\|^\circ)^2/\Sigma w^\circ\|F_o^\circ\|^2]^{1/2}$	0.036
$w = [\sigma(F_o^2)^2 + (0.005F_o^2)^2]^{-1/2}$	
Residual electron density (eÅ^3)	1.43

Table 2
Atomic coordinates and equivalent isotropic thermal parameters for NaAuSe (origin at $2/m$, ESDs in parentheses)

Atom	W.P.	x	y	z	B_{eq}
Na(1)	8e	0.500	0.250	−0.0520(6)	2.0(6)
Na(2)	8c	0.000	0.500	0.000	2.2(2)
Au	16g	0.33402(6)	0.58402	0.875	1.501(6)
Se	16h	0.2034(2)	0.750	−0.0086(1)	1.41(3)

$$B_{eq} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j.$$

angle reflections ($34° < 2\theta < 40°$), carefully centered at four different settings.

Averaging of the reduced data yielded a unique data set of 369 symmetry independent reflections ($R_{int} = 0.058$). The crystal structure was solved by direct methods (MULTAN 11/82 [9]). Isotropic refinement with the full (redundant) data set rapidly converged to $R = 0.061$. At this stage an empirical adsorption correction (DIFABS [10]) was applied. The following refinements with anisotropic temperature factors converged to $R = 0.030$, the final shift over error ratio was less than 0.005. A final difference Fourier synthesis showed no physically significant peaks. Further details on the refinement are given in Table 1. The final atomic positions and equivalent isotropic temperature factors are listed in Table 2. Interatomic distances and selected bond angles are summarized in Table 3. Structure factor tables and a list of anisotropic thermal parameters have been deposited under the deposition number CSD 56582 with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information m.b.H., D-76344 Eggenstein Leopoldshafen 2, Germany.

All calculations were performed on a DEC Microvax-3520 computer using programs of the MOLEN crystallographic software package [11]. Atomic scattering factors for the neutral atoms and coefficients for anomalous dispersion effects were taken from International Tables for X-ray Crystallography [12].

3. Discussion

An outstanding feature of the crystal structure of NaAuSe, which distinguishes it from the other equiatomic alkali gold chalcogenides [5–7], is the formation of discrete anionic moieties $[Au_4Se_4]^{4-}$. As can be seen from Fig. 1, these groups consist of highly symmetrical (point symmetry S_4) eight-membered rings of a unique V-shaped ('butterfly type") conformation. Au is in an almost linear coordination ($\angle$Se–Au–Se: 168.31(7)°) the bond angle on the Se atoms is considerably smaller than 90° ($\angle$Au–Se–Au:

Table 3
Interatomic distances (up to 4 Å) and bond angles (°) for NaAuSe
(ESDs are given in parentheses)

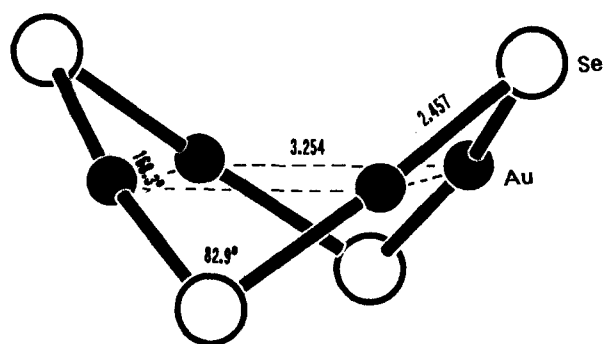|	
Na(1)–Se	2.988(4) × 2
Na(1)–Se	2.935(9) × 2
Na(1)–Au	3.083(9) × 4
Au(1)–Au	3.743(3) × 4
Na(1)–Na(2)	3.331(9) × 2
Se–Na(1)–Se	85.7(3)
Se–Na(1)–Se	100.2(2) × 4
Se–Na(1)–Se	152.0(5)
Na(2)–Se	3.015(2) × 2
Na(2)–Se	3.162(2) × 4
Na(2)–Au	3.665(1) × 4
Se–Na(2)–Se	78.40(4) × 2
Se–Na(2)–Se	85.33(5) × 4
Se–Na(2)–Se	94.67(5) × 4
Se–Na(2)–Se	101.60(4) × 2
Se–Na(2)–Se	180 × 3
Au–Se	2.457(2) × 2
Au–Se	3.833(1) × 2
Au–Au	3.254(1) × 2
Au–Au	3.311(1) × 2
Se–Au–Se	168.31(7)
Se–Se	3.995(2)
AU–Se–Au	82.94(7)

Fig. 1. The eight-membered anionic rings of NaAuSe.

82.94(7)°). The Au–Se bond length is 2.457(2) Å, comparable with that of $[(Ph_2PAu)_2Se\text{-}(pC_6F_4Cl)]^+SbF_6^-$ (2.458(2) Å) [13], but distinctly larger than in KAuSe (2.414(1) Å) [7]. Within the ring all Au atoms lie on the same plane, hence each Au has two homoatomic contacts (d_{Au-Au}–3.254 Å) to its ring neighbors.

The Na atoms occupy two crystallographically different positions (8e and 8c respectively) with very different chalcogen environments. The coordination polyhedron around Na(1) is a grossly distorted tetrahedron of symmetry C_{2v}. As will be shown below, this distortion is essentially due to packing effects, its main

characteristic is the large difference (approximately 1.8 Å) between the lengths of the two (viewed along [001]) opposing edges. The Na(1) atom is displaced from the center of the tetrahedron towards the longer edge, so that the Na(1)–Se distances lie close together (d_{Na-Se} = 2.96 Å). Na(2) occupies the center of a skew octahedron, the distances to the four Se atoms of the equatorial plane (virtually parallel to (001)) being considerably longer than those to the axial Se atoms (3.162 Å and 3.015 Å respectively).

In the [110] direction the Na(1)Se$_4$ tetrahedra are connected with the Au$_4$Se$_4$ rings via common selenium atoms to form an open layer (Fig. 2). The translation period c comprises four layers, crystallographically related to the 4$_1$ screw axes. The layers are intercalated by rows of Na(2) ions running parallel to the tetragonal axes.

The structural principle which underlies the atomic arrangement of NaAuSe is a distorted cubic close packed array of chalcogen atoms. In this sense, Fig. 2 may be conceived as representing a sheet of tetrahedra out of the c.c.p. array. The gold atoms may be thought to occupy one half of these tetrahedra (in a chess-board like arrangement) having being shifted from their centers towards one of the edges, however, in order to attain a linear coordination. The Au$_4$Se$_4$ rings formed in this way envelop a tetrahedron which cannot be occupied by Na$^+$ ions since its center is surrounded by four Au at a distance of only 2.31 Å. Thus, in contrast to the otherwise closely related structures of Na$_3$AgS$_2$ [14] and Na$_4$Cu$_2$S$_3$ [15], where all tetrahedral sites are occupied, the Na$^+$ ions have
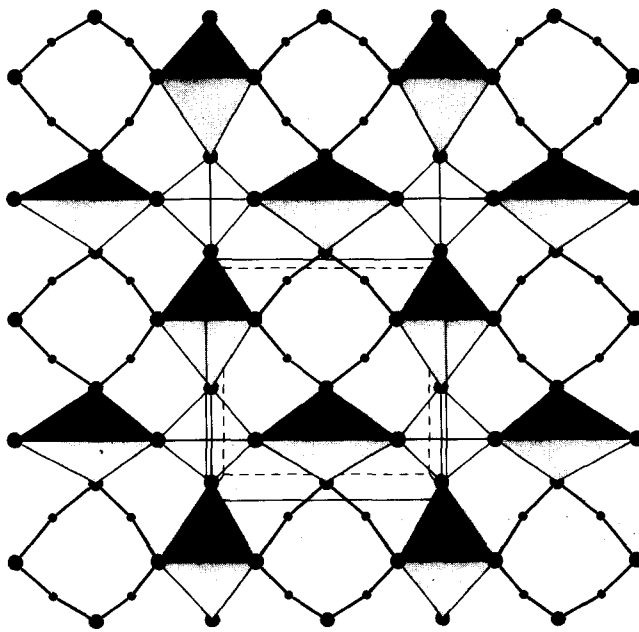

Fig. 2. Linkage of the Na(1)Se$_4$ tetrahedra (shaded) and the Au$_4$Se$_4$ rings viewed along the tetragonal axis of NaAuSe. The drawing represents a sheet of tetrahedra out of distorted c.c.p.-packing of Se atoms. Au atoms are shifted from the tetrahedral centers to the edges. 1/4 of the tetrahedral sites remains unoccupied.

now to be distributed between tetrahedral and octahedral sites. Of the remaining tetrahedral sites only two thirds are occupied by Na(1) while the other are evidently too small to accommodate further Na ions. The Na(2) ions hence occupy one half of the octahedral sites of the packing. The $NaSe_6$ octahedra form a three-dimensional framework of condensed *trans*-octahedral chains, mutually perpendicular to each other along c (Fig. 3). Each octahedron shares faces with two Na(1)Se$_4$ tetrahedra. As can be seen in greater detail from Fig. 4, unfavorable cation–cation repulsion between Na(1) and Na(2) is overcome by deformations (mainly affecting the tetrahedra) and by an off-center shift of the Na(1) ions.

The conformation of the rings found in NaAuSe is unique among the ternary chalcogenides of the coinage metals. Essentially planar quadratic rings, $[M_4^IX_4]^{4-}$, are, however, long known as anionic groups in the structures of KAgO [16,17], KCuO [17,18] and CsAuO [19]. With higher chalcogenide planar anionic ring systems, $[Au_4Te_4]^{4-}$, stabilized by tetraphenylphosphonium cations, have been reported for $[Ph_4P]_2[K_2Au_4Te_4(en)_4]$ and $[Ph_4P]_2[K_2Au_4Te_4 (dmf)_2(CH_3OH)_2]$ [20]. These rings are distorted from quadratic to diamond shape, thus allowing pairwise attractive interactions between the gold atoms
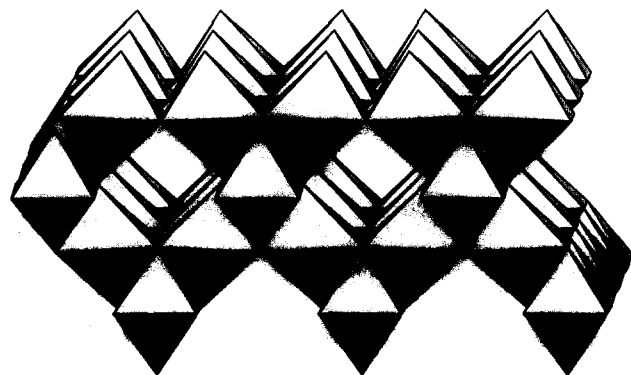

Fig. 3. The framework formed by the Na(2)Se$_6$ octahedra; *trans*-octahedral chains (running along the a-axis) are crosswise linked together via common chalcogen atoms.
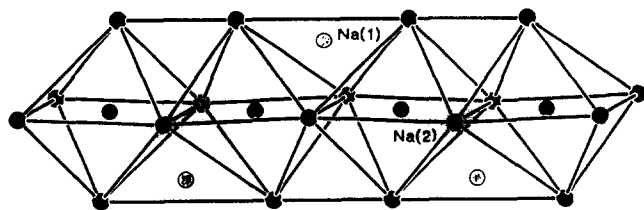

Fig. 4. Distortion of the coordination polyhedra of Na(1) and Na(2) sharing common triangular faces. The off-centered position of Na(1) reduces cation–cation repulsion.

$(d_{Au-Au} = 3.05$ Å and 3.25 Å respectively). In the $[Au_4Se_4]^{4-}$ anion short Au–Au contacts become possible because of the twisted shape of the ring. In our opinion the conformation of the ring is, however, predominantly determined by the packing and not by potential attractive force between the gold atoms. Since each gold atom has two further homoatomic contacts of 3.311(1) Å (which are only longer by 0.06 Å than the intramolecular contacts) attractive Au–Au interactions, if present, should be effective throughout the crystal structure.

Acknowledgements

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