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The Crystal Structure of AuSeBr

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Gold selenide bromide, AuSeBr, crystallizes with space group *Pnma* and eight formula units per unit cell. The lattice parameters are: $a = 6.77$ Å, $b = 12.22$ Å, and $c = 7.38$ Å. The crystal structure was determined from a complete set of three-dimensional Mo-$K\alpha$ diffractometer data. Two gold atoms on mirror planes of the space group and one nonmetal atom of each kind in general positions form infinite ribbons parallel to the *a* axis. In these ribbons Au(1) is bonded to two Br atoms at 2.46 Å and two Se atoms at 2.45 Å, while Au(2) makes four bonds at 2.49 Å to Se atoms only. In both cases the coordination is of a planar distorted square type. For the bridging Se atom the coordination is trigonal pyramidal. The Br atom occupies terminal positions. The ribbons are interlocked into sheets perpendicular to the *b* axis.

Introduction

Gold chalcogenide halides have not been known until recently. The existence of telluride halides is now well established (*1*). The preparation of pure selenide halides proved to be very difficult. Most of the evidence had to be based on a few small crystals grown in anhydrous HBr and HCl, respectively (*2*). The structure determination of gold selenide bromide, AuSeBr, therefore seemed to be the best way to support the published results. No indication with respect to the existence of sulfide halides could be obtained so far.

With AuSeBr the first structure within this group of compounds has been determined.

Experimental and Crystallographic Data

Crystals of AuSeBr are of dark-grey metallic colour. Oscillation, Weissenberg and precession photographs confirmed the orthorhombic symmetry and the content and approximate dimensions of the unit cell as reported by Rabenau, Rau, and Rosenstein (*2*). Improved lattice parameters were obtained by a least-squares fit of angular measurements on a diffractometer: $a = 6.77(1)$ Å, $b = 12.22(1)$ Å, $c = 7.38(1)$ Å. With eight formula units AuSeBr in the unit cell, the calculated density is 7.75 g cm^{-3}. The measured value (*2*) is 7.8. The systematic extinctions $0kl$ for $k + l = 2n + 1$ and $hk0$ for $h = 2n + 1$ point to $Pn2_1a$ and *Pnma* as possible space groups. The latter, centrosymmetric one, proved adequate for a successful structure determination.[1]

A crystal of approximate dimensions $0.13 \times 0.13 \times 0.09$ mm^3 was used for the intensity measurements on an automatic diffractometer. The instrument of the Siemens type was paper tape controlled and run in the $\theta/2\theta$ scanning mode. With Nb-filtered Mo-$K\alpha$ radiation 871 independent reflections up to a limit of $2\theta = 60°$ were measured, of which 262 were classified as unobserved by the criterion $I < \sigma_1$. With the linear absorption coefficient as high as 761.0 cm^{-1} no correction for absorption was attempted.

Structure Determination and Refinement

The structure was found from the Patterson function to be made up of two independent gold

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[1] In order to achieve the conventional setting, as given above, for this space group, the *b* and *c* axis directions of the earlier work (*2*) have been interchanged. In (*2*) the space group was incorrectly given.

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TABLE I

ATOMIC POSITIONAL PARAMETERS GIVEN IN FRACTIONS OF THE LATTICE TRANSLATIONS[a]

Atom	X	Y	Z
Au(1)	0.5870(3)	0.25	0.3583(3)
Au(2)	0.3344(3)	0.25	0.7493(3)
Se	0.5843(6)	0.1243(3)	0.6166(5)
Br	0.5878(7)	0.1038(4)	0.1286(5)

[a] Estimated standard deviations given in parentheses refer to the least significant figures.

atoms on mirror planes of the space group and one selenium and one bromine atom in general positions. After four cycles of full matrix refinement minimizing the function $\sum w(|F_0| - |F_c|)^2$ the initial R-factor of 0.40 was reduced to 0.15. Due to the extremely high absorption the isotropic thermal parameters converged at very small values: $B_{\mathrm{Au(1)}} = 0.08$, $B_{\mathrm{Au(2)}} = 0.09$, $B_{\mathrm{Se}} = 0.10$, and $B_{\mathrm{Br}} = 0.75$ Å^2. After three more cycles in the anisotropic mode, R was 0.124 for the observed reflections.

The atomic scattering factors were taken from (*3*), the reflections were weighted according to $w = 1.0$ for $|F_0| \leqq K$ and $w = K^2/|F_0|^2$ for $|F_0| > K$ with $K = 200.0$. The final atomic coordinates and their standard deviations are listed in Table I. The anisotropic thermal parameters are not given, since they did not stay positive definite.

Results and Discussion

The crystal structure of AuSeBr consists of infinite atomic ribbons parallel to the crystallographic *a* axis. Within these ribbons, one of which is depicted in a perspective view in Fig. 1, the gold atoms extend four coplanar bonds to the nonmetal atoms. The assignment of selenium and bromine with their very similar scattering factors to the nonmetal atom positions was based on the general structural behavior of these elements and considerations of favorable charge distribution.

Atom Au(1), off the axis of the ribbon, makes two terminal bonds to Br atoms of length 2.46 Å and two bonds to the bridging Se atoms at 2.45 Å. Atom Au(2), very close to the central line of the ribbon, bonds only to Se atoms at equal distances of 2.49 Å. With angles at the two Au atoms ranging from 78 to 95° and from 76 to 104°, respectively, the ligand atoms form distorted squares. The coordination of the Se atom is

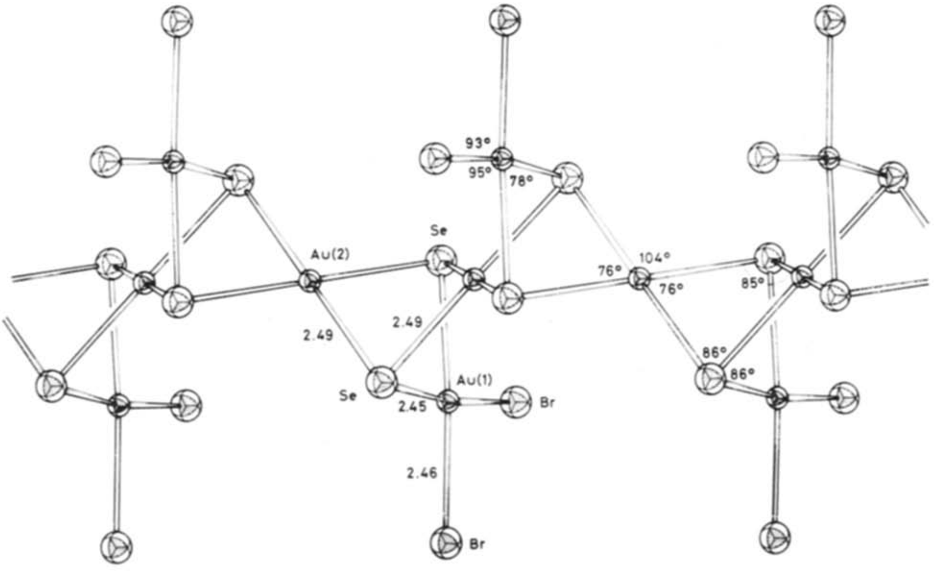

FIG. 1. Perspective view of an atomic ribbon of the crystal structure of AuSeBr. The only crystallographic symmetry is a mirror plane through all the gold atoms. Independent bond lengths in Å and bond angles are given.[2]

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[2] The estimated standard deviations for interatomic distances and angles as resulting from the least-squares values of Table I are 0.005 Å and 0.2°. Nevertheless, because of the high absorption, all numbers in Figs. 1–3 have been rounded to two decimal places for distances and unit positions for angles.

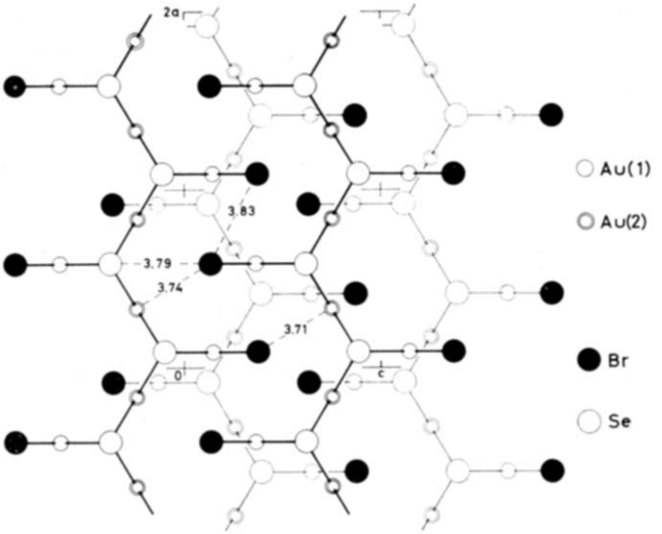

FIG. 2. Projection of the crystal structure of AuSeBr down the *b* axis. Shortest distances in Å between ribbons translated by *c* are shown. The elements of crystallographic symmetry are not shown.

trigonal pyramidal, the three Au–Se–Au angles being 85, 86, and 86°. Thus, the ribbon-type structure of AuSeBr presents an elegant way of realizing 1:1:1 stoichiometry together with the usual planar 4-fold coordination for Au(III) and of utilizing the different preference of the nonmetal atoms for bridging versus terminal positions.

The three shortest Au–Au distances of 3.34, 3.35, and 3.38 Å are much larger than the shortest Au–Au contact in metallic gold at 2.88 Å but somewhat smaller than the corresponding value of 3.43 Å in the planar Au_2Cl_6 molecule (*4*). The Au–Br bond is similar in length to the average of 2.43 observed for $RbAuBr_4$ (*5*).

The arrangement of neighboring ribbons is shown in Figs. 2 and 3. The shortest metal–nonmetal distances at 3.71 and 3.74 Å are between

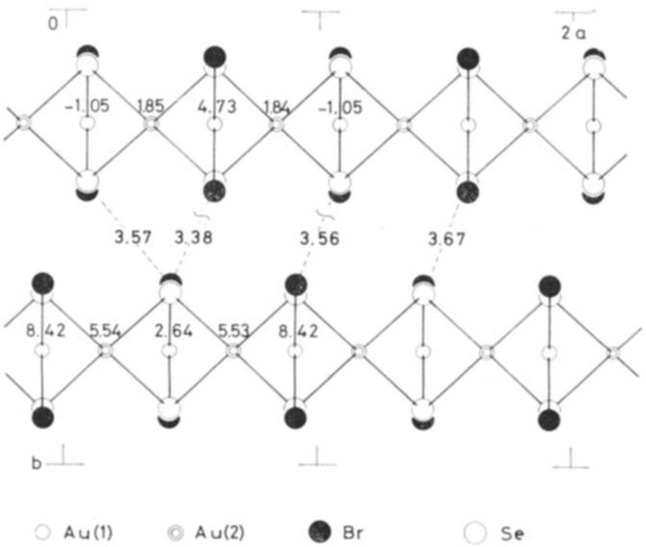

FIG. 3. Projection of the crystal structure of AuSeBr in direction of the negative *c* axis. Close approaches in Å between two ribbons related by symmetry are shown. The elements of crystallographic symmetry are not shown. Heights of Au(1) and Au(2) in Å upon the plane of drawing is given.

ribbons translationally equivalent in the c axis direction. Such ribbons are interlocked (Fig. 2) and thus form sheets perpendicular to the b axis. Approximately, such a sheet can be regarded as the result of congruent stacking of two identical close-packed layers of nonmetal atoms with the gold atoms in certain positions enclosed in between. Stacking of the sheets, then, is analogous to hexagonal stacking of close-packed layers. Some stacking disorder was indicated by weak streaking parallel to b^* of reflections on the Weissenberg films.

Acknowledgments

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