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The Crystal Structure of Gold Telluride Iodide AuTeI

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The crystal structure of AuTeI has been determined. It is monoclinic with space group $P2_1/c$, $a = 7.3130$, $b = 7.6242$, $c = 7.2550$ Å, $\beta = 106.263°$, and $Z = 4$. Intensities were measured on an automatic diffractometer, and the structure was refined, with anisotropic temperature factors, to $R = 0.055$. With a distorted square-planar coordination by three bridging Te atoms and one terminal I atom the Au atom is in the oxidation state 3+. The atoms form corrugated nets parallel to the *b/c*-plane, which are translationally equivalent along the *a*-axis direction.

The six known gold chalcogenide halides occur in four different structural types (*1*, *2*). Three of these have been characterized by complete X-ray analysis; $AuTe_2Cl$ (isotype $AuTe_2Br$) (*3*), $AuTe_2I$ (*3*), and AuSeBr (isotype AuSeCl) (*4*). The atomic arrangement of the remaining type and compound, AuTeI, has now been determined.

Experimental

Greyish-black crystals of AuTeI in the form of thin plates were prepared from the elements by hydrothermal synthesis in hydroiodic acid as in (*1*). Oscillation, Weissenberg, and precession photographs confirmed the basic crystallographic data given in (*1*). They are summarized in Table I with refined values of the lattice parameters from diffractometric measurements.

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TABLE I

CRYSTALLOGRAPHIC DATA[a]

$a = 7.3130(4)$ Å	M(AuTeI) $= 451.471$
$b = 7.6242(4)$ Å	Z(AuTeI) $= 4$
$c = 7.2550(2)$ Å	$d_m(1) = 7.73$ g cm^{-3}
$\beta = 106.263(4)$ Å	$d_x = 7.72$ g cm^{-3}
$V = 388.32(3)$ Å^3	$\mu_{MoK\alpha} = 545.2$ cm^{-1}

[a] Symmetry and space group: monoclinic, $P2_1/c$.

Intensity measurements were made on a Syntex $P2_1$ automatic diffractometer using monochromated Mo$K\alpha$ radiation and a sample crystal of $0.03 \times 0.12 \times 0.18$ mm in size. The instrument was run in the ω scanning mode with a scanning range of 1.0° for each reflection. The offset from the peak position for measuring the background intensity was $\pm 1.0°$ and the ratio for measuring times for background intensity and peak intensity was one. Intensities of two reference reflections remained constant during data collection.

Of 1772 independent reflections with $2\theta \leq 71°$ ($\sin \theta/\lambda \leq 0.82$ Å^{-1}) 1172 had significant

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intensities ($I \geqq 3\sigma_I$). Only these were used in the calculations. They were corrected for absorption using the Gaussian grid method. The value of A^* in the expression $I_{corr} = I_{obs} \cdot A^*$ varied from 5.27 to 38.61.

Structure Determination and Refinement

The structure was solved by application of the MULTAN program (*5*). An *E* map with 240 reflections with $E \geqq 1.5$ showed two outstanding peaks which were interpreted as two of the three independent atoms of the structure, Au and Te (or I). The remaining I (or Te) could be located by a round of structure factor and Fourier calculation. The structure was refined by anisotropic full-matrix least-squares to $R = 0.055$ and $R_w = 0.052$, with $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. The function minimized was $\sum w(|F_{o,rel}| - |F_c|/K)^2$ with $w = 1/\sigma_F^2$.

The atomic scattering factors used were those of Cromer and Mann (*6*). A dispersion correction was made for all atoms using Templeton-type factors (*7*). An isotropic correction for extinction after the method of Larson (*8*) converged from an initial preset 0.0 to 0.98(5). All calculations were done with programs of the systems XTL (*9*) and X-ray (*10*). Table II contains the atomic parameters with their standard deviations. A list of the observed and calculated structure factors is available from the authors.

TABLE II

THE ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS[a]

	Au	Te	I
x	0.4654(1)	0.6720(2)	0.1758(2)
y	0.1395(1)	0.1301(2)	0.0857(2)
z	0.2370(1)	−0.0090(1)	0.3892(2)
U_{11}	2.17(3)	1.78(5)	2.00(6)
U_{22}	2.11(3)	2.26(5)	3.58(7)
U_{33}	1.37(3)	1.29(4)	2.29(5)
U_{12}	−0.16(3)	−0.01(5)	−0.08(5)
U_{13}	0.79(2)	0.51(4)	0.96(5)
U_{23}	−0.15(3)	−0.13(4)	0.19(5)

[a] The U_{ij} as multiples of 0.01 Å^2 refer to $-2\pi^2(U_{11}h^2a^{*2} + 2U_{23}klb^*c^* + \cdots)$ as exponent of the anisotropic temperature factor.

Results and Discussion

The atomic arrangement is shown in Fig. 1, interatomic distances and angles are listed in Table III. The assignment of Te and I with their very similar scattering factors to the nonmetal atom positions (bridging and terminal, respectively) was based on general crystal chemical reasoning.

As in the nonisotypic AuSeBr (*4*) and different from CuTeI of analogous composition (*11*) the metal atom in AuTeI is not in the 1+ but in the 3+ state, indicated by a distorted square-planar coordination and the absence of primary bonding distances between the nonmetal atoms. The Au atom and the I and three Te atoms bonded to it at distances between 2.642 and 2.684 Å are coplanar within 0.224 Å. The smallest distance between nonmetal atoms is a contact of 3.235 Å between two Te atoms. This is distinctly shorter than the double Van der Waals radius

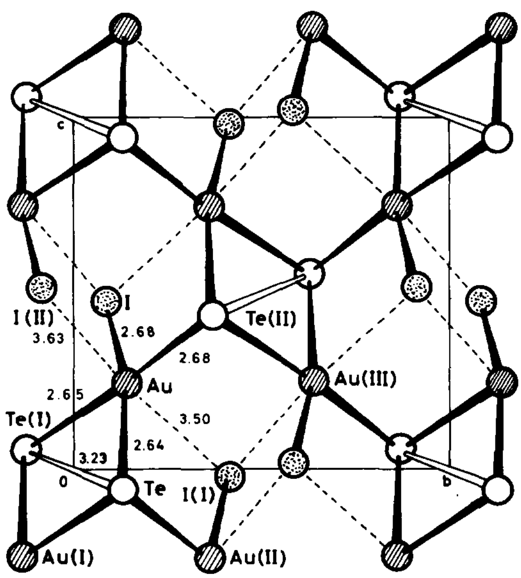

FIG. 1. A corrugated net of the AuTeI structure, ORTEP plot (*16*).

TABLE III

INTERATOMIC DISTANCES AND ANGLES WITHIN A NET[a]

Au–I	2.680 Å	Te···Te(I)	3.235 Å
Au–Te	2.642	Au···I(I)	3.500
Au–Te(I)	2.654	Au···I(II)	3.633
Au–Te(II)	2.684		
		Au···Au(I)	4.193 Å
I–Au–Te	160.26°	Au···Au(II)	4.000
I–Au–Te(I)	81.17	Au···Au(III)	3.843
I–Au–Te(II)	100.09		
Te–Au–Te(I)	75.29	Au–Te–Au(I)	104.71°
Te–Au–Te(II)	99.40	Au–Te–Au(II)	97.34
Te(I)–Au–Te(II)	167.71	Au(I)–Te–Au(II)	92.12

[a] Standard deviations from 0.001 to 0.002 Å and from 0.03 to 0.05°. Atom designations as in Table II and Fig. 1.

at 4.40 Å and other observed nonbonding distances I...I and I...Te in the AuTeI structure at above 3.6 Å and thus indicates a certain degree of interaction. At the same time it is much longer than the ca. 2.8 Å associated with a covalent Te–Te bond, e.g., 2.7781(6) Å in $AuTe_2I$ where the Te atoms form pairs (*3*), 2.772(2) Å in CuTeI (*11*), and 2.835(2) in elemental Te (*12*) with unlimited screws of Te atoms in both cases and from 2.67 to 2.93 Å in the various tellurium subhalides (*13*).

The four bonds between Au and the nonmetal atoms generate a corrugated two-dimensional net parallel to the *b*/*c*-plane. Adjacent nets are stacked on each other by the lattice translation along the *a*-axis. Geometrically, the net can be derived from the double layer of nonmetal atoms of the CdI_2 structure with the metal atoms enclosed in octahedral voids. This is evident from Fig. 1 by ignoring the Te...Te interactions described above and accepting the shortest nonbonding distances from Au, two Au...I at 3.500 and 3.633 Å, as fifth and sixth sites of a fictitious octahedral Au coordination. This geometrical relation may be of crystal chemical meaning inasmuch as a telluride iodide of analogous composition, BiTeI, is reported once as a *true* isotype of CdI_2 (*14*), with disorder of Te and I atoms, and once with a hexagonal structure *similar* to that of CdI_2 (*15*), with an ordered distribution of all atoms.

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