Preparation and Crystal Structure of [TeBr₃][AuBr₄]·1/2 Br₂, a Compound with “Bromine of Crystallization”

Cristina Freire-Erdbrügger, Dieter Jentsch, Peter G. Jones*, and Einhard Schwarzmann*
Institut für Anorganische Chemie der Universität, Tammanstraße 4, D-3400 Göttingen, FRG
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Tellurium(IV), Gold(III), Bromide Complex, Bromine of Crystallization, Crystal Structure

The reaction between elemental gold, tellurium and bromine leads to a crystalline product of empirical formula AuBr₄Te. The crystal structure determination of AuBr₄Te shows that it is composed of dimeric [TeBr₃·AuBr₄]₂ units with secondary Te–Br interactions and of isolated Br₂ molecules.

Introduction

We have recently published crystal structure determinations of compounds MCl₅[AuCl₄]− (M = Te [1], Se [2]). Such salts display secondary interactions between the atom M and the accompanying anions, leading to an extended coordination geometry at M that is usually distorted octahedral (but was distorted square pyramidal for M = Te). Here we report the extension of these studies to bromide derivatives.

Experimental

0.25 mmol gold, 0.25 mmol tellurium and 3 ml bromine were introduced into a glass tube, which was then evacuated and sealed off and heated to 160 °C for 7 days. When the temperature was lowered to 80 °C for 1 day, black prismatic crystals formed. These are sensitive to atmospheric moisture and would therefore be immersed in inert oil and mounted in glass capillaries for crystallographic investigation.

Crystal Structure Determination of AuBr₄Te

Crystal data: M = 963.8, triclinic, space group P1, a = 7.936(3), b = 8.992(3), c = 9.595(4) Å, α = 86.48(3), β = 73.34(3), γ = 82.86(3)°, V = 675.3 Å³, Z = 2, D = 4.74 g cm⁻³, F(000) = 822, μ(MoKa) = 36.2 mm⁻¹. A crystal 0.08 x 0.06 x 0.04 mm was used to measure 2786 profile-fitted intensities [3] on a Stoe-Siemens four-circle diffractometer (MoKα radiation, 2Θmax 50°). The data were corrected for crystal decay (ca. 20%, based on three check reflections) and absorption (ψ-scans; transmission factors 0.40–0.98). Of 2379 unique reflections, 1384 with F > 4σ(F) were used for all calculations (program SHELX-76). Cell constants were refined from setting angles of 48 reflections in the range 20 20–23°.

The structure was solved by the heavy-atom method and refined anisotropically on F to R 0.074, R. 0.052. An extinction correction of the form

Fcorr = F/[1 + xF²/sin 2Θ]⁰.25

was applied; x refined to 1.4(1)×10⁻⁶. The weighting scheme was

w⁻¹ = σ²(F) + 0.0001 F².

92 parameters were refined. The maximum residual electron density was 2 e Å⁻³.

Final atomic coordinates are presented in Table I, with derived bond lengths and angles in Table II [4].

Discussion

The structure is composed of three primary units: AuBr₄⁺ and TeBr₃⁺ ions and Br₂ molecules.

The AuBr₄⁺ ions display the expected square-planar coordination, with Au–Br bond lengths

<table>
<thead>
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<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)*</th>
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<tr>
<td>Au</td>
<td>21(2)</td>
<td>1077(1)</td>
<td>3140(2)</td>
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<tr>
<td>Te</td>
<td>6998(3)</td>
<td>2581(2)</td>
<td>7261(2)</td>
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<td>Br(1)</td>
<td>2958(4)</td>
<td>809(3)</td>
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<td>727(4)</td>
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<td>Br(8)</td>
<td>794(5)</td>
<td>4120(4)</td>
<td>703(4)</td>
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* Equivalent isotropic U defined as one third of the trace of the orthogonalized Uij tensor.
The Au—Br bond lengths in RbAuBr₄ (2.417, 2.434 Å [5]) and Cs₃(AuBr₄)₂(Br₃) (eight bonds, 2.417–2.432 Å [6]) are in good agreement with the values observed here; in Bu₄N⁺AuBr₄⁻, however, the bonds are somewhat shorter (2.404 Å [7]), perhaps because there are no interactions between the bromide ligands and the cations.

The TeBr₃⁺ ions are pyramidal, with Te—Br bond lengths 2.457–2.466 Å and Br—Te—Br angles 94.3–97.4°. In TeBr₅⁺AsF₆⁻ the corresponding values are 2.428–2.438 Å, 95.9–99.5° [8].

The bromine molecule lies across a centre of symmetry and has a bond length of 2.294 Å. In solid bromine the corresponding value is 2.27 Å, but the structure determination was carried out in 1936 [9] and its precision is uncertain; to the best of our knowledge the structure has never been redetermined.

The structure displays the expected secondary contacts [10] between the tellurium atom and the anion bromine atoms; these complete a distorted octahedral coordination at Te (Fig. 1; Te···Br 3.131–3.173 Å) and lead to the formation of centrosymmetric dimers [TeBr₃⁺AuBr₄⁻]. The bond Au—Br(4) is the shortest Au—Br bond, consistent with the lack of secondary interactions at Br(4).

Surprisingly, the bromine molecule does not take part in secondary interactions, unless the contact Br₈···Br(4) (3.316 Å, second atom at −x, 1−y, 1−z) is considered as such; cf. 3.31 Å in solid bromine [9].

<table>
<thead>
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<th>Bond Lengths</th>
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<td>Au—Br(1)</td>
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<td>Br(1') — Te — Br(3')</td>
<td>81.6(2)</td>
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</table>

Symmetry operators: see Fig. 1.

Fig. 1. Thermal ellipsoid plot (50% level) of the dimeric [TeBr₃⁺AuBr₄⁻] unit and the Br₂ molecule in the crystal. Symmetry operators (referred to the coordinates of Table I): (') - 1 + x, y, z; (') - y, 1−z, 1−x; (#) - y, -x, -z; (a) -x, 1−y, −z.

In adducts with organic solvents, weak contacts to donor oxygen or nitrogen atoms are observed [11] and in bromide/bromine species polybromides are formed, e.g. Br···Br 2.89 Å in (Me₄N)₅SbBr₉·Br₂ [12]. We believe that the current structure is the first containing essentially “free” bromine of crystallization. Fig. 2 shows the crystal packing.

We thank the Fonds der Chemischen Industrie for financial support.
Fig. 2. Stereographic packing plot of the title compound. Radii are arbitrary.

[4] Further details of the crystal structure determination have been deposited at the Fachinformationszentrum Energie, Physik, Mathematik, 7514 Eggenstein-Leopoldshafen 2, FRG. Any request for this material should be accompanied by a full literature citation and should quote the reference number CSD 52492.