# Synthesis and Crystal Structure of $[Re_2Br_4(Te_2)(TeBr)_2(TeBr_2)_2]$, a Dinuclear Complex with $Te_2^{2-}$, $TeBr^-$ , and $TeBr_2$ Ligands

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The reaction of $ReBr_4$, Te and $TeBr_4$ in $SiBr_4$ as solvent in a sealed glass ampoule at 150 °C yields black crystals of $Re_2Te_6Br_{10}$. As the X-ray crystal structure determination shows [monoclinic, $P2_1$, $Z = 2$, $a = 1127.5(1)$, $b = 861.85(9)$, $c = 1231.0(2)$pm, $\beta = 105.47(9)°$], the structure consists of discrete dinuclear complexes. A Re–Re dumb-bell with $d$(Re–Re) = 279.9 pm is coordinated by a μ-$Te_2$ group and two μ-TeBr groups. Additionally, each Re atom is coordinated to two terminal bromine atoms and a $TeBr_2$ ligand leading to the formula $[Re_2Br_4(Te_2)(TeBr)_2(TeBr_2)_2]$. $Re_2Te_6Br_{10}$ is one of only a few compounds known in the ternary system Re/Te/Br.

## Introduction

In lower oxidation states rhenium is known to form dinuclear complexes with multiple Re−Re bonds as well as a large variety of clusters.[1] Among the rhenium chalcogenide halides hexanuclear octahedral cluster compounds are predominant,[2] but trinuclear triangular clusters like $Re_3E_7X_7$ (E = S, Se; X = Cl, Br)[3−5] and tetranuclear clusters like $Re_4S_4Te_4$[6] or $[Re_4(\mu_3\text{-}Te)_4(TeBr_2)_4Br_8]$ with a $Re_4Te_4$ heterocubane core[7] are known, too.

In the ternary system Re/Te/Br only very few compounds are known so far. Two examples of hexanuclear clusters were reported, $[Re_6Te_8(TeBr_2)_6]Br_2$[8], $Re_6Te_4Br_{10}$,[9] and the above-mentioned tetranuclear complex $[Re_4(\mu_3\text{-}Te)_4(TeBr_2)_4Br_8]$. Recently, we discovered that $ReCl_4$, Te and $TeCl_4$ yield $Te_8[ReCl_6]$.[10] We extended our synthetic attempts to the reactions of $ReBr_4$ with elemental chalcogen and its tetrabromides. Here we report the synthesis and crystal structure of a new dinuclear complex containing unusual ligands.

## Results and Discussion

### Synthesis

The reaction of $ReCl_4$, Te and $TeCl_4$ leads to $Te_8[ReCl_6]$ and is carried out in a sealed, evacuated ampoule at 230°C under the conditions of the chemical vapor transport.[10] All attempts to obtain polycation-containing compounds starting from $ReBr_4$, Te and $TeBr_4$ failed. The only crystalline material which could be identified was $Re_3Br_9$.[11][12] The use of $SiBr_4$ as solvent allowed a moderate reaction temperature of 150°C and proved to be successful for the synthesis of a ternary compound. Within two weeks black cuboid crystals of $Re_2Te_6Br_{10}$ were deposited from the solution besides silvery crystals of tellurium.

$$4\,ReBr_4 + 11\,Te + TeBr_4 \xrightarrow{SiBr_4} 2\,Re_2Te_6Br_{10}$$

An excess of tellurium was found to be necessary for the formation of the ternary phase. In other solvents like $SnBr_4$ or $S_2Br_2$, $Re_2Te_6Br_{10}$ was not obtainable.

### Crystal Structure

The crystal structure is built of discrete molecular complexes with the formula $Re_2Te_6Br_{10}$ (Figure 1). Central unit is an Re−Re dumb-bell coordinated by a $Te_2$ group and two TeBr groups, bridging both Re atoms. Additionally, each Re atom has two terminal Br ligands. The coordination sphere is completed by two $TeBr_2$ molecules, bound to each Re atom. The Re−Re distance is 279.9(2) pm which represents a weak bond. In $Re^{III}$ halides containing an $Re_3$ triangle with a formal Re−Re double bond, distances between 245 and 250 pm are observed.[11][13] However, the Re−Re distance in $Re_2Te_6Br_{10}$ is in good agreement with $[Re_4Te_4(TeBr_2)_4Br_8]$, for which 277.4 pm and 283.1 pm were found.[7] The angles Re−Te−Re are all in the range from 61.9 to 64.2° and thus notably acute. In the complex $[(\mu\text{-}Te)\{Cp^*Re(CO)_2\}_2]$, which contains a comparable Re−Te−Re unit, this angle is 71.8° and the Re−Re distance 314 pm.[14] Apparently, steric hindrance and the requirements for orbital overlap in the Re−Te−Re units are limiting factors for the Re−Re distances. All Re−Te bonds in $Re_2Te_6Br_{10}$ are in the narrow range from 261.7(2) to 273.5(2) pm. The Te(3)−Te(4) distance in the $Te_2$ group is 268.7(4) pm, slightly shorter than a Te−Te single bond of 275 pm, but comparable to other compounds containing $Te_2$ groups, e.g. $Nb_2Te_2X_6$ (X = Br, I) with 267.0 and 268.5 pm.[15] The distance Te(2)−Te(5) is 324.9(3) pm, indicating only a very weak interaction and the absence of a second $Te_2$ group. Two Br atoms are bound to Te(2) and Te(5) with Te−Br distances of 260.9(4) and 264.5(5) pm. Thus, $Re_2Te_6Br_{10}$ contains two TeBr groups, a type of ligand

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which so far has been only observed in $Mo_4Te_7Br_8$, and as the analogous TeCl groups in $Mo_4Te_7Cl_8$.[16]

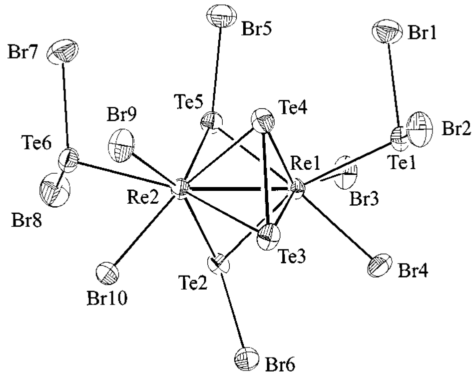

Figure 1. The structure of the molecular complex $[Re_2Br_4(Te_2)(TeBr)_2(TeBr_2)_2]$; thermal ellipsoids are drawn at a 50% probability level[27]

$TeBr_2$ is unstable in the solid state,[17] but can be stabilized by coordination, which was already shown in the structures of $[Re_4(\mu_3\text{-}Te)_4(TeBr_2)_4Br_8]$[7] and $[Re_6Te_8(TeBr_2)_6]Br_2$.[8] With mean Te−Br bond lengths of 252.6 pm and Br−Te−Br angles of 96.7° the conformation of the coordinated $TeBr_2$ molecules in the structure of $Re_2Te_6Br_{10}$ is quite similar to that in the gas phase (251 pm and 98°).[18]

Together with the two terminal Br ligands each Re atom is sevenfold coordinated in a piano-stool fashion. The bonding in the complex can be rationalized by an ionic formula. Counting the terminal bromine ligands as $Br^-$, the $Te_2$ groups as $Te_2^{2-}$, the TeBr groups as $TeBr^-$ and thus analogous to a hypochlorite ion, and the $TeBr_2$ ligands as neutral molecules, one obtains the ionic formula $[(Re^{4+})_2(Br^-)_4(Te_2^{2-})(TeBr^-)_2(TeBr_2)_2]$. This formula is consistent with the assumption of a bonding Re−Re interaction. The presence of $Re^{4+}$ has also been suggested for the heterocubane cluster $[Re_4Te_4(TeBr_2)_4Br_8]$. The mean Re−Br bond lengths between the central atom and the terminal bromide ligands generally are very sensitive to changes in the oxidation state of the central atom. Figure 2 shows the arrangement of the molecules in the unit cell.

Molybdenum and tungsten form a class of dinuclear chalcohalide complexes of the general formula $M_2E_6X_{10}$ (M = Mo, W; E = S, Se, Te; X = Cl, Br).[19][20] Although the formula is analogous to $Re_2Te_6Br_{10}$, these complexes are not isostructural. Mo and W compounds contain two $E_2^{2-}$ groups, three terminal halide ligands for each metal atom and two $EX_2$ molecules connected with the metal atoms through the chalcogen atoms, but no $TeX^-$ groups. Therefore, the ionic formula is $[(M^{5+})_2(X^-)_6(E_2^{2-})_2(EX_2)_2]$. The significant difference between this family of complexes and $Re_2Te_6Br_{10}$ lies in the function of two halide ligands. In the Mo and W complexes they act as terminal ligands bound to the metal atoms resulting in a coordination number of eight for Mo/W, while in $Re_2Te_6Br_{10}$ they are bound to the Te atoms of a "former" $Te_2$ group with the consequence of loss of the Te−Te bond and the formation of the unusual $TeBr^-$ ligands.

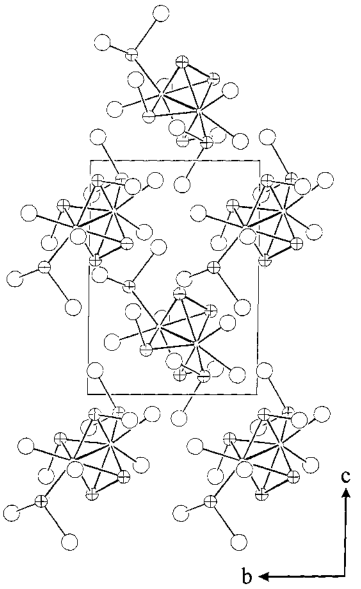

Figure 2. The unit cell of $[Re_2Br_4(Te_2)(TeBr)_2(TeBr_2)_2]$ in a view along the *a* axis showing the noncentrosymmetry of the structure; rhenium atoms are shown as small, bromine atoms as large white circles, tellurium atoms as cross-hatched circles

## Experimental Section

**General:** Tellurium (Alfa Chemicals) was sublimed before use, $TeBr_4$ was prepared from the elements,[21] using bromine (Riedel-

Table 1. Crystal data, details of the diffraction data collection and structure analysis for $Re_2Te_6Br_{10}$

| Formula | $Re_2Te_6Br_{10}$ |
|---|---|
| Molecular mass [g mol$^{-1}$] | 1937.1 |
| Crystal system | monoclinic |
| Space group | $P2_1$ |
| *a* [pm] | 1127.5(1) |
| *b* [pm] | 861.95(9) |
| *c* [pm] | 1231.0(2) |
| β [°] | 105.47(9) |
| *Z* | 2 |
| Density (calculated) [g cm$^{-3}$] | 5.58 |
| μ (Mo-$K_\alpha$) [cm$^{-1}$] | 325.4 |
| Temperature [K] | 293(2) |
| Scan range (2 θ) [°] | 3.3, 52.1 |
| *hkl* range | −13 to 13, −10 to 10, −15 to 15 |
| Measured reflections | 7204 |
| Reflections without overlap with second twin individual | 4176 |
| Unique reflections | 2525 |
| Data for refinement | 2525 |
| Parameters refined | 163 |
| Flack parameter | 0.037(20) |
| ρ[a]; max./min. [e pm$^{-3}$ 10$^{-6}$] | +3.51/−2.30 |
| $R(\|F\|)$[b] | 0.065 |
| $R(\|F\|)$[b]; $I > 2\,\sigma(I)$ | 0.063 |
| $wR(F^2)$[c] | 0.167 |

[a] Largest final difference hole and peak. − [b] $R(|F|) = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$. − [c] $wR(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]\}$.

Table 2. Selected distances [pm] and angles [°] between atoms of [$Re_2Br_4(Te_2)(TeBr)_2(TeBr_2)_2$]

| Atoms | Distance [pm] | Atoms | Distance [pm] | Atoms | Distance [pm] | Atoms | Distance [pm] |
|---|---|---|---|---|---|---|---|
| Re1−Re2 | 279.9(2) | Re1−Te2 | 262.4(3) | Re1−Te5 | 264.7(3) | Re1−Te4 | 267.3(3) |
| Re1−Te1 | 270.0(3) | Re1−Te3 | 273.5(2) | Re2−Te5 | 261.7(2) | Re2−Te2 | 264.5(3) |
| Re2−Te4 | 269.1(3) | Re2−Te3 | 271.1(3) | Re2−Te6 | 271.7(3) | Re1−Br3 | 261.3(4) |
| Re1−Br4 | 262.4(4) | Re2−Br10 | 261.4(4) | Re2−Br9 | 263.0(4) | Te1−Br1 | 251.9(5) |
| Te1−Br2 | 254.3(5) | Te1−Br3 | 292.4(5) | Te6−Br7 | 251.7(5) | Te6−Br8 | 252.6(6) |
| Te6−Br10 | 293.1(4) | Te2−Br6 | 260.9(4) | Te5−Br5 | 264.5(5) | Te3−Te4 | 268.7(4) |
| Te2−Te5 | 324.9(3) | Te4−Te5 | 330.3(3) | Te2−Te3 | 353.8(4) | | |

| Atoms | Angles [°] | Atoms | Angles [°] | Atoms | Angles [°] |
|---|---|---|---|---|---|
| Re2−Re1−Te2 | 58.27(6) | Re2−Re1−Te3 | 58.65(6) | Re2−Re1−Te4 | 57.36(6) |
| Re2−Re1−Te5 | 58.85(7) | Re1−Re2−Te2 | 57.56(6) | Re1−Re2−Te3 | 59.49(6) |
| Re1−Re2−Te4 | 58.24(7) | Re1−Re2−Te5 | 58.40(6) | Te3−Re1−Te4 | 59.57(8) |
| Te3−Re2−Te4 | 59.66(9) | Re1−Te2−Re2 | 64.16(7) | Re1−Te3−Re2 | 61.87(6) |
| Re1−Te4−Re2 | 62.91(7) | Re1−Te5−Re2 | 64.23(6) | | |

de Haën) dried with $P_4O_{10}$. $BBr_3$ (Riedel-de Haën) was used as received, $ReCl_5$ prepared from the elements, using Re (Riedel-de Haën), purified with $H_2$ at 1000°C, and chlorine gas dried with $H_2SO_4$. $ReBr_4$ was prepared from $ReCl_5$ and $BBr_3$.[22] $SiBr_4$ (Aldrich) was distilled prior to use. All compounds were handled in an argon glovebox or by standard vacuum techniques.

**Synthesis of [$Re_2Br_4(Te_2)(TeBr)_2(TeBr_2)_2$]:** The reaction of $ReBr_4$, Te and $TeBr_4$ was carried out in an evacuated glass ampoule of 14 mm diameter and 13 cm length. The ampoule was loaded with 250 mg of the solid starting materials in a glovebox, $SiBr_4$ was added under a flow of argon. The molar ratio of all starting materials was $ReBr_4$/Te/$TeBr_4$/$SiBr_4$ = 2:13:1:40. The solids showed only little solubility in the solvent. Within 14 d black crystals of [$Re_2Br_4(Te_2)(TeBr)_2(TeBr_2)_2$] were formed at 150°C. Yields were generally low and no increase was observed on prolonged heating or at higher temperatures. The solvent was decanted and the crystals were dried in vacuo. Crystals of [$Re_2Br_4(Te_2)(TeBr)_2(TeBr_2)_2$] are weakly moisture-sensitive. They decompose in moist air within several hours under evolution of HBr.

**Crystal Structure Determination:** Crystals of [$Re_2Br_4(Te_2)(TeBr)_2(TeBr_2)_2$] were sealed in glass capillaries under argon. The crystal finally chosen for the data collection had dimensions of 0.32 × 0.24 × 0.06 mm. Preliminary precession photographs showed a systematic twinning of all crystals examined with a twofold axis along the diagonal of the reciprocal $a-c$ plane as the twin element. The crystal system was determined to be monoclinic with the Laue group $2/m$. The systematic extinction $0k0$ only present for $k = 2n$ led to the spacegroups $P2_1/m$ and $P2_1$ of which the noncentrosymmetric group was confirmed by the structure analysis. Data were collected with a STOE Image Plate diffractometer using graphite monochromized radiation. The reflections of the two individuals were indexed separately with the aid of the programm RECIPE.[23] Overlapping reflex intensities were excluded from the data sets. A structure model was obtained by direct methods[24] and refined against $F^2$ by full-matrix least squares with anisotropic displacement parameters for all atoms and both sets of data.[25] A numerical absorption correction was applied,[26] although this is principially problematic for twinned crystals. Crystallographic data and details on the structure analysis are given in Table 1, selected distances and angles in Table 2. Further crystal structure data have been deposited at the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany. Inquiries should be accompanied by the depository number CSD-410190.

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