Rhenium Tellurobromide Re$_6$Te$_{16}$Br$_6$

Yuri V. Mironov,[†,‡,*] **Sung-Jin Kim,**[‡,*] **and Vladimir E. Fedorov**[†]

[†]*Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3, Acad. Lavrentiev pr., 630090, Novosibirsk, Russia. *E-mail: yuri@che.nsk.su*
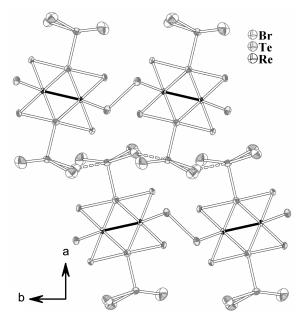[‡]*Division of Nano Sciences and Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea*
E-mail: sjkim@ewha.ac.kr
Received April 6, 2006

Key Words : Rhenium, Octahedral cluster, Tellurobromide, Crystal structure

Whereas Re$_6$ octahedral thio- and selenium halide clusters are well known[1-4] only few examples of tellurium halide clusters are known.[5-8] The known data have demonstrated that there is essential difference in the compositions and structures of chalcohalides containing cluster core {Re$_6$Q$_8$} for Q=Te compounds and S/Se derivatives. Earlier it was shown that in the compounds with cluster core {Re$_6$Q$_8$} often Te-rich compounds are formed in which Re atoms are coordinated by Te atoms of different unusual ligands such as neutral Te$_6$ and TeCl$_3^-$ found in Re$_6$Te$_{16}$Cl$_6$, Te$_{16}$Cl$_{18}^{2-}$ in Re$_6$Te$_{16}$Cl$_{18}$[6] or TeCl$_2$ in Re$_6$Te$_6$Cl$_{10}$ and TeBr$_2$ in Re$_6$Te$_{14}$Br$_{14}$.[7] As is evident from these data the chemistry of cluster rhenium tellurobromides is poorly understood. In this work we have continued the study of Re-Te-Br system and prepared a new tellurobromide Re$_6$Te$_{16}$Br$_6$.

The title compound, Re$_6$Te$_{16}$Br$_6$ is isostructural to known Re$_6$Te$_{16}$Cl$_6$.[6] It may be described as [{Re$_6$Te$_8$}(Te$_6$)(TeBr$_3$)$_2$] where cluster cores {Re$_6$Te$_8$} are joined together by neutral Te$_6$ and [TeBr$_3$]$^-$ ligands. The cluster core {Re$_6$Te$_8$} has a crystallographically imposed twofold axes. The bond lengths and angles in cluster core are similar to those observed in others compounds with {Re$_6$Te$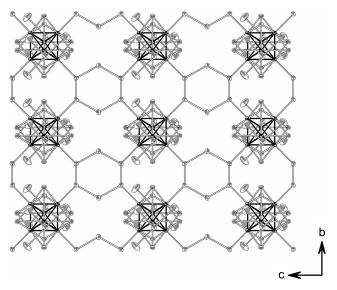_8$} cluster core. In Re$_6Te_{16}Br_6$ two rhenium atoms at opposite vertices of the Re$_6$ octahedron are capped by [TeBr$_3$]$^-$ ligands (Fig. 1). The four remaining Re atoms are capped with neutral Te$_6$ ligands. The Te$_6$ ligands have a chair conformation as in Re$_6$Te$_{16}$Cl$_6$ and recently described (AgI$_2$)$_2$Te$_6$.[9] In Te$_6$ units Te–Te bond lengths are ranging from 2.770(2) to 2.930(2) Å in the title compound, from 2.762(4) to 2.899(5) Å in Re$_6$Te$_{16}$Cl$_6$ and equal to 2.729(1) and 2.760(1) Å in (AgI$_2$)$_2$Te$_6$. In the present structure each Te$_6$ species are chelated four Re$_6$Te$_8$(TeBr$_3$)$_2$ clusters (Re-Te distances are 2.6567(13)-2.7166(13) Å) forming a two-dimensional network (Fig. 2). The four Re-bound Te atoms of the Te$_6$ chair are coplanar. The Te-Br bond lengths in the [TeBr$_3$]$^-$ ligands are 2.574(2), 2.585(2) and 2.969(2) Å. The Br atom that forms the longer Te-Br bond interacts further with Te^{2+} center of a [TeBr$_3$]$^-$ ligand from an adjacent layer, creating a square-planar geometry around the Te^{2+} center (Br$_3$Te $\cdots$Br distance is equal to 3.024(2) Å, Br-Te-Br angles are in the range 84.755(7)° - 94.56(7)°).

Experimental Section

Synthesis. The title compound was prepared by the reaction of Re$_6$Te$_{15}$ with elemental Te and Br$_2$ taken in molar

Figure 1. Structure of Re$_6$Te$_{16}$Br$_6$ viewed along [001]. Displacement ellipsoids are drawn at the 75% probability level.

Figure 2. Structure of Re$_6$Te$_{16}$Br$_6$ viewed along [100]. Displacement ellipsoids are drawn at the 75% probability level.

Table 1. Selected bond length (Å) and angles (°)

Bond	length (Å)	Bond	length (Å)
Re1–Te3	2.6761(12)	Re3–Te3^i	2.6567(13)
Re1–Re2	2.6849(10)	Re3–Te1	2.6590(12)
Re1–Re3	2.6880(9)	Re3–Te2	2.6790(16)
Re1–Re1^i	2.6948(13)	Re3–Te4	2.6892(15)
Re1–Re3^i	2.6958(10)	Re3–Te8	2.7307(13)
Re1–Te2	2.7057(13)	Te5–Te7^{ii}	2.7749(17)
Re1–Te1	2.7085(13)	Te5–Te5^{iii}	2.928(2)
Re1–Te5	2.7086(13)	Te6–Te7	2.7703(17)
Re1–Te2^i	2.7166(13)	Te6–Te6^{iii}	2.930(2)
Re2–Te3	2.6844(13)	Te8–Br2	2.574(2)
Re2–Re3	2.6919(10)	Te8–Br3	2.585(2)
Re2–Re3^i	2.6960(10)	Te8–Br1	2.969(2)
Re2–Te1	2.7046(13)		
Re2–Te4	2.7047(13)	Angle	(°)
Re2–Te4^i	2.7072(14)	Te7^{ii}–Te5–Te5^{iii}	93.21(5)
Re2–Re2^i	2.7077(14)	Te7–Te6–Te6^{iii}	93.31(5)
Re2–Te6	2.7199(13)	Te6–Te7–Te5^{iv}	106.37(5)

Symmetry codes: (i) −x, −y, z; (ii) x, y, 1+z; (iii) −x, 1−y, z; (iv) x, y, z−1.

ratio 1 : 2 : 5. An excess of Te and Br$_2$ were taken to promote the growth of single crystals of title compound. The synthesis was carried in an evacuated fused-silica tube heated at 723 K for 48 hours and then cooled 12 hours to room temperature. The reaction mixture was washed with CH$_3$CN. Single crystals suitable for X-ray analysis were selected from reaction mixture.

X-ray Crystallography: Single-crystal X-ray diffraction data were collected on Re$_6$Te$_{16}$Br$_6$ using graphite-monochromotized MoK$_\alpha$ radiation (λ = 0.71073 Å) with a Bruker Smart APEX CCD diffractometer with the operating program SMART. A face-indexed absorption correction was performed numerically with the use of XPREP. The program SADABS was then employed to make incident beam and decay corrections: T$_{min}$ = 0.1697, T$_{max}$ = 0.4916. The structure was solved by direct method with the SHELX-97 program set[10] for structure solution (direct methods) and refinement (full-matrix least-squares on F^2).

Re$_6$Te$_{16}$Br$_6$: (M = 3638.26), crystal size 0.1 × 0.024 × 0.018 mm, orthorhombic space group $P2_12_12$, a = 18.466(4), b = 8.5102(18), c = 10.784(2) Å, V = 1694.8(6) Å^3, Z = 2, ρ_{calcd} = 7.130 g cm^{-3}, μ = 41.912 mm^{-1}. 2.19 < θ < 28, 29°, T = 295(2) K. Reflections: 10528 collected, 3964 unique (R_{int} = 0.0432), 3093 observed [I > 2$\sigma(I)$]; 127 parameters refined with R = 0.0343 [I > 2$\sigma(I)$], wR_2 = 0.0709 (all data). GOF = 0.940, residual electron density: + 4.328, −1.680 eÅ^{-3}. Flack parameter = 0.008 (10).

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