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**The crystal structure of Bi₂W₆Br₁₈ and a new synthesis of
W₆Br₁₂**

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Figure Captions

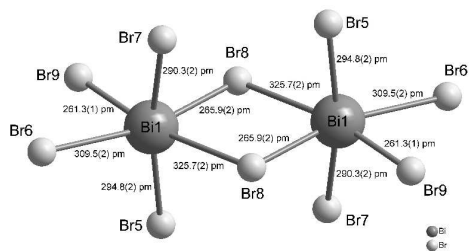


Figure 1. Projection of the environment of pairs of bismuth atoms in the structure containing two short Bi–Br distances each.



Figure 2. Connectivity of $(\text{BiBr}_2)_2$ units with outer bromide cluster ligands. $(\text{W}_6\text{Br}_8^i)$ clusters are shown as octahedra.

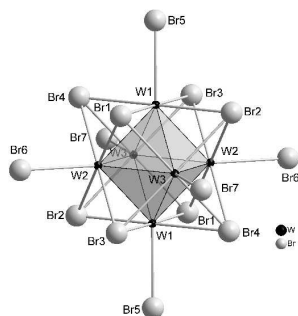


Figure 3. Projection of an isolated $[(\text{W}_6\text{Br}_8^i)\text{Br}_6^{\text{a}}]^{2-}$ cluster.

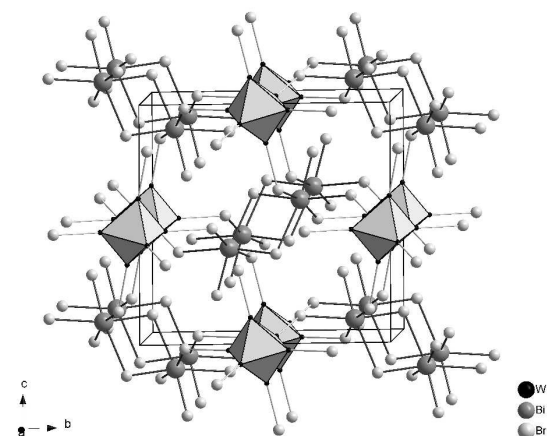


Figure 4. Unit cell of $(\text{BiBr}_2)_2[(\text{W}_6\text{Br}_8^i)\text{Br}_6^{\text{a}}]$ (inner Br ligands are omitted).

The crystal structure of $\text{Bi}_2\text{W}_6\text{Br}_{18}$ and a new synthesis of W_6Br_{12}

Markus Ströbele^[a] and H.-Jürgen Meyer^{*[a]}

Dedicated to Professor Bernd Harbrecht on the Occasion of his 60th Birthday

Keywords: Tungsten cluster; Bromide; Synthesis; Structure

Abstract. The new tungsten bromide cluster compound $\text{Bi}_2\text{W}_6\text{Br}_{18}$ was synthesized by reacting tungsten hexabromide with bismuth metal in a silica tube at 350 °C. The structure of $\text{Bi}_2\text{W}_6\text{Br}_{18}$ was refined by single crystal X-ray diffraction in the space group $P2_1/c$ with unit cell dimensions of $a = 981.8(2)$ pm, $b = 1305.9(2)$ pm, $c = 1256.8(2)$ pm and $\beta = 101.81(2)^\circ$. The crystal structure is constructed from $[(\text{W}_6\text{Br}_8)\text{Br}_6]^{2-}$ anions being interconnected by outer bromine ligands with (BiBr_2) units, which behave as cations in $(\text{BiBr}_2)_2[(\text{W}_6\text{Br}_8)\text{Br}_6]$. Short Bi–Br bonding distances at 261.3(1) pm and 265.9(2) pm in (BiBr_2) units suggest the presence of covalent interactions. Thermal decomposition of the compound leads to W_6Br_{12} .

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Introduction

Tungsten halide cluster chemistry is represented by a remarkable widespread domain of different compounds and structures. Currently known tungsten clusters are represented by the octahedral $[W_6X_{12}]$ type cluster of W_6Cl_{18} [1,2], the octahedral $[W_6X_8]$ type cluster of W_6X_{12} with $X = Cl, Br$ [3], and the centered trigonal prismatic cluster core in W_6CCl_{18} [4]. Mixtures of such clusters were obtained in the structure of $W_{30}C_2X_{68}$ ($X = Cl, Br$) containing carbon centered trigonal prismatic and octahedral cluster moieties in one structure [5]. More cluster types have been discovered in the field of tungsten iodides [6], just recently extended by the identification of the binary compound $W_{15}I_{47}$ containing a square pyramidal cluster core [7].

Based on these tungsten halide clusters, several salt-like compounds have been synthesized in which clusters act as bulky anions [8]. Compounds with $[W_6X_8]$ type clusters have been reported with monovalent A ions in AW_6Cl_{13} , $A_2W_6Cl_{14}$ [9,10,11], and with trivalent M ions in MW_6Cl_{15} $M = Bi$ [12,13], Gd, Tb, Dy [14]. Corresponding cluster bromides were reported as NaW_6Br_{13} [15], AW_6Br_{14} with $A = Na, Ag$ [16], and $A_2W_6Br_{14}$ with $A = Ag$ [16], K [17], Rb [17], Cs [18], Tl [17], Cd [19], and Cu [20].

The synthesis of W_6Cl_{12} has been recently established by a convenient low-temperature route based on the reduction of WCl_6 with bismuth metal at 335 °C [21]. The structural characterization of the intermediate BiW_6Cl_{15} revealed a constitutional isomerism of this compound, which may be described by the two formulas $(BiCl)[(W_6Cl_8^i)Cl_6^a]$ [12] and $(BiCl_2)[(W_6Cl_8^i)Cl_4^aCl_{2/2}^{a-a}]$ [13]. The main differences in these structures are expressed by short Bi–Cl distances at 249 pm for $(BiCl)^{2+}$ and at 245 pm for $(BiCl_2)^+$ with chloride ligands which remain unconnected with respect to the tungsten cluster. The similarity with the previously reported isotopic structure of $(BiCl)[Mo_6Cl_8^i]Cl_6^a$ [22] suggests a close relationship in chemistry of these compounds.

The present work proves the reactivity of tungsten hexabromide with metallic bismuth in order to develop a useful and comfortable synthesis of W_6Br_{12} as an alternative route to the reported reaction between tungsten metal and bromine. In course of this study, namely through reaction of WBr_6 and metallic bismuth, we discovered the new compound $Bi_2W_6Br_{18}$, whose crystal structure is reported herein.

Experimental Section

Synthesis of $Bi_2W_6Br_{18}$

Manipulations of the starting materials WBr_6 and Bi (Riedel-de Haen, 99 %) were performed in a dry box under argon atmosphere. A mixture of WBr_6 (0.5 g, 0.75 mmol) and elementary Bi (0.21 g, 1 mmol) were charged into a two chamber silica tube and sealed under vacuum. This mixture was heated in a tube furnace at 350 °C for 48 h. Afterwards, the coproduced

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3 BiBr₃ was sublimed off from the bulk part (later identified as Bi₂W₆Br₁₈) into the receiver
4 chamber of the silica vessel, being exposed with a lower temperature (near room
5 temperature) over the period of two days. Finally, the ampoule was cooled down to room
6 temperature, the receiver chamber was disconnected from the product chamber, and the
7 content of the product chamber was collected inside the dry box. Dark amber colored
8 rhombic crystals of the new Bi₂W₆Br₁₈ were selected for X-ray single crystal structure
9 analysis.

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15 When the mixture was treated at slightly higher temperatures (at 370 °C for one week)
16 Bi₂W₆Br₁₈ was decomposed into W₆Br₁₂ and coproduced BiBr₃, which was subsequently
17 sublimed off.
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19 20 21 **Synthesis of (H₃O)₂[W₆Br₁₄]·4H₂O**

22 Bi₂W₆Br₁₈ was dissolved in boiling concentrated HBr solution. Brownish crystals of
23 (H₃O)₂[W₆Br₁₄]·4H₂O were crystallized upon cooling the solution to room temperature.
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26 27 28 **Synthesis of WBr₆**

29 A Schlenk tube with two gas cocks was charged with 3 g (8.5 mmol) W(CO)₆ (ABCR, 99 %) in a dry box under argon atmosphere. Afterwards, the tube inlet was connected to an argon line in order to provide an inert gas atmosphere, and the outlet was equipped with three empty washing bottles. After the vessel was cooled with liquid nitrogen, 12.8 ml of liquid Br₂ (0.5 mol) were added to the solid W(CO)₆. The reaction was initiated by allowing the vessel to warm up slowly to room temperature by removing the liquid nitrogen coolant. After resting for 30 min. at room temperature the three washing bottles were filled with alkaline sodium sulfite solution and the Schlenk tube was heated in a water bath to remove the excess of bromine from the reaction. The residual dark gray WBr₆ powder was collected inside the dry box.
44

45 46 47 **X-ray Diffraction**

48 The XRD patterns of reaction products were collected with a Stadi-P (Stoe, Darmstadt) powder diffractometer using Cu-K_{α1} radiation (germanium monochromator), with Bi₂W₆Br₁₈ and (H₃O)₂[W₆Br₁₄]·4H₂O being obtained X-ray pure, although WBr₆ contained some small amounts of WOb₄ (about 5%) which may be a result of an oxygen contamination of W(CO)₆.
55 A single crystal of Bi₂W₆Br₁₈ was coated with lithelen grease and attached to the tip of a glass fibre. Single crystal diffraction data were collected with an IPDS diffractometer (STOE, Darmstadt) using monochromated Mo-K_α radiation. The unit cell refinement and data reduction were carried out using the STOE IPDS software. An absorption correction was applied by using the programs X-Shape/X-Red [23]. The structure was refined in the space
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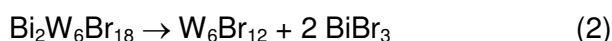
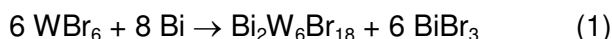
group $P2_1/c$ by full-matrix least-squares procedures using SHELX-97 [24]. All atoms were refined anisotropically. Crystallographic data and structure refinement results are summarized in Table 1, atom positions are listed in Table 2, and selected bond lengths are given in Table 3.

A brown single crystal of $(\text{H}_3\text{O})_2[\text{W}_6\text{Br}_{14}] \cdot 4\text{H}_2\text{O}$ was measured under analogous conditions as $\text{Bi}_2\text{W}_6\text{Br}_{18}$. The structure solution and refinement for $(\text{H}_3\text{O})_2[\text{W}_6\text{Br}_{14}] \cdot 4\text{H}_2\text{O}$ was performed with the space group $C2/c$ with $a = 1598.2(2)$ pm, $b = 1066.4(2)$ pm, $c = 1802.0(3)$ pm, and $\beta = 108.27(2)^\circ$, yielding R values of $R1 = 0.049$, $wR2 = 0.076$ based on all measured data.

Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-421436 for $\text{Bi}_2\text{W}_6\text{Br}_{18}$ and CSD-421437 for $(\text{H}_3\text{O})_2[\text{W}_6\text{Br}_{14}] \cdot 4\text{H}_2\text{O}$.

Results and Discussion

The compound $\text{Bi}_2\text{W}_6\text{Br}_{18}$ was prepared by metallothermic reduction of WBr_6 with bismuth metal at 350°C . However, $\text{Bi}_2\text{W}_6\text{Br}_{18}$ is thermally labile and decomposes slowly at temperatures above 370°C to yield W_6Br_{12} and BiBr_3 , of which the latter can be sublimed off into the colder section (room temperature) of the reaction vessel. This procedure, as emphasized in the following reaction equations permits a comfortable access to obtain pure W_6Br_{12} .



The composition $\text{Bi}_2\text{W}_6\text{Br}_{18}$ may suggest a relationship with $\text{A}_2[\text{W}_6\text{Cl}_{18}]$ compounds containing $[(\text{W}_6\text{Cl}_{12}^i)\text{Cl}_6^a]^{2-}$ ions [8]. However, the crystal structure of $\text{Bi}_2\text{W}_6\text{Cl}_{18}$ was refined to yield a structure which can be described as $(\text{BiBr}_2)_2[(\text{W}_6\text{Br}_8^i)\text{Br}_6^a]$, reflecting a structural relation to the already known bismuth chloro-tungstenate $(\text{BiCl})[(\text{W}_6\text{Cl}_8^i)\text{Cl}_6^a]$. The structure of $(\text{BiBr}_2)_2[(\text{W}_6\text{Br}_8^i)\text{Br}_6^a]$ contains two bromine atoms being involved in covalent bonding with bismuth, thus allowing a (BiBr_2) moiety to act as a monovalent cation like $\text{A}^{(+)}$ in $\text{A}_2[(\text{W}_6\text{Br}_8^i)\text{Br}_6^a]$ compounds.

The two short Bi–Br distances with Br(8) at $265.9(2)$ pm and Br(9) at $261.3(1)$ pm are contained in a strongly distorted edge-sharing bi-octahedral $\text{Bi}_2\text{Br}_{10}$ moiety, displayed in Figure 1. All the remaining bromide atoms of this moiety, with Bi–Br distances presented in Table 3 can be referred as outer ligands of the tungsten cluster (Figure 2).

The $[(\text{W}_6\text{Br}_{12}^i)\text{Br}_6^a]^{2-}$ cluster (Figure 3) in the structure exhibits W–W distances ranging from $261.94(7)$ to $264.13(7)$ pm, W–Brⁱ distances ranging from $260.1(2)$ to $262.8(1)$ pm, and W–Br^a distances ranging from $257.4(2)$ to $264.2(2)$ pm. All these distances reflect typical values among bromo-tungstenate cluster units of this type.

The crystal structure of $(\text{BiBr}_2)_2[(\text{W}_6\text{Br}_8^i)\text{Br}_6^a]$ is displayed in Figure 4 and shows a CsCl type

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3 like structural arrangement of bi-octahedral ($\text{Bi}_2\text{Br}_{10}$) units and (W_6Br_8) cluster units. Six out of
4 ten bromides of the bi-octahedral ($\text{Bi}_2\text{Br}_{10}$) unit are in fact outer bromide ligands of the cluster
5 (Figure 2).
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8 The given, straight forward synthesis of W_6Br_{12} would be challenging for the preparation of
9 the corresponding tungsten dichloride, W_6Cl_{12} , too. The related bismuth chloro-tungstenate
10 precursor having the formula $\text{BiW}_6\text{Cl}_{15}$ has shown to behave thermally stable up to 340 °C.
11 Thermal treatments at higher temperatures appeared inadequate for $\text{BiW}_6\text{Cl}_{15}$ because
12 W_6Cl_{12} has shown to react with quartz tubing above 350 °C. Therefore, a purification process
13 via solution has been used subsequently for the synthesis of W_6Cl_{12} [21]. Following this
14 procedure, both, the chloride and bromide compounds can be dissolved into their aqueous
15 HCl and HBr solutions to yield $(\text{H}_3\text{O})_2[\text{W}_6\text{Cl}_{14}] \cdot 7\text{H}_2\text{O}$ and $(\text{H}_3\text{O})_2[\text{W}_6\text{Br}_{14}] \cdot 4\text{H}_2\text{O}$, respectively. A
16 structure refinement based on a single crystal measurement of $(\text{H}_3\text{O})_2[\text{W}_6\text{Br}_{14}] \cdot 4\text{H}_2\text{O}$ (with
17 crystal data being deposited in the ICSD) has shown that the structures of both compounds
18 are closely related to each other (space group $C2/c$). In addition, both compounds can be
19 pyrolyzed to yield binary W_6X_{12} ($X = \text{Cl}, \text{Br}$) [3].
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Table 1. Crystal data and structure refinement data of $(\text{BiBr}_2)_2[(\text{W}_6\text{Br}_8)\text{Br}_6]^{\text{a}}$.

Empirical formula	$\text{Bi}_2\text{W}_6\text{Br}_{18}$	
Formula weight	2959.44 g/mol	
Temperature	293(2) K	
Wavelength	71.073 pm	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 981.8(2)$ pm	$\alpha = 90^\circ$
	$b = 1305.9(2)$ pm	$\beta = 101.81(2)^\circ$
	$c = 1256.8(2)$ pm	$\gamma = 90^\circ$
Volume	$1.5772(5)$ nm ³	
Z	2	
Density (calculated)	6.23 g/cm ³	
Absorption coefficient	55.7 mm ⁻¹	
F(000)	2480	
Crystal size	$0.16 \times 0.16 \times 0.04$ mm ³	
Θ range for data collection	2.12 to 24.94°	
Index ranges	$-11 \leq h \leq 11, -15 \leq k \leq 15, -14 \leq l \leq 14$	
Reflections collected	15341	
Independent reflections	2732 ($R_{\text{int}} = 0.073$)	
Completeness, $2\Theta = 24.94^\circ$	98.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / parameters	2732 / 118	
Goodness-of-fit on F^2	0.969	
Final R indices [$ I > 2\sigma(I)$]	$R1 = 0.032, wR2 = 0.069$	
R indices (all data)	$R1 = 0.043, wR2 = 0.072$	
Largest diff. peak and hole	2.743 and -1.813 e $\cdot\text{\AA}^{-3}$	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) of $(\text{BiBr}_2)_2[(\text{W}_6\text{Br}_8)\text{Br}_6^{\text{a}}]$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Bi(1)	72(1)	8578(1)	998(1)	27(1)
W(1)	5939(1)	6247(1)	40(1)	22(1)
W(2)	3577(1)	5643(1)	505(1)	20(1)
W(3)	5908(1)	4728(1)	1422(1)	20(1)
Br(1)	5427(2)	6607(1)	1970(1)	29(1)
Br(2)	8244(1)	5345(1)	956(1)	28(1)
Br(3)	6441(1)	5850(1)	-1888(1)	27(1)
Br(4)	3611(1)	7154(1)	-864(1)	26(1)
Br(5)	7164(2)	8048(1)	29(1)	40(1)
Br(6)	1572(2)	6481(1)	1228(1)	37(1)
Br(7)	7080(2)	4312(1)	3444(1)	35(1)
Br(8)	-786(2)	482(1)	1225(1)	39(1)
Br(9)	-251(2)	8094(1)	2948(1)	41(1)

Table 3. Selected bond lengths (in pm) of $(\text{BiBr}_2)_2[(\text{W}_6\text{Br}_8)\text{Br}_6^{\text{a}}]$.**W – W: 261.94(7) – 264.13(7)**

W(1)-W(2)	262.66(9)
W(1)-W(2)	263.10(8)
W(1)-W(3)	264.13(7)
W(1)-W(3)	263.11(9)
W(2)-W(3)	263.02(9)
W(2)-W(3)	261.94(7)

W – Brⁱ: 260.1(2) – 262.8(1)

W(1)-Br(1)	261.8(1)
W(1)-Br(2)	260.1(2)
W(1)-Br(3)	262.2(1)
W(1)-Br(4)	261.8(2)
W(2)-Br(1)	262.8(1)
W(2)-Br(2)	262.5(1)
W(2)-Br(3)	261.4(1)
W(2)-Br(4)	262.3(1)
W(3)-Br(1)	261.8(1)
W(3)-Br(2)	260.8(2)
W(3)-Br(3)	260.5(1)
W(3)-Br(4)	262.5(1)

W – Br^a: 257.4(2) – 264.2(2)

W(1)-Br(5)	264.2(2)
W(2)-Br(6)	257.4(2)
W(3)-Br(7)	262.2(1)

Bi – Br

Bi(1)-Br(5)	294.8(2)
Bi(1)-Br(6)	309.5(2)
Bi(1)-Br(7)	290.3(2)
Bi(1)-Br(8)	265.9(2), 325.7(2)
Bi(1)-Br(9)	261.3(1)

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