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**Constitutional Isomerism of BiW₆Cl₁₅: (BiCl)[W₆Cl₁₄] and
(BiCl₂)[W₆Cl₁₃]**

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Constitutional Isomerism of $\text{BiW}_6\text{Cl}_{15}$: $(\text{BiCl})[\text{W}_6\text{Cl}_{14}]$ and $(\text{BiCl}_2)[\text{W}_6\text{Cl}_{13}]$

Markus Ströbele and H.-Jürgen Meyer*

Keywords: Bismuth; Tungsten cluster; Isomerism; Structure

Abstract. The compound $(\text{BiCl})[\text{W}_6\text{Cl}_{14}]$ was previously characterized as a product of the reduction of tungsten hexachloride with elemental bismuth. Another modification of $\text{BiW}_6\text{Cl}_{15}$ is now presented as $(\text{BiCl}_2)[\text{W}_6\text{Cl}_{13}]$, based on the results of an X-ray single crystal structure determination (space group $P2_1/c$, $a = 1354.3(2)$ pm, $b = 1234.4(2)$ pm, $c = 1538.9(2)$ pm, and $\beta = 118.76(1)^\circ$). The structure of $(\text{BiCl}_2)[\text{W}_6\text{Cl}_{13}]$ contains chains of $[(\text{W}_6\text{Cl}_8)\text{Cl}_4^{\text{a}}\text{Cl}_{2/2}^{\text{a-a}}]^-$ clusters bridged by chlorine atoms. The $(\text{BiCl}_2)^+$ counter ion exhibits two short Bi–Cl distances of 244.1(4) and 245.9(3) pm, respectively.

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Introduction

The reduction of WCl_6 with bismuth metal can be used for the synthesis of reduced tungsten chlorides [1,2]. The raw product obtained from this reaction has brought up $(BiCl)[W_6Cl_{14}]$ after the coproduced $BiCl_3$ was sublimed off. The crystal structure of $(BiCl)[W_6Cl_{14}]$ was already determined by X-ray diffraction a short while ago [2]. However, the X-ray powder pattern of the raw product revealed the presence of several unknown X-ray reflections, evidenced after subtracting the pattern of the known $(BiCl)[W_6Cl_{14}]$.

This raw product, containing $(BiCl)[W_6Cl_{14}]$ and other minor phases, is used in course of the W_6Cl_{12} synthesis. Dissolution of the raw product into concentrated HCl yields the cluster acid $(H_3O)_2[W_6Cl_{14}] \cdot 7H_2O$ besides other compounds [2], and its pyrolysis yields deep yellow W_6Cl_{12} .

This entire synthesis was reproduced by us several times in order to collect larger quantities of W_6Cl_{12} . After finishing up the first reaction step and subliming off the $BiCl_3$, bright red crystals of an unknown phase appeared besides those of $(BiCl)[W_6Cl_{14}]$. The new structure was characterized as $(BiCl_2)[W_6Cl_{13}]$ by single crystal X-ray diffraction.

Experimental Section

All reactions were performed under the same reaction conditions as described very recently, using the same sources and purities of materials [2]. Bright red crystals, which later turned out to represent a new modification of BiW_6Cl_{15} , were selected from the raw product for X-ray single crystal structure analysis.

X-ray diffraction

Single crystal X-ray diffraction data of $(BiCl_2)[W_6Cl_{13}]$ were collected on an IPDS diffractometer (STOE, Darmstadt) using monochromatized Mo- K_α radiation. Cell refinements and the data reduction were carried out using the STOE IPDS software. An absorption correction was applied using the programs X-Shape/X-Red [3]. The structures were refined by full-matrix least-squares procedures using SHELX-97 [4]. Crystallographic data and structure refinement results are summarized in Table 1, atom positions are presented in Table 2, and a comparison of bond length is provided in Table 3.

Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on

quoting the depository number CSD-420528 for $(\text{BiCl}_2)[\text{W}_6\text{Cl}_{13}]$.

Results and Discussion

The reduction of WCl_6 with bismuth yields two modifications of $\text{BiW}_6\text{Cl}_{15}$. Both phases, the already known $(\text{BiCl})[\text{W}_6\text{Cl}_{14}]$ and the new $(\text{BiCl}_2)[\text{W}_6\text{Cl}_{13}]$ appeared in the same reaction batch. The reaction was performed in a fused silica tube at 355 °C as follows:



The crystal structure of $(\text{BiCl})[\text{W}_6\text{Cl}_{14}]$ described a short time ago contains isolated $[(\text{W}_6\text{Cl}_8^i)\text{Cl}_6^a]^{2-}$ clusters and $(\text{BiCl})^{2+}$ ions [2]. Both fragments are interconnected with each other by chlorine bridges. Bismuth is coordinated by six outer chlorine atoms (Cl^a) plus one terminal chlorine atom featuring one short Bi–Cl bond of 248.9(4) pm, all together resulting in a strongly distorted single-capped trigonal prismatic arrangement of chlorine atoms. The centers of gravities of $[(\text{W}_6\text{Cl}_8)\text{Cl}_6]^{2-}$ and $(\text{BiCl})^{2+}$ ions in the structure follow the motif of sodium and chloride ions in the NaCl type structure.

The crystal structure of the new $(\text{BiCl}_2)[\text{W}_6\text{Cl}_{13}]$ resembles a completely different pattern. The structure is characterized by chains of chlorine bridged $[(\text{W}_6\text{Cl}_8^i)\text{Cl}_4^a\text{Cl}_{2/2}^{a-a}]^-$ clusters, running along the crystallographic *c* direction, with each $(\text{W}_6\text{Cl}_8^i)$ cluster core being connected via trans $\text{W}(1)\text{--Cl}(11)^{a-a}\text{--W}(6)$ bridges into chains, as shown in Figure 1. A similar connectivity pattern of clusters has been previously reported in structures of $\text{AMo}_6\text{Cl}_{13}$ compounds with $A = \text{Li}, \text{Na}$ [5].

The W–Cl bond lengths of $\text{W}(1)\text{--Cl}(11)^{a-a}\text{--W}(6)$ bridges along $[(\text{W}_6\text{Cl}_8^i)\text{Cl}_4^a\text{Cl}_{2/2}^{a-a}]^-$ cluster chains are 251,3(3) and 252,1(3) pm (Table 3). The remaining four outer chlorine atoms of $[(\text{W}_6\text{Cl}_8^i)\text{Cl}_4^a\text{Cl}_{2/2}^{a-a}]^-$ have bridging functionalities with the bismuth atom. Noteworthy is the strongly distorted octahedral arrangement of six chlorine atoms around the bismuth atom in $(\text{BiCl}_2)[\text{W}_6\text{Cl}_{13}]$, displayed in Figure 2, with four Bi–Cl^a distances ranging from 278.8(3) to 310.7(3) pm and two short Bi–Cl distances being 244.1(4) and 245.9(3) pm. These short contacts with terminal Cl(1) and Cl(2) atoms make up for considerably stronger covalent Bi–Cl interactions as it is expressed by the formula $(\text{BiCl}_2)[\text{W}_6\text{Cl}_{13}]$. Bond lengths of both $\text{BiW}_6\text{Cl}_{15}$ phases are nicely in agreement as can be seen in Table 3.

The occurrence of the compound $(\text{BiCl})[\text{Mo}_6\text{Cl}_{14}]$ [6] raises questions regarding its dimorphic character, too.

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Table 1. Crystal data and results on the structure refinement of $(\text{BiCl}_2)[\text{W}_6\text{Cl}_{13}]$.

Formula	$(\text{BiCl}_2)[\text{W}_6\text{Cl}_{13}]$
Formula weight / $\text{g}\cdot\text{mol}^{-1}$	1843.83
Crystal system	monoclinic
Space group	$P 2_1/c$
Unit cell dimensions / pm	$a = 1354.3(2)$
	$b = 1234.4(2)$
	$c = 1538.9(2)$
Monoclinic angle / $^\circ$	$\beta = 118.76(1)$
Volume / nm^3	2.2554(5)
Z	4
Crystal size / mm^3	0.26 x 0.28 x 0.16
Temperature / K	293(2)
$\lambda(\text{Mo-K}\alpha)$ / pm	71.073
Calc. density / $\text{g}\cdot\text{mol}^{-3}$	5.430
Absorption coefficient / mm^{-1}	40.006
F(000)	3128
Θ range for data collection / $^\circ$	2.24 to 24.99
Index ranges	$-16 \leq h \leq 16, -14 \leq k \leq 14, -18 \leq l \leq 18$
Reflections collected	17067
Independent reflections	3818 [R(int) = 0.0769]
Refinement method	Full-matrix least-squares on F^2
Data / parameters	3818 / 200
Goodness-of-fit on F^2	1.000
Final R indices [$ I > 2\sigma(I)$]	R1 = 0.0334, wR2 = 0.0762
R indices (all data)	R1 = 0.0394, wR2 = 0.0785
Extinction coefficient	0.00108(3)
Largest diff. peak and hole / $e\text{\AA}^{-3}$	2.061 and -1.808

Table 2. Atom positions and equivalent isotropic displacement parameters (in 10^{-4} pm^2) for $(\text{BiCl}_2)[\text{W}_6\text{Cl}_{13}]$.

	x	y	z	U_{eq}
Bi(1)	0.7908(1)	0.1906(1)	0.6915(1)	0.027(1)
W(1)	0.2761(1)	0.3233(1)	0.4454(1)	0.019(1)
W(2)	0.1220(1)	0.2244(1)	0.4703(1)	0.020(1)
W(3)	0.2376(1)	0.3821(1)	0.5893(1)	0.021(1)
W(4)	0.4246(1)	0.2815(1)	0.6298(1)	0.021(1)
W(5)	0.3081(1)	0.1243(1)	0.5111(1)	0.021(1)
W(6)	0.2697(1)	0.1833(1)	0.6551(1)	0.021(1)
Cl(1)	0.9479(2)	0.1030(3)	0.6813(2)	0.041(1)
Cl(2)	0.7733(4)	0.3274(3)	0.5702(3)	0.068(1)
Cl(3)	0.1011(2)	0.4164(2)	0.4153(2)	0.027(1)
Cl(4)	0.3886(2)	0.4693(2)	0.5633(2)	0.027(1)
Cl(5)	0.4532(2)	0.2276(2)	0.4887(2)	0.028(1)
Cl(6)	0.1666(2)	0.1685(2)	0.3379(2)	0.027(1)
Cl(7)	0.0894(2)	0.2815(2)	0.6077(2)	0.028(1)
Cl(8)	0.3809(2)	0.3377(2)	0.7628(2)	0.029(1)
Cl(9)	0.4477(2)	0.0890(2)	0.6878(2)	0.029(1)
Cl(10)	0.1601(2)	0.0365(2)	0.5391(2)	0.028(1)
Cl(11)	0.2738(2)	0.4171(2)	0.2995(2)	0.030(1)
Cl(12)	-0.0778(2)	0.1806(2)	0.3561(2)	0.034(1)
Cl(13)	0.1889(3)	0.5510(3)	0.6384(3)	0.047(1)
Cl(14)	0.6225(2)	0.3181(3)	0.7362(2)	0.038(1)
Cl(15)	0.3569(2)	-0.0440(2)	0.4553(3)	0.042(1)

Table 3. Comparison of bond length (in pm) in crystal structures of $(\text{BiCl})[\text{W}_6\text{Cl}_{14}]$ [2] and $(\text{BiCl}_2)[\text{W}_6\text{Cl}_{13}]$.

Atoms	$(\text{BiCl})[\text{W}_6\text{Cl}_{14}]$	$(\text{BiCl}_2)[\text{W}_6\text{Cl}_{13}]$
Bi – Cl	248.9(3)	244.1(4), 245.9(3)
Bi – Cl	276.4(4) – 309.7(3) (6x)	278.8(3) – 310.7(3) (4x)
W – W	260.00(7) – 262.62(7)	259.87(7) – 262.18(8)
W – Cl ⁱ	246.5(3) – 250.2(3)	245.0(3) – 250,8(3)
W – Cl ^{a(-a)}	242.2(3) – 248.6(3)	241.5(4) – 252.1(3)

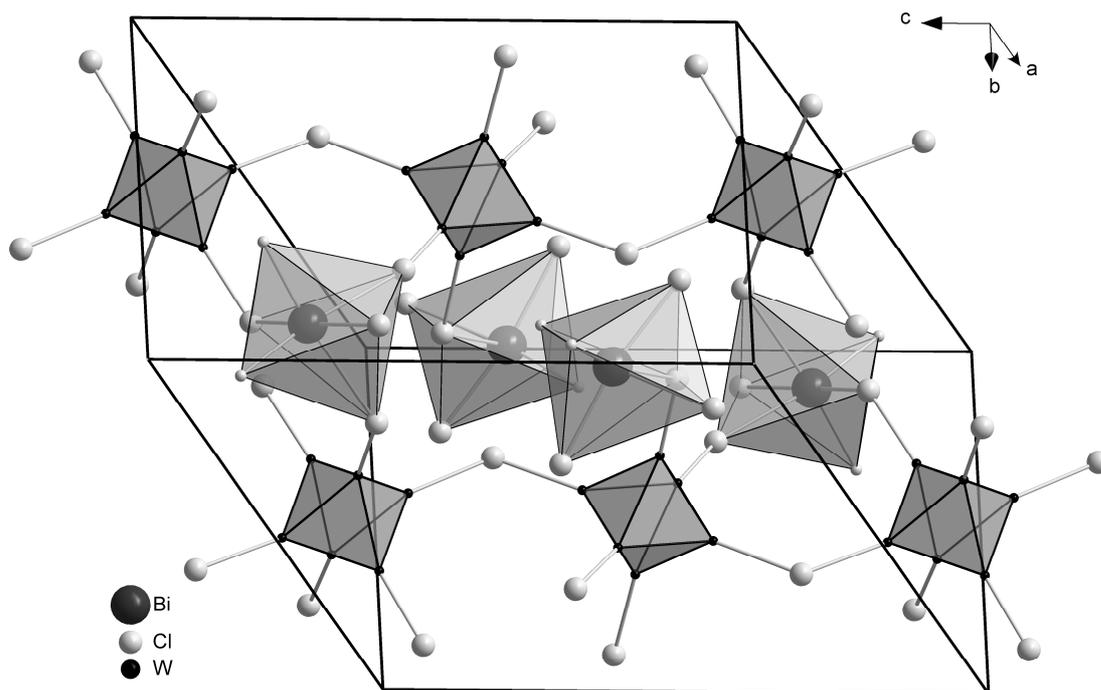


Figure 1. Crystal structure of $(\text{BiCl}_2)[(\text{W}_6\text{Cl}_8)\text{Cl}_4^a \text{Cl}_{2/2}^{a-a}]$ with dark gray octahedra representing the $[\text{W}_6]$ cores bridged by $\text{Cl}(11)^{a-a}$ atoms, and light gray octahedra showing distorted $[\text{BiCl}_6]$ units. Chlorine atoms which do not connect to the cluster are displayed as smaller spheres. All Cl^i atoms are suppressed from the drawing for a better illustration of the connectivity pattern.

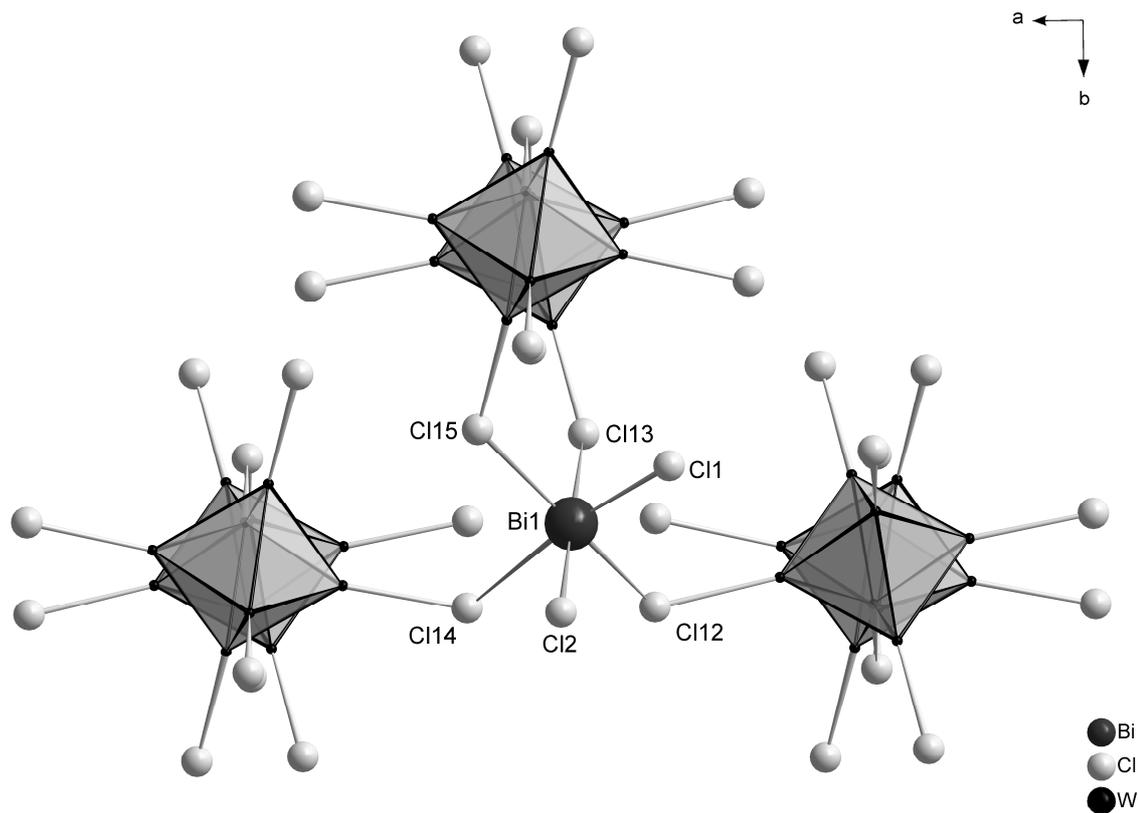


Figure 2. Connectivity of bismuth atoms in crystal structure of $(\text{BiCl}_2)[\text{W}_6\text{Cl}_{13}]$. Note the terminal Cl(1) and Cl(2) atoms of bismuth. All Cl^i atoms are suppressed from the drawing.