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Two Modifications of Copper(I) *Octahedro*-Hexatungsten(II) Tetradecabromide, $Cu_2[W_6Br_{14}]$

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Abstract. The reaction of W_6Br_{12} with CuBr sealed in an evacuated silica tube at the temperature gradient 925/915 K and annealing at 625/300 K yields a mixture of orthorhombic α-$Cu_2[W_6Br_{14}]$ and cubic β-$Cu_2[W_6Br_{14}]$ in the low temperature zone. α-$Cu_2[W_6Br_{14}]$ crystallizes in the space group *Pbca* (no. 61), a = 15.126 Å, b = 9.887 Å, c = 15.954 Å, Z = 4, *oP*88, and β-$Cu_2[W_6Br_{14}]$ crystallizes in the space group $Pn\bar{3}$ (no. 201), a = 13.391 Å, Z = 4, *cP*88. The crystal structures are built up by $[(W_6Br^i_8)Br^a_6]^{2-}$ cluster anions and Cu^+ cations. The cluster anions show only in the peripheral shells small deviation from $m\bar{3}m$ symmetry ($\bar{d}$(W–W) = 2.630 Å; $\bar{d}$(W–Br^i) = 2.618 Å; $\bar{d}$(W–Br^a) = 2.614 Å). The anions are arranged in a slightly compressed *bcc* pattern (α) and *ccp* (β) pattern, respectively. The Cu^+ cations are trigonal-planar coordinated by Br^a ligands with $\bar{d}$(Cu–Br) = 2.377 Å (α) and 2.378 Å (β). The cubic β-modification is diamagnetic with an unexpected large susceptibility ($\chi_{mol} = -884 \times 10^{-6}\ cm^3\ mol^{-1}$) and have a band gap of 2.8 eV. It decomposes under dynamic vacuum in two steps at 795 K und 1040 K.

Keywords: Ternary copper tungsten bromides; $Cu_2[W_6Br_{14}]$; cluster compound; syntheses; crystal structure; properties

Zwei Modifikationen von Kupfer(I)-*octahedro*-hexawolframat(II)-tetradecabromid, $Cu_2[W_6Br_{14}]$

Inhaltsübersicht. Bei der Umsetzung von W_6Br_{12} mit CuBr in einer evakuierten Quarzampulle im Temperaturgradienten 925/915 K und nachfolgendem Tempern bei 625/300 K entsteht ein Gemisch von orthorhombischem α-$Cu_2[W_6Br_{14}]$ und kubischem β-$Cu_2[W_6Br_{14}]$ in der kalten Zone. α-$Cu_2[W_6Br_{14}]$ kristallisiert in der Raumgruppe *Pbca* (Nr. 61), a = 15,126 Å, b = 9,887 Å, c = 15,954 Å, Z = 4, *oP*88, und β-$Cu_2[W_6Br_{14}]$ in der Raumgruppe $Pn\bar{3}$ (Nr. 201), a = 13,391 Å, Z = 4, *cP*88. Die Kristallstrukturen sind aus den Cluster-Anionen $[(W_6Br^i_8)Br^a_6]^{2-}$ und Cu^+-Kationen aufgebaut. Die Cluster-Anionen zeigen in beiden Modifikationen nur in den peripheren Schalen kleine Abweichungen von der Symmetrie $m\bar{3}m$ ($\bar{d}$(W–W) = 2,630 Å; $\bar{d}$(W–Br^i) = 2,618 Å; $\bar{d}$(W–Br^a) = 2,614 Å). Die Packung der Anionen entspricht in α einer leicht gestauchten *bcc*-Struktur und in β einem *ccp*-Muster. Die Cu^+-Kationen sind in beiden Modifikationen trigonal-planar von Br^a-Liganden koordiniert mit $\bar{d}$(Cu–Br) = 2,377 Å (α) und 2,378 Å (β). Die kubische β-Modifikation ist diamagnetisch mit einer unerwartet großen Suszeptibilität ($\chi_{mol} = -884 \times 10^{-6}\ cm^3\ mol^{-1}$), besitzt eine Bandlücke von 2,8 eV, und zersetzt sich im dynamischen Vakuum in zwei Stufen bei 795 K und 1040 K.

1 Introduction

In the group of ternary-*octahedro* hexatungsten cluster bromides of the alkali metals, we have successfully prepared $Na[W_6Br_{13}]$ [1, 2], $Na[W_6Br_{14}]$ [2, 3] and $A_2[W_6Br_{14}]$ with A = K, Rb, Cs [2, 4]. The structure of $Na[W_6Br_{13}]$ contains one-dimensional anionic chains *trans*-$^1_\infty[(W_6Br^i_8)Br^a_4Br^{a-a}_{2/2}]^{1-}$ and Na^+ ions. $Na[W_6Br_{14}]$ is isostructural with $Hg[Mo_6Cl_{14}]$ [5] and contains isolated monovalent $[(W_6Br^i_8)Br^a_6]^{1-}$ cluster

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anions. The compounds $A_2[W_6Br_{14}]$ are derivatives of divalent $[(W_6Br^i_8)Br^a_6]^{2-}$ cluster anions, forming a filled variant of $Hg[Mo_6Cl_{14}]$ [5]. The comparison of the two cubic compounds, $Na[W_6Br_{14}]$ and $K_2[W_6Br_{14}]$, do not indicate cationic size effects in the structure, but much more changes by electronic effects. This prompted us to try the synthesis of Cu(I) compounds, which leads to the discovery of two modifications of $Cu_2[W_6Br_{14}]$. During our studies, *Ihmaine, Perrin* and *Sergent* [6] reported about the cubic modification of $Cu_2[W_6Br_{14}]$, which was prepared by heating a mixture of WBr_5, $CuBr_2$ and W powder at 750 °C. In this work, we report our results on the crystal structures of orthorhombic and cubic $Cu_2[W_6Br_{14}]$ as well as on magnetic, optical and thermal properties.

2 Syntheses

A mixture of 500 mg (0.252 mmol) W_6Br_{12} [7] and 72 mg (0.50 mmol) CuBr (Fluka, p. a.) was sealed in an evacuated silica tube ($\varnothing_{inner}$ = 12 mm, L = 100 mm) and heated at the temperature gradient 925/915 K for 4 weeks with the starting materials in the high temperature zone. $Cu_2[W_6Br_{14}]$ was deposited in the low temperature zone. The silica tube was then kept at 625/300 K with the product at 625 K for 2 days to sublime WBr_5 and WBr_6 to the low temperature zone. Pure cubic $Cu_2[W_6Br_{14}]$ was obtained in high yield (> 95%) from the outmost end of the tube. It forms a dark green sintered aggregate. Next to the sintered clumps, in direction to the low temperature zone, grew a small amount of greenish yellow bipyramidal crystals of the orthorhombic phase.

On grinding, the sintered dark green aggregates turns greenish yellow. Both modifications are stable in air. It was difficult to gather sufficient amount of the orthorhombic phase, and, therefore, the investigations of properties were done with samples of the cubic phase.

3 Structure determination

Suitable single crystals were selected and fixed in sealed capillaries. The quality was checked by Laue photographs and the intensities were measured on a four-circle diffractometer. The lattice parameters were refined from the 2 values of 20 carefully centered reflections. Detailed information about the crystal data and structure determination are summarized in Table 1. The final positional and displacement parameters are given in Tables 2 and 3. Additional material can be ordered referring to the no. CSD-408570 (α-$Cu_2[W_6Br_{14}]$) and CSD-408569 (β-$Cu_2[W_6Br_{14}]$), names of the authors and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany.

α-$Cu_2[W_6Br_{14}]$: The structure was solved by direct methods and final full-matrix least squares refinement. It was recognized later that α-$Cu_2[W_6Br_{14}]$ is isotypic with $Cu_2[Mo_6I_{14}]$ [10].

β-$Cu_2[W_6Br_{14}]$: The cubic unit cell and the space group (Table 1) suggested that this compound may be isostructural with $Na[W_6Br_{14}]$ [2, 3] or $K_2[W_6Br_{14}]$ [2, 4], but the refinement was not successful with the parameters of these compounds. Nevertheless, the po-

Table 1 Crystal data for orthorhombic α-$Cu_2[W_6Br_{14}]$ and cubic β-$Cu_2[W_6Br_{14}]$ (T = 293 K)

Phase	α	β
Formula; mole mass	$Cu_2W_6Br_{14}$; 2348.85 amu	$Cu_2W_6Br_{14}$; 2348.85 amu
Crystal shape	greenish yellow bipyramid	greenish yellow cube
Crystal size (mm)	0.10 × 0.10 × 0.10	0.12 × 0.10 × 0.10
Space group	*Pbca* (no. 61)	$Pn\bar{3}$ (no. 201)
Formula units	Z = 4	Z = 4
Pearson code	*oP*88	*oP*88
Unit cell (Å)	a = 15.126(2), b = 9.887(1), c = 15.954(2)	a = 13.391(1)
V ($Å^3$); D_x (g cm^{-3})	2385.9(9), 6.539	2401.3(5), 6.479
Measurement	Siemens R3m/V four-circle diffractometer, Mo Kα radiation (λ = 0.71073 Å); Wyckoff scan mode; $2\vartheta_{max} = 55°$	
Calculations	direct methods, DIFABS, difference Fourier syntheses; full-matrix least squares refinement, unit weights; CSD package [8]	
N (parameter)	100	35
μ (mm^{-1})	57.08	57.08
extinction coefficient	0.0009(1)	0.00019(1)
N(*hkl*) (meas./unique)	3950/2747	3102/934
N(*hkl*) ≥ $4\sigma(F_o)$	1627	715
R(*F*)	0.073	0.048

Table 2 Positional and displacement parameters (pm^2) for the orthorhombic α-$Cu_2[W_6Br_{14}]$; (standard deviations); displacement factor: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2\,U_{23}klb^*c^*)]$

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Function
W1	8 *c*	0.9593(1)	0.1574(2)	0.4489(1)	80(8)	43(8)	74(8)	19(7)	–5(6)	24(7)	W_6
W2	8 *c*	0.0633(1)	0.1032(2)	0.5762(1)	59(8)	67(8)	55(7)	6(7)	–9(6)	3(7)	W_6
W3	8 *c*	0.0972(1)	–0.0015(2)	0.4285(1)	75(8)	74(8)	56(7)	23(7)	4(6)	–10(8)	W_6
Br1	8 *c*	0.8002(3)	0.0555(5)	0.4441(3)	120(20)	150(20)	130(20)	40(20)	–40(20)	–10(20)	Br^i
Br2	8 *c*	0.6194(3)	0.2422(5)	0.5458(3)	130(20)	110(20)	180(20)	50(20)	–10(20)	10(20)	Br^i
Br3	8 *c*	0.9917(3)	0.0510(6)	0.3022(3)	140(20)	230(30)	60(20)	–10(20)	–10(20)	60(20)	Br^i
Br4	8 *c*	0.4253(3)	0.2383(5)	0.4028(3)	140(20)	100(20)	210(20)	–40(20)	10(20)	–50(20)	Br^i
Br5	8 *c*	0.4081(4)	0.1173(5)	0.6225(4)	250(30)	130(20)	340(30)	–30(2)	70(20)	130(20)	Br^a
Br6	8 *c*	0.6495(3)	0.2489(6)	0.3159(3)	170(20)	160(20)	170(20)	40(20)	40(20)	–90(20)	Br^a
Br7	8 *c*	0.2388(3)	0.0007(7)	0.3342(3)	110(20)	330(30)	140(20)	–20(20)	40(20)	–20(20)	Br^a
Cu	8 *c*	0.2831(4)	0.1300(9)	0.7084(5)	160(30)	410(50)	310(40)	–10(30)	40(30)	60(30)	

Table 3 Positional and displacement parameters (pm^2) for the cubic β-$Cu_2[W_6Br_{14}]$; origin at $\overline{3}$ (choice 2) (standard deviations); displacement factor: $\exp[-2\pi^2(U_{11}h^2a^{*2}+\cdots+2\,U_{23}klb^*c^*)]$

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Function
W	24*h*	0.13271(6)	–0.02570(6)	0.03214(6)	61(4)	79(4)	76(4)	–5(3)	–19(3)	5(3)	W_6
Br1	8*e*	0.1393(2)	x	x	164(8)	U_{11}	U_{11}	–47(8)	U_{12}	U_{12}	Br^i
Br2	24*h*	0.1886(2)	0.0736(2)	–0.1267(2)	85(9)	172(10)	159(10)	–36(8)	33(8)	3(8)	Br^i
Br3	24*h*	0.3170(2)	–0.0667(2)	0.0809(2)	112(10)	245(12)	264(12)	6(9)	–66(9)	78(10)	Br^a
Cu	8*e*	0.4339(3)	x	x	285(13)	U_{11}	U_{11}	35(15)	U_{12}	U_{12}	

sitions of W and Br were found to be correct and, after several cycles, the Cu atoms were located from difference Fourier syntheses. The final refinement gave the composition $Cu_2[W_6Br_{14}]$.

4 Physical Measurements

4.1 The magnetic susceptibility was measured on a powdered sample (202.3 mg) with the use of a SQUID magnetometer (Quantum Design Model MPMS 5.5) in the temperature range $5 \leq T(K) \leq 300$ with an applied field of 1 Tesla.

4.2 The diffuse reflectivity was measured with a Perkin-Elmer Lambda 9 spectrometer in the range of 250–800 nm. The powdered sample was loaded under inert condition into a flat quartz container which was then sealed under dynamic vacuum.

4.3 Combined thermogravimetric and mass spectrum measurements (TG–MS) were carried out with a thermogravimetric analyzer (STA 429, Netzsch Gerätebau, Selb) coupled to a mass spectrometer (Fa. Balzers). The powdered sample (15.1 mg) was heated with 10 K min^{-1} under dynamic vacuum up to 1273 K.

5 Results and Discussion

5.1 Thermal stability

As shown in section 2, the two modifications of $Cu_2[W_6Br_{14}]$ are formed under the conditions of synthesis at separated zones in the reaction tube. The cubic modification seems to be formed first and will be transformed into the orthorhombic modification below 625 K (annealing in temperature gradient 625/300 K to sublime the higher tungsten bromides). This corresponds to the smaller mole volume of the orthorhombic form (359.2 $cm^3\,mol^{-1}$ vs. 361.5 $cm^3\,mol^{-1}$; Table 1). We have, therefore, designated the orthorhombic phase as the low-temperature modification α-$Cu_2[W_6Br_{14}]$. With these arguments, the higher symmetric cubic β-$Cu_2[W_6Br_{14}]$ is the HT-modification which should be metastable at room temperature. The expected exothermic phase transformation $\alpha \rightarrow \beta$ at higher temperatures was not yet observed directly, but the sudden evaporation of some CuBr at about 600 K (Fig. 1) indicates such a small exothermic process.

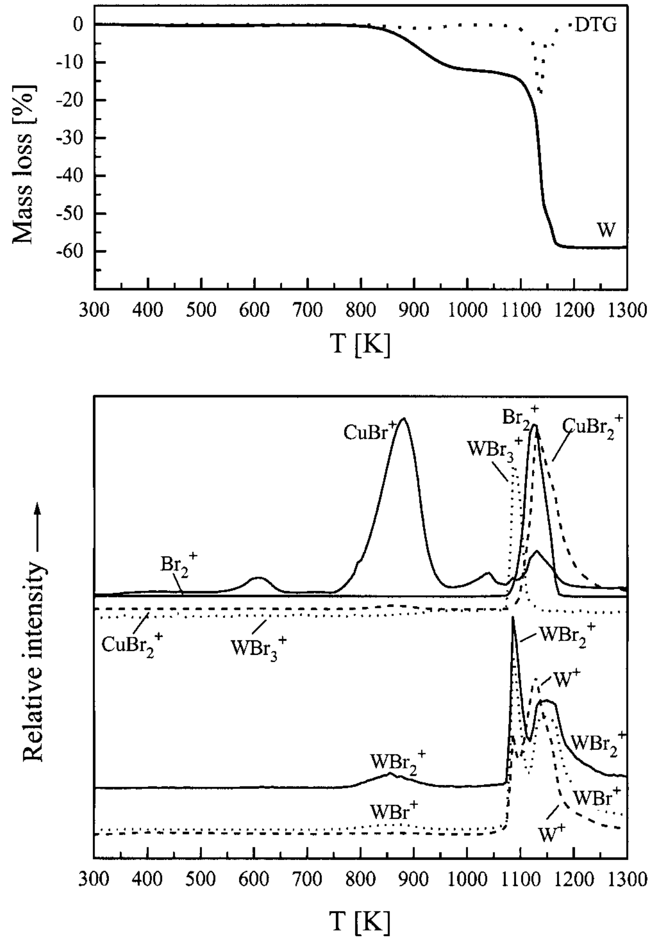


Fig. 1 Cubic $Cu_2[W_6Br_{14}]$: mass loss with temperature under dynamic vacuum (upper) and simultaneously recorded mass spectrum (below)

Under dynamic vacuum, the thermal decompsition of $Cu_2[W_6Br_{14}]$ starts at 795 K (Fig. 1) with the complete loss of 2 CuBr (–12.2%). The residue at 1010 K was confirmed to be W_6Br_{12} by X-ray powder patterns. In the second step, W_6Br_{12} is decomposed to tungsten at about 1040 K. The gas phase analysis (mass spectra) shows the evaporation of CuBr in the first step, and the evaporation of tungsten bromides in the second step (Fig. 1). The $CuBr_2^+$ fragment observed at 1150 K has nothing to do with the thermal decomposition of $Cu_2[W_6Br_{14}]$, because the stoichiometrical CuBr mass loss is complete at the first step (795 K). The $CuBr_2^+$ fragment, therefore, indicates a reaction of elementary bromine with CuBr or Cu outside the Knudsen cell.

5.2 Magnetism and optical reflection

Cubic β-$Cu_2[W_6Br_{14}]$ is diamagnetic with $\chi_{mol} = -884 \times 10^{-6}$ cm^3 mol^{-1} in agreement with the presence of divalent $[W_6Br_{14}]^{2-}$ cluster anions and monovalent Cu^+ ions. The diamagnetic susceptibility is unexpected large. On one hand, the value fits the sum of the diamagnetic increments of about -830×10^{-6} cm^3 mol^{-1} [9]. On the other hand, one misses the contribution of van Vleck paramagnetism (TIP) which is usually observed with this type of cluster compounds ($400 \leq \chi(\mathrm{TIP}) \cdot 10^6 \leq 600$ cm^3 mol^{-1}), e. g. with the close related cubic $Tl_2[W_6Br_{14}]$ [2]. The unique coordina-

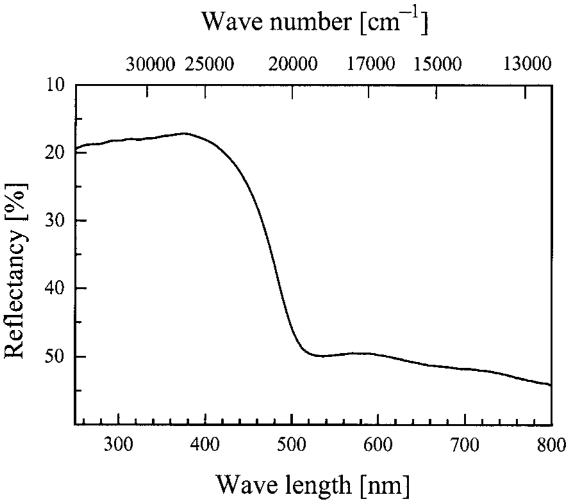
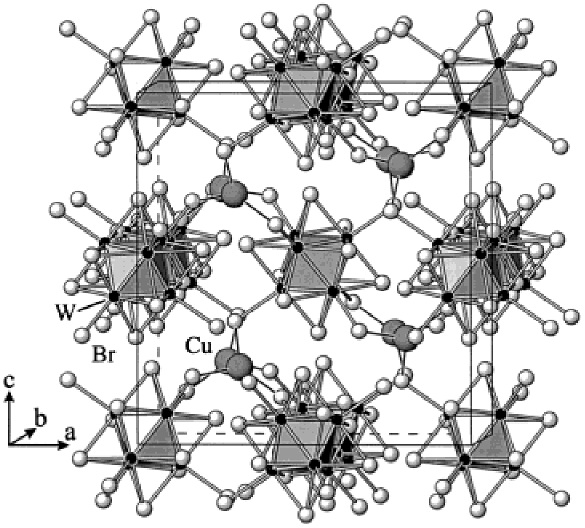


Fig. 2 Spectrum of diffuse reflection of cubic $Cu_2[W_6Br_{14}]$



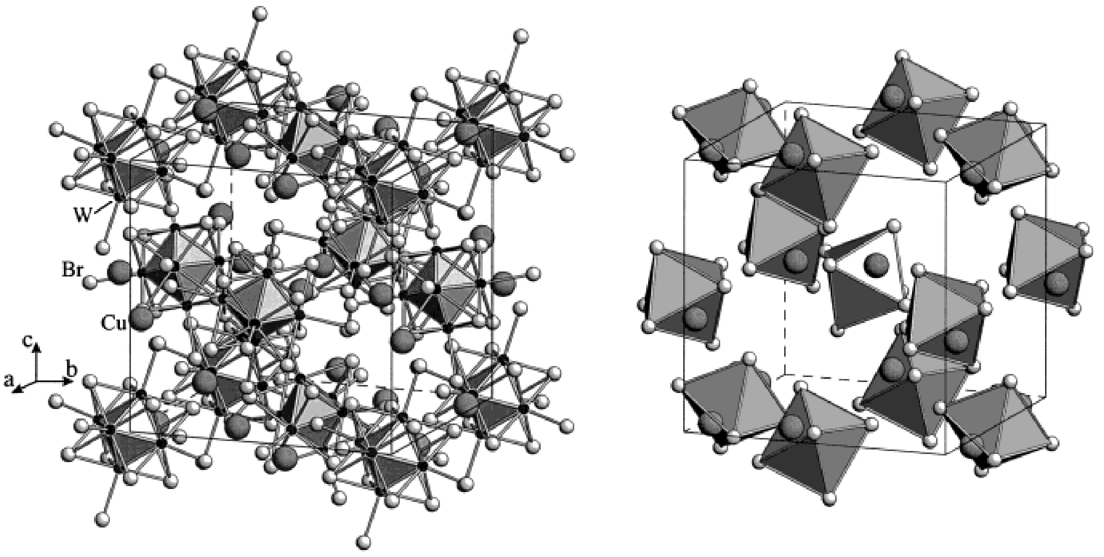


Fig. 3 Unit cells of α-$Cu_2[W_6Br_{14}]$ (upper) and β-$Cu_2[W_6Br_{14}]$ together with the trigonal antiprismatic Cu_2Br_6 polyhedra (below)

tion of the Cu^+ cations is the main structural difference between β-$Cu_2[W_6Br_{14}]$ and all the other corresponding cubic cluster compounds. Maybe this detail is responsible for the suppressed TIP contribution.

The diffuse reflection spectrum (Fig. 2) shows the onset of the strong absorption at 22600 cm^{-1} which corresponds to the colour of the compound. The band gap is $E_g = 2.80$ eV. The weak irregularity at 17400 cm^{-1} may indicate a d–d transition.

5. 3 *Crystal structures*

Orthorhombic α-$Cu_2[W_6Br_{14}]$ is isostructural with $Cu_2[Mo_6I_{14}]$ [10], while cubic β-$Cu_2[W_6Br_{14}]$ has the structure of $Cu_2[Mo_6Cl_{14}]$ and $Cu_2[Mo_6Br_{14}]$ [10]. Compared with the recently reported cubic $Cu_2[W_6Br_{14}]$ with a = 13.3866(6) Å [6], our unit cell is slightly larger (a = 13.391(1) Å), but no significant differences occur in the atomic parameters.

The two modifications (Fig. 3) differ mainly by the packing of the cluster anions, which corresponds to a slightly compressed *bcc* pattern in α and a *fcc* pattern in β. In the α modification, the clusters are centered at the orthorhombic point configuration *F*, which is very close to a tetragonal point configuration *I* with $(c/a)_t = 0.900$ $(a_t = (a/\sqrt{2} + c/\sqrt{2})/2 = 10.988$ Å; $c_t = b = 9.887$ Å). In the β modification, the clusters are centered at the cubic point configuration *F*.

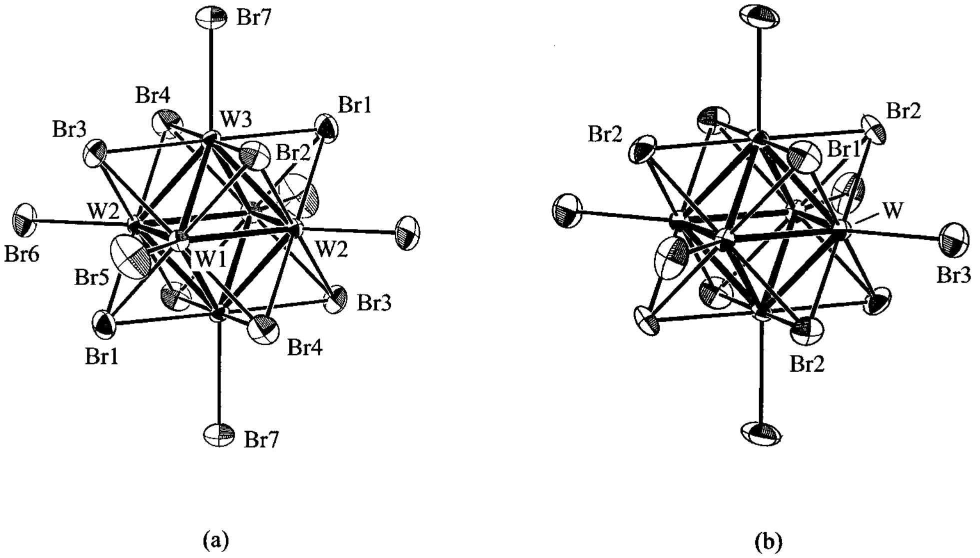


Fig. 4 The $[(W_6Br^i_8)Br^a_6]^{2-}$ cluster anions in α-$Cu_2[W_6Br_{14}]$ (a) and β-$Cu_2[W_6Br_{14}]$ (b) with displacement ellipsoids (90% probability) (Atomic labelling see Table 2 and 3)

Table 4 Selected interatomic distances (Å) and bond angles (°) for α-$Cu_2[W_6Br_{14}]$ and β-$Cu_2[W_6Br_{14}]$

	α			β	
W1–W2	2.624(2)	W3–Br7	2.618(5)	W–W	2.629(1) (2×)
–W2	2.630(3)	Br1–Br2	3.702(7)	–W	2.633(1) (2×)
–W3	2.632(2)	–Br3	3.677(7)	–Br1	2.636(3)
–W3	2.633(2)	–Br4	3.702(7)	–Br2	2.602(3)
W2–W3	2.624(2)	–Br5	3.776(7)	–Br2	2.616(3)
–W3	2.629(2)	–Br6	3.735(7)	–Br2	2.618(3)
W1–Br1	2.610(5)	–Br7	3.629(7)	–Br3	2.611(2)
–Br2	2.619(5)	Br2–Br3	3.714(7)	Br1–Br2	3.728(4) (3×)
–Br3	2.612(5)	–Br4	3.718(7)	–Br3	3.727(4) (3×)
–Br4	2.632(5)	–Br5	3.776(7)	Br2–Br2	3.677(4) (2×)
–Br5	2.619(6)	–Br6	3.697(7)	–Br3	3.653(4)
W2–Br1	2.613(5)	–Br7	3.659(8)	–Br3	3.665(4)
–Br2	2.616(5)	Br3–Br4	3.703(7)	–Br3	3.771(4)
–Br3	2.604(5)	–Br5	3.714(8)	Cu–Cu	3.066(8)
–Br4	2.632(5)	–Br6	3.678(8)	Cu–Br3	2.378(5) (3×)
–Br6	2.608(5)	–Br7	3.805(6)		
W3–Br1	2.612(5)	Br4–Br5	3.713(8)	W–Br^i–W	60.3(4)
–Br2	2.618(5)	–Br6	3.665(6)	Br3–Cu–Br3	120.0(2) (3×)
–Br3	2.622(5)	–Br7	3.754(8)		
–Br4	2.627(5)	W–Br^i–W	60.3(2)		
Cu–Br5	2.339(9)	Br5–Cu–Br6	128.2(4)		
–Br6	2.381(9)	Br5–Cu–Br7	124.8(4)		
–Br7	2.410(10)	Br6–Cu–Br7	106.8(3)		

The divalent $[W_6Br_{14}]^{2-}$ cluster anions (Fig. 4) differ by small distortion in the corresponding crystal fields, namely with respect to the symmetry $\overline{1}$ in the orthorhombic phase and $\overline{3}$ in the cubic structure (Table 4). On average, however, the $[W_6Br_{14}]^{2-}$ cluster anions in both modifications have practically the same shape (Table 5). The mean bond lengths and intracluster distances are $\overline{d}(W–W) = 2.630$ Å, $\overline{d}(W–Br^i) = 2.618$ Å, $\overline{d}(W–Br^a) = 2.614$ Å, $\overline{d}(Br^i–Br^i) = 3.703$ Å, $\overline{d}(Br^i–Br^a) = 3.711$ Å (Table 5). These values are almost identical with those of other compounds with the cluster anion $[W_6Br_{14}]^{2-}$ [2, 4]. Again, the W atoms are shifted outside the Br_8^i cube by 0.008 Å. With respect to the inner W_6 octahedra, the Br_6^a octahedra are rotated from the ecliptic positions by 0.7–1.7° and 1.1° in both modifications, which is also observed with other compound, and which is related to the coordination of the cations by the Br^a ligands.

The trigonal-planar coordination of Cu^+ by Br^a ligands is shown in Fig. 5. The bond lengths in the α modification (d(Cu–Br) = 2.339–2.410 Å) demonstrate a considerable distortion (bond angles: 107°, 125°, 128°). The shortest Cu–Cu distance is 5.044 Å. In the β modification, however, the Cu atoms are perfectly triangular coordinated with d(Cu–Br) = 2.378 Å. But, the two Cu atoms center two opposite triangular faces of the slightly compressed trigonal antiprism formed by six Br^a ligands around the point configuration $F(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. This brings the Cu atoms pairwise at a distance d(Cu–Cu) = 3.066 Å. A detailed analysis of this cubic structure shows [11] that the compression of the trigonal antiprism around $F(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ results from the cluster rotation around the threefold axis at $F(000)$ and do not indicate Cu–Cu interactions.

Table 5 Mean interatomic distances (Å) and angles (°) in the $[(W_6Br_8^i)Br_6^a]^{2-}$ cluster anions of orthorhombic (α) and cubic (β) $Cu_2[W_6Br_{14}]$. $\Delta = \frac{1}{2}[\overline{d}(W–W) \cdot \quad 2 - \overline{d}(Br^i–Br^i)]$

	α	β	mean values
Local symmetry	$\overline{1}$	$\overline{3}$	$m\overline{3}m$
d(W–W)	2.629(4)	2.631(3)	2.630(1)
$d(W–Br^i)$	2.618(8)	2.618(14)	2.618(0)
$d(W–Br^a)$	2.615(6)	2.612(2)	2.614(2)
$d(Br^i–Br^i)$	3.703(14)	3.703(36)	3.703(0)
$d(Br^i–Br^a)$	3.717(54)	3.704(55)	3.711(9)
$W–Br^i–W$	60.2(4)	60.3(4)	60.3
Δ	0.008	0.009	0.008
Cu–Br	2.377(36)	2.378(5)	2.378

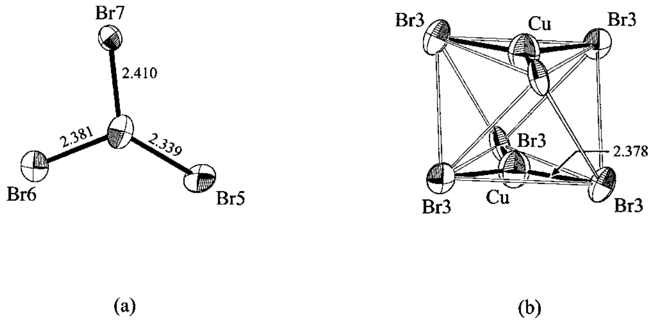


Fig. 5 Coordination of the Cu^+ cations in the orthorhombic (a) and cubic (b) modifications with displacement ellipsoids (90% probability)

Compared with cubic $K_2[W_6Br_{14}]$ with the same arrangement of $[W_6Br_{14}]^{2-}$ cluster anions but with different arrangement of cations [4], the distribution of the copper atoms in the present cubic modification is strongly related to the covalence and size of Cu^I. It is obvious that the Cu–Br distances of 2.825 Å and 2.997–3.457 Å would be too large to accomodate Cu^+ ions in the octahedral and tetrahedral holes if $Cu_2W_6Br_{14}$ would adopt the structure of $K_2W_6Br_{14}$ [4].

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