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CRYSTAL STRUCTURE OF WI_4

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Tungsten tetraiodide WI_4 (**1**) is produced by a high-temperature reaction of WTe_2 and I_2 in a vacuum sealed ampoule. The crystals of **1** belong to the triclinic crystal symmetry, space group P-1, $Z = 4$, $a = 7.9291(3)$ Å, $b = 10.7695(4)$ Å, $c = 10.8117(4)$ Å, $\alpha = 85.668(1)°$, $\beta = 71.772(1)°$, $\gamma = 71.559(1)°$, $V = 831.60(5)$ Å^3, $d_{calc} = 5.523$ g/cm^3. The structure of **1** consists of tetrameric W_4I_{16} molecules in which W atoms are in a distorted octahedral environment formed by I atoms.

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There are two basic methods to synthesize tungsten iodide: 1) a method based on the interaction of metallic tungsten with iodine vapor under temperature gradient conditions (transport reactions); 2) a method using the reaction of tungsten hexacarbonyl with iodine under elevated temperature and pressure. These reactions yield binary compounds such as W_4I_{13}, W_5I_{16}, W_6I_{12}, W_6I_{14}, W_6I_{15}, W_6I_{16}, W_6I_{17}, W_6I_{18}, $W_{15}I_{47}$, $WI_{3.3}$, and WI_4 [1-3]. For the time being, the majority of compounds of this series can be considered as sufficiently characterized, including the methods of structural analysis. On the other side, while studying the interaction of WTe_2 with iodine, we have obtained WI_4 crystals (this compound is known in the literature, but its crystal structure is not determined yet). In order to determine the structure of this compound and to confirm its composition, we have selected single WI_4 crystals and studied them by the single crystal X-ray diffraction (XRD).

Experimental. Initial tungsten telluride WTe_2 was obtained by the reaction of stoichiometric quantities of metallic tungsten and elemental tellurium in a vacuum-sealed quartz ampoule at a temperature of 800°C. The ratio of heavy elements was determined by energy dispersive X-ray spectroscopy (EDS) using the Hitachi TM3000 TableTop SEM desk-top scanning microscope assembled with a Bruker QUANTAX 70 EDS equipment. The powder X-ray diffraction analysis of the gross body of products was carried out on a Philips PW1700 diffractometer using CuK_α radiation ($\lambda = 1.54060$ Å).

Synthesis of WI_4 (1). 0.300 g (0.683 mmol) of WTe_2 and 0.867 g (0.683 mmol) of I_2 were put into a glass ampoule. The ampoule was sealed, heated in an oven up to 520°C, and kept under this temperature for 48 h, afterwards it was cooled for 12 h. Black crystals of WI_4 were formed. Judging by the EDS data, the ratio of the elements in the sample was as follows: W:I = 1:3.9. Crystals suitable for the XRD analysis were manually selected from the reaction medium.

Single crystal X-ray diffraction (XRD) analysis. The structure of compound **1** was determined by the XRD method using the standard procedures on an automated four-circle Bruker-Nonius X8 Apex diffractometer equipped with a two-dimensional CCD detector, at a temperature of 296(2) K using MoK_α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator.

The crystallographic data are as follows: triclinic crystal symmetry, space group P-1, $Z = 4$, $M = 691.45$, $a = 7.9291(3)$ Å, $b = 10.7695(4)$ Å, $c = 10.8117(4)$ Å, $\alpha = 85.668(1)°$, $\beta = 71.772(1)°$, $\gamma = 71.559(1)°$, $V = 831.60(5)$ Å^3,

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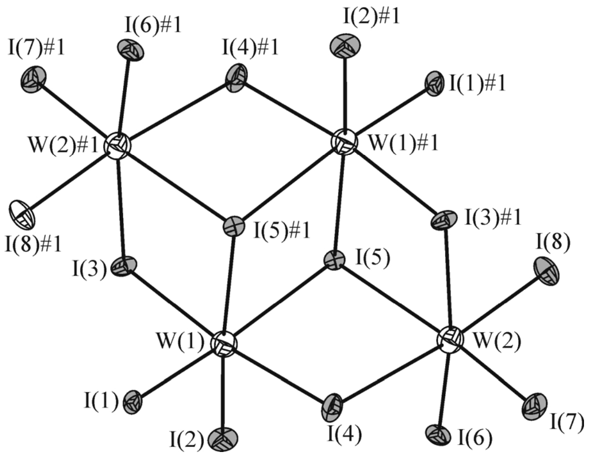

Fig. 1. Structure of the W_4I_{16} tetrameric molecule (50% probability ellipsoids are shown).

$d_{calc} = 5.523$ g cm^{-3}, $\mu = 28.629$ mm^{-1}. The crystal dimensions are 0.08×0.08×0.05 mm. Total 3119 reflections were measured in the θ range for data collection of 1.98-25.68° ($-9 \le h \le 9$, $-13 \le k \le 13$, $-13 \le l \le 13$), out of which 3123 were independent and 2799 observed reflections ($I \ge 2\sigma(I)$). The final data of the R-factors were as follows: $R_1 = 0.0599$, $wR_2 = 0.1741$ for 2799 reflections observed and $R_1 = 0.0646$, $wR_2 = 0.1796$ for all 3123 independent reflections. The S-factor on F^2 was 1.142.

The absorption was corrected empirically (by intensities of equivalent reflections) using the SADABS software [4]. The crystal structure was solved by the direct method. The final structure refinement was carried out by the matrix least-square technique in the anisotropic approximation for all atoms against independent reflections. All the calculations were carried out using the SHELXTL software package [4]. The atomic coordinates and values of thermal parameters have been deposited with the Inorganic Crystal Structure Database (ICSD) under no. CSD 428712, and they can be obtained from the following web-site: http://www.fiz-karlsruhe.de/request_for_deposited_data.html.

Results and discussion. The structure of **1** is formed by centrosymmetric tetrameric W_4I_{16} molecules (Fig. 1). This structural fragment has two crystallographically independent W atoms and six I atoms. The W(1) and W(2) atoms are located in the nonequivalent distorted octahedral coordination environment. Thus, in particular, the environment of the W(1) atoms

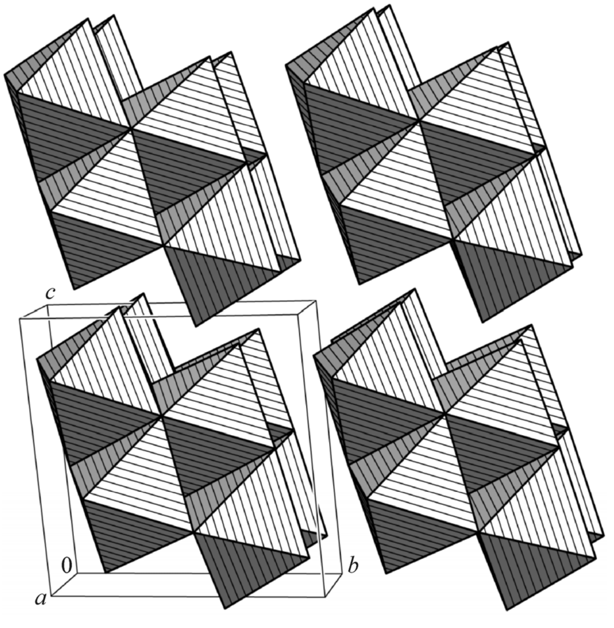

Fig. 2. General view of the WI_4 structure along the *a* axis.

consists of two terminal (I(1), I(2), two μ_2-I(3), I(4), and two μ_3-bridging I(5), I(5)#1; #1 – symmetry operation $-x$, $1-y$, $1-z$) atoms of iodine, while the environment of the W(2) atom has three terminal I(6), I(7), I(8), two μ_2- I(3)#1, I(4), and one μ_3-bridging I(5) atoms. Therefore, geometrically, the W_4I_{16} tetramer consists of four $\{WI_6\}$ octahedra sharing their edges. The $W-I_t$, $W-\mu_2$-I, $W-\mu_3$-I bond lengths (I_t are the terminal iodine atoms; the average values are given in parentheses) are in the following ranges: 2.7405(14)-2.7678(14) (2.75) Å, 2.9532(13)-3.3253(14) (3.1) Å, and 3.2245(14)-3.3265(14) (3.27) Å, respectively. The $W\cdots W$ intramolecular distances are 535(11) Å and 4.6556(11) Å. The $I\cdots I$ intermolecular contact lengths are in the range from 3.8111(18) Å to 4.4450(17) Å with the average value of 4.1 Å, which is a slightly smaller than the sum of the van der Waals radii of the iodine atoms (4.3 Å [5]). In the crystal of **1,** the tetrameric W_4I_{16} molecules are in the sites of the primitive pseudocubic lattice (Fig. 2).

First-row transition metals in compounds with halogens are known to tend to the formation of metallocluster compounds of various nuclearities. Thus, nearly all tungsten binary iodides, which have been already studied, and their derivatives have a cluster structure with cores containing 3-6 metal atoms. Thus, WI_4 as well as high-valent tungsten chlorides and bromides WX_5 [6, 7] and WX_6 [8, 9] ($X = Cl, Br$), are an interesting example of tungsten halide in which metal-metal bonds are absent.

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