Tellurium Polycations by Oxidation of Tellurium with Tungsten Halides – Syntheses and Crystal Structures of $Te_6(WOCl_4)_2$ and $Te_6I_2(WCl_6)_2$

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$WOCl_4$ reacts at 200°C with tellurium in a sealed, evacuated ampoule with the formation of $Te_6(WOCl_4)_2$. The structure consists of six-membered tellurium rings in a boat conformation with significant transannular interactions and of pyramidal $WOCl_4$ units which are linked by linear asymmetric O···W=O bridges to polymeric $(WOCl_4)_n$ chains. The observed paramagnetism is consistent with the ionic formulation $Te_6^{2+}[(WOCl_4^-)_2]_n$. In the reaction of WCl_6, I_2 and Te in a 2:1:6 ratio $Te_6I_2(WCl_6)_2$ is formed at 150°C. The crystal structure consists of $Te_6I_2^{2+}$ cations and of slightly distorted octahedral WCl_6^- anions. The $Te_6I_2^{2+}$ ions are isostructural with $Se_6I_2^{2+}$ and consist of a six-membered ring of Te atoms in the chair conformation with two I atoms bound in the 1,4-positions.

The oxidation of tellurium by transition-metal halides is a useful synthetic route to new tellurium polycations[1]. Tungsten halides turn out as selective oxidants towards tellurium, which makes the synthesis of polycations possible that cannot be obtained by the classical oxidation with AsF_5/SbF_5 in liquid SO_2[2], e.g. Te_8^{2+}[3] or $[Te_7^{2+}]_n$[4,5]. Two further specific reactions of tungsten halides are now presented. The reaction of $WOCl_4$ with tellurium leads to the often predicted[6–8] but never confirmed polycation Te_6^{2+}, and from WCl_6, I_2 and tellurium $Te_6I_2^{2+}$ can be obtained, which is isostructural with the selenium analogue $Se_6I_2^{2+}$[9].

Preparation and Properties of $Te_6(WOCl_4)_2$ and $Te_6I_2(WCl_6)_2$

Elemental tellurium is selectivly oxidized by $WOCl_4$ at 210–230°C to Te_6^{2+}, $WOCl_4$ is reduced to $WOCl_4^-$.

$$6\,Te + 2\,WOCl_4 \rightarrow Te_6^{2+}(WOCl_4^-)_2$$

The reaction is carried out in a sealed, evacuated glass ampoule, $Te_6(WOCl_4)_2$ is obtained in the colder part of the ampoule in nearly quantitative yield as black, lustrous, predominantly needle-shaped crystals which are slowly hydrolyzed in air. If any part of the ampoule is allowed to become colder than 190°C, crystalline $WOCl_4$ deposits and $Te_6(WOCl_4)_2$ will decompose completely into tellurium and $WOCl_4$. Also at temperatures higher than 230°C $Te_6(WOCl_4)_2$ decomposes into elemental tellurium and molten $WOCl_4$. The temperature range of stability is limited to 190–230°C. The magnetic properties have been studied in the temperature range from 20 to 300 K by means of a SQUID magnetometer. $Te_6(WOCl_4)_2$ is paramagnetic, the reciprocal susceptibility increases linearly with temperature with a Curie-Weiss constant $\Theta = -17$ K. The magnetic moment amounts to 1.15 B.M. for the smallest formula unit Te_3WOCl_4, slightly less than the expected value of 1.73 B.M. for one unpaired electron.

$Te_6I_2(WCl_6)_2$ is obtained from tellurium, iodine and WCl_6.

$$6\,Te + I_2 + 2\,WCl_6 \rightarrow Te_6I_2^{2+}(WCl_6^-)_2$$

The reaction is carried out in a sealed glass ampoule under Ar. At 300°C the components are molten to a black liquid, which on cooling forms a black amorphous mass. Annealing at 150°C yields $Te_6I_2(WCl_6)_2$ in quantitative yield. To prevent the decomposition into the different volatile starting compounds Te, I_2 and WCl_6 it is essential to minimize the temperature gradient along the ampoule. Under these conditions, the content of the ampoule crystallizes within three months as black plate-like moisture-sensitive crystals that can reach 5 × 5 × 1 mm in size.

Crystal Structure of $Te_6(WOCl_4)_2$

The crystal structure is built of discrete Te_6^{2+} ions and of one-dimensional strands of $WOCl_4^-$ ions. Table 1 contains the crystal data and atomic coordinates; Figure 1 gives a view of the ions, Figure 2 shows a section of the unit cell. The $(WOCl_4)_n$ strands run along the *c* axis and contain square-pyramidal $WOCl_4$ monomers which are linked by asymmetric, nearly linear ···W=O···W=O bridges. The asymmetric unit of the unit cell contains four monomers forming a $(WOCl_4)_4$ tetramer. These tetramers are repeated by a crystallographic glide-plane operation yielding the polymeric chain in which every ninth monomer is translationally identical. The Cl atoms in each tetrameric unit are in a nearly eclipsed arrangement with rotation angles between the four $WOCl_4$ groups of only 2 to 4°, but adjacent $(WOCl_4)_4$ units are rotated by 20°. The $(WOCl_4)_n$ structural part of $Te_6(WOCl_4)_2$ shows a close relationship to the structure of $WOCl_4$ which is built of polar strands of

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$WOCl_4$ monomers in an eclipsed arrangement[10]. The main difference lies in evidently longer W−Cl distances of averaged 235.7 pm in $Te_6(WOCl_4)_2$ compared with 228 pm in $WOCl_4$. An elongation of W−Cl bonds up to 10 pm is typical of the transition of W^{VI} to W^{V} and has already been found in compounds with $WOCl_4^-$ anions ($AsPh_4^+$ $WOCl_4^-$: W−Cl 238 pm[11]; PPh_4^+ $WOCl_4$ · THF^-: W−Cl 236 pm[12]).

Table 1. Crystallographic data, structure determination[a] and fractional atomic coordinates for $Te_6(WOCl_4)_2$

W(1)	.53232(4)	.25125(3)	-.06632(1)	W(2)	.50225(4)	.25200(3)	.05433(1)
W(3)	.54404(4)	.25062(3)	.18481(1)	W(4)	.52398(4)	.24835(3)	.30741(1)
Te(1)	.02407(8)	.60082(5)	.31919(3)	Te(2)	-.23457(8)	.50198(5)	.30005(3)
Te(3)	-.22436(8)	.49914(5)	.39004(3)	Te(4)	.03833(8)	.59642(5)	.44043(3)
Te(5)	.16308(9)	.44677(5)	.43927(3)	Te(6)	.15388(9)	.45047(5)	.34940(3)
Te(7)	-.18180(8)	.47690(5)	.03813(3)	Te(8)	-.00337(9)	.61353(6)	.07736(3)
Te(9)	.00717(9)	.61051(5)	.16743(3)	Te(10)	-.18258(9)	.47740(6)	.15650(4)
Te(11)	.12573(9)	.42304(6)	.18323(3)	Te(12)	.12266(9)	.41882(6)	.09415(3)
Cl(1)	.5829(3)	.1110(2)	-.0474(1)	Cl(2)	.8088(3)	.2771(2)	-.0152(1)
Cl(3)	.4787(3)	.3920(2)	-.0661(1)	Cl(4)	.2474(3)	.2244(2)	-.1000(1)
Cl(5)	.5454(3)	.1109(2)	.0695(1)	Cl(6)	.7854(3)	.2774(2)	.0998(1)
Cl(7)	.4494(3)	.3927(2)	.0569(1)	Cl(8)	.2227(3)	.2292(2)	.0285(1)
Cl(9)	.6115(3)	.1124(2)	.2025(1)	Cl(10)	.8219(3)	.2819(2)	.2300(1)
Cl(11)	.4912(3)	.3930(2)	.1878(1)	Cl(12)	.2632(3)	.2231(2)	.1582(1)
Cl(13)	.5603(3)	.1077(2)	.3216(1)	Cl(14)	.8094(3)	.2732(2)	.3555(1)
Cl(15)	.4723(3)	.3915(2)	.3096(1)	Cl(16)	.2425(3)	.2299(2)	.2781(1)
O(1)	.5354(7)	.2484(4)	-.1213(2)	O(2)	.5050(7)	.2527(4)	-.0010(2)
O(3)	.5250(6)	.2533(4)	.1268(2)	O(4)	.5367(6)	.2511(4)	.2538(2)

[a] Cl_4OTe_3W; monoclinic; $P2_1/c$; $a = 917.8(1)$, $b = 1633.2(1)$, $c = 3084.6(3)$ pm; $\beta = 117.10(1)°$; $Z = 16$; four-circle diffractometer STOE AED 2; Mo-K_α; 23°C; 12856 reflections collected in the range $2° < 2\Theta < 50°$; 6466 unique reflections; $R_{merge} = 0.024$; 5670 reflections with $I > 1\sigma(I)$ used in full-matrix least squares; 325 parameters; $\mu = 195$ cm^{-1}; numerical absorption correction; $R(|F|) = 0.029$; $R_w(|F|) = 0.026$ with $w = 1/\sigma^2(F)$; largest difference peak/hole $+1.53/-1.07$ e/10^6 pm^3.

The two symmetrically independent but nearly isostructural Te_6^{2+} ions form six-membered rings in the boat conformation. The cations form one-dimensional strands parallel to the polymeric $(WOCl_4^-)_n$ chains but without interactions. The shortest distance between Te atoms of two neighboring polycations is 461 pm and longer than the sum of the van der Waals radii (440 pm[13]). The Te−Te distances within the individual cations of 270.3−273.6 pm are in the range of single bonds. Additionally, two further transannular weak Te−Te bonds of the mean distance 328 pm are observed. The structure can alternatively be derived from a triangular prism with one prism edge opened and two weak bonds in the triangular faces.

The Te_6^{2+} ions in $Te_6(WOCl_4)_2$ belong to the family of prismatic chalcogen cations. In the heteroatomic ions $Te_3S_3^{2+}$[14] and $Te_2Se_4^{2+}$[15] two edges of the prism are unconnected. Both polycations contain two triply bound Te atoms that carry formally the positive charges, according to the Zintl-Klemm concept[16]. For the homoatomic Te_6^{4+} the Zintl-Klemm concept requires four triply bound Te atoms. The structure is also prismatic with six very short bonds of 267 pm within the triangular faces and three very long bonds of 312 pm[17]. The deviation from the expected structure, a prism with one edge opend and all other bonds in the range of single bonds, can be explained by the delocali-

Figure 1. Two independent Te_6^{2+} ions and the symmetrically independent part of the $[WOCl_4^-]_n$ chain in the structure of $Te_6(WOCl_4)_2$; thermal ellipsoids are scaled to enclose 70% of the probability density (ORTEP[29]); symmetry operation I: x, $1/2-y$, $1/2+z$; selected distances [pm] and angles [°]: W−Cl 233.4(1)−239.3(1), W−O 170.9(7)−172.0(6) and 214.0(6)−215.9(7), Te−Te in the six-membered rings 270.3(1)−273.6(1), Te(3)−Te(5) 328.1(1), Te(2)−Te(6) 328.5(1), Te(9)−Te(11) 321.1(1), Te(8)−Te(12) 334.3(1) Te(1)−Te(4) 368.3(1), Te(7)−Te(10) 365.4(1); O−W−O 173.2(2)−174.7(2), Te−Te−Te at Te(1), Te(4), Te(7), Te(10), 72.7(1)−76.4(1), all other Te−Te−Te 99.5(1)−100.5(1)

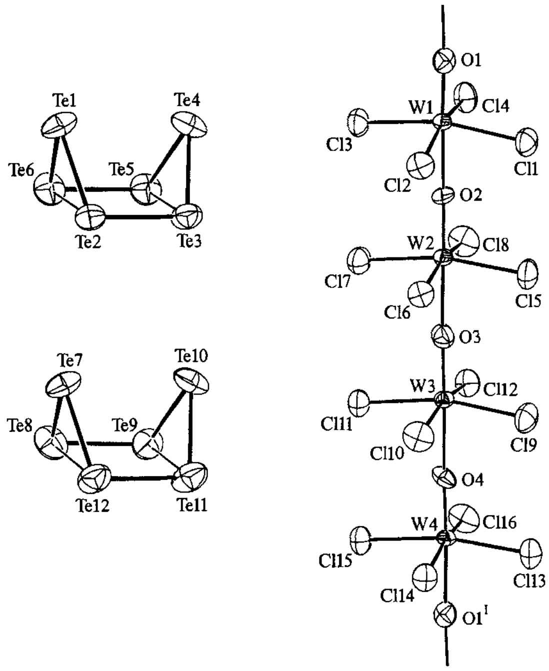


Figure 2. A section of the structure of $Te_6(WOCl_4)_2$ in a view along the b axis

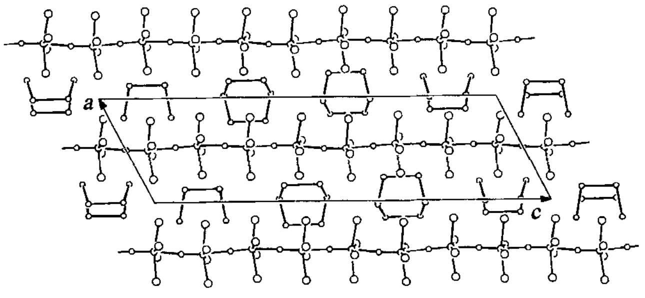


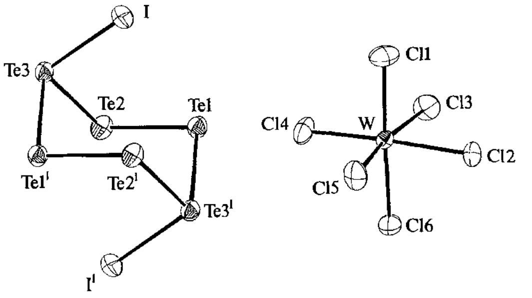
Table 2. Crystallographic data, structure determination[a] and fractional atomic coordinates for $Te_6I_2(WCl_6)_2$

W	.63591(1)	-.00591(1)	.28499(2)	Te(1)	.06290(2)	.21155(2)	-.04894(3)
Te(2)	-.11541(2)	.19028(3)	.04310(3)	Te(3)	-.00961(2)	-.00726(2)	.22048(3)
I	.23162(2)	.02920(3)	.26401(3)				
Cl(1)	.5583(1)	.1192(1)	.4014(1)	Cl(2)	.8424(1)	.0048(1)	.4416(1)
Cl(3)	.6921(1)	.1753(1)	.2023(1)	Cl(4)	.4479(1)	-.0191(1)	.1242(1)
Cl(5)	.6092(1)	-.1849(1)	.3808(1)	Cl(6)	.7228(1)	-.1267(1)	.1638(1)

[a] Cl_6ITe_3W; monoclinic; $P2_1/c$; $a = 1156.3(3)$, $b = 1056.1(2)$, $c = 1159.8(2)$ pm; $\beta = 112.33(1)°$; $Z = 4$; four-circle diffractometer STOE AED 2; Mo-K_α; −70°C; 6818 reflections collected in the range $3° < 2\Theta < 60°$; 3824 unique reflections; $R_{merge} = 0.020$; 3553 reflections with $I > 1\sigma(I)$ used in full-matrix least squares; 100 parameters; $\mu = 178$ cm^{-1}; numerical absorption correction; $R(|F|) = 0.020$; $R_w(|F|) = 0.017$ with $w = 1/\sigma^2(F)$; largest difference peak/hole $+0.83/-0.82$ e/10^6 pm^3.

zation of the positive charges over all six Te atoms. The structure of Te_6^{2+} can also be interpreted by the delocalization of the two positive charges over four Te atoms. A localized Te−Te bond resulting in a Te_3 triangle as in $Te_3S_3^{2+}$ or a Te_2Se triangle in $Te_2Se_4^{2+}$ is not observed. Instead, two elongated transannular Te−Te bonds are present[18]. The observed paramagnetism is consistent with the ionic formula $Te_6^{2+}(WOCl_4^-)_2$ and tungsten in the oxidation state +V. The diminished magnetic moment and the otherwise nearly ideal paramagnetic behavior can be interpreted by a partial coupling of the d^1 electrons along the linear W=O···W=O chain.

Figure 3. The $Te_6I_2^{2+}$ and WCl_6^- ions in the structure of $Te_6I_2(WCl_6)_2$; thermal ellipsoids are scaled to enclose 70% of the probability density (ORTEP[29]); symmetry operation I: $-x$, $-y$, $-z$; selected distances [pm] and angles [°]: W−Cl 226.9(1)−238.7(1), Te(1)−Te(2) 267.0(1), Te(2)−Te(3) 286.1(1), Te(1)−Te(3^I) 284.2(1), Te(3)−I 267.0(1), Te−Te−Te and Te−Te−I 97.5(1)−102.8(1)



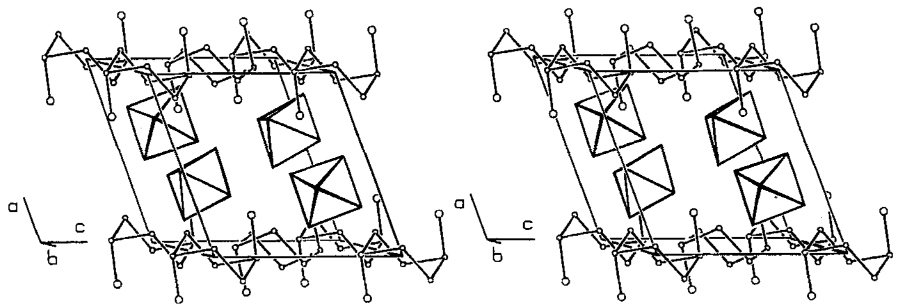
Crystal Structure of $Te_6I_2(WCl_6)_2$

The crystal structure is built of discrete $Te_6I_2^{2+}$ ions and of discrete WCl_6^- ions. Table 2 contains the crystal data and atomic coordinates; Figure 3 shows the structure of the ions, Figure 4 gives a stereoscopic view of the unit cell. The WCl_6^- anions form distorted octahedra with W−Cl bond lengths ranging from 226−239 pm. The Cl−W−Cl angles of 85.4(1)−92.0(1)° show also a marked deviation from ideal symmetry. The mean W−Cl distance of 232.8 pm is in good agreement with other hexachlorotungstate(V) anions[3,19,20]. The distortion of the anions is caused by strong cation-anion interactions.

The centrosymmetric $Te_6I_2^{2+}$ ions consist of a six-membered ring of Te atoms in the chair conformation with two I atoms bound in the 1,4-positions in the *endo* conformation. $Te_6I_2^{2+}$ is isostructural with the selenium analogue in $Se_6I_2(AsF_6)_2 \cdot 2\ SO_2$[9]. The bond lengths in $Te_6I_2^{2+}$ show distinctly alternations. The Te(3)−I distance of 267 pm is shorter than every Te−I bond length in all known tellurium iodides starting with 268.3 pm in one of the five modifications of TeI_4[21]. The bonds Te(3)−Te(2) (286 pm) and Te(3)−Te(1^I) (284 pm) are relatively long, while the remaining bonds Te(2)−Te(1) and Te(1^I)−Te(2^I) with an average of 267 pm are significantly shorter than a Te−Te single bond (275 pm). This separation into long and short bonds is also found in $Se_6I_2^{2+}$[9]. The simplest bonding model, single bonds between all atoms and localization of the positive charges at the triply bound Te atoms, cannot explain the alternating bond lengths. If some degree of double bonding is assigned to the shortened bonds, the positive charges are delocalized over all atoms of the cation, including the iodine atoms[22]. This interpretation is made plausible by several short contacts of chlorine atoms of the surrounding WCl_6^- ions to the Te and I atoms of the cation. Figure 5 gives a stereoscopic view of the cation with all Te,I···Cl contacts up to 380 pm. The shortest contact is observed between Te(3) and Cl(6^{II}) with 317.4(1) pm, the three contacts of the I atoms have distances of 350.0(1), 362.7(1) and 372.7(1) pm.

The packing of the ions in the structure of $Te_6I_2(WCl_6)_2$ can be derived from the basic AB_2 structure type $MoSi_2$[23] with the symmetry centers of the $Te_6I_2^{2+}$ ions in the Mo positions and the W atoms of the WCl_6^- ions in the Si positions. The monoclinic structure of $Te_6I_2(WCl_6)_2$ can be deduced by a series of supergroup-subgroup relations from the tetragonal structure of $MoSi_2$[24] (Figure 6). Like Mo in the $MoSi_2$ structure, each $Te_6I_2^{2+}$ is surrounded by ten anions in the form a bicapped cube.

Figure 4. Stereoscopic view of the unit cell of $Te_6I_2(WCl_6)_2$; WCl_6^- ions are drawn as white octahedra, small circles = Te, large circles = I



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Experimental

All experiments were carried out under dry Ar. Glass ampoules were heated to 300°C before use. Charging and opening of the ampoules were performed in an Ar-filled glove box. Tungsten hexachloride[25] and tungsten tetrachloride oxide[25] were prepared according to literature procedures, iodine was sublimed *in vacuo* before used, tellurium (powder; Aldrich Company) was used as obtained.

Figure 5. Stereoscopic view of the $Te_6I_2^{2+}$ cation in the structure of $Te_6I_2(WCl_6)_2$; all Cl atoms with distances up to 380 pm to the Te and I atoms are included; symmetry operations: II: $x - 1, y, z$; III: $-x + 1, -y, -z$; IV: $-x + 1, y, -z + 1$; V: $-x + 1, 1/2+y, 1/2-z$; VI. $x - 1, 1/2- y, (1/2+z) - 1$

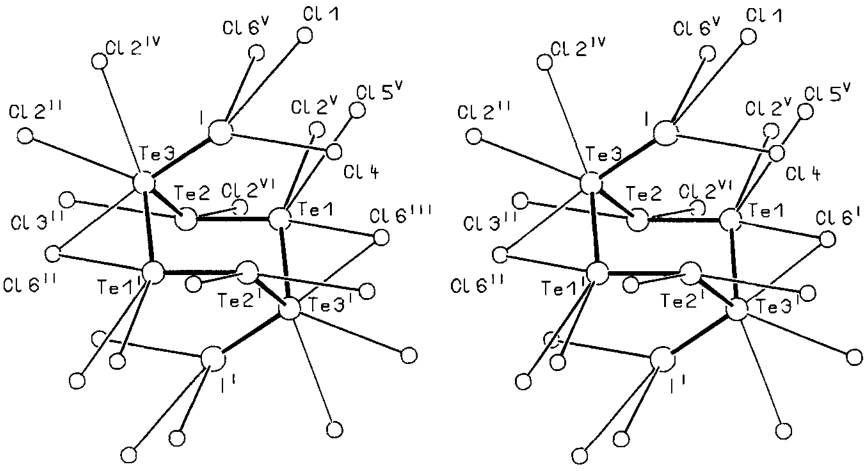
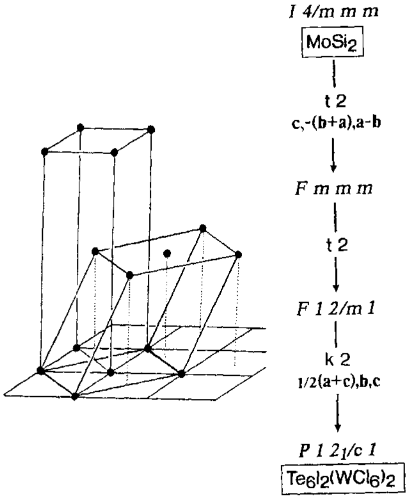


Figure 6. Symmetry relation between the structures of $MoSi_2$ and $Te_6I_2(WCl_6)_2$ depicted as a supergroup-subgroup family tree (right); the relation between the unit cells is given on the left; black circles represent the Mo positions in $MoSi_2$ and the centers of the cations in $Te_6I_2(WCl_6)_2$, respectively



cyclo-Hexatellurium(2+) Bis[tetrachlorooxotungstate(−)] $[Te_6^{2+}(WOCl_4^-)_2]$: $WOCl_4$ (1 g, 2.9 mmol) and tellurium (1.12 g, 8.8 mmol) were filled in an ampoule (15 cm length and 1 cm diameter) which was evacuated and sealed. The ampoule was placed in a horizontal tube furnace (temperature gradient 230 → 210°C). Black, needle- and plate-shaped crystals are formed in the colder part of the ampoule within two weeks. To prevent the deposition of $WOCl_4$ from the gas phase on the crystals on cooling it was advantageous to cool the formerly hot side of the ampoule first. Together with $Te_6(WOCl_4)_2$ a thin layer of white crystals of WO_2Cl_2 is formed, but the black crystals of $Te_6(WOCl_4)_2$ could be separated mechanically.

1,4-Diiodo-cyclo-hexatellurium(2+) Bis[hexachlorotungstate(−)] $[Te_6I_2^{2+}(WCl_6^-)_2]$: WCl_6 (1.5 g, 3.8 mmol), tellurium (1.45 g, 11.3 mmol) and iodine (0.24 g, 1.9 mmol) were filled in a glass ampoule (15 cm length and 1.5 cm diameter) which was sealed under Ar and heated to 300°C until a homogeneous black melt had formed. The ampoule was then placed at 150 °C horizontally in an oven with as little temperature gradient as possible. Within three months the glassy and partially molten mass was completely transformed into black, plate-like crystals of $Te_6I_2(WCl_6)_2$.

Crystal-Structure Determinations of $Te_6(WOCl_4)_2$ and $Te_6I_2(WCl_6)_2$[26]: Tables 1 and 2 contain the crystal data, details of data collection, refinement, and the positional parameters of the atoms. In order to avoid decomposition by hydrolysis in moist air the crystals were sealed in quartz capillaries under Ar. Both structures were solved by direct methods[27], all atoms were refined with anisotropic displacement parameters[28].

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[26] Further crystal-structure data of both structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, F.R.G.; inquiries should be accompanied by the depository number CSD-58492, the name of the author, and the full literature reference.

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[28] G. M. Sheldrick, *SHELX76, Program for Crystal Structure determination*, University of Cambridge, U.K., **1976**.

[29] C. K. Johnson, *ORTEP; Thermal Ellipsoid plot program,* Oak Ridge National Laboratory, Tennessee, U.S.A., **1965**.

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