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Te₆O₁₁Cl₂ – a Revision of Crystal Symmetry

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Abstract

A redetermination of the crystal structure of the tellurium oxochloride hexatellurium dichloride undecaoxide, Te₆O₁₁Cl₂, is described. The title compound is isostructural with Te₆O₁₁Br₂ and is correctly described in the space group *Ccmm*. Te^{IV} atoms are coordinated to four or three O atoms with average Te—O distances of 2.01 and 1.91 Å, respectively. Te—Cl distances are in the range 2.99–3.45 Å. The structure consists of infinite (Te₆O₁₁)²⁺ chains parallel to [001].

Comment

Khodadad (1965) and Khodadad, Laruelle & Etienne (1965) reported the synthesis of Te₆O₁₁Cl₂ and proposed the orthorhombic space group *Ccmm* on the basis of Debye–Scherrer photographs. A structure determination of Te₆O₁₁Br₂ (Khodadad & Rodier, 1977) also led to the space group *Ccmm* and the authors suggested, because of similar cell dimensions, that it was isostructural with the oxochloride compound. Contrarily, Abriel (1981) investigated Te₆O₁₁Cl₂ and described it with monoclinic symmetry. This structure determination was carried out with single crystals on a two-circle diffractometer. In spite of the fact that Guinier film data could be indexed orthorhombically and that the crystal structure resembles that of Te₆O₁₁Br₂, the author persisted in the lower symmetry based on Weissenberg photographs. The present study aimed to ensure a definite choice of the space group.

Abriel (1981) described Te₆O₁₁Cl₂ in space group *P112₁/m* with $a = 6.844$ (4), $b = 6.800$ (4), $c = 15.227$ (9) Å and $\gamma = 120.19^\circ$, indicating a pseudo-hexagonal cell, with transformed, slight deviations from orthogonal metrics. A transformation of Abriel's monoclinic cell ($-\bar{a}, \bar{a} + 2\bar{b}, -\bar{c}$) leads to $a = 6.844$, $b = 11.755$, $c = 15.227$ Å, $\alpha = \beta = 90.0$ and $\gamma = 90.024^\circ$.

In the present redetermination, a conventional reduced monoclinic unit cell in *P12₁/m1* was chosen initially, with $a = 6.797$ (2), $b = 15.228$ (3), $c = 6.798$ (2) Å and $\beta = 119.56$ (1)°, which transforms ($\bar{a} + \bar{c}, \bar{a} - \bar{c}, -\bar{b}$) to $a = 6.843$ (2), $b = 11.748$ (3), $c = 15.228$ (3) Å, $\alpha = \beta = 90.0$ and $\gamma = 90.006$ (10)°, and turns out to be orthogonal, at least within the accuracy of measurements. In order not to overlook measured intensities that might contradict an orthorhombic space group, the crystal structure refinements were carried out in both space groups. In the monoclinic refinement (92 variables, $R = 0.028$), bond distances and angles of all coordination polyhedra, related in *Ccmm*, proved to be equal within one standard deviation. Te₆O₁₁Cl₂ seems, therefore, to be correctly described in *Ccmm* and is obviously isostructural with Te₆O₁₁Br₂.

Recently, Popolitov, Telegenov & Bondareva (1992) refined the lattice parameters of Te₆O₁₁Br₂ with a four-circle diffractometer. Stimulated by the work of Abriel, as the authors note, they believed in a monoclinic metric and assigned the monoclinic space group *P112₁/m* to Te₆O₁₁Br₂ with $a = 6.8354$ (9), $b = 6.8347$ (7), $c = 15.5073$ (20) Å, $\alpha = \beta = 90.0$ and $\gamma = 119.4888$ (83)°. Unfortunately, they too failed to realize the higher symmetry. As expected, a simple transformation ($\bar{a} + \bar{b}, -\bar{a} + \bar{b}, \bar{c}$)

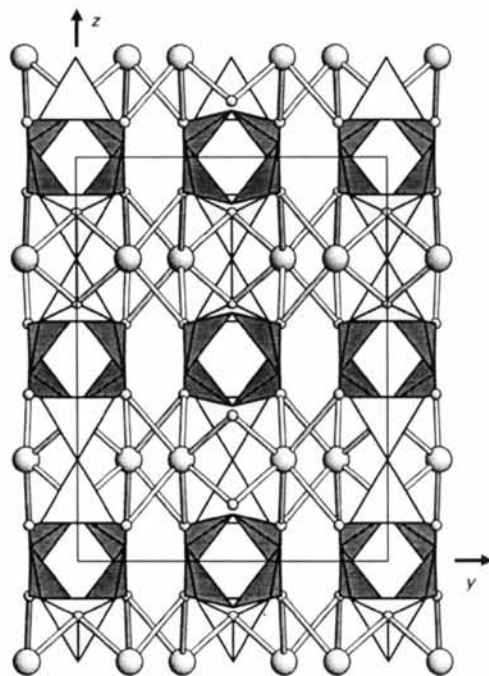


Fig. 1. Crystal structure of Te₆O₁₁Cl₂ in a projection parallel to [100]. The figure was drawn using the program *ATOMS* (Dowty, 1993). The Cl atoms are indicated by large circles, the Te atoms by small circles and the Te—Cl bonds by sticks.

shows that the correct unit-cell parameters of tellurium oxobromide are $a = 6.888$, $b = 11.808$, $c = 15.507$ Å, $\alpha = \beta = 90.0$ and $\gamma = 90.007^\circ$ (i.e. equal to 90.0° within the limits of error) and the true space group is *Ccmm*.

Fig. 1 illustrates the atomic arrangement in a projection parallel to [100]. The Te^{IV} atoms are bound to O atoms (1.89–2.18 Å) and additionally to Cl atoms with Te—Cl distances ranging from 2.99 to 3.45 Å. Te(1)O₄ ψ -trigonal bipyramids share a common edge forming Te(1)₂O₆ units, which in turn share corners to build Te(1)₄O₁₀ rings. Furthermore, each two Te(2)O₃ ψ -tetrahedral groups share a common corner. Both these structural parts, Te(1)₄O₁₀ and Te(2)₂O₅, are alternately corner-linked building infinite chains parallel to [001]. The Cl atoms are coordinated to six Te atoms, forming a distorted trigonal prism.

The Te—O polyhedra in Te₆O₁₁Cl₂ and Te₆O₁₁Br₂ have remarkably similar geometry, while the differences refer, of course, to bonding to the respective halogen atoms.

Experimental

Crystal data

Te₆O₁₁Cl₂
 $M_r = 1012.5$
 Orthorhombic
Ccmm
 $a = 6.843$ (2) Å
 $b = 11.748$ (3) Å
 $c = 15.228$ (3) Å
 $V = 1224.2$ Å³
 $Z = 4$
 $D_x = 5.494$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 48 reflections
 $\theta = 21$ – 24°
 $\mu = 13.628$ mm⁻¹
 $T = 295$ K
 Parallelepiped
 $0.14 \times 0.07 \times 0.05$ mm
 Yellow

Data collection

Stoe AED-2 diffractometer
 $2\theta/\omega$ scans
 Absorption correction:
 empirical
 $T_{\min} = 0.29$, $T_{\max} = 0.39$
 7163 measured reflections
 1439 independent reflections
 1267 observed reflections
 $[F_o > 3\sigma(F_o)]$

$R_{\text{int}} = 0.076$
 $\theta_{\text{max}} = 35^\circ$
 $h = -11 \rightarrow 11$
 $k = -18 \rightarrow 18$
 $l = -24 \rightarrow 0$
 3 standard reflections
 frequency: 120 min
 intensity variation: none

Refinement

Refinement on F
 $R = 0.036$
 $wR = 0.036$
 $S = 2.89$
 1267 reflections
 54 parameters
 $w = 1/[\sigma(F_o)]^2$
 $(\Delta/\sigma)_{\text{max}} < 0.01$
 $\Delta\rho_{\text{max}} = 2.9$ e Å⁻³
 $\Delta\rho_{\text{min}} = -3.9$ e Å⁻³

Extinction correction:
 Zachariasen (1967)
 Extinction coefficient:
 $g = 2.3$ (1) $\times 10^{-6}$
 Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{\text{eq}} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
Te1	0.36751 (5)	0.15605 (3)	0.08765 (2)	0.92 (1)
Te2	0.92198 (6)	0.0	0.13947 (4)	0.85 (1)
Cl	0.1982 (3)	0.3352 (2)	0.25	1.60 (4)
O1	0.4223 (8)	0.0	0.1157	1.32 (9)
O2	0.1644 (5)	0.3485 (4)	0.0361 (3)	1.14 (7)
O3	0.0770 (6)	0.1198 (4)	0.0941 (3)	1.36 (8)
O4	0.0620 (3)	0.0	0.25	1.43 (15)

Table 2. Interatomic bond lengths (Å) and angles (°) with interpolyhedral O...O distances (Å) given in square brackets

Te1—O1	1.919 (1)	Te1—Cl	3.448 (1)
Te1—O2	1.898 (4)	Te2—O3 (×2)	1.893 (4)
Te1—O2	2.178 (3)	Te2—O4	1.937 (3)
Te1—O3	2.035 (3)	Te2—Cl (×2)	2.988 (1)
Te1—Cl	3.353 (1)		
O1—Te1—O2	82.8 (2)	[2.717 (6)]	
O1—Te1—O2	102.5 (3)	[2.978 (7)]	
O1—Te1—O3	88.9 (2)	[2.770 (6)]	
O2—Te1—O2	75.5 (2)	[2.504 (7)]	
O2—Te1—O3	86.0 (2)	[2.684 (6)]	
O2—Te1—O3	157.4 (4)	[4.132 (5)]	
O3—Te2—O3	96.1 (3)	[2.817 (9)]	
O3—Te2—O4 (×2)	92.3 (2)	[2.762 (4)]	

Te₆O₁₁Cl₂ was prepared in Teflon-lined steel vessels of 50 cm³ capacity. A mixture of TeO₂, HCl and H₂O was heated to 500 K, kept at that temperature for one week and then slowly cooled to room temperature. The crystals obtained formed clusters with individual crystal sizes up to a few tenths of a mm.

Initial atomic coordinates were taken from those of Te₆O₁₁Br₂ (Khodadad & Rodier, 1977). Full-matrix least-squares refinement was performed with anisotropic thermal parameters for all atoms.

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Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71409 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1049]

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