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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{Ta}-\text{Cl}) = 0.002$ Å
 R factor = 0.029
 wR factor = 0.067
Data-to-parameter ratio = 23.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tetrapotassium dodeca- μ -chloro-hexachloro-
octahedro-hexatantalate, $\text{K}_4[\text{Ta}_6\text{Cl}_{12}]\text{Cl}_6$ $\text{K}_4[\text{Ta}_6\text{Cl}_{12}]\text{Cl}_6$ was obtained as a by-product during the reaction of VCl_3 and KCl in a sealed tantalum container. The compound is isotypic to $\text{K}_4\text{Nb}_6\text{Cl}_{18}$ [Simon, von Schnering & Schäfer (1968). *Z. Anorg. Allg. Chem.* **361**, 235–246] and contains octahedral $([\text{Ta}_6\text{Cl}_{12}]\text{Cl}_6)^{4-}$ clusters with $2/m$ site symmetry.

Received 28 June 2004

Accepted 13 July 2004

Online 24 July 2004

Comment

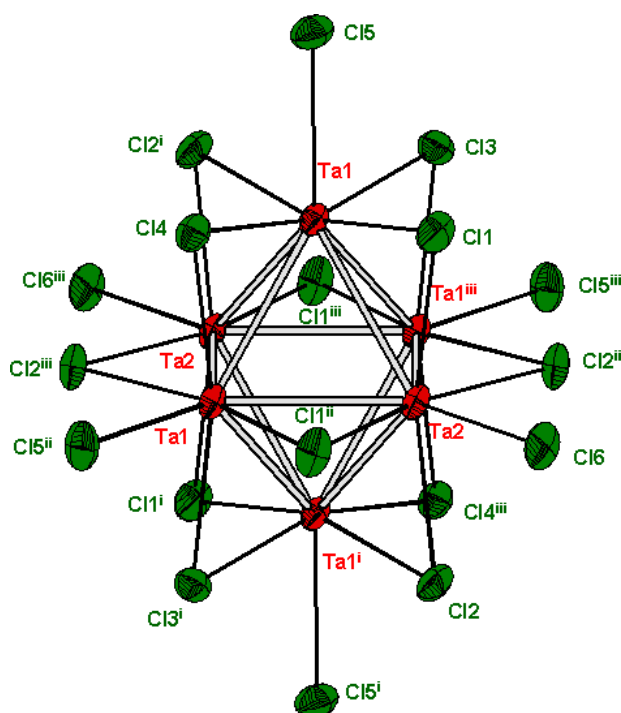
Tantalum ampoules are often used as reaction containers for halide melts because of the refractory and inert nature of the metal. With unstable transition metal halides such as VCl_3 (Böcker, 1996), tantalum may, however, take part in the reaction. In an attempt to prepare KVCl_3 from the reaction of KCl , VCl_3 and vanadium powder, we have not only obtained K_2TaCl_6 as a by-product (Jongen & Meyer, 2004), but also $\text{K}_4[\text{Ta}_6\text{Cl}_{12}]\text{Cl}_6$. This appears to be the first report of such a ternary complex cluster tantalate, although the binary clusters $\text{Ta}_6\text{Cl}_{15}$ (von Schnering *et al.*, 1999), $\text{Ta}_6\text{Br}_{14}$ (Bajan & Meyer, 1995) and Ta_6I_{14} (Artelt & Meyer, 1993) are well known. Furthermore, with niobium there is a rich chemistry with $[\text{Nb}_6\text{Cl}_{12}]$ -type cores in both binary and ternary compounds, for example, $\text{Nb}_6\text{Cl}_{14}$ (Simon *et al.*, 1965), $\text{K}_4\text{Nb}_6\text{Cl}_{18}$ (Simon *et al.*, 1968) and $\text{Rb}_4\text{Nb}_6\text{Cl}_{18}$ (Reckeweg & Meyer, 1996).

Figure 1

The $([\text{Ta}_6\text{Cl}_{12}]\text{Cl}_6)^{4-}$ cluster anion. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, -y, -z$; (ii) $x, -y, z$; (iii) $-x, y, -z$.]

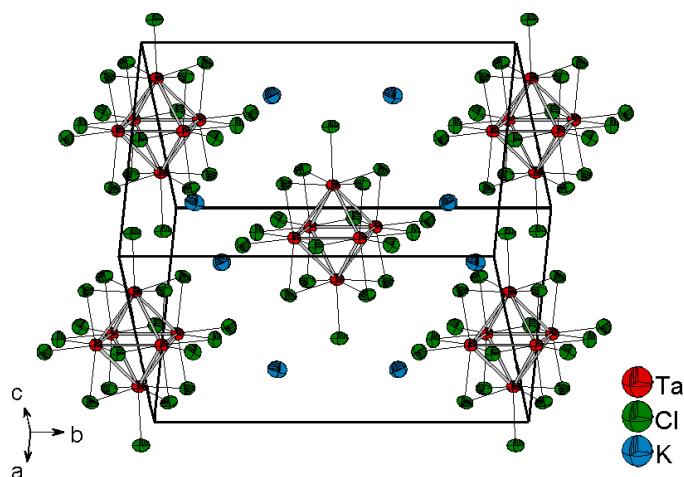


Figure 2
The unit-cell contents of $K_4[Ta_6Cl_{12}]Cl_6$.

$K_4[Ta_6Cl_{12}]Cl_6$ crystallizes isotypic to $K_4[Nb_6Cl_{12}]Cl_6$ (Simon *et al.*, 1968) and contains octahedral clusters of Ta atoms, with Ta–Ta distances between 2.8901 (7) and 2.9011 (5) Å, which are in good agreement with the Ta–Ta distances observed in Ta_6Cl_{15} (von Schnering *et al.*, 1999). Twelve chloride ions bridge the edges of the Ta_6 octahedron, in order to form $[Ta_6Cl_{12}]^{2+}$ cationic cores. The coordination of the Ta_6 octahedron is completed by a further six chloride ions that are placed terminally at the vertices of the octahedron. The Ta–Cl distances for the terminal Cl atoms are 2.553 (3) and 2.600 (2) Å, slightly longer than those for the bridging chloride atoms [Ta–Cl = 2.455 (2)–2.474 (2) Å]. The $[(Ta_6Cl_{12})Cl_6]^{4-}$ anions with site symmetry $2/m$ form a face-centred arrangement, whereby the potassium ions hold the $[Ta_6Cl_{18}]^{4-}$ anions together by electrostatic forces.

Experimental

$K_4[Ta_6Cl_{12}]Cl_6$ was obtained as a by-product in the attempt to synthesize $KVCl_3$, starting from VCl_3 , KCl, and V powder in a sealed tantalum container jacketed by a silica ampoule. The reaction mixture was heated to 1123 K for 10 d, and then cooled slowly to room temperature. Black single crystals of $K_4[Ta_6Cl_{12}]Cl_6$ were selected under a microscope in an argon-filled dry-box.

Crystal data

$K_4[Ta_6Cl_{12}]Cl_6$	$D_x = 4.406 \text{ Mg m}^{-3}$
$M_r = 1880.20$	Mo $K\alpha$ radiation
Monoclinic, $C2/m$	Cell parameters from 18943 reflections
$a = 9.9900$ (12) Å	$\theta = 1.9\text{--}28.2^\circ$
$b = 16.5228$ (18) Å	$\mu = 25.34 \text{ mm}^{-1}$
$c = 9.4745$ (10) Å	$T = 293$ (2) K
$\beta = 115.005$ (8)°	Polyhedron, black
$V = 1417.3$ (3) Å ³	$0.2 \times 0.2 \times 0.1 \text{ mm}$
$Z = 2$	

Data collection

Stoe IPDS-II diffractometer	1608 independent reflections
ω and φ scans	1423 reflections with $I > 2\sigma(I)$
Absorption correction: numerical [<i>X-RED32</i> (Stoe & Cie, 2002) and <i>X-SHAPE</i> (Stoe & Cie, 1999)]	$R_{\text{int}} = 0.066$
$T_{\text{min}} = 0.034$, $T_{\text{max}} = 0.101$	$\theta_{\text{max}} = 27.0^\circ$
9391 measured reflections	$h = -12 \rightarrow 12$
	$k = -21 \rightarrow 21$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.067$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 1.75 \text{ e \AA}^{-3}$
1608 reflections	$\Delta\rho_{\text{min}} = -1.75 \text{ e \AA}^{-3}$
70 parameters	Extinction correction: <i>SHELXL97</i>
	Extinction coefficient: 0.00046 (6)

Table 1

Selected geometric parameters (Å, °).

Ta1–Cl2 ^{iv}	2.455 (2)	Ta1–Ta2 ^{iv}	2.8920 (5)
Ta1–Cl1	2.469 (2)	Ta1–Ta1 ^v	2.8944 (6)
Ta1–Cl3	2.473 (2)	Ta1–Ta2	2.9011 (5)
Ta1–Cl4	2.474 (2)	Ta2–Cl2	2.464 (2)
Ta1–Cl5	2.600 (2)	Ta2–Cl1	2.472 (2)
Ta1–Ta1 ⁱⁱ	2.8901 (7)	Ta2–Cl6	2.553 (3)
Ta1 ⁱⁱ –Ta1–Ta2 ^{iv}	60.022 (8)	Ta1 ^v –Ta1–Ta2	59.869 (14)
Ta1 ⁱⁱ –Ta1–Ta1 ^v	90	Ta1 ^v –Ta2–Ta1 ⁱⁱ	89.831 (15)
Ta2 ^{iv} –Ta1–Ta1 ^v	60.179 (13)	Ta1 ^{iv} –Ta2–Ta1 ⁱⁱ	59.952 (14)
Ta1 ⁱⁱ –Ta1–Ta2	60.125 (8)	Ta1–Ta2–Ta1 ⁱⁱ	59.750 (16)
Ta2 ^{iv} –Ta1–Ta2	90.169 (15)		

Symmetry codes: (ii) $x, -y, z$; (iv) $-x, -y, 1 - z$; (v) $-x, y, 1 - z$.

The highest peak and deepest hole in the final difference map are 1.39 and 0.88 Å from Ta2.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1996); software used to prepare material for publication: *SHELXL97*.

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