Crystal structure redetermination of the *octahedro*-hexatantalum(2.5+) pentadecahalides, $\text{Ta}_6\text{Cl}_{15}$ and $\text{Ta}_6\text{Br}_{15}$

H. G. von Schnering, D. Vu, S.-L. Jin and K. Peters

Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany

Received September 24, 1998, transferred 1st update to database ICSD in 1999, CSD-No. 409386 and CSD-No. 409387

1. *octahedro*-Hexatantalum(2.5+) pentadecachloride, $\text{Ta}_6\text{Cl}_{15}$

Source of material

Synthesis and crystal growth were carried out according to [1, 2]. Lattice parameter from Guinier photographs and high angle measurements are much more reliable as in [1, 3].

Discussion

$[\text{Ta}_6\text{Cl}_{12}]\text{Cl}_{3/2}^{\text{a-a}}$ forms *one* 3D network via the bridging $\text{Cl}^{\text{a-a}}$ ligands Cl3 (figure) as described in [1]. Cl1 and Cl2 represent the inner ligands Cl^{i} forming cuboctahedra. Small deviations from $m\bar{3}m$ symmetry result from inter cluster repulsions of the Cl^{i} ligands and a shift of the $\text{Cl}^{\text{a-a}}$ atoms from the ideal parameter $y(\text{Cl}3) = 3/4 - \sqrt{2}/8 = 0.57322$ (lowering the Ta– $\text{Cl}^{\text{a-a}}$ –Ta bond angle from 142.72° to 139.0°). Cluster size averaged under $m\bar{3}m$ symmetry: Ta–Ta = $2.9185(7)$ Å; Ta– Cl^{i} = $2.436(9)$ Å; Ta– $\text{Cl}^{\text{a-a}}$ = 2.599 Å; Cl^{i} – Cl^{i} = 3.410 Å; Cl^{i} – $\text{Cl}^{\text{a-a}}$ = 3.300 Å; $R(\text{Ta}_6) = 2.0637$ Å; $R(\text{Cl}_{12}^{\text{i}}) = 3.410$ Å; $R(\text{Cl}_3^{\text{a-a}}) = 4.663$ Å. The Ta atoms are shifted from the $\text{Cl}_{12}^{\text{i}}$ squares toward the cluster center by 0.347 Å.

Abstract

$\text{Cl}_{15}\text{Ta}_6$, cubic, $Ia\bar{3}d$ (No. 230), $a = 20.326(1)$ Å, $V = 8397.6$ Å³, $Z = 16$, $R_{\text{gt}}(F) = 0.033$, $R_{\text{w}}(F) = 0.027$, $T = 293$ K.

$\text{Br}_{15}\text{Ta}_6$, cubic, $Ia\bar{3}d$ (No. 230), $a = 21.309(2)$ Å, $V = 9675.9$ Å³, $Z = 16$, $R_{\text{gt}}(F) = 0.049$, $R_{\text{w}}(F) = 0.048$, $T = 293$ K.

Table 1. Data collection and handling.

Crystal:	dark olive-colored octahedron, 0.08 x 0.12 x 0.15 mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	330.40 cm ^{−1}
Diffractometer, scan mode:	Syntex P3, ω
$2\theta_{\text{max}}$:	55°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	5266, 822
Criterion for F_{obs} , $N(hkl)_{\text{gt}}$:	$F_{\text{obs}} > 3 \sigma(F_{\text{obs}})$, 777
$N(\text{param})_{\text{refined}}$:	33
Program:	SHELXTL-plus [4]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Ta(1)	96 <i>h</i>	0.05852(2)	−0.03305(2)	0.07609(2)	0.0172(2)	0.0175(2)	0.0167(2)	0.0009(1)	−0.0002(1)	0.0012(1)
Cl(1)	96 <i>h</i>	0.1577(1)	0.0294(1)	0.0505(1)	0.021(1)	0.031(1)	0.025(1)	−0.0031(7)	−0.0039(7)	0.0039(8)
Cl(2)	96 <i>h</i>	0.1105(1)	−0.1241(1)	0.0184(1)	0.028(1)	0.024(1)	0.023(1)	0.0083(7)	−0.0016(7)	0.0003(7)
Cl(3)	48 <i>g</i>	1/8	0.5718(1)	1/4− <i>y</i>	0.0326(9)	0.0247(9)	0.025(2)	−0.0056(8)	<i>U</i> ₁₂	−0.002(1)

2. octahedro-Hexatantalum(2.5+) pentadecabromide, Ta₆Br₁₅

Source of material

Synthesis see Ta₆Cl₁₅. Lattice parameters from Guinier photographs and high angle measurements are much more reliable as in [1, 3].

Discussion

[Ta₆Br₁₂]₂Br₃²⁻ is isotypic with Ta₆Cl₁₅ (see above). Cluster size averaged under $m\bar{3}m$ symmetry: Ta–Ta = 2.958(2) Å; Ta–Br¹ = 2.576(8) Å; Ta–Br^a = 2.804 Å; Br¹–Br¹ = 3.591 Å; Br¹–Br^a = 3.468 Å; R(Ta₆) = 2.091 Å; R(Br₁₂) = 3.591 Å; R(Br₃) = 4.895 Å. Shift of the Ta atoms toward the center by 0.448 Å, bond angle Ta–Br^a–Ta = 138.2°.

Table 3. Data collection and handling.

Crystal:	black (brownish) octahedron, 0.05 x 0.07 x 0.11 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	517.90 cm ⁻¹
Diffractometer, scan mode:	Syntex P3, ω
2 $\theta_{\max}$:	55°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	6178, 931
Criterion for $F_{\text{obs}}, N(hkl)_{\text{gt}}$:	$F_{\text{obs}} > 3 \sigma(F_{\text{obs}})$, 879
$N(\text{param})_{\text{refined}}$:	33
Program:	SHELXTL-plus [3]

Table 4. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Ta(1)	96h	0.05675(2)	–0.03194(3)	0.07342(2)	0.0056(3)	0.0062(3)	0.0052(3)	0.0012(2)	0.0002(2)	0.0011(2)
Br(1)	96h	0.15824(7)	0.02982(7)	0.05058(7)	0.0087(6)	0.0179(7)	0.0131(7)	–0.0031(5)	–0.0027(5)	0.0045(5)
Br(2)	96h	0.11187(7)	–0.12390(7)	0.01796(6)	0.0156(7)	0.0125(6)	0.0098(6)	0.0071(5)	–0.0015(5)	0.0004(5)
Br(3)	48g	1/8	0.57108(7)	1/4– <i>y</i>	0.0115(6)	0.0115(6)	0.0154(9)	–0.0052(5)	<i>U</i> ₁₂	–0.0017(7)

References

1. Bauer, D.; von Schnering, H. G.: Die Struktur der Tantalhalogenide Ta₆Cl₁₅ und Ta₆Br₁₅. Z. Anorg. Allg. Chem. **362** (1968) 259–276.
2. Simon, A.: Präparative und strukturelle Untersuchungen an niederen Niobhalogeniden mit Me_n-Gruppen. Dissertation, Universität Münster 1966.
3. Bauer, D.: Untersuchungen an niederen Tantalhalogeniden mit Metall-Metall-Bindungen. Dissertation, Westfälische Wilhelms-Universität Münster 1967.
4. Sheldrick, G. M.: Program Package SHELXTL-plus. Release 4.1. Siemens Analytical X-Ray Instruments Inc., Madison (WI 53719), USA 1990.