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Tetrakis(tetramethylammonium) dodeca-μ-chloro-hexachloro-*octahedro*-hexatantalate chloride

Marija Vojnović,[a] Dražan Jozić,[a] Ivan Bašic,[a]* Sanda Rončević[b] and Pavica Planinić[a]

[a]Rudjer Bošković Institute, POB 180, HR-10002 Zagreb, Croatia, and [b]Faculty of Science, University of Zagreb, HR-10000 Zagreb, Croatia
Correspondence e-mail: basic@rudjer.irb.hr

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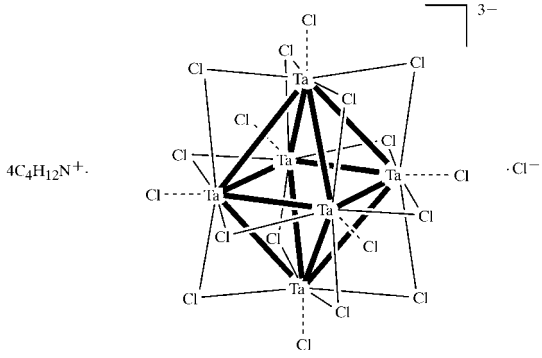
The title compound, $(C_4H_{12}N)_4[Ta_6Cl_{18}]Cl$, crystallizes in the cubic space group $Fm\bar{3}m$. The crystal structure contains two different types of coordination polyhedra, *i.e.* four tetrahedral $[(CH_3)_4N]^+$ cations and one octahedral $[(Ta_6Cl_{12})Cl_6]^{3-}$ cluster anion, and one Cl^- ion. The presence of three different kinds of Cl atoms [bridging (μ_2), terminal and counter-anion] in one molecule makes this substance unique in the chemistry of hexanuclear halide clusters of niobium and tantalum. The Ta_6 octahedron has an ideal O_h symmetry, with a Ta—Ta interatomic distance of 2.9215 (7) Å.

Comment

In the hexanuclear halide clusters $[M_6X_{12}]^{n+}$ (M = Nb and Ta, X = Cl and Br, and n = 2, 3 and 4), the lowest oxidation potentials for the oxidation of $[M_6X_{12}]^{2+}$ to $[M_6X_{12}]^{3+}$ to $[M_6X_{12}]^{4+}$ have been found for $[Ta_6Cl_{12}]^{n+}$ (Eisenbraun & Schäfer, 1985). Consequently, the largest number of compounds containing $[M_6X_{12}]^{n+}$ (n = 3 or 4) has been isolated for this cluster, by using oxidants that are not common for the oxidation of other members in the $[M_6X_{12}]^{n+}$ series. For example, fast air-oxygen oxidation of $[Ta_6Cl_{12}]^{2+}$ to $[Ta_6Cl_{12}]^{4+}$ in an alkaline medium has been used as a method of preparation of crystalline cluster hydroxides $[Ta_6Cl_{12}(OH)_6]^{2-}$ (Brničević *et al.*, 1984) or methoxides (Brničević *et al.*, 1988). A direct synthesis of the title compound, (I), which contains $[Ta_6Cl_{12}]^{3+}$ ions, has now been accomplished in a one-step oxidation of the $[Ta_6Cl_{12}]Cl_2{\cdot}6C_2H_5OH$ precursor in ethanol solution in the presence of Me_4NCl, using air as an oxidant.

Compound (I) consists of four tetrahedral $[(CH_3)_4N]^+$ cations, one octahedral $[(Ta_6Cl_{12})Cl_6]^{3-}$ cluster anion and one Cl^- counter-anion (Fig. 1). The Ta_6 octahedron has an ideal O_h symmetry, with a Ta—Ta interatomic distance of 2.9215 (7) Å (Table 1). This value is in good agreement with the Ta—Ta bond lengths found for other compounds containing the $[Ta_6Cl_{12}]^{3+}$ cluster unit, specifically with the values [2.925 (1) and 2.911 (1) Å, respectively] found in $CsPb[(Ta_6Cl_{12})Cl_6]$ (Cordier *et al.*, 1999) and $[(Ta_6Cl_{12})Cl(H_2O)_5][HgBr_4]{\cdot}9H_2O$ (Vojnović *et al.*, 1997). Simultaneously, the Ta—Ta bond length in (I) is intermediate between the Ta—Ta bond lengths [2.889 (1) and 2.973 (1) Å] found in $In_4[(Ta_6Cl_{12})Cl_6]$ (Bájan & Meyer, 1995) and $[N(CH_3)_4]_2[Ta_6Cl_{12}(OH)_6]{\cdot}21H_2O$ (Beck *et al.*, 1997), which contain $[Ta_6Cl_{12}]^{2+}$ and $[Ta_6Cl_{12}]^{4+}$ ions.



(I)

Compound (I) is the first in the chemistry of hexanuclear halide clusters of niobium and tantalum to have three different kinds of Cl atoms present simultaneously in the same

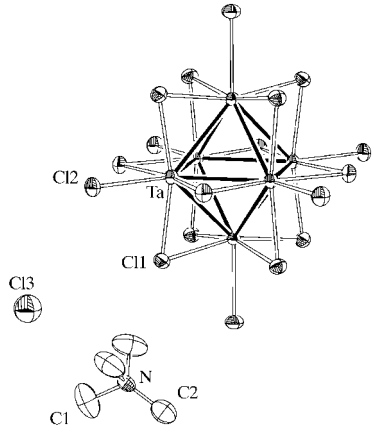


Figure 1
A view of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted.

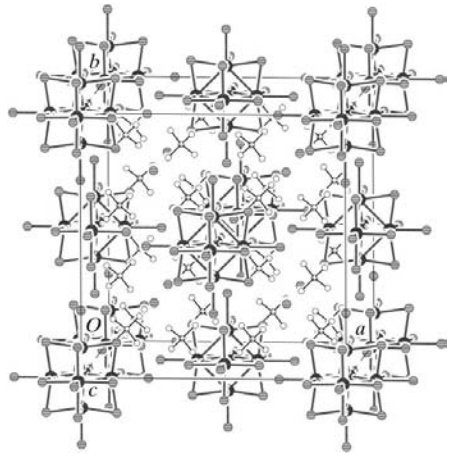


Figure 2
A packing diagram of (I), viewed along the *c* axis. Ta atoms are shown as black circles, Cl atoms as circles filled with horizontal lines, N atoms as crossed circles and C atoms as open circles.

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molecule; 12 Cl atoms are bridging (μ-Cl), six Cl atoms occupy terminal octahedral coordination sites and one Cl atom is a counter-anion. The Ta—(μ-Cl) interatomic distance [2.449 (2) Å] is the same as that found for $[(CH_3)_4N][Ta_6Cl_{12}(H_2O)_6]Br_4$ (Brničević *et al.*, 1985), *i.e.* intermediate between the mean values [2.464 (2) and 2.414 (5) Å] found for $[Ta_6Cl_{12}(C_2H_5OH)_6][(Mo_6Cl_8)Cl_6]$ (Bašic *et al.*, 1998) and $H_2[(Ta_6Cl_{12})Cl_6]\cdot 6H_2O$ (Thaxton & Jacobson, 1971), which contain $[Ta_6Cl_{12}]^{2+}$ and $[Ta_6Cl_{12}]^{4+}$ entities, respectively. The $Ta-Cl_{terminal}$ bond length [2.540 (3) Å] is comparable to the values [2.531 (4) and 2.574 (2) Å, respectively] found for *trans*-$[(Ta_6Cl_{12})Cl_2(PEt_3)_4]\cdot CHCl_3$ (Imoto *et al.*, 1990) and CsPb-$[(Ta_6Cl_{12})Cl_6]$ (Cordier *et al.*, 1999).

The interatomic C—N distances in the tetrahedral $[(CH_3)_4N]^+$ cations are as expected for a single C—N bond [mean 1.408 (9) Å].

The crystal packing of cations and anions in the unit cell of (I) is shown in Fig. 2. The packing is influenced exclusively by attractive interionic forces. The $[(Ta_6Cl_{12})Cl_6]^{3-}$ cluster anions are situated at the corners and centers of the faces of the unit cell, while the Cl^- counter-anions lie in the centers of eight octants that make up the unit cell, in a manner similar to that observed in CaF_2-type structures. The $[(CH_3)_4N]^+$ cations, located around the cluster anion, and Cl^- counter-anions occupy one-half of the possible crystallographic positions, thus satisfying the charge neutrality of the compound.

The title compound is paramagnetic, as found for the $[Ta_6Cl_{12}]^{3+}$ ion. The magnetic susceptibility in the temperature range 5–300 K is nearly constant (μ_{eff} = 1.4–1.6 BM), indicating that there are no interacting $[Ta_6Cl_{12}]^{3+}$ cluster entities.

Experimental

Ethanol solutions of freshly prepared $[Ta_6Cl_{12}]Cl_2\cdot 6C_2H_5OH$ (10 ml, 0.376 g, 0.202 mmol) and $(CH_3)_4NCl$ (5 ml, 0.133 g, 1.212 mmol) were mixed in air. The reaction flask was degassed with a stream of dry nitrogen and the reaction mixture was stirred with a magnetic stirrer for half an hour, after which the contents of the flask were transferred into an ampoule, which was filled with dry nitrogen, sealed and left at room temperature. Dark-green octahedral single crystals appeared on the walls of the ampoule after one month.

Crystal data

$(C_4H_{12}N)_4[Ta_6Cl_{18}]Cl$
M_r = 2055.83
Cubic, $Fm\bar{3}m$
a = 18.1781 (4) Å
V = 6006.8 (2) Å^3
Z = 4
D_x = 2.273 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 20.4–23.2°
μ = 11.75 mm^{-1}
T = 100 (2) K
Octahedron, dark green
0.15 × 0.12 × 0.12 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (North *et al.*, 1968)
T_{min} = 0.201, T_{max} = 0.244
1958 measured reflections
412 independent reflections
351 reflections with $I > 2\sigma(I)$
R_{int} = 0.063
θ_{max} = 27.9°
$h = -23 \rightarrow 0$
$k = -23 \rightarrow 0$
$l = -23 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: 54%

Table 1
Selected geometric parameters (Å, °).

Ta—Ta^{i}	2.9215 (7)	N—C2	1.41 (1)
Ta—Cl1^{ii}	2.449 (2)	N—C1	1.407 (8)
Ta—Cl2	2.540 (3)		
Ta^{iii}—Cl1—Ta	73.23 (6)	Cl1^{ii}—Ta—Cl1^{vi}	163.23 (6)
Cl1^{ii}—Ta—Ta^{i}	95.92 (2)	Cl1^{ii}—Ta—Cl1^{v}	88.781 (9)
Cl1^{v}—Ta—Ta^{i}	53.39 (3)	Cl1^{ii}—Ta—Cl2	81.61 (3)
Cl1—Ta—Ta^{i}	143.39 (3)	C1—N—C1^{vii}	110.4 (6)
Cl2—Ta—Ta^{i}	135	C2—N—C1	108.6 (7)

Symmetry codes: (i) $\frac{1}{2}-y, \frac{1}{2}-z, 1-x$; (ii) $z, x-\frac{1}{2}, \frac{1}{2}+y$; (iii) $\frac{1}{2}+y, z-\frac{1}{2}, x$; (iv) $1-z, \frac{1}{2}-x, \frac{1}{2}-y$; (v) $x, -y, 1-z$; (vi) $z, \frac{1}{2}-x, \frac{1}{2}-y$; (vii) $\frac{3}{2}-z, x-\frac{1}{2}, 1-y$.

Refinement

Refinement on F^2
$R(F)$ = 0.027
$wR(F^2)$ = 0.068
S = 1.15
412 reflections
24 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2 + 58.2675P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.91 e Å^{-3}
$\Delta\rho_{min}$ = −1.10 e Å^{-3}

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1988); cell refinement: *CAD*-4 *Software*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *WinGX* (Farrugia, 1999); software used to prepare material for publication: *ORTEP*-3 (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1032). Services for accessing these data are described at the back of the journal.

References

Bájan, B. & Meyer, H.-J. (1995). *Z. Naturforsch. Teil B*, **50**, 1373–1376.
Bašic, I., Brničević, N., Beck, U., Simon, A. & McCarley, R. E. (1998). *Z. Anorg. Allg. Chem.* **624**, 725–732.
Beck, U., Simon, A., Širac, S. & Brničević, N. (1997). *Z. Anorg. Allg. Chem.* **623**, 59–64.
Brničević, N., Mesarić, S. & Schäfer, H. (1984). *Croat. Chem. Acta*, **57**, 529–535.
Brničević, N., Muštović, F. & McCarley, R. E. (1988). *Inorg. Chem.* **27**, 4532–4535.
Brničević, N., Ružić-Toroš, Ž. & Kojić-Prodić, B. (1985). *J. Chem. Soc. Dalton Trans.* pp. 455–457.
Cordier, S., Loisel, C., Perrin, C. & Sergent, M. (1999). *J. Solid State Chem.* **147**, 350–357.
Eisenbraun, R. & Schäfer, H. (1985). *Z. Anorg. Allg. Chem.* **530**, 222–226.
Enraf–Nonius (1988). *CAD*-4 *Software*. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Imoto, H., Hayakawa, S., Morita, N. & Saito, T. (1990). *Inorg. Chem.* **29**, 2007–2014.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968) *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1997). *HELENA*. Utrecht University, The Netherlands.
Thaxton, C. B. & Jacobson, R. A. (1971). *Inorg. Chem.* **10**, 1460–1463.
Vojnović, M., Antolić, S., Kojić-Prodić, B., Brničević, N., Miljak, M. & Aviani, I. (1997). *Z. Anorg. Allg. Chem.* **623**, 1247–1254.