

## Bis(tetramethylammonium) hexa-aquadodeca- $\mu$ -bromo-octahedro-hexatantalum tetrabromide dihydrate

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The novel title compound,  $[(\text{CH}_3)_4\text{N}]_2[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6]\text{Br}_4 \cdot 2\text{H}_2\text{O}$ , with a  $[\text{Ta}_6\text{Br}_{12}]^{2+}$  cluster unit, has been prepared and structurally characterized. The compound crystallizes in space group  $C2/c$ , with a twofold axis passing through the cluster and the centre of symmetry located between the clusters. The nearest neighbouring cluster units are aligned along the crystallographic  $c$  axis, forming a one-dimensional chain pattern.

### Comment

Due to difficulties in the preparation of single crystals of  $[\text{Ta}_6\text{Br}_{12}]^{n+}$  ( $n = 2, 3$  or  $4$ ) cluster compounds, there are only a limited number of reported structures containing this cluster unit. The structures known to date with  $n = 2$  are  $(\text{Ta}_6\text{Br}_{12})\text{Br}_2$

(Bajan & Meyer, 1995),  $\text{CsEr}[(\text{Ta}_6\text{Br}_{12})\text{Br}_6]$  (Cordier *et al.*, 1995), and a series of cubic clusters  $[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6][\text{MBr}_4] \cdot 12\text{H}_2\text{O}$  ( $M = \text{Zn}, \text{Cd}$  or  $\text{Hg}$ ; Vojnović *et al.*, 1997, 1999, 2001) exhibiting semiconducting properties.  $(\text{Ta}_6\text{Br}_{12})\text{Br}_3$  (von Schnering *et al.*, 1999) is the only structure reported for  $n = 3$ .  $[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6]X_2 \cdot \text{trans}[\text{Ta}_6\text{Br}_{12}(\text{OH})_4(\text{H}_2\text{O})_2] \cdot 18\text{H}_2\text{O}$  ( $X = \text{Cl}$  or  $\text{Br}$ ; Vojnović *et al.*, 2002) are the only structures reported with  $n = 2$  and  $4$  present simultaneously in the same compound. Interesting magnetic properties are observed within these cluster compounds (diamagnetic for  $n = 2$  and  $4$ , paramagnetic for  $n = 3$ ; Converse & McCarley, 1970). Some of the latter are low-dimensional magnetic materials, as a consequence of the specific crystal packing.

The title compound consists of two different kinds of cations, namely two  $[(\text{CH}_3)_4\text{N}]^+$  and one  $[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6]^{2+}$  cluster, four  $\text{Br}^-$  anions and two further water molecules (Fig. 1). In the  $[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6]^{2+}$  cluster cation, six Ta atoms are arranged octahedrally, and 12 Br atoms are located over the bridges of the  $\text{Ta}_6$  octahedron as  $\mu_2$  ligands. The cluster cation possesses  $C_2$  symmetry, with a twofold axis passing through atoms Br6 and Br7 and bisecting the  $\text{Ta}2-\text{Ta}2^i$  and  $\text{Ta}3-\text{Ta}3^i$  bonds [symmetry code: (i)  $-x, y, \frac{1}{2} - z$ ]. Six water molecules occupy terminal octahedral coordination sites. The  $\text{Ta}_6$  octahedron is distorted, being slightly elongated along the  $\text{Ta}1-\text{Ta}1^i$  direction.

The Ta—Ta bond distances are in the range 2.8899 (7)–2.9111 (7) Å (mean 2.9026 Å), and these are comparable with the mean value of 2.898 Å in  $\text{CsEr}[(\text{Ta}_6\text{Br}_{12})\text{Br}_6]$  and the value of 2.9000 (8) Å in  $[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6][\text{HgBr}_4] \cdot 12\text{H}_2\text{O}$ . These values and local charge neutrality requirements dictate the presence of  $[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6]^{2+}$  explicitly.

The Ta—Br bond distances are in the range 2.5885 (9)–2.6170 (7) Å (mean 2.6074 Å), as expected for  $[\text{Ta}_6\text{Br}_{12}]^{2+}$  (Vojnović *et al.*, 1997, 1999, 2001). The Ta1—O1 bond distance is the shortest [2.218 (4) Å], in comparison with Ta2—O2 [2.251 (5) Å] or Ta3—O3 [2.269 (5) Å]. The C—N bond distances in  $[(\text{CH}_3)_4\text{N}]^+$  are as expected for a C—N single bond (mean 1.486 Å).

The crystal packing is governed by strong ionic interactions between cations and anions, and by hydrogen bonds. The system of hydrogen bonds (Table 1) is a complex one and involves coordinated and free water molecules and  $\text{Br}^-$  anions. The  $\text{Br}^-$  anions are triple (Br8) and quadruple (Br9) acceptors, indicating their charge-assisted character (CAHB; Giacobozzo, 1992). In spite of the stronger interactions in these 'charge-assisted hydrogen bonds', the shortest hydrogen bond is formed between coordinated and free water molecules (Table 1).

The distances between cluster cations are shortest along the  $c$  axis

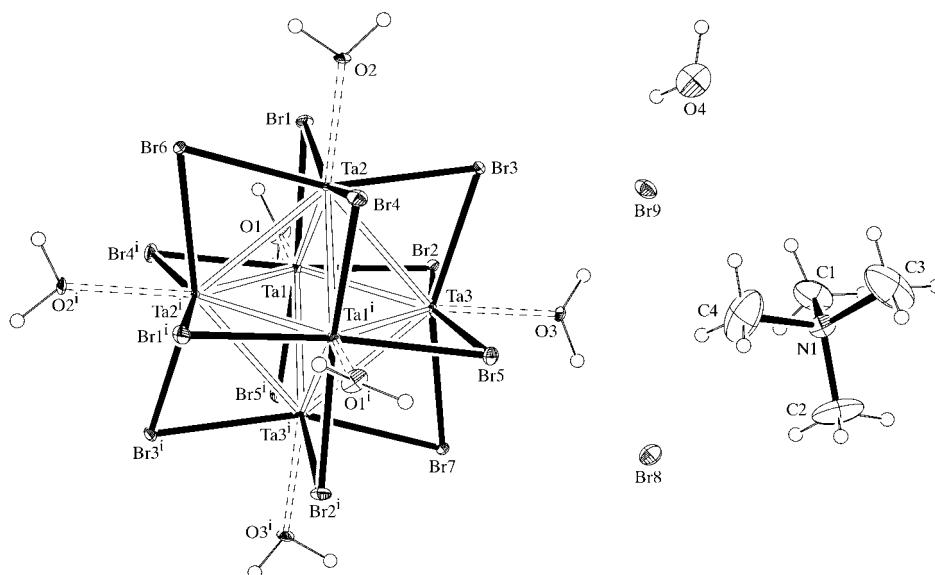
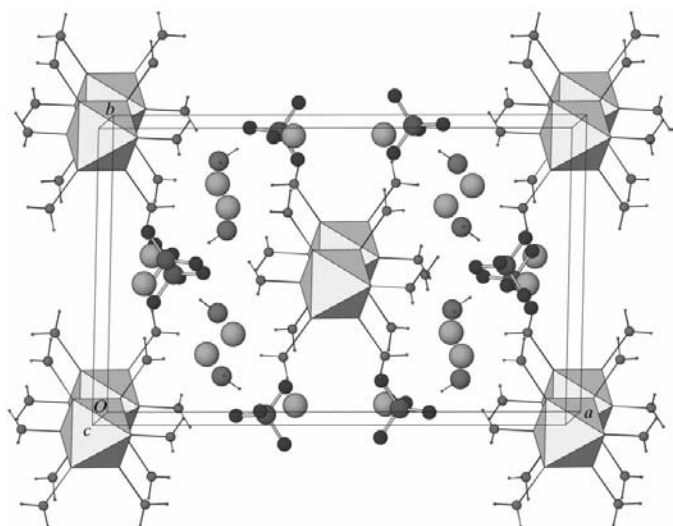


Figure 1

A view of  $[(\text{CH}_3)_4\text{N}]_2[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6]\text{Br}_4 \cdot 2\text{H}_2\text{O}$  with 30% probability displacement ellipsoids [symmetry code: (i)  $-x, y, \frac{1}{2} - z$ ].



**Figure 2**  
The crystal packing of the title compound. Octahedra are constructed from six Ta atoms. Bridging Br atoms and H atoms from  $[(\text{CH}_3)_4\text{N}]^+$  cations have been omitted for clarity.

[9.2586 (1) Å between cluster centres]. The one-dimensional cluster chains that extrude along the *c* axis are surrounded by  $[(\text{CH}_3)_4\text{N}]^+$  cations,  $\text{Br}^-$  anions and free water molecules (Fig. 2).

## Experimental

Methanolic solutions of  $[(\text{Ta}_6\text{Br}_{12})\text{Br}_2(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$  (10 ml, 0.200 g, 0.085 mmol) and  $[(\text{CH}_3)_4\text{N}]\text{Br}$  (5 ml, 0.052 g, 0.341 mmol) were mixed and filtered over a G-4 frit. In a stream of nitrogen, the volume was reduced to 5 ml at 308 K. The reaction mixture was left to crystallize under ambient conditions. Dark-green nearly black cube-like crystals appeared within a few days.

### Crystal data

$(\text{C}_4\text{H}_{12}\text{N})_2[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6]\text{Br}_4\cdot 2\text{H}_2\text{O}$	$D_x = 3.982 \text{ Mg m}^{-3}$
$M_r = 2656.52$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 12 960 reflections
$a = 24.388$ (5) Å	$\theta = 2.1\text{--}30.5^\circ$
$b = 12.470$ (2) Å	$\mu = 29.21 \text{ mm}^{-1}$
$c = 18.425$ (4) Å	$T = 200 \text{ K}$
$\beta = 127.74$ (3) $^\circ$	Prism, dark green
$V = 4431$ (2) Å <sup>3</sup>	$0.10 \times 0.07 \times 0.05 \text{ mm}$
$Z = 4$	

**Table 1**

Hydrogen-bonding geometry (Å,  $^\circ$ ).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$\text{O1--H11}\cdots\text{Br9}^i$	0.94 (7)	2.35 (6)	3.230 (4)	156 (10)
$\text{O1--H12}\cdots\text{O4}^{ii}$	0.94 (6)	1.69 (6)	2.627 (7)	173 (8)
$\text{O2--H21}\cdots\text{Br8}^{iii}$	0.96 (5)	2.29 (4)	3.222 (4)	164 (8)
$\text{O2--H22}\cdots\text{Br9}^{iv}$	0.96 (9)	2.32 (9)	3.279 (6)	177 (6)
$\text{O3--H31}\cdots\text{Br9}$	0.94 (7)	2.32 (7)	3.259 (5)	176 (3)
$\text{O3--H32}\cdots\text{Br8}$	0.95 (3)	2.30 (3)	3.223 (4)	163 (8)
$\text{O4--H41}\cdots\text{Br8}^{iv}$	0.96 (11)	2.51 (10)	3.339 (7)	144 (7)
$\text{O4--H42}\cdots\text{Br9}$	0.93 (6)	2.58 (8)	3.347 (6)	140 (8)

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

### Data collection

Nonius KappaCCD area-detector diffractometer	6770 independent reflections
$\omega$ scans	5864 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan ( <i>DENZO-SCALEPACK</i> ; Otwinowski & Minor, 1997)	$R_{\text{int}} = 0.033$
$T_{\text{min}} = 0.054, T_{\text{max}} = 0.232$	$\theta_{\text{max}} = 30.5^\circ$
12 960 measured reflections	$h = -34 \rightarrow 34$
	$k = -17 \rightarrow 17$
	$l = -26 \rightarrow 26$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0172P)^2 + 7.5089P]$
$R(F) = 0.028$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.069$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 2.50 \text{ e \AA}^{-3}$
6770 reflections	$\Delta\rho_{\text{min}} = -2.94 \text{ e \AA}^{-3}$
219 parameters	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.000407 (10)

H atoms bonded to O atoms were located from a difference Fourier synthesis and refined freely, while those bonded to C atoms were placed in calculated positions and constrained to ride on the parent atoms. In the final cycles of refinement, the geometries of the water molecules were restrained to ideal values. The highest peak and the deepest hole in the difference Fourier synthesis are in the vicinity of the  $\text{Br8}^-$  anion.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO-SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO-SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2001) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1533). Services for accessing these data are described at the back of the journal.

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