

Hexaaquadodeca- $\mu$ -bromo-octahedro-  
hexatantalum bromide chloride octa-  
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The title compound,  $[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6](\text{Br}_{0.4}\text{Cl}_{1.6})\cdot 8\text{H}_2\text{O}$ , crystallizes in space group  $P\bar{1}$ . The structure contains two crystallographically independent  $[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6]^{2+}$  cluster cations forming distinct layers parallel to the  $ab$  plane. The compound is isoconfigurational with the double salts  $[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6]X_2\text{-trans-}[\text{Ta}_6\text{Br}_{12}(\text{OH})_4(\text{H}_2\text{O})_2]\cdot 18\text{H}_2\text{O}$  ( $X = \text{Cl}, \text{Br}$ ).

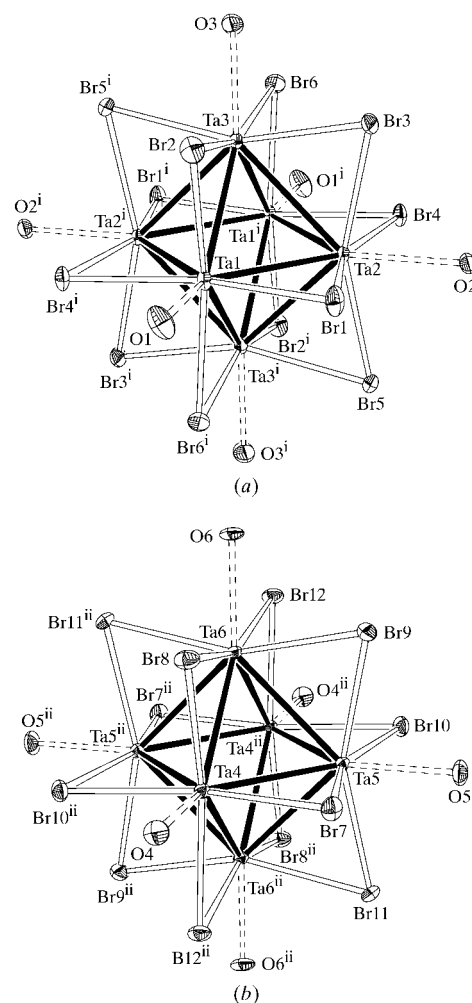
## Comment

The  $(M_6X_{12})X_2\cdot 8\text{H}_2\text{O}$  ( $M = \text{Nb}, \text{Ta}; X = \text{Cl}, \text{Br}$ ) and  $(M_6X_{12})X_2\cdot 6\text{ROH}$  ( $R = \text{CH}_3, \text{C}_2\text{H}_5$ ) cluster compounds are usually used as starting materials for reactions in aqueous or non-aqueous media. The only structure within these two series which has thus far been solved is that of  $[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_2(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$  (Burbank, 1966). The six Ta atoms form a nearly regular octahedron and the 12 Cl atoms are bridging. The terminal octahedral coordination sites are occupied by four  $\text{H}_2\text{O}$  molecules and two Cl atoms in *trans* positions. The crystal structure determination of the title compound, (I), revealed that two additional halogen atoms are not coordinated to the cluster  $[\text{Ta}_6\text{Br}_{12}]^{2+}$  entity.

The structure of the title compound consists of two cluster cations of the same chemical composition, *i.e.*  $[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6]^{2+}$  (denoted **A** and **B**; Fig. 1), together with  $\text{Cl}^-$  or  $\text{Br}^-$  as counter-ions and free  $\text{H}_2\text{O}$  molecules (Fig. 2). One cluster cation (**A**) is located at the origin, while the other (**B**) is located at the centre of inversion with fractional coordinates  $(0, 0, \frac{1}{2})$ . Thus, both clusters are centrosymmetric and very close to having octahedral  $O_h$  symmetry. The Ta—Ta bond lengths of clusters **A** and **B** are in the ranges 2.8908 (10)–2.9113 (9) Å (average 2.8981 Å) and 2.8950 (8)–2.9110 (11) Å (average 2.9036 Å), respectively, and are comparable to the average values of 2.898 and 2.9000 (8) Å found for  $\text{CsEr}[(\text{Ta}_6\text{Br}_{12})\text{Br}_6]$  (Cordier *et al.*, 1995) and  $[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6](\text{HgBr}_4)\cdot 12\text{H}_2\text{O}$  (Vojnović *et al.*, 1997), respectively. These values and local

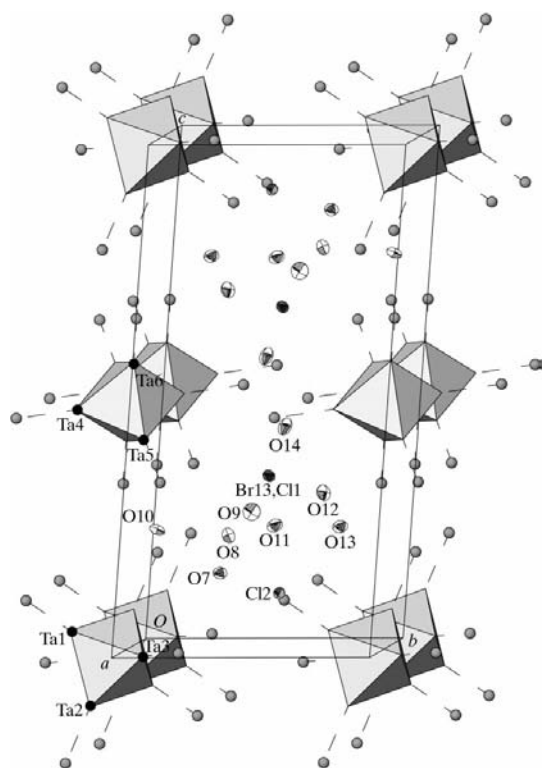
charge-neutrality requirements dictate the presence of  $[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6]^{2+}$  explicitly. The Ta—Br interatomic distances, with average values of 2.6054 and 2.6110 Å in clusters **A** and **B**, respectively, are as expected for  $[\text{Ta}_6\text{Br}_{12}]^{2+}$  (Cordier *et al.*, 1995; Vojnović *et al.*, 1997). The Ta—O bond lengths, in the ranges 2.217 (4)–2.336 (5) and 2.236 (4)–2.254 (4) Å for clusters **A** and **B**, respectively, are as expected for Ta—O( $\text{H}_2\text{O}$ ) interatomic distances.

Cluster cations **A** and **B** form two distinct layers parallel to the  $ab$  plane of the unit cell (Fig. 2). Each face of the  $\text{Ta}_6$  octahedron defines a plane which forms three angles with the crystallographic axes. The planes of two faces of an octahedron uniquely define the orientation of that cluster in the unit cell. Faces (Ta1, Ta2, Ta3) and (Ta1, Ta2<sup>i</sup>, Ta3) [symmetry code: (i)  $-x, -y, -z$ ] define the orientation of clusters **A**, while faces (Ta4, Ta5, Ta6) and (Ta4, Ta5<sup>ii</sup>, Ta6) [symmetry code: (ii)  $-x, -y, 1-z$ ] define the orientation of clusters **B** (Table 1 and Fig. 2). It is evident that faces (Ta1, Ta2, Ta3) and (Ta4, Ta5, Ta6) have similar orientations [the angle between them is 7.88 (2)°]. In contrast, the angle between the (Ta1, Ta2<sup>i</sup>, Ta3) and (Ta4, Ta5<sup>ii</sup>, Ta6) faces is 53.60 (1)°. This means



**Figure 1**  
An ORTEP-3 (Farrugia, 1997) drawing of clusters (a) **A** and (b) **B** in (I), shown with 50% probability displacement ellipsoids. [Symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $-x, -y, 1-z$ .]

that clusters **B** are rotated with respect to clusters **A** by an angle of  $\sim 60^\circ$  around the normal to the (Ta1, Ta2, Ta3) face. By this rotation, and by translation along the  $c$  axis by a half of the period, Ta1 coincides with Ta4, Ta2 with Ta5 and Ta3 with Ta6. This is a non-crystallographic symmetry operation and results in the crystallographic independence of the **A** and **B** cluster cations. A similar type of crystal packing has been observed recently in the crystal structures of double salts  $[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6]X_2 \cdot \text{trans}-[\text{Ta}_6\text{Br}_{12}(\text{OH})_4(\text{H}_2\text{O})_2] \cdot 18\text{H}_2\text{O}$  ( $X = \text{Cl}$ , compound (II), and  $X = \text{Br}$ , compound (III)), which contain  $[\text{Ta}_6\text{Br}_{12}]^{n+}$ , with  $n = 2$  and 4, simultaneously in the same compound (Vojnović *et al.*, 2002). These clusters crystallize in space group  $P\bar{1}$  with a similar unit cell; the dimensions are:  $a = 9.3264$  (2) Å,  $b = 9.8272$  (2) Å,  $c = 19.0158$  (4) Å,  $\alpha = 80.931$  (1)°,  $\beta = 81.772$  (2)° and  $\gamma = 80.691$  (1)° for (II), and  $a = 9.3399$  (2) Å,  $b = 9.8796$  (2) Å,  $c = 19.0494$  (4) Å,  $\alpha = 81.037$  (1)°,  $\beta = 81.808$  (1)° and  $\gamma = 80.736$  (1)° for (III). The orientations of clusters **A** and **B** in the unit cell of compound (I) are compared with the orientations of the corresponding cluster entities in the unit cells of (II) and (III), where *trans*- $[\text{Ta}_6\text{Br}_{12}(\text{OH})_4(\text{H}_2\text{O})_2]$  is denoted as **A** and  $[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6]^{2+}$  as **B** (Table 1). Considering the clusters of type **B**, the particular angles are essentially the same for all three compounds. The orientations of clusters **A** in (I) differ slightly (to a



**Figure 2**

The crystal packing of (I). Octahedra are constructed from six Ta atoms. Bridging Br atoms have been omitted for clarity. Six crystallographically independent Ta atoms are labelled and shown as black circles, O atoms from coordinated  $\text{H}_2\text{O}$  molecules are shown as grey circles, and O atoms from free  $\text{H}_2\text{O}$  molecules and counter-anions are labelled and shown in ORTEP II (Johnson, 1976) style with 50% probability displacement ellipsoids.

maximum of  $5^\circ$ ) from those in (II) and (III), most probably due to the difference in the chemical composition of  $[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6]^{2+}$  in relation to *trans*- $[\text{Ta}_6\text{Br}_{12}(\text{OH})_4(\text{H}_2\text{O})_2]$ . The locations of the counter-ions and free  $\text{H}_2\text{O}$  molecules are similar in all three structures with respect to the cluster positions. The position of the Cl2 counter-anion in (I) (Fig. 2) is occupied by a free  $\text{H}_2\text{O}$  molecule (O15) in both (II) and (III).

In conclusion, the present analysis indicates that the three structures are isoconfigurational (Lima-de-Faria *et al.*, 1990), in spite of the difference in chemical composition, the charges of the cluster entities and the number of counter-anions or free  $\text{H}_2\text{O}$  molecules. These structures can be used as a starting model in Rietveld refinements for other compounds in this series which crystallize in space group  $P\bar{1}$  and which have similar values of the unit-cell parameters.

## Experimental

Aqueous solutions of  $(\text{Ta}_6\text{Br}_{12})\text{Br}_2 \cdot 8\text{H}_2\text{O}$  (5 ml, 0.200 g, 0.085 mmol) and  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$  (2 ml, 0.0305 g, 0.085 mmol) were mixed and filtered through a G-4 frit, then left to evaporate under ambient conditions. Plate-like single crystals formed over a period of one week.

### Crystal data

$[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6](\text{Br}_{0.4}\text{Cl}_{1.6}) \cdot 8\text{H}_2\text{O}$	$Z = 2$
$M_r = 2385.53$	$D_x = 4.426 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	MoK $\alpha$ radiation
$a = 9.729$ (2) Å	Cell parameters from 20 232 reflections
$b = 9.823$ (2) Å	$\theta = 2.1\text{--}30.5^\circ$
$c = 19.392$ (4) Å	$\mu = 32.29 \text{ mm}^{-1}$
$\alpha = 81.92$ (3)°	$T = 200$ (3) K
$\beta = 80.28$ (3)°	Plate, dark-green
$\gamma = 80.34$ (3)°	$0.09 \times 0.05 \times 0.02 \text{ mm}$
$V = 1788.7$ (7) Å <sup>3</sup>	

**Table 1**

The orientations of clusters **A** and **B** in (I), (II) and (III) (°).

Angle	(I)	(II) <sup>a</sup>	(III) <sup>a</sup>
<b>Cluster A</b>			
(Ta1, Ta2, Ta3) – $a^b$	75.82 (1)	78.72	78.85
(Ta1, Ta2, Ta3) – $b$	2.46 (1)	3.25	3.34
(Ta1, Ta2, Ta3) – $c$	0.82 (1)	2.14	1.98
(Ta1, Ta2 <sup>i</sup> , Ta3) – $a$	30.06 (1)	31.11	31.03
(Ta1, Ta2 <sup>i</sup> , Ta3) – $b$	16.49 (1)	21.08	21.34
(Ta1, Ta2 <sup>i</sup> , Ta3) – $c$	68.66 (1)	64.78	68.82
<b>Cluster B</b>			
(Ta4, Ta5, Ta6) – $a$	75.92 (1)	75.51	76.01
(Ta4, Ta5, Ta6) – $b$	4.42 (1)	5.18	4.64
(Ta4, Ta5, Ta6) – $c$	8.08 (1)	7.15	7.18
(Ta4, Ta5 <sup>ii</sup> , Ta6) – $a$	10.40 (1)	9.22	9.60
(Ta4, Ta5 <sup>ii</sup> , Ta6) – $b$	36.59 (1)	37.22	37.21
(Ta4, Ta5 <sup>ii</sup> , Ta6) – $c$	43.88 (1)	42.42	42.21

Notes: (a) faces corresponding to (Ta1, Ta2, Ta3), (Ta1, Ta2<sup>i</sup>, Ta3), (Ta4, Ta5, Ta6) and (Ta4, Ta5<sup>ii</sup>, Ta6) are (Ta6, Ta5<sup>iii</sup>, Ta4), (Ta6, Ta5, Ta4), (Ta2<sup>iv</sup>, Ta1, Ta3<sup>iv</sup>) and (Ta2<sup>iv</sup>, Ta1<sup>iv</sup>, Ta3<sup>iv</sup>) in (II) and (III) (Vojnović *et al.*, 2002), respectively. (b) The angle between the plane defined by atoms Ta1, Ta2 and Ta3 and the crystallographic  $a$  axis. Complete symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $-x, -y, 1 - z$ ; (iii)  $1 - x, -y, 1 - z$ ; (iv)  $1 - x, -y, -z$ .

*Data collection*

Nonius KappaCCD diffractometer  $\omega$  scans  
 Absorption correction: multi-scan  
 (DENZO-SCALEPACK;  
 Otwinowski & Minor, 1997)  
 $T_{\min} = 0.055$ ,  $T_{\max} = 0.524$   
 20 232 measured reflections

10 753 independent reflections  
 8662 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.033$   
 $\theta_{\text{max}} = 30.5^\circ$   
 $h = -13 \rightarrow 13$   
 $k = -13 \rightarrow 13$   
 $l = -27 \rightarrow 27$

*Refinement*

Refinement on  $F^2$   
 $R(F) = 0.031$   
 $wR(F^2) = 0.063$   
 $S = 1.04$   
 10 753 reflections  
 309 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0157P)^2 + 6.9837P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 1.62 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -2.56 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.000817 (19)

All the Ta and bridging Br atoms of the clusters were located. The remainder of the atoms (except for the H atoms) were located from a difference Fourier synthesis. During isotropic refinement, it was observed that the displacement parameter of the Br13 atom was too large. Assuming that its position is also occupied by Cl anions in a disordered way, the remainder of the refinement cycles were performed constraining the Br13 and Cl1 anions to the same site and constraining the sum of their occupation factors to 1. The refinement converged to a value of 0.397 (5) for the site occupation of the Br13 anion, from which the chemical formula of the compound was deduced.

Data collection: COLLECT (Nonius, 1998); cell refinement: DENZO-SCALEPACK (Otwinowski & Minor, 1997); data reduc-

tion: DENZO-SCALEPACK; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ATOMS (Dowty, 2002) 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: BR1370). Services for accessing these data are described at the back of the journal.

**References**

- Burbank, R. D. (1966). *Inorg. Chem.* **5**, 1491–1496.  
 Cordier, S., Perrin, C. & Sergent, M. (1995). *J. Solid State Chem.* **118**, 274–279.  
 Dowty, E. (2002). *ATOMS for Windows*. Version 6.0. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.  
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
 Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 Lima-de-Faria, J., Hellner, E., Liebau, F., Makovicky, E. & Parthé, E. (1990). *Acta Cryst.* **A46**, 1–11.  
 Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.  
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.  
 Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.  
 Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.  
 Vojnović, M., Antolić, S., Kojić-Prodić, B., Brničević, N., Miljak, M. & Aviani, I. (1997). *Z. Anorg. Allg. Chem.* **623**, 1247–1254.  
 Vojnović, M., Brničević, N., Bašić, I., Planinić, P. & Giester, G. (2002). *Z. Anorg. Allg. Chem.* **628**, 401–408.