

## Cation distribution in the zirconium chloride cluster phase Cs[(Zr<sub>6</sub>C)Cl<sub>15</sub>]

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Poly[caesium [[ $\mu_6$ -carbido-dodecakis- $\mu_2$ -chloro-hexazirconium]-tri- $\mu_2$ -chloro]], Cs[(Zr<sub>6</sub>C)Cl<sub>15</sub>], crystallizes in the orthorhombic space group *Pmma*. The structure is built up of two symmetry-independent [(Zr<sub>6</sub>C)Cl<sub>12</sub>Cl<sub>6/2</sub><sup>a</sup>] cluster units (where 'inner' and 'outer' ligands are denoted by i and a, respectively), which are three-dimensionally connected to form a cluster network through all six halogen atoms on the *exo* positions of each octahedral (Zr<sub>6</sub>C) metal unit, forming Cl<sup>a</sup>-a bridges. The caesium cations are distributed in several voids within the cluster network. 16 of the 23 independent atoms lie on crystallographic special positions.

### Comment

In the present paper, we describe the structure of the cluster compound Cs[(Zr<sub>6</sub>C)Cl<sub>15</sub>], which was prepared using Al<sub>4</sub>C<sub>3</sub> as the carbon source, reactor grade (extreme low Hf content) Zr powder and ZrCl<sub>4</sub> [for reviews on Zr cluster chemistry, see Corbett (1992, 1995, 1996, 2000)]. Being a member of the K[(Zr<sub>6</sub>C)Cl<sub>15</sub>] structure type (Ziebarth & Corbett, 1987), this compound crystallizes in the orthorhombic space group *Pmma*. This structure type is based on two symmetry-independent anionic cluster units, [(Zr<sub>6</sub>C)Cl<sub>12</sub>Cl<sub>6/2</sub><sup>a</sup>]<sup>-</sup> [where 'inner' and 'outer' ligands are denoted by i and a, respectively (Schäfer & von Schnering, 1964)] (Fig. 1), sharing the outer ligands with neighbouring units, forming two different types of cluster chains. One linear chain runs along the *c* axis, where all cluster units are connected by linear chlorine bridges, and the other type is built up of bent chlorine bridges (Zr2—Cl<sup>a</sup>—Zr2), forming a zigzag chain of clusters along the *a* axis (Fig. 2). Additional bent chlorine bridges (Zr1—Cl<sup>a</sup>—Zr3; Table 1) interconnect the two groups of chains, leading to a three-dimensional cluster network. Within the cluster network, the Cs cations are distributed on several sites. The title compound is structurally comparable to the boron-centered zirconium cluster compound CsK[(Zr<sub>6</sub>B)Cl<sub>15</sub>], in which the potassium site is fully occupied and the caesium cation is distributed over two sites (Ziebarth & Corbett, 1987). However, the cation distribution within the cluster network in the title phase is

different from that in CsK[(Zr<sub>6</sub>B)Cl<sub>15</sub>]. Apparently, the size of the cavities plays an important role. Whereas in CsK[(Zr<sub>6</sub>B)Cl<sub>15</sub>] the Wyckhoff site 4*k* is completely occupied by potassium, in Cs[(Zr<sub>6</sub>C)Cl<sub>15</sub>] the occupation is rather small (0.08). This site is surrounded by ten Cl atoms with Cs3—Cl distances as short as 3.297 (6) Å; the sum of the ionic radii of Cs and Cl is 3.55 Å (Shannon, 1976). Therefore, we can assume that this site is too small to accommodate more than marginal numbers of Cs cations.

The two remaining cation sites are filled with caesium ions as in CsK[(Zr<sub>6</sub>B)Cl<sub>15</sub>]. For both sites, the Cs atoms had to be refined on split positions (Cs1/Cs2 and Cs4/Cs5). Both sites have longer distances to the surrounding Cl atoms [3.42 (1) and 3.46 (1) Å, respectively]; therefore, size restrictions are much less pronounced. The Cs4/Cs5 site is especially interesting because the Cs atoms are disordered along a channel running down the [001] direction (Fig. 3). This might suggest

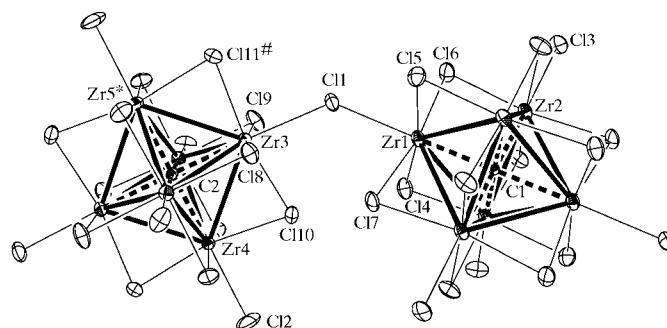


Figure 1

The independent cluster components of the title phase, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (\*)  $x, y, z - 1$ ; (#)  $\frac{1}{2} - x, y, z - 1$ .]

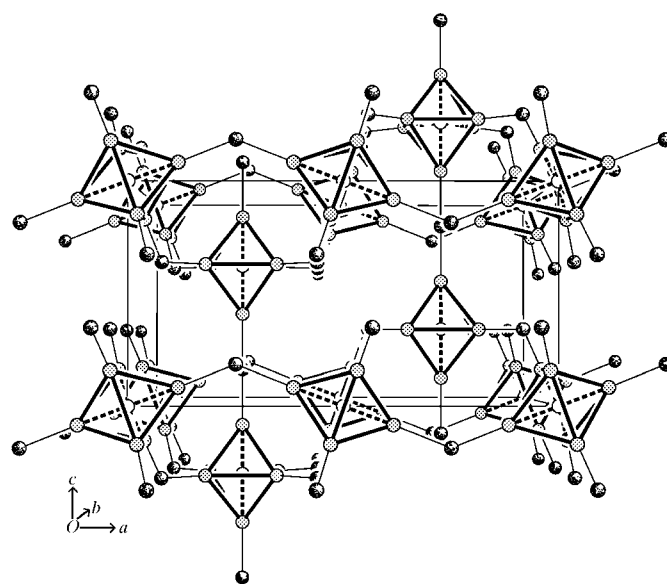
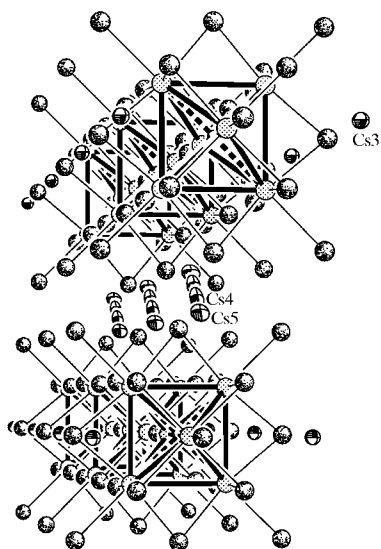


Figure 2

A view of the structure of the title phase down [010], showing the two independent cluster chain types. C atoms are shown as white circles, Zr atoms as regularly dotted circles and outer Cl atoms as irregularly dotted circles. Inner halides and Cs atoms have been omitted for clarity.


**Figure 3**

Disordered Cs4 and Cs5 atoms located between cluster chains, viewed down [001] (Cs atoms are represented by displacement ellipsoids of 50% probability, Cl atoms as irregularly dotted circles, Zr atoms as regularly dotted circles and C atoms as shaded circles).

that this phase could be an acceptable ionic conductor. Conductivity measurements are being planned.

The coordination polyhedron of atom Cs3 can be described as an irregular twofold capped tetragonal prism, whereas the other two coordination environments are rather irregular. The coordination environment of each Zr atom consists of a tetragonal–pyramidal arrangement of Cl atoms, a square arrangement of Zr atoms and one additional C atom.

## Experimental

Cs[(Zr<sub>6</sub>C)Cl<sub>15</sub>] is conventionally prepared from appropriate mixtures of CsCl, ZrCl<sub>4</sub>, elemental Zr and Al<sub>4</sub>C<sub>3</sub>, which are enclosed in welded niobium (or tantalum) ampoules, which in turn are sealed in evacuated silica ampoules. Reactions were carried out by heating the enclosed ampoules at 1123 K for two to three weeks. The air- and moisture-sensitive compound was obtained as dark-red crystals.

### Crystal data

Cs[(Zr <sub>6</sub> C)Cl <sub>15</sub> ]	Mo K $\alpha$ radiation
$M_r = 1223.99$	Cell parameters from 42 reflections
Orthorhombic, <i>Pmma</i>	$\theta = 2.9\text{--}19.9^\circ$
$a = 18.513 (2) \text{ \AA}$	$\mu = 5.47 \text{ mm}^{-1}$
$b = 13.916 (1) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 9.6383 (7) \text{ \AA}$	Irregular block, dark red
$V = 2483.1 (4) \text{ \AA}^3$	$0.52 \times 0.43 \times 0.40 \text{ mm}$
$Z = 4$	
$D_x = 3.274 \text{ Mg m}^{-3}$	

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Zr–C (average)	2.278 (7)	Zr–Cl <sup>ii</sup> (average)	2.643 (2)
Zr–Zr (average)	3.221 (1)	Zr–Cl <sup>i</sup> (average)	2.527 (2)
Zr2 <sup>i</sup> –Cl3–Zr2 <sup>ii</sup>	137.7 (1)	Zr4–Cl2–Zr5	180.0
Zr1–Cl1–Zr3	132.84 (6)		

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

### Data collection

Siemens P4 diffractometer  
 $\omega$  scans  
 Absorption correction:  $\psi$  scan (Farrugia, 1999)  
 $T_{\min} = 0.047, T_{\max} = 0.112$   
 4087 measured reflections  
 3223 independent reflections  
 2627 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$   
 $\theta_{\text{max}} = 28.0^\circ$   
 $h = -1 \rightarrow 24$   
 $k = -18 \rightarrow 1$   
 $l = -12 \rightarrow 1$   
 2 standard reflections  
 every 98 reflections  
 intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.128$   
 $S = 1.08$   
 3223 reflections  
 141 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0687P)^2 + 15.1304P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 2.00 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.62 \text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.00071 (11)

During structure refinement, it quickly became obvious that the Cs cation is distributed over several disordered positions. As in the CsK[(Zr<sub>6</sub>B)Cl<sub>15</sub>] structure (Ziebarth & Corbett, 1987), Wyckoff sites  $4k$ ,  $2f$  and  $2c$  are involved. Unconstrained refinements of all five positions (two sites split into two positions) including variations of the occupation factors indicated the  $2f$  site to be fully occupied, which accounts for one-half of a Cs atom per formula unit. The refinement of this atom was carried out using a split position (Cs1 and Cs2), the sum of the site-occupation factors being fixed to full occupation (occupation factors are given in the deposited CIF). Using a restrained occupation for atoms Cs3, Cs4 and Cs5, the total Cs content per formula unit refines to Cs<sub>1.00(7)</sub>[(Zr<sub>6</sub>C)Cl<sub>15</sub>]. The two independent interstitial C atoms were refined isotropically. All other atoms were refined using anisotropic displacement parameters.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1155). Services for accessing these data are described at the back of the journal.

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