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# The Synthesis and Structure of a New Zirconium Iodide Carbide Cluster Phase, $Cs_2Zr_7I_{18}C$

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The title compound is obtained from reactions of CsI, $ZrI_4$, Zr, and C in sealed Ta at 800°C (but not at 850°C). Both $Zr_6I_{12}C$ and $Zr_6I_{14}C$ are unstable in the presence of CsI. The $Cs_2Zr_7I_{18}C$ is shown by X-ray crystallography to be isostructural with $K_2Zr_7Cl_{18}H$ and is better described as $Cs_2ZrI_6 \cdot Zr_6I_{12}C$, the iodine in the $ZrI_6^{2-}$ groups bonding to metal vertices in six separate carbon-centered clusters ($R\bar{3}$, $Z = 3$ for $a = 10.744(1)$ Å, $c = 29.409(5)$ Å, $R(F)/R_w = 3.5/4.4\%$).

## Introduction

Previous studies have identified $Zr_6I_{14}C$, $CsZr_6I_{14}C$, $Zr_6I_{12}C$ (*1*), and $Cs_2ZrI_6$ (*2*) as the important ternary and quaternary phases in the Zr–I–C and Cs–Zr–I–C systems. Carbon (or another nonmetal) is essential for the thermodynamic stability of the first three reduced phases, these being constructed from carbon-centered $Zr_6I_{12}$-type octahedral clusters that are interbridged at all metal vertices by iodine. This article reports investigations of cesium-richer carbide and boride cluster systems that demonstrate the existence of the new compound $Cs_2Zr_7I_{18}C$ (= $Cs_2ZrI_6 \cdot Zr_6I_{12}C$) in the $K_2Zr_7Cl_{18}H$ structure (*3, 4*). This phase is important to any consideration of possible fission-product chemistry within Zircaloy-clad fuel elements in pressurized water reactors (*5*) since the fission yield of cesium well exceeds that of iodine.

## Experimental Section

The synthetic and characterizational techniques employed, including reactions in sealed Ta containers, have been described earlier (*1, 2*). The new phase was originally produced in ~10% yield through the intervention of adventitious carbon (e.g., grease) during only one of several unsuccessful attempts to prepare $CsZr_6I_{14}Rh$. Crystals of the carbide are well formed and easily noticed, and only a very small amount of impurity carbon is necessary with the other, heavy elements (*1*). The heavy atom structure and the probable presence of carbon were established crystallographically (below). Subsequent stoichiometric reactions of sublimed $ZrI_4$, CsI (Alpha), powdered Zr (reactor grade, via the hydride), and spectroscopic grade graphite (Union Carbide) in tantalum at 850°C gave only $CsZr_6I_{14}C$, $Cs_2ZrI_6$, and $ZrI_x$ ($x = 3, 4$). However, reactions of the same components at 800°C either in stoichiometric proportions or with an excess of metal for ~26 days gave the title phase in high yields. A 25% deficiency of CsI provided $CsZr_6I_{14}C$ as a second phase, not $Zr_6I_{12}C$, even with excess Zr. In other words, $Zr_6I_{12}C$ is evidently not stable in the presence of an equal or greater

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TABLE I

DIFFRACTION COLLECTION AND REFINEMENT DATA FOR $Cs_2Zr_7I_{18}C$

| | |
|---|---|
| Space group, $Z$ | $R\bar{3}$ (No. 148), 3 |
| Lattice parameters[a] | |
| $a$, Å | 10.744(1) |
| $c$, Å | 29.409(5) |
| $V$, Å$^3$ | 2939.8(8) |
| Crystal size, mm | 0.45 × 0.52 × 0.40 |
| Data collection instrument | Rigaku AFC6R |
| Radiation (monochromated in incident beam) | Mo$K\alpha$ |
| Temperature, °C | 23 |
| Scan method | $\theta$–$2\theta$ |
| Octants measured | 4; $h$, $\pm k$, $\pm l$ |
| $2\theta_{max}$, degrees | 65 |
| Refl. meas. | 7354 |
| unique | 2353 |
| obs, $F_o^2 > 3\sigma(F_o^2)$ | 1781 |
| $\mu$(Mo$K\alpha$), cm$^{-1}$ | 184.5 |
| Trans. factor range | 0.776–1.17 |
| Number of variables | 45 |
| Sec. extinct. param ($10^{-9}$) | 4.2 (9) |
| $R_{ave}$, % | 12.6[b] |
| $R$, %[c] | 3.5 |
| $R_w$, %[d] | 4.4 |
| Goodness-of-fit indicator[e] | 1.10 |
| Largest shift/esd, final cycle | <0.00 |
| Largest ΔF peak, e/Å$^3$ | 2.39 (0.53 Å from I3) |

[a] From Guinier powder data refinement with Si as an internal standard, λ = 1.540562 Å.

[b] All data.

[c] $R = \Sigma \| |F_o| - |F_c| \| / \Sigma |F_o|$.

[d] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(F_o)^2]^{1/2}$; $w = [\sigma(F)]^{-2}$.

[e] $S = \Sigma ((|F_o| - |F_c|)/\sigma_i)/(N_{obs} - N_{para})$.

amount of CsI. Attempts to prepare the less reduced, 15-electron $Cs_2Zr_6I_{18}B$ gave the 14-electron $CsZr_6I_{14}B$ (*6*) instead, plus $Cs_2ZrI_6$.

The well-formed crystals first encountered (above) were strongly diffracting. One was readily indexed as rhombohedral by the Rigaku diffractometer programs, the triclinic cell parameters falling within 1$\sigma$ of the expected constrained (hexagonal) values. The Laue symmetry was indicated to be $R\bar{3}$. Diffraction data were collected at room temperature over one hemisphere with a 2$\theta$ limit of 65° (see Table I). The symmetry and dimensions suggested the phase might be analogous to $K_2Zr_7Cl_{18}H$ (*3*), and the corresponding $Cs_2Zr_7I_{18}$ model refined without incident when absorption was corrected with the aid of five psi scans ($\mu$ = 184 cm$^{-1}$). The rhodium present in the first reaction had far too much electron density to be refined at the cluster center, but the density observed in a Fourier map relative to Cs, I, and Zr scaled well for carbon ($Z_{calc}$ = 5.58, 6.05, and 5.56, respectively). Furthermore, the distance from zirconium to the cluster center, 2.29 Å, agreed well with that in iodide cluster carbides already known (*1*) as well as in four chloride cluster analogues (*7*). (This supposition of a carbon interstitial was later confirmed by the synthesis of the same phase in high yields, above.) Refinement with this composition converged well. A cesium occupancy refinement of 0.969(4) was reset to unity in the final refinement. Even the carbon thermal ellipsoid could be varied once the absorption correction had been improved with the aid of DIFABS (*8*); $R(F)$, $R_w$ = 3.5, 4.4%, or 4.3, 5.0% with all data ($F_o \geq 0$). Positional, distance, and angle data are given in Tables II and III; anisotropic displacement parameters and $F_o/F_c$ data are available from J.D.C.

## Results and Discussion

The structure of $Cs_2Zr_7I_{18}C$ or, more definitively, $Cs_2ZrI_6 \cdot Zr_6(C)I_{12}$ consists of

TABLE II

POSITIONAL PARAMETERS AND $B_{eq}$ FOR $Cs_2Zr_7I_{18}C$[a]

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Cs | 0 | 0 | 0.22324(3) | 2.18(2) |
| I1 | 0.23671(4) | 0.18586(4) | 0.11134(1) | 0.66(1) |
| I2 | 0.42268(3) | 0.13597(4) | 0.00026(1) | 0.66(1) |
| I3 | 0.09375(4) | 0.46359(4) | 0.10938(1) | 0.94(1) |
| Zr1 | 0.04171(5) | 0.19214(5) | 0.04485(1) | 0.23(1) |
| Zr2 | 0 | 0 | $\frac{1}{2}$ | 0.34(2) |
| C | 0 | 0 | 0 | 0.6(3) |

[a] Space group $R\bar{3}$.

TABLE III

IMPORTANT ATOMIC DISTANCES (Å) AND ANGLES (°) IN $Cs_2Zr_7I_{18}C$

| | | | |
|---|---|---|---|
| | Distances | | |
| Zr1–C | 2.2922(8) | I3–Zr2 | 2.928(1) |
| Zr1–Zr1 | 3.234(1) | I3–Zr1 | 3.278(1) |
| Zr1–Zr1 | 3.249(2)[a] | Cs–I1 (×3) | 4.019(1) |
| I1–Zr1 | 2.885(1) | Cs–I1 (×3) | 4.056(2)[a] |
| I1–Zr1 | 2.892(1) | Cs–I2 (×3) | 4.023(1) |
| I2–Zr1 | 2.875(1) | Cs–I3 (×3) | 4.063(2)[a] |
| I2–Zr1 | 2.881(1) | | |
| | Angles | | |
| Zr1–Zr1–Zr1 | 60.30(3) | Zr1–C–Zr1 | 89.74(3) |
| Zr1–Zr1–Zr1 | 59.85(2) | Zr1–C–Zr1 | 89.71(1) |
| Zr1–Zr1–Zr1 | 60.00[a] | Zr1–C–Zr1 | 180.00 |

[a] Normal to **c**.

rhombohedrally ordered carbon-centered $Zr_6(C)I_{12}$ clusters, a unit that is already known as the ternary compound $Zr_6I_{12}C$ (*1*). The strongly bonding exo positions at each zirconium vertex in the present structure are filled, and the clusters are interconnected, by iodine in formal $ZrI_6^{2-}$ units that are each bonded to six different clusters. A [110] section is shown in Fig. 1. The I3 atoms that bridge in this role are distinctly closer to the isolated Zr(2) atoms, 2.928(1) Å, than to the Zr(1) vertices in the cluster, 3.278(1) Å, thereby supporting the (somewhat arbitrary) assignment of $Zr_6(C)I_{12}$ and $ZrI_6^{2-}$ units. As in $K_2Zr_7Cl_{18}H$ (*3*), the structure can also be described in terms of close-packed iodine layers. Two-thirds of these have one-seventh of the atoms substituted by cesium and the other one-third of the layers, by the carbon at the cluster center, the I2 atoms in the latter lying about the waist of the ($\bar{3}$) clusters. Zirconium(1) atoms in neighboring octahedral interstices cluster about the carbon member to generate the formal clusters, while the isolated zirconium(2) is bound between pairs of the cesium-substituted layers. The cesium atoms are located at the ends of the cluster antiprisms (Fig. 1). The R-centering gives a $(chh)_3$ ordering in which the *c* iodine layers also contain carbon.

Dimensionally, the $Zr_6I_{12}C$ cluster is very much like examples seen before. The Zr–C distance, 2.292(1) Å, is slightly longer than in $Zr_6I_{12}C$ itself, 2.259(1) Å, and the average Zr–Zr distance in the cluster is correspondingly 0.046 Å longer. The 0.125 Å closer approach of the two-coordinate and more basic exo iodine atoms to the zirconium vertices in the present cluster must be responsible for both of these differences; in $Zr_6I_{12}C$, the exo iodine is three-coordinate and an inner member of a neighboring like cluster. Cluster metal–interstitial distances (and the geometrically related metal–metal values) are well known to vary inversely with the distance and character of the *trans*

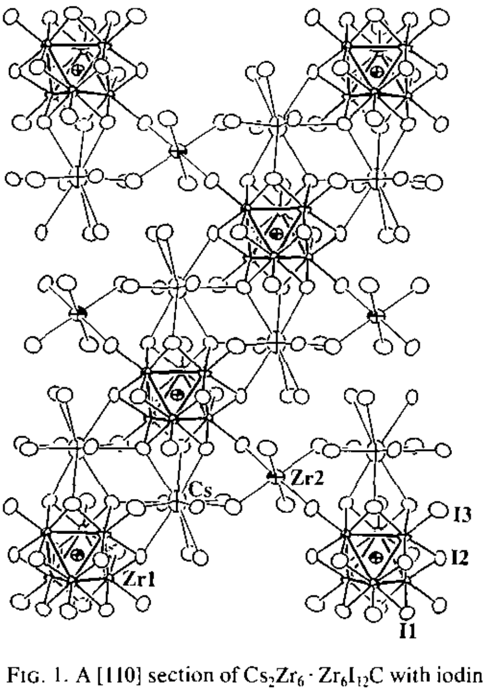

FIG. 1. A [110] section of $Cs_2Zr_6 \cdot Zr_6I_{12}C$ with iodine as open, cluster zirconium(1) and cesium as small and large crossed ellipsoids, respectively, and carbon and zirconium(2) as shaded ellipsoids. The cesium and carbon are members of close-packed layers while both zirconium(1) (in the clusters) and zirconium(2) (in nominal $ZrI_6^{2-}$ groups) lie between the layers.

exo atoms; these and the interstitial atoms are in effect competing for the same zirconium orbitals (*7, 9*).

Examples of the $K_2ZrCl_6 \cdot Zr_6Cl_{12}H$ (or $K_2Zr_7Cl_{18}H$) structure type have previously been limited to that phase, the sodium and cesium analogues (*3*), and the corresponding beryllide $K_2Zr_7Cl_{18}Be$ (*4*). A large family of $M_2M'Zr_6Cl_{18}Z$ derivatives have now been established wherein other metal atoms $M'$ substitute at the center of the $ZrCl_6^{2-}$ trigonal antiprism (*10*), and a superstructure variation is found for $Ba_2(Ba)Zr_6Cl_{18}Be$ (*11*). On the other hand, a chloride carbide version of $M_2Zr_7I_{18}C$ is not found with either potassium or cesium cations, rather only less reduced phases like $CsZr_6Cl_{15}C$ and $Cs_3Zr_6Cl_{16}C$ (*12*). This changes when the larger iodide is used, affording the present $Cs_2Zr_7I_{18}C$ with its 16-electron cluster, but it must be noted that the identities of most of the competing phases change as well. There is no iodide analogue of either of the two cesium chloride carbides just cited and no chloride equivalent of $Zr_6I_{12}C$ or $CsZr_6I_{14}C$ (*1, 4, 6*).

It is important to note that neither the unusual $Zr_6I_{12}C$ structure nor the $Zr_6I_{14}C$ composition is stable when CsI is available. In other words, both react with CsI (or $Cs_2Zr_6I_{18}C$) to form $CsZr_6I_{14}C$ or $Cs_2Zr_7I_{18}C$ (plus minor products), depending on proportions (see the Experimental Section). The presence of excess zirconium does not appear to influence the equilibrium products either, even though $CsZr_6I_{14}C$ is less reduced than the other phases.

The new compound $Cs_2Zr_7I_{18}C$ represents another potential product that may form from fission product iodine within PWR fuel rods, which are constructed from a zirconium-rich Zircaloy. This chemistry is particularly important because iodine seems to be clearly responsible for stress-corrosion-cracking of the cladding under certain circumstances. Cesium is also a potential component if this more abundant fission product is sufficiently mobile and not tied up as cesium zirconates, uranates, fission product molybdates, etc. Finally, the essential role of carbon (or other) interstitial atoms in producing these particularly stable (and thus less damaging) cluster iodides also seems plausible (*5*). Graphite has been regularly added to the fuel pellets in some reactor systems where it has been supposed to function as a lubricant in reducing stress-corrosion-cracking by iodine through "pellet-cladding interactions" (*13*). An alternative chemical explanation of the effect in terms of these cluster iodide carbides appears reasonable (*5*), and there is some evidence that these compounds form under such conditions (*14*).

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