well expect the overlap integrals to be in a ratio close to 2.

To conclude, we will point out that the design of the alternating bimetallic chain described in this paper represents a significant step in the field of the low-dimensional magnetism. We are looking for novel systems in which the spin order would be even more subtle.

Registry No. $MnCu(obp)(H_2O)_3{\cdot}H_2O$, 111436-56-7; diethyl oxalate, 95-92-1; β-alanine, 107-95-9.

Supplementary Material Available: Table SI, listing the anisotropic thermal parameters (1 page); a table of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

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Zirconium Iodide Clusters That Encapsulate Silicon, Germanium, Phosphorus, or Pyrex

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The phases $Zr_6I_{14}Z$ (Z = Si, Ge, P) as well as $M_xZr_6I_{14}P$ (M = Cs, Rb) have been synthesized by reaction of stoichiometric amounts of ZrI_4, Z (as the element), M^I when appropriate, and excess Zr in sealed Ta containers at 700–850 °C. Experiments with a longer list of main-group elements from the third and fourth periods as the potential interstitial Z gave only negative results as far as the formation of either the corresponding ternary or quaternary phase. The structure of $Cs_{0.35(1)}Zr_6I_{14}P$ was established by single-crystal X-ray diffraction (space group *Cmca*, Nb_6Cl_{14} type; $a = 15.934$ (1), $b = 14.287$ (1), $c = 12.939$ (1) Å; $R = 0.050$, $R_w = 0.064$ for 1428 reflections with $2\theta \le 55°$). Distortions and bonding within the cluster are described. Some of the problems associated with adventitious impurities and mixed interstitials are also considered. The silicon and boron from a few percent of Pyrex glass impurity produce a moderate yield of well-crystallized $Cs_{0.54}Zr_6I_{14}(B,Si)$ (plus ZrO_2); the structural refinement and the dimensions of the cluster indicate about a 50:50 mixture of the two elements is encapsulated.

Introduction

An unprecedented variety of metal cluster halide phases of the early transition metals has recently been obtained through the bonding of an additional heteroelement in the center of the metal octahedra. Although the first examples[1] of these interstitially stabilized clusters arose via adventitious impurities, namely as what are now known to be $Zr_6Cl_{15}N$, $Sc_7Cl_{12}C$, and $Zr_6I_{12}C$,[2-4] our explorations demonstrate that a considerable number of other interstitial atoms may also be encapsulated. Variations of not only the interstitial element (*Z*) but also the oxidation state of the M_6X_{12}-type clusters through the addition of halide at terminal positions, countercations to the cluster framework, or both allow the preparation of a wide range of structural types and compositions.[5]

Although the greatest variety of structures presently known, eight all told, involve $Zr_6Cl_{12}Z$-type clusters in which chlorine bridges edges of the octahedron, these have been largely limited to examples containing interstitial Z = H, Be, B, C, or N.[2,5,6] On the other hand, the analogous zirconium iodide clusters appear to allow the inclusion of a greater range of interstitial elements, but to date only the $Zr_6I_{12}Z$ or $Zr_6I_{14}Z$ compositions and structures plus the alkali-metal derivatives of the second have been identified. In these cases, Z may be not only K, Al, or Si[7,8] but also Cr, Mn, Fe, or Co as in recently discovered examples.[9,10] Zirconium chloride and bromide clusters containing iron are now also known.[11]

Table I. Data Collection and Refinement Parameters for $Cs_{0.35}Zr_6I_{14}P$

space group	*Cmca*
Z	4
cryst dimens, mm	0.20 × 0.15 × 0.15
2θ(max), deg; octants	55; *hkl*, $\bar{h}\bar{k}l$
no of reflcns: measd, obsd,[a] indep	3850, 2692, 1428
R(av), %	2.8
abs coeff μ, cm^{-1} (Mo Kα)	180
range of transm coeff (normalized)	0.62–1.0
sec ext coeff (10^{-7})	0.6 (1)
R,[b] %	5.0
R_w,[c] %	6.4

[a] $F_o \ge 3\sigma_F$ and $I_o > 3\sigma_I$. [b] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Exploration of the range of main-group elements that may be so encapsulated in the iodides has now been extended to other third- and fourth-period elements. This paper reports on the formation of several cluster phases containing germanium or phosphorus and on a new silicon composition as well as on a longer list of main-group elements for which incorporation in a zirconium iodide cluster has not been successful. The considerable driving force associated with the formation of this type of compounds is also revealed by the preparation of a mixed silicon–boron example when Pyrex glass is the source of the interstitial elements.

Experimental Section

Syntheses. The purity, preparation, and handling of reactor grade Zr and ZrI_4 have been described.[12] Reagent grade CsI, RbI, and KI were vacuum sublimed prior to use. Red P (J. T. Baker) and zone-refined Si and Ge were employed as interstitial sources. All reactions were run in sealed Ta tubes with the aid of techniques described previously.[13] Stoichiometric amounts of ZrI_4, elemental Z, and, where appropriate, CsI, RbI, or KI were generally utilized together with about a 12-fold

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(1) Corbett, J. D.; Daake, R. L.; Poeppelmeier, K. R.; Guthrie, D. H. *J. Am. Chem. Soc.* **1978**, *100*, 652.
(2) Ziebarth, R. P.; Corbett, J. D. *J. Less-Common Met.*, in press.
(3) Hwu, S.-J.; Corbett, J. D. *J. Solid State Chem.* **1986**, *64*, 331.
(4) Smith, J. D.; Corbett, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5704.
(5) Ziebarth, R. P.; Corbett, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 4571.
(6) Ziebarth, R. P.; Corbett, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 4844.
(7) Smith, J. D.; Corbett, J. D. *J. Am. Chem. Soc.* **1984**, *106*, 4618.
(8) Smith, J. D.; Corbett, J. D. *J. Am. Chem. Soc.* **1986**, *108*, 1927.
(9) Hughbanks, T.; Rosenthal, G.; Corbett, J. D. *J. Am. Chem. Soc.* **1986**, *108*, 8289.
(10) Hughbanks, T.; Rosenthal, G.; Corbett, J. D. *J. Am. Chem. Soc.*, in press.
(11) Zhang, J.; Ziebarth, R. P.; Hughbanks, T.; Corbett, J. D., unpublished research.
(12) Guthrie, D. H.; Corbett, J. D. *J. Solid State Chem.* **1981**, *37*, 256.
(13) Hwu, S.-J.; Corbett, J. D.; Poeppelmeier, K. R. *J. Solid State Chem.* **1985**, *57*, 43.

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Table II. Lattice Constants (Å) and Cell Volumes ($Å^3$) for New Cluster Phases[a]

compd[b]	*a*	*b*	*c*	*V*
$Zr_6I_{14}Si$	15.939 (4)	14.254 (6)	12.953 (3)	2943 (2)
$Zr_6I_{14}Ge$	16.028 (5)	14.277 (4)	12.982 (3)	2970 (2)
$Zr_6I_{14}P$	15.916 (2)	14.275 (2)	12.902 (2)	2931 (1)
$Cs_{0.35}Zr_6I_{14}P$	15.934 (1)	14.287 (1)	12.939 (1)	2946 (1)
$Cs_xZr_6I_{14}P$[c]	15.963 (1)	14.277 (1)	12.980 (1)	2958 (1)
$Rb_xZr_6I_{14}P$[d]	15.928 (4)	14.278 (2)	12.941 (2)	2943 (2)
$Cs_{0.54}Zr_6I_{14}$("Pyrex")	15.923 (2)	14.284 (2)	12.970 (2)	2950 (1)

[a] Dimensions and their standard deviations are deduced from Guinier powder data; λ = 1.54056 Å. [b] Zr_6I_{14} types are isostructural with Nb_6Cl_{14}, space group *Cmca*.[14] [c] The same as the previously listed phase except that excess CsI was used in the synthesis; $x > 0.35$. [d] Loaded for $x = 1$.

excess of metal as strips ca. 0.5 × 2 × 25 mm. Containers were loaded and later opened in a drybox. Temperatures from 700 to 850 °C were found to be effective with reaction times of 2–4 weeks.

Yields were estimated from careful analysis of X-ray powder patterns and by microscopic inspection. Except for $Cs_xZr_6I_{14}P$, which was studied by single-crystal means, product identity was established first by semiquantitative comparisons of the positions and intensities in the powder patterns with those in known or calculated patterns and, second, on the basis of refined unit cell parameters and volumes. X-ray powder diffraction film data were collected with a focusing Guinier camera (Enraf-Nonius) equipped with a quartz monochromator that gave clean Cu $K\alpha_1$ radiation. Powdered silicon (NBS, SRM-640) was included in samples as an internal standard, the positions of the five observed lines being fit to known diffraction angles by a quadratic function. Lattice constants were determined by standard least-squares refinements of sample data indexed on basis of known structures.

Single-Crystal Diffraction. The best crystallized of all of the new products was $Cs_{0.35}Zr_6I_{14}P$, which occurred as large, well-faceted, black crystals. The cesium content was established and the location of the phosphorus confirmed by single-crystal means. Single-crystal data were collected at room temperature on a DATEX diffractometer with monochromatized Mo Kα radiation (λ = 0.71069 Å) and variable scan speeds of 1.5–29.3° min^{-1}. Data collection and refinement parameters are given in Table I. Empirical absorption corrections were carried out by using full-circle ϕ-scan data at two values of 2θ. Programs used in the structure refinement have been referenced previously.[13] Atomic scattering factors included corrections for contributions to anomalous dispersion.

Initial positions for the heavy atoms were taken from data obtained earlier for the silicide,[8] which in turn is isostructural with Nb_6Cl_{14}[14] except for the cesium and the cluster-centered interstitial. A residual *R* of 11% was obtained after six cycles of refinement ($w = 1/\sigma_F^2$), isotropic thermal parameters for all atoms also being varied in the last few cycles. Conversion to anisotropic parameters, variation of the cesium occupancy (=0.350 (7)), and reassignment of group weights for 30 overlapping groups of the data set sorted on F_o in order to remove systematic variations in $[w(|F_o| - |F_c|)^2]$ for the weaker reflections in these[14] quickly yielded convergence at $R = 0.050$, $R_w = 0.064$. The final difference map contained no residuals above 0.7 e $Å^{-3}$.

Results and Discussion

New Phases. Table II lists the new compounds synthesized together with their Guinier lattice constants. These and their cluster-based electron counts in parentheses are $Zr_6I_{14}Si$ (14), $Zr_6I_{14}Ge$ (14), $Zr_6I_{14}P$ (15), $Cs_{0.35}Zr_6I_{14}P$ (15.35), and $Rb_xZr_6I_{14}P$ (15 + *x*). The $Cs_xZr_6I_{14}P$ product listed with the larger cell was obtained when excess CsI was employed in the synthesis and presumably represents the upper limit for the cesium content. The situation with the Pyrex-derived product will be presented later following a description of impurity-based results and problems. All of these phases occur in the frequently encountered[4,5,7-10] Nb_6Cl_{14}-type structure[15] with the inclusion of the indicated Si, Ge, or P in the center of all clusters plus, in some cases, a second interstitial Cs or Rb in a halide environment between the clusters. As shown in Figure 1, this particular structural framework contains four halogen atoms X^{a-a} (I3) that only bridge between metal vertices in different clusters, while two of what would be inner halides in the $M_6X^i_{12}$ unit (I4) complete bonding to metal vertices in other clusters, viz., $M_6X_{14} = M_6X^i_{10}X^{i-a}_{2/2}X^{a-i}_{2/2}X^{a-a}_{4/2}$.

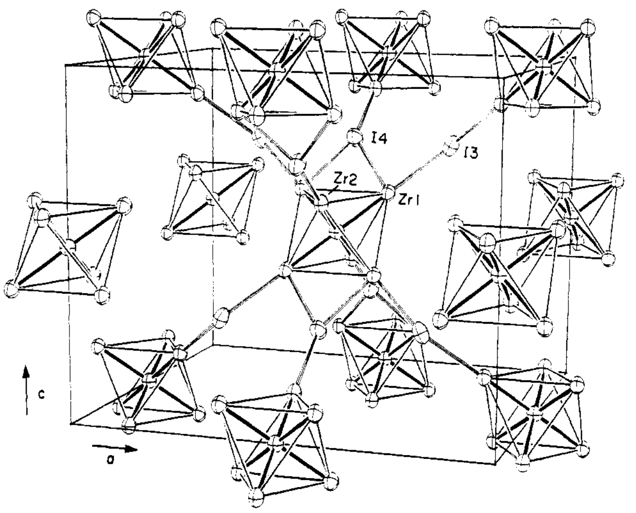

Figure 1. Cluster orientations and intercluster bonding in $Cs_{0.35}Zr_6I_{14}P$. The latter involves I3 as I^{a-a} and I4 as I^{i-a}. (The cesium and inner iodine atoms have been omitted for clarity.)

Although one can never be sure that negative synthetic results mean instability rather than just the use of inappropriate conditions, a considerable list of main-group elements did not form cluster or other new phases when comparable reactions were carried out in the neighborhood of 700–800 °C. Quaternary $Cs_xZr_6I_{14}Z$ compounds were not obtained for Z = Mg, Ca, Cu, Zn, Ga, In, Sn, As, S, or Se (as the elements), rather only the usual ZrI_2 and ZrI_3 products that are formed when a workable Z element is not present. The absence of products with the $Zr_6I_{14}Z$ or $Zr_6I_{12}Z$ structures from these reactions presumably rules out all of the corresponding ternary possibilities as well, *except* that $Zr_6I_{14}Ge$ was found to be stable. Ternary reactions were also explicitly examined for Z = Mg, Ga, Ge, As, and Se, but all except that with germanium gave generally negative results. The results with arsenic were a little equivocal, however.

Sulfur apparently cannot be bound, and interestingly, an attempt to make $K_xZr_6I_{14}S$ led instead to the smaller $Zr_6I_{14}K_{0.5}$[7] ($x \sim 0.5$, $V = 2929$ $Å^3$), showing that even potassium is better than nothing. One competitive experiment, resulting from an attempt to make $KZr_6I_{14}Ge$ at 850 °C, also led to the same potassium compound rather than to germanium incorporation. (Note that $Cs_xZr_6I_{14}Ge$ could not be obtained either.) The germanium-centered cluster $Zr_6I_{14}Ge$ may be of marginal stability; it represents the largest $Zr_6I_{14}Z$-type cell achieved to date with a main-group element (but the result is still smaller than with iron[9,10]). The volume of $Cs_{0.30}Zr_6I_{14}Si$[8] is comparable to that of $Zr_6I_{14}Ge$, but the former includes an expansion of ~23 $Å^3$ from that for $Zr_6I_{14}Si$ owing to the inclusion of the cesium.

A caveat is necessary regarding the foregoing negative results because of the mechanism by which these phases must form. The quantitative conversions that can be achieved at temperatures in the range 650–900 °C when both zirconium metal and many quite nonvolatile interstitial elements are involved (e.g., B, C, Si, or Fe) suggest a fairly efficient vapor-phase transport process must occur. Zirconium metal can be transported as ZrI_3, and we presume gaseous halides of the interstitial elements must also be involved. With carbon we have shown that hydrocarbons work well in the range 450–600 °C whereas graphite alone (presumably via a halide) serves only at 650 °C and above.[16] However, higher yields of the iodide clusters containing transition metals M have been obtained when the more volatile MI_2 was added rather than just the metal. This circumstance may also apply with some of the Z element reactions above for which the syntheses were unsuccessful. In addition, the formation of binary compounds between

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(14) Jacobson, R. A. "OMEGA" (unpublished program), Ames Laboratory, 1980.

(15) Simon, A.; von Schnering, H.-G.; Wöhrle, H.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1965**, *339*, 155.

(16) Chen, T.-M.; Kauzlarich, S. M.; Corbett, J. D. *J. Nucl. Mater.*, in press.

Table III. Positional Parameters for $Cs_{0.35}Zr_6I_{14}P^a$

	x	y	z
Zr1	0.38880 (7)	0.06714 (8)	0.88639 (8)
Zr2	0	0.3586 (1)	0.8954 (1)
I1	0.12561 (5)	0.08979 (5)	0.24726 (6)
I2	0.12570 (4)	0.25535 (6)	0.00694 (6)
I3	0.25	0.34587 (8)	0.25
I4	0	0.15748 (8)	0.76628 (9)
I5	0.24639 (7)	0	0
Cs^b	0	0	0
P	0.5	0.5	0.5

[a] Space group *Cmca*. [b] Occupancy 0.350 (7).

Table IV. Principal Distances (Å) in $Cs_{0.35}Zr_6I_{14}P$

Zr–Zr Intralayer[a]			
Zr1–Zr1 (×2)	3.544 (2)	Zr1–Zr2 (×4)	3.468 (2)
Zr–Zr Interlayer			
Zr1–Zr1 (×2)	3.510 (2)	av	3.498
Zr1–Zr2 (×4)	3.498 (2)		
Zirconium–Interstitial			
Zr1–P (×4)	2.494 (1)	av	2.473
Zr2–P (×2)	2.432 (2)		
Zirconium–Iodine			
$Zr–I^i$ (av)	2.879	$Zr2–I4^{a-i}$ (×2)	3.324 (2)
$Zr1–I4^{i-a}$ (×2)	2.951 (1)	$Zr1–I3^{a-a}$ (×4)	3.090 (1)
Cesium–Iodine			
Cs–I1 (×4)	3.986 (1)	Cs–I5 (×2)	3.926 (1)
Cs–I2 (×4)	4.163 (1)	av	3.999
Cs–I4 (×2)	3.769 (1)		

[a] Referred to the approximately close packed iodine layers that run from upper left to lower right in Figure 2.

zirconium and the potential interstitial may provide an alternate sink for the latter. However, the temperatures utilized in many of the successful reactions suggest that equilibrium is attained and that these Zr–Z sinks are in most cases kinetic rather than thermodynamic diversions.

Structural Results. The positional parameters determined from a single crystal of $Cs_{0.35}Zr_6I_{14}P$ are given in Table III, and some important distances calculated therefrom are in Table IV. Thermal parameter and structure factor data are available as supplementary material. Figure 1 shows the arrangement of metal clusters within the cell together with the intercluster iodine bridging mode, and an isolated cluster with all halides is shown in Figure 2 in a depiction that emphasizes the strong Zr–P bonds.

Comparison of our results for $Cs_{0.35}Zr_6I_{14}P$ with the results obtained earlier for $Cs_{0.30}Zr_6I_{14}Si$ is reasonable since the cesium contents are so similar. The Zr–Z distances are found to decrease from 2.53 to 2.47 Å on going from silicon to phosphorus, a logical trend although this must also include the effect of the addition of one more electron to the slightly antibonding a_{2u} cluster orbital.[4,8] Nonetheless, the last effect must be small since the rate of decrease in average Zr–Z distances here parallels very closely that observed between the boron and carbon analogues[8] where the added electron is slightly bonding. The use of the 0.86-Å crystal radius of six-coordinate zirconium(IV)[17] as an arbitrary size for the metal gives a 1.61-Å "radius" for phosphorus in the cluster. This is 0.15 Å less than similarly deduced in α-ZrP (NaCl type),[18] a common difference for these clusters relative to analogous Zr–Z binary compounds.

As has been discussed before,[4] the pseudotetragonal compression of the metal cluster found in all M_6X_{14}-type phases goes hand-in-hand with the unsymmetric character of the halogen bridging that occurs between the metal vertices in different clusters (Figure 1). In the present case, four cluster vertices of the $Zr_6I^i{}_{12}$ core are bridged to other clusters via two-coordinate I^{a-a} atoms at distances of 3.09 Å (Table IV), while the other two are bonded at notably longer distances, 3.32 Å, by less basic inner (I4′) iodines in other clusters (I^{a-i}). The evidently weaker bonding to the latter produces stronger Zr–Zr (and Zr–Z) bonding at these two vertices of the cluster and hence the observed tetragonal compression at Zr2 (Figure 1). In the case of the silicon-to-phosphorus conversion, a 0.07-Å *increase* in the longer $d(Zr–I^{a-i})$ is accompanied by a like contraction of the shorter, opposed Zr–Z bond, that part of the metal cluster in effect "breathing" within a fairly fixed iodine matrix determined by I–I contacts (matrix effect). The changes in the shorter and stronger $d(Zr–I^{a-a})$ are parallel but smaller, 0.02 Å for silicon–phosphorus.

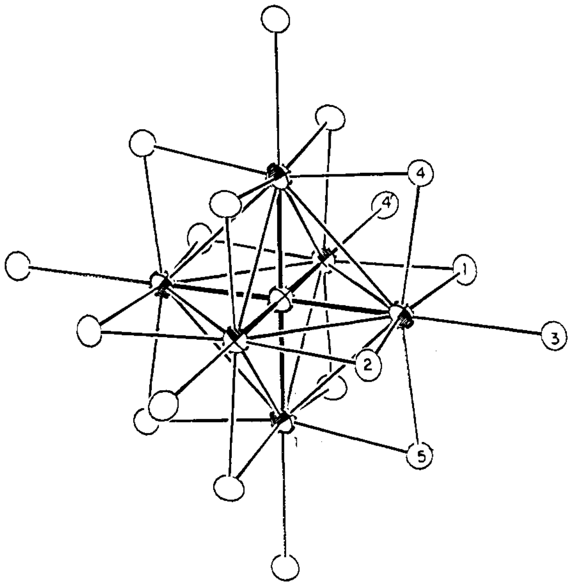

Figure 2. $Zr_6I_{12}P$ cluster unit together with the intercluster bridging atoms in $Cs_{0.35}Zr_6I_{14}P$. The centrosymmetric cluster exhibits C_{2h} symmetry with I4, I4′, P, and Zr2 in a mirror plane normal to the page and I5 and P on the twofold axis.

Cluster Stability. Zirconium clusters containing nitrogen are known with chlorine but not with iodine, and we have previously[8] speculated that this might result from the larger matrix effect with iodine, the nitrogen atom simply being too small to allow simultaneously good Zr–N and Zr–I bonding. The preparation of the iodide phosphide is in accord with this idea; the corresponding chloride phosphide has not (yet) been obtained, but neither has any other chloride involving a main-group element beyond the second period.

The MO description of these cluster systems[3,4,8] suggests the greatest stability is associated with 14 cluster-based electrons and a $t_{2g}{}^6$ HOMO, and this is in accord with observation. Only one iodide appears to fall short of this count, $Cs_{0.7}Zr_6I_{14}Al$ with 13.7.[8] Several chlorides, but still a small proportion, are known with 13, including the hydride,[19] but a larger variety of structures and countercation proportions have been investigated in this series.[2,5,6] Addition of one or even two more electrons to a metal–metal-bonding, metal–iodine-antibonding a_{2u} level does not seem to be precluded, other examples including $CsZr_6I_{14}C$ (15) and $Zr_6I_{12}C$ (16).[4] Of course, factors other than electron count enter into cluster stability and phase stability in general. The magnitude of the H_{ii} (valence state orbital) energies for the interstitial relative to those of zirconium 4d orbitals in the cluster is an obvious one. The relatively high and perhaps limiting value of H_{ii} for the aluminum p orbitals has been used to explain the unusually small cluster found in that case.[8] However, the magnitude of the valence-state energies alone will not account for the absence of clusters centered by Ga, In, Sn, As, Se, and others. The strength of the Zr–Z bonds formed is also reflected in overlap, and the loss of Zr–Zr and Zr–I bonding in the cluster during an expansion

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(17) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*

(18) Irani, K. S.; Gingerich, K. A. *J. Phys. Chem. Solids* **1963**, *24*, 1153.

(19) Chu, P. J.; Ziebarth, R. P.; Corbett, J. D.; Gerstein, B. C., submitted for publication in *J. Am. Chem. Soc.*

necessary to accommodate larger interstitials is obviously significant. Even so, considerations or correlations like the above are made in isolation as they ignore alternate phases that the interstitials may form during the attempted syntheses. These are usually not known at the small concentration levels involved.

Impurity Problems. The means and the problems associated with establishing the existence of new phases of this kind from synthesis results require further comment. Experience with zirconium as well as other halide cluster systems[4,13,20,21] has repeatedly demonstrated that the most reliable synthetic criteria for the occurrence of a known new phase are its preparation in high yield and in a reproducible manner. These conditions are particularly important because of the uncommon degree to which relatively small amounts of adventitious interstitial atoms can also produce significant amounts of similar cluster phases, generally of the $Zr_6I_{12}Z$, $Zr_6I_{14}Z$, or $M^I_xZr_6I_{14}Z$ types. Carbon seems to be the most pervasive and, when first unrecognized, led to the first identification of these structure types for the zirconium iodides,[22] although wide and unexplained variations in the cell volumes obtained for some of the earlier materials were later recognized as evidence for other, probably mixed, interstitial impurities.

In the absence of a suitable interstitial element, a $Zr-ZrI_4$ reaction will produce only the layered ZrI_2 (and, often, the less reduced ZrI_3), plus $Cs_3Zr_2I_9$ (and perhaps Cs_2ZrI_6), as well in the presence of CsI. However, large excesses of metal surface, i.e., molar $Zr:ZrI_4$ ratios of $\sim$(50–250):1 appear necessary to get complete reduction of ZrI_3 to ZrI_2 under typical reaction conditions,[16] and so ZrI_3 may also appear when insufficient metal reductant is present.

Under the above circumstances, a low yield of one of the common cluster structure types cannot be taken as evidence that a reaction carried out in the presence of a prospective interstitial element has been successful. Of course, cell volumes deduced from such an unexpected impurity product may also be inappropriate, and these are also characteristically highly variable when impurities are responsible. Variation in cell sizes may also result when the amount of a countercation is also substoichiometric and variable, as seen for $Cs_xZr_6I_{14}P$ in Table II and earlier for the cesium silicide[8] and the potassium carbide[4] analogues. Since the lattice dimensions of the Zr_6I_{14} cell change at very different and not highly predictable rates with the alteration of cation or interstitial size, the individual dimensions seem to be less useful criteria than volumes.

Our attempts to prepare $Cs_xZr_6I_{14}S$ derivatives were particularly vexing along these lines in that small or even moderate (30%) yields of a Zr_6I_{14}-type cluster phase were often (but not always) encountered as a microcrystalline powder when cesium iodide was present. The lattice dimensions were quite variable. The persistence of these products was greater than in any other group of unsuccessful experiments. We were left with the unsatisfying conclusion that problems associated with mixed and partly adventitious interstitials may have been particularly important here, the electronic-rich character of sulfur at some sites possibly being compensated by electron-poorer contaminants (C, Si, B, Al?) in other clusters. Mixed clusters represent both a specter and an opportunity, one for which analysis presents particular problems.

Finally, it appears that just such a mixed interstitial result can be generated solely from the boron and silicon components of Pyrex glass. One attempt to make a cluster containing interstitial indium produced a 40–50% yield of excellent crystals. A quite comparable X-ray diffraction analysis proceeded to a very satisfactory result,[23] but the scattering by the interstitial and the size of the cavity were both too small for indium. The peak height at the cluster center in Fourier and difference Fourier maps indicated an atomic number of about 10. Linear interpolation of cavity size between the known dimensions in $Cs_{0.3}Zr_6I_{14}Si$ and $CsZr_6I_{14}B$[8] using the four most rapidly changing distances ($Zr-Zr$, $Zr-Z$, $Zr-I^{a-i}$, $Zr-I^{a-a}$) yielded a boron content of $\sim$47% ($Z \simeq 9.2$). Not surprising, the synthetic result could not be duplicated with only added indium.

Our confidence in a Pyrex impurity hypothesis was boosted by the subsequent preparation of a material with a visually *identical* Guinier powder pattern in $\sim$40% yield by the purposeful inclusion of only powdered Pyrex in an otherwise clean $CsI-Zr-ZrI_4$ reaction. The other products were just ZrI_4, Cs_2ZrI_6, and a trace of ZrI_3. Our choice of contaminant was based on the fact that the ZrI_4 reactant is stored in evacuated and sealed glass ampules when not in use in loading reactions in the drybox, and small chips of glass are sometimes discovered in the orange-red iodide after the container has been broken open. In the particular test reaction described, the added Pyrex was 3 wt % of the ZrI_4 while the amount of powdered metal used made it the limiting reactant with respect to just encapsulation of the added silicon and boron, that is, neglecting the fate of the oxygen from the glass. Oxygen alone does not give an interstitial phase but readily forms ZrO_2 or, in lesser amounts, dissolves in zirconium metal. Metathetical reactions of ZrI_4 with SiO_2 or B_2O_3 to form ZrO_2 and SiI_4 or BI_x are reasonable means for transport of these interstitials, and that with silica has been demonstrated.[16]

The estimate of about a 50:50 mixture of interstitial silicon and boron in this product is somewhat of a simplification, as it does not allow for the smaller amount of aluminum also available or for the fact that oxygen may cosubstitute in smaller amounts with other interstitials. A quantitative analysis of individual crystals would be necessary to be more definitive in such a complex system.

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Registry No. $Zr_6I_{14}Si$, 111793-40-9; $Zr_6I_{14}Ge$, 111793-37-4; $Zr_6I_{14}P$, 111793-38-5; $Cs_{0.35}Zr_6I_{14}P$, 111717-69-2; $RbZr_6I_{14}P$, 111793-39-6; $Cs_{0.54}Zr_6I_{14}(B,Si)$, 111717-68-1; ZrI_4, 13986-26-0; CsI, 7789-17-5; RbI, 7790-29-6; KI, 7681-11-0; Zr, 7440-67-7; Si, 7440-21-3; Ge, 7440-56-4; P, 7723-14-0; Mg, 7439-95-4; Ca, 7440-70-2; Cu, 7440-50-8; Zn, 7440-66-6; Ga, 7440-55-3; In, 7440-74-6; Sn, 7440-31-5; As, 7440-38-2; S, 7704-34-9; Se, 7782-49-2.

Supplementary Material Available: A table of anisotropic thermal parameters (1 page); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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(20) Ford, J. E.; Corbett, J. D. *Inorg. Chem.* **1985**, *24*, 4120.

(21) Hwu, S.-J.; Dudis, D. S.; Corbett, J. D. *Inorg. Chem.* **1987**, *26*, 469.

(22) Guthrie, D. H.; Corbett, J. D. *Inorg. Chem.* **1982**, *21*, 3290.

(23) The refinement resulted in $R = 3.3\%$, $\bar{d}(Zr-Z) = 2.450$ (1) Å and a cesium occupancy of 0.54 (1) when aluminum was used as the interstitial (not refined).