Centered Zirconium Chloride Clusters. Synthetic and Structural Aspects of a Broad Solid-State Chemistry

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A marked increase in both interest and research activity in solid-state materials chemistry has been evident in recent years. One important direction for this has been, and continues to be, the search for new compounds and, therewith, new or unusual properties and new phenomena. The flow of surprising discoveries makes it clear that our knowledge in many areas of solid-state chemistry—that is, what is possible chemically and in structure and bonding—is very incomplete. There is also a great lack of understanding regarding the coupling between structure and physical properties, and the prediction of phase stability among a collection of clear alternatives remains one of the great challenges in solid-state science.

The lack of a firm descriptive base in a great many systems, one from which one can rationally extrapolate a chemistry, means that synthesis is often an *exploration* in the real sense of the word. On the other hand, the discovery of the totally unexpected, even hitherto unimagined, is certainly one of the greatest delights in a synthetic exploration of new territory. The best discoveries in an unprincipled area are often those that one stumbles upon during experiments designed on plausible but often incorrect ideas regarding target compounds or structures, or even from a "wild shot".

The other side of the story is that solid-state products often put significant strictures on characterizational methods available to the investigator. Such phases are, by definition, those with compositions, structural components, or properties that are unique to the solid state. Thus workup, identification, and characterization of products that are truly infinite usually must forego all of the solution or gas-phase methods and many of the instrumental techniques so well developed for a world of small independent molecules. Single-crystal X-ray studies are the usual way by which new solid-state products and structures are first characterized. Reactions must accordingly be carried out at relatively elevated temperatures in order to overcome the characteristically low interphase reactivity between solids. Additives that give chemical transport reactions under the strongly reducing conditions of the present studies are unknown, and substantially all of the compounds to be described here were made at 800 °C or above. The general need to study new products formed largely under equilibrium conditions, in contrast to under kinetic control and at lower temperatures, is a major deficiency in solid-state synthesis.

Background

Impurity Problems. Our exploratory efforts have dealt with reduced halides of the early transition metals that lie along the metal–salt interface, that is, compounds exhibiting some combination of structure, bonding, and conduction properties that relate at least in concept to those of both conventional salts and metals. Our earlier reports dealt largely with new infinite sheet structures for zirconium and rare-earth-metal chlorides, all of which could be viewed in terms of condensed metal clusters.[1,2] It has since become amply clear that some, but by no means all, of the infinite structures were uniquely stabilized by common impurity atoms such as hydrogen or carbon acting in an interstitial role. This was particularly the case with rare-earth-metal examples.[3-5] A common characteristic under this circumstance was the pervasively low and irregular yields of new and supposedly simple compounds. Another feature of these troublesome cases was that they all consisted of condensed M_6Cl_{12}-type edge-bridged clusters (described below) and seemed to be particularly electron deficient. On the other hand, the more productive syntheses of real binary phases such as ZrCl, Gd_2Cl_3 and Sc_7Cl_{10}[2] pertained to products that derive from face-capped M_6X_8-type clusters where there is much less room for a centered interstitial atom.

These synthetic lessons also apply to a small number of early cluster examples. A phase Zr_6Cl_{15} that seemed to be isostructural with Ta_6Cl_{15} was seen only rarely, but as well-formed cubes.[6] New cluster phases Zr_6Cl_{12} and $K_2ZrCl_6 \cdot Zr_6Cl_{12}$ were obtained only when ZrCl was reacted (disproportionated) in the presence of hydrogen.[7] This last circumstance is, with hindsight, highly suspicious and a good hint that hydrogen may be bound in the cluster products. Unexplained electron-density residuals within the clusters were seen for "Zr_6Cl_{15}" as well as "$CsZr_6I_{14}$" and "$Sc(Sc_6Cl_{12})$"[6,8] following structural analysis, phases that are now known to bond interstitial nitrogen or carbon. In other cases, systematic

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(1) Corbett, J. D. *Adv. Chem. Ser.* **1980**, *No. 186*, 329.
(2) Corbett, J. D. *Acc. Chem. Res.* **1981**, *14*, 239.
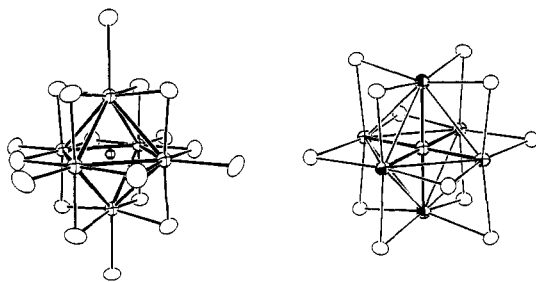(3) Ford, J. E.; Corbett, J. D.; Hwu, S.-J. *Inorg. Chem.* **1983**, *22*, 2789.
(4) Simon, A. *J. Solid State Chem.* **1985**, *57*, 2.
(5) Corbett, J. D.; McCarley, R. E. In *Crystal Chemistry and Properties of Materials with Quasi-One-Dimensional Structures*; Rouxel, J., Ed; Riedel Publishing Co.: Dordrecht, Holland, 1986; pp 179–204.
(6) Corbett, J. D.; Daake, R. L.; Poeppelmeier, K. R.; Guthrie, D. H. *J. Am. Chem. Soc.* **1978**, *100*, 652.
(7) Imoto, H.; Corbett, J. D.; Cisar, A. *Inorg. Chem.* **1981**, *20*, 145.
(8) Guthrie, D. H.; Corbett, J. D. *Inorg. Chem.* **1982**, *21*, 3290.

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Figure 1. Zr_6X_{12} clusters with interstitial atoms. Left: the $(Zr_6X_{12})X_6$ unit centered by an interstitial and with the essential terminal halide atoms bound at the six metal vertices. Right: the cluster core with a better representation of the strong Zr–interstitial bonding. Halogen atoms are the open ellipsoids in both views.

errors from secondary extinction effects obliterated impurity residuals quite well.[9] These observations, the systematics derived from first accidental and then purposeful insertion of H, C, and O into the double-metal-layered monohalides of zirconium, yttrium, and scandium,[5] and the reports of rare-earth-metal iodide clusters containing dicarbon[4] prompted us to make a systematic exploration of interstitials in what appeared to be only isolated examples of zirconium clusters. This has led to a broad new chemistry in which nearly two dozen elements have been found to play an interstitial role in a large family of Zr_6X_{12} cluster phases that span about 15 structure types. Although the iodides appear more versatile in the variety of third elements bound, the chlorides exhibit much greater structural variety and thereby reveal more of the systematics regarding bonding and electronic structure.

The building block in all of these zirconium phases is the Zr_6X_{12} cluster centered by interstitial Z, as shown in two views in Figure 1. The illustration on the left emphasizes a metal octahedron with all edges bridged by *inner* halide (X^i), but it also shows the inevitable exo or outer halides (X^a) bound at all metal vertices, a feature we shall return to shortly. The contrasting drawing on the right gives more appropriate emphasis to the bonding between the cluster metal and Z.

Empty Clusters. Few relevant examples of empty M_6X_{12} clusters are known, all for the neighboring niobium and its congener tantalum. If we limit ourselves to binary halides obtained by traditional high-temperature routes (this makes a difference), the principal examples are just Nb_6Cl_{14},[10] $Ta_6(Br,I)_{14}$,[11,12] and Ta_6-$(Cl,Br,I)_{15}$,[13] the halogen beyond 12 in each case being utilized in the X^a role. The novel Nb_6F_{15} is a structural singularity for a binary phase,[14] while Nb_6I_{11} (= $Nb_6I_8I_{6/2}$)[15,16] affords the alternative of a *face-capped* M_6I_8 cluster, probably because the anion gives excessive crowding in the unknown Nb_6I_{12} cluster (matrix ef-

fect[17]). A few ternary compounds containing 16-electron cluster cores may also be obtained, such as in the recently discovered $CsNb_6Cl_{15}$[18] as well as $M^I_4(Nb,$-$Ta)_6Cl_{18}$ (M^I = Na, K, Cs) and $K_4Nb_6Br_{18}$.[19–21] Halide in the last two groups occupies all terminal positions, viz., $(Nb_6Cl_{12})Cl_6{}^{4-}$. Fourteen-electron analogues of this first group can also be achieved, but only by solution means near room temperature.

All told, the niobium and tantalum cluster phases span only three compositions, $M_6X_{12}X_n$ with n = 2, 3, or 6, and five structure types, Nb_6Cl_{14},[10] Ta_6Cl_{15},[13] Nb_6F_{15},[14] $CsNb_6Cl_{15}$,[18] and $M_4Nb_6Cl_{18}$.[20] The narrow range of compositions reflects the fact that only cluster cores $M_6X_{12}{}^{2,3+}$ with 16 or 15 cluster-based electrons, respectively, are stable.

The ability—indeed, the necessity—to bond an interstitial element Z within all Zr_6X_{12} clusters, and therewith to vary the charge of the core over a greater range affords a much greater versatility in composition and structure and a far better basis on which to develop systematics regarding cluster synthesis, bonding, and structure. Over five dozen zirconium chloride cluster phases can be synthesized in high, often quantitative yields at 650–850 °C from proper amounts of interstitial element, alkali-metal halide, if any, Zr, and $ZrCl_4$.[22–29] Furthermore, the $Zr_6Cl_{12}Z$ cluster cores group rather tightly about those with 14 cluster-based electrons, not the 15 or 16 found with group 5 metals.

First Comes the Synthesis

Zirconium-rich systems require special container considerations because of the avidity with which this metal forms compounds with B, C, O, Al, Si, Pt, Au, etc., which, singly or in combination, represent most useful containers. Fortunately, tantalum is completely satisfactory, although its cost is some consideration.[30] Inclusion of an interstitial in a Zr_6Cl_{12} composition oxidizes the substrate to about zirconium(III), and this raises the equilibrium pressure above the phase at the 750–850 °C necessary for decent crystal growth. Bulging of the crimped containers is accordingly often seen ($P \sim$ 5–15 atm) although failure is uncommon.

Crystals of many cluster phases appear to form by autogenous vapor phase transport that mobilizes both interstitial and metal values. The intermediate $ZrCl_3$ is volatile and would serve for the latter, while chlorides are also reasonable means for transporting Be, B, and, presumably, C. Carbon transport at 650 °C has been seen in zirconium iodide cluster systems, and hydrocarbons serve as a source down to at least 450 °C

(9) Smith, J. D.; Corbett, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5704.
(10) Simon, A.; von Schnering, H.-G.; Wöhrle, H.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1965**, *339*, 155.
(11) McCarley, R. E.; Boatman, J. C. *Inorg. Chem.* **1965**, *4*, 1486.
(12) Bauer, D.; Schnering, H.-G; Schäfer, H. *J. Less-Common Met.* **1965**, *8*, 388.
(13) Bauer, D.; von Schnering, H.-G. *Z. Anorg. Allg. Chem.* **1968**, *361*, 259.
(14) Schäfer, H.; Schnering, H.-G.; Niehues, K.-J.; Nieder-Vahrenholz, H. G. *J. Less-Common Met.* **1965**, *9*, 95.
(15) Bateman, L. R.; Blount, J. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1966**, *88*, 1082.
(16) Simon, A.; von Schnering, H.-G.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1967**, *355*, 295.

(17) Corbett, J. D. *J. Solid State Chem.* **1981**, *37*, 335.
(18) Imoto, H.; Simon, A., unpublished research, 1980.
(19) Fleming, P. B.; Mueller, L. A.; McCarley, R. E. *Inorg. Chem.* **1967**, *6*, 1.
(20) Simon, A.; von Schnering, H.-G.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1968**, *361*, 235.
(21) Broll, A.; Juza, D.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1971**, *382*, 69.
(22) Ziebarth, R. P.; Corbett, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 4571.
(23) Ziebarth, R. P.; Corbett, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 4844.
(24) Ziebarth, R. P.; Corbett, J. D. *J. Less-Common Met.* **1988**, *137*, 21.
(25) Ziebarth, R. P.; Corbett, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 1132.
(26) Ziebarth, R. P.; Corbett, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 3272.
(27) Ziebarth, R. P.; Corbett, J. D. *Inorg. Chem.* **1989**, *28*, 626.
(28) Ziebarth, R. P.; Corbett, J. D. *J. Solid State Chem.* **1989**, *80*, 56.
(29) Ziebarth, R. P.; Corbett, J. D., to be published.
(30) Corbett, J. D. *Inorg. Synth.* **1983**, *22*, 15.

therein, but not in a reversible way.[31] Loss of interstitial Z is a potential problem since zirconium forms stable phases with many examples, but these probably represent only kinetic diversions during intermediate stages.

The compounds to be described are thermodynamically stable and therefore in equilibrium with an adjoining phase when the overall composition is off stoichiometry. Thus, the ability to synthesize a *single-phase* product from a reactant mixture of the correct stoichiometry is an excellent test that the investigator is on target regarding a new cluster phase, especially as to the identity of an interstitial for which X-ray diffraction is somewhat undiscriminating. In practice, purities of greater than 90% are reasonable considering weighing errors, dissociation, etc., and >95% is often achieved, the latter being a conservative estimate of the sensitivity of Guinier powder diffraction to the usual crystalline impurities. Combined Guinier and microscropic examinations of products from a series of reactions run with different proportions can often allow one to establish the relative proportions of the elements in a new phase to ±10–15% in each. Omission of just the interstitial from a reaction, or an attempt to insert an unsuitable one, will generally give only routine products like $ZrCl_n$ ($n = 1, 2, 3$), $M^I_2ZrCl_6$, or both. On the other hand, one should not misled or distracted by small amounts of well-formed crystals like $Zr_6Cl_{14}C$ and $Zr_6Cl_{15}N$ which can form from the more pervasive impurities that originate with traces of plastics, grease, air, and the like. These can often be differentiated from other products on the basis of powder patterns and lattice constants.

Fortunately or not, theory is presently in no position to assess well the stability of any new phase, as such conceptualization can at best be an extrapolation of the known. An even greater barrier to calculational success comes from the fact that theory cannot realistically ascertain the relative stability of *alternate* phases, which is the really important question regarding any new compound. This is clearly important in attempts to extend the range of cluster interstitials—what other combinations, known or new, of a particular Z are important? The amount of Z used is sufficiently small that it is frequently difficult to ascertain what other products formed when Z did not become a small but essential component of a cluster phase.

General Principles

Substantially all phases fall within the description $M^I_x[(Zr_6(Z)Cl_{12})]Cl_n$ where x and n variables each range between 0 and 6, and the interstitial Z can be H, Be, B, C, or N. A separate and smaller family has been found more recently for Z = Mn, Fe, etc.[32] Three factors appear to be important in determining the compositions and structures, deriving basically from the conservation of bonding orbitals.

1. Terminal Halides and Cluster Bridging. A simple M_6X_{12} cluster actually represents an unnatural configuration since basically a hemisphere about each metal vertex is empty (Figure 1, right). In fact, structures of all known M_6X_{12}-type clusters always have a halide (or other base) bound in the exo position, and

(31) Chen, T.-M.; Kauzlarich, S. M.; Corbett, J. D. *J. Nucl. Mater.* **1988**, *151*, 225.

(32) Zhang, J.; Corbett, J. D., unpublished research.

Table I
Stoichiometry and Connectivity of $(Zr_6Cl_{12})Cl_n$ Clusters, $0 \leq n \leq 6$, According to Halide Function[a]

halide functions	inner X ($\Sigma = 12$) i	outer X ($\Sigma = 6$) bridging i–a	a–i	a–a	a
Zr_6Cl_{12}	6	6/2	6/2		
Zr_6Cl_{13}[b]	(8)	(4/2)	(4/2)	(2/2)	
Zr_6Cl_{14}	10	2/2	2/2	4/2	
Zr_6Cl_{15}	12			6/2	
Zr_6Cl_{16}	12			4/2	2
Zr_6Cl_{17}	12			2/2	4
Zr_6Cl_{18}	12				6

[a] i: inner, edge-bridging. i–a and a–i: inner in one cluster, outer or exo to a metal vertex in another, and vice versa. a–a: bridging only between cluster vertices. a: exo on a single cluster. [b] This stoichiometry is presently known only with an irregular I^{i-i} connectivity.[22]

the same applies to infinite chain halides consisting of condensed octahedra as well as many comparable halides and chalcogenides of later transition metals.

The means by which this exo position is occupied is intimately tied to the number of additional halides n, and this in turn mainly determines structure type. The constraints are that (a) the 12 inner halide (X^i) positions are evidently immutable for uncondensed clusters and (b) six outer or terminal (X^a) ligands are also needed. The latter may be an edge-bridging inner halide in another cluster, X^{a-i} ($Zr \cdots X < Zr_2$), a halide that bridges between clusters X^{a-a} ($Zr–X–Zr$), or one that is terminal solely to one vertex ($Zr–X^a$). Algebraically, this gives $Zr_6X^i_{12-m}X^{i-a}_{n-p}X^a_p$ for which $m + 2(n - p) + p$ must total 6. A regular progression in the distribution of these halide functions with increasing n is to be expected, as shown in Table I. Cluster phases with $n \leq 3$ accordingly form three-dimensional networks, e.g., $[Zr_6(Z)Cl_{12}]Cl_{6/2}$, while $n = 4$ and 5 give sheet $\{[Zr_6(Z)Cl_{12}]Cl^{a-a}_{4/2}Cl^a_2\}$ and chain $\{[Zr_6(Z)Cl_{12}]Cl^{a-a}_{2/2}Cl^a_4\}$ structures, and $n = 6$ corresponds to isolated units.

2. Interstitial Atoms. *All* zirconium (and rare-earth-metal) clusters evidently *require* an interstitial atom. These provide additional electrons to an otherwise impoverished cluster as well as four (s and p) or five (d and s) orbitals for strong Zr–Z bonding. The Zr–Z bonding is an obvious difference from the longer known, empty clusters of the later transition metals. In a few cases—Nb_6I_{11}, $CsNb_6I_{11}$, ZrCl, and ZrBr, for example—empty cluster units occur that may also bond atoms such as H, C, N, or O within the metal framework, sometimes with internal structural rearrangement.[2,5]

The optimum electron count within the zirconium chloride cluster phases with main-group interstitials is 14, with only infrequent deviations of ±1 from this target, while 18 is the ideal with 3d interstitials. MO descriptions for these will be provided later. The magic number of 14 pertains to the number of electrons left over after all low-lying chlorine 2p valence orbitals are filled, a bookkeeping that is familiar to most chemists. Thus, the $CsZr_6Cl_{15}C$ cluster contains $1 + 6 \times 4 - 15 \times 1 + 4 = 14$ electrons. The carbon atom certainly does *not* donate its valence electrons to the cluster but shares them in covalent bonds, acquiring a somewhat negative charge when bonded to such an electropositive cluster

Table II
Examples of $(Zr_6Cl_{12})Cl_n$ Cluster Phases and Their Structure Types

n	examples	ref	structure type	space group	ref
0	$Zr_6Cl_{12}Be$, $Zr_6Cl_{12}H$,[a] $Zr_6Cl_{12}B$[a]	28	$Zr_6I_{12}C$ ($Sc_7Cl_{12}N$)	$R\bar{3}$	9 (8, 33)
0	$Cs_2ZrCl_6 \cdot Zr_6Cl_{12}Be$, $K(LaCl_6)Zr_6Cl_{12}CCs(LaCl_6)Zr_6Cl_{12}Fe$	28, 32	$K_2ZrCl_6 \cdot Zr_6Cl_{12}H$[a]	$R\bar{3}$	7
1	$Zr_6Cl_{13}B$, $(K,Rb)Zr_6Cl_{13}Be$	29	$KZr_6Cl_{13}B$	$Pnnm$	same
2	$Zr_6Cl_{14}C$, $Zr_6Cl_{14}B$,[a] $(Li-Cs)Zr_6Cl_{14}B$, $Zr_6Cl_{14}Fe$	28, 32	Nb_6Cl_{14}	$Cmca$	10
3	$Zr_6Cl_{15}N$, $Na_2Zr_6Cl_{15}B$[b]	24	Ta_6Cl_{15}	$Ia3d$	13
3	$(Cs,Rb,K)Zr_6Cl_{15}C$, $(CsK,Rb_2)Zr_6Cl_{15}B$, $KZr_6Cl_{15}N$,[a] $RbZr_6Cl_{15}Fe$	23, 32	$KZr_6Cl_{15}C$, $CsNb_6Cl_{15}$[c]	$Pmma$	23 / 18
3	$K_2Zr_6Cl_{15}B$, $K_2Zr_6Cl_{15}Be$[a]	25	$K_2Zr_6Cl_{15}B$	$Cccm$	same
3	$(K,Rb)_3Zr_6Cl_{15}Be$	25	$K_3Zr_6Cl_{15}Be$[d]	$C2c$	same
3	$Zr_6Cl_{15}Co$, $LiZr_6Cl_{15}Fe$, $Li_2Zr_6Cl_{15}Mn$	32	Nb_6F_{15}	$Im3m$	14
4	$Cs_3Zr_6Cl_{16}B$, $Cs_4Zr_6Cl_{16}Be$	27	$Cs_3Zr_6Cl_{16}C$[a]	$P2_1/n$	same
4	$Na_4Zr_6Cl_{16}Be$	27	$Na_4Zr_6Cl_{16}Be$	$Pccm$	same
5	$Ba_2Zr_6Cl_{17}B$	32	$Ba_2Zr_6Cl_{17}B$	$I4/m$	same
6	$Rb_5Zr_6Cl_{18}B$	26	$Rb_5Zr_6Cl_{18}B$	$Pmna$	same
6	$Li_6Zr_6Cl_{18}H$[a]	34	$Li_6Zr_6Cl_{18}H$	$R\bar{3}$	same

[a] Clusters with ±1 electron from the optimum. [b] Small tetragonal distortion. [c] These two types utilize different cation sites. [d] This structure is a distorted version of the preceding one.

metal. The C(1s) binding energy within the cluster is found to be approximately 3.0 eV less than in a hydrocarbon.[26]

3. Inclusion of Cations. Use of a relatively electron poor interstitial or use of a high Cl/Zr ratio to give products with higher n values are both means of "forcing" the inclusion of alkali-metal cations since these provide a counterreduction of the cluster. Incorporation of cations within a cluster network that is largely determined by the value of n may require occupation of sites that are of quite low symmetry or somewhat mis-sized. Although only one structure type is known for n = 0, 1, or 2, four different connectivities and structures may be realized with n = 3 in response to both the size and number of cations to be accommodated *and* the relative size of the cluster as determined by the size of Z. These will be described shortly.

Cluster Examples

A sampling of the phases so achieved for zirconium chlorides is given in Table II for each of the structure types and in order of increasing n. Their connectivities were described in Table I. The few examples that are not 14-e⁻ clusters will be considered shortly. Also included in the table for comparison are a few recent examples of 18-e⁻ clusters containing transition metals Mn–Co that form in some of these structure types, Nb_6F_{15} especially.

The versatility that can be achieved among the 14-e⁻ clusters can be focused better with some examples where only two of the variables x, Z, and n change. Isoelectronic series can be achieved by changing n and Z at the same rate and in the same direction since these give oxidation and reduction, respectively. An example is

$$Zr_6Cl_{12}Be, \ Zr_6Cl_{13}B, \ Zr_6Cl_{14}C, \ Zr_6Cl_{15}N$$
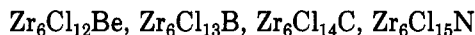
Insertion of one cation between the clusters in each and a simultaneous decrease of the valence electrons from Z by one may provide a series that is isostructural pairwise with that above, viz.,

$$Sc(Sc_6Cl_{12}N), \ KZr_6Cl_{13}Be, \ KZr_6Cl_{14}B, \ NaZr_6Cl_{15}C$$
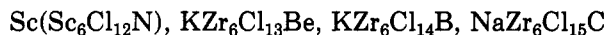
Although $KZr_6Cl_{12}Li$ is not known (yet!) to pair with $Zr_6Cl_{12}Be$, the nominally isostructural $Sc(Sc_6Cl_{12}N)$ is achieved when three more electrons each are provided
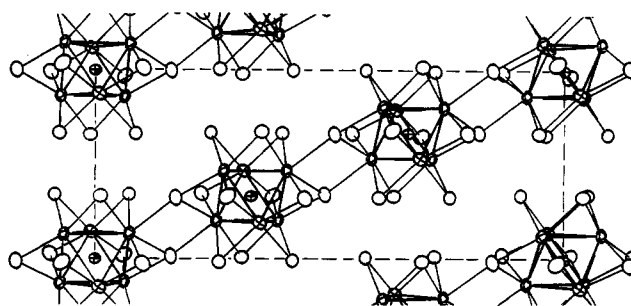

Figure 2. A [110] cross section of the structure of $Zr_6Cl_{12}Be$ showing the mode of intercluster bonding. The c axis lies vertical.

by the added Sc^{3+} cation and the interstitial and six fewer come from the cluster element.[33] Analogous phases have not yet been found with yttrium, surprisingly. Additionally, compensation of changes in cluster charge type with cation count for a fixed interstitial is found in a series like

$$Zr_6Cl_{13}B, \ RbZr_6Cl_{14}B, \ Rb_2Zr_6Cl_{15}B, \ Rb_3Zr_6Cl_{16}B,$$
$$Rb_5Zr_6Cl_{18}B$$
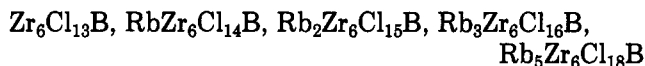
It is noteworthy that the syntheses of the last four involve principally an appropriate variation in the relative amount of RbCl added.

Structure Types. Illustration of some of the structural networks is helpful. All of the drawings emphasize the functionalities of the chlorines bound at metal vertices as these define the network and the structure type (Table I). The inner Cl^i atoms are much less important, and these are omitted from all but the first in order to improve the clarity.

Figure 2 shows a cross section of the structure of $Zr_6Cl_{12}Be$. The clusters are oriented around a crystallographic 3-fold inversion axis, vertical in this view, and a center of symmetry is located at each Be atom. Since this composition has no extra chlorine atoms to occupy terminal positions, this functionality is provided in a complementary manner by pairs of inner Cl^{i-a} atoms that are also terminal in an adjoining cluster, Cl^{a-i}, and vice versa. The $\bar{3}$ axis through the origin means that just the six Cl^i atoms about the waist of the cluster are involved in bridging, and the clusters are cubic-
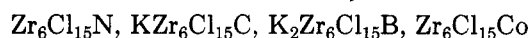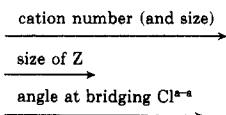
(33) Hwu, S.-J.; Corbett, J. D. *J. Solid State Chem.* **1986**, *64*, 331.
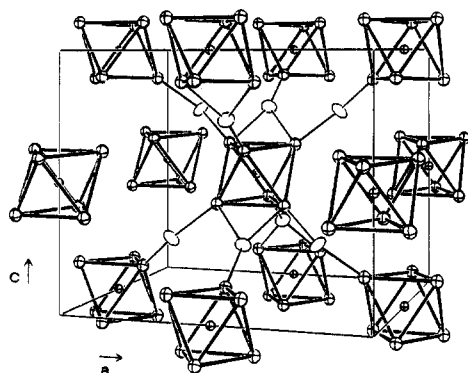
Figure 3. $Zr_6Cl_{14}C$: a view of the Zr_6C cluster cores and of the bridging of the central cluster by four Cl^{a-a} and two Cl^{i-a} atoms (90% probability ellipsoids).

Figure 4. The crisscrossed and interlinked linear chains of Zr_6B clusters in $K_2Zr_6Cl_{15}B$ with bridging chlorine represented by open ellipsoids. The crossed ellipsoids lie between the chains and represent the potassium ion positions. All Cl^i atoms have been omitted (90%).

close-packed. This behavior is closely analogous to the even tighter intercluster bonding found in Chevrel phases like Mo_6Se_8 that also provides an intercluster conduction path. The vacant octahedral site at 0, 0, $^1/_2$ is occupied by the isolated cation in $Sc(Sc_6Cl_{12}N)$ noted above.

Additional halide beyond the basic twelve allows Cl^{a-a} bonding to progressively replace some of the Cl^{a-i} functions. Actually this is observed first in the fairly common structure type shown in Figure 3 for $Zr_6Cl_{14}C$, where four shared Cl^{a-a} atoms link clusters in two directions, while two Cl^{a-i} functions remain. A single cation per cluster can be accommodated in a chlorine polyhedron about the origin.

In contrast, the structure of $Zr_6Cl_{13}B$ is irregular with both Cl^{i-i} atoms shared between clusters and Cl^a atoms that occupy *three* vertices, viz., $Zr_6Cl_{10}(B)Cl^{i-i}_{2/2}Cl^{a-a}_{6/3}$. This sharing of inner halide is the first step into the regime of hypoclusters and, ultimately, cluster condensation by sharing edges of the metal cluster.[2] A more regular example is found with isolated clusters in $Y_6I_{10}Ru$ ($=Y_6(Ru)I^i_8I^{i-i}_{4/2}$).[35] The unusual linkage in $Zr_6Cl_{13}B$ must represent a compromise, a reasonable three-dimensional packing coupled with the strong demand for a 12 + 6 arrangement of halogen ligands about each cluster.

With a Zr_6Cl_{15} composition we achieve a uniform linkage mode as $(Zr_6Cl_{12})Cl^{a-a}_{6/2}$ but, surprisingly, in four distinctly different structures. These four differ in the angles at the intercluster Cl^{a-a} atoms and, more precisely, in the size and disposition of the rings defined by the interlinked clusters, and they cannot be interconverted by twisting, rather only by breaking and rearranging bridge bonds.[23-25] The following series, with one member of each type, shows the systematics.

<div align="center">

cation number (and size)
———————————————————→

size of Z
———————————→

angle at bridging Cl^{a-a}
————————————————→

$Zr_6Cl_{15}N$, $KZr_6Cl_{15}C$, $K_2Zr_6Cl_{15}B$, $Zr_6Cl_{15}Co$

</div>

The first member of this series, $Zr_6Cl_{15}N$, contains only bent intercluster $Zr-Cl^{a-a}-Zr$, the 138° angles reflecting the need to fill space fairly efficiently. The three-dimensional linkage is rather complex and involves

(34) Ziebarth, R. P.; Zhang, J.; Corbett, J. D., unpublished research, 1986.
(35) Hughbanks, T.; Corbett, J. D. *Inorg. Chem.* **1989**, *28*, 631.
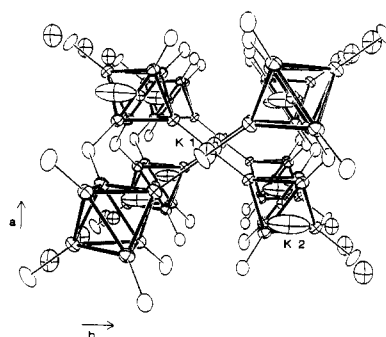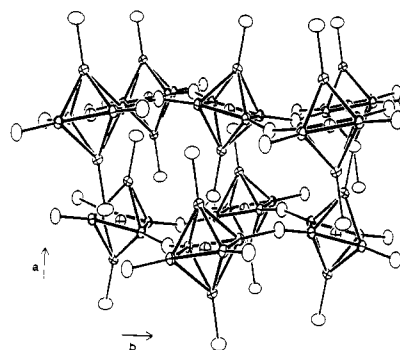
Figure 5. The layered network observed in $Na_4(Zr_6Cl_{12}Be)Cl_4$ (Cl^i omitted). Sodium cations occur within and between the layers (90%).

four-rings, $(-Zr_6-Cl^{a-a}-)_4$. Inclusion of a cation the size of K^+ or greater requires that the network expand, and this yields one-sixth linear bridges at Cl^{a-a} and three-rings through a combination of linear cluster chains interleaved with horizontal zig-zag versions. The network opens up even more when two (or three) potassium cations are bound in $K_2Zr_6Cl_{15}B$ structure, Figure 4. Here we see crisscrossing linear chains of bridged clusters interconnected by bent chlorine bridges while potassium is accommodated in two different chlorine polyhedra between chains (larger crossed ellipsoids).

Although one should never assert there are *no* further examples containing more open but still completely interlinked clusters, the next know illustration involves a sizable change in the character of the network. Increasingly large interstitial atoms such as Fe, Co, or Ni alter the cluster geometry by pushing the metal vertices outward, bringing them closer to the plane of the four neighboring halogen atoms that bridge the adjoining Zr–Zr edges. (The smaller fluoride allows the same thing.) At some point, a more open arrangement of only linearly bridged units is achieved, the Nb_6F_{15} structure,[14] with *two* interpenetrating but not interconnecting arrays, and now only small countercations like Li^+ will fit within the compound network.[32] Larger cations may provide as yet unrecognized intermediate structures.

Passage to Zr_6Cl_{16} compositions means that half of the outer chlorine atoms are terminal solely to one cluster, viz., $(Zr_6Cl^i_{12})Cl^{a-a}_{4/2}Cl^a_2$. The linkage affords two-dimensional cluster layers, two of which are shown in Figure 5 for $Na_4Zr_6Cl_{16}Be$. The clusters tilt from the normals to the layers even further when they must

Centered Zirconium Chloride Clusters

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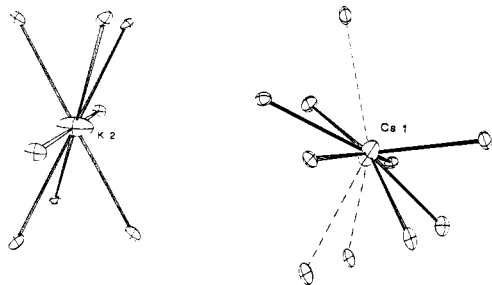
Figure 6. Left: the chlorine polyhedron about K2 in $K_2Zr_6Cl_{15}B$ (Figure 4). Right: the Cs1 site in $Cs_3Zr_6Cl_{16}C$. The seven shorter separations in the latter average 3.64 Å, while the three dashed ones are over 3.90 Å (50%).

accommodate cesium ions.

The orbital requirements of the zirconium clusters appear to dominate in all of these structures. In contrast, the cations may have to settle for relatively unsymmetric polyhedral sites defined by halogen. Two of the more extreme examples are shown in Figure 6. At the left is the polyhedron with $2/m$ symmetry about K2 in $K_2Zr_6Cl_{15}C$, where two chlorine atoms lie quite far from the normal to the plane of the other six.[25] The right side of the figure shows one of two similar cation polyhedra in $Cs_3Zr_6Cl_{16}C$.[27] The seven solid "bonds" average 3.64 Å, large compared with a crystal radius sum of 3.55 Å for CN8, while the more distant chlorines (dashed lines) are over 3.90 Å away.

Size Effects.[26] The effective size of a zirconium halide cluster, a feature that has already been seen to be of some importance in differentiating structures, depends mainly on the sizes of the halogen and the interstitial. The reproducibility of average Zr–Z distances in 14-e⁻ chloride with different structure types is good for a given Z, decreasing as expected from Be to C, for example. On the other hand, a clear "rattling" of the hydrogen in $Zr_6Cl_{12}H$ has been seen by NMR, where the radius of the cavity is about 0.16 Å larger than reasonable for good Zr–H contact.[36]

In most clusters, the bonding attraction between both Zr–Z and Zr–Zr appears to be opposed by closed-shell repulsions between relatively large halogen atoms. The last serve to expand the cube defined by edge-centered halogen relative to the face-centered metal or, alternatively, to pull the metals in from the cube faces, as seen at the top of the clusters in Figure 1. Such a matrix effect[17] should order I > Br > Cl > F and Nb > Zr > Y, other things being equal. This effect appears to be of some consequence in determining the most stable electron configurations of clusters (below).

Bonding and Cluster Stability

The bonding in these clusters can be represented particularly well in MO terms since they are well isolated in the solid state. Several extended-Hückel calculations have been reported.[9,26,33] These can be easily generalized by starting with the results for a hypothetical empty cluster like $(Zr_6Cl_{12})Cl_6^{4-}$ [37] shown schematically at the left below.
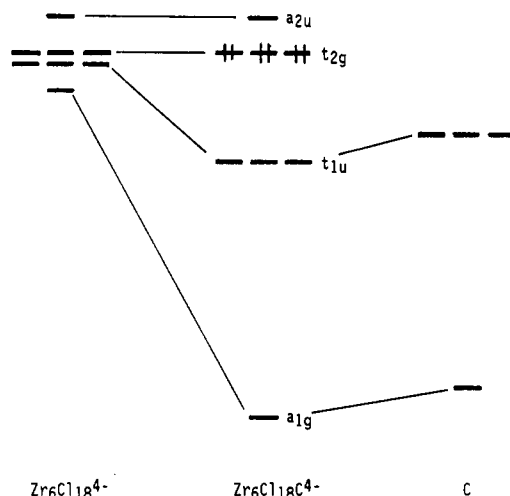
A narrow band of bonding Zr–Cl and nonbonding Cl 3p orbitals that fall in the large gap in the center of the figure have been omitted, while antibonding orbitals all lie above the highest metal-based orbital, a_{2u}. On the right are typical (charge consistent) valence orbital energies for carbon. The magnitudes of the decreases of the a_{1g} and t_{1u} orbital energies on bonding of carbon, center, reflect the strength of the Zr–C bonding. The unperturbed t_{2g}^6 is left as the HOMO for the experimentally optimal 14-e⁻ chloride cluster. (Substitution of a 3d interstitial results in both the reversal of the t_{1u} and t_{2g} functions and the addition of a nonbonding e_g^4 level, and an 18-e⁻ cluster is observed to have some special stability.) All of the 14-e⁻ cluster phases are reddish, and spectroscopic studies could be interesting. On the other hand, the structures suggest that electronic conduction is apt to be very low.

Matrix effects and distortions of the cluster from the ideal were noted above to originate with relative sizes of the $M_6(Z)$ unit and enveloping halogens. Expectations for these correlate very well with the utilization of the a_{2u} orbital and an increase of the cluster bonding complement from 14 to 16 electrons with or without a main-group Z.[26] An increase in cluster distortion will decrease the $M(xy)–X^i(p\pi)$ antibonding contributions at each vertex (Figure 1) to a_{2u}, which is otherwise M–M bonding. This change appears most directly with centered zirconium iodide carbides, where the trans X^i–M–X^i angles at the vertices are 5–15° less than in the chlorides, and the formation of 15- and 16-e⁻ clusters is notably easier.[9,39,40] Of course, a changing Zr–X overlap with halogen must also be a factor. In the other direction, M–M distances decrease by 0.2–0.4 Å between centered zirconium and empty niobium (or tantalum) chloride units, and 15- and 16-e⁻ clusters become the rule in high-temperature products, viz., in Nb_6Cl_{14}, $Ta_6(Cl,Br)_{15}$, and $Ta_6(Br,I)_{14}$.[10–13] Of course, we have also removed the bonding to the interstitial in the process, so the comparison is not completely simple. However, both niobium oxide and fluoride clusters follow the expected trend and form 14- and 15-e⁻ clusters.

We are compelled to note a caution regarding the foregoing "explanation" of cluster electron trends in

(36) Chu, P. J.; Ziebarth, R. P.; Corbett, J. D.; Gerstein, B. C. *J. Am. Chem. Soc.* **1988**, *110*, 5324.

(37) The importance of including the six terminal Zr–Cl^a bonds in cluster calculations should already be evident. This bonding feature is significant in empty clusters as well.

(38) Hughbanks, T.; Rosenthal, G.; Corbett, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 1511.

(39) Smith, J. D.; Corbett, J. D. *J. Am. Chem. Soc.* **1986**, *108*, 1927.

(40) Rosenthal, G.; Corbett, J. D. *Inorg. Chem.* **1988**, *27*, 53.

zirconium chlorides vs either zirconium iodide or niobium chloride examples—the alternate products have changed! Attempts to "overreduce" 14-e⁻ zirconium chloride clusters and utilize the a_{2u} level compete with the formation of ZrCl, a product not known for either the zirconium iodides or the group 5 chlorides where the next most reduced phases are the metals.

Exceptions to the 14-e⁻ rule for the zirconium chlorides are few. Three of the five 13-e⁻ examples listed in Table II are hydrides, $Zr_6Cl_{12}H$, $Li_6Zr_6Cl_{18}H$, and $M^I_2ZrCl_6 \cdot Zr_6Cl_{12}H$, perhaps meaning that "something is better than nothing". (The first listed is known to be properly paramagnetic.[36]) The other two are K_2-$Zr_6Cl_{15}Be$ and $Zr_6Cl_{14}B$, relatively large clusters for their structure types. Only two 15-e⁻ examples are known to date, $Cs_3Zr_6Cl_{16}C$ and $KZr_6Cl_{15}N$. The last occurs in a family of $Zr_6Cl_{15}Z$ compounds where structural factors are better understood. The occurrence of a 15-e⁻ cluster with the small nitride interstitial is the best place for an increased matrix effect to influence the a_{2u} level, as discussed above, and the compound was synthesized with that in mind.

It is interesting to note that 12- and 13-e⁻ centered zirconium clusters have recently been prepared from the 14-e⁻ solid-state examples via nonaqueous solution routes near room temperature,[41] quite analogous to the oxidized, 14-e⁻ niobium and tantalum counterparts achieved in aqueous systems.[42,43] All are probably metastable.

Other factors in cluster stability that have not been enumerated are the strengths of the Zr–Z bonds and, as a component of that, the valence-state ionization energies H_{ii} and Zr–Z overlaps for various interstitial atoms. The energies alone will ultimately generate some limits—first for those that are too low and allow little charge transfer to the cluster, a situation that probably applies to oxide and fluoride (and neon) relative to polar phases like ZrO_2 and ZrF_4. At the other extreme, main-group Z candidates with high-lying p orbitals that provide little interaction with zirconium relative to other products should also be less effective. Lithium in chlorides and aluminum in iodides[39] may be so categorized. *But, we again must caution that the stabilities of alternate phases are the really important considerations in equilibrium systems.*

Finally, there is speculation as to whether empty zirconium clusters might be prepared. One obvious way would be to utilize more highly charged countercations in phases such as $LaCaZr_6Cl_{15}$ ($CsKZr_6Cl_{15}B$ type) or $Ca(Zr_6Cl_{12})$, although experiments to introduce such polyvalent cations have to date been largely unsuccessful. Another way would be to remove hydrogen from a hydride at a lower temperature.

The assembly of suitable products via lower temperature routes and under kinetic rather than thermodynamic control is naturally a major goal of solid-state synthetic chemistry, but it may be some time before sufficiently crystalline examples of multidimensional solids of the sort described here can be so obtained. Many new and novel compositions and structures remain to be discovered by more traditional means.

(41) (a) Rogel, F.; Corbett, J. D., unpublished research. (b) Rogel, F.; Zhang, J.; Payne, M. W.; Corbett, J. D. *Adv. Chem. Ser.*, submitted.
(42) McCarley, R. E.; Hughes, B. G.; Cotton, F. A.; Zimmerman, R. *Inorg. Chem.* 1965, 4, 1491.
(43) Fleming, P. B.; Dougherty, T. A.; McCarley, R. E. *J. Am. Chem. Soc.* 1967, 89, 159.