The structural analogy to many transition metal tetrahalides, as indicated by the presence of chains of cis-edge-sharing octahedra, also extends on the arrangement of these structural units relative to each other. When considering the I-O substructure, isotypism to uranium tetraiodide becomes evident, that is, the oxygen atoms form a hexagonal close packing with the iodine atoms occupying a quarter of the octahedral holes. Every polymeric chain is connected to four adjacent chains through hydrogen bonds (Figure 4; $d(O \cdots O) = 269(2)$ pm).

**Experimental Section**

HIO$_4$· Oleum (25%, 15 mL) was slowly added to a solution of H$_2$IO$_6$ (3 g) in concd H$_2$SO$_4$ (40 g) at 50°C until an insoluble precipitate appeared. Upon standing for 12 h at 50°C a voluminous precipitate separated, which was isolated by filtration under an inert-gas atmosphere. It was treated with concd H$_2$SO$_4$ (15 mL), washed with trifluoroacetic acid (5 x 15 mL) to remove traces of H$_2$SO$_4$, and finally dried in vacuo. Elemental analysis: iodine: 65.5% (calcd 66.1%), active oxygen: 27.9% (calcd 29.2%), sulfate: not detected.

Structure determination of HIO$_4$. After indexing [9] the X-ray powder diagram (Stoe Stadi P, Cu$_{2}$K$_{4}$ radiation, $\lambda = 1.54051$) on the basis of a monoclinic system ($a = 936.88(5)$, $b = 629.59(4)$, $c = 495.30(3)$ pm; $\beta = 94.953(3)^\circ$), $C$ (no. 9) and $C2/c$ (no. 15) were considered as possible space groups from the systematic absences. In both space groups the iodine- and oxygen-atom positions were determined with direct methods [10], but a crystal-chemically consistent refinement (550 reflections, 30 parameters, $R = 0.0657$, $R_w = 0.219$, $R_b = 0.0522$ [11]) could only be achieved in the space group $C2/c$. The hydrogen bridges and, thus, the approximate positions of the hydrogen atoms were derived from crystal-chemical considerations. To verify these results optimized structure models (space group $C2/c$ with disordered H atoms and Ce with no disordering of H atoms) were refined on the basis of neutron diffraction data ($\bar{d}$ determined to 112.704 pm [11], two-circle neutron diffractometer SV7 equipped with a linear position-sensitive JULIUS detector from the Mineralogisches Institut der Universität Bonn at the reactor FRJ2 of the KFA Jülich). The model with space group $C2/c$ was unambiguously the correct one ($a = 936.60(18)$, $b = 628.86(13)$, $c = 495.75(19)$ pm; $\beta = 94.890(15)^\circ$; 282 reflections, 27 parameters, $R = 0.0185$, $R_w = 0.033$, $R_b = 0.21$ [11]).

**Keywords:** iodine · metaperiodic acid · neutron diffraction · structure elucidation

Ge$_4^{4+}$: A Deltahedral Zintl Ion Now Made in the Solid-State**

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All known main group deltahedral clusters are made either by crystallization from solution or by direct synthesis from the elements, that is by solid-state reactions. (We exclude gaseous clusters here since they are not structurally well characterized.) Members of the first group belong to the well known class of Zintl ions and include anions of group 14 (the tetrels Tl$_n$): Tl$_4^{4-}$

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Tr\(_3^–\), Tr\(_2^–\), Tr\(_4^–\), and Tr\(_{10}^–\), of group 15 (the pnictogens (Pn): Pn\(_3^–\)), and the mixed species Tr\(_2^–\)Pn\(_3^–\), Tr\(_3^–\)Pn\(_3^–\), and Tr\(_{10}^–\) (Tr = element of group 13).\(^{[1–3]}\) These clusters form when the corresponding alloy with Na or K (or mixtures of them) is dissolved in either liquid ammonia or ethylenediamine, often mixed with 2,2,2-crypt.\(^{[4]}\) Most of these clusters have been characterized in terms of nuclearity and charge by NMR spectroscopy in solution.\(^{[5]}\) Presumably, formation of the clusters takes place during the extraction with the solvent since no precipitate is observed in the starting alloys.\(^{[2]}\) The group of clusters made by solid-state reactions is somewhat smaller, but also includes a few species from groups 14 (Tt\(_2^–\)), 15 (Bi\(_2^+\), Bi\(_3^+\), Bi\(_4^+\)), and 16 (Se\(_2^+\) and Te\(_3^+\)).\(^{[6]}\) These clusters are found in solid-state compounds with alkali metals as counterions (or AlCl\(_3\), as counterion).\(^{[7]}\) In Ge\(_n^–\) we have found the first such species to bridge the two elements. Prior to this report the clusters of Ge\(_3^–\) were structurally characterized only in the salt K[2-222-crypt]Ge\(_3^–\)(JGe\(_3^–\)), made by crystallization of a solution of a K-Ge alloy dissolved in ethylenediamine.\(^{[8]}\) The tin-substituted isoelectronic clusters [Ge\(_n^–\)Sn\(_{n−1}^+\) (n = 1–8) have been characterized in solution by \(^{119}\)Sn NMR spectroscopy.\(^{[9]}\) Transition metal derivatives of these and similar deltahedral Zintl ions are also known. They include [Tt\(_{n+1}\)Cr(CO)\(_5\)]\(^–\) (Tt = Sn, Pb), [Sn\(_{n+2}\)Cr(CO)\(_5\)]\(^–\), and the recently synthesized Ge-centered [Ge\(_n^–\)Ni(PPh\(_3\))]\(^–\),\(^{[10]}\) all of which have been isolated with cryptated alkali metal cations and structurally characterized.\(^{[8]}\) Similarly [Tt\(_n^–\)Pn\(_{n−1}^+\)]\(^–\) (Tt = Sn, Pb; L = ligand) have been characterized in solution by \(^{119}\)Sn and \(^{207/208}\)Pb NMR spectroscopy.\(^{[9]}\)

We have now made the nacked Ge\(_n^–\) clusters in “neat” solids.\(^{[10]}\) These solids are Cs\(_n^–\)Ge\(_n\) and the isostructural Rb\(_2^–\)Ge\(_n\), both made by direct synthesis from the corresponding elements (see Experimental Section). Ge\(_3^–\) is the first deltahedron cluster of the tetrels in the solid state since Tr\(_3^–\) was made more than forty years ago in A\(_2^–\)Tr\(_3\) (A = alkali metal).\(^{[11]}\) Our attempts to make similar A\(_2^–\)Ge\(_n\) compounds with sodium or potassium proved unsuccessful. This supports the hypothesis that the precursors used for the solution studies (traditionally made with the light alkali metals) do not contain the clusters.

The structure of Cs\(_n^–\)Ge\(_n\) (Figure 1) was determined by single-crystal X-ray diffraction (see Experimental Section). It crystallizes in the rare noncentrosymmetric P4\(_1\) space group and contains four crystallographically different clusters.

![Figure 1. A general view of the tetragonal unit cell of Cs\(_n^–\)Ge\(_n\), (the c axis runs vertical). Bonds are drawn between the Ge atoms of the different Ge\(_n^–\) clusters. The Cs atoms are shown isolated. All atoms are drawn with 30% thermal ellipsoids.](image-url)

The geometry of the four clusters is virtually the same as that of the Ge clusters in the K-crypt salt.\(^{[17]}\) The distances of the latter are listed in Table 1 for comparison. Often it is difficult to distinguish between a nine-atom closo species (a tricapped trigonal prism) and a nine-atom nido species (a monocalcaded square antiprism). However, the four clusters in the present compound are unambiguously nido polyhedra according to their distances. The diagonals of the square bases, Ge\(_6^–\)Ge\(_8^–\) and Ge\(_7^–\)Ge\(_9^–\) (Table 1), which are the potential candidates for heights in even-
mium trigonal prisms, are quite longer than the "existing" heights, Ge3−Ge4, Ge2−Ge5, and Ge2−Ge3, Ge4−Ge5, respectively. The similarities in shape and distances between the four clusters in Cs8Ge20 and the one in K+[−222−2,2,2-crypt][Ge9−] (Ge9) support the assumption that the latter is indeed Ge9−.

This is contrary to a recent suggestion that the two clusters in the crypt-salt are both Ge8− similar to the recently discovered Sn6+[−222−2,2,2-crypt][Sn6−]3+ and K+[−222−2,2,2-crypt][PB6−]3+ (PB6−), respectively, as well as to Ge8− in K+[−222−2,2,2-crypt][PB6−]3+ (PB6−) and K+[−222−2,2,2-crypt][Ge9−].

The Cs8Ge20 compound is a semiconductor (or an insulator) according to its magnetic susceptibility (temperature independent and near zero, see Experimental Section) and its appearance (semitransparent, ruby-red color).

The Cs−Ge and Rb−Ge phase diagrams are quite uncertain especially in the regions with high alkali metal content.11,12 There are conflicting reports on the number of Cs−Ge and Rb−Ge compounds. Three possible stoichiometries, A2Ge, A3Ge2, and A6Ge3 (A = Rb or Cs), are suggested in each phase diagram, but only CsGe and RbGe have been structurally characterized. The compounds with the stoichiometries closest to A2Ge (30.8 at % alkali-metal) would be A2Ge (20 at % alkali metal), which melt congruently at 990 °C and 1110 °C for Cs and Rb, respectively.

The absence of large naked clusters of group 14 in the solid state may be explained by the large ratio of nuclearity to charge. According to Wade’s rules delahedral clusters of this group will have charges of −2, −4, and −6 for closo, nido, and arachno species, respectively. It is important to note that these charges are independent of the nuclearity of the cluster. The charge balancing cations therefore may not be enough to efficiently keep apart (shield) large clusters. This is especially true for the smaller alkali metals such as Na and K which have been traditionally used as counterions. The effect is even more pronounced when the corresponding tetrel is among the heaviest of the group (Sn or Pb), which results in even larger clusters. In the crypt salts the large alkali metal cryptate is sufficient to separate the clusters efficiently. The new compounds are most likely the result of the combination of large cations (cesium or rubidium) and clusters of the small germanium. Despite the relatively high nuclearity and the relatively small negative charge of −4, the clusters are small enough that four large cations can separate them efficiently.

Experimental Section

Synthesis: Ruby-red semitransparent Cs8Ge20 was initially isolated and its structure determined from a reaction of Cs, Ge, compound is a semiconductor (or an insulator) with Rb1.064 for 5128 independent reflections with I>3o, (R1/wR2

Keywords: caesium · clusters · germanium · solid-state structures · Zintl phases


[10] The use of "near" here (after J. D. Corbett in ref. [2]) is to distinguish solids made by solid-state reactions from "molecular" solids crystallized from solution.


