

FARADAY COMMUNICATIONS

Homoatomic Polyanions of Post-transition Elements

Synthesis, Structure and Characterization of the Paramagnetic Nonagermanide ($3-$) Ion Ge_9^{3-} , a C_{2v} Cluster with an odd Skeletal Electron Count

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The salt $\text{K}_3(2,2,2\text{-cryptand})_3(\text{PPh}_3)_3\text{Ge}_9$ has been obtained by complexation of the $\text{KGe}_{1.8}$ alloy by 2,2,2-cryptand in ethylenediamine with solute triphenylphosphine. The structure of the anion has been determined crystallographically and the results are supported by EPR and extended Hückel calculations.

So far, many homopolyatomic Zintl anions have been isolated in the solid state, using the procedure described by Corbett:¹ Sn_4^{2-} ,² Pb_2^{2-} and Sn_2^{2-} ,³ Sb_7^{3-} ,^{4,5} Te_3^{2-} ,⁶ Bi_4^{2-} ,⁷ Sb_4^{2-} ,⁵ As_3^{1-} ,⁸ Sn_9^{3-} ⁹ and As_2^{4-} ,¹⁰ all of which except Sn_9^{3-} exhibit the customary diamagnetism. Sn_9^{3-} was found to be a 21-skeletal electron cluster which was confirmed to be paramagnetic by EPR and magnetic susceptibility measurements.⁹ For germanium, at least three varieties of crystal were obtained in the past by Corbett and co-workers. Only the structure of the compound $\text{K}_6^+(2,2,2\text{-cryptand})_6\text{Ge}_9^{4-}\cdot 2.5\text{en}$ has been established;¹¹ this compound is characterized by two kinds of anion: the tricapped triangular prismatic (C_{2v} , rather than D_{3h}) Ge_9^{2-} with 10 skeletal electron pairs (S.E.P.) and the monocapped square antiprismatic (C_{4v}) Ge_9^{4-} anion with 11 S.E.P.

An alloy of stoichiometry $\text{KGe}_{1.8}$ reacts with 2,2,2-cryptand in ethylenediamine. The brown–green dichroic solution turns instantaneously red when treated with PPh_3 . After a few hours, black flat crystals are deposited on the bottom of the reactor. Slight evaporation of the remaining solution leads to a large amount of dark-red rods. Only the latter type of crystal was suitable for X-ray diffraction studies.[†]

The centrosymmetric unit cell contains six $\text{K}^+(2,2,2\text{-cryptand})$ cations and two neutral PPh_3 molecules and the anion is presumed to have a $3-$ charge. The EPR spectrum of a single crystal that exhibits a single resonance ($g = 1.9989$) confirms the paramagnetic character of the compound in agreement within the $3-$ charge of the anion, which is then described as a 21 skeletal-electron cluster.

Ge_9^{3-} is depicted in Fig. 1 as a tricapped non-regular trigonal prism, in fact, the prism heights of 2.824(3), 3.202(4) and 3.268(4) Å indicate a relatively strong distortion from the ideal D_{3h} tricapped trigonal prism towards a C_{2v} configuration. This may appear surprising compared to the isoelec-

tronic anion Sn_9^{3-} ,⁹ which has been found to deviate only slightly from the ideal D_{3h} configuration.

With 21 skeletal electrons, Ge_9^{3-} is intermediate between Ge_9^{2-} (20 e) and Ge_9^{4-} (22 e). Ge_9^{2-} is a tricapped trigonal prism of which one height is elongated by 0.33 Å (C_{2v}) and the Ge_9^{4-} configuration is quite close to the ideal (C_{4v}), monocapped square antiprism. Conversely, the Ge_9^{2-} anions with two additional electrons will go from C_{2v} to C_{4v} , undergoing a supplementary elongation by 0.41 Å of its prism height to form a square base.

Corbett has shown that the height-to-edge ratio ($h:e$) of the trigonal prism for D_{3h} or pseudo- D_{3h} nine-atom clusters provides the best correlation of configuration with the electron count. A mean ratio of 1.03 has been found for the 20 e family ($\text{B}_9\text{H}_9^{2-}$,¹³ TiSn_8^{3-} ¹⁴ and Ge_9^{2-} ¹¹), 1.08 for the 21 e, Sn_9^{3-} cluster and 1.15 for Bi_9^{5+} ¹⁵ (22 e). The same calculation gives an $h:e$ ratio of 1.17 for Ge_9^{3-} , which is close to that calculated (1.18) for the C_{4v} , 22 e Ge_9^{4-} on the basis of its converse trigonal prism. Complementarily, the comparison of some dihedral angles has been put forward by Corbett¹⁵ as a useful guide for configurational discussions. The three most useful angles are those involving two atoms describing a height of the prism and the corresponding capping atoms (for example 4–6–8 vs. 4–6–9 in Fig. 1).

For a D_{3h} species, the dihedral angles are ca. 20° (Table 1), for Ge_9^{4-} the dihedral angle corresponding to the square base is 5° while the angles relative to the elongated heights are 14 and 17° for Ge_9^{3-} . Curiously both Ge_9^{3-} and Ge_9^{4-} present a dihedral angle of 32°, which nearly corresponds to the sums (31 and 29°, respectively) of the other two. Since the elongation of one of the prism heights and flattening of the corresponding dihedral angle (8°) has long been considered as an inexplicable aberration for Ge_9^{2-} , and a puzzling problem has been encountered in the case of Ge_9^{3-} , extended Hückel MO calculations have been performed for Ge_9^{3-} , Ge_9^{2-} and Ge_9^{4-} .

Ge_9^{2-} (C_{2v}) has a HOMO–LUMO gap of only 0.9 eV, with the LUMO (b_1) essentially σ antibonding along the trigonal prism heights and π bonding within the prism bases and along cap to prism edges. In Ge_9^{3-} , this orbital is lowered by 0.5 eV to become the HOMO (b_1) with less σ antibonding along the shortest prism height (2.82 Å), π bonding at the prism bases and caps to edges and in addition further stabilization by the appearance of σ bonding within the prism bases. The paramagnetic character is not incompatible with the one-electron occupation of the HOMO (b_1) with a HOMO–LUMO separation of 4.42 eV, of the order of that observed for Ge_9^{4-} (4.93 eV). For Ge_9^{3-} (C_{2v}), the HOMO (b_1) then lies just 0.4 eV above that which could be the HOMO (a_1) of a 20 e species. Calculations have been performed in the

[†] Crystal data: $\text{K}_3(2,2,2\text{-cryptand})_3(\text{PPh}_3)_3\text{Ge}_9$, $M_r = 2131.1$, triclinic, space group $P\bar{1}$, $a = 14.356(4)$ Å, $b = 14.994(3)$ Å, $c = 25.641(5)$ Å, $\alpha = 105.65(1)^\circ$, $\beta = 84.76(3)^\circ$, $\gamma = 115.83(3)^\circ$, $Z = 2$, $F(000) = 2202$, $D_c = 1.48$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 31.6$ cm⁻¹. Intensity data were collected by the $\omega - \theta$ technique on a Nonius CAD-4 diffractometer in the range $4 \leq 2\theta/^\circ \leq 44$ [11 529 unique reflections of which 5135 had $I > 3\sigma(I)$]. The data were corrected for background and Lorentz polarization and numerical absorption corrections were applied. The structure was solved by direct methods and refined by the full-matrix least-squares of to a final R of 0.083 ($R_w = 0.089$) with anisotropic thermal parameters for germanium, potassium and phosphorus atoms, isotropic for light atoms; atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

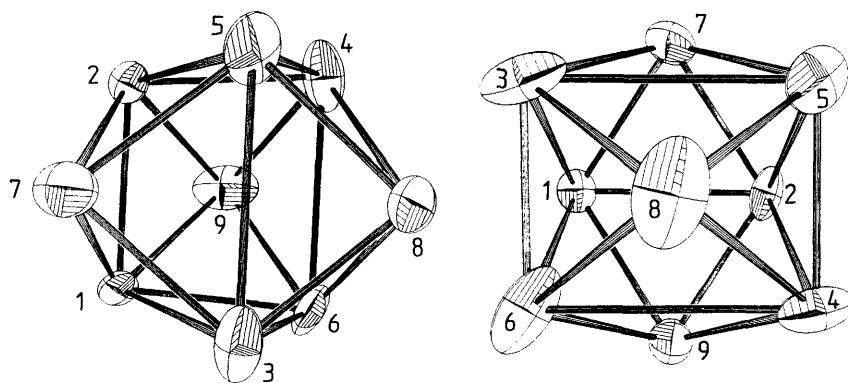


Fig. 1 Two views of the geometry of the Ge_9^{3-} in $\text{K}_3(2,2,2\text{-cryptand})_3(\text{PPh}_3)_3\text{Ge}_9$. Thermal ellipsoids are shown at the 50% probability level. Interatomic distances (Å): Ge(1)–Ge(2) 2.824(3), Ge(1)–Ge(3) 2.721(4), Ge(1)–Ge(6) 2.679(4), Ge(1)–Ge(7) 2.579(4), Ge(1)–Ge(9) 2.552(4), Ge(2)–Ge(4) 2.687(4), Ge(2)–Ge(5) 2.705(4), Ge(2)–Ge(7) 2.561(3), Ge(2)–Ge(9) 2.578(4), Ge(3)–Ge(5) 3.202(4), Ge(3)–Ge(6) 2.545(4), Ge(3)–Ge(7) 2.534(4), Ge(3)–Ge(8) 2.568(4), Ge(4)–Ge(5) 2.537(4), Ge(4)–Ge(6) 3.268(4), Ge(4)–Ge(8) 2.584(4), Ge(4)–Ge(9) 2.539(4), Ge(5)–Ge(7) 2.536(4), Ge(5)–Ge(8) 2.572(4), Ge(6)–Ge(8) 2.585(4), Ge(6)–Ge(9) 2.562(4).

alternative idealized D_{3h} configuration using an $h : e$ ratio of 1.08 found for the 21 e Sn_9^{3-} species. For germanium, this configuration appears to be less favourable since the sum of one-electron energies is 1 eV lower and, although the HOMO–LUMO separation would be a little larger in the latter case (5.1 against 4.4 eV), the HOMO (a_2'') would then be 1.3 eV above the e' orbital (HOMO for the ideal D_{3h} , 20 e species). Other calculations in the D_{3h} configuration with $h : e$ ranging from 1.08 to 1.02 proved no more satisfactory.

In conclusion, the C_{2v} configuration for Ge_9^{3-} , i.e. a strong deviation from D_{3h} by the elongation of two prism heights, is very likely. This elongation cannot be the result of disorder produced by the 50 : 50 occupation of the crystallographic site by two Ge_9^{2-} and Ge_9^{4-} anions in this case, as some of the thermal ellipsoids would be larger and would show some preferential orientation. Furthermore, as indicated by computed interatomic distances, the elongation cannot be pro-

duced by electrostatic interactions between either the anion and cations, or the anion and the lone pair of the phosphine molecule [$r(\text{Ge}–\text{P}) > 7.9 \text{ Å}$].

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Table 1 Characteristic dihedral angles ($^\circ$) and $h : e$ ratios for some nine-atom clusters

cap to cap (vicinal)					$h : e$
D_{3h}	$\{\text{Bi}_9^{5+}$	22	22	22	1.15
	$\{\text{Sn}_9^{3-}$	17	18	18	1.08
C_{2v}	$\{\text{Ge}_9^{2-}$	8	25	23	1.10
	$\{\text{Ge}_9^{3-}$	14	32	17	1.17
C_{4v}	Ge_9^{4-}	5	32	24	1.18

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