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The *closo*-Ge_5^{2-} Anion: Synthesis, Crystal Structure, and Raman Spectrum of $(2,2,2\text{-crypt-}K^+)_2Ge_5^{2-}\cdot$THF

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The isolation and structural characterization of the *closo*-Ge_5^{2-} cluster anion by X-ray crystallography and Raman spectroscopy is reported, completing the series of five-atom homopolyatomic anions of the group 14 elements, M_5^{2-} (M = Ge, Sn, Pb). The *closo*-Ge_5^{2-} anion was obtained as the $(2,2,2\text{-crypt-}K^+)_2Ge_5^{2-}\cdot$THF salt which crystallizes in the triclinic system, space group P1, in a unit cell of dimensions $a = 10.9657(4)$ Å, $b = 12.1750(5)$ Å, $c = 12.9142(5)$ Å, $\alpha = 62.163(1)°$, $\beta = 67.776(1)°$, and $\gamma = 84.187(1)°$. The trigonal bipyramidal geometry observed for the Ge_5^{2-} anion ($\sim D_{3h}$ point symmetry) is in accord with that predicted by Wade's rules for a $2n + 2$ skeletal electron system and has been observed for the Sn_5^{2-} and Pb_5^{2-} homologues and for the isovalent Tl_5^{7-} and Bi_5^{3+} ions. The Raman spectrum of the Ge_5^{2-} anion is compared and assigned by analogy with that of the Bi_5^{3+} cation.

Introduction

Homopolyatomic main-group element anions were electrochemically prepared by Zintl and co-workers[1−4] in the 1930's and identified by potentiometric titrations of sodium/liquid ammonia solutions with salts of the main-group elements. Evaporation of ammonia from these solutions resulted in the formation of amorphous amine complexes which lost ammonia forming intermetallic phases, thus precluding the isolation and characterization in the solid state of the species present in solution.[4]

Although electrochemical preparations of homopolyatomic germanium anions were unsuccessful,[1,3] Zintl and Kaiser[3] generated pale brown solutions by ammonia extraction of sodium−germanium alloys, while Johnson and Wheatly[5] reported that the reaction of sodium and finely divided germanium in liquid ammonia produced an intense red solution. Diehl *et al.*[6] reported that the sodium−germanium alloy $NaGe_2$ slowly dissolved in warm ethylenediamine (en) and copper-colored crystals of composition $Na_4Ge_9\cdot5$en were isolated. A general route to the stabilization of homopolyatomic anions was discovered by Corbett and co-workers[7] and employs the use of 2,2,2-crypt as a sequestering agent for the alkali metal cations in order to prevent electron transfer from the anions to the cations upon removal of the solvent. More recently, the use of 2,2,2-crypt allowed the isolation and structural characterization of the homopolyatomic germanium anions Ge_4^{2-},[8] Ge_9^{n-} (n = 2,[9] 3,[10,11] 4[9]), and Ge_{10}^{2-}.[10]

To date, trigonal bipyramidal *closo*-M_5 clusters containing group 13 (Tl_5^{7-}),[12,13] group 14 (Sn_5^{2-} and Pb_5^{2-}),[14] and group 15 (Bi_5^{3+})[15] metals have been synthesized and structurally characterized in the solid state. Of these clusters, only Bi_5^{3+} has been characterized in solution by spectroscopic methods.[16]

The present work reports the preparation and structural characterization of the Ge_5^{2-} anion in $(2,2,2\text{-crypt-}K^+)_2Ge_5^{2-}\cdot$THF by X-ray crystallography and solid-state Raman spectroscopy. The isolation of Ge_5^{2-} completes the series of group 14 five-atom cluster anions.

Results and Discussion

Synthesis of $(2,2,2\text{-crypt-}K^+)_2Ge_5^{2-}\cdot$THF. The experimental approach involved the formation of $KGe_{1.67}$ by fusion of the elements followed by extraction of the powdered alloy in en in the presence of a stoichiometric deficit of 2,2,2-crypt with respect to K^+ (K^+:2,2,2-crypt = 1.00:0.44). Orange-colored single crystals were isolated from the en solution upon addition of tetrahydrofuran (THF). The synthetic approach used to isolate $(2,2,2\text{-crypt-}K^+)_2Ge_5^{2-}\cdot$THF differs from that used to prepare other salts containing germanium cluster anions. The $(2,2,2\text{-crypt-}K^+)_6Ge_9^{2-}Ge_9^{4-}\cdot2.5$en salt[9] was obtained upon addition of a slight excess of 2,2,2-crypt (with respect to K^+) to an en extract of the $KGe_{1.8}$ alloy, while addition of triphenylphosphine and tetrakis(triphenylphosphine)nickel(0) to this en solution led to the isolation of $(2,2,2\text{-crypt-}K^+)_3P(C_6H_5)_3\text{-}Ge_9^{3-}$ and $(2,2,2\text{-crypt-}K^+)_2Ge_{10}^{2-}$, respectively.[10,11] The amount of 2,2,2-crypt added to an en alloy extract can dramatically influence the nature of the anions that are obtained, as exemplified by the isolation of the Pb_9^{4-} and Pb_9^{3-} anions;[17] the paramagnetic Pb_9^{3-} anion was isolated in the presence of a stoichiometric excess of 2,2,2-crypt while a stoichiometric deficit of 2,2,2-crypt was required for the isolation of the Pb_9^{4-} anion.

X-ray Crystal Structure of $(2,2,2\text{-crypt-}K^+)_2Ge_5^{2-}\cdot$THF. Details of the data collection parameters and other crystal-

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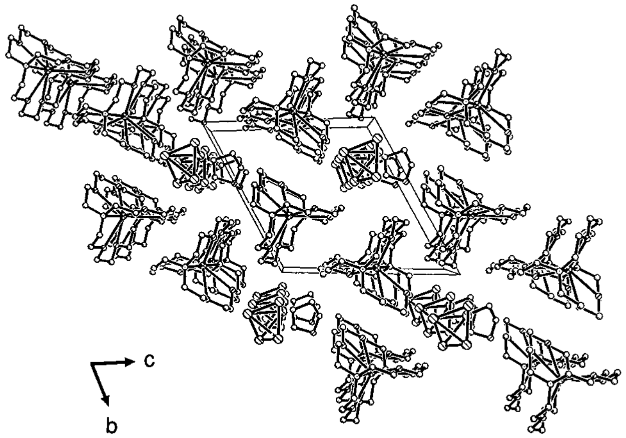

Figure 1. Unit cell of (2,2,2-crypt-K^+)$_2$$Ge_5^{2-}$·THF viewed down the *a*-axis. For clarity, only the non-hydrogen atoms have been included.

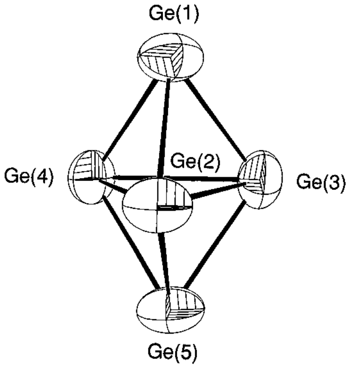

Figure 2. View of the Ge_5^{2-} anion in (2,2,2-crypt-K^+)$_2$$Ge_5^{2-}$·THF. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Summary of Crystal Data and Refinement Results for (2,2,2-crypt-K^+)$_2$$Ge_5^{2-}$·THF

chem formula $C_{40}H_{80}Ge_5K_2N_4O_{13}$	fw 1266.23
$a = 10.9657(4)$ Å	space group $P1$ (No. 1)
$b = 12.1750(5)$ Å	$T = 24$ °C
$c = 12.9142(5)$ Å	$\lambda = 0.710\ 73$ Å
$\alpha = 62.163(1)°$	$\rho_{calcd} = 1.496$ g cm^{-1}
$\beta = 67.776(1)°$	$\mu = 28.5$ cm^{-1}
$\gamma = 84.187(1)°$	$R_1{}^a = 0.0432$
$V = 1405.4(1)$ Å^3	$wR_2{}^b = 0.1068$
$Z = 1$	

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$.

lographic information are given in Table 1. The final atomic coordinates and equivalent isotropic thermal parameters for all non-hydrogen atoms are given in Table 2. The contact distances and angles in the Ge_5^{2-} anion are listed in Table 3.

The structure of the (2,2,2-crypt-K^+) cation is similar to that determined previously in the (2,2,2-crypt-K^+)$_2$$Pb_2Te_3^{2-}$·$CH_3CN$ salt,[18] which also crystallizes in the $P1$ space group, with average K−O and K−N distances of 2.826(14) and 2.943(9) Å, respectively. A complete list of bond lengths and angles in the cations and THF is provided in the Supporting Information.

The crystal structure consists of a Ge_5^{2-} anion, (2,2,2-crypt-K^+) cations, and a THF solvent molecule. In contrast to the high symmetry and centrosymmetric packing in the (2,2,2-crypt-K^+)$_2$$M_5^{2-}$ (M = Sn, Pb) salts, which contain positionally disordered M_5^{2-} anions,[15] the packing in the unit cell of (2,2,2-crypt-K^+)$_2$$Ge_5^{2-}$·THF is noncentrosymmetric and contains a well-ordered Ge_5^{2-} anion. The packing consists of layers of (2,2,2-crypt-K^+) cations separated by layers of Ge_5^{2-} anions and THF, as shown in Figure 1.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for the Non-Hydrogen Atoms in (2,2,2-crypt-K^+)$_2$$Ge_5^{2-}$·THF

	x	*y*	*z*	*U*(eq)^a
Ge(1)	5319(1)	1632(1)	9138(1)	96(1)
Ge(2)	5284(1)	2414(1)	7001(1)	86(1)
Ge(3)	5269(1)	3935(1)	7996(1)	94(1)
Ge(4)	3149(1)	2346(1)	8959(1)	85(1)
Ge(5)	3869(1)	4153(1)	6804(1)	101(1)
K(1)	1468(1)	9557(1)	5571(1)	54(1)
N(100)	4349(4)	9558(4)	4699(4)	68(1)
C(101)	4763(6)	9081(7)	3771(7)	90(2)
C(102)	4205(7)	9655(7)	2779(6)	93(2)
O(103)	2811(4)	9377(4)	3326(3)	74(1)
C(104)	2258(8)	9992(6)	2366(6)	88(2)
C(105)	826(8)	9684(7)	2934(7)	92(2)
O(106)	203(4)	10064(4)	3879(4)	77(1)
C(107)	−1193(7)	9839(8)	4372(8)	100(2)
C(108)	−1795(6)	10241(8)	5374(8)	99(2)
N(109)	−1418(4)	9548(5)	6466(5)	82(1)
C(110)	−2003(6)	8280(7)	7180(8)	113(3)
C(111)	−1514(7)	7444(8)	8196(8)	114(3)
O(112)	−129(5)	7370(4)	7639(4)	88(1)
C(113)	424(8)	6703(6)	8575(6)	94(2)
C(114)	1768(8)	6506(6)	7998(7)	97(2)
O(115)	2584(4)	7681(3)	7181(4)	76(1)
C(116)	3914(7)	7512(6)	6635(7)	87(2)
C(117)	4713(6)	8736(7)	5774(7)	90(2)
C(118)	4927(6)	10853(7)	4090(8)	97(2)
C(119)	4320(8)	11553(7)	4817(9)	112(2)
O(120)	2990(4)	11709(4)	4886(5)	91(1)
C(121)	2382(11)	12256(8)	5716(9)	119(3)
C(122)	1059(11)	12411(9)	5862(12)	139(4)
O(123)	292(5)	11208(4)	6513(5)	103(2)
C(124)	−1059(8)	11391(9)	6686(10)	116(3)
C(125)	−1819(7)	10159(8)	7275(9)	110(2)
K(2)	927(1)	16250(1)	2195(1)	55(1)
N(200)	−1991(4)	16296(4)	3095(5)	72(1)
C(201)	−2443(5)	16652(7)	4114(6)	82(2)
C(202)	−1844(6)	16004(6)	5076(6)	84(2)
O(203)	−456(4)	16361(3)	4520(3)	67(1)
C(204)	140(7)	15770(6)	5417(5)	82(2)
C(205)	1556(7)	16154(6)	4840(6)	86(2)
O(206)	2184(4)	15795(4)	3870(4)	75(1)
C(207)	3581(7)	16048(8)	3358(7)	99(2)
C(208)	4192(6)	15566(9)	2413(7)	101(2)
N(209)	3828(4)	16214(5)	1291(4)	77(1)
C(210)	4437(6)	17503(8)	510(7)	99(2)
C(211)	3888(7)	18294(7)	−485(6)	98(2)
O(212)	2533(4)	18382(3)	107(3)	76(1)
C(213)	1986(7)	19201(5)	−794(5)	81(2)
C(214)	616(7)	19402(5)	−128(6)	81(2)
O(215)	−207(4)	18251(3)	643(4)	74(1)
C(216)	−1518(7)	18429(6)	1244(7)	87(2)
C(217)	−2359(6)	17174(6)	2032(7)	86(2)
C(218)	−2595(6)	15033(6)	3587(7)	86(2)
C(219)	−1952(7)	14411(7)	2783(8)	97(2)
O(220)	−637(4)	14189(4)	2713(4)	83(1)
C(221)	−20(8)	13607(6)	1954(7)	91(2)
C(222)	1324(9)	13366(6)	1915(7)	97(2)
O(223)	2101(4)	14490(4)	1392(4)	86(1)
C(224)	3445(7)	14292(8)	1190(8)	104(2)
C(225)	4228(6)	15522(8)	559(7)	98(2)
O(300)	7985(23)	4062(20)	9934(21)	324(9)
C(301)	7109(15)	2977(14)	10819(14)	176(5)
C(302)	7940(19)	2045(18)	10800(17)	217(7)
C(303)	8944(18)	2499(17)	9451(17)	198(6)
C(304)	8937(26)	3663(24)	8974(24)	270(10)

^{a} *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The trigonal bipyramidal geometry (∼D_{3h} point symmetry) exhibited by the Ge_5^{2-} anion (Figure 2) has been observed for its group 14 homologues Sn_5^{2-} and Pb_5^{2-} [15] and for the isovalent Bi_5^{3+} [16] and Tl_5^{7-} [12,13] ions. The Ge_5^{2-} anion and related M_5 clusters contain 22 valence (s and p) electrons, of which 10 are

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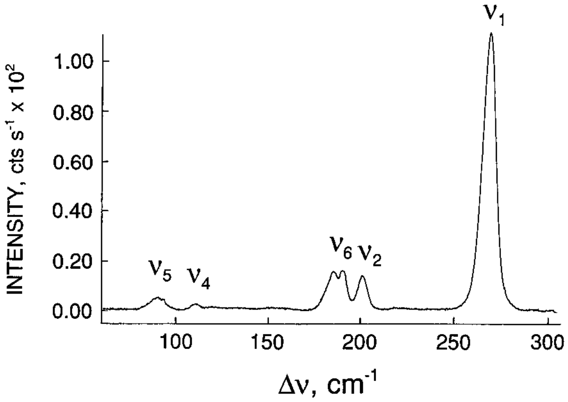

Figure 3. Raman spectrum of the Ge_5^{2-} anion in (2,2,2-crypt-K^+)$_2$-Ge_5^{2-}·THF recorded in a glass capillary on crystals at room temperature using 647.1-nm excitation.

Table 3. Contacts (Å) and Angles (deg) for the Ge_5^{2-} Anion in (2,2,2-crypt-K^+)$_2$$Ge_5^{2-}$·THF

Contacts (Å)

Ge(1)−Ge(2)	2.479(1)	Ge(1)−Ge(3)	2.491(1)	Ge(1)−Ge(4)	2.506(1)
Ge(2)−Ge(3)	2.698(1)	Ge(2)−Ge(4)	2.691(1)	Ge(2)−Ge(5)	2.466(1)
Ge(3)−Ge(4)	2.678(1)	Ge(3)−Ge(5)	2.474(1)	Ge(4)−Ge(5)	2.486(1)

Angles (deg)

Ge(2)−Ge(1)−Ge(3)	65.75(3)	Ge(2)−Ge(1)−Ge(4)	65.35(3)
Ge(3)−Ge(1)−Ge(4)	64.81(3)	Ge(1)−Ge(2)−Ge(5)	103.26(3)
Ge(1)−Ge(3)−Ge(5)	102.67(3)	Ge(1)−Ge(4)−Ge(5)	101.91(3)
Ge(2)−Ge(3)−Ge(4)	60.08(3)	Ge(3)−Ge(2)−Ge(4)	59.59(3)
Ge(3)−Ge(4)−Ge(2)	60.33(3)	Ge(2)−Ge(5)−Ge(3)	66.19(3)
Ge(2)−Ge(5)−Ge(4)	65.84(3)	Ge(3)−Ge(5)−Ge(4)	65.35(3)

allocated to the *exo*-skeletal electron pairs leaving 12 skeletal bonding electrons so that the cluster obeys the simplified $(2n + 2)$ rule for *closo*-clusters.[19,20]

The Ge−Ge contacts range from 2.466(1) to 2.698(1) Å and are comparable to those found in the homopolyatomic germanium clusters [Ge_9^{n-} ($n = 2$, 2.528(6)−2.811(6) Å;[9] $n = 3$, 2.534(4)−3.268(4) Å;[10,11] $n = 4$, 2.533(7)−2.962(7) Å[9]) and Ge_{10}^{2-} (2.504(6)−2.946(7) Å)[10]] and to the Ge−Ge bonds found in [((CH$_3$)$_3$Si)$_3$GeCl]$_4$·C$_6$H$_6$ (2.509(1)−2.558(2) Å)[21] and Ge$_4$-Ph$_{10}$·2C$_6$H$_6$ (2.463(2) Å).[22] The Ge−Ge contacts from the apical Ge(1) and Ge(5) atoms to the equatorial Ge(2), Ge(3), and Ge(4) atoms are shorter than those between the equatorial atoms by 0.21 Å. This trend has also been observed in Sn_5^{2-}, Pb_5^{2-}, Tl_5^{7-}, and Bi_5^{3+} in which the differences between these distances generally are similar, i.e., 0.23 (Sn),[14] 0.24 (Pb),[14] 0.09−0.47 (Tl),[12] and 0.31 (Bi)[15] Å. As expected, the Ge−Ge−Ge angles in Ge_5^{2-} are comparable to the corresponding angles observed in the Sn_5^{2-} and Pb_5^{2-} clusters.[14]

Vibrational Spectrum of the Ge_5^{2-} Anion. The solid-state Raman spectrum of (2,2,2-crypt-K^+)$_2$$Ge_5^{2-}$·THF is shown in Figure 3 and covers only that region in which the fundamental vibrations of the anion are found. The observed frequencies and their assignments are listed in Table 4.

The vibrational modes of the gas-phase Ge_5^{2-} anion (D_{3h} point symmetry) belong to the irreducible representation $\Gamma_{vib} = 2A_1' + A_2'' + 2E' + E''$. A total of 6 vibrational bands (9 modes) are expected of which 5 bands ($2A_1' + 2E' + E''$) are Raman active and 3 bands ($A_2'' + 2E'$) are infrared active. Correlation of the free anion symmetry (D_{3h}) to the crystallographic anion site symmetry (C_1) and the unit cell symmetry (C_1) indicated that the vibrational modes of the anion in the unit cell should, in principle, be Raman and infrared active. However, failure to observe the counterpart to the formally infrared active A_2'' mode in the Raman spectrum indicates that vibrational coupling within the unit cell is not significant. Consequently, vibrational assignments for the Ge_5^{2-} anion of (2,2,2-crypt-K^+)$_2$$Ge_5^{2-}$·THF are for the gas-phase Ge_5^{2-} anion and were made by analogy with those of the isovalent Bi_5^{3+} cation.[16] Both the solid-state infrared and Raman spectra, including solution Raman depolarization measurements, have been obtained for Bi_5^{3+} (Table 4), and the assignments have been confirmed by a normal coordinate analysis. Although the vibrational spectra of Sn_5^{2-} and Pb_5^{2-} have not been reported, their calculated vibrational frequencies have been reported along with those of Bi_5^{3+}, using extended Hückel and Hartree−Fock methods.[15] With the exception of $\nu_4(E')$ and $\nu_5(E')$ for Bi_5^{3+}, the remaining calculated frequencies at the MP2 level agree, to within ±8 cm^{-1}, with the experimental values. Because a better overall agreement between calculated and experimental values could be obtained by interchanging $\nu_2(A_1')$ and $\nu_4(E')$, a reassignment of the experimental spectrum was suggested. The suggested reassignment, however, requires $\nu_2(A_1')$ to be infrared active contradicting the vibrational selection rules, which require $\nu_2(A_1')$ to be Raman active and $\nu_4(E')$ to be both Raman and infrared active. In addition, the experimental vibrational activities in the solid-state infrared and Raman spectra and solution Raman polarization measurements of the Bi_5^{3+} cation do not support this interchange of vibrational modes. Thus, the assignments originally reported for the experimental vibrational spectra of Bi_5^{3+} have been retained.

Table 4. Vibrational Frequencies and Assignments for Ge_5^{2-} in (2,2,2-crypt-K^+)$_2$$Ge_5^{2-}$·THF and Bi_5^{3+} in $Bi_5(AsF_6)_3$·2SO$_2$ and in $Bi_5(AlCl_4)_3$[a]

frequency, cm^{-1}				
	$Bi_5(AlCl_4)_3$			
$Bi_5(AsF_6)_3$· 2SO$_2$ solid	solid	soln (NaAlCl$_4$, 180 °C)	Ge_5^{2-}	assgn[b]
142 (10.0)	146 (4.2), 139 (5.3)[c]	135 (3.6) p	269 (10.0)	ν_1 (A_1')
124 (1.8)	125 (1.3), 121 (1.3)[c]	119 (4.1) p	201 (1.2)	ν_2 (A_1')
130 s, sp[d]	125 s, sp[d]			ν_3(A_2'')
103 (3.8), 98 (4.1)[c]	100 (4.0)	97 (1.2) dp	190 (1.4), 185 (1.4)	ν_6(E'')
64 (8.5)	64 (10.0)	62 (2.0) p	111 (0.2)	ν_4(E')
52 (5.2)	51 (4.8)	48 (1.9) p	91 (0.4)	ν_5(E')

[a] Relative intensities are given in parentheses. The vibrational frequencies for the Bi_5^{3+} cation are from ref (13). The symbols p and dp denote polarized and depolarized bands. [b] See Figure 4. [c] Factor-group split bands. [d] Obtained from an infrared spectrum. The symbols s and sp denote strong and sharp.

As expected, the Ge_5^{2-} anion modes were shifted to higher frequency relative to those of Bi_5^{3+} by virtue of the reduced mass effect (Table 4). Descriptions of the vibrational modes of the Ge_5^{2-} anion are depicted in Figure 4. The most intense band at 269 cm^{-1} is assigned to $\nu_1(A_1')$, the totally symmetric stretching mode of the Ge$_5$ cluster, and the band at 201 cm^{-1} is assigned to the totally symmetric stretching mode mainly associated with the apical Ge atoms. The degenerate modes, $\nu_4(E')$ and $\nu_5(E')$, are assigned to the bands at 111 and 91 cm^{-1}, respectively. The remaining degenerate mode, $\nu_6(E'')$, is split and appears at 185 and 190 cm^{-1}. The splitting of the doubly degenerate $\nu_6(E'')$ mode has also been observed in the Raman spectrum of the Bi_5^{3+} cation in $Bi_5(AsF_6)_3$·2SO$_2$ and is attributed to lowering of the free Ge_5^{2-} anion symmetry to C_1 site symmetry in the crystal.

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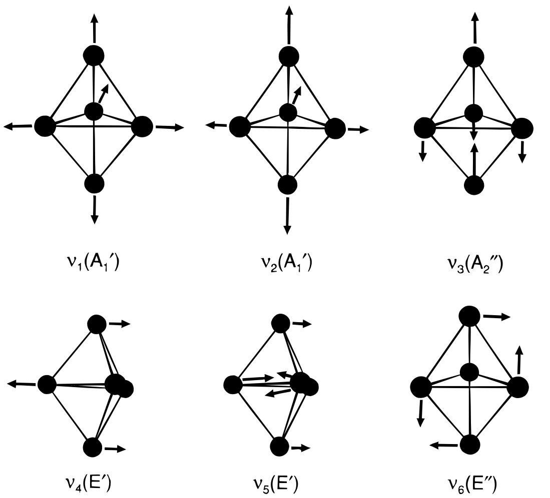

Figure 4. Vibrational modes of the Ge_5^{2-} anion.

Experimental Section

Apparatus and Materials. All manipulations were carried out under anhydrous and oxygen-free conditions on a glass vacuum line, equipped with glass/Teflon grease-free stopcocks (J. Young Scientific Glassware), and in a two-station nitrogen-atmosphere drybox (Vacuum Atmosphere Model DLX). Drybox moisture and oxygen levels were <0.1 ppm.

Potassium metal (MCB, >99%), treated as described previously,[17] germanium (Strem Chemicals, 99.999%), and 2,2,2-crypt (4,7,13−16,-21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; Merck, 99%) were dried in the evacuated port of the drybox for at least 45 min followed by exposure to the atmosphere of the drybox for at least 2 days prior to use. Ethylenediamine (Fisher, 99%) and tetrahydrofuran (Fisher, 99%) were initially dried over CaH_2 powder (MCB) and sodium wire, respectively, for several weeks and then vacuum distilled onto and stored over fresh CaH_2 and sodium for at least an additional 1 week prior to use.

Preparation of $KGe_{1.67}$. The alloy $KGe_{1.67}$ was prepared by fusing potassium (0.5661 g, 14.48 mmol) and germanium (1.7527 g, 24.15 mmol) in a dry quartz tube over a Meeker burner flame, until completely molten. After complete reaction, the alloy was allowed to cool and solidify and was transferred to the drybox where it was ground to a fine dark gray powder.

Preparation and Isolation of (2,2,2-crypt-K^+)$_2$$Ge_5^{2-}$·THF. The $KGe_{1.67}$ powder (0.0928 g, 0.579 mmol) was transferred into one arm of a two-arm Pyrex vessel and extracted in en in the presence of a nonstoichiometric amount of 2,2,2-crypt (0.0961 g, 0.255 mmol) with respect to K^+. After 1 week, the red solution was carefully decanted off the unreacted $KGe_{1.67}$ residue into the second arm of the reaction vessel. An excess of THF (1:1.5 v/v) was condensed under static vacuum at 0 °C into the first arm of the reactor. The reactor was allowed to stand for several months over which period the THF slowly vapor diffused into the en solution, resulting in the formation of orange parallelepiped-shaped crystals. The mother liquor was decanted back into the first arm of the Pyrex vessel and slowly pumped off under dynamic vacuum. The dry crystalline sample was transferred to a drybox equipped with a stereomicroscope and the reaction vessel cut open. Single crystals were sealed in 0.3−0.5 mm Lindemann glass capillaries.

Collection and Reduction of X-ray Data. Data were collected using a P4 Siemens diffractometer, equipped with a Siemens SMART 1K charge-coupled device (CCD) area detector (using the program SMART[23]) and a rotating anode using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The crystal-to-detector distance was 3.991 cm, and the data collection was carried out in a 512 × 512 pixel mode utilizing 2 × 2 pixel binning. A complete sphere of data was collected, to better than 0.8 Å resolution. Upon completion of the data collection, the first 50 frames were recollected in order to improve the decay corrections analysis. Processing was carried out by using the program SAINT,[24] which applied Lorentz and polarization corrections to three-dimensionally integrated diffraction spots. The program SADABS[25] was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections.

Solution and Refinement of the Structure. The XPREP program[26] was used to confirm the original cell and showed the lattice to be triclinic ($R_{int} = 0.0205$). The structure was solved in the $P1$ space group by using the direct methods procedure in the Siemens SHELXTL program,[26] which located the general positions of five germanium atoms, indicating the presence of a trigonal bipyramidal Ge_5^{2-} anion, and the positions of the potassium, carbon, nitrogen, and oxygen atoms of the two (2,2,2-crypt-K^+) cations. The full-matrix least-squares refinement of their positions and isotropic thermal parameters gave an R-factor of 0.195, and the successive difference Fourier synthesis revealed the general positions of carbon and oxygen atoms of the THF solvent molecule. Least-squares refinement of the positions and isotropic thermal parameters of the solvent molecule showed that the molecule was disordered over two positions. However, the two positions could not be completely resolved. The final refinement was obtained by refining the non-hydrogen atoms of the anion and the cations with anisotropic thermal parameters, setting the calculated positions of the hydrogen atoms [$d(\text{C}-\text{H}) = 0.96$ Å, $U(\text{H})$ fixed to $1.2U(\text{C})$], and by setting the weight factor to $1/[\sigma^2(F_o^2) + (0.0620P)^2 + 0.4889P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$, giving rise to a residual R_1, of 0.0432 ($wR_2 = 0.1068$). In the final difference map, the maximum and minimum electron densities were 0.47 and −0.36 e Å^3. The largest peaks were located near the disordered solvent.

Raman Spectroscopy. The Raman spectrum was recorded on a Jobin-Yvon Mole S-3000 triple spectrograph system equipped with a 0.32-m prefilter, adjustable 25-mm entrance slit, and a 1.00-m double monochromator. Holographic gratings were used for the prefilter (600 groves mm^{-1}, blazed at 500 nm) and monochromator (1800 groves mm^{-1}, blazed at 550 nm) stages. An Olympus metallurgical microscope (Model BHSM-L-2) was used for focusing the excitation laser beam to a 1-μm spot on the sample. The 647.1-nm line of a Kr ion laser was used for excitation of the sample. The spectrum was acquired at ambient temperature on crystals sealed inside a baked-out Pyrex melting point capillary. The spectrum was recorded by signal averaging with a Spectraview-2D CCD detector equipped with a 25-mm chip (1152 × 298 pixels) and at a laser power of 100 mW and slit settings corresponding to a resolution of 1 cm^{-1}. A total of 10 reads having 45 s integration times were used. The Raman spectrometer was frequency calibrated by using the 1018.3 cm^{-1} line of neat indene.[27]

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Supporting Information Available: Structure determination parameters for (2,2,2-crypt-K^+)$_2$$Ge_5^{2-}$·THF (Table S1), distances and angles in the (2,2,2-crypt-K^+) cations and THF (Table S2), anisotropic thermal parameters for (2,2,2-crypt-K^+)$_2$$Ge_5^{2-}$·THF (Table S3), and atomic coordinates for the hydrogen atoms (Table S4) (8 pages). X-ray crystallographic files, in CIF format, are available. Ordering and access information is given on any current masthead page.

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