Ge_5^{2-} Zintl anions: synthesis and crystal structures of $[K([2.2.2]\text{-crypt})]_2Ge_5\cdot 4NH_3$ and $[Rb([2.2.2]\text{-crypt})]_2Ge_5\cdot 4NH_3$

Christof Suchentrunk and Nikolaus Korber*

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The new compounds $[K(C_{18}H_{36}N_2O_6)]_2Ge_5\cdot 4NH_3$ (**1**) and $[Rb(C_{18}H_{36}N_2O_6)]_2Ge_5\cdot 4NH_3$ (**2**) were prepared by the extraction of a binary phase of the nominal composition $KGe_{1.67}$ and a ternary phase of the composition $Rb_{0.5}Cs_{0.5}Ge_{2.25}$ with liquid ammonia in the presence of cryptand [2.2.2]. The resulting crystalline materials were characterized by low temperature X-ray structure analysis. Compounds **1** and **2** contain isolated trigonal-bipyramidal Ge_5^{2-} cage anions, the symmetries of which were investigated and compared to the previously reported pentagermanide anion. Despite the nearly identical formulae, the two compounds are not isotypic, as the space group type changes from the acentric group *P*1 (no. 1) for the potassium compound to $P\bar{1}$ (no. 2) for the rubidium compound.

Introduction

The extraction of alloys between germanium and alkali metals with solvents like ethylenediamine and subsequent crystallization with the help of alkali metal cation ligands like crown ethers or cryptands is an established method for obtaining homoatomic polygermanide Zintl anions without any organic or organometallic substituents. In the majority of the reactions reported so far, this route leads to monomeric nonagermanide anions Ge_9^{x-} (x = 2, 3, 4),[1–3] which have the monocapped square-antiprismatic shape of the most commonly encountered Zintl anions of the group 14 elements. These nonagermanide cages can be linked to yield dimers, trimers, tetramers or to form infinite chains.[4–7] A comprehensive review on nonatetrelide cages was published by Fässler.[8] Beside the nonagermanides, other cages such as Ge_4^{2-} or Ge_{10}^{2-} can be isolated from solutions,[9,10] but they are far less common. Additionally, a Ge_5^{2-} pentagermanide anion was reported by Schrobilgen and Campbell in the compound $[K(C_{18}H_{36}N_2O_6)]_2Ge_5\cdot THF$, investigated using several methods including Raman spectroscopy.[11] Analogous dianions, which take the shape of rather regular trigonal bipyramids, have been reported for other group 14 elements, namely Si_5^{2-}, Sn_5^{2-} and Pb_5^{2-}.[12,13] There also exist similarly shaped isoelectronic homoatomic cages of other main group elements, examples are Tl_5^{7-} and Bi_5^{3+}.[14,15] Calculations using density functional theory showed the trigonal bipyramid with the point group symmetry D_{3h} to be the energetic minimum for the dianion Ge_5^{2-}.[16]

Despite this stability, Ge_5^{2-} anions seemed to be rather elusive, as only one compound had been reported so far. We were looking for additional pentagermanides that might be formed by extraction of alkali metal germanides with liquid ammonia. In this article, we report on the new compounds $[K(C_{18}H_{36}N_2O_6)]_2Ge_5\cdot 4NH_3$ (**1**) and $[Rb(C_{18}H_{36}N_2O_6)]_2Ge_5\cdot 4NH_3$ (**2**).

Experimental

All work was done excluding moisture and air in an atmosphere of purified argon. The compounds were prepared by extraction of binary or ternary phases with liquid ammonia in the presence of cryptand [2.2.2]. For the crystal preparation we adapted the technique described by Kottke and Stalke.[17] The thermally unstable (decomposition due to loss of ammonia above −20 °C) and moisture sensitive ammoniate crystals were transferred directly from the mother liquor to the diffractometer using an endcapped perfluoropolyether oil to protect them.

Synthesis

$[K(C_{18}H_{36}N_2O_6)]_2Ge_5\cdot 4NH_3$ (1). A mixture of 0.48 g (12.23 mmol) K and 1.5 g (20.65 mmol) Ge was heated in a glass ampoule to 450 °C (25 °C h^{-1}), annealed at 450 °C for 240 hours, and finally cooled to room temperature (25 °C h^{-1}). 0.15 g (0.17 mmol) of the resulting binary phase with the nominal composition $K_{5.38}Ge_9$ and 0.13 g (0.35 mmol) cryptand [2.2.2] (4,7,13,16,21,4-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane) were placed into a Schlenk tube and 30 cm^3 of sodium-dried liquid ammonia was added, yielding a dark-red solution. The reaction vessel was stored at −40 °C for four months. After this period, red needle-shaped crystals of (**1**) had precipitated at the vessel wall. Due to their extreme sensitivity to temperatures above −40 °C, as well as to air and moisture, only an orange-coloured, slightly decomposed crystal could be mounted on the diffractometer. No yield could be determined.

$[Rb(C_{18}H_{36}N_2O_6)]_2Ge_5\cdot 4NH_3$ (2). 0.26 g (3.04 mmol) Rb, 0.4 g (3.01 mmol) Cs and 1.0 g (13.77 mmol) Ge were heated in a stainless steel ampoule to 800 °C (20 °C h^{-1}), annealed at 800 °C for 3 hours, and finally cooled down to room temperature (30 °C h^{-1}). 0.15 g (0.14 mmol) of the resulting binary phase

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Institut für Anorganische Chemie der Universität Regensburg, Universitätsstrasse 31, 93053 Regensburg, Germany. E-mail: nikolaus.korber@chemie.uni-regensburg.de.; Fax: +49 941 9431812; Tel: +49 941 9434448

Table 1 Crystal data and refinement results for the compounds **1** and **2**

Empirical formula	$[K(C_{18}H_{36}N_2O_6)]_2 Ge_5 \cdot 4NH_3$	$[Rb(C_{18}H_{36}N_2O_6)]_2 Ge_5 \cdot 4NH_3$
Formula weight/g mol^{-1}	1262.3	1355.0
Crystal system	Triclinic	Triclinic
Space group	$P1$ (no. 1)	$P\bar{1}$ (no. 2)
a/Å	11.2887(9)	11.316(2)
b/Å	11.8949(9)	12.333(2)
c/Å	11.9433(9)	20.915(3)
α/°	117.911(8)	89.183(1)
β/°	98.650(9)	83.60(2)
γ/°	91.797(9)	78.26(2)
Volume/$Å^3$	1391.5(2)	2840.3(7)
Z	1	2
μ/mm^{-1}	2.876	4.374
Refl. coll./unique/obs. ($I > 2\sigma(I)$)	10669/8934/8001	36788/10249/7057
R_{int}	0.0293	0.0794
R_1 (all data)	0.0501	0.0671
wR_2 (all data)	0.1205	0.1014

of the nominal composition $Rb_2Cs_2Ge_9$ and 0.026 g (0.069 mmol) cryptand [2.2.2] were placed in a Schlenk tube and 30 cm^3 of sodium-dried liquid ammonia was added, yielding a deep-red solution. The reaction vessel was stored at −40 °C for 10 months. After this period red crystals of (**2**) were obtained.

Crystal structure determination†

The diffraction data were collected with graphite monochromated Mo-K_α (λ = 0.71073 Å) radiation on a STOE IPDS (imaging plate diffraction system) at −150 °C. For compound **1**, the data collection was made with a 0.8° oscillation step of φ, 360 s exposure time and 70 mm scanner distance. 242 frames were collected. For compound **2** data collection was made with a 0.8° oscillation step of φ, 420 s exposure time and 70 mm scanner distance. 410 frames were collected. The data were integrated with the STOE IPDS software. The structures were solved by direct methods (SHELXS-97) and refined on F^2 (SHELXL-97).[18] A DIFABS-type absorption correction was applied which is integrated into the PLATON program package.[19] All of the atoms, except the hydrogen atoms, were refined with anisotropic displacement parameters. The nitrogen atoms of ammonia were localised in the Fourier synthesis. The hydrogen atoms of the cryptand [2.2.2] and the ammonia molecules were inserted using a riding model. The selection of the space groups was certified using PLATON.[19] The crystal data and the details of the structure refinements are given in Table 1.

Results and discussion

The asymmetric unit of compound **1** consists of a Ge_5^{2-} anion (Fig. 1), two potassium cations, each of which is surrounded by a molecule of cryptand [2.2.2], and four additional molecules of ammonia of crystallization. As compound **1** crystallizes in the acentric space group $P1$ (no. 1), the Ge_5^{2-} anion cannot have any crystallographic symmetry. Nevertheless, a close inspection of the bond lengths and angles within the anion reveals a highly symmetric cage for which D_{3h} point group symmetry is a very good approximation.[20] The equatorial Ge–Ge contacts within the trigonal base Ge(2)–Ge(3)–Ge(4) range from 2.688(1) Å to 2.7039(9) Å and are remarkably longer than the axial bonds to the capping atoms Ge(1) and Ge(5) with 2.495(1) Å to 2.511(1) Å. The eq–eq/eq–ax length ratio is found to be 1.08, which is in good agreement with the ratio found for the anion of $[K(C_{18}H_{36}N_2O_6)]_2Ge_5 \cdot THF$.[11] The cage has 22 valence electrons, of which 12 are used for skeletal bonding. In accordance with Wade's rules,[21] the pentagermanide has the shape of a *closo*-cluster. In a simpler view of the chemical bonding, the 22 electrons can even be attributed to nine 2e2c bonds between the germanium atoms and two lone pairs at the capping atoms. The cages are arranged in distorted hexagonal layers with the $[K([2.2.2]\text{-crypt})]^+$ units filling the space between them (Fig. 2). Three of the adjacent $[K([2.2.2]\text{-crypt})]^+$ units shown in Fig. 2 are situated above, and the other three below the layer of the Ge_5^{2-} anions. The smallest distance between two cages is 7.438(1) Å. Due to the cryptands, cations and anions are completely separated. The K–O distances within the cryptand lie between 2.735(5) Å and 2.902(5) Å and the K–N distances between 2.955(6) Å and 2.994(6) Å.

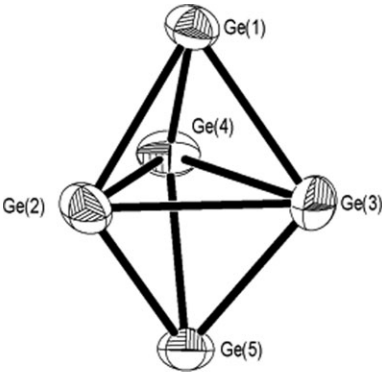

Fig. 1 The pentagermanide cage in compound **1** (50% probability ellipsoids). Selected interatomic distances [Å]: Compound **1**: Ge(1)–Ge(2) 2.5000(9), Ge(1)–Ge(3) 2.505(1), Ge(1)–Ge(4) 2.511(1), Ge(2)–Ge(3) 2.7039(9), Ge(3)–Ge(4) 2.689(1), Ge(4)–Ge(2) 2.688(1), Ge(2)–Ge(5) 2.504(1), Ge(3)–Ge(5) 2.5051(9), Ge(4)–Ge(5) 2.495. Compound **2**: Ge(1)–Ge(2) 2.5035(9), Ge(1)–Ge(3) 2.500(1), Ge(1)–Ge(4) 2.514(1), Ge(2)–Ge(3) 2.718(9), Ge(3)–Ge(4) 2.697(1), Ge(4)–Ge(2) 2.691(1), Ge(2)–Ge(5) 2.517(1), Ge(3)–Ge(5) 2.4956(9), Ge(4)–Ge(5) 2.5348(9).

The asymmetric unit of compound **2** again consists of one Ge_5^{2-} anion, two rubidium cations surrounded by cryptand [2.2.2], and four molecules of ammonia. In contrast to compound **1**, compound **2** crystallizes in the space group $P\bar{1}$ (no. 2) with two asymmetric units per unit cell. All atoms reside on general sites with the Wyckoff letter 2*i*. The Ge_5^{2-} anion has the same shape as the anion in **1**, and the same atom designation scheme as in Fig. 1 is used. The centre of gravity of the cage is located on a general site, so that again no crystallographic site symmetry is observed for the anion. An inspection of the distances and angles within this polyhedron reveals it to be close to D_{3h} symmetry with only slightly larger deviations than those in compound **1**.[20] The eq–eq/eq–ax

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† CCDC reference numbers 615430 (**1**) and 615431 (**2**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b610547e

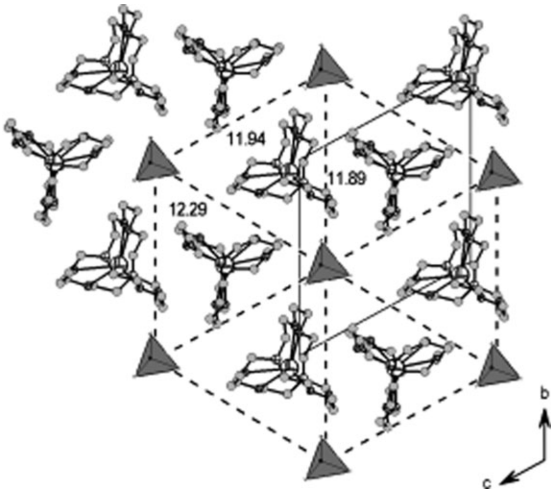

Fig. 2 Hexagonal layer of the pentagermanide cages in compound **1**. (50% probability isotropic ellipsoids).

length ratio is again 1.08. In contrast to compound **1**, the cages are arranged in very distorted layers where the distances between the centres of the polyhedra range from 10.31 Å to 15.03 Å. The smallest distance between two cages has a value of 7.441(1) Å. The interstices between the Ge_5^{2-} cages are occupied by the $[Rb([2.2.2]\text{-crypt})]^+$ units. They exhibit Rb–O distances ranging from 2.841(4) Å to 2.930(4) Å and Rb–N distances between 3.017(5) Å and 3.039(4) Å.

The pentagermanide cages of the compounds **1** and **2** are very similar to the one reported by Schrobilgen and Campbell.[11] All cages show approximately D_{3h} symmetry even though their centre of gravity lies on a general site with no symmetry. They all show significant differences between axial and equatorial bond lengths. The equatorial bond lengths of the previously reported Ge_5^{2-} anion range from 2.678(1) Å to 2.698(1) Å, the axial bonds have values between 2.466(1) Å and 2.506(1) Å.[11]

Conclusions

The isolation of two further examples of Ge_5^{2-} anions confirms the calculations, which predict the trigonal bipyramid to be the energetic minimum for dianionic pentagermanide cages.[16] Close approximations to idealized D_{3h} point group symmetry were observed for the anions of the two compounds **1** and **2**. Noteworthy is the difference in the space groups, the nearly identical chemical formulas would lead one to expect the compounds to be isostructural. The difference in packing must be due to the cationic units consisting of the alkali metal cations and the cryptand. The usage of the cryptand [2.2.2] seems to facilitate the formation of this cage anion in liquid ammonia. However, it does not seem to matter whether the cryptand is applied in excess (**1**), in an equimolar ratio[11] or in a half molar ratio (**2**). Despite the different alkali metals and solvate molecules, all the up-to-now known Ge_5^{2-} cages have very similar shapes, whereas the shape of the nonagermanide cage is very sensitive to changes in the alkali metal counterions, leading to a higher structural diversity.[2] Highly reduced phases were utilized in the preparation of compound **1** ($KGe_{1.67}$) and $[K(C_{18}H_{36}N_2O_6)]_2Ge_5 \cdot THF$ ($KGe_{1.8}$),[11] whereas for compound **2** the solvation of the less reduced phase $Rb_{0.5}Cs_{0.5}Ge_{2.25}$ was successful. Up to now, Ge_5^{2-} containing compounds crystallize from the extraction reactions only by serendipity. While a connection between the Ge_9^{4-} anions detected in binary solids like Cs_4Ge_9 and in the compounds isolated from solutions of similar solids may be postulated,[22] no such easy rationality exists for the pentagermanide cages, as no analogous solid containing Ge_5^{2-} is known up to now.

References

1 C. H. E. Belin, J. D. Corbett and A. Cisar, *J. Am. Chem. Soc.*, 1977, **99**, 7163–7169.

2 (*a*) T. F. Fässler, M. Hunziker, M. E. Spahr, H. Lueken and H. Schilder, *Z. Anorg. Allg. Chem.*, 2000, **626**, 692–700; (*b*) T. F. Fässler and U. Schütz, *Inorg. Chem.*, 1999, **38**, 1866–1870; (*c*) T. F. Fässler and M. Hunziker, *Inorg. Chem.*, 1994, **33**, 5380–5381; (*d*) C. Suchentrunk and N. Korber, *Inorg. Chim. Acta*, 2006, **359**, 267–272.

3 (*a*) M. Somer, W. Carillo-Cabrera, E. M. Peters and H. G. von Schnering, *Z. Anorg. Allg. Chem.*, 1998, **624**, 1915–1921; (*b*) R. Hauptmann and T. F. Fässler, *Z. Kristallogr. – New Cryst. Struct.*, 2003, **218**, 370–372; (*c*) C. Suchentrunk, J. Daniels, M. Somer, W. Carillio-Cabrera and N. Korber, *Z. Naturforsch., B: Chem. Sci.*, 2006, **60**, 277–283.

4 R. Hauptmann and T. F. Fässler, *Z. Anorg. Allg. Chem.*, 2003, **629**, 2266–2273.

5 A. Ugrinov and S. C. Sevov, *J. Am. Chem. Soc.*, 2002, **124**, 10990–10991.

6 A. Ugrinov and S. C. Sevov, *Inorg. Chem.*, 2003, **42**, 5789–5791.

7 C. Downie, Z. Tang and A. M. Guloy, *Angew. Chem., Int. Ed.*, 2000, **39**(2), 337–340.

8 T. F. Fässler, *Coord. Chem. Rev.*, 2001, **215**, 347–377.

9 S. C. Critchlow and J. D. Corbett, *J. Chem. Soc., Chem. Commun.*, 1981, 236–237.

10 C. Belin, H. Mercier and V. Angilella, *New J. Chem.*, 1991, **15**, 931–938.

11 J. Campbell and G. J. Schrobilgen, *Inorg. Chem.*, 1997, **36**, 4078–4081.

12 J. M. Goicoechea and S. C. Sevov, *J. Am. Chem. Soc.*, 2004, **126**, 6860–6861.

13 P. A. Edwards and J. D. Corbett, *Inorg. Chem.*, 1977, **16**, 903–907.

14 (*a*) Z. Dong and J. D. Corbett, *J. Am. Chem. Soc.*, 1994, **116**, 3429–3435; (*b*) Z.-C. Dong and J. D. Corbett, *Inorg. Chem.*, 1996, **35**, 3107–3112.

15 S. Ulvenlund, K. Stahl and L. Bengtsson-Kloo, *Inorg. Chem.*, 1996, **35**, 223–230.

16 (*a*) R. B. King, I. Silaghi-Dumitrescu and A. Kun, *J. Chem. Soc., Dalton Trans.*, 2002, 3999–4004; (*b*) S.-D. Li, Q.-L. Guo, X.-F. Zhao, H.-S. Wu and Z.-H. Jin, *J. Chem. Phys.*, 2002, **117**, 606–614.

17 T. Kottke and D. Stalke, *J. Appl. Crystallogr.*, 1993, **26**, 615.

18 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997; G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.

19 A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34.

20 Selected angles [°] within the Ge_5^{2-} cages of compound **1**: Ge(2)–Ge(1)–Ge(3) 65.39(3), Ge(3)–Ge(4)–Ge(1) 64.84(3), Ge(4)–Ge(1)–Ge(2) 64.88(3), Ge(2)–Ge(3)–Ge(4) 59.79(3), Ge(3)–Ge(4)–Ge(2) 60.36(3), Ge(4)–Ge(2)–Ge(3) 59.85(3), Ge(2)–Ge(5)–Ge(3) 65.33(3), Ge(3)–Ge(5)–Ge(4) 65.09(3), Ge(4)–Ge(5)–Ge(2) 65.06(3), Ge(1)–Ge(2)–Ge(5) 103.26(3), Ge(1)–Ge(3)–Ge(5) 103.09(3), Ge(1)–Ge(4)–Ge(5) 103.19(4). Compound **2**: Ge(2)–Ge(1)–Ge(3) 65.81(3), Ge(3)–Ge(1)–Ge(4) 65.06(3), Ge(4)–Ge(1)–Ge(2) 64.88(3), Ge(2)–Ge(3)–Ge(4) 59.61(3), Ge(3)–Ge(4)–Ge(2) 60.60(2), Ge(4)–Ge(2)–Ge(3) 59.80(2), Ge(2)–Ge(5)–Ge(3) 65.68(3), Ge(3)–Ge(5)–Ge(4) 64.84(3), Ge(4)–Ge(5)–Ge(2) 64.39(2), Ge(1)–Ge(2)–Ge(5) 103.19(3), Ge(1)–Ge(3)–Ge(5) 103.90(3), Ge(1)–Ge(4)–Ge(5) 102.37(3).

21 K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1–66.

22 V. Queneau and S. C. Sevov, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**(16), 1754–1756.