[1]Institute of Nanotechnology (INT)
Karlsruher Institute of Technology, D-76131 Karlsruhe

Quantum Chemical Investigations on the New Binary Anions $[GeSb_3]^{5-}$, $(Ge_2Sb_2)^{2-}$, $(Ge_4Sb_{12})^{4-}$, and $(Ge_4Sb_{14})^{4-}$

Lukas Guggolz[1], Katrin Beuthert, Stefanie Dehnen[1]*

Introduction

From its beginnings more than a hundred years ago to its developments in recent years, *Zintl* chemistry has become remarkably diverse.[1–5] Our group has been actively involved in these endeavours.[6–10] Among other methods, we use quantum chemical calculations to deepen our understanding of the geometric and electronic structures of binary Zintl anions.

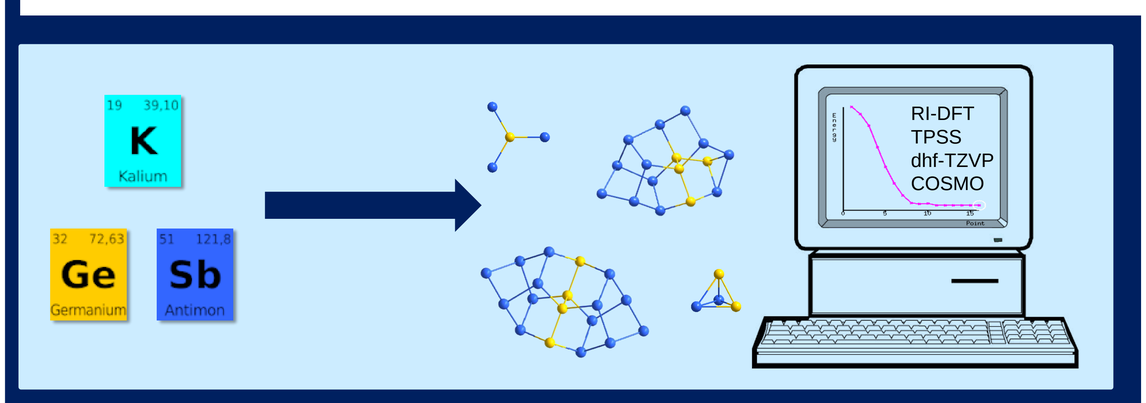
Starting from the new solid phase of the nominal composition "K_2GeSb", we were able to afford a number of novel distinct anions, namely the carbonate-analogous $[GeSb_3]^{5-}$ (**1**), the *pseudo*-tetrahedral anion $(Ge_2Sb_2)^{2-}$ (**2**), $(Ge_4Sb_{12})^{4-}$ (**3**), and $(Ge_4Sb_{14})^{4-}$ (**4**).[11] One of these anions, $(Ge_2Sb_2)^{2-}$, was predicted to be synthetically accessible in one of our earlier works.[12]

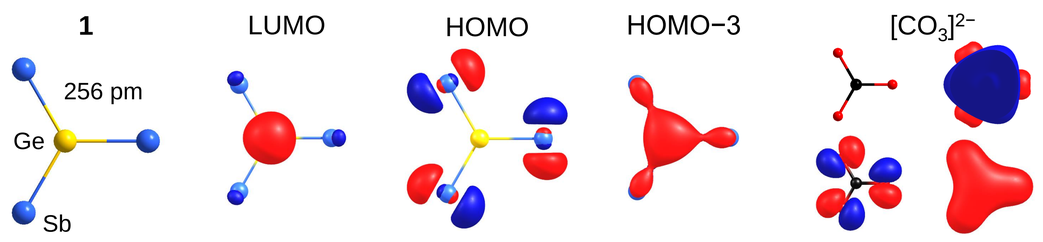
Herein, we present in-depth results of the quantum chemical studies of these heretofore unknown Zintl anions.

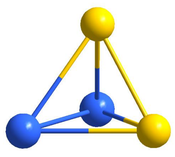
Results

The starting mixture afforded the single-crystalline alloy $K_{12}Ge_{3.5}Sb_6$, which is comprised of a double-salt of "$K_2Ge_{1.5}$" and $K_5[GeSb_3]$, with $[GeSb_3]^{5-}$ being a new member of a series of carbonate analogs. We furthermore obtained the heretofore unknown anions $(Ge_2Sb_2)^{2-}$ and $(Ge_4Sb_{12})^{4-}$ upon extraction with crypt-222 and en. Addition of $[AuMe(PPh_3)]$ yielded the anion $(Ge_4Sb_{14})^{4-}$, the lighter homolog of the already known $(Ge_4Bi_{14})^{4-}$.[8]

Synthetic details are given by Katrin Beuthert at **Poster 12**.

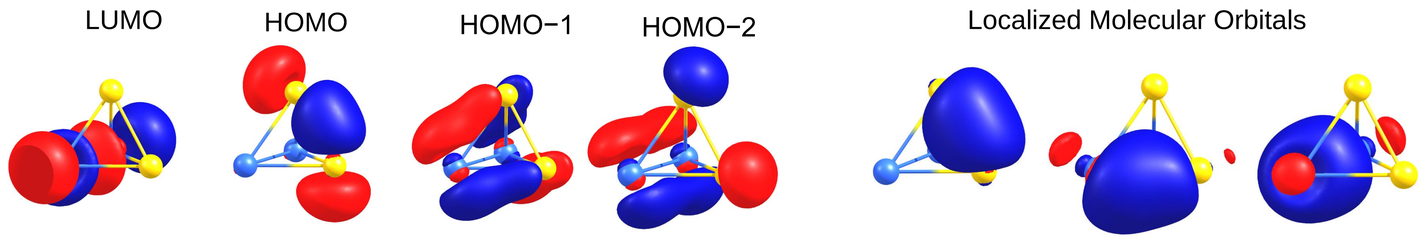


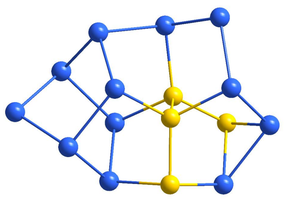




2

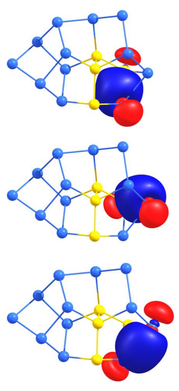
Bond Lengths / Å		
	Calculated	Experiment
Ge–Ge	2.55	2.5316
Ge–Sb	2.73	2.6941 – 2.7057
Sb–Sb	2.83	2.7889



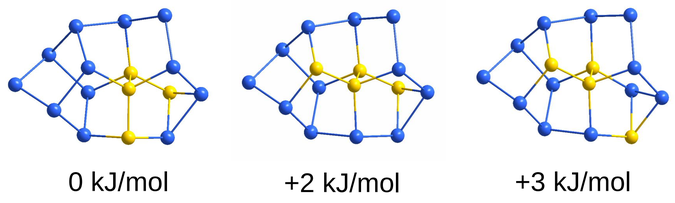


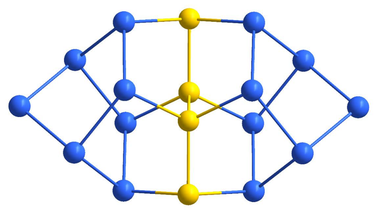
3

Only 2e2c bonds



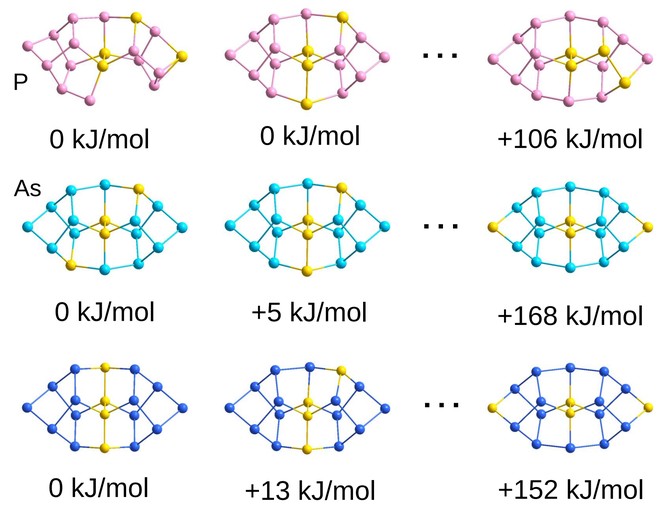
Eight isomers are found to be within 10 kJ/mol with respect to the global minimum structure.





4

The ratio of the covalent radii (Q_{cr}) determines the distribution of the different atom types within the $(Ge_4Pn_{14})^{4-}$ anions (Pn: P, As, Sb, Bi).



Conclusion

- Four novel binary anions were obtained from "K_2GeSb".
- DFT studies helped to elucidate their geometric and electronic structures.
- A mixture of different isomers of **3** is likely to be present in solution.
- The distribution of different atom types over the respective sites is heavily influenced by the ratio of the ovalent radii (Q_{cr}).

Outlook

- Further investigations of the reactions of binary *Zintl* anions with transition metal complexes are currently underway.
- They are being accompanied by extensive quantum chemical studies.

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