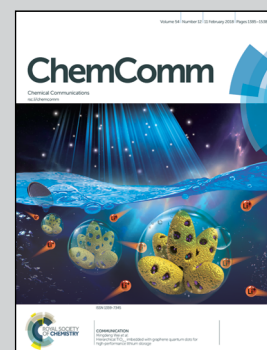


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$(\text{Ge}_2\text{P}_2)^{2-}$: a binary analogue of P_4 as a precursor to the ternary cluster anion $[\text{Cd}_3(\text{Ge}_3\text{P})_3]^{3-}$

The novel binary P_4 analogue $(\text{Ge}_2\text{P}_2)^{2-}$ was used for the synthesis of the ternary cluster anion $[\text{Cd}_3(\text{Ge}_3\text{P})_3]^{3-}$. The latter comprises an unusual triangular Cd_3 moiety and $(\text{Ge}_3\text{P})^{3-}$ units that form from $(\text{Ge}_2\text{P}_2)^{2-}$ in solution. Fragmentation and rearrangement of this P_4 analogue was monitored by NMR spectroscopy and mass spectrometry.

As featured in:



See Florian Weigend,
John F. Corrigan,
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$(\text{Ge}_2\text{P}_2)^{2-}$: a binary analogue of P_4 as a precursor to the ternary cluster anion $[\text{Cd}_3(\text{Ge}_3\text{P})_3]^{3-}$ †

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The novel binary P_4 analogue $(\text{Ge}_2\text{P}_2)^{2-}$ proved to be a suitable precursor for heteroatomic cluster synthesis. Over time in solution, it rearranges to form $(\text{Ge}_7\text{P}_2)^{2-}$, as shown by NMR studies and X-ray diffraction. Reactions of $(\text{Ge}_2\text{P}_2)^{2-}$ with CdPh_2 afford $[\text{K}(\text{crypt-222})_2][\text{Cd}_3(\text{Ge}_3\text{P})_3]$, containing an unprecedented ternary cluster anion with a triangular Cd_3 moiety.

Homoatomic polyanions of germanium, Ge_9^{4-} and Ge_4^{4-} , are actively used for the synthesis of binary transition metal-main group metal complexes and intermetalloid clusters. Their relative stability and yet demonstrated reactivity towards organic and inorganic compounds has been reported for numerous examples,^{1–4} like the silylated cages $[\text{Ge}_9(\text{SiPh}_2\text{CHCH}_2)_3]^-$,⁵ metal complexes like $[(\text{Ge}_9\{\text{Si}(\text{TMS})_3\}_2)\text{tBu}_2\text{P}]\text{Au}(\text{NHC}^{\text{DIPP}})$,⁶ or the intermetalloid cluster $[\text{Ru}@\text{Ge}_{12}]^{3-}$.⁷ Within the last decade, a large variety of novel compounds was thus discovered: these compounds are exemplary for the high chemical flexibility of these homoatomic systems, which also includes mixed Ge/Si or Ge/Sn intertetrelide species.⁸

A complementary branch of transition metal-main group element cluster chemistry is based on the activation and derivatization of white phosphorus (P_4) as a reagent, which has led to a multitude of beautiful and spectacular new compounds and molecular architectures.^{9–13}

We transferred this concept to binary analogs¹⁴ by using the isoelectronic $(\text{E}_2^{14}\text{E}_2^{15})^{2-}$ species $(\text{Ge}_2\text{As}_2)^{2-}$,¹⁶ $(\text{Sn}_2\text{Sb}_2)^{2-}$,^{17,18} $(\text{Sn}_2\text{Bi}_2)^{2-}$,^{19–21} or $(\text{Pb}_2\text{Bi}_2)^{2-}$.²² This way, the two aforementioned areas of research are bridged, with significant electronic and structural consequences for the reaction products. Isoelectronic substitution has proven a very powerful tool in the formation of intermetalloid cluster anions and heterometallic complexes in the recent past.^{22–27} The inclusion of E^{15} atoms to produce binary $(\text{E}_2^{14}\text{E}_2^{15})^{2-}$ anions reduces their charge relative to their E^{14} analogues, $(\text{E}_4^{14})^{4-}$, while retaining the overall valence electron number. The solubility is thus significantly enhanced. However, to date all studies with binary Zintl anions have so far addressed (semi-)metals of the fourth period upwards. In this work, we intended to approach the intriguing P_4 chemistry even more closely by explicitly including this element type while retaining the Zintl anion style of chemistry.

A solid mixture of potassium, germanium and red phosphorus of the nominal composition “ $\text{K}_2\text{Ge}_2\text{P}_2$ ” was formed by fusing the elements in a 1 : 1 : 1 ratio at 950 °C in an Nb ampoule. According to a comprehensive time-dependent electrospray ionization mass spectrometry (ESI-MS) study of the extraction process of “ $\text{K}_2\text{Ge}_2\text{P}_2$ ”/crypt-222 in ethane-1,2-diamine (ethylene diamine, en), the $(\text{Ge}_2\text{P}_2)^{2-}$ anion is the only Zintl anion detected at the beginning of the extraction. It was detected as its protonated, mono-charged derivative $(\text{Ge}_2\text{P}_2\text{H})^-$ (Fig. S10 and S13, ESI†), as a typical consequence of the ESI procedure of (especially light element) Zintl ions from en solutions, and in contrast to some anions that were intrinsically protonated and even crystallized in this form.^{28,29} Upon extracting the solid mixture with en/crypt-222 and subsequent layering with toluene, $[\text{K}(\text{crypt-222})_2](\text{Ge}_2\text{P}_2)\text{-en}$ (1-en) crystallized as yellow tabular prisms in approximately 20% yield within 3 days (Fig. S1, ESI†). Larger amounts of **1** can be obtained by enforcing its precipitation by the rapid addition of THF to the filtered extraction mixture (yield approx. 70%). If undisturbed, dark orange cubes of $[\text{K}(\text{crypt-222})_2](\text{Ge}_7\text{P}_2)$ (**2**) also crystallize, in approximately 10% yield after two weeks (Fig. S2, ESI†). If left undisturbed for several weeks, crystals of **1-en** dissolve completely and large amounts of **2** crystallize. As the $(\text{Ge}_7\text{P}_2)^{2-}$

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† Electronic supplementary information (ESI) available: Synthesis details, crystallography, EDX spectroscopy, ESI mass spectrometry, NMR spectroscopy, quantum chemical calculations. CCDC 1579583–1579585. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc08348c

cluster anion contained in **2** has not been detected in the ESI(−) mass spectrum upon fresh extraction of the solid mixture in en, we anticipate its formation upon oxidation in solution over time.

The reactivity of the $(\text{Ge}_2\text{P}_2)^{2-}$ cluster anion towards d-block metal compounds was demonstrated by the addition of CdPh_2 , giving rise to the formation of $[\text{K}(\text{crypt-222})]_3[\text{Cd}_3(\text{Ge}_3\text{P})_3]\text{-tol}$ (**3**-tol; tol = toluene). A reaction with the lighter homologue, ZnPh_2 , has not afforded identifiable products so far. Compound **1**-en crystallizes as red, elongated square prisms that dendritically agglomerate into a leaf-like morphology (Fig. S3, ESI†). **3** represents a new example of the rare family of compounds that contain direct Cd–Ge contacts, such as $[\text{CdGe}(\text{SiMe}_3)_2]\text{I}_3$ ³⁰ and $[\text{Ge}_9(\text{Si}(\text{SiMe}_3)_3)_2]\text{Cd}$.² At the same time the anion in **3** is the first species comprising more than two Cd atoms within an intermetalloid cluster structure.

The compositions of **1–3** were confirmed by means of ESI(−)MS and energy-dispersive X-ray (EDX) spectroscopy. Their crystal structures were determined by means of single-crystal X-ray diffraction^{31,32} (see ESI† for details).

1 crystallizes with one molecule of en per unit cell in the triclinic space group *P1* (*Z* = 1). The bond lengths of the tetrahedral anion were found to vary between 2.387(2) and 2.635(2) Å. The shortest bond is thus notably longer than the P–P bonds in white phosphorus (2.209(5) Å),³³ while the longest contact is slightly longer than the Ge–Ge bonds in the Ge_4^{4-} anion in K_4Ge_4 (2.563(3) Å).³⁴ However, the bond lengths are similar to known Ge–P distances (e.g., 2.34 Å for a Ge atom coordinated to a P_4 unit;³⁵ e.g., 2.50–2.52 Å for Ge atoms coordinated to a P_7 unit).³⁶ Due to intrinsic disorder in the solid state structure, we cannot discriminate between specific Ge–P, Ge–Ge and P–P bonds.

The ³¹P-NMR spectrum, measured on a fresh solution of **1** in DMF-*d*₇ at room temperature, shows a singlet at $\delta = -432$ ppm (Fig. 1, bottom). This is slightly less shifted upfield than the values reported for white phosphorus itself (−488 to −527 ppm).³⁷ However, the comparison of these values is problematic due to very

different solvent environments. Recently, a planar Ge_2P_2 four-membered ring was reported that was synthesized *via* CO elimination of a phosphaketenyl germylene. For this compound, the ³¹P-NMR spectrum shows a singlet at 131.9 ppm, hence significantly deshielded in comparison with its parent molecule, which exhibits a singlet at −301.7 ppm before decarbonylation.³⁸ However, a comparison with the anion in **1** is questionable for the Ge_2P_2 moiety being planar and not charged. A butterfly-type Ge_2P_2 motif was reported in a Ge(II) phosphinidene dimer, which also exhibits a low-field resonance ³¹P-NMR signal at 270.2 ppm.³⁹ Here, the P atoms form four bonds each, again complicating a direct comparison with **1**. The NMR data of $(\text{Ge}_2\text{P}_2)^{2-}$ compare best with butterfly-shaped Ge–P heterocycles reported by Drieß *et al.*: with all P atoms bound three-fold, the ³¹P-NMR resonance singlet is observed at −365 ppm,⁴⁰ hence between the values reported herein for **1** and **2**. This confirms the angles and the number of bonds to be the most important parameters for controlling the (de)shielding of the P atoms.

Time-dependent ³¹P-NMR spectroscopy in DMF-*d*₇ in a flame-sealed NMR tube (Fig. 1) indicates the continuous formation of a second species over time. As mentioned above, this species was identified as the $(\text{Ge}_7\text{P}_2)^{2-}$ anion by crystallization of compound **2**. The NMR data showed a complete conversion of $(\text{Ge}_2\text{P}_2)^{2-}$ to $(\text{Ge}_7\text{P}_2)^{2-}$ anions after two weeks, together with precipitation of red phosphorus, consistent with the lower relative phosphorus content in $(\text{Ge}_7\text{P}_2)^{2-}$ (3.5 : 1) with regard to that in $(\text{Ge}_2\text{P}_2)^{2-}$ (1 : 1). The loss of phosphorus by precipitation is reflected by a decrease of the ³¹P-NMR signal intensity. The ³¹P-NMR spectrum of the products features a singlet at $\delta = -252$ ppm, in accordance with the less shielding chemical environment of seven neighboring Ge atoms with a total charge of 2− in $(\text{Ge}_7\text{P}_2)^{2-}$, opposed to only two neighboring Ge atoms with the same total charge in $(\text{Ge}_2\text{P}_2)^{2-}$. The ESI(−) mass spectrum recorded after the described conversion (Fig. S11, ESI†) exhibits peaks for the corresponding single charged species $(\text{Ge}_7\text{P}_2\text{H})^-$ and $\{[\text{K}(\text{crypt-222})](\text{Ge}_7\text{P}_2)\}^-$, respectively, in agreement with the described formation of $(\text{Ge}_2\text{P}_2)^{2-}$ into $(\text{Ge}_7\text{P}_2)^{2-}$. Noteworthy, this result supports a recent assumption regarding the formation mechanism of the *nido*-type cages from tetrahedral anions, which was made based on quantum chemical calculations.¹⁵ Some calculations have also been done on the structure of neutral $[\text{Ge}_2\text{P}_2]$,⁴¹ which are in full agreement with the known feature of a two-electron oxidation of the tetrahedral anions to result in the cleavage of the $\text{E}^{14}\text{–E}^{14}$ bond, which represents the clusters' HOMO.¹⁹

Compound **2** crystallizes in the trigonal space group *P* $\bar{3}c1$ (*Z* = 2). The cluster anion is disordered over three positions around a common center of gravity (Fig. S5 and S6, ESI†). Each orientation shares two atom positions with another orientation. Its crystallographic constitution is therefore similar to that of the homologous $(\text{Ge}_7\text{As}_2)^{2-}$ cluster anion.¹⁵ The Ge–Ge distances are in accordance with those observed in the $(\text{Ge}_7\text{As}_2)^{2-}$ homolog.

The ternary cluster compound **3** crystallizes in the hexagonal space group *P6*₃*22* (*Z* = 6) with one equivalent of toluene solvent (3-tol). Two cluster orientations, that can be converted into each other by a two-fold rotation, are disordered on the same anionic

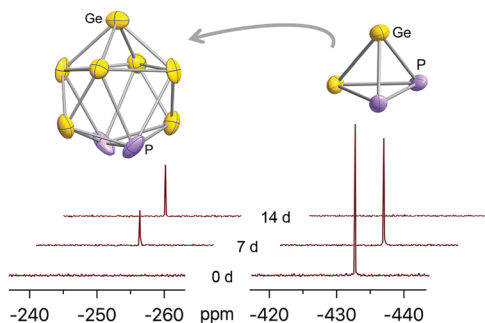


Fig. 1 Time-dependent ³¹P-NMR spectroscopy, indicating full conversion of $(\text{Ge}_2\text{P}_2)^{2-}$ anions to $(\text{Ge}_7\text{P}_2)^{2-}$ anions in the course of 14 days. The spectrum at the bottom was measured on a fresh solution of single crystals of compound **1** in DMF-*d*₇, and comprises the singlet signal of the $(\text{Ge}_2\text{P}_2)^{2-}$ anion (see structure diagram to the right) at −432.38 ppm only. The spectrum in the centre was recorded from the same sample after 7 days, the topmost spectrum after 14 days. The latter comprises the singlet signal of the $(\text{Ge}_7\text{P}_2)^{2-}$ anion (see structure diagram to the left) at −252.21 ppm only, which is identical to the signal measured from single crystals of **2**.

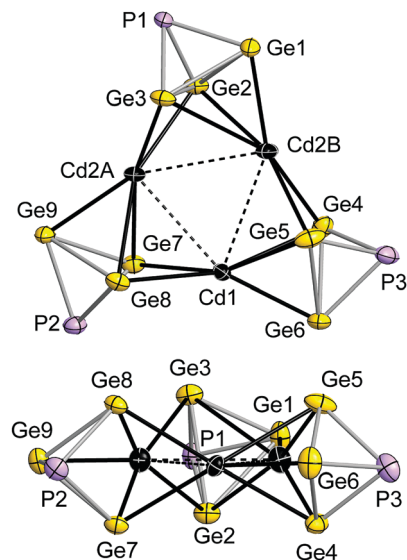


Fig. 2 Top view (top) and side view (bottom) of the molecular structure of the anion in **3**-tol, shown for one of the two disordered positions. Selected distances [Å] and angles [°]: Cd1...Cd2A 2.985(3), Cd1...Cd2B 3.251(3), Cd2A...Cd2B 3.358(3), Cd-Ge 2.686(4)–3.170(4), Ge-Ge 2.232(6)–2.566(5), Ge-P 2.309(9)–2.440(14), Cd...Cd...Cd 10.70(4), 35.35(14), Ge-P-Ge 66.2(2)–71.5(6), Ge-Ge-Ge 57.3(2)–66.68(11), P-Ge-Ge 51.48(19)–57.01(17). Dashed Cd...Cd contacts are not meant to represent bonds.

position, with site occupation factors of 0.5 for all atoms (Fig. S9, ESI†). The structure of one of the orientations is shown in Fig. 2. The crystallographic assignment of Ge and P atoms is supported by quantum chemical calculations as well as ^{31}P -NMR and ^{113}Cd -NMR studies (see below).

The anion in compound **3** is based on three Cd atoms forming a nearly isosceles triangle (Cd...Cd 2.985(3)–3.358(3) Å) that is coordinated and thereby connected by three $(\text{Ge}_3\text{P})^{3-}$ tetrahedra. Notably, only Ge atoms of the latter interact with the Cd atoms, while the P atoms point outwards. Each of the Cd atoms interacts with two of the neighboring $(\text{Ge}_3\text{P})^{3-}$ units, one coordinating in a η^3 -type fashion, thereby forming a $\text{P}(\text{Ge}_3)\text{Cd}$ bipyramid, the other one coordinates in a η^2 -type manner. This leads to an idealized C_{3h} symmetric structure, which is, however, perturbed by the irregularity of the central Cd_3 ring.

Quantum chemical calculations of the anion that are carried out without symmetry restrictions did not reproduce the exact structure as global energy minimum, but a diversity of similar ones within 30 kJ mol^{-1} , exhibiting weak modes (below 10 cm^{-1}) for a rotation of the $(\text{Ge}_3\text{P})^{3-}$ unit about the virtual Cd...P_{opposite} axes (see Fig. S19, ESI†). This indicates a high fluxionality of the cluster at least under the given experimental conditions, which is in agreement with the NMR spectroscopic data of the cluster in solution.

The ^{113}Cd -NMR spectrum of a solution of **3** in DMF- d_7 revealed only one signal ($\delta = 636 \text{ ppm}$ (t), $^2J_{^{113}\text{Cd}-^{31}\text{P}} = 72 \text{ Hz}$; see Fig. S18, ESI†). The ^{31}P -NMR is more complex and consists of a central singlet at -129 ppm with two symmetric satellites (72 Hz apart) and symmetric shoulders. After evaluation of several couplings enabled due to various Cd isotopes, an integral distribution of 2 : 19 : 58 : 19 : 2 was calculated and also

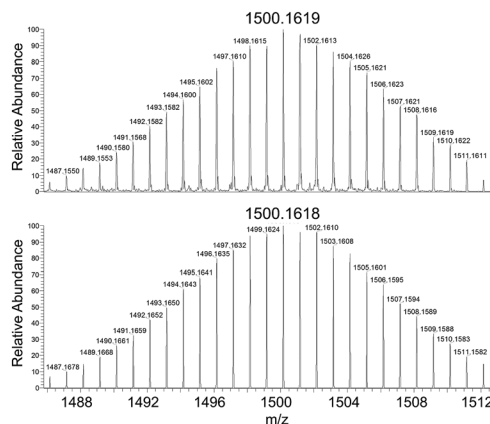


Fig. 3 High resolution ESI mass peak of the $[\text{Cd}_3(\text{Ge}_3\text{P})_3]^{3-}$ anion in **3**, detected as $\{[\text{K}(\text{crypt-222})\text{H}][\text{Cd}_3(\text{Ge}_3\text{P})_3]^{-}\}$ at m/z 1500. Top: Measured spectrum. Bottom: Calculated spectrum.

observed in the experimental spectrum (see ESI† for more details). The value of the ^{113}Cd - ^{31}P coupling of 72 Hz is similar to 2J coupling constants reported for Cd-enriched enzyme phosphate complexes (30 Hz),⁴² whereas it deviates by more than one order of magnitude from reported values for a $^1J_{^{113}\text{Cd}-^{31}\text{P}}$ coupling (1123–2960 Hz).^{43,44} This supports the assignment of the P atoms in the $(\text{Ge}_3\text{P})^{3-}$ moiety in **3** as pointing outwards.

The originally unexpected presence of $(\text{Ge}_3\text{P})^{3-}$ units in the molecular structure of the anion in **3** was unambiguously confirmed by SCXRD as well as by ESI(-)MS of re-dissolved single-crystals (Fig. 3), and it is in perfect agreement with the total 3- charge of that anion that results from a combination of three $(\text{Ge}_3\text{P})^{3-}$ units with three Cd^{2+} ions, balanced by three $[\text{K}(\text{crypt-222})]^+$ cations. Therefore, we propose that upon addition of CdPh_2 , the $(\text{Ge}_2\text{P}_2)^{2-}$ anions undergo a transformation into $(\text{Ge}_3\text{P})^{3-}$ anions and some phosphorus species, such as $(\text{GeP}_3)^-$ (for the simplest possible way to comply with atom and charge balance), or some yet unidentified polyphosphides.

Moreover, in a detailed mass spectrometric study of the Ge/P system under different solvent conditions, we found evidence for “ GeP_3 ” moieties with solvent fragments (Fig. S14, ESI†), which may support this first assumption. In our previous study of the Ge/As system¹⁵ a corresponding “ (Ge_3As) ” moiety was detected in the ESI mass spectrum, which suggests that a similar process in solution is occurring in Ge/As and Ge/P systems. The mechanism of and the stimulus for this transformation remains puzzling and needs further investigation.

In conclusion, we were able to demonstrate the successful use of the novel P_4 homolog $(\text{Ge}_2\text{P}_2)^{2-}$ for the synthesis of multi-metallic clusters using CdPh_2 as a reagent. The novel trimeric cluster anion comprises an unusual triangular Cd geometry and a new $(\text{Ge}_3\text{P})^{3-}$ fragment which forms from $(\text{Ge}_2\text{P}_2)^{2-}$ in solution at a so far unknown pathway, that most probably releases $(\text{Ge}_3\text{P})^{3-}$ and $(\text{GeP}_3)^-$ fragments. The tetrahedral cluster anion $(\text{Ge}_2\text{P}_2)^{2-}$ undergoes an irreversible transformation in solution resulting in the 9-vertex-cluster anion $(\text{Ge}_7\text{P}_2)^{2-}$. The novel homolog of P_4 can be synthesized as the $[\text{K}(\text{crypt-222})]^+$ salt in high purity with approx. 70% yield and is

therefore a good precursor for the development of new binary Ge/P cluster compounds. Although many questions remain unanswered in this process, we can conclude that these binary Zintl-type clusters possess a rich chemistry in solution. Their reactivity is to a degree solvent-specific, and they can undergo transformations into larger binary clusters. The quantitative understanding of this process alone would be of great value to develop a comprehensive chemistry around the so far selective knowledge we possess of multi-metallic clusters. This will be addressed in the future.

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Conflicts of interest

There are no conflicts to declare.

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