

ChemComm

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Frontiers in Molecular Main Group Chemistry web themed issue

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Cite this: *Chem. Commun.*, 2012, **48**, 7720–7722

www.rsc.org/chemcomm

Water compatibility and organic transformations of organo-Zintl deltahedral clusters^{†‡}

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Received 28th March 2012, Accepted 26th April 2012

DOI: 10.1039/c2cc32263c

We report the remarkable stability of di-substituted organo-Zintl deltahedral clusters in the presence of water. This has been exploited in a reaction at the organic substituents of the cluster which produces water as a by-product. Also reported are the synthesis, characterization, and crystal structure of [K-krypt]-[Ge₉-(CH=CH-CH₂NH₂)₂] involved in the reaction.

The field of Zintl chemistry has diversified dramatically over the last decade. For a long time anionic Zintl clusters were assumed to be the purview of solid-state chemists alone, and were considered far too reducing and reactive to be compatible with more conventional solution chemistry. But this bias has been rapidly eroding in recent years.¹ Several new sub-fields have emerged, namely: intermetallic-,² organometallic-,³ and organo-Zintl cluster chemistry. The latter field has proved particularly rich. Several methods for functionalizing Zintl clusters with organic substituents have been developed. Reactions of the clusters with alkyl halides yield mono- and di-substituted monomers and di-substituted dimers for both Sn₉ⁿ⁻ and Ge₉ⁿ⁻, such as [Sn₉-ⁿBu]³⁻,⁴ [Ge₉-(ⁿBu)₂]²⁻, and [ⁿBu-Ge₉-Ge₉-ⁿBu]⁴⁻.⁵ This methodology is convenient, given the abundance of alkyl halides, and is effective for primary, secondary, tertiary, and alkenyl carbon substrates. Alternatively, reactions with alkynes yield mono- and di-substituted clusters functionalized with alkenyl substituents, as in [Ge₉-(CH=CH-Fc)₂]²⁻ (where Fc = ferrocenyl),⁶ [Ge₉-(CH=CH₂)₂]²⁻,⁷ and [GeSn₈-CH=CH-Ph]³⁻.⁸ The mechanisms for these reactions have been worked out in some detail, indicating that the clusters primarily act as strong nucleophiles, following a substitution pathway with alkyl halides or an addition pathway with alkynes.⁹ It appeared as if two substituents were the maximum until recently when a trisubstituted cluster, [Ge₉-(Si(SiMe₃)₃)₃]⁻, was rationally synthesized by a reaction of the naked Ge₉⁴⁻ clusters with the corresponding halide (Me₃Si)₃SiCl.^{10a}

(The same tri-substituted species had been previously synthesized by a not well understood disproportionation GeBr.^{10b}) Collectively, these results demonstrate the wealth of structure and functionality accessible through organo-Zintl chemistry. Moreover, the dianionic clusters, like [Ge₉-(CH=CH₂)₂]²⁻, can be readily dissolved in conventional organic solvents like benzene, toluene, ether, *etc.*, after appropriate cation exchange.⁷ These developments help to bring organo-Zintl chemistry in line with more traditional organic synthesis. Herein we report the next step forward, namely the water-stability of the organo-Zintl clusters and a proof-of-concept organic reaction at their organic tails, thus laying to rest the faulty notion of the incompatibility of organo-Zintl clusters with broader synthetic chemistry.

Our results show that organo-Zintl clusters (Ge₉-R₂)²⁻ are significantly less reducing than their “naked” counterpart Ge₉⁴⁻. Thus, with aldehydes the latter is readily oxidized to Ge₉³⁻, Ge₉²⁻ (as monomers, dimers, and/or oligomers), and/or Ge₁₀^{2-,3a,11} and is oxidized and functionalized to (Ge₉-R)³⁻ and (Ge₉-R₂)²⁻ when combined with tertiary alkyl halides.⁹ In contrast, NMR evidence clearly shows that [Ge₉-(CH=CH₂)₂]²⁻ is stable in the presence of aldehydes and tertiary alkyl halides (Fig. S1–2 in Supporting Information[†]). The increased resistance towards oxidation is in keeping with the changes in frontier orbitals upon functionalization of the cluster. Lohr¹² and others^{1c,13} have shown that there is a significant increase in the HOMO/LUMO gap of the functionalized clusters relative to Ge₉⁴⁻ or Ge₉³⁻. The widening of the HOMO/LUMO gap translates into increased stability in the presence of oxidizing organic substrates.

Greater still and significantly more remarkable is the compatibility of the functionalized Zintl clusters with water. Systematic investigations with intentional water spiking showed that the di-substituted clusters are stable in the presence of water. The tests were carried out with [Ge₉-(CH₂CH(CH₂)₂)₂]²⁻, [Ge₉-(CH=CH₂)₂]²⁻, and [Ge₉-(Sn(CH₃)₃)₂]²⁻.^{6,7,9,14} The ¹H NMR spectra in *d*₅-pyridine of each of these species taken before and after the addition of water show no change other than the new resonance corresponding to H₂O (Fig. 1 and S3–4 in Supporting Information). Integration of the water-added spectrum shown for [Ge₉-(CH=CH₂)₂]²⁻ in Fig. 1 indicates an approximate water-to-cluster ratio of 50 : 1. Mass spectrometry measurements taken after water exposure likewise show the anionic clusters intact. The solutions were monitored by NMR

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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c2cc32263c

[‡] This article is part of the *ChemComm* ‘Frontiers in Molecular Main Group Chemistry’ web themed issue.

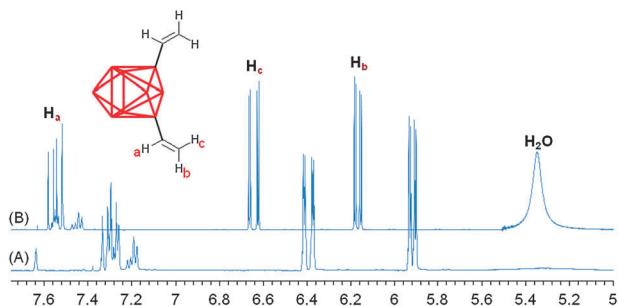


Fig. 1 ^1H NMR of $[\text{Ge}_9\text{-(CH=CH}_2)_2]^{2-}$ before (A) and after (B) the addition of H_2O (the spectra are shifted with respect to each other for better visibility).

for over two months and showed no changes, indicating their high stability (Fig. S5). The stability appears to be intrinsic to the clusters themselves and not related to the solvent as the same compatibility is observed in DMF and ethylenediamine (Fig. S6). In spite of their inertness towards water, though, when crystals of $[\text{K-crown}]_2[\text{Ge}_9\text{-(CH=CH}_2)_2]$ were placed in water, they did not dissolve or change in any way. The lack of solubility in water may be as much a function of the organic substituents and/or cations as it is of the cluster. Subsequent solubility studies are underway. The compatibility with water is particularly fortuitous as many organic reactions require catalytic amounts of water or generate water as a by-product.

The combination of observations of water stability and compatibility with aldehydes led us to investigate whether an aldehyde condensation reaction could be performed in the presence of the cluster. Schiff-base formation is a well-established reaction, and the so-called Jacobsen catalysts formed by transition-metal coordination have proven to be a fruitful area in catalysis.¹⁵ Organo-Zintl clusters are intense chromophores and have the potential for rich electrochemistry. The prospect of combining these properties with those of transition-metal complexes is promising, and led us to pursue the synthesis of an organo-Zintl salen-like compound that can potentially coordinate to transition metals.

The first step towards this goal was to synthesize an organo-Zintl cluster with amine pendants. By reacting Ge_9^{4-} (from K_4Ge_9 dissolved in ethylenediamine) with propargylamine ($\text{H-C}\equiv\text{C-CH}_2\text{NH}_2$) the diamine cluster, $[\text{Ge}_9\text{-(CH=CH-CH}_2\text{NH}_2)_2]^{2-}$ was synthesized (Fig. 2). The 3-aminopropenyl functionalized cluster shows similar structural features to that of other di-substituted clusters.⁶⁻⁹ It exhibits the commonly observed tricapped trigonal prismatic structure with one substantially elongated edge. Since the crystal structure[¶] of $[\text{Ge}_9\text{-(CH=CH-CH}_2\text{NH}_2)_2]^{2-}$ shows two equally occupied cluster positions superimposed upon one another, there are two slightly different distances for the elongated edge, 3.124(2) and 3.162(2) Å. The two shorter edges are 2.686(1) and 2.674(1) Å, and are common for the two cluster positions. The organic substituents are bonded to the two Ge-atoms forming the elongated edge with Ge-C distances of 1.962(7) and 2.005(4) Å in one of the cluster positions and 1.988(7) and 2.005(4) Å in the other. These distances compare well with the statistical mean of 1.96 Å for Ge-C(sp^2) distances, and are within the range of 1.82–2.05 Å for such

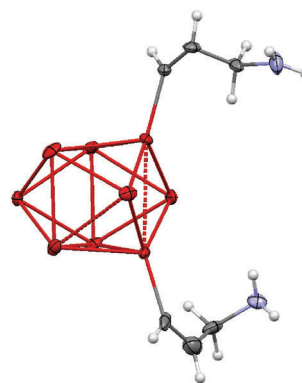


Fig. 2 Thermal ellipsoid plot (50% probability) of $[\text{Ge}_9\text{-(CH=CH-CH}_2\text{NH}_2)_2]^{2-}$. The elongated trigonal prismatic edge is shown with a broken line.

distances in the Cambridge Structural Database.¹⁶ These distances are slightly longer than those seen in $[\text{Ge}_9\text{-(CH=CH}_2)_2]^{2-}$, where the Ge-C bond distances are 1.951(2) and 1.961(2) Å.⁷

The ^1H NMR spectrum of $[\text{Ge}_9\text{-(CH=CH-CH}_2\text{NH}_2)_2]^{2-}$ in d_5 -pyridine is consistent with the solid-state structure (Fig. S7), showing a doublet for the vinyl proton on the α -carbon (7.05 ppm, 11.5 Hz) while the proton on the β -carbon is a doublet of a triplet (6.54 ppm, 11.5 Hz, 6.7 Hz) as a result of coupling to both the other olefinic proton and the two methylene protons. The methylene protons are split into a pseudo-quartet (doublet of a triplet, 4.07 ppm, 6.7 Hz, 6.7 Hz) by equal coupling to both the β -olefin proton and the protons on the amine group. Similarly, the amine protons are a triplet (1.45 ppm, 6.7 Hz).

In a straightforward condensation reaction, $[\text{Ge}_9\text{-(CH=CH-CH}_2\text{NH}_2)_2]^{2-}$ was combined with ferrocene-carboxaldehyde (FcCHO) in pyridine and stirred for one hour. Pyridine is an effective solvent for this reaction as it is capable of shuttling the proton between the ammonium center and the alkoxide anion formed during the course of the reaction. The mass spectrometry measurements taken of the sample clearly show that the aldehyde has reacted with the amine such that the clusters are now functionalized with imine pendants (Fig. 3). Such an organic transformation is possible because of the stability of the organo-Zintl clusters in the presence of water: $[\text{Ge}_9\text{-(CH=CH-CH}_2\text{NH}_2)_2]^{2-} + 2\text{FcCHO} \rightarrow [\text{Ge}_9\text{-(CH=CH-CH}_2\text{N=CHFc)}_2]^{2-} + 2\text{H}_2\text{O}$. This reaction clearly demonstrates that organo-Zintl clusters are capable of undergoing secondary organic transformations. The combination of a wide range of accessible solvents through cation exchange,⁷ as well as the numerous functional groups that can now be attached to the clusters through the ‘halide’ and ‘alkyne’ synthetic routes,^{8,9} leave open the possibility for the rational design of more complex systems incorporating Zintl clusters. The prospect of being able to combine organo-Zintl clusters with transition metal complexes is a promising lead. Simple coordination by the organic tethers of the organo-Zintl clusters to M^{2+} transition metals could provide overall neutral, albeit Zwitterionic, complexes. The ability to make Schiff-base functionalized clusters *via* an aldehyde condensation reaction puts all of this chemistry within reach.

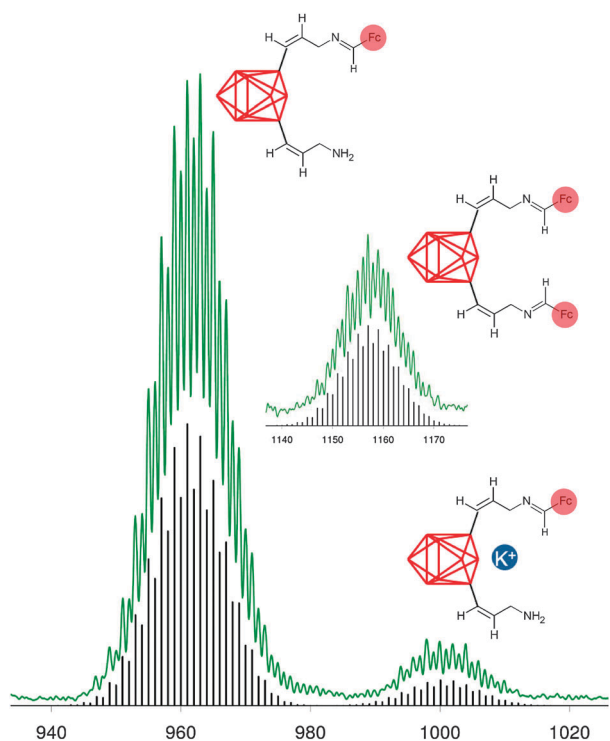


Fig. 3 An electrospray mass spectrum showing the imine formation in the condensation of $[\text{Ge}_9\text{-(CH=CH-CH}_2\text{NH}_2)_2]^{2-}$ with FcCHO .

The results presented here demonstrate, for the first time, the robust stability of the organo-Zintl clusters: namely their surprising compatibility with water and inertness towards a variety of organic substrates. Since a large number of organic transformations involve water in some role, the former is of particular importance. The aldehyde condensation reaction involving $[\text{Ge}_9\text{-(CH=CH-CH}_2\text{NH}_2)_2]^{2-}$ provides a proof of concept that such organic transformations are possible with the substituents of the organo-Zintl clusters.

We thank the National Science Foundation (CHE-0742365) for the financial support of this research.

Notes and references

§ All operations were carried out under an inert atmosphere or vacuum using standard Schlenk-line or glovebox techniques. Ethylenediamine (Alfa-Aesar, 99%) was distilled over sodium metal and stored in a gastight ampule under nitrogen. K_4Ge_9 was synthesized by heating a stoichiometric mixture of the elements (K: 99+%, Strem; Ge: 99.999%, Alfa Aesar) at 950 °C for 2 days in sealed niobium containers jacketed in evacuated fused-silica ampoules according to previously reported synthetic procedures. 2,2,2-krypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane, Acros, 98%) and $\text{H-C}\equiv\text{C-CH}_2\text{NH}_2$ (propargylamine, Acros, 99%), were used as received. **CAUTION!!!: Propargylamine is highly toxic; all personal protection steps recommended in the MSDS should be followed.** $[\text{K-crown}]_2\text{-}[\text{Ge}_9\text{-(CH=CH}_2)_2]$ was synthesized as previously reported. See Supporting Information for full experimental details. Synthesis of $[\text{K-krypt}]_2[\text{Ge}_9\text{-(CH=CH-CH}_2\text{NH}_2)_2]$. K_4Ge_9 (0.090 g, 0.11 mmol) was dissolved in 1.5 mL of ethylenediamine (red solution) in a test tube inside the glovebox. Propargylamine (0.034 g, 0.62 mmol) was added dropwise slowly and the reaction mixture was stirred for four hours. The solution was centrifuged, filtered, and 2,2,2-krypt added (0.149 g, 0.36 mmol). The solution was layered with toluene and left undisturbed for a week. After diffusion large red-orange crystals formed on the side of the test tube. The identical cluster anion can be synthesized with 18-crown-6-sequestered potassium cations by substitution 0.126 g

18-crown-6 in place of 2,2,2-krypt. The latter complex did not yield crystals suitable for X-ray diffraction.

¶ **Structure Determination.** Single-crystal X-ray diffraction data of $[\text{K-krypt}]_2[\text{Ge}_9\text{-(CH=CH-CH}_2\text{NH}_2)_2]$ was collected on a Bruker X8 APEX-II diffractometer equipped with a CCD area detector at 100 K using graphite-monochromated Mo-K α radiation. The crystal was selected under Paratone-N oil, mounted on the fiber, and positioned in the cold stream of the diffractometer. The structure was solved by direct methods and refined on F^2 using the SHELXTL V6.21 package.¹⁷ Crystallographic data for $[\text{K-krypt}]_2[\text{Ge}_9\text{-(CH=CH-CH}_2\text{NH}_2)_2]$: triclinic, $P\bar{1}$, $a = 10.8104$, $b = 12.87$, and $c = 22.1394$ Å, $\alpha = 83.5$, $\beta = 88.19$, and $\gamma = 86.68^\circ$, $V = 3054.34$ Å³, $Z = 2$, $T = 100(2)$ K, $R1/wR_2 = 3.4/7.5\%$ for the observed data ($I \geq 2\sigma$), $R1/wR_2 = 4.7/10.4\%$ for all data (CCDC 873396).

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