



# Synthesis and characterization of pristine *closo*-[Ge<sub>10</sub>]<sup>2-</sup>†

Manuel M. Bentlohner, Christina Fischer and Thomas F. Fässler\*

Cite this: *Chem. Commun.*, 2016, 52, 9841

Received 17th May 2016,  
Accepted 12th July 2016

DOI: 10.1039/c6cc04143d

www.rsc.org/chemcomm

**The first [Ge<sub>10</sub>]<sup>2-</sup> Zintl anion, which is neither filled nor connected to another metal atom is presented in terms of X-ray structure, Raman-spectrum and ESI-MS. Pure [Ge<sub>10</sub>]<sup>2-</sup>, adapting a D<sub>4d</sub> symmetric *closo*-structure, were crystallized from a Rb<sub>4</sub>Ge<sub>9</sub>/ethylenediamine solution, containing 7-amino-1-trimethylsilyl-5-aza-hepta-3-en-1-yne. The role of the latter on the formation of [Rb(222-crypt)]<sub>2</sub>[Ge<sub>10</sub>](en)<sub>1.5</sub> is discussed.**

The soft oxidation of *nido*-[E<sub>9</sub>]<sup>4-</sup> Zintl anions (E = Ge, Sn, Pb) with 22 skeleton electrons (SE) is a powerful method for the synthesis of new types of the heavier representatives of group 14 clusters and led to a large variety of cage-like structures.<sup>1–5</sup> By that strategy new element allotropes<sup>4–5</sup> as well as ordered, (nano)porous forms of germanium have been obtained.<sup>6–8</sup> Although a comprehensive understanding of the cluster oxidation and thus a control over the reaction outcome is still lacking, a large number of investigations on the oxidation of [E<sub>9</sub>]<sup>4-</sup> clusters in solution has been performed during the last couple of years,<sup>1,2</sup> and a broad variety of coupled clusters {[(Ge<sub>9</sub>)<sub>m</sub>]<sup>q-</sup> (m = 2–4, ∞)} has been obtained by soft oxidation of [Ge<sub>9</sub>]<sup>4-</sup> in ethylenediamine (en), *N,N*-dimethylformamide (dmf) and liquid ammonia. Even though in most cases the reactions are not understood in detail,<sup>9–16</sup> mild oxidative properties have been ascribed to the involved solvents,<sup>5,17–19</sup> and recently we have shown that the solvent en indeed plays an important role in the cluster formation.<sup>8</sup>

It has been found that oxidative reaction conditions not only can trigger the coupling but also the growth of clusters.<sup>20</sup> Theoretical investigations showed that for E = Ge a full oxidation to novel germanium allotropes under retention of the polyhedral structure is reasonable.<sup>21</sup> The reaction of [E<sub>9</sub>]<sup>4-</sup> with organometallic complexes ML<sub>a</sub> (M = metal, L = ligand) in en, dmf and liquid ammonia yielded a broad variety of endohedrally filled

clusters [M@E<sub>n</sub>]<sup>q-</sup> (n ≥ 9),<sup>1–3</sup> which in special cases adapt non-deltahedral structures and transition metal complexes of clusters with up to 45 covalently connected Ge atoms.<sup>22–25</sup> The formation of [M@E<sub>n</sub>]<sup>q-</sup> (n > 9), from [E<sub>9</sub>]<sup>4-</sup> cages, highlights the ability of these tetrel clusters to structurally reorganize in solution.<sup>26,27</sup>

The Zintl anions [Pb<sub>10</sub>]<sup>2–28</sup> and [(Ge<sub>10</sub>)Mn(CO)<sub>4</sub>]<sup>3–29</sup> are scarce examples of empty homoatomic ten-vertex tetrel clusters, and recently we extended the series of structurally characterized heteroatomic correspondents.<sup>26,30,31</sup> In [Ge<sub>9</sub>SnGe<sub>9</sub>]<sup>4-</sup> a formally *closo*-[Ge<sub>9</sub>Sn]<sup>2-</sup> unit coordinates to a [Ge<sub>9</sub>]<sup>2-</sup> cluster.<sup>32</sup> In case of [M@E<sub>n</sub>]<sup>q-</sup> a stabilizing effect of the interstitial M atom on the surrounding [E<sub>n</sub>] cage has been evidenced by quantum-chemical calculations, indicating the preferred formation of endohedrally filled clusters with n > 9 instead of their empty correspondents.<sup>1–3,20</sup>

The formation of the empty pristine [Pb<sub>10</sub>]<sup>2-</sup> unit on the one hand and of [(Ge<sub>10</sub>)Mn(CO)<sub>4</sub>]<sup>3-</sup> on the other also suggests the existence of an unbound [Ge<sub>10</sub>]<sup>2-</sup> Zintl anion. An earlier report on such a [Ge<sub>10</sub>]<sup>2-</sup> cluster<sup>33</sup> turned out to be rather questionable because a disordered *closo*-[Ge<sub>9</sub>]<sup>2-</sup> cluster (Fig. S1, ESI†) was unequivocally characterized in similar crystals.<sup>‡</sup><sup>34</sup> Although the isolation of crystals containing the unbound and empty [Ge<sub>10</sub>]<sup>2-</sup> Zintl anion has been unsuccessful so far, the latter is a frequently observed species in mass spectra obtained by laser desorption experiments or from solutions of Zintl phases in polar organic solvents.<sup>29,32,35,36</sup>

Herein we report on the synthesis and characterization of [Rb(222-crypt)]<sub>2</sub>[Ge<sub>10</sub>](en)<sub>1.5</sub> (**1**) which contains such an empty and unbound [Ge<sub>10</sub>]<sup>2-</sup> Zintl anion. Compound **1** was characterized by single crystal X-ray structure analysis, Raman-spectroscopy and electrospray ionization mass spectrometry (ESI-MS). Further, we present an ESI-MS investigation on the involved reaction solutions in order to shed some light on the formation of **1**.

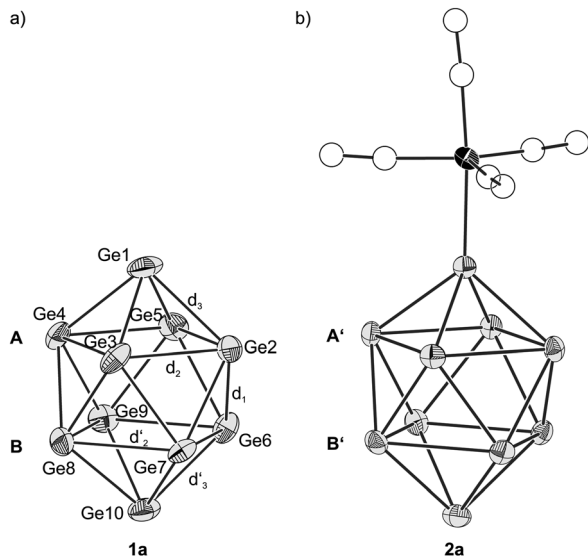
Dark purple pillars of **1** were obtained (yield ca. 10–20%) from a solution of Rb<sub>4</sub>Ge<sub>9</sub> (1 eq.) and 7-amino-1-trimethylsilyl-5-aza-hepta-3-en-1-yne (1 eq.)<sup>37</sup> in en after layering of the solution with toluene/cryptand[2.2.2] (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; for experimental details see ESI†).

Crystals of **1** (Fig. S2, ESI†) contain two [Rb(222-crypt)]<sup>+</sup> cations per cluster unit, and thus a formal charge of –2 can be assigned

Technische Universität München, Department Chemie, Lichtenbergstrasse 4, 85747 Garching, Germany. E-mail: Thomas.fassler@lrz.tum.de; Fax: +49 89 289 13186; Tel: +49 89 289 13131

† Electronic supplementary information (ESI) available: Experimental details, crystallographic details, ESI-MS spectra. CCDC 1479637. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc04143d





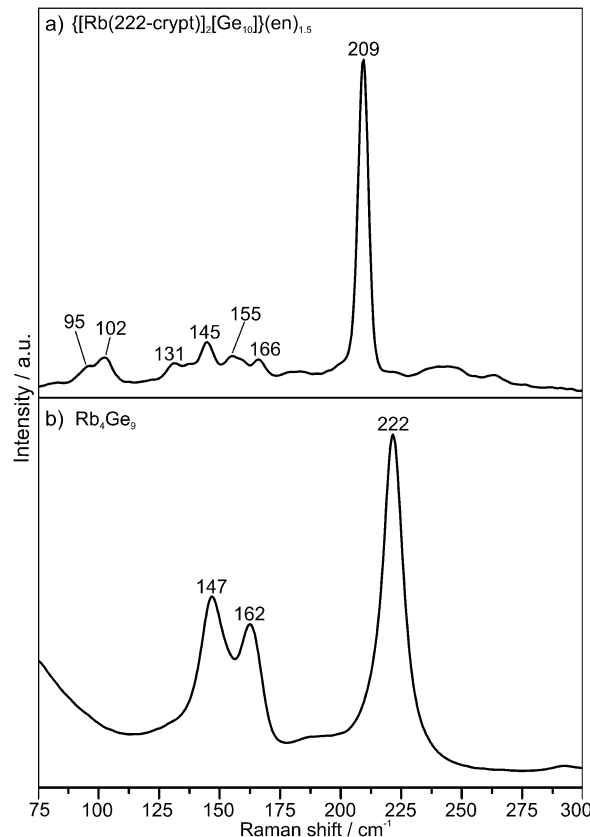
**Fig. 1** (a) *closo*-[Ge<sub>10</sub>]<sup>2-</sup> (**1a**) and (b) [(Ge<sub>10</sub>)Mn(CO)<sub>4</sub>]<sup>3-</sup> (**2a**)<sup>29</sup> for comparison. Square planes of **1a** and **2a** are labeled with **A/B** and **A'/B'**, respectively. (a and b) Ge and Mn atoms are shown as grey and black ellipsoids, respectively, at a probability level of 50%. C and O atoms are shown as empty spheres.

to the anionic cluster entity (Fig. 1a). [Ge<sub>10</sub>]<sup>2-</sup> (**1a**) consists of ten symmetry-independent germanium atoms and adapts the shape of a bi-capped square antiprism. The atoms of the planes **A** (Ge2 to Ge5) and **B** (Ge6 to Ge9) are nearly perfect squares with ratios of the face diagonals of 1.01 and 1.00 and torsion angles of 179.8° and 179.9°, respectively. The side lengths of **A** and **B** are in the narrow ranges of 2.760(1) Å (Ge2–Ge3) to 2.799(1) Å (Ge4–Ge5) and 2.780(1) Å (Ge7–Ge8) to 2.822(1) Å (Ge6–Ge9). Moreover, similar inter-square Ge–Ge distances from 2.535(1) Å (Ge3–Ge7) to 2.566(1) Å (Ge4–Ge9) indicate that **A** and **B** are in parallel. The mean inter-square Ge–Ge distance  $d_1(\mathbf{1a}) = 2.55(1)$  Å is considerably shorter than the mean Ge–Ge distances within **A** and **B** [ $d_2(\mathbf{1a}) = 2.79(2)$  Å,  $d_2'(\mathbf{1a}) = 2.80(2)$  Å]. The two atoms Ge1 and Ge10 cap the quadratic antiprism, whereby  $d_3(\mathbf{1a}) = 2.583(7)$  Å and  $d_3'(\mathbf{1a}) = 2.59(2)$  Å are slightly longer than  $d_1(\mathbf{1a}) = 2.55(1)$  Å. In summary **1a** adopts a nearly perfect *D*<sub>4d</sub> symmetry.

The geometrical parameters of **1a** are very similar to those of [(Ge<sub>10</sub>)Mn(CO)<sub>4</sub>]<sup>3-</sup> (**2a**) (Fig. 1b). Like for **1a**, the [Ge<sub>10</sub>] cluster in **2a** adapts *D*<sub>4d</sub> symmetry. The mean Ge–Ge distances  $d_3(\mathbf{2a})$  and  $d_3'(\mathbf{2a})$  are both 2.58(1) Å, suggesting that  $d_3(\mathbf{2a})$  is not influenced by the coordination of the Mn(CO)<sub>4</sub> fragment. However, in contrast to the square planes in **1a**, **A'** is significantly widened [ $d_2(\mathbf{2a}) = 2.85(2)$  Å] compared to **B'** [ $d_2'(\mathbf{2a}) = 2.77(1)$  Å], which might be attributed to the neighboring Mn(CO)<sub>4</sub> fragment. The inter-square Ge–Ge distances are almost identical for **1a** and **2a** [ $d_1(\mathbf{1a}) = 2.55(1)$  Å,  $d_1(\mathbf{2a}) = 2.547(8)$  Å].<sup>29</sup>

According to Wade's rules, **1a** can be described as a *closo*-deltahedron with 22 skeleton electrons (SE), whereby each vertex atom contributes two electrons, plus two extra electrons due to the two-fold negative charge.<sup>38</sup>

In order to study the vibrational behavior of **1a**, single crystals of **1** were investigated by Raman spectroscopy. The



**Fig. 2** Raman spectrum of (a) **1** and (b) Rb<sub>4</sub>Ge<sub>9</sub>. Characteristic modes are labeled with the corresponding Raman shifts.

spectrum (Fig. 2a) shows a very strong signal at 209 cm<sup>-1</sup> and several very weak bands in the range from 95 to 166 cm<sup>-1</sup>. In comparison, the Raman spectrum of the compound [K(222-crypt)]<sub>2</sub>[Ge<sub>9</sub>] exhibits one very intensive peak at 212 cm<sup>-1</sup> and three signals below 200 cm<sup>-1</sup> of medium intensity. Quantum-chemical calculations showed that the most intensive mode at 212 cm<sup>-1</sup> corresponds to the “breathing” of the *closo*-[Ge<sub>9</sub>]<sup>2-</sup> cluster. At least one of the medium intensive signals is attributed to vibrations of the central trigonal prism.<sup>34</sup> For *nido*-[Ge<sub>9</sub>]<sup>4-</sup> clusters (Fig. 2b) the “breathing” mode appears at higher wavenumbers of ca. 222 cm<sup>-1</sup>, and below 150 cm<sup>-1</sup> medium-intensive signals are visible.<sup>39–41</sup> However, the latter appear in a neat solid with stronger alkaline metal–Ge interactions. In the spectrum of **1** the absence of intensive signals below 200 cm<sup>-1</sup> evidences, that **1** does not contain [Ge<sub>9</sub>]<sup>2-</sup> clusters, and thus we conclude that the mode at 209 cm<sup>-1</sup> corresponds to the “breathing” vibration of **1a**.<sup>34,39–41</sup>

Crystals of **1** were obtained only from Rb<sub>4</sub>Ge<sub>9</sub>/en mixtures in the presence of 7-amino-1-trimethylsilyl-5-aza-hepta-3-en-1-yne (**3**), but not in the absence of **3**. Therefore we investigated several solutions by ESI-MS, namely **1** in acetonitrile (acn) (Fig. S3, ESI<sup>†</sup>) as well as Rb<sub>4</sub>Ge<sub>9</sub>/en and Rb<sub>4</sub>Ge<sub>9</sub>/en/**3** with a molar ratio Rb<sub>4</sub>Ge<sub>9</sub>/**3** = 1 : 1 at an equal concentration of Rb<sub>4</sub>Ge<sub>9</sub> in en for both mixtures (Fig. S4, ESI<sup>†</sup>).

Crystals of **1** readily dissolve in acn (denoted as **1/acn**) giving a deep brown solution. Immediate injection of this solution into the mass spectrometer leads to peaks indicative for the presence of



$\text{Ge}_{10}^-$  ( $m/z = 725$ ),  $\{\text{Ge}_{10}\text{Rb}\}^-$  ( $m/z = 812$ ), and  $\{\text{Ge}_{10}\text{Rb}(222\text{-crypt})\}^-$  ( $m/z = 1188$ ), with the latter one as the most prominent species. The occurrence of solely  $\text{Ge}_{10}$  units hints for an enhanced stability of this cluster. By contrast, the ESI-MS of  $\text{Rb}_4\text{Ge}_9/\text{en}$  (Fig. S4a, ESI†) reveals the presence of  $\{\text{H}_x\text{Ge}_9\}^-$  ( $x = 0-2$ ;  $m/z = 653, 654, 655$ ),  $\{\text{HGe}_{10}\}^-$  ( $m/z = 726$ ) and  $\{\text{Ge}_9\text{Rb}\}^-$  ( $m/z = 738$ ) with an approximate ratio of intensities of 3 : 1 : 1. The high abundance of  $\{\text{HGe}_{10}\}^-$  indicates that **1a** is readily formed upon solution of  $\text{Rb}_4\text{Ge}_9$  in en, by a not yet understood fragmentation of the original  $[\text{Ge}_9]^{4-}$  cluster. §¶

Interestingly, the mass spectrum of the solution of  $\text{Rb}_4\text{Ge}_9/3/\text{en}$  (Fig. S4b, ESI†), from which the crystals of **1a** were obtained, shows dominant signals of  $\{\text{Ge}_9\text{R}\}^-$  ( $m/z = 764$ ),  $\{\text{Ge}_8\text{R}\}^-$  ( $m/z = 692$ ) and  $\{\text{Ge}_7\text{R}\}^-$  ( $m/z = 618$ ) ( $\text{R} = 7\text{-amino-5-aza-hepta-2,4-dien-2-yl}$ ) as well as the non-alkenylated species  $\{\text{H}_x\text{Ge}_9\}^-$  ( $x = 0-2$ ),  $\{\text{Ge}_9\text{Rb}\}^-$  and  $\{\text{HGe}_{10}\}^-$ . The high abundance of clusters bearing organic ligands R, that arise from the nucleophilic addition of one and two molecules of **3** to the  $[\text{Ge}_9]^{4-}$  unit, documents the higher reactivity of the  $[\text{Ge}_9]^{4-}$  unit compared to that of  $[\text{Ge}_{10}]^{2-}$ .<sup>37,42</sup> The appearance of  $\{\text{HGe}_{10}\}^-$  suggests that a fraction of the initial  $[\text{Ge}_9]^{4-}$  clusters reacts to **1a** prior to the reaction with **3**. Thus, layering of a  $\text{Rb}_4\text{Ge}_9/3/\text{en}$  solution with cryptand[2.2.2] in toluene preferably produces crystals of **1** since the functionalized species  $[\text{Ge}_9\text{R}]^{3-}$  obviously do not crystallize under these conditions. The binding mode of the organic group R to the cluster is shown in Fig. S5 (ESI†).

Our investigations shed some light onto the formation of the  $[\text{Ge}_{10}]^{2-}$  Zintl anion. ESI-MS investigations revealed that the  $[\text{Ge}_{10}]^{2-}$  unit is readily formed upon simple dissolution of  $\text{Rb}_4\text{Ge}_9$  in en, highlighting the flexibility of the dissolved tetrel element  $[\text{Ge}_9]^{4-}$  clusters which can grow and thereby change their shape. It turned out that the crystallization of the bare  $[\text{Ge}_9]^{y-}$  ( $y = 2-4$ ) clusters is favored over the crystallization of  $[\text{Ge}_{10}]^{2-}$ , both of which are present in  $\text{Rb}_4\text{Ge}_9/\text{en}$  solutions. Obviously, the  $[\text{Ge}_{10}]^{2-}$  unit can only be obtained when the  $\text{Ge}_9$  clusters are “masked” by the reaction with 7-amino-1-trimethylsilyl-5-aza-hepta-3-en-1-yne, leading to  $[\text{RGe}_9]^{3-}$ , which remains in solution and does not crystallize by layering with cryptand[2.2.2] in toluene. By adjusting the experimental conditions, it might be possible to obtain even larger empty germanium cages, and it also is feasible that other representatives of the  $[\text{E}_{10}]^{2-}$  series can be synthesized by this method.

The authors are grateful to the SolTech (Solar Technologies go Hybrid) program of the State of Bavaria for financial support. Moreover, the authors thank Herta Slavik for Raman-spectroscopic measurements and Dr Wilhelm Klein for the help with the crystal structure analysis.

## Notes and references

‡ Both Belin and Akerstedt isolated  $[\text{K}(222\text{-crypt})]_2[\text{Ge}_9]$ , which undergoes a disorder/order transition between 250 K and 100 K. Belin *et al.* performed single-crystal X-ray structure analysis at 250 K, and described the disordered  $[\text{Ge}_9]^{2-}$  clusters as  $[\text{Ge}_{10}]^{2-}$ . Akerstedt *et al.* reinvestigated the same compound (identical unit cell and cell volume) at 100 K, and observed a fully ordered *closo*- $[\text{Ge}_9]^{2-}$  cluster.<sup>33,34</sup>

§ The formation of **1a** is an oxidative process (Scheme S1, ESI†), as the formal number of valence electrons per Ge atom, reduces from 22/9 in case of  $[\text{Ge}_9]^{4-}$  to 22/10 for **1a**.

¶ Layering of such solutions with cryptand[2.2.2] or 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) in toluene has yielded a variety of crystals containing (connected)  $\text{Ge}_9$  clusters, but none comprising **1a**.<sup>17</sup>

|| The occurrence of also  $\text{Ge}_9^-$  and  $(\text{Ge}_9\text{Rb})^-$  in ESI-MS most likely is attributed to the cleavage of the Ge-C bonds of  $[\text{Ge}_9\text{R}]^{3-}$  under ESI-MS conditions.<sup>42</sup>

- 1 T. F. Fässler and S. D. Hoffmann, *Angew. Chem., Int. Ed.*, 2004, **43**, 6242.
- 2 S. C. Sevon and J. M. Goicoechea, *Organometallics*, 2006, **25**, 5678.
- 3 S. Scharfe, F. Kraus, S. Stegmaier, A. Schier and T. F. Fässler, *Angew. Chem., Int. Ed.*, 2011, **50**, 3630–3670.
- 4 A. M. Guloy, R. Ramlau, Z. Tang, W. Schnelle, M. Baitinger and Y. Grin, *Nature*, 2006, **443**, 320.
- 5 T. F. Fässler, *Angew. Chem., Int. Ed.*, 2007, **46**, 2572.
- 6 D. Sun, A. E. Riley, A. J. Cadby, E. K. Riechman, S. D. Korlann and S. H. Tolbert, *Nature*, 2006, **441**, 1126.
- 7 G. S. Armatas and M. G. Kanatzidis, *Science*, 2006, **313**, 817.
- 8 M. M. Bentlohner, M. Waibel, P. Zeller, K. Sarkar, P. Müller-Buschbaum, D. Fattakhova-Rohlfing and T. F. Fässler, *Angew. Chem., Int. Ed.*, 2016, **55**, 2441.
- 9 L. Xu and S. C. Sevon, *J. Am. Chem. Soc.*, 1999, **121**, 9245.
- 10 C. Downie, Z. J. Tang and A. M. Guloy, *Angew. Chem., Int. Ed.*, 2000, **39**, 337.
- 11 A. Ugrinov and S. C. Sevon, *J. Am. Chem. Soc.*, 2002, **124**, 10990.
- 12 R. Hauptmann and T. F. Fässler, *Z. Anorg. Allg. Chem.*, 2003, **629**, 2266.
- 13 A. Ugrinov and S. C. Sevon, *Inorg. Chem.*, 2003, **42**, 5789.
- 14 L. Yung, S. D. Hoffmann and T. F. Fässler, *Z. Anorg. Allg. Chem.*, 2004, **630**, 1977.
- 15 A. Nienhaus, S. D. Hoffmann and T. F. Fässler, *Z. Anorg. Allg. Chem.*, 2006, **632**, 1752.
- 16 S. Scharfe and T. F. Fässler, *Z. Anorg. Allg. Chem.*, 2011, **637**, 901.
- 17 A. Ugrinov and S. C. Sevon, *J. Am. Chem. Soc.*, 2003, **125**, 14059.
- 18 A. Ugrinov and S. C. Sevon, *Chem. – Eur. J.*, 2004, **10**, 3727.
- 19 C. Downie, J. G. Mao, H. Parmar and A. M. Guloy, *Inorg. Chem.*, 2004, **43**, 1992.
- 20 E. N. Esenturk, J. Fettinger, Y.-F. Lam and B. Eichhorn, *Angew. Chem., Int. Ed.*, 2004, **43**, 2132.
- 21 A. J. Karttunen, T. F. Fässler, M. Linnolahti and T. A. Pakkanen, *ChemPhysChem*, 2010, **11**, 1944.
- 22 A. Spiekermann, S. D. Hoffmann, T. F. Fässler, I. Krossing and U. Preiss, *Angew. Chem., Int. Ed.*, 2007, **46**, 5310.
- 23 J.-Q. Wang, S. Stegmaier and T. F. Fässler, *Angew. Chem., Int. Ed.*, 2009, **48**, 1998.
- 24 B. Zhou, M. S. Denning, D. L. Kays and J. M. Goicoechea, *J. Am. Chem. Soc.*, 2009, **131**, 2802.
- 25 G. Espinoza-Quintero, J. C. A. Duckworth, W. K. Myers, J. E. McGrady and J. M. Goicoechea, *J. Am. Chem. Soc.*, 2014, **136**, 1210.
- 26 M. M. Gillett-Kunnath, I. Petrov and S. C. Sevon, *Inorg. Chem.*, 2010, **49**, 721.
- 27 M. M. Gillett-Kunnath, A. G. Oliver and S. C. Sevon, *J. Am. Chem. Soc.*, 2011, **133**, 6560.
- 28 A. Spiekermann, S. D. Hoffmann and T. F. Fässler, *Angew. Chem., Int. Ed.*, 2006, **45**, 3459.
- 29 D. Rios and S. C. Sevon, *Inorg. Chem.*, 2010, **49**, 6396.
- 30 M. Waibel and T. F. Fässler, *Inorg. Chem.*, 2013, **52**, 5861.
- 31 D. Rios, M. M. Gillett-Kunnath, J. D. Taylor, A. G. Oliver and S. C. Sevon, *Inorg. Chem.*, 2011, **50**, 2373.
- 32 M. M. Bentlohner, L.-A. Jantke, T. Henneberger, C. Fischer, K. Mayer, W. Klein and T. F. Fässler, *Chem. – Eur. J.*, 2016, DOI: 10.1002/chem.201601706.
- 33 C. Belin, H. Mercier and V. Angilella, *New J. Chem.*, 1991, **15**, 931.
- 34 J. Åkerstedt, S. Ponou, L. Kloos and S. Lidin, *Eur. J. Inorg. Chem.*, 2011, 3999.
- 35 T. F. Fässler, H.-J. Muhr and M. Hunziker, *Eur. J. Inorg. Chem.*, 1998, 1433–1438.
- 36 S. Mitzinger, L. Broeckaert, W. Massa, F. Weigend and S. Dehnen, *Nat. Commun.*, 2016, **7**, 10480.
- 37 M. M. Bentlohner, W. Klein, Z. H. Fard, L.-A. Jantke and T. F. Fässler, *Angew. Chem., Int. Ed.*, 2015, **54**, 3748.
- 38 K. Wade, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 559.
- 39 H. G. Von Schnering, M. Baitinger, U. Bolle, W. Carrillo-Cabrera, J. Curda, Y. Grin, F. Heinemann, J. Llanos, K. Peters, A. Schmeding and M. Somer, *Z. Anorg. Allg. Chem.*, 1997, **623**, 1037.
- 40 M. Somer, W. Carrillo-Cabrera, E. M. Peters, K. Peters and H. G. v. Schnering, *Z. Anorg. Allg. Chem.*, 1998, **624**, 1915.
- 41 V. Hlukhyy, T. F. Fässler, S. Ponou, S. Lidin, N. P. Ivleva and R. Niessner, *Inorg. Chem.*, 2012, **51**, 4058.
- 42 M. W. Hull and S. C. Sevon, *J. Am. Chem. Soc.*, 2009, **131**, 9026.

