

Cite this: *Dalton Trans.*, 2014, **43**, 14514Received 25th July 2014,  
Accepted 13th August 2014

DOI: 10.1039/c4dt02265c

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## The preparation and structure of Ge<sub>3</sub>F<sub>8</sub> – a new mixed-valence fluoride of germanium, a convenient source of GeF<sub>2</sub>†

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The new binary mixed-valence fluoride of germanium, Ge<sub>3</sub>F<sub>8</sub>, has been obtained by heating GeF<sub>4</sub> with powdered Ge in an autoclave (390 K/4 bar/48 h). The structure contains pyramidal Ge<sup>II</sup>F<sub>3</sub> and octahedral Ge<sup>IV</sup>F<sub>6</sub> units, linked by fluoride bridges. The new compound is the missing member of the series (GeF<sub>2</sub>)<sub>n</sub>-GeF<sub>4</sub> (*n* = 2, 4, or 6). Sublimation of (GeF<sub>2</sub>)<sub>n</sub>-GeF<sub>4</sub> *in vacuo* provides a convenient source of GeF<sub>2</sub> in ca. 30% overall yield.

Although germanium is technologically very important both as the element and in oxide or chalcogenide compounds, with key applications in electronics, ceramics and optics,<sup>1</sup> its chemistry was neglected for many years compared with those of silicon and tin. It is now a very active area of main group chemistry and, in addition to the extensive chemistry of Ge(IV),<sup>2</sup> recent work has identified a large and complex coordination chemistry of Ge(II);<sup>2,3</sup> the latter contrasting with the limited coordination chemistry of Si(II).<sup>2</sup> In Group 14 as well as the common tetrahalides MX<sub>4</sub> (M = Si, Ge, Sn; X = F–I),<sup>4</sup> there are dihalides MX<sub>2</sub> (M = Ge, Sn), and the subhalides, GeBr and SnBr.<sup>5</sup> Of these, the chemistry of GeF<sub>2</sub> has been very little explored since it is not readily available commercially and its preparation by repeatedly passing GeF<sub>4</sub> over heated germanium, is both inconvenient and time consuming,<sup>6</sup> while the alternative method, involving the reaction of Ge with anhydrous HF in an autoclave, is hazardous. Both routes also require special equipment.<sup>7</sup> A number of intermediate halides have also been identified.<sup>2</sup> The latter are of two types; the most common are those with element–element (E–E) bonds, including Si<sub>2</sub>F<sub>6</sub>, Si<sub>2</sub>Cl<sub>6</sub>, Si<sub>3</sub>Cl<sub>8</sub>, Si<sub>6</sub>Cl<sub>14</sub>, Ge<sub>2</sub>Cl<sub>6</sub> and Ge<sub>5</sub>Cl<sub>12</sub>,<sup>8</sup> with structures analogous to the corresponding alkanes. Much

rarer, and limited to Ge and Sn, are a second group of mixed-valence materials, including Sn<sub>3</sub>F<sub>8</sub>, Ge<sub>5</sub>F<sub>12</sub>, and Ge<sub>7</sub>F<sub>16</sub>, which are without direct E–E bonds, but are fluoride-bridged and contain distinct environments attributable to M<sup>II</sup> and M<sup>IV</sup> centres.<sup>9–11</sup>

We are currently developing new routes for electrodeposition of p-block materials from non-aqueous media, using reagents including halometallate anions as the p-block element source,<sup>12</sup> and have recently reported the electrochemistry of [GeX<sub>3</sub>]<sup>–</sup> (X = Cl, Br or I) and [GeCl<sub>6</sub>]<sup>2–</sup> in CH<sub>2</sub>Cl<sub>2</sub> solution.<sup>13</sup> During the course of this work we have extended our studies to the fluoride systems. We report here the preparation and characterisation of a new binary, mixed-valence fluoride of germanium and its use to provide a convenient route to GeF<sub>2</sub>.

Depending upon the experimental conditions, repeatedly passing GeF<sub>4</sub> at low pressure over heated germanium yields either GeF<sub>2</sub>,<sup>6</sup> or mixed valence Ge<sup>II</sup>–Ge<sup>IV</sup> fluorides.<sup>10,11,14</sup> Two of the latter identified by single crystal X-ray diffraction (XRD) studies are Ge<sub>5</sub>F<sub>12</sub>† and Ge<sub>7</sub>F<sub>16</sub>,<sup>10,11</sup> which are members of the series (GeF<sub>2</sub>)<sub>n</sub>-GeF<sub>4</sub>.<sup>14</sup> These flow reactions are inconvenient and low yielding, hence we have investigated the reduction of GeF<sub>4</sub> with Ge powder in an autoclave under modest pressure (390 K/4 bar/48 h, see ESI†). Initial attempts at temperatures <370 K resulted in little reaction, but on increasing the temperature to 390 K/48 h, much of the GeF<sub>4</sub> was consumed (as indicated by the drop in pressure), and upon opening the autoclave in a glove-box, a mass of white microcrystalline material was found on the cooler lid. The crystals are extremely moisture sensitive, converting into a pool of liquid immediately on exposure to air. Single crystal X-ray diffraction data were collected from one of the small crystals and the structure solution identified this product as Ge<sub>3</sub>F<sub>8</sub>, the missing third member of the series (GeF<sub>2</sub>)<sub>n</sub>-GeF<sub>4</sub>, with *n* = 2. Unit cell measurements on several other crystals confirmed these as the same compound. Powder X-ray diffraction (PXRD) data were also collected on the bulk material and that showed smaller amounts of Ge<sub>5</sub>F<sub>12</sub> and Ge<sub>7</sub>F<sub>16</sub>, as well as traces of GeF<sub>2</sub> were also present. The simulated and experimental powder XRD data from this mixture are shown in the ESI.†

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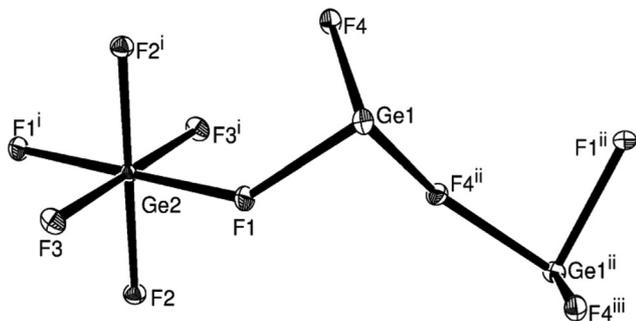
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† Electronic supplementary information (ESI) available: Experimental details for the syntheses of Ge<sub>3</sub>F<sub>8</sub> and GeF<sub>2</sub>, and the PXRD data for all the products. Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request\_for\_deposited\_data.html) on quoting CSD number 427896. See DOI: 10.1039/c4dt02265c

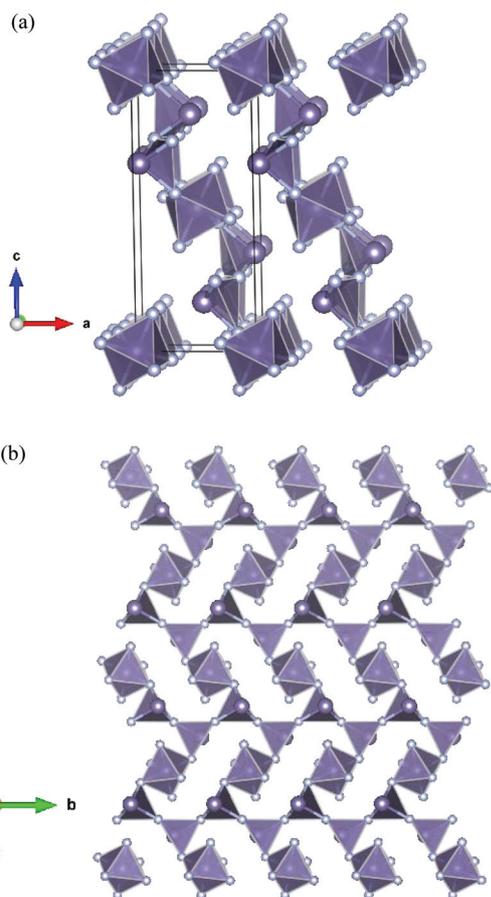


Sublimation of the mixture (390 K/0.5 mm) gave ~30% yield of  $\text{GeF}_2$  (based on elemental Ge used in the first step), which was identified by PXRD (see ESI†). Some involatile orange material (*cf.* ref. 6) was also formed.

Germanium difluoride has a polymeric chain structure based upon trigonal pyramidal  $\text{GeF}_3$  units ( $\text{Ge-F} = 1.79(2)$ ,



**Fig. 1** The  $\text{Ge}^{\text{II}}$  and  $\text{Ge}^{\text{IV}}$  units in  $\text{Ge}_3\text{F}_8$  with ellipsoids drawn at the 50% level. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ):  $\text{Ge2-F1} = 1.855(1)$ ,  $\text{Ge2-F2} = 1.767(1)$ ,  $\text{Ge2-F3} = 1.782(1)$ ,  $\text{Ge1-F1} = 2.010(1)$ ,  $\text{Ge1-F4}^{\text{II}} = 1.938(1)$ ,  $\text{Ge1-F4} = 1.980(1)$ ,  $\text{F1-Ge1-F4} = 83.28(5)$ ,  $\text{F4-Ge-F4}^{\text{II}} = 86.35(3)$ ,  $\text{F4}^{\text{II}}-\text{Ge1-F1} = 85.42(6)$ . Symmetry codes: (i)  $1-x, 1-y, 1-z$ ; (ii)  $0.5-x, -0.5+y, 1.5-z$ ; (iii)  $x, -1+y, z$ .

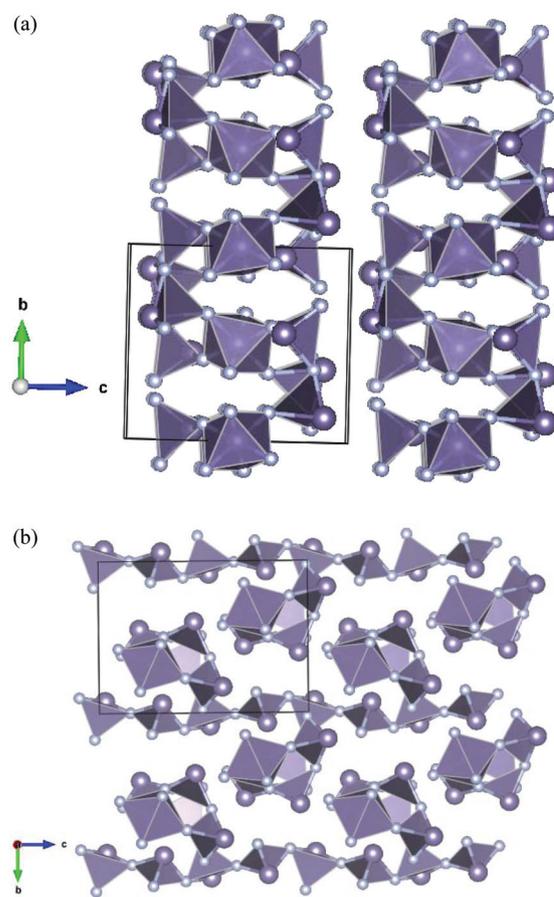


**Fig. 2** The  $\text{Ge}_3\text{F}_8$  structure viewed along: (a) the  $b$  axis to observe the sheets, and (b) the  $a$  axis, showing the connectivity within the sheets.

$1.91(2)$ ,  $2.09(2)$   $\text{\AA}$ ), with a distant fourth fluoride at  $2.57(2)$   $\text{\AA}$  that cross-links the chains.<sup>15</sup> The new preparation is a convenient way to obtain  $\text{GeF}_2$  in useful quantity for further studies of its coordination and organometallic chemistry.

The single crystals of the mixed-valence  $\text{Ge}_3\text{F}_8$  are isomorphous with  $\text{Sn}_3\text{F}_8$ ,<sup>9</sup> adopting the monoclinic space group  $P2_1/n$ . The structure is composed (Fig. 1) of slightly distorted  $\text{GeF}_6$  octahedra with four terminal  $\text{Ge-F}$  bonds ( $1.767(1)$ ,  $1.782(1)$   $\text{\AA}$ ), and two slightly longer  $\text{Ge-F}$  bonds ( $1.855(1)$   $\text{\AA}$ ) that are involved in bridging to the  $\text{Ge}^{\text{II}}$  units. The germanium (ii) core environment is trigonal pyramidal, composed of one terminal ( $\text{Ge-F} = 1.938(1)$   $\text{\AA}$ ) and two bridging ( $\text{Ge-F} = 1.980(1)$ ,  $2.010(1)$   $\text{\AA}$ ) fluorides, one linked to  $\text{Ge}^{\text{IV}}$  and one to a second  $\text{Ge}^{\text{II}}$  centre. There are also longer  $\text{Ge}^{\text{II}}\cdots\text{F}$  contacts ( $2.56$   $\text{\AA}$ ), and if these are included, the germanium(ii) geometry is a distorted saw-horse shape, reminiscent of  $\text{GeF}_2$ . Overall, the packing is best considered as sheets in the (101) planes (Fig. 2a), with each sheet being made up of puckered chains of  $\text{GeF}_3$  units along [010] connected together by the  $\text{GeF}_6$  octahedra (Fig. 2b).

Considering the structures of  $\text{Ge}_5\text{F}_{12}$ <sup>10</sup> and  $\text{Ge}_7\text{F}_{16}$ ,<sup>11</sup> the same basic building blocks are present (trigonal pyramidal  $\text{GeF}_3$  and octahedral  $\text{GeF}_6$ ), but as the F/Ge ratio declines, the



**Fig. 3** (a) View of the structure of  $\text{Ge}_5\text{F}_{12}$ .<sup>10</sup> (b) View of the structure of  $\text{Ge}_7\text{F}_{16}$ .<sup>11</sup>



structures become more distorted to maintain the germanium coordination numbers. In  $\text{Ge}_5\text{F}_{12}$ , if we ignore the distant fourth fluoride at 2.44 Å, the  $\text{GeF}_3$  trigonal pyramids ( $\text{Ge}-\text{F} = 1.80(2), 1.99(2), 2.20(2)$  Å) form corrugated sheets in (001), based on  $\text{GeF}_6$  octahedra linked to dimers of two corner-linked  $\text{GeF}_3$  pyramids. As a consequence of the 4 : 1  $\text{Ge}^{\text{II}} : \text{Ge}^{\text{IV}}$  constitution, the  $\text{GeF}_6$  units are linked to four dimers (rather than two as in  $\text{Ge}_3\text{F}_8$ ) (Fig. 3a). The structure of  $\text{Ge}_7\text{F}_{16}$  is complicated in that there are seven distinct germanium sites,<sup>11</sup> but again, the building blocks are trigonal pyramidal  $\text{GeF}_3$  and octahedral  $\text{GeF}_6$  units. The structure is best described as chains of  $\text{GeF}_3$  pyramids along [001] with side chains of four  $\text{GeF}_3$  units terminated by a  $\text{GeF}_6$  octahedron attached to every second  $\text{GeF}_3$  of the main chain (Fig. 3b).

In conclusion, the missing member of the unique series of mixed-valence germanium fluorides  $(\text{GeF}_2)_n\text{-GeF}_4$  ( $n = 2, 4$ , or 6) has been obtained by reaction of  $\text{GeF}_4$  and Ge powder under modest pressure and temperature, its structure determined and the structural relationships within the series established. Sublimation of the  $(\text{GeF}_2)_n\text{-GeF}_4$  *in vacuo* provides a convenient route to the previously rather inaccessible  $\text{GeF}_2$ . Further work to explore the chemistry of  $\text{GeF}_2$  formed by this route is underway and will be reported in due course.

## Acknowledgements

We thank EPSRC for support (EP/1033394/1 and EP/1010890/1). The SCFED Project (<http://www.scfed.net>) is a multidisciplinary collaboration of British universities investigating the fundamental and applied aspects of supercritical fluids.

## Notes and references

‡  $\text{Ge}_5\text{F}_{12}$  was originally formulated as  $\text{Ge}_2\text{F}_5$ ,<sup>14</sup> the correct formula subsequently being established from the crystal structure determination.<sup>10</sup>

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