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The new binary mixed-valence fluoride of germanium,  $\text{Ge}_3\text{F}_8$ , has been obtained by heating  $\text{GeF}_4$  with powdered Ge in an autoclave (390 K/4 bar/48 h). The structure contains pyramidal  $\text{Ge}^{\text{II}}\text{F}_3$  and octahedral  $\text{Ge}^{\text{IV}}\text{F}_6$  units, linked by fluoride bridges. The new compound is the missing member of the series  $(\text{GeF}_2)_n \cdot \text{GeF}_4$  ( $n = 2, 4$ , or 6). Sublimation of  $(\text{GeF}_2)_n \cdot \text{GeF}_4$  in *vacuo* provides a convenient source of  $\text{GeF}_2$  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  $\text{MX}_4$  ( $\text{M} = \text{Si, Ge, Sn}$ ;  $\text{X} = \text{F-I}$ ),<sup>4</sup> there are dihalides  $\text{MX}_2$  ( $\text{M} = \text{Ge, Sn}$ ), and the subhalides,  $\text{GeBr}$  and  $\text{SnBr}$ .<sup>5</sup> Of these, the chemistry of  $\text{GeF}_2$  has been very little explored since it is not readily available commercially and its preparation by repeatedly passing  $\text{GeF}_4$  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  $\text{Si}_2\text{F}_6$ ,  $\text{Si}_2\text{Cl}_6$ ,  $\text{Si}_3\text{Cl}_8$ ,  $\text{Si}_6\text{Cl}_{14}$ ,  $\text{Ge}_2\text{Cl}_6$  and  $\text{Ge}_5\text{Cl}_{12}$ ,<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  $\text{Sn}_3\text{F}_8$ ,  $\text{Ge}_5\text{F}_{12}$ , and  $\text{Ge}_7\text{F}_{16}$ , which are without direct E–E bonds, but are fluoride-bridged and contain distinct environments attributable to  $\text{M}^{\text{II}}$  and  $\text{M}^{\text{IV}}$  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  $[\text{GeX}_3]^-$  ( $\text{X} = \text{Cl, Br or I}$ ) and  $[\text{GeCl}_6]^{2-}$  in  $\text{CH}_2\text{Cl}_2$  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  $\text{GeF}_2$ .

Depending upon the experimental conditions, repeatedly passing  $\text{GeF}_4$  at low pressure over heated germanium yields either  $\text{GeF}_2$ ,<sup>6</sup> or mixed valence  $\text{Ge}^{\text{II}}\text{-Ge}^{\text{IV}}$  fluorides.<sup>10,11,14</sup> Two of the latter identified by single crystal X-ray diffraction (XRD) studies are  $\text{Ge}_5\text{F}_{12}\ddagger$  and  $\text{Ge}_7\text{F}_{16}$ ,<sup>10,11</sup> which are members of the series  $(\text{GeF}_2)_n \cdot \text{GeF}_4$ .<sup>14</sup> These flow reactions are inconvenient and low yielding, hence we have investigated the reduction of  $\text{GeF}_4$  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  $\text{GeF}_4$  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  $\text{Ge}_3\text{F}_8$ , the missing third member of the series  $(\text{GeF}_2)_n \cdot \text{GeF}_4$ , 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  $\text{Ge}_5\text{F}_{12}$  and  $\text{Ge}_7\text{F}_{16}$ , as well as traces of  $\text{GeF}_2$  were also present. The simulated and experimental powder XRD data from this mixture are shown in the ESI.†

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† Electronic supplementary information (ESI) available: Experimental details for the syntheses of  $\text{Ge}_3\text{F}_8$  and  $\text{GeF}_2$ , 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](mailto:crysdata@fiz-karlsruhe.de), [http://www.fiz-karlsruhe.de/request\\_for\\_deposited\\_data.html](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  $\sim$ 30% yield of  $\text{GeF}_2$  (based on elemental Ge used in the first step), which was identified by PXRD (see ESI<sup>†</sup>). 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 ( $\text{Ge}-\text{F} = 1.79(2)$ ,

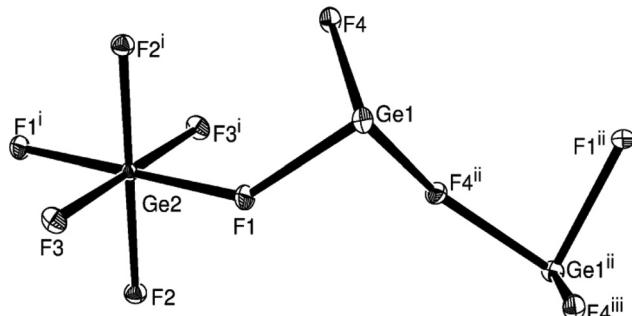


Fig. 1 The  $\text{Ge}^{\text{II}}$  and  $\text{Ge}^{\text{IV}}$  units in  $\text{Ge}_3\text{F}_8$  with ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°):  $\text{Ge}2-\text{F}1 = 1.855(1)$ ,  $\text{Ge}2-\text{F}2 = 1.767(1)$ ,  $\text{Ge}2-\text{F}3 = 1.782(1)$ ,  $\text{Ge}1-\text{F}1 = 2.010(1)$ ,  $\text{Ge}1-\text{F}4^{\text{II}} = 1.938(1)$ ,  $\text{Ge}1-\text{F}4 = 1.980(1)$ ,  $\text{F}1-\text{Ge}1-\text{F}4 = 83.28(5)$ ,  $\text{F}4-\text{Ge}1-\text{F}4^{\text{II}} = 86.35(3)$ ,  $\text{F}4^{\text{II}}-\text{Ge}1-\text{F}1 = 85.42(6)$ . Symmetry codes: (i)  $1 - x, 1 - y, 1 - z$ ; (ii)  $0.5 - x, -0.5 + y, 1.5 - z$ ; (iii)  $x, -1 + y, z$ .

$1.91(2)$ ,  $2.09(2)$  Å, with a distant fourth fluoride at  $2.57(2)$  Å 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  $\text{Ge}-\text{F}$  bonds (1.767(1), 1.782(1) Å), and two slightly longer  $\text{Ge}-\text{F}$  bonds (1.855(1) Å) that are involved in bridging to the  $\text{Ge}^{\text{II}}$  units. The germanium (II) core environment is trigonal pyramidal, composed of one terminal ( $\text{Ge}-\text{F} = 1.938(1)$  Å) and two bridging ( $\text{Ge}-\text{F} = 1.980$  (1), 2.010(1) Å) 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 Å), 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

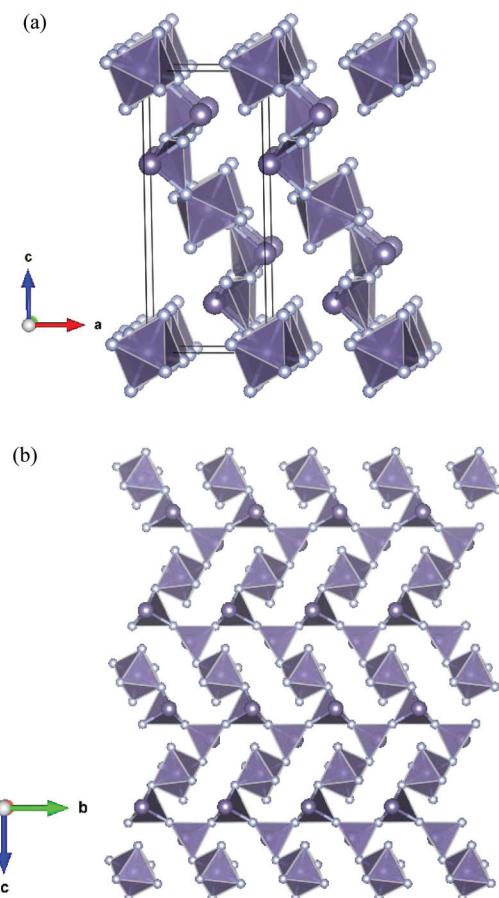


Fig. 2 The  $\text{Ge}_3\text{F}_8$  structure viewed along: (a) the  $b$  axis to observe the sheets, and (b) the  $a$  axis, showing the connectivity within the sheets.

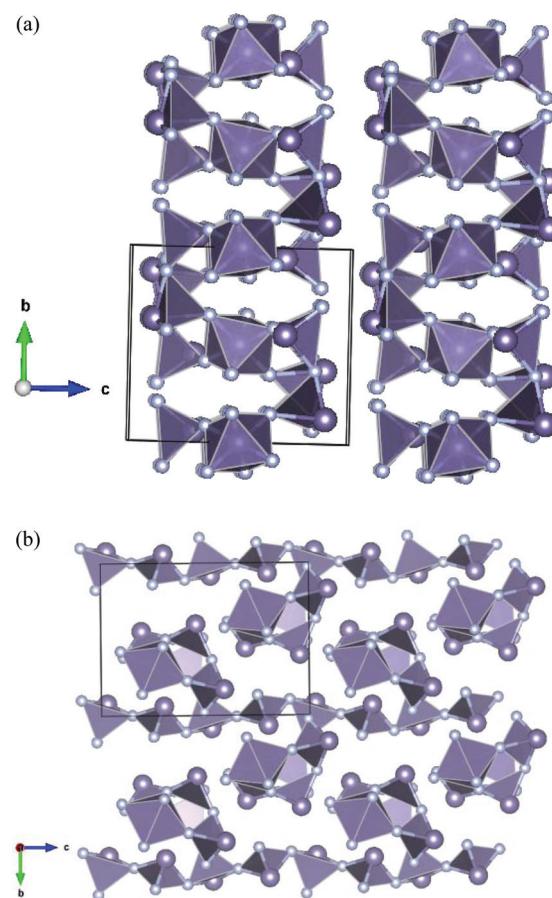


Fig. 3 (a) View of the structure of  $\text{Ge}_5\text{F}_{12}$ .<sup>10</sup> (b) View of the structure of  $\text{Ge}_7\text{F}_{16}$ .<sup>11</sup>

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  $(\text{GeF}_2)_n \cdot \text{GeF}_4$  ( $n = 2, 4$ , 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  $(\text{GeF}_2)_n \cdot \text{GeF}_4$  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.

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## Notes and references

<sup>‡</sup> $\text{Ge}_5\text{F}_{12}$  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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