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The preparation and structure of Ge₃F₈ – a new mixed-valence fluoride of germanium, a convenient source of GeF₂†

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The new binary mixed-valence fluoride of germanium, Ge₃F₈, has been obtained by heating GeF₄ with powdered Ge in an autoclave (390 K/4 bar/48 h). The structure contains pyramidal Ge^{II}F₃ and octahedral Ge^{IV}F₆ units, linked by fluoride bridges. The new compound is the missing member of the series (GeF₂)_n-GeF₄ (*n* = 2, 4, or 6). Sublimation of (GeF₂)_n-GeF₄ *in vacuo* provides a convenient source of GeF₂ 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,¹ 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),² recent work has identified a large and complex coordination chemistry of Ge(II);^{2,3} the latter contrasting with the limited coordination chemistry of Si(II).² In Group 14 as well as the common tetrahalides MX₄ (M = Si, Ge, Sn; X = F–I),⁴ there are dihalides MX₂ (M = Ge, Sn), and the subhalides, GeBr and SnBr.⁵ Of these, the chemistry of GeF₂ has been very little explored since it is not readily available commercially and its preparation by repeatedly passing GeF₄ over heated germanium, is both inconvenient and time consuming,⁶ while the alternative method, involving the reaction of Ge with anhydrous HF in an autoclave, is hazardous. Both routes also require special equipment.⁷ A number of intermediate halides have also been identified.² The latter are of two types; the most common are those with element–element (E–E) bonds, including Si₂F₆, Si₂Cl₆, Si₃Cl₈, Si₆Cl₁₄, Ge₂Cl₆ and Ge₅Cl₁₂,⁸ with structures analogous to the corresponding alkanes. Much

rarer, and limited to Ge and Sn, are a second group of mixed-valence materials, including Sn₃F₈, Ge₅F₁₂, and Ge₇F₁₆, which are without direct E–E bonds, but are fluoride-bridged and contain distinct environments attributable to M^{II} and M^{IV} centres.^{9–11}

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,¹² and have recently reported the electrochemistry of [GeX₃][–] (X = Cl, Br or I) and [GeCl₆]^{2–} in CH₂Cl₂ solution.¹³ 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 GeF₂.

Depending upon the experimental conditions, repeatedly passing GeF₄ at low pressure over heated germanium yields either GeF₂,⁶ or mixed valence Ge^{II}–Ge^{IV} fluorides.^{10,11,14} Two of the latter identified by single crystal X-ray diffraction (XRD) studies are Ge₅F₁₂† and Ge₇F₁₆,^{10,11} which are members of the series (GeF₂)_n-GeF₄.¹⁴ These flow reactions are inconvenient and low yielding, hence we have investigated the reduction of GeF₄ 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 GeF₄ 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 Ge₃F₈, the missing third member of the series (GeF₂)_n-GeF₄, 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 Ge₅F₁₂ and Ge₇F₁₆, as well as traces of GeF₂ 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 Ge₃F₈ and GeF₂, 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 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 GeF_3 units ($\text{Ge-F} = 1.79(2)$,

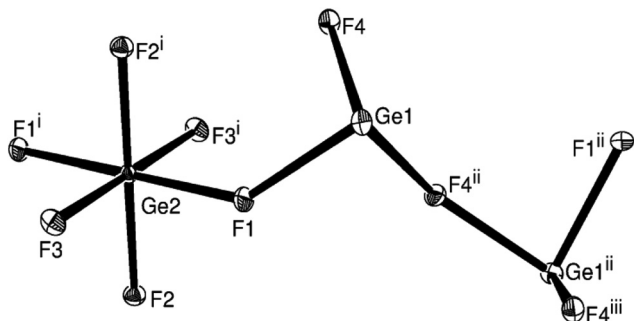


Fig. 1 The Ge^{II} and Ge^{IV} units in Ge_3F_8 with ellipsoids drawn at the 50% level. Selected bond lengths (\AA) and angles ($^\circ$): $\text{Ge2-F1} = 1.855(1)$, $\text{Ge2-F2} = 1.767(1)$, $\text{Ge2-F3} = 1.782(1)$, $\text{Ge1-F1} = 2.010(1)$, $\text{Ge1-F4}^{\text{II}} = 1.938(1)$, $\text{Ge1-F4} = 1.980(1)$, $\text{F1-Ge1-F4} = 83.28(5)$, $\text{F4-Ge-F4}^{\text{II}} = 86.35(3)$, $\text{F4}^{\text{II}}-\text{Ge1-F1} = 85.42(6)$. Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $0.5-x, -0.5+y, 1.5-z$; (iii) $x, -1+y, z$.

$1.91(2)$, $2.09(2)$ \AA), with a distant fourth fluoride at $2.57(2)$ \AA that cross-links the chains.¹⁵ The new preparation is a convenient way to obtain GeF_2 in useful quantity for further studies of its coordination and organometallic chemistry.

The single crystals of the mixed-valence Ge_3F_8 are isomorphous with Sn_3F_8 ,⁹ adopting the monoclinic space group $P2_1/n$. The structure is composed (Fig. 1) of slightly distorted GeF_6 octahedra with four terminal Ge-F bonds ($1.767(1)$, $1.782(1)$ \AA), and two slightly longer Ge-F bonds ($1.855(1)$ \AA) that are involved in bridging to the Ge^{II} units. The germanium (ii) core environment is trigonal pyramidal, composed of one terminal ($\text{Ge-F} = 1.938(1)$ \AA) and two bridging ($\text{Ge-F} = 1.980(1)$, $2.010(1)$ \AA) fluorides, one linked to Ge^{IV} and one to a second Ge^{II} centre. There are also longer $\text{Ge}^{\text{II}}\cdots\text{F}$ contacts (2.56 \AA), and if these are included, the germanium(ii) geometry is a distorted saw-horse shape, reminiscent of GeF_2 . Overall, the packing is best considered as sheets in the (010) planes (Fig. 2a), with each sheet being made up of puckered chains of GeF_3 units along [010] connected together by the GeF_6 octahedra (Fig. 2b).

Considering the structures of Ge_5F_{12} ¹⁰ and Ge_7F_{16} ,¹¹ the same basic building blocks are present (trigonal pyramidal GeF_3 and octahedral GeF_6), but as the F/Ge ratio declines, the

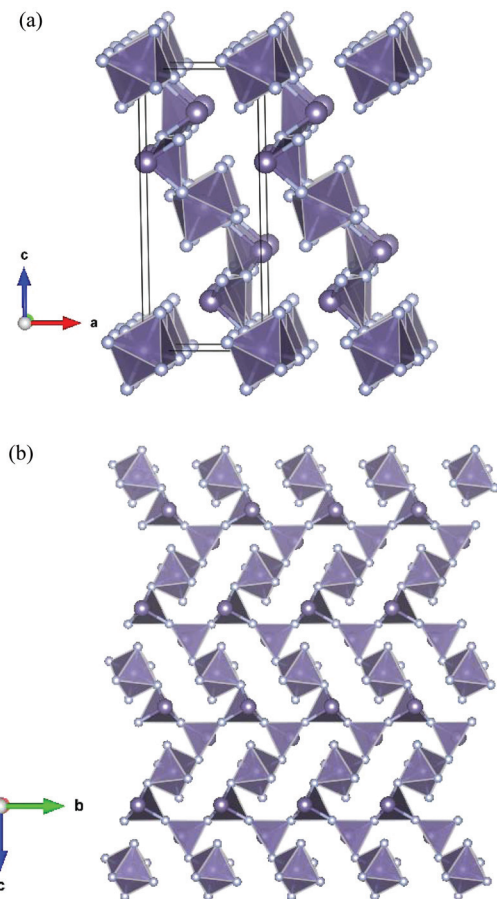


Fig. 2 The Ge_3F_8 structure viewed along: (a) the b axis to observe the sheets, and (b) the a axis, showing the connectivity within the sheets.

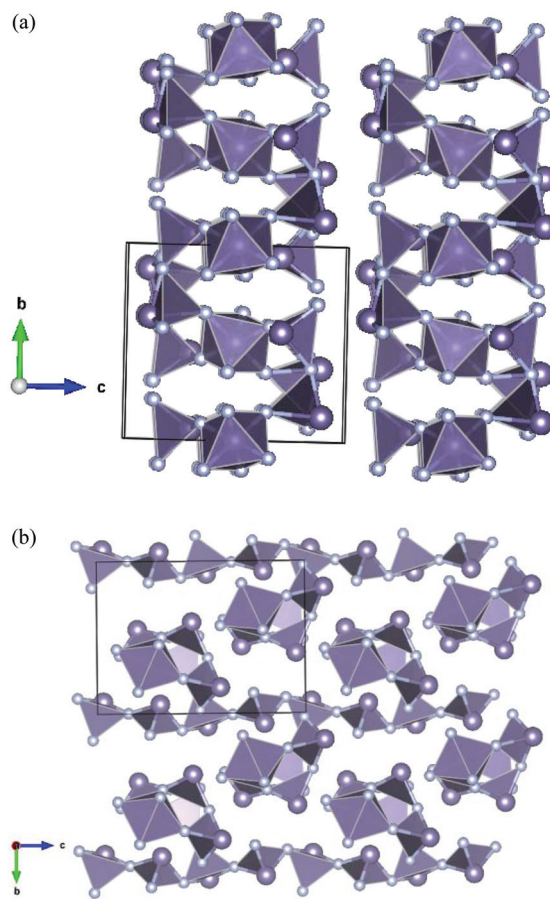


Fig. 3 (a) View of the structure of Ge_5F_{12} .¹⁰ (b) View of the structure of Ge_7F_{16} .¹¹



structures become more distorted to maintain the germanium coordination numbers. In Ge_5F_{12} , if we ignore the distant fourth fluoride at 2.44 Å, the 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 GeF_6 octahedra linked to dimers of two corner-linked GeF_3 pyramids. As a consequence of the 4 : 1 $\text{Ge}^{\text{II}} : \text{Ge}^{\text{IV}}$ constitution, the GeF_6 units are linked to four dimers (rather than two as in Ge_3F_8) (Fig. 3a). The structure of Ge_7F_{16} is complicated in that there are seven distinct germanium sites,¹¹ but again, the building blocks are trigonal pyramidal GeF_3 and octahedral GeF_6 units. The structure is best described as chains of GeF_3 pyramids along [001] with side chains of four GeF_3 units terminated by a GeF_6 octahedron attached to every second GeF_3 of the main chain (Fig. 3b).

In conclusion, the missing member of the unique series of mixed-valence germanium fluorides $(\text{GeF}_2)_n\text{-GeF}_4$ ($n = 2, 4, \text{ or } 6$) has been obtained by reaction of 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 GeF_2 . Further work to explore the chemistry of GeF_2 formed by this route is underway and will be reported in due course.

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Notes and references

‡ Ge_5F_{12} was originally formulated as Ge_2F_5 ,¹⁴ the correct formula subsequently being established from the crystal structure determination.¹⁰

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