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The preparation and structure of Ge_3F_8 – a new mixed-valence fluoride of germanium, a convenient source of GeF_2†

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The new binary mixed-valence fluoride of germanium, Ge_3F_8, has been obtained by heating GeF_4 with powdered Ge in an autoclave (390 K/4 bar/48 h). The structure contains pyramidal $Ge^{II}F_3$ and octahedral $Ge^{IV}F_6$ units, linked by fluoride bridges. The new compound is the missing member of the series $(GeF_2)_n{\cdot}GeF_4$ (n = 2, 4, or 6). Sublimation of $(GeF_2)_n{\cdot}GeF_4$ *in vacuo* provides a convenient source of 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,[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 MX_4 (M = Si, Ge, Sn; X = F–I),[4] there are dihalides MX_2 (M = Ge, Sn), and the subhalides, GeBr and SnBr.[5] Of these, the chemistry of GeF_2 has been very little explored since it is not readily available commercially and its preparation by repeatedly passing GeF_4 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 Si_2F_6, Si_2Cl_6, Si_3Cl_8, Si_6Cl_{14}, Ge_2Cl_6 and Ge_5Cl_{12},[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 Sn_3F_8, Ge_5F_{12}, and Ge_7F_{16}, 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 $[GeX_3]^-$ (X = Cl, Br or I) and $[GeCl_6]^{2-}$ in CH_2Cl_2 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 GeF_2.

Depending upon the experimental conditions, repeatedly passing GeF_4 at low pressure over heated germanium yields either GeF_2,[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 Ge_5F_{12}‡ and Ge_7F_{16},[10,11] which are members of the series $(GeF_2)_n{\cdot}GeF_4$.[14] These flow reactions are inconvenient and low yielding, hence we have investigated the reduction of 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 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 Ge_3F_8, the missing third member of the series $(GeF_2)_n{\cdot}GeF_4$, 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 Ge_5F_{12} and Ge_7F_{16}, as well as traces of 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 Ge_3F_8 and 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, 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 (Ge–F = 1.79(2), 1.91(2), 2.09(2) Å), with a distant fourth fluoride at 2.57(2) Å 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) Å), and two slightly longer Ge–F bonds (1.855(1) Å) that are involved in bridging to the Ge^{II} units. The germanium (II) core environment is trigonal pyramidal, composed of one terminal (Ge–F = 1.938(1) Å) and two bridging (Ge–F = 1.980 (1), 2.010(1) Å) fluorides, one linked to Ge^{IV} and one to a second Ge^{II} centre. There are also longer $Ge^{II}\cdots F$ contacts (2.56 Å), 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 (101) 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

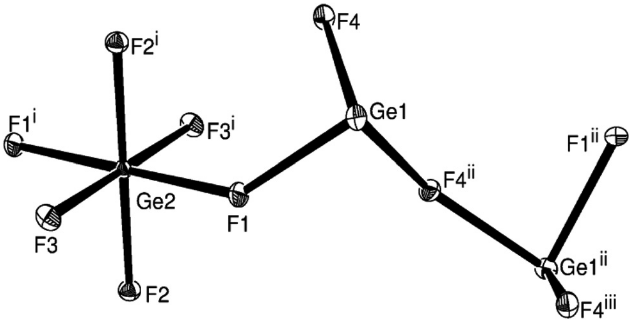

Fig. 1 The Ge^{II} and Ge^{IV} units in Ge_3F_8 with ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): Ge2–F1 = 1.855(1), Ge2–F2 = 1.767(1), Ge2–F3 = 1.782(1), Ge1–F1 = 2.010(1), Ge1–$F4^{ii}$ = 1.938(1), Ge1–F4 = 1.980(1), F1–Ge1–F4 = 83.28(5), F4–Ge–$F4^{ii}$ = 86.35(3), $F4^{ii}$–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) $x, -1 + y, z$.

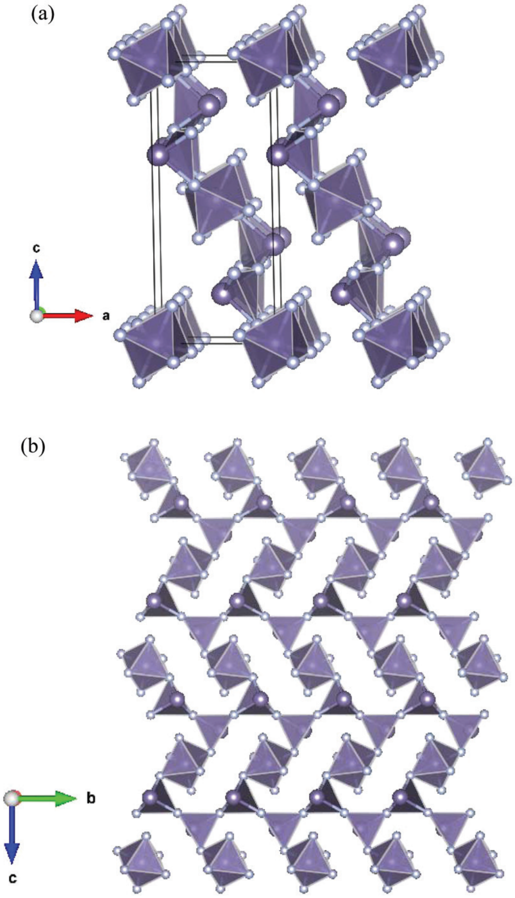

Fig. 2 The Ge_3F_8 structure viewed along: (a) the *b* axis to observe the sheets, and (b) the *a* axis, showing the connectivity within the sheets.

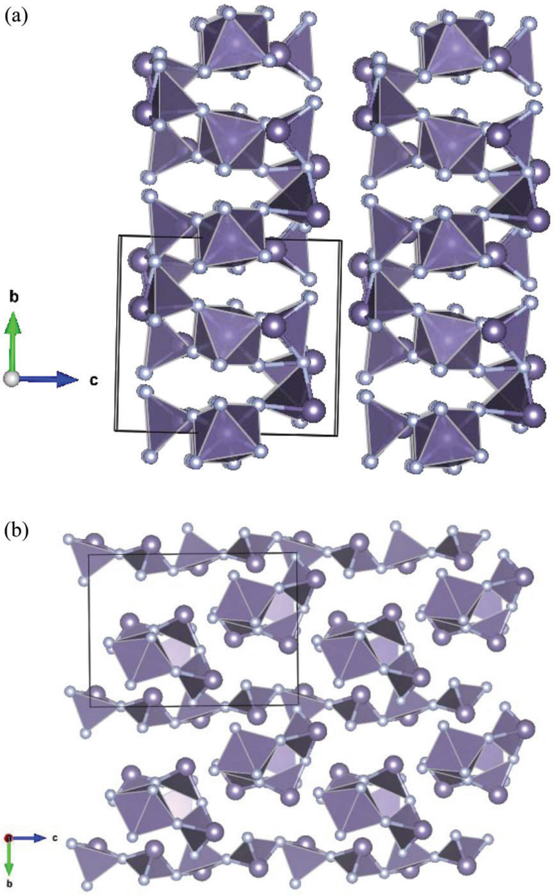

Fig. 3 (a) View of the structure of Ge_5F_{12}.[10] (b) View of the structure of Ge_7F_{16}.[11]

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 (Ge–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 $4:1$ $Ge^{II}:Ge^{IV}$ 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 $(GeF_2)_n{\cdot}GeF_4$ (n = 2, 4, 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 $(GeF_2)_n{\cdot}GeF_4$ *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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