

Tetrafluorodipyridinegermanium,  
[GeF<sub>4</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>]Dat T. Tran,<sup>a</sup> Peter Y. Zavalij<sup>b</sup>  
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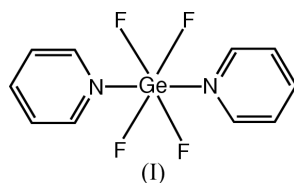
## Key indicators

Single-crystal X-ray study  
T = 298 K  
Mean  $\sigma$ (C–C) = 0.006 Å  
R factor = 0.039  
wR factor = 0.052  
Data-to-parameter ratio = 12.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The molecular title compound was solvothermally synthesized at 373 K and crystallized in the triclinic system, with space group  $P\bar{1}$ . The Ge(IV) atom lies on an inversion center and is coordinated by four fluoride anions and two pyridine molecules. Owing to the non-bridging nature of the fluoride anions, this material forms a molecular solid with close packing.

## Comment

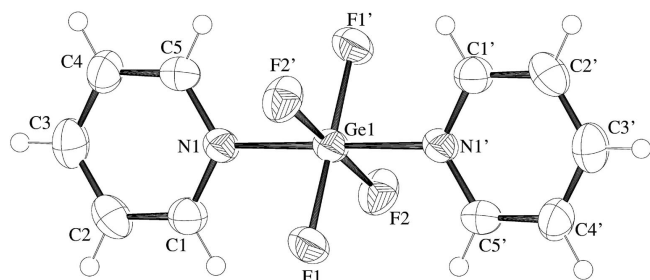
Our research is currently focused on the solvothermal synthesis of new layered and open-framework materials based on heavier group 14 elements. We have used both cationic and anionic structure-directing agents, for the formation of anionic and cationic germanium-, tin- (Salami *et al.*, 2001*a,b*, 2002; Lansky *et al.*, 2001) and lead-based compounds (Tran *et al.*, 2002). Our interest in these materials stems from their potential to yield chemically and thermally stable microporous zeotype materials, with advantageous materials properties, such as ion-exchange, separation and catalysis. We have successfully synthesized a series of new materials. We are also interested in these materials for their possible semiconducting properties, as well as for low-dimensional solid-state precursors to extended frameworks.



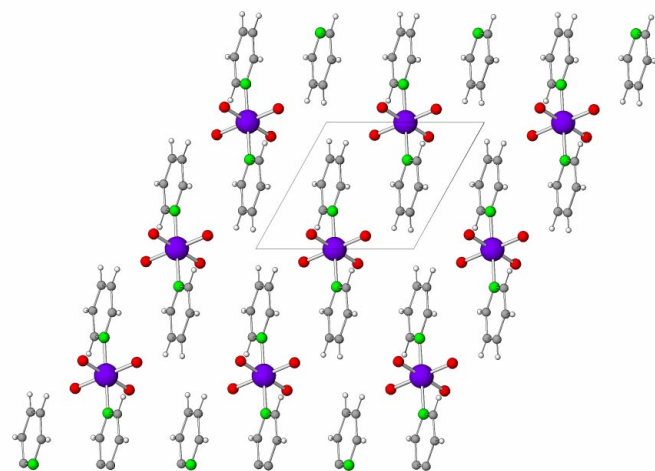
Recently, we used a predominantly non-aqueous environment, where the only source of water was present in the hexafluorophosphoric acid reagent (HPF<sub>6</sub>, 60 wt% solution in water), which was added to a pyridine solvent. Hexafluorophosphoric acid was selected as a potential anionic structure-directing agent. Instead, it acted as source of fluoride. Pyridine and fluoride combined with germanium to form the title compound, denoted BING-10 [where BING denotes the State University of New York at Binghamton and 10 represents structure type], an octahedral complex (Fig. 1). The key feature of BING-10 is the non-bridging terminal fluorides, resulting in the formation of a neutral molecular solid (Fig. 2). In the case of lead as the building block, the fluorides bridge the metal centers, to give rise to an extended layered material (BING-5; Tran *et al.*, 2002).

BING-10 exists as isolated octahedral units that form a neutral molecular solid. Pyridine solvent molecules are incorporated as ligands. There is only one crystallographically

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**Figure 1**  
View of the molecules of BING-10, shown with ellipsoids at the 50% probability level.



**Figure 2**  
The crystallographic projection of BING-10, highlighting the germanium tetrafluoride dipyrindine complex (colour scheme: Ge blue, F red, N green, C dark grey and H light grey).

unique germanium center, which is bonded to four fluorides and the N atoms of two pyridine molecules. The Ge–F distances are 1.768 (2) and 1.770 (2) Å, while the Ge–N distance is 2.014 (3) Å. All *trans* ligands define a 180° bond angle, since the molecule lies on an inversion center. The *cis* F–Ge–F bond angles are 89.96 (9) and 90.04 (9)°, while those of F–Ge–N vary from 89.82 (10) to 90.18 (10)°.

We are working further towards obtaining cationic and anionic germanates, especially new layered or open-framework materials. It would appear that a significant concentration of fluoride source in our systems is not suitable for the formation of an extended germanium oxide material. We are currently studying other combinations of germanium sources, solvents and structure-directing agents, to isolate inorganic materials with semiconducting or anion-exchange capabilities.

## Experimental

The reaction mixture consisted of pyridine, germanium tetraethoxide and HPF<sub>6</sub> in a molar ratio of 16:1:1. Solvothermal synthesis was conducted in a 23 ml capacity Teflon-lined Parr autoclave at 373 K for 6 d. The BING-10 crystals were colorless needles. The yield was 65.7%.

## Crystal data

[GeF<sub>4</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>]  
*M<sub>r</sub>* = 306.79  
 Triclinic, *P* $\bar{1}$   
*a* = 6.4729 (13) Å  
*b* = 7.0928 (14) Å  
*c* = 7.2643 (14) Å  
 $\alpha$  = 115.138 (4)°  
 $\beta$  = 94.921 (4)°  
 $\gamma$  = 109.954 (4)°  
*V* = 273.16 (9) Å<sup>3</sup>

*Z* = 1  
*D<sub>x</sub>* = 1.865 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 758 reflections  
 $\theta$  = 6.4–43.7°  
 $\mu$  = 2.84 mm<sup>-1</sup>  
*T* = 298 K  
 Needle, colorless  
 0.17 × 0.05 × 0.04 mm

## Data collection

Bruker SMART APEX CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (*XPREP*; Sheldrick, 1997)  
 $T_{\min}$  = 0.827,  $T_{\max}$  = 0.893  
 2925 measured reflections

1007 independent reflections  
 778 reflections with *I* > 2σ(*I*)  
 $R_{\text{int}}$  = 0.058  
 $\theta_{\text{max}}$  = 25.4°  
 $h$  = −7 → 7  
 $k$  = −8 → 8  
 $l$  = −8 → 8

## Refinement

Refinement on *F*<sup>2</sup>  
 $R[F^2 > 2\sigma(F^2)]$  = 0.039  
 $wR(F^2)$  = 0.052  
 $S$  = 0.77  
 1007 reflections  
 81 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.007P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Ge1–F2	1.7678 (19)	Ge1–N1	2.014 (3)
Ge1–F1	1.7696 (18)		
F1–Ge1–F2	89.96 (9)	F2–Ge1–N1	90.06 (10)
F1–Ge1–N1	90.18 (10)		
F2–Ge1–N1–C1	57.7 (2)	F1–Ge1–N1–C1	−32.3 (2)

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS90* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXL97*.

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