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Ethylenediammonium decafluorodineptunate(IV)

Tyler A. Sullens, Philip M. Almond and T. E. Albrecht-Schmitt*

Department of Chemistry and Leach Nuclear Science Center, Auburn University, Auburn, Alabama 36849, USA

Correspondence e-mail: albreth@auburn.edu

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An organically templated neptunium(IV) fluoride compound, $\{(C_2H_{10}N_2)[Np_2F_{10}]\}_n$, has been synthesized under mild hydrothermal conditions. The compound crystallizes in the monoclinic space group *C*2/*c* (No. 15). The structure consists of NpF_9 tricapped trigonal prisms connected through edge- and corner-sharing to form infinite two-dimensional $[Np_2F_{10}]^{2-}$ sheets, that are separated by the ethylenediammonium dications. The $C_2H_{10}N_2^{2+}$ cations form hydrogen-bonding interactions with the $[Np_2F_{10}]^{2-}$ layers.

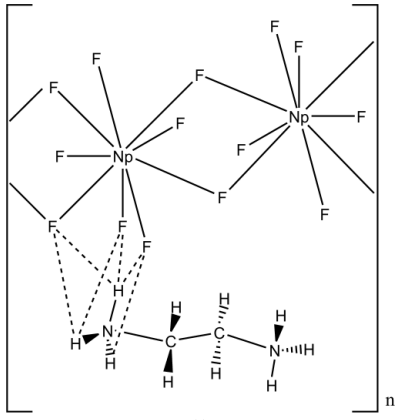
Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.005 Å
R factor = 0.014
wR factor = 0.033
Data-to-parameter ratio = 16.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

$(C_2H_{10}N_2)[Np_2F_{10}]$ was determined to be isostructural with both U^{IV} (Almond *et al.*, 2000) and Ce^{IV} (Sykora & Albrecht-Schmitt, 2001) variants of $(enH_2)[M_2F_{10}]$ (*M* = U and Ce; enH_2^{2+} is the ethylenediammonium dication). The structure of $(C_2H_{10}N_2)[Np_2F_{10}]$ contains one crystallographically unique Np atom in a nine-coordinate tricapped trigonal prism bound by fluoride anions. A view of the NpF_9 fundamental building unit is shown in Fig. 1.



(I)

The nine fluoride anions of each neptunium polyhedron form three edge-sharing and two corner-sharing interactions to adjacent Np atoms, a single fluoride being terminal. These interactions are the foundation of the formation of infinite $[Np_2F_{10}]^{2-}$ sheets that are separated by ethylene diammonium dications, as shown in Fig. 2. An individual sheet viewed down the *a* axis is shown in Fig. 3.

Np—F bond distances [2.209 (2)–2.434 (2) Å] are within the normal range, with F3 having the shortest Np—F bond distance owing to its terminal nature. The terminal fluorides are directed between the layers and form hydrogen bonds with the enH_2^{2+} cations. Hydrogen-bonding distances for enH_2^{2+} N atoms to the fluoride anions within the layers range from

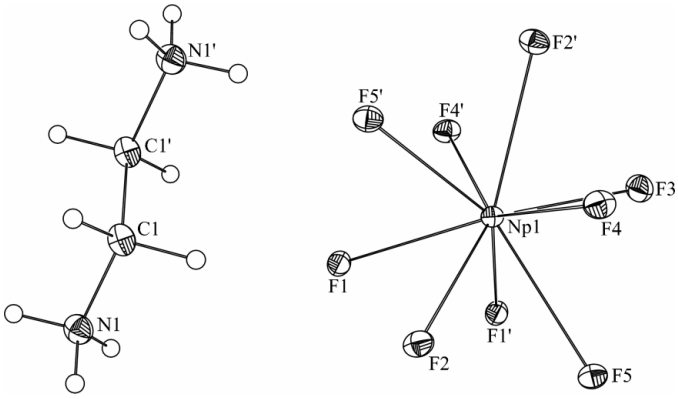


Figure 1
A depiction of the ethylenediammonium dication and NpF_9 fundamental building unit in $(C_2H_{10}N_2)[Np_2F_{10}]$. Displacement ellipsoids are drawn at the 50% probability level. **Symmetry code (i) as in Table 1.**

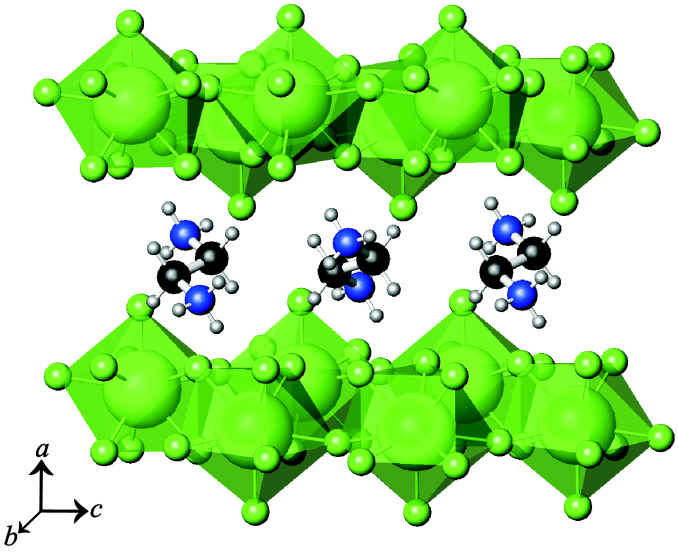


Figure 2
A view down the *b* axis, showing $[Np_2F_{10}]^{2-}$ sheets separated by enH_2^{2+} dications.

2.714 (7) to 3.133 (7) Å [distances of N1 to the nearest F3 atoms are 2.714 (7), 2.873 (7) and 3.133 (7) Å]. The N atom has the possibility of forming hydrogen-bonding interactions with six different fluoride anions, totaling 12 potential interactions for each enH_2^{2+} cation.

Experimental

$^{237}NpO_2$ (99.9%, Oak Ridge), HF (48% wt, Aldrich), and homopiperazine ($C_5N_2H_{12}$, 98%, Aldrich) were used as received. Distilled and Millipore filtered water with a resistance 18.2 MΩ·cm was used in all reactions. Reactions were conducted in Parr 4749 autoclaves with 10 ml PTFE liners.

[Caution! ^{237}Np ($t_{1/2}$ = 2.14 × 10^{-6} *y*) represents a serious health risk owing to its α and γ emission, especially because of its decay to the short-lived isotope ^{233}Pa ($t_{1/2}$ = 27.0 d), which is a potent β and γ emitter. All studies were conducted in a laboratory dedicated to studies on transuranium elements using procedures previously described (Albrecht-Schmitt *et al.*, 2003).]

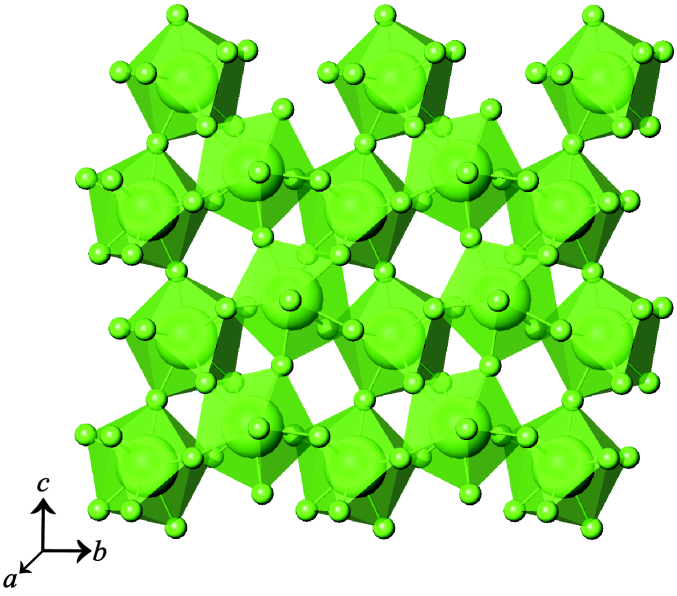


Figure 3
A view down the *a* axis, depicting the $[Np_2F_{10}]^{2-}$ sheets extending parallel to the *bc* plane. One NpF_9 tricapped trigonal prism is connected to neighboring neptunium fluorides through three edge-sharing and two corner-sharing interactions. The terminal F3 atoms are aligned along the *a* axis.

For the preparation of $(C_2H_{10}N_2)[Np_2F_{10}]$, NpO_2 (0.0100 g, 3.7 × 10^{-5} mol) and $C_5N_2H_{12}$ (0.0074 g, 7.4 × 10^{-5} mol) were loaded into a 10 ml PTFE-lined autoclave with 0.33 ml H_2O. 0.0094 ml 48% wt HF (4.7 × 10^{-4} mol) was then added dropwise to the reaction mixture. The autoclave was sealed and placed in a box oven pre-heated at 453 K. The autoclave was heated for 72 h and then cooled at a rate of 9 K h^{-1} to room temperature. The final reaction mixture was composed of a brown mother liquor and prismatic emerald green crystals of $(C_2H_{10}N_2)[Np_2F_{10}]$ bounded by ten faces.

Crystal data

$(C_2H_{10}N_2)[Np_2F_{10}]$
M_r = 726.12
Monoclinic, *C*2/*c*
a = 16.0190 (11) Å
b = 7.0570 (5) Å
c = 8.7203 (6) Å
β = 91.536 (1)°
V = 985.44 (12) Å^3
Z = 4
D_x = 4.894 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 4826 reflections
θ = 3.2–28.3°
μ = 21.10 mm^{-1}
T = 193 (2) K
Prism, green
0.11 × 0.07 × 0.05 mm

Data collection

Bruker SMART APEX diffractometer
ω scans
Absorption correction: analytical [*XPREP* in *SHELXTL* (Sheldrick, 2000) and *SADABS* (Sheldrick, 1997)]
T_{min} = 0.126, T_{max} = 0.371
4826 measured reflections
1224 independent reflections
1185 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 28.3°
h = −21 → 21
k = −9 → 9
l = −11 → 11

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.014
$wR(F^2)$ = 0.033
S = 1.15
1224 reflections
74 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0131P)^2 + 2.3052P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.84 e Å^{-3}
$\Delta\rho_{min}$ = −0.74 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.00049 (5)

Table 1
Selected bond lengths (Å).

Np1—F3	2.209 (2)	Np1—F2^{ii}	2.343 (2)
Np1—F1	2.2981 (19)	Np1—F4^{iii}	2.3467 (19)
Np1—F2	2.3029 (19)	Np1—F5	2.4341 (19)
Np1—F1^{i}	2.3053 (19)	Np1—Np1^{i}	3.8487 (3)
Np1—F5^{ii}	2.311 (2)	Np1—Np1^{iv}	3.9086 (3)
Np1—F4	2.3124 (19)		

Symmetry codes: (i) $\frac{1}{2}-x, -\frac{3}{2}-y, 1-z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iii) $x, -2-y, z-\frac{1}{2}$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$.

H atoms were positioned geometrically (N—H = 0.91 and C—H = 0.99 Å) and refined as riding, with U(H) = 1.5U_{eq}(N) and 1.2U_{eq}(C).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART* and *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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