

Andreas Fischer and
Zoltán Szabó*Inorganic Chemistry, Royal Institute of
Technology, 100 44 Stockholm, SwedenCorrespondence e-mail:
zoltan@inorchem.kth.se

Key indicators

Single-crystal X-ray study
 $T = 299\text{ K}$
Mean $\sigma(\text{U}-\text{F}) = 0.004\text{ \AA}$
H-atom completeness 50%
 R factor = 0.023
 wR factor = 0.047
Data-to-parameter ratio = 18.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Sodium pentafluorouranate(IV)
monohydrate, $\text{Na}[\text{UF}_5]\cdot\text{H}_2\text{O}$

$\text{Na}[\text{UF}_5]\cdot\text{H}_2\text{O}$ crystallizes in the orthorhombic space group *Pbcn*. It contains a uranium(IV) ion, which is coordinated by nine F^- ions yielding a tricapped trigonal prism. Some of the F^- ions function as bridging ligands coordinating to the Na^+ ion. The latter is coordinated by four F^- ions. Together with two molecules of water of crystallization, a distorted octahedral coordination around Na^+ is obtained.

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Comment

The behaviour of uranium species in different states of oxidation and in the presence of a number of coordinating ligands has been an important research topic for some time. The reason for this is the technical importance of the behaviour of uranium under a variety of conditions. The coordination chemistry of uranium depends strongly on its oxidation state and the prediction of its chemical properties is made difficult by the fact that the dominating species in uranium chemistry, UO_2^{2+} , is easily reduced under appropriate conditions. The resulting products, U^{IV} -containing compounds, show completely different behaviour regarding properties such as solubility. In our investigation of the coordinating behaviour of different ligands, we obtained the title compound by photochemical reduction of U^{VI} in a solution containing uranyl nitrate, sodium fluoride and quinic acid.

The structure features U^{IV} ions, which are coordinated by nine fluoride ions in the fashion of a tricapped trigonal prism. All fluoride ions function as bridging ligands, coordinating to further uranium ions and sodium ions yielding a complex three-dimensional network. The $\text{U}-\text{F}$ bond lengths [2.157 (4)–2.420 (4) Å] are in the same range as in other fluorouranates(IV), where the same coordination geometry can be found [$\delta\text{-Na}_2[\text{UF}_6]$; Cousson *et al.* (1979); $\beta\text{-Na}_2[\text{UF}_6]$; Zachariasen (1948)]. In the system $\text{Na}-\text{U}-\text{F}$, the tricapped trigonal prismatic coordination around uranium is one of the

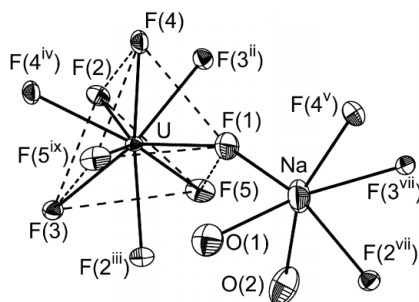


Figure 1

The U^{4+} and Na^+ cations and their respective coordination. Anisotropic displacement ellipsoids are drawn at the 70% probability level. Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (iv) $-x, 1 - y, 1 - z$; (v) $-x, y, \frac{1}{2} - z$; (vi) $\frac{1}{2} - x, y - \frac{1}{2}, z$; (vii) $\frac{1}{2} - x, \frac{1}{2} - y, z - \frac{1}{2}$; (viii) $1 - x, y, \frac{1}{2} - z$; (ix) $\frac{1}{2} - x, \frac{1}{2} + y, z$.

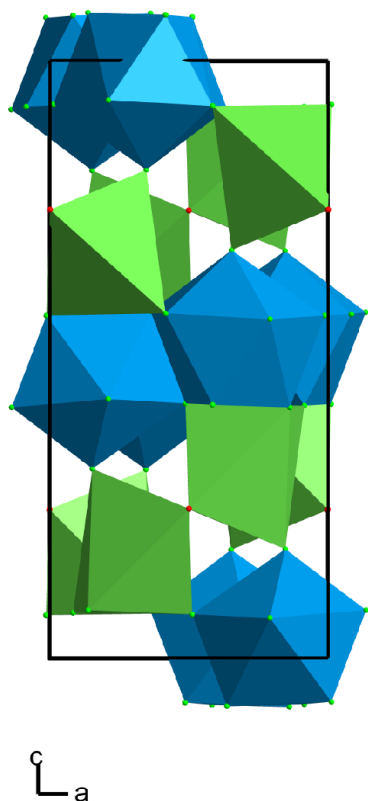


Figure 2

The unit cell contents of $\text{Na}[\text{UF}_5]\cdot\text{H}_2\text{O}$, viewed along b . Coordination polyhedra around U are blue, around Na are green. F atoms are represented as green spheres and the O atoms as red spheres.

common coordination geometries, besides a cubic coordination, which can be found in structures such as $\gamma\text{-Na}_2[\text{UF}_6]$ or $\text{Na}_3[\text{UF}_7]$ (Zachariasen, 1948), or the square antiprism in structures such as CaLi_2UF_8 (Vedrine *et al.*, 1973) or LiUF_5 (Brunton, 1966). The sodium ion is coordinated by four fluoride ions and two molecules of water of crystallization. The latter coordinate to a further Na^+ cation, yielding (albeit rather distorted) edge-sharing double octahedra.

Experimental

$\text{NaUF}_5\cdot\text{H}_2\text{O}$ was prepared by photochemical reduction of uranium(VI) with D-(–)-quinic acid. $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.0999 g, 0.19 mmol), NaF (0.055 g, 1.3 mmol) and D-(–)-quinic acid (0.1990 g, 1.03 mmol) were dissolved in water (10 ml). The pH of the solution was adjusted to 3 by adding NaOH. The solution was then exposed to light for a day, resulting in the formation of emerald-green plate-shaped crystals.

Crystal data

$\text{Na}[\text{UF}_5]\cdot\text{H}_2\text{O}$
 $M_r = 374.03$
 Orthorhombic, $Pbcn$
 $a = 6.9928$ (6) Å
 $b = 8.7617$ (4) Å
 $c = 15.0426$ (10) Å
 $V = 921.64$ (11) Å³
 $Z = 8$
 $D_x = 5.391$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 100 reflections
 $\theta = 4.0\text{--}21.0^\circ$
 $\mu = 35.33$ mm⁻¹
 $T = 299$ K
 Plate, emerald green
 $0.12 \times 0.10 \times 0.01$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: numerical (*HABITUS*; Herrendorf & Bärnighausen, 1997)
 $T_{\min} = 0.023$, $T_{\max} = 0.820$
 13694 measured reflections

1341 independent reflections
 1175 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\max} = 30.0^\circ$
 $h = -9 \rightarrow 9$
 $k = -12 \rightarrow 12$
 $l = -20 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.048$
 $S = 1.25$
 1341 reflections
 74 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + 17.16P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 4.05$ e Å⁻³
 $\Delta\rho_{\min} = -1.75$ e Å⁻³

Table 1

Selected geometric parameters (Å).

U–F1	2.157 (4)	U–F3 ⁱⁱ	2.420 (4)
U–F3	2.312 (4)	Na–F1	2.245 (5)
U–F5	2.317 (4)	Na–F3 ^{vii}	2.300 (5)
U–F4 ^{iv}	2.333 (4)	Na–F2 ^{vii}	2.317 (5)
U–F2 ⁱⁱⁱ	2.337 (4)	Na–O1	2.347 (6)
U–F5 ^{ix}	2.337 (4)	Na–O2	2.498 (7)
U–F4	2.369 (4)	Na–F4 ^v	2.528 (5)
U–F2	2.389 (4)		

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

H atoms bonded to the bridging O2 atoms were located in a difference Fourier map. Their parameters were refined using a riding model, with $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{O}2)$ and $\text{O}–\text{H} = 0.87$ Å. No H atoms could be located on O1. The highest peak in the difference map is 1.17 Å from F5 and the deepest hole is 1.57 Å from F4.

Data collection: *KappaCCD Software* (Nonius, 1997); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EvalCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *maXus* (Mackay *et al.*, 1999).

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