Supporting Information

Expanding Pentafluorouranates: Hydrothermal Synthesis and Characterization of β-NaUF5 and β-NaUF5•H2O

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Supporting Information Figure 1

SI Figure 1: Wireframe comparison of the uranium networks in all three products. Particularly note that, although the absorption spectra of 1 and 3 are nearly identical (Figure 4 in the text), and they have similar uranium coordination environments, they have very different uranium networks.
Supporting Information Figure 2

These layers of 1 are mirror images.

Sl Figure 2: The generation of the layer structure of the alpha-hydrate from the 1 motif.
When superimposed (left), they generate the $\alpha$-NaUF$_5$$\cdot$H$_2$O template (right).
Supporting Information Figure 3

SI Figure 3: Voronoi-Dirichlet polyhedra for O1 with all atoms considered (left) and only anions (right).

Supporting Information Figure 4

SI Figure 4: The coordination environment of O1 viewed down the c-axis, a distorted tetrahedron. Sodium atoms are yellow, and hydrogen atoms are white.
Supporting Information Table 1

All Non-Hydrogen Atoms Dirichlet Calculation of 1

# 1: Na, U F5, H2 O

Central atom: O1 OxSt:-2 CN:2 0.998 0.511 0.810 Rsd:1.655
D(CP): 0.244 (0.9819 0.5140 0.7811)  
D(VDP): 0.134 (0.9984 0.5114 0.7946)

Atom: 2.367 < r < 3.749  <r>=3.218   Top: 1.808 < R < 2.055  <R>=1.945
CN=16:0:2 NV=32 V=18.996/93.871 S=38.109 Cpac=0.365 Ccov=1.913
G3=0.081560699
Face distribution: {4/2 5/8 6/8}
Vertex distribution: {3/32}

| Atom | x    | y    | z    | Distance (Å) | D1 | D2 | Solid Angle % |
|------|------|------|------|--------------|----|----|---------------|
| 1    | Na1  | 1.13 | 0.30 | 1.02         | 2.37| 1.66| 0.71          | 16.34 |
| 2    | Na1  | 0.87 | 0.70 | 0.98         | 2.48| 1.66| 0.83          | 13.86 |
| 3    | F_3  | 1.13 | 0.66 | 0.57         | 2.87| 1.66| 1.22          | 10.12 |
| 4    | F_2  | 0.65 | 0.49 | 0.84         | 2.91| 1.66| 1.25          | 6.64  |
| 5    | F_4  | 0.65 | 0.58 | 0.55         | 2.99| 1.66| 1.34          | 8.32  |
| 6    | F_3  | 0.87 | 0.16 | 0.93         | 3.04| 1.66| 1.39          | 5.40  |
| 7    | F_5  | 1.37 | 0.71 | 0.89         | 3.15| 1.66| 1.49          | 6.96  |
| 8    | F_1  | 1.34 | 0.36 | 0.74         | 3.16| 1.66| 1.50          | 6.70  |
| 9    | F_3  | 1.13 | 0.85 | 1.07         | 3.20| 1.66| 1.54          | 4.55  |
| 10   | O_1  | 1.00 | 0.49 | 1.19         | 3.34| 1.66| 1.68          | 0.80  |
| 11   | F_3  | 0.87 | 0.35 | 0.43         | 3.34| 1.66| 1.69          | 5.37  |
| 12   | Na1  | 0.87 | 0.80 | 0.48         | 3.42| 1.66| 1.76          | 2.65  |
| *13  | F_2  | 1.35 | 0.51 | 1.16         | 3.45| 1.66| 1.79          | 1.37  |
| *14  | F_1  | 0.66 | 0.86 | 0.76         | 3.56| 1.66| 1.91          | 1.05  |
| 15   | F_5  | 0.63 | 0.21 | 0.61         | 3.57| 1.66| 1.92          | 2.57  |
| 16   | O_1  | 1.00 | 0.01 | 0.69         | 3.67| 1.66| 2.01          | 3.07  |
| 17   | O_1  | 1.00 | 1.01 | 0.69         | 3.67| 1.66| 2.01          | 3.07  |
| 18   | Na1  | 1.13 | 0.20 | 0.52         | 3.75| 1.66| 2.09          | 1.15  |

Elapsed time: 6.43 sec
Supporting Information Table 2

Anion-Only Dirichlet Calculation of 1

1:Na, U F5, H2 O

Central atom:O1 OxSt:-2 CN:2 0.998 0.511 0.810 Rsd:1.773
D(CP):0.157 ( 1.0075 0.4913 0.8088 )
D(VDP):0.066 ( 1.0036 0.5068 0.8163 )
Atom:2.871 < r < 4.003 <r>=3.328   Top: 1.808 < R < 2.336  <R>=2.048
CN=15:0 NV=26 V=23.366/94.889 S=43.477 Cpac=0.530 Ccov=2.284
G3=0.080107027
Face distribution: {4/3 5/6 6/6 }
Vertex distribution: {3/26 }

| Atom | x    | y    | z    | Distance (Å) | D1  | D2  | Solid Angle % |
|------|------|------|------|-------------|-----|-----|---------------|
| 1    | F_3  | 1.13 | 0.66 | 0.57        | 2.87| 1.77| 1.10          | 11.07 |
| 2    | F_2  | 0.65 | 0.49 | 0.84        | 2.91| 1.77| 1.14          | 10.06 |
| 3    | F_4  | 0.65 | 0.58 | 0.55        | 2.99| 1.77| 1.22          | 9.31  |
| 4    | F_3  | 0.87 | 0.16 | 0.93        | 3.04| 1.77| 1.27          | 10.20 |
| 5    | F_5  | 1.37 | 0.71 | 0.89        | 3.15| 1.77| 1.38          | 6.98  |
| 6    | F_1  | 1.34 | 0.36 | 0.74        | 3.16| 1.77| 1.38          | 8.43  |
| 7    | F_3  | 1.13 | 0.85 | 1.07        | 3.20| 1.77| 1.42          | 8.82  |
| 8    | O_1  | 1.00 | 0.49 | 1.19        | 3.34| 1.77| 1.57          | 6.72  |
| 9    | F_3  | 0.87 | 0.35 | 0.43        | 3.34| 1.77| 1.57          | 5.82  |
| 10   | F_2  | 1.35 | 0.51 | 1.16        | 3.45| 1.77| 1.68          | 5.85  |
| 11   | F_1  | 0.66 | 0.86 | 0.76        | 3.56| 1.77| 1.79          | 4.06  |
| 12   | F_5  | 0.63 | 0.21 | 0.61        | 3.57| 1.77| 1.80          | 2.57  |
| 13   | O_1  | 1.00 | 1.01 | 0.69        | 3.67| 1.77| 1.90          | 4.01  |
| 14   | O_1  | 1.00 | 0.01 | 0.69        | 3.67| 1.77| 1.90          | 4.01  |
| 15   | F_4  | 1.35 | 0.08 | 0.95        | 4.00| 1.77| 2.23          | 2.09  |

Elapsed time: 5.15 sec.
Supporting Information Table 3

Uranium-fluorine bond length and uranium-uranium distance comparison between Na₄CuU₆F₃₀ and 2

|                        | Na₄CuU₆F₃₀²⁻ | β-NaUF₅ (2) |
|------------------------|--------------|-------------|
| U-F non-bridging bond length (Å) | 2.250(4)     | 2.196(4)    |
| U-F (μ²) bond lengths (Å)      | 2.268(3)-2.418(3) | 2.287(4)-2.435(4) |
| U-U double-fluoride bridge distances (Å) | 4.0266(3)-4.0700(4) | 4.0442(4)-4.1019(6) |
| U-U single-fluoride bridge distances (Å) | 4.4851(3)-4.5088(2) | 4.5235(5)-4.5480(7) |

17 J. Yeon, M. D. Smith, J. Tapp, A. Möller and H.-C. zur Loye, Application of a Mild Hydrothermal Approach Containing an in Situ Reduction Step to the Growth of Single Crystals of the Quaternary U(IV)-Containing Fluorides Na₄MU₆F₃₀ (M = Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺) Crystal Growth, Structures, and Magnetic Properties, *Journal of the American Chemical Society*, 2014, **136**, 3955–3963.
Atomic coordinates and structural information of Product 1 - β-NaUF₅·H₂O

Crystal data

| Structure | Description |
|-----------|-------------|
| NaUF₅·H₂O | Monoclinic, P2₁/c |
| Mᵣ = 374.04 | Dᵣ = 5.334 Mg m⁻³ |
| a = 7.957 (3) Å | Mo Kα radiation, λ = 0.71073 Å |
| b = 7.027 (2) Å | Cell parameters from 996 reflections |
| c = 8.792 (3) Å | θ = 2.7–28.0° |
| β = 108.678 (7)° | µ = 34.96 mm⁻¹ |
| V = 465.7 (3) Å³ | T = 297 K |
| Z = 4 | Thin tetragonal plates, emerald green |
| F(000) = 632 | 0.05 × 0.05 × 0.02 mm |
| R[F² > 2σ(F²)] = 0.036 | wR(F²) = 0.105 |
| w = 1/[σ²(Fo²) + (0.0764P)²], where P = (Fo² + 2Fc²)/3 | Δρ_max = 2.84 e Å⁻³, Δρ_min = −2.47 e Å⁻³ |

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

| Atom | x   | y   | z   | U iso* / U eq |
|------|-----|-----|-----|---------------|
| U1   | 0.57881 (4) | 0.16299 (5) | 0.85335 (4) | 0.0074 (2) |
| F2   | 0.3390 (8) | 0.3605 (7) | 0.7381 (8) | 0.0121 (13) |
| F3   | 0.6455 (8) | 0.4858 (8) | 0.8413 (7) | 0.0138 (12) |
| F1   | 0.8667 (10) | 0.1548 (8) | 0.9336 (10) | 0.0236 (17) |
| F4   | 0.3451 (7) | 0.0822 (9) | 0.9506 (7) | 0.0139 (12) |
| F5   | 0.6300 (9) | 0.2883 (9) | 1.1107 (7) | 0.0189 (13) |
| Na1  | 1.1349 (7) | 0.2974 (7) | 1.0214 (6) | 0.0276 (11) |
| O1   | 0.9980 (11) | 0.5106 (13) | 0.8115 (11) | 0.0287 (19) |
| H1   | 0.915 (5) | 0.471 (7) | 0.730 (4) | 0.11 (9)* |
| H2   | 1.064 (6) | 0.585 (6) | 0.778 (6) | 0.03 (3)* |

Atomic displacement parameters (Å²)

| | U₁₁ | U₂₂ | U₃₃ | U₁₂ | U₁₃ | U₂₃ |
|---|-----|-----|-----|-----|-----|-----|
| U1  | 0.0088 (3) | 0.0065 (3) | 0.0074 (3) | −0.0006 (11) | 0.00308 (17) | 0.00032 (10) |
| F2  | 0.007 (3) | 0.012 (3) | 0.014 (3) | −0.001 (2) | −0.001 (2) | 0.001 (2) |
| F3  | 0.017 (3) | 0.011 (3) | 0.012 (3) | −0.001 (2) | 0.002 (2) | 0.000 (2) |
| F1  | 0.018 (4) | 0.019 (4) | 0.030 (4) | 0.001 (2) | 0.002 (3) | −0.001 (2) |
| F4  | 0.012 (3) | 0.014 (3) | 0.017 (3) | −0.001 (2) | 0.007 (2) | 0.002 (2) |
|    |   |   |   |   |   |   |
|----|---|---|---|---|---|---|
| F5 | 0.031 (4) | 0.012 (3) | 0.017 (3) | −0.003 (3) | 0.014 (3) | −0.003 (3) |
| Na1 | 0.026 (3) | 0.020 (2) | 0.031 (3) | 0.003 (2) | 0.001 (2) | −0.002 (2) |
| O1 | 0.021 (5) | 0.036 (5) | 0.031 (5) | −0.007 (4) | 0.011 (4) | 0.003 (4) |

Geometric parameters (Å, °)

| Bond/Angle | Distance/Angle |
|------------|---------------|
| U1—F1      | 2.171 (8)     |
| U1—F2      | 2.314 (6)     |
| U1—F5      | 2.340 (6)     |
| U1—F4      | 2.389 (6)     |
| U1—F3      | 2.339 (6)     |
| U1—Na1     | 2.258 (9)     |
| Na1—F3     | 2.341 (7)     |
| Na1—F2     | 2.435 (6)     |
| Na1—F4     | 2.349 (8)     |
| Na1—F5     | 2.374 (6)     |
| Na1—O1     | 2.356 (10)    |
| Na1—F1     | 2.477 (8)     |
| Na1—F2     | 2.374 (6)     |
| Na1—F3     | 2.352 (6)     |
| Na1—O1     | 2.356 (10)    |
| Na1—F4     | 2.349 (8)     |
| Na1—F5     | 2.349 (8)     |
| F2—Na1     | 2.349 (8)     |
| F2—U1      | 2.435 (6)     |
| F3—Na1     | 2.341 (7)     |
| F1—U1—F2  | 142.6 (2)     |
| F1—U1—F5  | 79.9 (3)      |
| F2—U1—F5  | 82.6 (2)      |
| F1—U1—F5  | 81.8 (3)      |
| F2—U1—F5  | 93.5 (2)      |
| F5—U1—F5  | 143.69 (18)   |
| F1—U1—F3  | 79.0 (2)      |
| F2—U1—F3  | 64.3 (2)      |
| F5—U1—F3  | 72.9 (2)      |
| F5—U1—F3  | 73.0 (2)      |
| F1—U1—F4  | 138.6 (3)     |
| F2—U1—F4  | 70.5 (2)      |
| F5—U1—F4  | 139.6 (2)     |
| F5—U1—F4  | 69.6 (2)      |
| F3—U1—F4  | 117.9 (2)     |
| F1—U1—F4  | 75.4 (2)      |
| Bond/Rotation  | Distance (Å) | Symmetry Code/Rotation  | Distance (Å) |
|---------------|--------------|-------------------------|--------------|
| F2—U1—F4     | 137.4 (2)    | U1—F4—U1               | 113.1 (2)    |
| F5—U1—F4     | 134.0 (2)    | U1—F4—Na1              | 128.3 (3)    |
| F5—U1—F4     | 69.3 (2)     | U1—F4—Na1              | 107.2 (3)    |
| F3—U1—F4     | 136.7 (2)    | U1—F5—U1               | 156.5 (3)    |
| F4—U1—F4     | 66.9 (2)     | F1—Na1—F3             | 158.8 (4)    |
| F1—U1—F3     | 133.4 (2)    | F1—Na1—F3             | 113.6 (3)    |
| F2—U1—F3     | 71.1 (2)     | F3—Na1—F2             | 71.4 (2)     |
| F5—U1—F3     | 74.3 (2)     | F1—Na1—O1             | 82.2 (3)     |
| F5—U1—F3     | 138.4 (2)    | F3—Na1—O1             | 94.1 (3)     |
| F3—U1—F3     | 126.94 (14)  | F2—Na1—O1             | 164.2 (4)    |
| F4—U1—F3     | 68.8 (2)     | F1—Na1—O1             | 84.7 (3)     |
| F4—U1—F3     | 95.7 (2)     | F3—Na1—O1             | 74.2 (3)     |
| F1—U1—F2     | 73.6 (2)     | F2—Na1—O1             | 95.3 (3)     |
| F2—U1—F2     | 130.53 (11)  | O1—Na1—O1             | 86.5 (3)     |
| F5—U1—F2     | 71.4 (2)     | F1—Na1—F4             | 106.5 (3)    |
| F5—U1—F2     | 131.8 (2)    | F3—Na1—F4             | 94.3 (3)     |
| F3—U1—F2     | 137.9 (2)    | F2—Na1—F4             | 64.4 (2)     |
| F4—U1—F2     | 103.7 (2)    | O1—Na1—F4             | 111.8 (3)    |
| F4—U1—F2     | 64.7 (2)     | O1—Na1—F4             | 159.3 (3)    |
| F3—U1—F2     | 61.7 (2)     | F1—Na1—Na1            | 81.1 (3)     |
| F1—U1—Na1    | 151.1 (2)    | F3—Na1—Na1            | 81.8 (2)     |
| F2—U1—Na1    | 35.64 (16)   | F2—Na1—Na1            | 135.2 (3)    |
| F5—U1—Na1    | 71.17 (19)   | O1—Na1—Na1            | 44.5 (2)     |
| F5—U1—Na1    | 123.10 (19)  | O1—Na1—Na1            | 42.0 (2)     |
| F3—U1—Na1    | 93.58 (16)   | F4—Na1—Na1            | 155.0 (3)    |
| F4—U1—Na1    | 69.43 (17)   | F1—Na1—U1             | 147.0 (3)    |
| F4—U1—Na1    | 124.63 (16)  | F3—Na1—U1             | 36.90 (16)   |
| F3—U1—Na1    | 36.05 (15)   | F2—Na1—U1             | 35.03 (16)   |
| F2—U1—Na1    | 95.28 (16)   | O1—Na1—U1             | 129.6 (3)    |
| F1—U1—Na1    | 55.05 (16)   | O1—Na1—U1             | 88.4 (2)     |
| F2—U1—Na1    | 160.85 (16)  | F4—Na1—U1             | 72.64 (18)   |
| F5—U1—Na1    | 97.07 (19)   | Na1—Na1—U1            | 114.1 (2)    |
| F5—U1—Na1    | 97.68 (18)   | F1—Na1—U1             | 97.5 (2)     |
| F3—U1—Na1    | 134.06 (18)  | F3—Na1—U1             | 97.0 (2)     |
| F4—U1—Na1    | 98.93 (17)   | F2—Na1—U1             | 36.00 (16)   |
Hydrogen-bond geometry (Å, °)

|            | D—H  | H···A | D···A  | D—H···A |
|------------|------|------|--------|---------|
| O1—H1···F1¹ | 0.85 (2) | 2.66 (3) | 3.356 (12) | 140 (4) |
| O1—H1···F4¹ii | 0.85 (2) | 2.30 (4) | 2.998 (11) | 139 (4) |
| O1—H2···F1¹ii | 0.86 (2) | 2.16 (3) | 2.884 (12) | 142 (5) |
| O1—H2···F5¹ii | 0.86 (2) | 2.48 (4) | 3.151 (11) | 136 (4) |
| O1—H1···F1¹ | 0.85 (2) | 2.66 (3) | 3.356 (12) | 140 (4) |
| O1—H1···F4¹i | 0.85 (2) | 2.30 (4) | 2.998 (11) | 139 (4) |
| O1—H2···F1¹i | 0.86 (2) | 2.16 (3) | 2.884 (12) | 142 (5) |
| O1—H2···F5¹i | 0.86 (2) | 2.48 (4) | 3.151 (11) | 136 (4) |

Symmetry codes: (i) x, −y+1/2, z−1/2; (ii) −x+1, −y, −z+2; (iii) −x+1, y−1/2, −z+3/2; (iv) x−1, −y+1/2, z−1/2; (v) −x+2, −y, −z+2; (vi) −x+1, y+1/2, −z+3/2; (vii) −x+2, −y+1, −z+2; (viii) x−1, y, z; (ix) x, −y+1/2, z+1/2; (x) x+1, −y+1/2, z+1/2; (xi) x+1, y, z.

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Atomic coordinates and structural information of Product 2 - β-NaUF₅

Crystal data

| NaUF₅ | Trigonal, P-3c1 |
|-------|----------------|
| Mᵣ = 1068.06 | Dᵣ = 6.276 Mg m⁻³ |
Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 883 reflections
θ = 2.4–27.8°
µ = 43.18 mm−1
T = 120 K

Blocky green hexagon, emerald green

0.07 × 0.07 × 0.05 mm

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|          | x       | y       | z       | Uiso*/Ueq | Occ. (<1) |
|----------|---------|---------|---------|-----------|-----------|
| U1       | 0.07583 | 0.39943 | 0.89893 | 0.00251   | (9)       |
| Na1      | −0.3333 | 0.3333  | 0.8421  | 0.0086    | (9)       |
| Na2      | 0.0000  | 0.0000  | 0.7500  | 0.0246    | (17)      |
| Na3      | 0.0000  | 0.0000  | 1.0000  | 0.045     | (3)       |
| Na4      | 0.3289 (15) | 0.2861 (14) | 0.7907 (10) | 0.041 (3) | 0.3333    |
| F1       | −0.4140 (4) | 0.1165 (4) | 0.9466 (3) | 0.0070 (7) |           |
| F2       | −0.1224 (4) | 0.1896 (4) | 0.9777 (3) | 0.0088 (7) |           |
| F3       | −0.1318 (4) | 0.3091 (5) | 0.7833 (3) | 0.0106 (8) |           |
| F4       | 0.0895 (5) | 0.2007 (5) | 0.8406 (3) | 0.0184 (9) |           |
| F5       | 0.3417 (4) | 0.5116 (4) | 0.8631 (3) | 0.0109 (8) |           |

Atomic displacement parameters (Å²)

| U11  | U22  | U33  | U12  | U13  | U23  |
|------|------|------|------|------|------|
| U1   | 0.00250 (12) | 0.00270 (12) | 0.00201 (12) | 0.00107 (9) | −0.00019 (7) | −0.00013 (7) |
| Na1  | 0.0081 (13) | 0.0081 (13) | 0.010 (2) | 0.0041 (7) | 0.000 | 0.000 |
| Na2  | 0.024 (3) | 0.024 (3) | 0.026 (4) | 0.0118 (13) | 0.000 | 0.000 |
| Na3  | 0.024 (3) | 0.024 (3) | 0.088 (8) | 0.0118 (15) | 0.000 | 0.000 |
| Na4  | 0.038 (7) | 0.036 (6) | 0.063 (8) | 0.028 (6) | −0.001 (6) | −0.015 (6) |
| F1   | 0.0057 (17) | 0.0055 (17) | 0.0084 (16) | 0.0017 (15) | −0.0012 (14) | 0.0018 (13) |
| F2   | 0.0081 (17) | 0.0058 (17) | 0.0119 (17) | 0.0031 (15) | 0.0012 (14) | 0.0020 (14) |
| F3   | 0.0076 (18) | 0.021 (2) | 0.0038 (17) | 0.0073 (16) | −0.0006 (14) | −0.0005 (15) |
|     | 0.026 (2) | 0.015 (2) | 0.017 (2) | 0.0125 (19) | −0.0078 (18) | −0.0040 (17) |
|-----|-----------|-----------|-----------|-------------|--------------|--------------|
| F5  | 0.0041 (17) | 0.0105 (19) | 0.0147 (18) | 0.0012 (15) | −0.0009 (14) | 0.0040 (15) |

**Geometric parameters (Å, °)**

| Bond | Distance (Å)          | Bond | Distance (Å)          | Bond | Distance (Å)          |
|------|-----------------------|------|-----------------------|------|-----------------------|
| U1—F4 | 2.196 (4)             | Na2—Na4 | 3.143 (13)            |      |                       |
| U1—F2 | 2.287 (4)             | Na3—F4^{ii} | 2.713 (4)            |      |                       |
| U1—F5^{i} | 2.318 (4)       | Na3—F4^{vii} | 2.713 (4)           |      |                       |
| U1—F1^{ii} | 2.326 (3)       | Na3—F4^{xi} | 2.713 (4)           |      |                       |
| U1—F3 | 2.351 (4)             | Na3—F4^{x} | 2.713 (4)            |      |                       |
| U1—F5 | 2.359 (4)             | Na3—F4^{vii} | 2.713 (4)           |      |                       |
| U1—F2^{ii} | 2.376 (4)       | Na3—F4 | 2.713 (4)            |      |                       |
| U1—F3^{iii} | 2.430 (4)       | Na3—F2^{ii} | 2.739 (4)           |      |                       |
| U1—F1^{iv} | 2.435 (4)       | Na3—F2 | 2.739 (4)            |      |                       |
| U1—Na4^{iv} | 3.539 (12)     | Na3—F2^{ii} | 2.739 (4)           |      |                       |
| U1—Na4 | 3.543 (11)             | Na3—F2^{vii} | 2.739 (4)          |      |                       |
| U1—Na4^{iv} | 3.743 (12)     | Na3—F2^{xi} | 2.739 (4)          |      |                       |
| Na1—F3 | 2.281 (4)             | Na3—F2^{x} | 2.739 (4)            |      |                       |
| Na1—F3^{vi} | 2.281 (4)       | Na4—Na4^{v} | 1.29 (3)            |      |                       |
| Na1—F3^{ix} | 2.281 (4)       | Na4—F4 | 2.200 (13)            |      |                       |
| Na1—F1^{iv} | 2.337 (4)       | Na4—F3^{x} | 2.319 (12)           |      |                       |
| Na1—F1 | 2.337 (4)             | Na4—F5 | 2.389 (12)            |      |                       |
| Na1—F1^{ix} | 2.338 (4)       | Na4—F4^{x} | 2.434 (13)           |      |                       |
| Na1—Na4^{vii} | 3.240 (12)    | Na4—F5^{x} | 2.580 (14)           |      |                       |
| Na1—Na4^{i} | 3.240 (12)      | Na4—F1^{x} | 2.695 (13)           |      |                       |
| Na1—Na4^{viii} | 3.240 (12)   | Na4—F2^{x} | 2.896 (14)           |      |                       |
| Na1—U1^{xi} | 3.8771 (10)   | Na4—Na1^{xiii} | 3.240 (12)       |      |                       |
| Na1—U1^{xiv} | 3.8771 (10)    | Na4—U1^{v} | 3.539 (12)           |      |                       |
| Na2—F4 | 2.105 (4)             | F1—U1^{xi} | 2.326 (3)            |      |                       |
| Na2—F4^{ix} | 2.105 (4)      | F1—U1^{xvi} | 2.435 (4)           |      |                       |
| Na2—F4^{x} | 2.105 (4)             | F1—Na4^{vii} | 2.695 (13)          |      |                       |
| Na2—F4^{iii} | 2.105 (4)      | F2—U1^{xi} | 2.376 (4)            |      |                       |
| Na2—F4^{vii} | 2.105 (4)      | F2—Na4^{vii} | 2.896 (14)          |      |                       |
| Na2—F4^{v} | 2.105 (4)             | F3—Na4^{vii} | 2.319 (12)          |      |                       |
| Na2—Na4^{v} | 3.143 (13)        | F3—U1^{iii} | 2.430 (4)            |      |                       |
| Na2—Na4^{iii} | 3.143 (13)     | F4—Na4^{v} | 2.434 (13)           |      |                       |
| Na2—Na4^{ix} | 3.143 (13)     | F5—U1^{xiv} | 2.318 (4)            |      |                       |
| Bond  | Length (Å) | Angle (°) |
|-------|------------|-----------|
| Na2—Na4 | 3.143 (13) |           |
| Na2—Na4 | 3.143 (13) |           |
| F4—U1—F2 | 75.09 (15) | F4—Na2—Na4 | 140.9 (2) |
| F4—U1—F5 | 140.11 (15) | Na4—Na2—Na4 | 107.5 (4) |
| F2—U1—F5 | 142.87 (13) | Na4—Na2—Na4 | 23.7 (5) |
| F4—U1—F1 | 137.54 (13) | Na4—Na2—Na4 | 134.4 (4) |
| F2—U1—F1 | 87.43 (13) | Na4—Na2—Na4 | 117.21 (14) |
| F5—U1—F1 | 71.71 (13) | F4—Na2—Na4 | 44.3 (2) |
| F4—U1—F3 | 82.68 (15) | F4—Na2—Na4 | 140.9 (2) |
| F2—U1—F3 | 75.03 (13) | F4—Na2—Na4 | 76.0 (3) |
| F5—U1—F3 | 95.01 (14) | F4—Na2—Na4 | 98.1 (3) |
| F1—U1—F3 | 130.12 (13) | F4—Na2—Na4 | 132.3 (3) |
| F4—U1—F5 | 78.23 (16) | F4—Na2—Na4 | 50.7 (3) |
| F2—U1—F5 | 141.18 (13) | Na4—Na2—Na4 | 23.7 (5) |
| F5—U1—F5 | 72.39 (19) | Na4—Na2—Na4 | 134.4 (4) |
| F1—U1—F5 | 93.76 (13) | Na4—Na2—Na4 | 107.5 (4) |
| F3—U1—F5 | 128.66 (13) | Na4—Na2—Na4 | 117.21 (14) |
| F4—U1—F2 | 69.09 (14) | Na4—Na2—Na4 | 117.21 (14) |
| F2—U1—F2 | 73.30 (14) | F4—Na3—F4 | 180.0 |
| F5—U1—F2 | 123.12 (14) | F4—Na3—F4 | 67.58 (14) |
| F1—U1—F2 | 68.88 (12) | F4—Na3—F4 | 112.42 (14) |
| F3—U1—F2 | 141.86 (14) | F4—Na3—F4 | 112.42 (14) |
| F5—U1—F2 | 71.09 (13) | F4—Na3—F4 | 67.58 (14) |
| F4—U1—F3 | 72.67 (14) | F4—Na3—F4 | 180.0 |
| F2—U1—F3 | 128.02 (13) | F4—Na3—F4 | 67.58 (14) |
| F5—U1—F3 | 71.46 (13) | F4—Na3—F4 | 112.42 (14) |
| F1—U1—F3 | 142.28 (13) | F4—Na3—F4 | 67.58 (14) |
| F3—U1—F3 | 61.42 (16) | F4—Na3—F4 | 112.42 (14) |
| F5—U1—F3 | 67.45 (13) | F4—Na3—F4 | 112.42 (14) |
| F2—U1—F3 | 127.86 (13) | F4—Na3—F4 | 67.58 (14) |
| F4—U1—F1 | 139.92 (15) | F4—Na3—F4 | 112.42 (14) |
| F2—U1—F1 | 72.68 (13) | F4—Na3—F4 | 67.58 (14) |
| F5—U1—F1 | 70.59 (13) | F4—Na3—F4 | 180.00 (11) |
| F1—U1—F1 | 63.72 (14) | F4—Na3—F4 | 72.96 (12) |
| F3—U1—F1 | 66.51 (12) | F4—Na3—F4 | 107.04 (12) |
| Bond                     | Distance (Å) | Reference | Error (Å) |
|--------------------------|--------------|-----------|-----------|
| F3—Na1—F3              | 109.29 (14)  | F2—Na3—F2 | 61.11 (3) |
| F3—Na1—F4              | 69.27 (13)   | F2i—Na3—F2i | 118.88 (3) |
| F3—Na1—F1x             | 158.69 (19)  | F2vii—Na3—F2x | 61.12 (3) |
| F3—Na1—F1v             | 90.62 (14)   | F4i—Na3—F2x | 56.90 (11) |
| F3—Na1—F1              | 90.62 (14)   | F4vii—Na3—F2x | 123.10 (11) |
| F3—Na1—F1              | 69.27 (13)   | F4xi—Na3—F2x | 119.83 (12) |
| F3—Na1—F1              | 158.68 (19)  | F4v—Na3—F2x | 60.17 (12) |
| F1—Na1—F1              | 89.41 (17)   | F4iv—Na3—F2x | 107.04 (12) |
| F3—Na1—F1vi            | 158.69 (19)  | F4—Na3—F2x | 72.96 (12) |
| F3—Na1—F1v             | 90.62 (14)   | F2xi—Na3—F2x | 61.11 (3) |
| F3—Na1—F1              | 69.27 (13)   | F2—Na3—F2x | 118.89 (3) |
| F1—Na1—F1vi            | 89.41 (17)   | F2vi—Na3—F2x | 61.12 (3) |
| F1—Na1—F1v             | 89.41 (17)   | F2vi—Na3—F2x | 118.88 (3) |
| F3—Na1—Na4viii         | 45.7 (2)     | F2v—Na3—F2x | 180.0 |
| F3—Na1—Na4viii         | 70.2 (2)     | Na4v—Na4—F4 | 84.1 (7) |
| F3—Na1—Na4viii         | 145.9 (3)    | Na4v—Na4—F3v | 122.4 (12) |
| F1—Na1—Na4viii         | 97.7 (3)     | F4—Na4—F3v | 123.2 (6) |
| F1—Na1—Na4viii         | 55.0 (2)     | Na4v—Na4—F5 | 83.3 (9) |
| F1—Na1—Na4viii         | 143.3 (2)    | F4—Na4—F5 | 77.5 (4) |
| F3—Na1—Na4              | 70.2 (2)     | F3v—Na4—F5 | 146.0 (6) |
| F3—Na1—Na4              | 145.9 (3)    | Na4v—Na4—F4v | 64.0 (7) |
| F3—Na1—Na4              | 45.7 (2)     | F4—Na4—F4v | 82.1 (5) |
| F1—Na1—Na4              | 55.0 (2)     | F3v—Na4—F4v | 70.6 (3) |
| F1—Na1—Na4              | 143.3 (2)    | F5—Na4—F4v | 143.1 (6) |
| F1—Na1—Na4              | 97.7 (3)     | Na4v—Na4—F5v | 66.8 (9) |
| Na4vi—Na1—Na4i          | 115.83 (17)  | F4—Na4—F5v | 146.1 (6) |
| F3—Na1—Na4viii          | 145.9 (3)    | F3v—Na4—F5v | 65.5 (3) |
| F3—Na1—Na4viii          | 45.7 (2)     | F5—Na4—F5v | 114.0 (5) |
| F3—Na1—Na4viii          | 70.2 (2)     | F4v—Na4—F5v | 69.9 (4) |
| F1—Na1—Na4viii          | 143.3 (2)    | Na4v—Na4—F1v | 139.0 (5) |
| F1—Na1—Na4viii          | 97.7 (3)     | F4—Na4—F1v | 111.8 (5) |
| F1—Na1—Na4viii          | 55.0 (2)     | F3v—Na4—F1v | 81.4 (4) |
| Na4vi—Na1—Na4viii       | 115.83 (17)  | F5—Na4—F1v | 65.1 (3) |
| Na4v—Na1—Na4viii        | 115.83 (17)  | F4v—Na4—F1v | 151.8 (5) |
| F3—Na1—U1vi            | 108.36 (10)  | F5v—Na4—F1v | 101.7 (4) |
| Bond                  | Angle (deg) | Bond                  | Angle (deg) |
|----------------------|-------------|----------------------|-------------|
| $F_3^{vi} - Na_1 - U_1^{vi}$ | 33.74 (10)  | $Na_4^{v} - Na_4 - F_2^{x}$ | 160.4 (5)   |
| $F_3^{vi} - Na_1 - U_1^{vi}$ | 135.20 (11) | $F_4 - Na_4 - F_2^{x}$ | 77.7 (4)    |
| $F_1^{iv} - Na_1 - U_1^{vi}$ | 125.26 (15) | $F_3^{v} - Na_4 - F_2^{x}$ | 64.5 (3)    |
| $F_1 - Na_1 - U_1^{vi}$ | 36.52 (9)   | $F_5 - Na_4 - F_2^{x}$ | 99.3 (5)    |
| $F_1^{iv} - Na_1 - U_1^{vi}$ | 83.79 (10)  | $F_4^{v} - Na_4 - F_2^{x}$ | 106.1 (4)   |
| $Na_4^{vii} - Na_1 - U_1^{vi}$ | 62.7 (2)    | $F_5^{v} - Na_4 - F_2^{x}$ | 127.7 (4)   |
| $Na_4^{iv} - Na_1 - U_1^{vi}$ | 178.5 (3)   | $F_1^{x} - Na_4 - F_2^{x}$ | 56.7 (3)    |
| $Na_4^{iv} - Na_1 - U_1^{vi}$ | 65.0 (2)    | $Na_4^{v} - Na_4 - Na_2$ | 78.1 (2)    |
| $F_3 - Na_1 - U_1^{vi}$ | 33.74 (10)  | $F_4 - Na_4 - Na_2$ | 41.9 (2)    |
| $F_3^{vi} - Na_1 - U_1^{vi}$ | 135.20 (11) | $F_3^{v} - Na_4 - Na_2$ | 91.2 (4)    |
| $F_3^{iv} - Na_1 - U_1$ | 108.36 (10) | $F_5 - Na_4 - Na_2$ | 117.7 (4)   |
| $F_1^{iv} - Na_1 - U_1$ | 36.52 (9)   | $F_4^{v} - Na_4 - Na_2$ | 42.0 (2)    |
| $F_1 - Na_1 - U_1^{iv}$ | 83.79 (10)  | $F_5^{v} - Na_4 - Na_2$ | 111.8 (4)   |
| $F_1^{xii} - Na_1 - U_1^{iv}$ | 125.26 (15) | $F_1^{x} - Na_4 - Na_2$ | 138.9 (5)   |
| $Na_4^{iv} - Na_1 - U_1^{iv}$ | 65.0 (2)    | $F_2^{x} - Na_4 - Na_2$ | 83.6 (3)    |
| $Na_4^{iv} - Na_1 - U_1^{iv}$ | 62.7 (2)    | $Na_4^{v} - Na_4 - Na_1^{xiii}$ | 127.9 (8)  |
| $Na_4^{iv} - Na_1 - U_1^{iv}$ | 178.5 (3)   | $F_4 - Na_4 - Na_1^{xiii}$ | 148.0 (6)   |
| $U_1^{iv} - Na_1 - U_1$ | 116.43 (4)  | $F_3^{v} - Na_4 - Na_1^{xiii}$ | 44.7 (2)    |
| $F_3 - Na_1 - U_1^{iv}$ | 135.20 (11) | $F_5 - Na_4 - Na_1^{xiii}$ | 102.7 (4)   |
| $F_3^{iv} - Na_1 - U_1^{iv}$ | 108.36 (10) | $F_4^{v} - Na_4 - Na_1^{xiii}$ | 110.7 (4)   |
| $F_3^{iv} - Na_1 - U_1^{iv}$ | 33.74 (10)  | $F_5^{v} - Na_4 - Na_1^{xiii}$ | 63.6 (3)    |
| $F_1^{iv} - Na_1 - U_1^{iv}$ | 83.79 (10)  | $F_1^{x} - Na_4 - Na_1^{xiii}$ | 45.2 (2)    |
| $F_1 - Na_1 - U_1^{iv}$ | 125.26 (15) | $F_2^{x} - Na_4 - Na_1^{xiii}$ | 70.7 (3)    |
| $F_1^{xii} - Na_1 - U_1^{iv}$ | 36.51 (9)   | $Na_2 - Na_4 - Na_1^{xiii}$ | 135.1 (4)   |
| $Na_4^{iv} - Na_1 - U_1^{iv}$ | 178.5 (3)   | $Na_4^{v} - Na_4 - U_1^{v}$ | 79.6 (10)   |
| $Na_4^{iv} - Na_1 - U_1^{iv}$ | 65.0 (2)    | $F_4 - Na_4 - U_1^{v}$ | 118.5 (5)   |
| $Na_4^{iv} - Na_1 - U_1^{iv}$ | 62.7 (2)    | $F_3^{x} - Na_4 - U_1^{v}$ | 43.0 (2)    |
| $U_1^{iv} - Na_1 - U_1^{iv}$ | 116.43 (4)  | $F_5 - Na_4 - U_1^{v}$ | 154.8 (5)   |
| $U_1 - Na_1 - U_1^{iv}$ | 116.43 (4)  | $F_4^{v} - Na_4 - U_1^{v}$ | 37.72 (19)  |
| $F_4 - Na_2 - F_4^{x}$ | 174.1 (2)   | $F_5^{v} - Na_4 - U_1^{v}$ | 41.79 (19)  |
| $F_4 - Na_2 - F_4^{x}$ | 91.55 (16)  | $F_1^{x} - Na_4 - U_1^{v}$ | 119.0 (4)   |
| $F_4^{x} - Na_2 - F_4^{x}$ | 92.8 (2)    | $F_2^{x} - Na_4 - U_1^{v}$ | 103.0 (3)   |
| $F_4 - Na_2 - F_4^{iii}$ | 84.4 (2)    | $Na_2 - Na_4 - U_1^{v}$ | 76.7 (3)    |
| $F_4^{x} - Na_2 - F_4^{iii}$ | 91.55 (16)  | $Na_1^{xiii} - Na_4 - U_1^{v}$ | 74.2 (2)   |
| $F_4^{x} - Na_2 - F_4^{iii}$ | 174.1 (3)   | $Na_4^{v} - Na_4 - U_1$ | 79.3 (9)    |
| Bond | Angle 1 | Angle 2 | Angle 3 |
|------|---------|---------|---------|
| F4—Na2—F4vii | 91.55 (16) | F4—Na4—U1 | 36.3 (2) |
| F4x—Na2—F4vii | 84.4 (2) | F3x—Na4—U1 | 152.8 (6) |
| F4x—Na2—F4vii | 91.55 (16) | F5—Na4—U1 | 41.4 (2) |
| F4x—Na2—F4vii | 92.8 (3) | F4v—Na4—U1 | 111.5 (4) |
| F4—Na2—F4v | 92.8 (3) | F5v—Na4—U1 | 141.6 (5) |
| F4x—Na2—F4v | 91.55 (16) | F1x—Na4—U1 | 91.8 (3) |
| F4—Na2—F4v | 84.4 (2) | F2x—Na4—U1 | 89.8 (3) |
| F4x—Na2—F4v | 91.55 (16) | Na2—Na4—U1 | 76.6 (3) |
| F4v—Na2—F4v | 174.1 (2) | Na1viii—Na4—U1 | 136.9 (4) |
| F4—Na2—Na4v | 50.7 (3) | U1v—Na4—U1 | 148.8 (4) |
| F4x—Na2—Na4v | 132.3 (3) | U1xi—F1—Na1 | 133.12 (17) |
| F4x—Na2—Na4v | 98.1 (3) | U1xi—F1—U1vi | 116.28 (14) |
| F4x—Na2—Na4v | 76.0 (3) | Na1—F1—U1vi | 108.65 (14) |
| F4x—Na2—Na4v | 140.9 (2) | U1xi—F1—Na4vii | 109.1 (3) |
| F4—Na2—Na4v | 44.3 (2) | Na1—F1—Na4vii | 79.8 (3) |
| F4—Na2—Na4vii | 98.1 (3) | U1vi—F1—Na4vii | 93.6 (3) |
| F4x—Na2—Na4vii | 76.0 (3) | U1—F2—U1vi | 151.86 (18) |
| F4x—Na2—Na4vii | 140.9 (2) | U1vi—F2—Na3 | 101.58 (13) |
| F4x—Na2—Na4vii | 44.3 (2) | U1vi—F2—Na3 | 99.29 (12) |
| F4v—Na2—Na4vii | 50.7 (3) | U1—F2—Na4vii | 95.6 (3) |
| F4x—Na2—Na4vii | 132.3 (3) | U1xi—F2—Na4vii | 101.5 (3) |
| Na4v—Na2—Na4vii | 117.21 (14) | Na3—F2—Na4vii | 94.2 (3) |
| F4—Na2—Na4vix | 140.9 (2) | Na1—F3—Na4vii | 89.5 (3) |
| F4x—Na2—Na4vix | 44.3 (2) | Na1—F3—U1vii | 113.65 (18) |
| F4—Na2—Na4vix | 50.7 (3) | Na4vi—F3—U1vii | 111.6 (4) |
| F4x—Na2—Na4vix | 132.3 (3) | Na1—F3—U1vii | 120.80 (19) |
| F4v—Na2—Na4vix | 98.1 (3) | Na4vii—F3—U1vii | 96.3 (4) |
| F4x—Na2—Na4vix | 76.0 (3) | U1—F3—U1vii | 118.16 (15) |
| Na4v—Na2—Na4vix | 117.21 (14) | Na2—F4—U1vii | 150.3 (2) |
| Na4v—Na2—Na4vix | 117.21 (14) | Na2—F4—Na4vii | 93.8 (3) |
| F4—Na2—Na4vix | 132.3 (3) | U1—F4—Na4vix | 107.4 (3) |
| F4x—Na2—Na4vix | 50.7 (3) | Na2—F4—Na4vix | 87.3 (3) |
| F4x—Na2—Na4vix | 44.3 (2) | U1—F4—Na4vix | 99.6 (3) |
| F4v—Na2—Na4vix | 140.9 (2) | Na4—F4—Na4vix | 31.9 (6) |
| F4v—Na2—Na4vix | 76.0 (3) | Na2—F4—Na3 | 84.21 (14) |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|----------------------|--------------|----------------------|--------------|
| F4—Na2—Na4           | 98.1 (3)     | U1—F4—Na3            | 104.92 (15)  |
| Na4—Na2—Na4          | 134.4 (4)    | Na4—F4—Na3           | 114.0 (4)    |
| Na4—Na2—Na4          | 107.5 (4)    | Na4—F4—Na3           | 144.1 (3)    |
| Na4—Na2—Na4          | 23.7 (5)     | U1—F5—U1             | 153.01 (19)  |
| F4—Na2—Na4           | 76.0 (3)     | U1—F5—Na4            | 105.4 (3)    |
| F4—Na2—Na4           | 98.1 (3)     | U1—F5—Na4            | 96.5 (3)     |
| F4—Na2—Na4           | 132.3 (3)    | U1—F5—Na4            | 115.4 (3)    |
| F4—Na2—Na4           | 50.7 (3)     | U1—F5—Na4            | 91.4 (3)     |
| F4—Na2—Na4           | 44.3 (2)     | Na4—F5—Na4           | 29.9 (6)     |

Symmetry codes: (i) −x+y, −x+1, z; (ii) y, −x+y, −z+2; (iii) −x, −x+y, −z+3/2; (iv) −y, x−y+1, z; (v) y, x, −z+3/2; (vi) −x+y−1, −x, z; (vii) −y, x−y, z; (viii) x−1, y, z; (ix) x−y, −y, −z+3/2; (x) −x+y, −x, z; (xi) x−y, x, −z+2; (xii) −x, −y, −z+2; (xiii) x+1, y, z; (xiv) −y+1, x−y+1, z.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.