Synthesis, Structure and Upconversion Studies on Organically Templated Uranium Phosphites

Sukhendu Mandal^a, Manabendra Chandra^b, and Srinivasan Natarajan^{a*}

^a Framework Solids Laboratory, Solid State and Structural Chemistry Unit, Indian Institute of Science,
Bangalore 560012, India

and

^b Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India.

Supplementary Materials

* E-mail: snatarajan@sscu.iisc.ernet.in

Table 1. Selected bond distances in the compound $[\text{C}_4\text{N}_2\text{H}_{12}][(\text{U}^{\text{VI}}\text{O}_2)_2\text{F}_2(\text{HPO}_3)_2]$, **3**.

Bond	Distance (Å)	Bond	Distance (Å)
U(1)-O(1)	1.772(9)	U(1)-F(1)#3	2.388(6)
U(1)-O(2)	1.773(9)	U(1)-F(1)	2.405(6)
U(1)-O(3)	2.288(8)	P(1)-O(3)	1.515(9)
U(1)-O(4)#1	2.301(8)	P(1)-O(4)	1.515(9)
U(1)-O(5)#2	2.354(8)	P(1)-O(5)	1.549(8)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z+1$; #2 $x, y-1, z$; #3 $-x+2, -$

$y+1, -z+2$

Table 2. Selected bond angles in $[\text{C}_2\text{N}_2\text{H}_{10}][\text{U}_2^{\text{IV}}\text{F}_6(\text{HPO}_3)_2]$, **1**, $[\text{C}_4\text{N}_2\text{H}_{12}][\text{U}_2^{\text{IV}}\text{F}_6(\text{HPO}_3)_2]$, **2** and $[\text{C}_4\text{N}_2\text{H}_{12}][(\text{U}^{\text{VI}}\text{O}_2)_2\text{F}_2(\text{HPO}_3)_2]$, **3**.

Moiety	Angle (°)	Moiety	Angle (°)
<i>Compound 1</i>			
F(1)-U(1)-O(1)	78.9(2)	F(3)#1-U(1)-F(2)#2	123.50(18)
F(1)-U(1)-O(2)	145.1(2)	F(1)-U(1)-U(1)#2	73.35(16)
O(1)-U(1)-O(2)	86.4(3)	O(1)-U(1)-U(1)#2	112.89(19)
F(1)-U(1)-F(2)	78.4(2)	O(2)-U(1)-U(1)#2	83.76(16)
O(1)-U(1)-F(2)	144.9(2)	F(2)-U(1)-U(1)#2	34.16(12)
O(2)-U(1)-F(2)	97.3(2)	O(3)-U(1)-U(1)#2	118.2(2)
F(1)-U(1)-O(3)	71.4(2)	F(3)-U(1)-U(1)#2	158.18(13)
O(1)-U(1)-O(3)	108.0(3)	F(3)#1-U(1)-U(1)#2	99.94(12)
O(2)-U(1)-O(3)	143.5(2)	F(2)#2-U(1)-U(1)#2	32.46(12)
F(2)-U(1)-O(3)	89.6(3)	F(1)-U(1)-U(1)#1	141.74(15)
F(1)-U(1)-F(3)	128.5(2)	O(1)-U(1)-U(1)#1	108.30(18)
O(1)-U(1)-F(3)	76.3(2)	O(2)-U(1)-U(1)#1	72.98(15)
O(2)-U(1)-F(3)	77.0(2)	F(2)-U(1)-U(1)#1	106.09(12)
F(2)-U(1)-F(3)	138.54(17)	O(3)-U(1)-U(1)#1	70.66(17)
O(3)-U(1)-F(3)	74.4(2)	F(3)-U(1)-U(1)#1	32.63(12)
F(1)-U(1)-F(3)#1	134.5(2)	F(3)#1-U(1)-U(1)#1	32.61(12)
O(1)-U(1)-F(3)#1	139.9(2)	F(2)#2-U(1)-U(1)#1	143.44(13)
O(2)-U(1)-F(3)#1	74.5(2)	U(1)#2-U(1)-U(1)#1	130.80(2)
F(2)-U(1)-F(3)#1	73.60(17)	O(1)#3-P(1)-O(3)#1	111.2(4)
O(3)-U(1)-F(3)#1	73.2(3)	O(1)#3-P(1)-O(2)	111.4(4)
F(3)-U(1)-F(3)#1	65.2(2)	O(3)#1-P(1)-O(2)	113.9(4)
F(1)-U(1)-F(2)#2	74.0(2)	P(1)#3-O(1)-U(1)	147.2(4)
O(1)-U(1)-F(2)#2	81.6(2)	P(1)-O(2)-U(1)	139.6(4)

O(2)-U(1)-F(2)#2	72.6(2)	U(1)-F(2)-U(1)#2	1113.38(19)
F(2)-U(1)-F(2)#2	66.62(19)	P(1)#1-O(3)-U(1)	142.5(4)
O(3)-U(1)-F(2)#2	141.2(2)	U(1)-F(3)-U(1)#1	114.8(2)
F(3)-U(1)-F(2)#2	143.24(17)		
<i>Compound 2</i>			
F(1)-U(1)-O(1)	79.6(2)	F(3)#1-U(1)-F(2)#2	140.26(15)
F(1)-U(1)-F(2)	77.58(18)	F(1)-U(1)-U(1)#2	73.12(15)
O(1)-U(1)-F(2)	141.1(2)	O(1)-U(1)-U(1)#2	108.81(16)
F(1)-U(1)-O(3)	71.8(2)	F(2)-U(1)-U(1)#2	33.93(11)
O(1)-U(1)-O(3)	106.0(2)	O(3)-U(1)-U(1)#2	124.10(15)
F(2)-U(1)-O(3)	96.27(18)	F(3)-U(1)-U(1)#2	102.54(11)
F(1)-U(1)-F(3)	133.89(17)	O(2)-U(1)-U(1)#2	84.67(16)
O(1)-U(1)-F(3)	140.22(19)	F(3)#1-U(1)-U(1)#2	156.75(11)
F(2)-U(1)-F(3)	76.16(16)	F(2)#2-U(1)-U(1)#2	31.35(10)
O(3)-U(1)-F(3)	74.21(18)	F(1)-U(1)-U(1)#1	142.28(14)
F(1)-U(1)-O(2)	144.73(19)	O(1)-U(1)-U(1)#1	108.06(15)
O(1)-U(1)-O(2)	82.2(2)	F(2)-U(1)-U(1)#1	109.30(11)
F(2)-U(1)-O(2)	99.0(2)	O(3)-U(1)-U(1)#1	70.59(14)
O(3)-U(1)-O(2)	142.8(2)	F(3)-U(1)-U(1)#1	33.14(11)
F(3)-U(1)-O(2)	76.89(18)	O(2)-U(1)-U(1)#1	72.38(14)
F(1)-U(1)-F(3)#1	129.91(18)	F(3)#1-U(1)-U(1)#1	31.89(10)
O(1)-U(1)-F(3)#1	76.79(18)	F(2)#2-U(1)-U(1)#1	143.10(10)
F(2)-U(1)-F(3)#1	141.19(15)	U(1)#2-U(1)-U(1)#1	132.89(2)
O(3)-U(1)-F(3)#1	73.26(18)	O(3)-P(1)-O(2)#1	112.1(3)
F(3)-U(1)-F(3)#1	65.04(18)	O(3)-P(1)-O(1)#3	111.2(3)
O(2)-U(1)-F(3)#1	73.58(19)	O(2)#1-P(1)-O(1)#3	110.0(3)
F(1)-U(1)-F(2)#2	74.21(18)	P(1)#4-O(1)-U(1)	163.0(4)
O(1)-U(1)-F(2)#2	78.41(19)	U(1)-F(2)-U(1)#2	114.72(17)

F(2)-U(1)-F(2)#2	65.28(17)	P(1)#1-O(2)-U(1)	134.2(4)
O(3)-U(1)-F(2)#2	144.16(17)	P(1)-O(3)-U(1)	135.5(3)
F(3)-U(1)-F(2)#2	125.20(16)	U(1)-F(3)-U(1)#1	114.96(18)
O(2)-U(1)-F(2)#2	72.68(18)		
Compound 3			
O(1)-U(1)-O(2)	176.3(4)	O(4)#1-U(1)-F(1)	151.0(3)
O(1)-U(1)-O(3)	91.5(4)	O(5)#2-U(1)-F(1)	131.3(2)
O(2)-U(1)-O(3)	90.6(4)	F(1)#3-U(1)-F(1)	63.6(3)
O(1)-U(1)-O(4)#1	94.2(4)	O(1)-U(1)-U(1)#3	90.9(3)
O(2)-U(1)-O(4)#1	89.3(4)	O(2)-U(1)-U(1)#3	85.6(3)
O(3)-U(1)-O(4)#1	80.0(3)	O(3)-U(1)-U(1)#3	103.3(2)
O(1)-U(1)-O(5)#2	89.5(4)	O(4)#1-U(1)-U(1)#3	173.9(2)
O(2)-U(1)-O(5)#2	89.7(4)	O(5)#2-U(1)-U(1)#3	99.71(19)
O(3)-U(1)-O(5)#2	156.9(3)	F(1)#3-U(1)-U(1)#3	31.95(15)
O(4)#1-U(1)-O(5)#2	76.9(3)	F(1)-U(1)-U(1)#3	31.70(15)
O(1)-U(1)-F(1)#3	88.9(4)	O(3)-P(1)-O(4)	113.2(5)
O(2)-U(1)-F(1)#3	87.4(3)	O(3)-P(1)-O(5)	107.1(5)
O(3)-U(1)-F(1)#3	135.3(3)	O(4)-P(1)-O(5)	111.8(5)
O(4)#1-U(1)-F(1)#3	144.6(3)	P(1)-O(3)-U(1)	166.0(6)
O(5)#2-U(1)-F(1)#3	67.8(2)	P(1)-O(4)-U(1)#1	136.6(5)
O(1)-U(1)-F(1)	92.6(4)	P(1)-O(5)-U(1)#4	136.6(4)
O(2)-U(1)-F(1)	85.1(3)	U(1)#3-F(1)-U(1)	116.4(3)
O(3)-U(1)-F(1)	71.7(3)		

Symmetry transformations used to generate equivalent atoms for **1**: #1 -x+1,-y+2,-z+1 #2 -x+1,-y+1,-z+1 #3 -x+2,-y+2,-z+1 #4 -x,-y+1,-z+2; for **2**: #1 -x+1,-y+2,-z+2 #2 -x+2,-y+2,-z+2 #3 -x+1,y-1/2,-z+3/2 #4 -x+1,y+1/2,-z+3/2 #5 -x,-y+2,-z+1; for **3**: #1 -x+1,-y+1,-z+1 #2 x,y-1,z #3 -x+2,-y+1,-z+2 #4 x,y+1,z #5 -x+1,-y+2,-z+2.

Fig S1: Simulated and experimental XRD pattern for $[\text{C}_2\text{N}_2\text{H}_{10}][\text{U}_2^{\text{IV}}\text{F}_6(\text{HPO}_3)_2]$, **1**.

Fig S2: Simulated and experimental XRD pattern for $[\text{C}_4\text{N}_2\text{H}_{12}][\text{U}_2^{\text{IV}}\text{F}_6(\text{HPO}_3)_2]$, **2**.

Fig S3: Simulated and experimental XRD pattern for $[\text{C}_4\text{N}_2\text{H}_{12}][(\text{U}^{\text{VI}}\text{O}_2)_2\text{F}_2(\text{HPO}_3)_2]$, **3**.

Fig S4: Thermogravimetric analysis curve for the compounds, $[\text{C}_2\text{N}_2\text{H}_{10}][\text{U}_2^{\text{IV}}\text{F}_6(\text{HPO}_3)_2]$, **1**, $[\text{C}_4\text{N}_2\text{H}_{12}][\text{U}_2^{\text{IV}}\text{F}_6(\text{HPO}_3)_2]$, **2** and $[\text{C}_4\text{N}_2\text{H}_{12}][(\text{U}^{\text{VI}}\text{O}_2)_2\text{F}_2(\text{HPO}_3)_2]$, **3**..

Fig S5: Infrared spectra of the compounds $[\text{C}_2\text{N}_2\text{H}_{10}][\text{U}_2^{\text{IV}}\text{F}_6(\text{HPO}_3)_2]$, **1**, $[\text{C}_4\text{N}_2\text{H}_{12}][\text{U}_2^{\text{IV}}\text{F}_6(\text{HPO}_3)_2]$, **2** and $[\text{C}_4\text{N}_2\text{H}_{12}][(\text{U}^{\text{VI}}\text{O}_2)_2\text{F}_2(\text{HPO}_3)_2]$, **3**..

Fig. S6: ORTEP diagram of (a) **1**, (b) **2** and (c) **3**. Thermal ellipsoids are given at 50% probability.

Fig. S7 (a) Coordination geometry around U^{6+} ions in $[\text{C}_4\text{N}_2\text{H}_{12}][(\text{U}^{\text{VI}}\text{O}_2)_2\text{F}_2(\text{HPO}_3)_2]$, **3**.

(b) The structure of **3** viewed along ac plane, showing the arrangement of the layers and the piperazine molecules. The dotted lines represent the possible hydrogen bond interactions.