Supplementary Material (ESI) for Chemical Communications

Actinide-Mediated Coupling of 4-Fluorobenzonitrile: Synthesis of an Eight-Membered Thorium(IV) Tetraazametallacycle

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Electronic Supplementary Information:

General Synthetic Considerations.

Reactions and manipulations were performed at 20 °C in a recirculating Vacuum Atmospheres Model HE-553-2 inert atmosphere (N_2 or He) drybox with a MO-40-2 Dri-Train, or using standard Schlenk and high vacuum line techniques. Glassware was dried overnight at 150 °C before use. All NMR spectra were obtained using a Bruker Avance 300 MHz spectrometer. Cyclic voltammetric data were obtained in the Vacuum Atmospheres drybox system described above. All data were collected using a Perkin-Elmer Princeton Applied Research Corporation (PARC) Model 263 potentiostat under computer control with PARC Model 270 software. All sample solutions were ~5 mM in complex with 0.1 M [(*n*-$C_4H_9)_4N][B(C_6F_5)_4]$ supporting electrolyte in THF solvent. X-ray data were collected using a Bruker APEX2 diffractometer. Structural solution and refinement was achieved using the SHELXL97 program suite. Details regarding data collection are provided in the CIF files.

Benzene-d_6 and toluene-d_8 were obtained from Cambridge Isotope Laboratories (CIL) and were purified by storage over activated 4 Å molecular sieves prior to use. Chemical shifts were referenced to protio solvent impurities, which are referenced to internal $Si(CH_3)_4$ at δ 0.00 ppm, or to $CFCl_3$ (^{19}F) at δ -63.48 ppm. Mass spectrometric (MS) analyses were obtained at the University of California, Berkeley Mass Spectrometry Facility, using either VG ProSpec (EI) or VG70-SE (FAB) mass spectrometers. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility, on a Perkin-Elmer Series II 2400 CHNS analyzer. 4-Fluorobenzonitrile (Aldrich) was used as received. Celite (Aldrich) and alumina (Brockman I, Aldrich) were dried in vacuo at 250 °C for 48 h prior to use. Anhydrous toluene (Aldrich) and pentane (Aldrich), diethyl ether (Aldrich), and tetrahydrofuran (Aldrich) were passed through a column of activated alumina (A2, 12 × 32, Purifry) under nitrogen and stored over activated 4 Å

molecular sieves prior to use. $(C_5Me_5)_2Th(CH_3)_2$ was prepared according to literature procedures.[1] *Caution*: Natural thorium (isotope ^{232}Th) is a weak α-emitter with a half-life 1.41 x 10^{10} years; manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere drybox in a radiation laboratory equipped with α- and β-counting equipment.

(1) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J., *J. Am. Chem. Soc.* **1981**, *103*, 6650-6667.

Synthesis of $(C_5Me_5)_2Th[-N=C(CH_3)(4\text{-}F\text{-}C_6H_4)]_2$ (2). A toluene solution (10 mL) of 4-fluorobenzonitrile (0.16 g, 1.4 mmol) was slowly added dropwise with stirring to a toluene solution (40 mL) containing $(C_5Me_5)_2Th(CH_3)_2$ (**1**) (0.23 g, 0.62 mmol). Excess nitrile solution was rinsed into the reaction mixture with additional toluene (3 x 2 mL). The reaction mixture immediately change color from clear and colorless to bright yellow. The solution was stirred for 1 h and the volatiles removed under reduced pressure. The resulting yellow residue was dissolved in ~ 50 mL pentane, filtered through a Celite-packed coarse-porosity frit, the filtrate was collected, and the volatiles were removed under reduced pressure to give crude **2** as a yellow solid. Recrystallization from pentane at –30 ºC afforded **2** as a bright yellow crystalline solid. Yield 0.23 g, 0.30 mmol, 48%. ^{1}H-NMR (C_6D_6, 300 MHz, 298 K): δ 7.64 (dd, J_1 = 8.7 Hz, J_2 = 5.3 Hz, 4H, meta Ar-*H*), 6.87 (t, J_{HH} = 8.6 Hz, 4H, ortho Ar-*H*), 2.31 (s, 6H, -C*H*$_3$), 1.97 (s, 30H, $C_5(CH_3)_5$). ^{13}C-NMR (C_6D_6, 300 MHz, 298 K): δ 167.89 (s, N=*C*), 164.46 (d, J_{CF} = 987 Hz, F-*C*), 138.21 (d, J_{CF} = 1.2 Hz, quat Ar-*C*), 129.42 (d, J_{CF} = 33 Hz, ortho Ar-*C*), 122.99 (s, $C_5(CH_3)_5$), 115.28 (d, J_{CF} = 84 Hz, meta Ar-*C*), 30.46 (s, -*C*H$_3$), 11.53 (s, $C_5(CH_3)_5$). ^{19}F-NMR (C_6D_6, 300 MHz, 298 K): δ -113.52 (m, C_6H_5F). UV-Vis-NIR, cm^{-1} (ε, M^{-1} cm^{-1}, toluene): 22,396 (250). Electrochemistry (V vs. Fc/Fc$^+$ in THF/0.1 M [^{n}Bu$_4$N][B(C_6F_5)$_4$]) $E_{p,a}$ = -2.53 V. Anal. Calcd for $C_{36}H_{44}N_2F_2Th$ (mol. wt. 774.78): C, 55.81; H, 5.72; N, 3.62. Found: C, 55.82; H, 5.82; N, 3.55.

Crystal Data and Structure Refinement for $(C_5Me_5)_2Th[-N=C(CH_3)(4\text{-}F\text{-}C_6H_4)]_2$ (2).

Empirical formula	$C_{36}\ H_{44}\ F_2\ N_2\ Th$	
Formula weight	774.77	
Temperature	141(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 12.9201(6) Å	α= 90°
	b = 14.0054(7) Å	β= 98.677(1)°
	c = 18.2113(9) Å	γ = 90°
Volume	3257.6(3) $Å^3$	
Z	4	
Density (calculated)	1.580 Mg/m^3	
Absorption coefficient	4.615 mm^{-1}	
F(000)	1528	
Crystal size	0.24 x 0.16 x 0.14 mm^3	
θ Range for data collection	2.16 to 28.85°	
Index ranges	$-17 \le h \le 17, -18 \le k \le 18, -23 \le l \le 23$	
Reflections collected	17967	
Independent reflections	4014 [R(int) = 0.0222]	
Completeness to θ = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5643 and 0.4038	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4014 / 0 / 192	
Goodness-of-fit on F^2	1.323	
Final R indices [I>2σ(I)]	R1 = 0.0180, wR2 = 0.0484	
R indices (all data)	R1 = 0.0197, wR2 = 0.0488	
Largest diff. peak and hole	1.510 and -0.277 $e.Å^{-3}$	

Bond Lengths [Å] and Angles [°] for $(C_5Me_5)_2Th[-N=C(CH_3)(4\text{-}F\text{-}C_6H_4)]_2$ (2).

Th(1)-N(1)#1	2.250(2)	N(1)#1-Th(1)-N(1)	108.67(11)
Th(1)-N(1)	2.250(2)	N(1)#1-Th(1)-C(2)	92.73(7)
Th(1)-C(2)	2.806(2)	N(1)-Th(1)-C(2)	124.27(7)
Th(1)-C(2)#1	2.806(2)	N(1)#1-Th(1)-C(2)#1	124.27(7)
Th(1)-C(3)	2.806(2)	N(1)-Th(1)-C(2)#1	92.73(7)
Th(1)-C(3)#1	2.806(2)	C(2)-Th(1)-C(2)#1	116.84(9)
Th(1)-C(4)	2.818(2)	N(1)#1-Th(1)-C(3)	121.60(7)
Th(1)-C(4)#1	2.818(2)	N(1)-Th(1)-C(3)	105.05(7)
Th(1)-C(1)	2.821(2)	C(2)-Th(1)-C(3)	29.36(7)
Th(1)-C(1)#1	2.821(2)	C(2)#1-Th(1)-C(3)	99.66(7)
Th(1)-C(5)#1	2.821(2)	N(1)#1-Th(1)-C(3)#1	105.05(7)
Th(1)-C(5)	2.821(2)	N(1)-Th(1)-C(3)#1	121.60(7)
F(1)-C(16)	1.358(4)	C(2)-Th(1)-C(3)#1	99.66(7)
N(1)-C(11)	1.260(3)	C(2)#1-Th(1)-C(3)#1	29.36(7)
C(1)-C(2)	1.413(3)	C(3)-Th(1)-C(3)#1	95.57(10)
C(1)-C(5)	1.418(3)	N(1)#1-Th(1)-C(4)	122.64(7)
C(1)-C(6)	1.508(3)	N(1)-Th(1)-C(4)	77.87(7)
C(2)-C(3)	1.422(3)	C(2)-Th(1)-C(4)	48.20(7)
C(2)-C(7)	1.504(3)	C(2)#1-Th(1)-C(4)	111.77(7)
C(3)-C(4)	1.420(3)	C(3)-Th(1)-C(4)	29.25(7)
C(3)-C(8)	1.512(3)	C(3)#1-Th(1)-C(4)	119.54(7)
C(4)-C(5)	1.421(3)	N(1)#1-Th(1)-C(4)#1	77.87(7)
C(4)-C(9)	1.505(3)	N(1)-Th(1)-C(4)#1	122.64(7)
C(5)-C(10)	1.507(3)	C(2)-Th(1)-C(4)#1	111.77(7)
C(11)-C(13)	1.504(4)	C(2)#1-Th(1)-C(4)#1	48.20(7)
C(11)-C(12)	1.520(3)	C(3)-Th(1)-C(4)#1	119.54(7)
C(13)-C(14)	1.397(4)	C(3)#1-Th(1)-C(4)#1	29.25(7)
C(13)-C(18)	1.408(3)	C(4)-Th(1)-C(4)#1	147.20(10)
C(14)-C(15)	1.381(4)	N(1)#1-Th(1)-C(1)	77.01(7)
C(15)-C(16)	1.381(4)	N(1)-Th(1)-C(1)	106.25(7)
C(16)-C(17)	1.375(5)	C(2)-Th(1)-C(1)	29.08(6)
C(17)-C(18)	1.377(4)	C(2)#1-Th(1)-C(1)	145.52(6)
		C(3)-Th(1)-C(1)	48.15(6)
		C(3)#1-Th(1)-C(1)	127.13(6)

C(4)-Th(1)-C(1)	48.03(7)	C(2)-C(1)-Th(1)	74.88(13)
C(4)#1-Th(1)-C(1)	129.94(7)	C(5)-C(1)-Th(1)	75.45(13)
N(1)#1-Th(1)-C(1)#1	106.25(7)	C(6)-C(1)-Th(1)	120.24(15)
N(1)-Th(1)-C(1)#1	77.01(7)	C(1)-C(2)-C(3)	108.1(2)
C(2)-Th(1)-C(1)#1	145.52(6)	C(1)-C(2)-C(7)	125.4(2)
C(2)#1-Th(1)-C(1)#1	29.08(6)	C(3)-C(2)-C(7)	126.3(2)
C(3)-Th(1)-C(1)#1	127.13(6)	C(1)-C(2)-Th(1)	76.04(13)
C(3)#1-Th(1)-C(1)#1	48.15(6)	C(3)-C(2)-Th(1)	75.31(12)
C(4)-Th(1)-C(1)#1	129.94(7)	C(7)-C(2)-Th(1)	118.47(15)
C(4)#1-Th(1)-C(1)#1	48.03(7)	C(4)-C(3)-C(2)	107.8(2)
C(1)-Th(1)-C(1)#1	174.58(8)	C(4)-C(3)-C(8)	124.8(2)
N(1)#1-Th(1)-C(5)#1	78.65(7)	C(2)-C(3)-C(8)	127.1(2)
N(1)-Th(1)-C(5)#1	94.38(7)	C(4)-C(3)-Th(1)	75.85(12)
C(2)-Th(1)-C(5)#1	140.88(7)	C(2)-C(3)-Th(1)	75.33(12)
C(2)#1-Th(1)-C(5)#1	48.11(7)	C(8)-C(3)-Th(1)	120.01(15)
C(3)-Th(1)-C(5)#1	143.62(7)	C(3)-C(4)-C(5)	108.0(2)
C(3)#1-Th(1)-C(5)#1	48.22(7)	C(3)-C(4)-C(9)	125.6(2)
C(4)-Th(1)-C(5)#1	158.64(7)	C(5)-C(4)-C(9)	126.1(2)
C(4)#1-Th(1)-C(5)#1	29.19(6)	C(3)-C(4)-Th(1)	74.90(13)
C(1)-Th(1)-C(5)#1	152.05(7)	C(5)-C(4)-Th(1)	75.52(13)
C(1)#1-Th(1)-C(5)#1	29.12(7)	C(9)-C(4)-Th(1)	120.12(15)
N(1)#1-Th(1)-C(5)	94.38(7)	C(1)-C(5)-C(4)	107.9(2)
N(1)-Th(1)-C(5)	78.65(7)	C(1)-C(5)-C(10)	125.8(2)
C(2)-Th(1)-C(5)	48.11(7)	C(4)-C(5)-C(10)	126.2(2)
C(2)#1-Th(1)-C(5)	140.88(7)	C(1)-C(5)-Th(1)	75.43(13)
C(3)-Th(1)-C(5)	48.22(7)	C(4)-C(5)-Th(1)	75.28(13)
C(3)#1-Th(1)-C(5)	143.62(7)	C(10)-C(5)-Th(1)	118.71(14)
C(4)-Th(1)-C(5)	29.19(6)	N(1)-C(11)-C(13)	122.3(2)
C(4)#1-Th(1)-C(5)	158.64(7)	N(1)-C(11)-C(12)	121.3(2)
C(1)-Th(1)-C(5)	29.12(7)	C(13)-C(11)-C(12)	116.4(2)
C(1)#1-Th(1)-C(5)	152.05(7)	C(14)-C(13)-C(18)	117.7(3)
C(5)#1-Th(1)-C(5)	168.14(9)	C(14)-C(13)-C(11)	119.29(19)
C(11)-N(1)-Th(1)	175.29(19)	C(18)-C(13)-C(11)	123.0(2)
C(2)-C(1)-C(5)	108.2(2)	C(15)-C(14)-C(13)	121.5(2)
C(2)-C(1)-C(6)	126.3(2)	C(16)-C(15)-C(14)	118.3(3)
C(5)-C(1)-C(6)	125.2(2)	F(1)-C(16)-C(17)	118.9(2)

F(1)-C(16)-C(15)	118.5(3)
C(17)-C(16)-C(15)	122.6(3)
C(16)-C(17)-C(18)	118.4(2)
C(17)-C(18)-C(13)	121.5(3)

Crystal Data and Structure Refinement for $(C_5Me_5)_2Th[-N=C(4\text{-}F\text{-}C_6H_4)\text{-}N=C(4\text{-}F\text{-}C_6H_4)\text{-}N\text{-}C(4\text{-}F\text{-}C_6H_4)=N\text{-}C(4\text{-}F\text{-}C_6H_4)(CH_3)_2]$ (3).

Empirical formula	$C_{55}\ H_{64}\ F_4\ N_4\ Th$	
Formula weight	1089.14	
Temperature	141(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 24.6845(13) Å	α= 90°
	b = 18.9028(10) Å	β= 95.014(1)°
	c = 20.7781(11) Å	γ = 90°
Volume	9658.1(9) $Å^3$	
Z	8	
Density (calculated)	1.498 Mg/m^3	
Absorption coefficient	3.144 mm^{-1}	
F(000)	4384	
Crystal size	0.16 x 0.10 x 0.10 mm^3	
θ Range for data collection	1.63 to 25.65°.	
Index ranges	$-29 \le h \le 29$, $-21 \le k \le 22$, $-25 \le l \le 25$	
Reflections collected	40160	
Independent reflections	9059 [R(int) = 0.0631]	
Completeness to θ = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7439 and 0.6331	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9059 / 0 / 544	
Goodness-of-fit on F^2	1.011	
Final R indices [I>2σ(I)]	R1 = 0.0363, wR2 = 0.0929	
R indices (all data)	R1 = 0.0505, wR2 = 0.0985	
Largest diff. peak and hole	1.273 and -1.136 $e.Å^{-3}$	

Bond Lengths [Å] and Angles [°] for $(C_5Me_5)_2Th[-N=C(4\text{-}F\text{-}C_6H_4)\text{-}N=C(4\text{-}F\text{-}C_6H_4)\text{-}N\text{-}C(4\text{-}F\text{-}C_6H_4)=N\text{-}C(4\text{-}F\text{-}C_6H_4)(CH_3)_2]$ (3).

Th(1)-N(4)	2.234(4)	C(4)-C(5)	1.397(7)
Th(1)-N(2)	2.451(4)	C(4)-C(9)	1.529(7)
Th(1)-N(1)	2.727(4)	C(5)-C(10)	1.503(7)
Th(1)-C(3)	2.797(5)	C(11)-C(12)	1.406(7)
Th(1)-C(4)	2.828(5)	C(11)-C(15)	1.418(7)
Th(1)-C(11)	2.837(5)	C(11)-C(16)	1.516(8)
Th(1)-C(2)	2.843(5)	C(12)-C(13)	1.416(7)
Th(1)-C(12)	2.846(5)	C(12)-C(17)	1.515(7)
Th(1)-C(5)	2.864(5)	C(13)-C(14)	1.427(7)
Th(1)-C(15)	2.865(5)	C(13)-C(18)	1.510(7)
Th(1)-C(13)	2.873(5)	C(14)-C(15)	1.401(8)
Th(1)-C(1)	2.875(6)	C(14)-C(19)	1.514(8)
Th(1)-C(14)	2.892(5)	C(15)-C(20)	1.506(7)
Th(1)-C(30)	3.057(5)	C(21)-C(23)	1.503(8)
Th(1)-N(3)	3.879(4)	C(21)-C(22)	1.520(7)
F(1)-C(27)	1.405(6)	C(21)-C(24)	1.540(7)
F(2)-C(34)	1.346(6)	C(24)-C(29)	1.388(7)
F(3)-C(41)	1.344(5)	C(24)-C(25)	1.386(6)
F(4)-C(48)	1.380(5)	C(25)-C(26)	1.360(8)
N(1)-C(30)	1.313(6)	C(26)-C(27)	1.338(9)
N(1)-C(21)	1.518(6)	C(27)-C(28)	1.376(9)
N(2)-C(30)	1.378(6)	C(28)-C(29)	1.390(8)
N(2)-C(37)	1.383(6)	C(30)-C(31)	1.510(7)
N(3)-C(37)	1.285(6)	C(31)-C(36)	1.402(7)
N(3)-C(44)	1.406(6)	C(31)-C(32)	1.408(7)
N(4)-C(44)	1.268(6)	C(32)-C(33)	1.385(8)
C(1)-C(5)	1.400(7)	C(33)-C(34)	1.385(9)
C(1)-C(2)	1.417(7)	C(34)-C(35)	1.359(7)
C(1)-C(6)	1.520(7)	C(35)-C(36)	1.373(7)
C(2)-C(3)	1.413(7)	C(37)-C(38)	1.513(6)
C(2)-C(7)	1.493(7)	C(38)-C(43)	1.371(7)
C(3)-C(4)	1.411(7)	C(38)-C(39)	1.419(8)
C(3)-C(8)	1.514(7)	C(39)-C(40)	1.404(8)

C(40)-C(41)	1.348(9)	C(4)-Th(1)-C(12)	164.01(16)
C(41)-C(42)	1.363(8)	C(11)-Th(1)-C(12)	28.65(14)
C(42)-C(43)	1.399(7)	C(2)-Th(1)-C(12)	128.47(14)
C(44)-C(45)	1.513(6)	N(4)-Th(1)-C(5)	92.79(15)
C(45)-C(46)	1.377(7)	N(2)-Th(1)-C(5)	84.48(14)
C(45)-C(50)	1.405(7)	N(1)-Th(1)-C(5)	86.46(13)
C(46)-C(47)	1.381(7)	C(3)-Th(1)-C(5)	47.61(15)
C(47)-C(48)	1.346(7)	C(4)-Th(1)-C(5)	28.41(15)
C(48)-C(49)	1.372(8)	C(11)-Th(1)-C(5)	165.97(16)
C(49)-C(50)	1.383(7)	C(2)-Th(1)-C(5)	47.29(14)
		C(12)-Th(1)-C(5)	165.27(15)
N(4)-Th(1)-N(2)	69.78(13)	N(4)-Th(1)-C(15)	75.15(15)
N(4)-Th(1)-N(1)	120.09(12)	N(2)-Th(1)-C(15)	121.85(15)
N(2)-Th(1)-N(1)	50.49(12)	N(1)-Th(1)-C(15)	130.34(13)
N(4)-Th(1)-C(3)	81.60(15)	C(3)-Th(1)-C(15)	95.22(15)
N(2)-Th(1)-C(3)	122.67(15)	C(4)-Th(1)-C(15)	116.66(16)
N(1)-Th(1)-C(3)	131.85(14)	C(11)-Th(1)-C(15)	28.79(15)
N(4)-Th(1)-C(4)	70.98(16)	C(2)-Th(1)-C(15)	103.50(16)
N(2)-Th(1)-C(4)	93.75(15)	C(12)-Th(1)-C(15)	47.36(14)
N(1)-Th(1)-C(4)	112.92(14)	C(5)-Th(1)-C(15)	142.64(15)
C(3)-Th(1)-C(4)	29.05(15)	N(4)-Th(1)-C(13)	119.61(14)
N(4)-Th(1)-C(11)	74.50(15)	N(2)-Th(1)-C(13)	122.61(15)
N(2)-Th(1)-C(11)	96.33(14)	N(1)-Th(1)-C(13)	92.21(14)
N(1)-Th(1)-C(11)	104.90(14)	C(3)-Th(1)-C(13)	114.69(16)
C(3)-Th(1)-C(11)	122.83(15)	C(4)-Th(1)-C(13)	143.62(16)
C(4)-Th(1)-C(11)	137.87(16)	C(11)-Th(1)-C(13)	47.05(14)
N(4)-Th(1)-C(2)	110.56(15)	C(2)-Th(1)-C(13)	99.88(14)
N(2)-Th(1)-C(2)	131.55(14)	C(12)-Th(1)-C(13)	28.67(14)
N(1)-Th(1)-C(2)	111.82(13)	C(5)-Th(1)-C(13)	142.42(14)
C(3)-Th(1)-C(2)	29.00(14)	C(15)-Th(1)-C(13)	47.05(14)
C(4)-Th(1)-C(2)	47.34(14)	N(4)-Th(1)-C(1)	117.42(14)
C(11)-Th(1)-C(2)	131.39(15)	N(2)-Th(1)-C(1)	105.54(14)
N(4)-Th(1)-C(12)	101.41(16)	N(1)-Th(1)-C(1)	85.88(13)
N(2)-Th(1)-C(12)	96.70(14)	C(3)-Th(1)-C(1)	47.35(14)
N(1)-Th(1)-C(12)	83.08(13)	C(4)-Th(1)-C(1)	46.61(15)
C(3)-Th(1)-C(12)	138.07(14)		

C(11)-Th(1)-C(1)	157.60(14)	C(4)-Th(1)-N(3)	76.99(12)
C(2)-Th(1)-C(1)	28.69(14)	C(11)-Th(1)-N(3)	87.96(11)
C(12)-Th(1)-C(1)	139.85(15)	C(2)-Th(1)-N(3)	124.33(11)
C(5)-Th(1)-C(1)	28.23(14)	C(12)-Th(1)-N(3)	104.97(13)
C(15)-Th(1)-C(1)	131.77(16)	C(5)-Th(1)-N(3)	84.57(12)
C(13)-Th(1)-C(1)	114.19(14)	C(15)-Th(1)-N(3)	101.84(13)
N(4)-Th(1)-C(14)	102.04(15)	C(13)-Th(1)-N(3)	132.87(12)
N(2)-Th(1)-C(14)	141.96(15)	C(1)-Th(1)-N(3)	112.67(12)
N(1)-Th(1)-C(14)	120.79(14)	C(14)-Th(1)-N(3)	129.90(13)
C(3)-Th(1)-C(14)	91.07(15)	C(30)-Th(1)-N(3)	61.58(10)
C(4)-Th(1)-C(14)	119.38(15)	C(30)-N(1)-C(21)	124.2(4)
C(11)-Th(1)-C(14)	46.83(14)	C(30)-N(1)-Th(1)	91.5(3)
C(2)-Th(1)-C(14)	86.44(14)	C(21)-N(1)-Th(1)	140.5(3)
C(12)-Th(1)-C(14)	47.14(14)	C(30)-N(2)-C(37)	125.3(4)
C(5)-Th(1)-C(14)	133.55(14)	C(30)-N(2)-Th(1)	102.3(3)
C(15)-Th(1)-C(14)	28.16(15)	C(37)-N(2)-Th(1)	132.4(3)
C(13)-Th(1)-C(14)	28.66(15)	C(37)-N(3)-C(44)	121.2(4)
C(1)-Th(1)-C(14)	110.77(15)	C(37)-N(3)-Th(1)	65.0(3)
N(4)-Th(1)-C(30)	94.84(13)	C(44)-N(3)-Th(1)	56.6(2)
N(2)-Th(1)-C(30)	26.13(12)	C(44)-N(4)-Th(1)	141.3(3)
N(1)-Th(1)-C(30)	25.42(11)	C(5)-C(1)-C(2)	108.7(4)
C(3)-Th(1)-C(30)	137.18(14)	C(5)-C(1)-C(6)	126.5(5)
C(4)-Th(1)-C(30)	109.64(15)	C(2)-C(1)-C(6)	123.7(5)
C(11)-Th(1)-C(30)	96.49(14)	C(5)-C(1)-Th(1)	75.4(3)
C(2)-Th(1)-C(30)	129.59(14)	C(2)-C(1)-Th(1)	74.4(3)
C(12)-Th(1)-C(30)	84.62(13)	C(6)-C(1)-Th(1)	125.9(3)
C(5)-Th(1)-C(30)	90.37(14)	C(3)-C(2)-C(1)	107.3(4)
C(15)-Th(1)-C(30)	125.28(15)	C(3)-C(2)-C(7)	127.6(5)
C(13)-Th(1)-C(30)	104.15(15)	C(1)-C(2)-C(7)	124.3(5)
C(1)-Th(1)-C(30)	100.99(13)	C(3)-C(2)-Th(1)	73.7(3)
C(14)-Th(1)-C(30)	130.95(14)	C(1)-C(2)-Th(1)	76.9(3)
N(4)-Th(1)-N(3)	34.42(11)	C(7)-C(2)-Th(1)	123.3(4)
N(2)-Th(1)-N(3)	35.74(11)	C(2)-C(3)-C(4)	107.5(4)
N(1)-Th(1)-N(3)	86.22(9)	C(2)-C(3)-C(8)	126.2(5)
C(3)-Th(1)-N(3)	100.41(12)	C(4)-C(3)-C(8)	126.0(5)

C(2)-C(3)-Th(1)	77.3(3)	C(13)-C(14)-C(19)	124.4(6)
C(4)-C(3)-Th(1)	76.7(3)	C(15)-C(14)-Th(1)	74.9(3)
C(8)-C(3)-Th(1)	117.6(4)	C(13)-C(14)-Th(1)	74.9(3)
C(5)-C(4)-C(3)	108.9(4)	C(19)-C(14)-Th(1)	126.6(4)
C(5)-C(4)-C(9)	125.3(5)	C(14)-C(15)-C(11)	107.8(4)
C(3)-C(4)-C(9)	125.4(5)	C(14)-C(15)-C(20)	124.2(6)
C(5)-C(4)-Th(1)	77.2(3)	C(11)-C(15)-C(20)	127.4(6)
C(3)-C(4)-Th(1)	74.2(3)	C(14)-C(15)-Th(1)	77.0(3)
C(9)-C(4)-Th(1)	120.2(4)	C(11)-C(15)-Th(1)	74.5(3)
C(4)-C(5)-C(1)	107.6(4)	C(20)-C(15)-Th(1)	121.6(4)
C(4)-C(5)-C(10)	123.1(5)	C(23)-C(21)-N(1)	114.3(4)
C(1)-C(5)-C(10)	128.8(5)	C(23)-C(21)-C(22)	106.0(5)
C(4)-C(5)-Th(1)	74.4(3)	N(1)-C(21)-C(22)	104.7(4)
C(1)-C(5)-Th(1)	76.3(3)	C(23)-C(21)-C(24)	113.0(5)
C(10)-C(5)-Th(1)	121.1(3)	N(1)-C(21)-C(24)	110.5(4)
C(12)-C(11)-C(15)	108.6(5)	C(22)-C(21)-C(24)	107.6(4)
C(12)-C(11)-C(16)	126.9(6)	C(29)-C(24)-C(25)	117.6(5)
C(15)-C(11)-C(16)	124.1(5)	C(29)-C(24)-C(21)	121.1(4)
C(12)-C(11)-Th(1)	76.1(3)	C(25)-C(24)-C(21)	121.2(4)
C(15)-C(11)-Th(1)	76.7(3)	C(26)-C(25)-C(24)	122.0(6)
C(16)-C(11)-Th(1)	118.6(3)	C(27)-C(26)-C(25)	117.9(5)
C(11)-C(12)-C(13)	107.7(4)	C(26)-C(27)-C(28)	124.9(5)
C(11)-C(12)-C(17)	124.2(5)	C(26)-C(27)-F(1)	119.2(6)
C(13)-C(12)-C(17)	126.8(5)	C(28)-C(27)-F(1)	115.9(7)
C(11)-C(12)-Th(1)	75.3(3)	C(27)-C(28)-C(29)	115.8(6)
C(13)-C(12)-Th(1)	76.7(3)	C(24)-C(29)-C(28)	121.8(5)
C(17)-C(12)-Th(1)	124.4(3)	N(1)-C(30)-N(2)	111.3(4)
C(12)-C(13)-C(14)	107.7(4)	N(1)-C(30)-C(31)	129.0(4)
C(12)-C(13)-C(18)	127.4(5)	N(2)-C(30)-C(31)	118.6(4)
C(14)-C(13)-C(18)	124.2(5)	N(1)-C(30)-Th(1)	63.1(2)
C(12)-C(13)-Th(1)	74.6(3)	N(2)-C(30)-Th(1)	51.6(2)
C(14)-C(13)-Th(1)	76.4(3)	C(31)-C(30)-Th(1)	151.6(3)
C(18)-C(13)-Th(1)	122.8(4)	C(36)-C(31)-C(32)	117.9(5)
C(15)-C(14)-C(13)	108.2(4)	C(36)-C(31)-C(30)	118.1(4)
C(15)-C(14)-C(19)	126.1(6)	C(32)-C(31)-C(30)	123.9(5)

C(33)-C(32)-C(31)	119.7(6)
C(32)-C(33)-C(34)	119.1(5)
F(2)-C(34)-C(35)	119.4(6)
F(2)-C(34)-C(33)	117.4(5)
C(35)-C(34)-C(33)	123.1(6)
C(34)-C(35)-C(36)	117.5(5)
C(35)-C(36)-C(31)	122.6(5)
N(3)-C(37)-N(2)	125.3(4)
N(3)-C(37)-C(38)	114.1(4)
N(2)-C(37)-C(38)	120.2(4)
C(43)-C(38)-C(39)	118.5(4)
C(43)-C(38)-C(37)	120.2(5)
C(39)-C(38)-C(37)	121.1(5)
C(40)-C(39)-C(38)	118.8(5)
C(41)-C(40)-C(39)	120.3(6)
F(3)-C(41)-C(40)	118.6(5)
F(3)-C(41)-C(42)	119.1(5)
C(40)-C(41)-C(42)	122.3(5)
C(41)-C(42)-C(43)	118.4(5)
C(38)-C(43)-C(42)	121.7(5)
N(4)-C(44)-N(3)	127.2(4)
N(4)-C(44)-C(45)	121.7(4)
N(3)-C(44)-C(45)	111.1(4)
C(46)-C(45)-C(50)	118.1(4)
C(46)-C(45)-C(44)	123.1(4)
C(50)-C(45)-C(44)	118.8(4)
C(45)-C(46)-C(47)	121.3(5)
C(48)-C(47)-C(46)	118.9(5)
C(47)-C(48)-C(49)	122.8(5)
C(47)-C(48)-F(4)	118.3(5)
C(49)-C(48)-F(4)	118.8(5)
C(48)-C(49)-C(50)	118.2(5)
C(49)-C(50)-C(45)	120.7(5)