Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

For

Versatile New Uranyl(VI) Dihalide Complexes Supported by Tunable Organic Amide Ligands

Shanmugaperumal Kannan, Charles L. Barnes and Paul B. Duval*

Department of Chemistry, University of Missouri-Columbia, 601 S. College Ave., Columbia, Missouri, 65211, USA. Fax: 573-882-2754; Tel: 573-882-1735; E-mail: duvalp@missouri.edu

- **Experimental Section**
- **Table S1: Summary of X-ray Crystallographic Data**
- **Table S2: Selected Bond Distances and Bond Angles for 2a**
- **Table S3: Selected Bond Distances and Bond Angles for 3c**
- **Figure S1: X-ray Crystal Structure of 3c**

Experimental Section

General Considerations. All manipulations were conducted on the benchtop under ambient conditions. All solvents (Fisher) and reagents (Aldrich) were used as received. ^{1}H NMR spectra (referenced to non-deuterated impurity in the solvent) were recorded on a Bruker AMX-250 or -300 spectrometer. Chemicals shifts are reported in ppm and all coupling constants are reported in Hz unless otherwise noted. Infrared spectra were obtained as a mull in a mixture of type NVH and type B immersion oil pressed between KBr plates on a Thermo Nicolet Nexus 670 FT-IR spectrometer. The *N,N*-dialkyl amides *i*-PrC(O)NR_2 (**1**) were prepared according to general synthetic procedures *via* acylation of the corresponding secondary amine with isobutyryl chloride. An example of the procedure followed is given below for **1a**.

Synthesis of *N,N*-diisopropylisobutyramide (1a). A solution of *N,N*-diisopropylamine (18.0 mL, 0.10 mol) was added to a stirred benzene solution containing isobutyryl chloride (10.0 g, 0.09 mol) and 20 mL of triethylamine, causing the immediate precipitation of $HNEt_3Cl$. The reaction mixture was stirred 1 hr and treated with 200 mL of 5% $HCl_{(aq)}$. The organic layer was separated, dried over magnesium sulfate, and filtered. The solid **1a** (17.5 g, 93%) obtained upon evaporation of this filtrate was used without further purification.

Synthesis of $UO_2Cl_2L^{1a}_2$ (2a). UO_3 (1.00 g, 3.50 mmol) was dissolved in 10 mL of HCl and evaporated to dryness. The yellow-orange solid was re-dissolved in 10 mL of methanol, and to this was added dropwise a solution of **1a** (1.30 g, 8.20 mmol) in 10 mL of methanol. The yellow solution was stirred 1 hr, after which the volume was reduced to 5-6 mL and diethyl ether was added. The resulting yellow precipitate was filtered, washed with diethyl ether and dried. The solid **2a** (2.24 g, 92%) was recrystallized from CH_2Cl_2/heptane. ν_{max}/cm^{-1} 1555 (CO) and 921 (UO); δ_H(250 MHz; CH_3OD, Me_4Si) 1.08 (d, 12H, $^{3}J_{HH}$ = 7 Hz, $CH(CH_3)_2$), 1.24 (d, 12H, $^{3}J_{HH}$

Supplementary Material (ESI) for Chemical Communications

= 7 Hz, NCH(C*H*$_3$)$_2$), 1.34 (d, 12H, $^3J_{HH}$ = 7 Hz, NCH(C*H*$_3$)$_2$), 2.86 (sept, 2H, $^3J_{HH}$ = 7 Hz, NC*H*(CH$_3$)$_2$), 3.65 (br m, 2H, C*H*(CH$_3$)$_2$) and 4.14 (sept, 2H, $^3J_{HH}$ = 7 Hz, NC*H*(CH$_3$)$_2$).

Synthesis of $UO_2Cl_2L^{1b}_2$ (2b). The procedure followed was analogous to that for **2a** above, using (1.02 g, 3.57 mmol) of UO_3 and 1.50 g (8.00 mmol) of **1b** to give **2b** (2.30 g, 87%) ν_{max}/cm^{-1} 1543 (CO) and 924 (UO); δ_H(250 MHz; CH_3OD, Me_4Si) 0.84 (d, 12H, $^3J_{HH}$ = 7 Hz, CH$_2$CH(C*H*$_3$)$_2$), 0.95 (d, 12H, $^3J_{HH}$ = 7 Hz, CH$_2$CH(C*H*$_3$)$_2$), 1.11 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.98 (sept, 2H, $^3J_{HH}$ = 7 Hz, CH$_2$C*H*(CH$_3$)$_2$), 2.00 (sept, 2H, $^3J_{HH}$ = 7 Hz, CH$_2$C*H*(CH$_3$)$_2$), 2.99 (sept, 2H, $^3J_{HH}$ = 7 Hz, C*H*(CH$_3$)$_2$), 3.21 (d, 4H, $^3J_{HH}$ = 7 Hz, C*H*$_2$CH(CH$_3$)$_2$) and 3.24 (d, 4H, $^3J_{HH}$ = 7 Hz, C*H*$_2$CH(CH$_3$)$_2$).

Synthesis of $UO_2Cl_2L^{1c}_2$ (2c). The procedure followed was analogous to that for **2a** above, using (1.01 g, 3.53 mmol) of UO_3 and 1.50 g (8.00 mmol) of **1c** to give **2c** (2.35 g, 90%) ν_{max}/ cm^{-1} 1545 (CO) and 933 (UO); δ_H(250 MHz; CH_3OD, Me_4Si) 0.86 (t, 6H, $^3J_{HH}$ = 7 Hz, NCH(CH$_3$)CH$_2$C*H*$_3$), 0.88 (t, 6H, $^3J_{HH}$ = 7 Hz, NCH(CH$_3$)CH$_2$C*H*$_3$), 0.95 (d, 6H, $^3J_{HH}$ = 7 Hz, NCH(C*H*$_3$)CH$_2$CH$_3$), 0.97 (d, 6H, $^3J_{HH}$ = 7 Hz, NCH(C*H*$_3$)CH$_2$CH$_3$), 1.08 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.26 (m, 4H, NCH(CH$_3$)C*H*$_2$CH$_3$), 1.31 (m, 4H, NCH(CH$_3$)C*H*$_2$CH$_3$), 2.92 (sept, 2H, $^3J_{HH}$ = 7 Hz, C*H*(CH$_3$)$_2$), 3.20 (br m, 2H, NC*H*(CH$_3$)CH$_2$CH$_3$) and 3.88 (br m, 2H, NC*H*(CH$_3$)CH$_2$CH$_3$).

Synthesis of $UO_2Br_2L^{1a}_2$ (3a). The procedure followed was analogous to that for **2a** above, using (1.00 g, 3.50 mmol) of UO_3 and 1.30 g (8.20 mmol) of **1a** to give **3a** (2.51 g, 93%) ν_{max}/ cm^{-1} 1545 (CO) and 933 (UO); δ_H(250 MHz; CH_3OD, Me_4Si) 1.08 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.25 (d, 12H, $^3J_{HH}$ = 7 Hz, NCH(C*H*$_3$)$_2$), 1.33 (d, 12H, $^3J_{HH}$ = 7 Hz, NCH(C*H*$_3$)$_2$), 2.87 (sept, 2H, $^3J_{HH}$ = 7 Hz, NC*H*(CH$_3$)$_2$), 3.67 (br m, 2H, $^3J_{HH}$ = 7 Hz, C*H*(CH$_3$)$_2$) and 4.14 (sept, 2H, $^3J_{HH}$ = 7 Hz, NC*H*(CH$_3$)$_2$).

Synthesis of $UO_2Br_2L^{1b}_2$ (3b). The procedure followed was analogous to that for **2a** above, using (1.00 g, 3.50 mmol) of UO_3 and 1.50 g (8.00 mmol) of **1b** to give **3b** (2.76 g, 95%) ν_{max}/cm^{-1} 1562 (CO) and 925 (UO); δ_H(250 MHz; CH_3OD, Me_4Si) 0.85 (d, 12H, $^3J_{HH}$ = 7 Hz, CH$_2$CH(C*H*$_3$)$_2$), 0.96 (d, 12H, $^3J_{HH}$ = 7 Hz, CH$_2$CH(C*H*$_3$)$_2$), 1.11 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.98 (sept, 2H, $^3J_{HH}$ = 7 Hz, CH$_2$C*H*(CH$_3$)$_2$), 2.00 (sept, 2H, $^3J_{HH}$ = 7 Hz, CH$_2$C*H*(CH$_3$)$_2$), 2.99 (sept, 2H, $^3J_{HH}$ = 7 Hz, C*H*(CH$_3$)$_2$), 3.22 (d, 4H, $^3J_{HH}$ = 7 Hz, C*H*$_2$CH(CH$_3$)$_2$) and 3.23 (d, 4H, $^3J_{HH}$ = 7 Hz, C*H*$_2$CH(CH$_3$)$_2$).

Synthesis of $UO_2Br_2L^{1c}_2$ (3c). The procedure followed was analogous to that for **2a** above, using (1.01 g, 3.53 mmol) of UO_3 and 1.50 g (8.00 mmol) of **1c** to give **3c** (2.67 g, 91%) ν_{max}/ cm^{-1} 1544 (CO) and 925 (UO); δ_H(250 MHz; CH_3OD, Me_4Si) 0.86 (t, 6H, $^3J_{HH}$ = 7 Hz, NCH(CH$_3$)CH$_2$C*H*$_3$), 0.88 (t, 6H, $^3J_{HH}$ = 7 Hz, NCH(CH$_3$)CH$_2$C*H*$_3$), 0.95 (d, 6H, $^3J_{HH}$ = 7 Hz, NCH(C*H*$_3$)CH$_2$CH$_3$), 0.98 (d, 6H, $^3J_{HH}$ = 7 Hz, NCH(C*H*$_3$)CH$_2$CH$_3$), 1.08 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.25 (m, 4H, NCH(CH$_3$)C*H*$_2$CH$_3$), 1.30 (m, 4H, NCH(CH$_3$)C*H*$_2$CH$_3$), 2.91 (sept, 2H, $^3J_{HH}$ = 7 Hz, C*H*(CH$_3$)$_2$), 3.05 (br m, 2H, NC*H*(CH$_3$)CH$_2$CH$_3$) and 3.88 (br m, 2H, NC*H*(CH$_3$)CH$_2$CH$_3$).

Supplementary Material (ESI) for Chemical Communications

Table S1. Summary of X-ray Crystallographic Data.

	$UO_2Cl_2L_2$ (**2a**)	$UO_2Br_2L_2$ (**3c**)
Empirical formula	$C_{20}H_{42}Cl_2N_2O_4U$	$C_{24}H_{50}Br_2N_2O_4U$
Formula Weight	683.49	828.51
Space group	$P2_1/c$	$P2_1/c$
a, Å	8.5267(4)	16.8340(11)
b, Å	11.3761(5)	14.0098(9)
c, Å	13.8153(6)	14.4084(9)
β, °	96.7450(10)	106.0300(10)
V, $Å^3$	1330.82(10)	3266.0(4)
Z	2	4
ρ_{calc}, g cm^{-3}	1.706	1.685
T, K	173(2)	173(2)
μ, mm^{-1}	6.324	7.444
θ range, °	2.33 to 27.11	1.92 to 27.14
total reflections	9261	22823
unique reflections	2905	7182
parameters	139	313
R1	0.0247	0.0396
wR2	0.0494	0.0662
max, min peaks, e $Å^{-3}$	0.305, -1.438	1.024, -0.968
GOF	1.128	1.154

Table S2. Bond lengths (Å) and angles (°) for **2a**.

U(1)-O(2)#1	1.770(2)
U(1)-O(2)	1.770(2)
U(1)-O(1)#1	2.3151(18)
U(1)-O(1)	2.3151(18)
U(1)-Cl(1)	2.6468(8)
U(1)-Cl(1)#1	2.6468(8)
O(1)-C(1)	1.270(3)
N(1)-C(1)	1.329(3)
N(1)-C(5)	1.489(3)
N(1)-C(8)	1.492(3)
C(1)-C(2)	1.508(4)
C(2)-C(4)	1.525(4)
C(2)-C(3)	1.539(5)

Supplementary Material (ESI) for Chemical Communications

C(5)-C(7)	1.518(4)
C(5)-C(6)	1.530(4)
C(8)-C(10)	1.526(4)
C(8)-C(9)	1.533(4)
O(2)#1-U(1)-O(2)	180.00(12)
O(2)#1-U(1)-O(1)#1	91.43(8)
O(2)-U(1)-O(1)#1	88.57(8)
O(2)#1-U(1)-O(1)	88.57(8)
O(2)-U(1)-O(1)	91.43(8)
O(1)#1-U(1)-O(1)	180.00(10)
O(2)#1-U(1)-Cl(1)	89.06(8)
O(2)-U(1)-Cl(1)	90.94(8)
O(1)#1-U(1)-Cl(1)	90.60(5)
O(1)-U(1)-Cl(1)	89.40(5)
O(2)#1-U(1)-Cl(1)#1	90.93(8)
O(2)-U(1)-Cl(1)#1	89.07(8)
O(1)#1-U(1)-Cl(1)#1	89.40(5)
O(1)-U(1)-Cl(1)#1	90.60(5)
Cl(1)-U(1)-Cl(1)#1	180.00(3)
C(1)-O(1)-U(1)	160.83(18)
C(1)-N(1)-C(5)	123.5(2)
C(1)-N(1)-C(8)	121.1(2)
C(5)-N(1)-C(8)	115.4(2)
O(1)-C(1)-N(1)	118.7(2)
O(1)-C(1)-C(2)	118.5(2)
N(1)-C(1)-C(2)	122.7(2)
C(1)-C(2)-C(4)	111.0(2)
C(1)-C(2)-C(3)	108.9(3)
C(4)-C(2)-C(3)	111.1(2)
N(1)-C(5)-C(7)	110.8(2)
N(1)-C(5)-C(6)	111.0(2)
C(7)-C(5)-C(6)	112.5(3)
N(1)-C(8)-C(10)	112.9(2)
N(1)-C(8)-C(9)	112.5(2)
C(10)-C(8)-C(9)	112.9(3)

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

Supplementary Material (ESI) for Chemical Communications

Table S3. Bond lengths (Å) and angles (°) for **3c**.

U(1A)-O(2A)#1	1.741(5)
U(1A)-O(2A)	1.741(5)
U(1A)-O(1A)	2.281(4)
U(1A)-O(1A)#1	2.281(4)
U(1A)-Br(1A)	2.8153(7)
U(1A)-Br(1A)#1	2.8153(7)
O(1A)-C(1A)	1.279(7)
N(1A)-C(1A)	1.320(8)
N(1A)-C(5A)	1.496(8)
N(1A)-C(9A)	1.510(9)
C(1A)-C(2A)	1.489(8)
C(2A)-C(3A)	1.507(10)
C(2A)-C(4A)	1.526(9)
C(5A)-C(6A)	1.525(10)
C(5A)-C(7A)	1.532(11)
C(7A)-C(8A)	1.515(12)
C(9A)-C(11A)	1.489(16)
C(9A)-C(10A)	1.529(15)
C(11A)-C(12A)	1.530(19)
U(1B)-O(2B)#2	1.757(4)
U(1B)-O(2B)	1.757(4)
U(1B)-O(1B)	2.303(4)
U(1B)-O(1B)#2	2.303(4)
U(1B)-Br(1B)	2.8127(7)
U(1B)-Br(1B)#2	2.8127(7)
O(1B)-C(1B)	1.274(7)
N(1B)-C(1B)	1.320(8)
N(1B)-C(9B)	1.491(8)
N(1B)-C(5B)	1.512(8)
C(1B)-C(2B)	1.516(9)
C(2B)-C(3B)	1.493(11)
C(2B)-C(4B)	1.540(12)
C(5B)-C(6B)	1.511(11)
C(5B)-C(7B)	1.519(11)
C(7B)-C(8B)	1.497(13)
C(9B)-C(11B)	1.511(12)
C(9B)-C(10B)	1.549(11)

C(11B)-C(12B)	1.508(13)

O(2A)#1-U(1A)-O(2A)	180.0(3)
O(2A)#1-U(1A)-O(1A)	90.8(2)
O(2A)-U(1A)-O(1A)	89.2(2)
O(2A)#1-U(1A)-O(1A)#1	89.2(2)
O(2A)-U(1A)-O(1A)#1	90.8(2)
O(1A)-U(1A)-O(1A)#1	180.0(2)
O(2A)#1-U(1A)-Br(1A)	90.26(17)
O(2A)-U(1A)-Br(1A)	89.74(17)
O(1A)-U(1A)-Br(1A)	91.59(11)
O(1A)#1-U(1A)-Br(1A)	88.41(11)
O(2A)#1-U(1A)-Br(1A)#1	89.74(17)
O(2A)-U(1A)-Br(1A)#1	90.26(17)
O(1A)-U(1A)-Br(1A)#1	88.41(11)
O(1A)#1-U(1A)-Br(1A)#1	91.59(11)
Br(1A)-U(1A)-Br(1A)#1	180.0
C(1A)-O(1A)-U(1A)	171.9(5)
C(1A)-N(1A)-C(5A)	124.7(5)
C(1A)-N(1A)-C(9A)	119.8(5)
C(5A)-N(1A)-C(9A)	115.4(5)
O(1A)-C(1A)-N(1A)	120.0(5)
O(1A)-C(1A)-C(2A)	116.7(6)
N(1A)-C(1A)-C(2A)	123.3(5)
C(1A)-C(2A)-C(3A)	109.4(6)
C(1A)-C(2A)-C(4A)	110.3(6)
C(3A)-C(2A)-C(4A)	111.1(6)
N(1A)-C(5A)-C(6A)	114.6(6)
N(1A)-C(5A)-C(7A)	111.9(6)
C(6A)-C(5A)-C(7A)	114.3(6)
C(8A)-C(7A)-C(5A)	116.4(7)
C(11A)-C(9A)-N(1A)	110.5(8)
C(11A)-C(9A)-C(10A)	114.2(9)
N(1A)-C(9A)-C(10A)	110.7(8)
C(9A)-C(11A)-C(12A)	113.5(10)
O(2B)#2-U(1B)-O(2B)	180.000(1)
O(2B)#2-U(1B)-O(1B)	90.55(19)
O(2B)-U(1B)-O(1B)	89.45(19)
O(2B)#2-U(1B)-O(1B)#2	89.45(19)
O(2B)-U(1B)-O(1B)#2	90.55(19)
O(1B)-U(1B)-O(1B)#2	180.000(1)

Supplementary Material (ESI) for Chemical Communications

O(2B)#2-U(1B)-Br(1B)	89.40(15)
O(2B)-U(1B)-Br(1B)	90.60(15)
O(1B)-U(1B)-Br(1B)	89.18(11)
O(1B)#2-U(1B)-Br(1B)	90.82(11)
O(2B)#2-U(1B)-Br(1B)#2	90.60(15)
O(2B)-U(1B)-Br(1B)#2	89.40(15)
O(1B)-U(1B)-Br(1B)#2	90.82(11)
O(1B)#2-U(1B)-Br(1B)#2	89.18(11)
Br(1B)-U(1B)-Br(1B)#2	180.00(2)
C(1B)-O(1B)-U(1B)	168.2(4)
C(1B)-N(1B)-C(9B)	125.3(6)
C(1B)-N(1B)-C(5B)	120.3(5)
C(9B)-N(1B)-C(5B)	114.4(6)
O(1B)-C(1B)-N(1B)	120.3(6)
O(1B)-C(1B)-C(2B)	117.0(6)
N(1B)-C(1B)-C(2B)	122.6(6)
C(3B)-C(2B)-C(1B)	111.5(7)
C(3B)-C(2B)-C(4B)	110.7(8)
C(1B)-C(2B)-C(4B)	109.3(7)
C(6B)-C(5B)-N(1B)	111.3(7)
C(6B)-C(5B)-C(7B)	116.2(7)
N(1B)-C(5B)-C(7B)	109.0(6)
C(8B)-C(7B)-C(5B)	115.3(8)
N(1B)-C(9B)-C(11B)	112.9(7)
N(1B)-C(9B)-C(10B)	112.9(7)
C(11B)-C(9B)-C(10B)	115.8(7)
C(12B)-C(11B)-C(9B)	109.9(9)

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

Figure S1. Thermal ellipsoid drawing of **3c**, showing thermal ellipsoids at 50% probability. X-ray data (Table S1) and selected bond angles and bond distances (Table S3) are provided.

Supplementary Material (ESI) for Chemical Communications