

## Supporting Information

### Uranyl Sequestration: Synthesis and Structural Characterization of Uranyl Complexes with a Tetradentate Methylterephthalamide Ligand

Chengbao Ni,<sup>a</sup> David K. Shuh,<sup>a</sup> Kenneth N. Raymond<sup>a,b\*</sup>

<sup>a</sup>Chemical Science Division, Lawrence Berkeley National Laboratory and <sup>b</sup>Department of Chemistry,  
University of California, Berkeley, CA, 94720, USA.

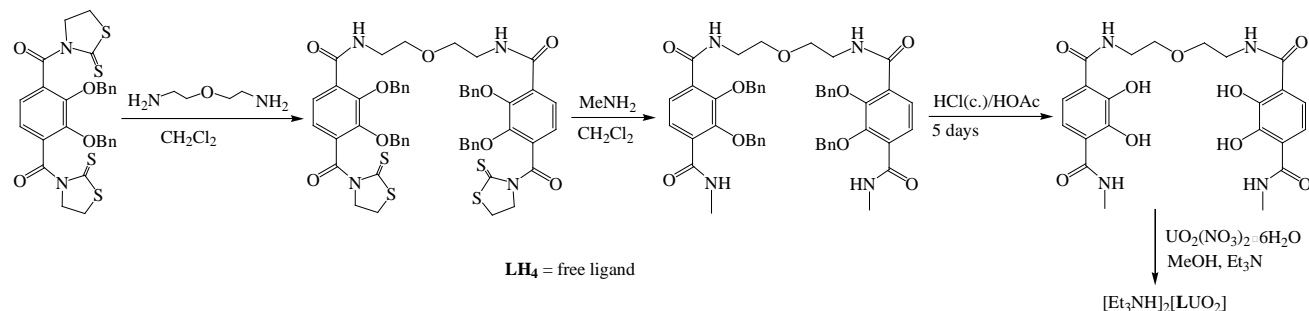
raymond@socrates.berkeley.edu

#### The supporting information contains:

1. Experimental Details
2. Crystallographic Studies

#### 1. Experimental Details

**General Information.** Unless otherwise noted, all chemicals and solvents were purchased from commercial sources and used as received. 2,3-dibenzoyloxy-1,4-dicarbonyl(2-mercaptothiazolide) (TAM-thiaz) and 3-oxapentane-1,5-diamine were synthesized according to published procedures.<sup>1, 2</sup> NMR spectra were collected using a Bruker AV-300 spectrometer in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub>. <sup>1</sup>H (or <sup>13</sup>C) NMR resonances are reported in ppm relative to the solvent resonances, taken as 7.26 (77.23) for CDCl<sub>3</sub> and 2.50 (39.51) for DMSO. Mass spectrometry and elemental analyses were performed at the QB3/Chemistry Mass Spectrometry Facility and the Microanalytical Facility, College of Chemistry, University of California, Berkeley. Reactions were monitored by TLC on 60 mesh F<sub>254</sub> silica gel from EMD Chemicals, Inc. and silica gel chromatography was performed on EcoChrom Silica (32-63 D 60 Å). Organic solutions were dried using anhydrous sodium sulfate and solvents were removed by rotary evaporation or under high vacuum on a Schlenk line. Yields indicate the amount of isolated compound and reactions are un-optimized.



**5LiO-(TAM(Bn)<sub>2</sub>-Thiaz):** 3-oxapentane-1,5-diamine (0.42 g, 4.00 mmol) in *ca.* 500 mL of CHCl<sub>3</sub> was added via a capillary into a solution of TAM-thiaz (30.00 g, 51.70 mmol) in *ca.* 200 mL of

CH<sub>2</sub>Cl<sub>2</sub> during the course of 24 hours. The solution was concentrated and loaded onto a silica column. The product was isolated as a bright yellow solid. Yield 3.67 g (89.4%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 2.94 (t, *J* = 6.6 Hz, CH<sub>2</sub>, 4H), 3.34-3.39 (m, CH<sub>2</sub>, 8H), 4.38 (t, *J* = 6.0 Hz, CH<sub>2</sub>, 4H), 5.08 (s, br., CH<sub>2</sub>, 8H), 7.22 (d, *J* = 6.0 Hz, 2H), 7.32-7.37 (m, 20H), 7.89 (d, *J* = 6.0 Hz, 2H), 7.99 (s, br., NH, 2H). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): δ 28.8, 39.6, 55.7, 69.2, 76.2, 76.9, 124.6, 126.9, 128.1, 128.5, 128.7, 128.8, 128.9, 130.0, 130.1, 133.6, 135.8, 137.0, 149.5, 150.1, 164.3, 166.9, 201.5. MS (ESI+): *m/z* 1049.23 (M+Na<sup>+</sup>).

**5LiO-(MeTAM(Bn)<sub>2</sub>):** To a yellow solution of 5LiO-(TAM(Bn)<sub>2</sub>-Thiaz) (3.00 g, 2.92 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was added MeNH<sub>2</sub> (2 M in THF, 1.50 mL, 3.00 mmol). The yellow solution became colorless in *ca.* 3 hours. The mixture was concentrated and loaded onto a silica column and the product was isolated as a white solid. Yield 2.12 g (85.3%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 2.82 (d, *J* = 6.0 Hz, CH<sub>3</sub>, 6H), 3.39-3.47 (m, CH<sub>2</sub>, 8H), 5.06 (s, CH<sub>2</sub>, 4H), 5.11 (s, CH<sub>2</sub>, 4H), 7.31-7.40 (m, CH, 20H), 7.71 (q, *J* = 4.2 Hz, NHCH<sub>3</sub>, 2H), 7.85 (s, br., CH, 4H), 7.93 (t, *J* = 4.2 Hz, NHCH<sub>2</sub>, 2H). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): δ 26.5, 39.6, 69.2, 77.1, 77.5, 126.5, 126.6, 128.6, 128.9, 129.0, 130.7, 130.9, 135.6, 135.9, 150.4, 150.5, 164.5, 164.9. MS (ESI+): *m/z* 851.36 (M+H<sup>+</sup>).

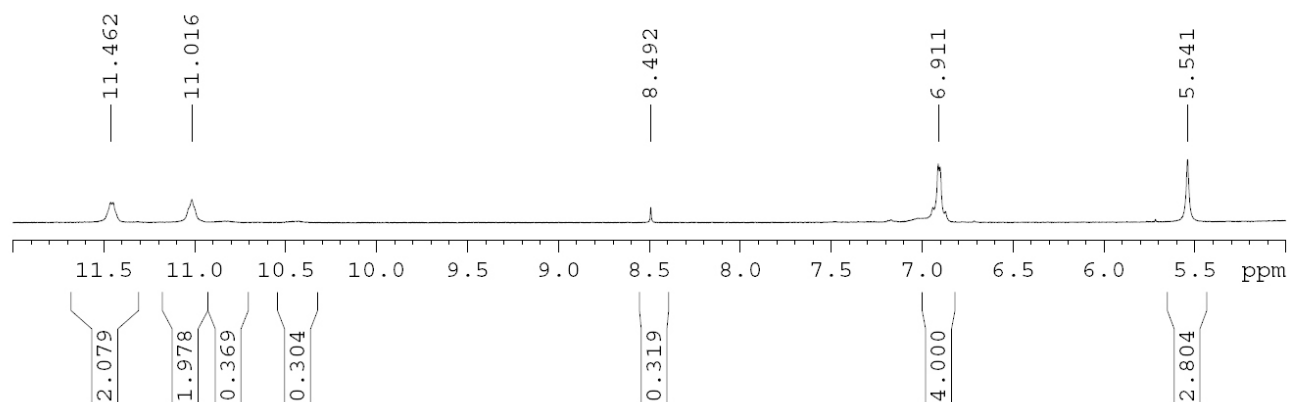
**5LiO-(MeTAM(OH)<sub>2</sub>) (LH<sub>4</sub>):** 5LiO-(MeTAM(Bn)<sub>2</sub>) (1.87 g, 2.19 mmol) was dissolved in 15 mL of acid solution (HCl(12 M) : HOAc = 1:1) and stirring was continued for 5 days, affording a pale yellow (almost colorless) solution. The solvents were removed under high vacuum to yield a beige solid. Yield 0.96 g (89.2%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ 2.82 (d, *J* = 4.5 Hz, CH<sub>3</sub>, 6H), 3.38-3.60 (m, CH<sub>2</sub>, 8H), 7.27 (d, *J* = 8.7 Hz, CH, 2H), 7.32 (d, *J* = 8.7 Hz, CH, 2H), 8.87-8.91 (m, NH, 4H), 12.56 (s, br., OH, 2H), 12.91 (s, br., OH, 2H). <sup>13</sup>C NMR (75.5 MHz, DMSO-*d*<sub>6</sub>): δ 26.1, 68.3, 115.6, 115.9, 117.0, 117.3, 149.9, 150.3, 168.6, 169.2. MS (ESI+): *m/z* 491.18 (M+H<sup>+</sup>). Elemental analysis calculated (found) for C<sub>22</sub>H<sub>26</sub>N<sub>4</sub>O<sub>8</sub>: C, 53.87(53.79); H, 5.34(5.22); N, 11.42(11.26).

**[Et<sub>3</sub>NH]<sub>2</sub>[LUO<sub>2</sub>]:** To a mixture of LH<sub>4</sub> (45.0 mg, 0.092 mmol) and UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (44.7 mg, 0.089 mmol) in MeOH (*ca.* 3 mL) was added 5 drops of Et<sub>3</sub>N under N<sub>2</sub>. The reaction mixture was heated to 55 °C for *ca.* 5 hours, yielding a homogenous deep red/brown solution. The solution was cooled down to room temperature and Et<sub>2</sub>O (*ca.* 10 mL) was added to the solution with vigorous stirring, causing a brown precipitate, which was collected by filtration. Yield 88.6 mg (87.2%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ 1.15 (t, *J* = 7.2 Hz, CH<sub>3</sub>, 18H), 3.03-3.17 (m, CH<sub>3</sub> + CH<sub>2</sub>, 16H), 3.69-3.73 (m, CH<sub>2</sub>, 4H), 7.00 (d, *J* = 8.7 Hz, CH, 2H), 7.05 (d, *J* = 8.7 Hz, CH, 2H), 8.92 (s, br., Et<sub>3</sub>NH, 2H), 10.38 (t, *J* = 4.5 Hz, CH<sub>2</sub>NH, 2H), 10.76 (q, *J* = 4.2 Hz, CH<sub>3</sub>NH, 2H). <sup>13</sup>C NMR (75.5 MHz, DMSO-*d*<sub>6</sub>): δ 8.7, 25.6, 45.7, 70.8, 114.3, 114.5, 118.2, 118.3, 167.1, 167.4, 167.5, 168.3. MS (ESI-): *m/z* 378.09 (LUO<sub>2</sub><sup>2-</sup>) and 757.19 (LHUO<sub>2</sub><sup>-</sup>). Elemental analysis calculated (found) for

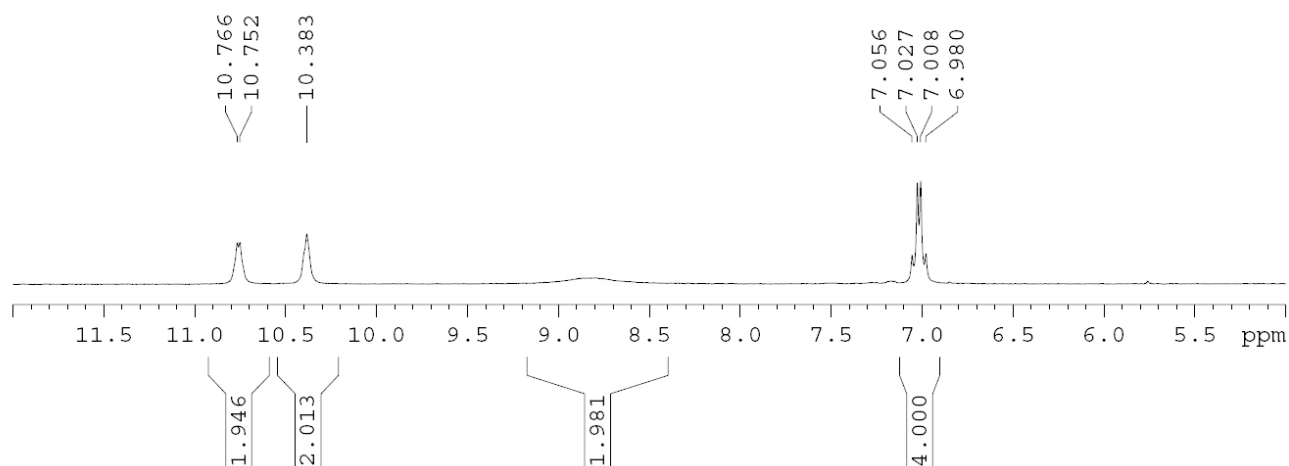
$C_{34}H_{54}N_6O_{11}U \cdot 2H_2O$ : C, 40.96(41.03); H, 5.86(6.08); N, 8.43(8.67). MS (ESI-) of  $[Me_4N]K_2[LUO_2(OMe)]$  crystals:  $m/z$  378.09 ( $LUO_2^{2-}$ ) and 757.19 ( $LHUO_2^-$ ). MS (ESI-) of  $[Me_4N]_8[LUO_2]_4$ :  $m/z$  378.09 ( $LUO_2^{2-}$ ), 757.19 ( $LHUO_2^-$ ), and 830.28 ( $[L(UO_2)(Me_4N)]$ ).

**$K_3[LUO_2(OMe)]$ :** To the  $[Et_3NH]_2[LUO_2] \cdot 2H_2O$  solution in  $DMSO-d_6$  was added 5 drops of 0.505 N KOH in MeOH. The brown solution became bright red immediately.  $^1H$  NMR shows the formation of  $Et_3N$  and other new species (Fig. S1). According to the chemical shifts, the dominant species is the uranyl methoxide complex  $[LUO_2(OMe)]^{3-}$ .  $^1H$  NMR (300 MHz,  $D_6$ -DMSO):  $\delta$  2.98 (d,  $J = 4.2$  Hz,  $CH_3$ , 6H), 3.68-3.72 (m,  $CH_2$ , 8H), 5.54 (s,  $CH_3$ , 3H), 6.89-6.93 (m,  $CH$ , 4H), 11.02 (s, br.,  $CH_2NH$ , 2H), 11.46 (q,  $J = 4.2$  Hz,  $CH_3NH$ , 2H).

KOH in MeOH added into  $[Et_3NH]_2[LUO_2]$  in DMSO



$[Et_3NH]_2[LUO_2]$  in DMSO



**Fig. S1.**  $^1H$  NMR spectra (5 ~ 12 ppm) of  $K_3[LUO_2(OMe)]$  (up) and  $[Et_3NH]_2[LUO_2]$  (down) in  $DMSO-d_6$ .

## 2. Crystallographic Studies

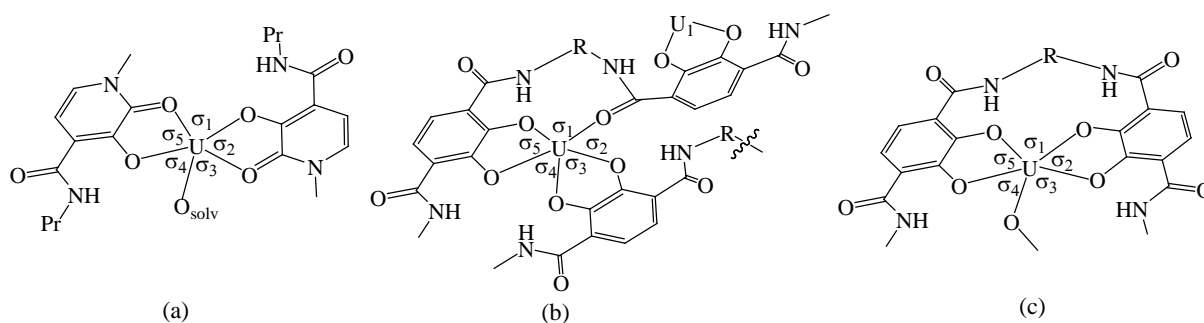
**X-ray Crystallographic Studies.** To a solution of  $[Et_3NH]_2[LUO_2] \cdot 2H_2O$  in MeOH/DMF (*ca.*

50:1) was added two equivalents of Me<sub>4</sub>NOH, giving a reddish brown solution. Diffusing Et<sub>2</sub>O into this solution at room temperature readily afforded crystals of [Me<sub>4</sub>N]<sub>8</sub>[[LUO<sub>2</sub>]<sub>4</sub>. Crystals of [Me<sub>4</sub>N]K<sub>2</sub>[LUO<sub>2</sub>(OMe)] were obtained by diffusing Et<sub>2</sub>O into a MeOH solution of [Et<sub>3</sub>N]<sub>2</sub>[[LUO<sub>2</sub>]<sub>2</sub>·2H<sub>2</sub>O, KOH, and Me<sub>4</sub>NOH at room temperature.

Suitable crystals were selected and mounted on a capstan loop with Paratone oil and cooled under a controlled temperature stream of liquid nitrogen. X-ray data were collected on a Bruker SMART Apex II diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at the UC Berkeley X-ray crystallographic facility. Absorption corrections were applied using SADABS.<sup>3</sup> The structures were solved using direct methods and refined by the full-matrix least-squares procedure in SHELXL.<sup>4,5</sup> All non-hydrogen atoms were refined anisotropically. Due to the quality of the X-ray diffraction data sets, all hydrogen atoms in both structures were placed at calculated positions and included in the refinement using a riding model.

**Table S1.** Crystallographic parameters for [Me<sub>4</sub>N]<sub>8</sub>[LUO<sub>2</sub>]<sub>4</sub> and [Me<sub>4</sub>N]K<sub>2</sub>[LUO<sub>2</sub>(OMe)].

	[Me <sub>4</sub> N] <sub>8</sub> [LUO <sub>2</sub> ] <sub>4</sub> ·(MeOH) <sub>10.56</sub> (H <sub>2</sub> O) <sub>2.4</sub>	[Me <sub>4</sub> N] <sub>2</sub> K <sub>4</sub> [LUO <sub>2</sub> (OMe)](MeOH) <sub>6</sub> (H <sub>2</sub> O) <sub>1.5</sub>
formula	C <sub>130.56</sub> H <sub>231.04</sub> N <sub>24</sub> O <sub>56.96</sub> U <sub>4</sub>	C <sub>60</sub> H <sub>101.5</sub> K <sub>4</sub> N <sub>10</sub> O <sub>29.5</sub> U <sub>2</sub>
fw	3993.85	2066.45
color, habit	dark red, block	dark red, rod
cryst syst	tetragonal	triclinic
space group	<i>I4<sub>1</sub>/acd</i>	<i>P-1</i>
<i>a</i> , Å	30.576(4)	9.9029(11)
<i>b</i> , Å	30.576(4)	18.940(2)
<i>c</i> , Å	45.263(6)	22.970(3)
$\alpha$ , deg	90	105.053(2)
$\beta$ , deg	90	94.799(2)
$\gamma$ , deg	90	102.429(2)
<i>V</i> , Å <sup>3</sup>	42316(8)	4018.4(8)
<i>Z</i>	8	2
<i>d</i> <sub>calcd</sub> , Mg/m <sup>3</sup>	1.261	1.734
$\theta$ range, deg	1.30~25.36	0.93~25.38
$\mu$ , mm <sup>-1</sup>	3.124	4.319
obs data, <i>I</i> >2 $\sigma$ ( <i>I</i> )	9701	14601
R1(obs data)	0.0502	0.0239
wR2(all data)	0.1785	0.0602



**Fig. S2.** Equatorial O-U-O bond angle designations for uranyl complexes: (a) (Pr-Me-3,2-HOPO)<sub>2</sub>UO<sub>2</sub>(DMF)<sub>6</sub><sup>6</sup>; (b) [Me<sub>4</sub>N]<sub>8</sub>[LUO<sub>2</sub>]<sub>4</sub>; (c) [Me<sub>4</sub>N]K<sub>2</sub>[LUO<sub>2</sub>(OMe)]. Uranyl oxo atoms are not shown for clarity.

**Table S2:** Comparison of equatorial O-U-O angles (deg) in uranyl complexes.

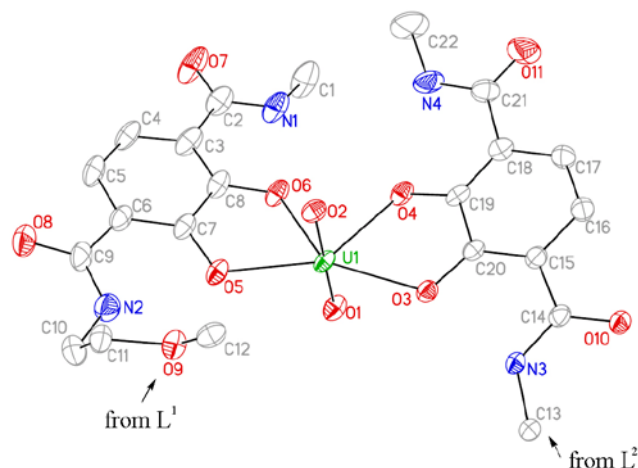
	$\sigma_1$	$\sigma_2$	$\sigma_3$	$\sigma_4$	$\sigma_5$
(Pr-Me-3,2-HOPO) <sub>2</sub> UO <sub>2</sub> (DMF) <sub>6</sub> <sup>6</sup>	76.8(2)	66.6(2)	76.1(2)	74.2(2)	66.4(2)
5Li-(Me-3,2-HOPO)UO <sub>2</sub> <sup>a, 6</sup>	90.26(14)	65.96(9)	69.87(7)	69.87(7)	65.96(7)
<i>m</i> -xyl-(Me-3,2-HOPO)UO <sub>2</sub> <sup>a, 7</sup>	92.8(1)	66.2(1)	67.4(1)	67.9(1)	66.0(1)
[Me <sub>4</sub> N] <sub>8</sub> [LUO <sub>2</sub> ] <sub>4</sub>	<b>77.1(2)</b>	<b>74.6(2)</b>	66.1(2)	<b>76.0(2)</b>	66.7(2)
[Me <sub>4</sub> N]K <sub>2</sub> [LUO <sub>2</sub> (OMe)] <sup>b</sup>	<b>75.53(8)</b>	66.44(8)	<b>74.79(9)</b>	<b>77.64(8)</b>	65.95(8)
	<b>73.91(8)</b>	65.81(8)	<b>78.02(9)</b>	<b>76.39(9)</b>	66.31(8)

*a*: the angle designations are similar to that in Fig. S2 (c), due to similar ligand orientations; *b*: two independent [LUO<sub>2</sub>(OMe)]<sup>3-</sup> units in the asymmetric unit;

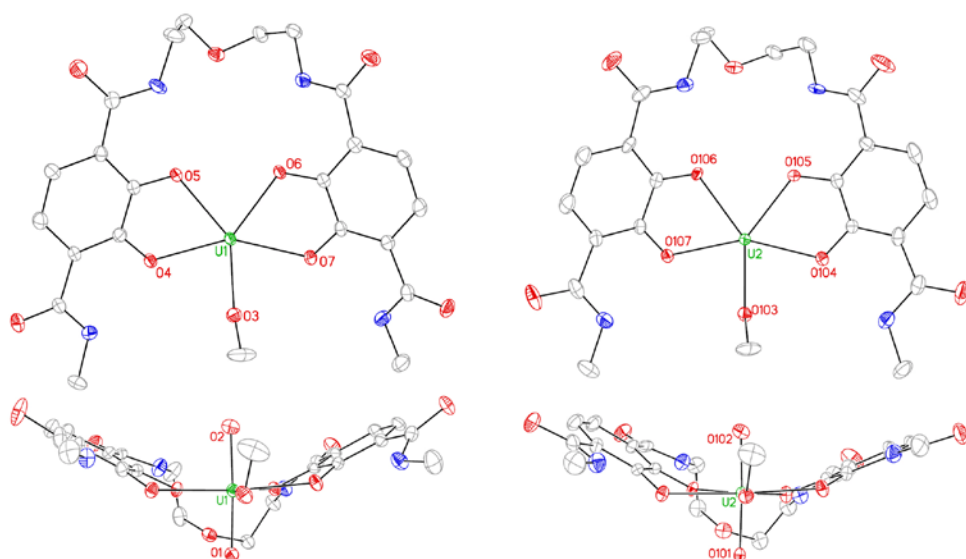
**Table S3:** U-O distances (Å) in [Me<sub>4</sub>N]<sub>8</sub>[LUO<sub>2</sub>]<sub>4</sub> and [Me<sub>4</sub>N]K<sub>2</sub>[LUO<sub>2</sub>(OMe)].

	U-O(oxo)	U-O <sub>phenolate</sub>	U-O <sub>(amide/methoxide)</sub>
[Me <sub>4</sub> N] <sub>8</sub> [LUO <sub>2</sub> ] <sub>4</sub>	1.785(5), 1.794(6)	2.342(6), 2.347(5), 2.362(6), 2.397(5)	2.365(5)
[Me <sub>4</sub> N]K <sub>2</sub> [LUO <sub>2</sub> (OMe)] <sup>a</sup>	1.788(3), 1.798(2)	2.360(2), 2.372(2), 2.377(2), 2.397(2)	2.288(3)
	1.804(2), 1.812(2)	2.352(2), 2.357(2), 2.402(2), 2.412(2)	2.218(2)

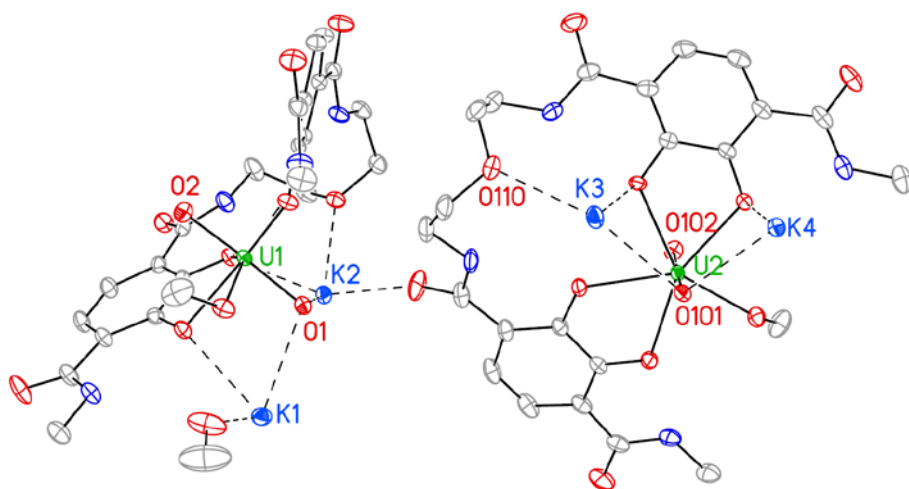
*a*: two independent [LUO<sub>2</sub>(OMe)]<sup>3-</sup> units in the asymmetric unit.



**Fig. S3.** The asymmetric unit of [LUO<sub>2</sub>]<sub>4</sub><sup>8-</sup> (30% probability) without hydrogen atoms.



**Fig. S4.** Two independent  $[\text{LUO}_2(\text{OMe})]^{3-}$  units in  $[\text{Me}_4\text{N}]\text{K}_2[\text{LUO}_2(\text{OMe})]$  (30% probability) without H and K atoms. Up: top view without oxo groups; down: side view.



**Fig. S5.** Asymmetric unit of  $\text{K}_2[\text{LUO}_2(\text{OMe})]^-$  (30% probability) without methanol and hydrogen atoms.

## References:

1. D. M. J. Doble, M. Melchior, B. O'Sullivan, C. Siering, J. D. Xu, V. C. Pierre and K. N. Raymond, *Inorg. Chem.*, 2003, **42**, 4930.
2. P. L. Anelli, F. Montanari and S. Quici, *J. Org. Chem.*, 1985, **50**, 3453.
3. SADABS, Bruker AXS: Madison, WI, 1998.
4. SHELXL, Bruker AXS: Madison WI, 1998.
5. Bruker, SADABS. Bruker AXS Inc., Madison, WI, 2007.
6. J. D. Xu and K. N. Raymond, *Inorg. Chem.*, 1999, **38**, 308.
7. G. Szigethy and K. N. Raymond, *Inorg. Chem.*, 2010, **49**, 6755.