

Supplementary information for
Competitive Coordination of Uranium(VI) and Thorium(IV) by Tetradentate
Phenanthroline Ligands: Structural and Spectroscopic Investigation of U(VI)-Th(IV)
Mixed Ion Pair Formation

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UV-vis

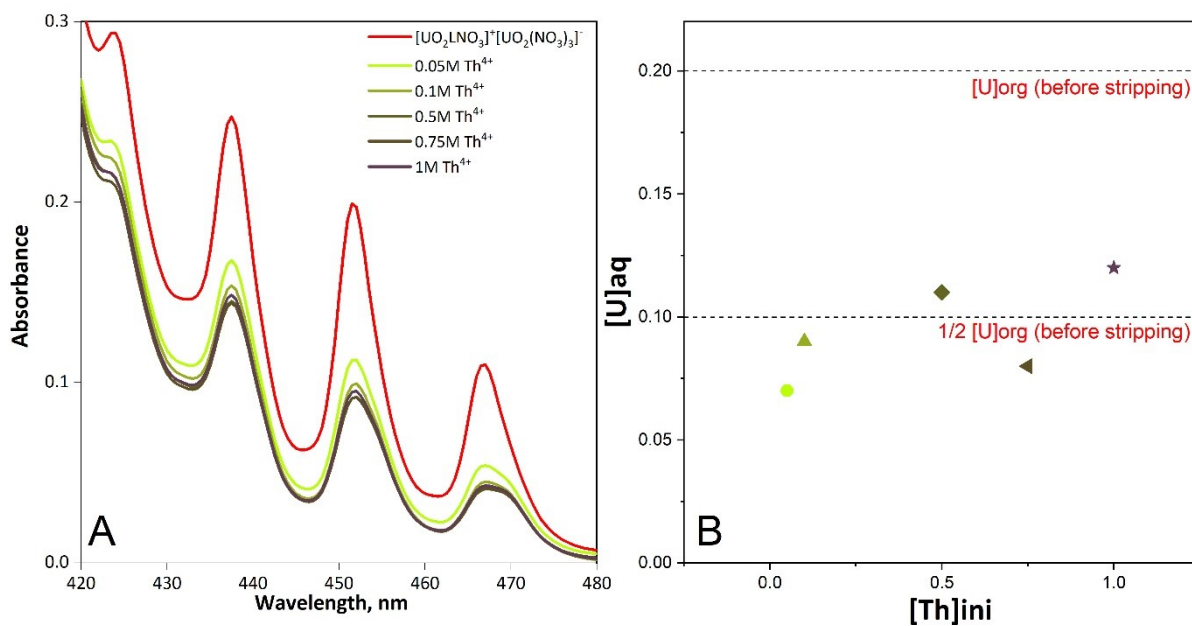


Figure S1. (A) UV-Vis absorption spectra of the organic phase of $1 \text{ mol}\cdot\text{L}^{-1}$ U(VI) in $3 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 and after stripping with 0.05 , 0.1 , 0.5 , 0.75 and $1 \text{ mol}\cdot\text{L}^{-1}$ Th(IV). (B) The ratio of the concentration of U(VI) in the aqueous phase after extraction to the initial concentration of Th(IV). Organic phase: $0.1 \text{ mol}\cdot\text{L}^{-1}$ L in F-3.

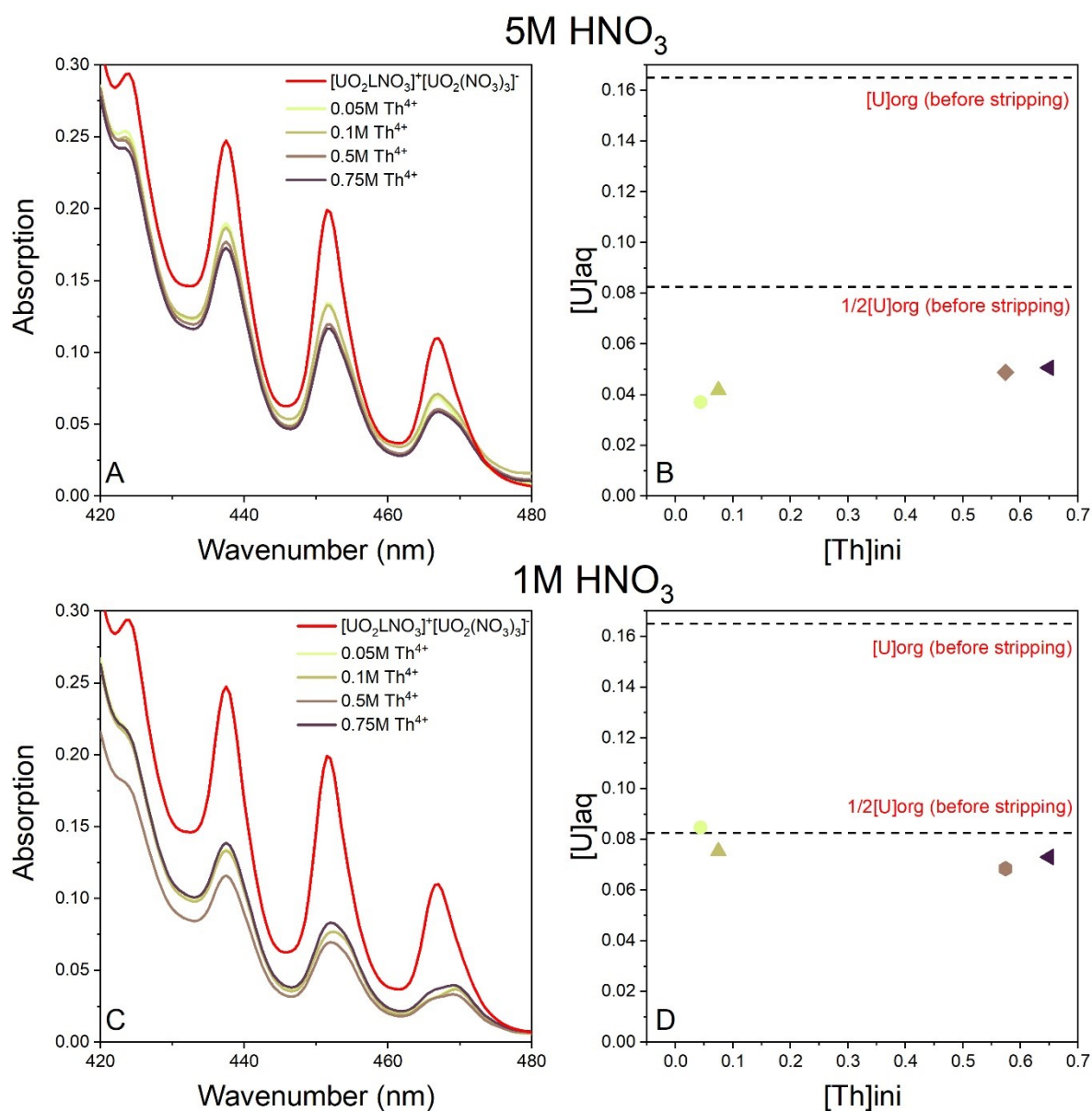


Figure S2. UV-Vis absorption spectra of the organic phase of 1 mol·L⁻¹ U(VI) in 3 mol·L⁻¹ and after stripping with 0.05, 0.1, 0.5 and 0.75 Th(IV) in 5 mol·L⁻¹ HNO₃ (A) and 1 mol·L⁻¹ HNO₃ (C). The ratio of the concentration of U(VI) in the aqueous phase after extraction to the initial concentration of Th(IV) in 5 mol·L⁻¹ HNO₃ (B) and 1 mol·L⁻¹ HNO₃ (D). Organic phase: 0.1 mol·L⁻¹ L in F-3.

XRD data

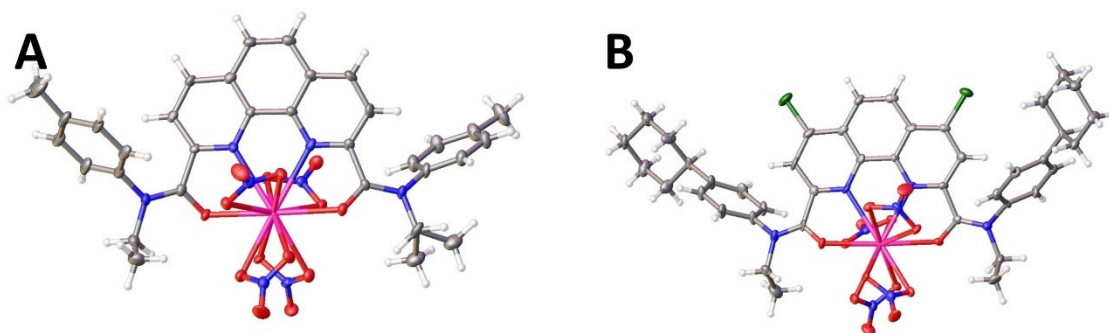


Figure S3 - General view of $\text{ThL}(\text{NO}_3)_4$ (where **L** – different phenanthroline diamide-based ligands: **L5** and **L6**) in representation of atoms by thermal ellipsoids ($p = 50\%$). Grey, blue, red, dark green and pink colors denote C, N, O, Cl and Th atoms, respectively.

Table S1 Crystallographic data for uranyl nitrate complex with **L0**.

Empirical formula	$\text{C}_{30}\text{H}_{40}\text{Cl}_2\text{N}_8\text{O}_{18}\text{U}_2$
Formula weight	1347.66
Crystal system	monoclinic
Space group	$\text{P2}_1/\text{n}$
$a/\text{\AA}$	16.0546(16)
$b/\text{\AA}$	16.1875(14)
$c/\text{\AA}$	18.9986(19)
$\alpha/^\circ$	90
$\beta/^\circ$	112.367(3)
$\gamma/^\circ$	90
Volume/ \AA^3	4566.0(8)
Z	4
$\rho_{\text{calc}}/\text{g/cm}^3$	1.960
μ/mm^{-1}	7.277
F(000)	2552.0
Crystal size/ mm^3	$0.21 \times 0.18 \times 0.02$
2θ range for data collection/ $^\circ$	3.422 to 50
Index ranges	$-15 \leq h \leq 19, -19 \leq k \leq 18, -22 \leq l \leq 22$
Reflections collected	29810
Independent reflections	8031 [$R_{\text{int}} = 0.0549, R_{\text{sigma}} = 0.0521$]
Data/restraints/parameters	8031/47/554
Goodness-of-fit on F^2	1.025
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0777, wR_2 = 0.2096$
Final R indexes [all data]	$R_1 = 0.0995, wR_2 = 0.2336$

Table S2 Crystallographic data for thorium nitrate complex with **L4**.

Empirical formula	$\text{C}_{37.5}\text{H}_{37}\text{Cl}_{3.5}\text{N}_{10.5}\text{O}_{14.5}\text{Th}$
Formula weight	1222.89
Crystal system	triclinic
Space group	P-1
$a/\text{\AA}$	16.5634(7)
$b/\text{\AA}$	17.5931(7)
$c/\text{\AA}$	20.1553(8)

$\alpha/^\circ$	65.5780(10)
$\beta/^\circ$	75.7710(10)
$\gamma/^\circ$	62.9860(10)
Volume/ \AA^3	4752.1(3)
Z	4
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.709
μ/mm^{-1}	3.409
F(000)	2404.0
Crystal size/ mm^3	$0.22 \times 0.2 \times 0.17$
2 θ range for data collection/ $^\circ$	3.424 to 50
Index ranges	$-19 \leq h \leq 19, -20 \leq k \leq 20, -23 \leq l \leq 23$
Reflections collected	32173
Independent reflections	16607 [$R_{\text{int}} = 0.0445, R_{\text{sigma}} = 0.0807$]
Data/restraints/parameters	16607/49/1124
Goodness-of-fit on F^2	0.979
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0399, wR_2 = 0.0755$
Final R indexes [all data]	$R_1 = 0.0600, wR_2 = 0.0805$

Table S3 Crystallographic data for thorium nitrate complex with **L5**.

Empirical formula	$\text{C}_{34}\text{H}_{36}\text{N}_9\text{O}_{15.5}\text{Th}$
Formula weight	1050.76
Crystal system	monoclinic
Space group	$P2_1/n$
a/ \AA	13.0013(4)
b/ \AA	10.9427(3)
c/ \AA	28.4236(9)
$\alpha/^\circ$	90
$\beta/^\circ$	101.2730(10)
$\gamma/^\circ$	90
Volume/ \AA^3	3965.8(2)
Z	4
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.760
μ/mm^{-1}	3.842
F(000)	2068.0
Crystal size/ mm^3	$0.6 \times 0.22 \times 0.18$
2 θ range for data collection/ $^\circ$	3.242 to 53.998
Index ranges	$-16 \leq h \leq 15, -13 \leq k \leq 13, -36 \leq l \leq 36$
Reflections collected	31043
Independent reflections	8645 [$R_{\text{int}} = 0.0455, R_{\text{sigma}} = 0.0480$]
Data/restraints/parameters	8645/64/545
Goodness-of-fit on F^2	1.132
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0369, wR_2 = 0.0896$
Final R indexes [all data]	$R_1 = 0.0465, wR_2 = 0.0925$

Table S4 Crystallographic data for thorium nitrate complex with **L6**.

Empirical formula	$\text{C}_{43}\text{H}_{46}\text{Cl}_3\text{N}_8\text{O}_{14}\text{Th}$
Formula weight	1237.27
Crystal system	monoclinic
Space group	$P2_1/n$
a/ \AA	12.1106(8)
b/ \AA	25.9428(18)

c/Å	16.7328(11)
$\alpha/^\circ$	90
$\beta/^\circ$	99.142(2)
$\gamma/^\circ$	90
Volume/Å ³	5190.4(6)
Z	4
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.583
μ/mm^{-1}	3.096
F(000)	2452.0
Crystal size/mm ³	0.33 × 0.16 × 0.04
2 θ range for data collection/ $^\circ$	3.75 to 49.994
Index ranges	-14 ≤ h ≤ 14, -30 ≤ k ≤ 30, -19 ≤ l ≤ 18
Reflections collected	30699
Independent reflections	9142 [R _{int} = 0.0758, R _{sigma} = 0.0820]
Data/restraints/parameters	9142/18/624
Goodness-of-fit on F ²	1.028
Final R indexes [I >= 2 σ (I)]	R ₁ = 0.0426, wR ₂ = 0.0766
Final R indexes [all data]	R ₁ = 0.0731, wR ₂ = 0.0836

Table S5 Crystallographic data for mixed uranium-thorium complex with **L0**.

Empirical formula	C ₇₄ H ₉₆ Cl ₄ N ₁₆ O ₃₂ ThU ₂
Formula weight	2571.56
Crystal system	monoclinic
Space group	C2/c
a/Å	31.6621(12)
b/Å	19.8030(8)
c/Å	32.2455(11)
$\alpha/^\circ$	90
$\beta/^\circ$	93.9240(10)
$\gamma/^\circ$	90
Volume/Å ³	20170.7(13)
Z	8
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.694
μ/mm^{-1}	4.862
F(000)	10000.0
Crystal size/mm ³	0.2 × 0.16 × 0.05
2 θ range for data collection/ $^\circ$	3.444 to 52.866
Index ranges	-39 ≤ h ≤ 37, -24 ≤ k ≤ 24, -39 ≤ l ≤ 40
Reflections collected	83531
Independent reflections	20699 [R _{int} = 0.0626, R _{sigma} = 0.0587]
Data/restraints/parameters	20699/45/1164
Goodness-of-fit on F ²	1.039
Final R indexes [I >= 2 σ (I)]	R ₁ = 0.0486, wR ₂ = 0.1076
Final R indexes [all data]	R ₁ = 0.0728, wR ₂ = 0.1172

Table S6 Crystallographic data for mixed uranium-thorium nitrate complex with **L8**.

Empirical formula	C ₆₈ H ₅₆ Cl ₄ N ₁₆ O ₃₂ ThU ₂
Formula weight	2459.18
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	13.3179(5)

b/Å	10.8403(4)
c/Å	31.2259(11)
$\alpha/^\circ$	90
$\beta/^\circ$	90.3840(10)
$\gamma/^\circ$	90
Volume/Å ³	4508.0(3)
Z	2
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.812
μ/mm^{-1}	5.434
F(000)	2348.0
Crystal size/mm ³	0.23 × 0.12 × 0.07
2 Θ range for data collection/ $^\circ$	3.978 to 55.996
Index ranges	-17 ≤ h ≤ 17, -14 ≤ k ≤ 14, -41 ≤ l ≤ 41
Reflections collected	60599
Independent reflections	10730 [$R_{\text{int}} = 0.0432$, $R_{\text{sigma}} = 0.0339$]
Data/restraints/parameters	10730/0/556
Goodness-of-fit on F ²	1.051
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0325$, $wR_2 = 0.0702$
Final R indexes [all data]	$R_1 = 0.0416$, $wR_2 = 0.0731$