

Heterobimetallic Uranyl(VI) Alkoxides of Lanthanoides: Trimerisation through simple ligand exchange

Supporting Information

General Information

Chemicals and Starting Materials

All reactions were performed under inert conditions in a glovebox with an argon atmosphere and less than 0.1 ppm H₂O and O₂ or using standard Schlenk techniques. Chemicals were obtained from Sigma-Aldrich Chemical Co., Acros Organics, Alfa Aesar, VWR, Fischer Scientific and Strem Chemical Co. Solvents were distilled from technical solvents and were dried and stored over potassium under argon atmosphere. *Tert*-butanol was dried by refluxing over CaH₂ for 2 days.¹ After degassing with freeze-pump-thaw technique it was brought into the glovebox and stored over molecular sieves 3 Å. Ln(N'')₃ was obtained using the literature procedure from *Bradley* and co-workers and was purified by sublimation under reduced pressure (10⁻³ mbar) at 130-135 °C.² [UO₂(OAc)₂(H₂O)₂] was dried under reduced pressure (10⁻³ mbar) at 150 °C for 2 days. [UO₂(N'')₂(THF)₂] was synthesised using the procedure from *Arnold* and co-workers.³

Elemental Analysis

CHN were carried out on a HEKAtech CHNS Euro EA 3000 by Mr. Dirk Pullem. The sample preparation was performed in a glove box whereas the reweighing of the cartridges was done outside under environmental atmosphere. There is a discrepancy between the calculated and found values. This seems to be a systematic error. This may indeed be due to carbide formation, which is reported for uranium to occur with CH₄ from the metal below 900 °C, however, we have no proof for this.

Physical Properties Measurements System (PPMS)

Magnetisation isotherms and susceptibility measurements were performed with a Vibrating Sample Magnetometer unit (VSM) in a Quantum Design Physical Property Measurement System (PPMS). Data were collected with field strengths of ±50 kOe between temperatures of 2.1-300 K using a PPMS MultiVu software package.⁴

UV-Vis spectroscopy

UV/vis spectra were recorded on a Varian 50 Scan UV-visible photometer using quartz glass cuvettes with a length of 1 cm. The spectra were baseline corrected.

X-ray crystallographic analysis

SXRD data were obtained mounting a suitable single crystal on a glass capillary or MiTiGen Microloop™ and attaching this to the goniometer head of an SC-XRD Bruker D8 Venture. The crystal was cooled to 100-120 K by an Oxford Cryostream low temperature device.⁵ The full data set was recorded and the images processed using APEX2.⁶ Structure solution by direct methods was achieved through the use of SHELXS programs,⁷ and the structural model refined by full matrix least squares on F² using SHELX97.⁸ Molecular graphics were plotted using Mercury.⁹ Editing of CIFs and construction of tables and bond lengths and angles was achieved using and PLATON¹⁰ and Olex2.¹¹

Infrared Spectroscopy

Infrared spectra were obtained using a Platinum ATR Spectrometer on a crystal plate with samples analysed using OPUS software. Uranyl stretching frequencies can be found within the region of 960 to 910 cm^{-1} .¹²

Syntheses

Synthesis of $[\text{Sm}_2\text{UO}_2(\text{O}^t\text{Bu})_8(\text{thf})]$ 1-Sm

To a suspension of 41.0 mg dried $\text{UO}_2\text{N}''_2(\text{thf})_2$ (0.056 mmol, 1.0 eq.) in 1 ml benzene, 70.4 mg SmN''_3 (0.111 mmol, 2.0 eq.) in 3 ml benzene were added dropwise. The reaction mixture was stirred for 1 h at room temperature and 100 mg HO^tBu (1.349 mmol, 24.1 eq.) were added. After stirring for 4 h at room temperature all volatiles were removed under reduced pressure to afford $[\text{Sm}_2\text{UO}_2(\text{O}^t\text{Bu})_8(\text{thf})]$ as an orange oil in a yield of 73% (49.9 mg, 0.041 mmol). Suitable single crystals for SXR D were grown from saturated benzene solutions at 5 °C.

Elemental Analysis: Anal. Calcd for $\text{C}_{36}\text{H}_{79}\text{Sm}_2\text{O}_{11}\text{U}$ (mol. wt. 1226.77): C, 35.25; H, 6.49; N, 0.00. Found: C, 33.80; H, 6.22; N, 0.00.

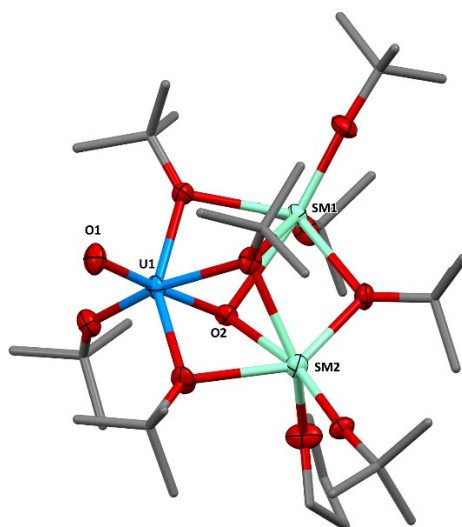


Figure S 1: Molecular structure of **1-Sm**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity.

Synthesis of $[\text{Gd}_2\text{UO}_2(\text{O}^t\text{Bu})_8(\text{thf})]$ 1-Gd

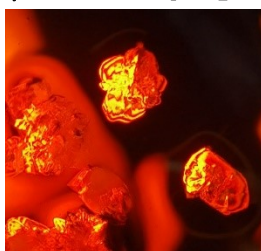


Figure S 2: Orange crystals of **1-Gd**. (Field of view ca. 1 mm).

To a suspension of 22.3 mg $\text{UO}_2\text{N}''_2(\text{thf})_2$ (0.034 mmol, 1.0 eq.) in 1 ml benzene, 42.9 mg GdN''_3 (0.067 mmol, 2.0 eq.) in 3 ml benzene were added dropwise. The reaction mixture was stirred for 1 h at room temperature and 82.5 mg HO^tBu (1.113 mmol, 32.7 eq.) were added. After stirring for 4 h at room temperature all volatiles were removed under reduced pressure to afford $[\text{Gd}_2\text{UO}_2(\text{O}^t\text{Bu})_8(\text{thf})]$ as an orange oil in a yield of 76% (32.1 mg, 0.026 mmol). Suitable single crystals for SXR D were grown from saturated benzene solutions at 5 °C.

IR (cm^{-1}): 2971 (m), 2935 (w), 2865 (w), 1471 (w), 1457 (w), 1382 (w), 1362 (m), 1241 (m), 1185 (s), 960 (m), 930 (s), 840 (m), 767 (m), 745 (m), 714 (s), 507 (s), 469 (s).

Elemental Analysis: Anal. Calcd for $\text{C}_{36}\text{H}_{79}\text{Gd}_2\text{O}_{11}\text{U}$ (mol. wt. 1240.55): C, 34.86; H, 6.42; N, 0.00. Found: C, 33.88; H, 6.17; N, 0.00.

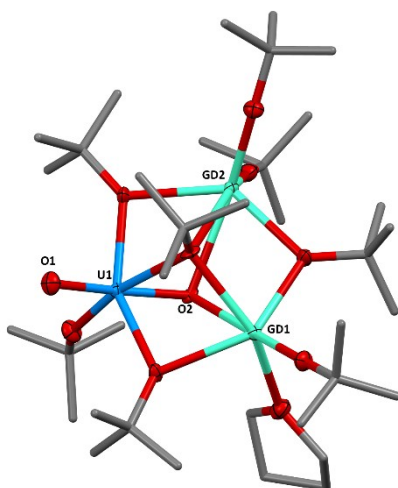


Figure S 3: Molecular structure of **1-Gd**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity.

Synthesis of $[\text{Nd}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})_2]_2$ 2-Nd

To a suspension of 0.520 g dried $\text{UO}_2(\text{OAc})_2$ (1.330 mmol, 2.0 eq.) in 10 ml THF, 1.670 g NdN''_3 (2.660 mmol, 4.0 eq.) in 30 ml toluene were added dropwise. The reaction mixture was stirred for 1 h at room temperature and 1.084 g HO^tBu (14.630 mmol, 33.0 eq.) were added. Care was taken that no $\text{UO}_2(\text{OAc})_2$ was left at the bottom before adding the *tert*-butanol. After stirring for 4 h at room temperature all volatiles were removed under reduced pressure to afford $[\text{Nd}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})_2]_2$ as a bright orange solid in a yield of 81% (1.216 g, 0.539 mmol). Suitable single crystals for SXRD were grown from saturated toluene solutions at 5 °C.

IR (cm^{-1}): 2968 (m), 2936 (w), 2903 (w), 2876 (w), 1554 (s), 1418 (m), 1341 (m), 1226 (w), 1183 (s), 981 (s), 938 (s), 900 (s), 834 (s), 757 (s), 697 (s), 665 (m), 642 (w), 615 (w), 611 (s), 517 (s), 473 (s).

Elemental Analysis: Anal. Calcd for $\text{C}_{60}\text{H}_{32}\text{Nd}_4\text{O}_{22}\text{U}_2$ (mol. wt. 2258.72): C, 31.91; H, 5.89; N, 0.00. Found: C, 30.92; H, 5.69; N, 0.00.

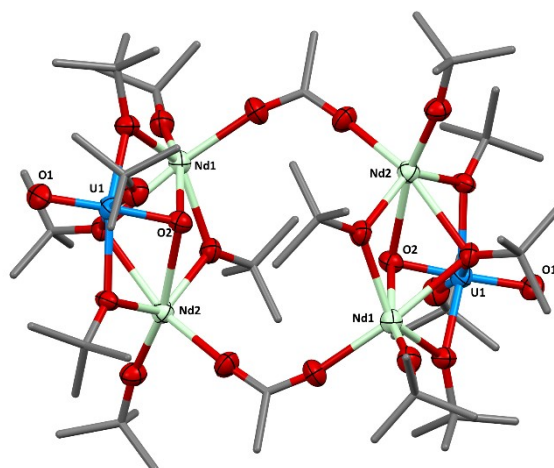


Figure S 4: Molecular structure of **2-Nd**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity.

Synthesis of $[\text{Gd}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})_2]_2$ 2-Gd

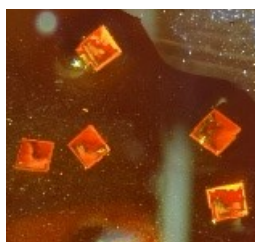


Figure S 5: Orange crystals of **2-Gd**. (Field of view ca. 1 mm).

To a suspension of 66.4 mg dried $\text{UO}_2(\text{OAc})_2$ (0.171 mmol, 2.0 eq.) in 1 ml THF, 218.5 mg GdN^{III} (hmds = $\text{N}\{\text{Si}(\text{CH}_3)_3\}_2$) (0.342 mmol, 4.0 eq.) in 5 ml benzene were added dropwise. The reaction mixture was stirred for 1 h at room temperature and 139.4 mg HO^tBu (1.881 mmol, 22.0 eq.) were added. Care was taken that no $\text{UO}_2(\text{OAc})_2$ was left at the bottom before adding the *tert*-butanol. After stirring for 4 h at room temperature all volatiles were removed under reduced pressure to afford $[\text{Gd}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})_2]_2$ as a bright orange solid in a yield of 66% (130.4 mg, 0.056 mmol). Suitable single crystals for SXR D were grown from saturated benzene solutions at 5 °C.

IR (cm^{-1}): 2973 (m), 2935 (w), 2908 (w), 2874 (w), 1578 (s), 1449 (m), 1362 (m), 1229 (w), 1176 (s), 1000 (m), 957 (m), 922 (s), 896 (s), 849 (s), 767 (m), 719 (m), 671 (m), 650 (m), 611 (s), 507 (s), 477 (s).

Elemental Analysis: Anal. Calcd for $\text{C}_{60}\text{H}_{32}\text{Gd}_4\text{O}_{22}\text{U}_2$ (mol. wt. 2310.75): C, 31.19; H, 5.76; N, 0.00. Found: C, 30.14; H, 5.65; N, 0.00.

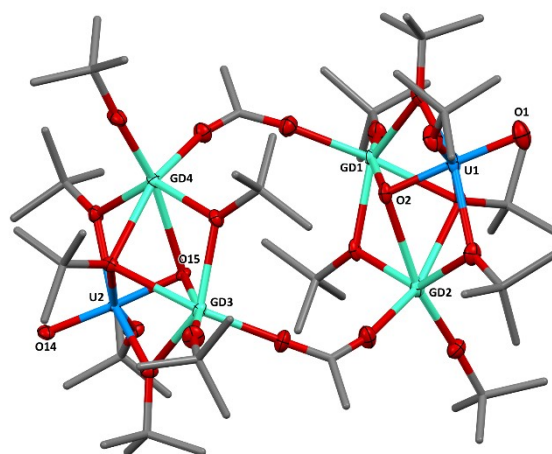


Figure S 6: Molecular structure of **2-Gd**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity.

Synthesis of $[\text{Dy}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})_2]_2$ 2-Dy

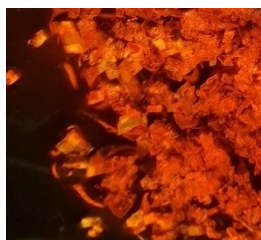


Figure S 7: Orange crystals of **2-Dy**. (Field of view ca. 1 mm).

To a suspension of 61.7 mg dried $\text{UO}_2(\text{OAc})_2$ (0.159 mmol, 2.0 eq.) in 1 ml THF, 204.8 mg DyN^{III} (0.318 mmol, 4.0 eq.) in 5 ml benzene were added dropwise. The reaction mixture was stirred for 1 h at room temperature and 129.6 mg HO^tBu (1.749 mmol, 22.0 eq.) were added. Care was taken that no $\text{UO}_2(\text{OAc})_2$ was left at the bottom before adding the *tert*-butanol. After stirring for 4 h at room temperature all volatiles were removed under reduced pressure to afford $[\text{Dy}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})_2]_2$ as a bright orange solid in a yield of 77% (142.7 mg, 0.061 mmol). Suitable single crystals for SXR D were grown from saturated benzene solutions at 5 °C.

IR (cm^{-1}): 2976 (m), 2930 (w), 2872 (w), 1579 (s), 1448 (m), 1364 (m), 1228 (w), 1175 (s), 1000 (m), 916 (s), 845 (s), 766 (m), 714 (m), 643 (m), 610 (w), 507 (s), 480 (s).

Elemental Analysis: Anal. Calcd for $\text{C}_{60}\text{H}_{32}\text{Dy}_4\text{O}_{22}\text{U}_2$ (mol. wt. 2331.75): C, 30.91; H, 5.71; N, 0.00. Found: C, 29.92; H, 5.52; N, 0.00.

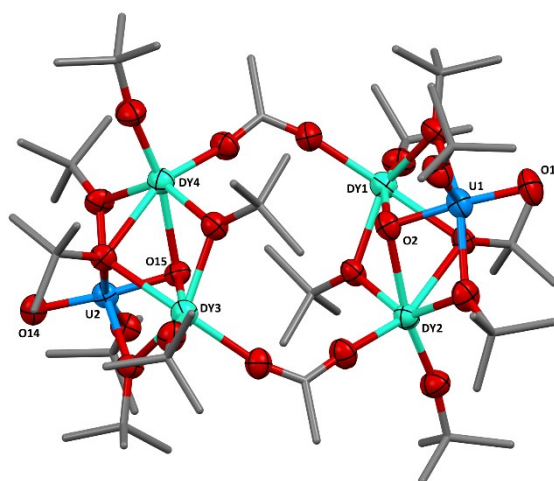


Figure S 8: Molecular structure of **2-Dy**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity.

Synthesis of $[\text{Ho}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_2$ **2-Ho** and $[\text{Ho}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_3$ **3-Ho**



Figure S 9: Orange crystals of **2-Ho** (right) and **3-Ho** (left). (Field of view ca. 1 mm).

To a suspension of 70.0 mg dried $\text{UO}_2(\text{OAc})_2$ (0.180 mmol, 2.0 eq.) in 1 ml THF, 233.1 mg HoN^{III} (0.361 mmol, 4.0 eq.) in 5 ml benzene were added dropwise. The reaction mixture was stirred for 1 h at room temperature and 146.8 mg HO^tBu (1.980 mmol, 22.0 eq.) were added. Care was taken that no $\text{UO}_2(\text{OAc})_2$ was left at the bottom before adding the *tert*-butanol. After stirring for 4 h at room temperature all volatiles were removed under reduced pressure to afford a bright orange solid in a yield of 75% (158.0 mg, 0.067 mmol, assuming conversion to $[\text{Ho}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_2$ (**2-Ho**)). Suitable single crystals for SXRD were grown from saturated benzene solutions at 5 °C. $[\text{Ho}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_2$ (**2-Ho**) along with $[\text{Ho}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_3$ (**3-Ho**). The crystals were crystallographically distinguishable and allowed for enough material for CHN to be set aside, however, the bulk material could not be synthetically separated.

IR (cm⁻¹) (2-Ho): 2975 (m), 2936 (w), 2896 (w), 1581 (m), 1447 (m), 1363 (m), 1234 (w), 1178 (s), 1005 (m), 960 (m), 920 (s), 893 (m), 848 (s), 770 (m), 719 (m), 652 (m), 613 (w), 506 (s), 473 (s).

Elemental Analysis: Anal. Calcd for $\text{C}_{60}\text{H}_{32}\text{Ho}_4\text{O}_{22}\text{U}_2$ (**2-Ho**) (mol. wt. 2341.47): C, 30.78; H, 5.68; N, 0.00. Found: C, 29.76; H, 5.49; N, 0.00.

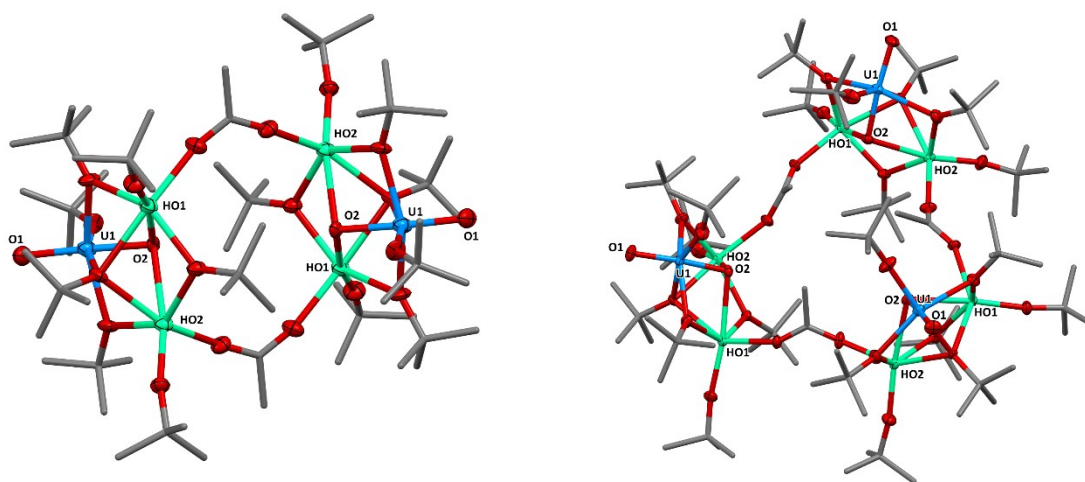


Figure S 10: Molecular structure of **2-Ho** and **3-Ho**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity.

Synthesis of $[\text{Er}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_2$ 2-Er

To a suspension of 10.8 mg dried $\text{UO}_2(\text{OAc})_2$ (0.026 mmol, 1.0 eq.) in 1 ml THF, 33.3 mg ErN''_3 (0.052 mmol, 2.0 eq.) in 5 ml benzene were added dropwise. The reaction mixture was stirred for 1 h at room temperature and 134.0 mg HO^tBu (1.808 mmol, 70.0 eq.) were added. Care was taken that no $\text{UO}_2(\text{OAc})_2$ was left at the bottom before adding the *tert*-butanol. After stirring for 4 h at room temperature all volatiles were removed under reduced pressure to afford $[\text{Ho}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_2$ as a bright orange solid in a yield of 85% (26.0 mg, 0.022 mmol). With SXRD analysis connectivity could be solved but due to heavy disorder and an insufficient dataset a refined structural model could not be obtained.

IR (cm^{-1}): 2975 (m), 2963 (w), 2875 (w), 1580 (m), 1441 (m), 1360 (m), 1229 (m), 1175 (s), 993 (m), 920 (s), 898 (s), 848 (s), 763 (m), 713 (m), 663 (m), 646 (m), 613 (w), 512 (s), 473 (s).

Elemental Analysis: Anal. Calcd for $\text{C}_{60}\text{H}_{32}\text{Er}_4\text{O}_{22}\text{U}_2$ (mol. wt. 2350.79): C, 31.28; H, 5.84; N, 0.00. Found: C, 31.47; H, 4.80; N, 0.00.

Synthesis of $[\text{Yb}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_3$ 3-Yb



Figure S 11: Orange crystals of **3-Yb**. (Field of view ca. 1 mm).

To a suspension of 70.0 mg dried $\text{UO}_2(\text{OAc})_2$ (0.180 mmol, 3.0 eq.) in 1 ml THF, 236.0 mg YbN''_3 (0.361 mmol, 6.0 eq.) in 5 ml benzene were added dropwise. The reaction mixture was stirred for 1 h at room temperature and 146.8 mg HO^tBu (1.980 mmol, 33.0 eq.) were added. Care was taken that no $\text{UO}_2(\text{OAc})_2$ was left at the bottom before adding the *tert*-butanol. After stirring for 4 h at room temperature all volatiles were removed under reduced pressure to afford $[\text{Yb}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_3$ as a bright orange solid in a yield of 76% (162.4 mg, 0.046 mmol). Suitable single crystals for SXRD were grown from saturated benzene solutions at 5 °C.

IR (cm^{-1}): 2975 (m), 2963 (w), 2875 (w), 1581 (m), 1453 (m), 1363 (m), 1246 (m), 1178 (s), 1016 (m), 976 (m), 920 (s), 842 (s), 769 (m), 713 (m), 646 (m), 613 (w), 512 (s), 478 (s).

Elemental Analysis: Anal. Calcd for $\text{C}_{90}\text{H}_{198}\text{Yb}_6\text{O}_{33}\text{U}_3$ (mol. wt. 3560.95): C, 30.36; H, 5.60; N, 0.00. Found: C, 30.45; H, 5.43; N, 0.00.

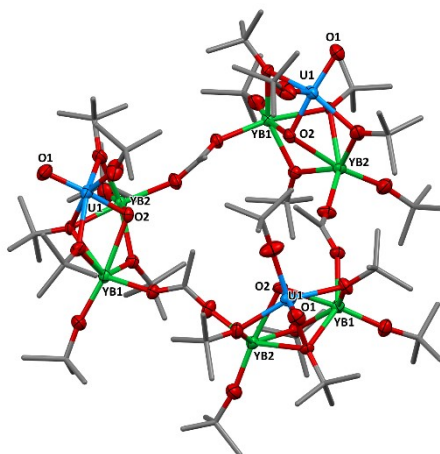


Figure S 12: Molecular structure of **3-Yb**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity.

Synthesis of $[\text{Sm}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_4$ **4-Sm**

To a suspension of 30.2 mg dried $\text{UO}_2(\text{OAc})_2$ (0.071 mmol, 4.0 eq.) in 1 ml THF, 89.9 mg SmN''_3 (0.142 mmol, 8.0 eq.) in 5 ml toluene were added dropwise. The reaction mixture was stirred for 1 h at room temperature and 57.9 mg HO^tBu (0.781 mmol, 44.0 eq.) were added. Care was taken that no $\text{UO}_2(\text{OAc})_2$ was left at the bottom before adding the *tert*-butanol. After stirring for 4 h at room temperature all volatiles were removed under reduced pressure to afford $[\text{Sm}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_4$ as a bright orange solid in a yield of 85% (68.9 mg, 0.015 mmol). Suitable single crystals for SXR D were grown from saturated toluene solutions at 5 °C.

IR (cm⁻¹): 2981 (m), 2935 (w), 2871(w), 1580 (m), 1440 (m), 1361 (m), 1232 (m), 1174 (s), 998 (m), 920 (s), 900 (s), 848 (s), 764 (m), 711 (m), 647 (m), 608 (w), 517 (s), 478 (s).

Elemental Analysis: Anal. Calcd for $\text{C}_{120}\text{H}_{264}\text{Sm}_8\text{O}_{44}\text{U}_4$ (mol. wt. 4566.38): C, 31.56; H, 5.83; N, 0.00. Found: C, 30.58; H, 5.66; N, 0.00.

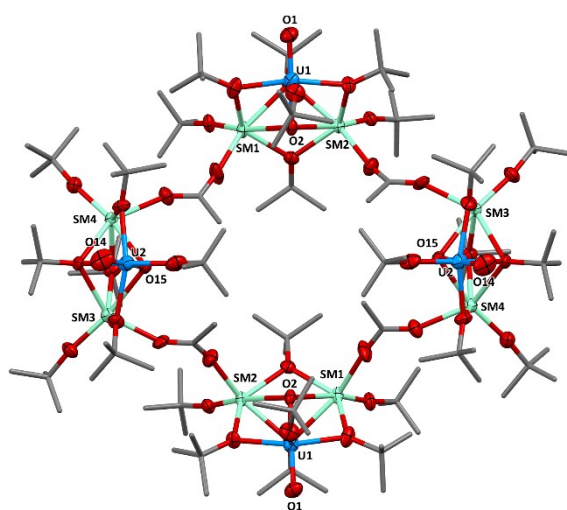


Figure S 13: Molecular structure of **4-Sm**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity.

Synthesis of $[\text{Dy}_3\text{UO}_2(\text{O}^t\text{Bu})_{10}\text{Cl}(\text{H}_2\text{O})]$ 5-Dy

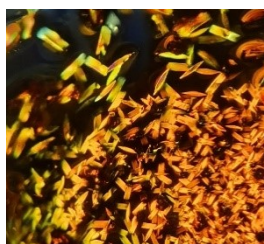


Figure S 14: Orange crystals of **5-Dy**. (Field of view ca. 1 mm).

To a solution of 107.1 mg $\text{UO}_2\text{N}''_2(\text{thf})_2$ (0.146 mmol, 1.0 eq.) in 2 ml benzene, 250.9 mg DyN''_3 (0.390 mmol, 2.67 eq.) and 18.2 mg $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ (0.048 mmol, 0.33 eq.) in 3 ml benzene were added dropwise. The reaction mixture was stirred for 1 h at room temperature and 210 mg HO^tBu (2.833 mmol, 19.4 eq.) were added. After stirring for 4 h at room temperature all volatiles were removed under reduced pressure to afford $[\text{Dy}_3\text{UO}_2(\text{O}^t\text{Bu})_{10}\text{Cl}(\text{H}_2\text{O})]$ as a bright orange solid in a yield of 42% (93.4 mg, 0.061 mmol). Suitable single crystals for SXR D were grown from saturated benzene solutions at 5 °C.

IR (cm^{-1}): 2970 (m), 2935 (w), 2872 (w), 1468 (w), 1358 (m), 1241 (m), 1201 (s), 1175 (s), 1000 (m), 915 (m), 844 (w), 825 (m), 760 (m), 654 (s), 506 (s), 480 (s).

Elemental Analysis: Anal. Calcd for $\text{C}_{40}\text{H}_{92}\text{ClDy}_3\text{O}_{13}\text{U}$ (mol. wt. 1542.14): C, 31.15; H, 6.01; N, 0.00. Found: C, 30.62; H, 5.77; N, 0.00.

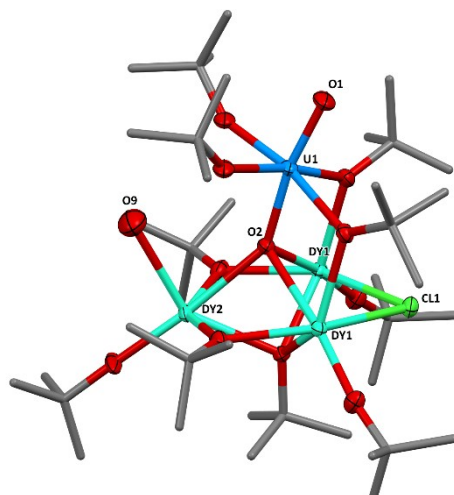


Figure S 15: Molecular structure of **5-Dy**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity.

Synthesis of $[\text{Ho}_3\text{UO}_2(\text{O}^t\text{Bu})_{10}\text{Cl}(\text{H}_2\text{O})]$ 5-Ho



Figure S 16: Orange crystals of **5-Ho**. (Field of view ca. 1 mm).

To a solution of 111.2 mg $\text{UO}_2\text{N}''_2(\text{thf})_2$ (0.151 mmol, 1.0 eq.) in 2 ml benzene, 261.0 mg HoN''_3 (0.404 mmol, 2.67 eq.) and 18.9 mg $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$ (0.050 mmol, 0.33 eq.) in 3 ml benzene were added dropwise. The reaction mixture was stirred for 1 h at room temperature and 220 mg HO^tBu (2.97 mmol, 19.7 eq.) were added. After stirring for 4 h at room temperature all volatiles were removed under reduced pressure to afford $[\text{Ho}_3\text{UO}_2(\text{O}^t\text{Bu})_{10}\text{Cl}(\text{H}_2\text{O})]$ as a bright orange solid in a yield of 71% (166.1 mg, 0.107 mmol). Suitable single crystals for SXR D were grown from saturated benzene solutions at 5 °C.

Elemental Analysis: Anal. Calcd for $\text{C}_{40}\text{H}_{92}\text{ClHo}_3\text{O}_{13}\text{U}$ (mol. wt. 1549.43): C, 31.01; H, 5.99; N, 0.00. Found: C, 30.02; H, 5.59; N, 0.00.

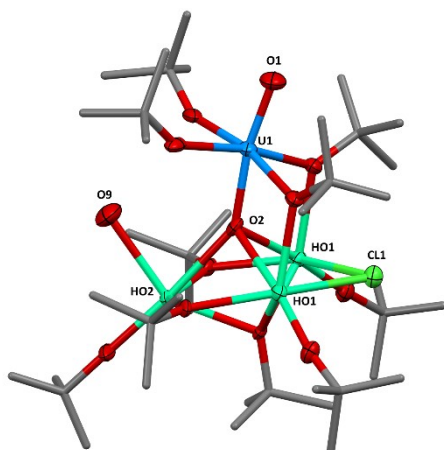


Figure S 17: Molecular structure of **5-Ho**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity.

Synthesis of $[\text{Ho}_3\text{UO}_2(\text{O}^t\text{Bu})_{10}(\text{OH})(\text{H}_2\text{O})]$ **6-Ho**



Figure S 18: Orange crystals of **6-Ho**. (Field of view ca. 1 mm).

To a solution of 35.5 mg $\text{UO}_2\text{N}''_2(\text{thf})_2$ (0.048 mmol, 1.0 eq.) in 2 ml benzene, 93.0 mg unsublimed HoN''_3 (0.144 mmol, 3.0 eq.) in 3 ml benzene were added dropwise. The reaction mixture was stirred for 1 h at room temperature and 126 mg HO^tBu (1.700 mmol, 35.4 eq.) were added. After stirring for 4 h at room temperature all volatiles were removed under reduced pressure to afford $[\text{Ho}_3\text{UO}_2(\text{O}^t\text{Bu})_{10}(\text{OH})(\text{H}_2\text{O})]$ as a red solid in a yield of 42% (30.9 mg, 0.020 mmol). Suitable single crystals for SXR D were grown from saturated benzene solutions at 5 °C.

Elemental Analysis: Anal. Calcd for $\text{C}_{40}\text{H}_{93}\text{Ho}_3\text{O}_{14}\text{U}$ (mol. wt. 1530.99): C, 31.38; H, 6.12; N, 0.00. Found: C, 30.87; H, 5.85; N, 0.00.

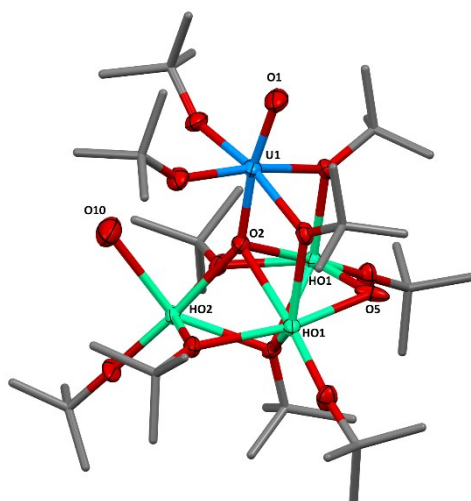


Figure S 19: Molecular structure of **6-Ho**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity.

Synthesis of $[\text{LiHo}_2\text{UO}_2(\text{O}^t\text{Bu})_9]$ 7-Ho

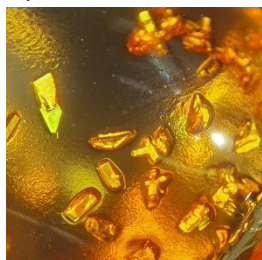


Figure S 20: Orange crystals of **7-Ho**. (Field of view ca. 2 mm).

To a solution of 40.1 mg $\text{UO}_2\text{N}''_2(\text{thf})_2$ (0.055 mmol, 1.0 eq.) in 2 ml benzene, 70.5 mg HoN''_3 (0.109 mmol, 2.0 eq.) and 9.1 mg LiN'' (0.055 mmol, 1.0 eq.) in 2 ml benzene were added dropwise. The reaction mixture was stirred for 1 h at room temperature and 100 mg HO^tBu (1.35 mmol, 24.5 eq.) were added. After stirring for 4 h at room temperature all volatiles were removed under reduced pressure to afford $[\text{LiHo}_2\text{UO}_2(\text{O}^t\text{Bu})_9]$ as a bright yellow solid in a yield of 89% (61.9 mg, 0.049 mmol). Suitable single crystals for SXR D were grown from saturated benzene solutions at 5 °C.

Elemental Analysis: Anal. Calcd for $\text{C}_{36}\text{H}_{81}\text{Ho}_2\text{LiO}_{11}\text{U}$ (mol. wt. 1264.83): C, 34.19; H, 6.46; N, 0.00. Found: C, 33.26; H, 6.26; N, 0.00.

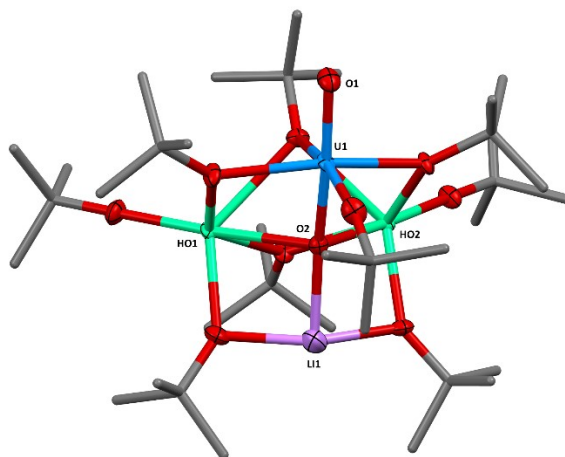


Figure S 21: Molecular structure of **7-Ho**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms are omitted for clarity.

Synthesis of $[\text{KHo}_2\text{UO}_2(\text{O}^t\text{Bu})_9(\text{HO}^t\text{Bu})]$ 8-Ho



Figure S 22: Orange crystals of **8-Ho**. (Field of view ca. 2 mm).

To a solution of 42.0 mg $\text{UO}_2\text{N}''_2(\text{thf})_2$ (0.057 mmol, 1.0 eq.) in 2 ml benzene, 73.8 mg HoN''_3 (0.114 mmol, 2.0 eq.) and 11.4 mg KN'' (0.057 mmol, 1.0 eq.) in 2 ml benzene were added dropwise. The reaction mixture was stirred for 1 h at room temperature and 100 mg HO^tBu (1.35 mmol, 23.7 eq.) were added. After stirring for 4 h at room temperature all volatiles were removed under reduced pressure to afford $[\text{KHo}_2\text{UO}_2(\text{O}^t\text{Bu})_9(\text{HO}^t\text{Bu})]$ as a bright orange solid in a yield of 74% (59.5 mg, 0.042 mmol). Suitable single crystals for SXR D were grown from saturated benzene solutions at 5 °C.

Elemental Analysis: Anal. Calcd for $\text{C}_{43}\text{H}_{94}\text{Ho}_2\text{KO}_{12}\text{U}$ (mol. wt. 1410.17): C, 36.62; H, 6.72; N, 0.00. Found: C, 35.08; H, 6.44; N, 0.00.

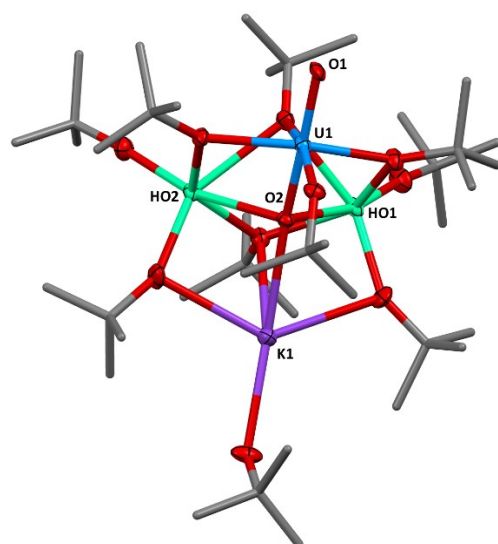


Figure S 23: Molecular structure of **7-Ho**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms are omitted for clarity.

Physical Properties Measurements System (PPMS)

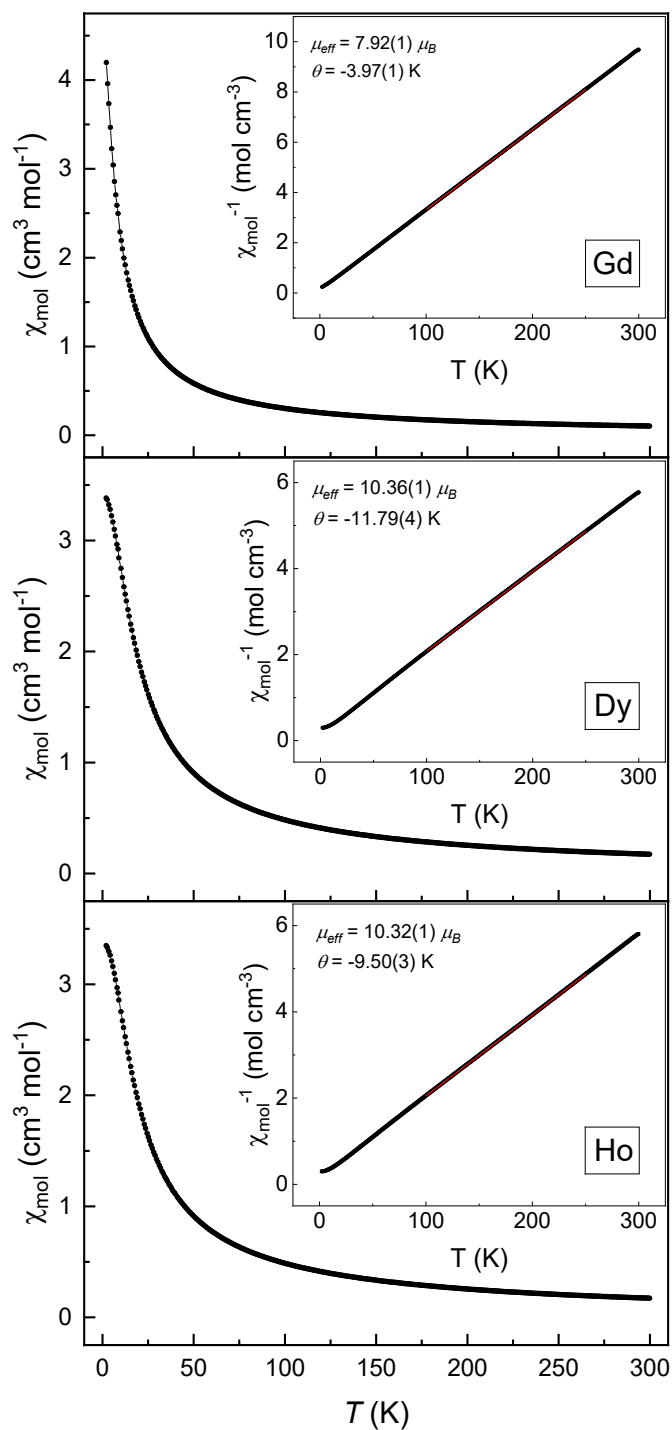


Figure S 24: Magnetic susceptibilities and inverse susceptibilities (inset) of $[\text{Gd}_2\text{UO}_2(\text{O}^i\text{Bu})_7(\text{OAc})]_2$ (**2-Gd**) (top), $[\text{Dy}_2\text{UO}_2(\text{O}^i\text{Bu})_7(\text{OAc})]_2$ (**2-Dy**) (centre) and $[\text{Ho}_2\text{UO}_2(\text{O}^i\text{Bu})_7(\text{OAc})]_2$ (**2-Ho**) (bottom). $B = 3 \text{ T}$. Curie-Weiss fits in red. Parameters obtained from the fits are given in the insets. Measurements were performed on free and randomly oriented powders.

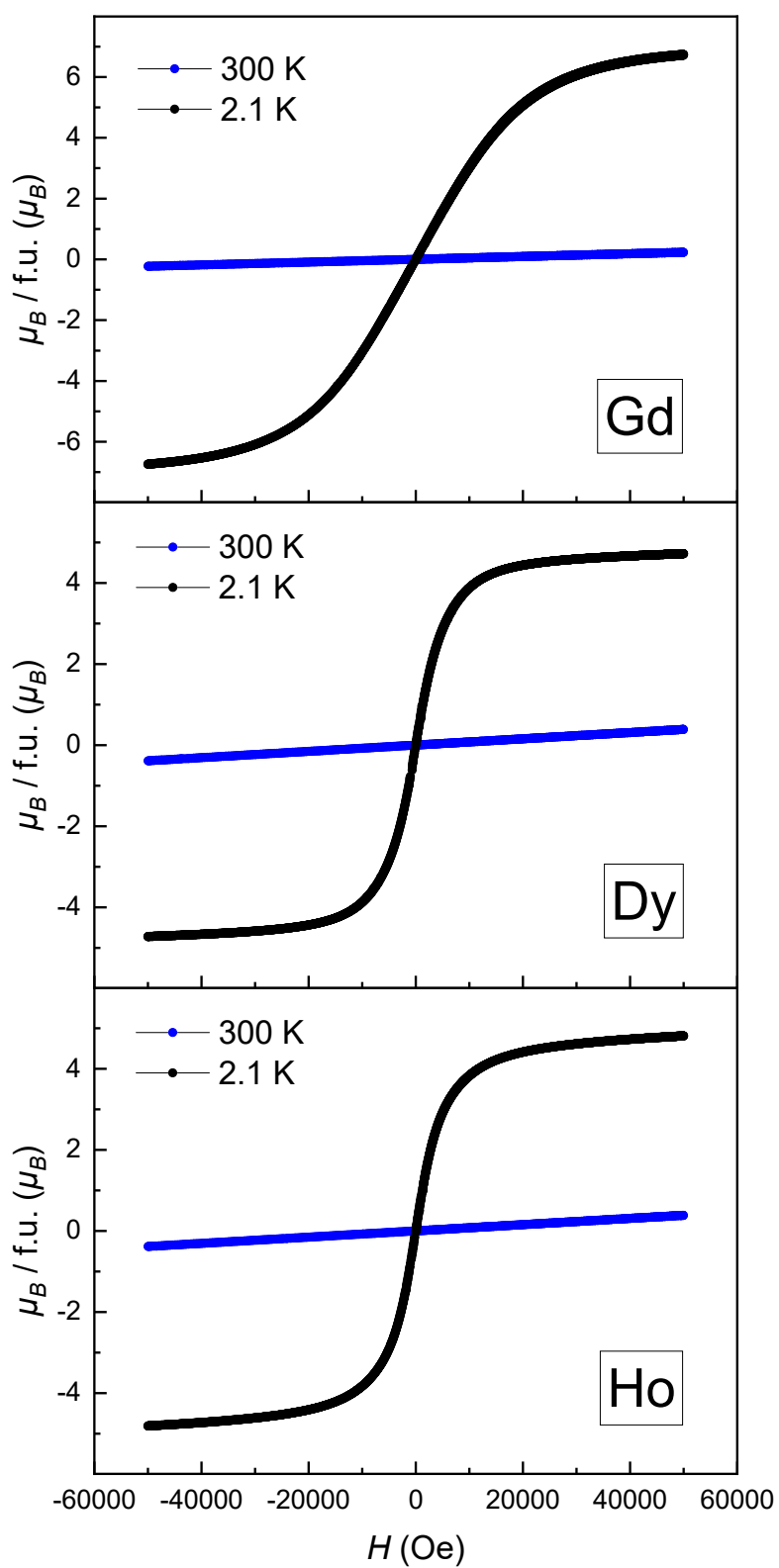


Figure S 25: Isothermal magnetisation of $[\text{Gd}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})_2]$ (**2-Gd**) (top), $[\text{Dy}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})_2]$ (**2-Dy**) (centre) and $[\text{Ho}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})_2]$ (**2-Ho**) (bottom) at 300 K and 2.1 K.

UV-Vis

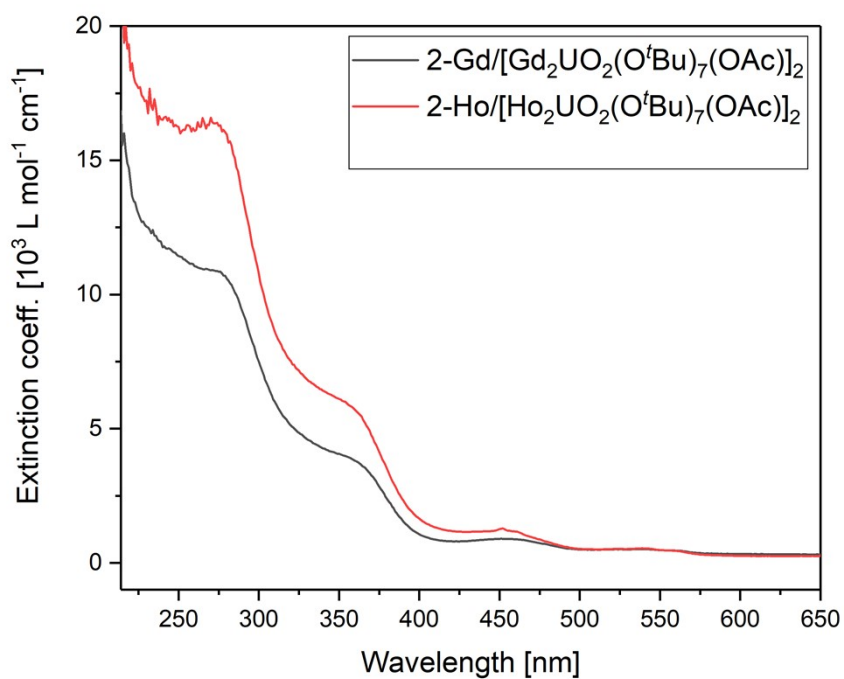


Figure S 26: Compared UV-Vis spectra of [Gd₂UO₂(O^tBu)₇(OAc)]₂ (**2-Gd**) and [Ho₂UO₂(O^tBu)₇(OAc)]₂ (**2-Ho**) measured at 278 K under inert conditions.

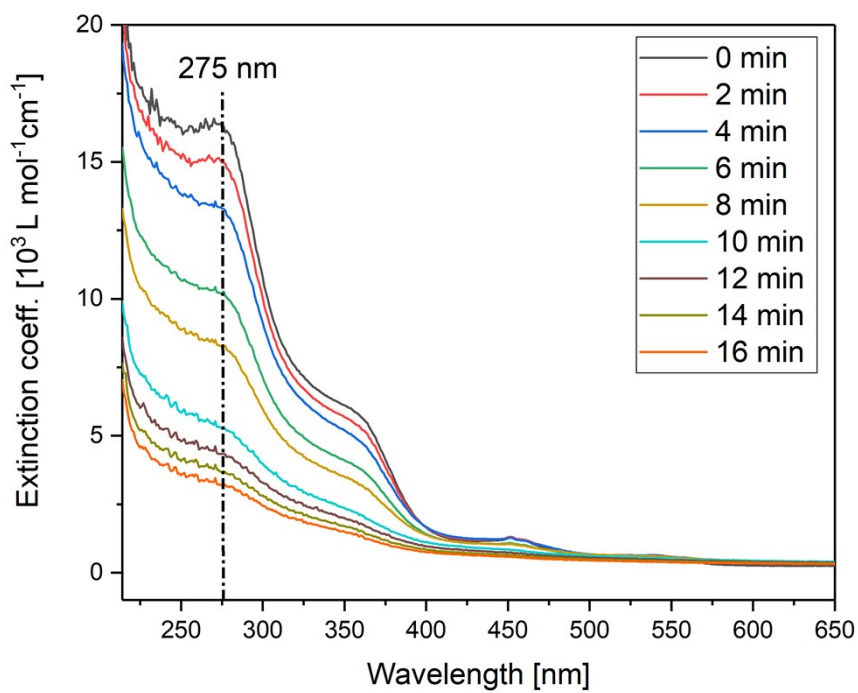


Figure S 27: UV-Vis spectra of [Ho₂UO₂(O^tBu)₇(OAc)]₂ (**2-Ho**) under atmospheric conditions over a time span of 16 min.

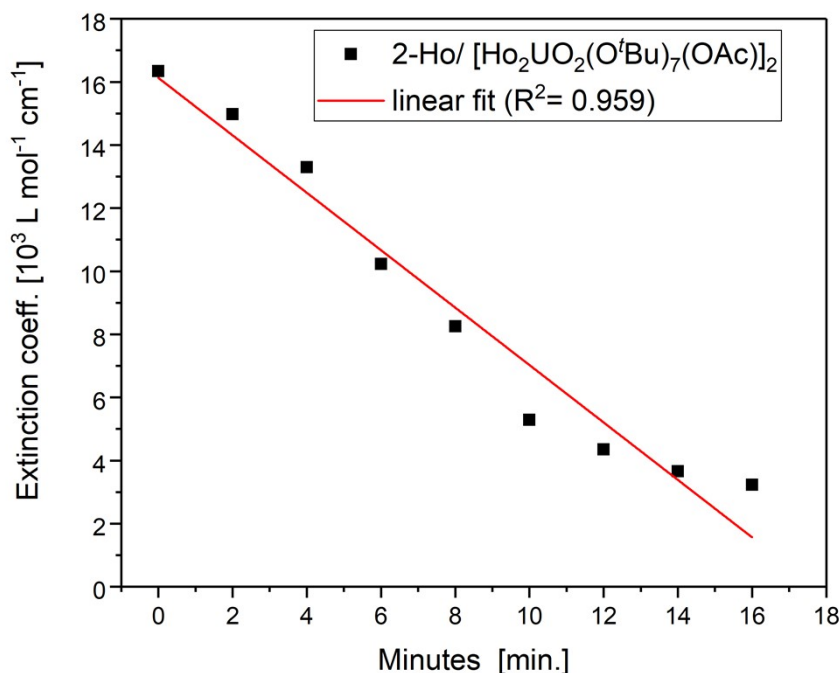


Figure S 28: Hydrolysis curve of $[\text{Ho}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_2$ (**2-Ho**) with linear fit (red). The rate of hydrolysis was determined by the decreasing absorption of the complex at 275 nm.

X-ray crystallographic analysis

Table S 1: Selected bond lengths (Å) and angles (°) of monomeric **1-Ln**, dimeric **2-Ln**, trimeric **3-Ln** and $[\text{Ln}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_n$ (Ln = Nd, Sm, Gd, Dy, Ho, Er, Yb; n = 2 – 4), as well as the chloride substituted complexes **5-Ln** $[\text{Ln}_3\text{UO}_2(\text{O}^t\text{Bu})_{10}\text{Cl}(\text{H}_2\text{O})]$ (Ln = Dy, Ho), the hydroxide substituted complex **6-Ho** $[\text{Ho}_3\text{UO}_2(\text{O}^t\text{Bu})_{10}(\text{OH})(\text{H}_2\text{O})]$ and the alkali metal (M = Li, K) substituted complexes **7-Ho/8-Ho** $[\text{MHo}_2\text{UO}_2(\text{O}^t\text{Bu})_9(\text{HO}^t\text{Bu})]$.

	Compound	U=O _{terminal}	U=O _{μ3}	Ln–O _{μ3}	O=U=O
	$\text{UO}_2(\text{OAc})_2\text{THF}_2$	1.780(6)	-	-	178.5(1)
1-Sm	$[\text{Sm}_2\text{UO}_2(\text{O}^t\text{Bu})_8(\text{THF})]$	1.793(4)	1.874(3)	2.5444(3)	173.1(1)
1-Gd	$[\text{Gd}_2\text{UO}_2(\text{O}^t\text{Bu})_8(\text{THF})]$	1.789(8)	1.86(8)	2.569(9)	173.9(4)
2-Nd	$[\text{Nd}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_2$	1.781(6)	1.866(6)	2.6250(7)	171.7(3)
2-Gd	$[\text{Gd}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_2$	1.794(9)	1.878(8)	2.575(9)	171.2(5)
2-Dy	$[\text{Dy}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_2$	1.793(9)	1.891(8)	2.507(9)	171.4(4)
2-Ho	$[\text{Ho}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_2$	1.81(2)	1.90(1)	2.497(1)	170.3(5)
3-Ho	$[\text{Ho}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_3$	1.789(4)	1.873(4)	2.492(4)	171.6(1)
3-Yb	$[\text{Yb}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_3$	1.792(7)	1.885(5)	2.447(5)	171.4(2)
4-Sm	$[\text{Sm}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})]_4$	1.76(1)	1.8584(9)	2.561(9)	172.1(5)
5-Dy	$[\text{Dy}_3\text{UO}_2(\text{O}^t\text{Bu})_{10}\text{Cl}(\text{H}_2\text{O})]$	1.799(3)	1.957(3)	2.475(2)	169.1(1)
5-Ho	$[\text{Ho}_3\text{UO}_2(\text{O}^t\text{Bu})_{10}\text{Cl}(\text{H}_2\text{O})]$	1.790(8)	1.948(7)	2.461(5)	169.5(3)
6-Ho	$[\text{Ho}_3\text{UO}_2(\text{O}^t\text{Bu})_{10}(\text{OH})(\text{H}_2\text{O})]$	1.802(7)	1.938(5)	2.470(4)	170.3(3)
7-Ho	$[\text{LiHo}_2\text{UO}_2(\text{O}^t\text{Bu})_9]$	1.790(5)	1.887(5)	2.494(8)	173.0(4)
8-Ho	$[\text{KHo}_2\text{UO}_2(\text{O}^t\text{Bu})_9(\text{HO}^t\text{Bu})]$	1.814(1)	1.905(1)	2.515(9)	175.6(4)

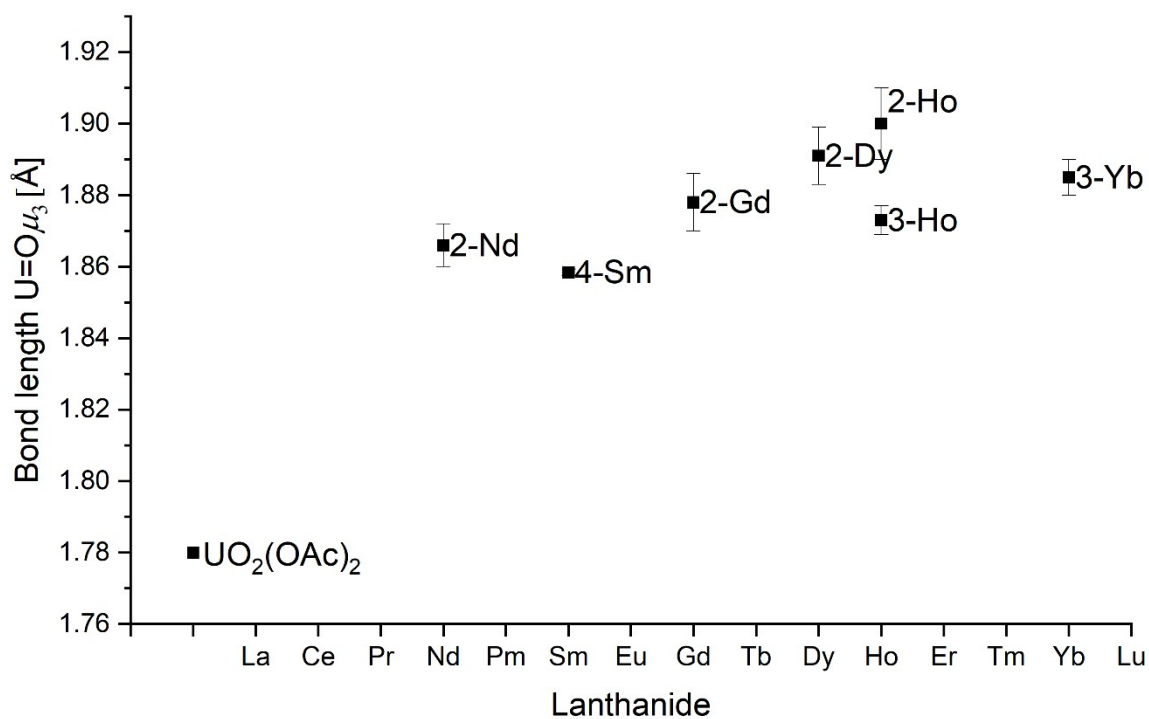


Figure S 29: Bond lengths of endogenous $U=O_{\mu_3}$ in Å which is coordinated to two lanthanide ($Ln = Nd, Sm, Gd, Dy, Ho, Yb$) centres. Only acetate bridged complexes are plotted for comparability.

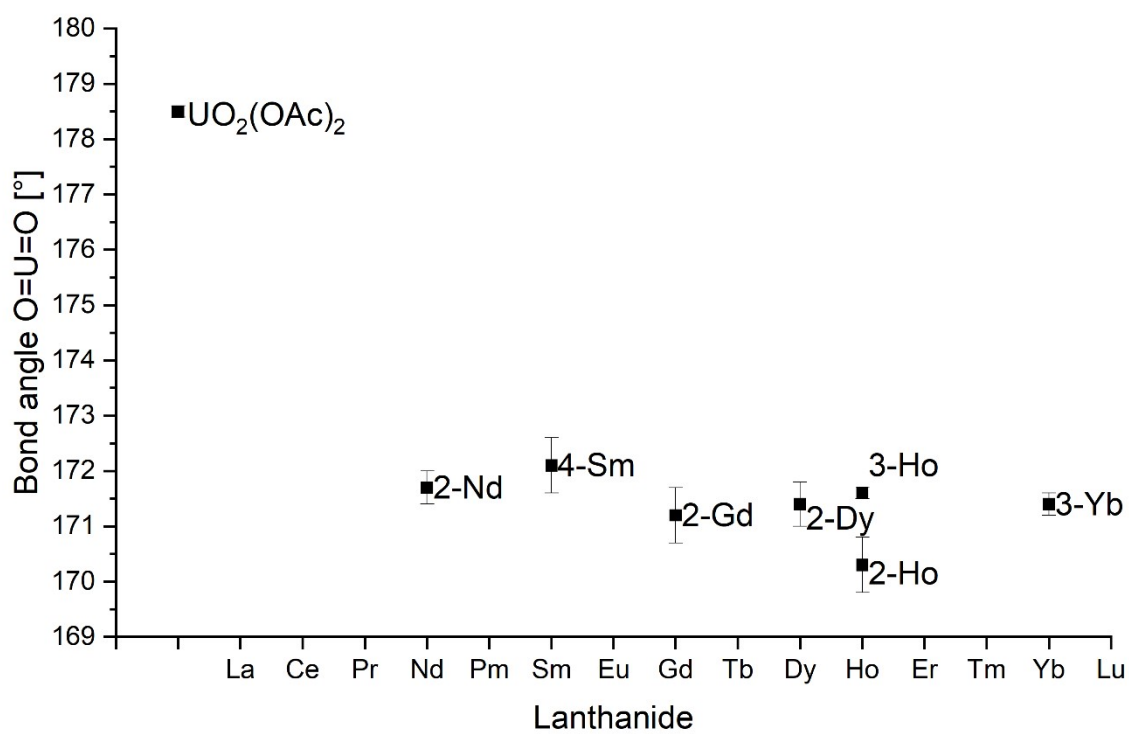


Figure S 30: Bond angles of the uranyl subunit $O=U=O$ in °. Only acetate bridged complexes are plotted for comparability.

Table S 2

Identification code	mo_DG075_full (1-Sm)	mo_DG059_A_210512_2 (1-Gd)	uo2nd (2-Nd)
CCDC Number	2110472	2110473	2110474
Empirical formula	C ₃₆ H ₈₀ O ₁₁ Sm ₂ U	C ₃₆ H ₈₀ Gd ₂ O ₁₁ U	C ₇₂ H ₁₄₄ Nd ₄ O ₂₂ U ₂
Formula weight	1227.73	1241.53	2414.88
Temperature/K	100.0	100.0	100
Crystal system	monoclinic	monoclinic	triclinic
Space group	P2 ₁ /c	P2 ₁ /c	P-1
a/Å	11.2945(5)	14.5453(16)	15.2728(7)
b/Å	24.6729(11)	16.8302(17)	16.2896(7)
c/Å	17.6410(7)	19.905(2)	20.7284(9)
α/°	90	90	104.640(3)
β/°	94.931(2)	93.193(4)	90.796(4)
γ/°	90	90	106.853(3)
Volume/Å ³	4897.8(4)	4865.1(9)	4754.0(4)
Z	4	4	2
ρ _{calc} /g/cm ³	1.665	1.695	1.687
μ/mm ⁻¹	5.710	6.061	5.597
F(000)	2400.0	2416.0	2352.0
Crystal size/mm ³	0.37 × 0.231 × 0.182	0.236 × 0.194 × 0.113	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.444 to 54.968	4.098 to 50.7	3.254 to 53.762
Index ranges	-14 ≤ h ≤ 14, -32 ≤ k ≤ 32, -21 ≤ l ≤ 22	-17 ≤ h ≤ 17, -20 ≤ k ≤ 18, - 23 ≤ l ≤ 23	-19 ≤ h ≤ 19, -20 ≤ k ≤ 20, -26 ≤ l ≤ 26
Reflections collected	227112	32832	108865
Independent reflections	11236 [R _{int} = 0.0781, R _{sigma} = 0.0260]	8902 [R _{int} = 0.1695, R _{sigma} = 0.1485]	20211 [R _{int} = 0.1982, R _{sigma} = 0.1326]
Data/restraints/parameters	11236/0/475	8902/454/439	20211/0/890
Goodness-of-fit on F ²	1.037	1.015	0.870
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0321, wR ₂ = 0.0701	R ₁ = 0.0700, wR ₂ = 0.1141	R ₁ = 0.0492, wR ₂ = 0.0967
Final R indexes [all data]	R ₁ = 0.0409, wR ₂ = 0.0738	R ₁ = 0.1305, wR ₂ = 0.1324	R ₁ = 0.1110, wR ₂ = 0.1177
Largest diff. peak/hole / e Å ⁻³	5.79/-2.59	1.51/-2.04	1.43/-3.05

Table S 3

Identification code	DG043_UGd_fa_sq	db053_0m_a (2-	DG054plate_tw_monoC
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	(2-Gd)	Dy)	(2-Ho)
CCDC Number	2110475	2110476	2110477
Empirical formula	C ₇₂ H ₁₄₄ Gd ₄ O _{23.25} U ₂	C ₇₂ H ₁₄₂ Dy ₄ O ₂₂ U ₂	C ₅₈ H ₁₂₀ Ho ₄ O ₂₄ U ₂
Formula weight	2486.92	2485.91	2337.31
Temperature/K	100.0	100.0	100.0
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /n	P2 ₁ /n	C2/m
a/Å	16.4891(13)	16.5252(13)	19.351(2)
b/Å	17.6043(14)	17.6822(13)	17.629(2)
c/Å	32.610(3)	32.478(3)	16.5056(19)
α/°	90	90	90
β/°	99.701(3)	99.612(5)	124.648(4)
γ/°	90	90	90
Volume/Å ³	9330.6(13)	9356.9(13)	4632.1(9)
Z	4	4	2
ρ _{calc} /g/cm ³	1.770	1.765	1.676
μ/mm ⁻¹	6.322	26.849	6.914
F(000)	4808.0	4792.0	2224.0
Crystal size/mm ³	0.10 × 0.10 × 0.10	0.5 × 0.1 × 0.1	0.23 × 0.224 × 0.148
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.99 to 52.772	5.52 to 146.054	4.622 to 55.754
Index ranges	-18 ≤ h ≤ 20, -22 ≤ k ≤ 14, -40 ≤ l ≤ 40	-20 ≤ h ≤ 20, -21 ≤ k ≤ 21, -39 ≤ l ≤ 40	-25 ≤ h ≤ 25, -23 ≤ k ≤ 21
Reflections collected	103999	189088	124112
Independent reflections	19090 [R _{int} = 0.0509, R _{sigma} = 0.0435]	18536 [R _{int} = 0.1387, R _{sigma} = 0.0722]	5680 [R _{int} = 0.0678, R _{sigma} = 0.0226]
Data/restraints/parameters	19090/910/933	18536/892/943	5680/66/375
Goodness-of-fit on F ²	1.417	1.090	1.184
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0878, wR ₂ = 0.2005	R ₁ = 0.0751, wR ₂ = 0.1639	R ₁ = 0.0565, wR ₂ = 0.1363
Final R indexes [all data]	R ₁ = 0.1004, wR ₂ = 0.2049	R ₁ = 0.1060, wR ₂ = 0.1845	R ₁ = 0.0650, wR ₂ = 0.1419
Largest diff. peak/hole / e Å ⁻³	8.33/-5.46	3.56/-1.92	2.19/-2.61

Table S 4

Identification code	mo_DG120_full2a (6-Ho)	mo_DG089new2_Pa-3a_sq (3-Yb)	shelx_sq (4-Sm)
CCDC Number	2110478	2111075	2110479

Empirical formula	C ₄₀ H ₉₂ Ho ₃ O ₁₄ U	C ₉₀ H ₁₉₈ O ₃₃ U ₃ Yb ₆	C ₆₀ H ₁₃₂ O ₂₂ Sm ₄ U ₂
Formula weight	1529.95	3560.80	2283.11
Temperature/K	100.0	100.0	293(2)
Crystal system	orthorhombic	cubic	orthorhombic
Space group	Pnma	Pa-3	Pnn2
a/Å	14.0962(5)	29.6894(10)	24.442(2)
b/Å	22.0046(8)	29.6894(10)	29.447(3)
c/Å	17.7241(7)	29.6894(10)	12.7021(10)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
Volume/Å ³	5497.7(4)	26170(3)	9142.2(14)
Z	4	8	4
ρ _{calc} /cm ³	1.848	1.808	1.659
μ/mm ⁻¹	7.259	8.001	6.112
F(000)	2948.0	13584.0	4400.0
Crystal size/mm ³	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1	0.26 × 0.04 × 0.02
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.692 to 58.26	3.88 to 50.668	3.87 to 50.156
Index ranges	-19 ≤ h ≤ 19, -30 ≤ k ≤ 30, -24 ≤ l ≤ 24	-35 ≤ h ≤ 35, -35 ≤ k ≤ 35, -35 ≤ l ≤ 35	-29 ≤ h ≤ 29, -35 ≤ k ≤ 35, -15 ≤ l ≤ 15
Reflections collected	232734	1207924	149356
Independent reflections	7578 [R _{int} = 0.0517, R _{sigma} = 0.0182]	7994 [R _{int} = 0.1253, R _{sigma} = 0.0129]	16179 [R _{int} = 0.1397, R _{sigma} = 0.0788]
Data/restraints/parameters	7578/0/297	7994/0/419	16179/766/837
Goodness-of-fit on F ²	1.103	1.185	1.027
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0226, wR ₂ = 0.0541	R ₁ = 0.0382, wR ₂ = 0.0817	R ₁ = 0.0427, wR ₂ = 0.0872
Final R indexes [all data]	R ₁ = 0.0247, wR ₂ = 0.0557	R ₁ = 0.0546, wR ₂ = 0.0956	R ₁ = 0.0663, wR ₂ = 0.0967
Largest diff. peak/hole / e Å ⁻³	1.74/-1.75	3.25/-1.51	0.85/-1.82

Table S 5

Identification code	mo_DG078_full_oP_r einta (5-Dy)	mo_DG107_Pnmaa (5-Ho)	mo_DG054_new2_0 m_full (3-Ho)
CCDC Number	2111783	2111784	2110480
Empirical formula	C ₄₀ H ₉₁ ClDy ₃ O ₁₃ U	C ₄₀ H ₉₂ ClHo ₃ O ₁₃ U	C ₃₀ H ₆₆ Ho ₂ O ₁₁ U
Formula weight	1541.10	1549.40	1170.71
Temperature/K	100.0	100.0	100.0

Crystal system	orthorhombic	orthorhombic	cubic
Space group	Pnma	Pnma	Pa-3
a/Å	14.2375(8)	14.1829(11)	29.7219(5)
b/Å	21.6260(13)	21.6096(13)	29.7219(5)
c/Å	17.8051(8)	17.8158(15)	29.7219(5)
α /°	90	90	90
β /°	90	90	90
γ /°	90	90	90
Volume/Å ³	5482.2(5)	5460.3(7)	26256.1(13)
Z	4	4	24
ρ_{calc} /g/cm ³	1.867	1.885	1.777
μ /mm ⁻¹	7.086	7.356	7.317
F(000)	2968.0	2984.0	13440.0
Crystal size/mm ³	0.1 × 0.1 × 0.1	0.249 × 0.126 × 0.088	0.1 × 0.1 × 0.1
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.118 to 54.964	4.126 to 50.724	4.112 to 50.694
Index ranges	-18 ≤ h ≤ 18, -28 ≤ k ≤ 28, -23 ≤ l ≤ 23	-17 ≤ h ≤ 17, -26 ≤ k ≤ 25, -21 ≤ l ≤ 21	-35 ≤ h ≤ 35, -34 ≤ k ≤ 35, -35 ≤ l ≤ 27
Reflections collected	219967	256608	134674
Independent reflections	6465 [R _{int} = 0.1138, R _{sigma} = 0.0263]	5141 [R _{int} = 0.1623, R _{sigma} = 0.0328]	8010 [R _{int} = 0.1000, R _{sigma} = 0.0416]
Data/restraints/parameters	6465/0/336	5141/323/337	8010/0/419
Goodness-of-fit on F ²	1.027	1.111	1.092
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0230, wR ₂ = 0.0471	R ₁ = 0.0362, wR ₂ = 0.0896	R ₁ = 0.0316, wR ₂ = 0.0694
Final R indexes [all data]	R ₁ = 0.0348, wR ₂ = 0.0506	R ₁ = 0.0559, wR ₂ = 0.1044	R ₁ = 0.0427, wR ₂ = 0.0746
Largest diff. peak/hole / e Å ⁻³	1.72/-0.93	1.26/-1.46	1.79/-1.05

Table S 6

Identification code	mo_DG122_full (7-Ho)	mo_DG127_fullc3_c (8-Ho)
CCDC Number	2110481	2110482
Empirical formula	C ₃₆ H ₈₁ Ho ₂ LiO ₁₁ U	C ₄₃ H ₉₄ Ho ₂ KO ₁₂ U
Formula weight	1264.83	1410.17
Temperature/K	100.0	100.0
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	10.5390(6)	11.0759(14)

b/Å	10.9635(6)	13.4602(17)
c/Å	21.2841(13)	20.604(3)
α /°	85.160(2)	89.721(5)
β /°	88.706(2)	85.951(5)
γ /°	79.534(2)	67.983(4)
Volume/Å ³	2409.7(2)	2839.8(6)
Z	2	2
ρ_{calc} /cm ³	1.743	1.649
μ /mm ⁻¹	6.650	5.725
F(000)	1228.0	1386.0
Crystal size/mm ³	0.453 × 0.351 × 0.282	0.195 × 0.166 × 0.133
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.362 to 54.966	3.964 to 50.7
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -27 ≤ l ≤ 27	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -24 ≤ l ≤ 24
Reflections collected	122129	213575
Independent reflections	11046 [R_{int} = 0.0840, R_{sigma} = 0.0390]	10402 [R_{int} = 0.0699, R_{sigma} = 0.0249]
Data/restraints/parameters	11046/0/487	10402/533/565
Goodness-of-fit on F ²	1.102	1.218
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0323, wR_2 = 0.0667	R_1 = 0.0638, wR_2 = 0.1661
Final R indexes [all data]	R_1 = 0.0394, wR_2 = 0.0696	R_1 = 0.0731, wR_2 = 0.1724
Largest diff. peak/hole / e Å ⁻³	1.59/-3.35	5.08/-8.12

Infrared spectra

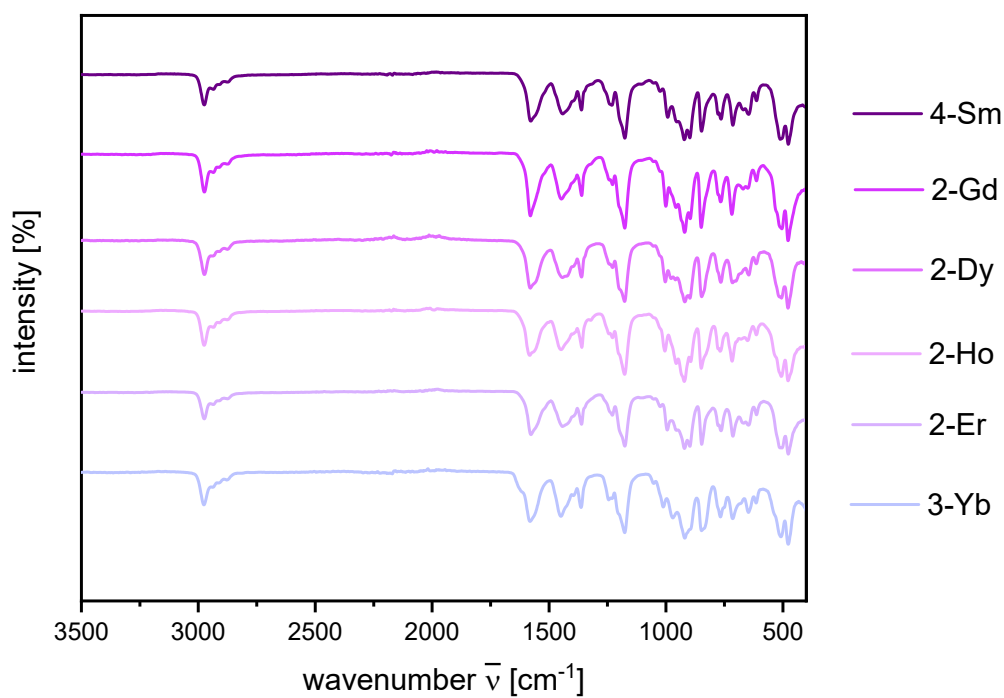


Figure S 31: Comparison of the IR spectra of $[Ln_2UO_2(O^tBu)_7(OAc)]_n$ (2-4-Ln).

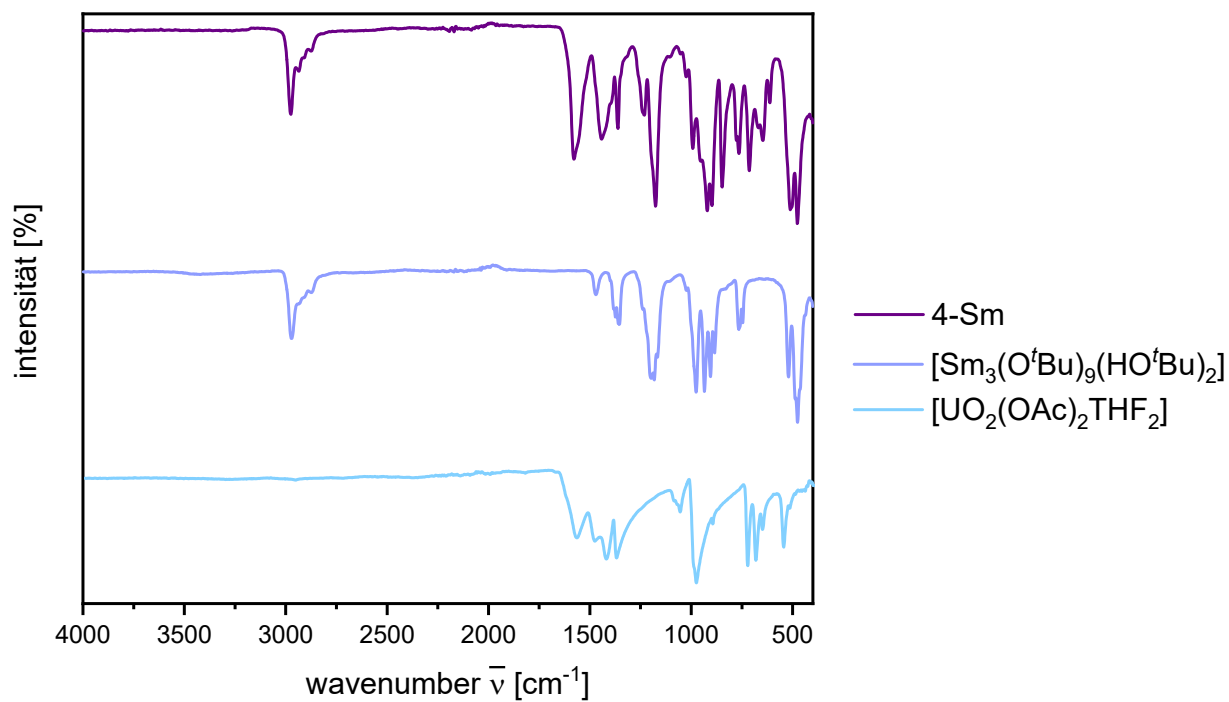


Figure S 32: Comparison of IR spectra of $[Sm_2UO_2(O^tBu)_7(OAc)]_4$ (4-Sm) with the starting materials $[Sm_3(O^tBu)_9(O^tBu)_2]$ and $[UO_2(OAc)_2(THF)_2]$.

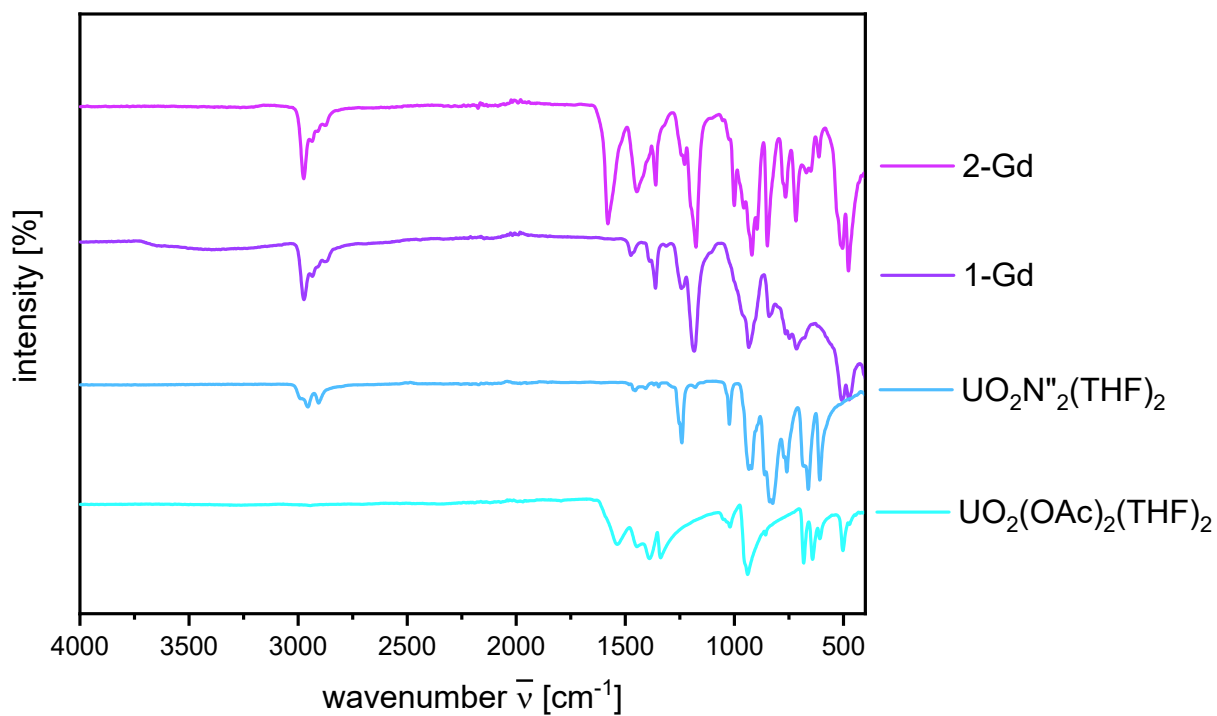


Figure S 33: Comparison of IR spectra of the dimeric $[\text{Gd}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})_4]$ (**2-Gd**) and the monomeric $[\text{Gd}_2\text{UO}_2(\text{O}^t\text{Bu})_8(\text{THF})_4]$ (**1-Gd**) with the starting materials $[\text{UO}_2(\text{OAc})_2(\text{THF})_2]$ and $[\text{UO}_2\text{N}''_2(\text{THF})_2]$.

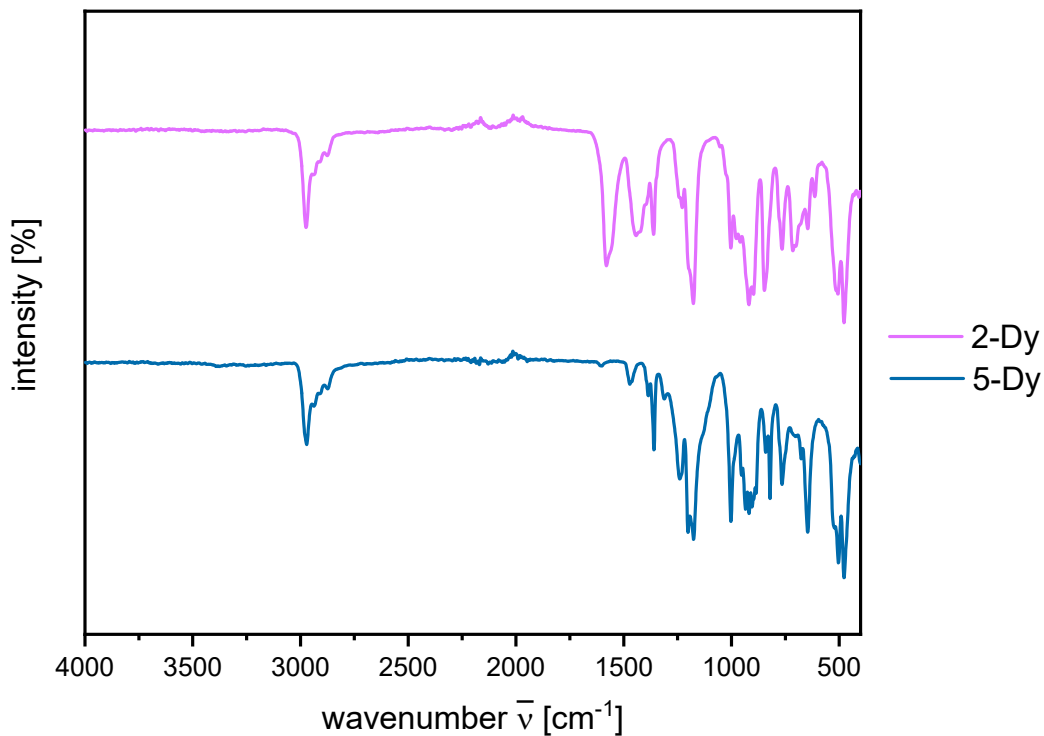


Figure S 34: Comparison of IR spectra of $[\text{Dy}_2\text{UO}_2(\text{O}^t\text{Bu})_7(\text{OAc})_2]$ (**2-Dy**) with $[\text{Dy}_3\text{UO}_2(\text{O}^t\text{Bu})_{10}\text{Cl}(\text{H}_2\text{O})]$ (**5-Dy**).

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