Differential uranyl(V) oxo-group bonding between the uranium and metal cations from groups 1, 2, 4, and 12; a high-energy X-ray absorption, computational, and synthetic study

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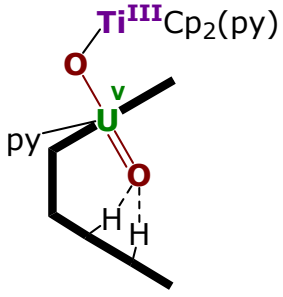
1. Synthetic and analytical details

All manipulations were carried out under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or an MBraun Unilab glovebox. Deuterated pyridine and deuterated benzene were boiled over potassium, distilled and freeze-pump-thaw degassed three times prior to use. All other solvents were purged with nitrogen and dried using Vacuum Atmospheres drying towers. Pyridine was degassed and distilled from potassium. ^{1}H NMR spectra were recorded on a Bruker ava400 spectrometer at 298 K operating at 399.90 MHz. ^{13}C{^{1}H} NMR spectra were recorded on a Bruker ava500 spectrometer operating at 125.76 MHz. Chemical shifts are given in parts per million (ppm) and referenced to residual resonances of the respective solvent. IR spectra were recorded in the range of 400-4000 cm^{-1} on a Nicolet Avatar 360 FT-IR spectrometer as nujol mulls between NaCl disks. Elemental analyses were carried out by Mr. Stephen Boyer, London Metropolitan University. Variable temperature magnetic susceptibility (dc and ac) measurements were carried out at the University of Edinburgh and made on a Quantum Design Magnetic Property Measurement System (SQUID magnetometer) equipped with a 7T magnet operating in the 350±2 K temperature range. Diamagnetic corrections were applied using Pascal's constants. The sample was placed in a gelatine capsule and fitted inside a plastic straw. The data analysis was carried out at the Institute for Transuranium Elements in Karlsruhe, Germany.

1.1 Syntheses

$[(UO_2)(py)(H_2L)]$[2] **A**, $Cp_2Ti(\eta^2\text{-}C_2(SiMe_3)_2$[3], $[Cp_2TiCl]_2$[4] and $Cp_2Zr(\eta^2\text{-}C_2(SiMe_3)_2)\cdot py$[5] were synthesised according to literature procedures.

$[(py)(Cp_2Ti^{III}OUO)(py)(H_2L)]$ 1



A brown suspension of $[(UO_2)(py)(H_2L)]$ **A** (300 mg, 0.226 mmol) in C_6H_6 (5.0 mL) was combined with $Cp_2Ti(\eta^2\text{-}C_2(SiMe_3)_2$ (78.9 mg, 0.226 mmol) at room temperature to form a light brown solution. The solvent was reduced to *ca.* 1.5 mL under vacuum to afford $[(py)(Cp_2TiOUO)(py)(H_2L)]$ **1** as a beige powder. The mother liquor was filtered and the powder recrystallised from pyridine to afford red crystals suitable for X-ray diffraction. The pyridine was decanted and the crystals were isolated and dried under vacuum. Yield: 230 mg (73%).

^{1}H-NMR (C_6D_6, 400 MHz): δ_H -5.71 (s, 3H, CH_3), -5.09 (s, 3H, CH_3), -3.57 (s, 2H), -1.53 (s, 6H, Ph-CH_3), -0.07 (s, 6H, Ph-CH_3), 0.16 (s, 10H, C_5H_5), 0.51 (s, 2H, pyrrole), 0.99 (s, 2H, pyrrole), 7.70 (s, 2H), 8.27 (s, 3H, CH_3), 10.63 (d, 2H, pyrrole, $^{3}J_{H\text{-}H}$ = 4 Hz), 12.53 (d, 2H, pyrrole, $^{3}J_{H\text{-}H}$ = 4 Hz), 21.24 (s, 3H, CH_3), 71.35 (br, 2H, NH); ^{1}H-NMR (C_5D_5N, 400 MHz): δ_H -11.09 (s, 3H, CH_3), -5.95 (s, 3H, CH_3), -3.02 (s, 2H), -2.38 (br, 6H, Ph-CH_3), -1.64 (s, 10H, C_5H_5), -0.62 (s, 6H, Ph-CH_3), 1.13 (s, 2H), 8.21 (s, 2H), 9.10 (s, 2H), 11.08 (s, 3H, CH_3), 13.18 (s, 2H), 25.54 (s, 3H, CH_3), 75.40 (br, 2H, NH);

$^{13}C\{^{1}H\}$-NMR (C_6D_6): δ_C 10.06, 15.92, 18.15, 20.80, 34.23, 52.63, 106.46, 109.15, 114.54, 116.34, 122.54, 123.17, 123.42, 125.90, 126.47, 146.04, 149.26, 163.54; Analysis. Found: C, 59.71; H, 5.12; N, 11.53 % $C_{67}H_{67}N_{11}O_2TiU$ requires: C, 59.86; H, 5.02; N, 11.46 %; FTIR (nujol, cm^{-1}): n 2925 (w, NH), 2854 (w, NH), 1581 (w, imine), 1461 (s, L), 1377 (s, L), 1288 (m, L), 1268 (m, L), 1181 (w, L), 1044 (m, L), 1019 (m, L), 893 (w, asymm. UO stretch), 865 (w, L), 800 (s, L), 722 (w, L). L = stretches attributed to the Pacman ligand.

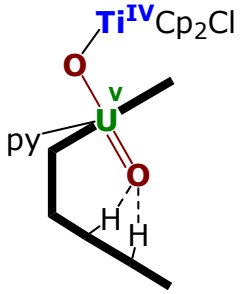
Magnetic measurements and calculations

The magnetic properties of the Ti(III)-U(V) complex **1** were modelled assuming that the former $3d^1$ ion is represented by a pure-spin moment $S = 1/2$ and the latter $5f^1$ ion by a total (orbital+spin) moment $J = 5/2$. The Hamiltonian which describes the quantum states of the U-Ti pair in an external magnetic field **B** can then be written as $-2J_{ex}S \cdot J + B_2^0O_2^0(J) + B_4^0O_4^0(J) - \mu_B B \cdot (g_S S + g_J J)$, where J_{ex} is the exchange coupling constant, the B_k^q's (O_k^q's) are the ligand-field parameters (operators) for the U(V) ion, and the *g*'s are the gyromagnetic factors. No ligand-field parameters have been explicitly considered for the Ti(III) sites because its orbital moment is expected to be quenched; for the same reason, we can safely assume that $g_S = 2$. The choice of a purely axial ligand-field potential for U(V) was made assuming that the two linearly arranged O atoms account for the large majority of it, and that the five N's in the equatorial plane mostly contribute with a term proportional to $O_6^5(J)$ which, however, does not affect a $J = 5/2$ moment (the Stevens factor γ is equal to zero). Mixing of the ground state with the excited $J = 7/2$ spin-orbit multiplet was not investigated in detail, but it was effectively taken into account by using g_J as a variable fitting parameter instead of fixing its value to the usual Landé factor (6/7 for the f^1 configuration); this can also account for covalency, to the extent where it can be described by an orbital reduction factor k_L defined so that $g_J J = k_L L + 2S$. The best fit of the susceptibility curve, shown in the main panel of Fig. X as χT-vs-T, was found with the parameters $g_J = 0.80$, $B_2^0 = -30$ cm^{-1}, $B_4^0 = 1.9$ cm^{-1}, and $J_{ex} = -0.97$ cm^{-1}. The relatively small value of the coupling constant explains why no clear antiferromagnetic behaviour is visible above 5 K, for example as a maximum in the χ-*vs*.-T curve. The signs of B_2^0 and B_4^0 are the same as for the Stevens factors α and β for the f^1 configuration, which means that their geometrical factor is positive in both cases, as expected for two O ligands coordinated at an angle close to 180°.

According to the above calculations, the single-ion ground state of U(V) is the $J_z = \pm 3/2$ doublet, separated from the ±5/2 level by 95 cm^{-1} and from the ±1/2 level by 760 cm^{-1}. Indeed, the dc susceptibility plotted as 1/χ vs *T* is nearly linear in the low-temperature region, where only the ground state is thermally populated. The best fit to a Curie-Weiss behaviour $1/\chi = (T - \theta)/C$ gives $\theta = -1.7\ K$ and $C = 0.585\ emu\ K/mol$. The sum of the contribution to *C* of a pure-spin $S_z = \pm 1/2$ doublet (0.375 emu K/mol) and of a $J_z = \pm 3/2$ ligand-field doublet (0.207 emu K/mol) gives 0.574 emu

K/mol, in excellent agreement with the experimental value, and the small negative value of θ confirms that the U and Ti ions are weakly antiferromagnetically coupled.

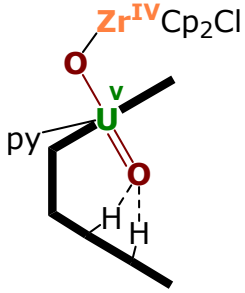
[ClCp$_2$Ti^{IV}OUO(py)(H$_2$L)] 2



A brown suspension of [(UO$_2$)(py)(H$_2$L)] A (40.6 mg, 0.033 mmol) in C$_6$D$_6$ (0.5 mL) was combined with [Cp$_2$TiCl]$_2$ (7.1 mg, 0.0165 mmol) to form a light orange-brown solution. The suspension was sonicated at 70 °C for 70 minutes to afford an orange-yellow solution. The mixture was centrifuged and allowed to crystallise by solvent evaporation to afford [ClCp$_2$TiOUO(py)(H$_2$L)] 2 as dark red crystals suitable for X-ray diffraction. The crystals were isolated by decanting the mother liquor and dried under vacuum. Yield: 29 mg (72%).

^{1}H-NMR (C$_6$D$_6$): δ_H -5.49 (s, 3H, C*H*$_3$), -4.24 (s, 2H), -4.19 (s, 3H, C*H*$_3$), -0.95 (s, 6H, Ph-C*H*$_3$), -0.47 (s, 6H, Ph-C*H*$_3$), 0.03 (s, 2H), 0.41 (s, 2H, pyrrole), 0.89 (s, 2H, pyrrole), 2.55 (s, 2H), 6.68 (br, 2H, pyridine), 6.99 (br, 1H, pyridine), 7.38 (s, 3H, C*H*$_3$), 8.45 (s, 2H), 8.56 (s, 2H, pyridine), 10.40 (d, 2H, pyrrole, $^3J_{H\text{-}H}$ = 4 Hz), 11.89 (d, 2H, pyrrole, $^3J_{H\text{-}H}$ = 4 Hz), 16.48 (s, 10H, C$_5$*H*$_5$), 18.21 (s, 3H, C*H*$_3$), 63.95 (s, 2H, N*H*); ^{13}C{^{1}H}-NMR (C$_6$D$_6$): δ_C 15.94, 16.35, 16.78, 22.88, 32.99, 50.46, 50.57, 68.16, 73.35, 107.03, 108.14, 110.65, 112.84, 113.48, 115.34, 119.12, 121.76, 122.75, 123.91, 124.75, 125.81, 127.20, 127.49, 131.12, 135.60, 137.48, 145.38, 151.98, 161.52; Analysis. Found: C, 55.66; H, 4.52; N, 10.18 % C$_{57}$H$_{57}$ClN$_9$O$_2$TiU requires: C, 56.05; H, 4.70, N, 10.32 %; FTIR (nujol, cm^{-1}): n 2926, (w, NH/nujol), 2854 (w, nujol), 1580 (w, imine), 1462 (s, nujol), 1377 (s, nujol), 1288 (m, L), 1265 (m, L), 1216 (m, L), 1076 (m, L), 1038 (m, L), 1018 (m, L), 893 (w, asymm. UO stretch), 811 (w, L), 766 (s, L), 722 (w, nujol). L = stretches attributed to the Pacman ligand.

[ClCp$_2$ZrOUO(py)(H$_2$L)] 3



In situ reduction with Mg: A brown suspension of [(UO$_2$)(py)(H$_2$L)] **A** (100 mg, 0.076 mmol) in C$_5$D$_5$N (0.5 mL) was combined with Cp$_2$ZrCl$_2$ (22.0 mg, 0.076 mmol) and one piece of Mg turnings at room temperature to form a pale brown suspension. The suspension was sonicated at 70 °C for 70 minutes to afford an orange-yellow solution. The mixture was centrifuged and allowed to crystallise by solvent evaporation to afford [ClCp$_2$ZrOUO(py) (H$_2$L)]·MgCl$_2$ **3-MgCl2** as beige crystals suitable for X-ray diffraction. The crystals were isolated by decanting the mother liquor and dried under vacuum. Yield: 63 mg (66%).

In situ reduction with Zr(II): A mixture of Cp$_2$ZrCl$_2$ (200 mg, 0.69 mmol) and Cp$_2$Zr(η^2-C$_2$(SiMe$_3$)$_2$)·py (324.6 mg, 0.69 mmol) in pyridine was added to a brown suspension of [(UO$_2$)(py)(H$_2$L)] **A** (383 mg, 0.35 mmol) in benzene (3 mL) at room temperature and allowed to stir for 24 hours. The resulting red

solution was evaporated to 1 mL and the yellow precipitated isolated by centrifugation (2 min, 6000 rpm). The mother liquor was removed and the precipitate was recrystallised from THF to afford light red crystals of [$ClCp_2ZrOUO(py)(H_2L)$] **3** suitable for X-ray diffraction. The crystals were isolated by decanting the mother liquor and dried under vacuum. Yield: 260 mg (60%).

^{1}H-NMR (C_6D_6, 600MHz): δ_H -6.14 (s, 3H, CH_3), -3.92 (s, 3H, CH_3), -2.31 (s, 3H, CH_3), -0.85 (s, 6H, Ph-CH_3), -0.67 (s, 2H), -0.26 (s, 6H, Ph-CH_3), 0.23 (s (br), 2H, pyrrole), 1.64 (s (br), 2H, pyrrole), 2.58 (s, 2H), 7.05 (s, 2H), 8.35 (s, 2H), 10.20 (s, 2H, pyrrole), 11.58 (s, 2H, pyrrole), 14.94 (s, 10H, C_5H_5), 16.96 (s, 3H, CH_3), 61.82 (br, 2H, N*H*); ^{1}H-NMR (C_5D_5N, 400 MHz): δ_H -5.65 (s, 3H, CH_3), -4.18 (s, 3H, CH_3), -1.92 (s, 3H, CH_3), -0.85 (s, 6H, Ph-CH_3), -0.15 (s, 6H, Ph-CH_3), 1.30 (d, 2H, pyrrole, $^3J_{H\text{-}H}$ = 4 Hz), 1.41 (d, 2H, pyrrole, $^3J_{H\text{-}H}$ = 4 Hz), 2.50 (s, 2H), 7.35 (s, 2H), 8.44 (s, 2H), 10.38 (d, 2H, pyrrole, $^3J_{H\text{-}H}$ = 4 Hz), 11.80 (d, 2H, pyrrole, $^3J_{H\text{-}H}$ = 4 Hz), 15.57 (s, 10H, C_5H_5), 17.87 (s, 3H, CH_3), 63.32 (br, 2H, N*H*); ^{1}H-NMR (THF-d_8, 500 MHz): δ_H -5.54 (s, 3H, CH_3), -3.86 (s, 3H, CH_3), -1.89 (s, 2H), -0.66 (s, 6H, Ph-CH_3), -0.03 (s, 6H, Ph-CH_3), 1.30 (d, 2H, pyrrole, $^3J_{H\text{-}H}$ = 5 Hz), 1.54 (d, 2H, pyrrole, $^3J_{H\text{-}H}$ = 5 Hz), 2.71 (s, 2H), 7.29 (s, 2H), 8.48 (s, 2H), 10.24 (d, 2H, pyrrole, $^3J_{H\text{-}H}$ = 5 Hz), 11.61 (d, 2H, pyrrole, $^3J_{H\text{-}H}$ = 5 Hz), 15.10 (s, 10H, C_5H_5), 17.26 (s, 3H, CH_3), 61.37 (br, 2H, N*H*); ^{13}C{^{1}H}-NMR (THF-d_8): δ_C 0.33, 16.01, 16.53, 23.90, 32.94, 42.74, 50.02, 78.11, 107.48, 111.06, 111.22, 114.52, 114.98, 115.05, 116.77, 120.72, 122.35, 122.53, 126.77, 131.06, 136.18, 145.16, 150.81, 151.22, 160.53 Analysis. Found: C, 54.26; H, 4.63; N, 9.86% $C_{57}H_{57}ClN_9O_2ZrU$ requires: C, 54.13; H, 4.54, N, 9.97 %; FTIR (nujol, cm^{-1}): n 2924 (w, nujol), 2854 (w, nujol), 1580 (w, imine), 1462 (s, nujol), 1377 (s, nujol), 1286 (m, L), 1263 (m, L), 1046 (m, L), 1019 (w), 894 (w, asymm. UO stretch), 803 (w, L), 722 (m, nujol). L = stretches attributed to the Pacman ligand.

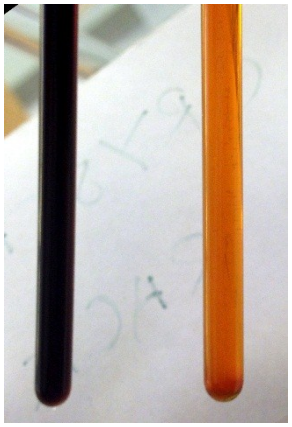
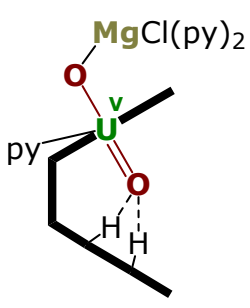


Figure S1: NMR samples of **A** (left) and **3** (right) in pyridine-d_5. (Photo: Max McMullon)

[$(py)_2ClMgOUO(py)(H_2L)$] 4



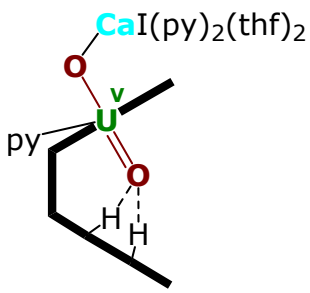
A mixture of **A** (274.2 mg, 0.246 mmol), $MgCl_2$ (11.7 mg, 0.123 mmol) and Mg (3.0 mg, 0.123 mmol) was suspended in pyridine (5 mL), sonicated for 160 minutes and stirred for 72 hours to form a cherry red solution. The mixture was

dried and recrystallised from pyridine, affording beige crystals of $[(py)_2(ClMgOUO)(py)(H_2L)]$ **12** suitable for X-ray structural analysis. The crystals were decanted and dried under vacuum. Yield: 210.0 mg (69%).

From mixture with Cp_2TiCl_2: To a mixture of **A** (300.0 mg, 0.18 mmol), Cp_2TiCl_2 (45.5 mg, 0.18 mmol) and Mg (4.4 mg, 0.18 mmol) pyridine (2 mL) was added and the dark brown suspension was allowed to stir at room temperature for 48 hours to give a dark red solution. The solution was centrifuged (2 min, 6000 rpm) and the mother liquor was allowed to evaporate slowly to afford light beige crystals of $[(py)_2ClMgOUO(py)(H_2L)]$ **4** suitable for X-ray diffraction. The crystals were isolated by decanting the mother liquor and dried under vacuum. Yield: 129 mg (58%).

^{1}H-NMR (C_5D_5N): δ_H -6.20 (s, 3H, C*H*$_3$), -5.99 (s, 3H, C*H*$_3$), -2.04 (s, 6H, Ph-C*H*$_3$), -1.76 (s, 3H, C*H*$_3$), -1.13 (s, 2H), -0.29 (s, 2H), 0.23 (s, 6H, Ph-C*H*$_3$), 0.99 (s, 2H), 2.83 (s, 2H), 6.85 (s, 2H), 9.32 (s, 3H, C*H*$_3$), 10.64 (s, 3H, C*H*$_3$), 13.08 (s, 2H), 77.28 (br, 2H, N*H*); ^{13}C{^{1}H}-NMR (C_5D_5N): δ_C 12.32, 15.08, 16.23, 16.78, 17.62, 27.07, 36.81, 56.16, 67.03, 69.09, 94.29, 100.89, 106.05, 108.55, 112.93, 118.06, 119.72, 122.33, 127.19, 129.99, 141.38, 146.26, 147.64, 148.59, 165.89, 179.11 Analysis. Found: C, 55.68; H, 4.58; N, 12.46% $C_{57}H_{57}ClMgN_{11}O_2U$ requires: C, 55.84; H, 4.69, N, 12.57 %; FTIR (nujol, cm^{-1}): n 2925 (w, NH/nujol), 2725 (w, NH), 1580 (w, imine), 1462 (s, nujol), 1377 (s, nujol), 1286 (m, L), 1213 (w, L), 1155 (w, L), 1041 (m, L), 973 (s), 891 (w, asymm. UO stretch), 827 (w, L), 722 (s, nujol). L = stretches attributed to the Pacman ligand.

$[(py)_2(thf)_2ICaOUO(py)(H_2L)]$ 5

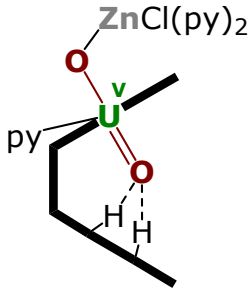


A mixture of **A** (200.0 mg, 0.180 mmol), CaI_2 (26.4 mg, 0.090 mmol) and Ca (3.6 mg, 0.090 mmol) was suspended in pyridine (3 mL), sonicated for 60 minutes at 50°C and stirred for 48 hours at room temperature to form a red solution. The mixture was dried and recrystallised from tetrahydrofuran, affording pale red translucent plates of $[(py)_2(thf)_2ICaOUO(py)(H_2L)]$ **5** suitable for X-ray structural analysis. The liquors were decanted and the crystals dried under vacuum. Yield: 210.0 mg (69%).

^{1}H-NMR (C_5D_5N): δ_H -8.41 (s, 2H), -6.32 (s, 3H, C*H*$_3$), -2.65 (s, 2H), -2.17 (s, 6H, Ph-C*H*$_3$), -0.63 (s, 3H, C*H*$_3$), -1.36 (s, 2H), -1.23 (s, 2H), 0.23 (s, 6H, Ph-C*H*$_3$), 0.85 (s, 2H), 1.59 (s, 2H), 6.83 (s, 2H), 9.76 (s, 3H, C*H*$_3$), 10.80 (s, 2H), 13.38 (s, 2H), 28.16 (s, 3H, C*H*$_3$), 79.30 (br, 2H, N*H*); ^{13}C{^{1}H}-NMR (C_5D_5N): δ_C 13.80, 15.16, 16.34, 17.67, 22.14, 23.00, 26.02, 31.86, 36.15, 55.82, 60.71, 68.08, 89.47, 96.42, 106.99, 108.18, 112.91, 114.36, 117.05, 121.04, 125.86, 147.11, 165.55 Analysis. Found: C, 49.00; H, 4.35; N, 10.03% $C_{51}H_{55}CaIN_9O_3U$ requires: C, 49.12; H, 4.45, N, 10.11 %; FTIR (nujol, cm^{-1}): n 2932 (w, nujol), 2725 (w, NH), 1552 (w, imine), 1462 (s, nujol), 1377 (s, nujol), 1272 (m, L), 1214

(w, L), 1179 (w, L), 1042 (m, L), 970 (s), 891 (w, asymm. UO stretch), 828 (w, L), 722 (s, nujol). L = stretches attributed to the Pacman ligand.

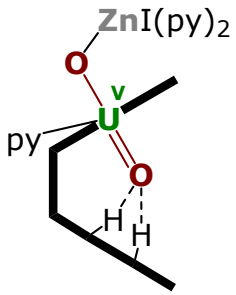
[(py)$_2$ClZnOUO(py)(H$_2$L)] 6



A mixture of **A** (100.0 mg, 0.092 mmol), $ZnCl_2$ (6.3 mg, 0.046 mmol) and Zn (3.0 mg, 0.046 mmol) was suspended in pyridine (3 mL), sonicated for 80 minutes to form a red solution which was left stirring overnight at room temperature to form a lemon yellow suspension. The mixture was centrifuged and the precipitate extracted with fresh pyridine, forming a yellow solution from which yellow, translucent plates of [(py)$_2$ClZnOUO(py)(H$_2$L)] **6** crystallised, which were suitable for X-ray structural analysis. The crystals were isolated by decanting the mother liquor, followed by drying under vacuum. Yield: 83.0 mg (71%).

^{1}H-NMR (C_5D_5N): δ_H -5.83 (s, 3H, C*H*$_3$), -4.30 (s, 2H), -1.77 (s, 6H, Ph-C*H*$_3$), -1.41 (s, 2H), -0.29 (s, 2H), -0.22 (s, 2H), 0.58 (s, 6H, Ph-C*H*$_3$), 3.65 (s, 2H), 6.67 (s, 2H), 9.24 (s, 3H, C*H*$_3$), 10.51 (s, 2H), 12.93 (s, 2H), 25.98 (s, 3H, C*H*$_3$), 75.37 (br, 2H, N*H*); ^{13}C{^{1}H}-NMR (C_5D_5N): δ_C 9.61, 11.55, 14.66, 15.47, 16.96, 23.27, 24.51, 26.25, 32.14, 35.57, 39.52, 68.28, 95.12, 101.33, 108.09, 110.57, 116.86, 117.61, 126.79, 147.79, 164.28 Analysis. Found: C, 49.00; H, 4.35; N, 10.03% $C_{57}H_{57}ClN_{11}O_2UZn$ requires: C, 54.03; H, 4.53, N, 12.16 %; FTIR (nujol, cm^{-1}): n 2954 (w, NH), 2723 (w, NH), 1563 (w, imine), 1462 (s, nujol), 1377 (s, nujol), 1287 (m, L), 1217 (w, L), 1154 (w, L), 1040 (m, L), 972 (s, L), 893 (w, asymm. UO stretch), 770 (w, L), 722 (s, nujol). L = stretches attributed to the Pacman ligand.

[(py)$_2$IZnOUO(py)(H$_2$L)] 7

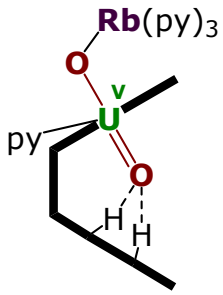


A mixture of **A** (100.0 mg, 0.092 mmol), ZnI_2 (14.6 mg, 0.046 mmol) and Zn (3.0 mg, 0.046 mmol) was suspended in pyridine (3 mL), sonicated for 30 minutes to form a red solution which was left stirring overnight at room temperature to form a lemon yellow suspension. The mixture was centrifuged and the precipitate extracted with fresh pyridine, forming a yellow solution from which yellow, translucent plates of [(py)$_2$IZnOUO(py)(H$_2$L)] **7** crystallised, which were suitable for X-ray structural analysis. The crystals were isolated by decanting the mother liquor, followed by drying under vacuum. Yield: 91.2 mg (73%).

^{1}H-NMR (C_5D_5N): δ_H -5.71 (s, 3H, C*H*$_3$), -4.86 (s, 2H), -1.75 (s, 6H, Ph-C*H*$_3$), -1.33 (s, 2H), -0.57 (s, 2H), -0.11 (s, 2H), 0.47 (s, 6H, Ph-C*H*$_3$), 3.35 (s, 2H), 6.74 (s, 2H), 9.14 (s, 3H, C*H*$_3$), 10.47 (s, 2H), 12.84 (s, 2H), 25.75 (s, 3H, C*H*$_3$), 74.52 (br, 2H, N*H*); Analysis. Found: C, 50.51; H, 4.35; N, 11.31% $C_{57}H_{57}IN_{11}O_2UZn$ requires: C, 50.40; H, 4.23, N, 11.34 %; FTIR (nujol, cm^{-1}): n 2928 (w, nujol), 2853 (w, nujol), 1559 (w, imine), 1462 (s, nujol), 1377 (s, nujol), 1287 (m, L), 1215 (w, L), 1182 (w, L),

1046 (m, L), 978 (s, L), 892 (w, asymm. UO stretch), 769 (w, L), 722 (s, nujol). L = stretches attributed to the Pacman ligand.

[(py)$_3$RbOUO(py)(H$_2$L)] 8



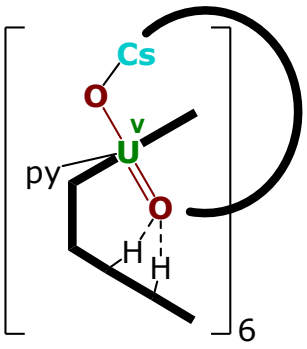
Rb metal (6.6 mg, 0.077 mmol) was added to a dark brown solution of **A** (82.9 mg, 0.076 mmol) in C_5D_5N (1.0 mL) in a Teflon-tapped reaction ampoule and allowed to react at room temperature for 3 h to form an intensely dark red solution. The solution was centrifuged (6000 rpm/ 1 min) and syringe filtered (0.45 µm PTFE filter) into a Teflon-tapped NMR tube. The volume was concentrated by removing the solvent under vacuum to a volume of ca. 0.3 mL to afford dark red prismatic crystals of [(py)$_3$RbOUO(py)(H$_2$L)] **8** suitable for X-ray diffraction. The crystals were decanted and dried under vacuum. Yield: 66.0 mg (64%).

[RbOUO(py)(H$_2$L)]$_6$ 8b dark red-brown crystals of the less-solvated form, the Rb congener to the hexamer **9** [(py)$_3$RbOUO(py)(H$_2$L)] **8b** were grown by evaporation of a pyridine solution of **8** over a period of 21 months.

Spectroscopic data for **8** (not 8b)**:** ^{1}H-NMR (C_5D_5N): δ_H -7.36 (s, 3H, C*H*$_3$), -6.15 (s, 3H, C*H*$_3$), -3.60 (s, 2H), -2.63 (s, 6H, Ph-C*H*$_3$), -2.47 (s, 2H), -0.94 (s, 2H), 0.05 (s, 2H), 0.84 (s, 6H, Ph-C*H*$_3$), 5.20 (s, 2H), 5.38 (s, 2H), 10.98 (s, 2H), 11.12 (s, 3H, C*H*$_3$), 14.32 (s, 2H), 32.82 (s, 3H, C*H*$_3$), 92.37 (br, 2H, N*H*); ^{13}C{^{1}H}-NMR (C_5D_5N): δ_C 15.30, 16.98, 19.67, 19.69, 19.72, 20.11, 106.15, 106.43, 108.28, 109.32, 112.88, 115.06, 115.10, 115.18, 115.57, 118.22, 118.48, 118.94, 120.47, 120.86, 122.38, 122.86, 126.54, 133.10, 133.21, 134.03, 134.74, 135.06, 140.51, 141.29, 141.81, 142.85, 144.37, 144.76, 146.44, 147.04, 148.33, 152.42, 159.49; Analysis. Found: C, 56.12; H, 4.63; N, 12.70 % $C_{62}H_{62}N_{12}O_2RbU$ requires: C, 55.96; H, 4.70, N, 12.63 %; FTIR (nujol, cm^{-1}): n 3368 (w, NH) 2927 (nujol), 2854 (w, nujol), 1582 (w, imine), 1462 (s, nujol), 1377 (s, nujol), 1290 (m, L), 1214 (w, L), 1039 (m, L), 1000 (w, L), 963 (s), 892 (w, asymm. UO stretch), 771 (m, L), 722 (s, nujol). L = stretches attributed to the Pacman ligand.

Figure S2: Single crystals of **8**. Dimensions: 5 mm × 3 mm × 2.5 mm (left, on cap of Young's 5mm diameter tube NMR spectroscopy tube); 1.5 mm × 1.5 mm × 0.8 mm (right, seen through microscope). (Photos: Rianne M. Lord)

[CsOUO(py)(H$_2$L)]$_6$ 9



Cs metal (24.7 mg, 0.186 mmol) was added to a dark brown solution of **A** (202 mg, 0.186 mmol) in C_5D_5N (1.0 mL) in a Teflon-tapped reaction ampoule and allowed to react at room temperature for 30 minutes to form an intensely dark red solution. The solution was syringe filtered (0.45 µm PTFE filter) into a Teflon-tapped NMR tube. The volume was concentrated by removing the solvent under vacuum to a volume of ca. 0.3 mL to afford after three weeks small rectangular red crystals of [CsOUO(py)(H$_2$L)]$_6$ **9** suitable for X-ray diffraction. The liquors were decanted and the crystals dried under vacuum. Yield: 144.0 mg (68 %).

^{1}H-NMR (C_5D_5N): δ_H -7.01 (s, 3H, C*H*$_3$), -5.73 (s, 3H, C*H*$_3$), -3.46 (s, 2H), -2.65 (s, 6H, Ph-C*H*$_3$), -0.82 (s, 2H), 0.98 (s, 6H, Ph-C*H*$_3$), 2.05 (br, 4H), 5.42 (br, 2H), 5.69 (br, 2H), 11.06 (s, 2H), 11.37 (s, 3H, C*H*$_3$), 14.48 (s, 2H), 33.78 (s, 3H, C*H*$_3$), 92.21 (br, 2H, N*H*); Analysis. Found: C, 49.56; H, 4.26; N, 11.02 % $C_{47}H_{47}CsN_9O_2U$ requires: C, 49.48; H, 4.15, N, 11.05 %; FTIR (nujol, cm^{-1}): n 3368 (w, NH) 2906 (nujol), 1582 (s, imine), 1461 (s, nujol), 1377 (s, nujol), 1289 (m, L), 1213 (w, L), 1041 (m, L), 1017 (w, L), 960 (w), 892 (m, asymm. UO stretch), 775 (m, L), 721 (s, nujol). L = stretches attributed to the Pacman ligand.

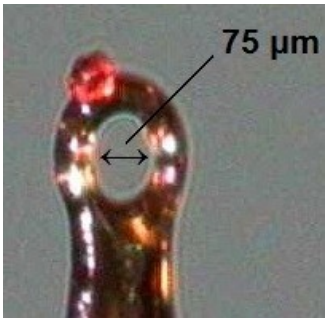


Figure S3: Single crystal of **9** mounted on the goniometer head MicroLoop™ for X-ray diffraction studies. Size of the crystal: 0.05 mm × 0.04 mm × 0.03 mm.

A + Mg

To a brown suspension of **A** (84.0 mg, 0.074 mmol) in C_5H_5N (2 ml) Mg metal (0.89 mg, 0.037 mmol) was added and the mixture was allowed to stir for 24 hours at room temperature to form an orange-red suspension. The suspension was filtered and the ^{1}H-NMR spectrum recorded. The spectrum showed the formation of paramagnetic resonances which can be attributed to a uranyl(V) complex. Any attempts to isolate this complex have failed. The solvent of the filtered solution was removed under vacuum to yield a thick red viscous material. Cooling a concentrated solution to -35 ºC or diffusion of hexane failed to give any isolable material.

^{1}H-NMR (C_5D_5N): δ_H -6.91 (s, 2H), -3.10 (s, 6H, Ph-C*H*$_3$), -2.34 (s, 3H, C*H*$_3$), -1.50 (s, 2H), -0.46 (s, 2H), 0.76 (s, 6H, Ph-C*H*$_3$), 1.83 (s, 3H, C*H*$_3$), 6.25 (s, 2H), 8.43 (s, 2H), 10.72 (s, 2H), 10.98 (s, 3H, C*H*$_3$), 14.06 (s, 2H), 31.64 (s, 3H, C*H*$_3$), 88.16 (br, 2H, N*H*)

1.2 Crystallographic information

Single crystal X-Ray diffraction data was collected using an Oxford Diffraction Supernova instrument at 120 K, fitted with a CCD area detector using CuKα radiation (λ = 1.5418 Å) or MoKα radiation (λ = 0.7107 Å) or using an Eos Excalibur instrument at 170 K using MoKα radiation (λ = 0.7107 Å). Structural solution and refinement was carried out using either SHEL-XS-97 direct methods,[6] SHEL-XS-97 Patterson methods,[6] *SIR*92[7] or the SUPERFLIP charge-flipping program[8] and refined using a full-matrix least square refinement on $|F|^2$ using SHELXL-97.[6] All programs were used either within the *WinGx* suite[9] or *OLEX*2.[10] CCDC codes 1883750-1883758.

1.3 Crystallographic Data Summary Tables

Crystal data			
Compound	**[(py)Cp$_2$TiOUO(py)(H$_2$L)] 1**	**[ClCp$_2$TiOUO(py)(H$_2$L)] 2**	**[ClCp$_2$ZrOUO(py)(H$_2$L)] 3**
Chemical formula	$C_{80}H_{80}N_{13}O_2TiU$	$C_{87}H_{87}ClN_9O_2TiU$	$C_{82}H_{86}ClN_{12}O_3UZr$
MW	1541.50	1612.04	1652.33
Crystal system, space group	Triclinic, *P*-1	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	170	120	170
a, b, c (Å)	14.017 (5), 15.236 (5), 17.911 (5)	20.517 (5), 21.431 (5), 19.018 (5)	20.2769 (12), 21.7767 (10), 18.5794 (11)
α, β, γ (°)	87.225 (5), 69.531 (5), 77.365 (5)	90.00, 117.115 (5), 90.00	90.00, 115.829 (7), 90.00
V (Å^3)	3495 (2)	7443 (3)	7384.4 (7)
Z	2	4	4
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α
μ (mm^{-1})	2.49	2.37	2.43
Crystal size (mm)	0.12 × 0.11 × 0.07	0.21 × 0.10 × 0.07	0.53 × 0.23 × 0.17
	Data collection		
Diffractometer	Xcalibur, Eos	SuperNova, Dual, Cu at zero, Atlas	Xcalibur, Eos
Absorption correction	multi-scan	gaussian	multi-scan
T_{min}, T_{max}	0.926, 1.000	0.916, 0.965	0.626, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26501, 11901, 7334	156288, 18357, 15202	75846, 14015, 10516
R_{int}	0.122	0.058	0.105
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.588	0.680	0.610
	Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.080, 0.122, 0.99	0.036, 0.080, 0.92	0.072, 0.178, 1.09
No. of reflections	11901	18357	14015
No. of parameters	874	910	901
No. of restraints	58	0	1
H-atom treatment	mixed	constrained	mixed
$\Delta\rho_{max}$,$\Delta\rho_{min}$(e Å^{-3})	0.98, −0.90	1.12, −0.59	5.64, −1.57

	Crystal data		
Compound	**[ClCp$_2$ZrOUO(py)(H$_2$L)] × MgCl$_2$(py)$_4$ 3MgCl$_2$**	**[(py)$_2$ClMgOUO(py)(H$_2$L)] 4**	**[(py)$_2$(thf)$_2$ICaOUO(py)(H$_2$L)] 5**
Chemical formula	$C_{86.48}H_{86.48}Cl_3MgN_{15}O_2UZr$	$C_{175}H_{175}Cl_2Mg_2N_{33}O_4U_2$	$C_{65}H_{73}CaIN_{11}O_4U$
MW	1827.82	3400.06	1477.35
Crystal system, space group	Monoclinic, *C*2/*c*	Monoclinic, *I*2/*a*	Monoclinic, $P2_1/c$
Temperature (K)	170	120	170
a, b, c (Å)	47.424 (5), 14.484 (5), 30.602 (5)	24.852 (5), 23.010 (5), 28.754 (5)	17.4073 (7), 15.5310 (4), 33.3439 (15)
α, β, γ (º)	90.00, 127.576 (5), 90.00	90.00, 102.183 (5), 90.00	90.00, 114.157 (5), 90.00
V (Å^3)	16659 (7)	16072 (6)	8225.2 (5)
Z	8	4	4
Radiation type	Mo *K*α	Cu *K*α	Mo *K*α
μ (mm^{-1})	2.23	6.53	2.45
Crystal size (mm)	0.30 × 0.06 × 0.02	0.17 × 0.04 × 0.04	0.66 × 0.54 × 0.24
	Data collection		
Diffractometer	Xcalibur, Eos	SuperNova, Dual, Cu at zero, Atlas	Xcalibur, Eos
Absorption correction	Multi-scan	gaussian	multi-scan
T_{min}, T_{max}	0.971, 1.000	0.893, 0.972	0.527, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	49400, 14167, 7401	165331, 16761, 14608	130415, 11791, 10091
R_{int}	0.199	0.058	0.121
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.588	0.630	0.555
	Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.097, 0.203, 1.01	0.030, 0.074, 0.92	0.121, 0.282, 0.87
No. of reflections	14167	16761	11791
No. of parameters	979	984	724
No. of restraints	108	10	102
H-atom treatment	mixed	mixed	mixed
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.34, −1.08	1.36, −0.96	3.22, −9.14

	Crystal data		
Compound	**[(py)$_2$ClZnOUO(py)(H$_2$L)] 6**	**[(py)$_2$IZnOUO(py)(H$_2$L)] 7**	**[(py)$_3$RbOUO(py)(H$_2$L)] 8**
Chemical formula	$C_{57}H_{57}ClN_{11}O_2UZn$	$C_{62}H_{62}IN_{12}O_2UZn$	$C_{62}H_{62}N_{12}O_2RbU\cdot3(C_5H_5N)$
MW	1266.98	1437.54	1586.03
Crystal system, space group	Monoclinic, *I*2/*a*	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$
Temperature (K)	120	120	170
a, b, c (Å)	28.7327 (5), 22.9300 (3), 24.8036 (3)	13.2730 (1), 16.4368 (1), 27.8646 (2)	13.6821 (2), 21.8875 (3), 24.2440 (3)
α, β, γ (º)	90.00, 102.0775 (13), 90.00	90.00, 90.00, 90.00	90.00, 90.00, 90.00
V (Å^3)	15980.0 (4)	6079.10 (7)	7260.27 (18)
Z	8	4	4
Radiation type	Cu *K*α	Cu *K*α	Mo *K*α
μ (mm^{-1})	6.62	12.32	2.09
Crystal size (mm)	0.13 × 0.08 × 0.05	0.12 × 0.06 × 0.03	1.26 × 0.86 × 0.52
	Data collection		
Diffractometer	SuperNova, Dual, Cu at zero, Atlas	SuperNova, Dual, Cu at zero, Atlas	Xcalibur, Eos
Absorption correction	gaussian	multi-scan	analytical
T_{min}, T_{max}	0.889, 0.955	0.692, 1.000	0.425, 0.681
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	129575, 16675, 14839	99868, 12683, 12267	216174, 16642, 15775
R_{int}	0.081	0.054	0.076
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.630	0.631	0.649
	Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.098, 0.237, 1.14	0.020, 0.047, 0.90	0.025, 0.054, 1.05
No. of reflections	16675	12683	16642
No. of parameters	660	720	873
No. of restraints	12	0	76
H-atom treatment	constrained	mixed	constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	5.27, −3.70	0.46, −1.01	1.24, −0.86

	Crystal data	
Compound	**[RbOUO(py)(H_2L)]$_6$ 8b**	**[CsOUO(py)(H_2L)]$_6$ 9**
Chemical formula	$C_{282}H_{288}N_{48}O_{18}Rb_6U_6 \cdot 6(C_6H_6)$	$C_{282}H_{282}Cs_6N_{54}O_{12}U_6 \cdot 6(C_5H_5N)$
MW	7047.09	7319.84
Crystal system, space group	Trigonal, *R*3	Trigonal, *R*-3
Temperature (K)	293	120
a, b, c (Å)	27.6890 (5), 27.6890 (5), 35.9043 (8)	27.7671 (4), 27.7671 (4), 35.7644 (5)
α, β, γ (º)	90.00, 90.00, 120.00	90.00, 90.00, 120.00
V (Å^3)	23839.2 (10)	23880.5 (8)
Z	3.0	3
Radiation type	Mo *K*α	Cu *K*α
μ (mm^{-1})	4.02	14.25
Crystal size (mm)	0.24 × 0.16 × 0.03	0.05 × 0.04 × 0.03
	Data collection	
Diffractometer	Xcalibur, Eos	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	analytical	gaussian
T_{min}, T_{max}	0.425, 0.681	0.992, 0.995
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	182149, 12132, 8060	123779, 11060, 9096
R_{int}	0.183	0.096
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.649	0.630
	Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.100, 0.268, 1.02	0.066, 0.176, 1.03
No. of reflections	12132	11060
No. of parameters	265	579
No. of restraints	0	21
H-atom treatment	H-atoms not refined	constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	7.19, −3.82	12.92, −1.91

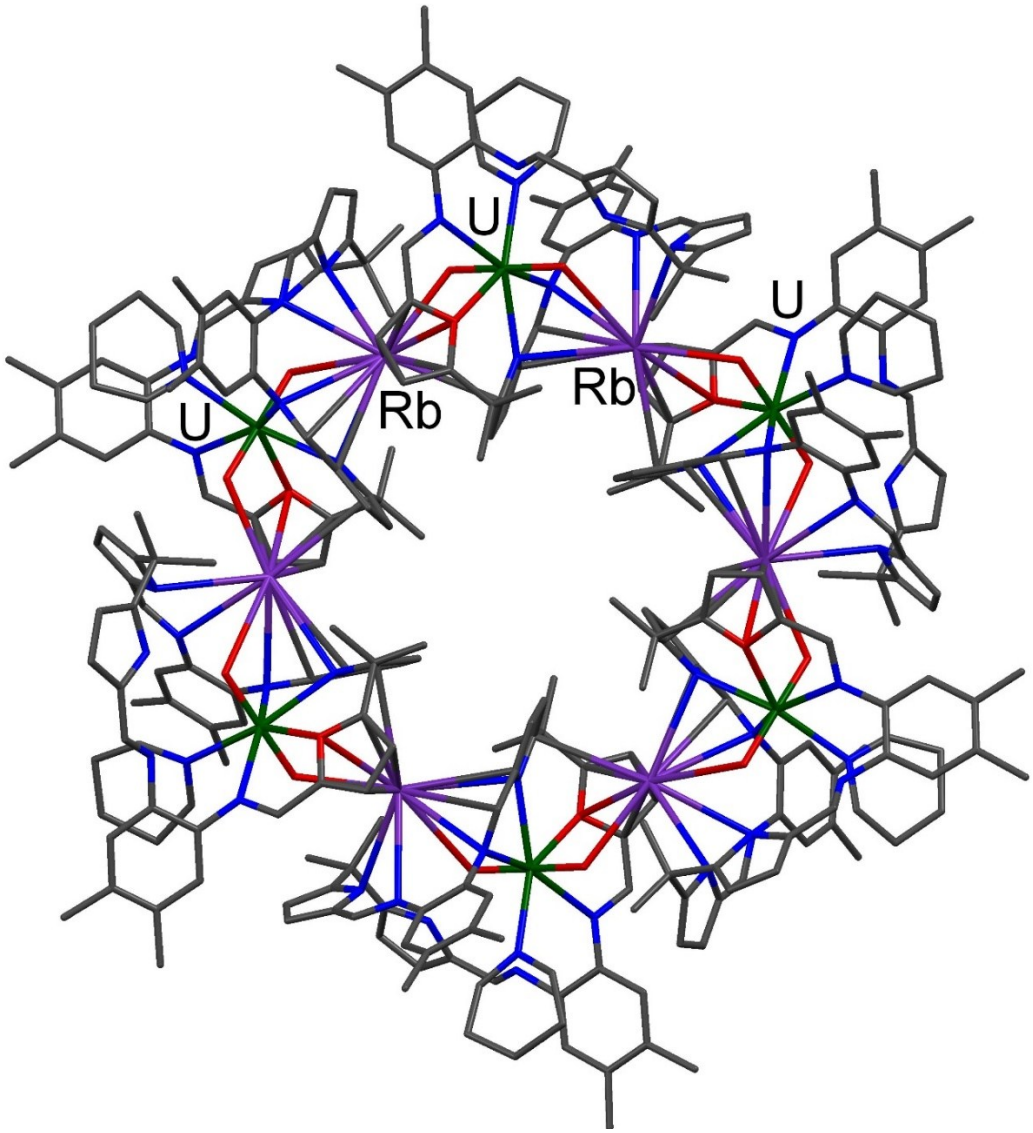


Figure S4: Solid state structure of **8b**, depicting the hexanuclear Rb(I)-uranyl(V) ring. For clarity, all hydrogen atoms except pyrrole N-Hs and all solvent molecules are omitted. U atoms green, Rb atoms purple, C atoms in grey, O atoms red, nitrogen atoms blue.

2. High energy resolution X-ray absorption Near Edge Structure (HR-XANES) and Resonant Inelastic X-ray Scattering (RIXS)

The U M_4 edge HR-XANES and 3*d*4*f* RIXS experiments (Figures S5, S6 and S7) were performed at the INE- or CAT-ACT-Beamlines at the Karlsruhe Research Accelerator (KARA, previous ANKA), Germany, using a multi-analyser Johann type X-ray emission spectrometer. All sample preparations were carried out in an inert gas glove box. 5 mg of each compound was mixed with 15 mg BN and pressed into a 7 mm diameter pellet. Each pellet was packed in a Kapton film with 8 µm thickness and shipped to the INE building next to the beamline in an air-tight container filled with N_2 gas. At INE in an inert gas glove box the samples were placed in an inert gas cell used as standard for transport and measurements of air sensitive samples.[1] Shortly before the start of the experiments the inert gas cell was transported to the INE-Beamline where it had been flushed with a continuous He flow. We did not detect any radiation damage of the samples during the experiments. No background function was subtracted and the spectra were normalised so that the absorption intensity at 3.789 eV equals 1. A second set of samples were shipped to INE and measured at the CAT-ACT-Beamline; very similar results were obtained.

For recording the U M_4 absorption edge (3728 eV)[11] HR-XANES/RIXS spectra of **A, 4** (Mg), **5** (Ca), **6** (ZnCl) and **7** (ZnI) the incident energy was monochromatised by a Si(111) double crystal monochromator (DCM) and focused to 0.5 x 0.5 mm full width at half maximum (FWHM) size onto the sample. Sample, five analyzer crystals and a single diode VITUS silicon drift detector (VITUS SDD KETEK) were arranged in a vertical Rowland geometry;[12] A box encompassing the spectrometer and maintaining constant He flow was installed to avoid intensity losses due to scattering and absorption of photons. The HR-XANES spectra were obtained by recording the maximum intensity of the M_β emission line (U M_β: 3339.8 eV) diffracted by five spherically bent Si(220) crystal analyzers (SAINT-GOBAIN) with 1 m bending radius and focused onto a single diode VITUS SDD. The crystals were aligned at 75.17° Bragg angle. The DCM was calibrated by assigning 3725.2 eV to the maxima of the most intense absorption peak of the U M_4 edge HR-XANES spectrum of a UO_2 sample. The experimental energy resolution was 1.2 eV estimated by measuring the FWHM of the incident beam elastically scattered from a Teflon sample. First five short spectra (7 eV) with 30 seconds recording time were measured at different positions on the sample. We did not observe any signs for radiation damage of the samples. After the beam was moved to a new position on the sample, two long (80 eV) U M_4 edge HR-XANES spectra were measured. The following scan parameters were applied defined with respect to the energy position of the absorption edge: -15 – -5 eV, step-size 0.5 eV, integration time 1 s; -5 – +15, 0.1, 1; +15 – +65, 0.5, 1. The RIXS maps were measured at the CAT-ACT Beamline. The emission and excitation energies were scanned as follows: excitation energy: 3.7215 3.7315 keV, 0.1 eV step size, emission energy: 3.3347 3.3410, 0.33 eV step size. A second set of samples was sent as powders packed in two independent glass vessels. They were opened in an Ar box and the powder was placed on a Kapton tape and covered with a Kapton film. The samples were transported and

measured in an inert gas cell (cf. text above). The measured U M_4 edge HR-XANES spectra differ only very slightly from the first measurements performed at the INE-Beamline due to variations in the experimental energy resolution (cf. Figure S7).

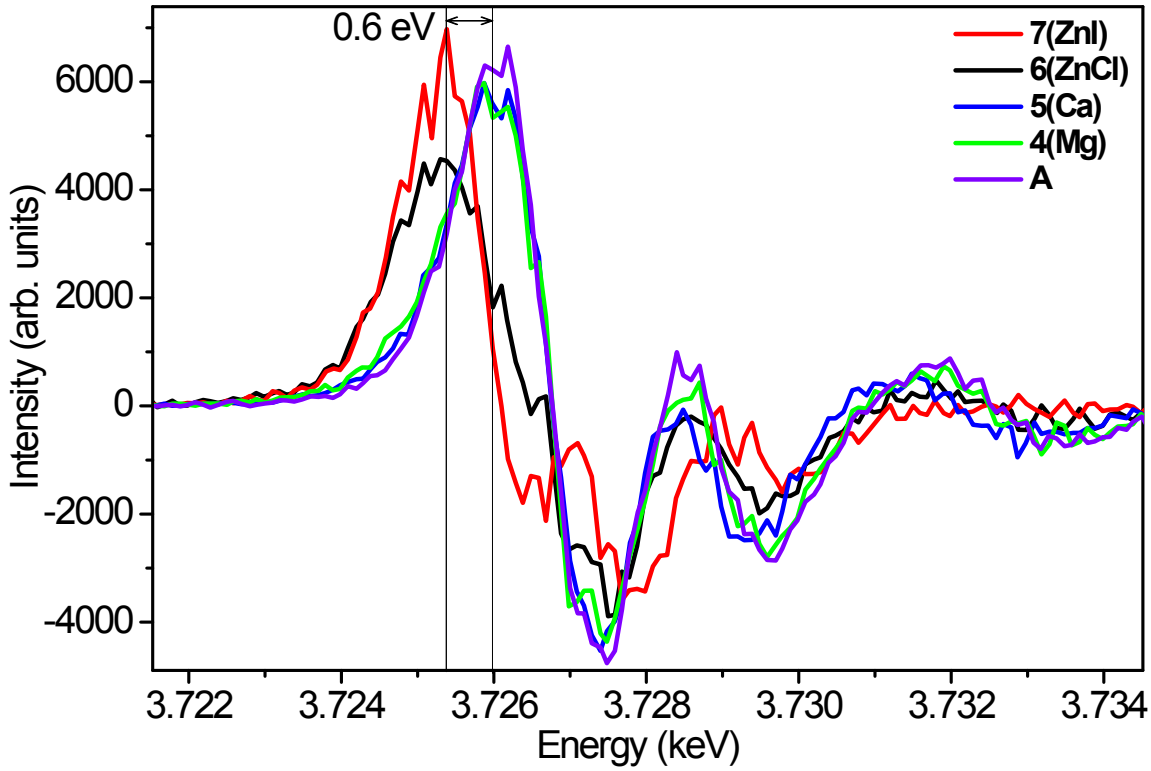


Figure S5: The first derivative of the U M_4 edge HR-XANES spectra of the **A, 4** (Mg)**, 5** (Ca)**, 6** (ZnCl) and **7** (ZnI) compounds. The energy difference between the energy positions of the maximum intensity of the first peaks is 0.6 eV.

Modeling of HR-XANES spectra. Linear combination least-squares (LCLS) fit analyses of the M_4 edge HR-XANES spectra were performed with the WINXAS program (www.winxas.de) using six pseudo-Voigt (PV) [f(x) = αGaussian + (1 − α)Lorentzian] and one arctangent functions. The Levenberg−Marquardt least-squares algorithm is used in the fit. The results are reported in Figure S6 and Table S1.

Table S1. Compound and absorption feature (Feature), height (Height), position (Position), and full width at half maximum (Fwhm) parameters of the pseudo Voigt (PV) functions used to model the U M_4 edge HR-XANES spectra and an arctangent used to model the edge jump, the Gauss part (α) and the area (Area) of the PV profiles, and the residual between experimental data and best fit.

Compound	Feature	Height ± 0.01	Position ± 0.1 (eV)	Fwhm ± 0.10 (eV)	α	Area	Residual (%)
ZnI	B	5.66	3725.8	0.002	0.73	0.010	2.8
ZnCl	B	7.07	3726.4	0.003	1.00	0.019	2.1
Ca	B	7.95	3726.7	0.002	0.75	0.018	2.3
Mg	B	8.02	3726.7	0.002	0.72	0.018	2.5
A	B	7.98	3726.7	0.002	0.80	0.016	2.0
ZnI	C	5.44	3727.2	0.002	0.80	0.013	2.8
ZnCl	C	2.45	3729.0	0.002	0.33	0.006	2.1
Ca	C	3.37	3728.8	0.002	0.80	0.007	2.3
Mg	C	3.65	3728.9	0.002	0.73	0.008	2.5
A	C	3.89	3728.9	0.002	0.71	0.009	2.0
ZnI	D	1.46	3729.4	0.001	0.91	0.003	2.8
ZnCl	D	0.75	3732.5	0.003	0.00	0.004	2.1
Ca	D	1.43	3731.9	0.003	1.00	0.004	2.3
Mg	D	1.36	3732.4	0.003	0.92	0.004	2.5
A	D	1.43	3732.5	0.003	0.69	0.004	2.0
ZnI	E	0.74	3732.1	0.008	1.00	0.006	2.8
ZnCl	E	0.47	3736.2	0.013	1.00	0.006	2.1
Ca	E	0.52	3736.0	0.005	1.00	0.003	2.3
Mg	E	0.54	3736.1	0.006	1.00	0.004	2.5
A	E	0.52	3736.2	0.007	1.00	0.004	2.0
ZnI	F	0.44	3742.9	0.012	1.00	0.006	2.8
ZnCl	F	0.27	3746.0	0.007	1.00	0.002	2.1
Ca	F	0.49	3743.8	0.014	1.00	0.007	2.3
Mg	F	0.50	3745.5	0.014	1.00	0.008	2.5
A	F	0.49	3745.5	0.014	1.00	0.007	2.0
ZnI	G	0.09	3758.3	0.006	1.00	0.001	2.8
ZnCl	G	0.06	3758.7	0.008	1.00	0.001	2.1
Ca	G	0.07	3762.7	0.007	1.00	0.001	2.3
Mg	G	0.08	3762.3	0.006	1.00	0.006	2.5
A	G	0.11	3761.8	0.006	1.00	0.001	2.0
ZnI	Arctan	0.94	3749.8	0.008	-	0.037	-
ZnCl	Arctan	0.94	3749.5	0.009	-	0.037	-
Ca	Arctan	0.98	3751.9	0.008	-	0.036	-
Mg	Arctan	0.94	3753.1	0.007	-	0.034	-
A	Arctan	0.94	3752.9	0.008	-	0.034	-

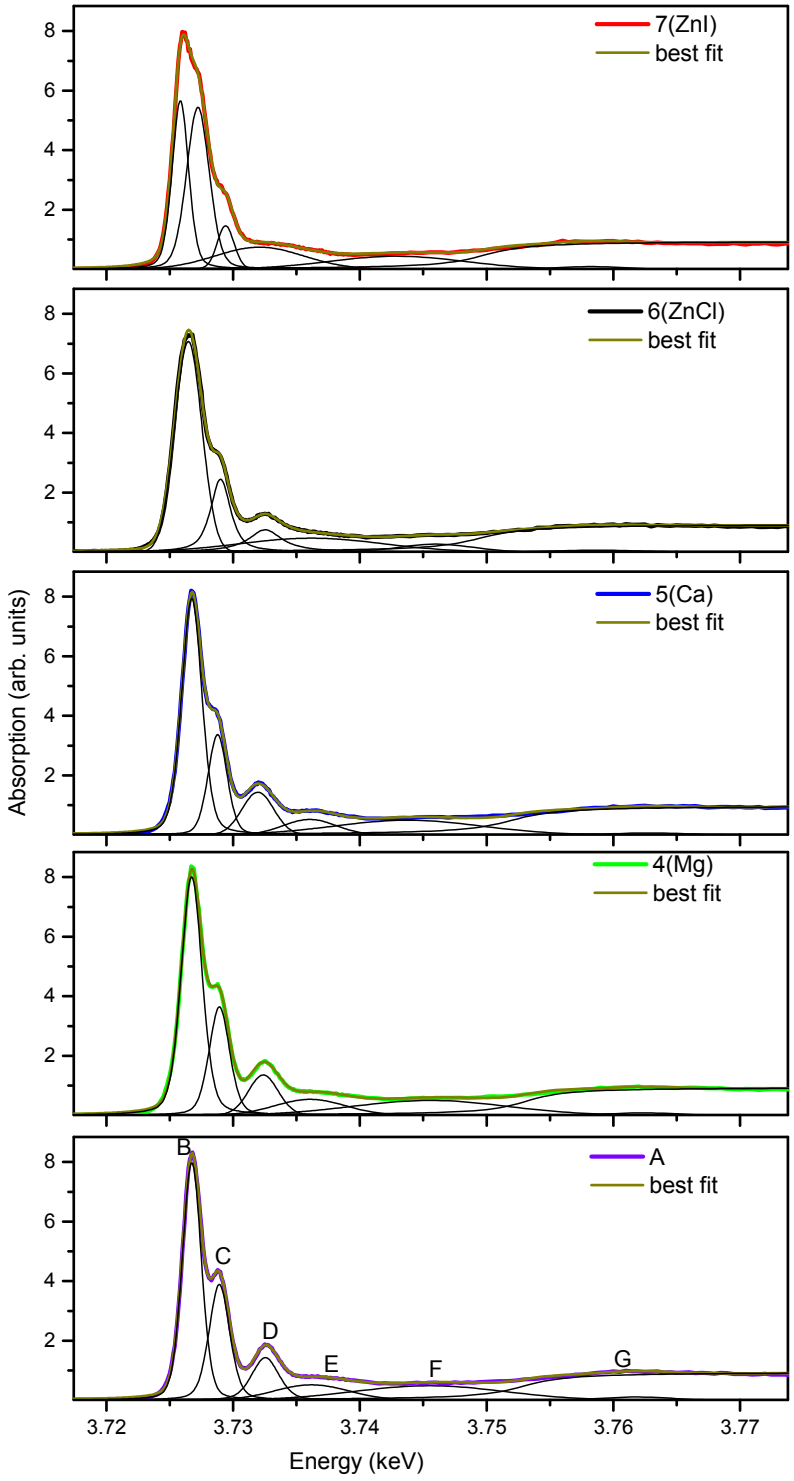


Figure S6: The U M_4 edge HR-XANES spectra of the **A**, **4** (Mg), **5** (Ca), **6** (ZnCl) and **7** (ZnI) compounds, their best fits and the Voigt profiles used to model the spectra (black lines).

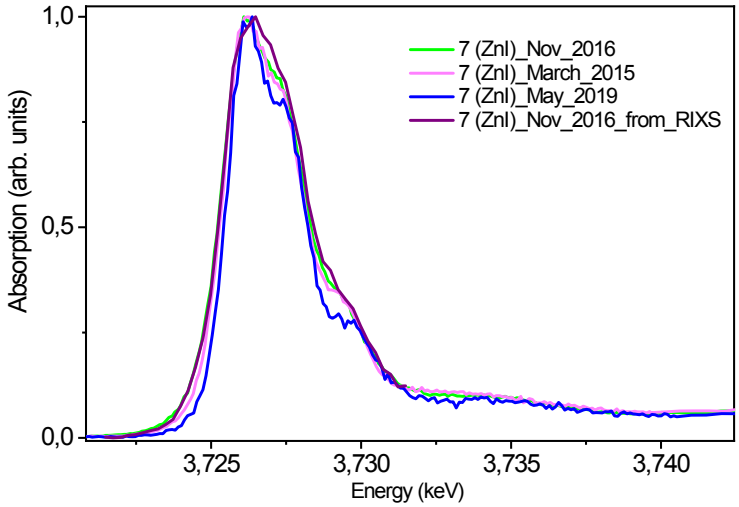


Figure S7: The U M_4 edge HR-XANES spectra of the **7** (ZnI) compound measured at different times and extracted from the RIXS map depicted in Figure 11. The spectra measured in November 2016 and in May 2019 are recorded at the CAT-ACT beamline, whereas the spectrum from March 2015 is recorded at the INE-Beamline, KARA. The spectrum measured in May 2019 is of the 7 (ZnI) compound dissolved in pyridine.

3. Computational procedures and results

Theoretical calculations were performed at the University of Manitoba, Canada. All geometries were fully optimised at the Density Functional Theory (DFT) level using the Perdew-Burke-Ernzerhof (PBE) functional[13,14] with correlation consistent all-electron cc-pVDZ basis sets for the large component and corresponding kinetically balanced basis sets for the small component,[15] using the Priroda code, version 13.[16] Priroda applies the full Dirac equation but with spin-orbit projected out and neglected.[17] Vibrational frequency calculations were performed at the same level of theory in order to verify that the geometries are real minima on the potential energy surfaces. Topology analysis such as QTAIM, Orbital composition analysis with Ros-Schuit (SCPA) partition[18,19] and Orbital composition analysis of localized orbitals with Hirshfeld partition were performed with the MultiWFN code.[20] Energy decomposition analysis (EDA) was interfaced with the Amsterdam Density Functional (ADF)[21–23] program. ADF calculations were performed using the PBE functional and the scalar zeroth order regular approximation (ZORA) method[24–28] with corresponding double zeta polarised (DZP) basis set for light elements and triple zeta polarised (TZP) for uranium. Due to the technical requirement of closed-shell fragments imposed by the ADF program, the fragments of [M-O↑↑] and [U-O↓↓] cannot converge properly, and only charged fragments converged, which means that the two fragments are $[M\text{-}O]^{2-}$ and $[U\text{-}O]^{2+}$(Figure S8). Considering the large ionic character of the bonds, this approach is still reasonable. However, as a consequence these results have qualitative meaning only.

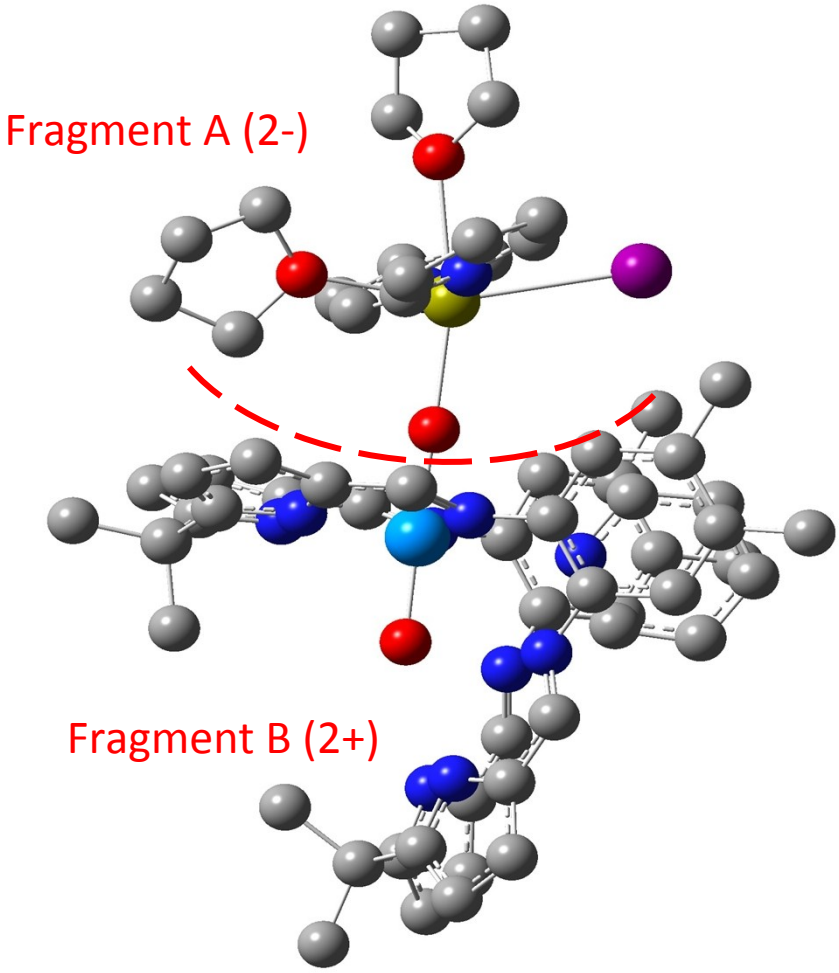


Figure S8: An example of fragments used for EDA. Hydrogen atoms are hidden.

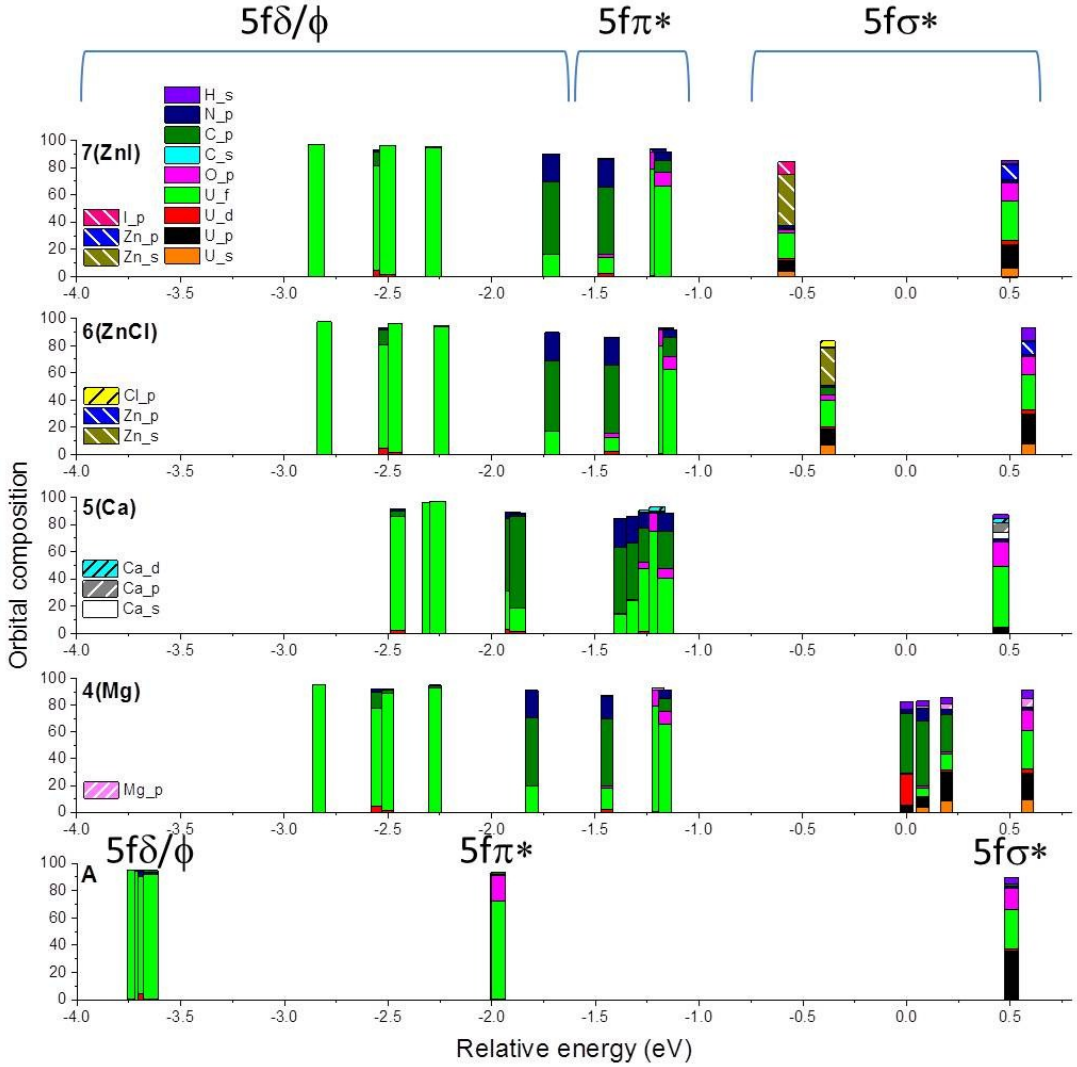


Figure S9: From bottom to top: relative energies and orbital compositions obtained by Mulliken population analyses for unoccupied valence orbitals with U 5f content for **A, 4** (Mg)**, 5** (Ca)**, 6** (ZnCl) and **7** (ZnI) compounds. Contributions smaller than 2 % contributions of atomic orbitals are not included.

Table S2 Selected calculated bond distances (Å)

Complex	M-O2	O2-U	U=O1
E[Al]	1.818	1.984	1.870
D[K]	2.808	1.870	1.882
1[Ti(III)]	2.101	1.967	1.867
2[Ti(IV)]	1.938	2.016	1.858
3[Zr]	2.026	2.039	1.860
4[Mg]	1.940	1.941	1.872
5[Ca]	2.324	1.925	1.877
6[ZnCl]	1.918	1.944	1.872
7[ZnI]	1.924	1.949	1.872
A[U(VI)]	-	1.801	1.837

Table S3 Properties of selected bond critical points

Complex	Parameter	$\nabla^2 \rho$	ρ	H
E[Al]	Al-O1	0.529	0.072	0.003
	O1-U	0.180	0.166	-0.074
	U=O2	0.419	0.230	-0.143
D[K]	K-O1	0.067	0.013	0.004
	O1-U	0.433	0.233	-0.146
	U=O2	0.431	0.225	-0.137
1[Ti(III)]	Ti(3)-O1	0.306	0.066	-0.003
	O1-U	0.431	0.174	-0.082
	U=O2	0.427	0.231	-0.145
2[Ti(IV)]	Ti(4)-O1	0.446	0.104	-0.016
	O1-U	0.410	0.154	-0.063
	U=O2	0.431	0.237	-0.152
3[Zr]	Zr-O1	0.404	0.110	-0.025
	O1-U	0.381	0.147	-0.058
	U=O2	0.431	0.236	-0.150
4[Mg]	Mg-O2	0.391	0.050	0.011
	O2-U	0.414	0.190	-0.098
	U=O1	0.415	0.229	-0.142
5[Ca]	Ca-O2	0.203	0.036	0.006
	O2-U	0.433	0.201	-0.109
	U=O1	0.438	0.228	-0.140
6[ZnCl]	Zn-O2	0.472	0.090	-0.017
	O2-U	0.454	0.183	-0.090
	U=O1	0.417	0.229	-0.142
7[ZnI]	Zn-O2	0.460	0.089	-0.017
	O2-U	0.451	0.180	-0.087
	U=O1	0.418	0.229	-0.142
A[U(VI)]	O1=U	0.439	0.277	-0.207
	U=O2	0.450	0.252	-0.171

Table S4 Selected calculated bond orders

Complex	Parameter	Mayer	Mulliken
E[Al]	Al-O1	0.829	0.653
	O1-U	1.465	0.605
	U=O2	2.159	0.850
D[K]	K-O1	0.083	0.043
	O1-U	2.224	0.937
	U=O2	2.091	0.837
1[Ti(III)]	Ti(III)-O1	0.655	0.441
	O1-U	1.668	0.729
	U=O2	2.197	0.885
2[Ti(IV)]	Ti(IV)-O1	0.883	0.507
	O1-U	1.424	0.643
	U=O2	2.230	0.875
3[Zr]	Zr-O1	0.897	0.493
	O1-U	1.382	0.649
	U=O2	2.220	0.871
4[Mg]	Mg-O1	0.643	0.524
	O1-U	1.642	0.651
	U=O2	2.134	0.852
5[Ca]	Ca-O1	0.540	0.371
	O1-U	1.750	0.678
	U=O2	2.157	0.851
6[ZnCl]	Zn-O1	0.599	0.427
	O1-U	1.704	0.745
	U=O2	2.149	0.860
7[ZnI]	Zn-O1	0.599	0.423
	O1-U	1.699	0.749
	U=O2	2.155	0.862
A[U(VI)]	O1=U	2.455	0.846
	U=O2	2.188	0.942

Table S5 Partial Atomic Charge of Uranium atoms

	Hirshfeld	Spin density
1[Ti(III)]	0.441	1.08
2[Ti(IV)]	0.481	1.01
3[Zr]	0.484	1.06
4[Mg]	0.450	1.03
5[Ca]	0.455	0.93
6[ZnCl]	0.439	1.05
7[ZnI]	0.438	1.05
[U(VI)]	0.520	-
A[U(V)]	0.415	0.76

Table S6.1 Uranium atomic orbital contribution of selected molecular orbitals related to U-O_{exo} Bonds

	4[Mg]		**5**[Ca]		**6**[ZnCl]		**7**[ZnI]	
	orbital#	contribution	orbital#	contribution	orbital#	contribution	orbital#	contribution
U-O_{exo} σ bond	294	4.92%	355	41.88%	304	7.09%	318	9.12%
	293	8.90%	353	14.74%	302	9.34%	317	38.40%
	291	38.72%	301	29.07%				
U-O_{exo} π bond	282	12.60%	346	8.89%	290	5.64%	311	14.47%
	280	6.58%	343	4.83%	291	8.52%	307	6.42%
	277	6.98%	341	3.66%	289	4.98%		
			340	4.58%				

Table S6.1 contains the uranium atomic orbital contributions to the O_{exo} dominant π and σ U-O bonding MOs of **4, 5, 6** and **7**. The π bonding orbitals are more stable then σ bonding orbitals, which may be due to a "pushing from below" effect. Although there are some arguments that orbital mixing and covalency should be separated in compounds of elements toward the middle of the actinide series, however, in uranium chemistry, they can be treated as synonymous.[29] One can see clearly the tendency in the sum of uranium atomic orbital contributions for σ bonds that are about as follows: **5** (Ca) (56%) ≥ **4** (Mg) (52%) > **6** (ZnI) (47%) ≥ **7** (ZnCl) (44%), which suggests a decrease of covalency. This agrees with QTAIM and EDA results. For π bonds, the contributions are about as follows: **4** (Mg) (26%) > **5** (Ca) (22%) ≥ **6** (ZnI) (21%) ≥ **7** (ZnCl) (19%). This may due to π bonds not being affected too much for symmetry reasons.

Table S6.2 Uranium atomic orbital contributions of localized U-O_{exo} bonding orbitals

	5[Ca]	4[Mg]	6[ZnCl]	7[ZnI]
σ	28.50%	26.70%	21.60%	22.80%
π	20.00%	17.10%	16.60%	18.20%
π	20.10%	17.70%	16.90%	18.70%

Due to the large number of split bonding MOs, we also localized those orbitals. Table S6.2 shows the U atomic orbital contributions to localized U-O_{exo} bonding orbitals. Increased U character can be taken as indicative of increased covalent character. Thus, we find an order of **5** (Ca) ≥ **4** (Mg) > **6** (ZnI) ≥ **7** (ZnCl)

Table S7 Properties of BCPs of hydrogen bonds

	Bond length

Complex	Parameter	$\nabla^2 \rho$	ρ	H	H···A cal.	D···A cal.
E[Al]	C1-H···O	0.0217	0.0064	0.0014	2.670	3.736
	C2-H···O	0.0361	0.0093	0.0022	2.435	3.475
	N1-H···O	0.0773	0.0218	0.0021	1.986	3.010
	N2-H···O	0.0806	0.0230	0.0019	1.964	2.991
D[K]	C1-H···O	0.0227	0.0067	0.0015	2.646	3.727
	C2-H···O	0.0360	0.0092	0.0022	2.440	3.470
	N1-H···O	0.0856	0.0249	0.0015	1.906	2.935
	N2-H···O	0.0905	0.0268	0.0011	1.935	2.962
1[Ti(III)]	C1-H···O	-	-	-	3.224	4.210
	C2-H···O	0.0342	0.0089	0.0021	2.450	3.510
	N1-H···O	0.0645	0.0176	0.0025	2.069	3.095
	N2-H···O	0.0685	0.0189	0.0024	2.041	3.066
2[Ti(IV)]	C1-H···O	0.0138	0.0044	0.0009	2.884	3.922
	C2-H···O	0.0282	0.0074	0.0018	2.542	3.591
	N1-H···O	0.0604	0.0158	0.0027	2.044	3.073
	N2-H···O	0.0682	0.0185	0.0025	2.107	3.128
3[Zr]	C1-H···O	0.0155	0.0040	0.0010	2.827	3.872
	C2-H···O	0.0297	0.0077	0.0019	2.521	3.567
	N1-H···O	0.0640	0.0170	0.0026	2.080	3.101
	N2-H···O	0.0710	0.0194	0.0024	2.025	3.054
4[Mg]	C1-H···O	0.0236	0.0069	0.0015	2.631	3.706
	C2-H···O	0.0366	0.0094	0.0022	2.431	3.467
	N1-H···O	0.0833	0.0241	0.0016	1.946	2.974
	N2-H···O	0.0820	0.0235	0.0018	1.956	2.982
5[Ca]	C1-H···O	0.0214	0.0062	0.0014	2.676	3.744

	C2-H···O	0.0308	0.0080	0.0020	2.508	3.548
	N1-H···O	0.0621	0.0125	0.0025	2.016	3.043
	N2-H···O	0.0724	0.0201	0.0023	2.010	3.035
6[ZnCl]	C1-H···O	0.0156	0.0049	0.0010	2.821	3.874
	C2-H···O	0.0389	0.0100	0.0023	2.400	3.443
	N1-H···O	0.0786	0.0224	0.0019	1.976	3.001
	N2-H···O	0.0791	0.0226	0.0019	1.973	2.997
7[ZnI]	C1-H···O	0.0153	0.0048	0.0010	2.832	3.880
	C2-H···O	0.0385	0.0099	0.0023	2.404	3.448
	N1-H···O	0.0781	0.0222	0.0020	1.979	3.004
	N2-H···O	0.0772	0.0219	0.0020	1.986	3.010
A[U(VI)]	C1-H···O	0.0176	0.0052	0.0011	2.767	3.818
	C2-H···O	0.0313	0.0079	0.0020	2.497	3.545
	N1-H···O	0.0669	0.0173	0.0027	2.065	3.086
	N2-H···O	0.0666	0.0172	0.0027	2.068	3.088

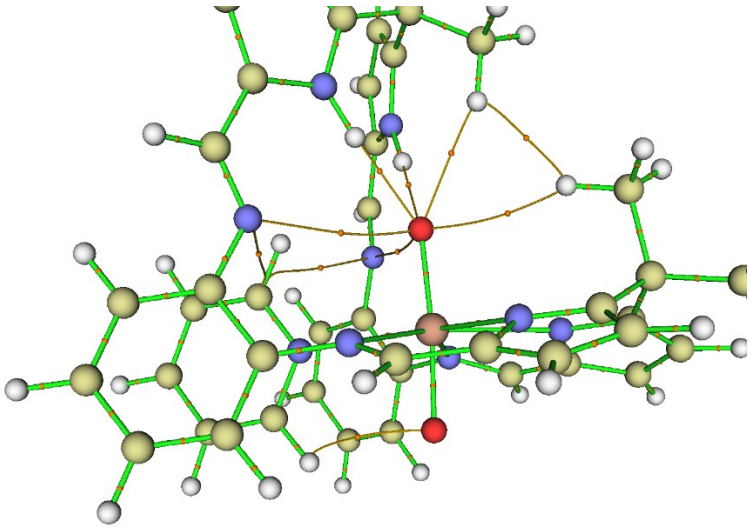


Figure S10: BCPs near O2 in complex **A**.

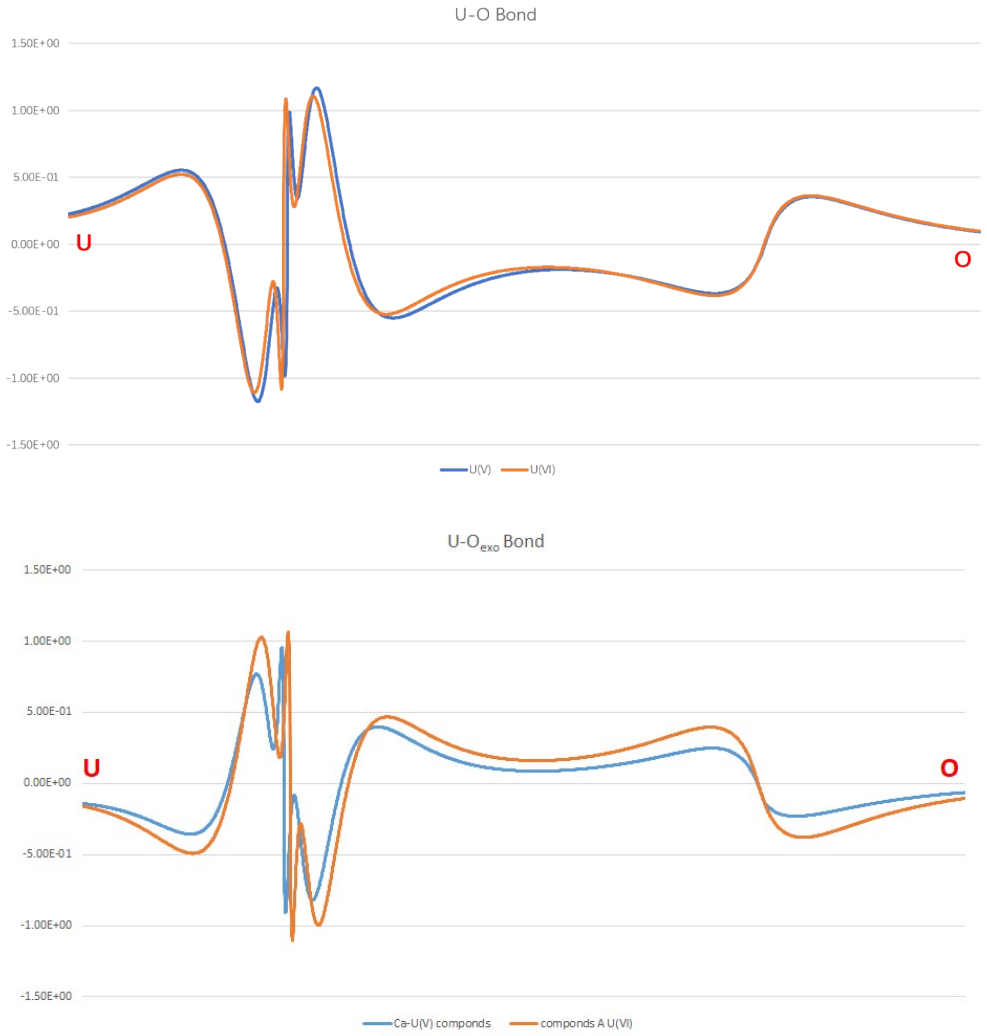


Figure S11: Bond contraction of the U-O_{yl} bond in uranyl(V) compared to uranyl(VI), traced along the U–O direction. **Top**: Bonding orbital (U($5f_{z3}$)–O($2p_z$) of UO_2^{2+} (orange) and UO_2^{+} (blue). **Bottom:** Bonding orbital (U($5f_{z3}$)–O_{exo}($2p_z$) of the U(VI) complex (**A**), orange, vs. the U(V) Ca complex (**5**), blue.

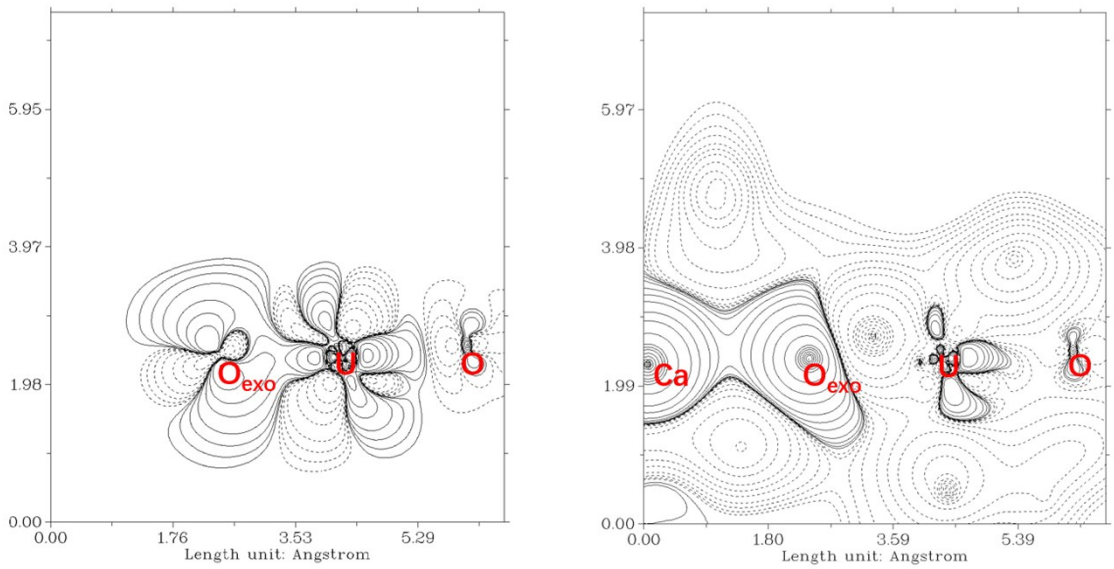


Figure S12 Electron density difference graph. In the graph, solid lines and dashed lines correspond to the regions having increased electron density and decreased electron density during formation of the U-O bonds of compound **A** and **5[Ca]**, respectively. Unrelated atoms and corresponding densities are omitted.

Optimised Coordinates:

A

6	1.531246500	-4.325060570	1.422524790
6	1.088145590	-5.665842810	1.316135880
1	1.644217210	-6.552025590	1.612447360
6	-0.188155030	-5.632526800	0.749691630
1	-0.831546320	-6.476926120	0.506945950
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1	-6.549009730	-2.587574760	0.402119940
1	-7.263964730	-2.522483280	-1.229130360
6	-5.128633080	-0.893570440	-2.251533220
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1	-6.046860000	0.257627770	-3.835312990
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1	-3.738562300	-0.009467790	-3.635882560
6	-2.685576190	-1.131117880	-2.126427810
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6	0.740844390	-0.225496610	-5.529482940
1	0.172597120	-0.266602830	-6.456415260
6	2.108207590	0.079507140	-5.381270200
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6	3.725051930	0.289456970	-3.290567570
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1	4.140458290	-1.810772080	-2.861985320
1	3.270159310	-0.993636020	-1.542249380
6	3.601897410	1.606759370	-2.540485840
6	4.190458350	2.852009860	-2.793312500
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6	2.046050170	3.497964590	0.117346000
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6	0.403461440	3.122390020	1.747171750
6	-0.182947560	4.397473640	1.835891870
1	0.001568470	5.113797760	1.028686470
6	-1.014108210	4.769688850	2.894749260
6	-1.628059010	6.147110310	2.929724280
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1	-0.929217160	1.815366920	4.606350040
6	0.116705970	2.180775870	2.767776240
6	1.419812530	0.491137520	3.713085250
1	1.594038290	1.168189380	4.563825540
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6	2.916966020	-1.323028250	4.683552810
1	3.211043510	-0.866308820	5.627381280
6	3.333468280	-2.549471190	4.160852850
1	4.020886420	-3.253160550	4.624131880
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1	3.129930810	-2.463491800	0.207470490
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1	-4.631540500	2.005677170	1.521436380
6	-3.536642430	2.767689690	-0.195828470
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6	-1.473124550	1.614047020	-0.605536070
1	-0.558023870	1.461116550	-1.177779220
7	0.583637170	-3.477096080	0.950996610
7	-1.676440570	-2.391391370	-0.298024280
7	-1.392614220	-0.875161150	-2.564701900
7	1.263291430	-0.306651510	-3.354427960
1	1.150204920	-0.492212490	-2.348267230
7	2.788266650	1.756266490	-1.450167330
1	2.251459430	1.025126410	-0.963724350
7	1.209963300	2.701151200	0.697819700
7	0.691974590	0.892696550	2.693511310
7	1.916133930	-1.628246610	2.637431300
7	-1.666518170	0.792422370	0.445877900
8	1.155874400	-0.596102730	-0.277698460
8	-1.118744700	-1.424404880	2.432184970
92	0.062242230	-1.077655360	1.116810970

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1	-0.740762130	4.273867850	-1.583873150
6	1.180318910	3.425115830	-1.070046100
7	-0.893778520	2.255869360	-1.055663400
6	2.064257420	4.495209140	-1.319901550
7	1.893303910	2.292105640	-0.698707080
6	-2.291446660	2.285137520	-1.258687030
92	0.540755910	0.355708300	0.109344630
1	1.785609340	5.497123610	-1.645439080
6	3.352157770	3.993232520	-1.097254260
6	3.206808490	2.636463180	-0.715356370
6	-2.855476870	1.419958540	-2.229611950
6	-3.128918440	3.144572620	-0.538853420
7	2.835985830	0.192708080	1.019302650

7	0.814388510	-1.522723240	1.947262660	6	2.405582770	3.995821000	2.306779160
7	-1.912803510	-0.640722860	0.274278150	6	2.653306320	3.046063430	4.414292760
8	0.080295410	1.428823240	1.713519730	1	-6.848336880	1.514979590	-2.666722360
8	0.870482020	-0.678428490	-1.413058560	1	-6.963736200	3.235650100	-2.218035350
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6	4.305711780	1.625750960	-0.431666020	6	-1.338409210	-1.188016530	-6.102121820
6	-4.250249780	1.437617920	-2.406338910	7	-0.152947500	-1.168985890	-4.200724400
7	-1.983312090	0.577082260	-2.904909280	6	-2.194114580	-3.092551300	5.592755820
6	-4.515339200	3.163907990	-0.728210160	6	-2.097280920	-4.272959360	3.342223900
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6	2.940565190	-0.487284850	2.227859700	1	-5.496825080	-2.127964220	0.535714880
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1	2.075541140	-1.945867890	3.564675110	6	0.658948770	-4.662499720	-1.663144430
6	-0.678700190	-2.347814530	3.721775790	1	4.001276200	5.212740550	1.561626890
6	-0.587991930	-3.477394550	1.572949820	6	4.408381980	4.434027070	3.555235170
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6	-3.629890180	-2.102749360	-0.560784220	6	1.754503120	-2.772904290	-4.656661050
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1	-2.176888680	3.874307330	2.822592780	7	0.977432060	-3.512773210	-2.361356710
6	-0.254277530	1.469678380	4.868300310	1	5.387167900	4.908927770	3.655880350
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7	1.906563080	3.236955210	3.305281980	1	0.717116230	-6.791528350	-2.268077630
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1	6.464628730	1.588547330	-0.156055900	1	0.958266130	-2.571519610	-1.929479060
1	5.688556960	3.058416600	0.501285240	1	2.437268840	-1.274389300	-3.179756820
1	3.406950310	0.097159510	-1.716626770	1	3.073796930	-1.042078680	-4.826824170
1	5.158248890	-0.125205930	-1.438086710	1	3.713729210	-2.356924470	-3.789543300
1	4.576643980	1.157424540	-2.556299240	1	3.268119740	-4.004883970	-5.613177950
6	-6.579376300	2.252377820	-1.895939230	1	2.627872110	-2.693562850	-6.645948770
6	-1.279955260	-0.650727700	-4.811425040	1	1.653585650	-4.161867420	-6.358573800
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1	5.887471030	0.995697120	2.053057480	6	4.138142050	-1.882774950	-1.845964010
1	4.565368440	-0.660516220	3.749891110	7	1.732682600	-1.221570720	-2.335743360
1	-0.347187270	-1.526480270	4.364967940	1	3.548788490	-2.838458740	-4.601059280
6	-1.641506340	-3.244472190	4.197543520	6	1.528603250	-1.926305910	-4.513617470
6	-1.563775320	-4.368015020	2.054783300	6	3.889412130	-2.018207400	-0.351850170
7	-0.056664260	-3.515139700	0.290975780	6	5.063116920	-3.020185260	-2.328181910
1	-4.675542150	-0.430978620	2.211751960	6	4.882338200	-0.530831070	-2.063536190
6	-4.490358280	-1.709049430	0.461758860	6	0.892437910	-1.261553660	-3.444981090
1	-3.932963480	-2.834522510	-1.312290350	92	0.706592350	-0.344344180	-0.248450150

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7	2.905580670	-1.358733260	0.311831520	1	-1.144754300	-7.048142960	-0.794973850
1	5.314859700	-2.884587750	-3.390077210	1	-2.931970770	-5.196261950	-1.578259840
1	4.589586450	-4.006358710	-2.201135670	1	-1.550474330	-3.037674300	-2.476836610
1	6.008833600	-3.007471050	-1.767044890	6	-3.198337050	-2.324530960	-0.001874860
1	4.250158510	0.302882450	-1.727232730	6	-3.671287900	-4.204821940	1.251699280
1	5.110972600	-0.391865940	-3.132913110	6	-4.722393570	1.730081780	-3.040371260
1	5.820163680	-0.516844320	-1.484354990	6	-5.802756890	-0.547568600	-3.370514590
6	-0.389953680	-0.677432580	-3.441386240	1	-3.658267120	3.586933410	-2.796277600
7	-0.930884630	-0.096010500	-2.394801540	6	-0.898738010	3.710258520	-3.155766850
7	1.260687590	-0.264763060	2.396057100	1	-0.385533570	3.315215320	4.764531730
7	-1.388869710	0.827660340	0.897011880	6	-0.899648460	1.420589670	5.649634460
8	1.438164430	1.347778340	-0.545684970	6	1.735061750	3.555895470	3.001688190
8	-0.153610340	-2.088549710	0.048152920	6	-1.388789740	-0.897306270	6.572466960
6	4.300036090	-2.344191910	1.850751450	1	-4.167466290	2.715791350	2.861176900
1	5.638645290	-3.249324060	0.329294740	1	-2.435419350	-1.719593010	-0.495756890
6	3.153479170	-1.543717490	1.669632300	6	-4.532532930	-1.923436950	0.027972930
1	-0.938641780	-0.693800370	-4.398045650	6	-5.015026500	-3.869916660	1.333329230
6	-2.199927670	0.505097310	-2.606426110	1	-3.297753070	-5.120887860	1.713685010
6	0.560753380	0.288695060	3.498304960	6	-6.058361000	2.402149740	-3.241188090
6	2.349933550	-0.948393490	2.663237030	1	-5.530116860	-1.613468380	-3.356552480
6	-1.637836570	2.132429600	0.664810520	1	-6.237387710	-0.323870350	-4.360467780
6	-2.125852010	0.202894130	1.836884430	1	-6.609633390	-0.392637930	-2.632396390
22	-0.618399060	-4.131069820	0.206146650	1	-1.595847200	4.097228390	-3.923921330
1	4.726136610	-2.648147560	2.806422960	6	0.326571980	4.428158170	-3.005682140
6	-3.346706600	-0.254817960	-2.865552240	6	-1.698866290	2.042753070	6.768305700
6	-2.305885260	1.918787290	-2.632806510	6	2.450371930	4.320837330	2.029128330
6	0.470428030	1.698216410	3.627952910	1	1.782118890	3.934943750	4.041438390
6	-0.033807940	-0.514496420	4.480161360	1	-2.483649000	-0.763221940	6.626385430
1	2.682276880	-1.065254840	3.708463500	1	-0.996973020	-0.701638730	7.585955040
1	-1.028747680	2.602881090	-0.111796570	1	-1.188444330	-1.952557910	6.332955960
6	-2.626878650	2.841092810	1.343299230	1	-4.808411140	-0.995120970	-0.476682810
6	-3.132812950	0.836766220	2.558893440	6	-5.466682340	-2.702167250	0.705787040
1	-1.885789830	-0.848504480	2.011452740	1	-5.697017130	-4.523929260	1.881093480
6	1.244084280	-4.599125950	1.618158430	1	-5.964223340	3.495508790	-3.165515230
6	0.424841020	-3.707539400	2.357151800	1	-6.797842630	2.072177990	-2.491051790
6	-0.803142220	-4.344462810	2.630759570	1	-6.484915290	2.166082880	-4.231487840
6	-0.761891190	-5.651577250	2.064816330	6	0.762050590	5.626289360	-3.582491050
6	0.515252070	-5.811886130	1.462756110	7	1.350427820	3.958899290	-2.204640560
6	0.264569460	-4.256250630	-2.011522510	1	-1.283319190	1.781146930	7.756769180
6	0.394788900	-5.551884100	-1.464850370	1	-2.746312450	1.694015330	6.763777520
6	-0.909875180	-6.074851780	-1.225427030	1	-1.706030150	3.139541220	6.683502300
6	-1.847969010	-5.100266950	-1.635427110	6	3.141310700	5.531377430	2.147563470
6	-1.126781830	-3.968992440	-2.107649970	7	2.600957370	3.883490640	0.727623790
7	-2.751177550	-3.453509190	0.598579320	1	-6.518893570	-2.412348730	0.749121540
1	-3.250070180	-1.344902100	-2.904791480	1	0.182733500	6.242710870	-4.266830790
6	-4.604034290	0.323544770	-3.085610600	6	2.063129900	5.873136550	-3.105324390
6	-3.574278030	2.495360110	-2.822890990	6	2.413298530	4.817098630	-2.253816290
7	-1.133807460	2.644234390	-2.463341520	1	1.302552150	3.049886870	-1.713848930
6	-0.278394520	2.227630900	4.694169970	6	3.704783860	5.817628030	0.889306730
7	1.129610550	2.462170150	2.676529140	1	3.214529790	6.128484440	3.054228290
6	-0.761225230	0.018531620	5.551046490	6	3.362045230	4.773583600	0.020827710
1	0.060495490	-1.602308420	4.395789720	1	2.217249860	2.979786460	0.400345980
1	-2.782935640	3.897145890	1.114036460	1	2.691829180	6.724897830	-3.348721580
6	-3.389003950	2.184353840	2.308140950	6	3.681181090	4.581438130	-1.451757070
1	-3.692758230	0.277724360	3.310976660	1	4.301419270	6.687335970	0.629030280
1	2.246183960	-4.379773830	1.248196720	6	4.759244200	5.591977280	-1.882634640
1	0.671127100	-2.676396920	2.585969760	6	4.216088140	3.151189000	-1.704338450
1	-1.644407060	-3.896399770	3.158547890	1	4.993140390	5.454544410	-2.949063050
1	-1.531509150	-6.420568260	2.133630140	1	5.676486530	5.428507110	-1.297274640
1	0.874680230	-6.716920290	0.977349640	1	4.429048450	6.630221740	-1.729240380

1	4.446742370	3.022233740	-2.773834040	1	6.187188270	2.672215630	0.945996770
1	3.486806270	2.378547930	-1.418733620	1	6.919943550	1.171560170	1.566652570
1	5.134228320	2.987435000	-1.118116540	1	6.779317670	2.583828200	2.625825040
2[Ti(VI)]				6	4.900293040	1.553975870	2.273616850
6	-2.969883030	2.210984080	-2.185612400	6	3.755860940	1.985857740	1.594198910
6	-3.566170960	2.055053710	-3.460526830	1	3.859461320	2.635187700	0.719332650
1	-4.246165040	2.752767060	-3.943828450	6	2.470437560	1.564002670	1.952744870
6	-3.136889910	0.824277330	-3.964571980	6	1.092526590	3.278347100	1.187830970
1	-3.415735840	0.358810360	-4.909407120	1	1.766060870	3.974075590	1.713079910
6	-2.285286250	0.272775210	-2.985495450	6	-0.030345810	3.829564600	0.535341840
6	-1.697033810	-1.010947190	-2.955300080	6	-0.425500210	5.178564970	0.447196770
1	-1.947515040	-1.695668480	-3.783171600	1	0.116693840	6.034064350	0.848387440
6	-0.519799640	-2.783511690	-2.016494070	6	-1.640184430	5.184323190	-0.244361160
6	0.202041540	-3.294958810	-3.103359030	1	-2.238813390	6.057213270	-0.493752230
1	0.444572210	-2.624384410	-3.932412550	6	-1.951454350	3.838043510	-0.549594870
6	0.637092500	-4.623362040	-3.166182960	6	-3.233384220	3.314085540	-1.175293210
6	1.436249550	-5.103736630	-4.351303150	6	-4.011388410	4.466376650	-1.837318150
1	0.935651230	-5.942828630	-4.865255320	1	-4.252798400	5.238011360	-1.090986150
1	2.433192390	-5.467334940	-4.046522890	1	-4.962076280	4.094655990	-2.248331100
1	1.582733600	-4.295625900	-5.083439050	1	-3.432304580	4.932759980	-2.649988670
6	0.805808420	-6.922089110	-2.096162020	6	-4.112721970	2.715948170	-0.041065000
1	0.415554070	-7.476894450	-2.966873140	1	-4.327881050	3.485646840	0.718067180
1	0.479246240	-7.447083010	-1.186329000	1	-3.586598110	1.880739830	0.442202260
1	1.906560820	-6.983749850	-2.149080210	1	-5.061661930	2.338354930	-0.456788570
6	0.330694650	-5.490513170	-2.094991510	6	2.844891050	-0.872304290	-0.018344900
6	-0.425841050	-4.999170310	-1.029463790	1	3.060911210	0.011445770	-0.626458150
1	-0.666561670	-5.666240600	-0.195190520	6	3.868656300	-1.711609630	0.411146810
6	-0.880742820	-3.669568170	-0.969530510	1	4.900076770	-1.489451130	0.130874260
6	-2.596370230	-3.880472920	0.595220320	6	3.547861790	-2.811081130	1.206455280
1	-2.865357300	-4.886566210	0.220082090	1	4.329042550	-3.487167470	1.562854050
6	-3.385715370	-3.392895730	1.680943830	6	2.212746430	-3.028114050	1.541334630
6	-4.373998970	-4.024081100	2.443622220	1	1.910391090	-3.871416460	2.165226240
1	-4.713617610	-5.049191940	2.310452210	6	1.246035320	-2.143013360	1.070606130
6	-4.818501380	-3.096837190	3.405445930	1	0.184800830	-2.285337880	1.292853210
1	-5.575104450	-3.265872950	4.166354620	6	3.555644730	-0.015304330	-3.669678050
6	-4.106986660	-1.905997670	3.212245670	1	4.362903100	-0.174586520	-2.958949540
6	-4.160144120	-0.596062020	3.979695610	6	2.254764320	-0.541122290	-3.583677540
6	-5.341935930	-0.624515670	4.965269770	1	1.874031990	-1.177013470	-2.788905830
1	-5.380758740	0.321426130	5.525911730	6	1.492525170	-0.017960780	-4.666951850
1	-5.251843670	-1.452597670	5.684006680	1	0.435819340	-0.202842540	-4.859079300
1	-6.285635570	-0.744179150	4.412073140	6	2.359355070	0.791475090	-5.451297030
6	-4.360838420	0.588570910	3.004008380	1	2.090692360	1.310668060	-6.368885890
1	-4.404621650	1.534313100	3.567367940	6	3.621197030	0.830996200	-4.814754080
1	-5.302631700	0.458859080	2.447402770	1	4.490504160	1.405829450	-5.131993040
1	-3.543328920	0.668088130	2.272995550	6	0.627484990	3.075672320	-4.866686550
6	-2.860610590	-0.427019090	4.748277590	1	0.140971820	2.540196750	-5.680677950
6	-2.602997610	-0.518762890	6.121373340	6	0.073777800	3.295452490	-3.585193260
1	-3.340861940	-0.725181030	6.891475990	1	-0.886807100	2.918936980	-3.236366250
6	-1.226600130	-0.290917890	6.317389020	6	1.013993660	4.031907950	-2.818773860
1	-0.688638660	-0.282841730	7.263066660	1	0.898633290	4.315766870	-1.772906050
6	-0.656181370	-0.074125820	5.059073950	6	2.140795650	4.289884770	-3.641940780
6	0.686059600	0.239582360	4.679278250	1	3.047819500	4.806647780	-3.336493660
1	1.394130550	0.409439440	5.513567900	6	1.916357980	3.691492320	-4.902980140
6	2.312582010	0.713083080	3.074924560	1	2.605206370	3.703345500	-5.746887910
6	3.468999740	0.266910320	3.740035010	7	-2.183399390	1.137543600	-1.900842870
1	3.352618580	-0.429438960	4.577029320	7	-0.949048940	-1.431521480	-1.962866330
6	4.752993100	0.664025520	3.361384550	7	-1.653279860	-3.167325190	0.071206830
6	5.958938580	0.146122020	4.105623800	7	-3.246702450	-2.107461240	2.167979320
1	6.649440050	-0.395301520	3.435696500	1	-2.624312370	-1.413979780	1.722722280
1	5.660301190	-0.539953100	4.912118930	7	-1.670668090	-0.162807150	4.126347850
1	6.538906090	0.969244010	4.557606970	1	-1.503611390	0.000658690	3.122252230
6	6.263830640	2.020270400	1.828420910	7	1.016025160	0.369626040	3.436486490

7	1.322945440	1.987654070	1.231805370	6	-0.873591970	6.881213120	2.047508250
7	-0.974137540	3.013934000	-0.086003000	1	-0.522556430	7.434721420	2.935351520
7	1.549257290	-1.082086610	0.295422020	1	-1.976658160	6.921332010	2.064388460
8	-1.413611510	0.074963130	1.018416790	1	-0.528451580	7.420914300	1.153178490
8	0.915568960	1.192904000	-1.865451200	6	-0.670146360	4.585137050	3.116489480
17	3.873134750	2.474660920	-1.980915240	6	-1.486795470	5.048903640	4.296135030
22	2.007680350	1.879671570	-3.311713230	1	-1.001513810	5.890723830	4.820107560
92	-0.314886810	0.660645980	-0.360249340	1	-1.630632870	4.234556560	5.022014930
3(Zr)				1	-2.485450640	5.401990510	3.984744970
6	1.977802840	-3.819816810	0.514828760	6	-0.208780020	3.265449610	3.055736540
6	1.648423200	-5.169737860	0.246372870	1	-0.442960930	2.588700110	3.882129420
1	2.248970530	-6.041771780	0.494529970	6	0.528731110	2.769771910	1.973083430
6	0.411157730	-5.168648740	-0.405019650	6	1.735641270	1.015277790	2.913349880
1	-0.149581370	-6.027799230	-0.771578890	1	1.974920340	1.700965090	3.743077790
6	0.022926040	-3.818414980	-0.508030940	6	2.340336910	-0.260283660	2.934461770
6	-1.113053920	-3.268917460	-1.139796890	6	3.209614360	-0.808896830	3.899733720
1	-1.811606670	-3.966868890	-1.627628890	1	3.494861940	-0.347336540	4.844556500
6	-2.485577190	-1.546570230	-1.902613810	6	3.644526360	-2.032220120	3.382428040
6	-3.767213510	-1.942125910	-1.502917420	1	4.335658480	-2.727340500	3.853565000
1	-3.858881940	-2.577683260	-0.616483650	6	3.031464190	-2.187637720	2.114772240
6	-4.922026110	-1.506155930	-2.162019080	6	3.276565770	-3.290347210	1.099811950
6	-6.280272590	-1.948752890	-1.677497620	6	4.076789550	-4.437750710	1.743312250
1	-6.922464880	-1.087819620	-1.421206070	1	4.301139630	-5.209809230	0.991998040
1	-6.190402280	-2.582102370	-0.782739840	1	3.521887810	-4.904935540	2.572155250
1	-6.818024970	-2.523760540	-2.451682520	1	5.036547460	-4.060955650	2.128102360
6	-4.789522620	-0.638764280	-3.269688340	6	4.121539620	-2.691043750	-0.058841410
6	-6.006479880	-0.121005580	-3.996066000	1	4.320079380	-3.461842240	-0.821516850
1	-6.675285720	0.441178040	-3.321296610	1	5.079683730	-2.307413150	0.329312380
1	-6.605869640	-0.946060440	-4.418338760	1	3.577587240	-1.860680080	-0.530462580
1	-5.718845620	0.545771400	-4.822538800	6	-2.782936790	0.959265520	0.025880860
6	-3.510059060	-0.263357520	-3.684973260	1	-2.991432680	0.102624960	0.672230000
1	-3.405935830	0.419210070	-4.534805560	6	-3.805640800	1.804403240	-0.393208120
6	-2.343614260	-0.711670960	-3.039209040	1	-4.829462870	1.617639600	-0.063711670
6	-0.741099380	-0.256348340	-4.676157820	6	-3.493163510	2.865855080	-1.241914390
1	-1.462252330	-0.430378630	-5.498275130	1	-4.273380180	3.545231600	-1.593853100
6	0.593469670	0.060695080	-5.079776220	6	-2.168213400	3.039195480	-1.636579340
6	1.137077590	0.281746900	-6.349383840	1	-1.872777490	3.851188970	-2.303756270
1	0.580615930	0.267867470	-7.284218720	6	-1.202675000	2.150479230	-1.170007090
6	2.514389150	0.524236400	-6.180742110	1	-0.149085370	2.261876930	-1.437396430
1	3.234537980	0.738724710	-6.965258120	6	0.127105100	-3.329781330	3.771060010
6	2.799832710	0.437092680	-4.812739110	1	1.073373290	-2.904536940	3.435129640
6	4.113109280	0.622423890	-4.071097160	6	-0.731466870	-4.164539630	3.006931060
6	5.272989810	0.667236620	-5.082003400	1	-0.558870810	-4.485486520	1.978660370
1	6.226563840	0.800043000	-4.549128160	6	-1.858757870	-4.483544520	3.809966090
1	5.156358930	1.494080730	-5.798320410	1	-2.710280130	-5.088008540	3.502177130
1	5.313127380	-0.277928450	-5.643795370	6	-1.713372090	-3.831902060	5.060265610
6	4.350939340	-0.560674150	-3.102026570	1	-2.416348950	-3.878247500	5.892313150
1	5.303288440	-0.419759590	-2.566736870	6	-0.477601170	-3.116340130	5.034907240
1	4.394515380	-1.504994570	-3.667866020	1	-0.054791600	-2.527734840	5.848770330
1	3.551076990	-0.651465870	-2.353114950	6	-3.703414320	-0.887980680	4.931850920
6	4.060396930	1.931318030	-3.301293070	1	-4.546147260	-1.500161950	5.252821420
6	4.751108160	3.131605960	-3.511510480	6	-2.446767130	-0.782851140	5.575029190
1	5.487886580	3.310142260	-4.289500130	1	-2.155389830	-1.283519260	6.496819500
6	4.316102590	4.053604700	-2.540634560	6	-1.623513000	0.080900350	4.798270930
1	4.644460310	5.083379720	-2.415973060	1	-0.585947970	0.339566950	5.012129520
6	3.353536930	3.410128560	-1.755151030	6	-2.401746760	0.552186670	3.702127500
6	2.575252970	3.892051760	-0.658716210	1	-2.053060940	1.218184950	2.915203950
1	2.831044710	4.906958360	-0.297552360	6	-3.674487040	-0.051131350	3.778155300
6	0.875944770	3.660616910	0.925554750	1	-4.488276520	0.065854960	3.064481170
6	0.398195480	4.982200810	0.984944620	7	0.992370410	-2.998525540	0.063818700
1	0.628643410	5.654352350	0.151810490	7	-1.325472480	-1.976173520	-1.208120650
6	-0.371600980	5.458857330	2.047996410	7	-1.051892340	-0.379990170	-3.427754000

7	1.625430890	0.159988630	-4.167115380	7	1.479230210	-4.703366250	0.254387280
1	1.482303430	-0.003779170	-3.158601660	17	4.517714910	-2.977211460	0.018725310
7	3.222142990	2.121706590	-2.237238170	1	4.540423310	-0.217759350	0.654282450
1	2.616709400	1.419297190	-1.781842600	6	4.987138350	1.252088760	2.171394630
7	1.652810070	3.166360490	-0.115347100	6	3.516935420	3.176228880	2.192973000
7	0.983024210	1.427415810	1.919997960	7	1.691699530	3.324142500	0.530710410
7	2.233250400	-1.120166390	1.846362240	6	-3.217105780	-0.392017020	3.919199070
7	-1.496611600	1.125999450	-0.344317930	7	-3.093520430	0.792740480	1.751496240
8	1.450785710	-0.081034220	-1.080779630	6	-2.418899840	-2.672998560	4.069394360
8	-0.881749160	-1.192112360	1.838532400	1	-1.636683320	-3.479633880	2.226779200
40	-1.975635990	-1.963954610	3.359836720	1	1.967022590	-0.644362760	4.693443410
92	0.358195560	-0.636709250	0.318573360	6	0.831957830	1.210912370	4.674728720
17	-3.921243340	-2.774343880	2.099621500	1	-0.366046620	2.979176630	4.267045940
4(Mg)				6	2.276444400	-5.576688240	0.903830040
6	0.721522930	-0.419396620	-4.061354820	6	3.471541090	-4.049539050	-3.237566080
6	1.882522430	-0.575767100	-4.858809980	6	1.170801510	-3.802206270	-3.386456780
6	-0.731555000	-0.573151720	-4.481224000	6	0.160504600	-4.974446540	0.173315640
7	1.060441170	-0.025796580	-2.807883250	6	6.138411280	0.458417150	2.737449780
1	1.911279830	-0.869571520	-5.906013880	6	4.599328560	2.485306510	2.743002300
6	2.977498490	-0.258065950	-4.049731830	1	3.196751940	4.117331800	2.652162760
6	-1.456757810	-1.509760990	-3.527710790	6	1.618692940	4.611118410	0.443872090
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6	-0.819425870	-1.099737200	-5.924461700	6	-2.981650420	-1.534297750	4.688445060
6	2.446870840	0.079750010	-2.786423250	6	-4.105029760	1.583226210	1.901275310
92	-0.036396990	0.010086030	-0.569893230	6	-2.131816370	-3.924500290	4.860998310
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7	-1.434119380	-1.315728200	-2.185237370	1	4.367129370	-3.880986330	-2.628316900
1	-2.475784610	0.731438740	-4.722762250	6	3.530296000	-4.655539700	-4.487574660
1	-0.905136380	1.520424020	-5.102922580	6	1.146782480	-4.414139190	-4.637580540
1	-1.373031390	1.222019770	-3.403958930	1	0.246415050	-3.423947700	-2.937673670
1	-1.872386820	-1.189099970	-6.232465940	6	-0.402923850	-6.121377650	0.726602670
1	-0.336603130	-2.084260070	-6.026565420	1	-0.458190410	-4.235092670	-0.348482100
1	-0.325412630	-0.396732310	-6.612359340	1	5.982970120	0.222621060	3.805008990
6	3.106789230	0.587695620	-1.642680290	1	7.088036630	1.018303980	2.672421440
7	2.447883910	0.941345800	-0.566277600	1	6.262869480	-0.489915100	2.194136300
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6	-2.765067130	-3.130338010	-2.640937450	6	-4.251821110	2.767523120	1.114324040
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6	3.181518110	1.446188950	0.528476240	1	-1.698939070	-4.705832970	4.218329260
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1	-3.222658110	-3.045747900	0.148211530	7	-0.618891500	4.559589180	-0.589625210
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7	2.310426430	-3.636102570	-2.685728980	1	0.011314890	-7.929793150	1.845820140

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6	-1.135907060	6.725947090	-0.743532380	6	-0.035420450	0.588602670	-4.864870810
6	-1.595857280	5.427676100	-0.996608780	6	0.385388140	-1.627178690	-4.052154290
1	-0.623031920	3.527346240	-0.678801870	1	0.457091240	-1.778943220	-1.902611430
6	-4.880707310	4.742193570	0.206370720	7	-1.865478610	-3.673214190	1.658077330
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1	-1.680801090	7.643006700	-0.949178970	1	3.947717780	-1.022667820	-0.746713210
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6	-0.898165220	4.194377180	2.741481340	6	5.453196380	-1.938483480	-2.815950710
6	-0.742622780	3.258720960	5.055982980	6	4.611467310	0.221088890	-3.855638170
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1	-0.834287610	3.971043860	1.667818590	1	-2.316072060	-2.078316470	2.919386070
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1	4.995582030	-1.055064380	-5.570312060
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6(ZnCl)

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1	2.952596160	2.489071680	-1.227629040
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6	-3.401435720	-0.970453250	3.342588590
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6	-0.593614400	-1.244516100	-6.151998970
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6	-0.429464260	-1.530445090	-4.798025240
1	0.289047930	-0.979760080	-4.183041020
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7	0.825581630	1.182983350	-2.637027500
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7	-0.168871220	4.322842740	1.562152200
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30	-0.791808910	-3.016719910	-2.187639600
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7(ZnI)

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1	3.968176520	2.782501050	4.307052880				

4. References

1 J. Rothe, S. Butorin, K. Dardenne, M. A. Denecke, B. Kienzler, M. Löble, V. Metz, A. Seibert, M. Steppert, T. Vitova, C. Walther and H. Geckeis, *Rev. Sci. Instrum.*, 2012, **83**, 043105.
2 P. L. Arnold, A. J. Blake, C. Wilson and J. B. Love, *Inorg. Chem.*, 2004, **43**, 8206–8208.
3 V. V. Burlakov, A. V. Polyakov, A. I. Yanovsky, Y. T. Struchkov, V. B. Shur, M. E. Vol'pin, U. Rosenthal and H. Görls, *J. Organomet. Chem.*, 1994, **476**, 197–206.
4 H. Arp, M. Zirngast, C. Marschner, J. Baumgartner, K. Rasmussen, P. Zark and T. Müller, *Organometallics*, 2012, **31**, 4309–4319.
5 U. Rosenthal, A. Ohff, M. Michalik, H. Görls, V. V. Burlakov and V. B. Shur, *Angew. Chem. Int. Ed.*, 1993, **32**, 1193–1195.
6 G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112–122.
7 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.
8 L. Palatinus and G. Chapuis, *J. Appl. Crystallogr.*, 2007, **40**, 786–790.
9 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.
10 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
11 W. T. Elam, B. D. Ravel and J. R. Sieber, *Radiat. Phys. Chem.*, 2002, **63**, 121–128.
12 A. Zimina, K. Dardenne, M. A. Denecke, D. E. Doronkin, E. Huttel, H. Lichtenberg, S. Mangold, T. Pruessmann, J. Rothe, T. Spangenberg, R. Steininger, T. Vitova, H. Geckeis and J.-D. Grunwaldt, *Rev. Sci. Instrum.*, 2017, **88**, 113113.
13 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
14 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.
15 D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151–156.
16 D. N. Laikov and Y. A. Ustynyuk, *Russ. Chem. Bull. Int. Ed.*, 2005, **54**, 820–826.
17 K. G. Dyall, *J. Chem. Phys.*, 1994, **100**, 2118.
18 T. Ziegler and A. Rauk, *Theor. Chim. Acta*, 1977, **46**, 1–10.

19 T. Lu and F.-W. Chen, *Acta Chim. Sin.*, 2011, **69**, 2393–2406.
20 T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580–592.
21 ADF2010, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com, http://www.scm.com/Doc/Doc2010/Background/References/page4.html, (accessed 26 March 2015).
22 C. Fonseca Guerra, J. G. Snijders, G. te Velde and E. J. Baerends, *Theor. Chem. Acc.*, 1998, **99**, 391–403.
23 G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders and T. Ziegler, *J. Comput. Chem.*, 2001, **22**, 931–967.
24 E. van Lenthe, E.-J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1993, **99**, 4597.
25 E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1994, **101**, 9783.
26 E. van Lenthe, A. Ehlers and E.-J. Baerends, *J. Chem. Phys.*, 1999, **110**, 8943.
27 E. van Lenthe, J. G. Snijders and E. J. Baerends, *J. Chem. Phys.*, 1996, **105**, 6505.
28 E. van Lenthe, R. van Leeuwen, E.-J. Baerends and J. G. Snijders, *Int. J. Quantum Chem.*, 1996, **57**, 281–293.
29 P. L. Arnold, J. H. Farnaby, R. C. White, N. Kaltsoyannis, M. G. Gardiner and J. B. Love, *Chem. Sci.*, 2014, **5**, 756-765.