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Citation for published version:
Arnold, PL, Patel, D, Pecharman, A-F, Wilson, C & Love, JB 2010, 'Equatorial ligand substitution by hydroxide in uranyl Pacman complexes of a Schiff-base pyrrole macrocycle', *Dalton Transactions*, vol. 39, no. 14, pp. 3501-3508. https://doi.org/10.1039/b922115h

Digital Object Identifier (DOI):
10.1039/b922115h

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Peer reviewed version

Published In:
Dalton Transactions

Post-print of a peer-reviewed article published by the Royal Society of Chemistry.
Published article available at: http://dx.doi.org/10.1039/B922115H

Cite as:
Arnold, P. L., Patel, D., Pecharman, A-F., Wilson, C., & Love, J. B. (2010). Equatorial ligand substitution by hydroxide in uranyl Pacman complexes of a Schiff-base pyrrole macrocycle. *Dalton Transactions*, 39(14), 3501-3508.

Manuscript received: 22/10/2009; Accepted: 12/02/2010; Article published: 02/03/2010

Equatorial ligand substitution by hydroxide in uranyl Pacman complexes of a Schiff-base pyrrole macrocycle**

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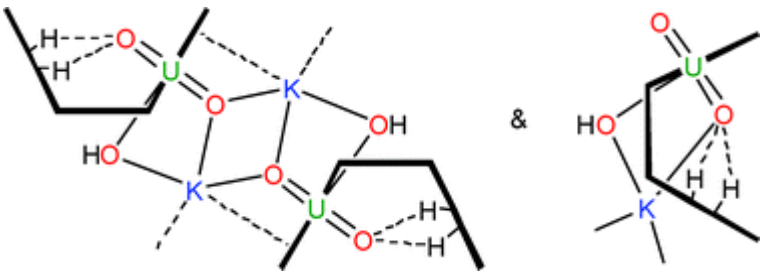
[**]We thank the Universities of Edinburgh and Nottingham for funding.

Supporting information:
[†]CCDC reference numbers 752122, 752123, 752124. For crystallographic data in CIF or other electronic format see http://dx.doi.org/10.1039/B922115H

Graphical abstract:



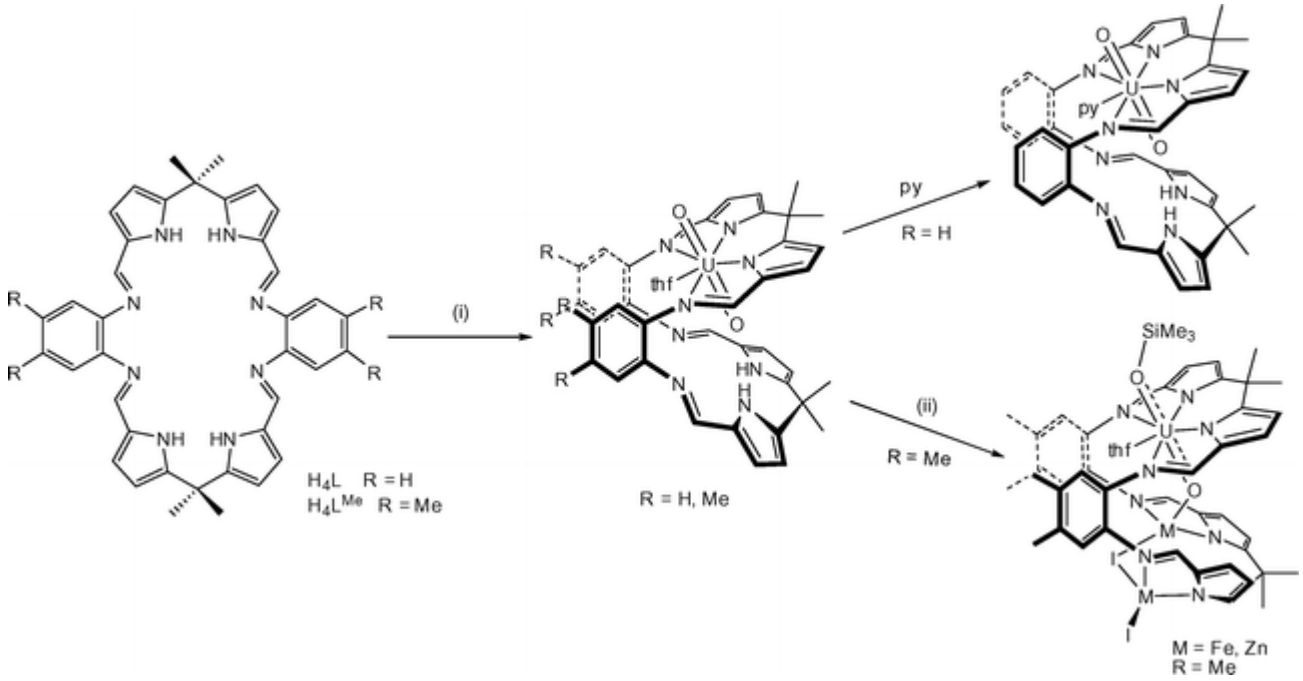
Abstract

The synthesis of the mono-uranyl complex $[UO_2(THF)(H_2L^{Me})]$ of a ditopic Schiff-base pyrrole macrocycle is described and is shown to adopt a Pacman wedge-shaped structure in which the uranyl dication is desymmetrised and sits solely in one N_4-donor compartment to leave the other vacant. While investigating the mechanism of the previously reported, base-initiated, reductive silylation chemistry of $[UO_2(THF)(H_2L^{Me})]$, we found that uranyl hydroxide complexes could be isolated. As such, the reaction between $[UO_2(THF)(H_2L^{Me})]$ and KH in THF generated the dimeric cation-cation hydroxide $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$ when crystallised from C_6H_6, or alternatively, when crystallised from THF, the monomeric THF-adducted cation-cation complex $[UO_2(OH)K(THF)_2(H_2L^{Me})]$ was isolated. These compounds result formally from the substitution of the equatorial THF molecule byhydroxide, and it was also shown that the reaction between dry KOH and $[UO_2(THF)(H_2L^{Me})]$ generated $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$.

Introduction

The uranyl dication, $[UO_2]^{2+}$ is the most prevalent form of uranium in solution chemistry and in the environment, and is characterised by strong and inert uranium oxo multiple bonding, with a rigorously linear O=U=O geometry and a formal U–O bond order of approximately 2.5 as a result of relativistic effects on the energies of the uranium valence orbitals.[1] Accordingly, ligand chemistry takes place almost exclusively in the equatorial plane.[2] We described recently the synthesis of mononuclear uranyl complexes of the macrocycle H_4L (Scheme 1), and showed that a folded, Pacman structure in solution and in the solid state was adopted and that substitution of the THF molecule that occupies the fifth, equatorial position by pyridine to form $[UO_2(C_5H_5N)(H_2L)]$ was straightforward.[3]

Significantly, we also found that reactions between $[UO_2(THF)(H_2L^{Me})]$, an analogue of $[UO_2(THF)(H_2L)]$, in which the aryl hinge groups are methylated, and $KN(SiMe_3)_2$ in the presence of two molar equivalents of a divalent transition metal halide, *e.g.* FeI_2 or ZnI_2 resulted in the remarkably selective reductive silylation of the uranyl dication, so forming the U^V complexes $[UO(OSiMe_3)(THF)(MI)_2(L^{Me})]$ (M = Fe, Zn; Scheme 1).[4] The use of KH as the base in the presence of either N–Si or C–Si substrates resulted in E–Si bond cleavage (E = N, C) and O–Si bond formation, with the generation of the same U^V reductively-silylated complexes. Therefore, we reasoned that the deprotonation of the vacant N_4-donor cavity by the potassium base caused the bonding in the $[UO_2]^{2+}$ group to be disrupted such that the *exo*-U=O bond was able to participate in radical abstraction reactions. This mechanism has been corroborated recently by theoretical calculations that show that the deprotonation of macrocyclic uranyl model complexes results firstly in the highly exergonic formation of an intermediate in which two potassium cations are bound to one U=O only. This activating-interaction then promotes an S_N2 radical reaction between the *exo* U=O group and silanes to form initially the reductively-silylated species which is then stabilised by addition of transition metal cations.[5]



Scheme 1. Synthesis and reactions of the macrocyclic uranyl complexes. Conditions: (i) $[UO_2(THF)_2\{N(SiMe_3)_2\}_2]$, -78 °C, THF, 88%; (ii) $KN(SiMe_3)_2$, MI_2, -78 °C, THF, M = Fe, 81%, M = Zn, 46% (alternatively: KH, $N(SiMe_3)_3$, MI_2 -78 °C, THF).

The interactions of the oxo groups of the uranyl dication with other metal cations are known as cation-cation interactions, or CCI's. Sullivan pioneered the study of CCI's, first noting the unusual interaction of the $[UO_2]^{2+}$ ion with the pentavalent $[NpO_2]^+$ cation in acidic solution,[6] and recognising that CCI's form much more readily in f^1 systems such as pentavalent uranyl, and also in neptunyl, and plutonyl salts that incorporate a more Lewis basic oxo group.[7] Weak interactions have been seen in a handful of X-ray structures of f^0 uranyl complexes such as $[Na(THF)_2][UO_2\{N(SiMe_3)_2\}_3]$,[8] and $Li_4[(UO_2)_{10}O_{10}(Mo_2O_8)]$.[9] CCI's change the solubilities of the actinyl salts in solution, and have important implications for the PUREX process that has been used for the last few decades by the nuclear industry to separate the dissolved components of spent nuclear fuel.[10] The precise interactions of solvated hydroxyl uranyl complexes with other cations is also attracting interest in the study of nuclear waste behaviour.[11]

Herein, we describe the full details of the synthesis and crystal structure of the uranyl complex $[UO_2(THF)(H_2L^{Me})]$ and its reaction with KH and K that generate complexes arising formally from addition of KOH to $[UO_2(THF)(H_2L^{Me})]$, isolated as two different solvates, $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$ and $[\{UO_2(OH)K(THF)_2(H_2L^{Me})\}_2]$. The single crystal X-ray structures of these solvates contain a variety of CCIs with potassium cations; as such, structural features of these complexes are compared with those in $[\{UO_2(O)K_2(C_6H_6)(H_2L)\}_2]$, the structure of which we communicated previously.[12]

Results and discussion

Formation and characterisation of the uranyl complex $[UO_2(THF)(H_2L^{Me})]$

In a manner similar to that described by us previously,[3] the transamination reaction between the uranyl silylamide $[UO_2(THF)_2\{N(SiMe_3)_2\}_2]$ and H_4L^{Me} in THF at low temperature resulted in the sole formation of the mono-uranyl complex $[UO_2(THF)(H_2L^{Me})]$ as an analytically-pure, dark brown solid in high yield (Scheme 1). Dark red columnar crystals suitable for X-ray diffraction studies were grown by the slow diffusion of hexane into a THF solution and the solid state structure was determined by X-ray diffraction (Fig. 1); selected bond lengths and angles are detailed in Table 1, with crystal data shown in Table 2. In a manner similar to that shown by us previously, one N_4-donor set of the macrocycle is sufficiently flexible to accommodate the large uranyl ion in a pentagonal bipyramidal geometry. The N-donors are found to occupy four equatorial sites with the fifth occupied by an oxygen atom of a bound THF molecule; the axial positions contain the two *trans*-oxo ligands. The second N_4-donor compartment of the macrocyclic ligand remains metal free with the pyrrole nitrogens protonated and results in a wedge-shaped geometry that differentiates between the two uranyl oxo groups. The uranyl-oxo bond lengths (U1-O1 1.787(3), U1-O2 1.770(3) Å) are similar to those in the related complex $[UO_2(THF)(H_2L)]$ (U1-O1 1.790(4), U1-O2 1.766(4) Å),[3] and show an elongation in the *endo* U=O bond distance of similar magnitude (0.017 Å) due to hydrogenbonding interactions with the pyrrole hydrogens of the vacant compartment.[13]

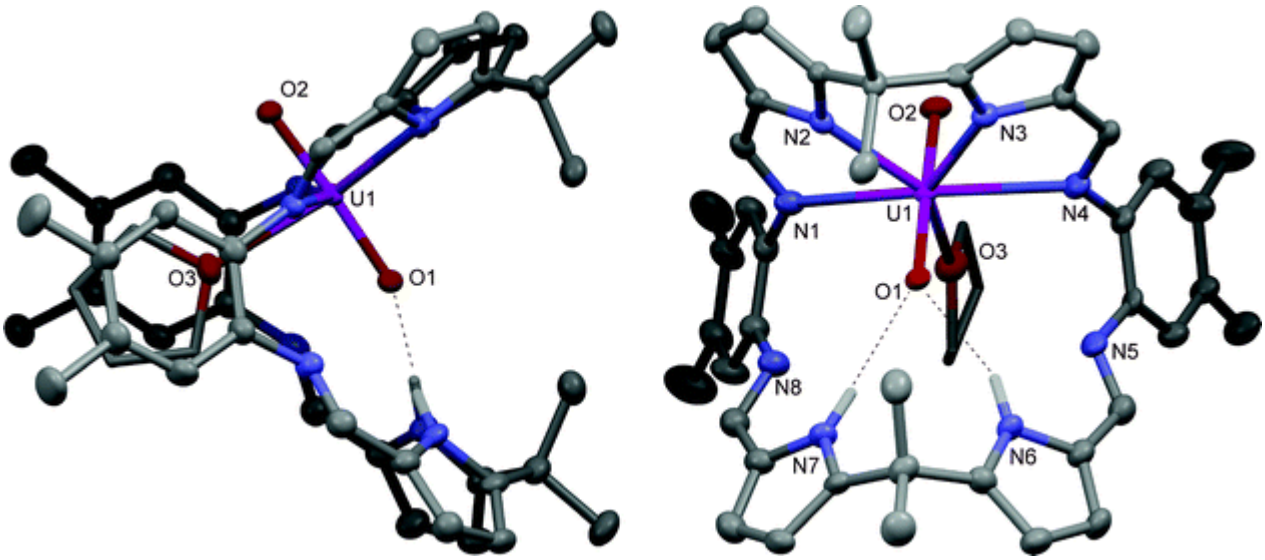
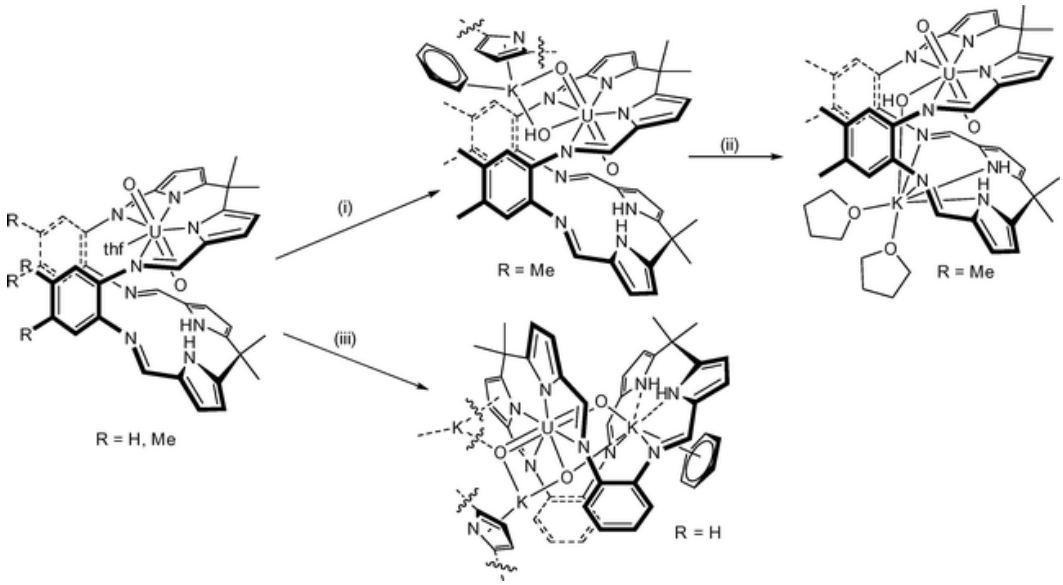


Figure 1. Side-on and face-on views of the solid state structure of the mono-uranyl complex $[UO_2(THF)(H_2L^{Me})]$. For clarity, solvent of crystallisation and all hydrogens except those on the pyrrole nitrogens are omitted (50% probability displacement ellipsoids).

The uranyl complex was characterised further by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, which revealed that the solid state structure is retained in solution. Discrete resonances are observed in the ^{1}H NMR spectrum for the metal free and complexed N_4-donor compartments, *e.g.* two distinct resonances at 8.74 and 7.99 ppm attributable to the Schiff base imine protons were seen, and also for the uranium-bound molecule of THF with four separate resonances at 4.83, 3.94, 0.86, 0.71 ppm. This equatorially-bound THF molecule is labile and undergoes fast exchange, as the ^{1}H NMR spectrum in d_8-THF no longer contains resonances due to coordinatedTHF. Furthermore, it has been shown previously by us that this THF molecule can be displaced by pyridine (Scheme 1).[3] The IR spectrum exhibits a strong absorption at 908 cm^{-1} that is attributed to the uranyl asymmetric stretch, is similar to that seen in $[UO_2(pyr)(H_2L)]$ (ν 910 cm^{-1}) and is indicative of a weakened U=O bond.

Reactions of $[UO_2(THF)(H_2L^{Me})]$ with KH, KOH, and K

While probing the mechanism of the reductive silylation of $[UO_2(THF)(H_2L^{Me})]$ (Scheme 1), in particular in an attempt to isolate and identify compounds such as $[UO_2(THF)K_2(L^{Me})]$ formed by deprotonation using a potassium base, we instead found that the reaction between $[UO_2(THF)(H_2L^{Me})]$ and some samples of KH in the absence of a silyl substrate formed a brown solid that, on crystallisation from benzene, generated the U^{VI} dimeric hydroxo complex $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$ in moderate yield (Scheme 2). Furthermore, recrystallisation of this material from a mixture of THF and benzene generated quantitatively the monomeric THF adduct $[UO_2(OH)K(THF)_2(H_2L^{Me})]$.



Scheme 2. Reactions of $[UO_2(THF)(H_2L^{Me})]$ with KH, KOH, and K. Conditions: (i) KH, -78 °C, THF, recrystallise from C_6H_6, 35% (alternatively: KOH, THF, recrystallise from C_6H_6, 25%), (ii) THF–C_6H_6, 100%; (iii) K, C_6H_6, 10% (ref.12).

It therefore appears likely that the incorporation of KOH in these complexes has resulted through either the use of impure KH (*i.e.* some KOH is present) or from the decomposition of the potassium salt $[UO_2(THF)(K_2L^{Me})]$ by reaction with adventitious water. To corroborate the presence of KOH and to find a reproducible route to these complexes, the reaction between dry KOH and $[UO_2(THF)(H_2L^{Me})]$ was carried out and was found to form $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$ aftercrystallisation from benzene in moderate isolated yield (effectively quantitative by ^{1}H NMR spectroscopy); X-ray quality crystals were grown and were found to have the same unit cell parameters as material derived from KH reactions.

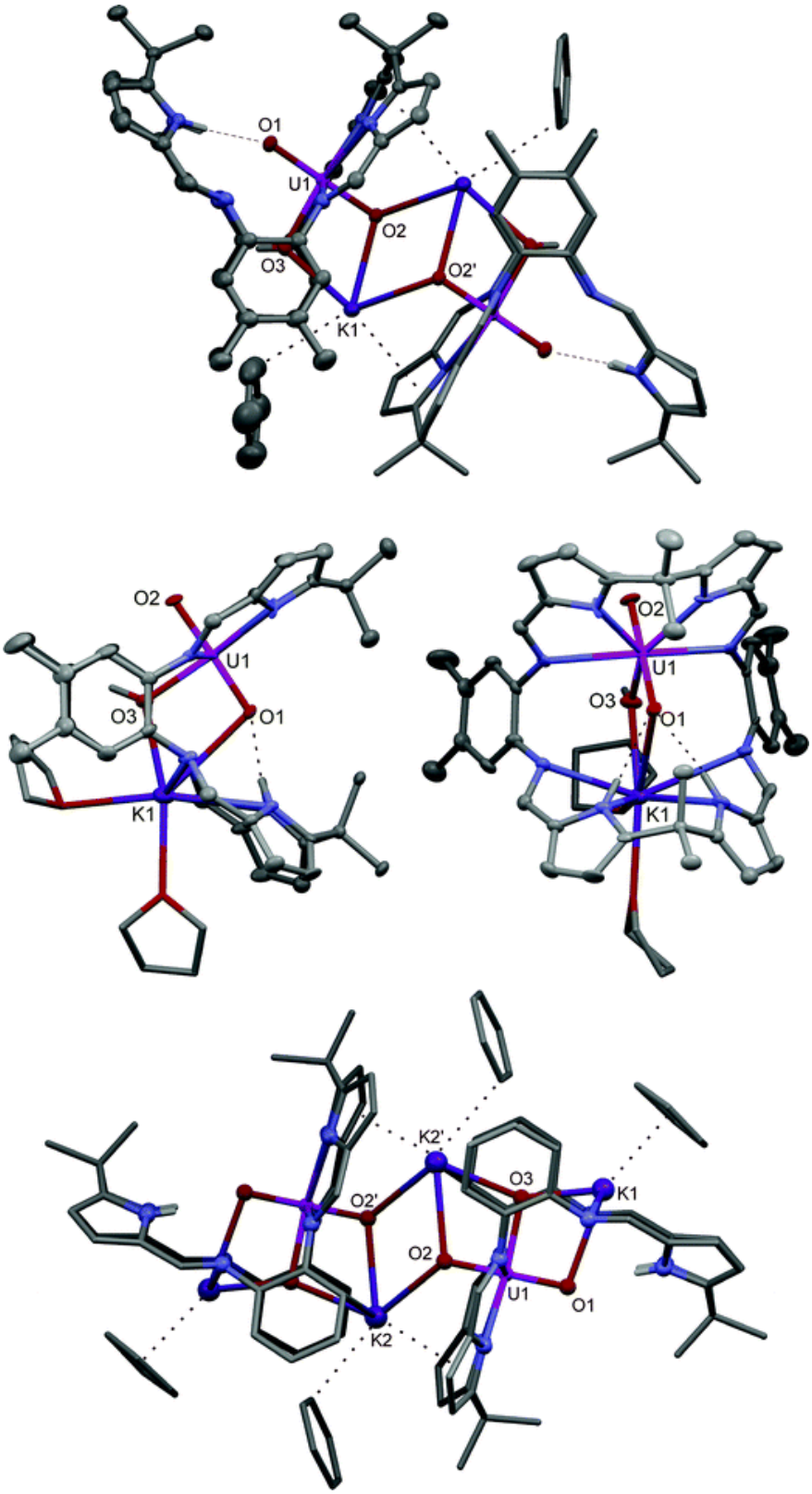
The ^{1}H NMR spectrum of $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$ in a mixture of C_6D_6 and THF supports the presence of the OH group with a characteristic broad resonance at 10.15 ppm and also suggests that the Pacman solid state structure is retained in solution with two separate resonances for the imine protons at 8.75 and 7.89 ppm associated with different N_4-donor compartments. The ^{1}H NMR spectrum of this complex derived from the reaction between $[UO_2(THF)(K_2L^{Me})]$ and KOH is very similar with subtle differences which is likely due to facile THF solvent exchange and the difficulty encountered in accurately defining concentrations andsolvent mixture ratios. The IR spectrum shows an absorption at 894 cm^{-1} and is attributed to the uranyl asymmetric stretch. This vibration lies within the expected range for the uranyl asymmetric stretch and is shifted to lower energy compared to that of the uranyl macrocyclic precursor $[UO_2(THF)(H_2L^{Me})]$ which may indicate slight elongation of the U=O bond (see below for solid state structure). There are also absorptions at 3608 and 3360 cm^{-1}, consistent with OH and NH stretches respectively that support further the presence of the hydroxo ligand and the metal-free N_4-donor compartment.

Dissolution of $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$ in a mixture of THF and benzene resulted in the quantitative deposition of red-orange rectangular block shaped crystals of the THF adduct $[UO_2(OH)K(THF)_2(H_2L^{Me})]$. Elemental analysis of this material supported its formulation, and the ^{1}H NMR spectrum is similar to that of $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$ in that the spectrum is diamagnetic and discrete resonances are observed for the separate uranyl-containing and metal-free N_4compartments; as such this indicates that a Pacman structure is adopted in solution. Notable features in the ^{1}H NMR spectrum of the complex are the imine resonances at 8.73 and 7.88 ppm, the broad resonance for the OH proton at 10.41 ppm, and the NH protons at 8.66 ppm. The IR spectrum of $[UO_2(OH)K(THF)_2(H_2L^{Me})]$ shows an absorption at 895 cm^{-1} that is similar to that seen for $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$. Also, there are absorptions at 3626 and 3329 cm^{-1} that support further the presence of a hydroxo ligand and a metal-free N_4-donor compartment.

X-ray crystallography

X-ray quality crystals of $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$ were grown from C_6H_6 and $[UO_2(OH)K(THF)_2(H_2L^{Me})]$ from a mixture of THF and C_6H_6; the solid state structures are shown in Fig. 2, with selected bond lengths and angles detailed in Table 1 and crystal data listed in Table 2. We have also

attempted previously the chemical reduction of $[UO_2(THF)(H_2L)]$ with an excess of potassium metal (Scheme 2), but only isolated a small quantity of orange crystalline material (*ca.* 10% yield) characterised as the dimeric potassium oxide adduct $[\{UO_2(O)K_2(C_6H_6)(H_2L)\}_2]$ by single crystal X-ray diffraction (Fig. 2, bottom, for comparison).[12]



← ***Figure 2.*** Solid state structures of the KOH uranyl adducts $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$ (top), $[UO_2(OH)K(THF)_2(H_2L^{Me})]$ (middle), and $[\{UO_2(O)K_2(C_6H_6)(H_2L)\}_2]$ (bottom, mixed 50 : 50 disorder between K2 andH, only oxo complex is shown).

For clarity, all hydrogens except those on thepyrrole nitrogens, and solvent of crystallisation are omitted (where present, displacement ellipsoids are drawn at 50% probability).

The presence of KOH in [{UO_2(OH)K(C_6H_6)(H_2L^{Me})}$_2$] does not disrupt the general Pacman structural motif, and the uranyl fragment remains complexed by the four nitrogen atoms (U1-N1 2.532(2), U1-N2 2.476(2), U1-N3 2.505(2), U1-N4 2.604(2) Å) in one half of the macrocycle. The uranium-oxo bond distances (U1-O1 1.7949(16), U1-O2 1.8029(16) Å) are longer than those reported for [UO_2(THF)(H_2L^{Me})] although they are still consistent with the hexavalent oxidation state.[14]The pentagonal bipyramidal coordination sphere of the uranium metal centre is completed in the equatorial plane by a hydroxo ligand, which resides in the same fifth equatorial site as the oxygen atom of the usually bound THF molecule, in-between the macrocyclic aryl rings. The uranyl-hydroxo U1-O3 bond length of 2.1854(19) Å is significantly shorter than those found in $(UO_2)_2$(μ-OH) complexes (range 2.29-2.51 Å, mean 2.34 Å)[15] with a relatively acute U1-O3-K1 angle of 102.25(6) ° (range for $(UO_2)_2$(μ-OH) complexes 102.0-145.4°, mean 113.4°);[15] there are no structurally-characterised hydroxyl bridged uranyl-alkali metal complexes for comparison.

The potassium cation resides above the plane of the macrocycle at a distance approximately equidistant from the *exo*-oxo atom (K1-O2 2.8130(19) Å) and the oxygen atom of the hydroxo ligand (K1-O3 2.657(2) Å) and leads to a slight elongation of the *exo*-oxo-uranium bond length compared to that of [UO_2(THF)(H_2L^{Me})] (*ca.* 0.03 Å). Hexavalent uranyl complexes with CCI interactions to a potassium cation are rare, and only a handful of calixarene and carboxylate complexes of the uranyl ion with potassium CCIs have been structurally characterised. For example, Thuéry and Masci reported the complex [(UO_2)K_2(L)(H_2O)$_2$(NC_5H_5)] (L = *p-tert*-butyltetrahomodioxacalix[4]arene) derived from the combination of uranyl nitrate, the free base calixarene and KOH. This complex incorporates potassium cations bridging pairs of uranyl cations to form polymeric chain structures, with the potassium–oxo interactions similar to those in [{UO_2(OH)K(C_6H_6)(H_2L^{Me})}$_2$].[16] The mean O–K distance in U=O···K CCI structures reported to date is 2.788 Å.[17] The presence of the potassium cation in [{UO_2(OH)K(C_6H_6)(H_2L^{Me})}$_2$] results in dimerisation as K1 not only interacts strongly with O3 of the hydroxyl ligand and the O2 oxo group, but also with O2′ of an adjacent complex in a symmetric bridging arrangement (K1-O2′ 2.8389(18) Å); this is reinforced by an intermolecular η^5-interaction to a pyrrole ring of the adjacent macrocycle. The coordination sphere of K1 is completed by an η^2-interaction with a molecule of benzene solvent of crystallisation. The bottom compartment of the macrocycle remains metal-free, and both the pyrrolic nitrogens are protonated. As in [UO_2(THF)(H_2L^{Me})], the *endo*-oxo ligand forms hydrogen bonds with the hydrogen atoms on the pyrroles (N6···O1 3.056 Å, N7···O1 3.202 Å), interactions that presumably help stabilise the complex. The structure of [{UO_2(OH)K(C_6H_6)(H_2L^{Me})}$_2$] is clearly related to that of the previously communicated K_2O adduct [{UO_2(O)K_2(C_6H_6)(H_2L)}$_2$] through exchange of (O)-H with (O)-K (Fig. 2, bottom).[12] This latter complex adopts a similar dimeric structural motif in which the two macrocycles are conjoined by K cations (Fig. 2, bottom), and the second K cation (K1) is bound to both the *endo*-uranyl oxygen and the oxo O3; the coordination sphere of K1 is completed through complexation by the macrocyclic imine nitrogens and an η^6-benzene.

In the X-ray crystal structure of $[UO_2(OH)K(THF)_2(H_2L^{Me})]$ (Fig. 2, middle), it is clear that the addition of THF has caused the scission of the intermolecular K-macrocycle interactions in the dimer of $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$ with the migration of the potassium cation K1 to the U-free half of the macrocyclic wedge. The geometry of the uranyl dication remains pentagonal bipyramidal with the oxo ligands *trans* (O1-U1-O2 178.5(3)°) and the equatorial coordination occupied by one N_4donor compartment and the hydroxo group; the bond distances between these donor atoms and U1 are similar to those seen in the structure of $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$. The potassium cation again adopts a bridging geometry, although in this case K1 bridges the hydroxo group O3 (K1-O3 2.547(5) Å) and the oxo ligand O1 (K1-O1 3.194(7) Å) in an asymmetric manner within the macrocyclic cleft. The remaining coordination sphere of K1 is completed by coordination with pyrrole andimine nitrogens of the vacant donor compartment and by two molecules of THF. This structural mode clearly affects the bonding in the uranyl fragment, as significant elongation of the *endo*-U1-O1 bond distance is seen (1.821(6) Å) compared to the *exo*-U1-O2 distance (1.788(6) Å) and also to the U–O bond distances in $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$ (1.8029(16) and 1.7949(16) Å). In a similar manner to $[UO_2(THF)(H_2L^{Me})]$ and $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$, a hydrogen bonding interaction between the *endo*-oxo group O1 and the pyrrole hydrogens is observed (N6···O1 3.046 Å, N7···O1 3.079 Å).

Conclusions

We have shown that reactions between the uranyl Pacman complex $[UO_2(THF)(H_2L^{Me})]$ and the potassium-based reagents K metal, KH, and KOH result in the isolation of KOH or K_2O adducts that have been characterised in the solid state and in solution. Structural data show that these complexes retain their overall Pacman structural motif in which the O-atoms at the uranyl are arranged in a T-shape. The K cations are coordinated either outside or within the macrocyclic framework which results in cation-cation interactions with the oxo-groups of the uranyl dication and bridging interactions with the equatorial hydroxide or oxide ligand.

Experimental details

All manipulations were carried out under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in MBraun Unilab or Vacuum Atmospheres OMNI-lab gloveboxes unless otherwise stated. THF and hexane were degassed and purified by passage through activated alumina towers prior to use, while benzenewas boiled over K and distilled. All deuterated solvents were boiled over potassium, vacuum transferred, and freeze-pump-thaw degassed three times prior to use. The compounds H_4L^{Me} and $[UO_2(THF)_2\{N(SiMe_3)_2\}_2]$ were synthesised according to literature procedures,[18] and KOH was prepared by the addition of degassed waterto potassium in toluene; all other reagents were used as purchased without

further purification. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX 300 and Avance 360 MHz NMR spectrometers at 300 K. Chemical shifts are reported in parts per million, and referenced to residual proton resonances calibrated against external TMS. Infrared spectra were recorded on Nicolet 210 and Jasco 410 spectrophotometers. Elemental analyses were carried out by Mr. Stephen Boyer at London Metropolitan University. Solutions for UV-vis spectrophotometry were made in a nitrogen filled glovebox and spectra were recorded in either a Teflon-tapped 10 mm quartz cell or a 1 mm quartz cell sealed by a tight fitting Subaseal on a Unicam UV1 spectrophotometer. Mass spectra were recorded by Mr. Tony Hollingsworth at the University of Nottingham on a VG Autospec instrument.

Synthesis of $[UO_2(THF)(H_2L^{Me})]$

A solution of H_4L^{Me} (2.64 g, 4.0 mmol) in THF (20 mL) was added slowly to a stirred solution of $[UO_2(THF)_2\{N(SiMe_3)_2\}_2]$ (2.94 g, 4.0 mmol) in THF (20 mL) at -78 °C. The resulting solution was allowed to warm to room temperature over 16 h, after which the volatiles were removed under vacuum and the residual solids redissolved in THF (15 mL). Addition of hexane (20 mL) to this solution resulted in a precipitate that was isolated by filtration, washed with hexane (2 × 10 mL), and dried under vacuum to yield $[UO_2(THF)(H_2L^{Me})]$ as a brown/red solid (3.76 g, 88%).

Analysis found: C 56.00, H 5.55, N 10.51%; $C_{50}H_{58}N_8O_4U$ requires: C 55.96, H 5.46, N 10.44%; ^{1}H NMR (C_6D_6): δ_H 8.74 (s, 2H, imine), 8.49 (s, 2H, N*H*), 7.99 (s, 2H, imine), 7.18 (s, 2H, aryl), 6.81 (s, 2H, aryl), 6.78 (d, 2H, pyrrole), 6.71 (d, 2H, pyrrole), 6.27 (d, 2H, pyrrole), 5.86 (d, 2H, pyrrole), 4.83 (m, 2H,THF), 3.94 (m, 2H, THF), 2.23 (s, 3H, methyl), 2.13 (s, 6H, 2 × methyl), 2.08 (s, 3H, methyl), 2.00 (s, 6H, 2 × methyl), 1.31 (s, 3H, methyl) 0.86 (m, 2H, THF), 0.71 (m, 2H, THF), 0.52 (s, 3H, methyl); ^{1}H NMR (d_8-THF): δ_H 8.87 (s, 2H, imine), 8.21 (s, 2H, imine), 8.09 (s, 2H, N*H*), 7.13 (s, 2H, aryl), 7.08 (s, 2H, aryl), 6.84 (d, 2H, J = 3.5 Hz, pyrrole), 6.34 (d, 2H, J = 3.5 Hz, pyrrole), 6.19 (d, 2H, pyrrole), 5.71 (d, 2H, pyrrole), 2.32 (s, 6H, 2 × methyl), 2.23 (s, 6H, 2 × methyl), 1.99 (s, 3H, methyl), 1.79 (s, 3H, methyl), 1.42 (s, 3H, methyl), 0.83 (s, 3H, methyl); $^{13}C\{^{1}H\}$ (C_6D_6): δ_C 164.9 (q), 161.0 (q), 148.1 (imine), 146.5 (imine), 144.1 (q), 143.2 (q), 139.3 (q), 134.0 (q), 132.0 (q), 124.5 (q), 122.2 (aryl), 117.8 (pyrrole), 114.7 (pyrrole), 109.8 (aryl), 105.7 (pyrrole), 75.6 and 78.0 (THF), 40.8 (q), 35.7 (methyl), 34.4 (quaternary), 29.1 (methyl), 27.7 (methyl), 26.2 and 25.7 (THF), 25.0 (methyl), 18.9 (methyl), 18.8 (methyl); EIMS: *m*/*z* 928.3 (3.87%, M^+), 913.2 (6.61%, $M\text{-}O^+$); IR (Nujol): ν 3373(br, NH), 1619, 1601, 1583, 1281(s), 1263, 1214, 1181, 1049(s), 1019, 959, 908 (s, U=O asymmetric stretch), 895, 780, 766 cm^{-1}; UV-vis (THF, 25 °C): 322 nm (ε = 42048 $dm^3mol^{-1}cm^{-1}$).

Reaction between $[UO_2(THF)(H_2L^{Me})]$ and KH: isolation of $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$

THF (20 mL) was added to a stirred mixture of $[UO_2(THF)(H_2L^{Me})]$ (0.10 g, 0.09 mmol) and KH (11 mg, 0.18 mmol) at -78 °C and was allowed to warm to room temperature over 16 h. After this time, the mixture was

filtered by cannula, the residual solids washed with THF (5 mL) and the washings and filtrate combined. The volatiles were removed under vacuum leaving a brown solid that was recrystallised from benzene to yield [{$UO_2(OH)K(C_6H_6)(H_2L^{Me})$}$_2$], (0.034 g, 35%). Orange hexagonal block-shaped crystals suitable for X-ray diffraction studies were grown from a saturated benzene solution.

Analysis. Found: C 54.22, H 4.60, N 10.47. $C_{48}H_{49}KN_8O_3U$ requires C 54.22, H 4.65, N 10.54%; ^{1}H NMR (C_6D_6 + THF, double presaturation): δ_H 10.15 (s, 1H, O*H*), 8.75 (s, 2H, imine), 8.62 (s, 2H, N*H*), 7.89 (s, 2H, imine), 7.05 (d, 2H, pyrrole), 6.89 (s, 2H, aryl), 6.68 (d, 2H, pyrrole), 6.63 (s, 2H, aryl), 6.14 (m, 2H,pyrrole), 5.72 (m, 2H, pyrrole), 2.17 (s, 6H, 2 × methyl), 2.10 (s, 6H, 2 × methyl), 2.04 (s, 3H, methyl), 0.71, (s, 3H, methyl), 0.18 (s, 3H, methyl). The remaining 1 ×methyl resonance is under the THF resonance of the solvent; IR (Nujol mull): *ν* 3608 (br, OH), 3360 (br, NH), 1620, 1601 (s), 1584, 1353, 1286 (s), 1267, 1214, 1179, 1047 (s), 1016, 960, 894 (U=O asymmetric), 860 (s), 779, 688 cm^{-1}.

Synthesis of [$UO_2(OH)K(THF)_2(H_2L^{Me})$]

Dissolution of the crystals of [{$UO_2(OH)K(C_6H_6)(H_2L^{Me})$}$_2$] in a mixture of THF and C_6H_6 resulted in the quantitative deposition of X-ray quality, red-orange rectangular block shaped crystals of [$UO_2(OH)K(THF)_2(H_2L^{Me})$]

Analysis. Found: C 53.18, H 5.27, N 9.95. $C_{50}H_{59}KN_8O_5U$ requires: C 53.18, H 5.27, N 9.92%; ^{1}H NMR (C_6D_6 + THF double presaturation): δ_H 10.41 (s, 1H, O*H*), 8.73 (s, 2H, imine), 8.66 (s, 2H, N*H*), 7.88 (s, 2H, imine), 7.06 (d, 2H, pyrrole), 6.71 (m, 4H, aryl), 6.66 (d, 2H, pyrrole), 6.15 (m, 2H, pyrrole), 5.75 (m, 2H,pyrrole), 2.19 (s, 6H, 2 × methyl), 2.08 (s, 6H, 2 × methyl), 2.06 (s, 3H, methyl), 0.64 (s, 3H, methyl), 0.22 (s, 3H, methyl); IR (Nujol): *ν* 3626 (br, OH), 3329 (br, NH), 1601 (s), 1583 (s), 1562 (sh), 1352, 1284 (s), 1269, 1215, 1184, 1153, 1043 (s), 1018, 960, 895 (U=O asymmetric), 866 (s), 795, 777, 760, 621, 594 cm^{-1}.

Direct synthesis of [{$UO_2(OH)K(C_6H_6)(H_2L^{Me})$}$_2$]

THF (20 ml) was added to an equimolar mixture of [$UO_2(THF)(H_2L^{Me})$] (0.089 g, 0.089 mmol) and dry KOH (0.005 g, 0.089 mmol) at 25 °C. The resulting solution was stirred for 16 h, and the volatiles removed under vacuum. The resulting pink red solid was recrystallised from benzene to yield [{$UO_2(OH)K(C_6H_6)(H_2L^{Me})$}$_2$] as orange rectangular block-shaped crystals (0.024 g, 25%). The crystals were analysed by X-ray crystallography and were found to have the same unit cell parameters as those formed using the above alternative route.

^{1}H NMR:(C_6D_6+THF double presaturation): δ_H 11.19 (s, 1H, OH), 9.17 (s, 2H, imine), 9.08 (s, 2H, NH), 8.59 (s, 2H, imine), 7.40 (s, 2H, aryl), 7.32 (s, 2H, aryl), 7.22 (d, 2H, pyrrole), 6.84 (d 2H, pyrrole), 6.68 (m, 2H, pyrrole), 6.22 (m, 2H, pyrrole), 2.72 (s, 6H, 2 × methyl), 2.68 (s, 6H, 2 × methyl), 1.34 (s, 3H,methyl), 0.55 (s, 3H, methyl); ^{1}H NMR ($CDCl_3$): δ_H 9.96 (s, 1H, OH), 9.00 (s, 2H, imine), 8.35 (s, 2H, NH), 8.25 (s, 2H, imine), 7.29 (d, 2H, pyrrole), 7.07(s, 2H, aryl), 6.89 (s, 2H, aryl), 6.69 (d 2H, pyrrole), 6.52 (m, 2H, pyrrole), 6.05 (m, 2H, pyrrole), 2.50 (s, 6H, 2 × methyl), 2.39 (s, 6H, 2 × methyl), 2.25 (s,3H,methyl), 2.13 (s,3H, methyl),1.68 (s, 3H, methyl), 1.09 (s, 3H, methyl).

Crystallographic details†

X-Ray diffraction data from single crystals of [UO_2(THF)(H_2L^{Me})], [UO_2(OH)K(THF)$_2$(H_2L^{Me})] and [{UO_2(OH)K(C_6H_6)(H_2L^{Me})}$_2$] were collected at 150 K usinggraphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker SMART APEX diffractometer equipped with a CCD detector. Details of the individual data collections and refinements are given in Table 2. All structures were solved by direct methods and refined using full-matrix least square refinement on $|F|^2$ using SHELXL-97. Unless otherwise stated, all non-hydrogen atoms were refined with anisotropic displacement parameters while hydrogen atoms were placed at calculated positions and included as part of a riding model. In [UO_2(THF)(H_2L^{Me})], two half-occupied THF solvent molecules per asymmetric unit were refined isotropically using distance and similarity restraints. In [{UO_2(OH)K(C_6H_6)(H_2L^{Me})}$_2$], some of the benzene solvent of crystallisation was disordered over two sites and was refined isotropically with 50 : 50 occupancy. In [UO_2(OH)K(THF)$_2$(H_2L^{Me})], the twin law (0 -1 0, -1 0 0, 0 0 -1) was applied and the twin component fraction refined to 0.1198(11). The two molecules of THF bound to the K, and one THF solvent of crystallisation could not be modelled accurately and so were refined isotropically. Furthermore, the two molecules of benzene that lie on crystallographic mirror planes could not be modelled accurately and so were also refined isotropically using distance and similarity restraints.

Tables

Table 1. Selected bond length (Å) and angles (°) for $[UO_2(THF)(H_2L^{Me})]$, $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$, and $[UO_2(OH)K(THF)_2(H_2L^{Me})]$

$[UO_2(THF)(H_2L^{Me})]$		**$[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$**		**$[UO_2(OH)K(THF)_2(H_2L^{Me})]$**	
Symmetry code/s: (i) -*x*+1, -*y*+1, -*z*+1.					
U1–O1	1.787 (3)	U1–O1	1.7956 (16)	U1–O2	1.788 (6)
U1–O2	1.770 (3)	U1–O2	1.8027 (16)	U1–O1	1.821 (6)
U1–O3	2.457 (3)	U1–O3	2.1863 (18)	U1–O3	2.186 (8)
U1–N1	2.557 (4)	U1–N1	2.531 (2)	U1–N1	2.598 (8)
U1–N2	2.473 (4)	U1–N2	2.476 (2)	U1–N2	2.499 (8)
U1–N3	2.443 (4)	U1–N3	2.504 (2)	U1–N3	2.519 (9)
U1–N4	2.583 (4)	U1–N4	2.603 (2)	U1–N4	2.550 (8)
		U1–K1	3.7853 (11)	U1–K1	3.966 (2)
		U1–K1^{i}	4.1083 (11)	K1–O3	2.574 (7)
		K1–O3	2.6610 (19)	K1–O4	2.688 (15)
		K1–O2	2.8127 (19)	K1–O5	2.758 (14)
		K1–O2^{i}	2.8382 (18)	K1–N8	2.900 (9)
		K1–N3^{i}	3.133 (2)	K1–N5	3.027 (9)
		O2–K1^{i}	2.8382 (18)	K1–O1	3.194 (7)
				K1–N6	3.254 (10)
				K1–N7	3.265 (9)
O1–U1–O2	176.97 (16)	O1–U1–O2	179.16 (7)	O1–U1–O2	178.5 (3)
O1–U1–O3	92.82 (13)	O1–U1–O3	94.51 (7)	O1–U1–O3	89.0 (3)
N1–U1–N2	66.25 (14)	N1–U1–N2	67.92 (7)	N2–U1–N1	65.5 (3)
N1–U1–N4	152.42 (14)	N1–U1–N4	153.28 (7)	N1–U1–N4	154.5 (2)
N2–U1–N3	70.86 (13)	N2–U1–N3	70.29 (7)	N2–U1–N3	70.0 (3)
N3–U1–N4	66.46 (13)	N3–U1–N4	65.71 (7)	N3–U1–N4	65.6 (3)
N1–U1–O3	79.72(13)	N1–U1–O3	79.14 (7)	N1–U1–O3	78.6 (3)
N4–U1–O3	75.64(13)	N4–U1–O3	76.04 (6)	N4–U1–O3	80.0 (3)
		O1–U1–K1	135.93 (6)	O2–U1–K1	126.3 (2)

Table 2. Crystal data for $[UO_2(THF)(H_2L^{Me})]$, $[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$, and $[UO_2(OH)K(THF)_2(H_2L^{Me})]$.

Experiments were carried out with Mo-Kα radiation

	$[UO_2(THF)(H_2L^{Me})]$	**$[\{UO_2(OH)K(C_6H_6)(H_2L^{Me})\}_2]$**	**$[UO_2(OH)K(THF)_2(H_2L^{Me})]$**
Chemical formula	$C_{46}H_{50}N_8O_3U\cdot C_4H_8O$	$C_{72}H_{73}KN_8O_3U$	$C_{55}H_{66}KN_8O_{5.50}U$
M_r	1073.07	1375.51	1204.29
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Triclinic, $P\bar{1}$	Orthorhombic, $P2_12_12$
a, b, c/Å	13.3919 (7), 14.7012 (8), 26.5250 (14)	13.864 (5), 15.187 (5), 18.151 (5)	22.7824 (11), 23.0693 (10), 10.9145 (5)
α,β,γ (°)	90, 90, 90	92.186 (5), 105.716 (5), 116.998 (5)	90, 90, 90
V/Å^3	5222.2 (8)	3219.7 (18)	5736.4 (5)
Z	4	2	4
μ/mm^{-1}	3.16	2.64	2.95
Crystal size/mm	0.28 × 0.13 × 0.13	0.35 × 0.33 × 0.32	0.26 × 0.13 × 0.13
Diffractometer	Bruker *SMART APEX* CCD area detector	Bruker *SMART APEX* CCD area detector	Bruker *SMART APEX* CCD area detector
Absorption correction	Multi-scan *SADABS*	Multi-scan *SADABS*	Multi-scan *SADABS*
T_{min}, T_{max}	0.712, 1.000	0.459, 0.486	0.514, 0.700
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	33639, 11976, 11239	73027, 17777, 15880	60407, 11782, 11517
R_{int}	0.040	0.032	0.074
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.087, 1.05	0.029, 0.071, 1.07	0.053, 0.138, 1.09
No. of reflections	11976	17777	11782
No. of parameters	576	731	563
No. of restraints	51	0	10
H-atom treatment	Riding model	Riding	Riding
	$w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 4.411P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2 + 1.2907P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0726P)^2 + 28.6785P]$ where $P= (F_o^2 + 2F_c^2)/3$
$D\rho_{max}$, $D\rho_{min}$/e Å^{-3}	1.14, -0.67	2.22, -0.72	2.22, -3.38
Flack parameter	0.084 (6)	–	0.052 (11)

Computer programs: Bruker *SMART* version 5.625 (Bruker, 2001), *SMART* (Siemans, 1993), Bruker *SAINT* version 6.36a (Bruker, 2000), *SAINT*(Siemans, 1995), Bruker *SAINT*; Bruker *SHELXTL* (Bruker, 2001), *SAINT* (Sienmansm 1995), *SHELXS97* (Sheldrick, 1990), *SHELXL97* (Sheldrick, 1997), *ORTEP-3 for Windows* (Farrugia, 1997), *enCIFer* (Allen *et al.*, 2004); *PLATON* (Spek, 2003), *WinGX* publication routines (Farrugia, 1999).

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