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Understanding the origins of $O_{yl}-U-O_{yl}$ bending in the uranyl (UO_2^{2+}) ion[§]

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The structure of the uranyl ion (UO_2^{2+}) has been the topic of investigation for almost a century. Since the first structural study of uranyl in 1935, over 4000 uranyl complexes have been characterized by X-ray crystallography. The vast majority of these complexes feature a linear uranyl group (e.g., $O_{yl}-U-O_{yl} = 180^\circ$); however, there are a handful of complexes that feature much more acute $O_{yl}-U-O_{yl}$ angles. In fact, the smallest experimentally observed $O_{yl}-U-O_{yl}$ angles are ca. 161° . This Frontier Article catalogs every reported uranyl complex that features an $O_{yl}-U-O_{yl}$ angle below 172° , and attempts to rationalize the origins of the observed $O_{yl}-U-O_{yl}$ bending. In particular, I describe two distinct causes of $O_{yl}-U-O_{yl}$ bending: (1) bending that occurs as a result of unfavourable steric interactions between the equatorial co-ligands and the uranyl oxo groups; and (2) bending that appears to have an electronic origin. In addition, I describe several possible avenues for future investigation. Understanding the effect that $O_{yl}-U-O_{yl}$ bending has on uranyl electronic structure could ultimately provide insight into several unique aspects of the uranyl ion, such as the inverse trans influence and the involvement of the “pseudo-core” U6p orbitals in U- O_{yl} bonding.

History

The structure of the uranyl ion (UO_2^{2+}) has intrigued chemists for decades. The earliest confirmation of the trans uranyl stereochemistry occurred in 1935, when Fankuchen determined the partial structure of $[Na][UO_2(OAc)_3]$ by X-ray crystallography.¹⁻³ Several years later, Zachariasen determined the structures of $[Ca]_2[UO_2(\mu_3-O)_2]$ and $[K]_3[UO_2F_5]$, placing the trans stereochemistry of the uranyl ion on even firmer experimental footing.^{4,5} Curiously, however, the solution phase structure of uranyl was still the subject of debate as late as 1958.^{6,7} This ambiguity was a consequence of the observation of weak ν_1 and ν_3 U=O stretching modes in the IR and Raman spectra, respectively, of a variety of uranyl compounds.^{2,8-10} For example, Conn and Wu observed a weak band at 860 cm^{-1} in their IR spectrum of UO_2Cl_2 ,¹¹ which they assign to the nominally forbidden ν_1 mode. Similarly, Sacconi and co-workers reported the observation of a weak ν_1 vibration at ca. 830 cm^{-1} for $[UO_2(acac)_2(py)]$.⁷ Rabinowitch and Belford suggested that these observations were not evidence for a bent uranyl group, but were instead a consequence of ligation of co-ligands to the uranyl equatorial plane, which weakened the vibrational selection rules.² Interestingly, in 1978, Alcock and co-workers

appeared to confirm by X-ray crystallography that the $O_{yl}-U-O_{yl}$ angle in $[UO_2(acac)_2(py)]$ was, in fact, slightly bent ($173.5(8)^\circ$).¹² However, a crystallographic reinvestigation of $[UO_2(acac)_2(py)]$ in 2006, by Kawasaki and co-workers, revealed a normal $O_{yl}-U-O_{yl}$ angle ($178.3(2)^\circ$) for this complex.¹³ Thus, it appears likely that observation of the ν_1 mode in this example (assuming the original assignment is correct) is due to other factors.

In the 1980s, several research groups performed electronic structure calculations on uranyl in an effort to understand the preference for the trans stereochemistry.¹⁴⁻¹⁶ These efforts renewed interest in $O_{yl}-U-O_{yl}$ bending and the synthesis of the cis isomer of uranyl. However, subsequent synthetic attempts to generate cis uranyl,^{17,18} most notably by Clark and co-workers at Los Alamos National Laboratory, were unsuccessful.^{19,20} Nonetheless, these efforts helped to illuminate the incredible stability of the trans uranyl fragment and highlighted the challenges inherent in the synthesis of a cis uranyl complex. Since these pioneering studies, little progress has been made toward the synthesis of an authentic cis uranyl species. A 2007 report on the isolation of a cis uranyl-containing ferrocenedicarboxylate complex²¹ came under scrutiny very soon after publication,²² while a 2015 example of a cis uranyl-containing succinate complex is also almost certainly erroneous.²³

While efforts to generate a cis uranyl complex appear to have temporarily stalled, these past studies have greatly expanded our understanding of the uranyl ion. In particular, past computational and spectroscopic investigations have uncovered two remarkable phenomena that are operative in uranyl, namely, the inverse trans influence and the involvement

[§]Dedicated to Prof. Phil Power on the occasion of his 65th birthday.

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of the “pseudo-core” U6p orbitals in the U-O bonding framework.^{24–28} Both phenomena appear to be unique to the actinyl ions, but the exact nature of these effects, and the role they play in dictating the chemical behavior of actinyls, is still not entirely clear. The study of O_{yl}-U-O_{yl} bending could provide answers to these questions.

The vast majority (93%) of the 4000+ structurally characterized uranyl complexes feature O_{yl}-U-O_{yl} angles of 175° or greater, according to a search of the Cambridge Structural Database.²⁹ Nonetheless, there are a handful of uranyl complexes that feature unusually bent uranyl fragments. Herein, I describe these complexes and attempt to identify the origins of the O_{yl}-U-O_{yl} perturbations. In particular, this survey has identified two distinct causes of O_{yl}-U-O_{yl} bending: (1) instances where O_{yl}-U-O_{yl} bending is the result of unfavourable steric interactions; and (2) instances where O_{yl}-U-O_{yl} bending has an electronic origin. In an effort to keep this Article a reasonable length, I have restricted my discussion to complexes that feature O_{yl}-U-O_{yl} angles below 172°, with a few exceptions. For convenience, I am also restricting the discussion to uranyl(VI) ions (e.g., U^{VI}O₂²⁺); however, I will note that there are several U^{VO}O₂⁺ compounds that feature small O_{yl}-U-O_{yl} angles.^{19, 30–34} Because of their weaker U=O bonds, the energy required to perturb the O_{yl}-U-O_{yl} angle in U^{VO}O₂⁺ is probably less than that required for U^{VI}O₂²⁺. Also, a handful of compounds with small O_{yl}-U-O_{yl} angles have been excluded from this discussion because of disorder,^{35–3839} or the use of crystallographic constraints on the uranyl fragment.⁴⁰ I will also very briefly describe previous computational efforts to explore O_{yl}-U-O_{yl} bending.

O_{yl}-U-O_{yl} Bending *in Silico*

The bending of uranyl has been explored computationally by several different groups.^{15, 41–45} In all cases, the trans isomer of uranyl was found to be more stable than the cis isomer. Interestingly, however, the relative energy difference of the trans and cis isomers appears to be strongly dependent on the identity of the equatorial co-ligands. For example, the cis isomer of [UO₂(OH)₄]²⁻ is 19 kcal/mol higher in energy than trans isomer,⁴² whereas the cis isomer of [UO₂(κ²-NO₃)₂(H₂O)₂] is 33 kcal/mol higher in energy than trans isomer.⁴⁵ Indeed, the lowest trans/cis isomerization energies are found for [UO₂(OH)₄]²⁻ and [UO₂(H₂O)₂(κ²-ONHCH=O)₂],^{42, 43, 45} which both feature strongly donating, anionic equatorial co-ligands. This observation is perhaps not surprising, as strong equatorial donors are known to weaken the U-O_{yl} bonds.⁴⁶ Also of note, adsorption of UO₂²⁺(aq) onto alumina is predicted to cause significant bending of the O_{yl}-U-O_{yl} angle (ca. 149°), according to DFT calculations.^{47, 48} This bending is likely a consequence of the close approach of the two oxo ligands to the alumina surface. Comparable O_{yl}-U-O_{yl} bending is predicted upon adsorption of uranyl onto rutile.^{49, 50} To my knowledge, however, O_{yl}-U-O_{yl} bending upon uranyl adsorption has not been confirmed experimentally.

Steric Perturbation of the O_{yl}-U-O_{yl} Angle

Of the thousands of uranyl complexes that appear in the chemical literature, only about 30 feature O_{yl}-U-O_{yl} angles smaller than 172°. Of these complexes, unfavourable steric interactions between the equatorial co-ligands and the uranyl oxo groups appear to be the primary cause of the O_{yl}-U-O_{yl} bending. For example, Wilkerson and co-workers suggest that the small O_{yl}-U-O_{yl} angle (167.8(4)°) in UO₂(O-2,6-^tBu₂C₆H₃)₂(THF)₂ (**1**) is a consequence of the steric repulsion between the *tert*-butyl substituents of the aryloxy ligands and the uranyl oxo groups (Table 1, Chart 1).⁵¹ Steric repulsion between the SiMe₃ groups in UO₂(N(SiMe₃)₂)₂(py)₂ and UO₂(NCN)₂(THF) (**2**) and their uranyl oxo ligands, also likely explains the small O_{yl}-U-O_{yl} angles in these complexes (170.5(3) and 169.7(2)°, respectively) (Table 1).^{52, 53} A handful of uranyl pentamethylcyclopentadienyl complexes are known (Table 1), and they all feature small O_{yl}-U-O_{yl} angles, ranging from 168.40(9)° for [NEt₄]₂[Cp*UO₂(CN)₃] (**3**) to 167.4(4)° for Cp*UO₂(^tBu-MesPDI^{Me}) (**4**).^{54, 55} The deviation away from linearity is a consequence of steric repulsion between the uranyl oxo ligands and methyl groups of the η⁵-Cp* ring. Interestingly, none of these complexes were made by salt metathesis between M[Cp*] (M = alkali metal) and a uranyl(VI) precursor. Instead, they were each made by O-atom transfer to a lower valent uranium pentamethylcyclopentadienyl complex.

Table 1. Uranyl complexes with small O_{yl}-U-O_{yl} angles as a result of steric and/or electrostatic repulsion

Complex	O _{yl} -U-O _{yl} Angle	Ref.
[UO ₂ (OTf)(THF)(^{Me} N4)][OTf]	161.7(5)	56
[UO ₂ Cl ₂ (phen) ₂] (7)	161.8(1)	57
UO ₂ (OTf) ₂ (^H N4) (6)	162.8(3)	56
UO ₂ Cl ₂ (^H N4)	164.1(3)	56
UO ₂ (κ ² -NO ₃) ₂ (ⁿ Pr-btp) (5)	166.2(1)	58
[NMe ₄] ₂ [UO ₂ (CS ₄)]·0.5H ₂ O	167.4(6)	59
Cp*UO ₂ (^t Bu-MesPDI ^{Me}) (4)	167.4(4)	55
UO ₂ (O-2,6- ^t Bu ₂ C ₆ H ₃) ₂ (THF) ₂ (1)	167.8(4)	51
UO ₂ Cl ₂ (^{Me} N4)	168.2(3)	56
[NEt ₄] ₂ [Cp*UO ₂ (CN) ₃] (3)	168.40(9)	54
Cp*UO ₂ (^{Me} SPDI ^{Me})	168.4(2)	55
UO ₂ (NCN) ₂ (THF) (2)	169.7(2)	53
[UO ₂ (MeOH)(salen-calix[4]arene)]	170.0	60
UO ₂ (κ ² -NO ₃) ₂ (Me-btp)	170.49(9)	58
[U(CyMe ₄ btp) ₂ (μ-O)UO ₂ (κ ² -NO ₃) ₃][OTf]	170.4(3)	58
UO ₂ (N(SiMe ₃) ₂) ₂ (py) ₂	170.5(3)	52
UO ₂ (κ ² -NO ₃) ₂ (Et(p)TDPA)	171.1(1)	61
UO ₂ (κ ¹ -O ₂ CC ₆ F ₅)(κ ² -O ₂ CC ₆ F ₅)(Ph ₃ PO) ₂	171(2)	62
[(UO ₂) ₂ (py) ₄ (LH ₄)]	171.1(9)	63
[C ₂ mim] ₃ [UO ₂ (NCS) ₅]	171.2(9)	64
[UO ₂ (salphen(C ₆ H ₄ -o-OMe) ₂)(NC ₅ H ₄ -p- ^t Bu)]	171.8	65
UO ₂ (κ ² -O ₂ CC ₆ F ₅) ₂ (bipy)	172(2)	62

Abbreviations: ^{Me}N4 = N,N'-dimethyl-2,11-diaza[3,3](2,6)pyridinophane; ^HN4 = 2,11-diaza[3,3](2,6)pyridinophane; ⁿPr =

btp = 2,6-bis(dipropyl-1,2,4-triazin-3-yl)pyridine; H_4CS_4 = *p*-sulfonatocalix[4]arene; $^t\text{Bu-MesPDI}^{\text{Me}}$ = 2,6-((*Mes*)- $\text{N}=\text{CMe}$)₂-*p*- $\text{C}(\text{CH}_3)_3\text{C}_5\text{H}_2\text{N}$; $^{\text{Mes}}\text{PDI}^{\text{Me}}$ = 2,6-((*Mes*)- $\text{N}=\text{CMe}$)₂ $\text{C}_5\text{H}_3\text{N}$; NCN = (Me_3SiN) $\text{CPh}(\text{NSiMe}_3)$; *Me*-btp = 2,6-bis(dimethyl-1,2,4-triazin-3-yl)pyridine; CyMe_4btbp = 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2'-bipyridine; Et(p)TDPA = *N,N'*-Diethyl-*N,N'*-bis(4-methylphenyl)pyridine-2,6-dicarboxamide; LH_8 = *p*-*tert*-butyloctahomotetraoxacalix[8]arene; C_2mim = 1-ethyl-3-methylimidazole.

Chart 1. Selected structural representations of uranyl complexes with small $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ angles as a result of steric and/or electrostatic repulsion

Several other ligands can also cause perturbations of the $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ angle. For example, the two κ^2 -bound nitrate ligands in $\text{UO}_2(\kappa^2\text{-NO}_3)_2(^n\text{Pr-btp})$ (**5**) bind perpendicular to the equatorial plane (Figure 1), which causes them to closely approach the uranyl oxo ligands, resulting in $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ bending ($166.2(1)^\circ$) (Table 1). This unusual binding mode is a consequence of steric crowding caused by coordination of the bulky tridentate $^n\text{Pr-btp}$ ligand to the uranyl equatorial plane.⁵⁸ $[\text{U}(\text{CpMe}_4\text{btbp})_2(\mu\text{-O})\text{UO}_2(\kappa^2\text{-NO}_3)_3][\text{OTf}]$, $\text{UO}_2(\kappa^2\text{-NO}_3)_2(\text{Me-btp})$, and $\text{UO}_2(\text{NO}_3)_2(\text{Et(p)TDPA})$ feature relatively small $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ angles, as well ($170.4(3)$, $170.49(9)$, and $171.1(1)^\circ$, respectively), for the

same reason (Table 1).^{58, 61} Similarly, the bipy ring in $\text{UO}_2(\kappa^2\text{-O}_2\text{CC}_6\text{F}_5)_2(\text{bipy})$ is somewhat displaced out of the equatorial plane because of steric crowding.⁶² This results in deflection of the uranyl oxo ligands ($172(2)^\circ$) because of the close approach of the hydrogens at the 3 position of the bipy ring.

Figure 1. Ball-and-stick diagram of $\text{UO}_2(\kappa^2\text{-NO}_3)_2(^n\text{Pr-btp})$ (**5**). $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ = $166.2(1)^\circ$. Green = uranium, red = oxygen, blue = nitrogen, grey = carbon.

Drawing on these results, my research group recently ligated the relatively rigid 12-membered pyridinophane macrocycles $^{\text{H}}\text{N}4$ (2,11-diaza[3,3](2,6) pyridinophane) and $^{\text{Me}}\text{N}4$ (*N,N'*-dimethyl-2,11-diaza[3,3](2,6) pyridinophane) to the uranyl fragment. We successfully isolated four uranyl pyridinophane complexes, including $\text{UO}_2\text{Cl}_2(^{\text{R}}\text{N}4)$ ($\text{R} = \text{H}, \text{Me}$), $\text{UO}_2(\text{OTf})_2(^{\text{H}}\text{N}4)$ (**6**), and $[\text{UO}_2(\text{OTf})(\text{THF})(^{\text{Me}}\text{N}4)][\text{OTf}]$.⁵⁶ We hypothesized that the rigid backbone of the pyridinophane macrocycle would force the coordination of its four N-donor atoms to the uranyl ion. Because all four N-donor atoms cannot occupy the uranyl equatorial plane, we expected to observe a considerable steric interaction between the macrocycle backbone and the uranyl oxo groups.

Gratifyingly, the solid-state structures of $\text{UO}_2\text{Cl}_2(^{\text{R}}\text{N}4)$ ($\text{R} = \text{H}, \text{Me}$) reveal small $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ angles (ranging from $164.1(3)^\circ$ to $168.2(3)^\circ$), on account of the steric clash between the oxo ligands and the macrocycle backbone (Table 1), as we initially hypothesized.⁵⁶ Even smaller $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ angles were observed for the triflate derivatives. For example, we observe $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ angles of $162.8(3)^\circ$ for **6** (Figure 2) and $161.7(5)^\circ$ for $[\text{UO}_2(\text{OTf})(\text{THF})(^{\text{Me}}\text{N}4)][\text{OTf}]$, which are amongst the smallest $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ angles yet recorded. We rationalized that the triflate derivatives feature smaller $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ angles than their chloride cousins on account of their shorter U-N bonds (a consequence of the presence of electron-withdrawing triflate ligands), which increases the steric clash between the pyridinophane ligand and the oxo groups. Finally, it is interesting to note that $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ bending does not cause any apparent lengthening of the U-O_{yl} bonds, which is likely because the $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ bending is still quite modest within this series of complexes. It is possible that a

larger amount of $O_{yl}-U-O_{yl}$ bending would result in an observable lengthening of the $U-O_{yl}$ bonds.

Figure 2. Ball-and-stick diagram of $UO_2(OTf)_2(HN4)$ (**6**). $O_{yl}-U-O_{yl}$ = $162.8(3)^\circ$. Green = uranium, yellow = sulfur, pink = fluorine, red = oxygen, blue = nitrogen, grey = carbon.

Very recently, Ikeda-Ohno and co-workers reported the structure of a uranyl bis(1,10-phenanthroline) complex, $[UO_2Cl_2(phen)_2]$ (**7**), which also features a significantly distorted $O_{yl}-U-O_{yl}$ angle ($161.8(1)^\circ$) (Figure 3, Table 1).⁵⁷ Indeed, the $O_{yl}-U-O_{yl}$ angle in this complex is comparable to the $O_{yl}-U-O_{yl}$ angles reported by us for $[UO_2(OTf)(THF)(Me_4N)][OTf]$.⁵⁶ Similar to $[UO_2(OTf)(THF)(Me_4N)][OTf]$, **7** also exhibits normal $U-O_{yl}$ distances. The X-ray structure of **7** reveals that one of its phen ligands coordinates to the uranyl ion in a manner that is orthogonal to the equatorial plane. The authors argue that this unusual coordination mode is a consequence of an intermolecular π -stacking network, which overrides the preference of uranyl to bind its co-ligands within the equatorial plane. As a result of this binding mode, the hydrogen atoms at the 2 and 9 positions of the phen ligand closely approach the uranyl oxo ligands, causing a large decrease the $O_{yl}-U-O_{yl}$ angle. It should be noted that $[UO_2Cl_2(phen)_2]$ (**7**) was not characterized in solution, so it is not clear if this unusual phen binding mode is maintained upon dissolution. Nonetheless, the observation that intermolecular networks can be harnessed to effect O-U-O bending suggests a new strategy for uranyl manipulation.

Intermolecular steric effects may also explain the small $O_{yl}-U-O_{yl}$ angle ($171.2(9)^\circ$) in $[C_2mim]_3[UO_2(NCS)_5]$ (Table 1), which would be a challenge to explain otherwise given the small steric profile of the thiocyanate ligand.⁶⁴ As with $[UO_2Cl_2(phen)_2]$, this effect is likely confined to the solid state. A similar intermolecular steric effect probably explains the small $O_{yl}-U-O_{yl}$ angle ($167.4(6)^\circ$) found in $[NMe_4]_2[UO_2(CS_4)] \cdot 0.5H_2O$ (Table 1). In this case, the close approach of a sulfonate oxygen atom in the solid state may cause an electrostatic repulsion of a uranyl oxo ligand, decreasing the $O_{yl}-U-O_{yl}$ angle.⁵⁹

Figure 3. Ball-and-stick diagram of $[UO_2Cl_2(phen)_2]$ (**7**). $O_{yl}-U-O_{yl}$ = $161.8(1)^\circ$. Green = uranium, aquamarine = chlorine, red = oxygen, blue = nitrogen, grey = carbon.

Our X-ray crystallographic analysis of $UO_2(OTf)_2(HN4)$ (**6**) and its analogues revealed that the uranyl-pyridinophane interaction is

quite weak (as evidenced by the long U-N bond lengths). Thus, attempts to cause further perturbation of the $O_{yl}-U-O_{yl}$ angle in uranyl will likely require a stronger interaction between the uranium center and the co-ligands. In this regard, we recently attempted to ligate the 14-membered dianionic tmtaa (H_2tmtaa = dibenzotetramethyltetraaza[14]annulene) macrocycle to the uranyl fragment,⁶⁶ which, because of its anionic charge, should

feature stronger (and shorter) U-N bonds. However, reaction of $[UO_2(N(SiMe_3)_2)_2(THF)_2]$ with H_2tmtaa , in an effort to form *cis*- $[UO_2(tmtaa)]$, resulted in only partial protonolysis and formation of $[UO_2(tmtaaH)(N(SiMe_3)_2)(THF)]$ (**8**) (Scheme 1), which features an essentially linear uranyl fragment ($174.0(2)^\circ$). This result highlights the thermodynamic stability of the *trans* uranyl configuration, as well as the surprising flexibility of the tmtaa ligand. The latter point is significant because unanticipated reaction outcomes have proven to be a major impediment in the effort to synthesize a *cis* uranyl complex.^{19, 20}

Scheme 1. Attempted synthesis of *cis*- $[UO_2(tmtaa)]$.

Electronic Perturbation of the O-U-O Angle

In contrast to the abovementioned examples, the uranyl methanediide complex, $\text{UO}_2(\text{BIPM}^{\text{TMS}})(\text{dmap})_2$ (**9**), reported in 2014 by Liddle and co-workers, does not feature any obvious steric repulsion between its equatorial co-ligands and its two oxo groups (Figure 4). Yet, it features a relatively small $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ angle ($167.16(9)^\circ$) (Table 2, Chart 2).⁶⁷ The related methanediide complex, $\text{UO}_2(\text{SCS})(\text{py})_2 \cdot 0.5\text{py}$ (**10**), which was reported by Ephritikhine and co-workers in 2011, also features a small $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ angle ($168.5(1)^\circ$).⁶⁸ Moreover, in both examples the two oxo ligands appear to be bending away from the strongly donating methanediide carbon. DFT calculations on **10** nicely reproduce the $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ bending observed in the solid-state. According to calculations, the U-C σ - and π -bonds feature some U-O antibonding character and Ephritikhine and co-workers argue that this antibonding character is likely the cause of the $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ bending in this complex.⁶⁸ Presumably, by bending the $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ angle, the amount of U-O antibonding is reduced, strengthening the U-C and U-O interactions.

Figure 4. Ball-and-stick diagram of $\text{UO}_2(\text{BIPM}^{\text{TMS}})(\text{dmap})_2$ (**9**). $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}} = 167.16(9)^\circ$. Green = uranium, gold = phosphorus, plum = silicon, red = oxygen, blue = nitrogen, grey = carbon.

Table 2. Uranyl complexes with small $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ angles as a result of electronic perturbation

Complex	$\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ Angle	Ref.
$\text{UO}_2(\text{BIPM}^{\text{TMS}})(\text{dmap})_2$ (9)	167.16(9)	67
$\text{UO}_2(\text{SCS})(\text{py})_2 \cdot 0.5\text{py}$ (10)	168.5(1)	68
$[(\text{UO}_2)_2(\mu_3\text{-O})(\text{C}_8\text{H}_{12}\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]_2$	171.1(3), 172.3(3), 176.6(2)	69
$[(\text{UO}_2(\text{CyMe}_4\text{BTBP}))_2(\mu\text{-O})][\text{I}]_2$ (11)	171.4(2)	70
$[(\text{UO}_2(\text{py})_4)_2(\mu\text{-O})][\text{OTf}]_2$	171.5(2), 173.1(2)	71
$\text{UO}_2(\text{SCS})(\text{py})_2$	171.8(2)	68

Abbreviations: $\text{BIPM}^{\text{TMS}} = \text{C}(\text{PPh}_2\text{NSiMe}_3)_2$; $\text{dmap} = 4$ -(dimethylamino)pyridine; $\text{SCS} = \text{C}(\text{PPh}_2\text{S})_2$; $\text{CyMe}_4\text{BTBP} = 6,6'$ -bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2'-bipyridine.

Chart 2. Selected structural representations of uranyl complexes with small $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ angles as a result of electronic perturbation

$\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ bending appears to have an electronic origin in several uranyl bridged-oxo clusters, as well. For example, the two $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ angles in $[(\text{UO}_2(\text{CyMe}_4\text{BTBP}))_2(\mu\text{-O})][\text{I}]_2$ (**11**) both deviate from linearity ($171.4(2)^\circ$) (Table 2).⁷⁰ This complex features two uranyl subunits which are connected via an equatorially-coordinated μ_2 -oxo ligand. Intriguingly, both uranyl units are deflected away from the strongly donating μ_2 -oxo in this example. Several other oxo-bridged uranyl clusters also feature uranyl groups with slightly bent $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ angles (Table 2).^{69, 71} This bending is presumably electronic in origin, although in some cases steric perturbation may also be operative.⁷¹ That said, it appears that an equatorial oxo ligand cannot induce as large a deviation in uranyl $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ angle as can a methanediide ligand, which may be a consequence of the stronger donating ability of the latter.

Conclusions and Outlook

Thus far, the degree of bending observed within the uranyl unit is still relatively small. The smallest observed $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ angles are ca. 161° , and they appear to be primarily a result of steric and/or electrostatic repulsion between the equatorial ligands and the uranyl oxo groups. While these changes are small, this review highlights several areas where further work could result in the observation of much larger degrees of $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ bending. For example, computational studies suggest that careful equatorial ligand tuning could make $\text{O}_{\text{yl}}\text{-U-O}_{\text{yl}}$ bending more

facile. In particular, it appears that ligation of strongly σ -donating ligands, such as alkoxide, amide, or alkyl, to the uranyl equatorial plane should reduce the energy penalty required to bend the uranyl group. The inclusion of these strongly electron donating groups into a ligand with a large steric footprint could be a particularly valuable approach for effecting $O_{yl}-U-O_{yl}$ bending. The use of unfavourable intermolecular steric interactions can also effect $O_{yl}-U-O_{yl}$ bending, as was observed for $[UO_2Cl_2(phen)_2]$. Future work should focus on implementing this promising (but underexplored) effect via the design of new ligands that can connect multiple uranyl units, but also place steric bulk next to an oxo ligand. That said, given the difficulty of predicting ligand binding modes upon coordination to uranyl, as revealed in the sections above, implementing this strategy in practice could be a challenge.

The coordination of strongly electron-donating equatorial ligands to uranyl can also perturb the $O_{yl}-U-O_{yl}$ angle, although the effect is usually not as large, nor as common, as the perturbations caused by steric repulsion. This effect is largest for the uranyl methanediide complexes, $UO_2(BIPM^{TM})_2(dmap)_2$ and $UO_2(SCS)(py)_2$, but its origins are still not well understood. Future work should attempt to better unravel the orbital interactions that result in $O_{yl}-U-O_{yl}$ bending. In addition, there are several synthetic avenues of investigation that could prove fruitful. For instance, it would be interesting to synthesize a uranyl complex that featured a terminal imido ligand coordinated to its equatorial plane. Like the methanediide ligand, imidos are also strongly-donating with a 2- charge, and a uranyl imido species would likely feature a bent uranyl fragment, as well. A bridged-nitrido uranyl cluster could also feature bent uranyl groups; however, such a complex would likely be a challenge to synthesize.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1. I. Fankuchen, *Z. Kristallogr.* **91**, 473 (1935).
2. E. Rabinowitch and R. L. Belford, *Spectroscopy and Photochemistry of Uranyl Compounds*, Macmillan, New York, 1964.
3. W. Zachariasen, *Acta Crystallogr.* **7**, 795-799 (1954).
4. W. Zachariasen, *Acta Crystallogr.* **1**, 281-285 (1948).
5. W. Zachariasen, *Acta Crystallogr.* **7**, 783-787 (1954).
6. L. Sacconi, G. Caroti and P. Paoletti, *J. Inorg. Nucl. Chem.* **8**, 93-103 (1958).
7. L. Sacconi, G. Caroti and P. Paoletti, *J. Chem. Soc.*, 4257-4264 (1958).
8. J. Sutton, *Nature* **169**, 235-236 (1952).
9. B. S. Satyanarayana, *Proc. Indian Acad. Sci. A* **15**, 414-416 (1942).
10. J. I. Bullock, *J. Chem. Soc. A*, 781-784 (1969).
11. G. K. T. Conn and C. K. Wu, *Trans. Faraday Soc.* **34**, 1483-1492 (1938).
12. N. W. Alcock, D. J. Flanders and D. Brown, *J. Chem. Soc., Dalton Trans.*, 679-681 (1984).
13. T. Kawasaki, T. Kitazawa, T. Nishimura, M. Nakada and M. Saeki, *Hyperfine Interact.* **166**, 417-423 (2005).
14. K. Tatsumi and R. Hoffmann, *J. Am. Chem. Soc.* **19**, 2656-2658 (1980).
15. W. R. Wadt, *J. Am. Chem. Soc.* **103**, 6053-6057 (1981).
16. P. Pyykko, L. J. Laakkonen and K. Tatsumi, *Inorg. Chem.* **28**, 1801-1805 (1989).
17. D. S. J. Arney and C. J. Burns, *J. Am. Chem. Soc.* **117**, 9448-9460 (1995).
18. T. Cantat, C. R. Graves, B. L. Scott and J. L. Kiplinger, *Angew. Chem. Int. Ed.* **48**, 3681-3684 (2009).
19. P. B. Duval, C. J. Burns, D. L. Clark, D. E. Morris, B. L. Scott, J. D. Thompson, E. L. Werkema, L. Jia and R. A. Andersen, *Angew. Chem. Int. Ed.* **40**, 3357-3361 (2001).
20. P. B. Duval, C. J. Burns, W. E. Buschmann, D. L. Clark, D. E. Morris and B. L. Scott, *Inorg. Chem.* **40**, 5491-5496 (2001).
21. A. E. Vaughn, C. L. Barnes and P. B. Duval, *Angew. Chem. Int. Ed.* **46**, 6622-6625 (2007).
22. C. Villiers, P. Thuéry and M. Ephritikhine, *Angew. Chem. Int. Ed.* **47**, 5892-5893 (2008).
23. Q. L. Guan, F. Y. Bai, Y. H. Xing, J. Liu and H. Z. Zhang, *Inorg. Chem. Commun.* **59**, 36-40 (2015).
24. R. G. Denning, *J. Phys. Chem. A* **111**, 4125-4143 (2007).
25. R. Denning, *Struct. Bonding* **79**, 215-276 (1992).
26. N. Kaltsoyannis, *Chem. Soc. Rev.* **32**, 9-16 (2003).
27. M. L. Neidig, D. L. Clark and R. L. Martin, *Coord. Chem. Rev.* **257**, 394-406 (2013).
28. H. S. La Pierre and K. Meyer, *Inorg. Chem.* **52**, 529-539 (2013).
29. Cambridge Structural Database, version 5.38, 2016.
30. P. L. Arnold, G. M. Jones, S. O. Odoh, G. Schreckenbach, N. Magnani and J. B. Love, *Nat. Chem.* **4**, 221-227 (2012).
31. G. M. Jones, P. L. Arnold and J. B. Love, *Angew. Chem. Int. Ed.* **51**, 12584-12587 (2012).
32. D. P. Mills, O. J. Cooper, F. Tuna, E. J. L. McInnes, E. S. Davies, J. McMaster, F. Moro, W. Lewis, A. J. Blake and S. T. Liddle, *J. Am. Chem. Soc.* **134**, 10047-10054 (2012).
33. V. Mougel, L. Chatelain, J. Pécaut, R. Caciuffo, E. Colineau, J.-C. Griveau and M. Mazzanti, *Nat. Chem.* **4**, 1011-1017 (2012).
34. M. F. Schettini, G. Wu and T. W. Hayton, *Inorg. Chem.* **48**, 11799-11808 (2009).
35. E. M. Villa, E. V. Alekseev, W. Depmeier and T. E. Albrecht-Schmitt, *Cryst. Growth Des.* **13**, 1721-1729 (2013).

36. S. G. Thangavelu and C. L. Cahill, *Inorg. Chem.* **54**, 4208-4221 (2015).
37. A. E. Bradley, C. Hardacre, M. Nieuwenhuysen, W. R. Pitner, D. Sanders, K. R. Seddon and R. C. Thied, *Inorg. Chem.* **43**, 2503-2514 (2004).
38. D. K. Unruh, K. Gojdas, E. Flores, A. Libo and T. Z. Forbes, *Inorg. Chem.* **52**, 10191-10198 (2013).
39. N. W. Alcock and S. Esperas, *J. Chem. Soc., Dalton Trans.*, 893-896 (1977).
40. D. M. Poojary, A. Cabeza, M. A. G. Aranda, S. Bruque and A. Clearfield, *Inorg. Chem.* **35**, 1468-1473 (1996).
41. K. G. Dyall, *Molecular Physics* **96**, 511-518 (1999).
42. G. Schreckenbach, P. J. Hay and R. L. Martin, *Inorg. Chem.* **37**, 4442-4451 (1998).
43. M. Bühl and G. Schreckenbach, *Inorg. Chem.* **49**, 3821-3827 (2010).
44. K. C. Mullane, A. J. Lewis, H. Yin, P. J. Carroll and E. J. Schelter, *Inorg. Chem.* **53**, 9129-9139 (2014).
45. M. A. Silver, W. L. Dorfner, S. K. Cary, J. N. Cross, J. Lin, E. J. Schelter and T. E. Albrecht-Schmitt, *Inorg. Chem.* **54**, 5280-5284 (2015).
46. S. Fortier and T. W. Hayton, *Coord. Chem. Rev.* **254**, 197-214 (2010).
47. L. V. Moskaleva, V. A. Nasluzov and N. Rösch, *Langmuir* **22**, 2141-2145 (2006).
48. H. Geckeis, J. Lützenkirchen, R. Polly, T. Rabung and M. Schmidt, *Chem. Rev.* **113**, 1016-1062 (2013).
49. Q.-J. Pan, S. O. Odoh, A. M. Asaduzzaman and G. Schreckenbach, *Chem. Eur. J.* **18**, 1458-1466 (2012).
50. H.-B. Zhao, M. Zheng, G. Schreckenbach and Q.-J. Pan, *Inorg. Chem.* **56**, 2763-2776 (2017).
51. M. P. Wilkerson, C. J. Burns, D. E. Morris, R. T. Paine and B. L. Scott, *Inorg. Chem.* **41**, 3110-3120 (2002).
52. G. M. Jones, P. L. Arnold and J. B. Love, *Chem. Eur. J.* **19**, 10287-10294 (2013).
53. M. J. Sarsfield and M. Helliwell, *J. Am. Chem. Soc.* **126**, 1036-1037 (2004).
54. J. Maynadie, J.-C. Berthet, P. Thuery and M. Ephritikhine, *Chem. Commun.*, 486-488 (2007).
55. J. J. Kiernicki, D. P. Cladis, P. E. Fanwick, M. Zeller and S. C. Bart, *J. Am. Chem. Soc.* **137**, 11115-11125 (2015).
56. E. A. Pedrick, J. W. Schultz, G. Wu, L. M. Mirica and T. W. Hayton, *Inorg. Chem.* **55**, 5693-5701 (2016).
57. S. Schöne, T. Radoske, J. März, T. Stumpf, M. Patzschke and A. Ikeda-Ohno, *Chem. Eur. J.* **23**, 13574-13578 (2017).
58. J.-C. Berthet, P. Thuéry, J.-P. Dognon, D. Guillaneux and M. Ephritikhine, *Inorg. Chem.* **47**, 6850-6862 (2008).
59. P. Thuery, *CrystEngComm* **14**, 6369-6373 (2012).
60. A. M. Reichwein, W. Verboom, S. Harkema, A. L. Spek and D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2*, 1167-1172 (1994).
61. J. L. Lapka, A. Paulenova, L. N. Zakharov, M. Y. Alyapyshev and V. A. Babain, *IOP Conf. Ser. Mater. Sci. Eng.* **9**, 012029 (2010).
62. G. B. Deacon, P. I. Mackinnon and J. C. Taylor, *Polyhedron* **4**, 103-113 (1985).
63. P. Thuéry and B. Masci, *Polyhedron* **22**, 3499-3505 (2003).
64. N. Aoyagi, K. Shimojo, N. R. Brooks, R. Nagaishi, H. Naganawa, K. V. Hecke, L. V. Meervelt, K. Binnemans and T. Kimura, *Chem. Commun.* **47**, 4490-4492 (2011).
65. A. R. Van Doorn, M. Bos, S. Harkema, J. Van Eerden, W. Verboom and D. N. Reinhoudt, *J. Org. Chem.* **56**, 2371-2380 (1991).
66. E. A. Pedrick, M. K. Assefa, M. E. Wakefield, G. Wu and T. W. Hayton, *Inorg. Chem.* **56**, 6638-6644 (2017).
67. E. Lu, O. J. Cooper, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake and S. T. Liddle, *Angew. Chem. Int. Ed.* **53**, 6696-6700 (2014).
68. J.-C. Tournieux, J.-C. Berthet, T. Cantat, P. Thuéry, N. Mézailles and M. Ephritikhine, *J. Am. Chem. Soc.* **133**, 6162-6165 (2011).
69. L. A. Borkowski and C. L. Cahill, *Cryst. Growth Des.* **6**, 2248-2259 (2006).
70. J.-C. Berthet, P. Thuéry, M. R. S. Foreman and M. Ephritikhine, *Radiochim. Acta* **96**, 189 (2008).
71. J.-C. Berthet, M. Lance, M. Nierlich and M. Ephritikhine, *Eur. J. Inorg. Chem.* **2000**, 1969-1973 (2000).