

Bending the Uranyl Ion through Unfavorable Steric Interactions

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Literature Seminar

November 6, 2018

Nuclear power generates one fifth of the total electricity used in the United States, and 53% of the electricity used in the state of Illinois.¹ Such reliance on nuclear energy has severe implications regarding the storage of nuclear waste. Currently, spent nuclear fuel is stored on-site in nuclear plants across the nation, with the long-term goal of disposal in a specialized geological site.¹ A major concern about current practices is the possibility of releasing uranium to the environment. When exposed to moisture and air, the uranium in spent nuclear fuel is oxidized to U(VI) as the uranyl dication (UO_2^{2+}).² The uranyl moiety is highly water soluble,² toxic,³ and chemically robust,⁴ making it a difficult contaminant to remedy.

The uranyl moiety is the most common fragment in uranium chemistry.⁴ This species is characterized by two short U–O bonds (*ca.* 1.78 Å) that always adopt a linear *trans*-dioxo configuration.⁵ The stereochemistry and chemical robustness of the uranyl unit are attributed to the strong covalency of the U–O bonds arising from appreciable mixing of $5f_z^3$ and “core-like” $6p_z$ metal orbitals with the $2p_z$ orbitals in O.⁶ As a consequence of the strong covalency, the reactivity of the uranyl unit is significantly suppressed and ligand coordination is limited to the equatorial plane. Therefore, enhancing the reactivity of UO_2^{2+} is relevant for improving storage and processing of spent nuclear fuel.

In contrast to the prevalence of *trans*-uranyl complexes, a *cis*-uranyl species remains unknown. Attempts to generate a *cis*-uranyl complex have resulted in ligand oxidation or decomposition,⁷ suggesting that a robust, redox-inactive ligand will be required to isolate such species. Inducing the *cis* isomerization of UO_2^{2+} is expected to increase the reactivity of the uranyl ion by reducing the degree of $5f$ - $6p$ mixing,⁶ as supported by density functional theory (DFT) calculations showing the *cis* isomers of $[\text{UO}_2(\text{OH})_4]^{2-}$ and $[\text{UO}_2(\text{N}(\text{SiH}_3)_2)_3]^-$ are 18 and 31 kcal/mol higher in energy, respectively, than the *trans* isomers.^{8,9} A promising approach to generate a *cis*-uranyl complex involves destabilizing the *trans* isomer through unfavorable steric interactions between equatorial ligands and the uranyl oxo groups (**Figure 1**), effectively bending the linear O–U–O unit.⁵ Among the thousands of structurally characterized uranyl complexes, fewer than 30 exhibit O–U–O angles smaller than 170° .⁵

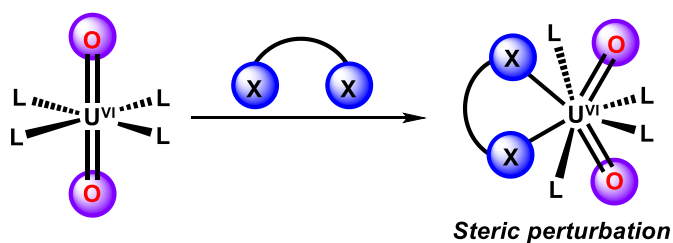


Figure 1. Bending of a uranyl moiety by unfavorable steric interactions of the ligand with the oxo groups.⁵

Drawing from this principle, Hayton and co-workers hypothesized that 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) could not accommodate the uranyl ion in the binding pocket, and thus would exhibit considerable steric interactions upon ligation to uranyl.¹⁰ The solid-state structures of the isolated complexes $\text{UO}_2\text{Cl}_2(^{\text{R}}\text{N}4)$ ($\text{R} = \text{H}, \text{Me}$), $\text{UO}_2(\text{OTf})_2(^{\text{H}}\text{N}4)$, and $[\text{UO}_2(\text{OTf})(\text{THF})(^{\text{Me}}\text{H}4)][\text{OTf}]$ reveal significantly bent O-U-O angles caused by steric interactions between the ligand backbone and the oxo groups on uranyl (**Figure 2**). The smaller O-U-O angles in the triflate derivatives relative to the chloride complexes can be attributed to shorter U-N bonds caused by the electron-withdrawing triflate ligands increasing the steric clash between the macrocycle and the oxo groups. Raman spectroscopy shows that these four complexes exhibit a decrease in the $\text{U}=\text{O}$ ν_{symm} frequency in the range of 10-20 cm^{-1} relative to the starting materials. Although the change in frequency can be interpreted as evidence of weaker $\text{U}=\text{O}$ bonds, this is not directly related to the O-U-O bending since the structures with the smallest angles exhibit the stronger bonds, and there is no appreciable lengthening of the U-O distances.¹⁰

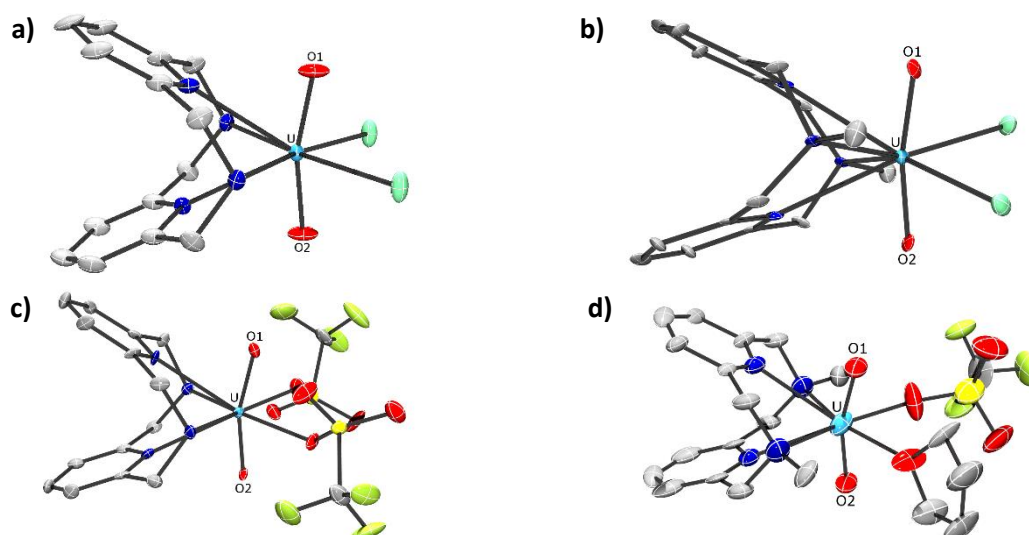


Figure 2. Solid-state structures of **a)** $\text{UO}_2\text{Cl}_2(^{\text{H}}\text{N}4)$, O-U-O angle: 164.1(3) $^\circ$; **b)** $\text{UO}_2\text{Cl}_2(^{\text{Me}}\text{N}4)$, O-U-O angle: 168.2(3) $^\circ$; **c)** $\text{UO}_2(\text{OTf})_2(^{\text{H}}\text{N}4)$, O-U-O angle: 162.8(3) $^\circ$; and **d)** $[\text{UO}_2(\text{OTf})(\text{THF})(^{\text{H}}\text{N}4)][\text{OTf}]$, O-U-O angle: 161.7(5) $^\circ$. Counter ions and hydrogen atoms omitted for clarity.¹⁰

More recently, Ikeda-Ohno and co-workers reported the first uranyl bis(1,10-phenanthroline) complex $\text{UO}_2\text{Cl}_2(\text{phen})_2$.¹¹ Interestingly, the solid-state structure complex exhibits unique coordination where the two phen ligands are essentially perpendicular to each other, and features an usually bent O-U-O angle of 161.8(1) $^\circ$ (**Figure 3**). The perturbation of the angle is attributed to the unusual coordination of a phenanthroline ligand on the plane of the molecule. In this binding mode, the H atoms at the 1 and 10 positions of the ligand approach the oxo ligands, bending the O-U-O angle. The authors propose that intermolecular π - π interactions between phen ligands lead to the stabilization of the structure. However, $\text{UO}_2\text{Cl}_2(\text{phen})_2$ was only characterized in the solid state, and it is unclear if it retains its geometry in solution, which could hinder future investigation of the reactivity of this bent uranyl species.

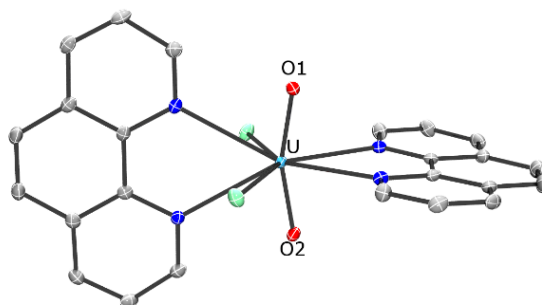


Figure 3. Solid-state structure of $\text{UO}_2\text{Cl}_2(\text{phen})_2$, O-U-O angle: $161.8(1)^\circ$. Hydrogen atoms omitted for clarity.¹¹

To conclude, the steric perturbation of the O-U-O angle in the uranyl dication is still relatively minor. Deviations from linearity have yet to surpass 20° . Although a *cis*-uranyl species remains elusive, recent developments show that unfavorable steric interactions between the ligand and the uranyl oxo groups are an effective strategy to decrease the O-U-O angle. Future work should focus on designing more rigid, strongly donating ligands that exhibit intermolecular interactions, which could eventually lead to *trans/cis* isomerization, and promote enhanced reactivity in uranyl.

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