**Bonding in electron-rich uranyl complexes (Burns)**

In 2021, Dr. Carol Burns received the American Chemical Society’s (ACS) Francis P. Garvan‒John M. Olin Medal. This national award recognizes distinguished service to chemistry by women chemists. Dr. Burns is Executive Officer for the Deputy Director for Science, Technology & Engineering at Los Alamos National Laboratory.

In recognition of this honor, this Learning Object explores a series of uranyl, UO22+, complexes reported by Dr. Burns and co-workers. This is but one example of Dr. Burn’s vast boundary-pushing synthetic f‑metal chemistry accomplishments.

“A Trigonal Bipyramidal Uranyl Amido Complex: Synthesis and Structural Characterization of [Na(THF)2][UO2(N(SiMe3)2)3]” Carol J. Burns, David L. Clark, Robert J. Donohoe, Paul B. Duval, Brian L. Scott, and C. Drew Tait *Inorg. Chem.* **2000**, *39*, 5464-5468, https://pubs.acs.org/doi/10.1021/ic0003168

This paper reports the synthesis and structure of [Na(THF)2][UO2(N(SiMe3)2)3]. The linear uranyl cation, UO22+, dominates the stereochemistry of uranium(VI) compounds. It is typically found with four or more additional ligands surrounding it in the equatorial plane. The tris(silylamide) compound in this paper is unusual because it has only three ligands in the equatorial plane.

Another unusual aspect of this uranyl complex is the electron-rich nature of the silylamide ligands. It has been reported that attempts to make uranium(VI) complexes with electron-rich amides leads to reduction of the metal. It is possible that the sterically demanding nature of this particular amide may stabilize this complex.

The following questions explore the bonding in this and two related uranyl silylamide complexes. The complex in this paper is called “tris” for its three equatorial silylamide ligands. The other two compounds are called “bis” and “tetrakis” for their two and four silylamide ligands, respectively.

(Hint for students: To answer the questions, skip to the “Metal-Ligand Bonding in Electron-Rich Uranyl Complexes” section of the paper.)

Shape

Description automatically generated with medium confidence

1. Amide ligands, **–**NR2, can act as both sigma-donors and pi-donors. Explain this using a Lewis structure of an amide.
2. The authors describe how the increased electron density in the equatorial plane from the amide ligands weakens the strong axial U=O bonds.
   1. According to the authors, how does an equatorial sigma-donating ligand weaken the U=O bond?
   2. According to the authors, how does an equatorial pi-donating ligand weaken the U=O bond?
3. List three examples (types of data) used to provide evidence of the weakening of the U=O bonds caused by the electron-rich amide ligands.
4. Infrared and Raman spectroscopy measure the energies associated with molecular vibrations. In your own words, explain how the vibrational frequency relates to bond strength.
5. List the Raman (symmetric O=U=O stretch) and IR (asymmetric O=U=O stretch) data for the three complexes.
6. Explain how these data support the authors’ hypothesis that the electron-rich amide ligands weaken the U=O bonds.