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CNA seminar

[Kevin P. Browne](#)

Brief Outline

- I. Introduction to the field of high-nitrogen chemistry
- II. Aqueous chemistry of Th with the high-nitrogen ligand bis(tetrazolylamine), BTA
- III. Water-free, oxygen-free chemistry of Th, U with high-nitrogen ligands using organometallic actinide precursors

What is “High-Nitrogen” (or “Nitrogen-Rich”)?

10% N

(Lewis 2012)

19% N

(Wang 2013)

33% N

(Sarkar 2003)

67% N

(Geisberger 2007)

75% N

(Tappan 2010)

100% N

(Crawford 2005)

High-Nitrogen Actinide Chemistry: Relatively Unexplored

Uranium Azides

Several researchers (Kiplinger, Evans, Hayton, shown).

Crawford, M.; et. al.
Angew. Chem. **2005**, 7874.

Uranyl AzoTetrazolate

Steinhauser, G.; et. al. *Inorg. Chem.* **2012**, 6739.

Fe-BTA Complexes: Synthesis and Combustion

laser
initiation

inert
atmosphere

Has been
extended to:

Ti, Fe, Co, Ni,
Cu, Zn, Pd, Ag,
Pt, Au

BC Tappan et al, *J. Am. Chem. Soc.*,
2006, 128, 6589

BC Tappan et al,
Angew. Chem. Int. Ed., **2010**, 49,
4544

Ln-BTA Complexes: Synthesis and Combustion

Ln = La, Ce, Pr, Nd

laser
initiation

inert
atmosphere

scale bar
= 20 μm

Ln-BTA

combustion
synthesis

[Ln-N]_x

Nanoporous
cerium nitride, [CeN]_x

work by Jacqueline
M. Veauthier, LANL

Why High-Nitrogen Actinides?

- **Nanoporous materials with new properties to explore for UO_2 , UN, UC, etc.**

- Nanoporosity will impart unique properties

- **Potential for new high purity routes to actinide nitrides and carbides.**

- Accident tolerant nuclear fuels (thermal stability, high conductivity, high m.p.)

- Difficult to make high purity bulk UN (CTR-N)

- **New field of science**

- New ligands lead to New Reactivity to Explore!

CTR-N for UN

UO₂-BTA Complexes: Synthesis

work by Nicholas E. Travia, LANL

UO₂-BTA Complexes: Combustion

- XRD confirms UO₂
- Nano-crystalline porous structure
 - Confirmed by TEM
- Heating UO₂-BTA under N₂ in calorimeter yields U₃O₈

work by Nicholas E. Travia, LANL

Th-BTA Complexes: Aqueous Synthesis

or

Aqueous High-Nitrogen Chemistry with Th: Characterization

reaction mixture

	carbon wt %	hydrogen wt %	nitrogen wt %
?	5.79	1.33	28.84
8.99	0.38	47.19
5.29	0.22	27.77
4.74	0.20	30.38

Aqueous High-Nitrogen Chemistry with Th: Characterization

Aqueous High-Nitrogen Chemistry with Th: Combustion

"Th-BTA" powder

press into pellet

Aqueous High-Nitrogen Chemistry with Th: Combustion

Aqueous High-Nitrogen Chemistry with Th: Combustion

video

Powder X-Ray Diffraction

**PXRD spectrum of
post-combustion
material**

Conclusion: product is
ThO₂

Aqueous High-Nitrogen Chemistry with Th: Combustion

Aqueous High-Nitrogen Chemistry with Th: Putting It All Together

Proposed mechanism and plausible final product

Organometallic High-N Chemistry with Th, U

- ✓ Vary available coordination sites
- ✓ Control source and reactivity of O atoms
- ✓ Tune oxidation states (U)

Synthetic Approach

Protonolysis chemistry

An = Th, U

Rationale:

- ✓ Cp* platform provides stability, solubility, and blocks metal center
- ✓ Protonolysis reactions very favorable, done within minutes, and...
- ✓ ... provide clear visual evidence (gas formation) of a reaction

Tetrazolates as High-N ligands

work by Nicholas E. Travia, LANL

Tetrazolates as High-N ligands

unstable

Tetrazolates as High-N ligands

or

Tetrazolates as High-N ligands

Synthetic Approach

Protonolysis chemistry

Rationale:

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Tetrazolates as High-N ligands

Tetrazolates as High-N ligands

Crystal Structure Analysis

	thorium (expt)	uranium (expt)
M–N, avg. (Å)	2.5142(19)	2.458(2)
C_{cent}–M, avg. (Å)	2.513(2)	2.445(3)
N–M–N, avg. (°)	31.23(6)	31.87(8)
C_{cent}–M–C_{cent} ' (Å)	136.65(7)	140.2(1)

Crystal Structure Analysis

	thorium (expt)	thorium (theory)	uranium (expt)	uranium (theory)
M–N, <i>avg.</i> (Å)	2.5142(19)	2.53	2.458(2)	2.48
C _{cent} –M, <i>avg.</i> (Å)	2.513(2)	2.58	2.445(3)	2.51
N–M–N, <i>avg.</i> (°)	31.23(6)	30.9	31.87(8)	31.5
C _{cent} –M–C _{cent} ' (Å)	136.65(7)	139.6	140.2(1)	138.4

Conformation of Tetrazolates

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Conformation of Tetrazolates

Conformation of Tetrazolates

T_2

$$K_{eq} = \frac{\delta_B - \delta}{\delta - \delta_A}$$

T_1

$$\delta = \frac{K_{eq} \delta_A + \delta_B}{1 + K_{eq}}$$

T_3

$$\delta = \frac{\exp\left(\frac{T\Delta S - \Delta H}{RT}\right) \delta_A + \delta_B}{1 + \exp\left(\frac{T\Delta S - \Delta H}{RT}\right)}$$

Conformation of Tetrazolates

Ideal behavior

Conformation of Tetrazolates

Electronic Characterization: UV-Visible

Electronic Characterization: Near-IR

Electronic Characterization: Summary for U

$\epsilon_{\text{UV-Vis}}: \sim 3000$
 $\epsilon_{\text{N-IR}}: \sim 70$

similar ϵ :

X = Cl
CH₃
CH₂Ph
SO₃CF₃

primarily σ -donor ligands

Conclusion: tetrazole functions primarily as σ -donor ligand

D. E. Morris *et. al.*, *Organometallics*, **2004**, 23, 5142

Electrochemical Characterization

Compound	$E_{1/2}$ (U^{IV}/U^{III})
$(C_5Me_5)_2U(SO_3CF_3)(CH_3)$	-1.83 V
$(C_5Me_5)_2UCl_2$	-1.85 V
1	-1.88 V
$(C_5Me_5)_2U(CH_2Ph)_2$	-1.95 V
$(C_5Me_5)U(CH_2Ph)_3$	-2.00 V
$(C_5Me_5)_2U(CH_3)_2$	-2.41 V

σ -donors

D. E. Morris *et. al.*, *Organometallics*, **2004**, 23, 5142

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