INL/CON-24-79158-Revision-0

Exploring the Structural Behavior of Hydrophilic Diglycolamide Complexes with the Lanthanides and Actinides

July 2024

Brian Matthew Rotermund, Nicholas Beck, Joseph M. Sperling, Gregory Peter Holmbeck, Thomas Albrecht

Changing the World's Energy Future

Idaho National Laboratory

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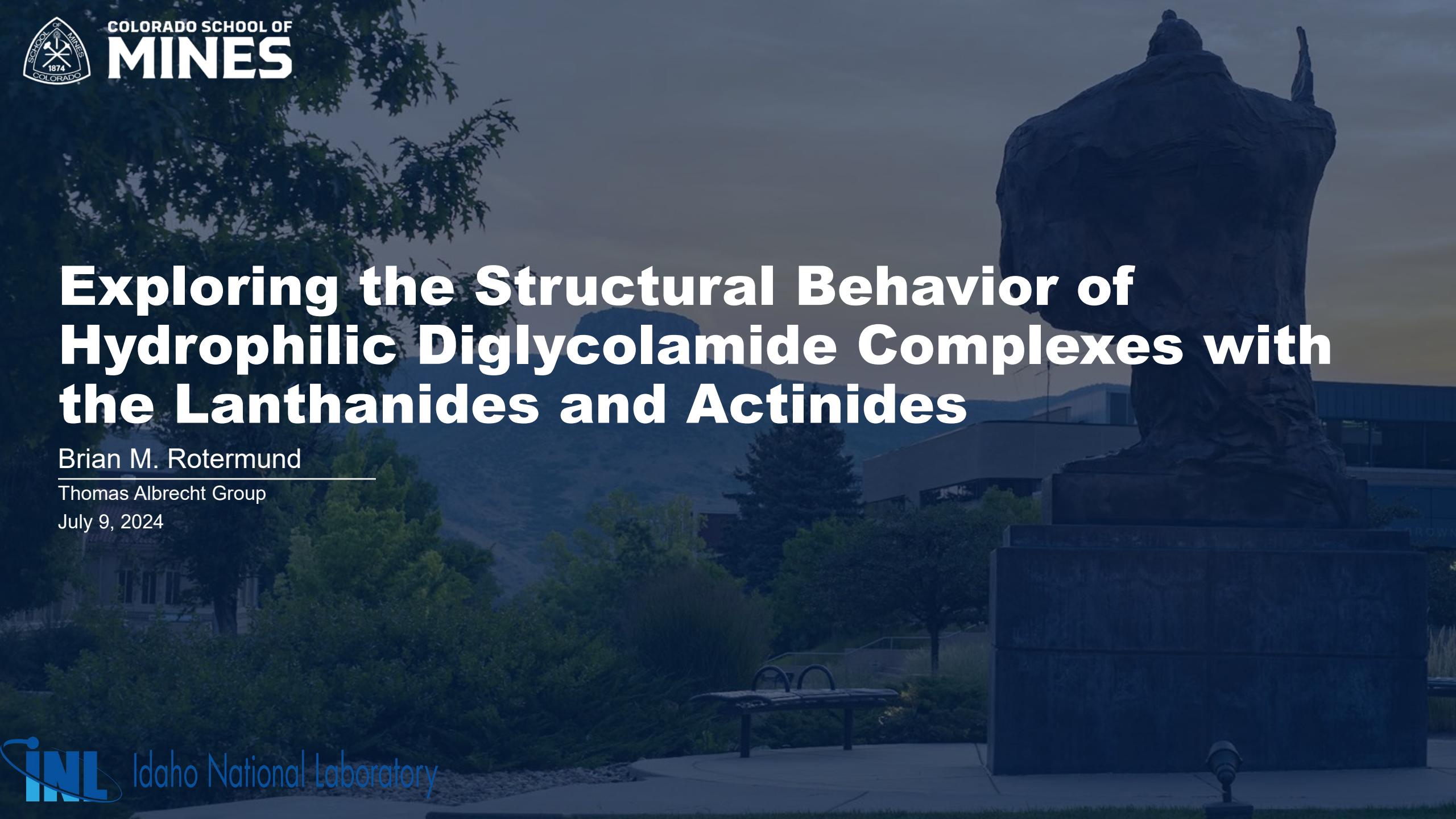


COLORADO SCHOOL OF MINES

Exploring the Structural Behavior of Hydrophilic Diglycolamide Complexes with the Lanthanides and Actinides

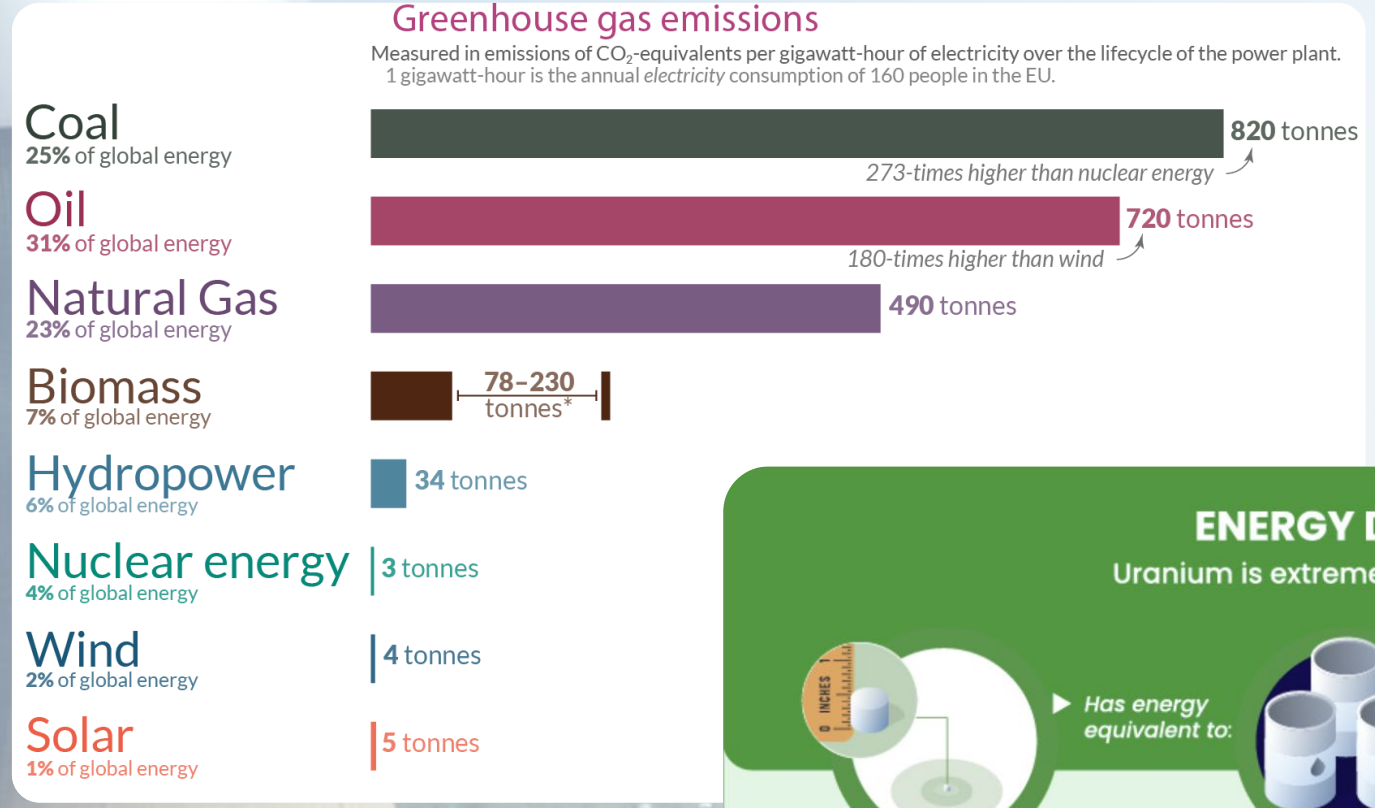
Brian M. Rotermund

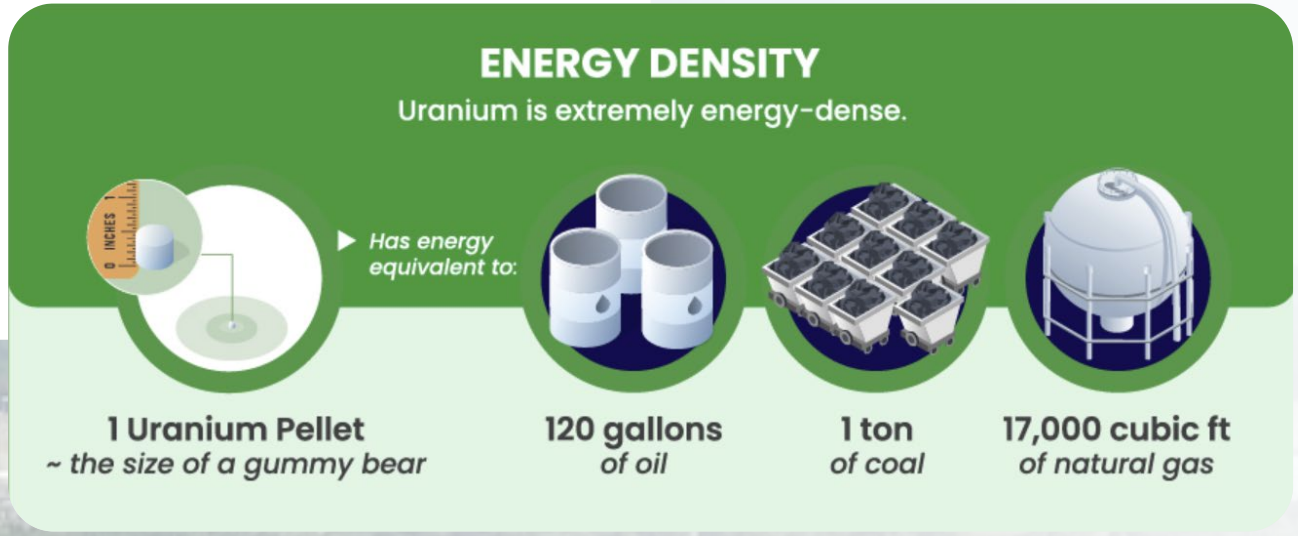
Thomas Albrecht Group

July 9, 2024

Idaho National Laboratory

Why Nuclear Power?

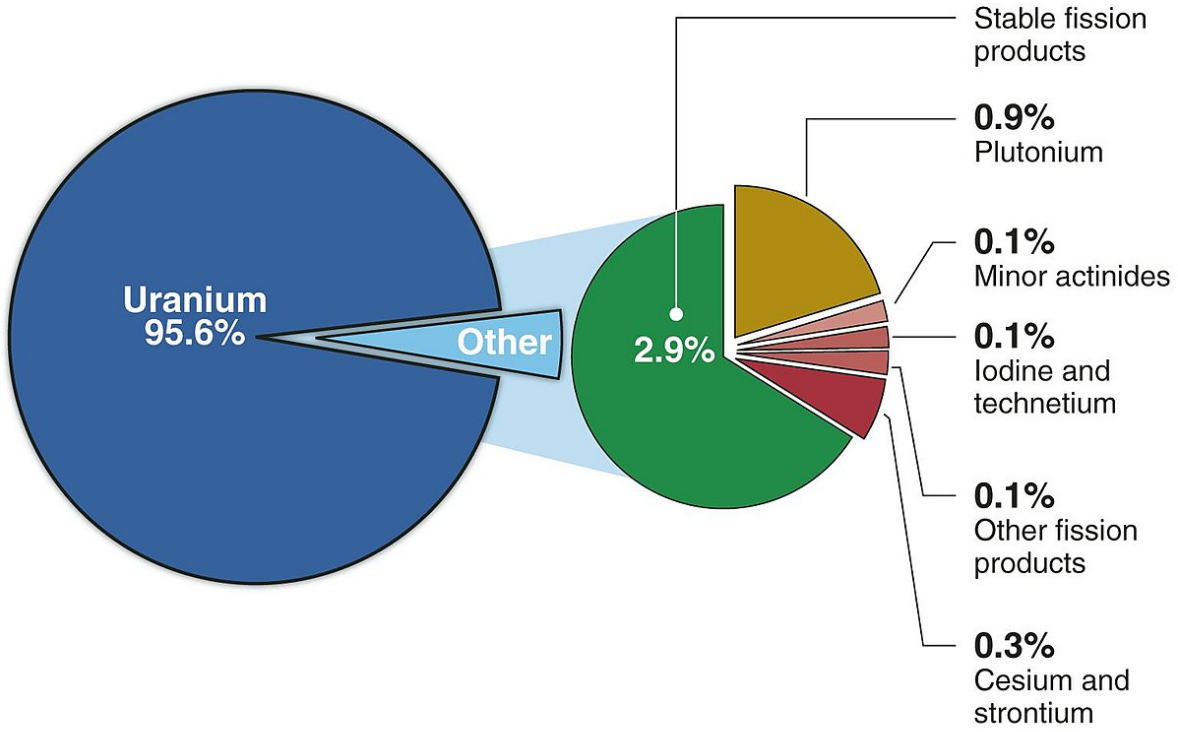




What are the Safest and Cleanest Sources of Energy?, 2020
The History of Uranium and Nuclear Power, 2021

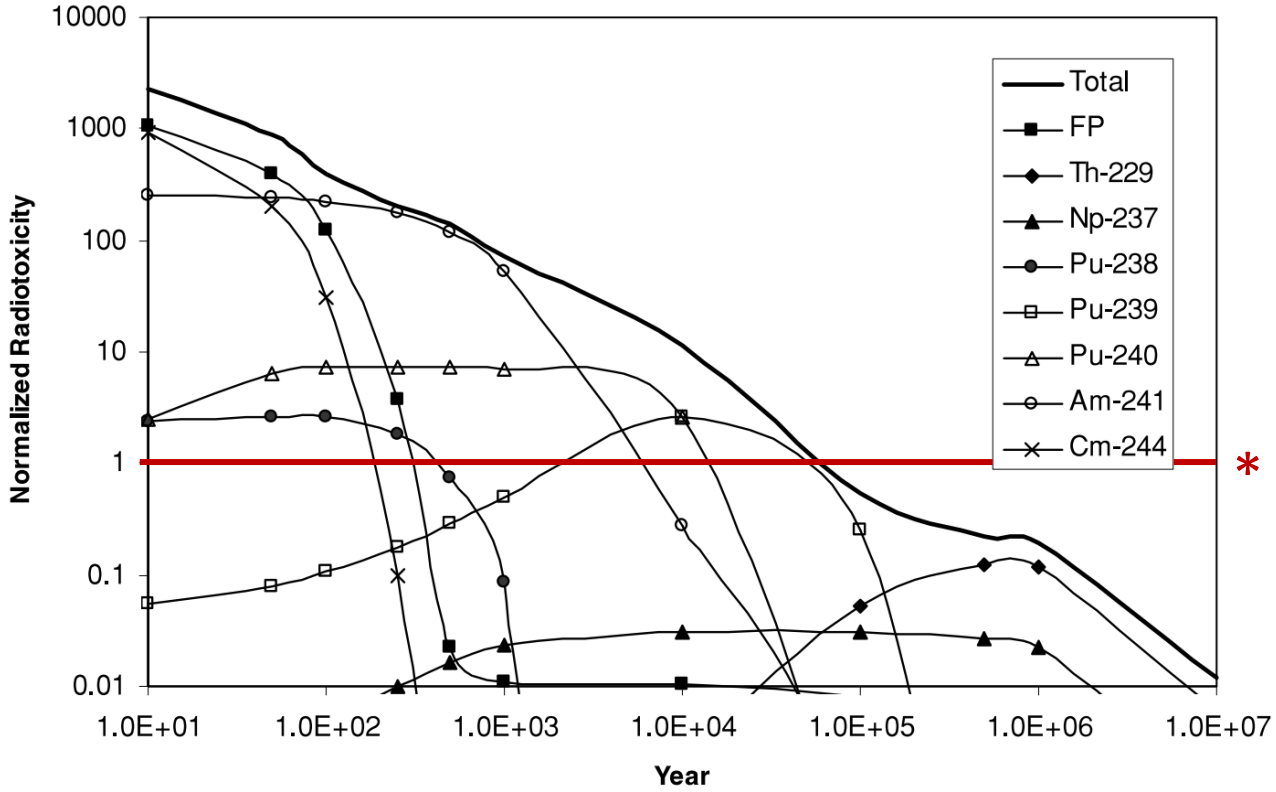
Problems with Used Nuclear Fuel

Used Nuclear Fuel (UNF) Composition



Source: GAO analysis of DOE data.

Radiotoxicity of Long-lived Isotopes in UNF



* Normalized to radiotoxicity of natural uranium ore

Aloise, G. *Nuclear Fuel Cycle Options.* 2011. DOE, GOA-12-70
Taiwo, T.A., *et al. Nucl.Technol.* **2006**. 155, 34-54

Challenges with Separation and Reprocessing

Alpha Emitters

^{237}Np, ^{241}Am, ^{244}Cm

$^{4}_{2}\alpha^{2+}$

Beta Emitters

^{93}Zn, ^{137}Cs, ^{249}Bk

$^{0}_{-1}\beta^{1-}$

Gamma Ray

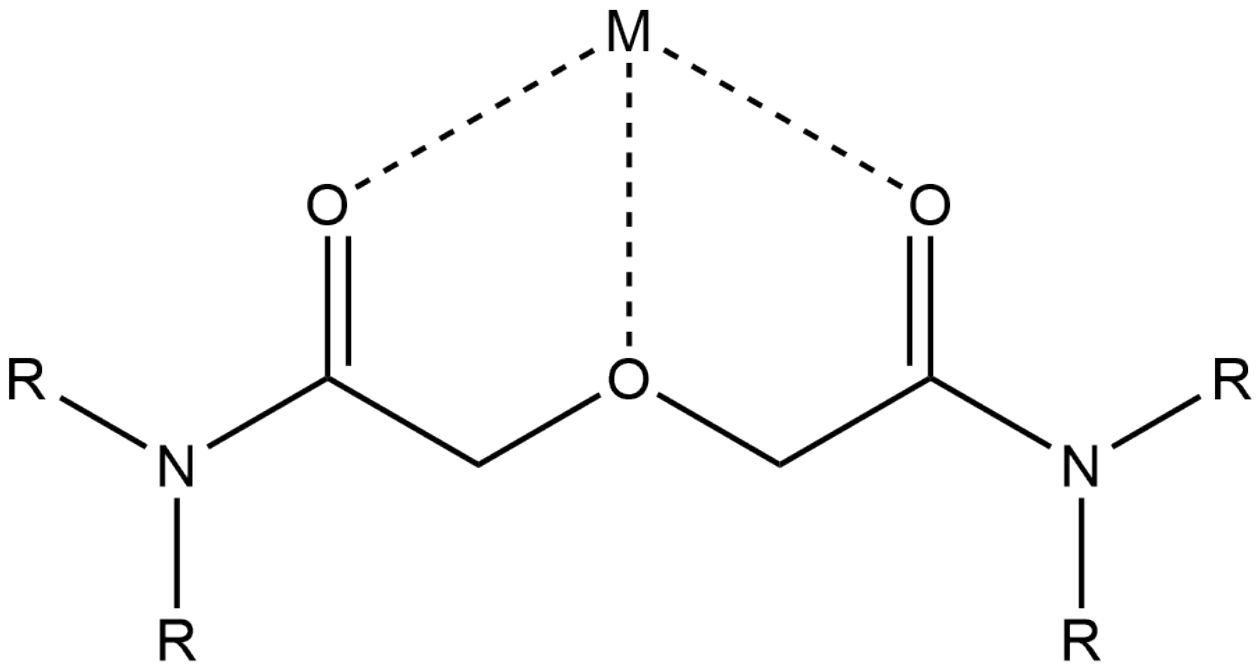
^{60}Co, ^{90}Sr, ^{249}Cf

$^{0}_{0}\gamma$

Multi-component Radiation Field

J.K. Conrad, *et al., Chem. Phys. Chem.* **2022**, *24*,

Diglycolamides (DGA)



Common diglycolamides:

- Tetramethyldiglycolamide (TMDGA), R = CH_3
- Tetraethyldiglycolamide (TEDGA), R = C_2H_5
- Tetraoctyldiglycolamide (TODGA), R = C_8H_{17}
- Tetra-2-ethylhexyldiglycolamide (TEHDGA), R = C_8H_{17}

Advantages:

- High affinity towards trivalent lanthanides and actinides
- Easy tunability through modification of the R groups
- Follows the C, H, O, N principal

Disadvantages

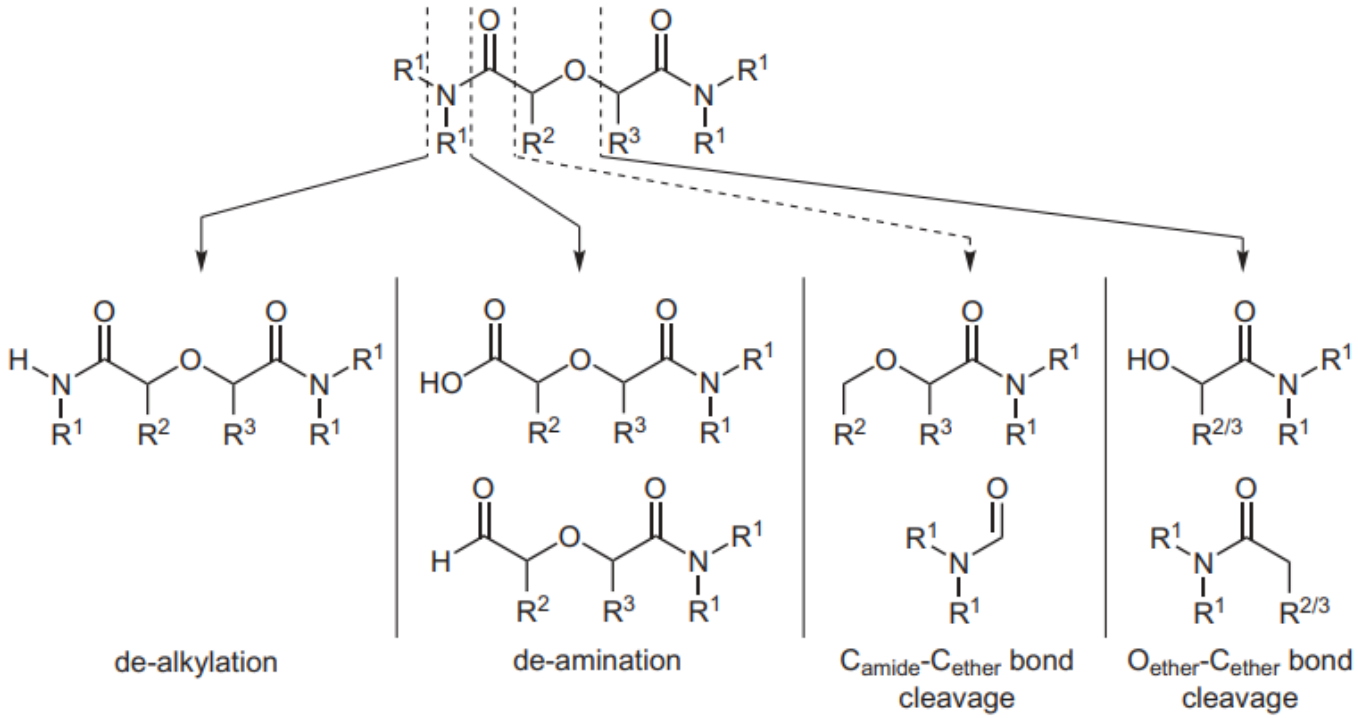
- Still relatively understudied
- Organic phase DGAs can be susceptible to third phase formation

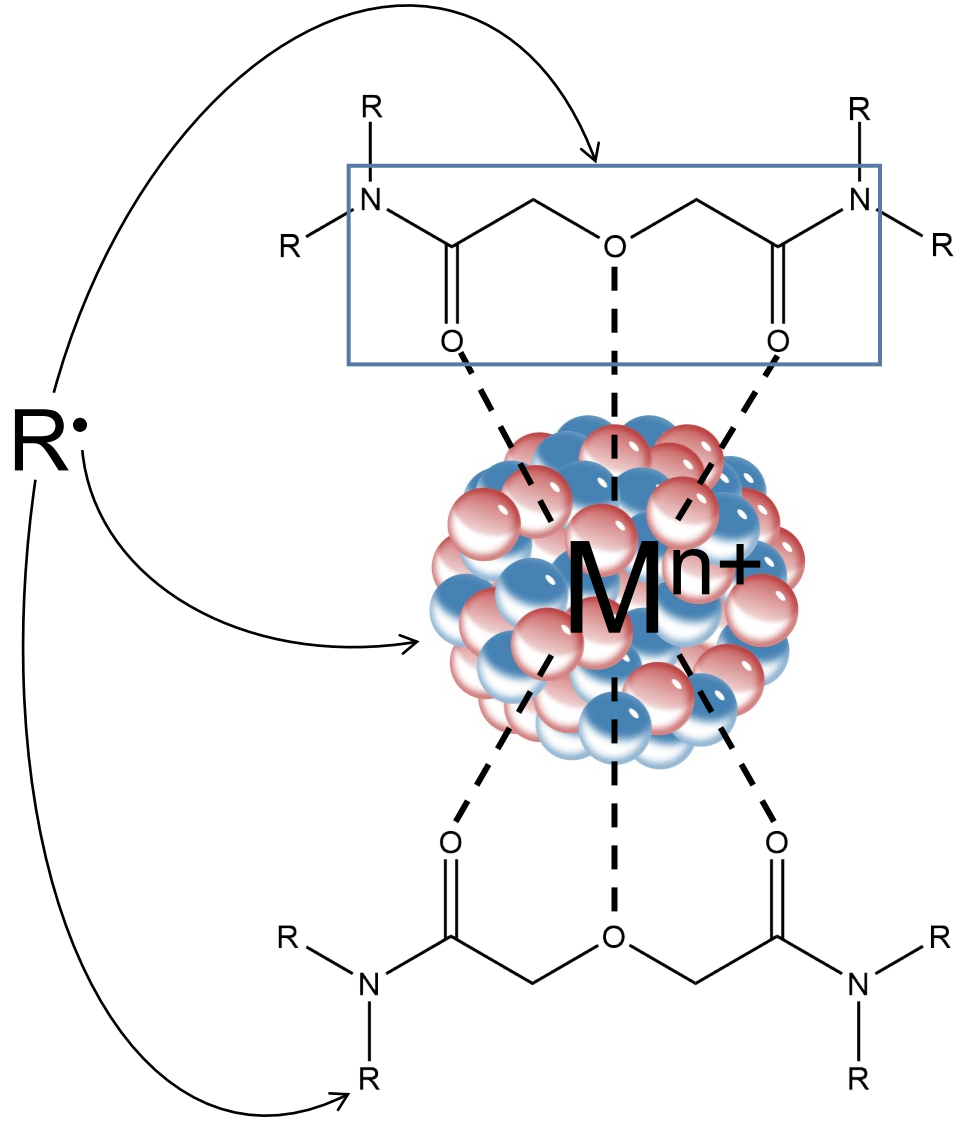
Properties and Advantages:

- Water Soluble
- Most simplified DGA structure
- Can be crystallized

S. A. Ansari, *et al.*, *Chem. Rev.* **2012**, *112* 3, 1751-1772

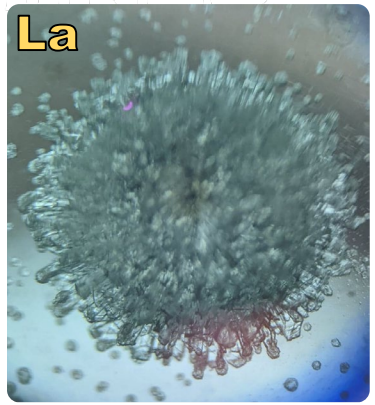
How Do Radicals React With TMDGA Complexes?

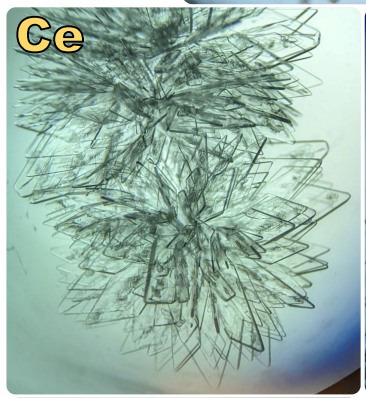


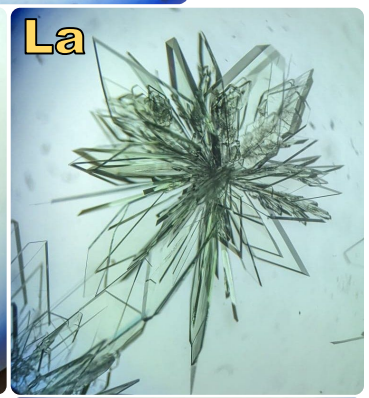


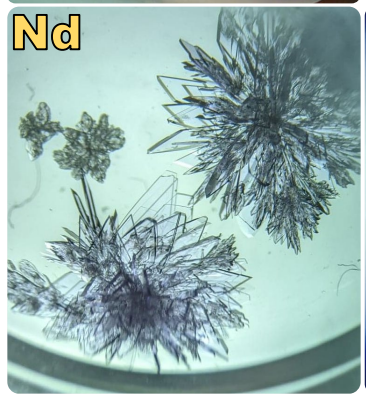
A. Wilden, *et al.*, *Solvent Extr. Ion Exch.* **2018**, *36*, 347-359

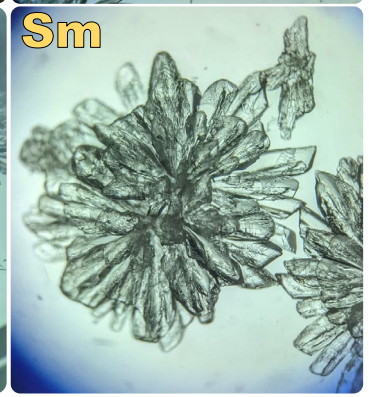
Lanthanide TMDGA Crystals





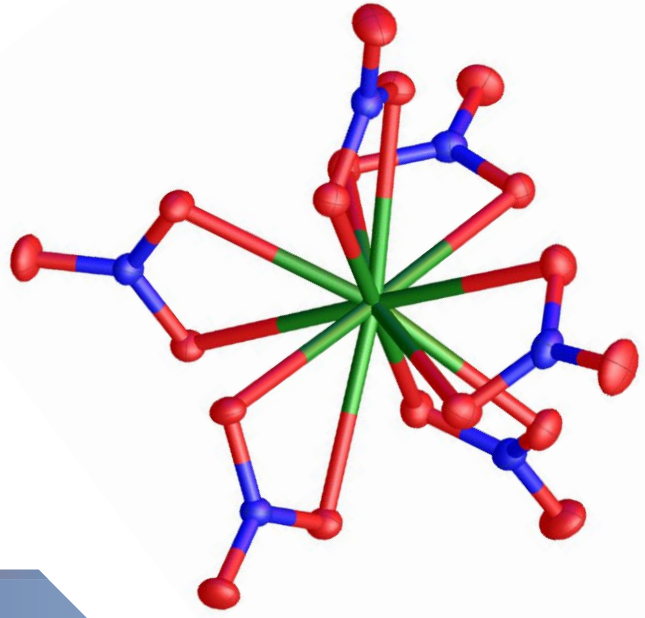


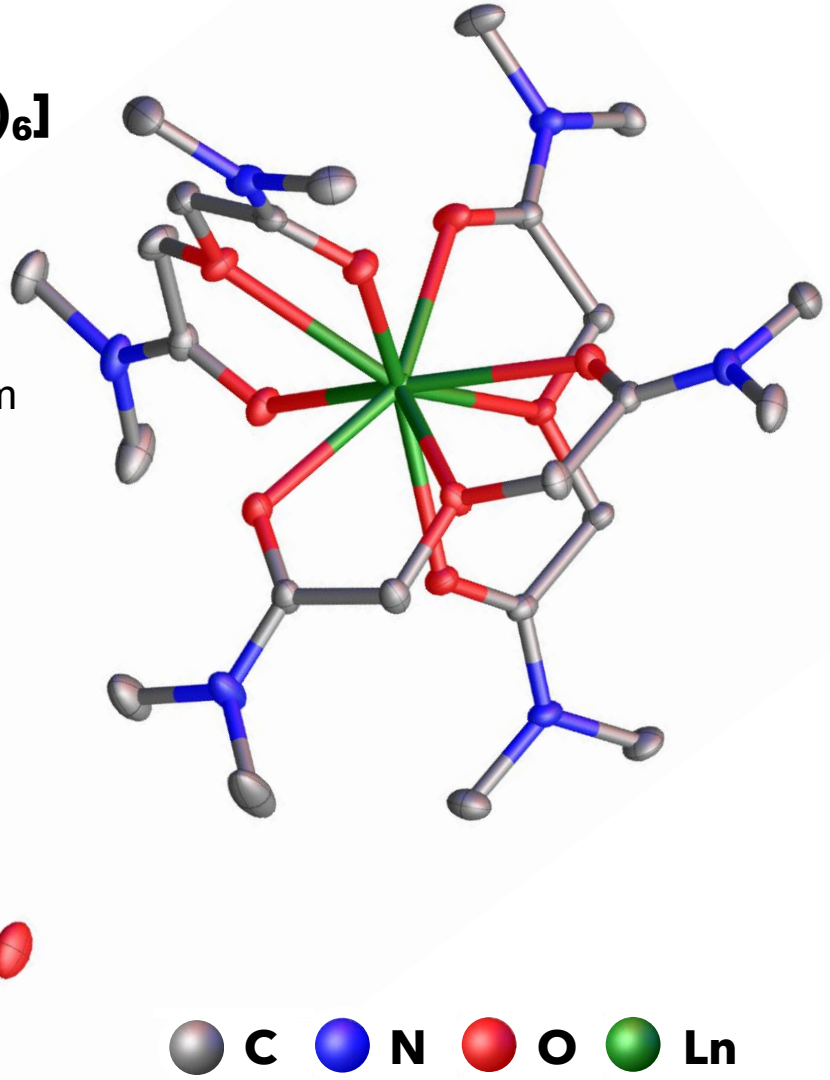




Formula: $[Ln(TMDGA)_3][Ln(NO_3)_6]$

- Ln = La, Ce, Pr, Nd, Sm
- Crystallizes in $P\bar{1}$
- Cation geometry: C_{4v}
  - Spherical capped square antiprism
- Anion Geometry: I_h
  - Icosahedron

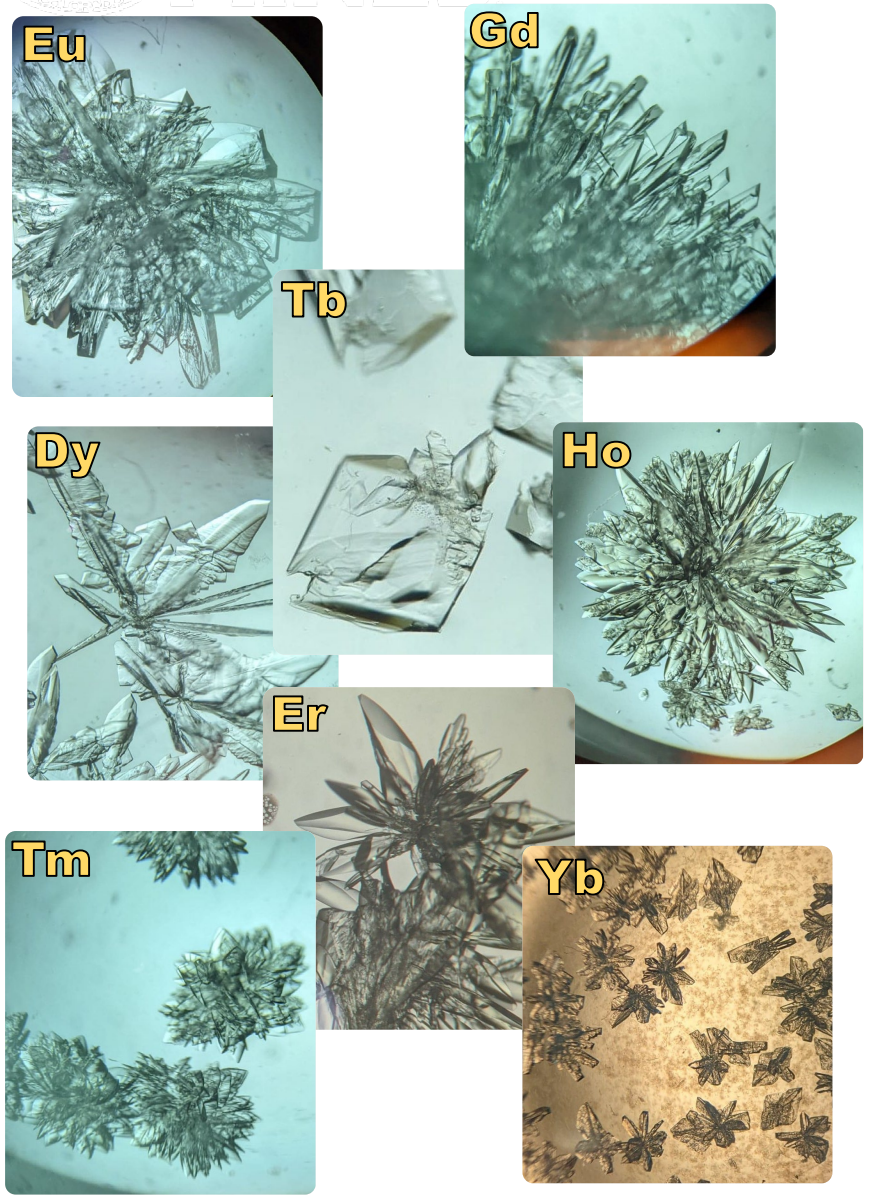




*Hydrogen removed for clarity

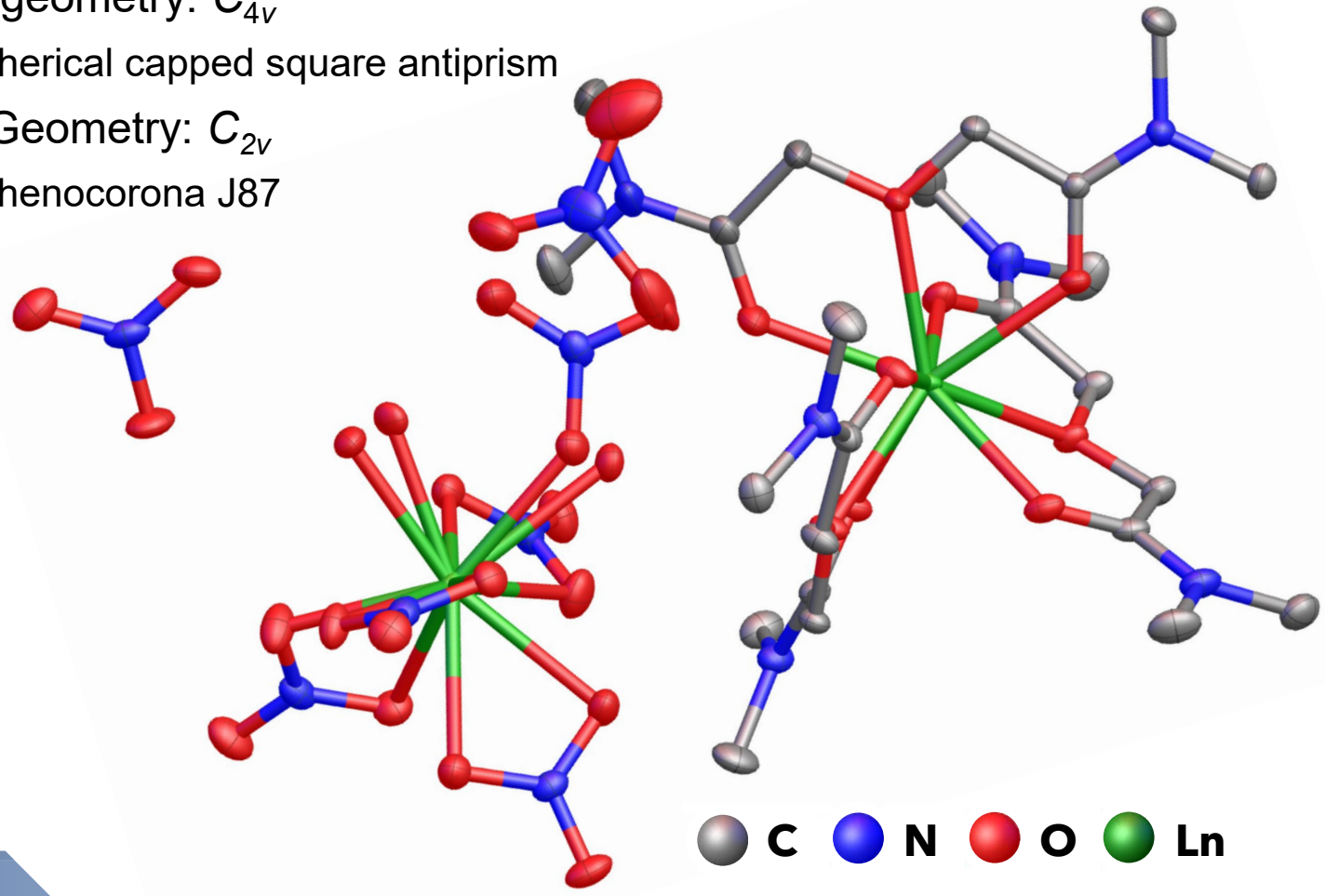
B.M. Rotermund, *et al.*, *Cryst. Growth Des.* ***Under Review***

Lanthanide TMDGA Crystals



Formula: $[M(TMDGA)_3][M(NO_3)_5(H_2O)]_{1-x}[M(NO_3)_4(H_2O)_2]_x(NO_3)_{1+x}$

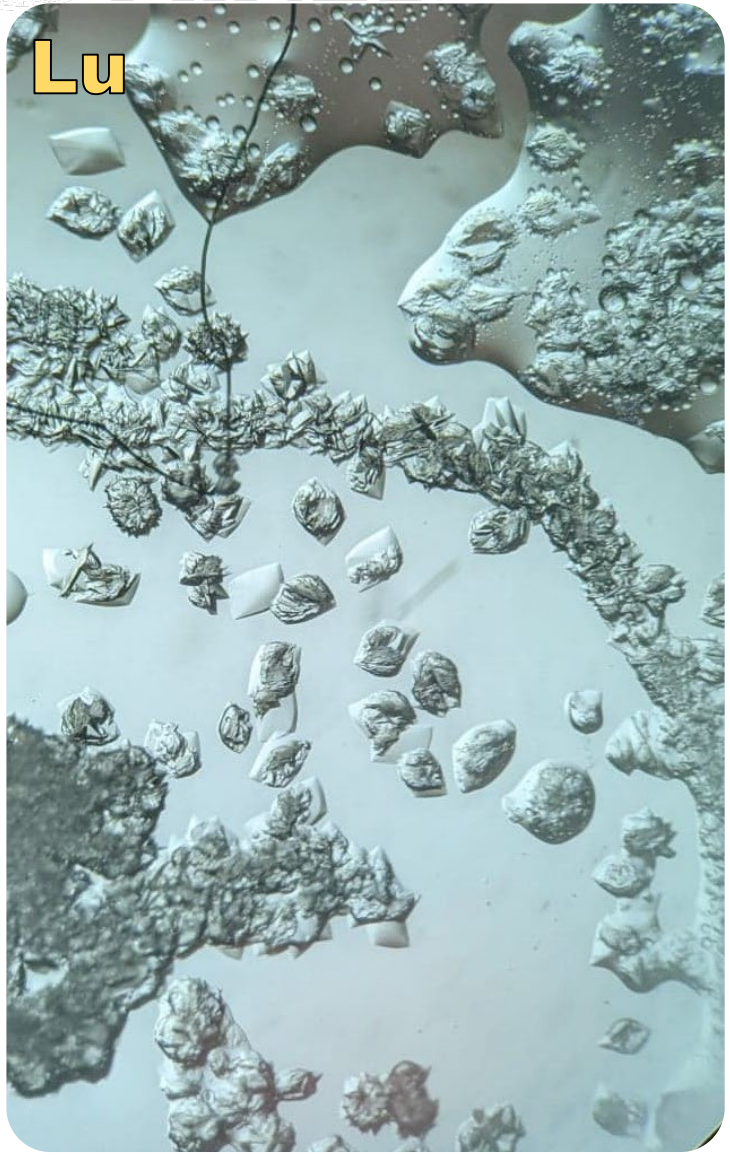
- Ln = Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb
- Crystallizes in $P\bar{1}$
- Cation geometry: C_{4v}
  - Spherical capped square antiprism
- Anion Geometry: C_{2v}
  - Sphenocorona J87



*Hydrogen removed for clarity

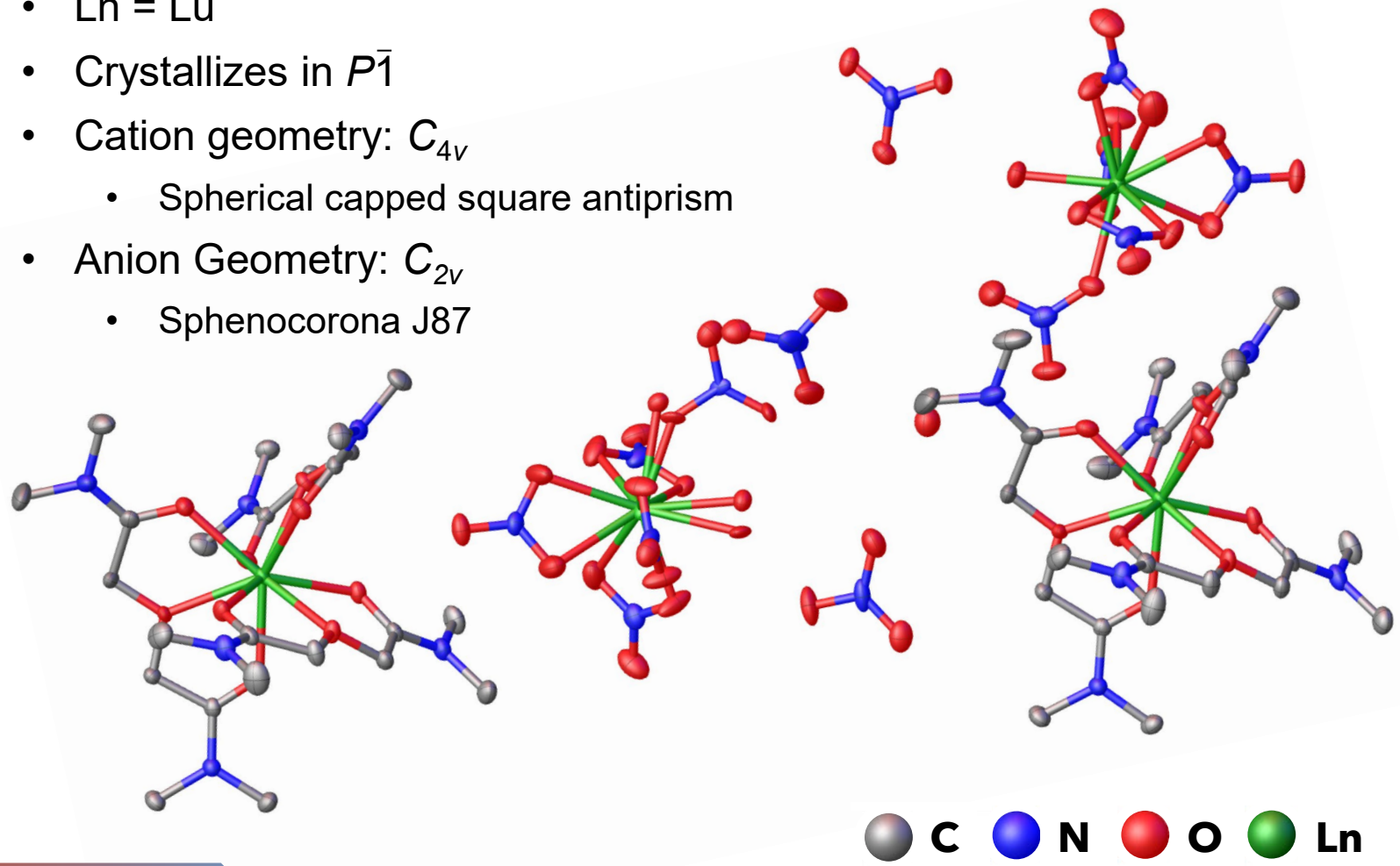
B.M. Rotermund, *et al.*, *Cryst. Growth Des.* ***Under Review***

Lanthanide TMDGA Crystals



Formula: $[Ln(TMDGA)_3]_2[Ln(NO_3)_4(H_2O)_2]_{0.75}[Ln(NO_3)_5(H_2O)]_{1.25}(NO_3)_{2.75}$

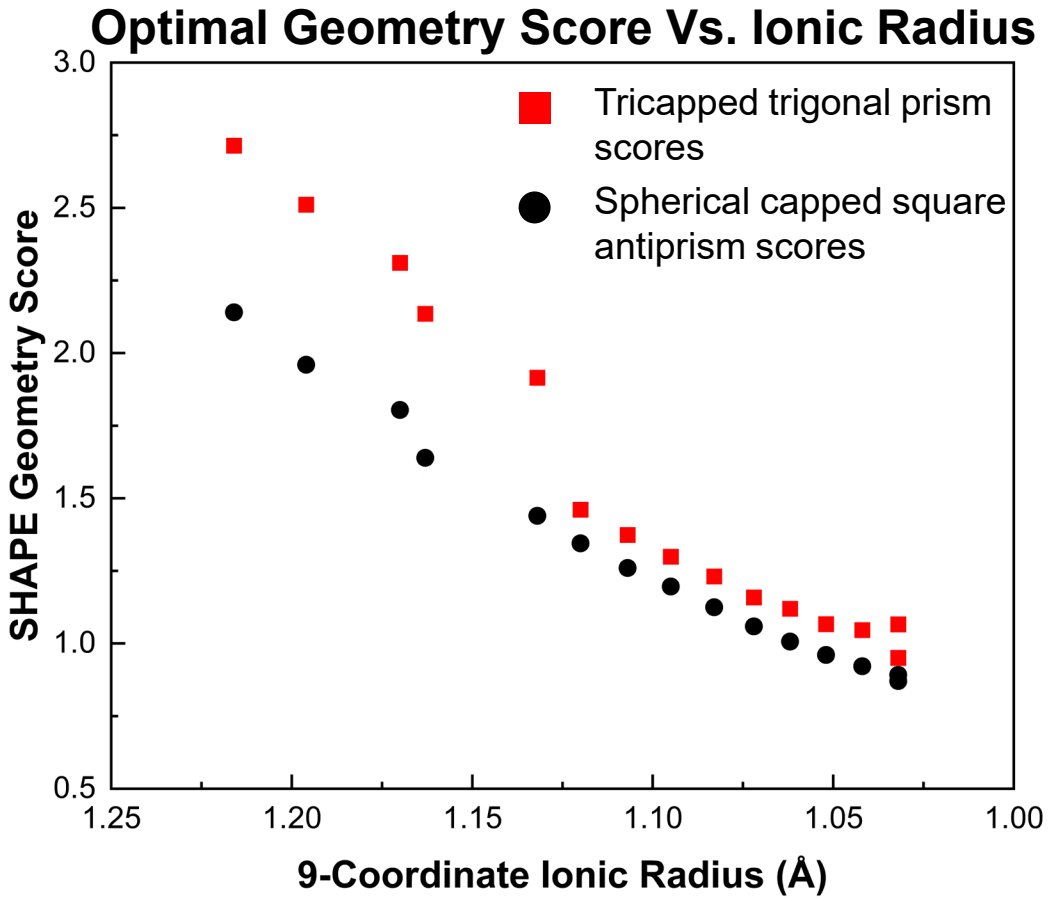
- Ln = Lu
- Crystallizes in $P\bar{1}$
- Cation geometry: C_{4v}
  - Spherical capped square antiprism
- Anion Geometry: C_{2v}
  - Sphenocorona J87

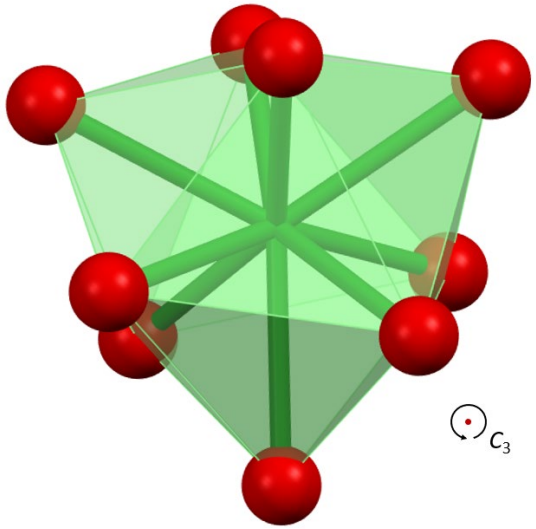


B.M. Rotermund, *et al.*, *Cryst. Growth Des.* ***Under Review***

*Hydrogen removed for clarity

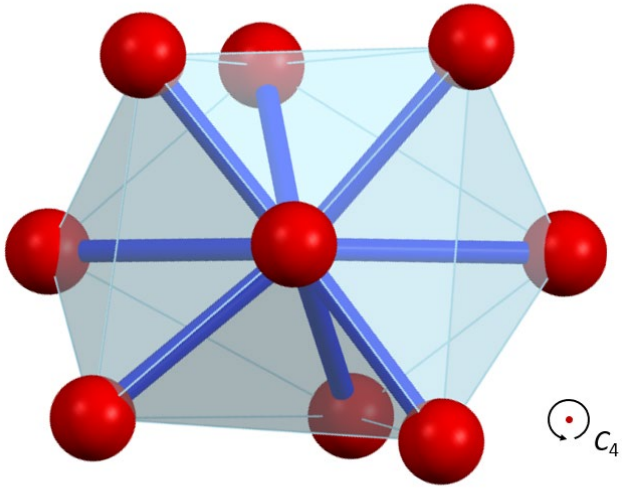
Lanthanide Geometry Across the Series





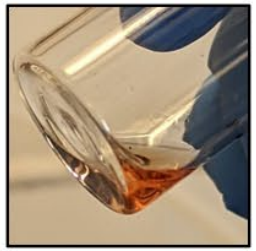
View of the three-fold rotation axis for the tricapped trigonal prism geometry

View of the four-fold rotation axis for the spherical capped square antiprism geometry



B.M. Rotermund, *et al., Cryst. Growth Des.* ***Under Review***
M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez, *SHAPE 2.1*

Pu TMDGA Crystallization

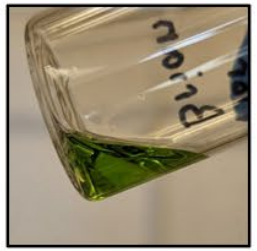


$Pu^{n+}(Cl)_{3\text{-}4\ (aq)}$

$NH_4OH_{\ (aq)}$

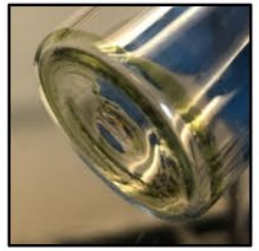
$Pu(OH)_{4\ (s)}$

$HNO_{3\ (aq)}$



$Pu(NO_3)_{4\ (aq)}$

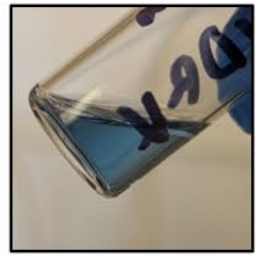
Δ



$Pu(NO_3)_{4\ (s)} + HONH_2 \bullet HCl$

Methanol

2 Hr.



$Pu(NO_3)_3$

$2\ Pu(NO_3)_3 + 3\ TMDGA$

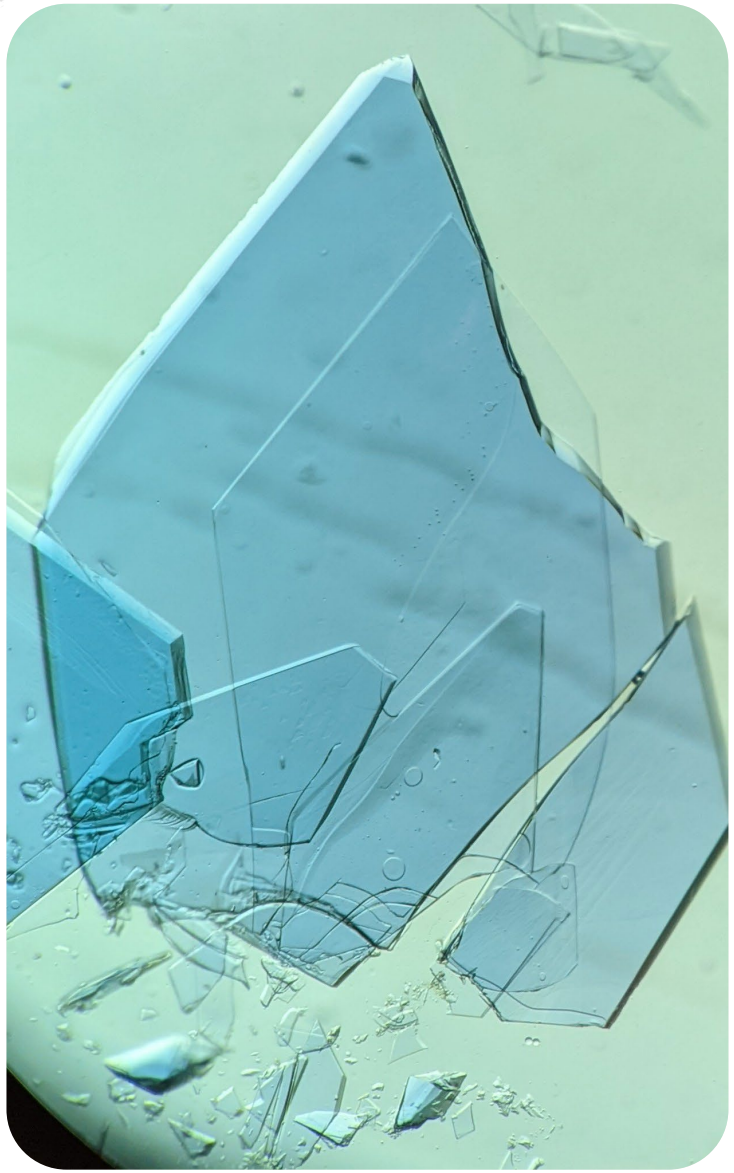
Ether

2 Hr.

$[Pu(TMDGA)_3][Pu(NO_3)_6]$

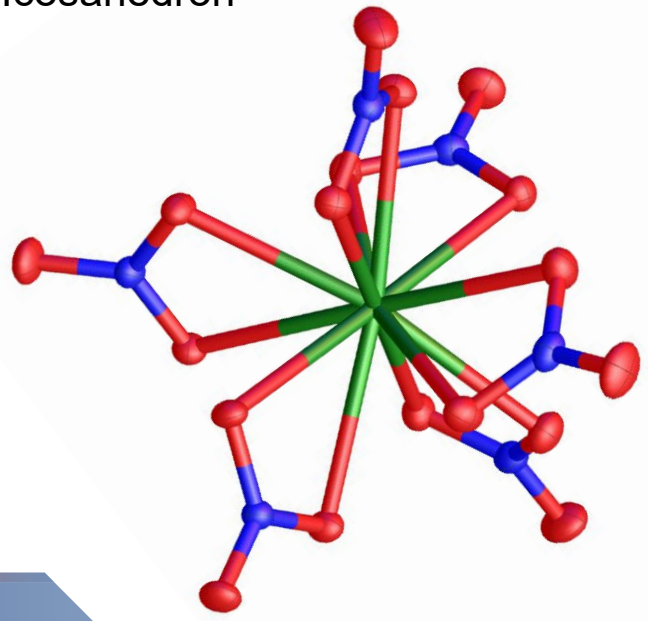
B.M. Rotermund, *et al., Inorg. Chem.* **2023**, *62*, 12905-12912

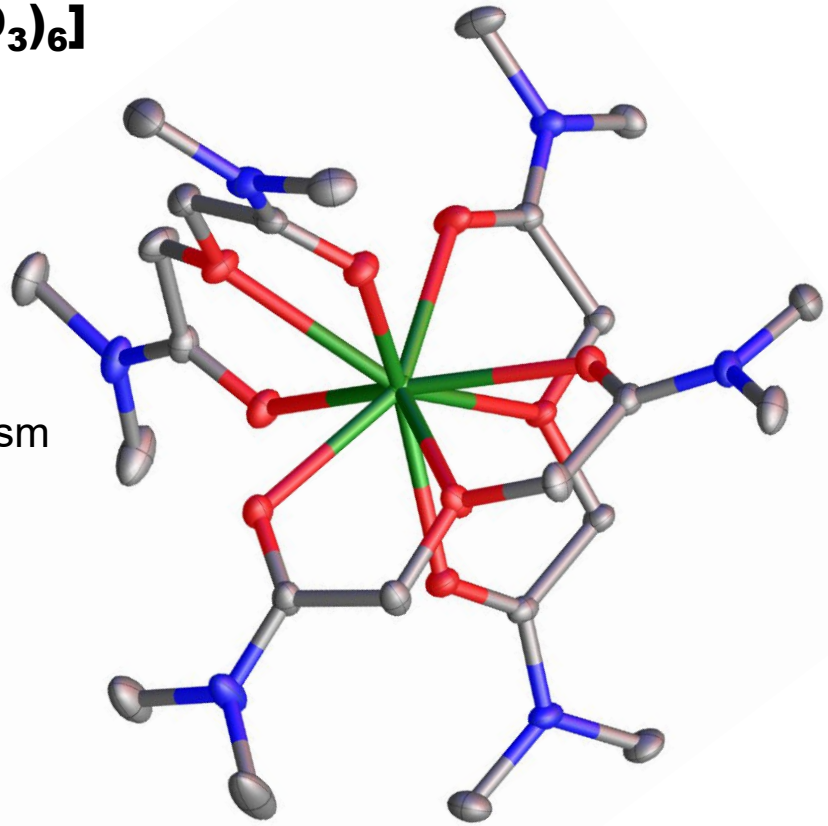
Plutonium(III) TMDGA Crystals



Formula: $[Pu(TMDGA)_3][Pu(NO_3)_6]$

- Crystallizes in $P\bar{1}$
- First isolation of plutonium(III) diglycolamide and plutonium(III) hexanitrato
- Cation geometry: C_{4v}
  - Spherical capped square antiprism
- Anion Geometry: I_h
  - Icosahedron





*Hydrogen removed for clarity

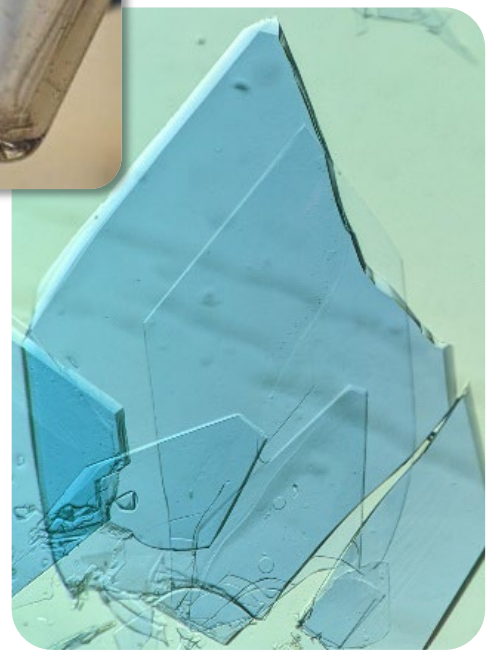
B.M. Rotermund, *et al.*, *Inorg. Chem.* **2023**, *62*, 12905-12912

Plutonium Crystal Oxidation

Pu(III)

O_2
24 h

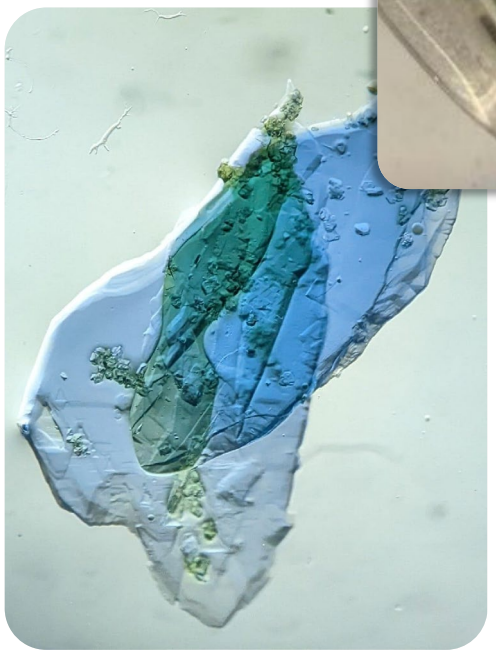
Pu(IV)



Exposed to air overnight

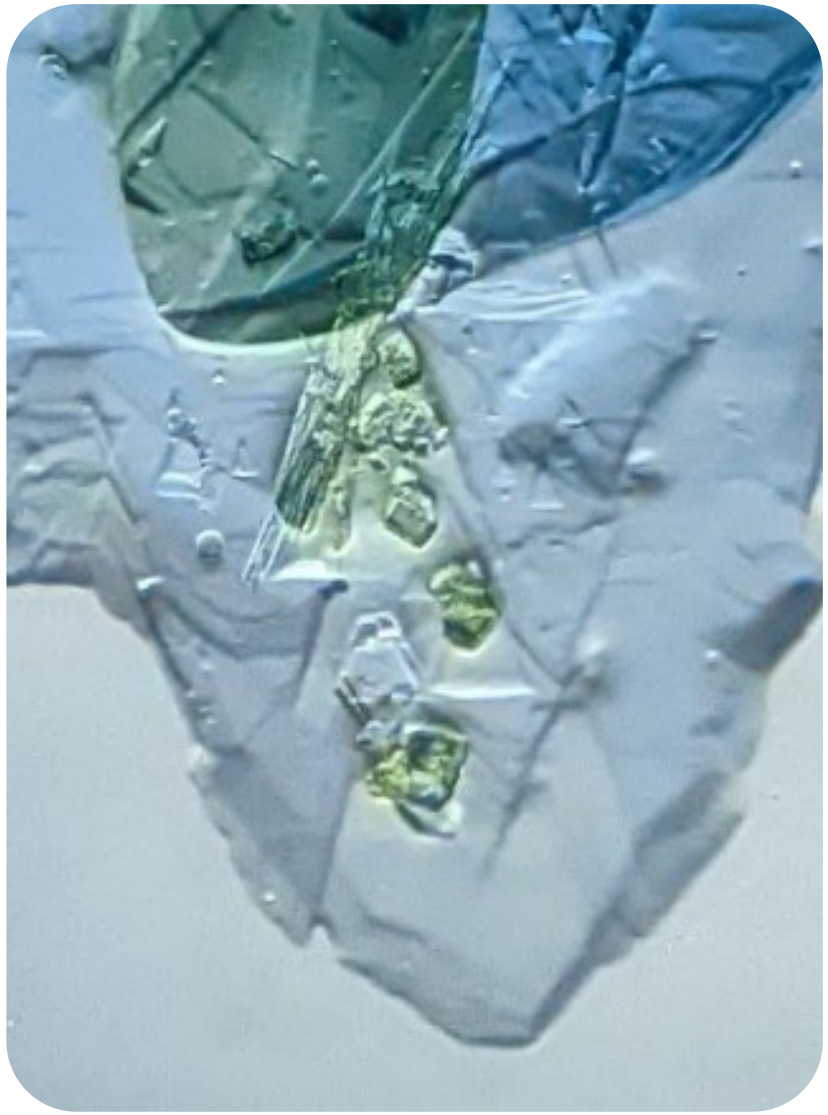
Oxidation of Plutonium (III)

Recrystallization
to plutonium (IV) species



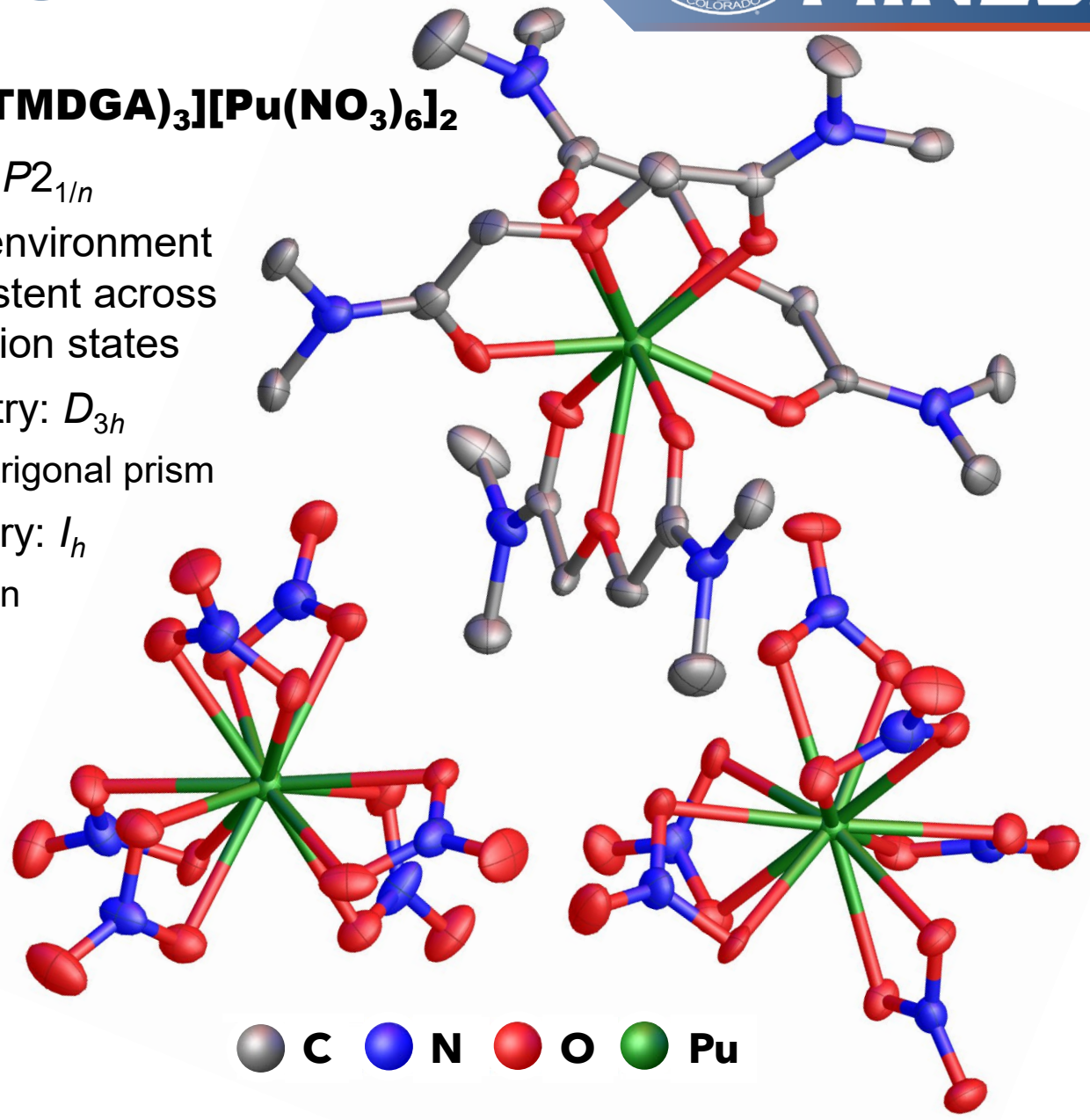
B.M. Rotermund, *et al.*, *Inorg. Chem.* **2023**, *62*, 12905-12912

Plutonium(IV) Crystals



Formula: $[Pu(TMDGA)_3][Pu(NO_3)_6]_2$

- Crystallizes in $P2_{1/n}$
- Coordination environment remains consistent across multiple oxidation states
- Cation geometry: D_{3h}
  - Tricapped trigonal prism
- Anion Geometry: I_h
  - Icosahedron

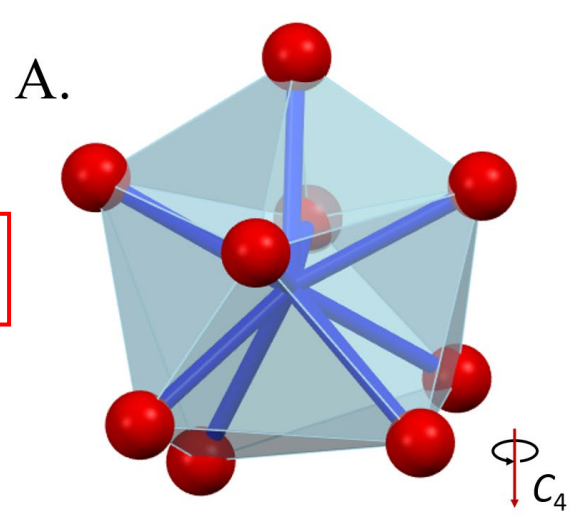


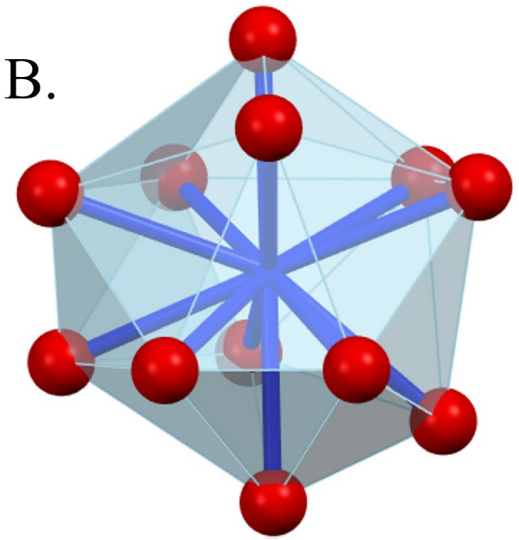
*Hydrogen & Lattice methanol removed for clarity

B.M. Rotermund, *et al.*, *Inorg. Chem.* **2023**, *62*, 12905-12912

Geometries of $Pu(TMDGA)_3$

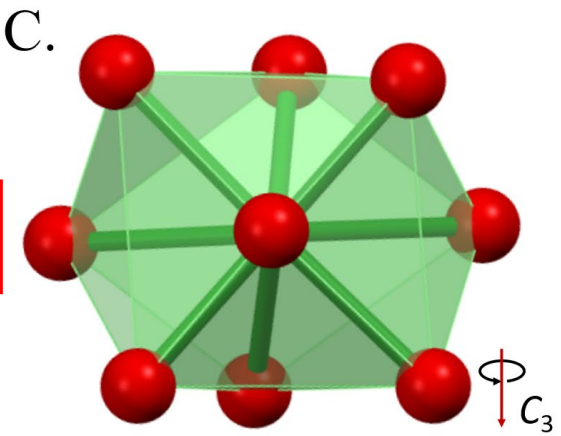
A) $[Pu(TMDGA)_3]^{3+}$ C_{4v}

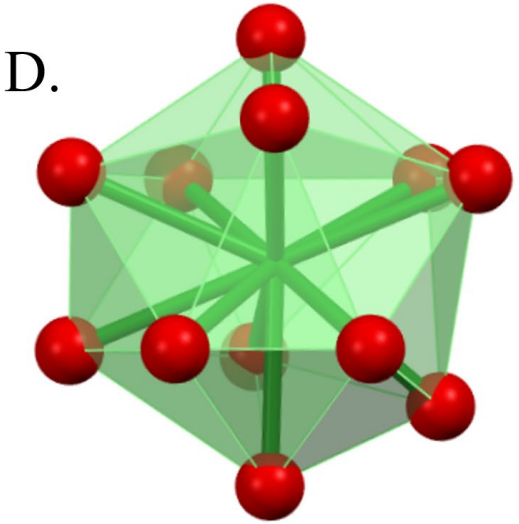




B) $[Pu(NO_3)_6]^{3-}$ I_h

C) $[Pu(TMDGA)_3]^{4+}$ D_{3h}

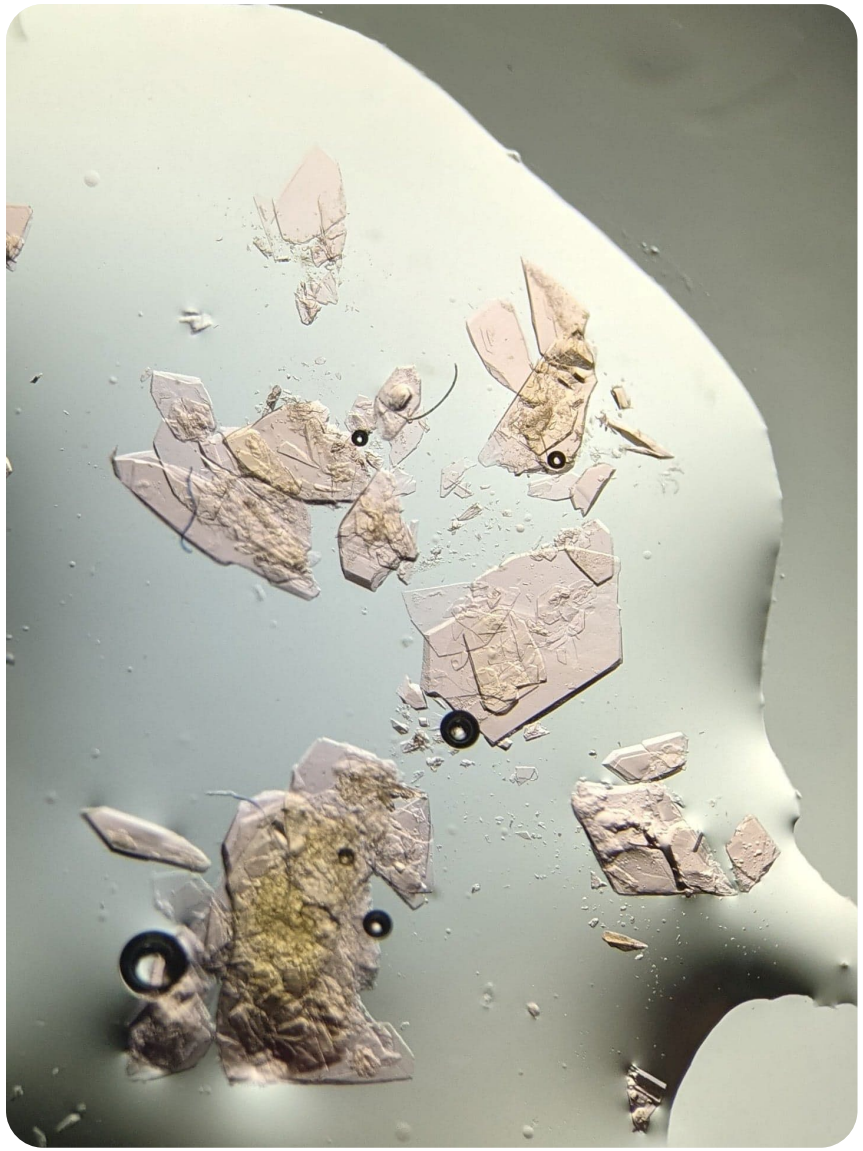




D) $[Pu(NO_3)_6]^{2-}$ I_h

B.M. Rotermund, *et al.*, *Inorg. Chem.* **2023**, *62*, 12905-12912
M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez, *SHAPE 2.1*

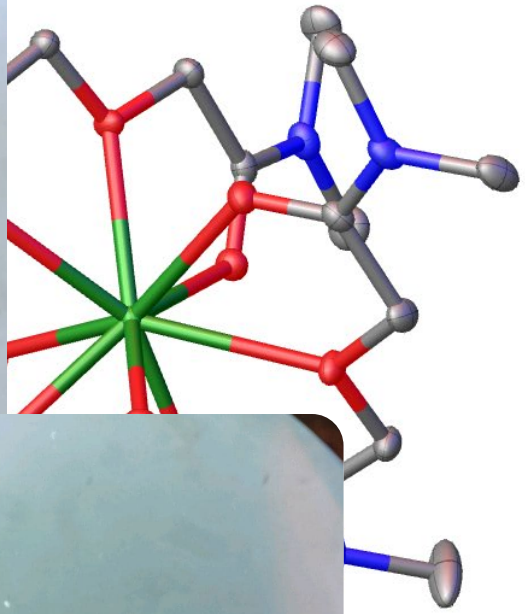
Americium(III) TMDGA Crystals

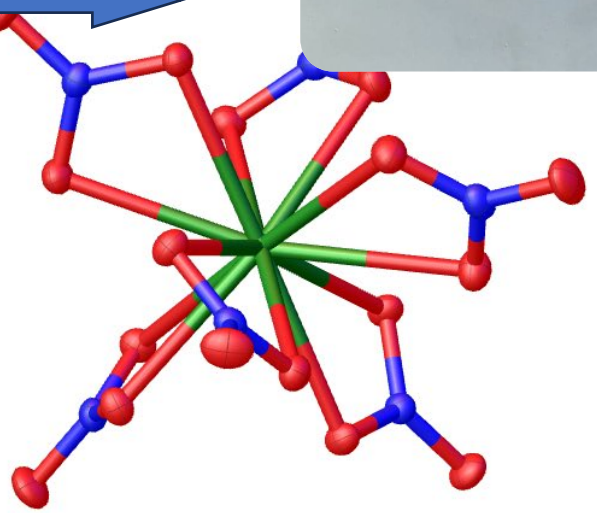


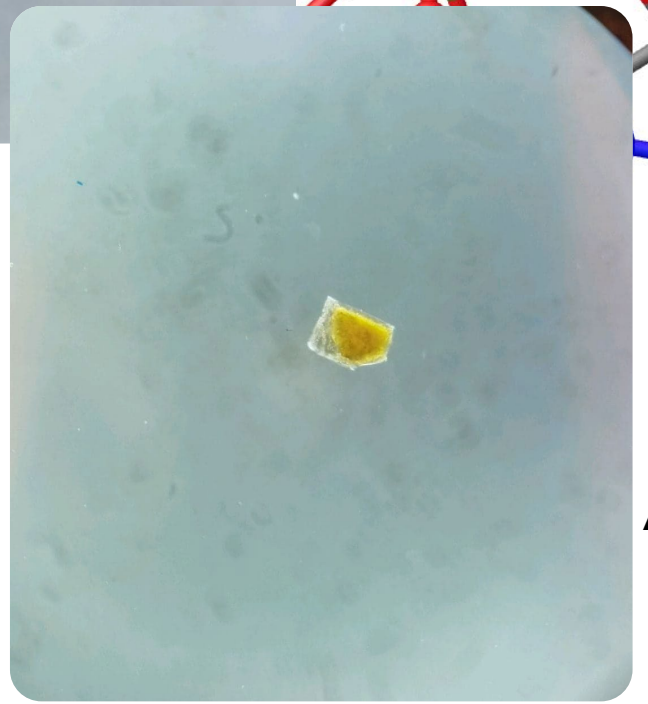
Formula: [Am(TMDG

- Crystallizes in $P\bar{1}$
- Same structure type
- Cation geometry: C_4
  - Spherical capped
- Anion Geometry: I_h
  - Icosahedron

300 Days





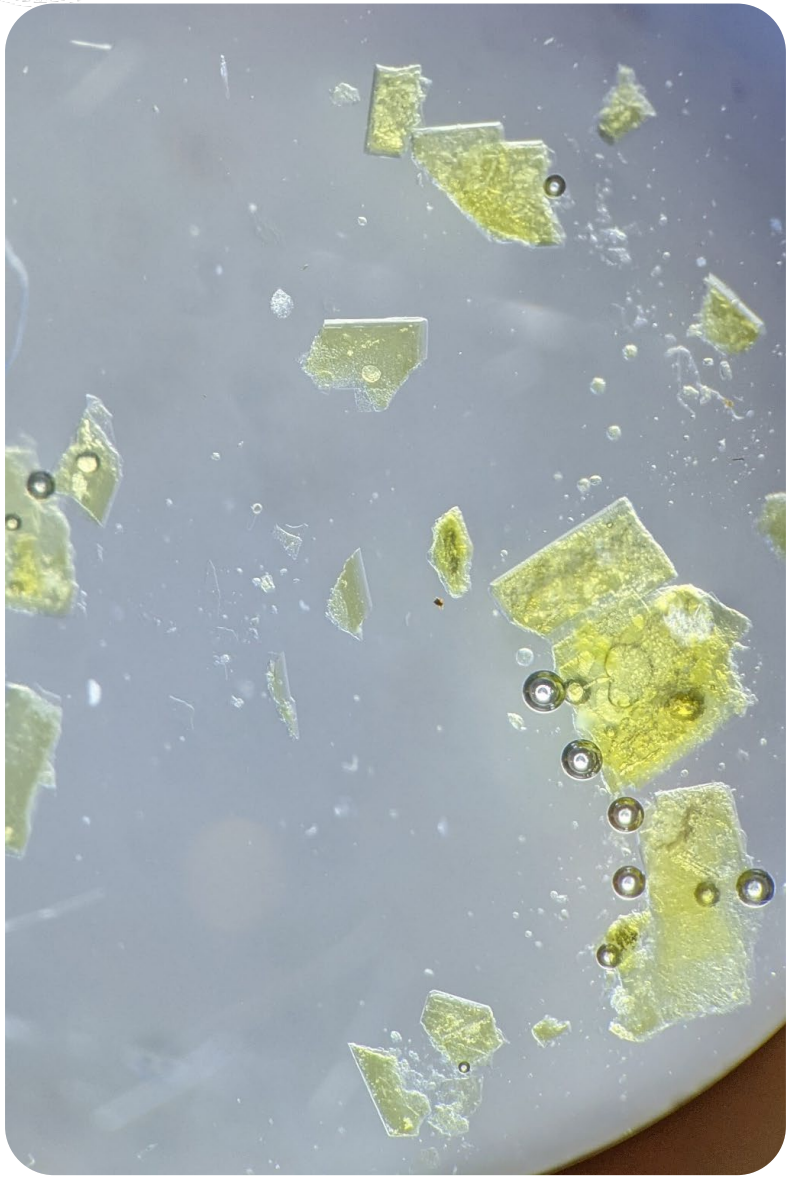


Am

B.M. Rotermund, *et al.*, *Inorg. Chem.* **2023**, *62*, 12905-12912

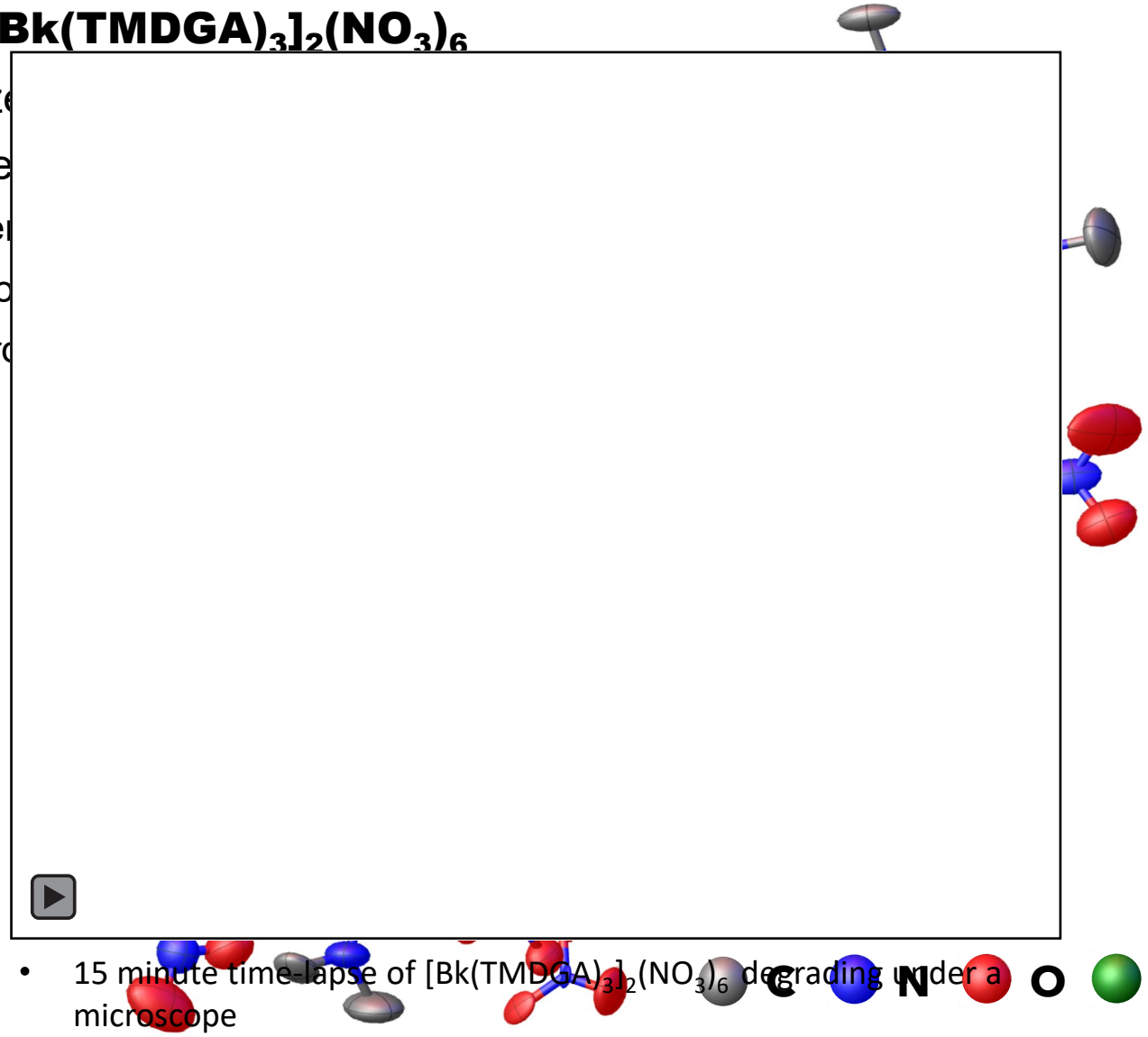
*Hydrogen removed for clarity

Berkelium(III) TMDGA Crystals



Formula: $[Bk(TMDGA)_3]_2(NO_3)_6$

- Crystallize
- Cation ge
  - Spher
- Nitrates do
- High disorc



- 15 minute time-lapse of $[Bk(TMDGA)_3]_2(NO_3)_6$ degrading under a microscope

C N O Bk

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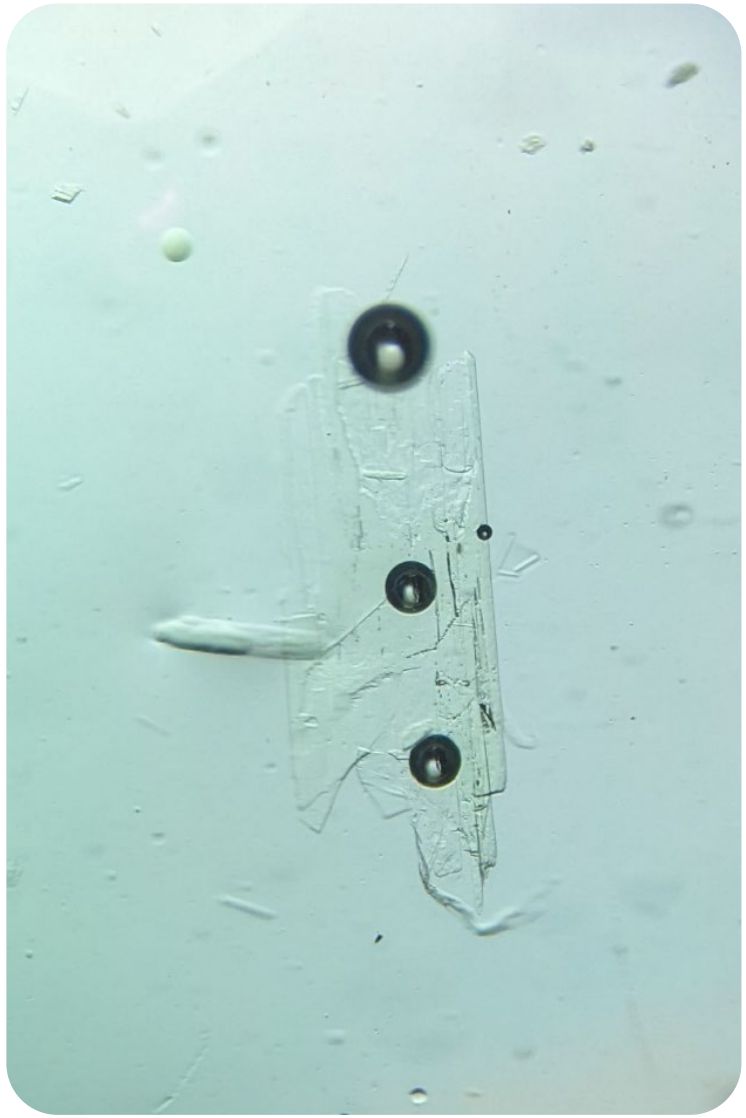
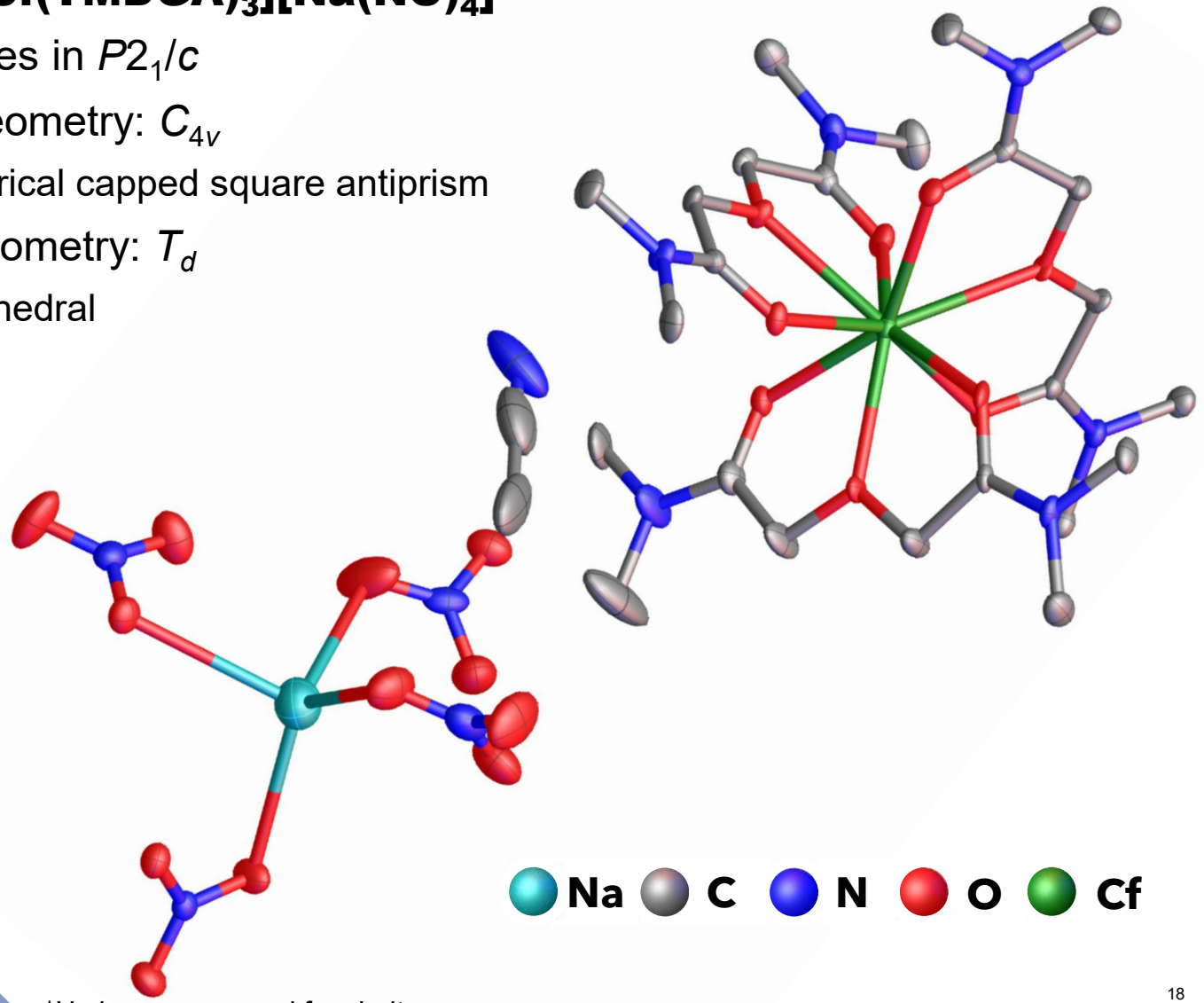
*Hydrogen & lattice water removed for clarity

Californium(III) TMDGA Crystals



Formula: $[Cf(TMDGA)_3][Na(NO)_4]$

- Crystallizes in $P2_1/c$
- Cation geometry: C_{4v}
  - Spherical capped square antiprism
- Anion Geometry: T_d
  - Tetrahedral



*Hydrogen removed for clarity

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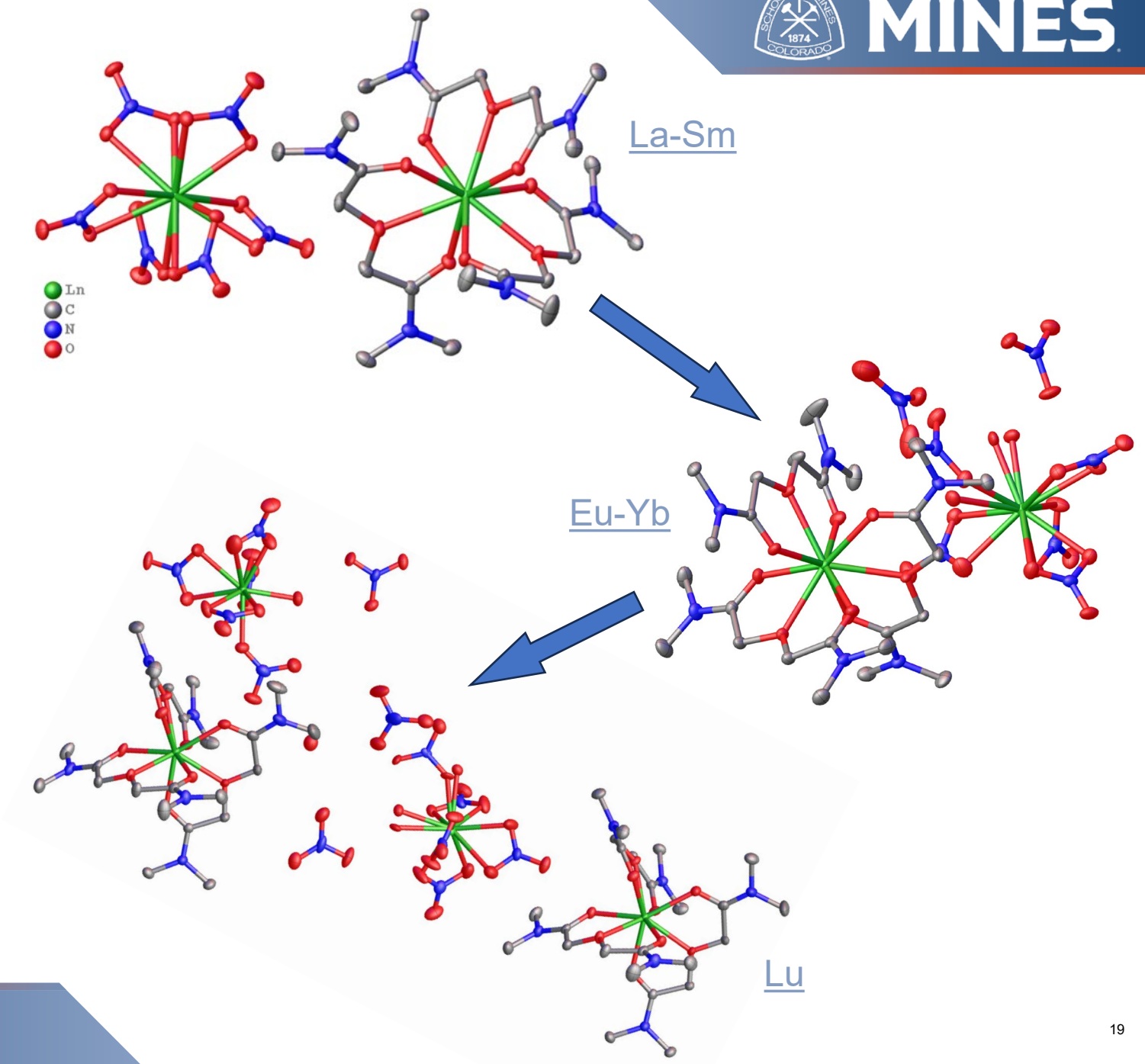
Summary

- Lanthanides show continued steric strain in the anionic environment across the Ln series
- Early actinides closely follow structural behavior of the early lanthanides
- Late actinides don't follow expected bonding behavior



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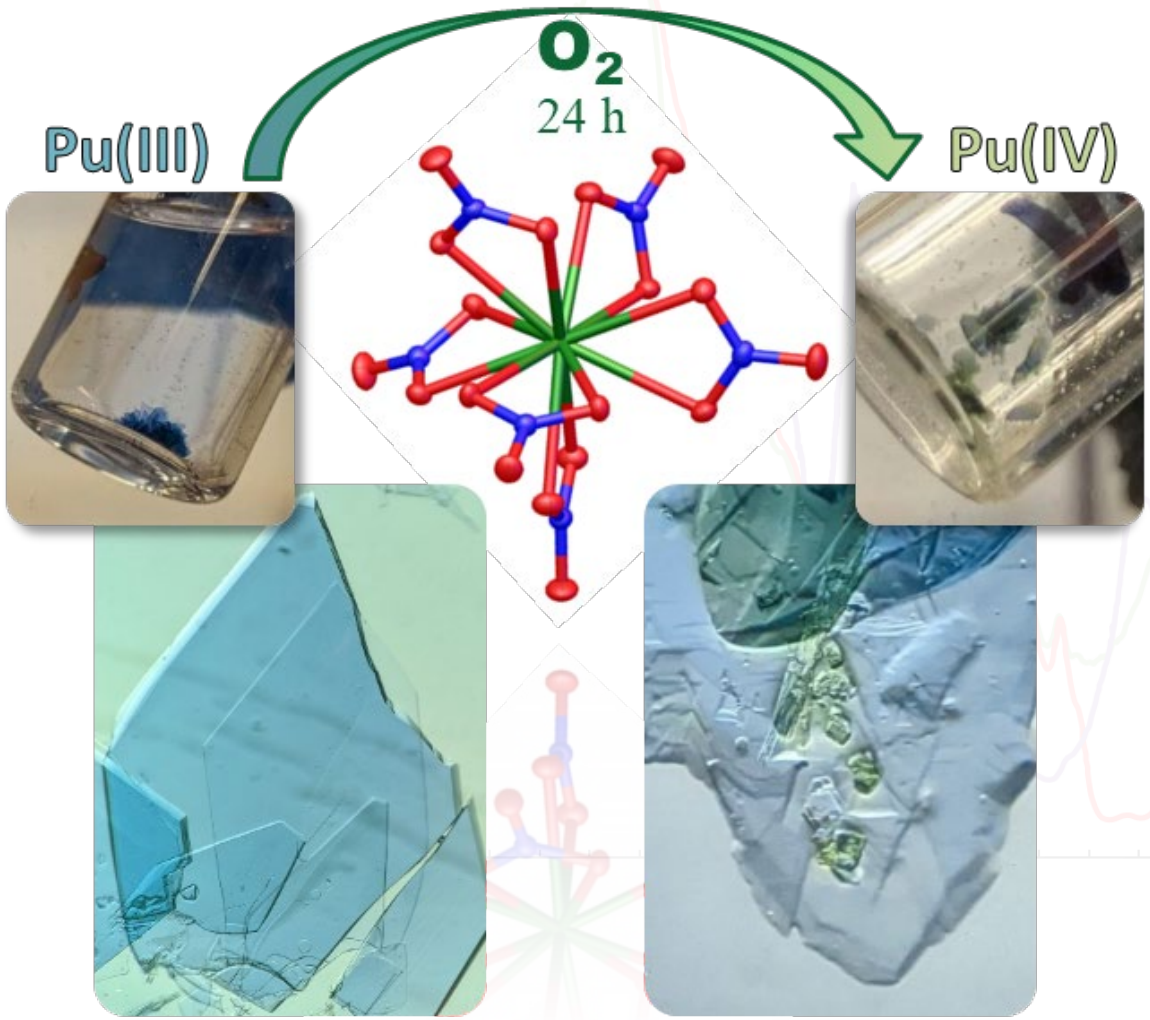
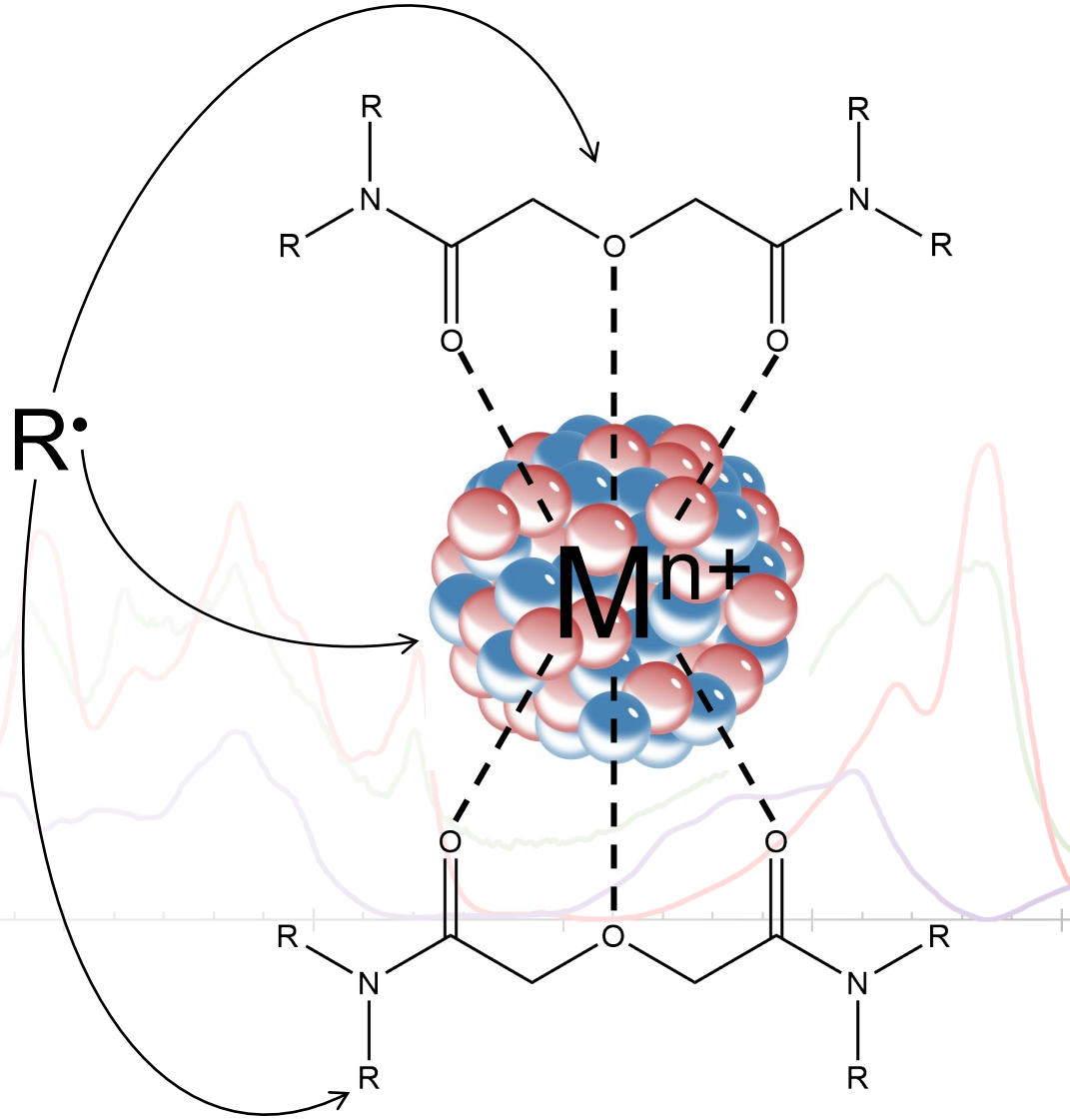
Questions?





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