INL/CON-24-80008-Revision-0

Impacts of Neodymium Complexation on Radiolysis of Tetramethyl Diglycolamide (TMDGA) in Aqueous Solutions

August 2024

Changing the World's Energy Future

Brian Matthew Rotermund

Idaho National Laboratory

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Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

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COLORADO SCHOOL OF MINES

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Albrecht Group

August 12, 2024

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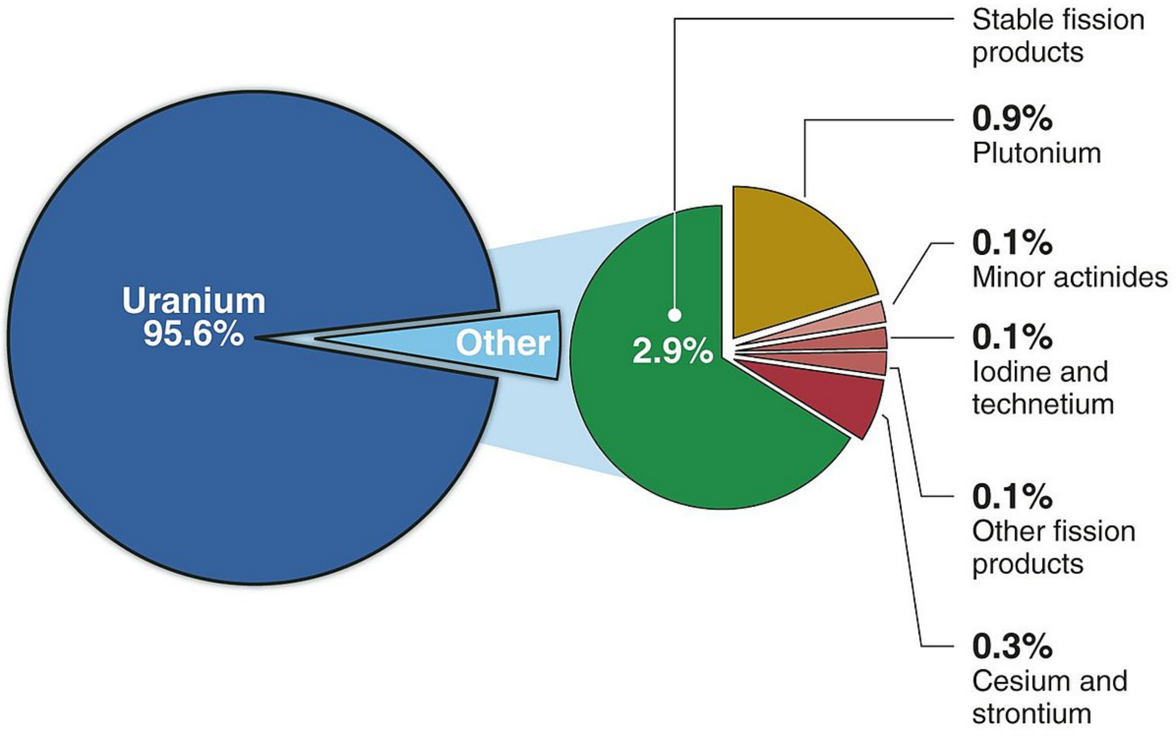
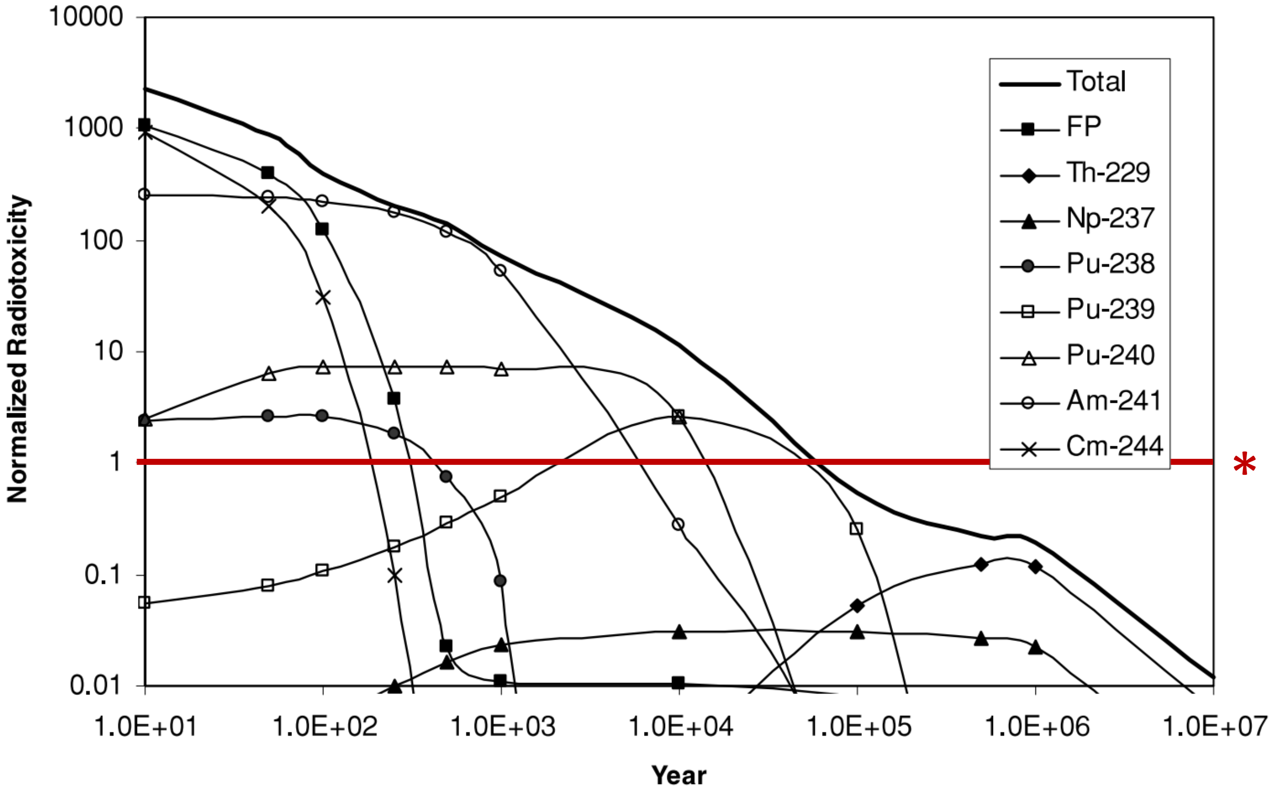
Challenges with Used Nuclear Fuel

Used Nuclear Fuel (UNF) Composition



Source: GAO analysis of DOE data.

Radiotoxicity of Long-lived Isotopes in UNF

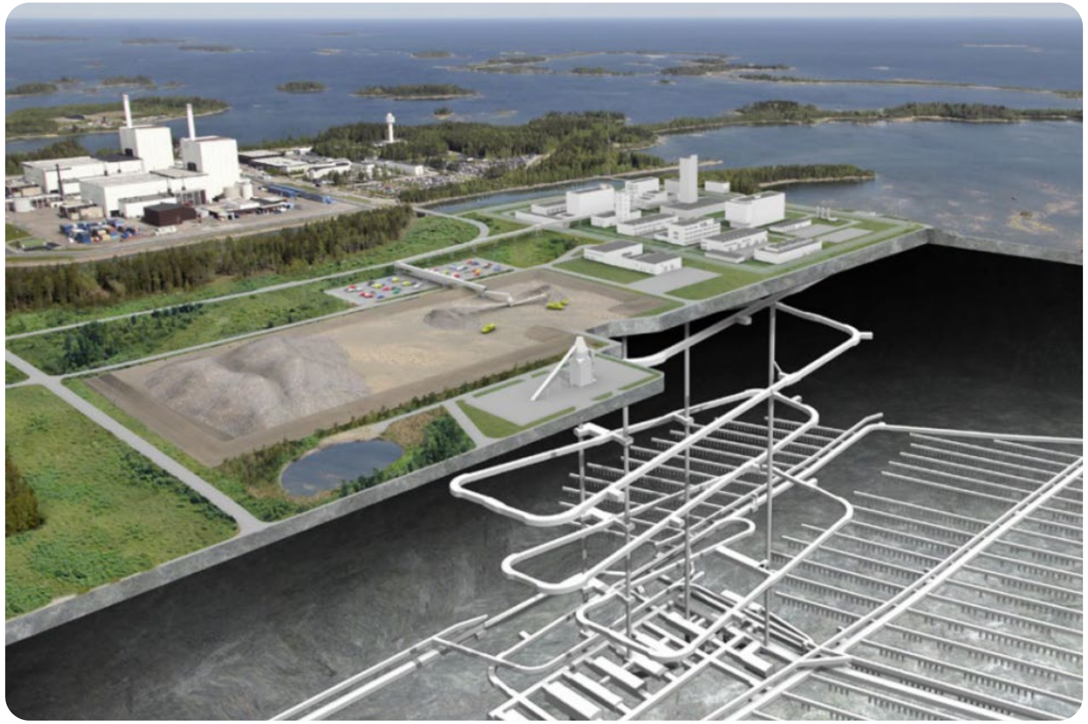


* Normalized to radiotoxicity of natural uranium ore

Aloise, G. *Nuclear Fuel Cycle Options.* 2011. DOE, GOA-12-70

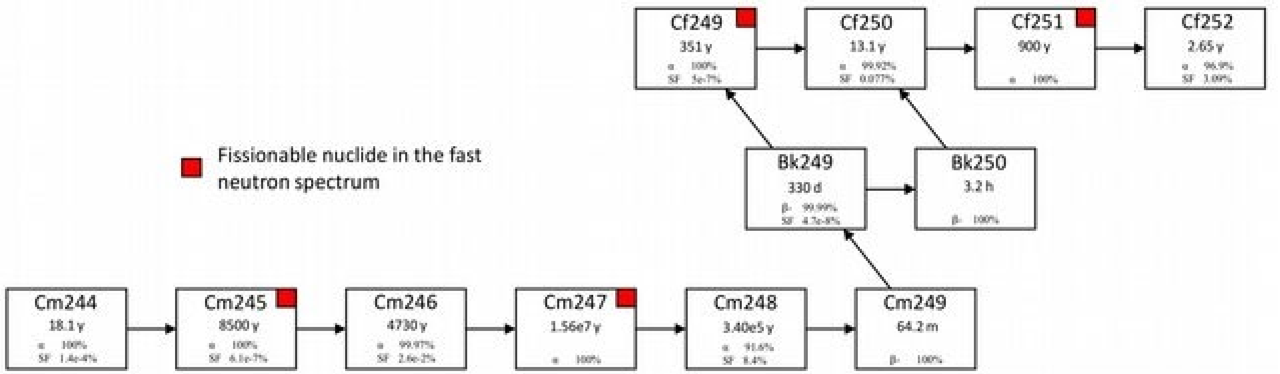
Taiwo, T.A., *et al. Nucl.Technol.* **2006**. 155, 34-54

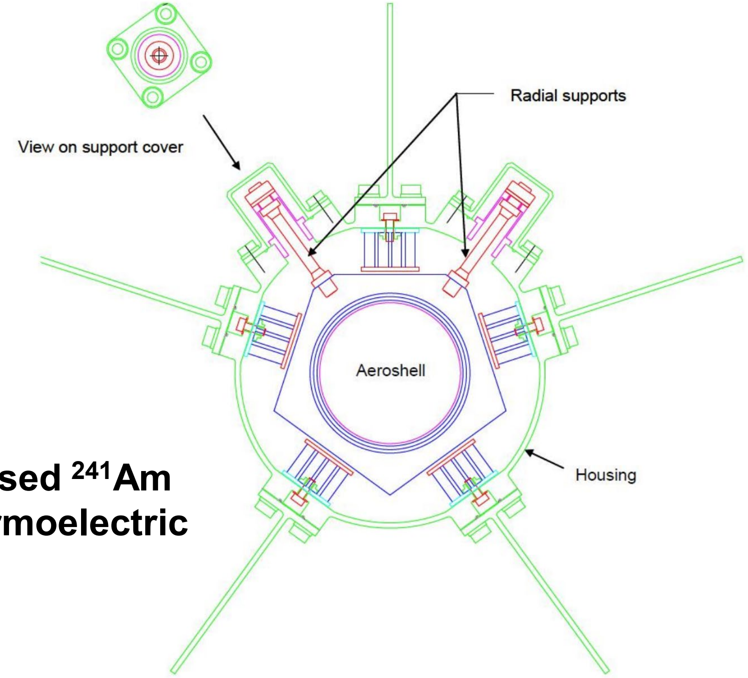
Minor Actinide Disposal and Applications



- **Future geological nuclear waste repository in Söderviken, Sweden planned to begin construction within the next few years**

- **Transmutation pathway for ^{244}Cm**

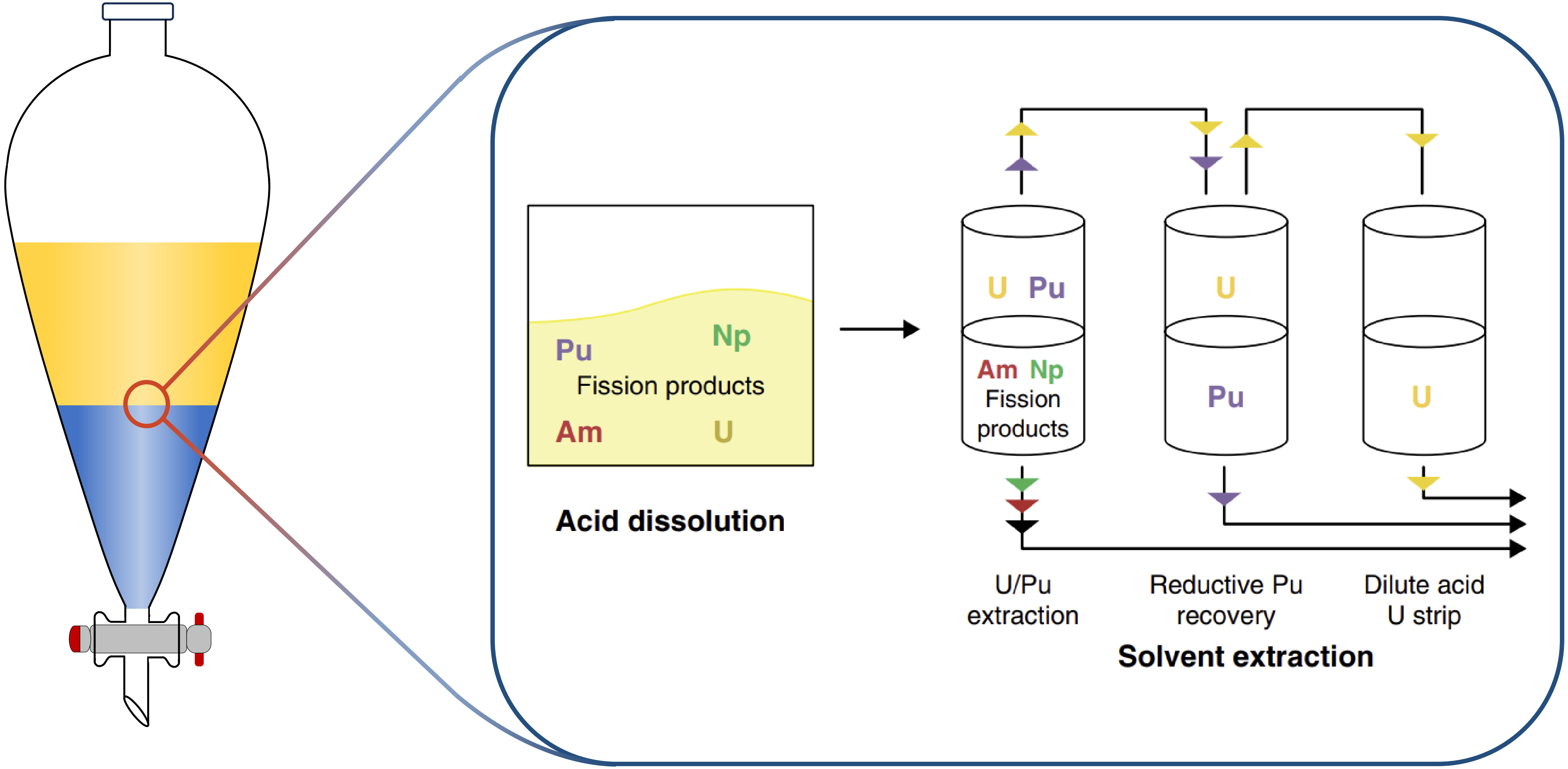




- **Cross-section for a proposed ^{241}Am sourced radioisotope thermoelectric generator**

Spent Fuel Repository Center, SKB. 2018
Ambrosi, R., et al., *International Nuclear Atlantic Conference*, Brazil, **2013**
Stanisz, P. AGH University of Science and Technology, **2017**

Hydroprocessing



Clark, A. E., *et al*. Experimental and Theoretical Approaches to Actinide Chemistry. **2018**. Wiley

Challenges with Separation and Reprocessing

Beta Emitters

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

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

Alpha Emitters

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

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

Gamma Ray

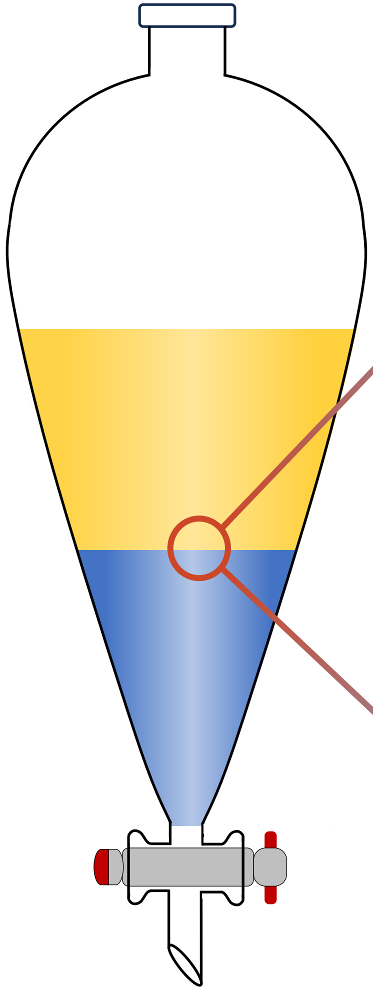
^{60}Co, ^{90}Sr, ^{249}Cf

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

Multi-component Radiation Field

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

Reprocessing Radiation Chemistry



Water Radiolysis

$H_2O \rightsquigarrow e^-, H^\bullet, {}^\bullet OH, H_2, H_2O_2, H_{aq}^+$

HNO_3 Radiolysis

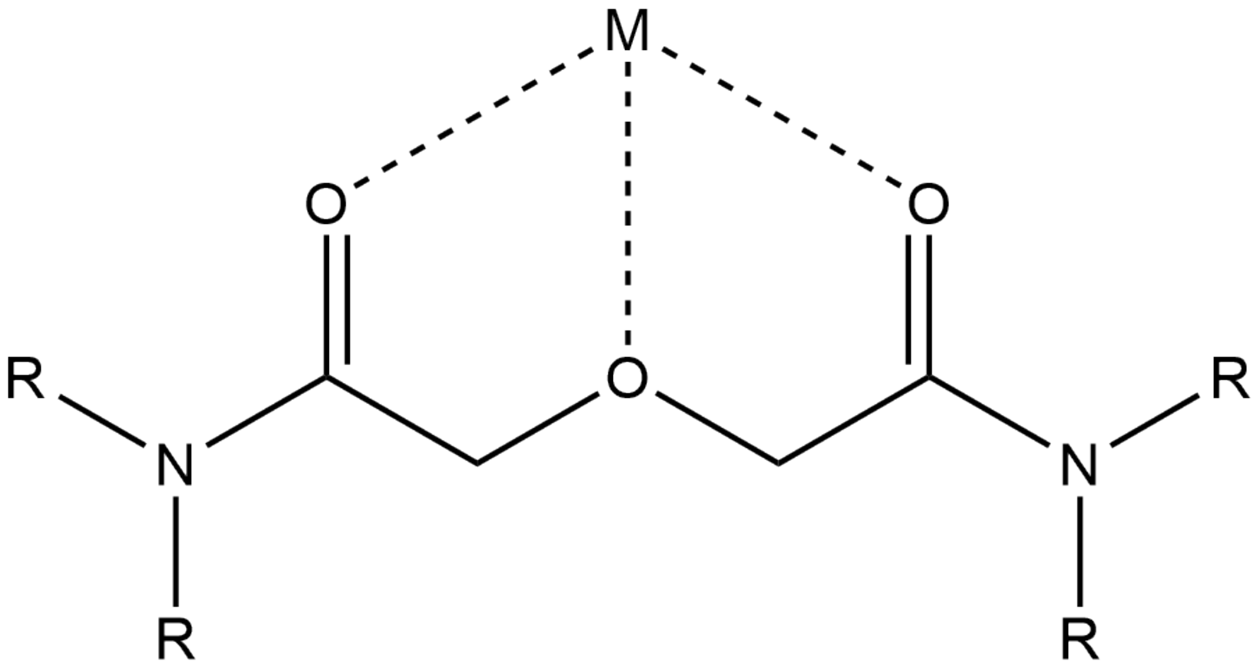
$NO_3^-/HNO_3 \rightsquigarrow e^-/H^\bullet, NO_3^\bullet, NO_2^-/HNO_2, O$

Alkane Radiolysis

$R\text{-}CH_3 \rightsquigarrow e^-, RH^{\bullet+}, RH^\bullet, {}^\bullet CH_3, H^\bullet, H_2$

Buxton *et al.*, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513
Katsumura, The Chemistry of Free Radicals: N-Centered Radicals, John Wiley & Sons, Chichester, **1998**.

Diglycolamides



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

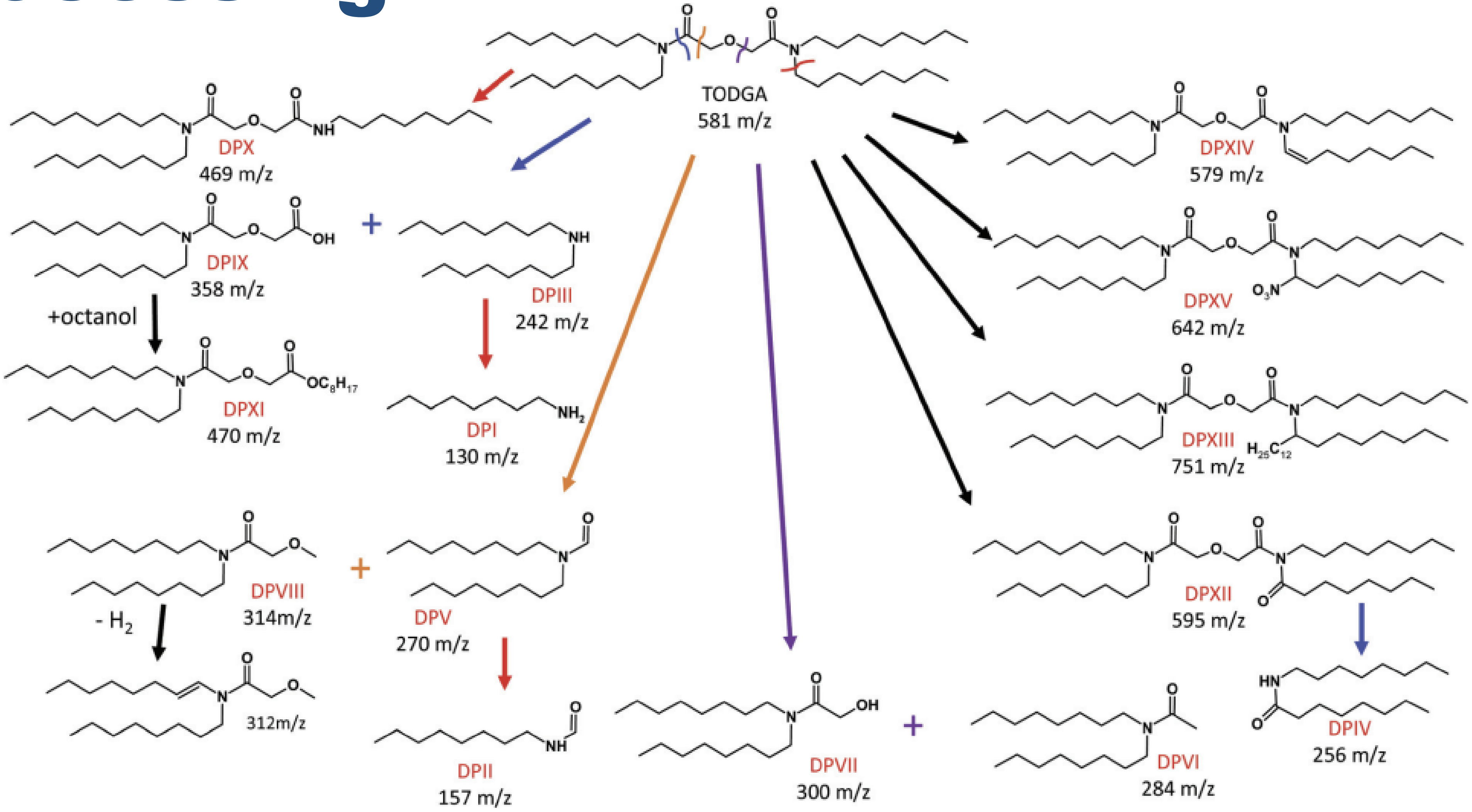
- Still fairly understudied
- Organic phase DGAs can be susceptible to third phase formation

Properties and Advantages:

- Water Soluble
- Most simplified DGA structure

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

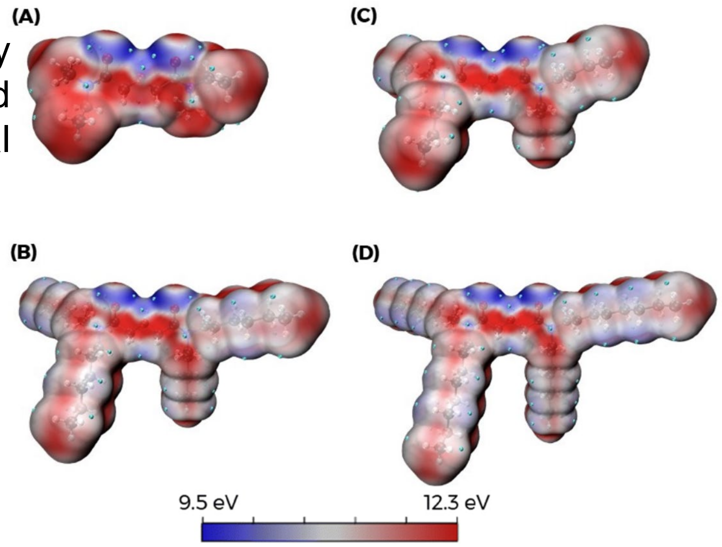
Challenges with Separation and Reprocessing

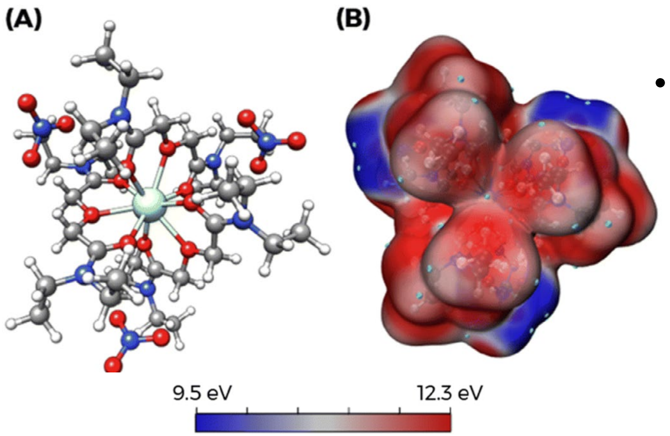


A. Kimberlin, *et al.*, *Phys. Chem. Chem. Phys.* **2022**, *24*, 9213

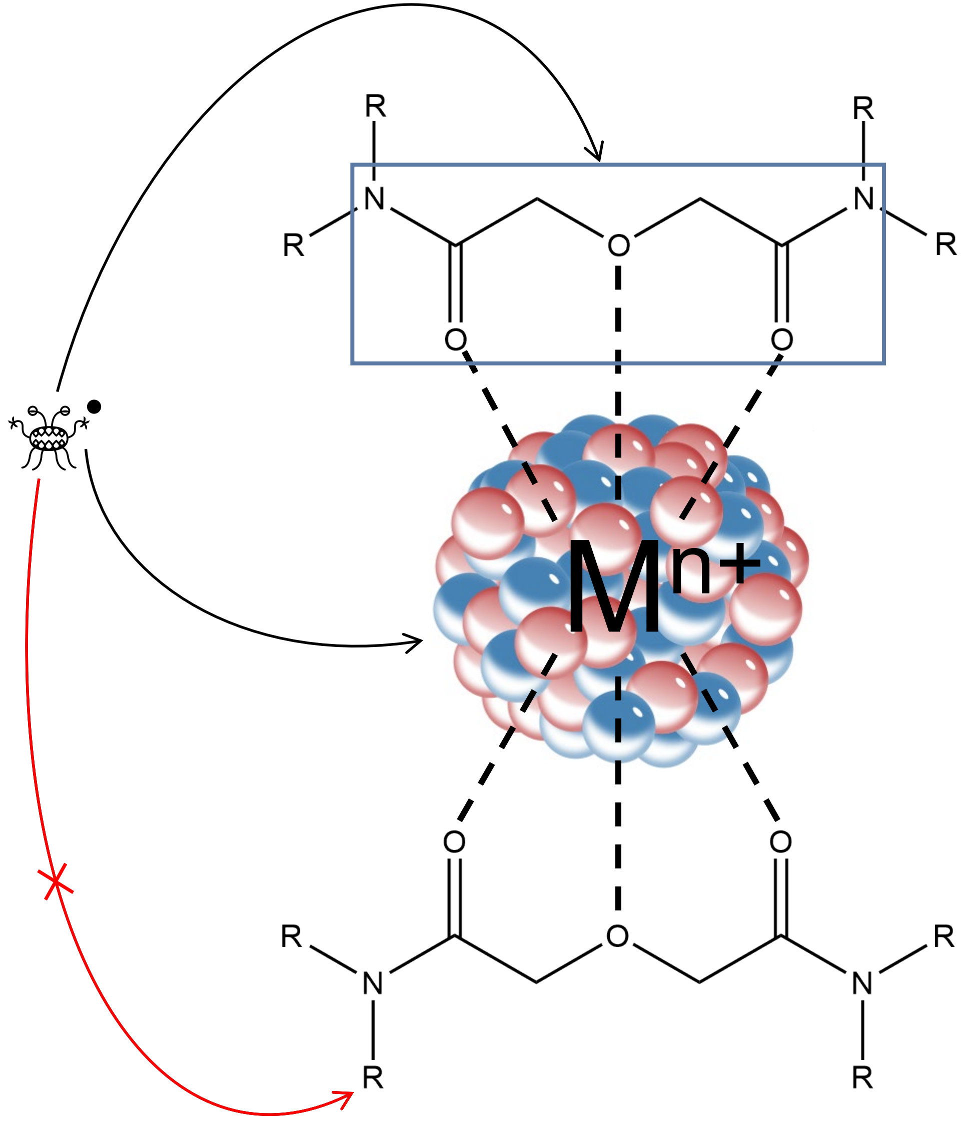
Radical Interactions

- Average Local Ionization Energy (ALIE) calculations on noncomplexed diglycolamides with varying terminal alkyl group lengths
  - **(A)** R = Ethyl
  - **(B)** R = Butyl
  - **(C)** R = Hexyl
  - **(D)** R = Octyl

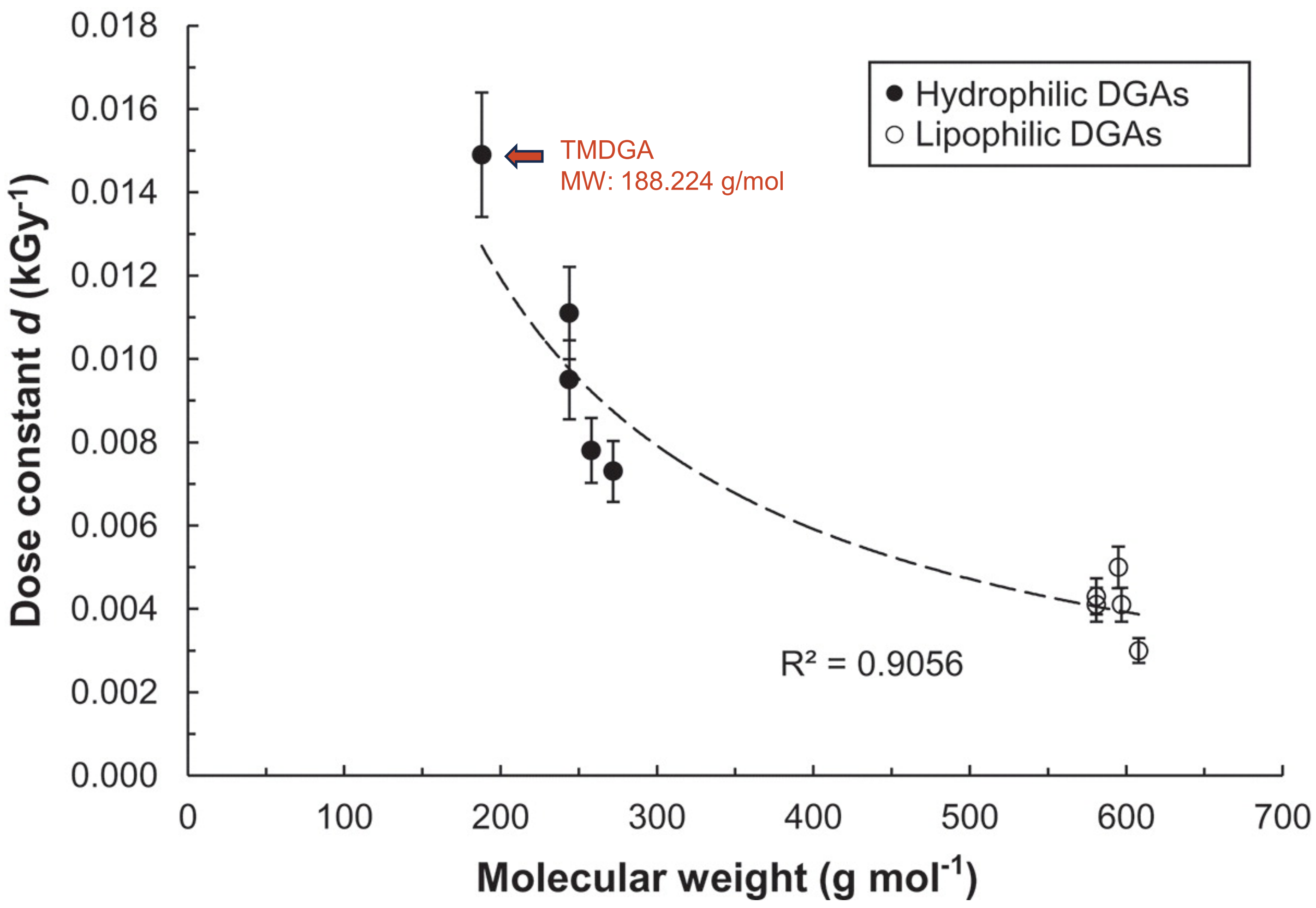




- ALIE calculations on tetraethyl diglycolamide (TEDGA) with neodymium metal
  - **(A)** $[Nd(TEDGA)_3](NO_3)_3$ without ALIE surfaces
  - **(B)** $[Nd(TEDGA)_3](NO_3)_3$ with ALIE surfaces



TMDGA Kinetics



Rate Coefficients Comparison

Common Reactive Radicals	Tetramethyl Diglycolamide TMDGA ($M^{-1}s^{-1}$)
$^{\bullet}OH$	$3.06 \pm 0.09 \times 10^9$
$NO_3^{\bullet}$	$3.05 \pm 0.12 \times 10^8$
$H^{\bullet}$	$1.22 \pm 0.03 \times 10^8$
e_{aq}^-	$4.51 \pm 0.39 \times 10^{8*}$

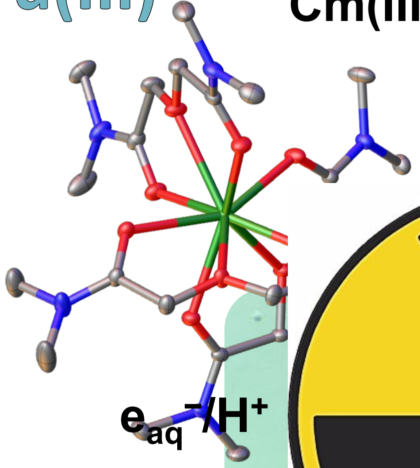
*Preliminary data yet to be published

Ligand	Rate coefficient (k, M^{-1} s^{-1})			
	$^{\bullet}OH$ (10^9)	$^{\bullet}NO_3$ (10^8)	$H^{\bullet}$ (10^8)	e_{aq}^- (10^8)
TEDGA	2.91 ± 0.10	11.19 ± 0.46	1.60 ± 0.09	2.24 ± 0.10

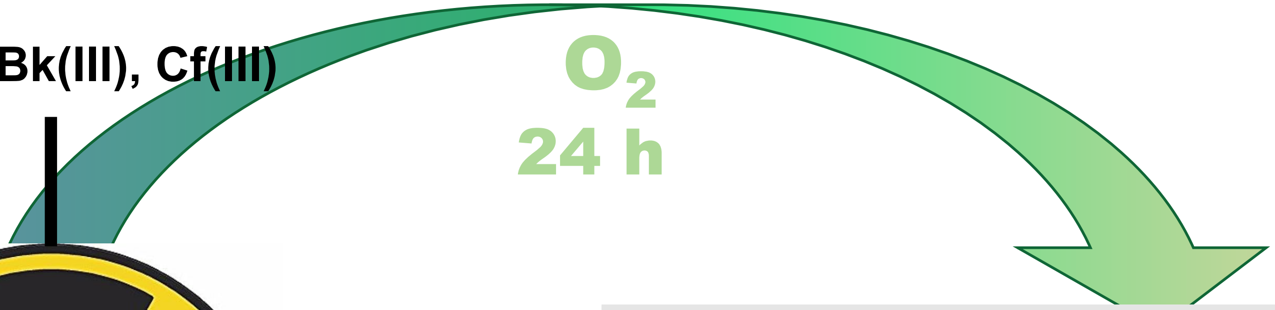
A. Wilden, *et al.*, *Solvent Extr. Ion Exch.* **2018**, *36*, 347-359
G.P. Horne, *et al.*, *Dalton Trans.* **2019**, *48* 45, 17005-17013

Coordination Across Oxidation States

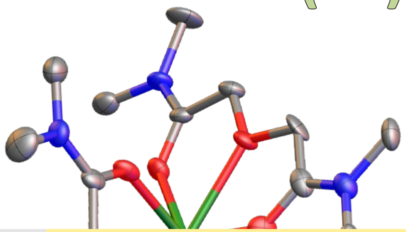
Pu(III)

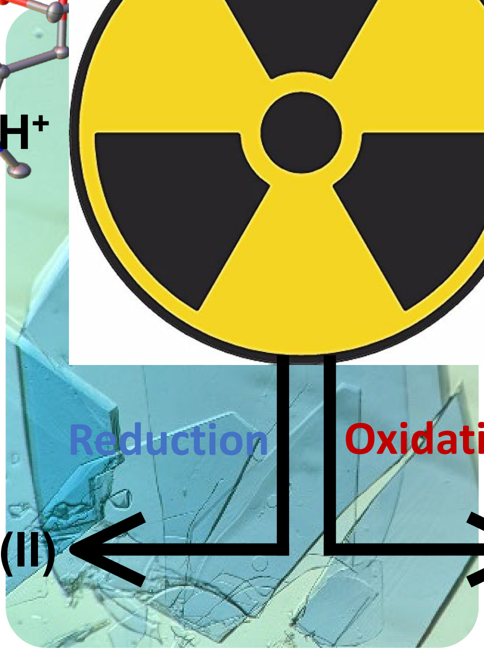


Cm(III), Bk(III), Cf(III)



Pu(IV)





e_{aq}^{-}/H^{+}

$^{\bullet}OH/NO_3^{\bullet}$

Exposed to a

xidation of P

Reduction

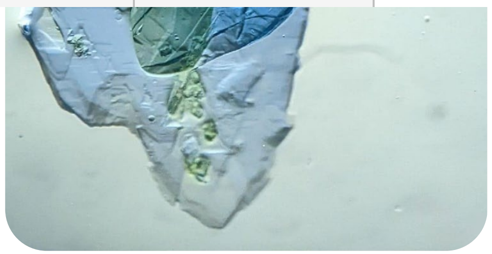
Oxidation

Cm(II), Bk(II), Cf(II)

Cm(IV), Bk(IV), Cf(IV)

Recrystallization to plutonium (IV) species

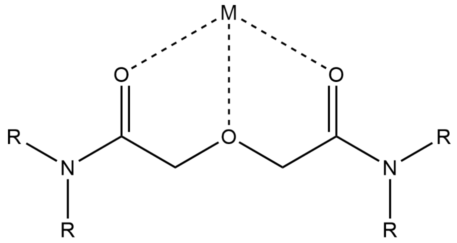
Element	Ion Charge	Coordination Number	Shannon-Prewitt Effective Ionic Radius
Americium	+2	7	121 pm
		8	126 pm
		9	131 pm
	+3	6	97.5 pm
		8	109 pm
	+4	6	85 pm
		8	95 pm

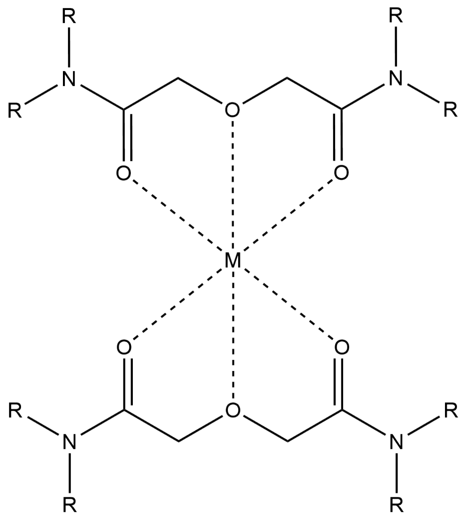


Hound, B. M.; Inorg. Chem. 2022, 61 (32), 12905-12912 / [illegible] et al., Inorg. Chem. 2023, 62 [illegible]
R. D. Shannon, *Acta Crystallographica Section A*, **1976**, 32 (5), 751-767

Metal:Ligand Speciation

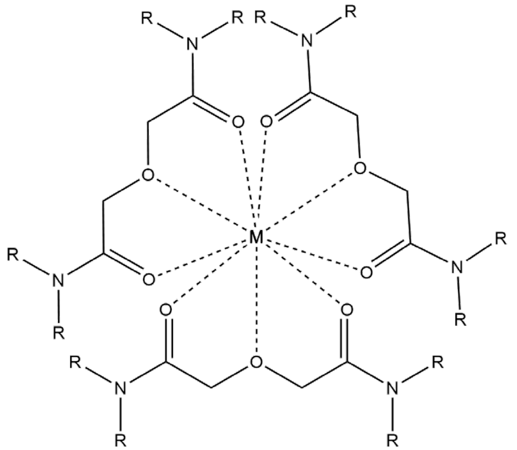
1:1 Complex

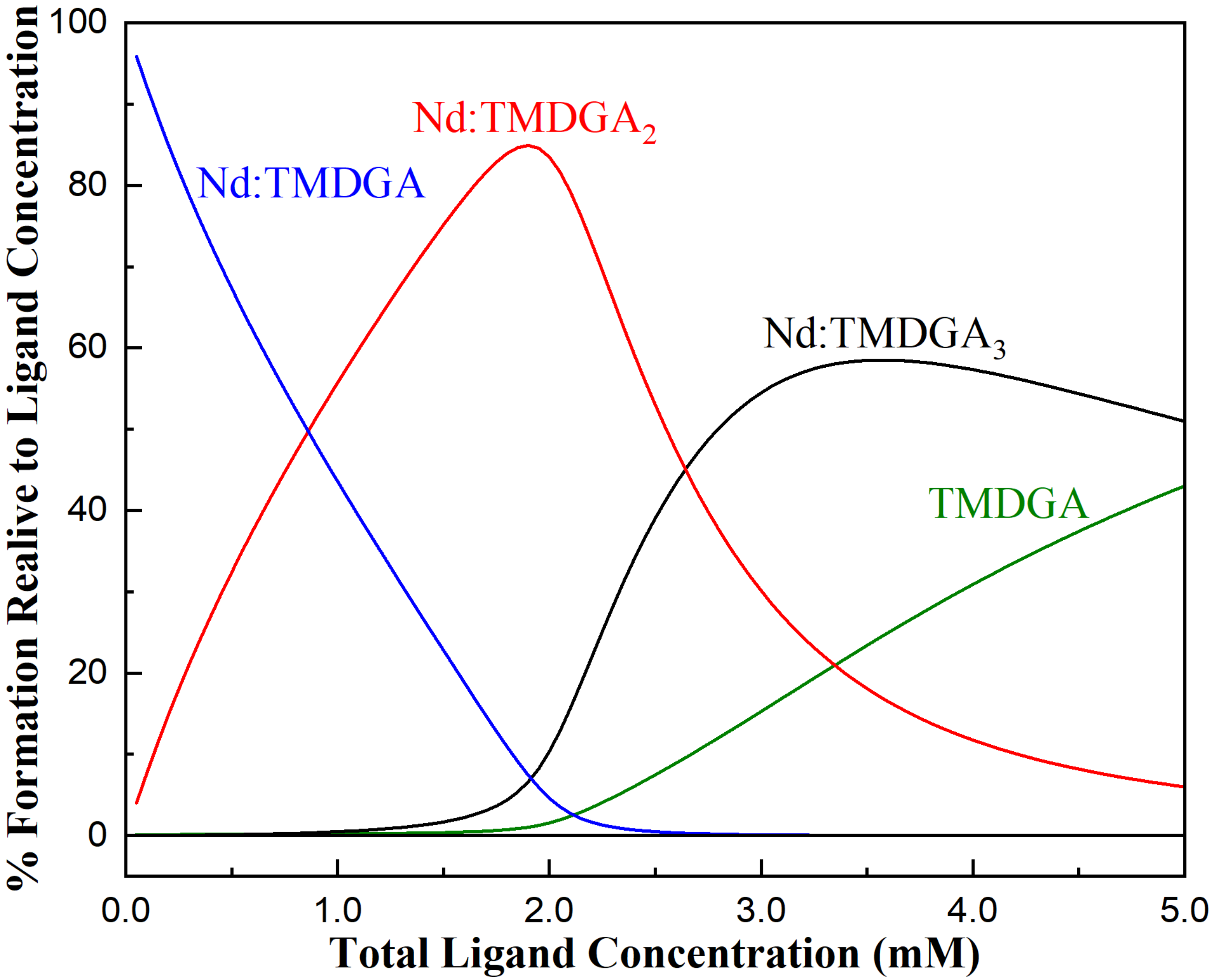




1:2 Complex

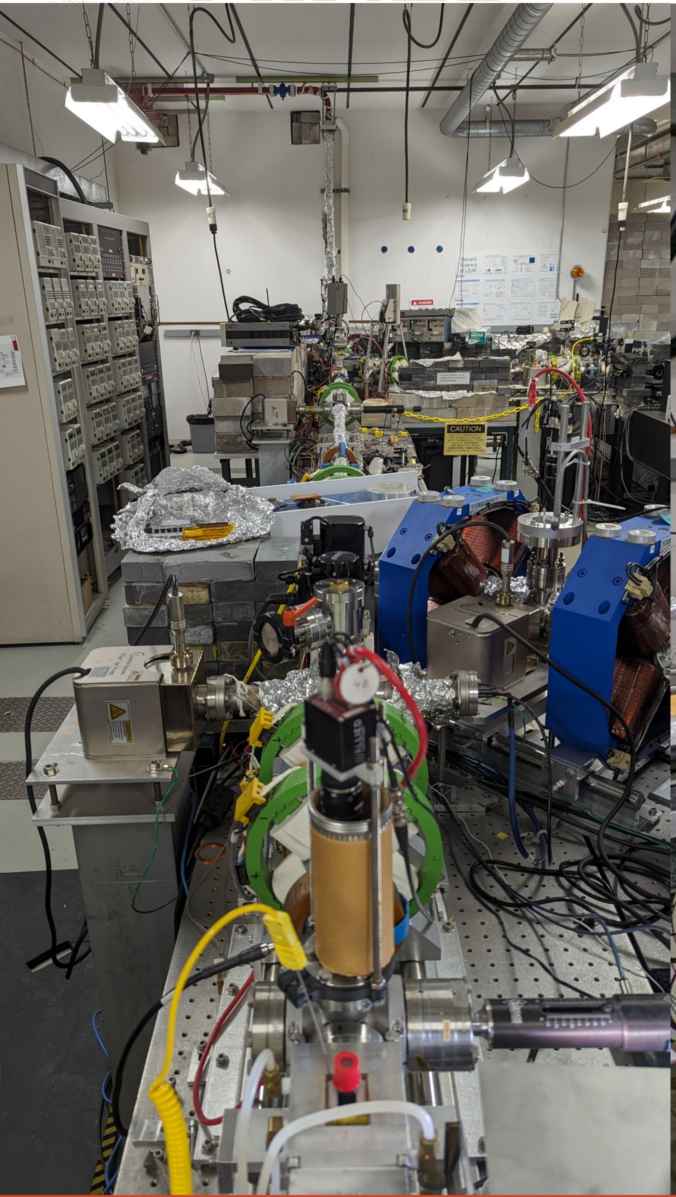
1:3 Complex

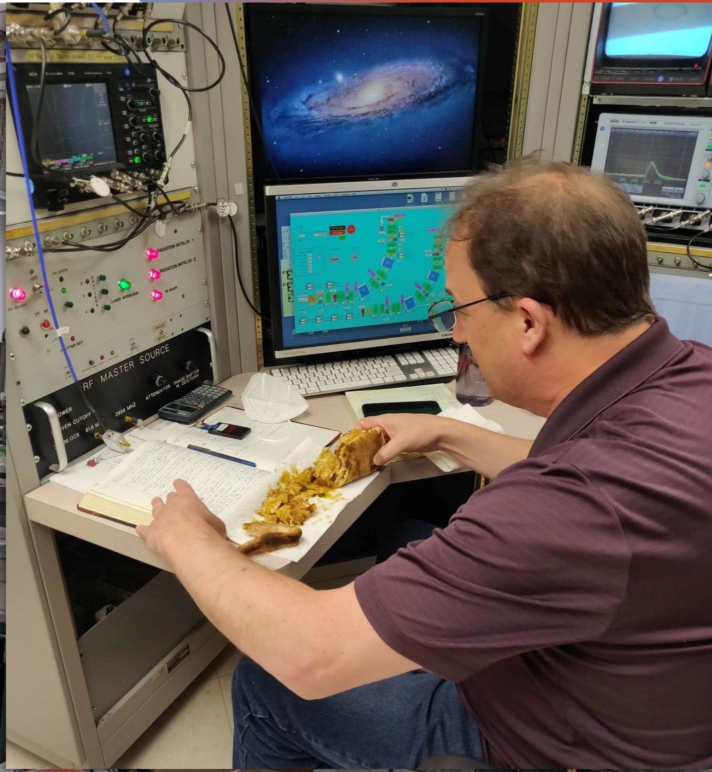




Rotermund, B. M.; et al., **2024**, ***In Preparation***

LEAF Experiments



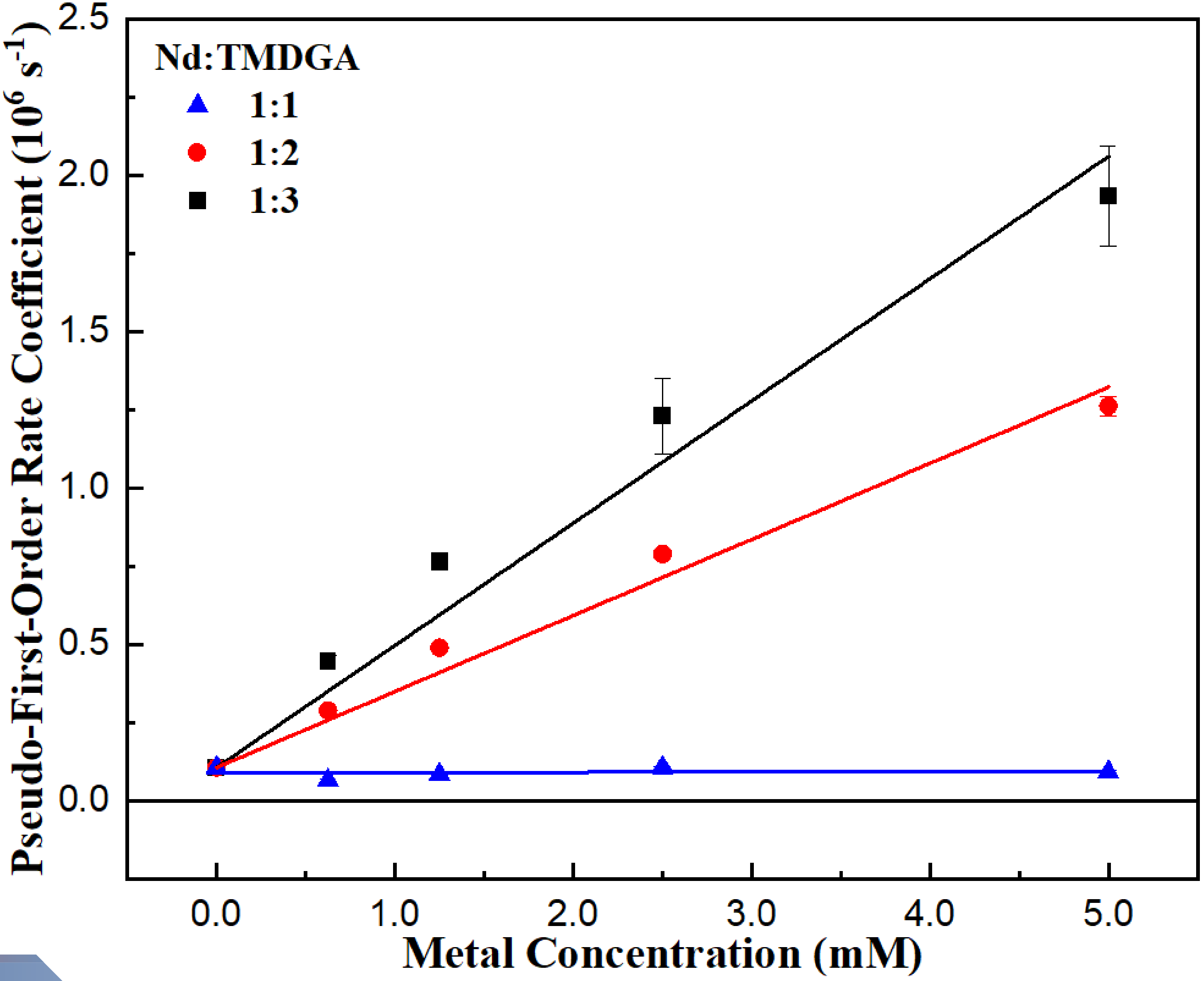


Brookhaven National Laboratory

Wishart, J. F.; et al., *Rev. Sci. Instrum.* **2004**, 75 (11), 4359-4366

Nitrate Radical Anion

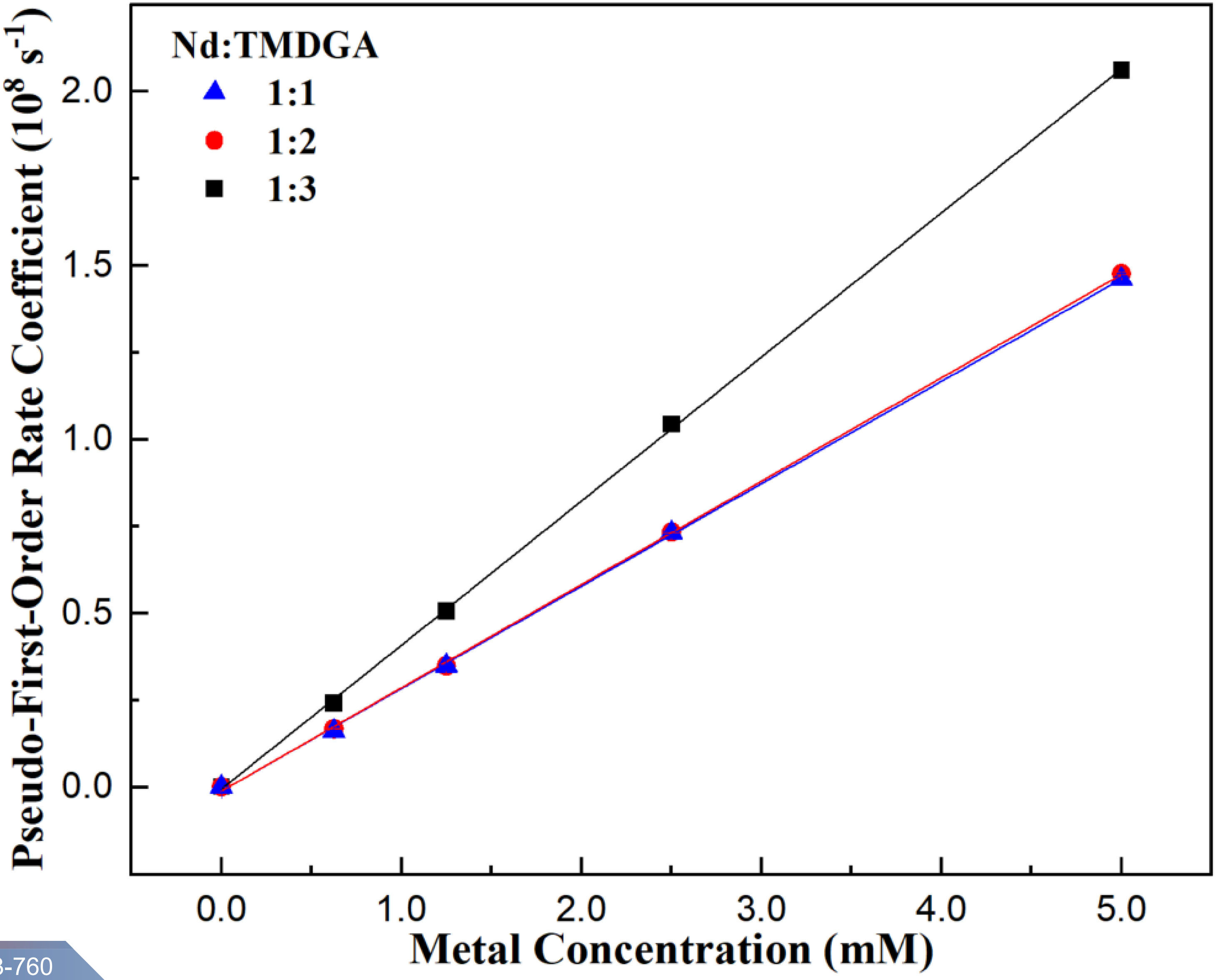
Speciation	Rate Coefficient ($M^{-1}s^{-1}$)
Free Ligand	$3.05 \pm 0.12 \times 10^8$
1:1	$1.24 \pm 0.49 \times 10^6$
1:2	$2.43 \pm 0.11 \times 10^8$
1:3	$3.90 \pm 0.24 \times 10^8$



G.P. Horne, *et al.*, *Dalton Trans.* **2019**, *48* 45, 17005-17013

Solvated Electron

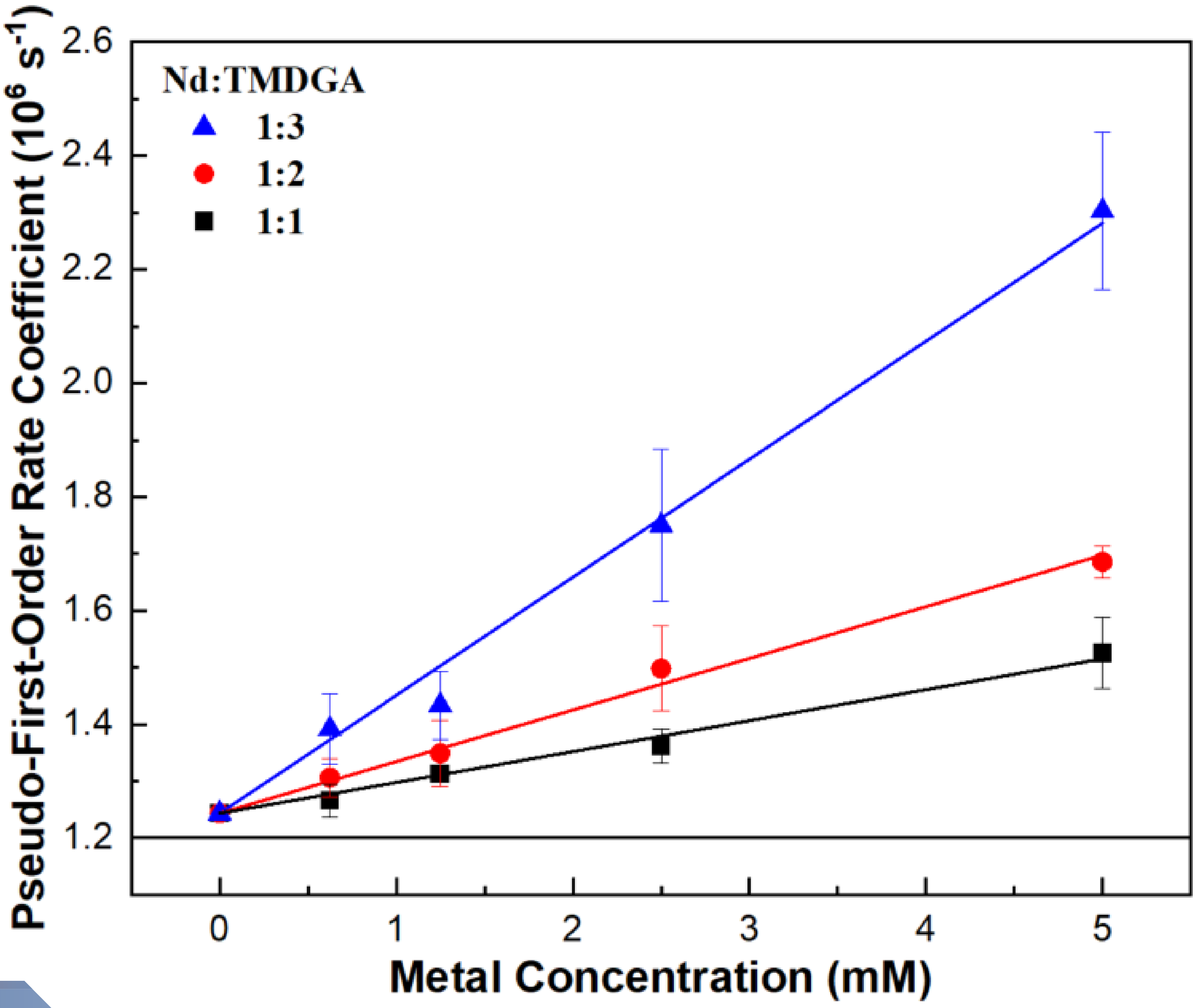
Speciation	Rate Coefficient ($M^{-1}s^{-1}$)
Free Nd^{3+}	2.3×10^6
Free Ligand	$4.51 \pm 0.39 \times 10^8$
1:1	$2.94 \pm 0.03 \times 10^{10}$
1:2	$2.97 \pm 0.03 \times 10^{10}$
1:3	$4.14 \pm 0.03 \times 10^{10}$



Gordon S., Pulsed Radiolysis of the Lanthanides and Actinides. **1977**. pp. 753-760
G.P. Horne, *et al*., *Dalton Trans.* **2019**, *48* 45, 17005-17013

Hydrogen Radical

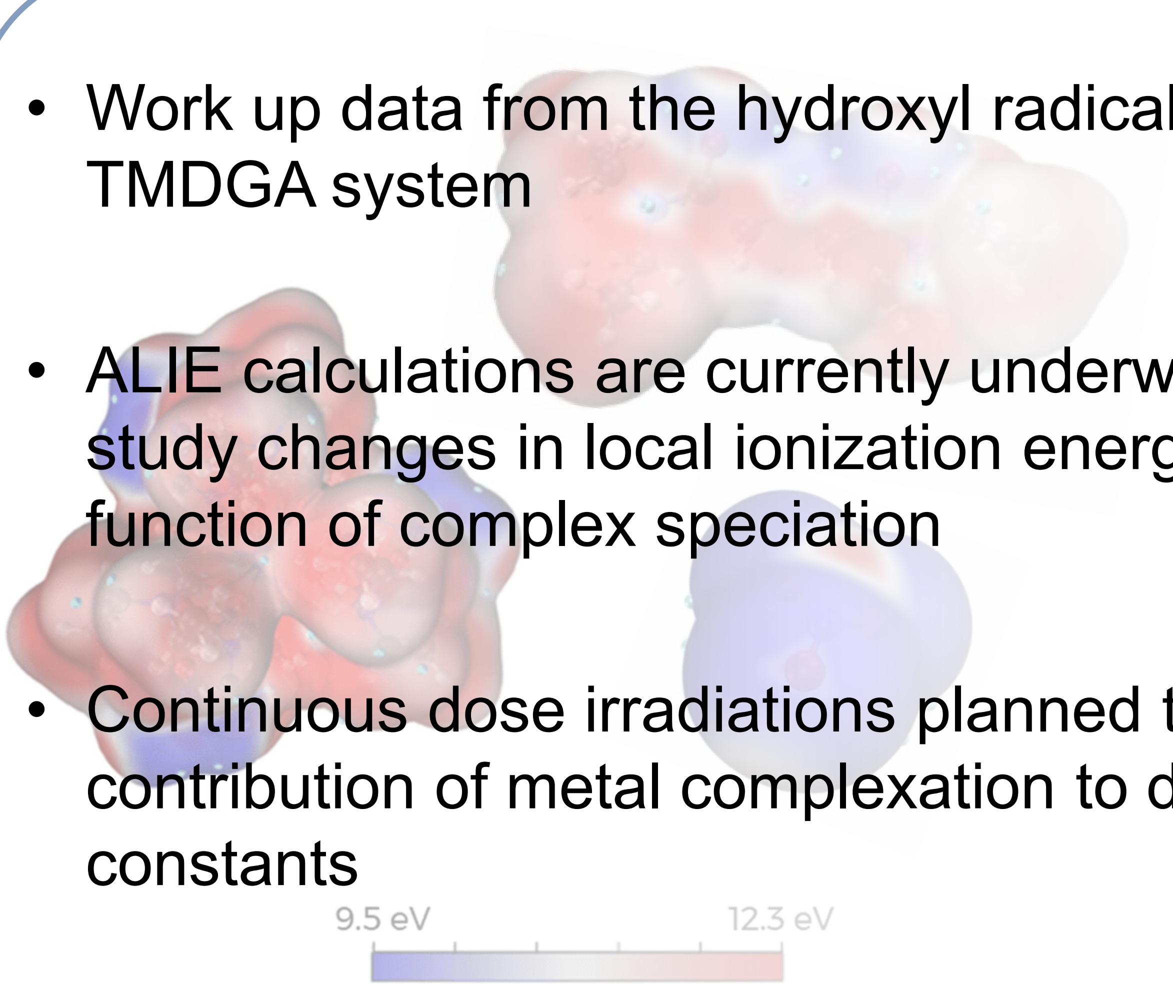
Speciation	Rate Coefficient ($M^{-1}s^{-1}$)
Free Ligand	$1.22 \pm 0.03 \times 10^8$
Free Metal	$1.99 \pm 0.18 \times 10^7$
1:1	$5.44 \pm 0.27 \times 10^7$
1:2	$9.07 \pm 0.27 \times 10^7$
1:3	$2.07 \pm 0.66 \times 10^8$

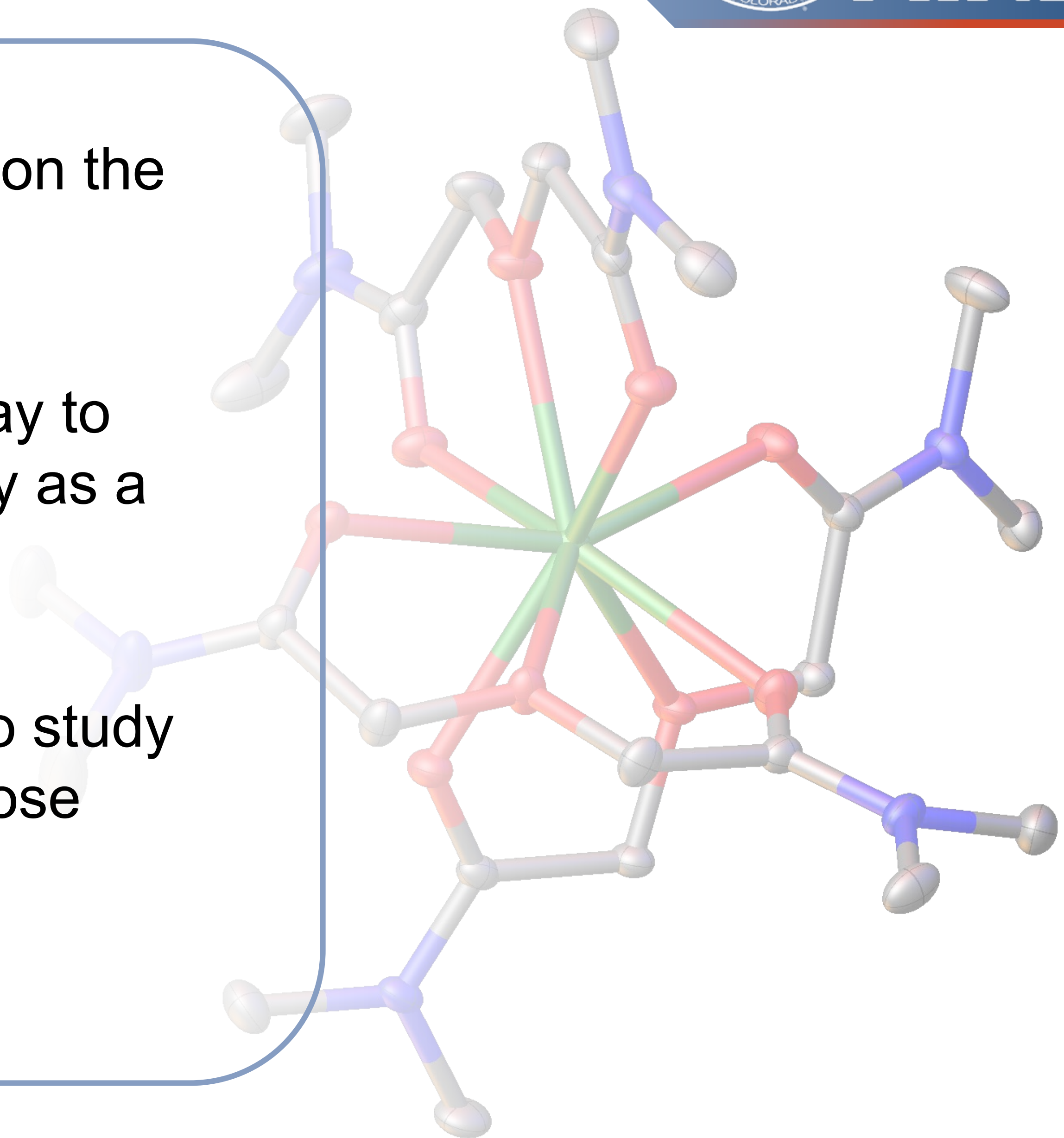


G.P. Horne, *et al.*, *Dalton Trans.* **2019**, *48* 45, 17005-17013
G.P. Horne, *et al.*, *Inorg. Chem.* **2022**, *61* 28, 10822-10832

Future Work

- Work up data from the hydroxyl radical on the TMDGA system
- ALIE calculations are currently underway to study changes in local ionization energy as a function of complex speciation
- Continuous dose irradiations planned to study contribution of metal complexation to dose constants





Horne, G. P.; et al., *Phys, Chem. Chem. Phys.* **2023**, 25, 16404-1613
B.M. Rotermund, *et al., Inorg. Chem.* **2023**, *62*, 12905-12912

Conclusions

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- Complexation with metal ions showed significant differences in the rates of the solvated electron and the nitrate radical anion relative to the free ligand

- The number of ligands complexed to the metal in some instances can have a significant effect on the rates of reaction

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

Acknowledgements

Thank you to...

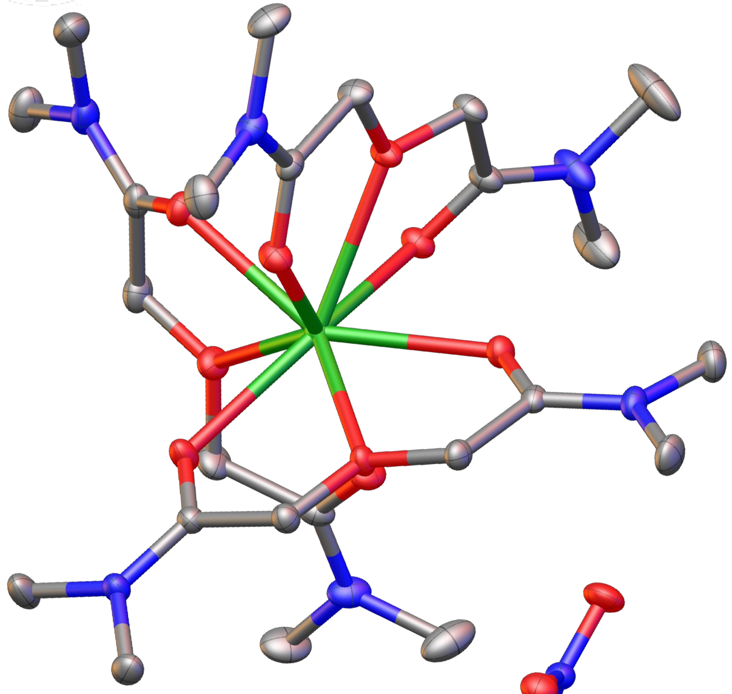
Dr. Gregory P. Horne

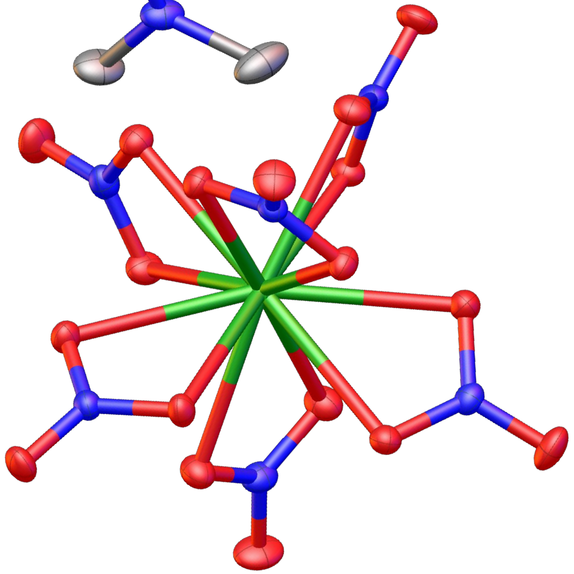
Prof. Thomas Albrecht

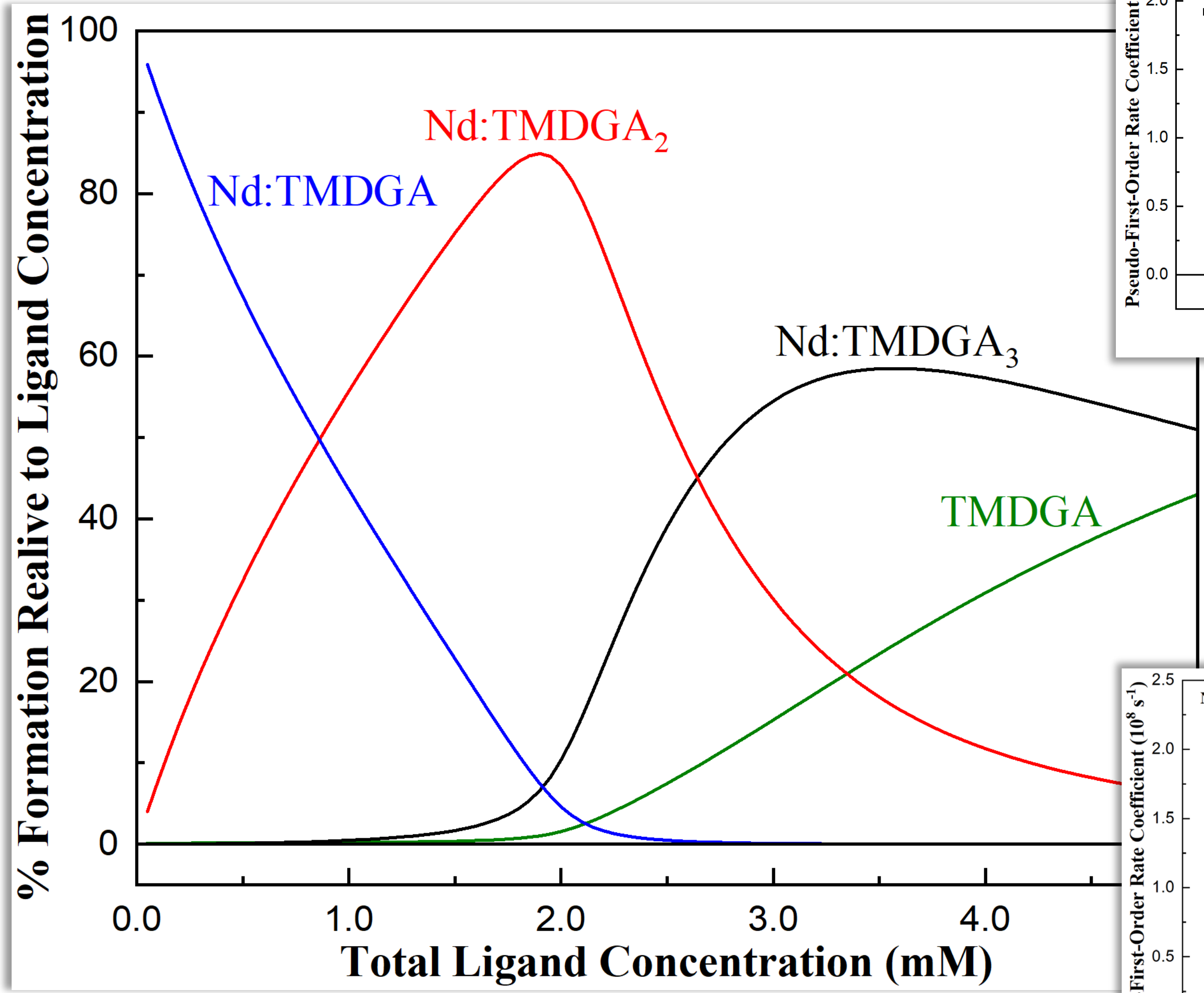
My Colleagues in the Thomas Albrecht Group and the Idaho National Lab

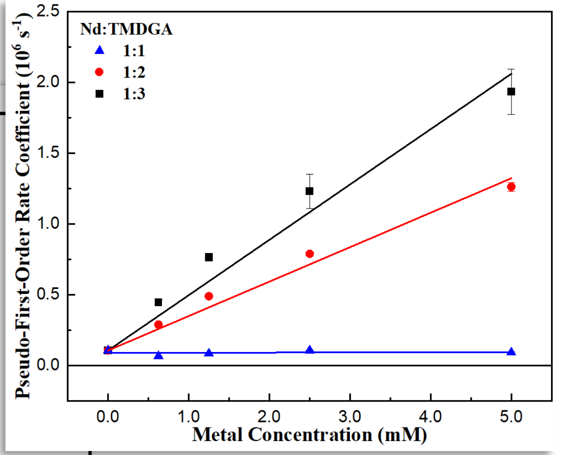
This work was supported by U.S Department of Energy (DOE), Basic Energy Sciences, Solar Photochemistry Program award number DE-SC0021372

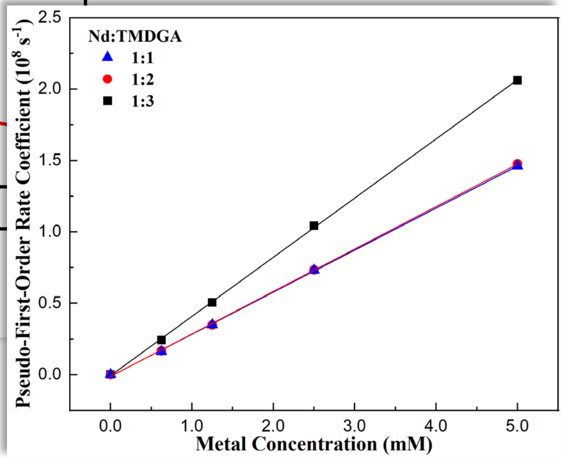
Questions?






% Formation Realive to Ligand Concentration
Total Ligand Concentration (mM)
Nd:TMDGA
Nd:TMDGA$_2$
Nd:TMDGA$_3$
TMDGA
0.0
1.0
2.0
3.0
4.0
0
20
40
60
80
100


Pseudo-First-Order Rate Coefficient (10^6 s^{-1})
Metal Concentration (mM)
Nd:TMDGA
1:1
1:2
1:3


Pseudo-First-Order Rate Coefficient (10^8 s^{-1})
Metal Concentration (mM)
Nd:TMDGA
1:1
1:2
1:3