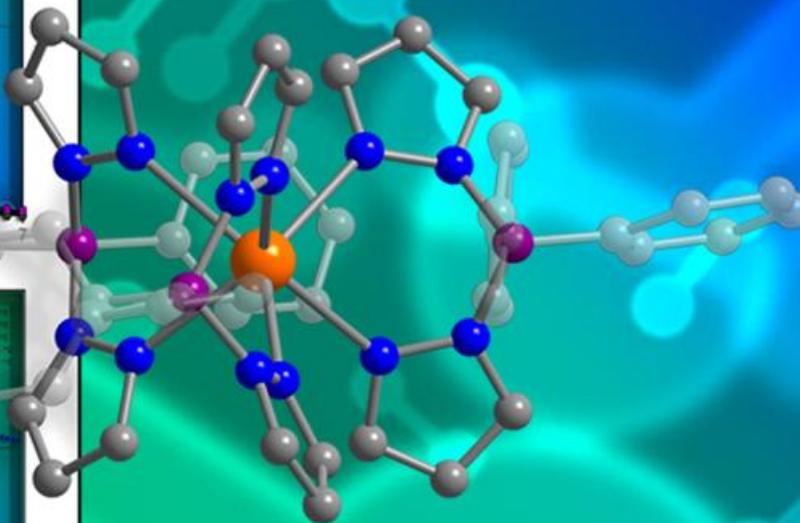
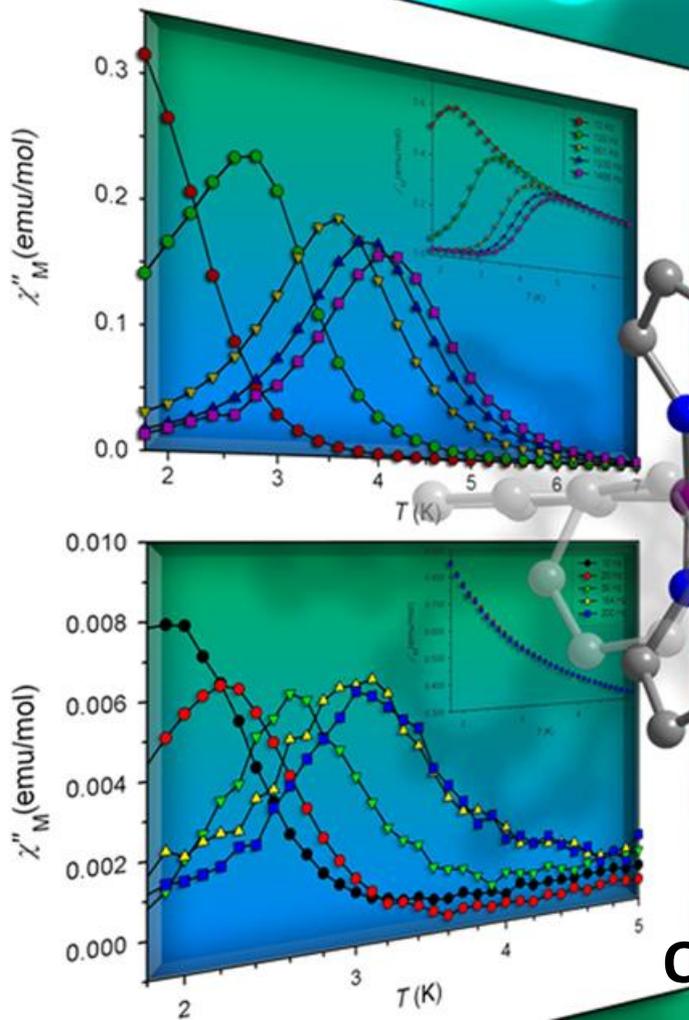


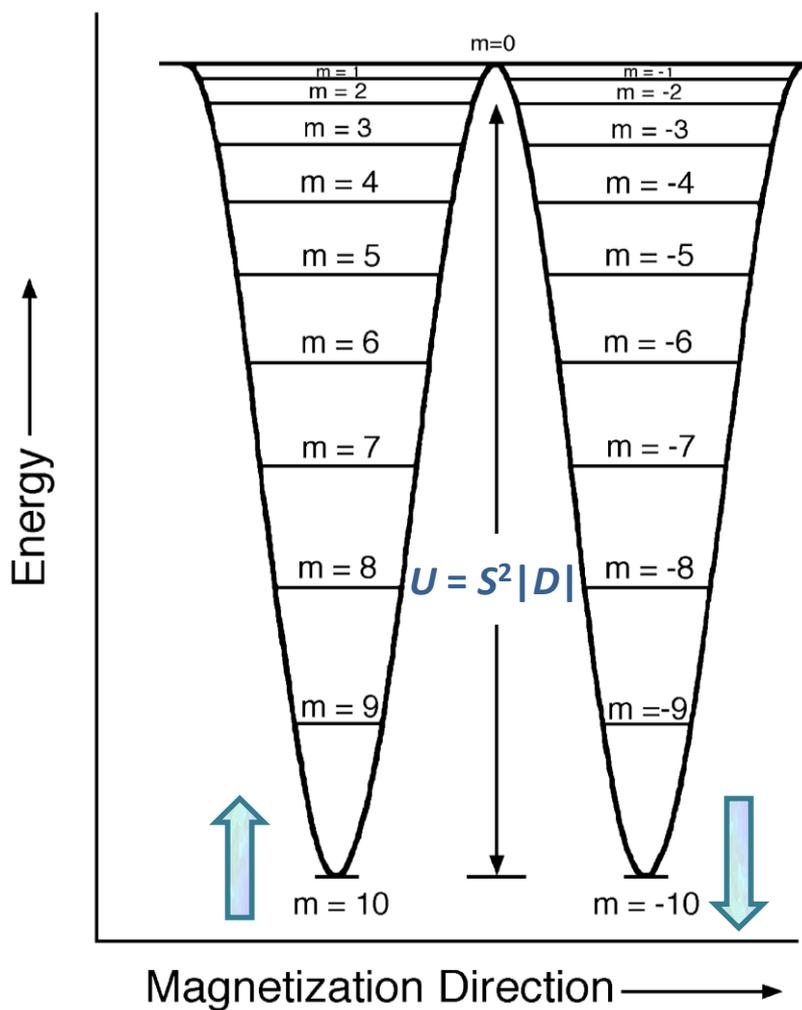
Uranium-Based Single-Molecule Magnetism



Jeffrey Rinehart
December 4th, 2009

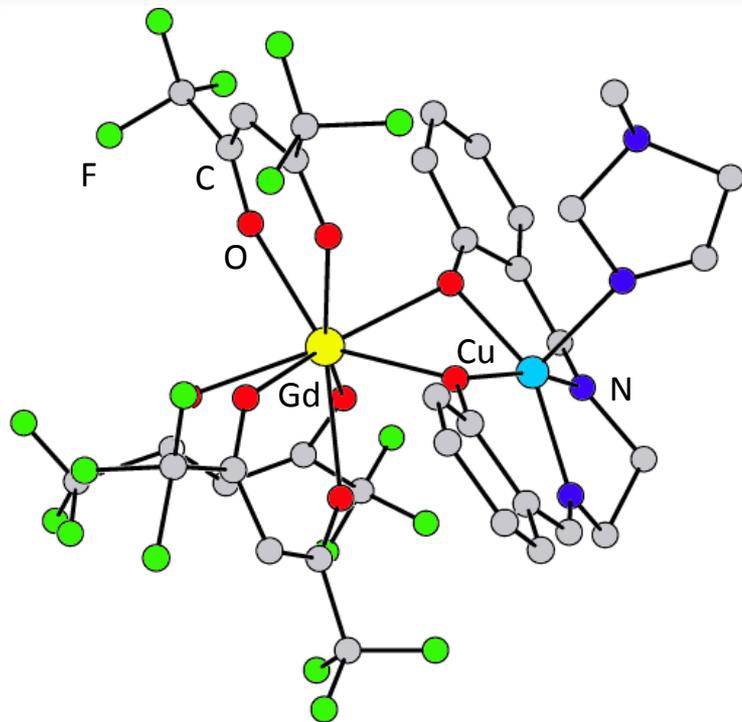
Quantum Properties of Coherent Spins II

Single-Molecule Magnets: Prospects in Uranium Chemistry



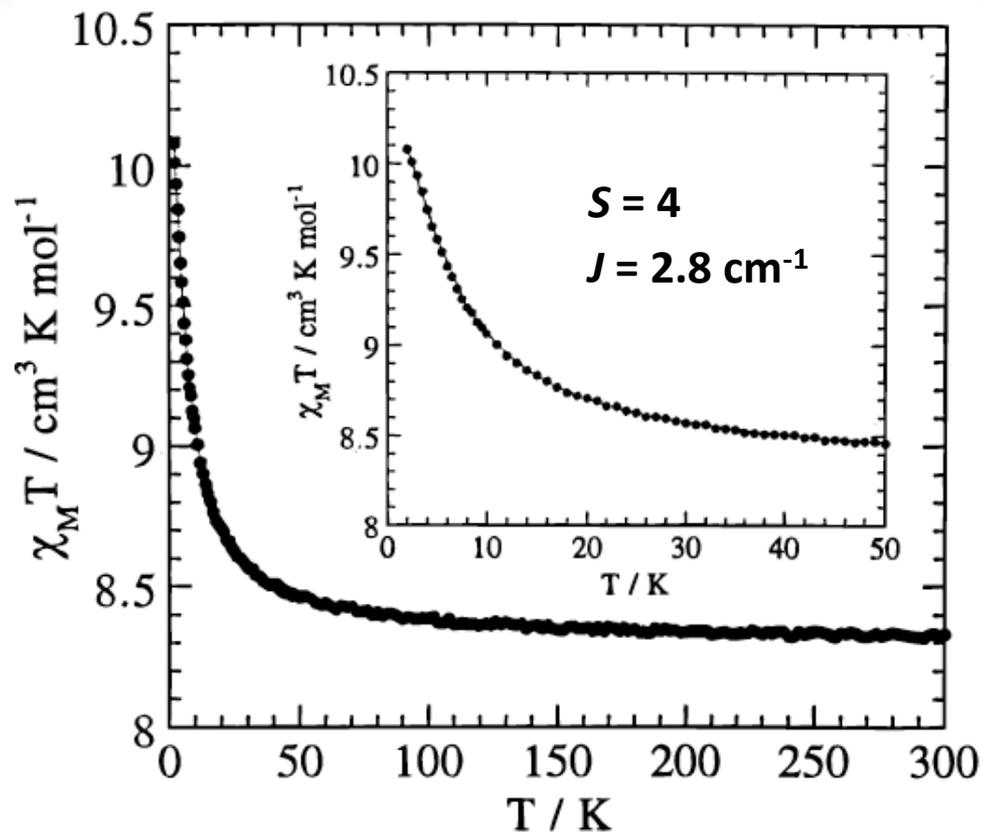
- Defined by two stable magnetic orientations of the ground state with an energy barrier to spin inversion
- Barrier arises from two factors:
 - ground-state spin
 - negative axial anisotropy
- Uranium systems:
 - (1) strong spin-orbit coupling can increase axial anisotropy
 - (2) $5f$ orbital extension allows for cooperative intramolecular interactions

Magnetic Coupling in Lanthanide Complexes



$\text{Gd}(\text{hfac})_3\text{Cu}(\text{salen})(\text{Melm})$

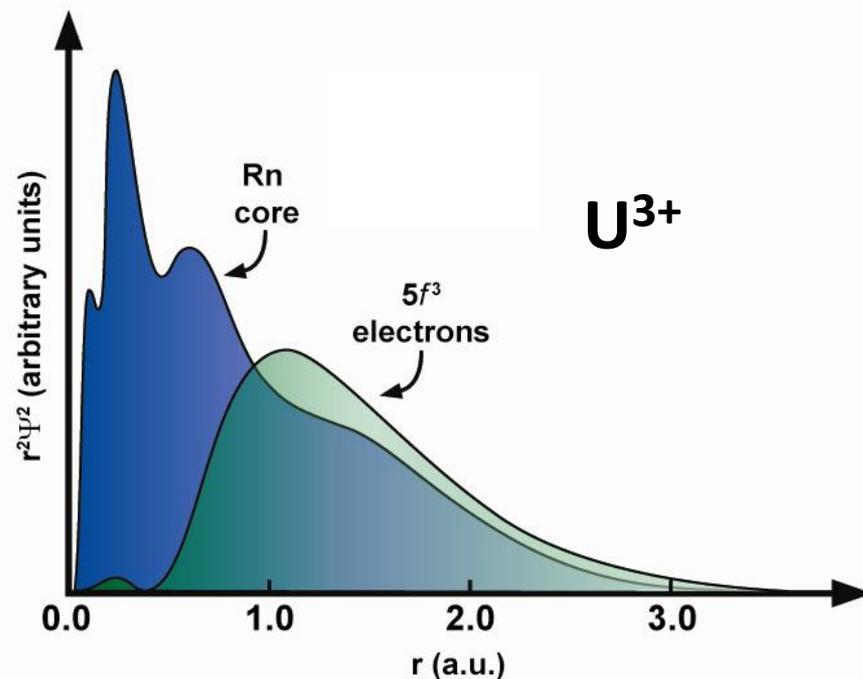
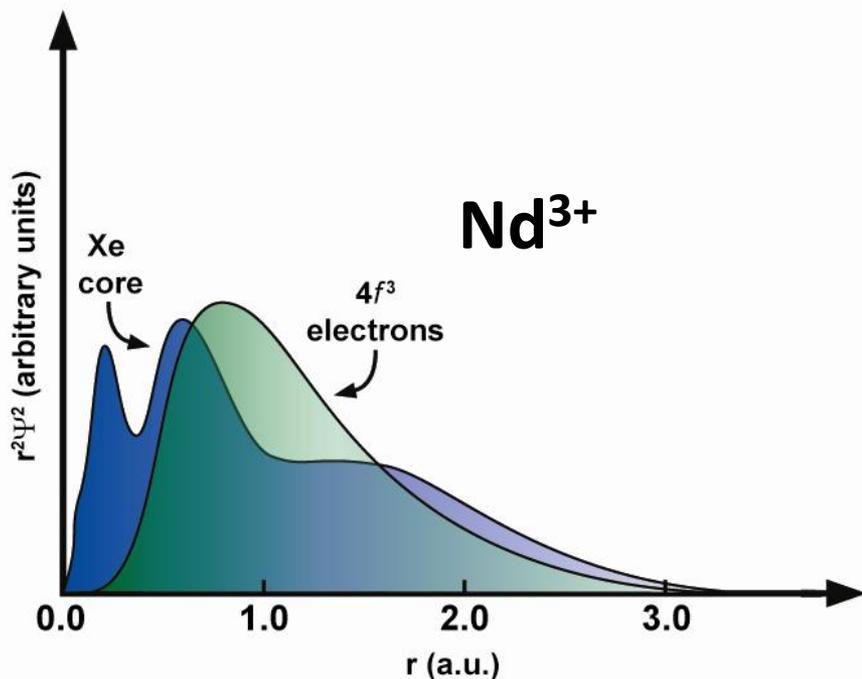
hfac = hexafluoroacetonato
Melm = 1-methylimidazole



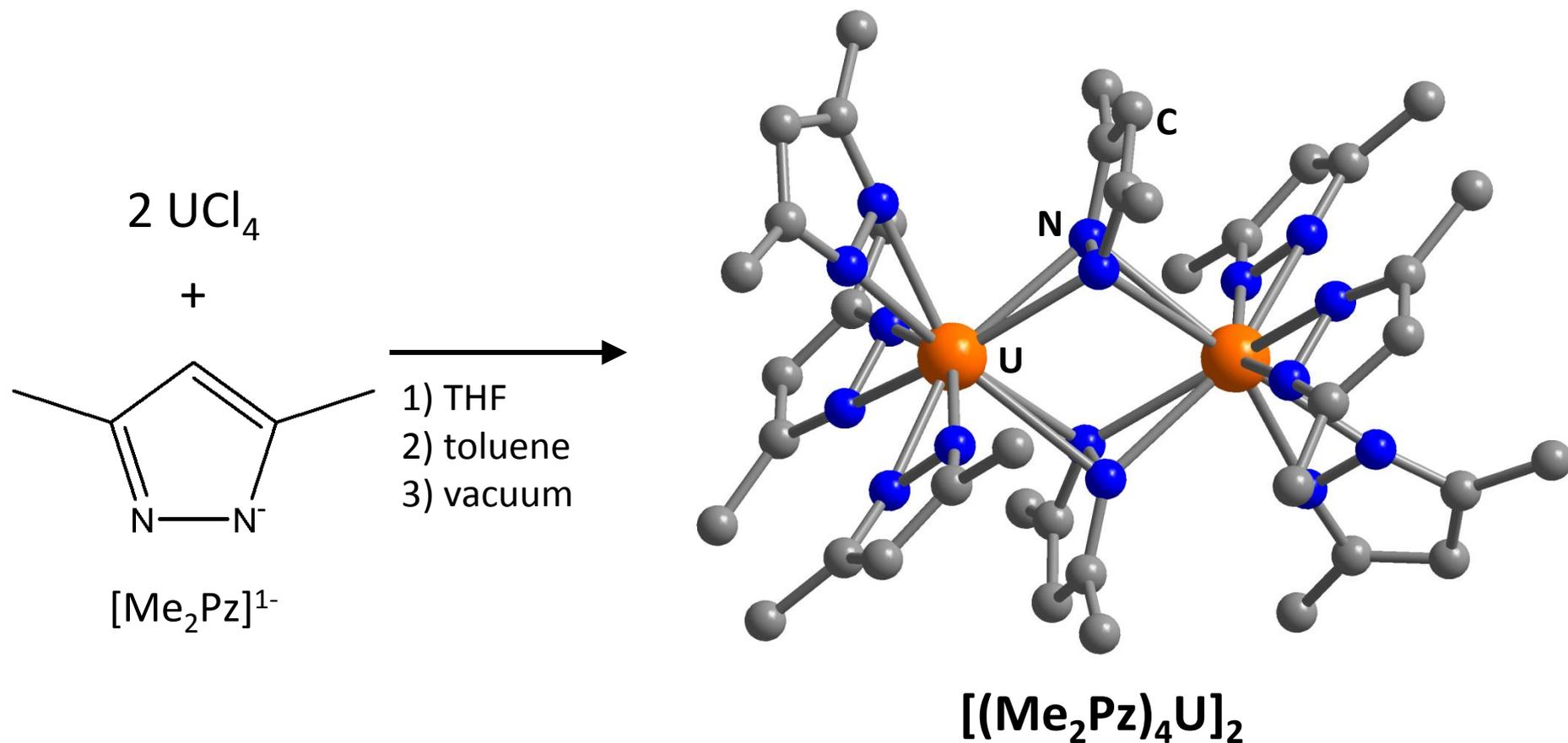
- High spin ground states, but magnetic exchange coupling is very weak

Radial Extension of 4f vs. 5f Metals

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

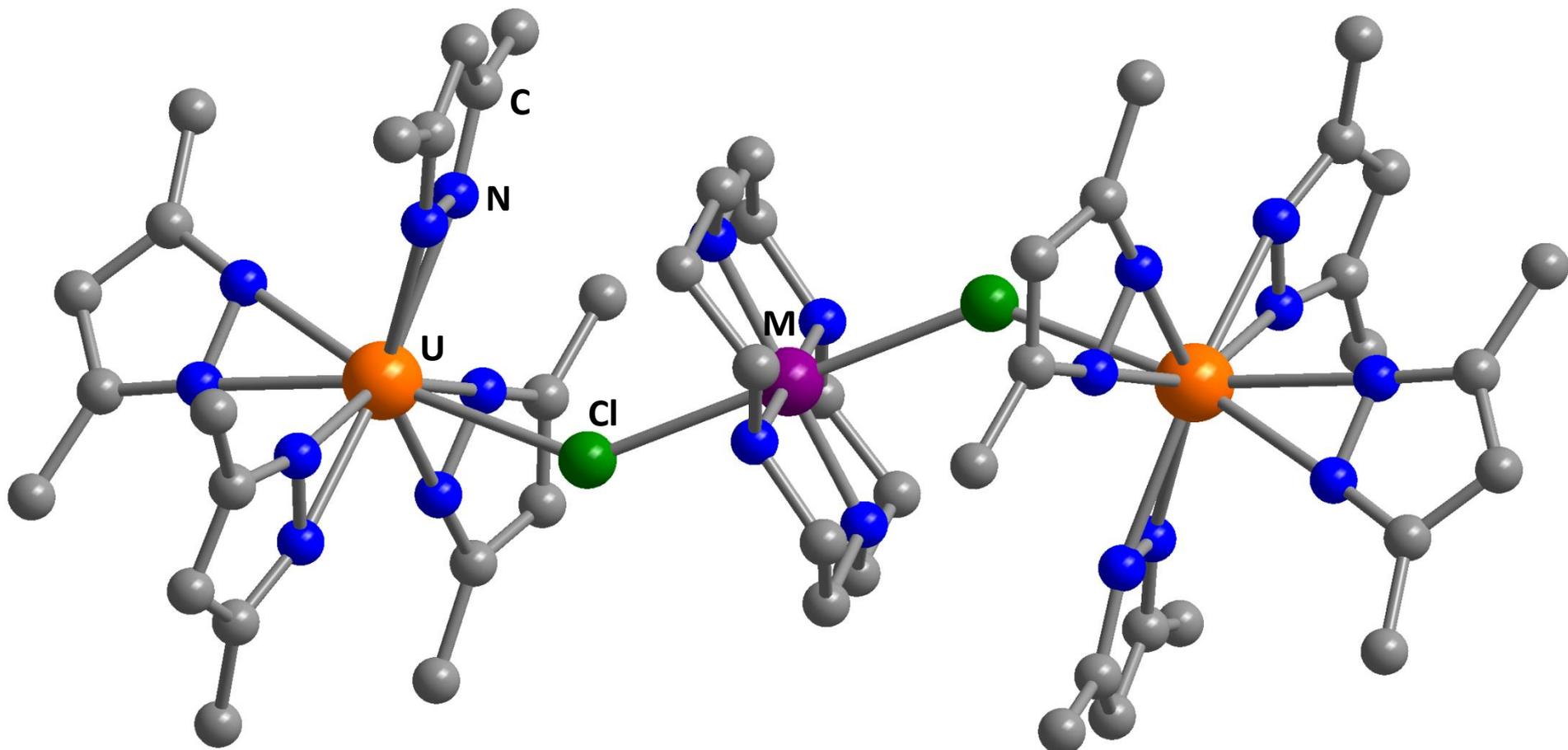
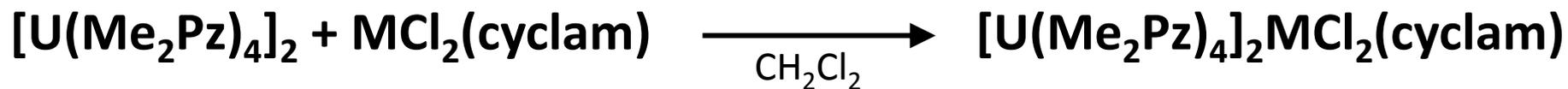


A Homoleptic Uranium(IV) Dimer



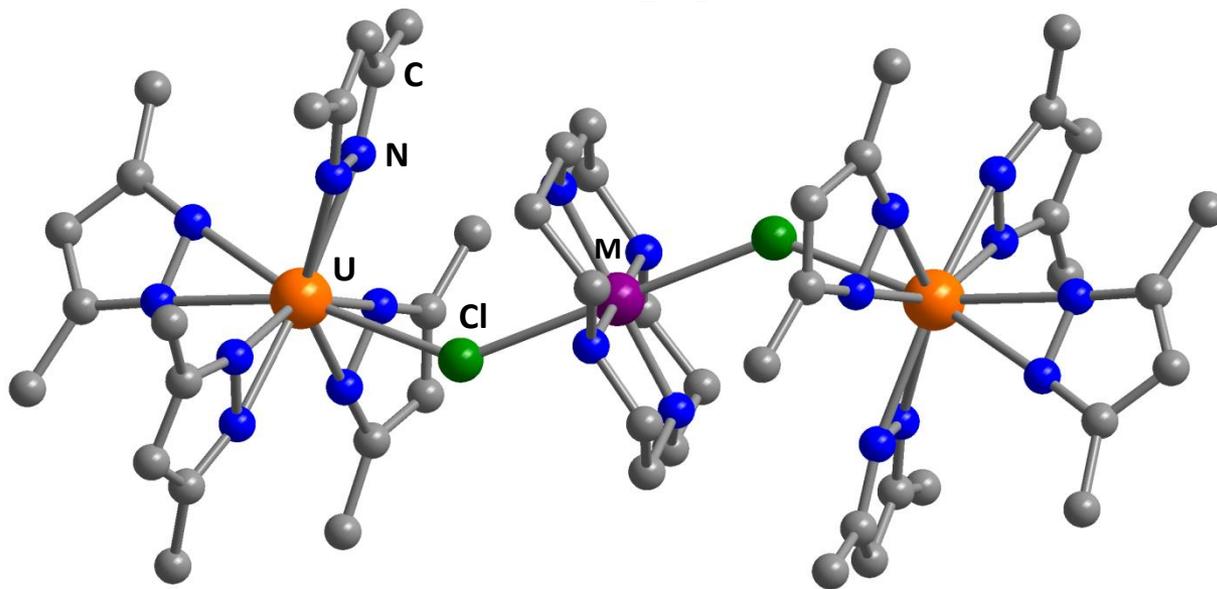
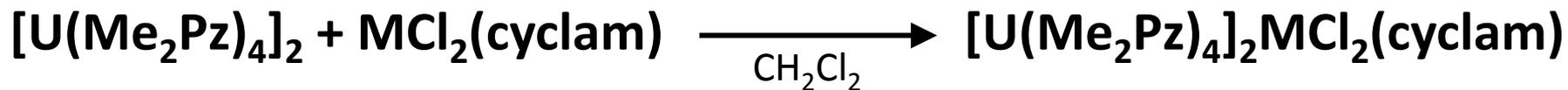
- Highly air-sensitive product isolated as green crystals in 86% yield

A Chloride-Bridged U₂M Cluster



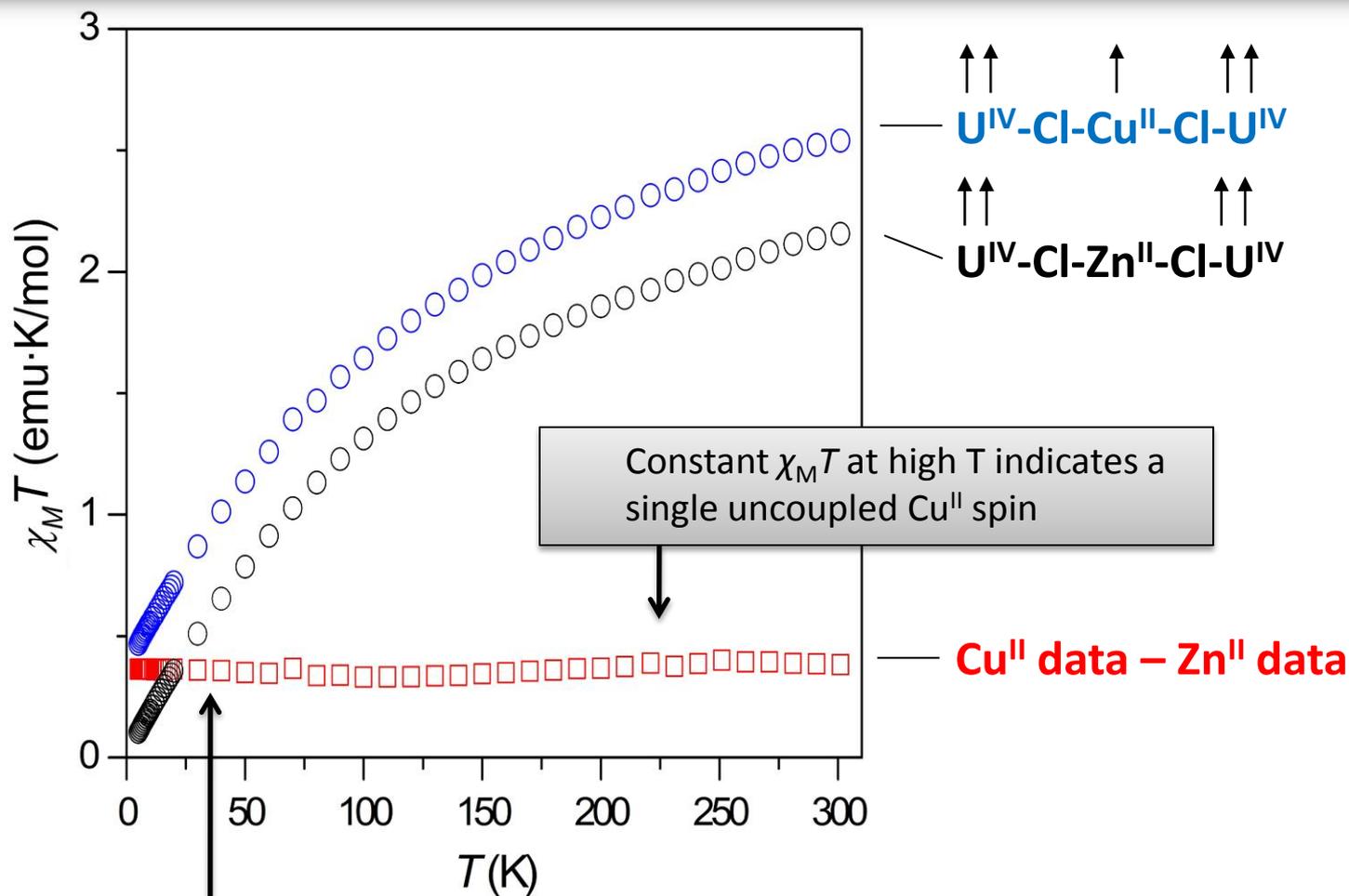
M = Cu, Co, Zn, Ni

Structural Comparisons of U₂M Clusters

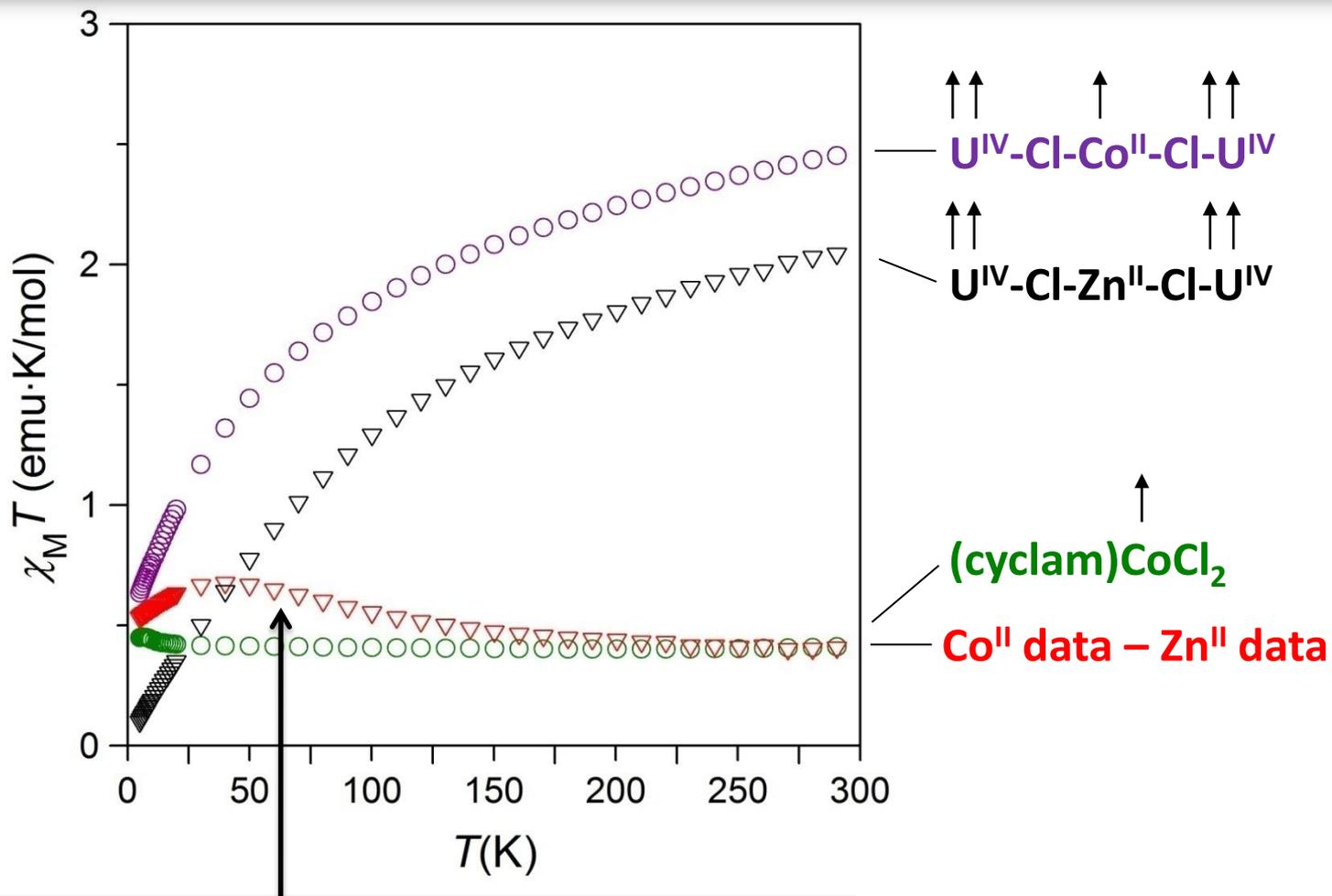


	U—Cl (Å)	M—Cl (Å)	U—Cl—M (deg)
M = Co(II)	2.800(2)	2.668(2)	138.76(8)
M = Ni(II)	2.838(2)	2.564(2)	139.47(9)
M = Cu(II)	2.785(2)	2.774(2)	137.61(7)
M = Zn(II)	2.822(2)	2.680(2)	138.31(6)

Magnetic Behavior of the $\text{U}^{\text{IV}}\text{-Cl-Cu}^{\text{II}}\text{-Cl-U}^{\text{IV}}$ Cluster

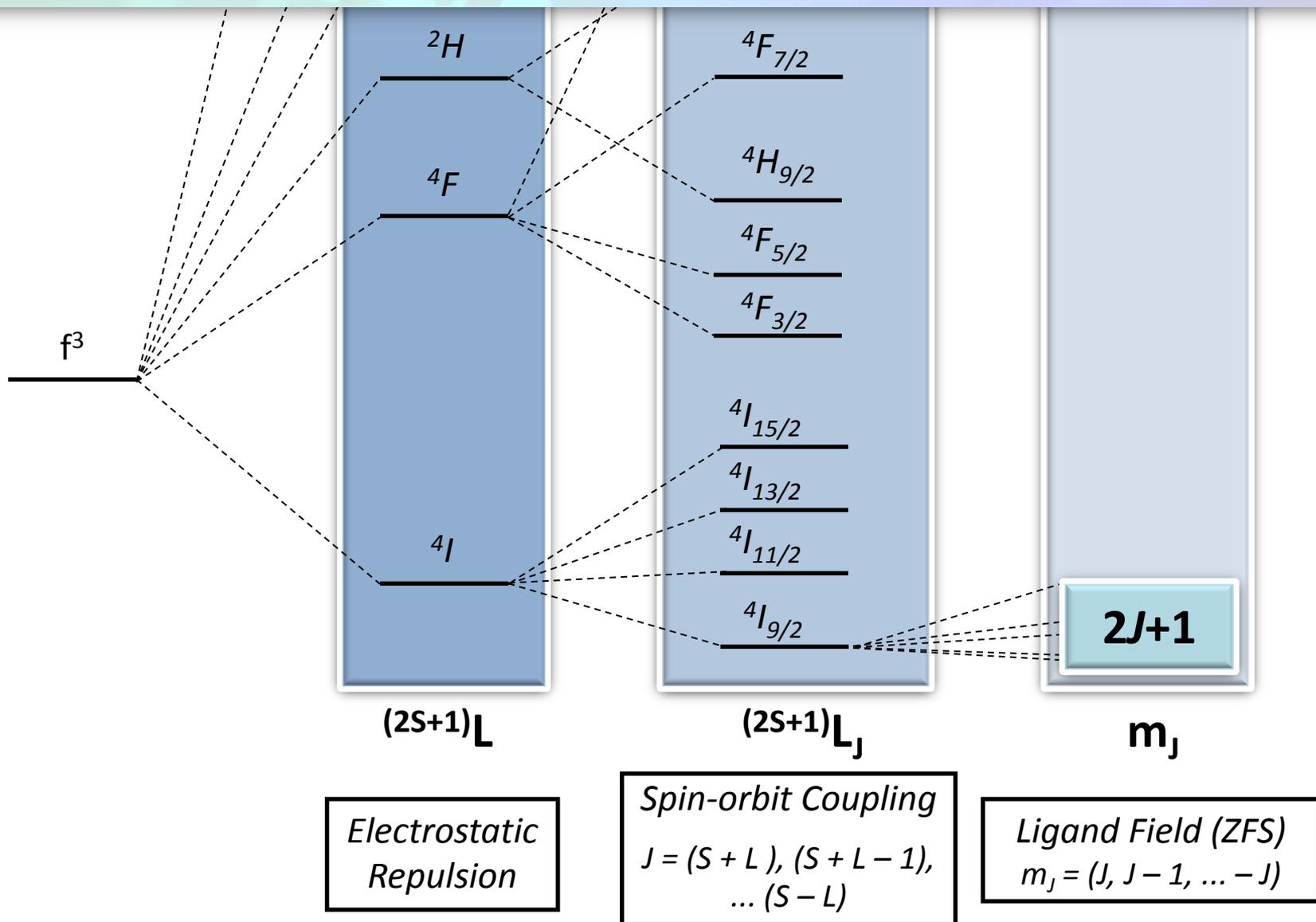


Magnetic Behavior of the $\text{U}^{\text{IV}}\text{-Cl-Co}^{\text{II}}\text{-Cl-U}^{\text{IV}}$ Cluster

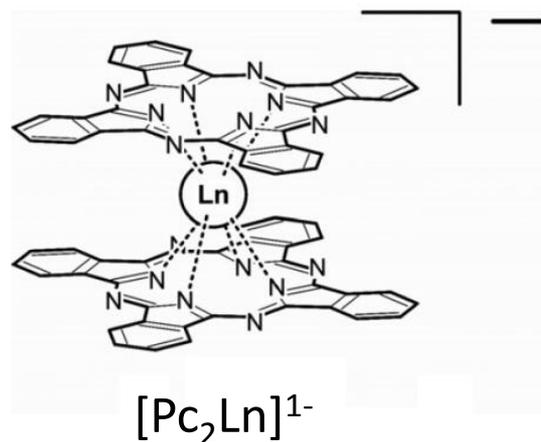


Rise in subtracted data indicates ferromagnetic exchange coupling between U^{IV} and Co^{II}

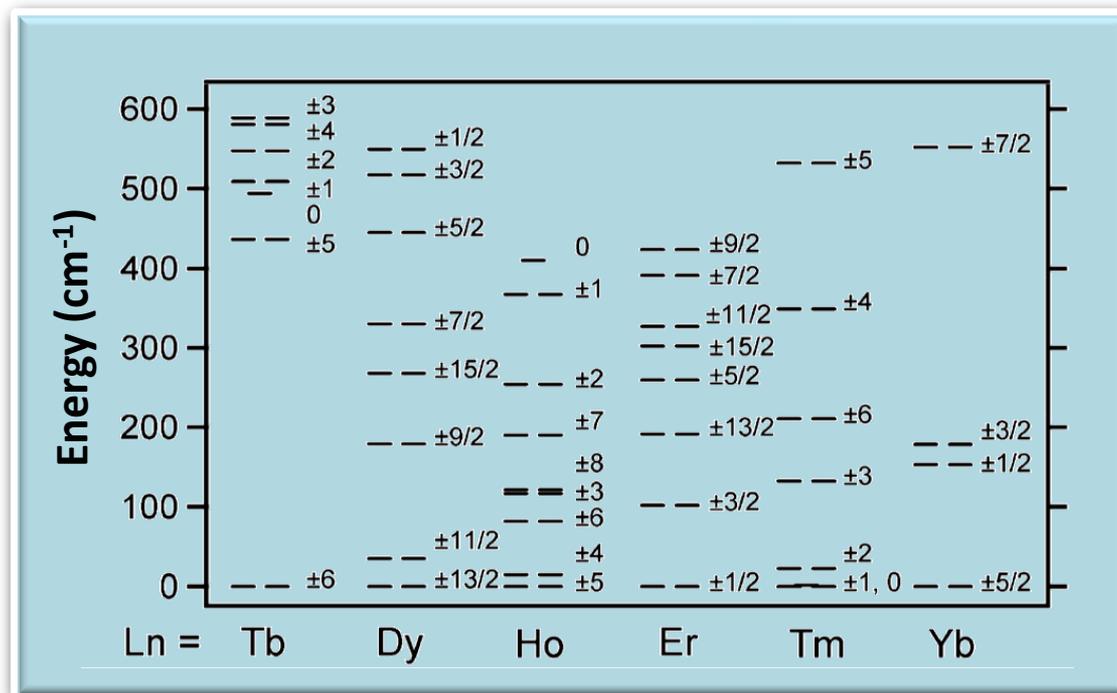
The Electronic Structure of Uranium(III): $5f^3$



Axial Anisotropy in Lanthanide Complexes



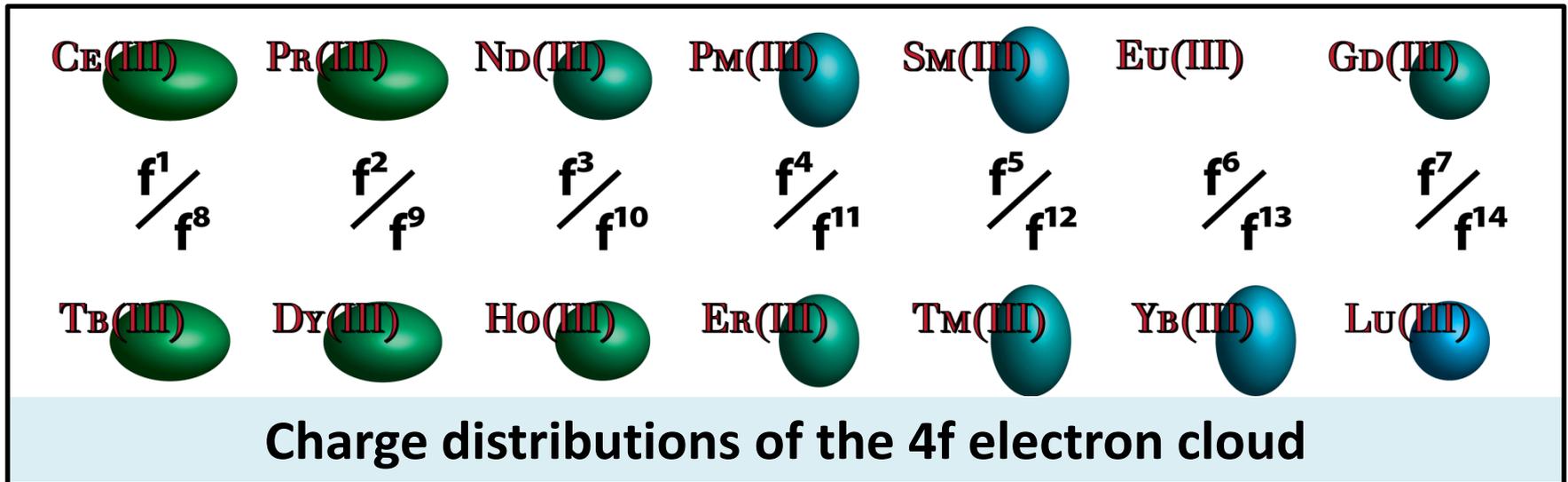
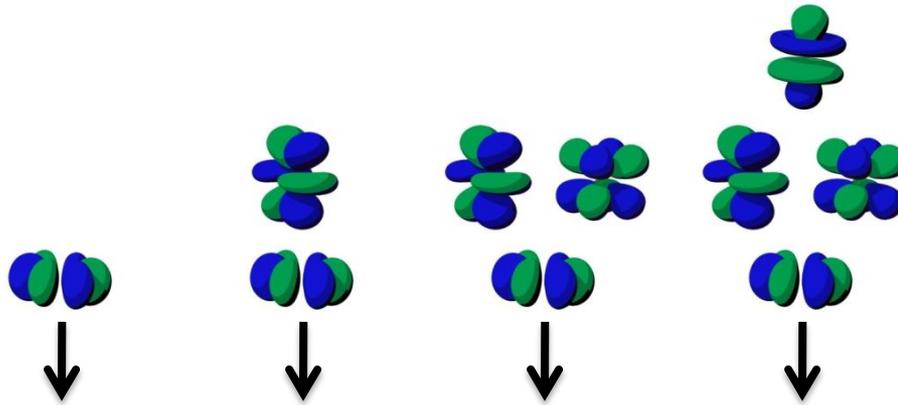
Splitting of ground J states by an axial ligand field



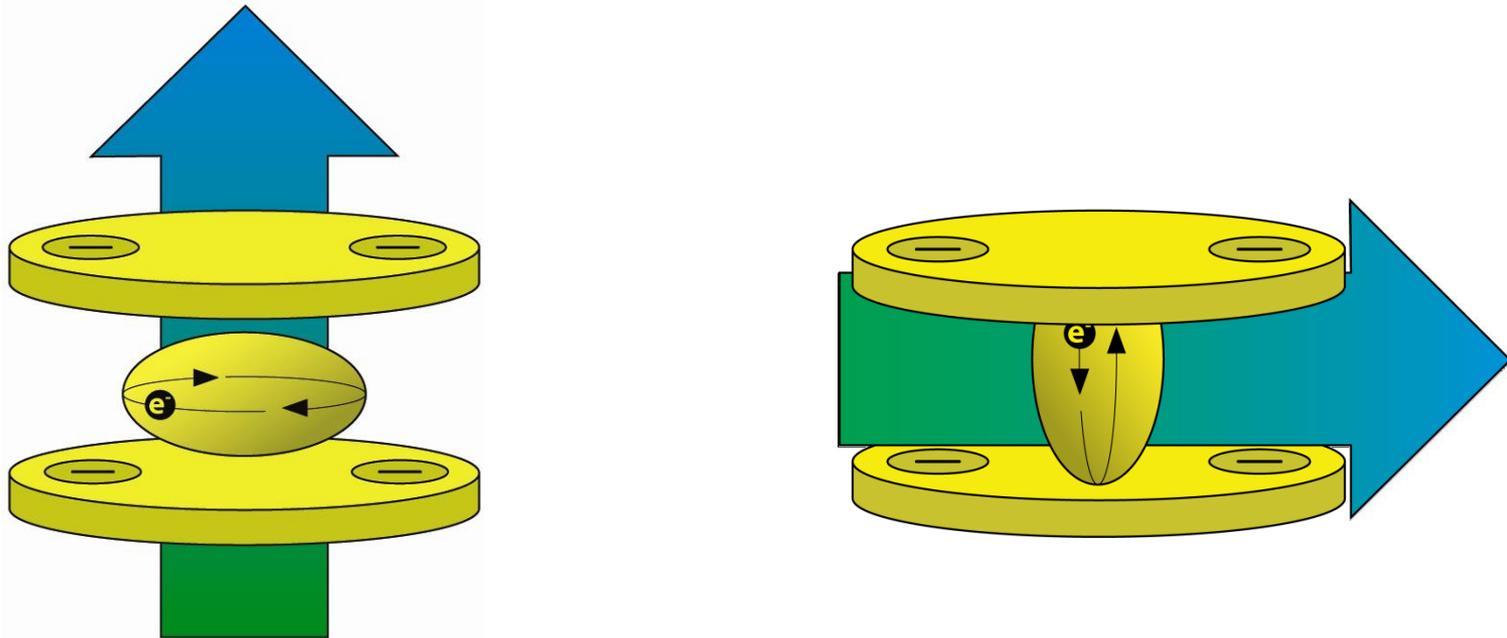
- Lanthanide phthalocyanine sandwich complexes show strong axial anisotropy for Ln = Tb and Dy

Custom-built Anisotropy from f -orbitals

- Placement of f electrons by Hund's second rule creates an asymmetric distribution of electron density

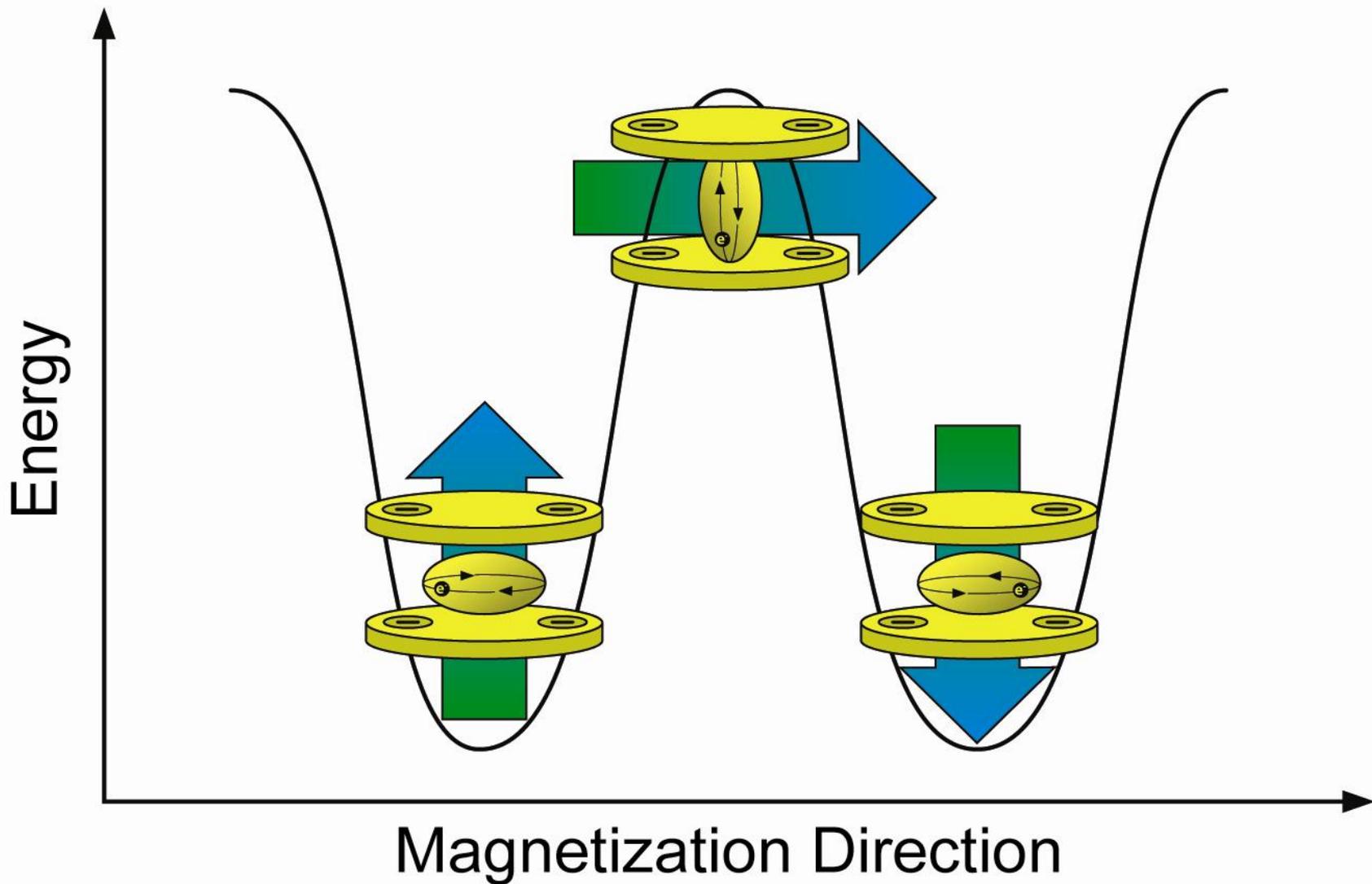


Creating Highly Anisotropic Metal-Ligand Interactions

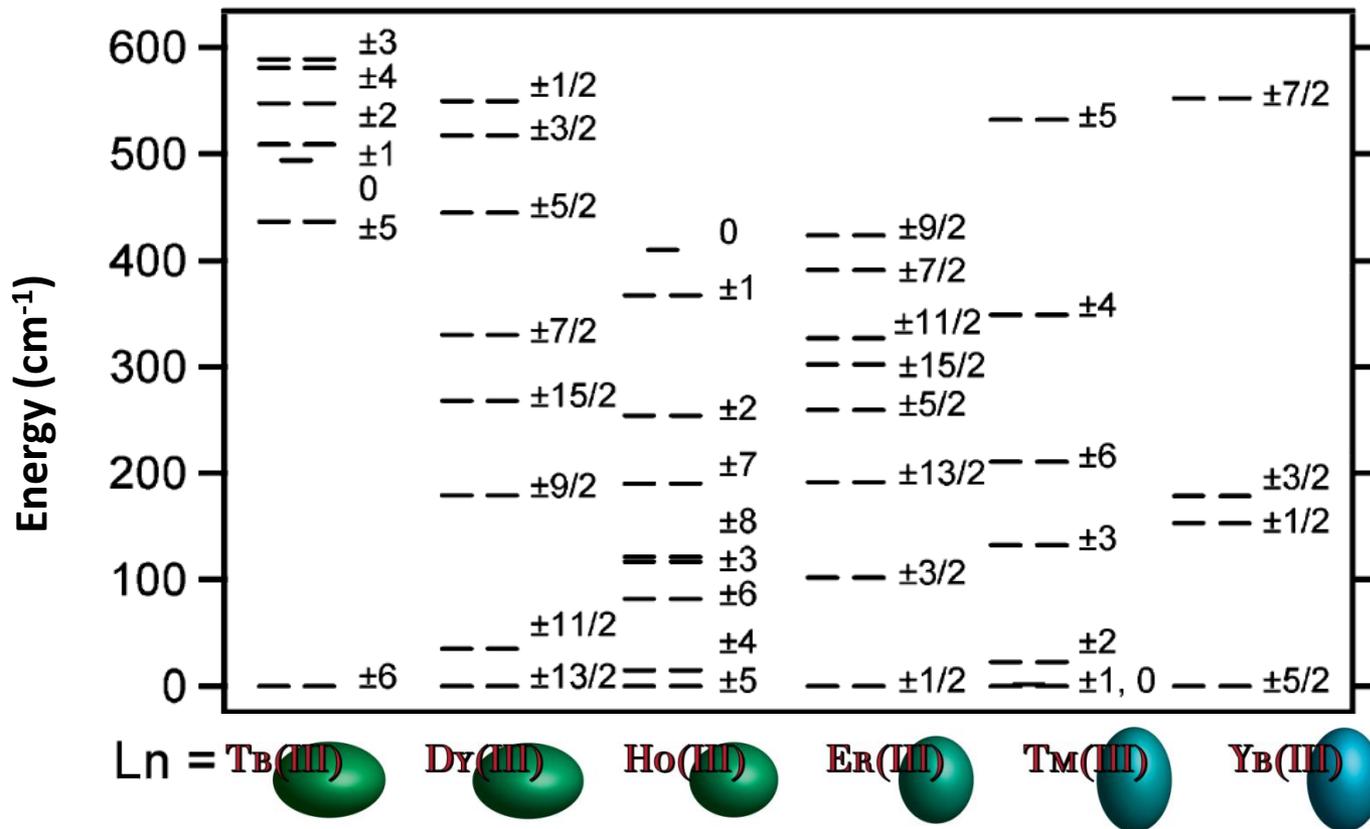
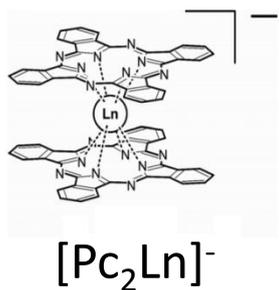


- Oblate electron density of Tb(III) and Dy(III) ground states should also be present in the ground state of U(III)

A Different Route to Magnetic Bistability

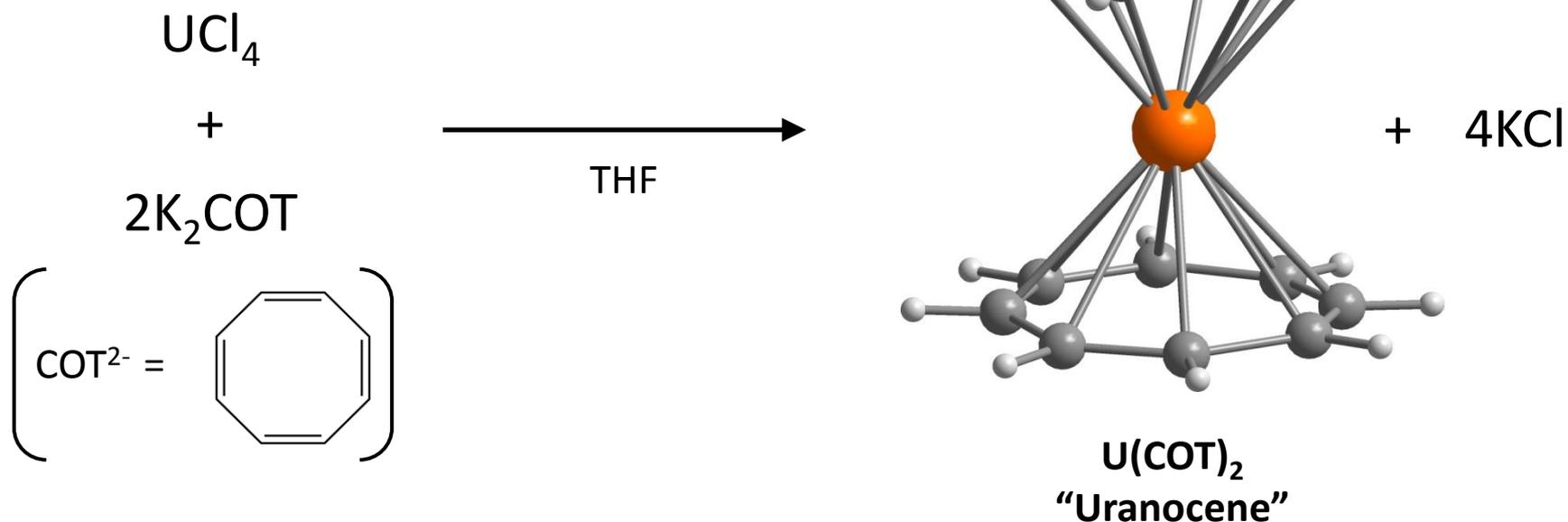


Rationalizing the Axial Anisotropy in LnPc_2



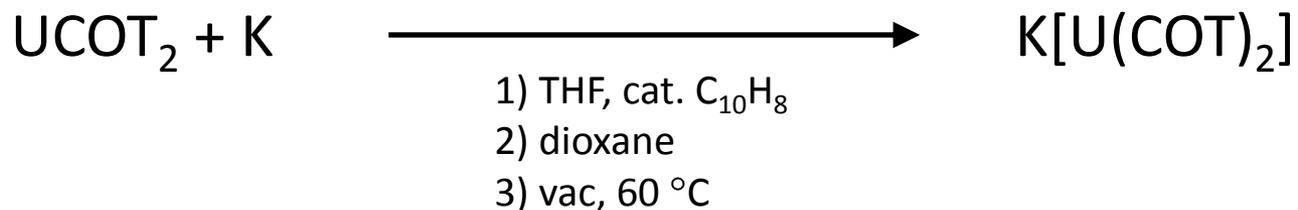
- Since the anisotropy is a function only of the f-electron count, we can use an oblate electron density lanthanide to predict behavior of U(III)

Uranocene: The Prototypical Organouranium Compound



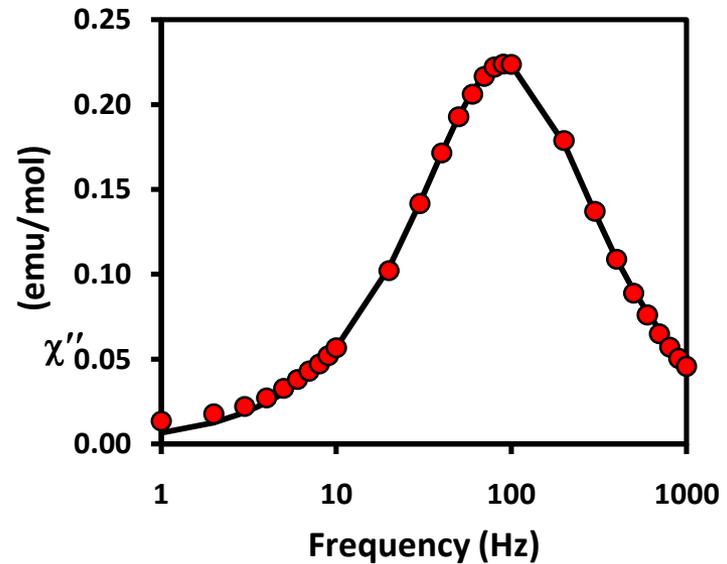
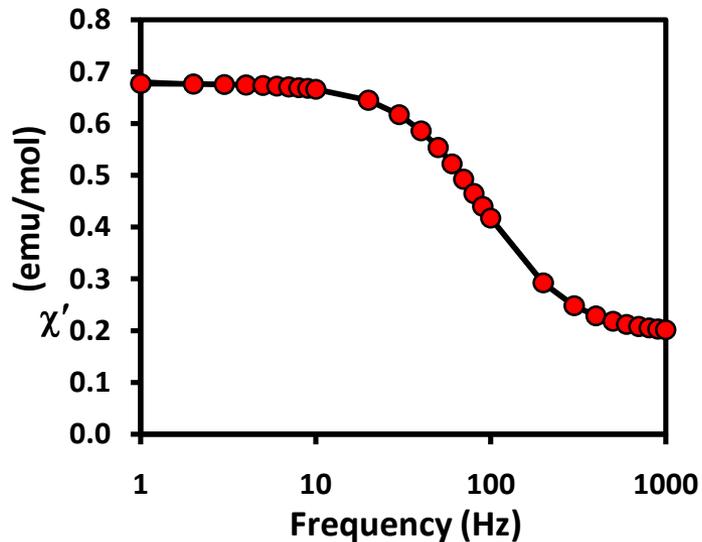
- Thermally stable, highly symmetric, synthetically and theoretically well characterized
- Not a Kramers ion (5f² valence electron configuration)

KUCOT₂ Synthesis



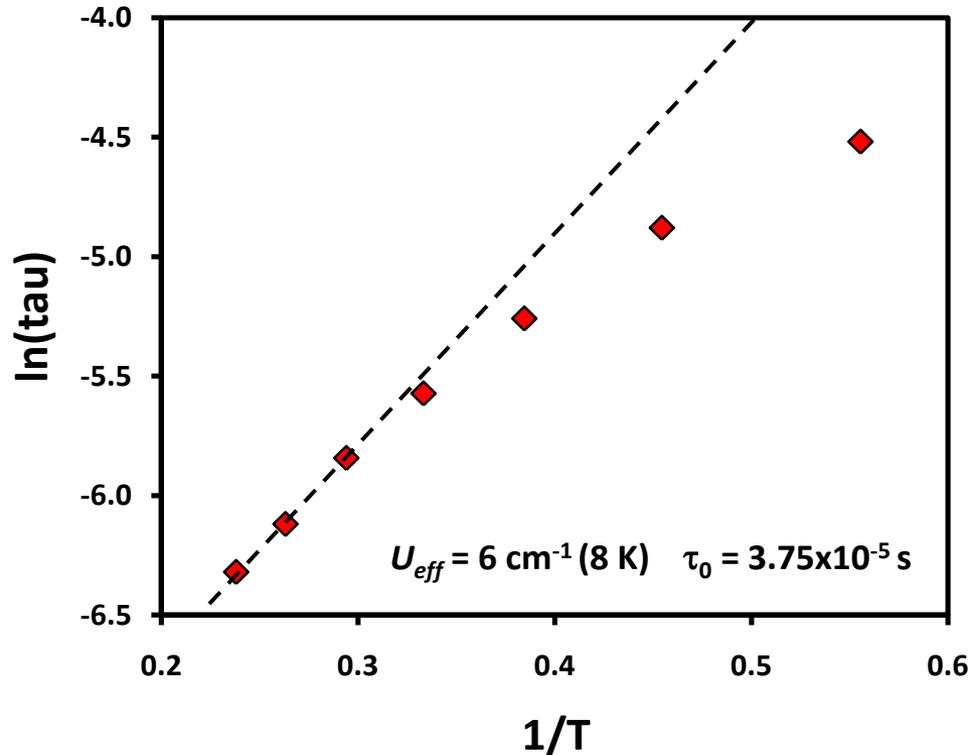
- Likely asymmetric in the solid state due to K – COT²⁻ ring interaction

AC Magnetic Susceptibility



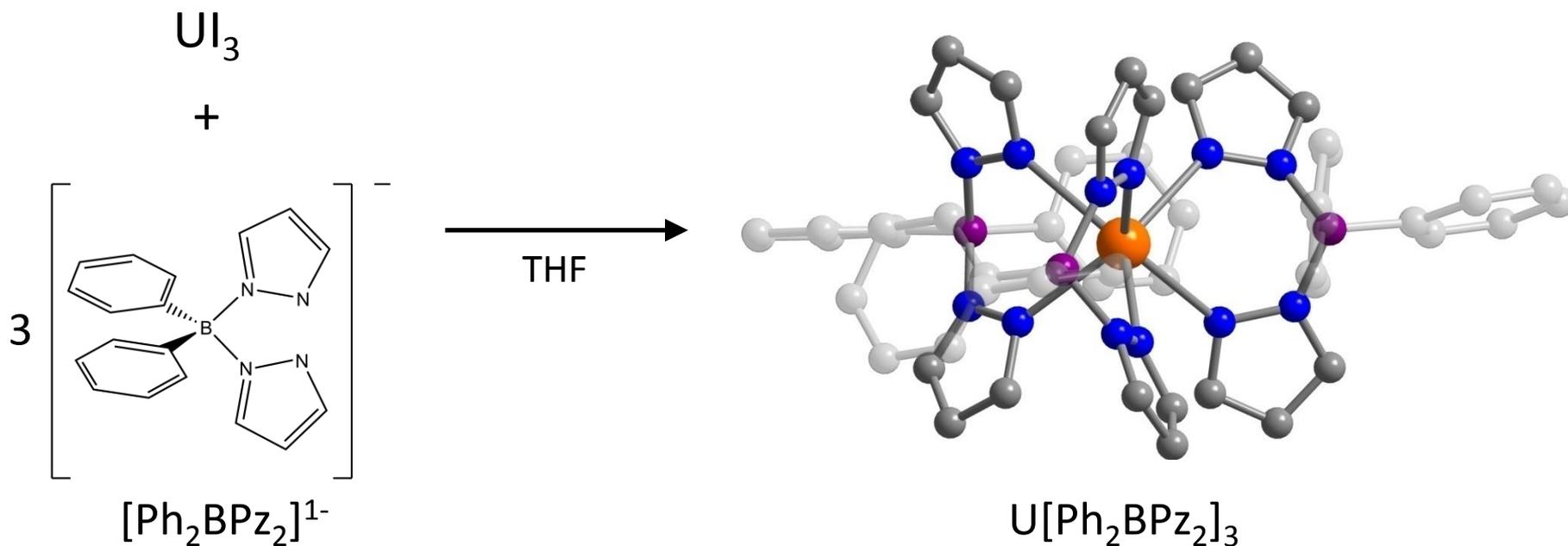
- No out-of-phase signal at zero applied dc field
- Generalized Debye model used to extract relaxation times for the magnetization
- Frequency dependence studied at multiple temperatures (1.8 K to 4.2 K)

Deviations from Arrhenius Behavior in Reduced Uranocene



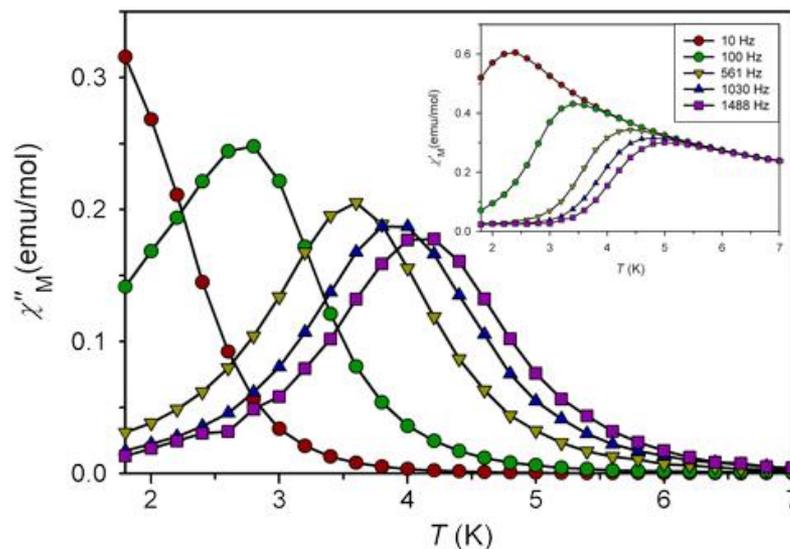
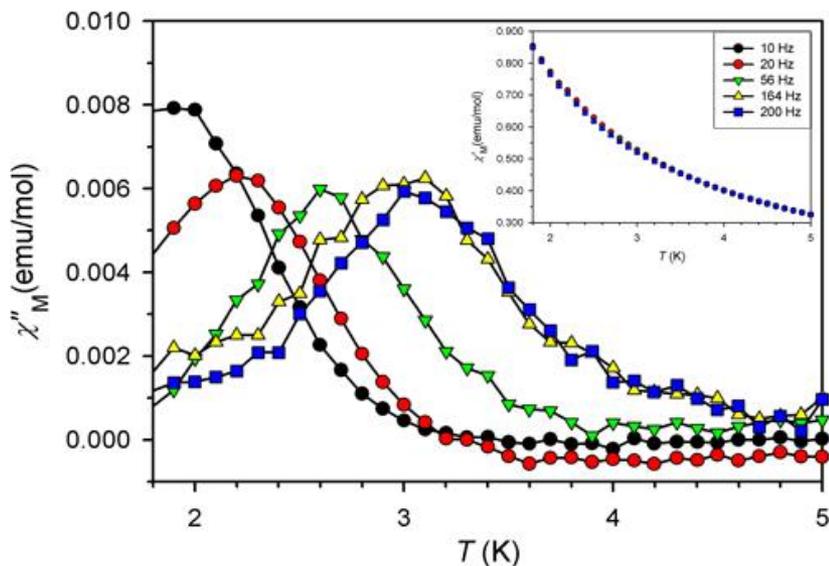
- Low barrier, large τ_0 , non-linear Arrhenius behavior, and no zero-field ac signal all point to the presence of a non-thermally dependent relaxation process

A Trigonal Prismatic U(III) Complex



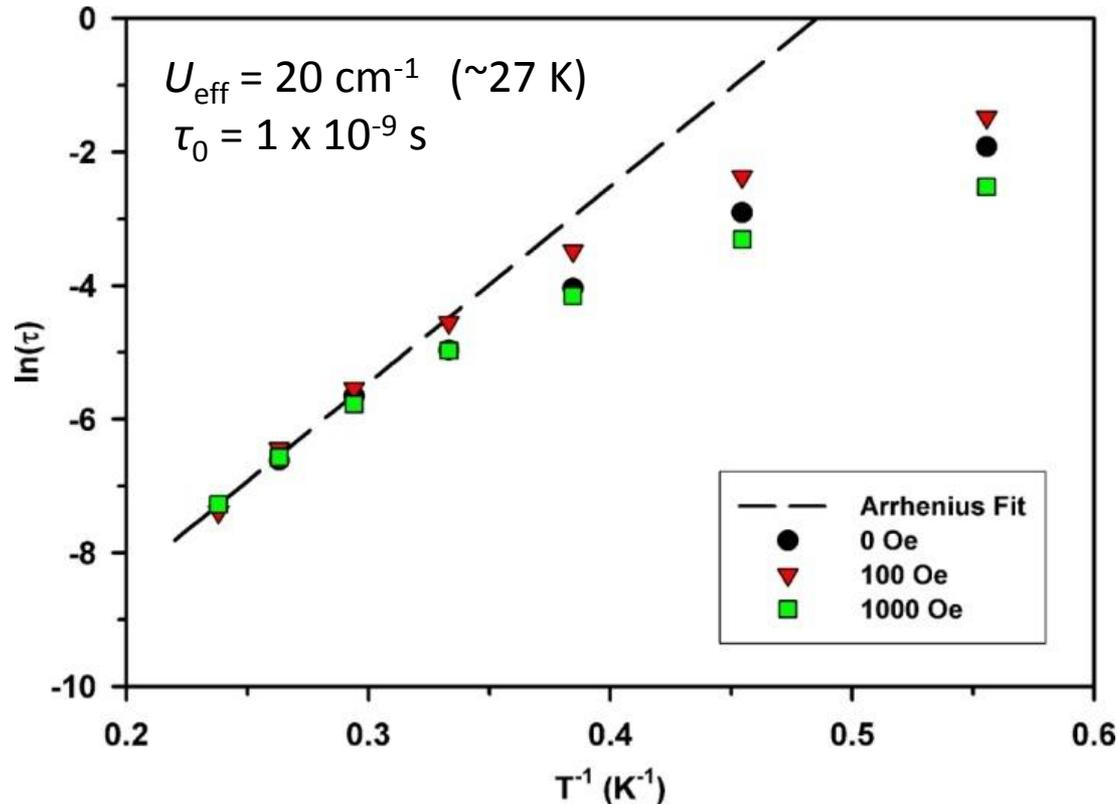
- Mononuclear U(III) molecular species with pseudo-3-fold symmetry axis
- Axially coordinated ligand density forms trigonal prismatic crystal field

Single-Molecule Magnetism in $U[Ph_2BPz_2]_3$



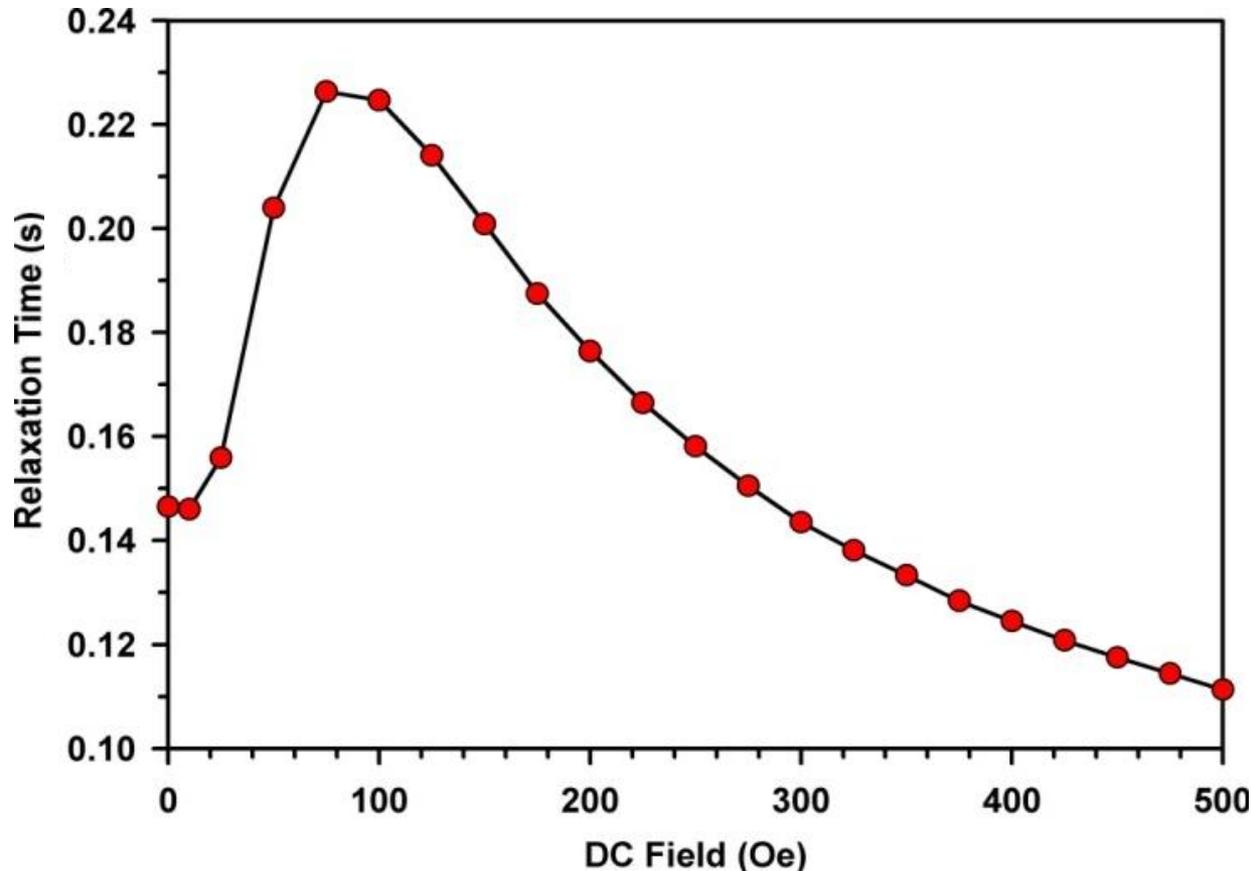
- Frequency dependency of out-of-phase susceptibility (χ'') is the signature of low-dimensional slow magnetic relaxation
- Effective barrier height is invariant to applied dc field, measurement technique, and sample preparation

DC Field Dependence of the Relaxation Time



- Relaxation times (τ) obtained by fitting both χ' and χ'' between 1-1000 Hz to a generalized Debye equation
- High temperature linear region defines the thermally-activated regime

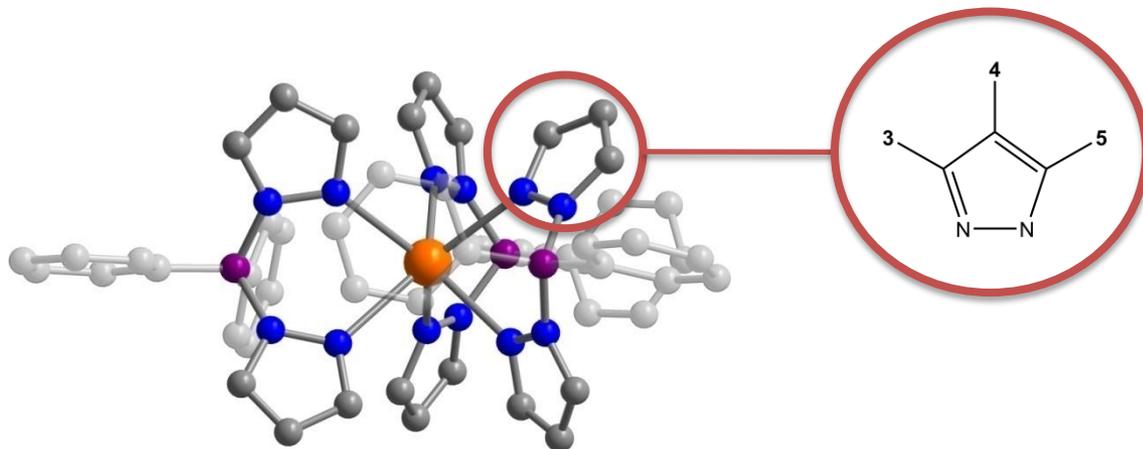
DC Field Effects on Relaxation Times in $U(\text{Ph}_2\text{BPz}_2)_3$



- Small applied dc fields may break ground state pathways and force slower thermal relaxation processes through excited states

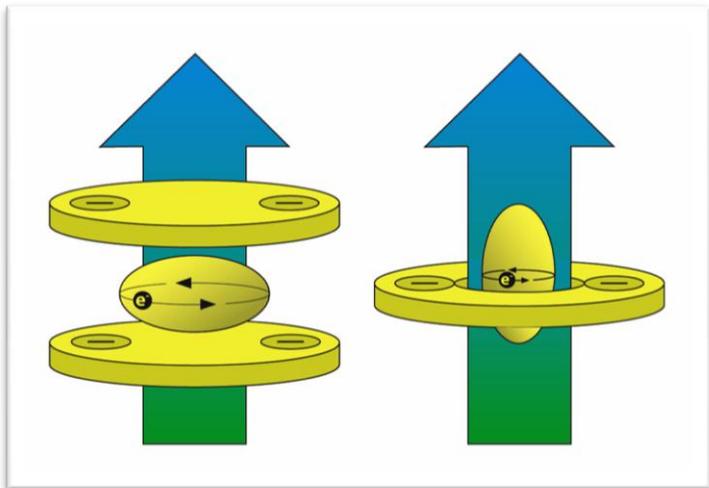
Tweaking the Electronic Structure of $U(\text{Ph}_2\text{BPz}_2)_3$

altering pyrazolate
structure



- Maintaining the Trigonal Prismatic geometry while altering the ligand field strength should help refine our model and point to optimal parameters for increasing relaxation times

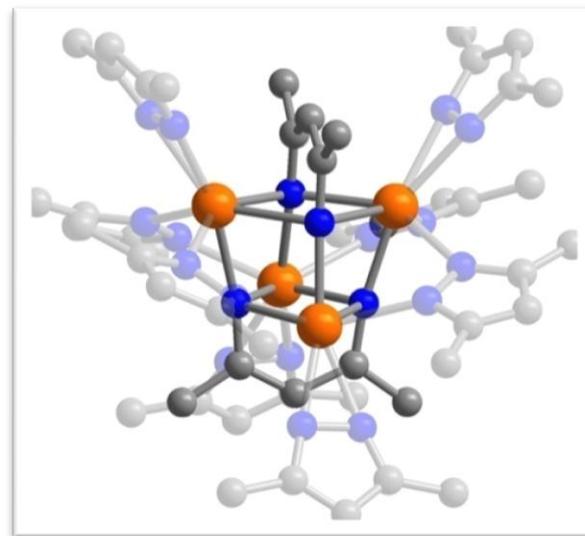
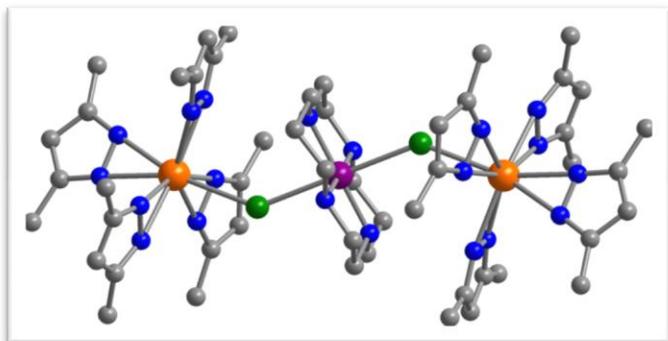
Further Directions for Actinides in Single-Molecule Magnetism



Study anisotropy variation with:

- *f*-electron count
- ligand geometry
- ligand-metal interaction

Construct high-anisotropy multinuclear clusters:



Acknowledgements



Prof. Jeffrey R. Long

Dr. Stosh A. Kozimor



T. David Harris



The Department of Energy