Coordination Chemistry and Reactivity of f Elements

Cours 5: Basic properties, electronic spectroscopy, luminescence and magnetism of 5f elements

Learning Outcomes

--Recall which actinides occur in nature and which are synthetic

-Recall the concepts of nuclear fission, nuclear power generation and nuclear fuel reprocessing

-Understand that R-S scheme is not a sufficient approximation

-Identify the range of magnetic moments available to uranium and their temperature dependency

-Explain the stability of different oxidation states for actinides

-Identify the nature of bonding in actinyl ions

- Recall the potential applications of actinyl luminescence

Actinides

89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
Actinium	Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium	Lawrencium
(227)	232.03806	231.03588	238.02891	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(262)

Discovery of actinides

1789 (U) – 1971 (Lr)

Naturally occurring: Th, Pa, U, (Np, Pu)

1828 – isolation of Th from thoria

1913 – discovery of ^{234}Pa ($t_{1/2}$ = 6.7 hr)

1916 – discovery of ^{231}Pa ($t_{1/2}$ = 32 760 hr)

1940 – synthesis of Np and Pu from ^{238}U with ^{1}n

1944 – synthesis of Am and Cm from ^{239}Pu

1947 – observation of Pm in decay of ^{235}U

1949 – synthesis of Bk

1955 – identification of Es and Fm in debris of thermonuclear explosions

1961–71 Synthesis of No and Lr by bombardment of $_{95}$Am or $_{98}$Cf

1996 – 2012 Reports of the synthesis of elements 112 – 118 ($_{114}$Fl and $_{116}$Lv named 30/05/12)

Natural Sources of Actinides

Th from monazite (Phosphate mineral)

Pa – byproduct from Uranium Extraction. 60 tons of pitchblende was treated and 126.75g Pa obtained. Most of the chemistry elucidated from this stock

U found in Pitchblende [U_3O_8] or Carnotite [$K_2(UO_2)_2(VO_4)_2.3H_2O$] (+ 130 others)

$$\boxed{\text{ORE}} \xrightarrow[\text{MnO}_2]{\text{H}_2\text{SO}_4} \boxed{UO_2^{2+}} \xrightarrow{NH_3} \boxed{(NH_4)_2U_2O_7} \xrightarrow{300\ ^{o}C} \boxed{UO_3} \xrightarrow[H_2]{700\ ^{o}C} \boxed{UO_2} \xrightarrow{HF} \boxed{UF_4} \xrightarrow{Mg} \boxed{U} \xrightarrow[250\ ^{o}C]{F_2} \boxed{UF_6} \rightarrow \boxed{UO_2}$$

Saskatchewan (Canada) mines the most Uranium 11 628 tonnes of U_3O_8 in 2005 (world total 49 052 t U_3O_8 in 2005)

Required
For enrichment

Uranium is a common element 40 times more common than silver

Characteristics of the Actinides

-Increased extension of f-orbitals
-Prefer hard donor atoms
-Covalent contribution to bonding

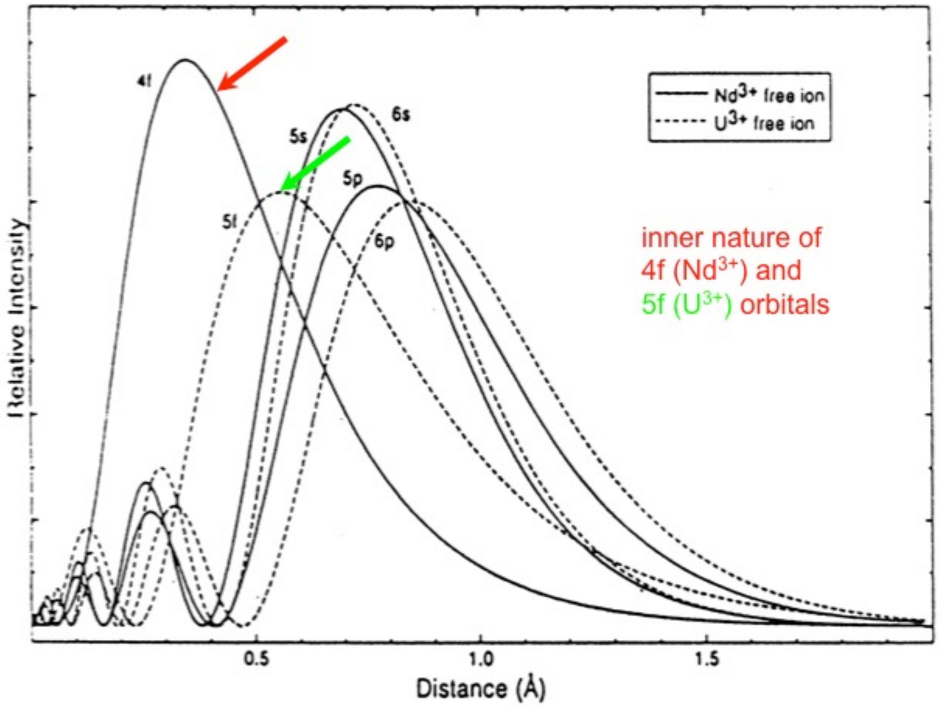
-Wide range of oxidation states
for early ions
-+3 oxidation common for later actinides

-Higher contribution of crystal field
compared to Ln

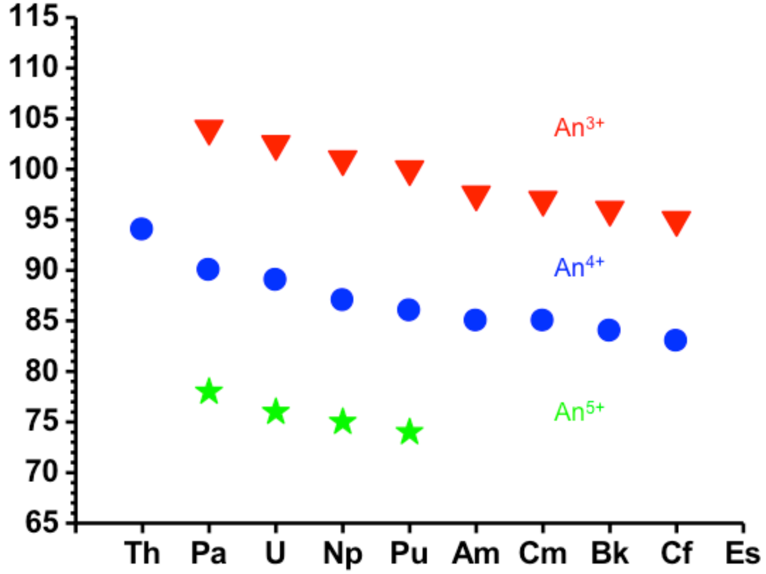
-Actinides contraction

-High coordination numbers common

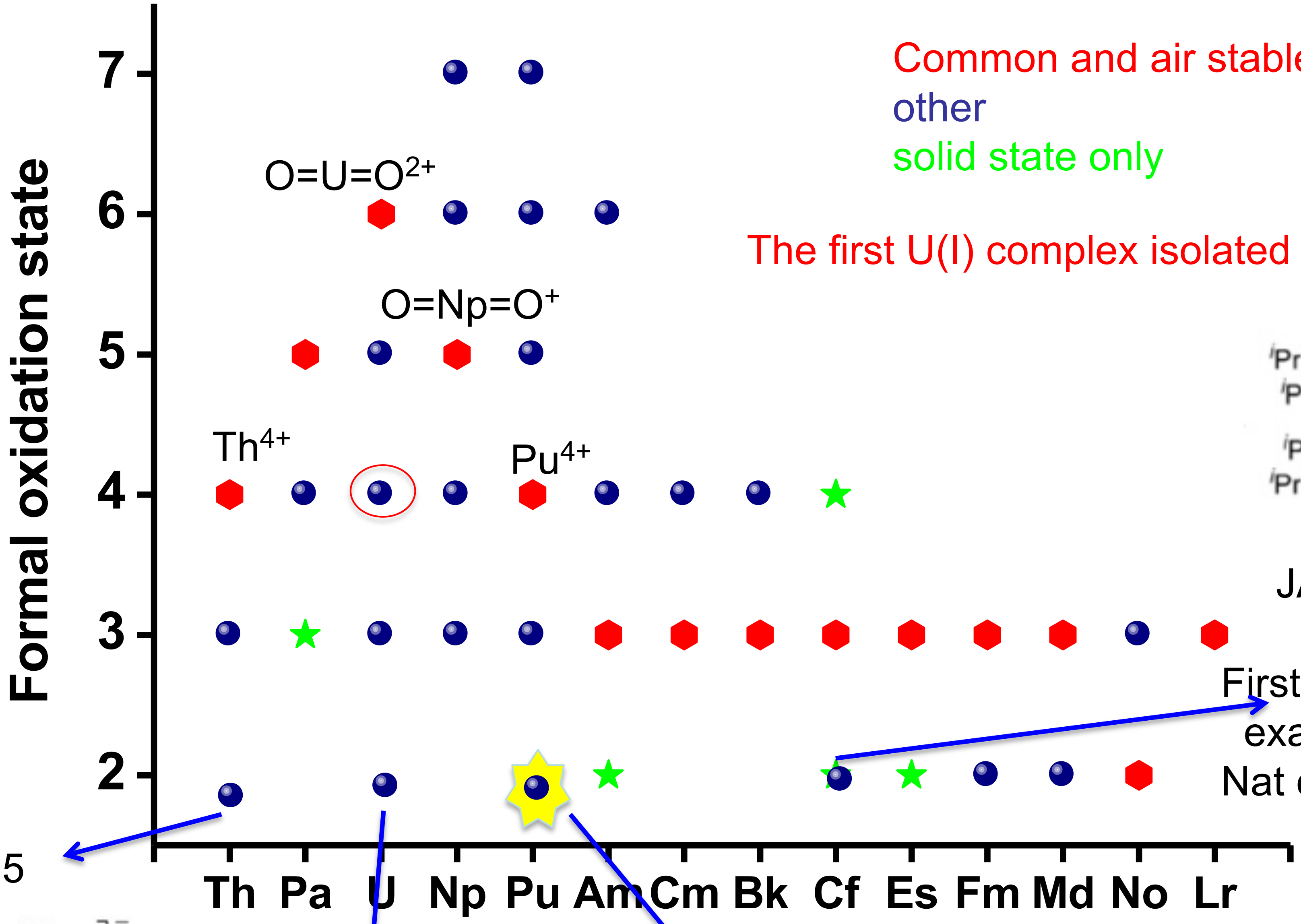
-Coordination polyhedra
dominated by steric effects



inner nature of 4f (Nd^{3+}) and 5f (U^{3+}) orbitals



Oxidation states of 5f elements An

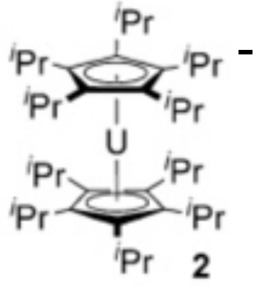


Common and air stable

other

solid state only

The first U(I) complex isolated in 2022

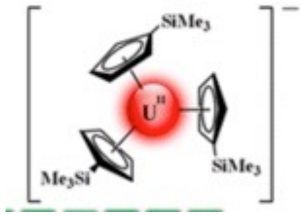


JACS 2022

First molecular example

Nat chem2023

2015



First example

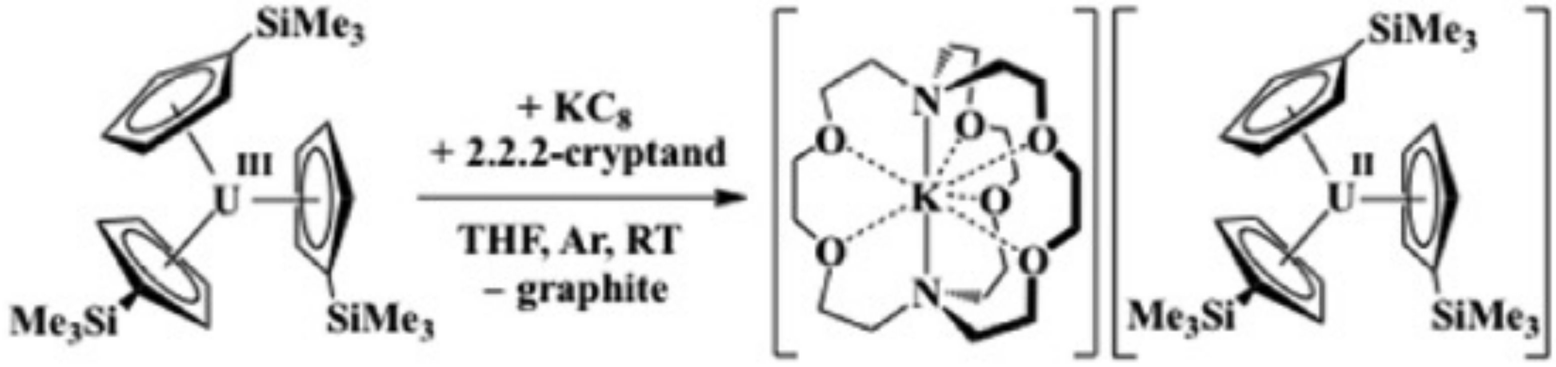
2013- now up to 4

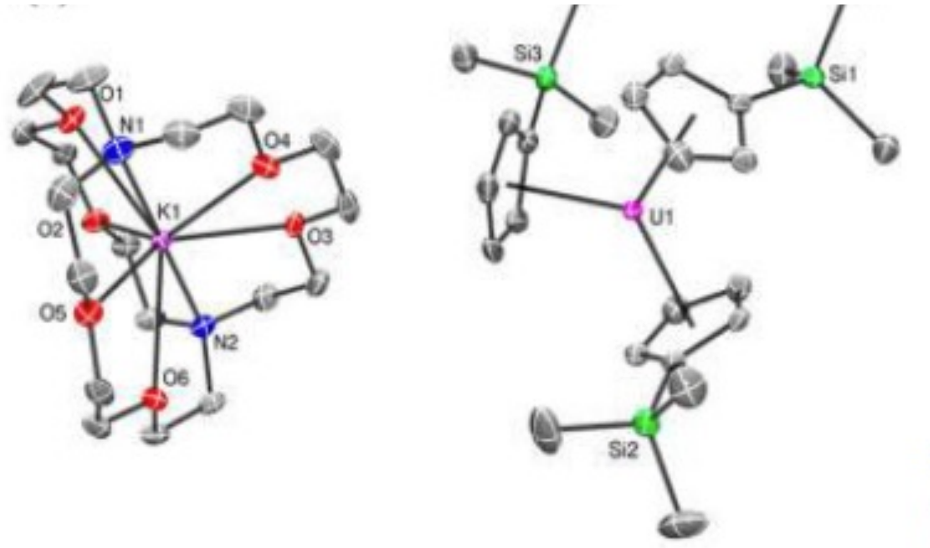
The First molecular structure published in 2017

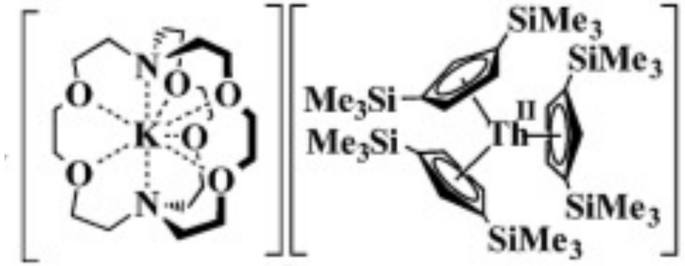
Pu officially the actinide with the largest

Number of oxidation states

The First Examples of U(II) and Th(II) Complexes







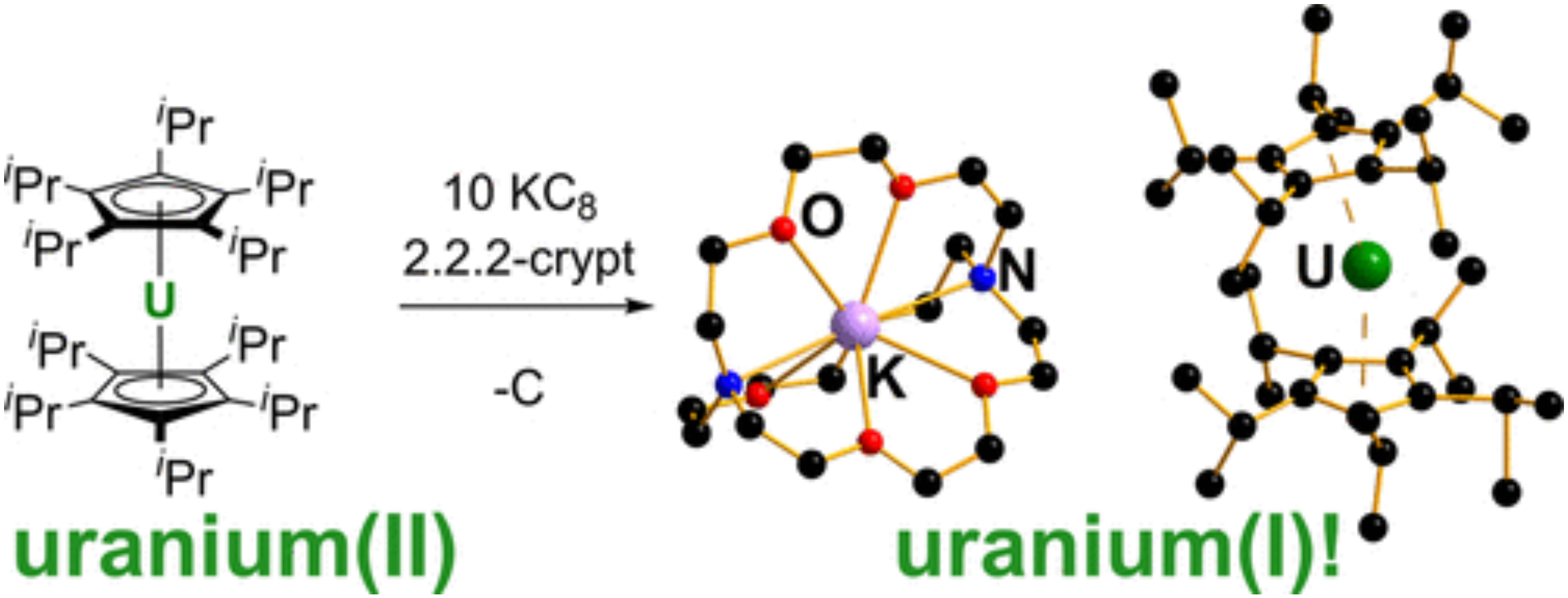
$5f^0 6d^2$ configuration for Th(II)

$5f^3 6d^1$ configuration for U(II)

$5f^6$ $6d^0$ Pu(II)

Evans, JACS 2013,135, 13310
Chem. Sci. 2015, 6, 517–521
Jacs 2017 ,3970

The First Example of U(I)



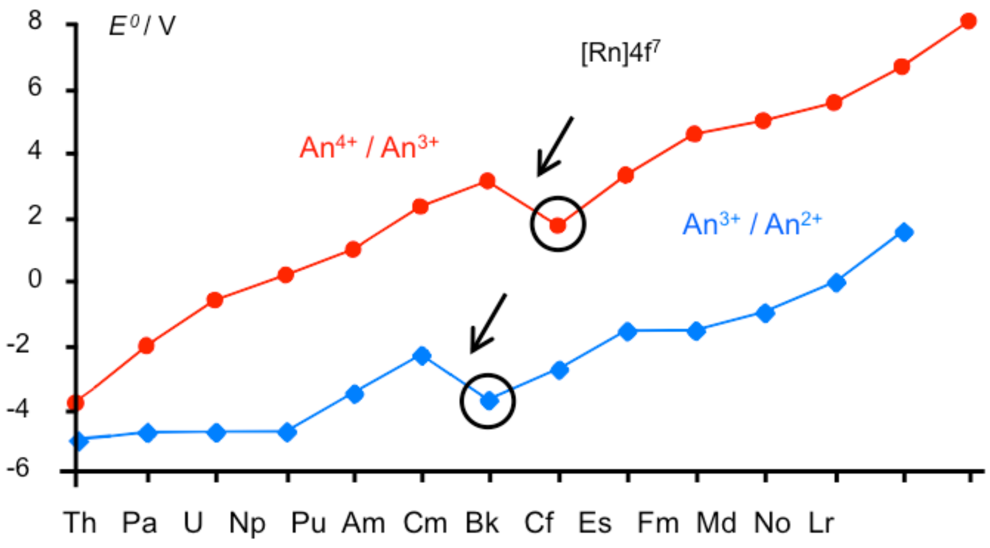
Taken from *J. Am. Chem. Soc.* **2022**, 144, 40, 18229-18233

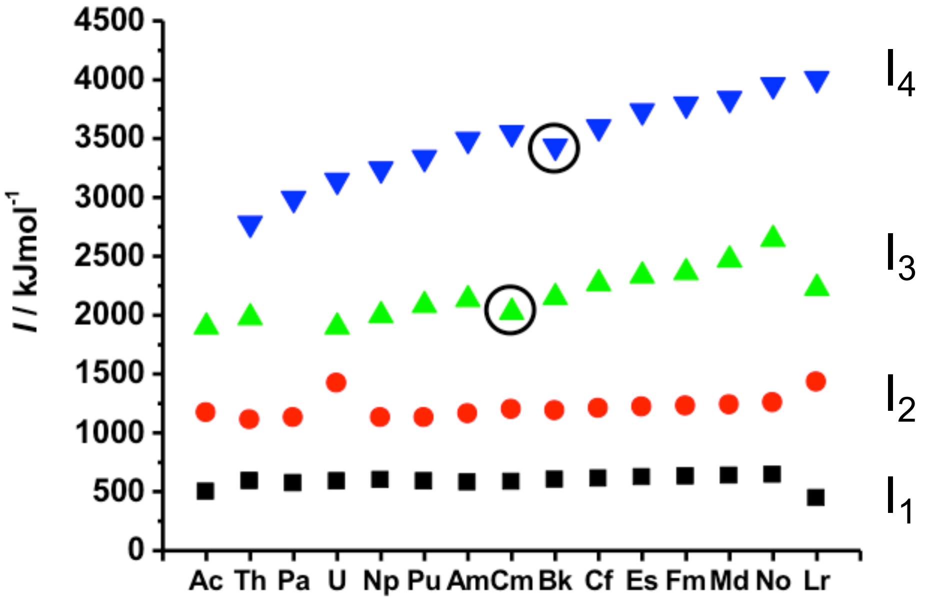
Oxidation states of 5f elements An

- The stability of An^{IV} decreases along the series Quite stable for Th, Pa, U, Np. Only found in solution with fluoride for Am, Cm, Bk

  The drop in E^0 (An^{4+}/An^{3+}) at Bk reflects the stability of [Rn]5f^7 (Bk^{IV}).

- The trend in E^0 (An^{3+}/An^{2+}) parallels the one in E^0 (An^{4+}/An^{3+}). The stability of An^{II} increases across the series. Note that the discontinuity appears at Cm, reflecting the stability of [Rn]5f^7 (Cm^{III}).



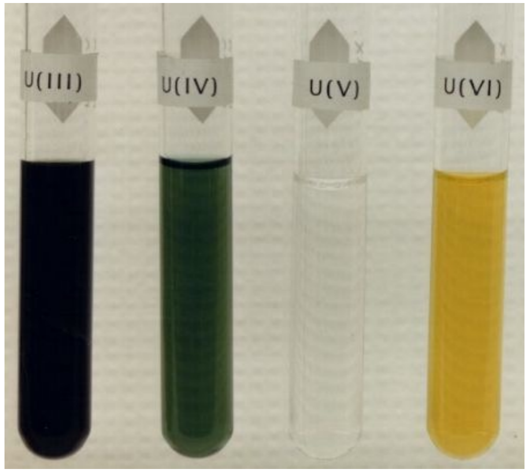


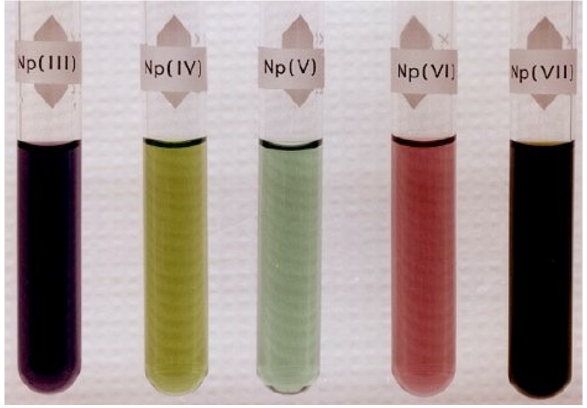
Most Stable Oxidation States of Actinides

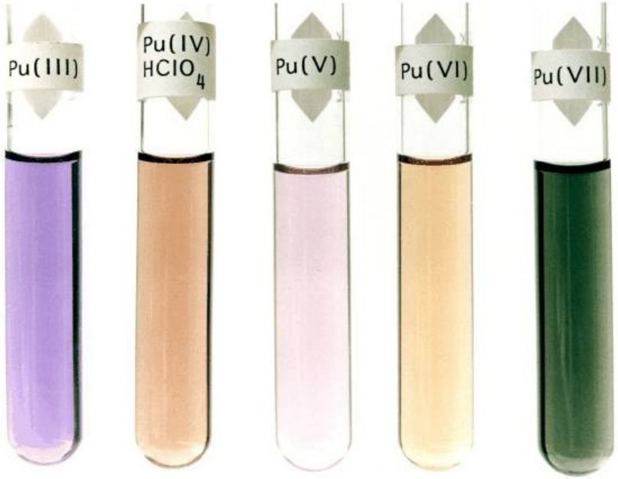
Thorium	Uranium		Neptunium		Plutonium	Americium	Curium
Th^{4+} (IV)	U^{4+} (IV)	UO_2^{2+} (VI)	Np^{4+} (IV)	NpO_2^{+} (V)	Pu^{4+} (IV)	Am^{3+} (III)	Cm^{3+} (III)
$5f^0$	$5f^2$	$5f^0$	$5f^3$	$5f^2$	$5f^4$	$5f^6$	$5f^7$

$O{=}U{=}O^{2+}$

$O{=}Np{=}O^{+}$



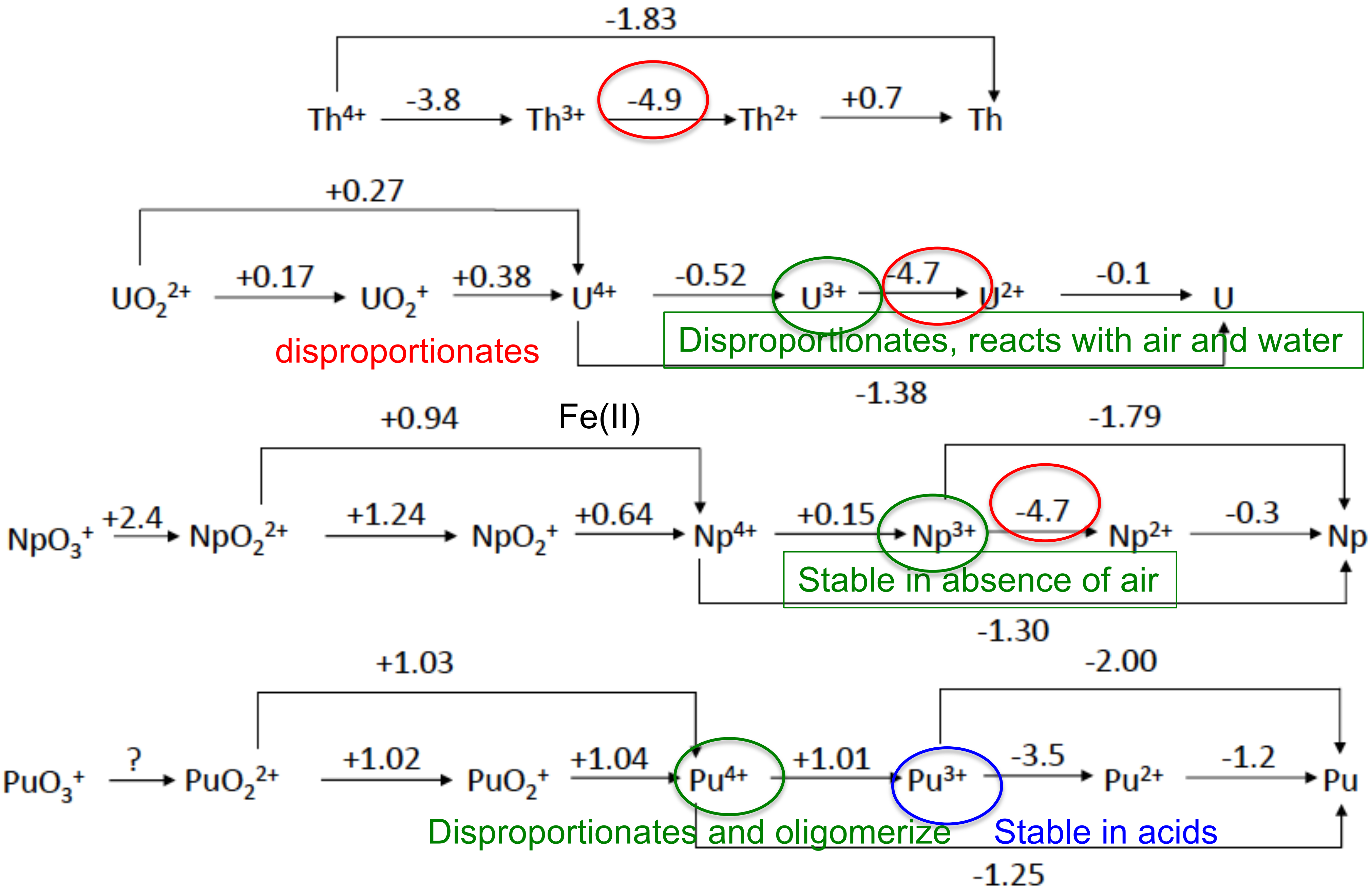




- The greater range of oxidation numbers of An elements compared with Ln is due to the nature of 5f orbitals

Redox Potentials of An

Maximum oxidation state correspond to the number of outer shell electrons like in d-block



$$Th^{4+} \xrightarrow{-3.8} Th^{3+} \xrightarrow{-4.9} Th^{2+} \xrightarrow{+0.7} Th$$

$$UO_2^{2+} \xrightarrow{+0.17} UO_2^{+} \xrightarrow{+0.38} U^{4+} \xrightarrow{-0.52} U^{3+} \xrightarrow{-4.7} U^{2+} \xrightarrow{-0.1} U$$

$$NpO_3^{+} \xrightarrow{+2.4} NpO_2^{2+} \xrightarrow{+1.24} NpO_2^{+} \xrightarrow{+0.64} Np^{4+} \xrightarrow{+0.15} Np^{3+} \xrightarrow{-4.7} Np^{2+} \xrightarrow{-0.3} Np$$

$$PuO_3^{+} \xrightarrow{?} PuO_2^{2+} \xrightarrow{+1.02} PuO_2^{+} \xrightarrow{+1.04} Pu^{4+} \xrightarrow{+1.01} Pu^{3+} \xrightarrow{-3.5} Pu^{2+} \xrightarrow{-1.2} Pu$$

disproportionates

Disproportionates, reacts with air and water

Fe(II)

Stable in absence of air

Disproportionates and oligomerize

Stable in acids

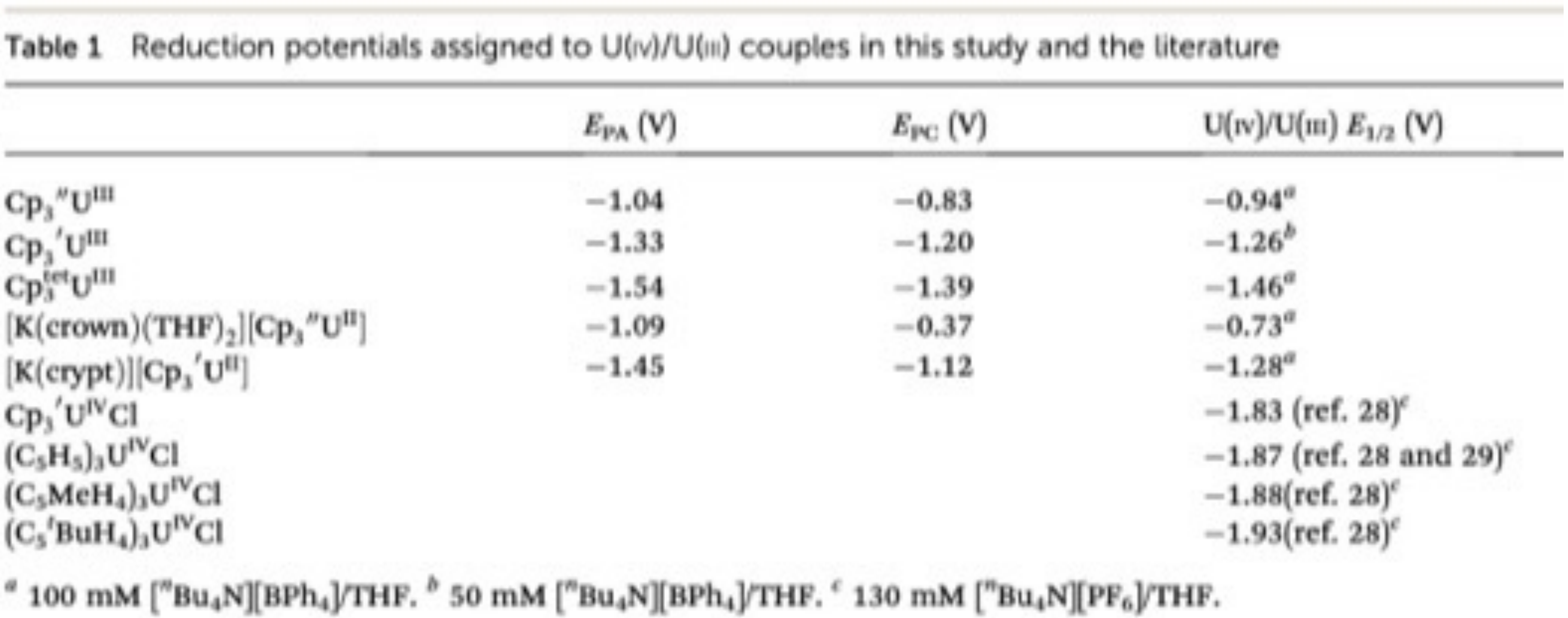


Table 1 Reduction potentials assigned to U(IV)/U(III) couples in this study and the literature

	E_{PA} (V)	E_{PC} (V)	U(IV)/U(III) $E_{1/2}$ (V)
$Cp_3''U^{III}$	−1.04	−0.83	−0.94[a]
$Cp_3'U^{III}$	−1.33	−1.20	−1.26[b]
$Cp_3^{tet}U^{III}$	−1.54	−1.39	−1.46[a]
$[K(crown)(THF)_2][Cp_3''U^{II}]$	−1.09	−0.37	−0.73[a]
$[K(crypt)][Cp_3'U^{II}]$	−1.45	−1.12	−1.28[a]
$Cp_3'U^{IV}Cl$			−1.83 (ref. 28)[c]
$(C_5H_5)_3U^{IV}Cl$			−1.87 (ref. 28 and 29)[c]
$(C_5MeH_4)_3U^{IV}Cl$			−1.88(ref. 28)[c]
$(C_5{}^tBuH_4)_3U^{IV}Cl$			−1.93(ref. 28)[c]

[a] 100 mM $[^nBu_4N][BPh_4]$/THF. [b] 50 mM $[^nBu_4N][BPh_4]$/THF. [c] 130 mM $[^nBu_4N][PF_6]$/THF.

Chem. Sci., 2021, 12, 8501–8511

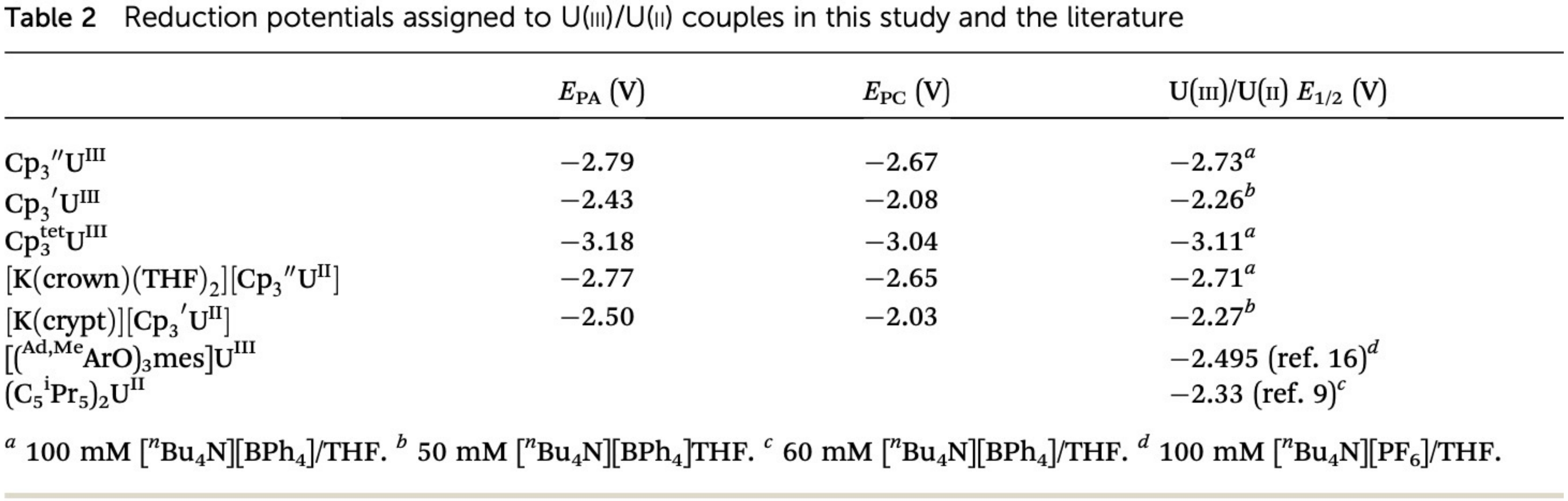


Table 2 Reduction potentials assigned to U(III)/U(II) couples in this study and the literature

	E_{PA} (V)	E_{PC} (V)	U(III)/U(II) $E_{1/2}$ (V)
$Cp_3''U^{III}$	−2.79	−2.67	−2.73[a]
$Cp_3'U^{III}$	−2.43	−2.08	−2.26[b]
$Cp_3^{tet}U^{III}$	−3.18	−3.04	−3.11[a]
$[K(crown)(THF)_2][Cp_3''U^{II}]$	−2.77	−2.65	−2.71[a]
$[K(crypt)][Cp_3'U^{II}]$	−2.50	−2.03	−2.27[b]
$[(^{Ad,Me}ArO)_3mes]U^{III}$			−2.495 (ref. 16)[d]
$(C_5{}^iPr_5)_2U^{II}$			−2.33 (ref. 9)[c]

[a] 100 mM $[^nBu_4N][BPh_4]$/THF. [b] 50 mM $[^nBu_4N][BPh_4]$THF. [c] 60 mM $[^nBu_4N][BPh_4]$/THF. [d] 100 mM $[^nBu_4N][PF_6]$/THF.

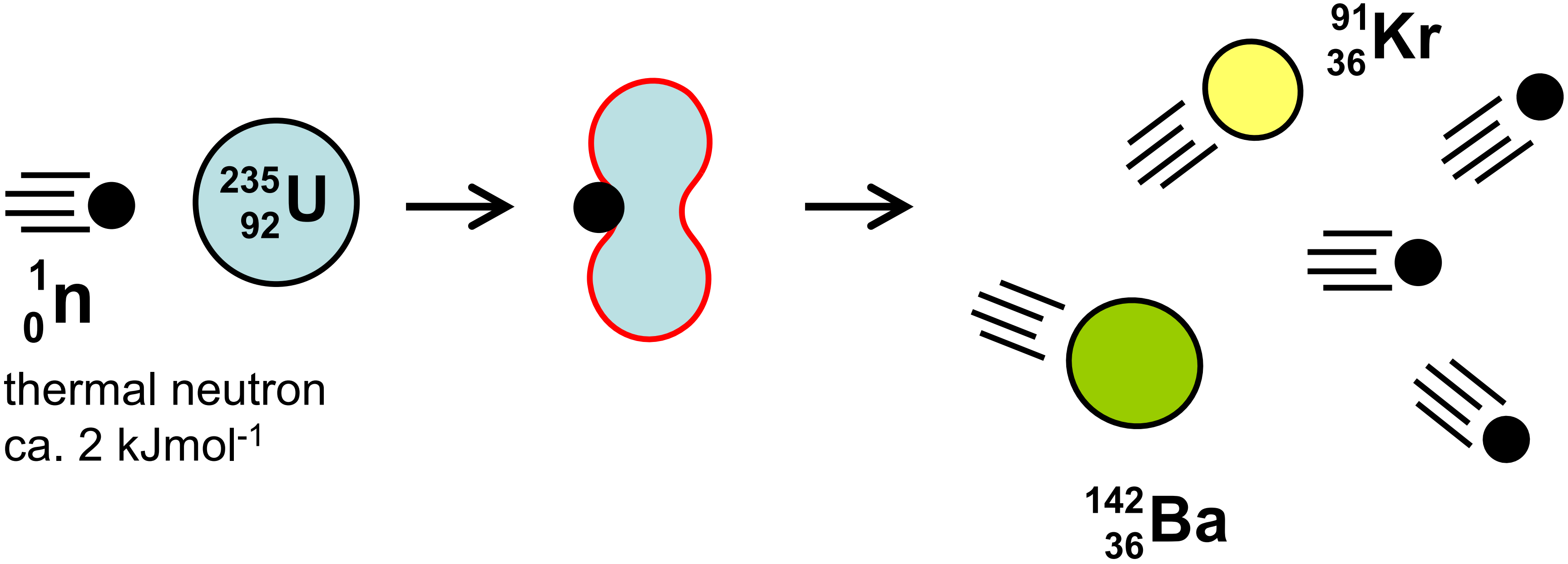
Radioactivity of the actinides

All of the An isotopes are radioactive, mostly α emitters.

Transuranium elements do not occur in sizeable quantities in nature and are commonly synthesized via nuclear reactions conducted with nuclear reactors. For example, under irradiation with reactor neutrons, uranium-238 partially converts to plutonium-239.

Z	El.	A	$t_{1/2}$ (* β^-, EC)	Z	El.	A	$t_{1/2}$
90	Th	232	1.40×10^{10} y	96	Cm	244	18.11 y
91	Pa	231	3.25×10^{4} y	97	Bk	247	1.38×10^{3} y
92	U	235	7.04×10^{8} y	98	Cf	249	351 y
		238	4.47×10^{9} y	99	Es	252	472 d
93	Np	236	1.55×10^{5} y*	100	Fm	257	100.5 d
94	Pu	239	2.41×10^{4} y	101	Md	258	56 d
		244	8.26×10^{7} y	102	No	259	1 h (α + EC)
95	Am	241	4.32×10^{2} y	103	Lr	262	3.6 h

Nuclear fission: discovered in 1938



thermal neutron
ca. 2 kJmol^{-1}

A large nucleus is split into two smaller (and more stable) ones by collision with a thermal neutron. The process releases several neutrons, which in turn collide with other nuclei, initiating the “chain reaction”, provided a “critical mass” exists, i.e. a minimum amount of the fissile product.


Enrico Fermi

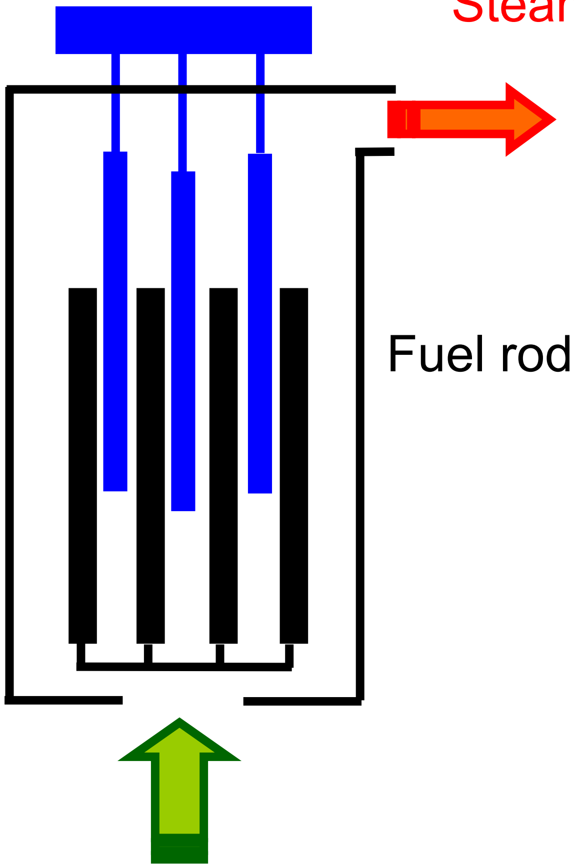

Ida Noddack


Lise Meitner


Otto Hahn

Natural uranium:
U-238 (99.2739–99.2752%)
U-235 (0.7198–0.7202%),
U-234 (0.0050–0.0059%)

Nuclear power generation



Control rods

Steam

Fuel rods

Cooling fluid

(H_2O, D_2O)

Best natural isotope: ^{235}U
Natural abundance: 0.72 %, henceforth the need for enrichment.

Fuel: UO_2 enriched to 2-3% ^{235}U, under the form of pellets stuffed into Zr tubes

Control rods: boron nitride or graphite (absorb neutrons)

The cooling fluid also acts as moderator, slowing down the produced neutrons (boric acid added).

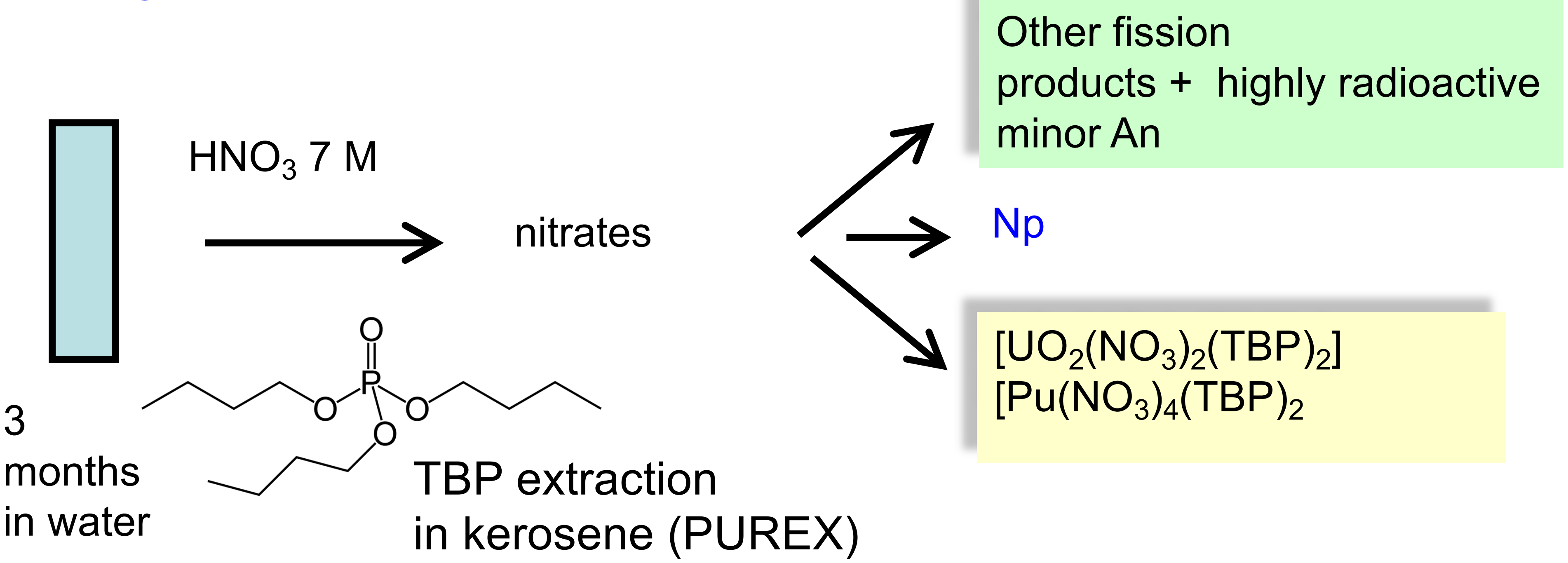
Fuel reprocessing and treatment

^{238}U produces ^{239}Pu, which can also be used as fuel

$$^{238}_{92}U + {}^{1}_{0}n \rightarrow {}^{239}_{92}U \rightarrow {}^{239}_{93}Np + {}^{0}_{-1}e \ (\beta^{-}, t_{1/2} = 24 \text{ min})$$

$$^{239}_{93}Np \rightarrow {}^{239}_{94}Pu + {}^{0}_{-1}e \ (\beta^{-}, t_{1/2} = 2.4 \text{ days})$$

1st stage: extraction of U and Pu



3 months in water

HNO_3 7 M

nitrates

TBP extraction in kerosene (PUREX)

Other fission products + highly radioactive minor An

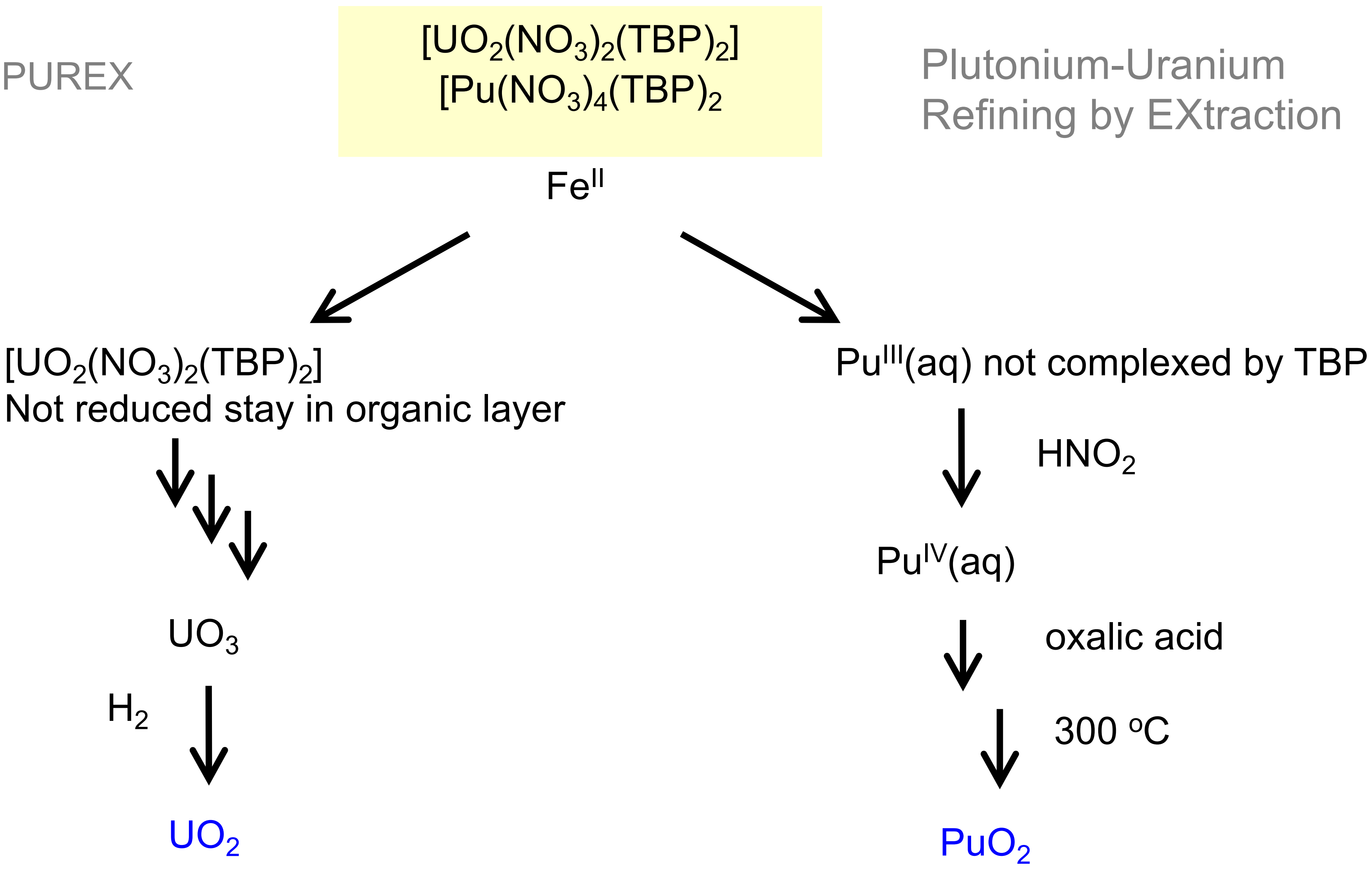
Np

$[UO_2(NO_3)_2(TBP)_2]$
$[Pu(NO_3)_4(TBP)_2$

Fuel reprocessing and treatment

PUREX

Plutonium-Uranium
Refining by EXtraction



$[UO_2(NO_3)_2(TBP)_2]$
$[Pu(NO_3)_4(TBP)_2$

Fe^{II}

$[UO_2(NO_3)_2(TBP)_2]$
Not reduced stay in organic layer

UO_3

H_2

UO_2

$Pu^{III}(aq)$ not complexed by TBP

HNO_2

$Pu^{IV}(aq)$

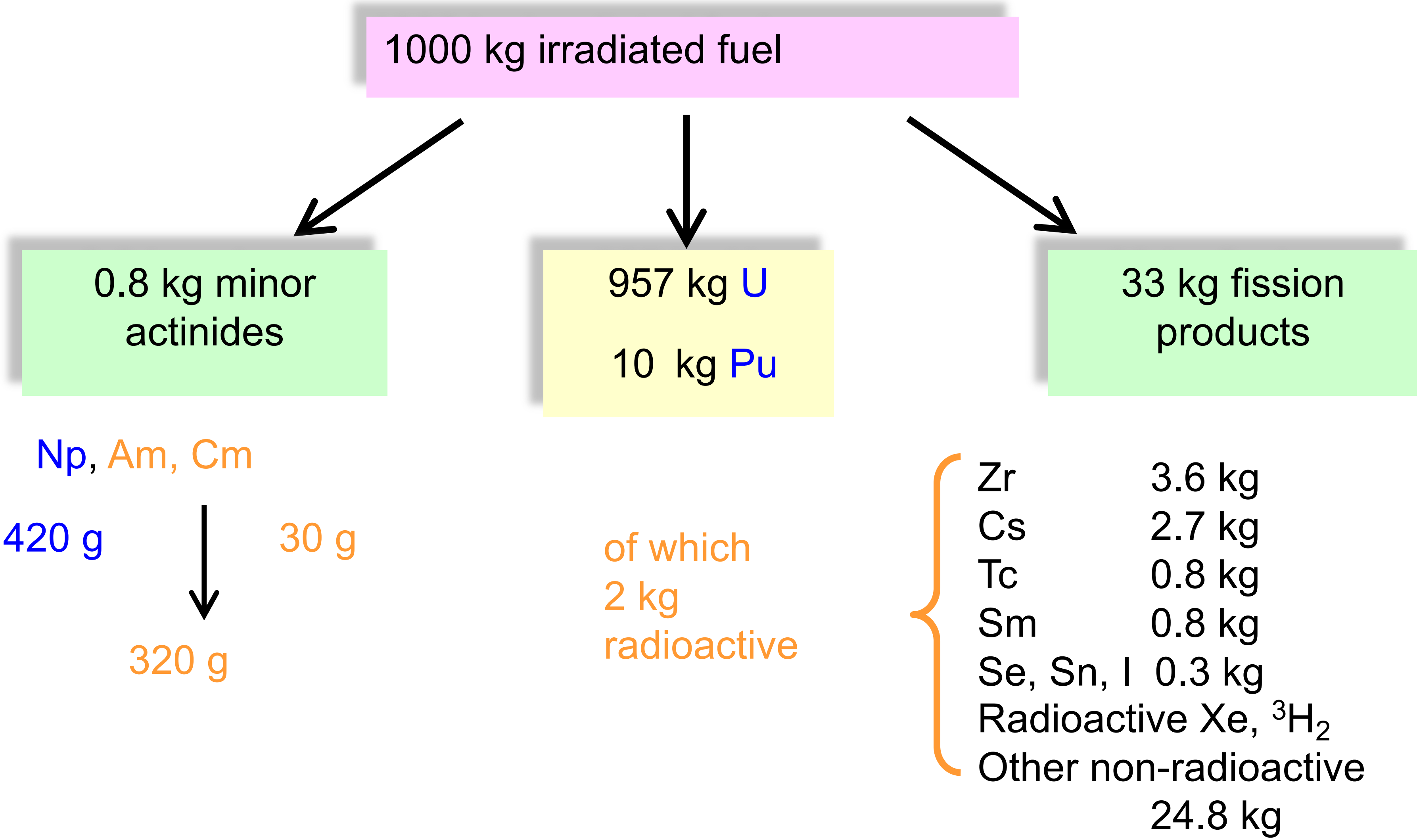
oxalic acid

300 °C

PuO_2

Fuel reprocessing and treatment

2nd stage: separation of radioactive wastes



1000 kg irradiated fuel

0.8 kg minor actinides

957 kg U

10 kg Pu

33 kg fission products

Np, Am, Cm

420 g

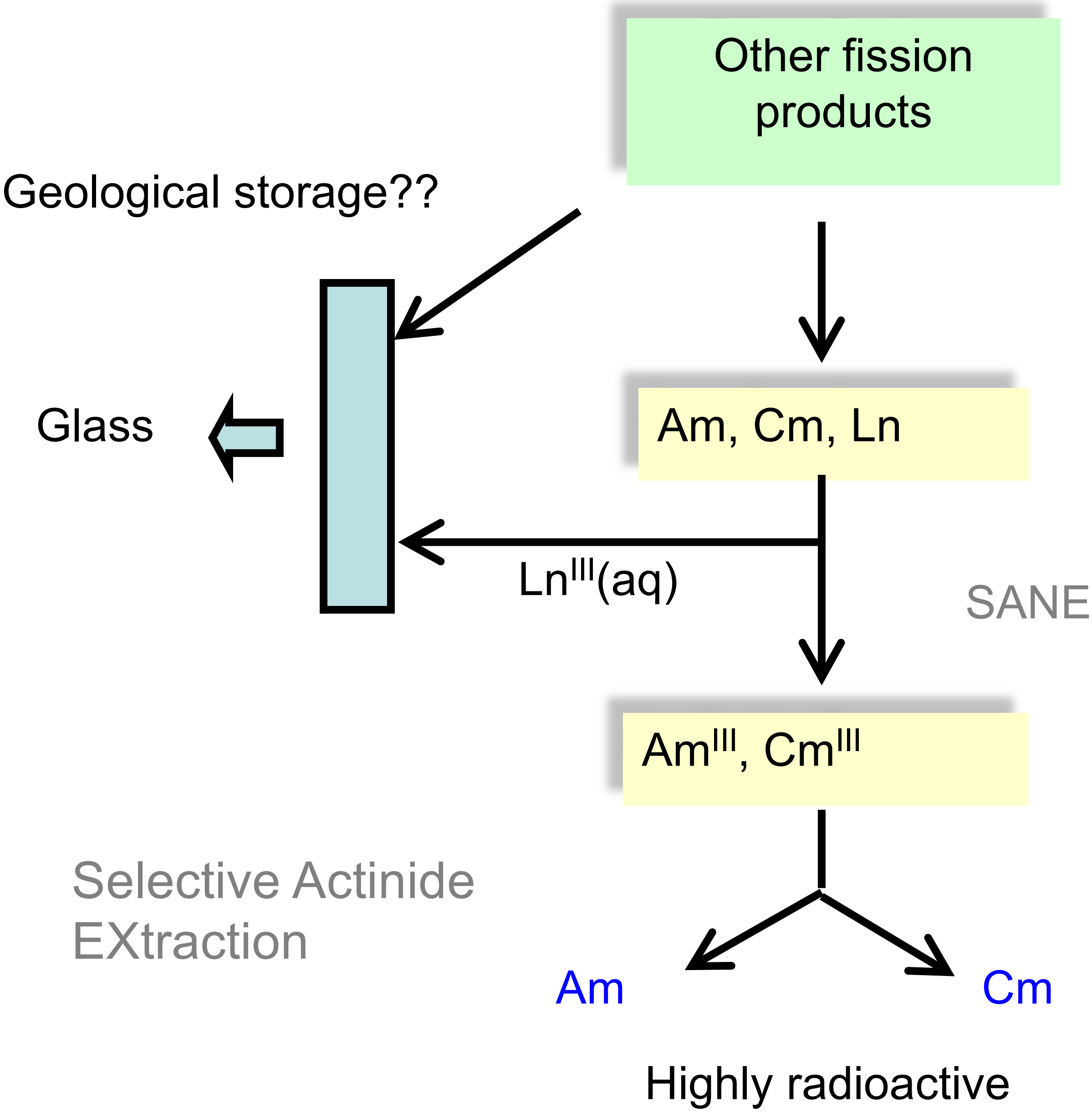
30 g

320 g

of which
2 kg
radioactive

Zr	3.6 kg
Cs	2.7 kg
Tc	0.8 kg
Sm	0.8 kg
Se, Sn, I	0.3 kg
Radioactive Xe, $^3H_2$	
Other non-radioactive	24.8 kg

Fuel Reprocessing or Storage???



Other fission products

Geological storage??

Glass

Am, Cm, Ln

Ln^{III}(aq)

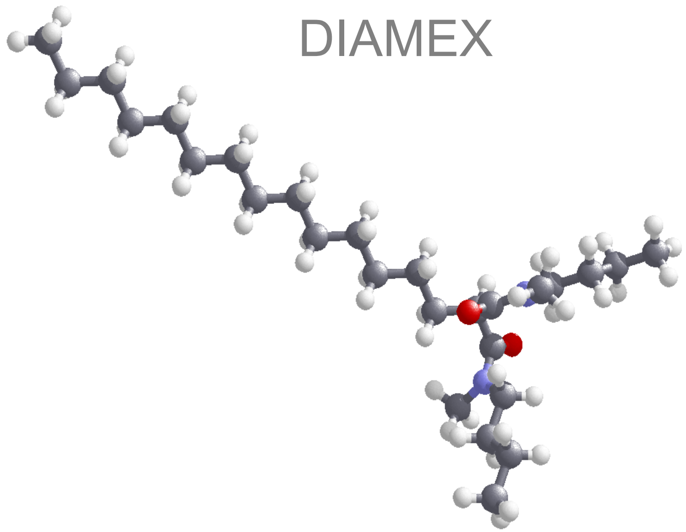
Am^{III}, Cm^{III}

Am

Cm

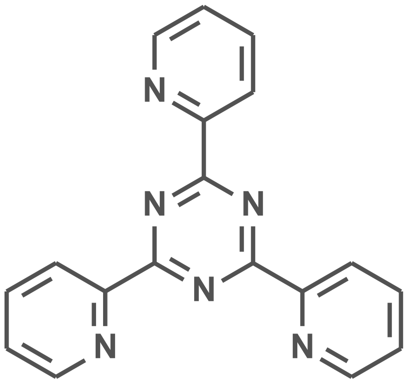
Highly radioactive

Selective Actinide EXtraction



DIAMEX

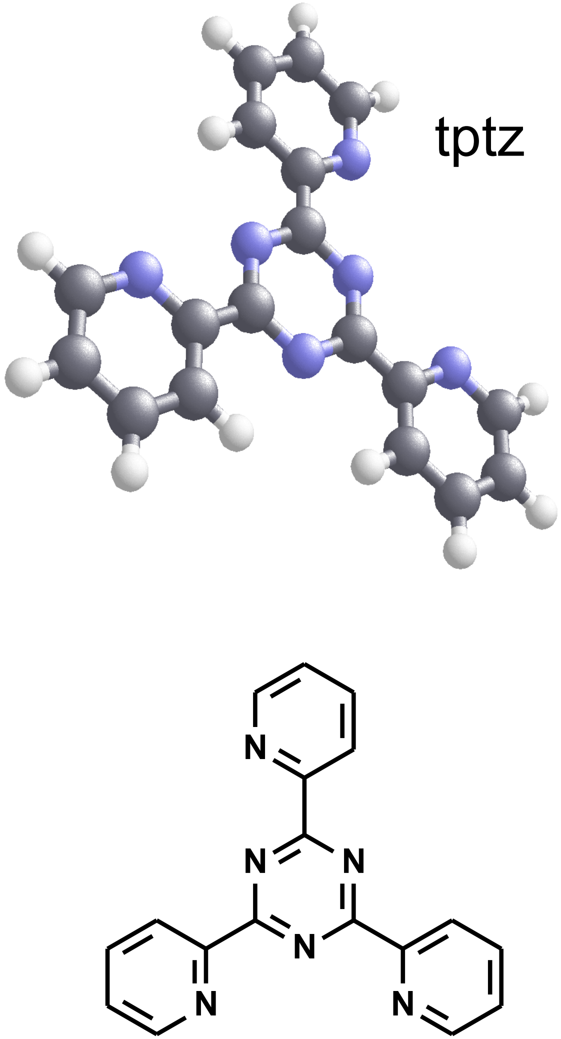
SANEX

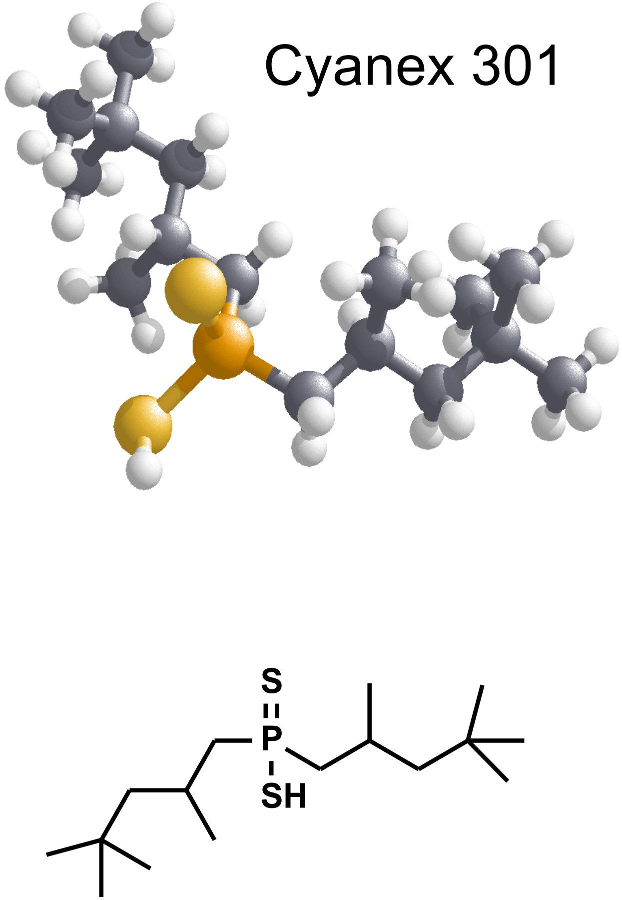


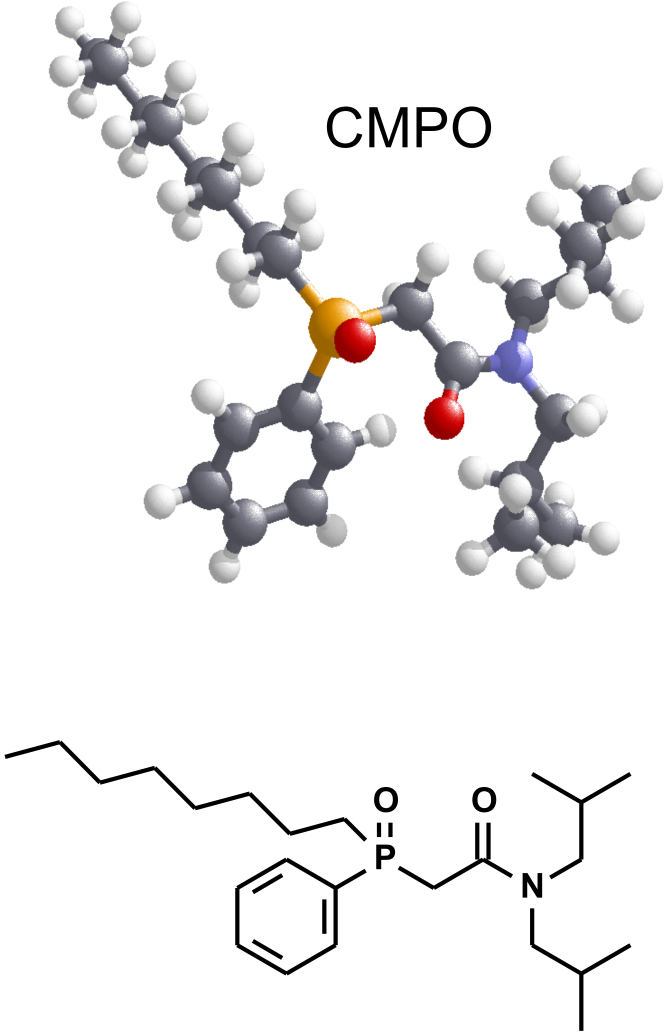
Fuel reprocessing and treatment

Some extraction molecules for An/Ln separation

exploiting the difference in hard/soft behavior


tptz


Cyanex 301


CMPO

Electronic structure of 5f elements

An	Atom [Rn]xxx	An^{3+}	An^{4+}	An	Atom [Rn]xxx	An^{3+}	An^{4+}
Ac	$6d^{1}7s^{2}$	[Rn]	-	Bk	$5f^{9}7s^{2}$	$5f^{8}$	$5f^{7}$
Th	$5f^{0}6d^{2}7s^{2}$	$5f^{1}$	[Rn]	Cf	$5f^{10}7s^{2}$	$5f^{9}$	$5f^{8}$
Pa	$5f^{2}6d^{1}7s^{2}$	$5f^{2}$	$5f^{1}$	Es	$5f^{11}7s^{2}$	$5f^{10}$	$5f^{9}$
U	$5f^{3}6d^{1}7s^{2}$	$5f^{3}$	$5f^{2}$	Fm	$5f^{12}7s^{2}$	$5f^{11}$	$5f^{10}$
Np	$5f^{4}6d^{1}7s^{2}$	$5f^{4}$	$5f^{3}$	Md	$5f^{13}7s^{2}$	$5f^{12}$	$5f^{11}$
Pu	$5f^{6}7s^{2}$	$5f^{5}$	$5f^{4}$	No	$5f^{14}7s^{2}$	$5f^{13}$	$5f^{12}$
Am	$5f^{7}7s^{2}$	$5f^{6}$	$5f^{5}$	Lr	$5f^{14}6d^{1}7s^{2}$	$5f^{14}$	$5f^{13}$
Cm	$5f^{7}6d^{1}7s^{2}$	$5f^{7}$	$5f^{6}$				

Electronic structure of 5f elements

Deciphering the electronic structure needs the use of
an adequate scheme for spin-orbit coupling.

The coupling is much greater than for 4f elements, so that Russel-Saunders scheme does not work.
Interpretation of magnetic and optical data is therefore more difficult than for 4f elements.

Sometimes, however, Russell-Saunders coupling scheme is
used as a first approach.

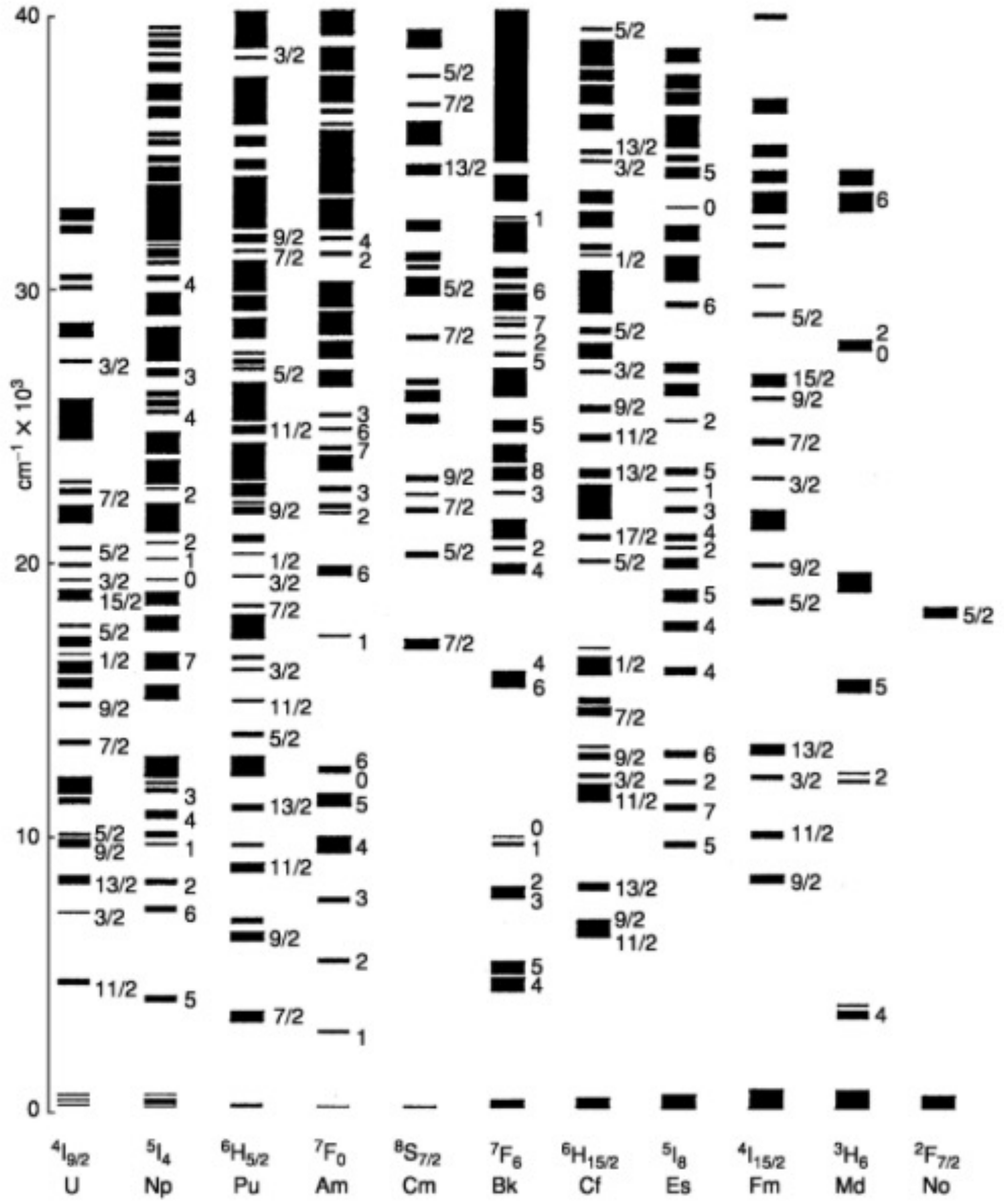
Example: U^{IV}, $5f^2$

Ground level: $^3H_4$
SO levels: $^3H_4$, $^3H_5$, $^3H_6$

Absorption spectra
contain f-f transitions (100-300 $M^{-1}cm^{-1}$) and more intense f-d absorptions (1000-3000 $M^{-1}cm^{-1}$). Higher radial extension of 5f compared to 4f results in more covalent M-L interaction and higher absorption coefficient of f-f transitions.

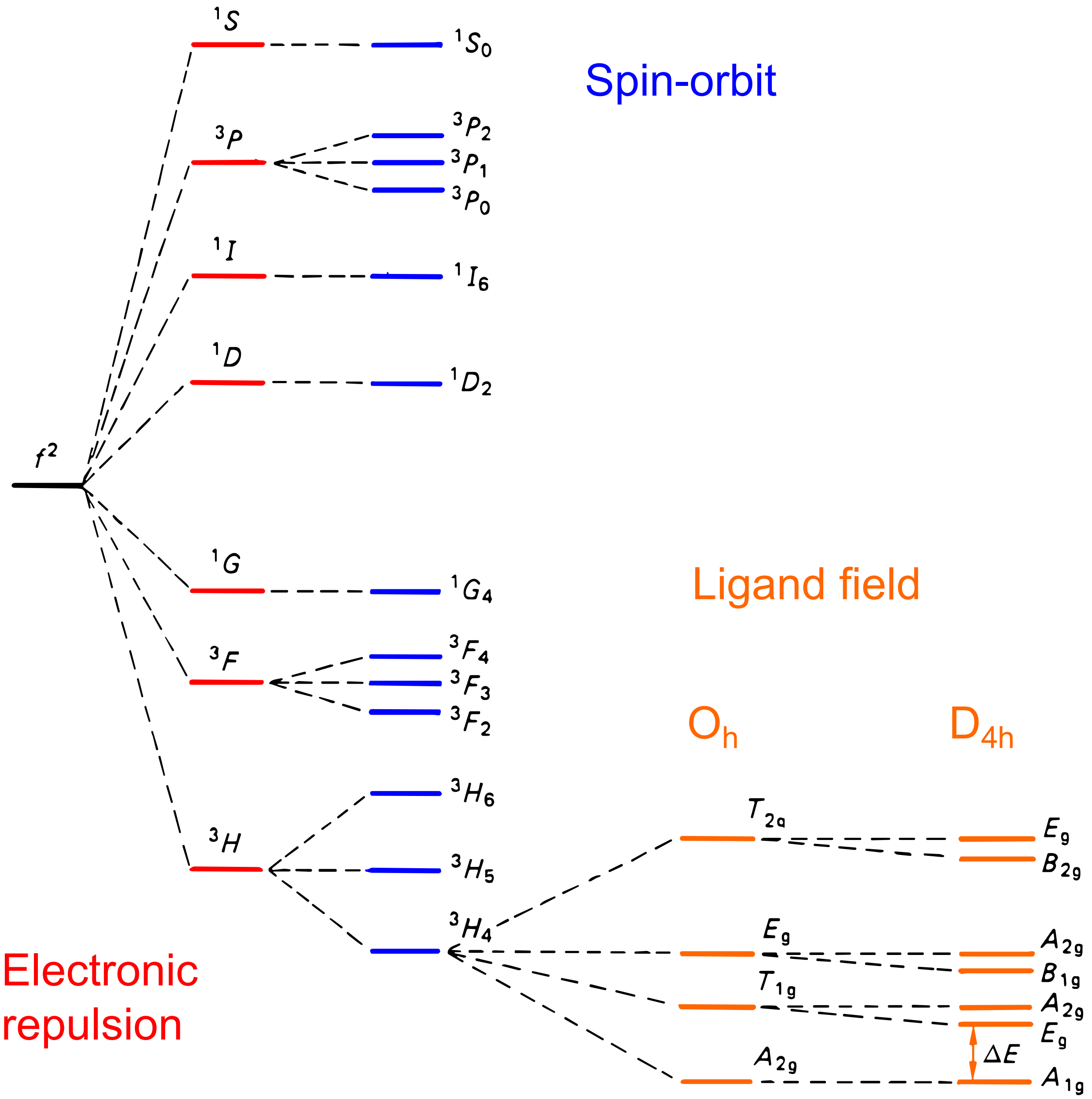
In later An^{3+} (from Bk) the 5f orbitals have lower radial extension and the absorption spectra have narrow lines not affected by ligands as for lanthanides.

Ground States and Excited Levels of An^{3+}



Electronic structure of 5f elements

U^{IV}, $5f^2$



Spin-orbit

Ligand field

O_h

D_{4h}

Electronic repulsion

Absorption Spectra of U^{4+} Complexes

The crystal field is more important for actinides , and therefore the geometry and coordination numbers have an effect on the spectrum

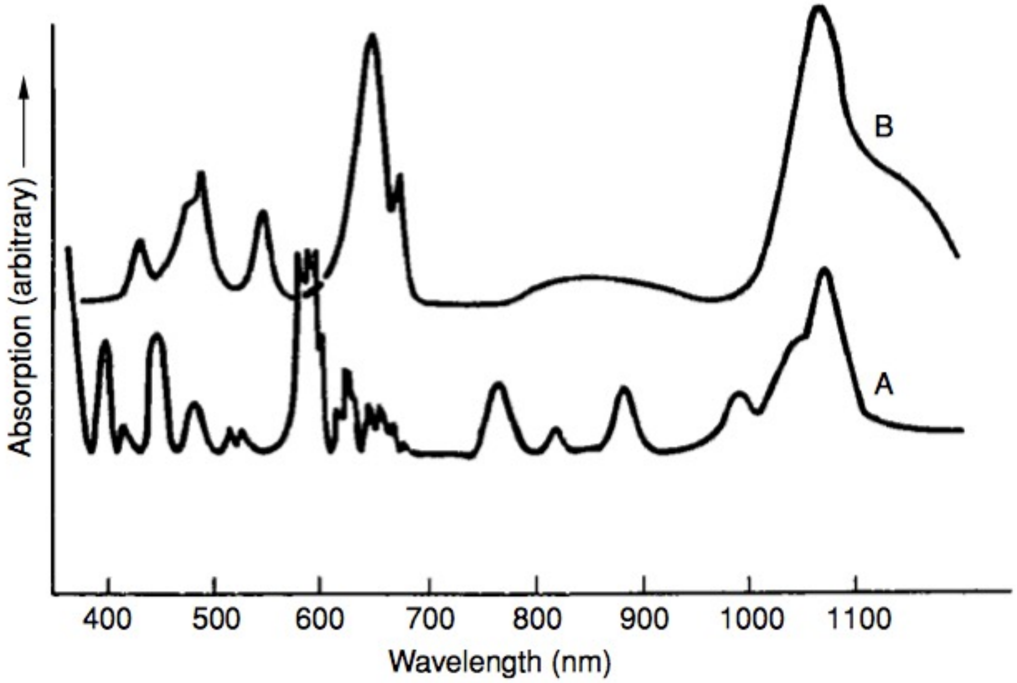
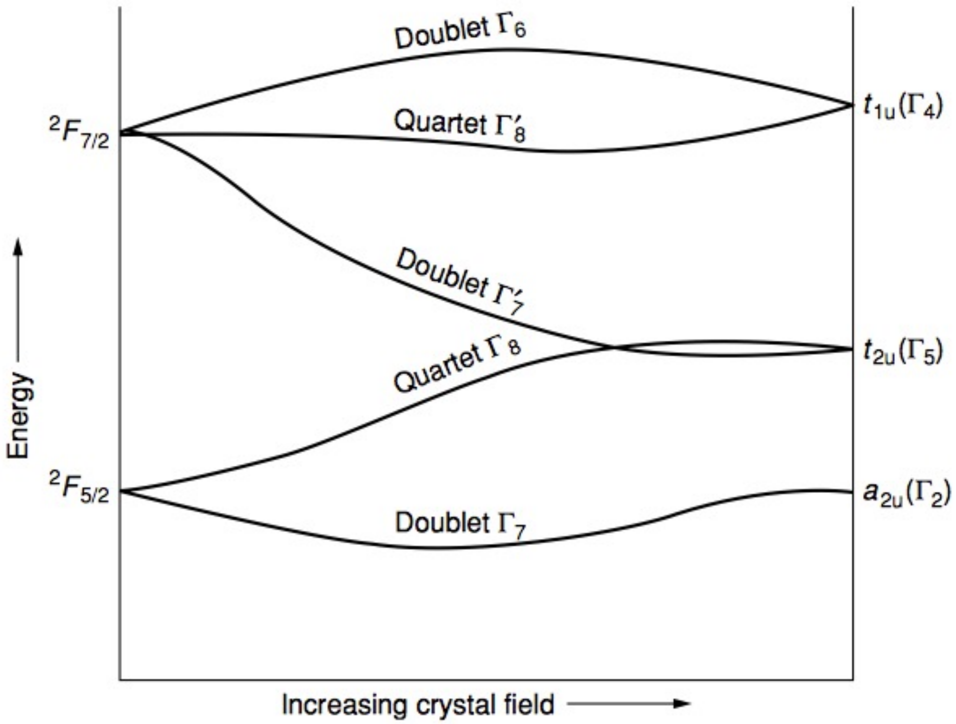


Figure 12.5
The absorption spectra of octahedral $[UCl_6]^{2-}$ (A) and 9–10-coordinate U^{4+}(aq) (B) (redrawn from D.M. Gruen and R.L. Macbeth, *J. Inorg. Nucl. Chem.*, 1959, **9**, 297 and reproduced by permission of Elsevier Science Publishers).

From S. Cotton book

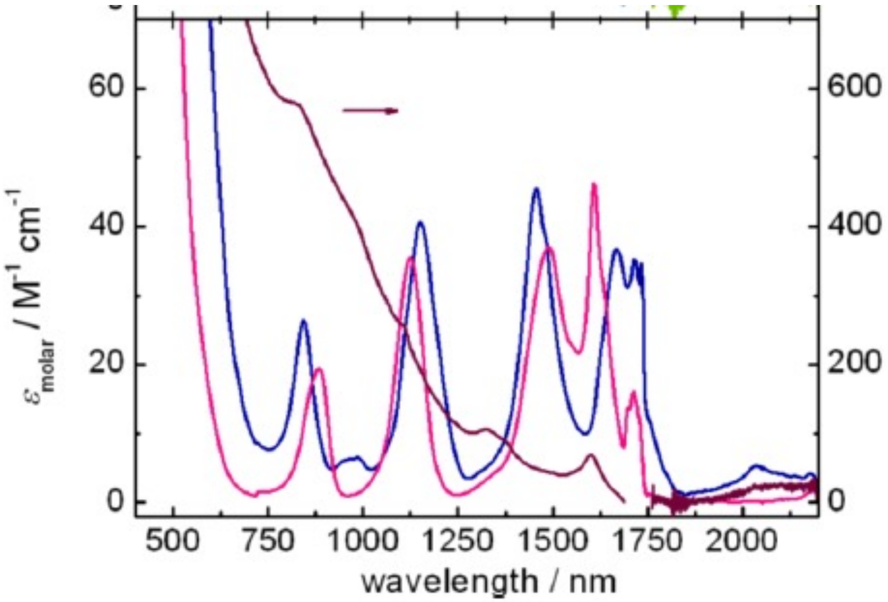
Absorption spectra in U(V)



Generally four lines observed
Between visible and the NIR region

4

5



Meyer 2014

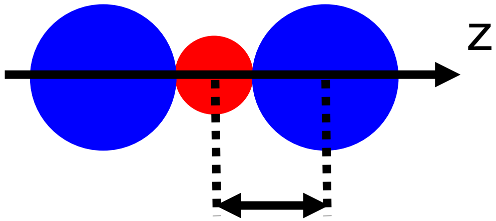
Angew. Chem. Int. Ed. 2015, 54, 8604 –8641

Bonding and spectra of uranyl(VI) moiety

High oxidation state actinides: main compounds halides and “yl complexes”

UF_6, UCl_6, UOF_4, $UOMe_6$, and UO_2^{2+} compounds

Uranyl :



1.7-1.9 Å
very short!

Linear molecule

Vibrational frequencies:
920-990 cm^{-1} ν_{as} IR spectrum
850-900 cm^{-1} ν_s Raman spectrum

U^{VI}-O bond distance similar to $Os^{VI}O_2^{2+}$ but ionic radius 0.2 Å larger

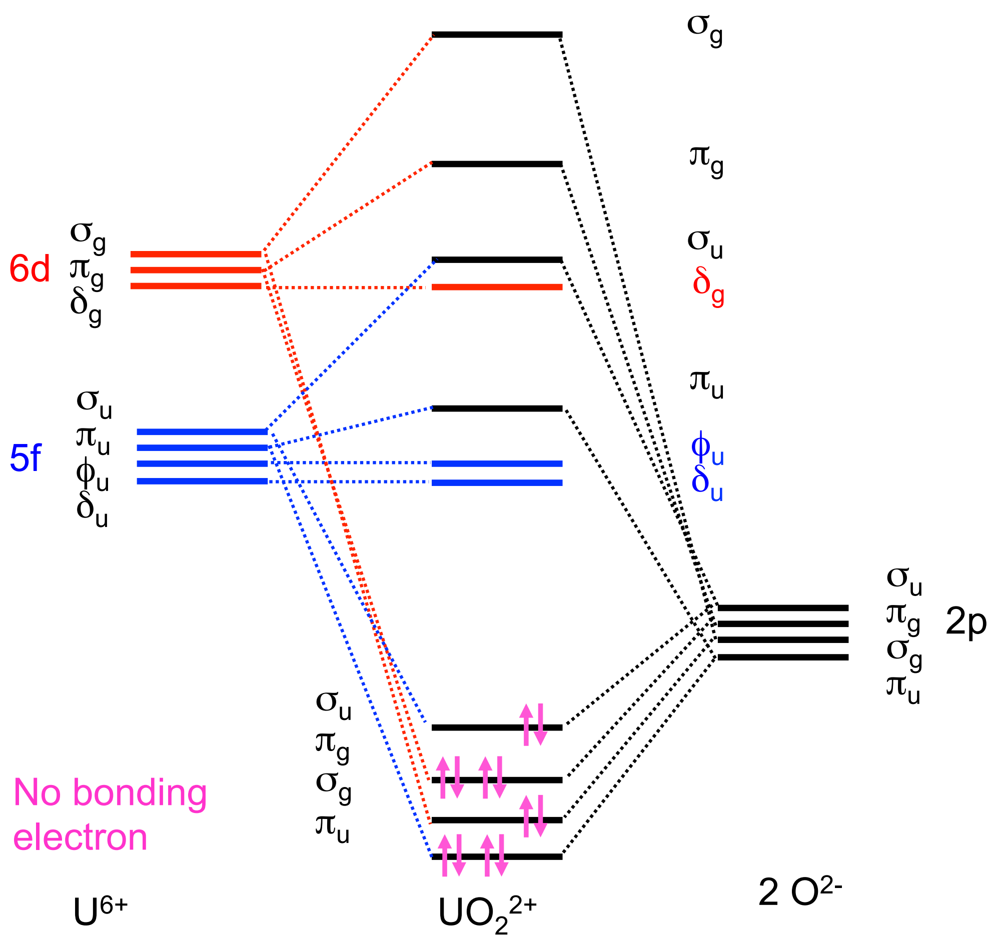
Symmetry $D_{\infty h}$:

The mean U-O bond enthalpy for dissociation to oxygen atoms, is 604 kJ mol^{-1} for UO_2^{2+}(g) and 746 kJ mol^{-1} for UO_2(g), comparable to that for many transition-metal gaseous dioxides.

However, ligands in the equatorial plane are weakly bound and labile (penta of hexacoordinated).

Denning, R. G. *Struct. Bonding* **1992**, *79*, 215-276.

Bonding in uranyl(VI) moiety



UO_2^{2+}
Approximate
MO diagram

Ground state:
$\ldots(\pi_u)^4(\sigma_u)^2$

Excited states:
$\ldots(\pi_u)^4(\sigma_u)^1(\delta_u)^1$
$\ldots(\pi_u)^4(\sigma_u)^1(\phi_u)^1$
$\ldots(\pi_u)^3(\sigma_u)^2(\delta_u)^1$
$\ldots(\pi_u)^3(\sigma_u)^2(\phi_u)^1$
etc.

Triple U-O bond

π bonding more
important
then σ

- The bent structure of MoO_2^{2+} $(5d^0)$ arises from the inability of Mo to use f orbitals (six electrons in d orbitals)
- Stability of AnO_2^{2+} decreases along the series
- Due to weaker overlap of 5f orbitals UO_2^+ tend to disproportionate:
$UO_2^+ = U^{4+} + UO_2^{2+}$

Uranyl(VI) Spectrum

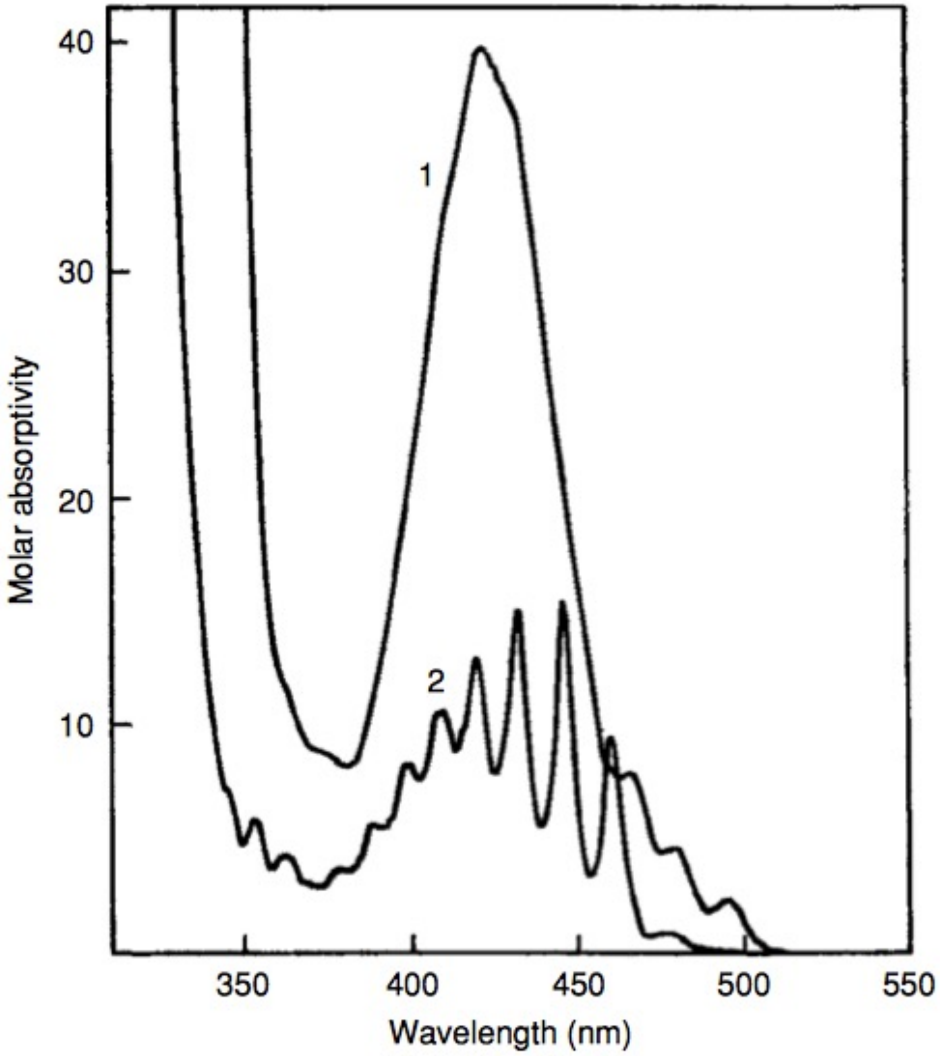
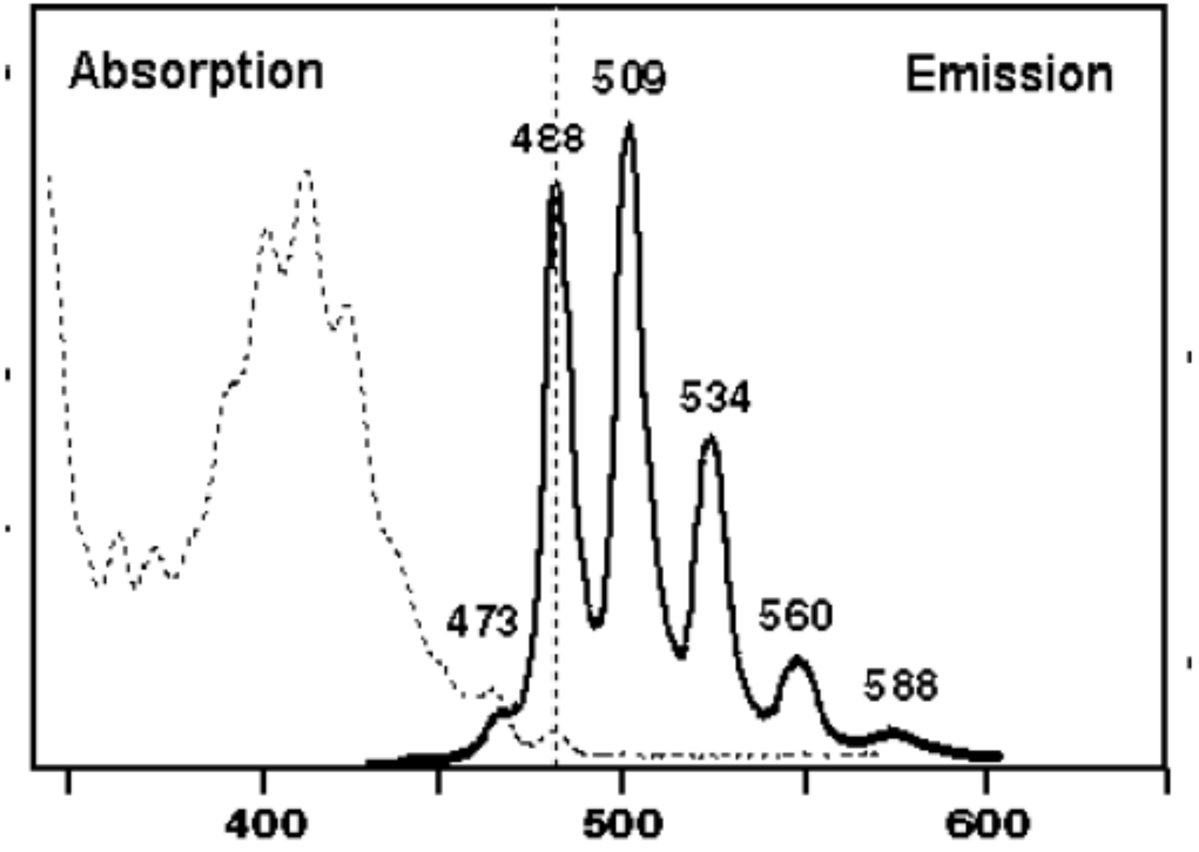


Figure 12.1

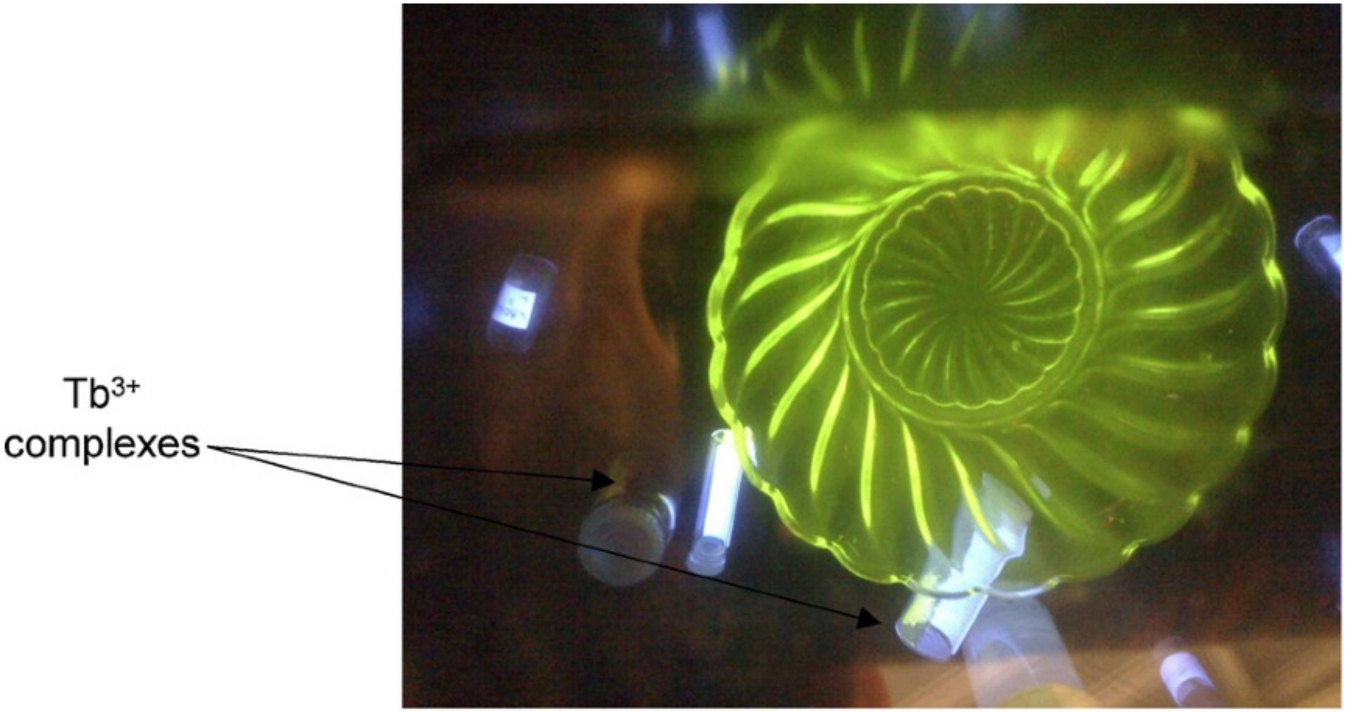
The absorption spectrum of (1) $[UO_2(OAc)_4]^{2-}$ in liquid $Et_4NOAc.H_2O$, showing the lack of vibronic structure, due to hydrogen bonding; (2) $[UO_2(OAc)_3]^-$ in MeCN solution, showing the progression due to the O═U═O stretching vibration (from J.L. Ryan and W.E. Keder, *Adv. Chem. Ser.*, 1967, **71**, 335 and reproduced by permission of the American Chemical Society).

Uranium(VI) Luminescence



- Formally a transition from ‘yl’ bonding orbital (σ_u, σ_g, π_u and π_g) to a non-bonding uranium $5f_\delta$ and $5f_\phi$ orbital
- strong coupling of the ground state symmetric vibrational O=U=O (ν_1) mode with the $^3\Pi_u$ electronic excited state

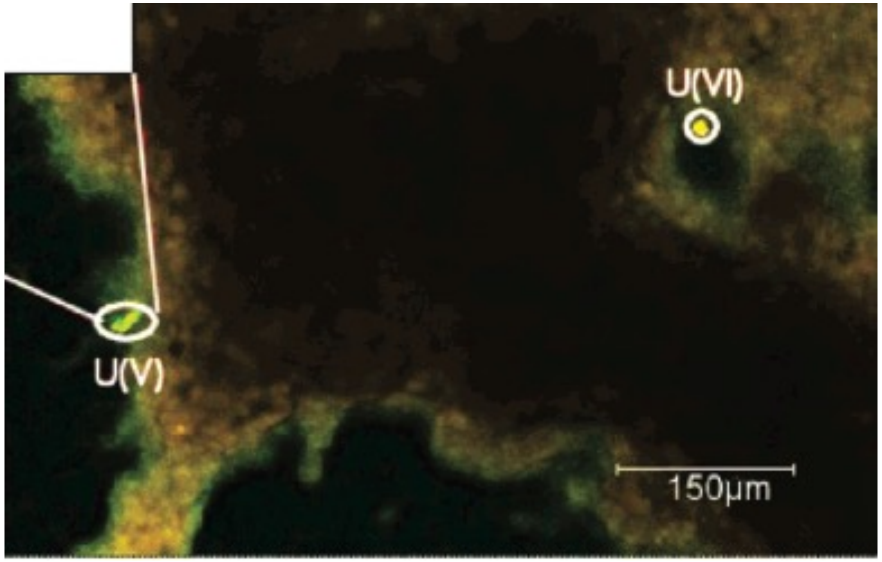
Uranium(VI) Luminescence

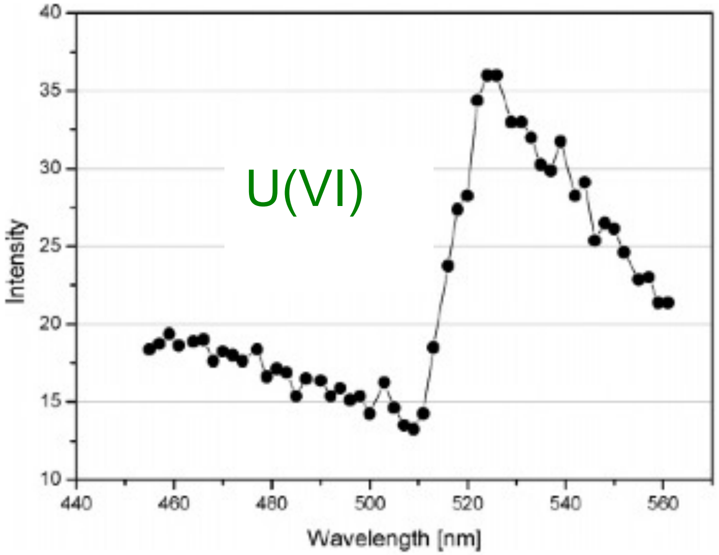


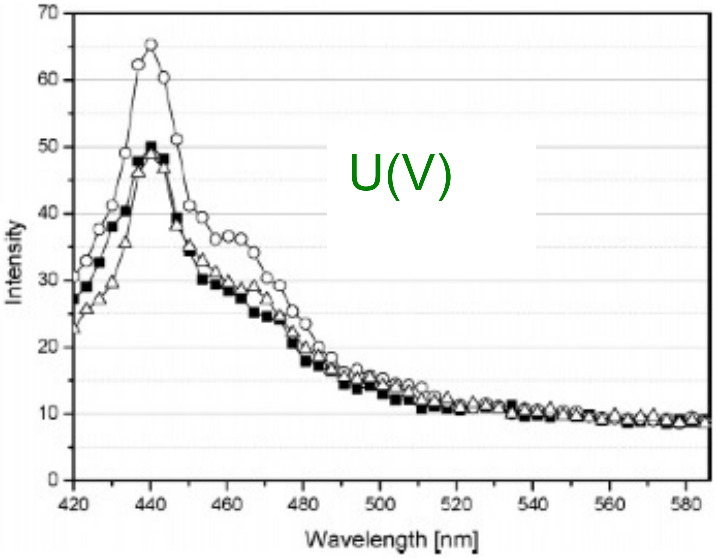
Tb^{3+} complexes

- Formally a Laporte forbidden transition
- Relaxation of selection rule by change in symmetry

Optical Imaging: a tool to investigate uranium biodreduction processes



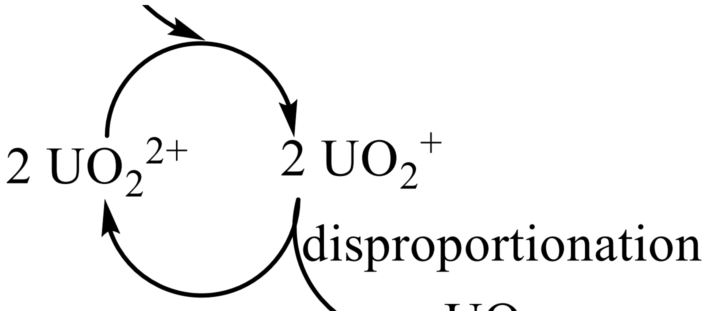


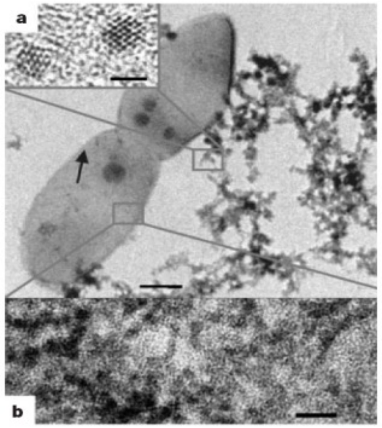


Groβman et al., Environ.Sci.Technol., 2007,41,6498-.-6504.

Bacterial Reduction of Soluble UO_2^{2+} to Insoluble UO_2

Bacteria in anaerobic conditions





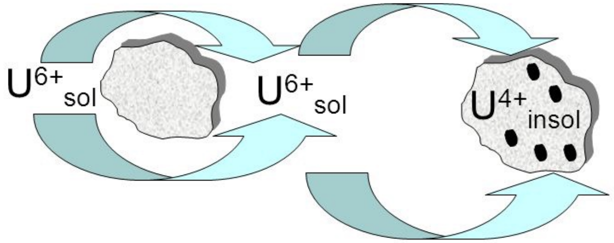
TEM image of floculated uranium nanoparticles

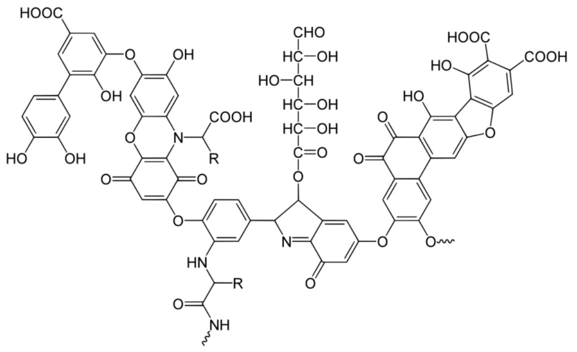
UO_2 produced from bacteria reduction as mobile nanoparticles (size 1.5-2.5 nm) (U-U distance of 0.370 nm).

Livens, May, Lloyd et al *Environ. Sci. Technol.* **2005**

Uranium reduction leads to uranium precipitation and immobilization

$U^{6+}_{sol} \longrightarrow U^{4+}_{insol}$





The U(IV) mobility of in the environment is modified by the presence of aromatic or humic acids in the media

Magnetism

When Russell-Saunders scheme for spin-orbit coupling is valid and when the ground state is pure and well separated from excited states, the following formulae are well adapted to predict the effective magnetic moment:

$$\mu_{eff} = \frac{\sqrt{3RT \cdot \chi_M}}{N_A \cdot \beta} = 2,828\sqrt{\chi_M \cdot T}$$

$$\boxed{\mu_{eff} = \mu_j = g_J\sqrt{(J(J+1)}}$$

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Magnetic moment of actinides

- More complicated behavior: large spin orbit coupling and RS coupling scheme for spin-orbit is not applicable.

- U^{VI} compounds [Rn]$5f^0$ ($^1S_0$) should be diamagnetic, but they often display temperature-independent paramagnetism (TIP) because of the mixing of excited states with the ground state.

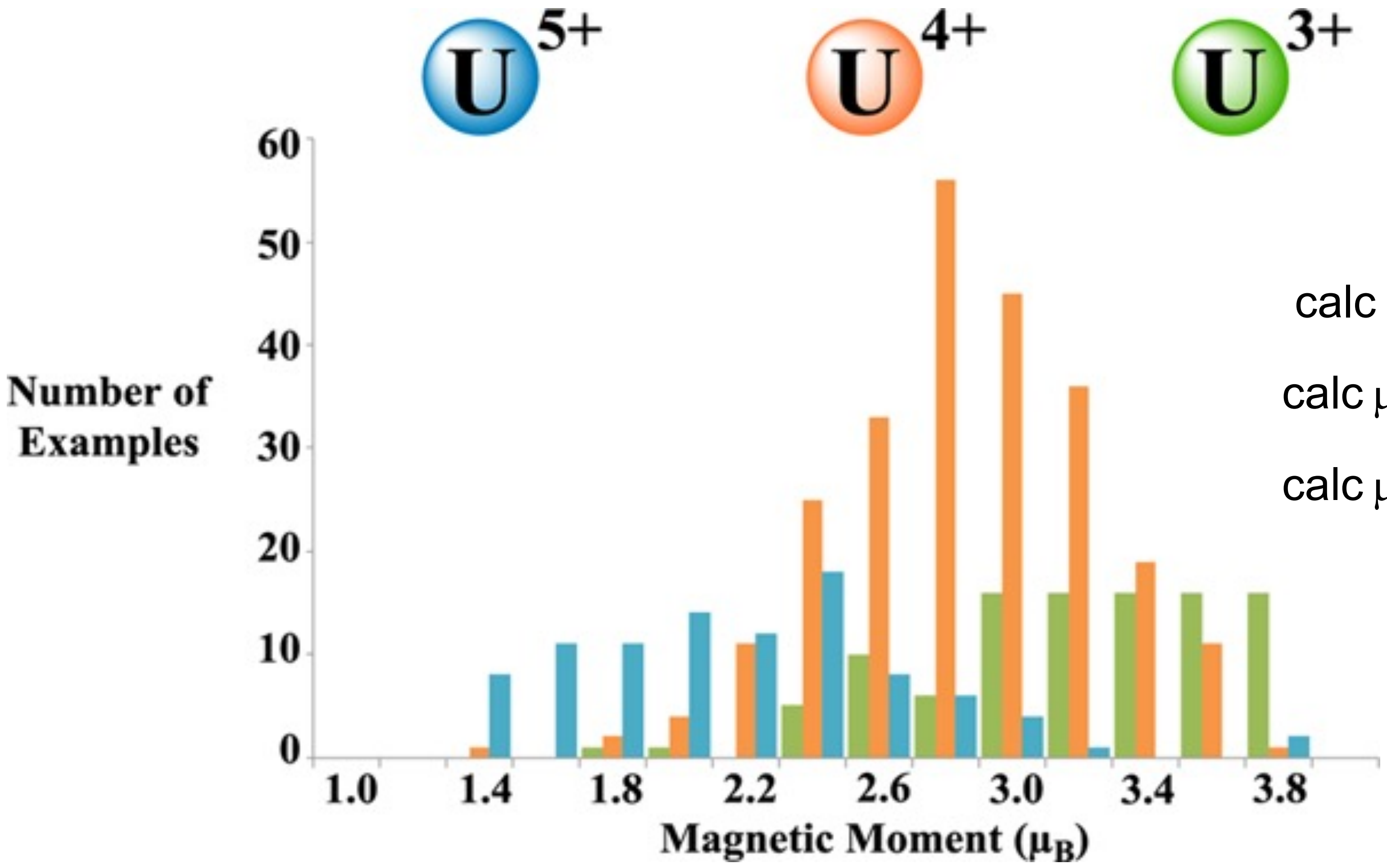
- U^{IV} compounds: [Rn]$5f^2$ ($^3H_4$). Predicted

$$g_J = 1 + (4x5 + 1x2 – 5x6)/2x4x5 = 1-0.2 = 0.8$$

$$\mu_{eff} = 0.8x(4x5)^{1/2} = 3.6\ \ \mu_B$$

measured for $[U(NCS)_8]^{4-}$: 2.9 μ_B

Magnetic Moment of Uranium Compounds



calc $\mu_{j\,U}^{3+}$= 3.62 $\mu_{\mathbf{B}}$

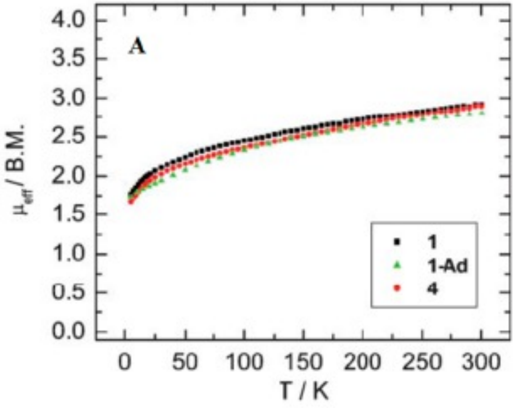
calc $\mu_{j\,U}^{4+}$= 3.58 $\mu_{\mathbf{B}}$

calc $\mu_{j\,U}^{5+}$ = 2.54 $\mu_{\mathbf{B}}$

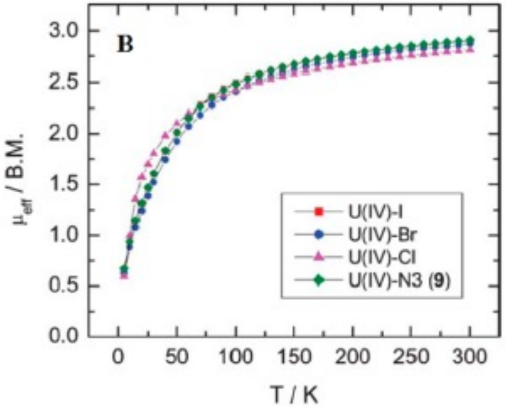
Neither spin-only or spin-orbit coupling approximations are satisfactory

W. Evans Chem. Rev. 2014, 114, 8865−8882

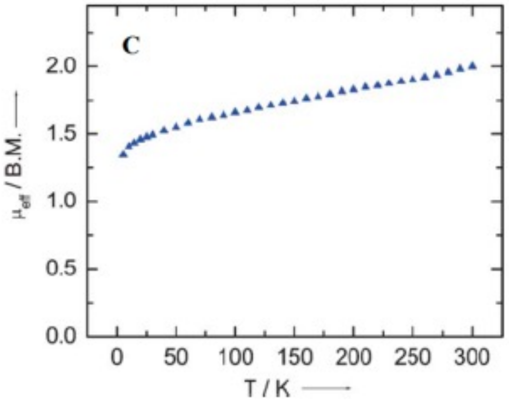
Temperature dependency of the magnetic moment of uranium compounds



U(III)

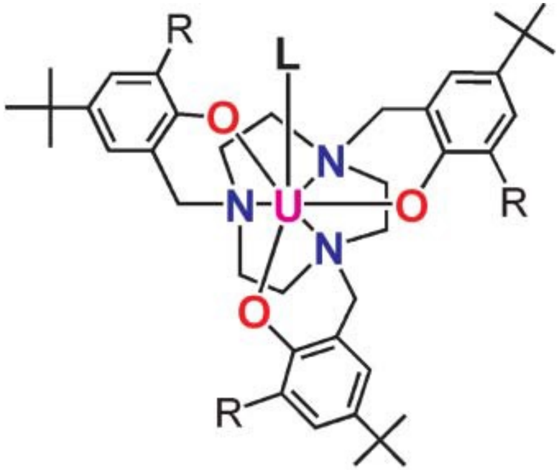


U(IV)



U(V)

$[((AdArO)_3tacn)U(NSi(CH_3)_3)]$



R = t-Bu	**1**	R = Ad	**1-Ad**
L = OAr	**2**	L = CO_2	**7**
μ–O	**3**	N_3	**10**
$NCCH_3$	**4**	$NSiMe_3$	**11**
μ–CO	**5**	NCO	**12**
μ–N_3	**6**	NCNMe	**13**
$NSiMe_3$	**8**	Cl	**14**
$NCPh_3$	**8b**	I	**14b**
NAd	**8c**		
N_3	**9**		

K. Meyer Chem Comm 2006

Summary

-Only few natural occurring actinides

-Importance in nuclear power generation

-Early actinides, intermediate properties between d-block and 4f elements

-Late actinides similar to 4f elements

- A wide range of oxidation states

- -R-S scheme is not a sufficient approximation for actinides*

Note: d-block crystal field dominates (15000-20000 cm-1)
Lanthanides : inter-electron repulsion dominates , spin-orbit becomes significant
Actinides: Crystal field (1000 cm^{-1}) and spin-orbit coupling are appreciable
Inter-electronic repulsion still dominates:
Difficulty in the interpretation of spectroscopic and magnetic properties

-Unique O≡U ≡O bond , involvement of f orbitals , very strong trans bond , high stability
Typical of actinides