4 Reasons why Scandium could be considered as main group 3
1. Sc^{3+} (r = 74 pm) is appreciably smaller than any of the rare earths - behaviour intermediate between the Lanthanides & Aluminium.
2. Sc_2O_3 is more like Al_2O_3 than Ln_2O_3: amphoteric in excess OH^-.
3. ScF_3 dissolves in excess F^- (N.B. scarcity of halogeno complexes for Lanthanides).
4. Anhydrous $ScCl_3$ is easily obtained by P_2O_5-dehydration of hydrated halide, but unlike $AlCl_3$, $ScCl_3$ is not a Friedel-Crafts catalyst.

Scandium may with similarly few exceptions be viewed as a 1st Row Transition Metal
Six-coordinate complexes are typical.
Aqua-ion is $Sc(H_2O)_6^{3+}$ and is susceptible to hydrolysis $\rightarrow$ O-H-bridged dimers...

Some CONTRASTS between Lanthanides & Pre-Transition & Transition Metals

Pre-Transition Metals	Lanthanides	Transition Metals
Essentially Monovalent - show Group (n+) oxidation state	Essentially Monovalent (+3). +2/+4 for certain configs	Show Variable Valence (extensive redox chemistry) control by environment - ligands, pH etc…
Periodic trends dominated by (effective nuclear) charge at noble gas config (i.e. on group valence).	Lanthanide Contraction of Ln^{3+}.	Size changes of M^{n+} less marked.
Similar Properties for a given group (differentiated by size).	Similar Properties (differentiated by size).	Substantial Gradation in Properties.
widespread on earth.	common mineralogy	diverse mineralogy
No Ligand Field Effects.	Insignificant Ligand Field Effects.	Substantial Ligand Field Effects.
Always 'hard' (O, Hal, N donors) (preferably -vely charged)	Always 'hard' (O, X, N donors) (preferably -vely charged)	Later (increasingly from Fe-Cu)/heavier metals may show a 'soft' side.
'Ionic' or 'Covalent' Organometallics	'Ionic' Organometallics.	'Covalent' Organometallics.
No Ligand Effects.	Paucity of Ligand Effects.	π-Acceptor Ligands - Extensive Chemistry.
Poor Coordination Properties (C.N. determined by size).	High Coordination Numbers (C.N. determined by size).	Extensive Coordination C.N. = 6 is typical maximum (but many exceptions).
Flexibility in Geometry.	Flexibility in Geometry.	Fixed (by Ligand Field effects) Geometries.
No Magnetism from the metal ions - noble gas configurations of ions	Free Ion-like Magnetism ground state magnetism	Orbital Magnetism 'Quenched' by Ligand Fields. excited J-states populated.
'Ionic' compound formulations $\rightarrow$ large HOMO-LUMO gaps $\rightarrow$ UV CT spectra	Weak, Narrow Optical Spectra. Forbidden, unfacilitated transitions.	Stronger, Broader Optical Spectra. Forbidden transitions. Vibronically-assisted.

THE ACTINIDES

Naturally Occurring Actinides
- Only Actinium, Thorium, Protactinium & Uranium occur naturally (i.e. Z ≤ 92).
- Actinium & Protactinium occur only in trace amounts.
- Neptunium & Plutonium occur in uranium minerals in minute amounts - not appreciated until after they had been synthesised that the synthesis route might occur naturally!
- All isotopes of all the actinides are radioactive.
- Most of the longer-lived isotopes decay by α-emission.
- Both Thorium and Uranium are far from rare.

Thorium
- Widely dispersed, accounts for > 3ppm of the earth's crust.
- Natural Thorium is essentially 100% ^{232}Th.
- Occurs in monazite [with the rare earths] and in uranothorite [a mixed Th, U silicate].
- Obtained as ThO_2, thoria, from mineral extraction process.
- Used as 99% ThO_2 / 1% CeO_2 in thoria gas mantles.

Uranium
- Widely distributed - found scattered in the faults of old igneous rocks.
- Natural Uranium is 99.27% ^{238}U & 0.72% ^{235}U.

⬥ Obtained usually as UO_2.
⬥ Used for nuclear fuel, and on a smaller scale for colouring glass/ceramics.

Basic Features of Nuclear Structure & Chemistry and Radiochemistry

All Radon isotopes are short half-life α-emitters (but give rise to short-lived β-emitters). Radon gas is derived from Thorium content in granite minerals - hazard in igneous areas.
Actinium and Protactinium occur in uranium ores in trace amounts, because of their participation in Actinium Decay series (from ^{235}U).
Synthesis of Trans-Uranium Elements – **bombardment** techniques.
Are there any **uses** for trans-Uranium elements?

Plutonium:
- ^{239}Pu - produced from ^{238}U by neutron capture in all nuclear reactors.
- Acts as nuclear fuel in fast-breeder reactors.
- Processed for nuclear weapon applications.
- Used as a compact energy source due to the heat from α-decay.
- N.B. α-emission is harmless, unless the emitter is ingested.
- Deep-sea diving suits are heated by ca. 750g of ^{238}Pu
- Combined with PbTe thermoelectric - totally reliable electricity.
- Used in Apollo space missions.
- Human heart pacemakers.

Americium:
- ^{241}Am is used as the α-emission source in smoke alarms

Actinide Metals

Preparation
General method for all Actinides:
Reduction of AnF_3 or AnF_4 with vapours of Li, Mg, Ca or Ba at 1100 - 1400°C
Highly Electropositive.
Typically react with:
- air → tarnishing
- boiling water or dilute acid → releasing Hydrogen
- most non-metals in direct combination

*Structures*
Very dense metals (e.g. U = 19 g cm^{-3}) with distinctive structures, e.g. Plutonium has at least 6 allotropes and forms numerous alloys.

General Observations (comparisons with Lanthanides)

➢ Electronic Configurations of Actinides are not always easy to confirm.

⬥ Atomic spectra of heavy elements are very difficult to interpret in terms of configuration. Competition between $5f^n7s^2$ and $5f^{n-1}6d7s^2$ configurations is of interest.
⬥ For early actinides promotion 5f → 6d occurs to provide more bonding electrons. Much easier than corresponding 4f → 5d promotion in lanthanides.
⬥ Second half of actinide series resemble lanthanides more closely.

➢ 5f orbitals have greater extension wrt 7s and 7p than do 4f relative to 6s and 6p orbitals, e.g. ESR evidence for covalent bonding contribution in UF_3, but not in NdF_3.
➢ 5f / 6d / 7s / 7p orbitals are of comparable energies over a range of atomic numbers, especially U–Am.

- Tendency towards variable valency.
- Greater tendency towards (covalent) complex formation than for lanthanides, including complexation with π-bonding ligands.
- Electronic structure of an element in a given oxidation state may vary between compounds and in solution.
- Often impossible to say which orbitals are being utilized in bonding.

➢ Ionic Radii of ions show a clear "Actinide Contraction"
- Actinide 3+ or 4+ ions with similar radii to their Lanthanide counterparts show similarities in properties that depend upon ionic radius
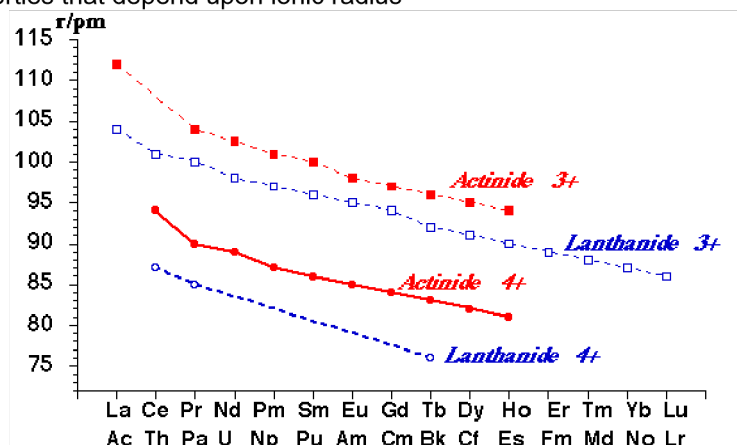
Electronic Spectra

- Narrow bands (compared to transition metal spectra).
- Relatively uninfluenced by ligand field effects.
- Intensities are ca. 10 x those of lanthanide bands.
- Complex to interpret.

Magnetic Properties

- Hard to interpret.
- Spin-orbit coupling is large & Russell-Saunders (L.S) Coupling scheme doesn't work.
- Ligand field effects are expected where 5f orbitals are involved in bonding.

Survey of Actinide Oxidation States

+2

- Unusual oxidation state.
- Common only for the heaviest elements.
- No^{2+} & Md^{2+} are more stable than Eu^{2+}.
- Actinide An^{2+} ions have similar properties to Lanthanide Ln^{2+} and to Ba^{2+} ions.

+3

- The most common oxidation state.
- The most stable oxidation state for all trans-Americium elements (except No).
- Of marginal stability for early actinides Th, Pa, U (But: Group oxidation state for Ac).
- General properties resemble Ln^{3+} and are size-dependent.
- Stability constants of complex formation are similar for same size An^{3+} & Ln^{3+}.
- Isomorphism is common.
- Later An^{3+} & Ln^{3+} must be separated by ion-exchange/solvent extraction.
- Binary Halides, MX_3 easily prepared, & easily hydrolysed to MOX.
- Binary Oxides, M_2O_3 known for Ac, Th and trans-Am elements.

+4

- ➕ Principal oxidation state for Th.
- ➕ Th^{4+} chemistry shows resemblance to Zr^{4+} / Hf^{4+} - like a transition metal.
- ➕ Very important, stable state for Pa, U, Pu.
- ➕ Am, Cm, Bk & Cf are increasingly easily reduced - only stable in certain complexes, e.g. Bk^{4+} is more oxidizing than Ce^{4+}.
- ➕ MO_2 known from Th to Cf (fluorite structure).
- ➕ MF_4 are isostructural with lanthanide tetrafluorides.
- ➕ MCl_4 only known for Th, Pa, U & Np.
- ➕ Hydrolysis / Complexation / Disproportionation are all important in (aq).

+5

- ➕ Principal state for Pa.
- ➕ Pa^{5+} chemistry resembles that of Nb^{5+} / Ta^{5+} - like a transition metal.
- ➕ For U, Np, Pu and Am the AnO_2^+ ion is known (i.e. quite unlike Nb/Ta).
- ➕ Comparatively few other An(V) species are known.
- ➕ e.g. fluorides, PaF_5, NbF_5, UF_5; fluoro-anions, AnF_6^-, AnF_7^{2-}, AnF_8^{3-}.
- ➕ e.g. oxochlorides, $PaOCl_3$, $UOCl_3$; uranates, $NaUO_3$.

+6

- ➕ AnO_2^{2+} ions are important for U, Np, Pu, Am.
- ➕ UO_2^{2+} is the most stable.
- ➕ Few other compounds e.g. AnF_6 (An = U, Np, Pu), UCl_6, UOF_4 etc..., $U(OR)_6$.

+7

- ➕ Only the marginally stable oxo-anions of Np and Pu, e.g. AnO_5^{3-}.

Actinide Aqueous Chemistry

- ➢ Latimer & Frost Diagrams for elements in acid & alkaline (aq) indicate actinides are quite electropositive.
- ➢ Pa - Pu show significant redox chemistry, e.g. all 4 oxidation states of Pu can co-exist in appropriate conditions in (aq).
- ➢ Stability of high oxidation states peaks at U (Np).
- ➢ An^{3+} is the maximum oxidation state for (Cf)Es – Lr.
- ➢ No^{2+}(aq) is especially stable ~ most stable state for No in (aq).
- ➢ Redox potentials show strong dependence on pH (data for Ac - Cm).
- ➢ High oxidation states are more stable in basic conditions.
- ➢ Even at low pH hydrolysis occurs - formation of polymeric ions. When hydrolysis leads to precipitation measurement of potentials is difficult, e.g. Pa^{5+} hydrolyses easily; potentials that indicate it to be the most stable oxidation state are recorded in presence of F^- or $C_2O_4^{2-}$.
- ➢ Tendency to disproportionation is particularly dependent on pH, e.g. at high pH $3Pu^{4+} + 2H_2O \Leftrightarrow PuO_2^{2+} + 2Pu^{3+} + 4H^+$.
- ➢ Early actinides have a tendency to form complexes - complex formation influences reduction potentials, e.g. Am^{4+}(aq) only exists when complexed by fluoride (15 M NH_4F(aq)).
- ➢ Radiation-induced solvent decomposition produces H• and OH• radicals, which lead to reduction of higher oxidation states e.g. Pu V/VI, Am IV/VI

Actinide Stereochemistries

Actinide Stereochemistries show similarities with the Lanthanides. High coordination numbers, e.g. $[Th(NO_3)_6]^{2-}$ has distorted icosahedral (C.N. = 12) geometry, and C.N. = 8, 9 are very common UF_8^{2-}, $Th(S_2CNEt_2)_4$

Distortions from idealised stereochemistries
e.g. PuF_6^{2-} is not octahedral, but widest range of stereochemistries is for An(IV) rather than An(III), possibly because chemistry of early actinides has received most attention!

Complexes
A wide range of complexes with monodentate and chelating ligands.
Complexing ability:- $[M^{5+}] > M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$

Geometry may be strongly influenced by covalent bonding effects, e.g. MO_2^{2+} unit is always linear
➔ $UO_2(\eta^2\text{-}NO_3)_2(H_2O)_2$ is hexagonal bipyramidal.

Compounds: Actinide Hydrides, Halides, Oxides, Oxyhalides ...
  ⵙ For a given oxidation state show similarly diverse C.N. to Lanthanides.
  ⵙ Different accessible oxidation states - even greater diversity of structure.
  ⵙ Wide variety of oxidation states of ligands & number of oxidation states.
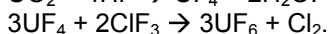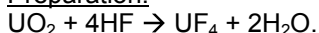 ⵙ Extraordinary range of stereochemistry in actinide complexes and compounds.

Uranium Chemistry

Halides
Fluorides
UF_6 - the most important fluoride.

Preparation:
$UO_2 + 4HF \rightarrow UF_4 + 2H_2O$.
$3UF_4 + 2ClF_3 \rightarrow 3UF_6 + Cl_2$.
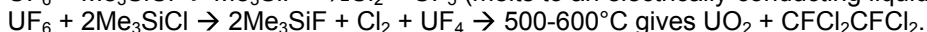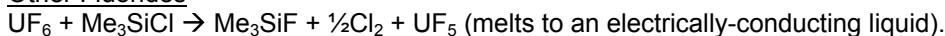
Properties:
mp. 64°C, vapour pressure = 115 mmHg at 25°C.
Made on a large scale to separate uranium isotopes.
Gas diffusion or centrifugation separates $^{235}UF_6$ from $^{238}UF_6$.
Uranium richer in ^{235}U is termed enriched, richer in ^{238}U is depleted.
Powerful **fluorinating** agent.

Other Fluorides
$UF_6 + Me_3SiCl \rightarrow Me_3SiF + \frac{1}{2}Cl_2 + UF_5$ (melts to an electrically-conducting liquid).
$UF_6 + 2Me_3SiCl \rightarrow 2Me_3SiF + Cl_2 + UF_4 \rightarrow$ 500-600°C gives $UO_2 + CFCl_2CFCl_2$.
Mixed-Valence fluorides such as U_2F_9 also form.
Reduction of UF_4 with $\frac{1}{2}H_2$ yields UF_3.

Chlorides
UCl_4 – is the usual starting material for the synthesis of other U(IV) compounds.

Preparation:
Liquid-phase chlorination of UO_3 by refluxing hexachloropropene.

Properties:
Soluble in polar organic solvents & in water.
Forms various adducts (2 - 7 molecules) with O and N donors.

UCl_3
Usually encountered as $UCl_3(thf)_x$ (a rather intractable material).
Unsolvated binary gives its name to the UCl_3 structure!

Actinide trihalides form a group with strong similarities (excepting redox behaviour) to the Lanthanides.

<u>UCl$_6$</u>
From chlorination of U$_3$O$_8$ + C.
Highly oxidising.
Moisture-sensitive : UCl$_6$ + 2H$_2$O $\rightarrow$ UO$_2$Cl$_2$ (Uranyl Chloride) + 4HCl.
In CH$_2$Cl$_2$ solution UCl$_6$ decomposes to U$_2$Cl$_{10}$ (Mo$_2$Cl$_{10}$ structure).

Halogeno Complexes
All Halides can form halogeno complexes, but F$^-$ and Cl$^-$ are best-known.

Occurrence:
U(III): UCl$_5$$^{2-}$, U$_2Cl_7$$^{2-}$ and UCl$_4$$^-$.
U(IV): UF$_7$$^{3-}$ and UF$_8$$^{4-}$ are common, UF$_6$$^{2-}$ and UCl$_6$$^{2-}$ are also known. Also pseudohalide complexes, e.g. [U(NCS)$_8$]$^{4-}$.
U(V): U(V) is usually unstable in (aq), but UF$_5$ in 48% HF $\rightarrow$ M+UF$_6$$^-$ (M$^+$ = Rb$^+$, Cs$^+$, H$_3$O$^+$) salts
U(VI): UF$_7$$^-$ and UF$_8$$^{2-}$ are known, the latter is more thermally-stable.

Hydrides
Principal Uranium Hydride is UH$_3$ – important as a source material for U(III) and U(IV) chemistry.

Oxides
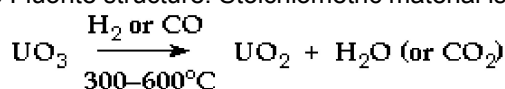Many binary phases UO$_x$ have been reported.
Many are not genuine phases.
Genuine phases show range of O-content.
The most important genuine phases are UO$_2$, U$_4$O$_9$, U$_3$O$_8$, UO$_3$.

<u>UO$_2$ & U$_4$O$_9$</u>
UO$_2$ (black-brown) has the Fluorite structure. Stoichiometric material is best obtained from:

$$UO_3 \xrightarrow[\text{300–600°C}]{\text{H}_2 \text{ or CO}} UO_2 + H_2O \text{ (or CO}_2\text{)}$$

Interstitial Oxide Ions may be incorporated into the structure - UO$_{2+x}$.
Neutron Diffraction studies indicate oxide vacancies in the normal fluorite lattice.
At UO$_{2.25}$ (U$_4$O$_9$) (black) - interstitials are ordered forming a distinct phase in the phase diagram.

<u>U$_3$O$_8$ & UO$_3$</u>
U$_3$O$_8$ is dark green.
conveniently made by heating uranyl nitrate or ethanoate in air.

$$3UO_2(NO_3)_2 \xrightarrow[\text{650–800°C}]{\text{O}_2} U_3O_8 + 6NO_2 + 2O_2$$
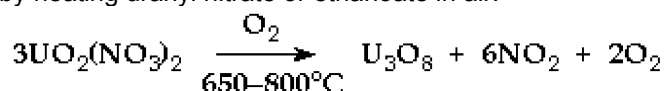
> 650°C Higher uranium oxides decompose to U$_3$O$_8$.
> 800°C loses U$_3$O$_8$ oxygen.

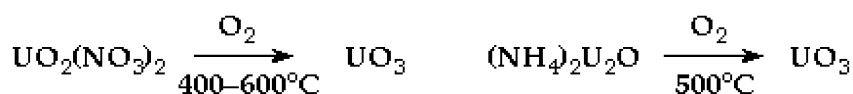Structure:
Mixed oxide - average oxidation state U$_{5.33}$.
Evidence suggests Class II/III mixed valence.
All U atoms have essentially identical environments.
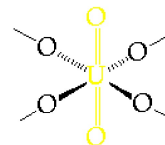Contains pentagonal bipyramidal UO$_7$ units.

UO$_3$ is orange-yellow.
Produced by a variety of methods:

$$UO_2(NO_3)_2 \xrightarrow[\text{400–600°C}]{\text{O}_2} UO_3 \qquad (NH_4)_2U_2O \xrightarrow[\text{500°C}]{\text{O}_2} UO_3$$

Structure:
> 6 modifications have been characterised.
Most contain O=U=O 'uranyl' groups linked by 4x equatorial bridging O - distorted octahedral environments.
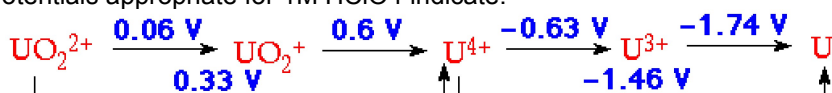

Uranates

Fusion of uranium oxides with alkali or alkaline earth carbonates – orange/yellow/brown mixed-oxides, Uranates.

Aqueous Chemistry
Complex aqueous chemistry due to extensive possibilities for complexation, hydrolytic reactions, often leading to polymeric ion species.

Reduction Potentials appropriate for 1M HClO4 indicate:

$$UO_2^{2+} \xrightarrow{0.06\ V} UO_2^{+} \xrightarrow{0.6\ V} U^{4+} \xrightarrow{-0.63\ V} U^{3+} \xrightarrow{-1.74\ V} U$$

$$UO_2^{2+} \xrightarrow{\hspace{1cm} 0.33\ V \hspace{1cm}} U^{4+} \xrightarrow{\hspace{1cm} -1.46\ V \hspace{1cm}} U$$

U^{3+}
Powerful reducing agent, reduces H_2O to H_2 (solutions in 1M HCl stable for days).
Obtained by reduction of UO_2^{2+} electrolytically or with Zn/Hg.

U^{4+}
Only slightly hydrolysed in 1M acid solution $U^{4+} + H_2O \Leftrightarrow U(OH)^{3+} + H^{+}$.
But, it can give rise to polymeric species in less acid solutions.
Regarded as a 'stable' oxidation state of uranium in (aq).

$UO_2^{\pm}$
Extremely unstable to disproportionation.
Evidence for its existence in (aq) from stopped-flow techniques.
More stable in DMSO (half-life ~ 30 mins).

UO_2^{2+}
The Uranyl ion.
Very stable, and forms many complexes.
A dominant feature of uranium chemistry.
Reduced to U^{4+} by e.g. Zinc, Cr^{2+}
Re-oxidation by $H_2^{18}O_2 \rightarrow U^{18}O_2^{2+}$
Re-oxidation by $^{18}O_2 \rightarrow U(^{18}O^{16}O)^{2+}$

Linear, symmetrical $(O=U=O)^{2+}$ structure.

Why is it trans linear, whereas WO_2^{2+} is cis, bent?
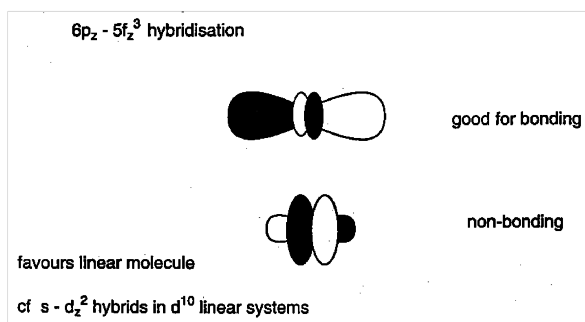WO_2^{2+} ($6d^0$) is cis bent because it allows π-donation from the 2 O to 2 independent d-orbitals, with a single d-orbital shared.
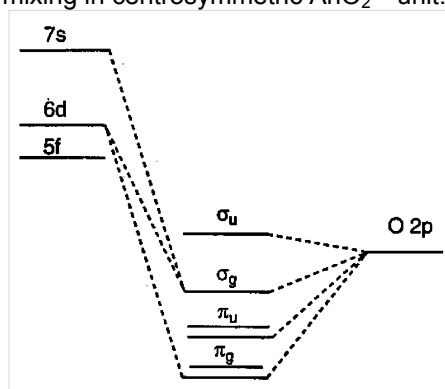ThO_2 ($6d^05f^0$) is bent (122°) for similar reasons i.e. no f-orbital participation.
UO_2^{2+} ($6d^05f^0$) is trans, linear because of the participation of its 5f orbitals.
U(5f) are of considerably lower energy than Th(5f).
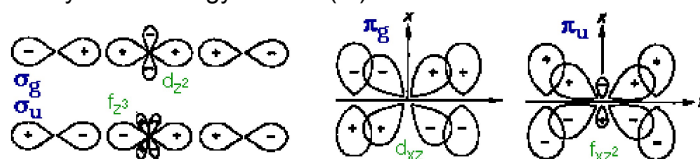
Details of the MO diagram for AnO_2^{2+} are controversial, but f-orbitals have ungerade symmetry, d-orbitals are gerade ➔ no d-f mixing in centrosymmetric AnO_2^{2+} unit.

UO_2^{2+} readily adds 4-6 donors in its equatorial plane → distinctive complexes
e.g. cyclic hexadentates.
UO_2^{2+} salts show characteristic (yellow) fluorescence.
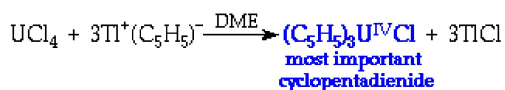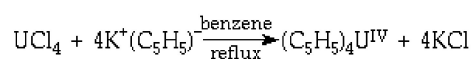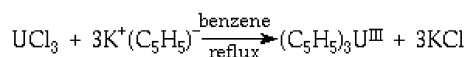

Organometallics
Organometallic chemistry of actinides is relatively recent.
Similar to lanthanides in range of cyclopentadienides / cyclo-octatetraenides / alkyls
Cyclopentadienides are π-bonded to actinides.
Compounds include:-

$$UCl_3 + 3K^+(C_5H_5)^- \xrightarrow[\text{reflux}]{\text{benzene}} (C_5H_5)_3U^{III} + 3KCl$$

$$UCl_4 + 4K^+(C_5H_5)^- \xrightarrow[\text{reflux}]{\text{benzene}} (C_5H_5)_4U^{IV} + 4KCl$$

$$UCl_4 + 3Tl^+(C_5H_5)^- \xrightarrow{\text{DME}} (C_5H_5)_3U^{IV}Cl + 3TlCl$$
<center>most important
cyclopentadienide</center>

$C_5H_5^-$ does not behave ionically, but Cl^- is labile ➔ formation of a wide variety of $(C_5H_5)_3UX$ compounds.

The most notable Cyclooctatetraenide is Uranocene
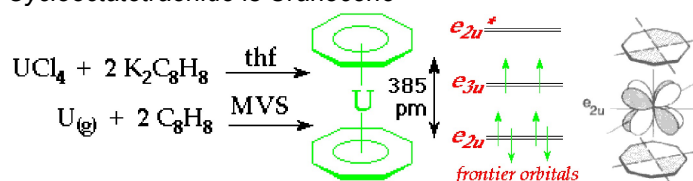
- Green crystals, paramagnetic and pyrophoric.
- Stable to hydrolysis.
- Planar 'sandwich'.
- Eclipsed D_{8h} conformation.

- UV-PES studies show that bonding in uranocene has 5f & 6d contributions.
- e_{2u} symmetry interaction shown can only occur via f-orbitals.

Nuclear Reactors, Atomic Energy & Uranium Chemistry

Principles of Nuclear Reactors
- Nuclear fission = large nucleus splitting into 2 highly energetic smaller nuclei + neutrons.
- Sufficient neutrons of suitable energy can induce fission of further nuclei → Chain reaction.
- To sustain chain reaction a critical mass of uranium must be achieved (prevents neutron loss).
- Kinetic energy of main fragments is converted to heat (106x energy of same mass of coal).
- Only naturally-occurring fissile nucleus is ^{235}U (0.72% natural abundance).

Modern Nuclear Reactors
- Current nuclear reactors use UO_2 fuel – less reactive than U metal.
- Enrichment is by fractional gaseous centrifugation of UF_6 (easily sublimed).
- Neutron capture by ^{238}U results in formation of ^{239}Pu, which is fissile. Significant amounts of Pu will only be produced in an unmoderated reactor (fuel reprocessing more dangerous!)

Coolants
- Water/Heavy Water – to keep it liquid it must be pressurized.
- CO_2 gas – in the Advanced Gas-Cooled Reactor.