LANTHANIDES & ACTINIDES NOTES

General Background

Mnemonics

Lanthanides

Lanthanide	**C**hemistry	**P**resents	**N**o	**P**roblems	**S**ince	**E**veryone	**G**oes	**T**o	**D**octor	**H**eyes'	**E**xcruciatingly	**T**horough	**Y**early	**L**ectures
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Actinides

Although	Theorists	Prefer	Unusual	New	Proofs	Able	Chemists	Believe	Careful	Experiments	Find	More	New	Laws
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Principal Characteristics of the Rare Earth Elements

1. Occur together in nature, in minerals, e.g. monazite (a mixed rare earth phosphate).
2. Very similar chemical properties. Found combined with non-metals largely in the 3+ oxidation state, with little tendency to variable valence.
3. Small difference in solubility / complex formation etc. of M^{3+} are due to size effects.
   Traversing the series $r(M^{3+})$ steadily decreases – the lanthanide contraction.
   Difficult to separate and differentiate, e.g. in 1911 James performed 15000 recrystallisations to get pure $Tm(BrO_3)_3$!

f-Orbitals

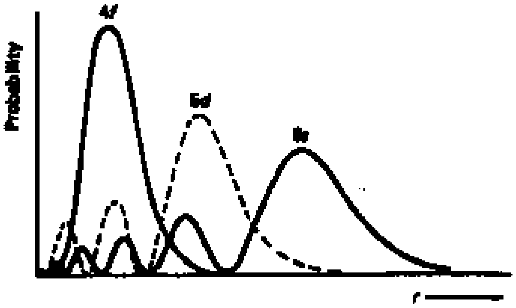
The Effective Electron Potential:

$$V_{eff} = -\frac{Z_{eff}}{r} + \frac{l(l+1)}{2r^2} \quad (a.u.)$$

Coulombic & Centrifugal potentials

- Large angular momentum for an f-orbital (*l* = 3).
- Large centrifugal potential tends to keep the electron away from the nucleus.
  - Aufbau order.
- Increased Z increases Coulombic attraction to a larger extent for smaller n due to a proportionately greater change in Z_{eff}.
  - Reasserts Hydrogenic order.

This can be viewed empirically as due to differing penetration effects.



Radial Wavefunctions $P_{n,l}{}^2$ for 4f, 5d, 6s in Ce

4f orbitals (and the atoms in general) steadily contract across the lanthanide series.
Effective electron potential for the excited states of Ba {[Xe] 6s 4f} & La {[Xe] 6s 5d 4f} show a sudden change in the broadness & depth of the 4f "inner well".

For Ba (Z = 56) 4f is an outer orbital with 4f close to its value for the H atom.
For La (Z = 57) 4f is an inner orbital with 4f ca. $0.7a_o$.

Though only for the next atom, Ce (Z = 58) is the 4f electron of sufficiently high binding energy to appear in the ground state configuration.

Which Elements are d-block or f-block?

Most current Periodic tables have:-

- La as first 5d transition element
- Ac as first 6d transition element

Reasons?
Possibly erroneous (early) interpretation of atomic spectra – misleading electronic configurations?

Some ground state electronic configurations:

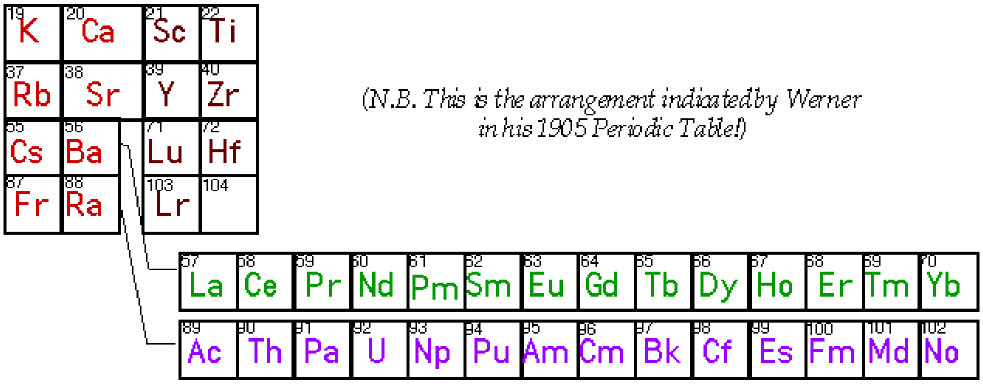
Calcium [Ar]$4s^2$	Scandium [Ar]$4s^2 3d^1$
Strontium [Kr]$5s^2$	Yttrium [Kr]$5s^2 4d^1$
Barium [Xe]$6s^2$	Lanthanum [Xe]$6s^2 5d^1$
Ytterbium [Xe]$6s^2 4f^{14}$	Lutetium [Xe]$6s^2 4f^{14} 5d^1$
Radium [Rn]7s2	Actinium [Rn]$7s^2 6d^1$
Nobelium [Rn]$7s^2 5f^{14}$	Lawrencium [Rn]$7s^2 5f^{14} 6d^1$

In each case: differentiation by (n-1)d^1 - as expected for the start of a transition series.
Lutetium and Lawrencium are just as good candidates to be the first elements of the 3rd and 4th transition series as Lanthanum and Actinium.

Some suggestions why Lu might best regarded as the first 5d transition element.

- Periodic Trends in Various Properties.
- Structures of Metal, Metal Sesquioxide (M_2O_3) and Metal Chloride (MCl_3).
- Similarities for Sc, Y, Lu.
- Differences from La.

Revised Medium-Block Format Periodic Table



(N.B. This is the arrangement indicated by Werner in his 1905 Periodic Table!)

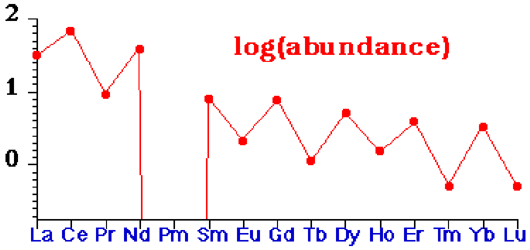
THE LANTHANIDES

Abundance & Distribution

- Not especially Rare(!), except Promethium which is produced artificially, e.g. La, Ce & Nd are more common than Pb.
- Most-common minerals:
  monazite (mixed La, Th, Ln phosphates) – widely-distributed, concentrated in sand & river beds due to relative insolubility.

bastnaesite (a La, Ln fluorocarbonate $M^{III}CO_3F$) – a vast deposit in Sierra Nevada, USA.

- Abundance of lanthanides in nature. Shows even-odd alternation with atomic number mirrored by several/few alternation of number of stable isotopes with even/odd Z.



Extraction

The extraction of the Lanthanides from minerals by:

- Alkali Digestion of Monazite/Xenotime.
  Monazite and Xenotime can also be opened-out through an Acid Route
- Acid Dissolution of Bastnaesite

Separation

$^2/_3$ of world production is actually used mixed in the proportions occurring naturally in the ore.

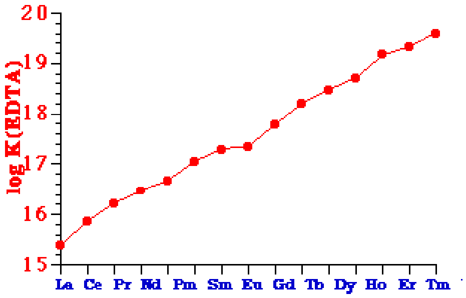
1. Cerium & Europium may be extracted **Chemically**:
Oxidise only Ce to M^{4+} by HClO or $KMnO_4$, then precipitate as CeO_2 or $Ce(IO_3)_4$.
On action of Zn/Hg only Eu forms a stable M^{2+} that doesn't reduce H_2O, then isolate by precipitation as $EuSO_4$.

2. Separation by **Fractionation**:
Small Scale methods used originally:

- Fractional Crystallization of e.g. $Ln(NO_3)_3.2NH_4NO_3.4H_2O$ or $Ln(BrO_3)_3$
- Fractional Thermal Decomposition of e.g. $Ln(NO_3)_3$

Current Small Scale Lab Separation:

- *Ion-Exchange Displacement Column*
  $Ln^{3+}(aq)$ are strongly adsorbed by a cation-exchange resin, add a ligand, typically chelating, e.g. EDTA.
  Ligand binds most strongly to smallest ion, e.g. the binding constants of the Ln(EDTA) complexes (right).



Current Large Scale Industrial Separation:

Solvent Extraction
$Ln^{3+}(aq)$ is extracted in a continuous counter-current process into a non-polar organic liquid (e.g. kerosene).
Solubility of Ln^{3+} in organic solvent increases with its relative atomic mass.

The Metals

Production of Elemental Metals

La, Ce, Pr, Nd, Gd:

$$2MCl_3 + 3Ca \rightarrow 2M + 3CaCl_2 \text{ (T > 1000°C)}$$

Tb, Dy, Ho, Er, Tm, Y:

$$2MF_3 + 3Ca \rightarrow 2M + 3CaF_2 \text{ (}MCl_3\text{ is too volatile)}$$

Pm:

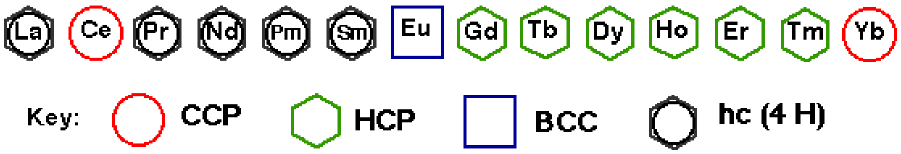
$$PmF_3 + 3\ Li \rightarrow Pm + 3LiF$$

Eu, Sm, Yb:

$$M_2O_3 + 2La \rightarrow 2M + La_2O_3 \text{ (}MCl_3\text{ reduced to }MCl_2\text{ by Ca)}$$

Mischmetall (mixed light Ln) :
electrolysis of fused $LnCl_3/NaCl$ with graphite anode & graphite or steel cathode.

Structures of Elemental Metals



Properties of the Metals

- Silvery white, but tarnish in air.
- Rather soft (later M are harder).
- High mp & bp.
- Very reactive: ($I_1 + I_2 + I_3$) comparatively low.
- Burn easily in air, but slowly in cold. Burn at T > 150 °C.
- Exothermic reaction with $H_2 \rightarrow MH_n$ (n = 2,3, often results in defect states).
- React readily with C, N_2, Si, P, halogens & other non-metals.
- Form binaries on heating with most non-metals (e.g. LnN, Ln_2S_3, LnB_6, LnC_2, ...).

Uses of Metals

<1% Mischmetall or Ln silicides improves strength & workability of low alloy steels for plate and pipes (also used in Mg alloys).
Mischmetall (50% Ce, 25% La, 25% other light lanthanides) is pyrophoric - alloyed with 30% Fe it is used in lighter flints.

Oxidation State Preferences

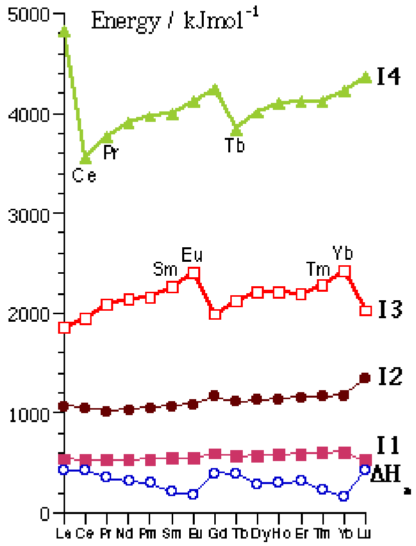
Chemistry is principally of Ln^{3+}.
Examine Thermodynamic Parameters: Ionisation Energies, Heats of Hydration and Atomisation.

Ionization

For any given Lanthanide:

- As successive electrons are removed from neutral Ln the stabilizing effect on the orbitals is related to their principal quantum number, 4f > 5d > 6s.
- For Ln^{2+} (except for La & Gd) the configuration is $[Xe]4f^n$
- For Ln^{3+} the configuration is always $[Xe]4f^n$
- The 4f binding energy is so great that remaining 4f electrons are regarded as "core-like" (i.e. incapable of modification by chemical means), except Ce.

Therefore in almost all cases Ln^{3+} provides the best energetics:



Observing trends across the Lanthanide Series:

- The general trend is for increasing ionization energies with increasing Z (i.e. with increase in Z_{eff})
- Marked Half-Shell Effects - magnitude as n in I_n

- Also Quarter/Three-Quarter Shell Effects (compare with transition metals - these are not seen clearly with d^n configurations).

Explanation:

Inter-electronic repulsion is related not just to electron pairing but also to angular momentum of the electrons.
e.g. in Pr^{2+} ($4f^3$) $\rightarrow$ Pr^{3+} ($4f^2$) ionization removes repulsion between e^- of like rotation, whereas Pm^{2+} ($4f^4$) $\rightarrow$ Pm^{3+} ($4f^3$) removes the stronger repulsion between e^- of unlike rotation (latter Ionization Energy is correspondingly lower - hence the local minimum in the I_3 graph at Pm).
The three-quarter effect is the bigger: interelectronic repulsion is bigger in smaller Ln^{n+}

Atomization

$\Delta_{atm}H$ follows the inverse trend to I_3, and therefore also to ($I_1 + I_2 + I_3$).
Metallic bonding is correlated with ease of ionization to Ln^{3+} state.
This trend is modified slightly due to the different structures of the Ln metals.

Some Thermodynamic Observations (Ionic Model style)

The trends in the formation of Ln^{III} Compounds, Δ_fH for $LnX_3(s)$ or $Ln^{3+}(aq)$ [E°($Ln^{3+}(aq)$ / Ln(s))] depends on the balance between:

Energy Supplied to effect:

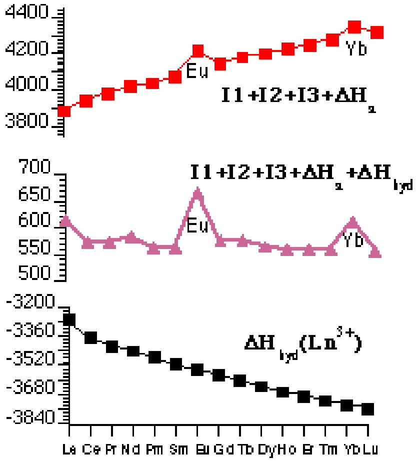
$$Ln(s) \rightarrow Ln(g) \rightarrow Ln^{3+}(g) + 3e^- \ [\ \Delta_{atm}H + I_1 + I_2 + I_3\ ]$$

vs.

Energy gained from:

$$Ln^{3+}(g) + 3X^-(g) \rightarrow LnX_3(s)\ [\ \Delta_LH(LnX_3(s))\ ]$$
$$\text{or } Ln^{3+}(g) \rightarrow Ln^{3+}(aq)\ [\Delta_{hyd}H(Ln^{3+})]$$

The energies determining trends in E°(Ln^{3+}(aq)/Ln(s)) are graphed below:



Production of Ln^{3+}(g) shows:

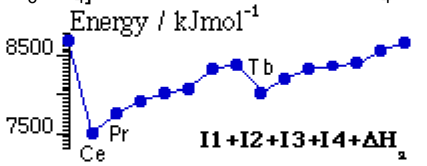
- A smooth trend based on size effects (trend based on Z_{eff}).
- Shell structure effects superimposed with clear maxima at half-shell (f^7) and full-shell (f^{14}).
- Also smaller quarter and three-quarter shell effects.

Hydration Energy of Ln^{3+} (also Lattice Energies of $LnX_3(s)$) shows:

- Only a smooth ionic-size-based trend (the trend based on Z_{eff}) and no shell structure effects.
- Balance of trends in Ionization + Atomization Energies with Hydration (Lattice) Energy removes size effects.
- Leaves only the Shell effects - see values of $\Delta_fH(Ln^{3+}(aq))$.

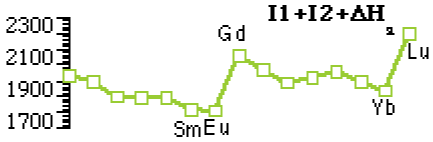
Overall:
The most important energy correlations are with I_3
Exceptions to +3 rule can also be rationalized.

Occurrence of +4 oxidation state
Predicted from [$\Delta_{atm}H + I_1 + I_2 + I_3 + I_4$] which follows trends in I_4.



Ce, Pr → Ce^{4+} [$4f^0$], Pr^{4+} [$4f^1$] - early in series 4f orbitals still comparatively high in energy.
Tb → Tb^{4+} [$4f^7$ valence shell] - half shell effect.

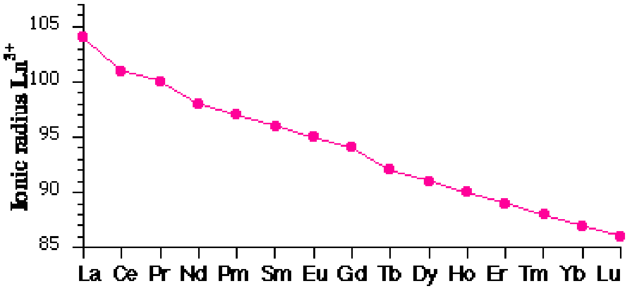
Occurrence of +2 oxidation state
Predicted from [$\Delta_{atm}H + I_1 + I_2$] which follows trends in $\Delta_{atm}H$, which is reverse of trend in I_3.



Eu, Sm, Yb → Eu^{2+} [$4f^7$], Sm^{2+} [$4f^6$], Yb^{2+} [$4f^{14}$] - clear influences of electronic shell structure & from $\Delta_{atm}H$.

General Features of Lanthanide Chemistry

1. similarity in properties, with gradual changes occurring across the lanthanide series: a size effect from the Lanthanide Contraction



Causes:
Poor screening of nuclear charge by 4f electrons → steady increase in Z_{eff}.
Relativistic effects influence the shielding characteristics of inner electrons.

2. Primarily the 3+ oxidation state adopted for all elements
Redox chemistry is commonly encountered only for Eu (3+/2+) and Ce (4+/3+).
Some solids formulated as Ln^{II} compounds actually contain Ln^{3+} & delocalized e^-.

3. Coordination chemistry is not especially extensive
Chelating ligands are preferred.

4. Bonding on coordination is primarily ionic in character
Complexes undergo rapid ligand exchange.

Why is the bonding so ionic?

$4f^n$ electrons are contracted into the core and unable to participate in bonding.

Other implications from lack of covalent bond-forming orbital-availability:

- No π-backbonding occurs.
- No simple carbonyl species (except in Ar matrix at 10 K).
- Cyclopentadienyls are ionic in nature [c.f. $Ln(C_5H_5)_3$ vs. $Fe(C_5H_5)_2$].
- Lanthanide organometallics have different properties from transition metal equivalents.

5. Ln^{3+} cations display typical a-class (hard) properties

preference for O-donor ligands.
Why not N too? O-donor ligands are more likely to be charged (importance of ionic bonding to lanthanides!)

6. Binding to water is common

Such that H_2O is often found included in products isolated from (aq).

7. Coordination numbers are high

> 6, typically 8, 9,... (up to 12 found).

8. Coordination polyhedra are often ill-defined

Determined by ligand requirements, not by bonding requirements.
No confirmed examples of isomerism.
Solid state structures of binaries are often rather different from those of other metals.

9. Ligand Field Effects are very small

Pale Colours from weak, narrow forbidden f-f optical transitions.

M^{3+} ions are:
Colourless (La, Ce, Gd, Yb, Lu)
Green (Pr, Tm)
Lilac (Nd, Er)
Yellow Pink (Pm, Ho)
Yellow (Sm, Dy)
Pale Pink (Eu, Tb)

Magnetic properties have spin-orbit coupled contributions (spin-orbit coupling >> ligand field splittings)

Magnetic & Optical properties are largely independent of environment (e.g. similar spectra in gas/solution/solid).

Renewed Technological interest in Lanthanides is mainly in optical/magnetic materials .

Solution Chemistry

Solubility

- Ln^{3+} are not especially soluble in water.
- No simple relationship of solubility to cation radius.
- Depends on small difference between large solvation and lattice energies.
- Depends on entropy effects.

Hydrated Lanthanide Ions

- Primary hydration numbers in (aq) are 8, 9.
- Primary hydration number decreases with Lanthanide Contraction.
- Secondary hydration number increases with Lanthanide Contraction.
- Increased polarization of primary hydration sphere by a smaller cation enhances hydrogen bonding to water in the secondary hydration sphere.
- Aqua ions hydrolyze - increasingly so from La to Lu as they become smaller.

$$Ln(H_2O)_n^{3+} + H_2O \rightarrow Ln(H_2O)_{n-1}^{2+} + H_3O^+$$

- Salts with common anions frequently contain $Ln(H_2O)_9^{3+}$ with tri-capped trigonal prismatic geometry.

Coordination Compounds

Strongly complexing, chelating ligands necessary to yield isolable products from (aq).
Some O-donor chelating ligands that form complexes include NO_3^- , which binds in its chelate mode.
Notable for high Coordination Numbers.
$Ce(NO_3)_5^{2-}$ - 10-coordinate bicapped dodecahedron.
$Ce(NO_3)_6^{3-}$ - 12-coordinate icosahedron.
Other favoured ligands include: Oxalate, Citrate, Tartrate.

Classic bidentate complexes formed as $Ln(L\text{-}L)_3L'$ (L' = H_2O, py, etc...) or $Ln(L\text{-}L)_4$ dehydrate in vacuo → $Ln(L\text{-}L)_3$ [now coordinatively unsaturated].

$Ln(L\text{-}L)_3$ with bulky R are thermally stable, volatile & sublimable, and soluble in non-polar solvents.

- Widely used as NMR shift reagents. Polar molecules may coordinate $Ln(L\text{-}L)_3$, their NMR resonances are perturbed by the paramagnetism of Ln, e.g. $Eu(facam)_3$.
- "Anti-knock" activity as petroleum additives.

Solution Chemistry of Other Lanthanide Oxidation States

Ln(IV)

Cerium is the only Ln^{4+} with significant aqueous or coordination chemistry.
E° (Ce^{4+}(aq) / Ce^{3+}(aq)) = 1.72 V (others estimated at 2.9 V).
Prepared by the action of a strong oxidizing agent, e.g. $S_2O_8^{2-}$, on Ce^{3+}(aq).
Widely used as an oxidant itself, e.g. quantitative analysis / organic chemistry.
E° (Ce^{4+}/Ce^{3+}) is markedly dependent on complexation and hydrolysis.
Strong oxidizing agent in perchloric acid solution. In other acids coordination occurs, e.g. $Ce(NO_3)_6^{2-}$ is generally used for oxidations as its NH_4^+ salt

Change in pH:
Hydrolysis to $Ce(OH)^{3+}$ occurs, then polymerization. Ultimately precipitation of yellow gelatinous $CeO_2.xH_2O$.
4+ charge stabilizes halogeno-complexes e.g. CeF_8^{4-}.

Ln(II)

Significant solution chemistry of Ln^{2+} is essentially confined to Sm^{II}, Eu^{II}, Yb^{II}

Preparation:
electrolytic reduction of Ln^{3+}(aq).
Eu^{2+} (the most stable Ln^{II}) is prepared by reduction of Ln^{3+}(aq) with Zn/Hg.

Properties:
Ln^{2+} Aquo-ion colours:

Sm^{2+} blood-red	Eu^{2+} colourless	Yb^{2+} yellow

- Ln^{2+}(aq) are readily oxidized by air, but Eu^{2+}(aq) is easily handled.
- Sm^{2+}(aq) & Yb^{2+}(aq) reduce water.
- Eu^{2+}(aq) is relatively stable in the dark.
- Carbonate and sulphate salts have been isolated.
- Sm^{2+} and Yb^{2+} salts are susceptible to oxidation by their water of crystallization.

- Eu & Yb dissolve in liquid ammonia to give intense blue, highly reducing solutions containing $[Ln(NH_3)_x]^{2+}$ and solvated electrons. Solutions decompose on standing, precipitating the amide $Ln(NH_2)_2$
- Properties of Ln^{2+} are closely-related to those of the alkaline earths. In particular Eu^{2+} is often likened to Ba^{2+}.
  Similar Salt Solubilities (like Ba, sulphates are insoluble, hydroxides are soluble).
  Behaviour in liquid NH_3 is very similar.
  Similar Coordination Chemistry (Not extensive / Hard ligands)
  BUT very different redox chemistry!

Magnetism & Spectra

Ln	**Ln^{3+} configuration**	**Ground State**	**No. of unpaired e-**	**Colour**	**$g_J\sqrt{(J(J+1))}$**	**Observed μ_{eff}/μ_B**
La	$4f^0$	$^1S_0$	0	colourless	0	0
Ce	$4f^1$	$^2F_{5/2}$	1	colourless	2.54	2.3 - 2.5
Pr	$4f^2$	$^3H_4$	2	green	3.58	3.4 - 3.6
Nd	$4f^3$	$^4I_{9/2}$	3	lilac	3.62	3.5 - 3.6
Pm	$4f^4$	$^5I_4$	4	pink	2.68	-
Sm	$4f^5$	$^6H_{5/2}$	5	yellow	0.85	1.4 - 1.7
Eu	$4f^6$	$^7F_0$	6	pale pink	0	3.3 - 3.5
Gd	$4f^7$	$^8S_{7/2}$	7	colourless	7.94	7.9 - 8.0
Tb	$4f^8$	$^7F_6$	6	pale pink	9.72	9.5 - 9.8
Dy	$4f^9$	$^6H_{15/2}$	5	yellow	10.65	10.4 - 10.6
Ho	$4f^{10}$	$^5I_8$	4	yellow	10.6	10.4 - 10.7
Er	$4f^{11}$	$^4I_{15/2}$	3	rose-pink	9.58	9.4 - 9.6
Tm	$4f^{12}$	$^3H_6$	2	pale green	7.56	7.1 - 7.6
Yb	$4f^{13}$	$^2F_{7/2}$	1	colourless	4.54	4.3 - 4.9
Lu	$4f^{14}$	$^1S_0$	0	colourless	0	0

Magnetic Properties

- Paramagnetism.
- Magnetic properties have spin & orbit contributions (contrast "spin-only" of transition metals).
- Magnetic moments of Ln^{3+} ions are generally well-described from the coupling of spin and orbital angular momenta - Russell-Saunders Coupling Scheme.
- Spin orbit coupling constants are typically large (ca. 1000 cm^{-1}).
- Ligand field effects are very small (ca. 100 cm^{-1}).
  - only ground J-state is populated.
  - spin-orbit coupling >> ligand field splittings.
  - magnetism is essentially independent of environment.
- Magnetic moment of a J-state is expressed by the Landé formula:

$$\mu = g_J\sqrt{J(J+1)}\,\mu_B \qquad g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

Ln^{3+} Magnetic Moments compared with Theory

Landé formula fits well with observed magnetic moments for all but Sm^{III} and Eu^{III}.
Moments of Sm^{III} and Eu^{III} are altered from the Landé expression by temperature-dependent population of low-lying excited J-state(s).

Uses of Ln^{3+} Magnetic Moments?

NMR Shift Reagents - paramagnetism of lanthanide ions is utilized to spread resonances in ^1H NMR of organic molecules that coordinate to lanthanides.

Ferromagnetism / Anti-Ferromagnetism / Ferrimagnetism

Lanthanide metals and alloys have interesting ordered magnetism effects.

$SmCo_5$, $Nd_2Fe_{14}B$ permanent magnets - FERROMAGNETIC

- light weight.
- high saturation moments.
- high coercivity.
- high magnetocrystalline anisotropy.
- Superior performance magnets for magnetic bearings / couplings / wavetubes & d.c. synchronous motors.

Rare Earth Garnets e.g. $Ln_3Fe_5O_{12}$ and $Y_3Fe_5O_{12}$.
FERRIMAGNETISM shows an unusual temperature-dependence.

- As T increases moment falls to zero at the Condensation Temperature.
- Above Condensation Temperature moment rises in the opposite direction to a maximum.
- Moment, then falls to zero at the Curie Temperature in the normal manner.

Reason?

- The magnetic moments of the rare earth and iron ions oppose each other.
- The rare earth moments dominate at low temperature.
- The rare earth moments randomize at a lower temperature than the iron moments.

Electronic Spectroscopy

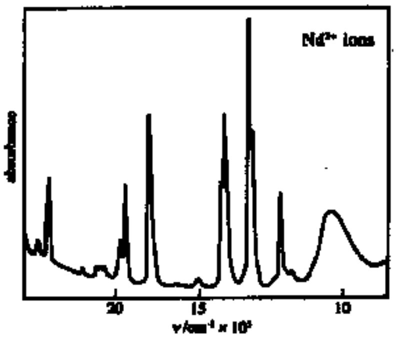
Transitions which involve only a redistribution of electrons within the 4f orbitals (f-f transitions) are orbitally-forbidden by the Selection Rules.

Pale colours of Ln^{III} compounds are usually not very intense.
Crystal/Ligand field effects in lanthanide 4f orbitals are virtually insignificant.
4f electrons are well shielded from external charge by $5s^2$ & $5p^6$ shells.
f-f absorption bands are very sharp (useful fingerprinting and quantisation of Ln^{III}).

[d↔d transitions in transition metal compounds are also orbitally forbidden, but gain intensity from and are broadened by the effects of molecular vibrations in distorting the crystal field].

Optical spectra are virtually independent of environment - similar spectra in gas/solution/solid (sharp lines like typical gas atom spectra).

Insensitivity of f-f transitions means of limited use in study of lanthanide materials.



Ce^{III} and Tb^{III} have high intensity bands in the UV due to $4f^n \rightarrow 4f^{n-1}5d^1$ transitions, i.e. f-d and therefore not orbitally forbidden.

Fluorescence / Luminescence

Of certain lanthanides e.g. Tb, Ho & Eu.
Luminescence: emission of light by material from its absorbing energy.
Photoluminescence: use of photons for excitation.

Fluorescence: short time lapse (~ 10^{-8}s) between excitation & emission.
Phosphorescence: long decay times - luminescence continues long after excitation source is removed.

Lasers

One of the most common high power lasers is the Neodymium YAG laser.
Host material is Yttrium Aluminium Garnet (YAG), $Y_3Al_5O_{12}$, doped with Nd^{3+}.

Solid State Chemistry

Halides

Halides of the form LnX_2, LnX_3 & LnX_4 exist.

LnX_4

- Only (Ce, Tb, Pr)F_4 are known.
- correlation with I_4 of Ln.
- fluorides only - most oxidising halogen.
- CeF_4 is comparatively stable e.g. crystallizes as a monohydrate from (aq).
- TbF_4, PrF_4 are thermally unstable and oxidize H_2O, i.e. prepare dry.
- MF_4 all white solids with the UF_4/ZrF_4 structure.
- Dodecahedral coordination of M.

LnX_3

All LnX_3 are known (except Pm [not attempted] & possibly EuI_3).
Typically crystalline / high mp / deliquescent.
Typically obtained as hydrates from (aq).
On heating, react with water to form oxyhalides: $LnX_3 + H_2O \rightarrow LnOX + 2HX$.
At high temperatures react even with glass: $2LnX_3 + SiO_2 \rightarrow 2LnOX + SiX_4$.

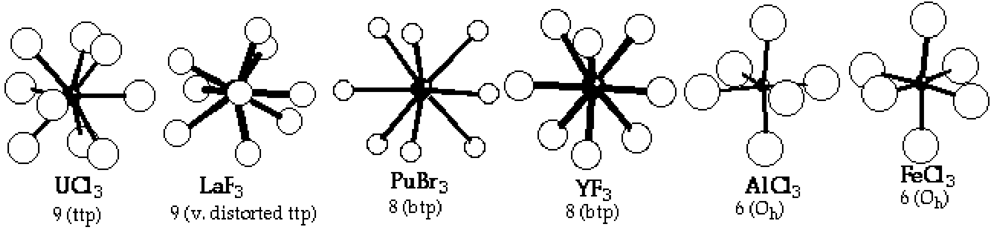
Preparation of anhydrous LnX_3

LnF_3: $Ln(NO_3)_3(aq) + 3HF \rightarrow LnF_3{\bullet}0.5H_2O$ (very insoluble).
Heat this under an HF atmosphere (for heavy Ln) to obtain anhydrous LnF_3.

$LnCl_3$: Ln_2O_3 / $Ln_2(CO_3)_3 + HCl(aq) \rightarrow LnCl_3{\bullet}6\text{-}8H_2O$ (rather soluble).
Heat this under HCl atmosphere (for heavy Ln) to obtain anhydrous $LnCl_3$.
or
Heat at 300°C, $Ln_2O_3 + 6NH_4Cl \rightarrow 2LnCl_3 + 3H_2O + 6NH_3$.

$LnBr_3$ / LnI_3: Best by direct combination (susceptible to hydrolysis to oxyhalides). Purify by sublimation (but avoid contact with hot silica!)

Structures:
Ln coordination varies from 9 for light trifluorides to 6 for heavy iodides.
Coordination Environments from LnX_3 structures:



LnX_2

Preparation - typically from comproportionation - $Ln + 2LnX_3 \Leftrightarrow 3LnX_2$
(Sm,Eu,Yb)I_2 are obtained from thermal decomposition of LnX_3
LnX_2 are easily oxidised.
Liberate H_2 from H_2O [Except for EuX_2].
Occurrence of dihalides - parallels high values for I_3.
Depends upon the oxidizing power of the halogen (iodides most numerous!)

Trends in the Stability of MX_2
Consider:

$$3MX_2(s) \Leftrightarrow M(s) + 2MX_3(s)$$

$$\Delta_m H° = 3\Delta_L H(MX_2) – 2\Delta_L H(MX_3) + 2I_3 - \Delta_{atm}H°(M) - (I_1 + I_2)$$

Irregularities should follow [$2I_3 - \Delta_{atm}H°(M)$], i.e. effectively follow I_3 [since variation in $-\Delta_{atm}H$ follows closely variation in I_3.

This explains occurrence of MCl_2:
- La, Ce, Pr MCl_2 unknown
- (Sm, Eu, Yb)Cl_2 are the most stable MCl_2 - may be prepared from $LnCl_3$(s) + ½H_2

Structures

- Coordination numbers from 9 to 6
- Fluorides are Fluorite (CaF_2) [C.N. = 8]
- Nd,Sm,Eu chlorides are $PbCl_2$-type [C.N. = 7 + 2]
- Nd,Sm,Eu bromides and iodides are $SrBr_2$ type [mixed CN=7 & 8]
- (Dy,Tm,Yb) I_2 have layer structures ($CdCl_2$,CdI_2) [CN=6] with polarization effects

Two *Classes* of dihalide
1. Most LnX_2 are regarded as "salt-like" halides (insulators).
2. (Ce,Pr,Gd) I_2 have metallic lustre, high conductivity.

Formulation as $Ln^{3+}(I^-)_2(e^-)$ with the electron in a delocalized conduction band.
Ln^{II} Compounds are finding increasingly more uses .

Lower Halides
LnX_3/Ln melts yield phases of reduced halide formulae e.g. Ln_2X_3 & LnX.
"Reduced Halides" contain "condensed metal clusters".
Black & metallic increase delocalization of electrons through the metal-metal bonded networks.
Gd_2X_3 single chains of edge-sharing metal octahedra with M_6X_8-type environment (i.e. face-capped by X).
Lowest Halides are stabilized by H, C or N atoms encapsulated in Ln_6 cluster octahedra.

e.g. $Gd_2Cl_2C_2$	Layers of edge-sharing M_6C units
e.g. Gd_3Cl_3C	Framework of M_6C units

Hydrides
Preparation: Heat at 300-350°C, Ln + H_2 → LnH_2

Properties of LnH_2
Black, reactive, highly conducting, with fluorite structure.
Most thermodynamically stable of all binary metal hydrides.
Formulated as $Ln^{3+}(H^-)_2(e^-)$ with e^- delocalized in a metallic conduction band.
Further H can often be accommodated in interstitial sites, and they are frequently non-stoichiometric, e.g. LuH_x where x = 1.83-2.23 & 2.78-3.00.

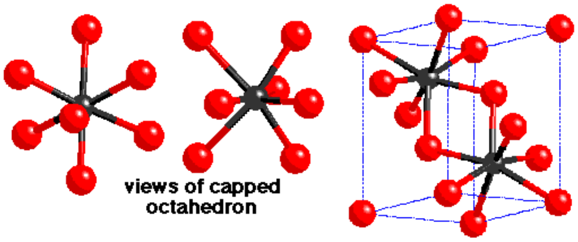
With a high pressure of H_2 forms LnH_3.
Reduced conductivity: salt-like $Ln^{3+}(H^-)_3$, except for Eu and Yb (the most stable Ln^{II}).

Possible Applications of Rare Earth Intermetallic Hydrides.
1. Production of ultra-pure hydrogen.
2. Isotope Separation of deuterium and hydrogen.
3. Source of fuel for motor vehicles.
4. Electrodes in Protonic Batteries/Fuel Cells.
5. Load Levelling in Power Stations.
6. Chemical heat-pump systems.
7. Useful hydrogenation agents in organic chemistry.

Binary Oxides

Ln_2O_3

The most common lanthanide oxide (notable exceptions; CeO_2, Pr_6O_{11}, Tb_4O_7).
Sesquioxides, Ln_2O_3, are strongly basic, and absorb water / CO from air, forming the hydroxide / carbonate salts.
They have pale colours, and properties strongly resemble alkaline earth oxides.
Adopt three structure types:



A-type
- light Ln
- unusual LnO_7 capped-octahedra

B-type
- middle Ln
- LnO_7 units of three types:
- 2 x capped trigonal prisms
- 1 x capped octahedron
- B-M_2O_3 structure is very complex. Densest of M_2O_3 structure types - favoured by increased pressure.

C-type
- heavy Ln
- LnO_6 units, but not octahedra
- (face & body - divacant cubic)
- C-type M_2O_3 is related to Fluorite (MO_2) with ¼ of anions removed.

Polymorphism

A (high T) B (medium T) C (low T)

$Ln(OH)_3$

Obtained by action of conc. NaOH on Ln_2O_3 under hydrothermal conditions.
9-coordinate Ln with tricapped trigonal prismatic geometry.
Basicity increases with Z - correlates with decrease in r(Ln^{3+})

LnO_2

CeO_2 (most stable).
Fluorite (CaF_2) structure.
Pr_6O_{11}, Tb_4O_7 (formed at high p(O_2) and high temperature)
Range of non-stoichiometric phases between Fluorite LnO_2 and C-type $LnO_{1.5}$ - intermediate phases were the first known examples of shear structures.

LnO

known for some Ln.
Preparation: Comproportionation Ln + Ln_2O_3 → 3LnO.
NaCl structure.
NdO, SmO lustrous golden yellow, conducting formulated as $Ln^{3+}(O^{2-})(e^-)$.
EuO (dark red), YbO (greyish-white) insulating genuine $Ln^{2+}O^{2-}$.
EuO is ferromagnetic and an insulator when pure.

Borides

A variety of binary borides exist e.g. YB_2, YB_4, YB_6, YB_{12}, YB_{66}.
Most important are LnB_6 – contain B_6 octahedral clusters, and are isomorphous with CaB_6.
Black, metallic conductivity (c.f. CaB_6 white, insulator).
formulated as $Ln^{3+}(B_6^{2-})(e^-)$, except EuB_6, YbB_6 which are $Ln^{2+}(B_6^{2-})$.

MT_4B_4 compounds
M = Sc, Y, Ln, Th, U.
T = Ru, Os, Co, Rh, Ir.
Of current interest for their superconductivity, e.g. $CeCo_4B_4$.

Carbides
Class III
Interstitial Carbides.
Close-Packed M with C in Octahedral Interstices, e.g. $(Tb,Ho,Y)_2C$.
anti-$CdCl_2$ structure.

Class II
Occurrence with La – Ho.

M_3C	C randomly distributed in ⅓ of Octahedral holes in CCP M.
M_2C_3	Pu_2C_3 structure - C_2 groups.
MC_2	CaC_2 structure - C_2 groups.

Metallic lustre & conductivity - not salt-like.
Hydrolysis of $(La,Ce)C_2$ at ambient temperature gives ethyne, C_2H_2.

Organometallic Chemistry

Organolanthanide chemistry is not as extensive as organotransition metal chemistry.
Currently receiving a lot of attention, especially in C-H Bond Activation studies.

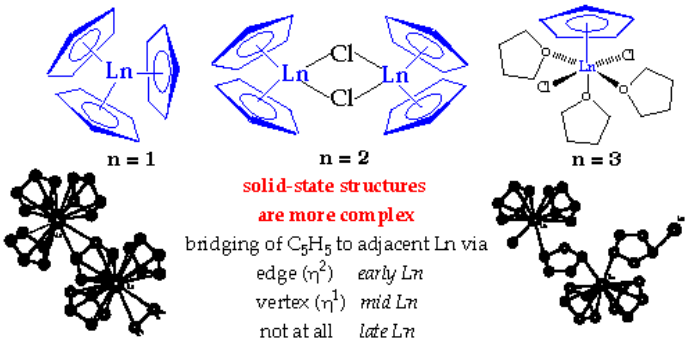
Primarily ionic in their bonding - contracted nature of the 4f valence orbitals.
Lanthanides cannot act as π-bases hence Ln-CO compounds are not stable.

Organolanthanides are extremely air & moisture sensitive - reflects highly carbanionic character of organic ligand & oxophilicity of $Ln^{2+/3+}$.

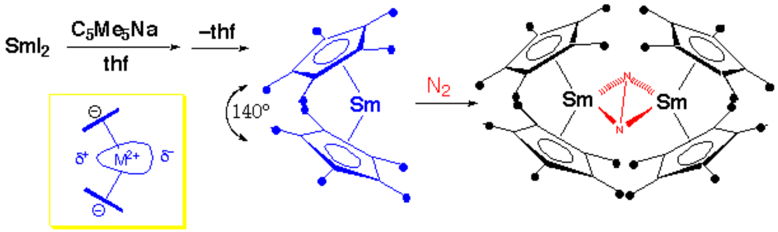
Cyclopentadienides
Preparation:

$$LnCl_3 + nNa(C_5H_5) \xrightarrow{THF} LnCl_{3-n}(C_5H_5)_n + nNaCl$$

Structure:



Also in +2 Oxidation State



Alkyls & Aryls

σ-bonded alkyls & aryls.
From metathesis in ether/THF.

$$LnCl_3 + 3LiR \xrightarrow{THF} LnR_3 + 3LiCl$$

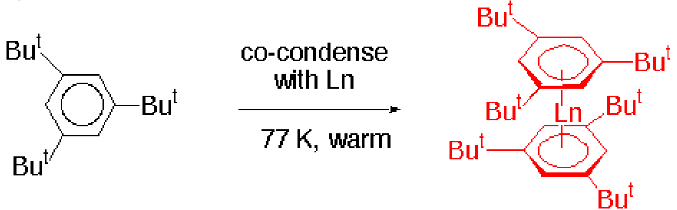
R = phenyl probably polymeric.
R = CH_2CMe_3 stable as $LnR_3(THF)_2$.
$[LnMe_6]^{3-}$ have been isolated for most Ln.

Mixed Alkyl Cyclopentadienides

C_5Me_5 (Pentamethyl-cyclopentadienyl) is a common organo-Ln ligand.
Large bulk - only 2 C_5Me_5 may be bound to Ln.
Causes major change in structural & chemical properties, especially novel chemistry in mixed alkyl cyclopentadienides, e.g. $(C_5Me_5)_2LuCH_3$.
- catalyzes alkene polymerization (Ziegler-Natta chemistry).
- reacts with C-H bonds of extremely low acidity e.g. CH_4.

Arenes

Lanthanide Bis-Arene 'sandwich' compounds.
prepared by metal vapour synthesis (MVS) techniques.
stable at ambient temperature.



Ln(0) - such compounds could not be expected for Ln^{III} with contracted 4f orbitals.

Comparisons and Contrasts

Yttrium - Why consider it with the Lanthanides?

- Occurs with lanthanides in rare earth minerals, e.g. monazite.
- Y occurs effectively exclusively in +3 oxidation state.
- combines with non-metals → $YHal_3$ Y_2O_3, $Y^{3+}(H^-)2(e^-)$, YH_3, etc...
- Y^{3+} has same radius as Ho^{3+} and is difficult to separate from it.
- Forms complexes of high coordination number with chelating O-donors, e.g. $Y(acac)_3(H_2O)$.
- Typical organometallics include: $Y(C_5H_5)_3$ (polymeric in the solid state).
- Dimeric $Y(C_5H_5)_2Cl$, monomeric form is a THF adduct

6 Reasons why Scandium could be considered with the Lanthanides

1. Sc occurs effectively exclusively in +3 oxidation state.
   Combines with non-metals → $ScHal_3$ Sc_2O_3, etc...
   But coordination octahedral (small size).
2. Sc forms reduced halides.
   e.g. Sc_7Cl_{12} which is $Sc^{3+}(Sc_6Cl_{12})^{3-}$ with Sc_6 clusters (but c.f. Nb).
3. Scandium Hydride ScH_2 is highly conducting $Sc^{3+}(H^-)_2(e^-)$.
4. Forms complexes of high coordination number with chelating O-donors, but forms octahedral complexes with monodentate ligands.
5. Nitrate & Sulphate are obtained as hydrated salts.
6. Typical organometallics include: $Sc(C_5H_5)_3$ (polymeric in the solid state). Dimeric $Sc(C_5H_5)_2Cl$, monomeric form is a THF adduct.

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 → 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 → large HOMO-LUMO gaps → 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. $Z \leq 92$).
- 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)

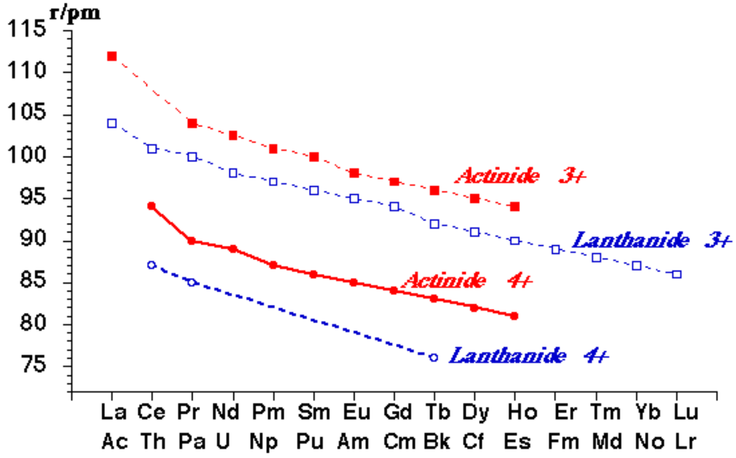
- Electronic Configurations of Actinides are not always easy to confirm.

  - 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 ...

- For a given oxidation state show similarly diverse C.N. to Lanthanides.
- Different accessible oxidation states - even greater diversity of structure.
- Wide variety of oxidation states of ligands & number of oxidation states.
- 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.

UCl_6

From chlorination of U_3O_8 + C.
Highly oxidising.
Moisture-sensitive : $UCl_6 + 2H_2O \rightarrow UO_2Cl_2$ (Uranyl Chloride) + 4HCl.
In CH_2Cl_2 solution UCl_6 decomposes to U_2Cl_{10} (Mo_2Cl_{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 $\rightarrow$ $M{+}UF_6^-$ ($M^+ = Rb^+, Cs^+, H_3O^+$) 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_4O_9, U_3O_8, UO_3.

UO_2 & U_4O_9

UO_2 (black-brown) has the Fluorite structure. Stoichiometric material is best obtained from:

$$UO_3 \xrightarrow[300\text{–}600^\circ C]{H_2 \text{ or } CO} UO_2 + H_2O \text{ (or } CO_2)$$

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_4O_9) (black) - interstitials are ordered forming a distinct phase in the phase diagram.

U_3O_8 & UO_3

U_3O_8 is dark green.
conveniently made by heating uranyl nitrate or ethanoate in air.

$$3UO_2(NO_3)_2 \xrightarrow[650\text{–}800^\circ C]{O_2} U_3O_8 + 6NO_2 + 2O_2$$

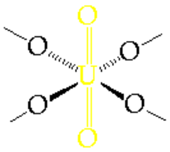
> 650°C Higher uranium oxides decompose to U_3O_8.
> 800°C loses U_3O_8 oxygen.

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:

$$UO_2(NO_3)_2 \xrightarrow[400\text{–}600^\circ C]{O_2} UO_3 \qquad (NH_4)_2U_2O \xrightarrow[500^\circ C]{O_2} UO_3$$

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

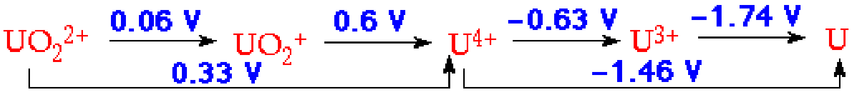


Uranates

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:



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.

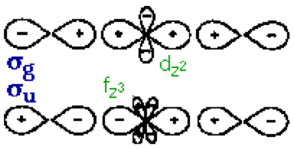
U^{4+}
Only slightly hydrolysed in 1M acid solution $U^{4+} + H_2O \Leftrightarrow U(OH)^{3+} + H^+$.
But, it can give rise to polymeric species in less acid solutions.
Regarded as a 'stable' oxidation state of uranium in (aq).

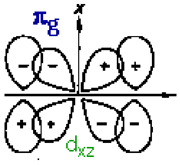
UO_2^+
Extremely unstable to disproportionation.
Evidence for its existence in (aq) from stopped-flow techniques.
More stable in DMSO (half-life ~ 30 mins).

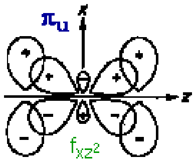
UO_2^{2+}
The Uranyl ion.
Very stable, and forms many complexes.
A dominant feature of uranium chemistry.
Reduced to U^{4+} by e.g. Zinc, Cr^{2+}
Re-oxidation by $H_2{}^{18}O_2 \rightarrow U^{18}O_2^{2+}$
Re-oxidation by ${}^{18}O_2 \rightarrow U({}^{18}O{}^{16}O)^{2+}$

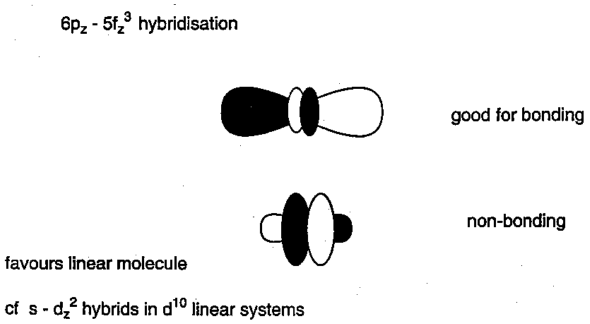
Linear, symmetrical $(O=U=O)^{2+}$ structure.

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).

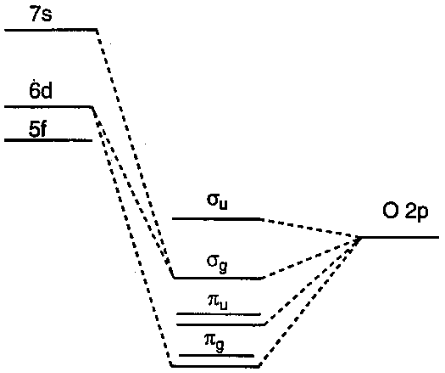








Details of the MO diagram for AnO_2^{2+} are controversial, but f-orbitals have ungerade symmetry, d-orbitals are gerade ➔ no d-f mixing in centrosymmetric AnO_2^{2+} unit.



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:-

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

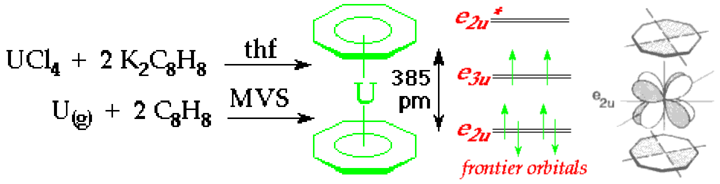
$$UCl_4 + 4K^+(C_5H_5)^- \xrightarrow[\text{reflux}]{\text{benzene}} (C_5H_5)_4U^{IV} + 4KCl$$

$$UCl_4 + 3Tl^+(C_5H_5)^- \xrightarrow{\text{DME}} \mathbf{(C_5H_5)_3U^{IV}Cl} + 3TlCl$$

most important cyclopentadienide

$C_5H_5^-$ 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.