

Uranium

CHEM-E4130 - Chemistry of the Elements



Aalto-yliopisto
Kemian tekniikan
korkeakoulu

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7.10.2022

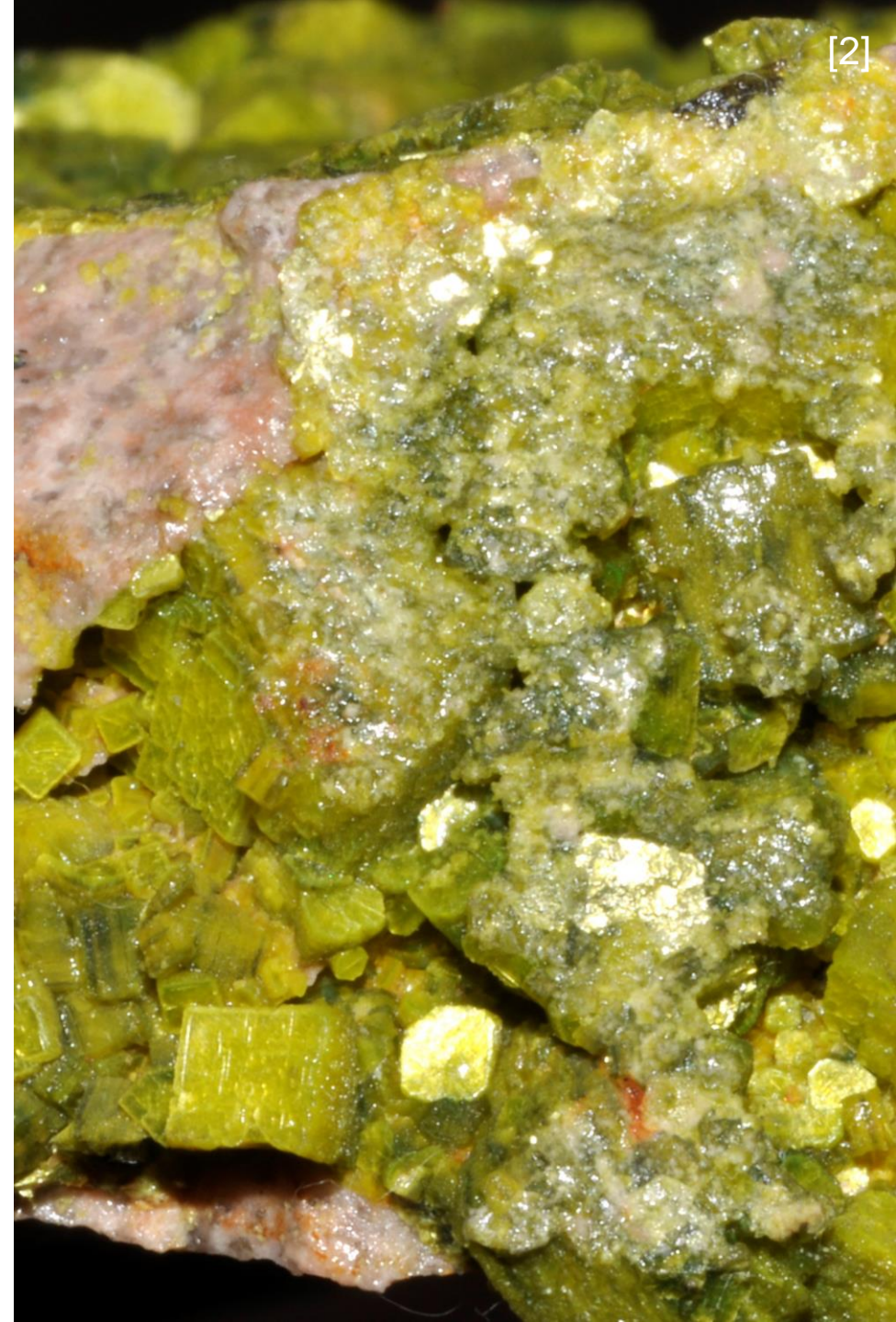
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General information

General information

- **Discovered in 1789 by Martin Heinrich Klaproth**
- **Named after the then recently discovered planet Uranus**
- **Radioactive properties discovered in 1896**
- **Silvery-grey and weakly radioactive metal when refined**
- **Highest atomic weight of the primordial occurring elements**
- **Nuclear power and military applications** ^[1]



Chemistry of uranium

1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																				
1 H Hydrogen 1.008	2 He Helium 4.0026	<div style="display: flex; justify-content: space-between;"> <div style="border: 1px solid black; padding: 5px; background-color: #1a3d4d; color: white; width: 150px;"> <p style="font-size: 24px; margin: 0;">92</p> <p style="font-size: 24px; margin: 0;">238.029</p> <p style="font-size: 36px; margin: 0;">U</p> <p style="margin: 0;">Uranium</p> <p style="margin: 0;">[Rn] 5f³6d¹7s²</p> <p style="margin: 0;">Actinides</p> </div> <div style="text-align: center;"> <p>Metals</p> <div style="display: flex; justify-content: space-around; font-size: 8px;"> Alkali metals Alkaline earth metals Lanthanoids Actinoids Transition metals Post-transition metals </div> </div> <div style="text-align: center;"> <p>Metalloids</p> </div> <div style="text-align: center;"> <p>Nonmetals</p> <div style="display: flex; justify-content: space-around; font-size: 8px;"> Reactive nonmetals Noble gases </div> </div> </div>										5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180	13 Al Aluminium 26.982	14 Si Silicon 28.085	15 P Phosphorus 30.974	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.948														
3 Li Lithium 6.94	4 Be Beryllium 9.0122	11 Na Sodium 22.990	12 Mg Magnesium 24.305	19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798																
5 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29	57-71 La-Lu	55 Rb Rubidium 85.468	56 Sr Strontium 87.62	57-71 La-Lu	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.05	71 Lu Lutetium 174.97		
6 Cs Caesium 132.91	56 Ba Barium 137.33	57-71 La-Lu	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)	87-103 Fr-Og	87 Fr Francium (223)	88 Ra Radium (226)	87-103 Fr-Og	89 Ac Actinium (227)	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (266)	
7 Fr Francium (223)	88 Ra Radium (226)	87-103 Fr-Og	104 Rf Rutherfordium (267)	105 Db Dubnium (268)	106 Sg Seaborgium (269)	107 Bh Bohrium (270)	108 Hs Hassium (277)	109 Mt Meitnerium (278)	110 Ds Darmstadtium (281)	111 Rg Roentgenium (282)	112 Cn Copernicium (285)	113 Nh Nihonium (286)	114 Fl Flerovium (289)	115 Mc Moscovium (290)	116 Lv Livermorium (293)	117 Ts Tennessine (294)	118 Og Oganesson (294)	87-103 Fr-Og	87-103 Fr-Og	87-103 Fr-Og	87-103 Fr-Og	87-103 Fr-Og	89 Ac Actinium (227)	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (266)

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.



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Melija, J., Coplan, T., Berglund, M., et al. (2016). Atomic weights of the elements 2013 (IUPAC Technical Report). Pure and Applied Chemistry, 88(3), pp. 265-291.

General information



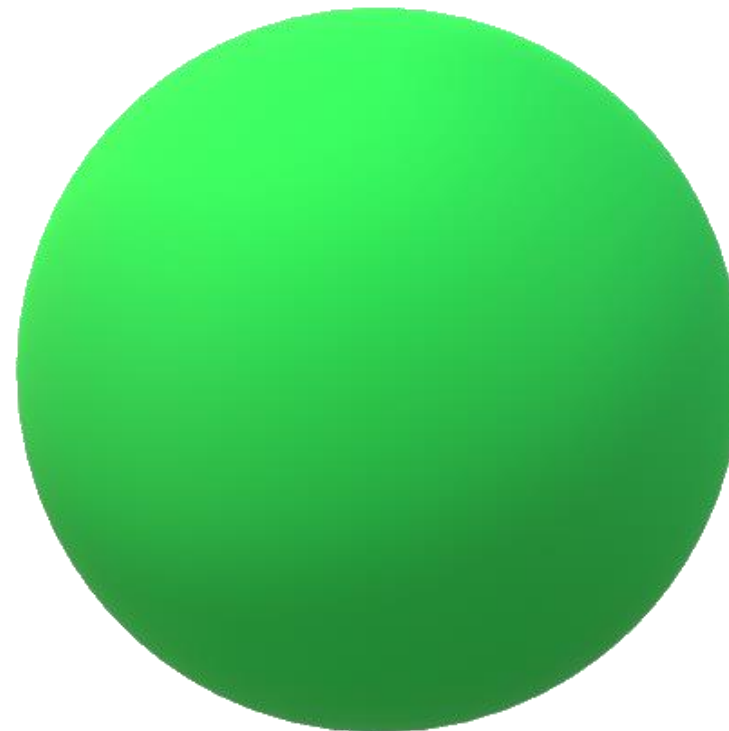
[3]

Properties of Uranium	
Atomic number	92
Atomic mass	238.029
Group	-
Period	7
Block	f-block
Electronic configuration	[Rn] 7s ² 5f ³ 6d ¹
Melting point	1132.2 °C
Boiling point	4131 °C
At RT	Solid
Crystal structure	Orthorombic (Cmcm)

Chemistry of uranium

- **Oxidation states:** +VI, V, IV, III
- **Isotopes:** all of them are radioactive:
 - Most common ^{238}U (99.3 %)
 - Others: ^{235}U , ^{234}U

[1,7]



U 156 pm

or U 156-175 pm



U⁶⁺ 73 pm

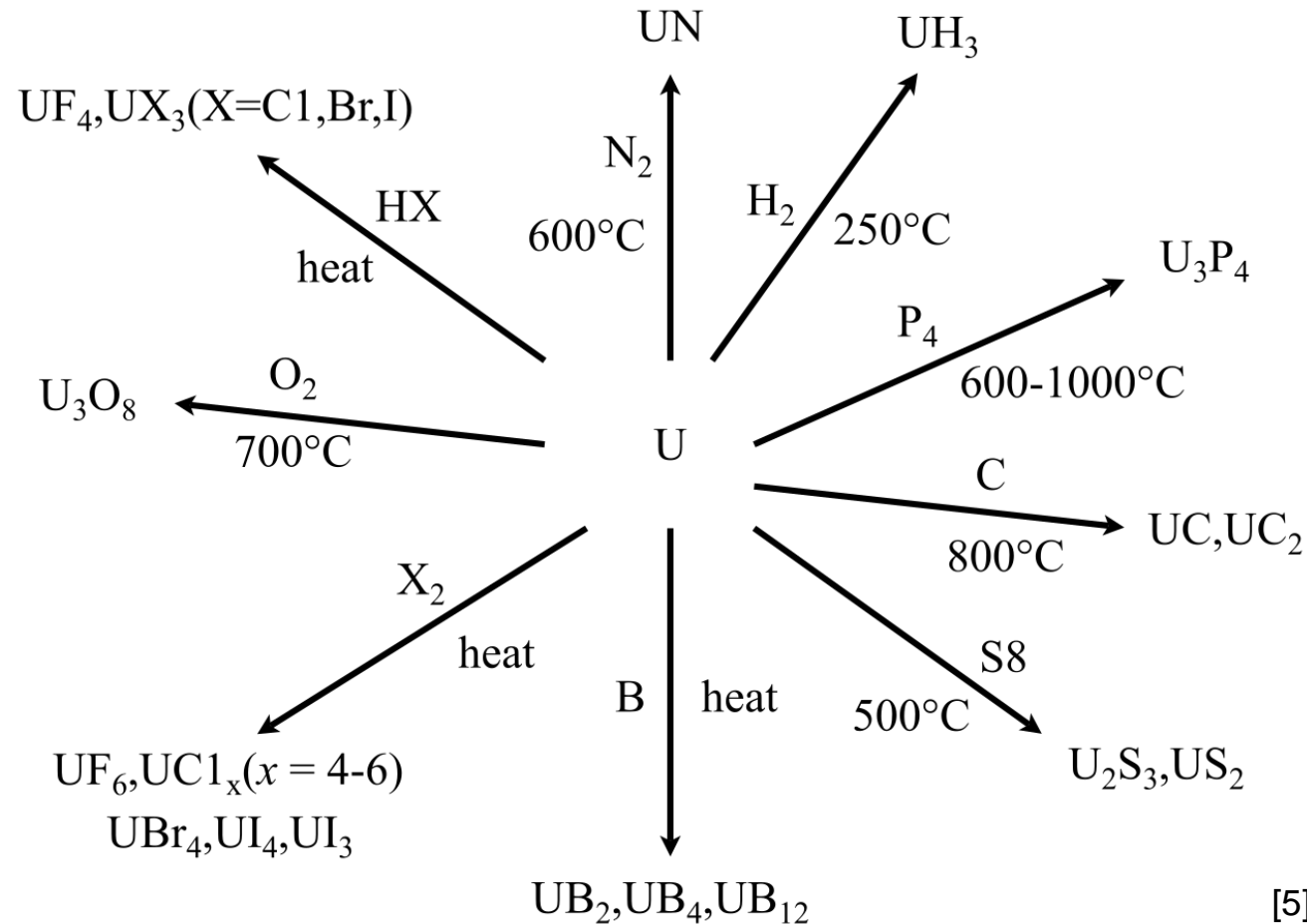
or U⁶⁺ 45-86 pm

[1] <https://en.wikipedia.org/wiki/Uranium>

[7] <http://abulafia.mt.ic.ac.uk/shannon/radius.php?Element=U>

Reactivity of uranium

Electron configuration $[Rn] 7s^2 5f^3 6d^1 \rightarrow +VI$ preferred oxidation state



Uranium compounds

Examples of uranium compounds

- **Uranium forms several oxides** [8, 11]
 - Uranium dioxide UO_2 (reactor fuel)
 - Diuranium pentoxide U_2O_5
 - Uranium trioxide UO_3
 - Triuranium octoxide U_3O_8 (most stable)
 - Uranyl peroxide UO_4
- **Uranium carbides** [9]
 - Uranium methanide UC
 - Uranium sesquicarbide U_2C_3
 - Uranium acetylide UC_2
- **Uranium tetrachloride** UCl_4 [10]

Triuranium octoxide U_3O_8

- Most stable uranium oxide
- Olive green to black solid, odorless [11]
- "Yellowcake" uranium concentrate powder contains around 70% - 90% U_3O_8 by weight
- Coarse powder that has a pungent odor
- Intermediate step in processing uranium ores [12]



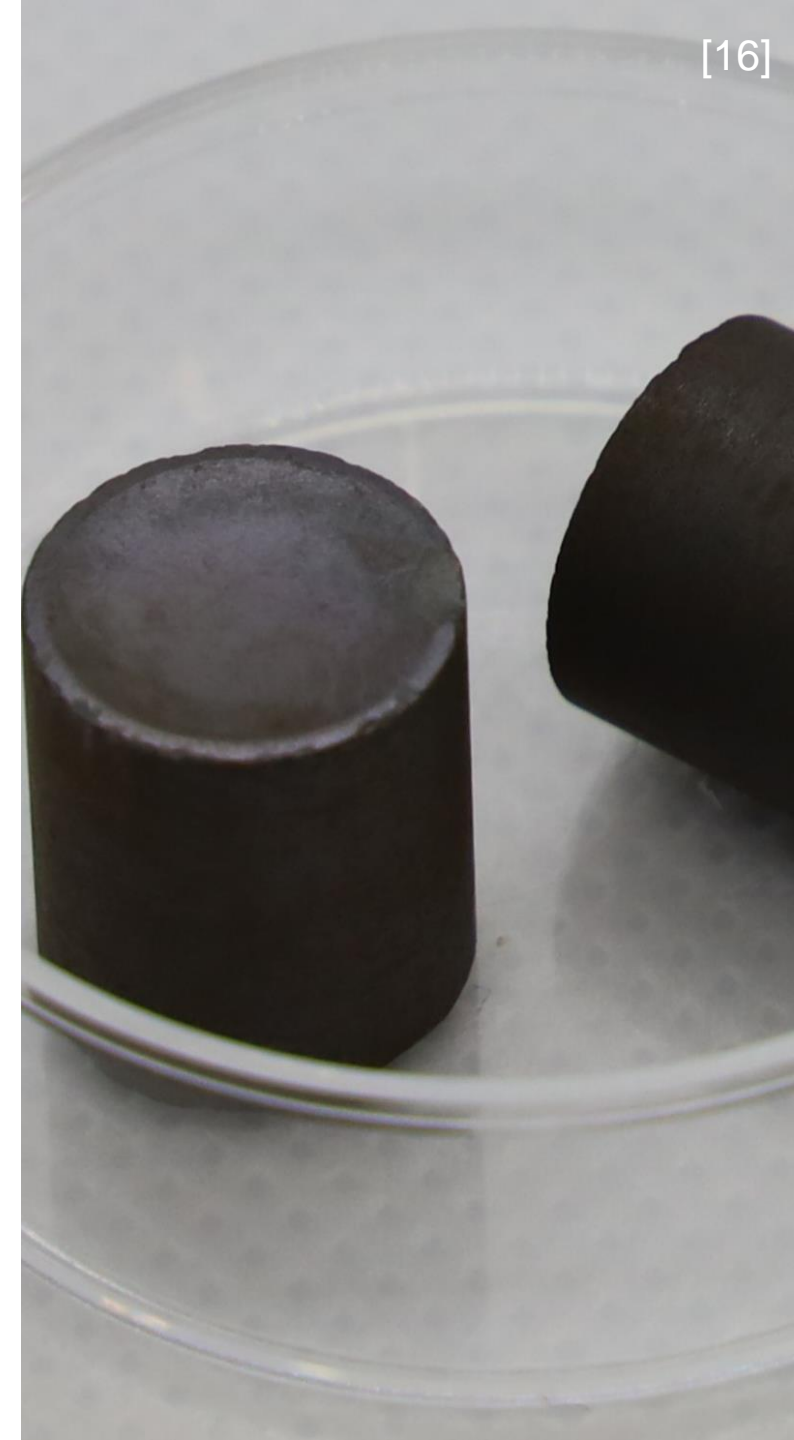
[13]



[14]

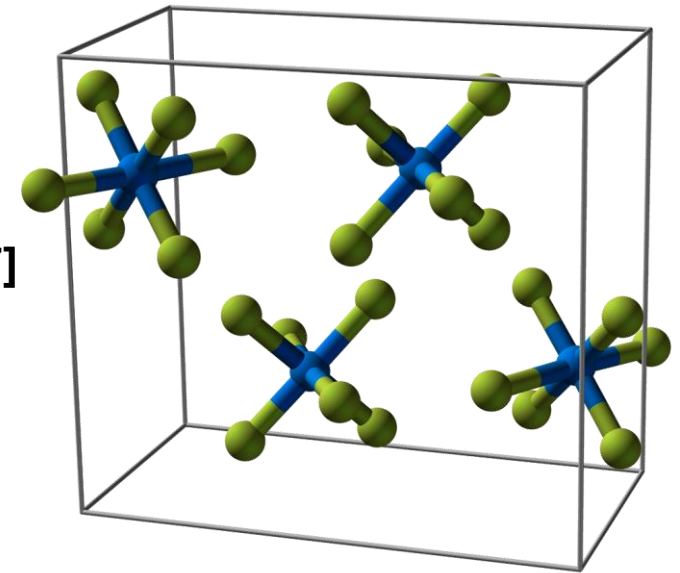
Uranium dioxide UO_2

- Used as nuclear fuel rods in nuclear rods
- Black, radioactive and crystalline powder
- Naturally occurs in the mineral uranitite
- Was used to colour glass and ceramics [15]



Uranium hexafluoride UF₆

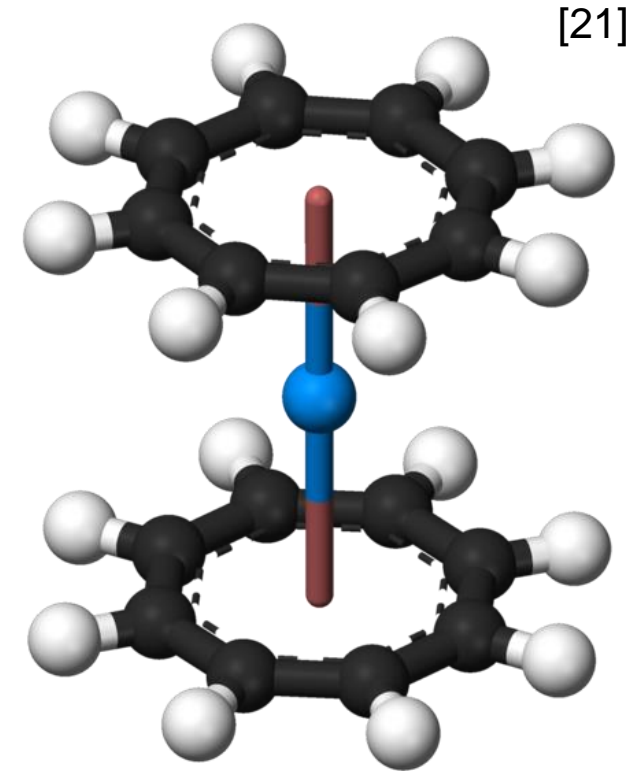
- Used in the process of enriching uranium
- A volatile white solid
- Relatively convenient to process
- Used in both main uranium enrichment methods: the gas centrifuge method and gaseous diffusion [17]



[18]

Organouranium compounds: Uranocene

- Organouranium compounds are organometallic compounds containing a carbon to uranium chemical bond
- Somewhat important to the nuclear industry [19]
- Uranocene $U(C_8H_8)_2$
- Uranium atom sandwiched between two cyclooctatetraenide rings
- No known practical applications [20]



Applications

Applications of uranium

- **Historically used for pottery and photographic chemicals**
- **Nuclear fuel and weapons [1]**
- **Depleted uranium as kinetic energy penetrator (military use) [22]**

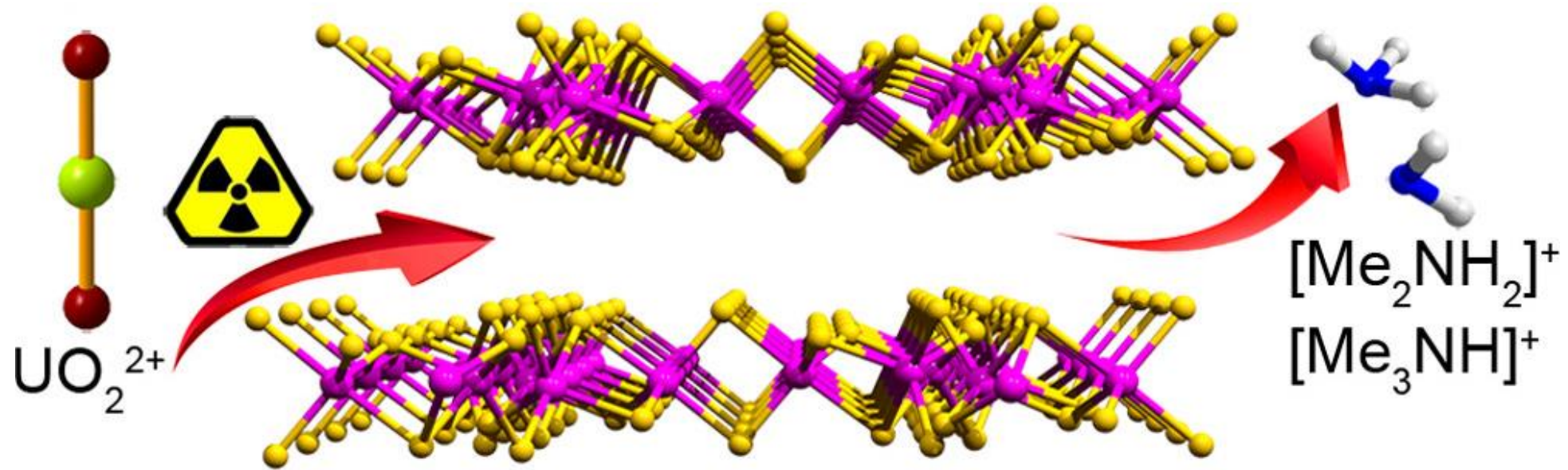
- **Uranium dioxide as a semiconductor material?**
- **Band gap comparable to silicon [15]**
- **A p-n-p transistor of UO₂ was manufactured in a lab [23]**

Recovery of Uranium by a Layered Organic–Inorganic Hybrid Thiostannate (1)

- Uranium is still left in nuclear waste
- $(\text{Me}_2\text{NH}_2)_{1.33}(\text{Me}_3\text{NH})_{0.67}\text{Sn}_3\text{S}_7 \cdot 1.25 \text{H}_2\text{O}$ (FJSM-SnS) is used for recovery of uranium
- Ion exchange with FJSM-SnS where UO_2^{2+} are exchanged for $[\text{Me}_2\text{NH}_2]^+$ and $[\text{Me}_3\text{NH}]^+$ ions

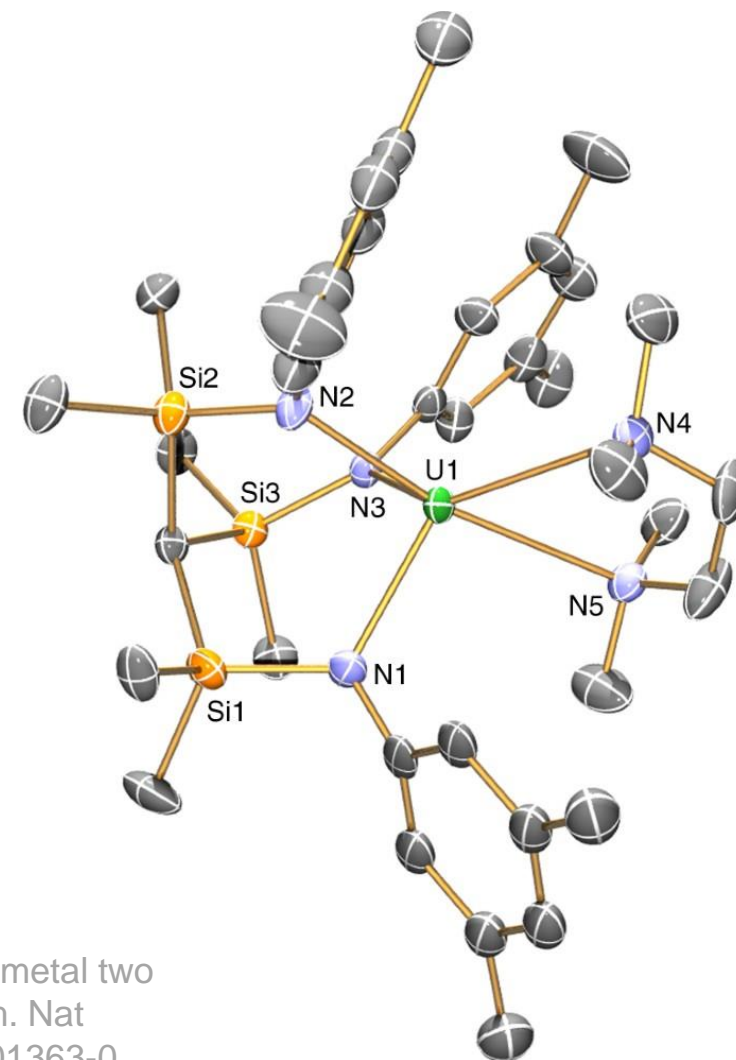


Recovery of Uranium by a Layered Organic–Inorganic Hybrid Thiostannate (2)



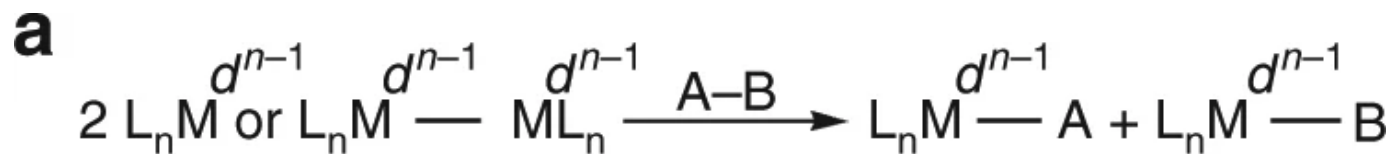
Single-metal two-electron oxidative addition and reductive elimination at uranium

- Single-metal two-electron oxidative addition possible for d-block metals
- Only one- or multi-electron oxidation or reduction reactions for f-block metals
- Possibility to oxidize uranium(III) complexes to uranium(V) complexes

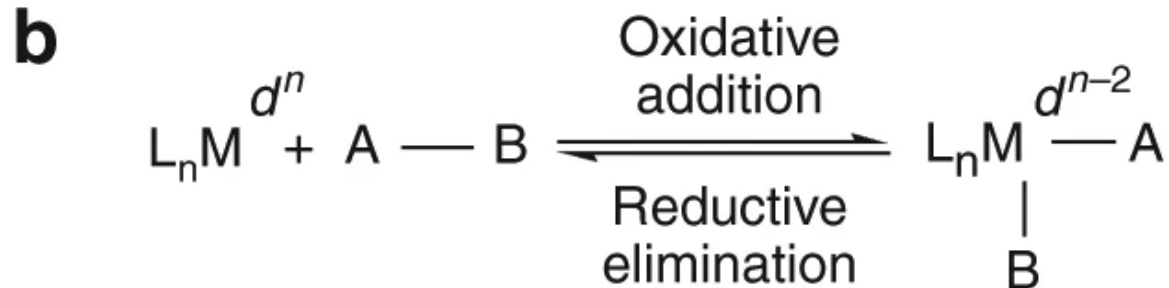


Gardner, B.M., Kefalidis, C.E., Lu, E. et al. Evidence for single metal two electron oxidative addition and reductive elimination at uranium. *Nat Commun* 8, 1898 (2017). <https://doi.org/10.1038/s41467-017-01363-0>

Single-metal two-electron oxidative addition and reductive elimination at uranium



$$\Delta \text{ OS} = +1; \Delta \text{ VE} = +1; \Delta \text{ C.N.} = +1$$



$$\Delta \text{ OS} = +2; \Delta \text{ VE} = +2; \Delta \text{ CN} = +2$$