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Element 92 Uranium

Jack Harrowfield^A and Pierre Thuéry^B

^A ISIS, Université de Strasbourg, 8 allée Gaspard Monge, 67083 Strasbourg, France

E-mail: harrowfield@unistra.fr

^B NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France

E-mail: pierre.thuery@cea.fr

If any element of the Periodic Table could be said to be the centre of controversies and unrest over its use and over the consequences of its use, uranium would be the obvious choice.^[1] While uranium minerals were used as pigments by the Romans^[2] and such use continues today in the preparation of uranium glasses, often referred to as "vaseline glasses" and admired for their yellow colour and green fluorescence (Fig. 1),^[3] Becquerel's discovery^[4] of radioactivity due to uranium dramatically changed the significance attached to the nature of the element. Research^[5] in the first few decades of the twentieth century largely conducted in France (Marie Curie), England (Ernest Rutherford), Germany (Otto Hahn, Lise Meitner, Fritz Strassman) and Italy (Enrico Fermi) established that natural radioactivity was associated with transmutation of one element into another involving emission of combinations of α (helium nuclei), β (electrons) and γ (high energy radiation) particles, that transmutation could be induced by bombarding one nucleus with another, and that uranium, in particular, was just the starting point of a long decay chain ultimately leading to lead as a stable species. It was Chadwick's 1932 discovery of the neutron, however, which led Fermi to experiment with neutron-induced transmutation and Hahn and Meitner to extend his experiments in a way which led to their 1938 discovery of nuclear fission by irradiating uranium with neutrons. The interpretation by Meitner and her nephew Otto Frisch of the processes involved and particularly of the origin of the enormous energy being released awoke the international community to the prospects, perhaps both good and bad, of this reaction and led, essentially within the context of World War II, to a race between scientists in the United States (Manhattan Project^[6]) and Germany^[7] to establish real applications. One of these, to use a controlled fission reaction as an energy source, was achieved by Fermi in Chicago in 1942, another, achieved within the Manhattan Project under Robert

Oppenheimer's direction, was the creation of the atomic bomb, exploited on Japan in 1945. While advocacy of peaceful uses of "atomic energy" was popular immediately after WWII and led eventually to many countries (notably, France) becoming dependent upon electricity generation in nuclear power stations, it was accompanied by a nuclear weapons arms race, now between the Soviet Union and the United States (and allies), constituting the "Cold War" which made for some 50 years study of uranium chemistry a rather restricted subject, very much focussed on methods of treating nuclear waste. In recent times, with a wider appreciation of its prospects,^[8,9,10] uranium chemistry has undergone remarkable developments, briefly considered below.

Uranium occurs naturally on Earth as three isotopes ^{234}U , ^{235}U and ^{238}U , while the isotope ^{233}U can be synthesised by neutron irradiation of thorium. As each isotope is radioactive and has a different half-life, the natural isotopic distribution is time dependent and the current estimates are 99.3 % ^{238}U , 0.7 % ^{235}U and 0.005 % ^{234}U , although since ^{235}U is the isotope of interest for the nuclear industry, commercially available uranium compounds contain "depleted" uranium and can be considered essentially as containing just ^{238}U . ^{238}U is described as being weakly radioactive^[9] and is an α emitter, so that its compounds can be used in the laboratory without too rigorous protection procedures provided inhalation or ingestion are avoided. ^{235}U is the only naturally occurring "fissile" nucleus, meaning that slow neutron irradiation induces a fragmentation to give a variety of lighter elements, including barium, which was the basis of Hahn's meticulous proof of the occurrence of such fission. Since the reaction produces extra neutrons, a "chain reaction" can be induced provided the amount of ^{235}U in the uranium sample is ~ 3 % or higher and this of course is the basis of the use, in different ways, of uranium in nuclear reactors and atomic bombs. Anomalies in terrestrial uranium isotope distributions, first detected in samples from the Oklo mine in Gabon,^[11] have been interpreted as evidence that at a time following nucleosynthesis^[12] of the isotopes when the ^{235}U level was approximately 3 %, some natural nuclear reactors were in operation.

The name uranium (firstly "uranit") was given to the element by Martin Heinrich Klaproth in 1789, partly in support of a Royal Academy colleague who favoured the name Uranus for the planet, at the time a matter of dispute. Thus, the element name derives from that of the ancient Greek god of the sky. Klaproth thought that he had isolated the element from an ore sample (obtained from a mine close to the present day

border between Germany and the Czech Republic) but he probably had just an oxide and elemental uranium metal was not isolated until 1841 by Eugène Péligot using reduction of the tetrachloride with potassium.^[13] The same ore, obtained from a nearby mine in what is now the Czech town of Jáchymov, was the "pitchblende" or uraninite (Fig. 2) used by Marie Curie in her celebrated work which included the isolation of polonium^[14] and radium. The name "pitchblende" derives from the German "pech blende", meaning "bad luck rock" since it was intrusions of this ore which signalled the end of silver ore deposits that were the basis of the wealth of the town then known as Joachimsthal. Silver coins minted there were known as Joachimsthaler, abbreviated to simply "thaler", a word which is the etymological origin of "dollar".

Pitchblende, with the approximate formula UO_2 , and carnotite, $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$, are the best known uranium minerals but there are many others,^[15] widely distributed, and the crustal abundance of uranium (2.3 ppm) is not particularly low, being greater than that of tin, for example, despite the fact that it has the greatest atomic number and heaviest nucleus of any element found naturally in significant concentrations on Earth. Processing of uranium ores^[16] can involve either acid (H_2SO_4) or base (Na_2CO_3) leaching, with the finally isolated product usually being "yellowcake", U_3O_8 , a mixed U(V)-U(VI) oxide. Australia, with approximately one third of the world's known uranium reserves, currently exports close to 6000 tonnes of yellowcake, with a value near one billion A\$, each year.^[17] Treatment^[18] of returned nuclear waste has been proposed as one form of uranium chemistry for Australia but has not proven to be a popular idea. Part of the research on waste treatment has involved efforts to find selective "uranophile" ligands, (Fig. 3) first considered^[19] for their possible use in extraction of the enormous total quantities, in very dilute solution, of the uranium dissolved in the world's oceans.

Putting the chemistry of nuclear applications aside, uranium chemistry still has both richness and diversity which exceed that of many familiar transition metals.^[8-10] In its compounds, oxidation states from +I to +VI are well characterised, with relativistic effects in its bonding leading to significant involvement of 5f orbitals in its valence shell.^[10] Compounds in the oxidation states IV and VI are most abundant but even oxidation state V, once thought to be inherently unstable, has been shown to have many stable forms.^[20] While the catalytic activity of uranium (in ammonia synthesis) was recognised by Haber as long ago as 1909,^[9] the burgeoning of uranium organometallic

and multidentate ligand chemistry which began in the 1960s, notably involving the synthesis of "uranocene" (*bis*(cyclo-octatetraenide)uranium(IV)),^[24] has led to the development of complexes (Fig. 4) able to activate important small molecules such as CO, CO₂ and N₂^[10] and to catalyse a variety of reactions including olefin polymerisation, Diels-Alder additions, hydroamination and hydrosilylation.^[8] A U(VI) complex with a terminal nitride ligand, although not organometallic, is very active in CH bond activation and was described in 2013 as an "actinide milestone".^[22]

The combination of the valence shell, size and shape of uranium in its various oxidation states and complexes is what determines their properties and the best-known examples of stereochemistry rarely found outside the actinide series are those in the myriad complexes of U(VI) incorporating the linear uranyl cation UO₂²⁺, where the uranium is, with rather few exceptions,^[23-25] in either pentagonal- or hexagonal-bipyramidal coordination (Fig. 5). Early crystal structure determinations established the coordination geometries of simple species such as Na[UO₂(O₂CCH₃)₃] (hexagonal-bipyramidal)^[26] and [UO₂(OH₂)₅](ClO₄)₂ (pentagonal-bipyramidal)^[27] but recent interest in exploiting the "unusual" coordination geometry of uranyl ion for the synthesis of novel coordination polymers/metal-organic frameworks^[23,28-31] has provided innumerable examples of both forms involving more complicated ligands. Both forms are also found in the large family of remarkable cluster complexes derived by peroxide complexation of uranyl ion.^[32]

A property of most uranyl compounds is that they show a green luminescence, long known in the case of uranium ("vaseline") glasses (Fig. 1). Typically, this luminescence displays a striking vibronic coupling (Fig. 6) due to the symmetric stretching mode of the UO₂²⁺ unit.^[33] Excited uranyl ion is well known as a photo-oxidant^[34] and one of the reasons^[31] for investigating the synthesis of framework solids incorporating uranyl centres has been the hope of finding solid state cavities suitable for selectively binding substrates in the vicinity of the photoactive centre. Success^[35] in this area has been limited to date, although simple uranyl salts deposited on supports such as titania or mesoporous silica^[36] have been shown to be active photocatalysts for oxidation of a variety of substrates and quite diverse solid coordination complex systems where moderately large molecules are included within cavities (Fig. 7) are now known.^[37,38] Optimism remains that real applications of uranium outside the nuclear and

military domains may continue to be found, with many areas yet to be fully investigated.^[39]

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Figures



Figure 1 Uranium glassware showing green fluorescence under UV light
<https://fr.wikipedia.org/wiki/Ouraline>



Figure 2 Crystals of pitchblende (uraninite)
<https://fr.wikipedia.org/wiki/Pechblende>

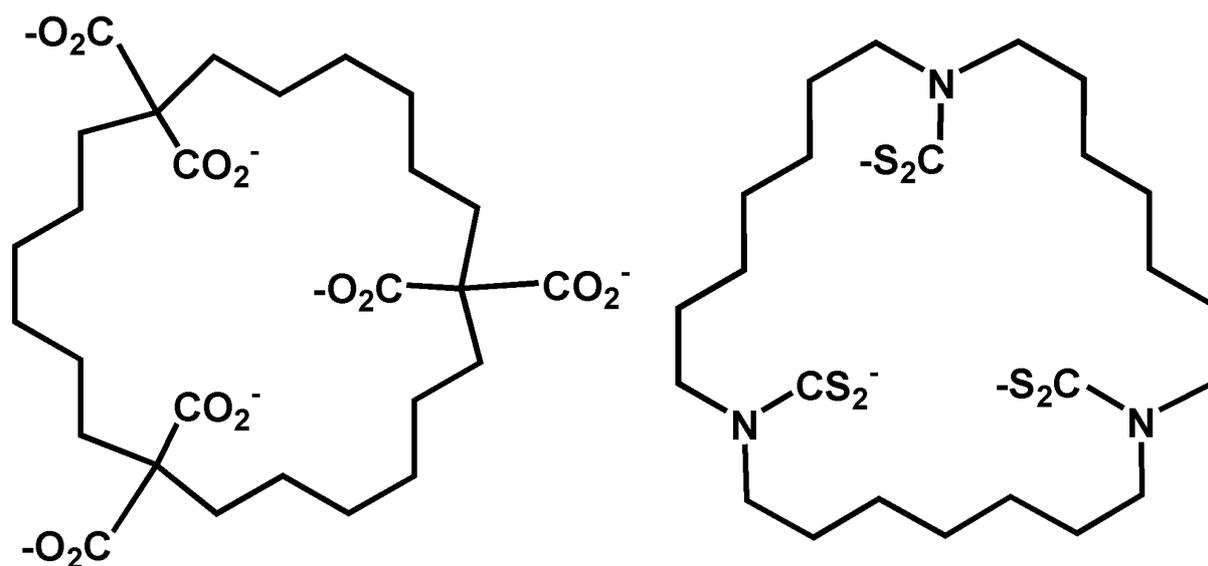


Figure 3 Macroyclic carboxylate and dithiocarbamate ligands as examples of "uranophiles"^[19] designed to be selective through their capacity to form a planar hexagonal array of donor atoms.

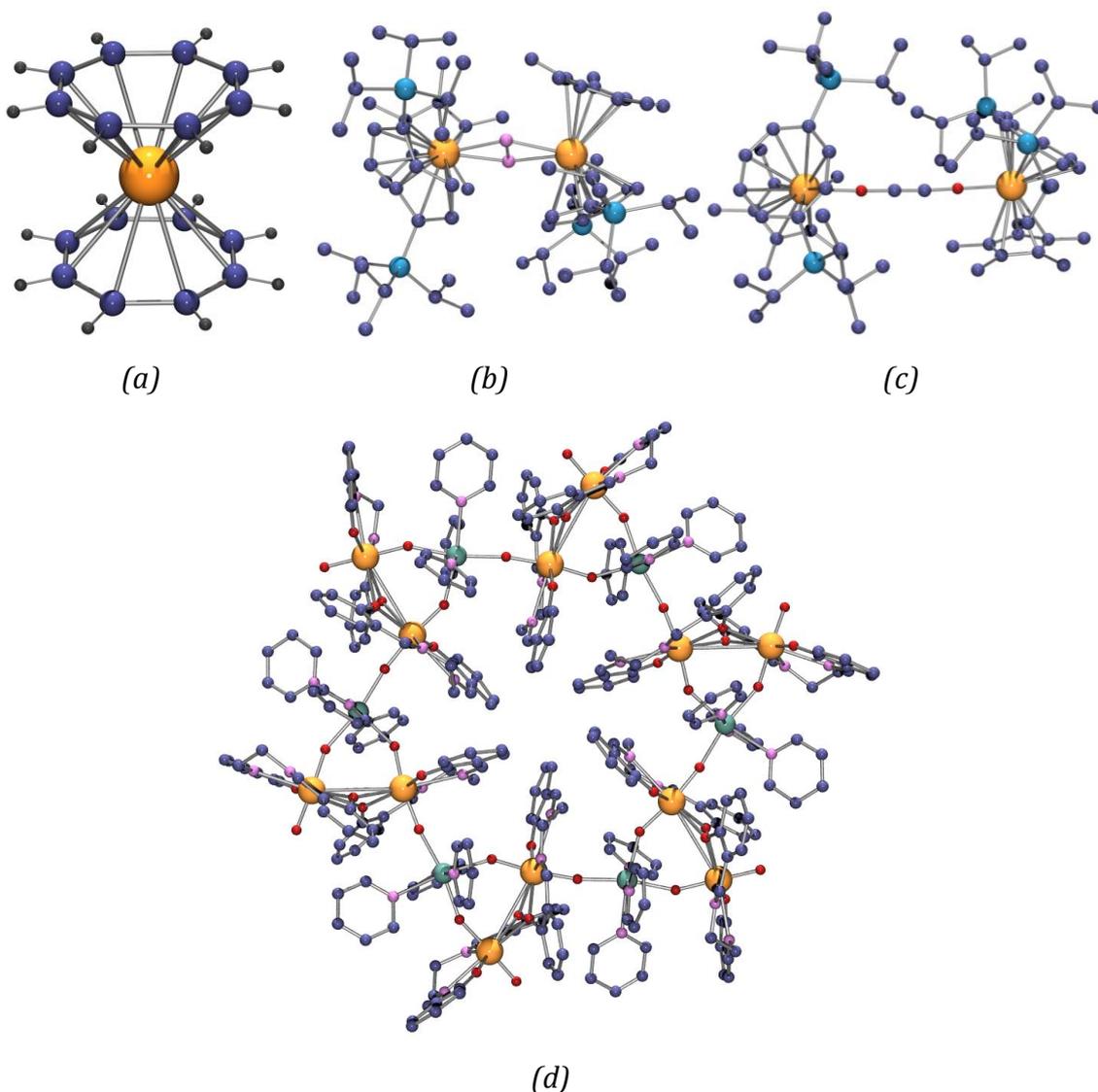


Figure 4 A selection of crystallographically characterised uranium complexes illustrating revelatory developments of the element's chemistry (see references [10], [21]): (a) uranocene, $[U^{IV}(C_8H_8)_2]$; (b) $[U(\eta^5-C_5Me_5)[\eta^8-1,4-(iPr_3Si)_2C_8H_4]_2(\mu-\eta^2:\eta^2-N_2)]$, a reactive dinitrogen complex; (c) the ethynediolate-bridged U^{IV} complex produced by reaction of $[U^{III}\{(iPr_3Si)_2C_8H_6\}(Cp^*)]$ with CO; (d) the octadecanuclear molecular magnet involving linkage of dimeric $[U^V(salen)]$ units by $Mn^{II}(py)_3$ bridges. Colour code: C dark blue, N purple, O red, Si light blue, Mn green, U yellow. Cp^* = pentamethylcyclopentadienide, salen = bis(salicylaldiminatoethylenediamine.)

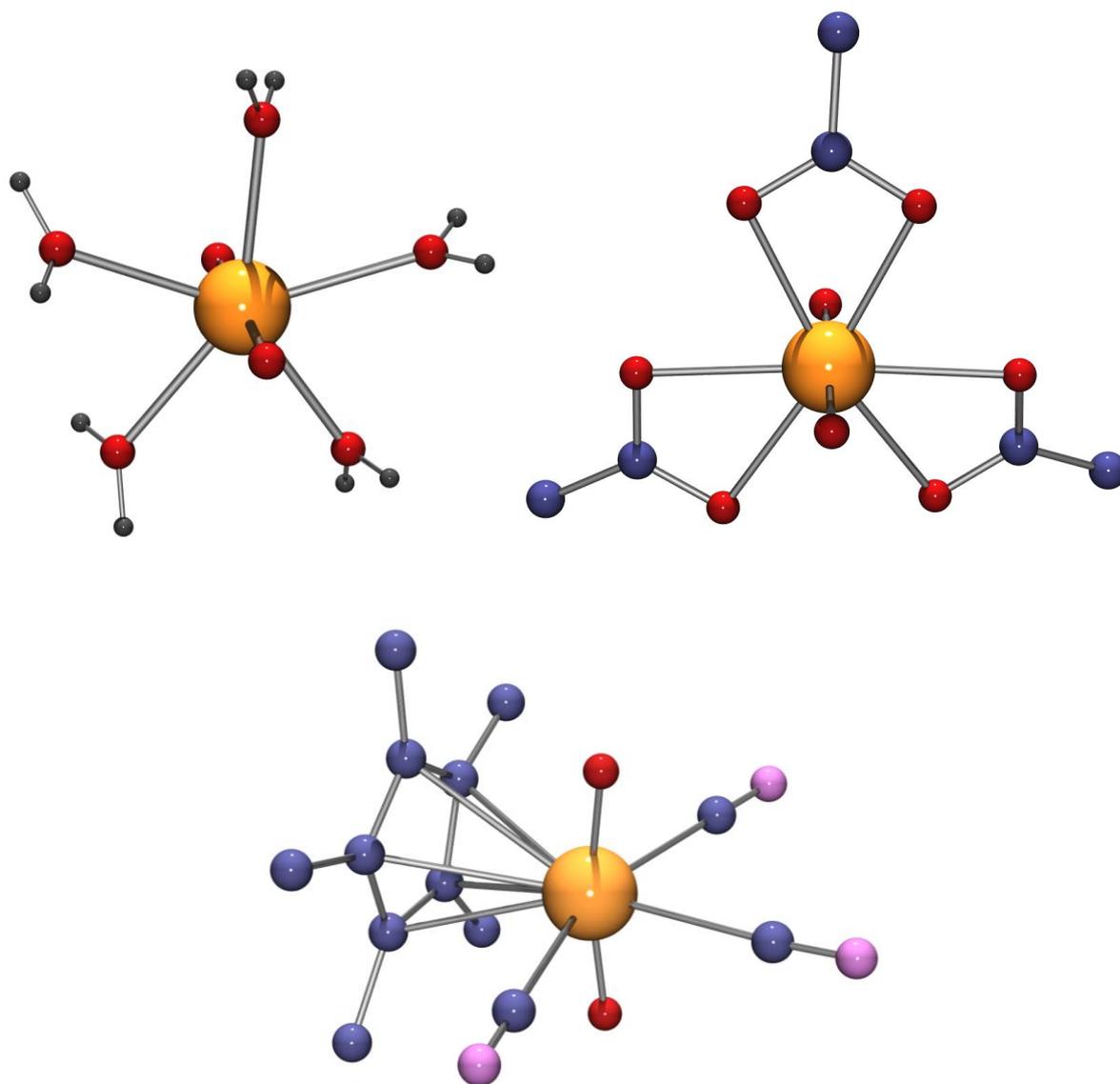


Figure 5 Representations of pentagonal-bipyramidal uranium(VI) as found^[27] in $[\text{UO}_2(\text{OH}_2)_5]^{2+}$ and hexagonal-bipyramidal uranium(VI) as found^[26] in $[\text{UO}_2(\text{O}_2\text{CCH}_3)_3]$ (top row). An unusual uranyl ion environment found in $[\text{UO}_2(\text{C}_5\text{Me}_5)(\text{CN})_3]^{2-}$ (lower row).^[25]

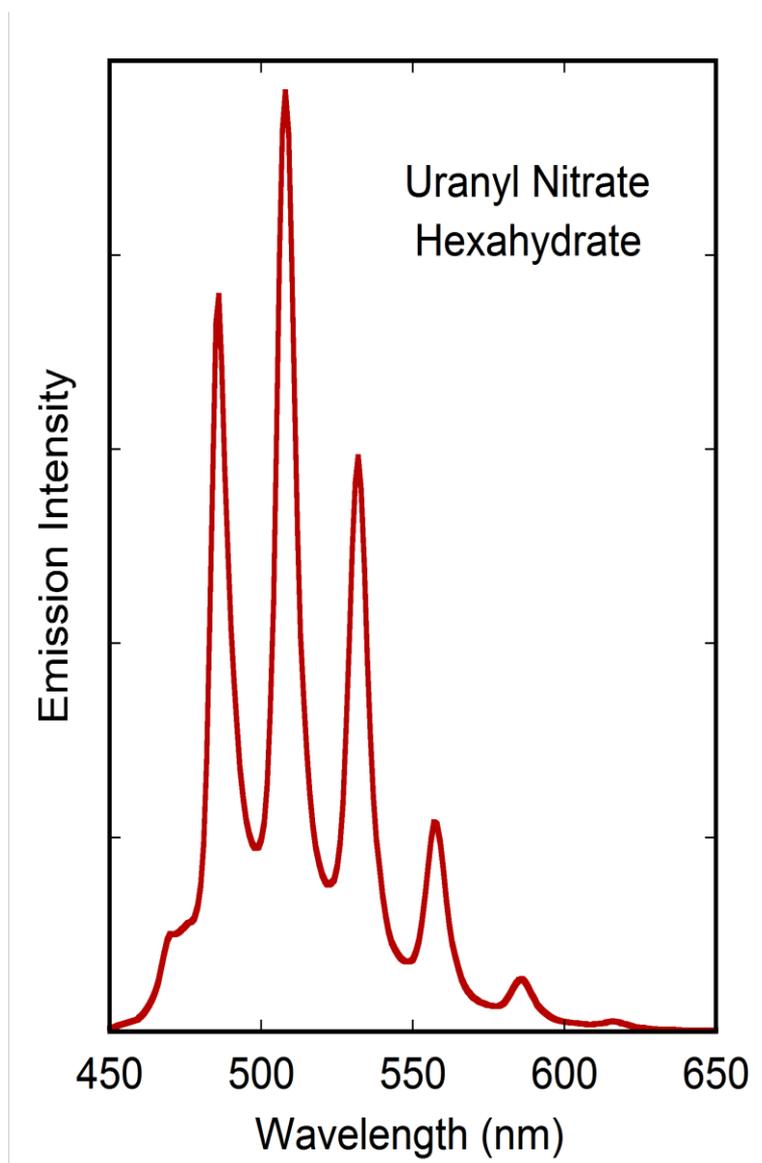


Figure 6 Solid state emission from pentagonal bipyramidal U(VI) in $UO_2(NO_3)_2 \cdot 6H_2O$

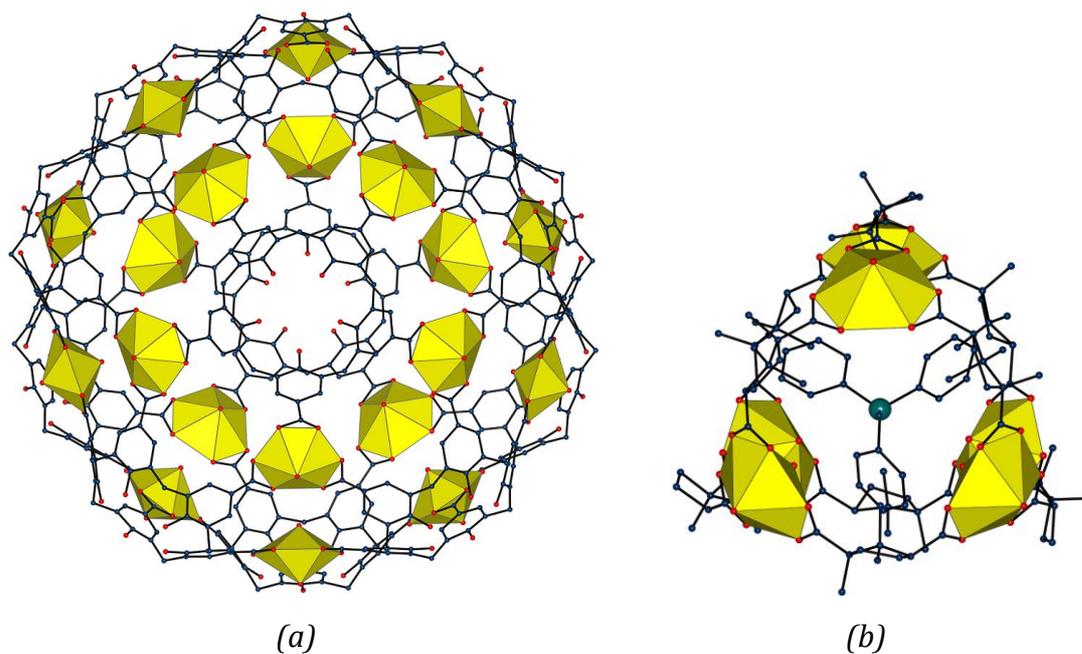


Figure 7 Cage species present in uranyl ion complexes of (a) *p*-carboxylatocalix[5]arene^[37] and (b) (1*R*,3*S*)-(+)-camphorate^[38]. The former is large enough to include diprotonated 1,4,7,10-tetra-azacyclododecane and the latter methyltriphenylphosphonium cation (shown with the phosphorus atom in blue). Uranyl units are shown as yellow polyhedra.