

Isolation of the Large {Actinide}₃₈ Poly-oxo Cluster with UraniumClément Falaise,[†] Christophe Volkringer,[†] Jean-François Vigier,[†] Arnaud Beaurain,[†] Pascal Roussel,[†] Pierre Rabu,[‡] and Thierry Loiseau^{*,†}[†]Unité de Catalyse et Chimie du Solide (UCCS), UMR CNRS 8181, Université de Lille Nord de France, USTL-ENSCL, Bat. C7, BP 90108, 59652 Villeneuve d'Ascq, France[‡]Département de Chimie des Matériaux Inorganiques, IPCMS and NIE, UMR 7504 CNRS-UdS, 23, rue du Loess, BP 43, 67034 Strasbourg cedex 2, France

S Supporting Information

ABSTRACT: By controlling the water content, a new poly-oxo-metalate species containing 38 uranium centers has been solvothermally synthesized in the presence of benzoic acid in tetrahydrofuran (THF). The {U₃₈} motif contains a distorted UO₂ core of fluorite type, stabilized by benzoate and THF molecules. This compound is analogous to the {Pu₃₈} motif and was characterized by X-ray photoelectron spectroscopy and magnetic analyses.

The chemistry of polynuclear oxo/hydroxo complexes bearing actinide metals has been extensively investigated in the past decade. Considering the most stable oxidation state, +6, for uranium under ambient conditions, a large number of molecular uranyl-based moieties have been identified by means of peroxo bridging ligands, which favor the formation of fullerene-type nanospheres with a wide range of nuclearities (from U₂₄ to U₆₈).¹ With organic ligands of calixarene types functionalized by carboxylate groups, the self-assembly of 20 discrete uranyl cations has been reported, giving rise to large icosahedral cages with nanoscale size.² Lower valence uranium is less investigated, although it can occur at the +4 state in biological redox systems involving bacteria in contaminated groundwater.³ Indeed, tetravalent actinides are also known to hydrolyze in aqueous media in order to undergo polycondensation processes through oxo or hydroxo bridges to form polynuclear species.⁴ With uranium, several atomic arrangements of oxo-hydroxo clusters based on U^{IV} have been reported so far.⁵ These structural records further our understanding of the oligomerization of nanospecies,⁶ which could be formed during geochemical reactions in the natural environment.⁷ Knowledge of how tetravalent uranium combines with carboxylate ligands such as oxalate moiety is also of significant interest for recycling spent nuclear fuel during the precipitation step.⁸ The hexanuclear moiety (U₆O₈) with an octahedral configuration of uranium nodes is a building block commonly encountered in some complexes stabilized by triflate,⁹ formate,¹⁰ or benzoate groups.¹¹ It was reported that the hydrolysis rate is a key parameter for controlling the condensation of such clusters. With this strategy, new polynuclear species have been isolated and crystallized in organic solvents upon addition of a precise water amount. This led to the isolation of several poly-oxo-hydroxo cores containing 10 (U₁₀O₁₄),^{5b} 12 (U₁₂O₂₀),^{5a} or 16 (U₁₆O₂₄)^{5b}

uranium centers, for which partial oxidation reactions occur, giving rise to mixed-valence U^{IV}/U^V systems. These species are usually decorated by monodentate O-donor and/or N-donor organic molecules, which complete the coordination sphere of uranium centers.

We recently started to investigate the reactivity of carboxylic acids with hexavalent¹² or tetravalent¹³ uranium and described a first extended 3D network involving trinuclear uranium(IV)-centered motifs with trimesate¹³ (tritopic) linker crystallizing in *N,N*-dimethylformamide under solvothermal conditions. Following this idea, new open frameworks have been synthesized and are built up from hexanuclear U^{IV} motifs with ditopic ligands (terephthalate and derived molecules).¹⁴ Herein, we describe the synthesis and characterization of a novel molecular polyoxometalate core involving the oxo condensation of 38 uranium centers {U₃₈} by means of monotopic benzoate linker.

Black crystals of U₃₈O₅₆Cl₁₈(THF)₈(bz)₂₄·8THF have been solvothermally synthesized at 130 °C for 36 h, by using uranium tetrachloride with benzoic acid and tetrahydrofuran (THF) as solvent under inert atmosphere (Ar). A controlled amount of water (5–70 μL, 0.28–3.89 mmol for 0.26 mmol of UCl₄) was typically added to the reaction mixture in order to allow the condensation of {U₃₈} [see synthesis details in Supporting Information (SI)]. A similar procedure has been previously described in the literature for the formation of a large iron core {Fe₁₁}.¹⁵ After the thermal treatment, {U₃₈} is obtained as a pure phase and easily observable as small black crystallites with octahedral shape (50–150 μm size, see Figure S1).

Single-crystal X-ray diffraction analysis revealed the formation of discrete polyoxometalate containing 38 uranium atoms based on the fluorite-type structural packing. It is closely related to that occurring in the Pu^{IV}-based anionic nanocluster [Pu₃₈O₅₆Cl₅₄(H₂O)₈]¹⁴⁻, exhibiting the same metal nuclearity,¹⁶ but is much more distorted due to the geometric constraints of monotopic organic ligands (benzoate and THF) attached to the uranium centers. The crystal symmetry is described in the *I4/m* space group, but a disorder of linked peripheral THF and benzoate molecules, or coupling of benzoate/chloride (1:1) groups, is observed for some of them (see Figure S2e–g). Attempts to refine in lower symmetry (*I4*) did not change the situation unambiguously.

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In addition to this symmetry, the crystals were systematically twinned (twin plane along $[110]$ direction) and treated with the twinning option in JANA2006.¹⁷ We also used the rigid-body approach for benzoate molecules. This is quite far from the ideal $Fm\bar{3}m$ symmetry expected for fluorite-type arrangement, which is reflected by a strong distribution of uranium–anion distances in the $\{U_{38}\}$ species. A first set of uranium atoms is observed for the 14 cations (U_{14}) occupying the center of the $\{U_{38}\}$ core (Figure 1). It corresponds to the nearly

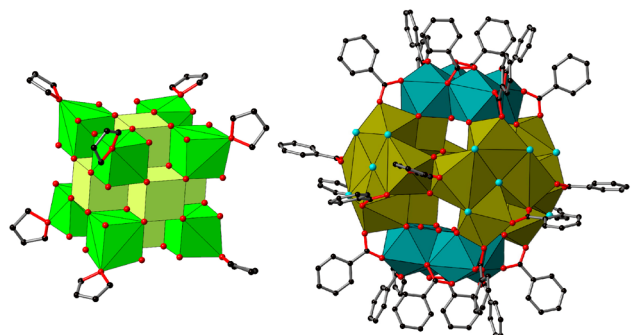


Figure 1. (Left) View of the internal (U_{14}) core in $U_{38}O_{56}Cl_{18}(THF)_8(bz)_{24}\cdot 8THF$, showing the almost ideal fluorite-type arrangement of the UO_8 cubic surroundings for uranium. Only THF molecules complete the coordination sphere of the external uranium atoms. (Right) View of the peripheral 24 uranium polyhedra around the $\{U_{14}\}$ core (the latter has been omitted for clarity). Only benzoate groups complete the coordination sphere of these uranium centers. Hydrogen atoms, THF, and benzoate/Cl disorders have been omitted for clarity.

ideally close packing of UO_2 , with the expected cubic coordination geometry for the uranium centers (UO_8 polyhedra) linked to each other through a μ_4 -oxo edge-sharing connection mode. U–O distances range from 2.228(8) to 2.427(8) Å, and the cubic environment is almost regular, except for one longer U–O distance from peripheral UO_8 polyhedra to a bonded THF molecule ($U-O^{THF} = 2.521(10)$ Å), which slightly distorts the cubic geometry. An identical fluorite-type (U_{14}) core has been observed in the $\{Pu_{38}\}$ cluster. It is interesting to notice the connection of $Ce^{IV}O_8$ cubic polyhedra as fragments of the ideal fluorite type (CeO_2) in the large $\{Ce_{22}\}$ oxo cluster.¹⁸

Each of the six faces of the (U_{14}) core is decorated by four additional uranium centers ($6(U_4)$), which leads to the formation of the $\{U_{38}\}$ motif, related to a truncated octahedral configuration of uranium nodes. Four of the faces are crystallographically equivalent and correspond to four uranium atoms with two $UO_4O^{bz}Cl_3$ and two $UO_4O^{bz}Cl_2$ coordination states, defining distorted square antiprismatic geometries (Figure 2). The U–O and U– O^{bz} distances are 2.230(9)–2.364(8) and 2.25(2)–2.50(2) Å, respectively. The U–Cl distances are 2.812(4)–2.848(4) and 3.032(12) Å, with a μ_2 coordination fashion, whereas a central μ_4 -Cl exists with U–Cl bond distances of 3.043(4)–3.114(4) Å. The carboxylate arm of the benzoate molecule adopts a bidentate connection mode between two adjacent uranium atoms. The two remaining faces decorating the fluorite-type core (U_{14}) possess one type of coordination for uranium, corresponding to a $UO_4O^{bz}_4Cl$ tricapped trigonal prismatic polyhedron (Figure 2).

The U–O and U– O^{bz} distances are 2.234(8)–2.375(8) and 2.403(7)–2.734(16) Å, respectively, and the μ_4 -chlorine is

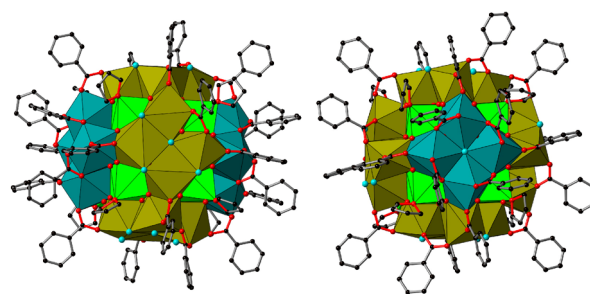


Figure 2. Two perpendicular views of the $\{U_{38}\}$ nanocluster in $U_{38}O_{56}Cl_{18}(THF)_8(bz)_{24}\cdot 8THF$. (Left) Capped face of the (U_{14}) core showing the μ_3 -chloro group bridging three uranium centers (brown polyhedra) together with a bidentate benzoate ligand. (Right) Capped face of the (U_{14}) core showing the μ_4 -chloro group bridging four uranium centers (teal polyhedra). Hydrogen atoms, THF, and benzoate/Cl disorders have been omitted for clarity.

located at the center between the four uranium atoms ($U-Cl = 3.023(3)$ Å). For this face, the benzoate molecules act as bidentate or chelate linkers. Other THF molecules are also found intercalated between the $\{U_{38}\}$ cores and contribute to the 3D cohesion of the structure.

Chemical and thermogravimetric analyses converge to eight free THF molecules per $\{U_{38}\}$ core, although only two disordered solvent species have been revealed from single-crystal analysis. Indeed, careful examinations of the crystal data indicate the presence of voids, which can be attributed to these solvent molecules, therefore resulting in a discrete $U_{38}O_{56}Cl_{18}(THF)_8(bz)_{24}$ motif, which possesses two extra negative charges. As no additional positive charge is observed from the XRD analysis, these two negative charges could be compensated by partial substitution of the O-bridge by an OH-bridge, with a ratio of $54O/2OH$ (3.6% for OH), of terminal Cl by H_2O species, with a ratio of $16Cl/2H_2O$, or of U^{IV} by U^V , with a ratio of $36U^{IV}/2U^V$ (5.2% for U^V). From the comparison with $\{Pu_{38}\}$ (containing only internal oxo bridges within the cluster), some hydroxo groups could occur with the U-based system since U^{IV} can be considered a weaker Brønsted acid cation, and therefore olation (versus oxolation) reaction could be favored during the condensation process.⁶ The second hypothesis could be related to the possible exchange of peripheral chloride groups by water. In fact, this type of interchange has also been observed in the $\{Pu_{38}\}$ cluster, without any perturbation of the inorganic core.^{16b} The occurrence of such OH or H_2O species is quite difficult to observe because of their low amount within the $\{U_{38}\}$ cluster. The presence of OH or H_2O groups should be observed by specific IR vibrations, but that was not the case (Figure S7). EDX analysis also indicated a U/Cl ratio of 69/31 ($\pm 2\%$), which is close to the values expected from XRD data (calcd 68/32 for $U_{38}Cl_{18}$). In a last hypothesis, the $\{U_{38}\}$ motif is formally neutral, considering uranium in a pentavalent state. These U^V species would be distributed over the cationic sites since the bond valence calculations (see Table S1) do not discriminate any preferential positions for them. The occurrence of mixed-valence U^{IV}/U^V , with a relatively low concentration of U^V , was typical of the large polynuclear uranium clusters previously reported by Mazzanti et al.,⁵ for instance, but was not present in the $\{Pu_{38}\}$ analogue.

Although the expected U^V content was low (5.2%), the $\{U_{38}\}$ compound has been characterized by X-ray photoelectron spectroscopy (XPS) analysis, and its magnetic behavior was

measured to examine the possibility of a mixed-valence state. The U 4f XPS spectrum (Figure S6) shows binding energies located at 380.6 eV (fwhm = 2.5 eV) and 391.5 eV (fwhm = 2.5 eV) for the main $U4f_{7/2}$ and $U4f_{5/2}$ components, respectively (Table S2). These binding energy values as well as their satellite shift (+6.6 eV) are similar to those observed in the previous U^{IV} trimesate¹³ or other U^{IV} compounds in the literature.¹⁹ However, a second set of components assigned to U^V is not observed, and the confirmation of its presence is rather difficult since the line width is larger in the $\{U_{38}\}$ complex.

The magnetic behavior of $U_{38}O_{56}Cl_{18}(THF)_8(bz)_{24} \cdot 8THF$ was investigated on crystal powder (see SI). The μ_{eff} value at room temperature ($2.57 \mu_B/U$) is consistent with that expected for U^{IV} and possibly a small amount of U^V as well. The thermal variation of the magnetic moment is representative of what was reported for U^{IV} compounds in the literature.^{5a,20} The lowering of the effective moment with temperature can stem from antiferromagnetic coupling and/or coupling of the non-magnetic ($m_j = 0$) ground state of U^{IV} in low-symmetry environments with low-lying excited states.²¹ The magnetization versus field curve indicates a small magnetic moment for the $\{U_{38}\}$ compound, which is still paramagnetic at 2 K. It confirms that the lowering of μ_{eff} is mainly due to thermal depopulation of excited states.

Previous works⁵ mentioned the influence of hydrolysis rate in controlling the formation of large poly-oxo clusters bearing low-valent uranium. Indeed, we examined this parameter by adding an accurate amount of water in our reaction medium. If no water is added to the chemical system, very few crystals of the $\{U_{38}\}$ phase are obtained, probably due to the presence of residual water from the starting reactants (benzoic acid or THF). However, the addition of controlled quantities of water in the range 0.28–3.89 mmol (for 0.26 mmol of UCl_4) led to a linear increase in the yield of the solvothermal reaction, with a maximum value reaching 72% (based on uranium) for 3.89 mmol (70 μ L) (Figure S2a). For higher water concentrations, we observed the formation of uranium oxide (UO_2 , fluorite type), which appeared gradually at the expense of $\{U_{38}\}$ when the amount of water increased. For the value of 16.7 mmol (300 μ L), only UO_2 is obtained (Figure S2b). Ongoing work is currently dedicated to the kinetic analysis concerning the formation mechanisms of the $\{U_{38}\}$ product.²²

We successfully synthesized and characterized the $\{U_{38}\}$ compound, which is, up to now, the largest polyoxo cluster encountered in the chemistry of low-valent uranium. This species is stabilized during the first steps of the poly-oxo condensation process by controlling the water content, before the formation of the 3D extended UO_2 fluorite-type network, when water content is further increased. Since the $\{Pu_{38}\}$ analogue¹⁶ was previously isolated, we may assume that the other parent {actinide₃₈} species may also exist with Th(IV), Np(IV), or Pu(IV). A similar trend has been already observed for smaller oxo clusters such as the hexanuclear moiety (An_6O_8 , An = actinide), isolated with Th(IV),^{10,23} U(IV),^{5a,9–11,14} Np(IV),²⁴ and Pu(IV).²⁵ For $\{U_{38}\}$, although consistent with all experimental findings, the presence of $2/38 U^V$, $54O/20H$, or $16Cl/2H_2O$ due to extra negative charges within the cluster is not demonstrated unambiguously since all U^{IV} is consistent with the data as well. The magnetic data suggest antiferromagnetic coupling between U ions owing to the presence of a fluorite-type UO_2 core. The behavior is the results of several contributions arising from U^{IV} in different environments.

■ ASSOCIATED CONTENT

■ Supporting Information

Synthesis procedures and analytical data; crystallographic data for **1** (CIF); SEM images, powder XRD patterns, XRD crystal data, thermogravimetric curve, IR spectrum, XPS spectrum, and magnetic curves (Figures S1–S9). This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC 905752 contains the supplementary crystallographic data. This file can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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