# Ligand assisted cleavage of uranium oxo-clusters†

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Dibenzoylmethanate replaces the bridging triflate ligands in uranium triflate polyoxo-clusters and cleaves the $U_{12}O_{20}$ core yielding the new $[U_6O_4(OH)_4(\eta\text{-dbm})_{12}]$ dibenzoylmethanate (dbm$^-$) cluster which slowly dissociates into a monomeric complex. This reactivity demonstrates the importance of bridging ligands in stabilizing uranium polyoxo-clusters.

Actinide oxo-clusters are of high current interest because of their implication in nuclear waste disposal and environmental mobility of actinides.[1–5] In particular, molecular-scale U(IV)-oxide-clusters have been shown to form in the bacterial reduction of U(VI) and the solubility and reactivity of these nanoparticles may impact the environmental fate of uranium and effect remediation strategies.[6] Moreover, uranium oxo-clusters represent good prospects for the design of uranium based single molecule magnets (SMM, discrete molecules presenting a slow magnetic relaxation).[7] A few high nuclearity oxo-clusters containing uranium in a reduced oxydation state (IV or V) have been obtained from the hydrolysis of trivalent uranium or the reduction of $UO_2^{2+}$ in non aqueous conditions and crystallographically characterised.[8–11] These clusters could provide an important model for the soluble colloidal nanoparticles involved in the transport of actinides in ground waters.[6,12,13] Nevertheless, the reactivity of these systems has never been studied and little information is available on their solution stability. We have recently reported the dodecanuclear U(IV)/U(V) cluster $[U_{12}(\mu_3\text{-OH})_8(\mu_3\text{-O})_{12}I_2(\mu_2\text{-OTf})_{16}(CH_3CN)_8]$, 1 having a $U_{12}O_{20}$ core and hexanuclear $[U_6(\mu_3\text{-O})_8(\mu_2\text{-OTf})_{12}]^{n-}$ ($n$ = 0, 2, 4) clusters.[8] These compounds provide suitable starting materials for reactivity studies because of the presence of the weakly coordinating triflate ligands.

Here we show that the dibenzoylmethanate (dbm$^-$) ligand can replace the triflate ligands in 1 resulting in the cleavage of the $U_{12}O_{20}$ core to yield the new hexanuclear U(IV) cluster $[U_6O_4(OH)_4(\eta\text{-dbm})_{12}]$ (2) which then slowly dissociates to form a monomeric complex. This is to our knowledge the first example of a reactivity study on uranium polyoxo-clusters. It shows that the formation of a uranium oxo-cluster can be controlled by the presence and the nature of ancillary ligands. Moreover, the reaction presented suggests that triflate

oxo-clusters are good starting materials for the synthesis of new polymetallic complexes of the f-elements.[14]

Complex 2 can be reproducibly prepared in a 48% yield by reacting 1 or a mixture of $[U_6(\mu_3\text{-O})_8(\mu_2\text{-OTf})_{12}]^{n-}$ ($n$ = 0, 2, 4) clusters[8] with dbmK in a 1 : 2 U : dbmK ratio in acetonitrile (Scheme 1).‡
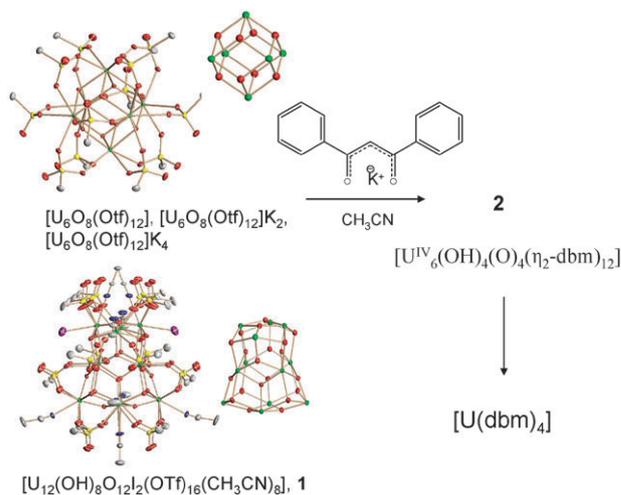


Scheme 1 Reaction of $U_6O_8$ and $U_{12}O_{20}$ clusters with dbmK.

The reaction of the $U_6O_8$ mixture with dbm$^-$ results in the replacement of the triflate ligands bridging adjacent uranium ions, but does not lead to an immediate cleavage of the $U_6O_8$ core to afford monomeric species as demonstrated by the solution NMR studies (see ESI†). In contrast, in the reaction of 1 with dbmK, ligand exchange results in the immediate cleavage of the $U_{12}O_{20}$ core to yield the cluster 2 where the 6 U(IV) ions are only connected by oxo and hydroxo bridges. Crystals of the cluster 2 can be isolated from pyridine/hexane and acetonitrile and X-ray diffraction studies revealed the same structure in both solvents (Fig. 1).

In the hexameric cluster $[U_6O_4(OH)_4(\eta\text{-dbm})_{12}]$ (2), the six uranium ions are arranged in a slightly distorted octahedron (U–U distances ranging from 3.805(1) to 3.851(1) Å). Each one of the eight triangular faces is capped by a triply bridging oxygen resulting in a $U_6O_8$ core. For four oxygens the value of the U–O distances are ranging from 2.211(10) to 2.271(11) Å and are in agreement with the presence of $\mu_3\text{-O}^{2-}$ groups[10] while the four others are ranging from 2.415(12) to 2.486(12) Å and indicate the presence of $\mu_3\text{-OH}^-$ groups.[8] The bond valence calculation carried out for the oxygen atoms using Burns' parameters[15] are also in agreement with the presence of 4 oxo and 4 hydroxo groups. Finally, the FTIR spectrum of 2 confirms the presence of coordinated O–H oscillators

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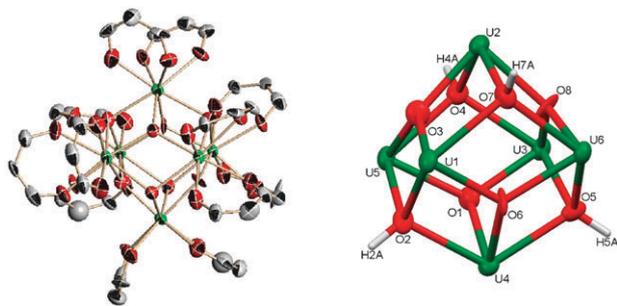
**Fig. 1** Ortep view of **2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules were omitted for clarity. Selected bonds lengths (Å) and angles (°) for **1**: average (av.) U–O 2.25(2) av. U–OH 2.44(2) av. U–U 3.84(1) av. O–U–OH 69.2(8)°.

($\nu$ = 3592 cm$^{-1}$) (see ESI†). The presence of bridging hydroxo groups had been proposed for the previously reported clusters $[U_6(\mu_3\text{-OH})_8(\eta_2\text{-O}_2(P(OPh)_2)_{12}]^{11}$ and $[U_6(\mu_3\text{-O}_4(\mu_3\text{-OH})_4(SO_4)_6]$ and were envisaged as a possibility for the $[U_6O_8(\mu_2\text{-OTf})_{12}$-$(H_2O)_{3.5}]K_4$ complex but the high symmetry of these systems did not allow to differentiate the oxo groups in the crystal structure leaving some ambiguity. Each uranium ion is also coordinated by two bidentate dbm$^-$ ligands. The U–O(dbm) distances are ranging from 2.318(10) and 2.448(10) Å and are close to those reported for the $[U(IV)(dbm)_4]$ monomer (2.329(2) to 2.3778(18) Å).[16] The overall charge of the 4 oxo groups, 4 hydroxo groups and the 12 dbm$^-$ ligands is balanced by six U(IV) ions.

The very low solubility of **2** in acetonitrile results in the immediate precipitation of **2**·2CH$_3$CN as a purple powder which can be recrystallized from pyridine/hexane solution. Additional products soluble in acetonitrile are formed in the reaction of the triflate clusters with dbmK which remain unidentified.§ The cluster **2** is stable in Py and thf solutions for a limited time sufficient to isolate it in a pure form. $^1$H NMR spectra of the isolated complex recorded immediately after dissolution in in pyridine or thf shows only traces of the monomeric $[U(dbm)_4]$ complex (see ESI†). The presence of the hexameric cluster in the thf solution was confirmed by the value of the translational diffusion coefficient $D$ ($D$ = 5.8(1) 10$^{-10}$ m$^2$s$^{-1}$) of **2** relative to the monomeric $[U(dbm)_4]$ complex (obtained from Pulsed-Field Gradient STimulated Echo[17] (PFGSTE) diffusion NMR) which can be related to their respective molecular weights by the Stokes–Einstein equation.[18] The measured molecular weight is $M$ = 4343 ± 300 gmol$^{-1}$, which is in good agreement with the expected value based on the formula of the cluster **2** ($M$ = 4239.21 gmol$^{-1}$).

NMR studies show that cluster **2** slowly decomposes in pyridine to yield the monomeric complex $[U(dbm)_4]$ which was identified by NMR spectroscopy and X-ray diffraction.[16,19] The decomposition is faster in thf solution or in the presence of an excess of dbmK (complete after 72 h). This behaviour contrasts with the solution stability of the previously reported hexanuclear and dodecanuclear triflate clusters in acetonitrile solution.[8] An important structural difference with respect to the starting U$_{12}$O$_{20}$ and U$_6$O$_8$ clusters containing triflate ligands bridging adjacent uranium ions, is the non-bridging mode adopted by the diketonate ligand in **2**. This results in the presence in **2** of longer U–U distances (U–U average = 3.84 Å

with respect to the analogous hexanuclear cluster $[U_6(\mu_3\text{-O})_8$-$(\mu_2\text{-OTf})_{12}(H_2O)_3]$ (U–U average = 3.71 Å). These results suggest that the U-oxo/U-hydroxo bonds are not sufficiently strong to stabilize polymetallic U(IV) assembly in the absence of ancillary bridging ligands. It should be noted that except for the $[Cp^*_4(bipy)_2U_6O_8]$ cluster containing an interstitial oxo group, all the previously reported polyoxo U(V)/U(IV) complexes contain supporting bridging ligands.[8–11,20] Preliminary studies also show that the substitution reaction on the hexanuclear cluster can be carried out efficiently with bridging ligands such as sulfonates without disruption of the hexameric structure. The characterisation of these compounds is in progress.

Temperature-dependent magnetic susceptibility data were collected for **2** in the temperature range from 6 to 300 K (Fig. 2). The $\chi$ *vs.* T data increases with decreasing temperature to reach a plateau between 20 and 6 K. The measured room temperature magnetic moment of **2** ($\mu_{\text{eff}}$ = 3.09 $\mu_B$ per U(IV) ion at 300 K and 5 G) is in the range of the values previously reported for other mononuclear and polymetallic U(IV) complexes (2.5-3.55 $\mu_B$).[21,22] The presence of temperature independent paramagnetism (TIP) is a typical magnetic response of molecular U(IV) compounds at low-temperature due to coupling between a non-magnetic ground state and low-lying excited states through a Zeeman perturbation.[21] The convoluting effect of the TIP, primary feature of the $\chi$ *vs.* T data render difficult the detection of possible magnetic coupling between uranium ions without further studies. A similar magnetic behaviour has been observed in the few other reported U(IV) multimetallic complexes for which magnetic data have been recorded.[23,24] The hexanuclear $[U_6O_4(OH)_4(\eta\text{-dbm})_{12}]$ complex is a rare example of oxo-hydroxo U(IV) cluster and provides an important addition to the few magnetically characterised multimetallic complexes of uranium(IV).
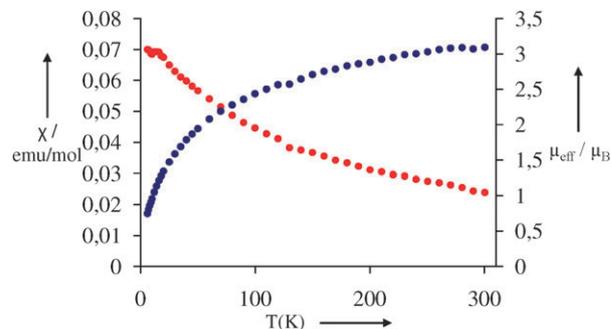


**Fig. 2** Temperature-dependent magnetization data per U(IV) ion of **2** from 6 to 300 K.

In conclusion, for the first time the presence in solution of polyoxo-clusters has been demonstrated thanks to the presence in **2** of the dbm ligands which give rise to well defined $^1$H NMR signals. This proved very useful in the study of the solution structure and stability. Finally, the first reactivity study on polymetallic clusters of uranium described here shows the importance of bridging ligands in stabilizing high nuclearity uranium polyoxo-cluster and suggests that ancillary ligands can be used to tune the cluster structure and stability. Future studies will be directed to elucidate further the

dissociation mechanism and to investigate the effect of protonation and oxidizing agents on the cluster structure.

## Notes and references

‡ Crystal data: Crystal data for (2·1.5py·0.5thf) [U$_6$O$_4$(OH)$_4$-(η-dbm)$_{12}$]·1.5py·0.5thf C$_{191.50}$H$_{151.50}$N$_{1.50}$O$_{32}$U$_6$, $M$ = 4413.82, triclinic, space group $P\bar{1}$, $a$ = 18.707(2), $b$ = 19.412(2), $c$ = 26.547(3) Å, $\alpha$ = 74.677(2), $\beta$ = 77.944(2), $\gamma$ = 63.905(2)°, $V$ = 8301.7(15) Å$^3$, $Z$ = 2, $\rho_c$ = 1.766 g cm$^{-3}$, $\mu$ = 5.906 mm$^{-1}$, $T$ = 223(2) K. Of the 34 061 reflections collected, 22 976 were unique ($R_{int}$ = 0.0364). $R_1$ = 0.0592, w$R_2$ = 0.1162. Max/min residual density 5.458 and −2.637 e Å$^{-3}$.

§ General details: All manipulations were carried out under an inert argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. Synthesis and characterisation of **2**: An emerald green solution of the complex [U$_{12}$(μ$_3$-OH)$_8$(μ$_3$-O)$_{12}$I$_2$-(μ$_2$-OTf)$_{16}$(CH$_3$CN)$_8$]·2CH$_3$CN·2H$_2$O (**1**) (33,0 mg, 5.24 μmol, 1 eq.) in acetonitrile (0.2 mL) was added to a solution of dbmK (34.2 mg, 130 μmol, 24 eq.) in acetonitrile (0.5 mL). It immediately formed a purple precipitate. The suspension was stirred for 2 h at room temperature. After filtration, the powder was washed with a small amount of acetonitrile and we obtained 28.0 mg of a purple powder (yield 48%). $^1$H NMR (Py-D$_5$, 400 MHz, 298 K): δ 15.29 (s, br, 12 H); 6.86 (s, br, 24 H); 3.87 (s, br, 48 H); 0.45 (s, br, 48 H). (thf-d$_8$, 400 MHz, 298 K): δ 15.08 (s, br, 12 H); 6.60 (s, br, 24 H); 3.54 (s, br, 48 H); 0.11 (s, br, 48 H). Anal. Calcd. for [U$_6$O$_4$(OH)$_4$(dbm)$_{12}$]·2Py·7KI (C$_{190}$H$_{146}$N$_2$O$_{32}$K$_7$I$_7$U$_6$): C 41.05, H 2.63, N 0.50. Found %C 41.01, H 3.05, N 0.67. NMR and mass spectrometry analysis of the acetonitrile solution show the presence of additional compounds soluble in acetonitrile probably of smaller nuclearity (a dimer was identified) which have not been characterised due to their low stability. Therefore it is difficult at this stage to know what is the fate of the uranium(v) ions which are present in the starting compounds.

The same result was obtained starting from complex **2** prepared *in situ* from the [UI$_3$(thf)$_4$] complex (see ESI† for details). A re-crystallisation from pyridine and hexane of the obtained compound allowed the isolation of X-ray suitable dark crystals of **2**·1.5py·0.5thf. The reaction carried out with an isolated mixture of [U$_6$(μ$_3$-O)$_8$-(μ$_2$-OTf)$_{12}$]$^{n-}$ ($n$ = 0, 2, 4) clusters lead to the same compound with similar yield. X-Ray quality crystals were also obtained after letting stand a dilute acetonitrile solution of **2**. Diffraction data for **2**·2CH$_3$CN are given in the supporting information.

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