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Kinetics vs thermodynamics: A unique crystal transformation from a uranyl peroxo- nanocluster to a nanoclustered uranyl polyborate †

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A novel method to prepare a nano-clustered uranyl polyborate in aqueous solution at room temperature has been developed. The initially formed kinetically favoured sodium uranyl peroxide yellow crystals transform, in the presence of boric acid, to the thermodynamically stable sodium uranyl polyborate in light yellow-green single crystal form.

Despite the importance of actinide (An) borates due to their close link with high-level nuclear waste conditioning, waste form interim storage and final geological disposal, the research on their formation and properties is still at a very early stage. In the literature, methods to make metal borates reported so far include hydrothermal synthesis, [1] solvothermal methods, [2] high temperature flux [3] and room temperature slow evaporation. [4] However for actinide borates, hydrothermal methods are not practical as water molecules always compete with borate for the inner coordination sphere of the actinide ions. In addition, the crystallization of actinide borate complexes is often greatly affected by the hydrolysis of actinide ions in solution. [5]

Uranyl metaborate and sodium uranyl borate were first reported in 1967. [6] In 1985, the first single crystal structure of potassium uranyl borate, $K_6[UO_2\{B_{16}O_{24}(OH)_8\}]\cdot 12H_2O$, was reported, [7] which was made by slow evaporation of a solution mixture of uranyl acetate and potassium borate. The crystal structure consists of isolated uranyl borate clusters with each uranyl group surrounded by a ring of 16-borates. However, no other characterization methods have been applied to this complex as the method only produced a few small orange coloured single crystals among a precipitate. From 1986 to 1991, several actinide borates including $UO_2(B_2O_4)$, $Li(UO_2)BO_3$, $Na(UO_2)BO_3$, $Ca(UO_2)_2(BO_3)_2$, $Mg(UO_2)B_2O_5$, $Ni_7(UO_2)(B_4O_{14})$ and $Th(B_2O_5)$ were made by using molten B_2O_3 as a flux in high temperature (>1000 °C) solid state reactions. [8] These actinide borates generally contain BO_3 triangles except for $Ni_7(UO_2)(B_4O_{14})$ which contains both BO_3 triangles and BO_4 tetrahedra. Since 2011, some new actinide borates have been made through a modified low temperature flux method using H_3BO_3. [9-11] These actinide borates feature 2D or 3D polymeric structures with low An/B (4-6) ratios. More recently a Th borate with a 3D cationic framework has been found to have the potential as a sorbent material for selective separation of some problematic radionuclides from aqueous radioactive wastes. [12]

In contrast to the recent advances on actinide borates prepared using boric acid flux at relatively low temperatures (180-280 °C), essentially no report of any effort to make actinide borates at room temperature has been recorded. In fact, to obtain crystalline actinide borates at room temperature, a slow reaction rate must be maintained to avoid precipitation of actinide borates due to their low solubilities in aqueous solution. In general, single crystals of compounds with low solubility have been prepared using slow diffusion methods. [13] We herein report a new method to make a nano-clustered uranyl polyborate in single crystal form at room temperature from a sodium uranyl peroxide compound.

The reaction of uranyl nitrate hexahydrate, sodium hydroxide, hydrogen peroxide and boric acid in an aqueous solution leads to the formation of a yellow crystalline product, Na-U28 (**1**), ‡ within a few days at pH ~8 followed by a crystal transformation with the yellow crystals of **1** dissolving gradually accompanied with the simultaneous formation of the light yellow-green crystals of $Na_6[UO_2\{B_{16}O_{24}(OH)_8\}]\cdot 14H_2O$ (**2**). ‡ The experimental details can be found in the online ESI† file and the overall reaction is outlined in Scheme 1. The optical images in Figure 1 highlight the crystal transformation process.

Scheme 1. Overall reaction to form the sodium uranyl polyborate.

$$UO_2(NO_3)_2\cdot 6H_2O + {\sim}12NaOH + {\sim}26H_2O_2 + {\sim}4H_3BO_3 \rightarrow$$
$$Na_{14}[(UO_2)(O_2)_{1.5}]_{28}\cdot nH_2O\ (\mathbf{1}) \rightarrow Na_6[UO_2\{B_{16}O_{24}(OH)_8\}]\cdot 14H_2O\ (\mathbf{2})$$

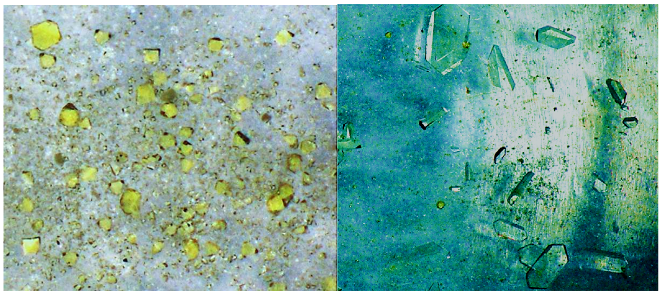

Fig. 1 The crystal transformation from the initially formed yellow crystals of **1** (left) to light yellow-green crystals of **2** (right).

In the asymmetric unit of **1**, six uranyl groups (U1 with full occupancy and rest with half occupancies) have been allocated. They are linked together by peroxide groups and charge balanced with sodium ions. The half occupancies for the five uranyl groups and numerous oxygen atoms close to uranyl peroxide units suggest that the structure is somewhat disordered. Extension by symmetry suggests that **1** contains very compact uranyl peroxo- ball shell with some unrealistic short U-U distances in six squares (Fig. 2a & 2b). Further examination of the 44 uranium polyhedra reveals that **1** is an orientationally disordered U28 shell (28 uranyl triperoxide polyhedra) with one rotating 90° from the other (Fig. 2c & 2d). Both U1 and U5 positions are shared by the two ball shells, not moving by rotating the sphere 90° through a rotation axis along the *c*-axis. However U2, U3, U4 and U6 positions are moving from one orientation (green) to the other (pink) causing the sphere orientation disorder in crystal packing. The U28 shell is composed of twelve pentagons and six hexagons (Fig. 2e & 2f) in the form of $[(UO_2)(O_2)_{1.5}]_{28}^{14-}$. The U=O bond lengths for uranyl groups range from 1.761(17) to 1.857(14) Å. Due to the structure disorder and some electron density overlapping, the Na^+ ions and H_2O molecules are unable to be located precisely leading to large solvent accessible voids inside and outside the spheres (Fig. 1S, ESI†). The size of the U28 sphere is ~1.75 nm measured from the most distant $-O_{yl}$ atoms outside the sphere, which is broadly consistent with the result of particle size and distribution measurement on the initial solution using dynamic light scattering [Fig. 2S, ESI†]. SEM-EDS analysis confirmed the presence of O, Na and U with nearly twice the atom numbers of U than Na (Figs. 3S-4S and Table 1S, ESI†). The Raman spectrum of **1** (Fig. 5S, ESI†) shows two prominent bands, the O-O symmetric stretching vibration ($\nu_{O\text{-}O}$) of the peroxo- ligand at 849 cm^{-1} and a symmetric stretching mode of the uranyl ion ($\nu_{O\text{-}U\text{-}O}$) at 803 cm^{-1}, corresponding to U=O bond length of 1.793(8) Å. [14]

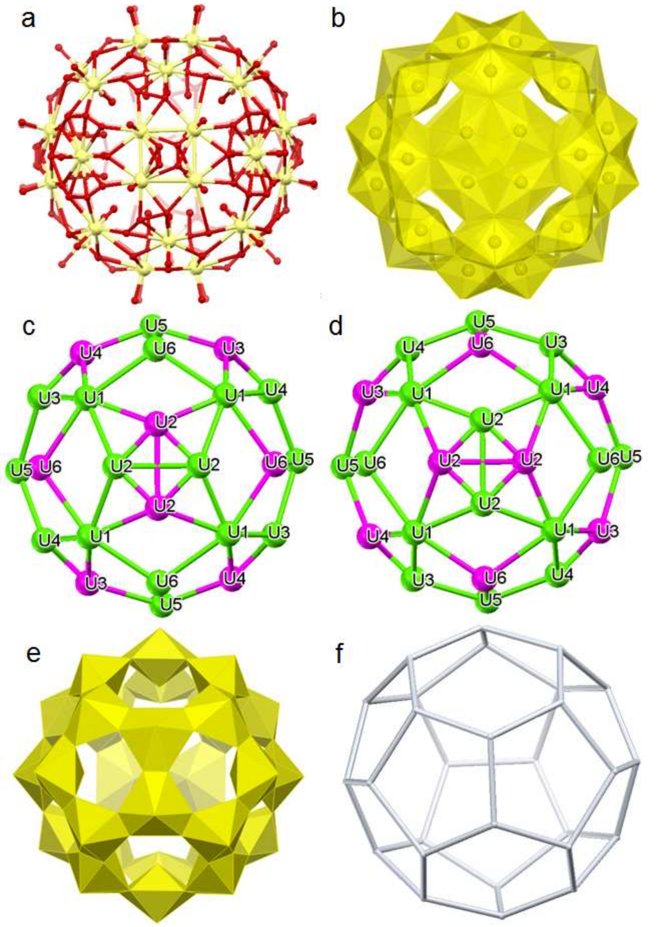

Fig. 2 Representative views of the U cluster in **1:** ball-stick (a); polyhedral (b); two orientational disordered positions (c and d with pink and green positions); U28 polyhedral (e) and U28 topology (f).

Orientation disorder is common among fullerene- type spheres such as C60 and its related compounds. [15] However, this phenomenon has not often been found in other polymetallate cluster systems. To our knowledge, **1** is the first fullerene- type uranyl peroxo- nanocluster with orientational disorder. Previous solution ^{23}Na NMR study [16] confirmed that Na^+ ions inside the U28 cluster involves in rapid exchange with cations in the solution which could be a reason leading to the orientational disorder in **1** and of course the main reason would be the free rotation of clusters along a rotation axis causing the clusters' disorder in the crystal packing. The isolation of many U28 compounds with large alkali cations, e.g. K^+, Rb^+ and Cs^+ has been reported [17] and a pattern of cation templating underneath various rings has been proposed based on the ionic sizes of the cations. However, the successful preparation of **1** and several other uranyl peroxo- nanoclusters [18] with Na^+ ions challenges the idea of cation templating according to their sizes in the formation of these uranyl peroxo- nanoclusters. In fact, the sizes of the cations are less important relative to their locations. [18]

The crystal structure of **2** consists of crown-shaped uranyl borate nano-clusters with each uranyl group surrounded by a ring of 16 connected borates (Fig. 3). The uranyl group is normal with U=O bond lengths ranging from 1.786(3) to 1.792(3) Å and coordinated by six borate O atoms in the equatorial plane forming hexagonal bipyramidal geometry for the uranium centre with U-O (BO_4) bond lengths in the range of 2.413(3) to 2.499(2) Å. The 16 borates are connected to form a ring around the uranyl group with 8 inner shell borates in the form of BO_4 tetrahedra and 8 outer shell borates in the form of BO_3 triangles (Figs. 3a & 3c). The size of the cluster is ~1.18 nm measured from the most distant borate O atoms. The polyhedral packing view along the *b*-axis (Fig. 3d) shows that slightly shifted face to face pairs of clusters stacking along the *a*-axis. Na^+ ions coordinated by H_2O molecules are located around the uranyl borate clusters. Extensive hydrogen bonds between O (BO_3) and water molecules lead the nano-clusters into three dimensions.

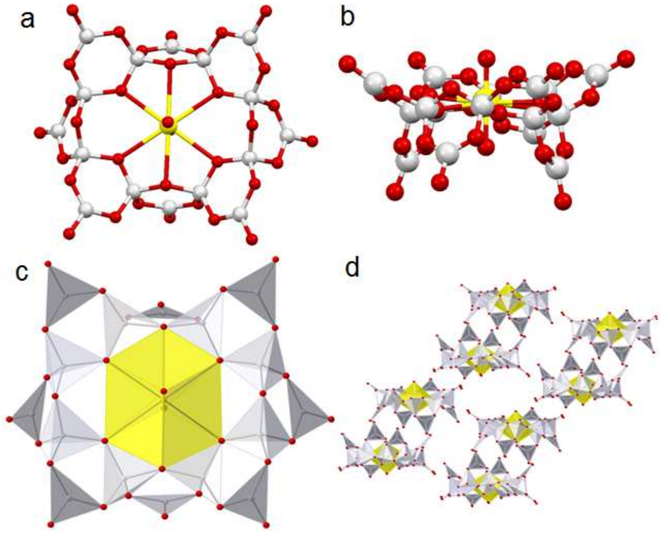

Fig. 3 Representative views of a single cluster in **2**: ball-stick (a & b); polyhedral (c) and a polyhedral packing along the *b*-axis (d).

The measured powder XRD pattern of **2** matches the simulated one well (Fig. 6S, ESI†) suggesting that the single crystal leading to the structure solution represents the bulk pure crystalline product. SEM-EDS characterization of **2** confirmed the presence of B, O, Na and U (Figs. 7S-8S and Table 2S, ESI†) with EDS determined U/Na ratio to be 1/6, consistent with the single crystal result. However, EDS gives higher B/U ratio as the method tends to give less reliable result for lighter elements. Raman spectroscopy has been proved to be useful in characterization of boron-based minerals [19] where the triangle BO_3 and tetrahedral BO_4 boron units have vibrational modes at different frequencies. The Raman spectrum of **2** (Fig. 5S, ESI†) shows a strong and sharp band at 822 cm^{-1} due to the symmetric vibration mode of the uranyl ion ($\nu_{\text{O-U-O}}$) with corresponding U=O bond length of 1.789(8) Å. [14] Raman bands at 967 and 751 cm^{-1} have been assigned to the asymmetric and symmetric stretching modes of B-O in BO_4 tetrahedra, respectively. Very weak bands at 1355 and 920 cm^{-1} are attributed to the asymmetric and symmetric stretching modes of B-O in BO_3. The vibrational modes of coordinated water molecules are located at both 1100-1050 and 696 cm^{-1}. The TG curve (Fig. 9S, ESI†) shows a weight loss in two steps from 50 to 500 °C of the total weight loss of ~25% corresponding to the removal of all H_2O molecules (calcd: 18.6%) and further weight loss of 6.4% equivalent to 5 hydroxyl groups.

It is well understood that the assembly of uranyl peroxo-nanoclusters is a rapid process [17] compared to the formation of polyborates at room temperature. [7] However, once formed, the polyborate will sequester uranyl ions from the preformed clusters forming the chelating uranyl polyborate, implying a possible entropical process from a high density state to a lower density state of metal ions. In addition, the solubility should be another driving force as **2** is relatively less soluble than **1**.

In conclusion, a new method based on a crystal transformation from an orientationally disordered Na-U28 to a nano-clustered sodium uranyl polyborate has been developed. The new Na-U28 is the first U28 compound with only Na^+ ions and the first fullerene-type uranyl peroxo- cluster with orientational disorder. The successful isolations of the Na-U28 and several other uranyl peroxo- clusters with Na^+ ions have proven that cation size is less important in controlling the size of the clusters. In fact, it is the unique cation locations which control the formations of various sizes of the uranyl peroxo-nanoclusters. The new nano-clustered sodium uranyl polyborate has been characterized using PXRD, SEM-EDS, TG/DTA, Raman spectroscopy and single crystal XRD. The method described here may shed light on the preparation of other actinide borates in non-polymeric forms. However, further work is needed to verify this.

The single crystal data for **1-2** were collected on the MX2 beamline at the Australian Synchrotron, Melbourne, Australia.

Notes and references

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† Electronic Supplementary Information (ESI) available: synthesis, particle size and distribution measurements, powder XRD, SEM-EDS, TG/DTA, Raman spectroscopy, single crystal X-ray diffraction and structure refinement details. The supporting information and crystallographic information files (CIF) can be found at DOI: 10.1039/c000000x/

‡ Crystal data for **1**: $O_{128}U_{28}$, FW = 8552.84; tetragonal, $P4/mnc$, a = 20.234(3) Å, c = 26.874(5) Å, V = 11002 (4) $Å^3$, Z = 2, ρ_{calcd} = 2.582 g cm^{-3}; μ = 20.582 mm^{-1}; F(000) = 7040, GOF = 1.255. A total of 132508 reflections were collected, 4962 of which were unique (R_{int} = 0.0539). R_1/wR_2 = 0.0605/0.2467 for 292 parameters and 4962 reflections ($I > 2\sigma(I)$). Crystal data for **2**: $H_{18}B_{16}Na_6O_{48}U$, FW = 1335.07; monoclinic, $P2_1$/n, a = 14.736(3) Å, b = 11.765(2) Å, c = 23.928(5) Å, V = 3989.5 (15) $Å^3$, Z = 4, ρ_{calcd} = 2.223 g cm^{-3}; μ = 4.461 mm^{-1}; F(000) = 2560, GOF = 1.097. A total of 62727 reflections were collected, 8723 of which were unique (R_{int} = 0.0300). R_1/wR_2 = 0.0449/0.1331 for 661 parameters and 8723 reflections ($I > 2\sigma(I)$). The crystallographic data of **1** and **2** have been deposit at ICSD with CSD-427908(**1**) and CSD-427907(**2**).

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Nanostructures

Graphic abstract

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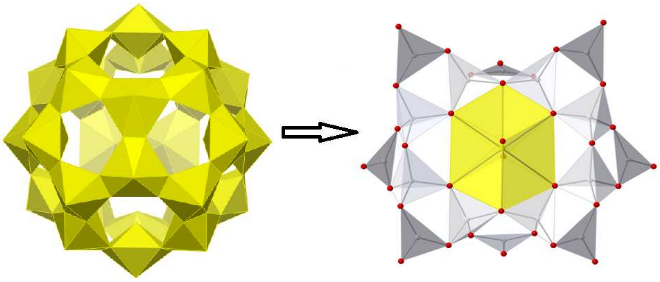

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