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H. Traustason,[a] S. M. Aksenov [b] and P. C. Burns* [a]

Li and H_2O encapsulated in the uranyl peroxide cage cluster U_{24} at 110 K are in square pyramidal and octahedral coordination, as dictated by the symmetry and topology of U_{24}, in contrast to Li cations between cages that are tetrahedrally coordinated by H_2O. The ordered distribution of Li found here deviate from earlier studies at higher temperatures that reported a dynamic distribution.

Nanoscale metal oxide clusters containing double or triple metal-oxygen bonds (polyoxometalates, POMs) are model systems for understanding structure-size-property relations,[1, 2] geochemical reactions at mineral surfaces,[3, 4] and have promising applications in catalysis, electronic materials, magnetism, and medicine, amongst others.[1] POMs containing group V/VI metals have been studied for several decades.[5] Uranyl peroxide nanoclusters were first described in 2005 (Fig. 1),[6] and now correspond to a large family of topologically and compositionally varied anionic uranyl cages.[7-9] Uranyl peroxide clusters self-assemble in water under ambient conditions and are usually charge-balanced by alkali cations.[9] Density functional theory simulations indicate that alkali cations potentially stabilize building units of uranyl peroxide clusters in solution, thereby promoting their formation.[10] The identity of the counter cations is important in determining aspects of cluster solution behaviour,[11] including solubility and aggregation into blackberries.[12-14] However, the role of alkali cations in determining topological aspects of uranyl peroxide cage clusters remains unclear.[15, 16]

The typical synthesis route for uranyl peroxide clusters is the dissolution of uranyl in water, followed by addition of hydrogen peroxide and an alkali base. The role of counter cations may include a templating role in some cases.[17-19] On the basis of density function theory simulations of cluster fragments, it was predicted that specific cations are energetically favoured at specific topological sites on the clusters: Li in topological square windows, Na/K in pentagonal windows, and Rb/Cs in hexagonal windows.[20, 21] However, recent studies have shown that $[(UO_2)_{24}\emptyset_{48}]^{24-}$ (where $\emptyset = O_2$, OH) clusters (U_{24}), with a sodalite-type cage topology formed by squares and hexagons, and $[(UO_2)_{28}\emptyset_{42}]^{28-}$ (U_{28}), with a fullerene topology consisting of pentagons and hexagons, both form with Li as the only available counter cation.[16]
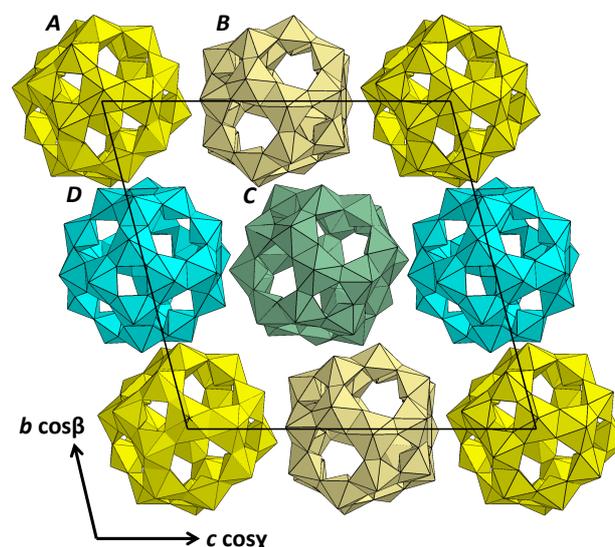
Figure 1: Polyhedral representation of the distribution of U_{24} cage clusters in the triclinic unit cell, showing four symmetrically distinct clusters by colour. Li and H_2O are omitted.

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U_{24} was amongst the first three uranyl peroxide cage clusters reported in 2005.[6] It was originally synthesized with Li as the counter cation (Li-U_{24}), and owing to the poorer overall quality of the X-ray diffraction data, the reported structure of Li-U24 contained only tentative Li positions that were constrained during refinement.[6] Xie et al. recently combined density function theory with NMR spectra to help locate some Li cations in the U_{24} cage in both the solid state and in solution.[22] U_{24} has also been isolated and characterized containing Na[23], Sr[15] and Ca.[15] Nyman's group have demonstrated encapsulation of $[Bi_6O_8]^{2+}$ and $[Pb_8O_6]^{4+}$ polycations in U_{24}.[24]

In the current work, synthesis of Li-U_{24} crystals was done by combining 1.0 mL of a 0.5 M uranyl nitrate hexahydrate aqueous solution with 1.0 mL of 30% hydrogen peroxide, followed by 0.75 mL of a 2.38 M solution of lithium hydroxide in a 25 mL scintillation vial. After O_2 bubbling ceased (several hours), the pH was measured at 8.5 and the vial was covered with Parafilm containing a few small holes to promote slow evaporation. Diffraction quality crystals formed after 7 weeks. As these crystals are unstable in air relative to dehydration, they were quickly transferred from their mother solution into oil for X-ray studies.

Chemical analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES) for solutions into which Li-U_{24} crystals had been dissolved yielded a uranium to lithium ratio of unity, consistent with charge-balance requirements (see supporting information).

Single-crystal X-ray diffraction revealed that Li-U_{24} crystallized with triclinic symmetry (space group *P*-1)*,* as reported earlier,[6] and the data was of sufficient quality to provide new structural detail, including coordinates and coordination environments of Li sites. Owing to the low symmetry and large unit cell, the highly complex asymmetric unit of our structure solution contains 513 non-H sites, including 48 U. The crystal chemical formula is ($Z = 4$): $^{IV}Li_{11}\{[^{V}Li_6{}^{VI}Li_7(H_2O)_{14}]@[(UO_2)_{24}(O_2)_{24}(OH)_{24}]\}\cdot31.5H_2O$, where Roman numbers denote the coordination number of Li sites.

The crystal structure of Li-U_{24} contains four symmetrically distinct U_{24} cages that differ in their orientation (Fig. 1). As in the initial and subsequent reports,[6, 15, 23, 24] the U_{24} cage has approximate O_h symmetry, the sodalite topology, and consists of 24 uranyl ions that are each coordinated by two side-on peroxide groups and two hydroxyl groups, with the peroxide in a *cis* arrangement in equatorial positions of hexagonal bipyramids. Uranyl ions are bridged by peroxide or two hydroxyl groups. Over the entire Li-U_{24} crystal structure determined here, the average uranyl ion U-O bond length is 1.802(13) Å, and that of the U-O equatorial bonds is 2.390(37) Å.

The spaces between the U_{24} clusters contain twenty-four symmetrically distinct Li sites. These Li sites are tetrahedrally coordinated by H_2O groups, with an overall average bond length of 2.05(15) Å. In several cases two Li tetrahedra share a vertex, forming $[Li_2(H_2O)_7]$-dimers. Linkages between the uranyl peroxide cages and interstitial components outside the cages are through three Li cations that are bonded to oxygen atoms of uranyl ions, and through H bonds emanating from interstitial H_2O to oxygen atoms of the cage,

or to interstitial H_2O from hydroxyl groups in equatorial positions of hexagonal bipyramids. Direct H bonds between a uranyl-bridging hydroxyl of one cluster and an O atom of a uranyl ion of an adjacent cluster are also likely, as there are five cases where the corresponding potential donor and acceptor oxygen atoms are separated by less than 2.87 Å.

We resolved Li and H_2O sites encapsulated by three symmetrically unique U_{24} cages (*A*, *C*, and *D*, Fig. 1), and partially resolved those encapsulated by the fourth cage (*B*). In the three fully resolved cages, two U_{24} clusters encapsulate 21 Li sites and 14 H_2O sites whereas the third one contains 19 Li sites and 14 H_2O sites, although not all of these sites are fully occupied. The coordination and chemical environments of the 21 or 19 Li cation sites encapsulated in the U_{24} clusters are different from those outside the clusters, as 19 are in octahedral or square pyramidal polyhedra (Fig. 2a). Some are bonded directly to the uranyl peroxide polyhedra.

Li sites are located inside each of the six square windows of the U_{24} cage, where they are coordinated by the four inward-pointing oxygen atoms of uranyl ions of the corresponding uranyl tetramer. The Li cations are located ~0.4 Å from the centre of the square defined by the uranyl ion oxygen atoms towards the centre of the cluster. The coordination is completed by a H_2O group, forming $LiO_4(H_2O)$ square pyramids (Fig. 2b). The apical H_2O groups of these six square pyramids define an octahedral environment around a Li site in the centre of the cluster with Li-H_2O distances of ~2.0 Å (Fig. 2c).
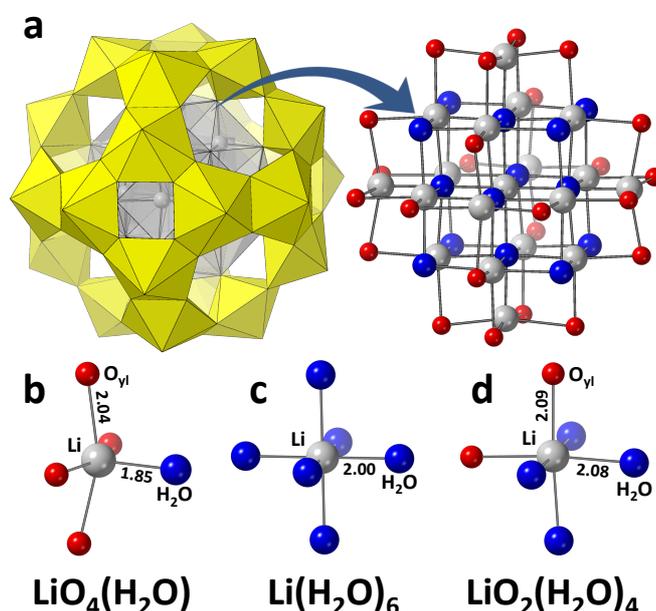
Figure 2. Representation of Li-U_{24} (left) and the encapsulated Li and H_2O positions (right) (a). Encapsulated Li coordination environments are square pyramid with four uranyl ion oxygen atoms and one H_2O (b), octahedral with six H_2O (c), and octahedral consisting of four H_2O and two oxygen atoms of uranyl ions (d). Oxygen atoms of uranyl are shown in red, Li cations are in silver, and oxygen atoms of H_2O are shown in blue.

H_2O groups are located inside each of the eight hexagonal windows of the U_{24} cage, close to the plane defined by the six
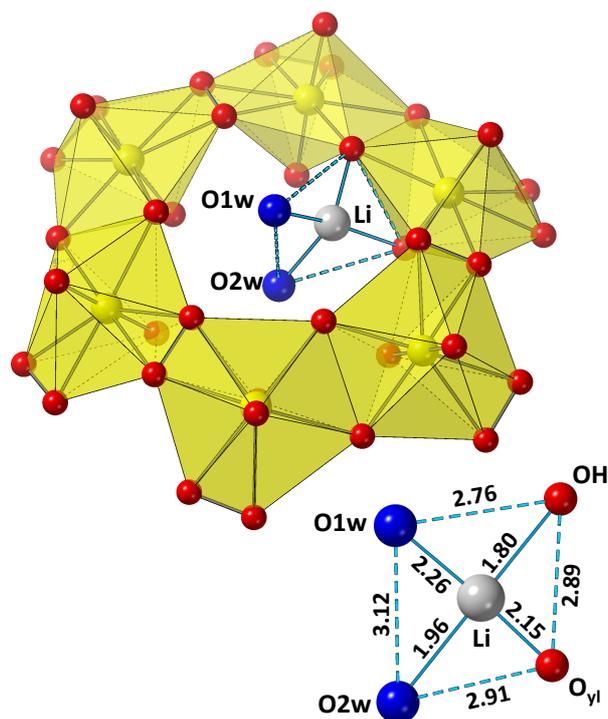
Figure 3: The coordination environment about Li cations located in some hexagonal windows of U_{24} where it is bound to an OH group that bridges two uranyl ions, an inward-pointing uranyl ion oxygen atom, and two H_2O. Oxygen bonded to uranium are shown in red, Li is in silver, and oxygen of H_2O groups are coloured blue.

inward-pointing oxygen atoms of the uranyl ions, where they may donate H bonds to the cage. These H_2O groups, together with oxygen atoms of uranyl ions and H_2O groups of the Li-centred square pyramids, form 12 octahedrally coordinated sites that are partially occupied by Li cations (Fig. 2d).

In the structure of Li-U_{24} there are two Li sites located within hexagonal windows of two of the U_{24} cages (at the same distance from the centre of the cluster as the U atoms). These Li sites bond to an O_{yl}–OH edge of uranyl polyhedron (Fig. 3). The coordination of these Li sites is completed by two H_2O groups, where one is towards the centre of the cluster and bonds to other Li cations, and the other is further from the centre, on the opposite side of the Li cation (Fig. 3).

The arrangement of Li and H_2O inside the U_{24} cage has a 3x3x3 halite-type core (Fig. 2a), which is surrounded by inward-facing oxygen atoms of uranyl ions and that contains 13 octahedrally coordinated $Li\phi_6$ sites (ϕ = O, H_2O). However, it is not possible for all of these to be occupied in the same U_{24} cage. In the case of full occupancy of the Li sites, the bond-valence sums at the H_2O sites (octahedrally coordinated by Li) would be 1 valence unit, corresponding to hydroxyl, rather than H_2O. The presence of hydroxyl is ruled out by the chemical analysis as the crystals contain exactly the quantity of Li needed to balance the charge of the cage (supplemental information). Moreover, full occupancy of the octahedra would leave no space to accommodate the H atoms of the H_2O groups, nor their H bonding requirements. We propose that the $LiO_4(H_2O)$ square pyramids associated with the square windows of the U_{24} cage

are fully occupied, whereas the other $LiO_2(H_2O)_4$ octahedra are about half occupied. Assuming that the Li sites sometimes contained within the two hexagonal windows of U_{24} are also about half occupied, U_{24} encapsulates approximately 13-14 Li cations. One possible local configuration consistent with the aforementioned constraints and that contains proposed H atom positions is shown in Figure 4. In this we assume that the Li cations in square pyramidal coordinated can shift towards the square window of the uranyl cluster.

The reported U_{24} structures that contain Na, Sr, Ca, and Bi each have the cations located in the square pyramidal sites located inside the square windows, as for Li in the current case.[15, 23, 24] In Pb-U_{24}, the cations are located in the hexagonal windows. The earlier structure report for Li-U24 included 48 tentative Li positions,[6] all of which were modelled as fully occupied. In the current model there are 68 partially occupied Li sites, with most of the additional sites encapsulated within U24.

Temperature variable [7]Li magic-angle-spinning nuclear magnetic resonance (MAS-NMR) spectra of Li-U_{24} reported earlier reveal chemical shift averaging with two overlapping environments at 0.3 and -2.9 ppm at 303 K.[25] Upon cooling to 283 K, two signals occur in the spectrum and remained for data collected at 273, 258, and 253 K, with signal enhancement occurring for lower temperatures for the resonance at ~-13 ppm that the authors attributed to encapsulated Li.[25] The diffraction data collected here at 110 K presents a well-ordered Li distribution both inside and between the clusters, which is consistent with the emergence of NMR signals assignable to encapsulated Li found earlier at considerably higher temperatures.
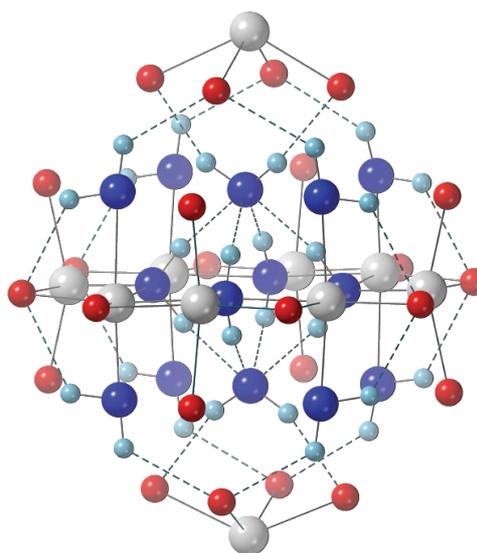
Figure 4: A possible local configuration of O, H_2O, and Li encapsulated in a U24 cage. Oxygen bonded to uranium are shown in red, Li is in silver, and oxygen of H_2O groups are coloured blue. H atoms are shown as small light blue spheres, and bonds to H atoms are shown as broken lines.

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A crystal structure of Li/K-U60 was reported from single crystal time-of-flight neutron diffraction data.[26] The topology of U60 is a fullerene with 20 hexagons and 12 pentagons.[26] The potassium cations are located inside the pentagonal windows and are bonded to the five inwards-pointing uranyl ions. The only lithium cations located in the structure are inside the hexagonal windows, where they are tetrahedrally coordinated by four water molecules.[26]

In summary, we located the Li atoms in crystals of U24 using single-crystal X-ray diffraction data, which showed that there are many encapsulated Li cations in square pyramidal and octahedral coordination environments, whereas Li cations located between the cages are tetrahedrally coordinated by water. The unusual coordination environments about the Li cations encapsulated by U24 are imposed by the structure and symmetry of the U24 cage.

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Conflicts of interest

There are no conflicts of interest to declare.

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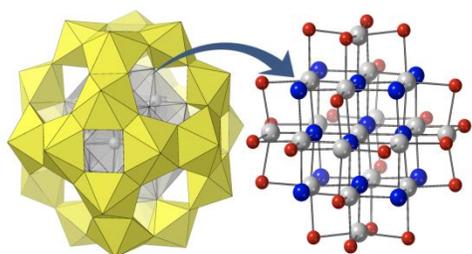
Lithium cations encapsulated within the U24 nanocapsule are in square pyramidal and octahedral coordination environments imposed by the topology of the cluster, whereas lithium outside the cages are in tetrahedral coordination.