



# Uranyl peroxide clusters stabilized by dicarboxylate ligands: A pentagonal ring and a dimer with extensive uranyl–cation interactions



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## ABSTRACT

Great effort has been made to synthesize larger uranyl peroxide clusters whilst the understanding of the basic construction units for these clusters still needs to be further explored. Two small uranyl peroxide clusters stabilized by simple dicarboxylate ligands have been synthesized and characterized.  $\text{Na}_{10}[(\text{UO}_2)(\text{O}_2)(\text{C}_3\text{H}_2\text{O}_4)]_5 \cdot 20\text{H}_2\text{O}$  (**1**) has a pentagonal ring stabilized by malonate and  $[\text{Na}_4\text{K}_2(\text{UO}_2)_2(\text{O}_2)(\text{C}_2\text{O}_4)_4] \cdot 6\text{H}_2\text{O}$  (**2**) has a dimer stabilized by oxalate. Cation–cation interactions between uranyl and alkali metal ions exist in both **1** and **2**, leading to the observation of elongated  $\text{U}=\text{O}_{-y1}$  bonds. Vibrational modes of uranyl ion, peroxide and malonate/oxalate ligands have been confirmed by Raman spectroscopy. The presence of malonate ligands prevents the pentagonal uranyl peroxide rings further assembling into larger clusters whilst the excess oxalate ligands inhibit the dimers further linking to nearby uranyl centers.

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## 1. Introduction

Actinide nano-structured materials have attracted recent research interest not only because their relevance to nuclear industry and potential impact on the environment, but also due to their unique and often unpredictable structure types making them potential new functional materials [1]. In addition to the production of  $^{99}\text{Mo}$  by alkaline processing of uranium targets [2], actinide peroxide phases form in aqueous solutions throughout the current nuclear fuel cycle, such as uranium yellow cake production, nuclear waste forms and spent nuclear fuels during storage [3,4]. Therefore, the peroxide ligand has long been recognized and considered in designing nuclear fuel reprocessing and separation of actinides, as well as transport codes for migration of actinides in the geological environment [3,4].

It is well established that uranyl peroxide and/or hydroxide nano-clusters form in many alkaline solutions [3–7] and the formations of small clusters in  $\text{UO}_2^{2+}-\text{H}_2\text{O}_2-\text{CO}_3^{2-}$  and  $\text{UO}_2^{2+}-\text{H}_2\text{O}_2-\text{OH}^-/\text{F}^-$  ternary aqueous systems have been well investigated [8]. A large numbers of these clusters have been synthesized with variety of topologies [4,9]. In general, uranyl peroxide  $[\text{UO}_2(\text{O}_2)_3]$

polyhedra can share edges (peroxide oxygen atoms) forming various spherical cages up to 60 uranium atoms. Great effort has been made trying to synthesize larger clusters whilst the basic understanding of the construction units still needs to be further explored. So far, the reported small uranyl peroxide clusters include a dimer, a pentagonal ring and a hexagonal ring stabilized by oxalate ligand and charge balanced with potassium ions [10]. Apart from this single crystallographic study with addition of oxalate ligand, there is no report of any other such uranyl peroxide small clusters stabilized by other dicarboxylate ligands and no detailed spectroscopic work available on these small clusters. In addition, the effect of sodium ion on the formation of these small clusters also needs to be further examined as sodium hydroxide has been widely used in the current nuclear fuel cycle. In this work, we continue to explore the formation of uranyl peroxide small clusters in the presence of dicarboxylate ligands, e.g. malonate and oxalate and herein report the synthesis, spectroscopic studies and crystal structures of a sodium uranyl peroxide malonate,  $\text{Na}_{10}[(\text{UO}_2)(\text{O}_2)(\text{C}_3\text{H}_2\text{O}_4)]_5 \cdot 20\text{H}_2\text{O}$  (**1**), with a pentagonal ring structure stabilized by malonate, and a sodium potassium uranyl peroxide oxalate,  $[\text{Na}_4\text{K}_2(\text{UO}_2)_2(\text{O}_2)(\text{C}_2\text{O}_4)_4] \cdot 6\text{H}_2\text{O}$  (**2**), with a dimer structure stabilized by oxalate. The spectroscopic results are in good agreement with the crystal structures revealed by single crystal X-ray diffraction studies.

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## 2. Results and discussion

### 2.1. Structure description

The crystal data and refinement details for **1** and **2** are summarized in Table 1. Complex **1** consists of five crystallographic distinguished uranyl units sharing five peroxide groups forming a pentagonal uranyl peroxide ring. Each uranyl unit has two bidentate peroxide groups and a bidentate malonate, making a pentagonal ring in the form of  $[(\text{UO}_2)(\text{O}_2)(\text{C}_3\text{H}_2\text{O}_4)]_5^{10-}$  (Fig. 1a and b) with hexagonal bipyramid geometry for each uranium centre. The uranyl groups are quite normal with U=O bond lengths ranging from 1.784(1) to 1.822(7) Å. U–O bond lengths for peroxide groups range from 2.312(6) to 2.429(7) Å. The closest U–U distances within the ring vary slightly ranging from 4.168(6) to 4.262(6) Å. The U–U distances between rings on (101) plane range from 13.240(8) to 15.599(8) Å whilst the U–U distance between stacking rings along the *b*-axis is about 8.480(8) Å. From the crystal structure, the diameter of the pentagonal ring is about 15.80(5) Å measured from the two most apart oxygen atoms. A uranium polyhedral packing view (Fig. 1c) highlights the nano-ring stacking along the crystallographic *b*-axis. All uranyl groups are involved in cation–cation interactions (CCIs) with Na ions, with the shortest  $\text{O}_{-yl}\text{--Na}$  bond length of 2.313(7) Å (Fig. 2a). Such uranyl alkali CCIs are common in alkali metal uranates and some minerals containing uranyl ions as well as uranyl organic complexes [11]. However, such short  $\text{O}_{-yl}\text{--Na}$  bond length is not commonly observed. Consequently, the U=O<sub>-yl</sub> bonds are typically elongated [up to 1.822(7) Å] relative to those observed in discrete uranyl complexes. Sodium ions are coordinated by both water molecules and carboxylate O atoms linking into a complicated 3D network. Sodium polyhedrons are linked together through both edge and corner sharing. They have only limited corner sharing with uranium polyhedra, three from the top and three from the bottom (Fig. 1d). Hydrogen bonding is very extensive involving uncoordinated carboxylate O atoms and water molecules.

The structure of **2** is made up of the uranyl peroxide oxalate dimer in the form of  $[(\text{UO}_2)_2(\text{O}_2)(\text{C}_2\text{O}_4)_4]^{6-}$  (Fig. 3a, b), charge balanced with both sodium and potassium ions. Two uranyl groups share one bidentate peroxide group and each is coordinated by two bidentate oxalate ligands, making hexagonal bipyramid geometry for each uranium centre. The U=O bond lengths for uranyl groups range from 1.786(4) to 1.801(4) Å whilst the U–O bond

lengths in the equatorial plane range from 2.320(4) to 2.354(4) Å for the peroxide group and 2.415(4) to 2.488(4) Å for the oxalate ligands. Sodium ions are coordinated by both water molecules and oxalate O atoms linking into a 3D network (Fig. 3c). Both uranyl groups have cation–cation interactions towards Na and K ions with  $\text{O}_{-yl}\text{--Na}$  bond lengths from 2.393(4) to 2.451(4) Å and  $\text{O}_{-yl}\text{--K}$  bond lengths from 2.792(4) to 2.934(4) Å (Fig. 2b). As a result, the U=O<sub>-yl</sub> bonds are elongated, up to 1.801(4) Å. Sodium and potassium polyhedrons are linked together through oxalate ligands and water molecules with limited corner sharing. They have both edge and corner sharing with uranium polyhedrons (Fig. 3d) forming pillared network along the crystallographic *a*-axis. Extensive hydrogen bonding involves coordinated carboxylate O atoms and water molecules.

### 2.2. Structure discussion

A survey on malonate complexes containing 6-membered chelate rings confirmed that the chelated malonate ring has a high degree of conformational flexibility [12] with as many as five different types of configurations. However, all malonate rings in **1** are in boat or slightly skewed boat configurations.

As pentagonal ring (**P**) and dimer (**D**) structures stabilized by oxalate and charge balanced with potassium ions were previously reported in a crystallographic study [10], it is of interest to compare the similarities and differences of **1** to **P** and **2** to **D**. The uranyl coordination environments of **1**, **2**, **P** and **D** are summarized in Table 2. Both **1** and **P** have similar average U=O<sub>-yl</sub>, U–O<sub>o-o</sub>, U–O<sub>COO</sub> bond lengths due to the similar ring structures. However, there are differences between them. Firstly, they were crystallized in different space groups [**P** in orthorhombic (*Pnma*) and **1** in monoclinic (*P2<sub>1</sub>/c*)] with different cell parameters. Secondly, they are stabilized by different dicarboxylate ligands, malonate in **1** and oxalate in **P**. Thirdly, they have slightly different ring conformations. **P** has relatively longer U–U distances and wider ranges of U–U–U angles leading to a more stretching flat ring conformation with five peroxide groups on one side of the ring. In contrast, **1** has a slightly distorted ring conformation with three peroxide groups on one side of the ring and two on the other. Furthermore, unlike **P** which has a K ion right in the centre of the ring bonding to five uranyl units with  $\text{O}_{-yl}\text{--K}$  bonds ranging from 2.680(5) to 2.804(5) Å, **1** has no Na ion in the centre of the ring.

On the other hand, both **2** and **D** have similar average U=O<sub>-yl</sub>, U–O<sub>o-o</sub>, U–O<sub>COO</sub> bond lengths. But they were crystallized in different space groups [**D** in monoclinic (*P2<sub>1</sub>/c*) and **2** in triclinic (*P $\bar{1}$* )] with different cell parameters. In addition, **2** has relatively shorter U–U distance and narrower U–O<sub>2</sub>–U angle compared to **D**, leading to a more bending dimer unit. Finally, it is worth mentioning that CCIs between uranyl and alkali metal ions have apparently elongated the U=O<sub>-yl</sub> bonds with more effect of Na<sup>+</sup> ions than K<sup>+</sup> ions observed as evidenced by slightly longer U=O<sub>-yl</sub> bonds for **1** and **2** compared to **P** and **D**.

### 2.3. Raman spectroscopy

Raman spectroscopy was used to study the vibrational modes of the two complexes. Band assignments are made with consultation of the relevant Ref. [13]. For both complexes, the Raman bands below 250 cm<sup>-1</sup> are due to the lattice modes.

The Raman spectrum of **1** (Fig. 4a) shows two very strong bands at 844 and 806 cm<sup>-1</sup>, corresponding to the symmetric stretching vibrations of the peroxo ligand,  $\nu_s(\text{OO})$  [14], and uranyl ion,  $\nu_s(\text{UO}_2)^{2+}$ , respectively, with the calculated U=O bond length of 1.805(8) Å [15], consistent with the U=O bond lengths [1.784(1)

**Table 1**  
Crystal data and refinement details for **1** and **2**.

Complex	<b>1</b>	<b>2</b>
Formula	C <sub>15</sub> O <sub>60</sub> Na <sub>10</sub> U <sub>5</sub>	C <sub>8</sub> O <sub>28</sub> Na <sub>4</sub> K <sub>2</sub> U <sub>2</sub>
Formula weight	2560.20	1190.30
Crystal system	monoclinic	triclinic
Space group	<i>P2<sub>1</sub>/c</i>	<i>P<math>\bar{1}</math></i>
<i>a</i> (Å)	26.196(5)	7.5190(15)
<i>b</i> (Å)	8.6950(17)	10.088(2)
<i>c</i> (Å)	30.831(6)	17.769(4)
$\alpha$ (°)		79.50(3)
$\beta$ (°)	110.81(3) <sup>a</sup>	83.07(3)
$\gamma$ (°)		86.57(3)
<i>V</i> (Å <sup>3</sup> )	6564(3)	1314.6(5)
<i>Z</i>	4	2
$\mu$ (mm <sup>-1</sup> )	12.479	12.805
Min./Max. $\theta$ (°)	1.36/25.00	1.17/27.89
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	2.591	3.007
Goodness-of-fit (GOF)	1.009	1.030
Final <i>R</i> <sub>1</sub> <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0453	0.0331
Final <i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.1250	0.1103

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>b</sup>  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ .

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