



Uranyl carboxyphosphonates that incorporate Cd(II)

Andrea N. Alsobrook^a, Evgeny V. Alekseev^c, Wulf Depmeier^c, Thomas E. Albrecht-Schmitt^{a,b,*}

^a Department of Civil Engineering and Geological Sciences, University of Notre Dame, 156 Fitzpatrick Hall, Notre Dame, IN 46556, USA

^b Department of Chemistry and Biochemistry, University of Notre Dame, 156 Fitzpatrick Hall, Notre Dame, IN 46556, USA

^c Institut für Geowissenschaften, Universität zu Kiel, 24118 Kiel, Germany

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ABSTRACT

The hydrothermal treatment of UO_3 , $\text{Cd}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, and triethyl phosphonoacetate results in the formation of $\text{Cd}_2[(\text{UO}_2)_6(\text{PO}_3\text{CH}_2\text{CO}_2)_3\text{O}_3(\text{OH})(\text{H}_2\text{O})_2] \cdot 16\text{H}_2\text{O}$ (CdUPAA-1), $[\text{Cd}_3(\text{UO}_2)_6(\text{PO}_3\text{CH}_2\text{CO}_2)_6(\text{H}_2\text{O})_{13}] \cdot 6\text{H}_2\text{O}$ (CdUPAA-2), and $\text{Cd}(\text{H}_2\text{O})_2[(\text{UO}_2)(\text{PO}_3\text{CH}_2\text{CO}_2)(\text{H}_2\text{O})]_2$ (CdUPAA-3). CdUPAA-1 adopts a cubic three-dimensional structure constructed from planar uranyl oxide clusters containing both UO_7 pentagonal bipyramids and UO_8 hexagonal bipyramids that are linked by Cd(II) cations and phosphonoacetate to yield large cavities approximately 16 Å across that are filled with disordered water molecules. CdUPAA-2 forms a rhombohedral three-dimensional channel structure that is assembled from UO_7 pentagonal bipyramids that are bridged by phosphonoacetate. CdUPAA-3 is layered with the hydrated Cd(II) cations incorporated directly into the layers linking one-dimensional uranyl phosphonate substructures together. In this structure, there are complex networks of hydrogen bonds that exist within the sheets, and also stitch the sheets together.

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1. Introduction

The development of the structural chemistry and function of actinide oxoanion compounds has undergone a renaissance in the last decade. While the importance of early actinide phosphates, silicates, and carbonates has been known for decades owing to their relevance in the environmental behavior of actinides, structure–property relationships of new actinide materials are underdeveloped. The reason why this family can expand almost without limit can be directly attributed to the flexibility of the coordination chemistry of actinides. Trivalent and tetravalent actinides adopt high coordination numbers, typically eight or nine, although 12 and higher are known [1,2]. In contrast, when higher oxidation states of +5 or +6 are obtained, linear dioxo cations form, termed actinyl cations, and these have highly anisotropic coordination chemistry, but again vary considerably from six to eight coordinate [3]. The solid-state chemistry of the actinides is reaching the point where topological relationships can be developed [4,5], and of equal importance, the rudiments of materials design are taking place; yielding solids with selective ion-exchange [6–12], mixed-valency [13,14], ionic conductivity [15–20], enhanced fluorescence [21–23], magnetic ordering

[11,24], nonlinear optical properties [12,25], and differential gas sorption [26,27].

Actinide carboxyphosphonates are one of the most rapidly expanding families of *f*-block oxoanion compounds. Almost 30 of these have been reported in the last few years with both Th(IV) and U(VI) [28–36]. As expected for compounds that contain uranyl cations, most of these compounds have layered structures [24]; whereas the more isotropic coordination of Th(IV) leads to three-dimensional networks [33,34]. The multifunctional nature of the carboxyphosphonates allows for the preparation of heterobimetallic compounds that incorporate both actinides and transition metals. The Pearson hardness of the phosphonate portion of the ligand is more compatible with the hard actinide metal ions leaving the carboxylate portion free to interact with softer transition metal ions. Thus far all of the metals have been first- and second-row divalent transition metals such as Mn(II) [35], Co(II) [35], Cu(II) [28], Zn(II) [32], and Cd(II) [35]. Additional anions, such as fluoride [33] and oxalate [34], can be incorporated into the networks substantially increasing their structural complexity.

We recently briefly communicated the existence of high symmetry heterobimetallic transition metal uranyl phosphonoacetates, $M_2[(\text{UO}_2)_6(\text{PO}_3\text{CH}_2\text{CO}_2)_3\text{O}_3(\text{OH})(\text{H}_2\text{O})_2] \cdot 16\text{H}_2\text{O}$ ($M = \text{Mn}(\text{II}), \text{Co}(\text{II}),$ and $\text{Cd}(\text{II})$), which adopt cubic three-dimensional network structures with large cavities approximately 16 Å in diameter that are filled with co-crystallized water molecules, and $[\text{Cd}_3(\text{UO}_2)_6(\text{PO}_3\text{CH}_2\text{CO}_2)_6(\text{H}_2\text{O})_{13}] \cdot 6\text{H}_2\text{O}$ which forms a rhombohedral channel structure with hydrated Cd(II) within the channels [35]. Herein, we

* Corresponding author at: Department of Chemistry and Biochemistry, University of Notre Dame, 156 Fitzpatrick Hall, Notre Dame, IN 46556.

E-mail address: talbre1@nd.edu (T.E. Albrecht-Schmitt).

expand on this work by providing a more detailed description and characterization of these Cd(II) compounds, as well as an addition to this family with $\text{Cd}(\text{H}_2\text{O})_2[(\text{UO}_2)(\text{PO}_3\text{CH}_2\text{CO}_2)(\text{H}_2\text{O})]_2$.

2. Experimental

2.1. Syntheses

Uranium trioxide (98%, Strem), triethyl phosphonoacetate (98%, Alfa Aesar), and $\text{Cd}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ (98%, Alfa Aesar) were used as received. Reactions were run in PTFE-lined Parr 4749 autoclaves with a 23 mL internal volume. Distilled and Millipore filtered water with a resistance of 18.2 M Ω cm was used in all reactions. Standard precautions were performed for handling radioactive materials during work with UO_3 and the products of the reactions. The products were thoroughly washed with water, then rinsed with methanol, and allowed to dry.

2.2. $\text{Cd}_2[(\text{UO}_2)_6(\text{PO}_3\text{CH}_2\text{CO}_2)_3\text{O}_3(\text{OH})(\text{H}_2\text{O})_2] \cdot 16\text{H}_2\text{O}$ (CdUPAA-1) and $[\text{Cd}_3(\text{UO}_2)_6(\text{PO}_3\text{CH}_2\text{CO}_2)_6(\text{H}_2\text{O})_{13}] \cdot 6\text{H}_2\text{O}$ (CdUPAA-2)

UO_3 (286.3 mg, 0.926 mmol), triethyl phosphonoacetic acid (0.120 mL, 0.602 mmol), $\text{Cd}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ (266.5 mg, 0.997 mmol), and 5 mL of water were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 150 P°C in a box furnace for 5 d. The autoclave was then cooled at an average rate of 9 °C/h to 35 P°C. CdUPAA-1 can be described as orange blocks and CdUPAA-2 as yellow blocks.

2.3. $\text{Cd}(\text{H}_2\text{O})_4[(\text{UO}_2)(\text{PO}_3\text{CH}_2\text{CO}_2)(\text{H}_2\text{O})]_2$ (CdUPAA-3)

UO_3 (286.3 mg, 0.827 mmol), triethyl phosphonoacetic acid (0.120 mL, 0.602 mmol), $\text{Cd}(\text{CO}_2\text{CH}_3)_2 \cdot 2\text{H}_2\text{O}$ (266.53 mg, 0.950 mmol), and 5 mL of water were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 200 P°C in a box furnace for 3 d. The autoclave was then cooled at an average rate of 9 °C/h to 35 P°C. CdUPAA-3 were yellow platelets. Yield 287.4 mg (67.13% based on uranium).

2.4. Crystallographic studies

Crystals of CdUPAA-1, CdUPAA-2, and CdUPAA-3 were mounted on glass fibers, and optically aligned on a Bruker APEXII Quazar X-ray diffractometer using a digital camera. Initial intensity measurements were performed using an I μ S X-ray source, a 30 W microfocused sealed tube (MoK α , $\lambda=0.71073$ Å) with high-brilliance and high-performance focusing Quazar multilayer optics. Standard APEXII software was used for determination of the unit cells and data collection control. The intensities of reflections of a sphere were collected by a combination of four sets of exposures (frames). Each set had a different φ angle for the crystal and each exposure covered a range of 0.5° in ω with exposure time per frame of 30–60 s, depending on the crystal.

For these compounds, determination of integrated intensities and global refinement were performed with the Bruker SAINT (v 6.02) software package using a narrow-frame integration algorithm. The data were treated with a semi-empirical absorption correction by SCALE (SADABS) [37]. The program suite SHELXTL (v 6.12) was used for space group determination (XPREP), direct methods structure solution (XS), and least-squares refinement (XL) [38]. The final refinements included anisotropic displacement parameters for all non-hydrogen atoms. Secondary extinction was not noted. Some crystallographic details are given in Table 1. Additional details can be found in the Supporting Information.

Table 1

Crystallographic data for $\text{Cd}_2[(\text{UO}_2)_6(\text{PO}_3\text{CH}_2\text{CO}_2)_3\text{O}_3(\text{OH})(\text{H}_2\text{O})_2] \cdot 16\text{H}_2\text{O}$ (CdUPAA-1), $[\text{Cd}_3(\text{UO}_2)_6(\text{PO}_3\text{CH}_2\text{CO}_2)_6(\text{H}_2\text{O})_{13}] \cdot 6\text{H}_2\text{O}$ (CdUPAA-2), and $\text{Cd}(\text{H}_2\text{O})_4[(\text{UO}_2)(\text{PO}_3\text{CH}_2\text{CO}_2)(\text{H}_2\text{O})]_2$ (CdUPAA-3).

Compound	CdUPAA-1	CdUPAA-2	CdUPAA-3
Formula mass	2579.98	1027.81	517.28
Color and habit	Orange, block	yellow, block	yellow, platelet
Space group	$Im\bar{3}$ (no. 204)	$R\bar{3}$ (no. 148)	$P\bar{1}$ (No. 2)
<i>a</i> (Å)	26.404(2)	18.962(2)	6.9135(4)
<i>b</i> (Å)	26.404(2)	18.962(2)	8.2817(4)
<i>c</i> (Å)	26.404(2)	14.0112(18)	8.7973(4)
α (deg)	90	90	70.453(1)
β (deg)	90	90	86.420(1)
γ (deg)	90	120	89.367(1)
<i>V</i> (Å ³)	18407(3)	4362.7(10)	473.71(4)
<i>Z</i>	16	3	1
<i>T</i> (K)	100	100	100
λ (Å)	0.71073	0.71073	0.71073
ρ_{calcd} (g cm ⁻³)	3.724	3.521	3.627
μ (MoK α) (cm ⁻¹)	221.65	180.11	184.30
<i>R</i> (<i>F</i>) for $F_o^2 > 2\sigma(F_o^2)^a$	0.0239	0.0253	0.0113
$R_w(F_o^2)^b$	0.0565	0.0494	0.0284

$$^a R(F) = \frac{\sum \|F_o\| - |F_c|}{\sum \|F_o\|}$$

$$^b R_w(F_o^2) = \left[\frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum wF_o^4} \right]^{1/2}$$

2.5. Fluorescence spectroscopy

Fluorescence data were acquired from all compounds from single crystals using a Craic Technologies UV–vis–NIR microspectrophotometer with a fluorescence attachment. Excitation was achieved using 365 nm light from a mercury lamp.

3. Results and discussion

3.1. Synthesis

The syntheses of CdUPAA-1 and CdUPAA-2 is achieved by reacting simple sources of U(VI) and Cd(II) with triethyl phosphonoacetate under mild hydrothermal conditions. During this reaction the triethyl phosphonoacetate slowly hydrolyzes to form phosphonoacetate. If phosphonoacetic acid is added directly to the starting reaction, crystalline products do not form in this reaction. The slow in situ formation of the ligand is the key to growing crystals [29,32,35]. Increasing the reaction temperature from 150 to 200 °C allows for the isolation of CdUPAA-3.

3.2. Structure of $\text{Cd}_2[(\text{UO}_2)_6(\text{PO}_3\text{CH}_2\text{CO}_2)_3\text{O}_3(\text{OH})(\text{H}_2\text{O})_2] \cdot 16\text{H}_2\text{O}$ (CdUPAA-1)

CdUPAA-1 crystallized in the high-symmetry cubic space group $Im\bar{3}$. Previous uranyl carboxyphosphonates have not crystallized in crystal systems with symmetries higher than orthorhombic. This three-dimensional, open framework is different from other uranyl carboxyphosphonates in that it incorporates both UO_7 pentagonal bipyramids and UO_8 hexagonal bipyramids; whereas all other carboxyphosphonates only contain UO_7 units. Other examples of high-symmetry structures that formed open frameworks are $(\text{NH}_4)_4[(\text{UO}_2)_5(\text{MoO}_4)_7](\text{H}_2\text{O})_5$ and $[(\text{UO}_2)_3(\text{PO}_4)\text{O}(\text{OH})(\text{H}_2\text{O})_2](\text{H}_2\text{O})$ [39,40]. The latter structure also contains UO_8 hexagonal and UO_7 pentagonal bipyramids. Furthermore, because UO_7 groups have point group symmetry of D_{5h} , one would not expect for such structures containing only these uranyl groups to solve in high crystal systems. The central portion of Fig. 1 shows the nearly planar cluster containing eight uranyl polyhedra in CdUPAA-1. Four such clusters are linked by additional

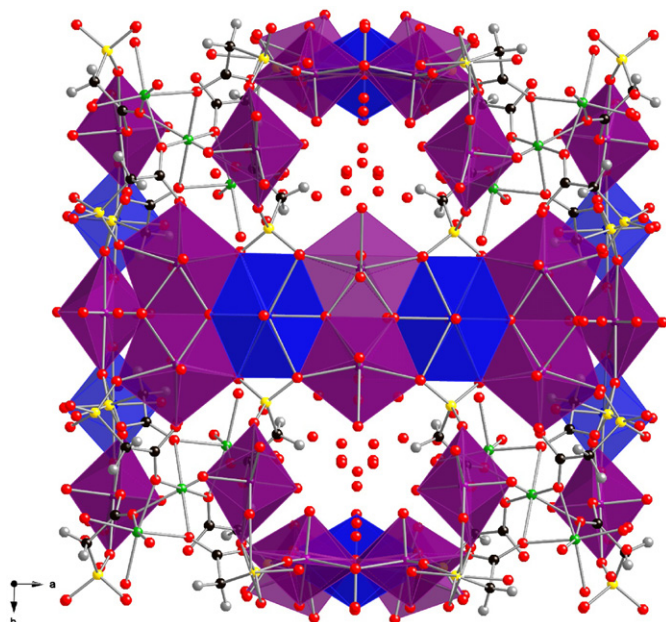


Fig. 1. A view of part of the structure of $\text{Cd}_2[(\text{UO}_2)_6(\text{PO}_3\text{CH}_2\text{CO}_2)_3\text{O}_3(\text{OH})(\text{H}_2\text{O})_2] \cdot 16\text{H}_2\text{O}$. The central portion of this figure shows the nearly planar, eight uranyl cluster that is made of both UO_7 pentagonal and UO_8 hexagonal bipyramids. Four of these clusters are linked together by intermediate uranyl groups to form this entire structure. There is also a cavity in this structure that is filled with disordered water molecules. UO_7 pentagonal bipyramids = purple, UO_8 hexagonal bipyramids = blue, cadmium = green, oxygen = red, phosphorus = yellow, carbon = black, and hydrogen = white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

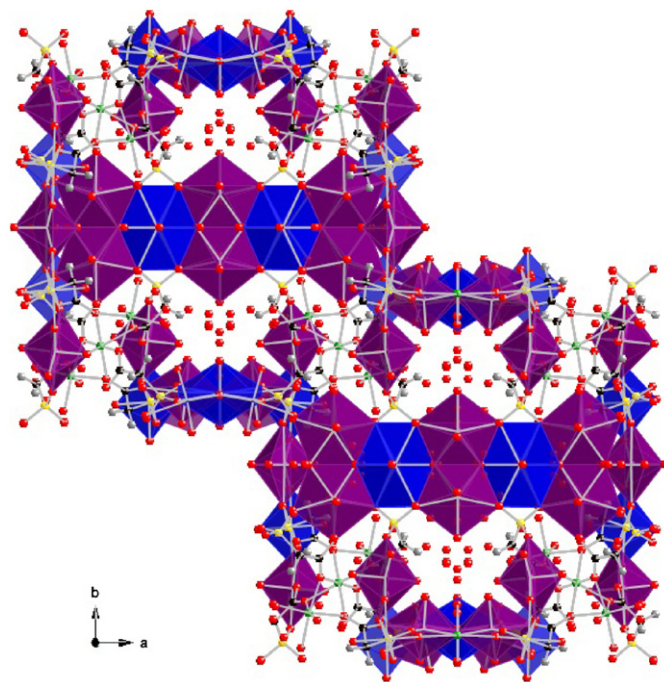


Fig. 2. An illustration of the cage-to-cage connection in the structure of $\text{Cd}_2[(\text{UO}_2)_6(\text{PO}_3\text{CH}_2\text{CO}_2)_3\text{O}_3(\text{OH})(\text{H}_2\text{O})_2] \cdot 16\text{H}_2\text{O}$ that is formed from uranyl clusters and intermediate uranyl groups bound by the phosphonate ligands. UO_7 pentagonal bipyramids = purple, UO_8 hexagonal bipyramids = blue, cadmium = green, oxygen = red, phosphorus = yellow, carbon = black, and hydrogen = white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

intermediate uranyl groups that are bound by phosphonates. These groups are linkers not only for the clusters within one cell, but also connect cage-to-cage as shown in Fig. 2. There are disordered cadmium cations that aligned along the edges of the structure that are coordinated by the carboxylate oxygen atoms of the phosphonoacetate ligand and water molecules. As required by the cubic symmetry, the top and bottom of the cavities are capped again by the clusters of UO_7 and UO_8 polyhedra. When assembled together, the subunits form a large cavity approximately 16 Å in diameter that is filled with co-crystallized water molecules that are disordered. In addition, there are channels between the cavities that are filled with the $\text{Cd}(\text{II})$ cations and water molecules.

The average uranyl $\text{U}=\text{O}$ bond length for $\text{U}(1)$ and $\text{U}(3)$ is 1.791(8) Å and the equatorial $\text{U}-\text{O}$ bonds range from 2.265(4) to 2.450(7) Å. The bond-valence sums for $\text{U}(1)$ and $\text{U}(3)$ are 6.08 and 6.07, both of which are consistent with $\text{U}(\text{VI})$ [3]. The $\text{U}(2)$ average uranyl $\text{U}=\text{O}$ bond is 1.811(6) Å, and its equatorial $\text{U}-\text{O}$ bonds range from 2.187(6) to 2.638(5) Å (Table 2). The bond-valence sum for $\text{U}(3)$ is 5.98, which again agrees well with $\text{U}(\text{VI})$ [3]. The cluster of uranyl polyhedral contains a total of eight edge-sharing uranyl groups, $\text{U}(1)$, $\text{U}(2)$, and $\text{U}(3)$, that are separated by octahedral $\text{Cd}(\text{II})$. There are three sets of uranyl pentagonal bipyramidal dimers, $\text{U}(1)$ and $\text{U}(3)$, that share edges with a neighboring uranyl hexagonal bipyramid, $\text{U}(2)$. There is also a phosphonoacetate ligand that shares a corner with one of the uranyl pentagonal bipyramids. The phosphonoacetate ligand again demonstrates bridging and chelating binding modes in this structure.

There are three crystallographically unique $\text{Cd}(\text{II})$ cations. Only two of the three crystallographically unique cadmium cations, $\text{Cd}(2)$ and $\text{Cd}(3)$, are shown in Figs. 1 and 2. The two cadmium cations share triangular faces to form a cluster. The final $\text{Cd}(\text{II})$ cation, $\text{Cd}(1)$, bridges between the uranyl hexagonal bipyramids.

Table 2

Selected bond distances (Å) and angles (deg) for $\text{Cd}_2[(\text{UO}_2)_6(\text{PO}_3\text{CH}_2\text{CO}_2)_3\text{O}_3(\text{OH})(\text{H}_2\text{O})_2] \cdot 16\text{H}_2\text{O}$ (CdUPAA-1).

Distances (Å)			
$\text{U}(1)-\text{O}(6)$	1.783(8)	$\text{Cd}(1)-\text{OW}(2\text{A})$	2.31(2)
$\text{U}(1)-\text{O}(7)$	1.789(8)	$\text{Cd}(1)-\text{OW}(2\text{A})$	2.31(2)
$\text{U}(1)-\text{O}(12)$	2.265(4)	$\text{Cd}(1)-\text{OW}(1\text{A})$	2.442(18)
$\text{U}(1)-\text{O}(12)$	2.265(4)	$\text{Cd}(1)-\text{OW}(1\text{A})$	2.442(18)
$\text{U}(1)-\text{O}(2)$	2.389(5)	$\text{Cd}(2)-\text{OW}(11)$	2.18(4)
$\text{U}(1)-\text{O}(2)$	2.389(5)	$\text{Cd}(2)-\text{O}(5)$	2.278(5)
$\text{U}(1)-\text{O}(13)$	2.450(7)	$\text{Cd}(2)-\text{O}(5)$	2.278(5)
$\text{U}(2)-\text{O}(8)$	1.794(6)	$\text{Cd}(2)-\text{O}(5)$	2.278(5)
$\text{U}(2)-\text{O}(9)$	1.829(7)	$\text{Cd}(2)-\text{OW}(3)$	2.326(9)
$\text{U}(2)-\text{O}(14)$	2.187(6)	$\text{Cd}(2)-\text{OW}(3)$	2.326(9)
$\text{U}(2)-\text{O}(12)$	2.205(6)	$\text{Cd}(2)-\text{OW}(3)$	2.326(9)
$\text{U}(2)-\text{O}(3)$	2.635(5)	$\text{Cd}(2)-\text{OW}(15)$	2.42(4)
$\text{U}(2)-\text{O}(3)$	2.635(5)	$\text{Cd}(2)-\text{OW}(15)$	2.42(4)
$\text{U}(2)-\text{O}(2)$	2.638(5)	$\text{Cd}(2)-\text{OW}(15)$	2.42(4)
$\text{U}(2)-\text{O}(2)$	2.638(5)	$\text{Cd}(3)-\text{O}(5)$	2.284(5)
$\text{U}(3)-\text{O}(10)$	1.796(5)	$\text{Cd}(3)-\text{O}(5)$	2.284(5)
$\text{U}(3)-\text{O}(11)$	1.798(5)	$\text{Cd}(3)-\text{O}(5)$	2.284(5)
$\text{U}(3)-\text{O}(14)$	2.271(3)	$\text{Cd}(3)-\text{O}(5)$	2.284(5)
$\text{U}(3)-\text{O}(15)$	2.339(4)	$\text{Cd}(3)-\text{O}(5)$	2.284(5)
$\text{U}(3)-\text{O}(1)$	2.355(4)	$\text{Cd}(3)-\text{O}(5)$	2.284(5)
$\text{U}(3)-\text{O}(4)$	2.396(4)	$\text{P}(1)-\text{O}(1)$	1.498(5)
$\text{U}(3)-\text{O}(3)$	2.407(4)	$\text{P}(1)-\text{O}(2)$	1.527(5)
$\text{Cd}(1)-\text{OW}(1)$	2.179(17)	$\text{P}(1)-\text{O}(3)$	1.537(5)
$\text{Cd}(1)-\text{OW}(1)$	2.179(17)	$\text{P}(1)-\text{C}(1)$	1.794(7)
$\text{Cd}(1)-\text{O}(9)$	2.231(7)	$\text{C}(2)-\text{O}(4)$	1.257(8)
$\text{Cd}(1)-\text{O}(9)$	2.231(7)	$\text{C}(2)-\text{O}(5)$	1.270(8)
$\text{Cd}(1)-\text{OW}(2)$	2.29(2)	$\text{C}(1)-\text{C}(2)$	1.512(9)
$\text{Cd}(1)-\text{OW}(2)$	2.29(2)		
Angles (deg)			
$\text{O}(6)-\text{U}(1)-\text{O}(7)$	173.5(4)	$\text{O}(8)-\text{U}(2)-\text{O}(9)$	178.8(3)

^a $\text{Cd}-\text{O}$ bond lengths include disordered oxygen atoms.

All of the cadmium cations are six-coordinate and have Cd–O bond lengths of 2.179(17) and 2.442(18) Å. Bond-valence sums for Cd(1), Cd(2), and Cd(3) are 2.22, 2.30, and 2.15, which agree with a +2 charge [41].

3.3. Structure of $[Cd_3(UO_2)_6(PO_3CH_2CO_2)_6(H_2O)_{13}] \cdot 6H_2O$ (CdUPAA-2)

CdUPAA-2 crystallizes in rhombohedral space group, $R\bar{3}$. Similar to the first compound, a high-symmetry three-dimensional network is adopted. Once again a cluster of face-sharing Cd(II) polyhedra play a substantial role in the structure. Here, they are found to align along the *c*-axis, and fill flower-shaped channels that extend in this same direction as shown in Fig. 3. The 3 symmetry is also evident from this view. These units make use of the carboxylate oxygen donors in their coordination sphere. However, the structure also contrasts sharply with the cubic compounds in that the uranium atoms are only found in UO_7 pentagonal bipyramids, as occurs in all other examples of uranyl carboxyphosphonates [28–36]. The structure can be viewed as forming from one-dimensional chains that extend along the *c*-axis that are bridged into hexameric channels by the phosphonates. The average uranyl U=O bond for U(1) is 1.739(4) Å and the equatorial U–O bonds range from 2.346(4) to 2.553(4) Å. The bond-valence sum for U(1) is 6.05, which is consistent with U(VI) [3]. There are two crystallographically unique cadmium cations, Cd(1) and Cd(2). The bond lengths range from 2.216(10) to 2.355(8) Å (Table 3). Bond-valence sums for Cd(1) and Cd(2) are 2.10 and 2.05, respectively, which agree with a +2 charge [41]. Cd(1) is a six-coordinate cation. However, the water molecules coordinating Cd(2) are partially disordered and there is a seventh oxygen donor.

3.4. Structure of $Cd(H_2O)_4[(UO_2)(PO_3CH_2CO_2)(H_2O)]_2$ (CdUPAA-3)

CdUPAA-3 is substantially different from the other two Cd(II) compounds in that it adopts a low-symmetry structure, and crystallizes in the triclinic space group $P\bar{1}$. There is only one crystallographically unique uranium atom, U(1), which is found as a UO_7 pentagonal bipyramid. The average uranyl U=O bond is 1.782(2) Å and the equatorial U–O bonds range from 2.2914(18)

Table 3

Selected bond distances (Å) and angles (deg) for $[Cd_3(UO_2)_6(PO_3CH_2CO_2)_6(H_2O)_{13}] \cdot 6H_2O$ (CdUPAA-2).

Distances (Å)			
U(1)–O(6)	1.763(4)	Cd(2)–O(9)	2.216(10)
U(1)–O(7)	1.764(4)	Cd(2)–O(5)	2.334(4)
U(1)–O(1)	2.346(4)	Cd(2)–O(5)	2.334(4)
U(1)–O(3)	2.350(4)	Cd(2)–O(5)	2.334(4)
U(1)–O(2)	2.375(4)	Cd(2)–O(10)	2.350(15)
U(1)–O(4)	2.376(4)	Cd(2)–O(11)	2.355(8)
U(1)–O(8)	2.553(4)	P(1)–O(1)	1.525(4)
Cd(1)–O(5)	2.293(4)	P(1)–O(2)	1.527(4)
Cd(1)–O(5)	2.293(4)	P(1)–O(3)	1.533(4)
Cd(1)–O(5)	2.293(4)	P(1)–C(1)	1.805(6)
Cd(1)–O(5)	2.293(4)	C(1)–C(2)	1.498(8)
Cd(1)–O(5)	2.293(4)	C(2)–O(4)	1.261(6)
Cd(1)–O(5)	2.293(4)	C(2)–O(5)	1.271(7)
Angles (deg)			
O(6)–U(1)–O(7)	176.74(18)		

^aCd–O bond lengths include disordered oxygen atoms.

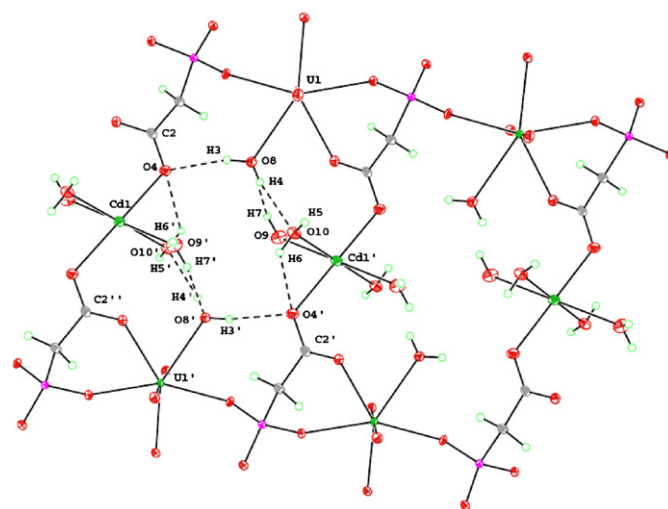


Fig. 4. A viewing of the hydrogen bonding between the layers of $Cd(H_2O)_4[(UO_2)(PO_3CH_2CO_2)(H_2O)]_2$ (CdUPAA-3). The hydrogen interactions are essential in stitching the uranyl phosphonate layers together and bonding the cadmium cations within the layers.

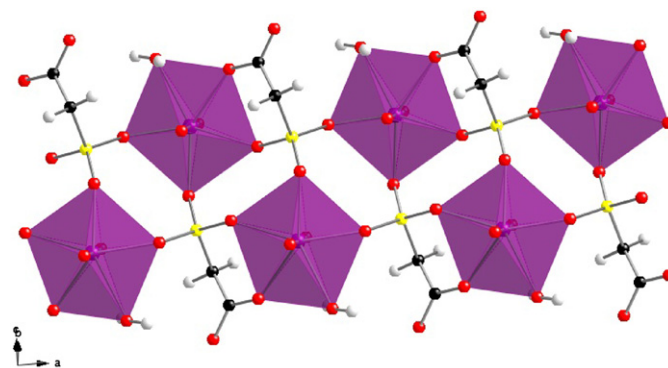


Fig. 5. A view of the one-dimensional uranyl phosphonoacetate chain in $Cd(H_2O)_4[(UO_2)(PO_3CH_2CO_2)(H_2O)]_2$ (CdUPAA-3). UO_7 pentagonal bipyramids = purple, phosphorus = yellow, oxygen = red, carbon = black, hydrogen = white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

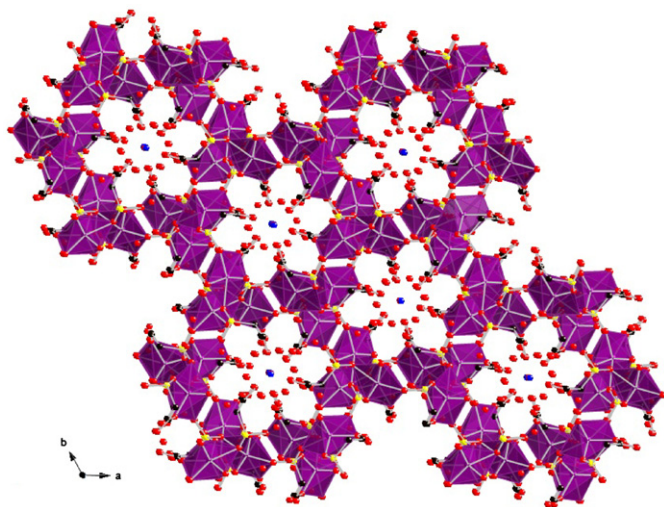


Fig. 3. A view along the *c*-axis of the three-dimensional network of $[Cd_3(UO_2)_6(PO_3CH_2CO_2)_6(H_2O)_{13}] \cdot 6H_2O$ (CdUPAA-2). UO_7 pentagonal bipyramids = purple, cadmium = blue, phosphorus = yellow, oxygen = red, carbon = black, hydrogen = white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

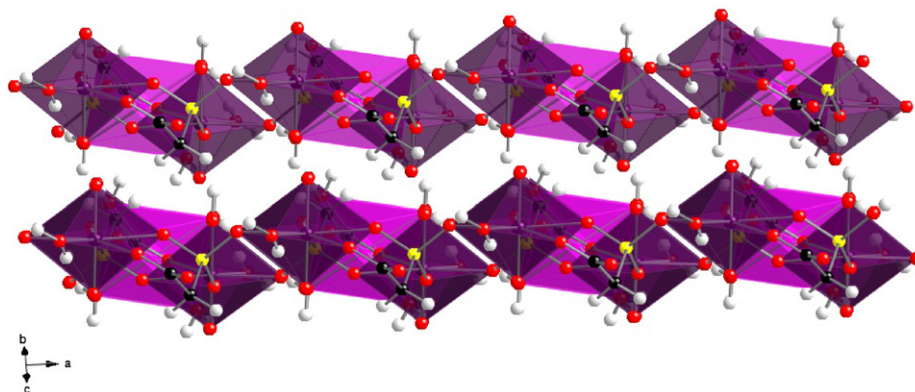


Fig. 6. A view of the stacking of layers in $\text{Cd}(\text{H}_2\text{O})_2[(\text{UO}_2)(\text{PO}_3\text{CH}_2\text{CO}_2)(\text{H}_2\text{O})]_2$ (CdUPAA-3). UO_7 pentagonal bipyramids=purple, cadmium=magenta, phosphorus=yellow, oxygen=red, carbon=black, hydrogen=white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 4

Selected bond distances (Å) and angles (deg) for $\text{Cd}(\text{H}_2\text{O})_4[(\text{UO}_2)(\text{PO}_3\text{CH}_2\text{CO}_2)(\text{H}_2\text{O})]_2$ (CdUPAA-3).

Distances (Å)			
U(1)–O(6)	1.7771(19)	Cd(1)–O(9)	2.337(2)
U(1)–O(7)	1.787(2)	Cd(1)–O(10)	2.349(2)
U(1)–O(1)	2.2914(18)	Cd(1)–O(10)	2.349(2)
U(1)–O(3)	2.3491(18)	P(1)–O(1)	1.5196(19)
U(1)–O(2)	2.3513(18)	P(1)–O(2)	1.5294(19)
U(1)–O(5)	2.395(2)	P(1)–O(3)	1.5311(19)
U(1)–O(8)	2.550(2)	P(1)–C(1)	1.805(3)
Cd(1)–O(4)	2.225(2)	C(1)–C(2)	1.517(4)
Cd(1)–O(4)	2.225(2)	C(2)–O(4)	1.252(3)
Cd(1)–O(9)	2.337(2)	C(2)–O(5)	1.264(3)
Angles (deg)			
O(6)–U(1)–O(7)	178.58(18)		
Hydrogen bonding contacts			
Distances (Å)			
O(8)⋯O(10)	2.84	O(10)⋯O(4)	2.76
O(9)⋯O(8)	3.06	O(8)⋯O(4)	3.10
O(10)⋯O(5)	3.04	O(10)⋯O(9)	3.04

to 2.550(2) Å. The longest U–O bond of 2.550(2) Å is to a coordinating water molecule and is within normal ranges for this type of interaction [42]. The bond-valence sum for U(1) is 6.01, which is consistent with U(VI) [3]. As shown in Fig. 4, the phosphonoacetate ligand differentiates between the metal centers by using the phosphonate portion to bind U(VI); whereas the carboxylate portion bonds to both the Cd(II) and U(VI). The uranyl cations are bridged by the phosphonate portion to create one-dimensional chains that extend along the *a*-axis (Fig. 5). The Cd(II) centers are then bound by the carboxylate moieties and link the chains together to form two-dimensional sheets. The Cd(II) center is six-coordinate with two trans interactions with carboxylate groups and four equatorial bonds with water molecules. The Cd–O bond length ranges from 2.225(2) to 2.349(2) Å, and the bond-valence sum is 2.06 [41]. The longer bonds are also with the coordinating waters of 2.337(2) (× 2) and 2.349(2) (× 2) Å.

As shown in Fig. 4, there is extensive hydrogen bonding in the structure. All of the hydrogen atoms in the structure were resolved despite the presence of two different heavy atoms owing to the remarkably low residuals. Hydrogen bonds exist within the sheets that join the water molecules that coordinate the U(VI) cations with the water molecules bound to Cd(II). The water molecule bound to U(VI) also forms short contacts with the

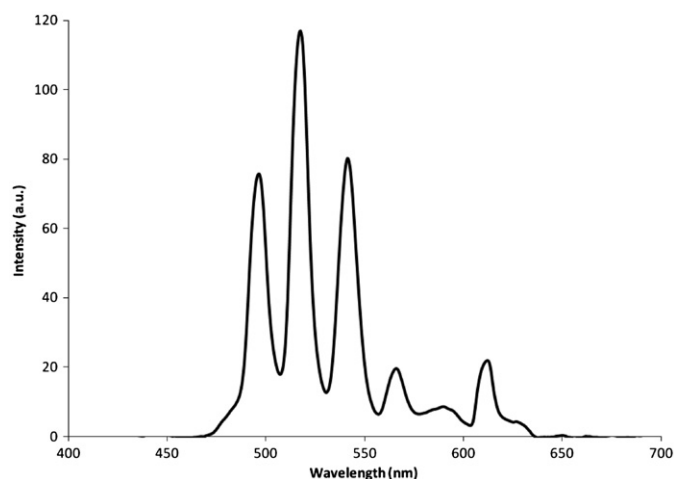


Fig. 7. Fluorescence spectrum of $\text{Cd}(\text{H}_2\text{O})_4[(\text{UO}_2)(\text{PO}_3\text{CH}_2\text{CO}_2)(\text{H}_2\text{O})]_2$ (CdUPAA-3) showing vibronically coupled charge-transfer transitions.

bridging carboxylate oxygen atoms that binds the Cd(II) cations. Hydrogen bonds also stitch the layers together (Fig. 6). A complete listing of the hydrogen bonding contacts is given in Table 4.

This family of Cd(II) uranyl carboxyphosphonates would be expected to be most similar with Zn(II) analogs [32]. In fact, the Zn(II) compounds show more similarities with Cu(II). However, CdUPAA-3 is very similar to $\text{Zn}(\text{H}_2\text{O})_4(\text{UO}_2)_2(\text{H}_2\text{O})_2(\text{PO}_3\text{CH}_2\text{CO}_2)_2$ [32]. An analysis of the unit cells demonstrates that the *a* and *b* axes are very similar and the *c*-axis of CdUPAA-3 is close to being half of the *c*-axis in $\text{Zn}(\text{H}_2\text{O})_4(\text{UO}_2)_2(\text{H}_2\text{O})_2(\text{PO}_3\text{CH}_2\text{CO}_2)_2$. The sheet topologies are the same. However, the Zn(II) system includes several layered compounds where the uranyl carboxyphosphonate layers are separated from one another by $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ [32]. These compounds are absent in the Cd(II) system. Likewise, the high-symmetry structures found for CdUPAA-1 and CdUPAA-2 are absent with Zn(II).

4. Fluorescence spectroscopy

Most uranyl compounds fluoresce when irradiated with long wavelength UV light. The emission is typically centered near 520 nm and consists of a series of strongly vibronically coupled charge-transfer features. Denning and co-workers have assigned these transitions for the $[\text{UO}_2\text{Cl}_4]^{2-}$ anion owing to its crystallization in a cubic space group [43]. At room-temperature, five

features are typically observed. Although, data acquired at 4 K shows far more resolved transitions [44]. Uranyl carboxyphosphonates fluoresce in much the same way as other uranyl compounds [28–36]. In transition metal uranyl carboxyphosphonates paramagnetic quenching and re-absorption by the *d–d* transitions of the transition metals are often responsible for loss of fluorescence. However, as shown in Fig. 6, Cd(H₂O)₄[(UO₂)(-PO₃CH₂CO₂)(H₂O)]₂ (CdUPAA-3) is luminescent, and show the typical fluorescence spectra of uranyl compounds with five vibronic transitions centered near 540 nm; albeit the intensity of emission is unusually weak (Fig. 7).

5. Conclusions

Cd₂[(UO₂)₆(PO₃CH₂CO₂)₃O₃(OH)(H₂O)₂]·16H₂O (CdUPAA-1) and [Cd₃(UO₂)₆(PO₃CH₂CO₂)₆(H₂O)₁₃]·6H₂O (CdUPAA-2) form high-symmetry structures that have not been observed before in uranyl carboxyphosphonates. A review of uranyl compounds in general demonstrates that this level of symmetry is rarely observed [4]. In both compounds, the Cd(II) cations are incorporated directly into the network either serving as linking atoms or as templates. Cd(H₂O)₄[(UO₂)(PO₃CH₂CO₂)(H₂O)]₂ (CdUPAA-3) continues some of these trends whereby the Cd(II) joins one-dimensional uranyl carboxyphosphonate features together into a higher dimensional structure; although the structure is still low-symmetry. The ability of Cd(II) to serve so many different roles in this family of compounds is surprising in light of the fact that it is generally a mundane transition metal being both redox inactive and typically octahedral.

Supporting information

Further details of the crystal structure investigation may be obtained from the Cambridge Crystallographic Data Centre on quoting numbers CSD 794933, 794935, and 801311.

Acknowledgments

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