

Cubic and rhombohedral heterobimetallic networks constructed from uranium, transition metals, and phosphonoacetate: new methods for constructing porous materials†

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Four heterobimetallic U(vi)/M(II) (M = Mn, Co, Cd) carboxyphosphonates have been synthesized. $M_2[(UO_2)_6(PO_3CH_2CO_2)_3O_3(OH)(H_2O)_2] \cdot 16H_2O$ (M = Mn(II), Co(II), and Cd(II)) adopt cubic three-dimensional network structures with large cavities approximately 16 Å in diameter that are filled with co-crystallized water molecules. $[Cd_3(UO_2)_6(PO_3CH_2CO_2)_6(H_2O)_{13}] \cdot 6H_2O$ forms a rhombohedral channel structure with hydrated Cd(II) within the channels. The cubic compound (Co) displays differential gas absorption with a surface area for CO₂ uptake of 40 m² g⁻¹ at 273 K, and no uptake of N₂ at 77 K.

The synthetic and materials chemistry of uranium is the best developed in the actinide series, and has expanded substantially over the past decade owing to advances in synthetic methods, instrumentation, and recognition of the importance of correlating structural features with physico-chemical properties for elements involved in the nuclear fuel cycle. U(vi) is typically found in the form of a linear UO₂²⁺ cation, called uranyl, and four to six additional donor atoms are usually found perpendicular to the uranyl axis yielding tetragonal, pentagonal, and hexagonal bipyramids. These polyhedra can be condensed into dense structures *via* corner- and edge-sharing, and are also bridged by various groups to yield extended structures. Most of the common oxoanions have been used to bind uranyl, and large families of uranyl oxoanion compounds are now known.¹ From these studies, it is recognized that oxoanions like iodate can be used to prepare one-dimensional compounds,² whereas the tetrahedral anion, selenate, can yield nanotubular structures under appropriate crystallization conditions.³ The use of peroxide in basic media has led to the discovery of a large family of uranyl peroxide nanoclusters with as many as sixty uranyl polyhedra.⁴ Uranyl compounds in general have also yielded some remarkable

properties that include ionic conductivity,⁵ selective ion-exchange,⁶ magnetic ordering,⁶ selective oxidation catalysis,⁷ non-linear optical properties,⁸ mixed-valency,⁹ and room-temperature phase transitions.¹⁰ One of the few examples of an actinide material with a porous structure that is capable of significant gas absorption is TOF-2, a Th(IV) metal-organic framework, which exhibits differential gas sorption with a surface area for CO₂ uptake of 293 m² g⁻¹ at 77 K.¹¹

One family of uranyl compounds that continues to rapidly yield unusual characteristics are the phosphonates. Unlike most other oxoanions, phosphonates can be chemically tuned through the modification of the organic residues.¹² Actinide phosphonates have relevance to nuclear waste stewardship and separation processes.¹³ They adopt a wide variety of structures including chains, layers, three-dimensional networks, and nanotubular architectures.¹² By placing a carboxylate-containing moiety in the organic residue, there is the potential for binding to a second metal center to yield heterobimetallic compounds with structures and properties not typically accessible.¹⁴ Herein we disclose the first examples of high-symmetry, porous (cubic and rhombohedral) heterobimetallic uranyl/transition metal carboxyphosphonates.

$[M_2(UO_2)_6(PO_3CH_2CO_2)_3O_3(OH)(H_2O)_2] \cdot 16H_2O$ (M = Mn(II), Co(II), Cd(II)) and $[Cd_3(UO_2)_6(PO_3CH_2CO_2)_6(H_2O)_{13}] \cdot 6H_2O$ can be prepared using common starting materials that are reacted together under mild hydrothermal conditions.† The key step in obtaining crystals of these compounds is the slow hydrolysis of triethyl phosphonoacetate to yield phosphonoacetate.¹⁵ The gradual introduction of this ligand allows for the crystallization of compounds that only form powders if phosphonoacetate is added directly to the reactions.

The structures of the Mn(II), Co(II) and Cd(II) variants of $[M_2(UO_2)_6(PO_3CH_2CO_2)_3O_3(OH)(H_2O)_2] \cdot 16H_2O$ are isotypic and adopt the high-symmetry cubic space group $Im\bar{3}$.§ Previous uranyl carboxyphosphonates have not crystallized in crystal systems with symmetries higher than orthorhombic. The structure is also different from other uranyl carboxyphosphonates in that it incorporates both UO₇ pentagonal bipyramids and UO₈ hexagonal bipyramids. These units assemble to form a nearly planar cluster containing eight uranyl polyhedra shown in the central portion of Fig. 1. Four such clusters are linked by additional 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 required by the cubic symmetry, the top and bottom of the cavities are capped again

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† Electronic supplementary information (ESI) available: For brevity we provide only the synthesis of the Co(II) compound. Replacement of the cobalt acetate with the acetate salts of the other transition metals yields the desired compounds. Both cadmium compounds are isolated from the same reaction. CCDC 794932–794935. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc03507f

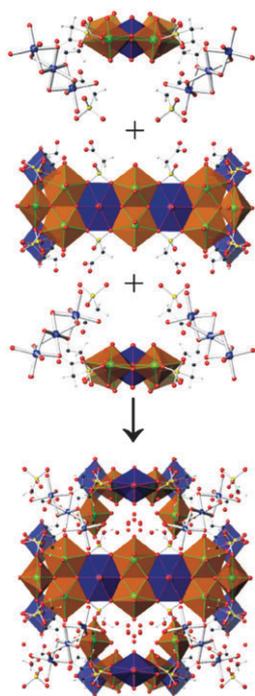


Fig. 1 An illustration of the assembly of the components that form the large cubic cavities in $[M_2(UO_2)_6(PO_3CH_2CO_2)_3O_3(OH)(H_2O)_2] \cdot 16H_2O$ ($M = Mn, Co, Cd$). UO_7 pentagonal bipyramids = brown, UO_8 hexagonal bipyramids = blue, cobalt = blue sphere, oxygen = red, phosphorus = yellow, carbon = black, and hydrogen = white.

by the clusters of UO_7 and UO_8 polyhedra. The subunits are assembled together by a disordered triad of $Co(II)$ cations that are bound by a variety of interactions that include bonds with the uranyl apical oxygen atoms, and bonds with phosphonate oxygen atoms. When assembled together, the subunits form a large cavity approximately 16 Å in diameter that is filled with co-crystallized water molecules. In addition there are channels between the cavities that are filled with the $M(II)$ cations and water molecules.

85% of uranyl compounds contain uranium in the form of a pentagonal bipyramid, and it is not surprising therefore that the family of uranyl carboxyphosphonates have thus far been found to exclusively contain this unit. This may be one of the reasons for the propensity for low-symmetry in this family. $[M_2(UO_2)_6(PO_3CH_2CO_2)_3O_3(OH)(H_2O)_2] \cdot 16H_2O$ ($M = Mn, Co, Cd$) are unusual in this regard in that they contain the much rarer, although certainly well-precedented,¹ UO_8 hexagonal bipyramid. These units create the previously described cluster that repeats itself to create part of the walls of the cavities. These clusters are recognized as portions of the infinite chains found within the sheets of the minerals with the $[(UO_2)_3(SeO_3)_2O_2]^{2-}$ sheet topology.¹ The structure is surprisingly rich in comparison to many of the actinide carboxyphosphonates.^{14,15}

The observation of large cavities filled with water led to the speculation that these might be compounds capable of gas sorption. In fact, the water molecules are easily removed upon heating as evidenced by TGA thermograms that show loss of the cage water molecules up to 230 °C, followed by loss of coordinating water molecules and decomposition. Despite

facile water loss, attempted assessments of nitrogen sorption demonstrated that the compound does not behave as a porous material, at least under cryogenic conditions (77 K). However, like TOF-2, this material does sorb CO_2 , yielding an NLDFT surface area of $40 \text{ m}^2 \text{ g}^{-1}$ ($142 \text{ m}^2 \text{ cm}^{-3}$ of framework) at 273 K. The CO_2 isotherm additionally yields a micropore volume of $122 \text{ cm}^3 \text{ g}^{-1}$ and an apparent average pore diameter of 4.8 angstroms.

The second high-symmetry cadmium compound, $[Cd_3(UO_2)_6(PO_3CH_2CO_2)_6(H_2O)_{13}] \cdot 6H_2O$, crystallizes in the rhombohedral space group, $R\bar{3}$. Similar to the first series of compounds, a high-symmetry three-dimensional network is adopted. Once again a cluster of disordered 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. 2. The $\bar{3}$ 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 with UO_7 pentagonal bipyramids, as occurs in all other examples of uranyl carboxyphosphonates.^{14,15} The structure can be viewed as forming from one-dimensional chains that extend along c that are bridged into hexameric channels by the phosphonates.

Most uranyl compounds fluoresce when irradiated with long-wavelength UV light.¹⁶ In these families of high-symmetry compounds, only the cadmium compounds are luminescent, and these compounds show the typical fluorescence spectrum of uranyl compounds with five vibronic transitions centered near 520 nm albeit the intensity of emission is unusually weak. Both paramagnetic quenching and re-absorption by the d-d transitions of the transition metals (Mn^{2+} and Co^{2+}) could be responsible for weakness or loss of fluorescence.

The synthesis and structural elucidation of $[M_2(UO_2)_6(PO_3CH_2CO_2)_3O_3(OH)(H_2O)_2] \cdot 16H_2O$ ($M = Mn(II), Co(II), Cd(II)$) and $[Cd_3(UO_2)_6(PO_3CH_2CO_2)_6(H_2O)_{13}] \cdot 6H_2O$ demonstrate three key features that have been absent in uranyl carboxyphosphonates. First, high-symmetry

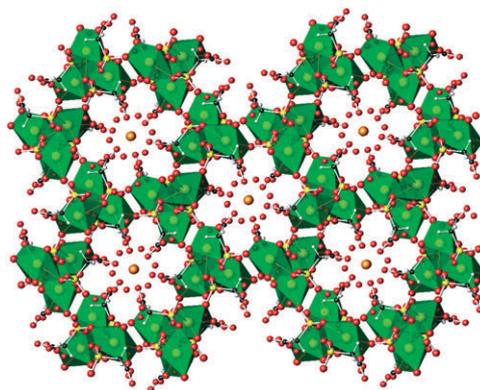


Fig. 2 A view down the c axis of the structure of $[Cd_3(UO_2)_6(PO_3CH_2CO_2)_6(H_2O)_{13}] \cdot 6H_2O$. The flower-shaped channels that extend along this axis are filled with disordered linear clusters of hydrated $Cd(II)$ cations. UO_7 pentagonal bipyramids = green, cadmium = orange, oxygen = red, phosphorus = yellow, carbon = black, and hydrogen = white.

structures can be synthesized. These crystal systems are not common for complex uranyl compounds, and much lower symmetry is typically found.^{1,14,15} The cubic compounds are among the most complex uranyl compounds ever synthesized. Second, structures with large voids can also be achieved leading to truly porous structures capable of differential gas sorption. The addition of the second rhombohedral cadmium compound to the family of uranyl carboxyphosphonates is important because, based in the structure of the cubic compounds, it might be assumed that the hexagonal bipyramids and the formation of condensed uranyl polyhedral features are requirements for high-symmetry. However, this is not the case. The common feature that both high-symmetry structures share is the presence of disordered divalent transition metals. These serve two different roles. In the cubic compounds this unit stitches the uranyl clusters together to create a framework, and in the rhombohedral structure, the network appears to form around these units. They may serve as a template for the structure. Finally, for the first time in the cubic compounds the phosphonate oxygen atoms are being used to bind the transition metals. In all previous carboxyphosphonates the phosphonate only interacts with the actinide centers.

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Notes and references

‡ $\text{Co}_2[(\text{UO}_2)_6(\text{PO}_3\text{CH}_2\text{CO}_2)_3\text{O}_3(\text{OH})(\text{H}_2\text{O})_2] \cdot 16\text{H}_2\text{O}$. UO_3 (286.3 mg, 0.870 mmol), triethyl phosphonoacetic acid (0.120 mL, 0.602 mmol), $\text{Co}(\text{CO}_2\text{CH}_3)_2 \cdot 4\text{H}_2\text{O}$ (249 mg, 1 mmol), and 5 mL of water were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 150 °C in a box furnace for 5 d. The autoclave was then cooled at an average rate of 9 °C h⁻¹ to 35 °C. Large red blocks of the desired compound were isolated. Yield 130 mg (36% based on uranium). Phase purity was confirmed using powder X-ray diffraction.

§ X-Ray structural analysis: $[\text{Co}_2(\text{UO}_2)_6(\text{PO}_3\text{CH}_2\text{CO}_2)_3\text{O}_3(\text{OH})(\text{H}_2\text{O})_2] \cdot 16\text{H}_2\text{O}$, FW: 2538.35, red block, crystal dimensions 0.087 × 0.050 × 0.017 mm, cubic, $I\bar{m}\bar{3}$, $Z = 16$, $a = 26.3861(3)$, $V = 18370.7(4)$ Å³ ($T = 100(2)$ K), $R_{\text{int}} = 0.0485$, $\mu = 220.12$ cm⁻¹, $R_1(\text{obs}) = 0.0188$, $wR_2(\text{all}) = 0.0431$. Bruker APEXII Quazar diffractometer: $\theta_{\text{max}} = 54.96^\circ$, MoK α , $\lambda = 0.71073$ Å, 0.5° ω scans, 110457 reflections measured, 3763 independent reflections all of which were included in the refinement. $[\text{Cd}_3(\text{UO}_2)_6(\text{PO}_3\text{CH}_2\text{CO}_2)_6(\text{H}_2\text{O})_{13}] \cdot 6\text{H}_2\text{O}$, FW: 3121.72, yellow tablet, crystal dimensions 0.102 × 0.081 × 0.062 mm, cubic, $R\bar{3}$,

$Z = 3$, $a = 18.962(2)$, $c = 14.0112(18)$, $V = 4362.7(1)$ Å³ ($T = 100(2)$ K), $R_{\text{int}} = 0.0473$, $\mu = 180.13$ cm⁻¹, $R_1(\text{obs}) = 0.0254$, $wR_2(\text{all}) = 0.0518$. Bruker APEXII Quazar diffractometer: $\theta_{\text{max}} = 55.00^\circ$, MoK α , $\lambda = 0.71073$ Å, 0.5° ω scans, 17130 reflections measured, 2230 independent reflections all of which were included in the refinement. The data were corrected for Lorentz-polarization effects and for absorption, structure was solved by direct methods, anisotropic refinement of F^2 by full-matrix least-squares. Further details of the crystal structure investigation may be obtained from the Cambridge Crystallographic Data Centre on quoting numbers CSD 794932, 794933, 794934, and 794935.

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