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

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Received 26th August 2010, Accepted 13th October 2010
DOI: 10.1039/c0cc03507f

Four heterobimetallic U(vi)/M(ii) (M = Mn, Co, Cd) carboxyphosphonates have been synthesized. M₂[UO₂]₆(PO₃CH₂CO₂)₃O₃(OH)(H₂O)₃·16H₂O (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. [Cd₃(UO₂)₆(PO₃CH₂CO₂)₆(H₂O)₁₃]·6H₂O 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. From these studies, it is recognized that oxoanions like iodate can be used to prepare one-dimensional compounds, whereas the tetraedral anion, selenate, can yield nanotubular structures under appropriate crystallization conditions. 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. Uranyl compounds in general have also yielded some remarkable properties that include ionic conductivity, selective ion-exchange, magnetic ordering, selective oxidation catalysis, non-linear optical properties, mixed-valency, and room-temperature phase transitions. 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.

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. Actinide phosphonates have relevance to nuclear waste stewardship and separation processes. They adopt a wide variety of structures including chains, layers, three-dimensional networks, and nanotubular architectures. 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. Herein we disclose the first examples of high-symmetry, porous (cubic and rhombohedral) heterobimetallic uranyl/transition metal carboxyphosphonates.

[M₂[UO₂]₆(PO₃CH₂CO₂)₃O₃(OH)(H₂O)₃]·16H₂O (M = Mn(ii), Co(ii), Cd(ii)) and [Cd₃[UO₂]₆(PO₃CH₂CO₂)₆(H₂O)₁₃]·6H₂O 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. 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 [M₂[UO₂]₆(PO₃CH₂CO₂)₃O₃(OH)(H₂O)₃]·16H₂O are isostructural and adopt the high-symmetry cubic space group Im3.‡ 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
much rarer, although certainly well-precedented, UO₈
Co, Cd) are unusual in this regard in that they contain the
surprisingly rich in comparison to many of the actinide
found to exclusively contain this unit. This may be one of the
family of uranyl carboxyphosphonates have thus far been
pentagonal bipyramid, and it is not surprising therefore 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.
[UO₂]₆(PO₃CH₂CO₂)₆O₃(OH)(H₂O)₂-16H₂O (M = Mn, Co, Cd) are unusual in this regard in that they contain the
much rarer, although certainly well-precedented, UO₈
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
[UO₂]₆(SeO₃)₂O₂⁻ sheet topology. The structure is
surprisingly rich in comparison to many of the actinide
carboxyphosphonates.

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 CO₂, yielding an NLDFT
surface area of 40 m² g⁻¹ (142 m² cm⁻³ of framework) at
273 K. The CO₂ isotherm additionally yields a micropore
volume of 122 cm³ g⁻¹ and an apparent average pore
diameter of 4.8 angstroms.

The second high-symmetry cadmium compound,
[Cd₃(UO₂)₆(PO₃CH₂CO₂)₆(H₂O)₁₁]6H₂O, crystallizes in the
rhombohedral space group, R3. 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 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
UO₇ pentagonal bipyramids, as occurs in all other examples of
uranyl carboxyphosphonates. The structure can be viewed
as forming from one-dimensional chains that extend along c
that are bridged into hexameric channels by the carboxylates.

Most uranyl compounds fluoresce when irradiated with
long-wavelength UV light. 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 (Mn²⁺ and Co²⁺) could be responsible for weakness
or loss of fluorescence.

The synthesis and structural elucidation of
[M₂(UO₂)₆(PO₃CH₂CO₂)₆O₃(OH)(H₂O)]₂-16H₂O (M = Mn(ii), Co(ii), Cd(ii)) and [Cd₃(UO₂)₆(PO₃CH₂CO₂)₆
(H₂O)₁₁]6H₂O demonstrate three key features that have been
absent in uranyl carboxyphosphonates. First, high-symmetry

![Fig. 1](image1.png)

**Fig. 1** An illustration of the assembly of the components that form
the large cubic cavities in [M₂(UO₂)₆(PO₃CH₂CO₂)₆O₃(OH)(H₂O)]-16H₂O (M = Mn, Co, Cd). UO₇ pentagonal bipyramids = brown, UO₈ hexagonal bipyramids = blue, cobalt = blue sphere, oxygen = red, phosphorus = yellow, carbon = black, and hydrogen = white.

![Fig. 2](image2.png)

**Fig. 2** A view down the c axis of the structure of
[Cd₃(UO₂)₆(PO₃CH₂CO₂)₆(H₂O)₁₁]6H₂O. The flower-shaped channels
that extend along this axis are filled with disordered linear clusters
of hydrated Cd(ii) cations. UO₇ 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.\textsuperscript{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 bipyramidal 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.

We are grateful for support provided by the Heavy Elements Program, U.S., Department of Energy under Grant DE-FG02-01ER16026, as well as DOE’s Separations Program (Grant DE-FG02-08165876) and by Deutsche Forschungsgemeinschaft within the DE 412/43-1 research project. This material is based upon work supported as part of the Materials Science of Actinides, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001089. J. T. H. also acknowledges AFOSR for support of this work.

Notes and references

\[ \text{Cu}_2[UO}_2\text{O}_4\text{(PO}_4\text{CH}_3\text{CO}_2\text{O}_3\text{OH(H}_2\text{O})_6\text{H}_2\text{O)}_6\text{H}_2\text{O} = 286.3 \text{ mg, 0.870 mmol), triethyl phosphonoacetic acid (0.120 mL, 0.602 mmol), } \]
\[ \text{CoC}_2\text{H}_3\text{O}_2\text{H}_2\text{O, FW: 2538.35, red block, crystal dimensions 0.087 mm, cubic, } \]
\[ \text{Z} = 3, a = 18.962(2), c = 14.0112(18), V = 4362.7(1) \text{ Å}^3 (T = 100 (2) K), R_{\text{int}} = 0.0473, \mu = 180.13 \text{ cm}^{-1}, R_{\text{obs}} = 0.0254, wR_{\text{all}} = 0.0518. \]
\[ \text{Bruker APEXII Quazar diffractometer; } \theta_{\text{max}} = 55.00^\circ, \text{ MoKz, } \lambda = 0.71073 \text{ Å, } 0.5^\circ \omega \text{ scans, 110457 reflections measured, 2230 independent reflections all of which were included in the refinement. The data were corrected for Lorentz-polarization effects and for absorption, structure was solved by direct methods, anisotropic refinement of } ^{F} \text{ by full-matrix least-squares. Further details of the crystal structure investigation may be obtained from the Cambridge Crystallographic Data Centre on quoting numbers CSD 794931, 794933, 794934, and 794935. } \]