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. M2[UO2]6(PO3CH2CO2)3O3(OH)(H2O)2•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 UO2+ 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 extended structures.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.

[M2(UO2)6(PO3CH2CO2)3O3(OH)(H2O)2•16H2O (M = Mn(ii), Co(ii), and 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.1 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 [M2(UO2)6(PO3CH2CO2)3O3(OH)(H2O)2•16H2O are isotypic 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

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much rarer, although certainly well-precedented. UO\(_8\) hexagonal bipyramids (M = Mn, Co, Cd) are unusual in this regard in that they contain the carboxyphosphonates. Surprisingly rich in comparison to many of the actinide carboxyphosphonates, 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. 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 m\(^2\) g\(^{-1}\) (142 m\(^2\) cm\(^{-3}\) of framework) at 273 K. The CO\(_2\) isotherm additionally yields a micropore volume of 122 cm\(^3\) g\(^{-1}\) and an apparent average pore diameter of 4.8 angstroms.

The second high-symmetry cadmium compound, [Cd\(_3\)(UO\(_2\))\(_6\)(PO\(_3\)CH\(_2\)CO\(_2\))\(_6\)(H\(_2\)O)\(_{13}\)] 6H\(_2\)O, 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\(^{\text{rd}}\) 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. 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. 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\(_3\)CH\(_2\)CO\(_2\))\(_3\)(OH)(H\(_2\)O)\(_2\)] 16H\(_2\)O (M = Mn, Co, Cd) and [Cd\(_3\)(UO\(_2\))\(_6\)(PO\(_3\)CH\(_2\)CO\(_2\))\(_6\) (H\(_2\)O)\(_{13}\)] 6H\(_2\)O demonstrate three key features that have been absent in uranyl carboxyphosphonates. First, high-symmetry...
structures can be synthesized. These crystal systems are not common for complex uranyl compounds, and much lower symmetry is typically found.\textsuperscript{1,4,15} 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 phosphate oxygen atoms are being used to bind the transition metals. In all previous carboxyphosphonates the phosphate only interacts with the actinide centers.

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Notes and references
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\item \textsuperscript{1}P. C. Burns, \textit{Can. Mineral.}, 2005, \textbf{43}, 1839.
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