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Uranyl Heteropolyoxometalate: Synthesis, Structure, and Spectroscopic Properties

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Ⓢ *Supporting Information*

ABSTRACT: A novel uranium heteropolyoxometalate, $[H_3O]_4[Ni(H_2O)_3]_4\{Ni[(UO_2)(PO_3C_6H_4CO_2)]_3(PO_4H)\}_4 \cdot 2.72H_2O$, has been prepared under mild hydrothermal conditions using the diethyl(2-ethoxycarbonylphenyl)phosphonate ligand and *in situ* ligand synthesis of the HPO_4^{2-} anion. The cluster is derived from a common UO_7, pentagonal bipyramid and is constructed by employing nickel(II) metal ions as linkers. The 3d−5f heteropolyoxometalate core incorporates 12 classical pentagonal uranyl groups and four Ni^{2+} octahedral units.

Polyoxometalate clusters have been the subject of intense inquiry for decades owing to their unique structures and versatile properties that give rise to applications in a variety of areas ranging from water oxidation[1] to antiviral activity.[2] While these clusters are well-known from the d block, only recently have polyoxometalate clusters been extensively developed for actinides.[3] While it is unlikely that these clusters will have the same applications as those with transition metals owing to their radioactivity, uranyl peroxide clusters hold promise for applications in mass-based separations of used nuclear fuel, and large clusters of plutonium (e.g., plutonium colloids) may be important in the transport of plutonium in the environment.[3a,4] Mixed 5f− and 4f−3d clusters are also of interest owing to the possibility of the magnetic coupling between the metal centers that may lead to the development of single molecule magnets.[5a,b] The incorporation of uranium atoms in heteropolytungstates has been investigated for use in sequestration and storage of actinide waste.[5c−e]

It has recently been shown that uranyl peroxide cluster chemistry can be expanded substantially through the incorporation of different anions such as oxalate,[6] phosphate,[7] and phosphonates.[8] We recently demonstrated that diphosphonates can be used to assemble hexanuclear clusters with thorium and plutonium, and many other uranium/thorium-based clusters with hexanuclear structures have been reported.[9] Herein, we demonstrate that a heteropolyoxometalate cluster can be assembled with uranyl, UO_2^{2+}, and a first-row transition metal using a 1,2-carboxyphenylphosphonate to assemble the cluster. This cluster is formulated as $[H_3O]_4[Ni(H_2O)_3]_4\{Ni[(UO_2)(PO_3C_6H_4CO_2)]_3(PO_4H)\}_4 \cdot 2.72H_2O$ (NiUcppe) and is easily synthesized from common starting materials using traditional hydrothermal methods.[10]

This compound crystallizes in the cubic space group $F\bar{4}3c$.[11] The cluster possesses T symmetry and consists of a core of 12 uranyl pentagonal bipyramids and four nickel(II) octahedra with four additional nickel(II) octahedra decorating the exterior of the cluster, as shown in Figure 1. The T symmetry group is the pure rotation subgroup of the T_d group, and the topology of this polyoxometalate cluster is similar to the T_d class of classical $M_{12}O_{40}$ polyoxometalates.[12] The ligand that bridges between the metal centers and terminates the surface of the cluster is 1,2-carboxyphenylphosphonate. Each of the UO_7 polyhedra shares an edge to form dimers that are connected via the PO_3 moiety. The nickel(II) metal ion octahedra are positioned at the four corners of a tetrahedron linking the uranyl dimers to form the $\{(UO_2)_{12}Ni_4\}$ core. The cluster is approximately 1.2 nm in diameter from the oxygen atoms of the uranyl centers and 1.4 nm from the diagonal of the oxygen atoms of the Ni^{2+} ion centers on the periphery. While one of the carboxylate oxygen atoms of the same ligand coordinates to the four nickel(II) metal ions in the 5f−3d polyoxo core; the second oxygen atom of the carboxylate moiety coordinates to the other four Ni^{2+} ion centers that are on the exterior of the cluster. The carboxylate moiety exclusively binds the softer metal cations, while the phosphonate moiety preferentially binds the uranyl centers. This trend is similar to what we have reported.[13a,b] This cluster is quite distinct from the uranyl peroxide clusters reported by Burns and co-workers, which are typically constructed from only uranyl peroxide hexagonal bipyramids, except for in a recently reported work where one of the fragments consists of two uranyl peroxide pentagonal bipyramids.[7a] This structure to our knowledge contrasts dramatically from the most common U_6O_8 topology of uranium clusters that are known, with the exceptions being discrete decanuclear oxo/hydroxo clusters, a dodecanuclear oxide cluster, and 16 uranium atoms consisting of fused octahedra, $[U_{16}O_{22}(OH)_2]$ cores.[9h,i]

Owing to the high symmetry, the cluster only contains one crystallographically unique uranium center that is coordinated by two nearly linear oxo atoms, forming a UO_2^{2+} unit, and the O═U═O bond angle is 178.1(3)° with normal U═O bond distances of 1.778(6) Å and 1.757(6) Å. Five oxygen atoms are coordinated to the uranyl center in the equatorial plane leading to U−O bonds that range from 2.306(7) to 2.544(6) Å; the longest bond corresponds to μ_2-O bridging atoms of the

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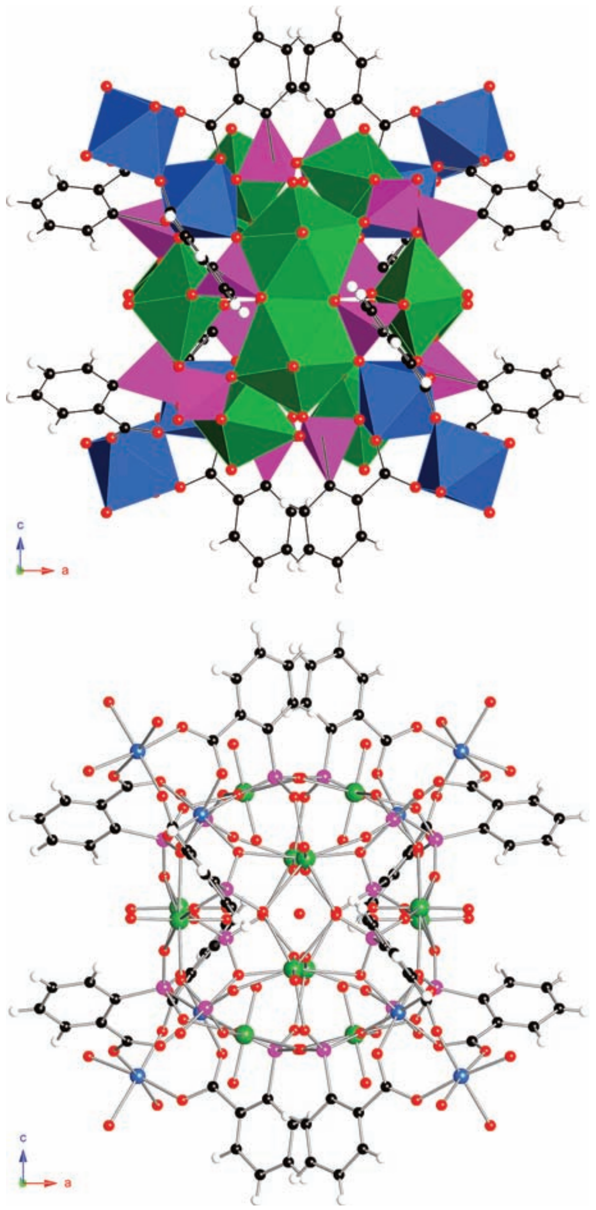

Figure 1. Both polyhedral and ball-and-stick representations of $[H_3O]_4[Ni(H_2O)_3]_4\{Ni[(UO_2)(PO_3C_6H_4CO_2)]_3(PO_4H)\}_4{\cdot}2.72H_2O$. UO_7, pentagonal bipyramids = green, Ni^{2+} = blue, phosphorus = magenta, oxygen = red, carbon = black, and hydrogen = white.

dimers. The calculated bond-valence sum of the uranium center is 6.03 and is in agreement with U(VI).[14]

The P(1)−O bond distances from the 2-carboxyphenylphosphonate ligand ranging from 1.544(7) Å to 1.568(6) Å correspond to μ_2-O bridging atoms and are longer than the terminal P(1)−O(5) of 1.518(6) Å. A single phosphate anion connects three uranyl dimers and is generated *in situ* via decomposition of some of the ligand. The P(2)−O bond distances from the phosphate moiety range from 1.487(7) Å to 1.607(18) Å. It is unlikely that this phosphate ion exists as PO_4^{3-} because only three of the P−O bonds are equidistant and $(HPO_4)^{2-}$ is essential to balancing the charge. There are two crystallographically distinct nickel(II) metal ion centers in this structure. Ni(1) forms six bonds with carboxylate and phosphonate oxygen atoms, and the Ni−O bond distance average is 2.046(6) Å. Ni(2) is coordinated by six oxygen atoms that range from 2.054(8) to 2.160(10) Å. Three equidistant oxygen atoms are from carboxylate moiety, and the remaining three are from water molecules. The packing diagram shows voids that are filled with disordered water and hydronium ions. These nickel metal ions have bond valences and absorption spectra that are consistent with divalent oxidation states, as shown in the Supporting Information.

The absorbance spectra for this uranyl heteropolyoxometalate and $UO_2(NO_3)_2{\cdot}6H_2O$ were collected (see Supporting Information). The characteristic equatorial U−O charge transfer band and axial U=O charge transfer band (vibronic coupling) were observed around 325 and 423 nm, respectively, which correspond to the $UO_2(NO_3)_2{\cdot}6H_2O$ spectrum.[13a] An additional absorbance peak was also observed around 753, which corresponds to the d−d transition of the Ni^{2+} metal ion. Although there is no clear difference in the position of the observed peaks relative to absorption spectra of two copper(II) complexes we reported before, the vibronic coupling of the CT bands is clearly observed here.[13b]

The fluorescence spectra for this compound and $UO_2(NO_3)_2{\cdot}6H_2O$ were also collected under the same experimental conditions and procedures and are shown in the Supporting Information. It has been demonstrated that the incorporation of Cu(II) metal ions resulted in the quenching of emission from uranyl complexes because of the overlap of emission from uranyl cations and the d−d absorption band of copper(II) ions, yielding energy transfer and nonradiative decay.[13d−f] Interestingly, we have also documented luminescence properties in $[Cu(H_2O)]_2Cu(H_2O)_2[(UO_2)(PO_3C_6H_4CO_2H)(PO_3C_6H_4CO_2)]_2$ complexes, and the mechanisms of the emission from uranyl compounds are most often difficult to explain.[13b,g] The luminescence spectrum of NiUcppe differs from that of the benchmark compound $(UO_2(NO_3)_2{\cdot}6H_2O)$. Five prominent peaks are clearly resolved for NiUcppe at about 488, 514, 543, 584, and 611 nm; these correspond to electronic and vibronic transitions $S_{11}-S_{00}$ and $S_{10}-S_{0\nu}$ (ν = 0−4). The most intense peak is positioned at 543 nm. The luminescent spectrum for the benchmark compound showed well-resolved sharp vibronic peaks at 487, 509, 532, 558, 586, and 612, and the most intense peak ($S_{10}-S_{00}$) is positioned at 509 nm. This uranyl heteropolyoxometalate exhibits a slight red shift of 35 nm compared to the benchmark compound. The slight difference observed in this compound and the benchmark may be attributed to the coordination environment around the uranium center, ligand field effects, and incorporated transition metals. The fluorescence spectra also differ from those reported for the uranyl carboxyphenylphosphonate compound, $UO_2(PO_3HC_6H_4CO_2H)_2{\cdot}2H_2O$.[13b] This nickel-containing uranyl polyoxometalate displayed a slight red shift of 15 nm compared to $UO_2(PO_3HC_6H_4CO_2H)_2{\cdot}2H_2O$. The fluorescence spectra observed here are similar to those reported for Cs^+/Ba^{2+} and $[Cu(H_2O)]_2Cu(H_2O)_2[(UO_2)(PO_3C_6H_4CO_2H)(PO_3C_6H_4CO_2)]_2$.[13a−c]

In the low wavenumber regions of the IR spectra the 664.9 cm^{-1} peak is indicative of O−P−O bending, and the 704.5 and 736.1 cm^{-1} peaks are dominated by phenyl ring and P−C stretching vibrations. The symmetric stretching mode of the uranyl cation, the UO_2^{2+} unit, is observed at 833 cm^{-1}, while the antisymmetric stretching modes are observed at 932.8 and 969.7 cm^{-1}. The two peaks at 1079 and 1144 cm^{-1} are at expected values for P−O and P=O symmetric and antisymmetric stretching modes of phosphonates. The band at 1385 cm^{-1} is characteristic of the O−C−O symmetric stretching of the carboxylate groups. The small peak at 1485 cm^{-1} is due to a phenyl ring stretching vibration. The peaks from 1538 to 1588 cm^{-1} are associated with the O−C−O antisymmetric stretching vibrations. The broad bands around 3080 cm^{-1} are associated with the overlap of O−H stretching of P−OH and free water/hydronium molecules.[15]

In conclusion, the assembly of the heteropolyoxometalate cage cluster described herein demonstrates that uranium polyoxometalates are not limited to U_6O_8 topology and that a mild hydrothermal *in situ* ligand synthetic approach can be used in the discovery of 5f−3d clusters that can be developed into a larger family of uranyl-based polyoxometalates in the future.[15a] We also demonstrate the importance of using an ortho-substituted phenylphosphonate ligand in stabilizing a high nuclearity uranyl polyoxometalate cage cluster.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files in CIF format for $[H_3O]_4[Ni(H_2O)_3]_4\{Ni[(UO_2)(PO_3C_6H_4CO_2)]_3(PO_4H)\}_4 \cdot 2.72H_2O$ (NiUcppe). Absorption, fluorescence, and infrared spectroscopic data are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(10) Synthesis: $UO_2(NO_3)_2 \cdot 6H_2O$ (50.1 mg, 0.1 mmol), $Ni(CH_3COO)_2 \cdot 4H_2O$ (25.6 mg, 0.1 mmol), diethyl(2-ethoxycarbonylphenyl)phosphonate (28.6 mg, 0.1 mmol), 0.5 mL of Millipore filtered water, and HF (∼10 μL, 0.006 mmol) were loaded into a PTFE-lined Parr 4749 autoclave with a 23 mL internal volume. The autoclave was sealed and heated to 160 °C in a box furnace for 1 h and was then cooled at an average rate of 0.5 °C/h to 25 °C. The resulting yellowish-green product was washed with distilled water and methanol and allowed to air-dry at room temperature. Green tablets of NiUcppe suitable for X-ray diffraction studies were isolated along with mixture of powders suspected to be decomposition products of the ligand. The uranyl polyoxometalate formed about 30% of the reaction products. The slow cooling of the reactions is highly critical to prevent the reactants from solidifying into glasses.

(11) X-ray structural analysis: $[H_3O]_4[Ni(H_2O)_3]_4\{Ni[(UO_2)(PO_3C_6H_4CO_2)]_3(PO_4H)\}_4 \cdot 2.72H_2O$: green tablet, crystal dimensions 0.12 × 0.08 × 0.06 mm, cubic, $F\bar{4}3c$ (No. 219), $Z = 8$, $a = 36.380(3)$ Å, $V = 48149(6)$ $Å^3$ ($T = 100$ K), $\mu = 88.3$ cm^{-1}, $R_1 = 0.034$, $wR_2 = 0.097$. Bruker APEXII Quazar CCD X-ray diffractometer: $\theta_{max} = 27.4°$, Mo Kα, $\lambda = 0.71073$ Å, 0.5° ω scans, 96 952 reflections measured, 4603 independent reflections, all of which were included in the refinement. The data was corrected for Lorentz-polarization effects and for absorption. The structure was solved by direct methods, anisotropic refinement of F^2 by full-matrix least-squares, 187 parameters. The final refinements included anisotropic displacement parameters for all atoms except H atoms. Selected bond distances and angles are listed in Table S1.

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