Th($As^{III}_4As^V_4O_{18}$): a Mixed-Valent Oxoarsenic(III)/arsenic(V) Actinide Compound Obtained under Extreme Conditions

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S *Supporting Information*

ABSTRACT: A high-temperature/high-pressure method was employed to investigate phase formation in the Th($NO_3)_4 \cdot 5H_2O$−As_2O_3−$CsNO_3$ system. It was observed that an excess of arsenic(III) in starting system leads to the formation of Th($As^{III}_4As^V_4O_{18}$), which is representative of a rare class of mixed-valent arsenic(III)/arsenic(V) compounds. This compound was studied with X-ray diffraction, energy-dispersive X-ray, and Raman spectroscopy methods. Crystallographic data show that Th($As^{III}_4As^V_4O_{18}$) is built from ($As^{III}_4As^V_4O_{18})^{4-}$ layers connected through Th atoms. The arsenic layers are found to be isoreticular to those in previously reported As_2O_3 and $As_3O_5(OH)$, and the geometric differences between them are discussed. Bands in the Raman spectrum are assigned with respect to the presence of AsO_3 and AsO_4 groups.

Figure 1. View of the crystal structure of Th($As^{III}_4As^V_4O_{18}$). ThO_8, AsO_4, and AsO_3 coordination polyhedra are yellow, green, and magenta, respectively, and O atoms are red. The $[As^{III}_4As^V_4O_{18}]^{4-}$ layer is marked with blue.

Interest in actinide chemistry has substantially expanded, especially in the last 20 years, because of its central roles in nuclear energy and nuclear waste management and, of equal importance, because the 5f series represents an area of the periodic table where many questions remain unanswered. To date, many investigations have been devoted to understanding the behavior of thorium and uranium phosphate/arsenate compounds because both of these elements have extremely long half-lives[1] and are present in far greater quantities than the heavier members of the actinide series. It led, for example, to the investigation of thorium phosphate diphosphate, which was shown to be suitable for actinide immobilization.[2−4] In addition, the compositional and structural diversity in this family is unparalled.[5−10]

There are few examples of mixed-valent phosphorus(III)/phosphorus(V) actinide compounds.[11,12] Although the phosphate compounds are generally better studied than the arsenate analogues, examples of mixed-valent arsenic(III)/arsenic(V) minerals, such as dixenite $Cu^IMn_{14}^{II}Fe^{III}(OH)_6(As^{III}O_3)_5$-$(Si^{IV}O_4)_2(As^VO_4)$,[13] hematolite $Mn_{10.39}Mg_{2.53}Al_{1.89}Fe_{0.19}$-$(OH)_{23}(AsO_3)(AsO_4)_2$,[14] and synadelphite $Mn_9(OH)_9(AsO_3)$-$(AsO_4)_2(H_2O)_2$[15] have been reported. Synthetic mixed-valent arsenic(III)/arsenic(V) compounds are also known,[16−18] although the data are still very limited, and no examples exist from the actinide series.
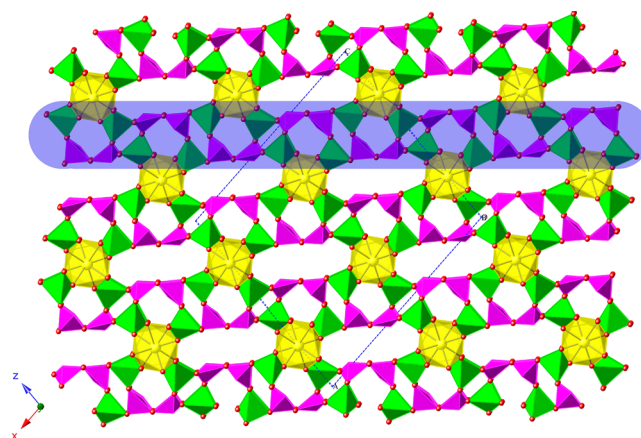
In this report, we applied high-temperature/high-pressure conditions to obtain the first example of a mixed-valent thorium arsenite/arsenate. The initial finely grounded mixture of Th($NO_3)_4 \cdot 5H_2O$, As_2O_3, and $CsNO_3$ in a ratio of 1:8:2 was sealed in a platinum capsule and placed in a high-pressure assembly, which was inserted in a piston cylinder apparatus. The whole synthesis procedure was performed at a pressure of 3 GPa. The capsule with the reaction mixture was heated to 1200 °C with a heating rate of 100 °C/min and then slowly cooled to room temperature with a cooling rate of 0.234 °C/min (a detailed description of the experiment is given in the Supporting Information, SI). The capsule was then broken, and colorless crystals of Th($As^{III}_4As^V_4O_{18}$) were isolated along with the amorphous phase and crystalline $CsAs_3O_8$.[19,20] Although analytical-grade As_2O_3 was used as an initial reagent, the resulting compound contains arsenic in both 3+ and 5+ oxidation states because of the presence of air and nitrate anions in the initial powdered mixture and in situ oxidation of As^{III} to As^V. Because no cesium is observed in the resulting compound, the role of
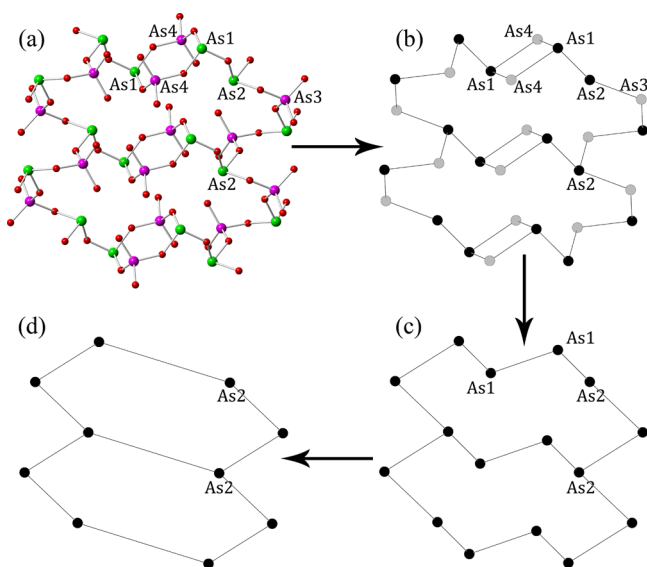
Figure 2. Simplification procedure applied to the $(As^{III}_4As^V_4O_{18})^{4-}$ layers. O, As^{III}, and As^V atoms are red, green, and magenta, respectively. In the graph representation, As^{III} and As^V nodes are black and gray, respectively.

cesium nitrate in the reaction mixture is to partially oxidize As_2O_3. This is accompanied by the fact that we have not observed any crystalline arsenic(III) compound after the reaction of the same reagents in a 1:3:2 ratio under similar conditions. Therefore, there should be a minimum amount of arsenic(III) with respect to the other reagents that provides formation of a mixed-valent arsenic(III)/arsenic(V) compound.

The crystal structure of $Th(As^{III}_4As^V_4O_{18})$ is based on a framework consisting of As^{III}/As^V layers and Th^{IV} centers (Figure 1). Each Th atom lies on a 2-fold rotational axis and is connected to eight O atoms of eight different AsO_4 tetrahedra to form a coordination polyhedron in the shape of a slightly distorted square antiprism. The Th−O bond distances are normal and range from 2.3688(18) to 2.4724(18) Å.[21]

There are four crystallographic As sites. The As1 and As2 positions are occupied by trivalent As ions, while As^V ions occupy the As3 and As4 atomic sites. The As3−O and As4−O bond distances are in the ranges 1.6504(18)−1.6624(18) and 1.7119(19)−1.7236(18) Å for terminal and bridging O atoms, respectively, and agree well with the previously reported values.[22] The O−As^V−O angles in AsO_4 tetrahedra vary from 102.96(10) to 118.35(9)°. As^{III} atoms form AsO_3 trigonal pyramids with As^{III}−O bond lengths in the range of 1.8068(19)−1.8218(19) Å for the O atoms bridging between As^{III} and As^V and at 1.7657(18) and 1.776(2) Å for those bridging between two As^{III} sites. The As^{III}−O bonds are influenced by the lone electron pairs of As^{III} atoms, and this is reflected in the strong deviation of the O−As^{III}−O angles, which lies in the range of 89.51(9)−98.32(9)°, from the tetrahedral arsenic(V) environments. To estimate the lone-pair effect, the D_A values of the As^{III} atomic Voronoi−Dirichlet polyhedra (VDP)[23] were calculated. This value reflects the shift of an atom in a crystal structure from the center of its VDP. The values of calculated D_A are 0.583, 0.556, 0.023, and 0.046 Å for As1−As4, respectively, and agree well with the previously reported average values of 0.63(7) and 0.05(3) Å for $As^{III}O_3$ and As^VO_4 VDPs,[24] respectively.

Both As^{III} and As^V atoms form layers that are connected to Th sites by terminal O atoms of AsO_4 groups. To reveal the topology of the layer (i.e., in the crystal structure considered without Th−O bonds), we applied a standard simplification procedure using the *ADS* program of the *TOPOS* software package.[25,26] The procedure applied to the $[As^{III}_4As^V_4O_{18}]^{4-}$ layer is shown in detail in Figure 2. The first step is the building of a cation topology graph and removal of the anions, i.e., O atoms (Figure 2a,b). This graph consists of vertices (nodes) and edges that correspond to the cationic groups and the connectivity between them, respectively (Figure 2b). The second step is the removal of bridging nodes (i.e., 2-coordinated), saving their connectivity (Figure 2b,c). At this step, one can see that, because of removal of the As4 nodes, the As1 nodes also become bridging and are to be simplified (Figure 2c). The resulting underlying net of the layer is built only of single As2 nodes and classified as the honeycomb
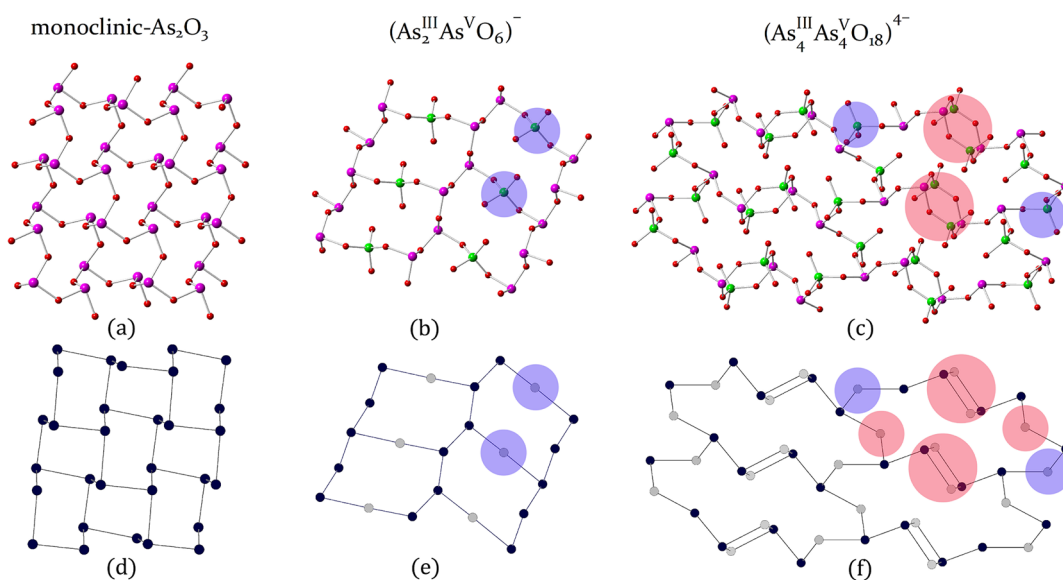

Figure 3. Arsenic layers (a−c) and their graph representations (d−f) in the crystal structures of monoclinic As_2O_3, $As^{III}_2As^VO_5(OH)$, and $Th(As^{III}_4As^V_4O_{18})$. The color scheme is the same as that in Figure 2. Blue and red transparent circles mark nodes and corresponding AsO_4 tetrahedra and $As^{III}_2As^V_2O_9$ ring fragments that are implemented in the edges of the initial As_2O_3 layer on each step in the d−e−f series.

(hcb) topological type (Figure 2d). Nevertheless, an underlying net of the whole crystal structure with the Th−O bonds taken into account is significantly more complicated (Figure 2b). To build this net, two-thirds of the edges of the initial hcb net should be complemented with 4-coordinated As3 nodes and the others with a $(As1As4)_2$ ring fragment. In this fragment, 3-coordinated As1 nodes form edges only with other As nodes, while 4-coordinated As4 nodes share edges with two As and two Th nodes. It is interesting to note that such a step-by-step complementation could be seen in the crystal structures of a [monoclinic As_2O_3]−[$As^{III}_2As^VO_5(OH)$]−[$Th(As^{III}_4As^V_4O_{18})$] series (Figure 3). The structure of monoclinic As_2O_3[27] is based on the layers with hcb underlying net, where the nodes correspond to As atoms. The same topological type is observed in the case of $As^{III}_2As^VO_5(OH)$, although additional AsO_4 tetrahedra are complemented in one-third of the hcb net edges (Figure 3b,e, marked with blue). Finally, the four-membered rings of As nodes as well as AsO_4 tetrahedra are complemented in a 1:1 ratio to the rest of the edges to build a layer observed in $Th(As^{III}_4As^V_4O_{18})$ (Figure 3c,f, marked with red).

The Raman spectrum (Figure 2S in the SI) was collected from a single crystal of $Th(As^{III}_4As^V_4O_{18})$. The band assignment shows the presence of three groups of bands in the spectrum: low frequency ($100-300$ cm^{-1}), medium frequency ($300-600$ cm^{-1}), and high frequency ($700-950$ cm^{-1}). Peaks of these groups were assigned as the crystal lattice, bending, and stretching vibrations for the low-, medium-, and high-frequency regions, respectively (Table 2S in the SI).

In conclusion, investigation of the interaction of thorium nitrate in a As_2O_3 flux demonstrates the possibility of stabilization of the mixed-valent arsenic(III)/arsenic(V) thorium phase with a complex 3D structure. Detailed topological analysis demonstrates that the chemical evolution from purely arsenic-(III)-based 2D phases to mixed arsenic(III)/arsenic(V) compounds is followed by the complication of the layered structure without topological changes of their underlying nets.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, experimental procedures, a Raman spectrum, band assignments, and energy-dispersive X-ray data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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