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Cerium(IV) Tellurite Halides $[Ce_2Te_7O_{17}]X_2$ ($X = Cl^-$ or Br^-): The First Cerium-Containing Cationic Frameworks

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Ⓢ *Supporting Information*

ABSTRACT: Two isotypic cerium tellurite halides with the formulas $[Ce_2Te_7O_{17}]Cl_2$ and $[Ce_2Te_7O_{17}]Br_2$ have been synthesized hydrothermally via the reactions of $CeCl_3$ and $CeBr_3$ with TeO_2. The structures of these compounds feature a cationic inorganic framework. The Ce^{IV} dimers are bound by a novel 3D $Te_7O_{17}{}^{6-}$ building unit, forming an unusual hexagonal-bipyramidal environment around Ce^{IV}.

Materials with extended structures are typically anionic in nature, and the charge is balanced by cations that fill the voids, leading to an overall neutral charge.[1] Only a handful of cationic inorganic materials exist where the charge is balanced by unbound anions.[2] Cationic inorganic frameworks with anion-exchange capabilities are much rarer. Owing to their stability under environmentally relevant conditions and the potential for trapping anions of concern, great effort has been placed on investigating inorganic cationic framework materials.[3] Our research efforts have successfully given rise to NDTB-1, an inorganic supertetrahedral cationic framework that selectively removes TcO_4^- from nuclear waste streams despite the presence of large excesses of competing anions such as Cl^-, NO_3^-, and NO_2^-.[4]

We have recently undertaken a study of the solid-state chemistry of lanthanides and actinides using different ligands, such as borate,[5] phosphite,[6] phosphate,[7] and tellurite. The reason tellurite is chosen as the ligand in this study is that the presence of stereochemically active lone-pair electrons on the Te^{IV} centers and the large variability in the coordination environments of the tellurite anion play important roles in the crystalline architecture of this family of compounds. Tellurite anions can be further interconnected to form dimers, trimers, and polymeric structures, which enable a variety of unusual structures to form.[8] For example, novel infinite tellurite tubes with lone-pair self-containment have been hydrothermally synthesized.[8d] Unusual uranyl tellurites containing $[Te_2O_6]^{4-}$ ions and 3D networks have been observed.[8c] A series of transition-metal tellurites with second-harmonic-generation, magnetic, and luminescent properties have been discovered.[9]

Herein, we report the preparation and structure elucidation of two new cerium tellurites with cationic inorganic frameworks, $[Ce_2Te_7O_{17}]Cl_2$ and $[Ce_2Te_7O_{17}]Br_2$, which are prepared hydrothermally via reactions of $CeCl_3$ and $CeBr_3$ with TeO_2.[10] The detailed structures were established by X-ray crystallographic analysis (cf. the Supporting Information).[11] Both compounds contain tetravalent cerium. The redox potential for Ce^{IV}/Ce^{III} is 1.28 V/NHE in 1 M HCl, and Ce^{III} is the preferred valence state under acid conditions.[12] However, different pH conditions and a possible solubility-driven mechanism suggest that Ce^{III} can be oxidized to Ce^{IV} under hydrothermal conditions, forming Ce^{IV} compounds. This solubility-driven mechanism has been proposed in our previous studies.[13]

$[Ce_2Te_7O_{17}]Cl_2$ and $[Ce_2Te_7O_{17}]Br_2$ are isotypic with cationic frameworks, where the Ce centers are chelated by $Te_7O_{17}{}^{6-}$ polynuclear clusters. The key features of $[Ce_2Te_7O_{17}]Cl_2$ and $[Ce_2Te_7O_{17}]Br_2$ are the channels that extend down the *b* axis. A view of the structure is shown in Figure 1. Ce atoms and $Te_7O_{17}{}^{6-}$ units do not fill all of the space in the crystals, and as a result of this architecture, large free voids in the structure are observed. The result of such a combination is a 3D cationic framework with a system of channels. These channels have dimensions of 10.644 Å × 5.050 Å for $[Ce_2Te_7O_{17}]Cl_2$ and 10.665 Å × 5.212 Å for $[Ce_2Te_7O_{17}]Br_2$. Paired Cl^-/Br^- anions reside in the channels,

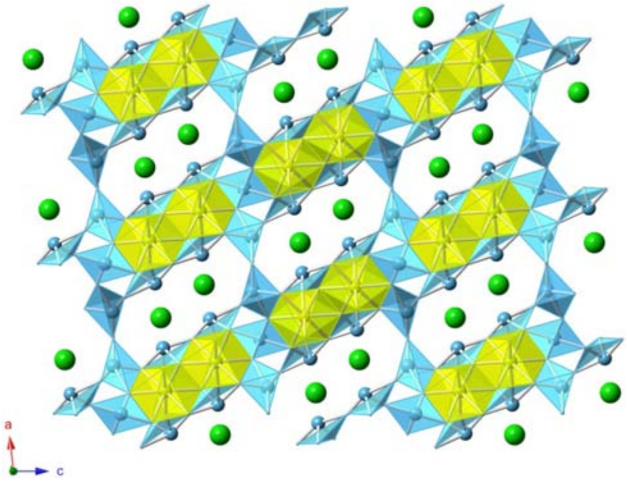

Figure 1. View of $[Ce_2Te_7O_{17}]X_2$ ($X = Cl^-$ or Br^-) showing the cationic framework extending down the *b* axis and the channels filled with halide anions. Cerium polyhedra are shown in yellow, TeO_4 polyhedra in blue, and halide anions in green.

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forming a highly ordered entity, and they do not covalently bond to any framework atoms. It is important to note that the interactions between Cl^-/Br^- anions do not result in a perturbation of the topology of the cationic framework. The cationic framework of these materials suggested the possibility for anion-exchange behavior. Anion exchange of $[Ce_2Te_7O_{17}]Cl_2$ and $[Ce_2Te_7O_{17}]Br_2$ crystals was conducted with common anions (F^-, Cl^-, Br^-, I^-, SO_4^{2-}, NO_3^-, and MnO_4^-) and measured by energy-dispersive X-ray spectroscopy. Unfortunately, the halides do not exchange with other anions. The nonbonded electron pairs on Te^{4+} point into the channels, forming electrostatic interactions with the halides. Te atoms retain their valence-shell electrons via the inert pair effect and effectively block halide mobility. Thus, the halides are locked within the channels, which is likely the reason these two compounds do not have anion-exchange abilities. This locking effect has been observed in a 3D mixed-metal oxychloride, $Te_4M_3O_{15}\cdot Cl$.[2c]

Another interesting feature of these cerium tellurite halide compounds is the coordination environment of the Ce center. Ce^{IV} is typically eight- or nine-coordinate when bound by oxygen, yielding different coordination geometries based on square antiprisms,[13a] trigonal dodecahedra,[13b,c,14] distorted dodecahedra,[15] etc. In $[Ce_2Te_7O_{17}]X_2$, a novel hexagonal-bipyramidal Ce^{IV} dimer with highly anisotropic Ce−O bond lengths has been discovered (cf. Figure 2). The hexagonal-bipyramidal geometry is very common for neptunyl and uranyl and can rarely be found for trivalent lanthanides.[16] In $[Ce_2Te_7O_{17}]X_2$, the capping O atoms have bond distances of 2.130(4) and 2.127(2) Å for $[Ce_2Te_7O_{17}]Cl_2$ and 2.126(6) and 2.133(2) Å for $[Ce_2Te_7O_{17}]Br_2$. The Ce−O bond distances in the hexagonal plane range from 2.323(9) to 2.527(5) Å for $[Ce_2Te_7O_{17}]Cl_2$ and from 2.325(1) to 2.531(4) Å for $[Ce_2Te_7O_{17}]Br_2$. The O atoms of the hexagon are not on the same plane for either compound (cf. Figure 2b). These cerium polyhedra edge-share to form dimers, and all O atoms bound to Ce^{IV} are donated from tellurite anions. Bond-valence-sum calculations indicate tetravalent cerium, which agrees with the charge-balanced formulas.[17]

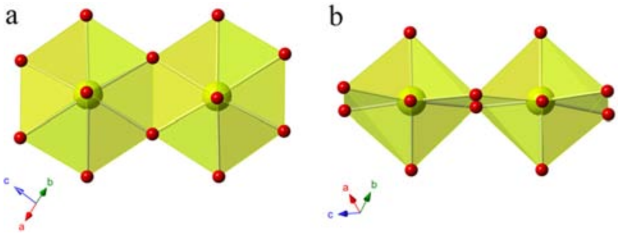

Figure 2. Top (a) and side (b) views of the edge-shared pseudo-hexagonal-bipyramidal Ce^{IV} dimer. The Ce^{IV} centers are yellow spheres, and the O atoms are red spheres.

Tellurites (Te^{IV}) have a rich structural chemistry attributable to their stereochemically active lone-pair electrons as well as their variable coordination environments. The ability of Te^{IV} to bind to three, four, or even five O atoms enables tellurites to form unusual structural building units, including 1D chains, 2D layers, and 3D frameworks.[8a] In this work, a novel 3D $Te_7O_{17}^{6-}$ framework is formed in $[Ce_2Te_7O_{17}]X_2$. Another example of $Te_7O_{17}^{6-}$ exists.[18] However, its structure is very different from the one described herein. The 3D tellurite framework is shown in Figure 3a,c with *ac* and *bc* views, respectively. Parts b and d of Figure 3 display the fundamental building unit of the 3D $Te_7O_{17}^{6-}$ framework. Each $Te_7O_{17}^{6-}$ unit is composed of one Te(1) atom, two Te(2) atoms, two Te(3) atoms, and two Te(4) atoms. All of the Te atoms in the $Te_7O_{17}^{6-}$ unit bind to four O atoms with alternating long/short distances. Te(2), Te(3), and Te(4) polyhedra corner-share with each other, forming zigzagging layered structures (cf. Figure 3c). Te(1) corner-shares with Te(2) and Te(3), holding the zigzag structures together and forming the 3D framework.

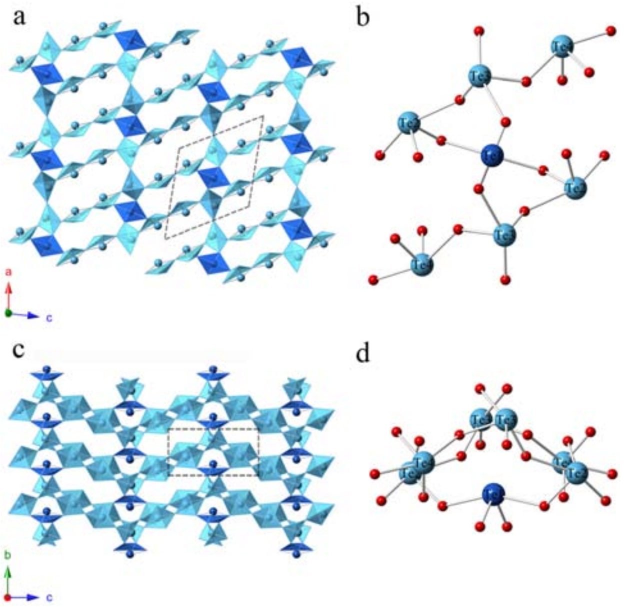

Figure 3. 3D $Te_7O_{17}^{6-}$ framework and the basic building unit. (a and b) 3D framework with *ac* and *bc* views. The building unit is marked with the dashed lines. (c and d) Ball-and-stick images of the $Te_7O_{17}^{6-}$ building unit. Te(1) atoms are dark-blue spheres, Te(2), Te(3), and Te(4) centers are light-blue spheres, and the O atoms are red spheres.

To the best of our knowledge, $[Ce_2Te_7O_{17}]Cl_2$ and $[Ce_2Te_7O_{17}]Br_2$ represent the first cerium-containing cationic inorganic frameworks. Cerium dimers exhibit an unusual edge-sharing hexagonal-bipyramidal environment. A novel 3D $Te_7O_{17}^{6-}$ structure is also featured in these two compounds. Investigations are underway to prepare Zr^{IV} and Th^{IV} analogues with cationic inorganic frameworks.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files in CIF format for $[Ce_2Te_7O_{17}]Cl_2$ and $[Ce_2Te_7O_{17}]Br_2$, detailed crystallographic information, photographs of the crystals, UV−vis−near-IR spectra, and SEM-EDX data. 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: $CeCl_3$ (99.5%, Alfa-Aesar), TeO_2 (99.99%, Alfa-Aesar), and $CeBr_3$ (99%, Alfa-Aesar) were all used as received. All of the reactions were run in a poly(tetrafluoroethylene) (PTFE)-lined Parr 4749 autoclave with a 23 mL internal volume. Distilled and Millipore-filtered water with a resistance of 18.2 MΩ·cm was used in all reactions. $[Ce_2Te_7O_{17}]X_2$ ($X = Cl^-$ or Br^-). CeX_3 (1 mM, 0.2465 g for $CeCl_3$, 0.3798 g for $CeBr_3$), TeO_2 (2 mM, 0.3192 g), and water (2 mL) were loaded into a 23 mL PTFE-lined autoclave. The autoclave was sealed and heated to 230 °C for 3 days, followed by slow cooling to room temperature at a rate of 5 °C/h. The products were washed with deionized water to remove soluble solids, followed by rinsing with methanol. For $[Ce_2Te_7O_{17}]Cl_2$, the products consisted of light-yellow block crystals of $[Ce_2Te_7O_{17}]Cl_2$ with 15% yield, coexisting with TeO_2 and $Te_6O_{11}Cl_2$. For $[Ce_2Te_7O_{17}]Br_2$, the products consisted of orange block crystals of $[Ce_2Te_7O_{17}]Br_2$ with 80% yield, conexisting with TeO_2 and $Te_6O_{11}Br_2$.

(11) Crystallographic data for $[Ce_2Te_7O_{17}]Cl_2$: light-yellow block, 0.10 mm × 0.04 mm × 0.02 mm, monoclinic, $P2/n$, $Z = 2$, $a = 9.6373(5)$ Å, $b = 5.3278\ (3)$ Å, $c = 18.8468(10)$ Å, $\beta = 96.0740(10)°$, $V = 962.27(9)$ Å^3, $T = 100(2)$ K, R1 = 0.0121 [$I > 2\sigma(I)$], wR2 = 0.0267. Crystallographic data for $[Ce_2Te_7O_{17}]Br_2$: light-orange block, 0.20 mm × 0.05 mm × 0.03 mm, monoclinic, $P2/n$, $Z = 2$, $a = 9.718(3)$ Å, $b = 5.3929(18)$ Å, $c = 19.025(6)$ Å, $\beta = 97.067(3)°$, $V = 989.5(6)$ Å^3, $T = 100(2)$ K, R1 = 0.0130 [$I > 2\sigma(I)$], wR2 = 0.0301.

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