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Cationic Framework Materials

NDTB-1: A Supertetrahedral Cationic Framework That Removes TcO_4^- from Solution**

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Materials with charged extended structures are typically based on an anionic network in which the charge is balanced by cations that fill the space between the anionic portions of the structure. This general description applies to a vast array of functional materials. There is, however, a rare alternative to this concept, and that is a solid with a cationic extended structure, whose charge is balanced by unbound anions. Until recently, materials of this kind were largely represented by the hydrotalcite clays.[1,2] These layered double hydroxides, which occur with many different metal ions, possess metal hydroxide slabs with interlayer anions that can be easily exchanged, making them extremely important for a variety of environmental applications. Other examples of cationic solids include the mineral francisite and its derivatives, $Cu_3BiSe_2O_8X$ (X = F, Cl, Br, I).[3,4] However, the anions in these compounds cannot be exchanged for larger ones without collapse of the framework. A series of heavy main-group hydroxides and fluorides have recently been reported that possess cationic layers.[5–7] The anions between these layers can be exchanged, thus allowing for the removal of key environmental contaminants from solution.[5–7]

There are two key anions that are inherent to the nuclear weapons complex legacy of the Cold War as well as to advanced nuclear fuel cycles: CrO_4^{2-} and TcO_4^-. The former is toxic from a chemical standpoint, and the latter is radioactive. Both are transported in the environment, and both are problematic during the vitrification of nuclear waste. Chromate forms spinels within the glass, weakening the integrity of the waste form,[8] and pertechnetate easily leaches from the glass.[7,9] Clearly, anion-exchange materials are needed that can remove these species from solution.

We have recently undertaken a study of the preparation, structure elucidation, and physicochemical property measurements of actinide borates, which is motivated in part by a desire to understand the crystallized portions of vitrified nuclear waste.[10] During the course of these studies, a highly unusual thorium borate was discovered, $[ThB_5O_6(OH)_6][BO(OH)_2]\cdot 2.5H_2O$ (Notre Dame thorium borate-1, NDTB-1). Thorium borates are poorly described in the literature, with only a single crystallographically characterized example known, ThB_2O_5.[11] This paucity is surprising in light of the fact that a thorium borate was reported by Berzelius in 1829.[12] This compound is thought to be $Th_3(BO_3)_4$, but the evidence is not convincing.[13] The preparation of NDTB-1 is accomplished through the use of a boric acid reactive flux. This species has probably not been observed before, because previous investigations either utilized aqueous precipitation at room temperature or high-temperature B_2O_3 melts.

The structure of NDTB-1 is a porous supertetrahedral 3D framework. The building blocks of this framework are twelve-coordinate Th^{4+} ions surrounded by BO_3 and BO_4 anions. The BO_4 anions chelate the thorium centers, and the BO_3 groups occupy single vertices (Figure 1a). All borate oxygen atoms are bound to thorium. All three oxygen atoms of the BO_3 groups are μ_3, whereas those within the BO_4 units are μ_2 or μ_3. The thorium atoms reside on $\bar{3}$ sites, thus yielding an almost

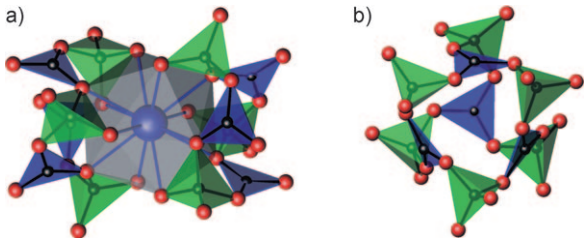

Figure 1. a) A view of the twelve-coordinate icosahedral geometry around the Th^{4+} centers in NDTB-1. b) A depiction of the $B_{10}O_{24}$ ($4\Delta 6\square$) clusters with threefold symmetry that bridge between the thorium centers in NDTB-1. BO_3 blue, BO_4 green.

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regular icosahedron with Th–O bond lengths of 2.566(3) (×6) and 2.575(2) Å (×6). This coordination number is known from classical anions such as $[Th(NO_3)_6]^{2-}$[14] and is allowed by a combination of the large size of the Th^{4+} cation (1.21 Å)[15] and the small size and chelating nature of the borate anions.[10]

The borate anions are polymerized and form $B_{10}O_{24}$ ($4\Delta6\square$) clusters with threefold symmetry that bridge between the thorium centers, and the hydroxide bridge between borate groups can be inferred from bond lengths and bond-valence considerations.[16] A view of one of these clusters is shown in Figure 1b. The bridging of the thorium centers by the borate clusters creates a supertetrahedral framework, depicted in two formats in Figure 2.

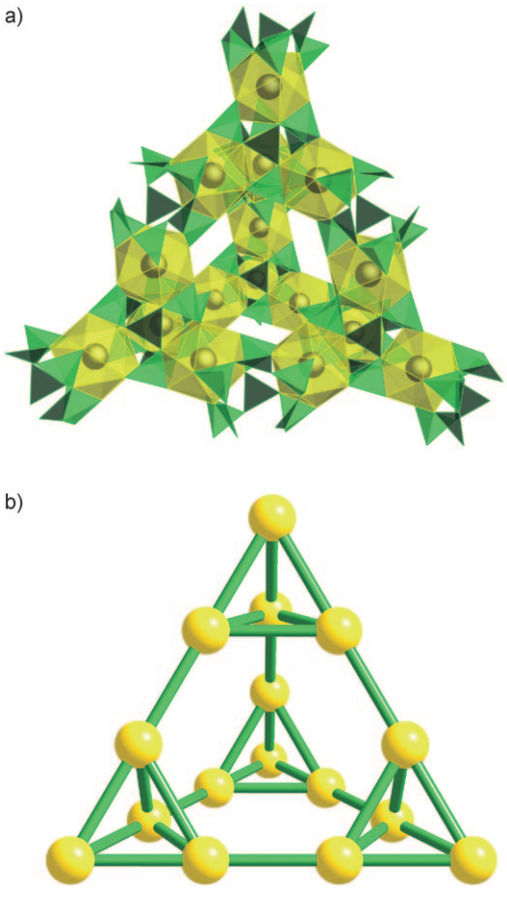

Figure 2. a) Supertetrahedral fragment in NDTB-1. Th yellow, B green. b) Topology of supertetrahedral 3D framework based on Th atoms (yellow).

The key feature of NDTB-1 is the channels that extend along [110]. A view of the structure of this material is shown in Figure 3. X-ray diffraction studies reveal the presence of a highly disordered entity within the channels.

Thorium atoms and crown-like $B_{10}O_{24}$ groups do not fill all of the space in the supertetrahedra, and as a result of this architecture, large free voids in the structure of NDTB-1 are observed. The result of such combination is a regular 3D

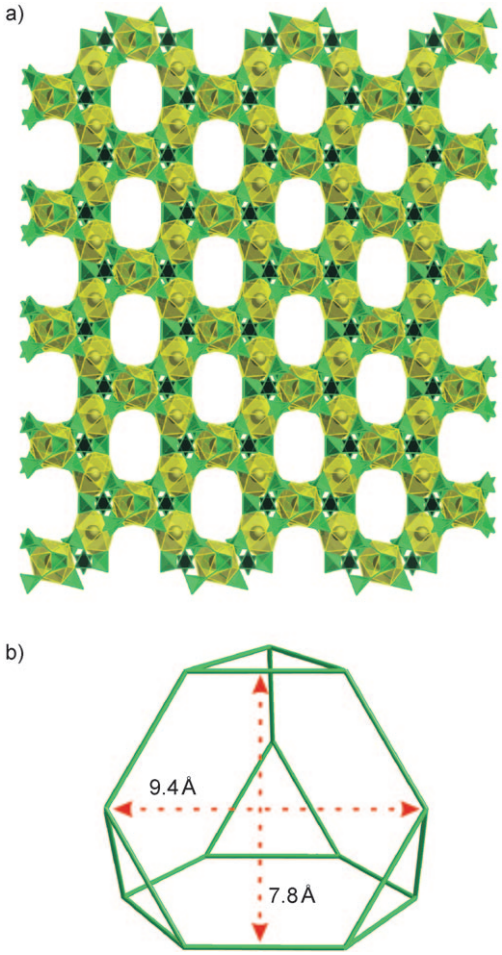

Figure 3. a) A view along [110] of the 3D structure of NDTB-1. The disordered BO_3 anions and water that reside in the channels have been omitted for clarity. b) Cage topology in the structure of NDTB-1.

framework with a system of channels and cages. A general view of the NDTB-1 structure is shown in Figure 3a. The six channels form a network that pierces the whole structure and allows facile anionic and molecular transport for the exchange processes (see below). These channels intersect in the center of the supertetrahedra. The gates into the intersecting chambers have a hexagonal form and are 9.4 × 7.8 Å in size (Figure 3b). Each cage has four identical gates and forms a truncated tetrahedron. Free void volume in NDTB-1 is 43%, which makes it the second most porous actinide compound known.[17] The channel directions are at an angle of 30° to the gates, and in Figure 3a an ellipse-like channel profile is observed. The preparation of this material from multiple sources as well as charge-balance considerations led us to suspect that disordered borate resided in the channels of NDTB-1.

Solid-state ^{11}B MAS NMR spectra (Figure 4a) show distinct signals from well-ordered BO_3 and BO_4 groups, as expected from the single-crystal XRD data. The ordered BO_3 groups yield a characteristic MAS powder pattern (Figure 4, blue) with horns that correspond to the steep edge near $\delta = +15$ ppm and the peak at $\delta = +7.5$ ppm, best fit with an isotropic chemical shift $\delta = 17.5$ ppm and quadrupolar cou-

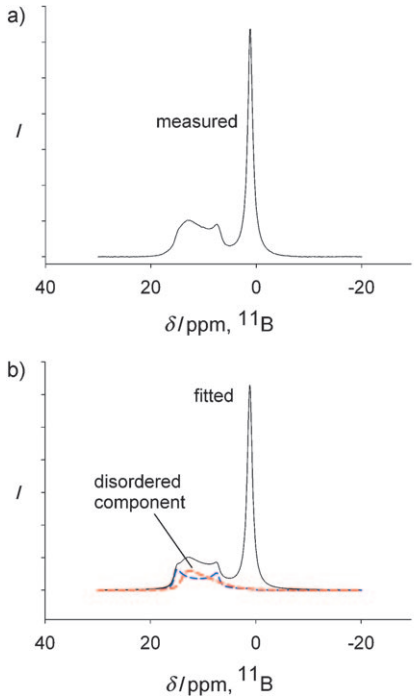

Figure 4. a) Solid-state ^{11}B MAS NMR spectrum of NDTB-1 at 160.45 MHz and 15 kHz spinning rate. b) Least-squares fit comprising a sum of the three components corresponding to ordered BO_3 (blue) and BO_4 groups and disordered BO_3^- anions (red) within the channels.

pling parameters Cq = 2.65 MHz, $\eta = 0$. However, a powder pattern for a well-ordered site cannot account for the broad area of intensity from 14 to 10 ppm, between the sharper BO_3 features. This intensity can be explained by the presence of a second BO_3 environment that experiences a range of local structures as reflected in the NMR parameters (Figure 4, red; calculated using the method described in Ref. [18]).

Preliminary ^{11}B MQ-MAS results show that this second type of BO_3 is characterized by a correlated distribution of isotropic chemical shift (from 17.0 to 14.5 ppm), Cq (from 2.55 to 2.35 MHz), and decreasing intensity. A sum of such component profiles accounts for the difference between the observed spectrum and the lineshape expected for well-ordered BO_3. This feature is in accord with the presence of a disordered BO_3 group, as was suspected from the crystal structure. Furthermore, the ratio of BO_3 to BO_4 integrated intensity (0.82(5)) exceeds that expected from the 2:3 crystallographic ratio of the framework and provides further support for the existence of additional BO_3 groups in the channels. When the single-crystal X-ray data and solid-state NMR spectroscopy are taken together, we can conclude that NDTB-1 is an exceedingly rare example of a cationic framework with extraframework borate anions residing in the symmetrical centers of the gates and being used to maintain charge neutrality.

Anion exchange experiments were conducted with a variety of common anions, beginning with halides. These studies, which combined inductively coupled plasma mass spectrometry (ICP-MS), energy-dispersive X-ray spectroscopy (EDS), and single-crystal and powder X-ray diffraction, revealed not only that anion exchange takes place, but that the structure remains intact throughout the exchange. More impressive is the fact that single crystals retain their integrity throughout the exchange, although with these small anions, disorder in the channels remains a crystallographic problem (Figure S1 in the Supporting Information).

Exchange experiments were conducted with a variety of highly colored anions, such as MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, and ReO_4^- (IO_3^- and SeO_3^{2-} were also studied). The single crystals show the color of the transition-metal anions within a few minutes (see picture in the table of contents). Using a microspectrophotometer, UV/Vis/NIR absorption data were collected from single crystals after exchange, and these clearly demonstrate the presence of the anions within the crystals (Figure S2 in the Supporting Information). The crystals can be cut, and the interior shows the same color as the surface. The critical anion exchange experiments involve replacing the extraframework borate anions with TcO_4^-. Owing to the intense nature of the charge-transfer bands of pertechnetate, we had to use relatively dilute solutions to monitor its removal from solution using UV/Vis spectroscopy. These studies of as-synthesized intact crystals of NDTB-1 (10 mg) show rapid uptake of TcO_4^- from solution, with 72% being removed in 36 h (Figure 5).

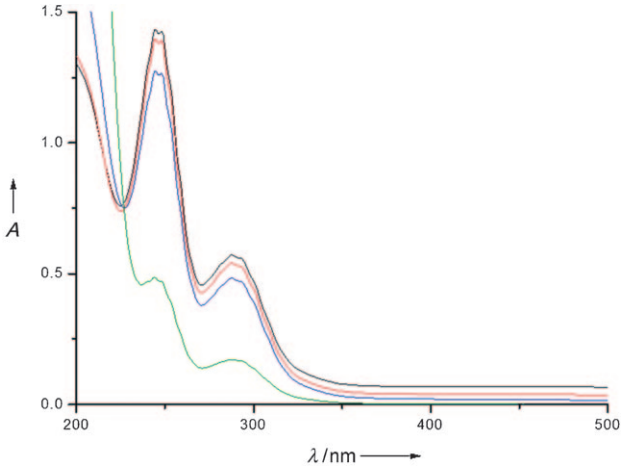

Figure 5. UV/Vis spectra of TcO_4^- showing its removal from solution by crystals of NDTB-1 at 0 (black), 1 (red), 8 (blue), and 36 h (green).

In conclusion, NDTB-1 represents a truly unprecedented supertetrahedral cationic framework with superb anion exchange capabilities. It is the first purely inorganic 3D cationic framework. Investigations are underway to prepare the Zr^{IV} and Ce^{IV} analogues of NDTB-1. These species should show utility outside of the nuclear industry.

Experimental Section

$Th(NO_3)_4{\cdot}4H_2O$ (0.2000 g, 0.416 mmol, 98%, International Bio-Analytical Industries), boric acid (0.6717 g, 10.86 mmol, 99.99%, Alfa-Aesar), and Millipore water (90 μL) were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 200°C in a box

furnace for 7 days. The autoclave was then cooled down to 160 °C at a rate of 1 °C h^{-1} and then cooled further to room temperature at a rate of 9 °C h^{-1}. The product was washed with boiling water to remove excess boric acid and subsequently rinsed with methanol. Crystals in the form of octahedra and their fragments were isolated. Crystals with improved morphology are obtained by using $ThOCO_3$ as the source of thorium. Single-crystal X-ray diffraction and powder X-ray diffraction studies reveal that NDTB-1 can be made as a pure phase with an average yield of 72.8% based on Th. The reaction is highly repeatable, but the slow cooling is absolutely essential. A Th/B ratio of 1:6 was verified using EDS.

X-ray structural analysis: $[ThB_5O_6(OH)_6][BO(OH)_2]\cdot 2.5\,H_2O$ (NDTB-1): colorless octahedron, crystal dimensions $0.131\times0.132\times0.134$ mm, cubic, space group $Fd\bar{3}$ (No. 203), $Z=16$, $a=17.4036(16)$ Å, $V=5271.3(8)$ Å^3 ($T=100$ K), $\mu=114.15$ cm^{-1}, $R_1=0.0194$, $wR2=0.0519$. Bruker APEXII Quazar diffractometer: $\theta_{max}=57.78°$, $Mo_{K\alpha}$, $\lambda=0.71073$ Å, 0.5° ω scans, 15189 reflections measured, 579 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 with anisotropic refinement of F^2 by full-matrix least-squares and 48 parameters.[19] Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-421217.

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[1] V. Rives, *LDHs: Layered Double Hydroxides: Present and Future*, Nova Science Publishers, Hauppauge, New York, USA, **2001**.
[2] D. G. Evans, R. C. T. Slade in *Layered Double Hydroxides* (Ed.: X. Duan, D. G. Evans), Springer, New York, NY, USA, **2006**, chap. 1, pp. 1–87.
[3] P. Millet, B. Bastide, V. Pashchenko, S. Gnatchenko, V. Gapon, Y. Ksari, A. Stepanov, *J. Mater. Chem.* **2001**, *11*, 1152–1157.
[4] K. M. Ok, P. S. Halasyamani, *Inorg. Chem.* **2002**, *41*, 3805–3807.
[5] C. H. Swanson, H. A. Shaikh, D. L. Rogow, A. G. Oliver, C. F. Campana, S. R. J. Oliver, *J. Am. Chem. Soc.* **2008**, *130*, 11737–11741.
[6] D. T. Tran, P. Y. Zavalij, S. R. J. Oliver, *J. Am. Chem. Soc.* **2002**, *124*, 3966–3969.
[7] S. R. J. Oliver, *Chem. Soc. Rev.* **2009**, *38*, 1868–1881.
[8] P. Izak, P. Hrma, B. W. Arey, T. J. Plaisted, *J. Non-Cryst. Solids* **2001**, *289*, 17–29.
[9] Y. F. Wang, H. Z. Gao, *J. Colloid Interface Sci.* **2006**, *301*, 19–26.
[10] S. Wang, E. V. Alekseev, J. Ling, S. Skanthakumar, L. Soderholm, W. Depmeier, T. E. Albrecht-Schmitt, *Angew. Chem.* **2009**, DOI: 10.1002/ange.200906127; *Angew. Chem. Int. Ed.* **2009**, DOI: 10.1002/anie.200906127.
[11] A. Cousson, M. Gasperin, *Acta Crystallogr. Sect. C* **1991**, *47*, 10–12.
[12] J. J. Berzelius, *Poggendorff's Ann. Phys.* **1829**, *92*, 385–415.
[13] S. P. Mushran, *Nature* **1946**, *158*, 95.
[14] M. R. Spirlet, J. Rebizant, C. Apostolidis, B. Kanellakopulos, E. Dornberger, *Acta Crystallogr. Sect. C* **1992**, *48*, 1161–1164.
[15] R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751–767.
[16] a) N. E. Brese, M. O'Keeffe, *Acta Crystallogr. Sect. B* **1991**, *47*, 192–197; b) I. D. Brown, *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*, Oxford University Press, Oxford, **2002**; c) I. D. Brown, D. Altermatt, *Acta Crystallogr. Sect. B* **1985**, *41*, 244–247.
[17] a) E. V. Alekseev, S. V. Krivovichev, W. Depmeier, *Angew. Chem.* **2008**, *120*, 559–561; *Angew. Chem. Int. Ed.* **2008**, *47*, 549–551; b) K. M. Ok, J. Sung, G. Hu, R. M. J. Jacobs, D. O'Hare, *J. Am. Chem. Soc.* **2008**, *130*, 3762–3763; c) R. E. Wilson, S. Skanthakumar, K. E. Knope, C. L. Cahill, L. Soderholm, *Inorg. Chem.* **2008**, *47*, 9321–9326.
[18] D. Coster, A. L. Blumenfeld, J. J. Fripiat, *J. Phys. Chem.* **1994**, *98*, 6201–6211.
[19] G. M. Sheldrick, SHELXTL PC, Version 5.0, Siemens Analytical X-Ray Instruments, Inc.: Madison, WI **1994**.

