

**TOWARD AN IMPROVED UNDERSTANDING OF STRUCTURE AND MAGNETISM
IN NEPTUNIUM AND PLUTONIUM PHOSPHONATES AND SULFONATES**

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Final Report

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List of Publications

69. T. E. Albrecht-Schmitt, "Structural Crystallography of Inorganic Oxysalts. IUCr Monographs on Crystallography No. 22. By Sergey V. Krivovichev," Book Review. *Angewandte Chemie, Int. Ed.* **2009**, 48, 5237. *Invited Article.*
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 1. P. M. Almond, L. Deakin, A. Mar, and T. E. Albrecht-Schmitt, “Hydrothermal Synthesis, Structure, and Magnetic Properties of a Layered Organically Templated Uranium Aquofluoride: [C₅H₁₄N₂][U₂F₁₀(H₂O)],” *Inorganic Chemistry* **2001**, *40*, 886-890.

General Summary

This grant supported the exploratory synthesis of new actinide materials with all of the actinides from thorium to californium with the exceptions of protactinium and berkelium. We developed detailed structure-property relationships that allowed for the identification of novel materials with selective ion-exchange, selective oxidation, and long-range magnetic ordering. We found novel bonding motifs and identified periodic trends across the actinide series. We identified structural building units that would lead to desired structural features and novel topologies. We also characterized many different spectroscopic trends across the actinide series. The grant support the preparation of approximately 1200 new compounds all of which were structurally characterized.

Selected abstract

T. H. Bray, J. Ling, E.-S. Choi, J. S. Brooks, J. V. Beitz, R. E. Sykora, R. G. Haire, D. M. Stanbury, and T. E. Albrecht-Schmitt, “Critical Role of Water Content in the Formation and Reactivity of Uranium, Neptunium, and Plutonium Iodates Under Hydrothermal

Conditions: Implications for the Oxidative Dissolution of Spent Nuclear Fuel,” *Inorganic Chemistry*, **2007**, 46, 3663-3668.

Abstract

The reactions of $^{237}\text{NpO}_2$ with excess iodate under acidic hydrothermal conditions result in the isolation of the Np(IV), Np(V), and Np(VI) iodates, $\text{Np}(\text{IO}_3)_4$, $\text{Np}(\text{IO}_3)_4 \cdot n\text{H}_2\text{O} \cdot n\text{HIO}_3$, $\text{NpO}_2(\text{IO}_3)$, $\text{NpO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$, and $\text{NpO}_2(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$, depending on both the pH and the amount of water present in the reactions. Reactions with less water and lower pH favor reduced products. While the initial redox processes involved in the reactions between $^{237}\text{NpO}_2$ or $^{242}\text{PuO}_2$ and iodate are similar, the low solubility of $\text{Pu}(\text{IO}_3)_4$ dominates product formation in Pu iodate reactions to a much greater extent than $\text{Np}(\text{IO}_3)_4$ does in the Np iodate system. UO_2 reacts with iodate under these conditions to yield U(VI) iodates solely. The isotopic structures of the An(IV) iodates, $\text{An}(\text{IO}_3)_4$ (An = Np, Pu) are reported and consist of one-dimensional chains of dodecahedral An(IV) cations bridged by iodate anions. The structure of $\text{Np}(\text{IO}_3)_4 \cdot n\text{H}_2\text{O} \cdot n\text{HIO}_3$ is constructed from NpO_9 tricapped trigonal prisms that are bridged by iodate into a polar three-dimensional framework structure. Second-harmonic generation measurements on a polycrystalline sample of the Th-analog of $\text{Np}(\text{IO}_3)_4 \cdot n\text{H}_2\text{O} \cdot n\text{HIO}_3$ reveals a response of approximately $12\times \alpha\text{-SiO}_2$. Single crystal magnetic susceptibility measurements of $\text{Np}(\text{IO}_3)_4$ show magnetically isolated Np(IV) ions.

Remaining Funds

All funds have been expended.