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


Framework Structure, Optical Properties, and EPR of the Mixed-Metal Uranyl Phosphate
Cs₂[UO₂(VO₂)₂(PO₄)₂·0.59H₂O],” Chemistry of Materials, 2005, 17, 6219-6222.
42. J. D. Woodward and T. E. Albrecht-Schmitt, “Molten Salt Flux Synthesis and Structure
of the New Layered Uranyl Tellurite, K₄[(UO₂)₅(TeO₃)₂O₅],” Journal of Solid State
41. T. E. Albrecht-Schmitt, “Actinide Materials Adopt Curvature: Recent Discoveries of
Actinide-Based Nanotubules and Nanospheres,” Angewandte Chemie 2005, 44, 4836-4838. Invited Highlight
40. J. D. Woodward, P. M. Almond, and T. E. Albrecht-Schmitt, “Cesium Thorium Silicate,
and the Raman and Emission Properties of Am(IO₃)₃ and Cm(IO₃)₃,” Inorganic
38. T. Y. Shvareva, P. M. Almond, and T. E. Albrecht-Schmitt, “Crystal chemistry and ion-
exchange properties of the layered uranyl iodate K[UO₂(IO₃)₃],” Journal of Solid State
Vanadyl Tellurate, Th(VO₂)₂(TeO₆)(H₂O)₂,” Inorganic Chemistry, 2005, 44, 2282-2286.
Structures, and Ion-Exchange Properties of the Three-Dimensional Framework Uranyl
Gallium Phosphates, Cs₆[(UO₂)₂(GaOH)₂(PO₄)₄]·H₂O and Cs[UO₂Ga(PO₄)₂],” Inorganic
Chemistry, 2005, 44, 300-305.
Synthesis, Structure, Raman Spectroscopy, and Self-Irradiation Studies of ²⁴⁸Cm(IO₃)₃,”
of Cs₆[(UO₂)₄(W₅O₂₁)(OH)₂(H₂O)₂]: A New Polar Uranyl Tungstate,” Journal of Solid
Dineptunium Decafluoride,” Acta Crystallogr. 2004, E60, m973-m975.


15. P. M. Almond and T. E. Albrecht-Schmitt, “Expanding the Remarkable Structural Diversity of Uranyl Tellurites: Hydrothermal Preparation and Structures of K[VO_2Te_2O_5(OH)], Tl_3[(UO_2)_2[Te_2O_5(OH)](Te_2O_6)]·2H_2O, β-Tl_2[(UO_2)_2(TeO_3)_2], and Sr_3[[(UO_2)(TeO_3)_2](TeO_3)_2],” Inorganic Chemistry, 2002, 41, 5495-5501.


(C₉H₁₀N₂)Zr₂F₁₀·H₂O and (C₄H₁₂N₂)ZrF₆·H₂O,” *Journal of Solid State Chemistry* **2001**, *159*, 198-203.


**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**


**Abstract**

The reactions of \(^{237}\text{NpO}_2\) with excess iodate under acidic hydrothermal conditions result in the isolation of the \(\text{Np(IV)}, \text{Np(V)}, \text{and Np(VI) iodates, Np(IO}_3)_4, \text{Np(IO}_3)_4\cdot\text{nH}_2\text{O}\cdot\text{nHIO}_3, \text{NpO}_2(\text{IO}_3), \text{NpO}_2(\text{IO}_3)_2(\text{H}_2\text{O}), \text{and NpO}_2(\text{IO}_3)_2\cdot\text{H}_2\text{O},\) 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 \(\text{Pu(IO}_3)_4\) dominates product formation in Pu iodate reactions to a much greater extent than \(\text{Np(IO}_3)_4\) does in the Np iodate system. \(\text{UO}_2\) reacts with iodate under these conditions to yield \(\text{U(VI) iodates solely.}\) The isotypic structures of the An(IV) iodates, \(\text{An(IO}_3)_4\) (An = Np, Pu) are reported and consist of one-dimensional chains of dodecahedral An(IV) cations bridged by iodate anions. The structure of \(\text{Np(IO}_3)_4\cdot\text{nH}_2\text{O}\cdot\text{nHIO}_3\) is constructed from \(\text{NpO}_9\) 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 \(\text{Np(IO}_3)_4\cdot\text{nH}_2\text{O}\cdot\text{nHIO}_3\) reveals a response of approximately \(12\times \alpha\text{-SiO}_2\). Single crystal magnetic susceptibility measurements of \(\text{Np(IO}_3)_4\) show magnetically isolated Np(IV) ions.

**Remaining Funds**

All funds have been expended.