New Insights Into The Pu/Sb/O System Found In Electrosynthetic Molten Salt And Hydroxide Fluxes

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The synthetic and structural chemistry of the transuranic elements has fallen behind their uranium counterparts, in part, because of the limited facilities that exist to investigate such materials, i.e., long-lived alpha emitters, and their diminished accessibility. The structural data from single crystal diffraction to support the higher oxidation (V, VI) states of plutonium, where the plutonyl (O=P=O) unit is found (Figure 1), is even more rare, with a few examples sited in the literature, i.e., $PuO_2(IO_3)_2 \bullet H_2O$,[1] $PuO_2(IO_3)_2 \bullet 0.5KCl \bullet 2.5H_2O$.[2] There is structural data from powder diffraction[3] and EXAFS,[4] however, data derived from single crystal X-ray crystallography would provide the most extensive and accurate information on bonding.

Recent efforts have been made at Los Alamos National Laboratory (LANL) to set up research conditions in order to probe the high oxidation state structural chemistry of plutonium compounds in molten fluxes. There are three methods that are combined to aid in the stabilization and isolation of high oxidation states of plutonium: molten flux reactions, electrosynthesis, and judicious choice of highly oxidizing anions. Electrosynthesis in molten hydroxide and salt fluxes is employed to synthesize single crystals of plutonium compounds. Molten fluxes, hydroxide fluxes in particular, offer several advantages over conventional high temperature methods and salt fluxes in that they are low melting and readily liquefy oxides.[5] Hydroxide fluxes are also known to dissolve lanthanide oxides, alkaline earth oxides, and first row transition metal oxides, and therefore, are likely to dissolve oxides of plutonium and can be used over a large temperature range (150-750°C). The addition of applied potentials in these molten hydroxide flux reactions has been used to isolate the unusually high oxidation states of Fe(IV) and Co(IV) in single crystals,[6,7] and therefore, can assist in stabilizing the Pu(V) and Pu(VI) oxidations as well. Compounds containing antimony and its analogous oxide anions, i.e., SbO_4, SbO_6, SbO_3, can have fascinating structural bonding[8] and in addition, can provide leads into interesting luminescent,[9] magnetic,[10] and catalytic[11] properities.

The synthesis and structural characterization of compounds found in the Pu/Sb/O system synthesized by both salt and hydroxide fluxes and electrosynthesis will be discussed. In addition, a comparison will be made with uranium analogues as well as actinide compounds synthesized by other methods, i.e., hydrothermal conditions.

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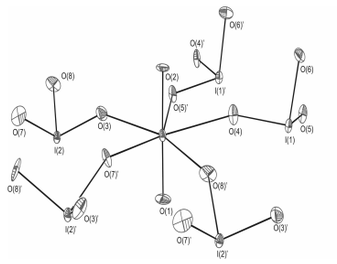

Figure 1. The first plutonyl iodate showing an example of the trans dioxo cation perpendicular to the equatorial plane.