Supporting Information for:

Conversion of Americia to Anhydrous Trivalent Americium Halides

Shane S. Galley¹, Joseph M. Sperling,² Cory J. Windorff,² Matthias Zeller,¹ Thomas E. Albrecht-Schmitt,² Suzanne C. Bart ¹*

¹H.C. Brown Laboratory, Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, United States
²Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306, United States

*To whom all correspondence should be addressed: sbart@purdue.edu
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Experimental Details:

Caution! $^{243}$Am is a high energy $\alpha$ emitter that has potentially serious health risks. All studies with this actinide were conducted in a laboratory equipped to study transuranium elements equipped with HEPA-filtered hoods and gloveboxes and with a series of instruments that continually monitor the radiation levels in the laboratory. All free-following actinide solids are handled in gloveboxes, and the products are only examined when coated with immersion oil. There are significant limitations in accurately determining yields of these actinide compounds because it requires drying, isolation and weighing a solid, which possess an inhalation hazard and manipulation difficulties given the small quantities of product from these reactions. Concentrated hydrochloric acid, hydrobromic acid, anhydrous tetrahydrofuran, 1,2-dimethoxyethane, trimethylsilyl chloride and trimethylsilyl bromide were purchased from Sigma-Aldrich and used without further purification.

Crystallographic Studies. Single crystals of each compound were mounted on a MiToGen™ mount with immersion oil and the crystals were optically aligned on a Bruker D8 Quest X-ray Diffractometer using a built in camera. Preliminary measurements were performed using an I-$\mu$-S X-ray source (Mo K$\alpha$, $\lambda = 0.71073$ Å) with high-brilliance and high-performance focusing quest multilayer optics. The APEX2 software was used for determining the unit cells and data collection. Data were collected at 100 or 130 K. The reflections’ intensities of a sphere were collected by a mixture of four sets of frames. Each set had a different phi angle for the crystal, and each exposure covered a range of 0.50 in $\omega$, totaling to 1464 frames. The frames
were collected with an exposure time of 5-25 seconds, dependent on the crystal. The SAINT software was used for data integration including polarization and Lorentz corrections, and data were scaled and corrected for absorption effects using the Sadabs or Twinabs software. The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs and refined by full matrix least squares against \( F^2 \) with all reflections using Shelxl2018 using the graphical interface Shelxle. H atoms attached to carbon were positioned geometrically and constrained to ride on their parent atoms with C-H bond distances of 0.99 Å. \( U_{iso}(H) \) values were set to 1.2 times of \( U_{eq}(C) \).

The crystal under investigation for 1-Am was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell_Now, with the two components being related by a 180° rotation around the reciprocal b-axis. The two components were integrated using Saint and corrected for absorption using twinabs, resulting in the following statistics:

- 5254 data (1769 unique) involve domain 1 only, mean \( I/\sigma \) 76.8
- 5163 data (1761 unique) involve domain 2 only, mean \( I/\sigma \) 22.9
- 6740 data (2647 unique) involve 2 domains, mean \( I/\sigma \) 63.4

The exact twin matrix identified by the integration program was found to be:

-0.99912 0.01349 -0.00633
The structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the overlapping ones), resulting in a BASF value of 0.1051(7).

The Rint value given is for all reflections and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (TWINABS (Sheldrick, 2012)).

PLATON and Checkcif were used to finalize the structure for any issues. CIFs are available from the Cambridge Crystallographic Data Centre (CCDC) and are 1877647 (1-Am) and 1557708 (2-Am).

UV-Vis-Near-IR (NIR) Spectroscopy. UV-vis- NIR data were collected for each compound using a Craic Technologies microspectrophotometer. Single crystals of each compound were paced on a quartz slide in immersion oil, and the data were collected from 300 nm to 1100 nm.

X-ray diffraction software references:

Apex2, Saint V8.37A: Bruker AXS Inc.: Madison (WI), USA, 2016.
SHELXTL suite of programs: Version 6.14, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison (WI), USA, 2000-2003.

Shelxs: Sheldrick GM. A short history of SHELX. Acta Crystallogr A. 2008, 64(1), 112–122.

Shelxl2018: a) Sheldrick GM. University of Göttingen, Germany, 2018. b) Sheldrick GM. Crystal structure refinement with SHELXL. Acta Crystallogr Sect C Struct Chem. 2015, 71(1), 3–8.

Shelxle: Hübschle CB, Sheldrick GM, Dittrich B. ShelXle: a Qt graphical user interface for SHELXL. J. Appl. Crystallogr. 2011, 44(6), 1281–1284.

Synthesis of 1-Am.²⁴³AmO₂ (5.0 mg, 0.018 mmol) was dissolved in concentrated hydrochloric acid. The solution was evaporated off slowly to leave a dry yellow residue. The vial was transferred to an argon-atmosphere glovebox by placing it under vacuum in the antechamber. The yellow residue was treated with 500 µL TMS-Cl and dried to completeness. The residue was brought up in a solution of THF and layered with pentane overnight to produce peach crystals of [AmCl(μ-Cl)₂(THF)₂]ₙ (1-Am).

Synthesis of 2-Am.²⁴³AmO₂ (5.0 mg, 0.018 mmol) was dissolved in concentrated hydrobromic acid. The solution was evaporated off slowly to a dry yellow residue. The vial was transferred to an argon-atmosphere glovebox by placing it under vacuum in the antechamber. The yellow residue was treated with 500 µL TMS-Br and dried to completeness. The residue was brought up
in a solution of THF was allowed to diffuse into polybutenes overnight to produce peach crystals of $\text{AmBr}_3(\text{THF})_4$ (2-Am).
Table S.1. Crystallographic Table of AmX₃(THF)ₙ (X: Cl, Br N: 2,4)

| Compound | 1-Am | 2-Am |
|----------|------|------|
| Formula Mass | 493.56 | 769.18 |
| Color and habit | Yellow, block | Peach, block |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (Å) | 8.2893 (13) | 8.2085 (5) |
| $b$ (Å) | 8.5726 (13) | 9.3333 (5) |
| $c$ (Å) | 9.7909 (15) | 15.3833 (9) |
| $\alpha$ (°) | 80.039 (3) | 78.9492 (12) |
| $\beta$ (°) | 70.683 (3) | 86.9269 (13) |
| $\gamma$ (°) | 83.012 (4) | 74.9655 (12) |
| $V$ (Å³) | 493.56 | 1117.10 (11) |
| $Z$ | 2 | 2 |
| $T$ (K) | 100(2) | 130(2) |
| $\lambda$ (Å) | 0.71073 | 0.71073 |
| Maximum 2θ (°) | 61.11 | 55.15 |
| $\rho$ calc (g/cm³) | 2.541 | 2.293 |
| $\mu$ (Mo Kα) (cm⁻¹) | 6.542 | 8.815 |
| $R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ | 0.0321 | 0.0308 |
| $R_w(F_o^2) \alpha$ | 0.0840 | 0.0638 |