

Synthesis and characterization of a channel framework in $K_3Am_3(IO_3)_{12} \cdot HIO_3$

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Single crystals of $K_3Am_3(IO_3)_{12} \cdot HIO_3$ were synthesized under hydrothermal conditions (180 °C) representing the first structurally characterized actinide(III) iodate.

The iodates of transition metals and lanthanides have attracted much interest owing to their potential as new nonlinear optical materials coupled with magnetic and polar properties.^{1–4} A series of 5f-iodates of general formula $Ln(IO_3)_3 \cdot xH_2O$, where $Ln = Pr$ to Lu and $x = 0–5$, have been synthesized. Two acidic lanthanide iodates,⁵ $Pr(IO_3)_3 \cdot HIO_3$, which is suggested to be isostructural with the La , Nd , and Sm double salts, and $3La(IO_3)_3 \cdot HIO_3 \cdot 7H_2O$,³ were reported with the La salt generating second harmonics. While the synthesis and crystal growth of 4f-lanthanides is driven by the search for new optical–magnetic properties, the search for new 5f-element compounds is motivated by the need for radiation-resistant and insoluble materials suitable for safe long-term nuclear material storage. The recently synthesized actinide borides are a recent example for this venture.⁶ Iodate offers the unique capability to precipitate actinides even under mildly acidic conditions, and in fact, was used for oxidation state determination of plutonium in October 1942.^{7,8} Application of hydrothermal conditions allowed the synthesis of single crystals of a variety of actinyl(vI) ($An = U$,^{9,10} Np ,¹¹ Pu^{11}) iodates. However, structural information on the light transplutonium (Am , Cm) compounds is still deficient.

We report herein the synthesis and structural characterization of the first ternary americium(III) iodate, $K_3Am_3(IO_3)_{12} \cdot HIO_3$ (**I**), and compare its structural features with those of the reported iodates of the chemically analogous lanthanides. Although hydrothermal conditions have been applied to the synthesis of transition metal, lanthanide and light actinide (U , Np , Pu) compounds, americium has been excluded from this approach because of safety and contamination concerns and the increased instability of Am crystals due to its own α -radiation damage. We were able to overcome these difficulties and reacted $^{243}Am(III)$ in 3 M HCl with KIO_4 solutions at 180 °C for 24 hours.[†] Although the high oxidation potential of the periodate anion in acid ($E^\circ(IO_4^-/IO_3^-) = 1.65$ V¹²) oxidizes $Pu(IV)$ completely to the hexavalent state ($E^\circ(Pu^{4+}/PuO_2^{2+}) = 0.98$ V¹³), no oxidation of $Am(III)$ to $Am(VI)$ ($E^\circ(Am^{3+}/AmO_2^{2+}) = 1.69$ V¹⁴) was observed. Pink crystals within large amounts of colorless salts formed with nearly quantitative removal of americium from solution. The X-ray crystal structure analysis[‡] revealed the crystalline product to be $K_3Am_3(IO_3)_{12} \cdot HIO_3$. This is the first actinide(III) iodate compound to be structurally characterized. It also represents a single crystal architecture of a f-element iodate compound that has not been observed with lanthanide elements.

The structure of **I** consists of a three-dimensional arrangement of $[AmO_8]$ units bridged by corner-sharing $[IO_3]$ pyramids. Four crystallographic unique IO_3^- anions possess one terminal oxygen atom with the remaining O atoms bonding in a monodentate fashion to one metal center, while also serving to bridge two americium atoms. Each iodine atom from the unique IO_3^- anions forms an independent trigonal pyramid with three close O atoms but deviating significantly from $3m$ point symmetry. The distortion of the $[I(2–5)O_3]$ pyramids is

reflected in a wide range of short I–O bonds between 1.75(3)–1.85(3) Å and O–I–O angles between 88(1)° and 101(1)°, still within the expected range for IO_3^- groups.¹⁵ In addition, there are three weak $I \cdots O$ interactions at longer distances of 2.67–3.01 Å as found in other transition metal and lanthanide iodates.^{2,15–18}

Three $[AmO_8]$ polyhedra and three $[I(5)O_3]$ groups are arranged to form irregular hexagonal channels that run along the c axis with about 4.6 Å in diameter (Fig. 1). The $[I(3)O_3]$ and $[I(4)O_3]$ units link the tubes together to form a three dimensional network, while $[I(2)O_3]$ groups add additional connection and stability to the channel periphery. The K atoms line the cavity with close contacts between the O(1) and K atoms of 2.40(4) Å. Additional interactions between K atoms and four O atoms from three of the four bridging IO_3 groups ($K \cdots O$

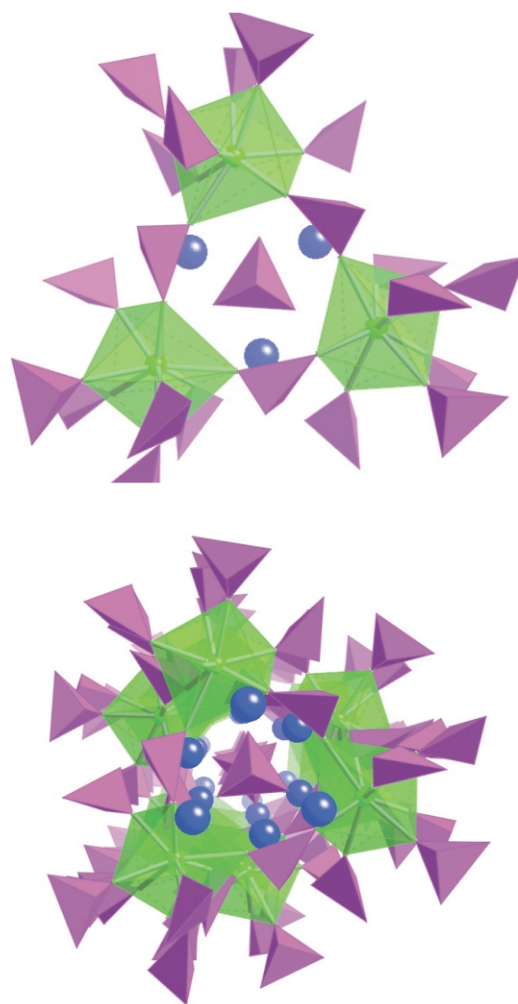


Fig. 1 Views of one segment (top) and along (bottom) the K^+ (blue)-lined channel of $K_3Am_3(IO_3)_{12} \cdot HIO_3$ formed along the c axis and built from alternating $[AmO_8]$ polyhedra (green) and three $[I(5)O_3]$ groups (purple) with neutral HIO_3 (purple) staggered in the channel center.

between 2.53 and 2.78 Å) indicate a complex three-dimensional bonding network. Neutral $\text{HI}(\text{O})_3$ molecules are staggered in the center of the void. The highly symmetrical HIO_3 pyramids contain three short $\text{I}(\text{O})_3$ bonds of 1.92(4) Å and an averaged $\text{O}-\text{I}-\text{O}$ angle of 88.2(2)°. Six additional oxygen atoms originating from the three $[\text{I}(\text{O})_3]$ units are less than 3.3 Å apart, *i.e.*, $\text{I}(\text{O})_3 \cdots \text{O}(11) = 2.86$ Å and $\text{I}(\text{O})_3 \cdots \text{O}(13) = 3.24$ Å. The oxygen–oxygen distances of 2.74 Å in the pyramidal plane of $[\text{I}(\text{O})_3]$ are within those found for the O–O distances in the bridging iodate groups (2.52–2.78 Å).

The americium $[\text{AmO}_8]$ polyhedra are comprised of eight $[\text{IO}_3]$ oxygen atoms to complete a distorted bicapped trigonal prismatic coordination (Fig. 2). The $\text{Am}-\text{O}$ distances range between 2.42(3) Å and 2.60(3) Å, which are similar to those observed in reported $\text{Ln}(\text{III})$ iodate compounds. In addition, one longer $\text{Am}-\text{O}(1)$ distance of 2.93(4) Å is observed for the weaker interaction of the Am atom with the nearest oxygen atom of the neutral HIO_3 molecule. It follows that all nine O atoms complete a distorted tricapped trigonal prismatic Am coordination sphere. The americium oxidation state was confirmed by the characteristic peak of $\text{Am}(\text{III})$ at about 503 nm in the diffuse reflectance spectrum of $\text{K}_3\text{Am}_3(\text{IO}_3)_{12}\cdot\text{HIO}_3$.

Only a few acidic lanthanide iodates have been prepared and structurally characterized.^{5,19} From X-ray powder diffraction data, Abrahams *et al.*⁵ determined that $\text{Pr}(\text{IO}_3)_3\cdot\text{HIO}_3$ crystallizes in the monoclinic space group $P2_1/a$ but no structural data are known. In the pyroelectric $3\text{La}(\text{IO}_3)_3\cdot\text{HIO}_3\cdot 7\text{H}_2\text{O}$, the La atoms are lying within a distorted bicapped trigonal (CN 8) or distorted tetragirdled trigonal prismatic (CN 10) arrangement of oxygen atoms.⁵ All $\text{La}-\text{O}$ distances are between 2.44 and 2.77 Å. Interestingly, the $\text{Ln}-\text{O}$ distances in the structurally characterized binary compounds $\text{Ln}(\text{IO}_3)_3\cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{Nd},^2 \text{Sm},^{16} \text{Gd},^1 \text{Lu}^{20}$) are slightly shorter ranging between 2.25 and 2.56 Å with eight-coordinate lanthanide atoms. In contrast, in the anhydrous compound $\text{Sc}(\text{IO}_3)_3$, the Sc atom is only six-coordinate in an approximately octahedral environment with expected short $\text{Sc}-\text{O}$ bonds between 2.08 and 2.11 Å.²⁰ In this compound the iodate groups form an octahedral hole with a 5.2 Å diameter that remains vacant.

The most interesting aspect of the compound derived from this work lies within the microporous channel framework and its potential application for cation exchange and catalysis. It still has to be shown if the trapped neutral molecules can be replaced by other molecules varying in size and shape and if the replacement of K cations along the channel exterior will affect the retention strength of the trapped molecules. Although to date this is the first architecture of its kind among the f-element iodates and this compound was derived by using the highly

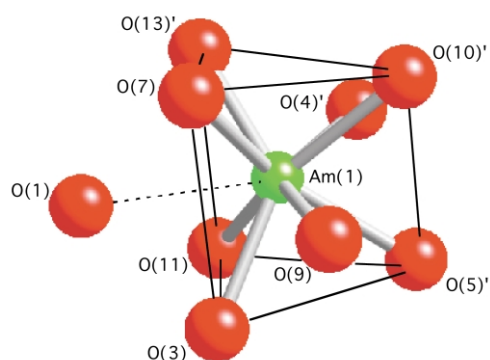


Fig. 2 Coordination environment of Am^{3+} in $\text{K}_3\text{Am}_3(\text{IO}_3)_{12}\cdot\text{HIO}_3$. Symmetry operations used to generate symmetry-equivalent atoms: $\text{O}(4)'$: $1 - y, 1 - x, -0.5 + z$. $\text{O}(5)'$: $-1/3 + x, 1/3 + x - y, -1/6 + x$. $\text{O}(10)'$: $4/3 - y, 2/3 + x - y, -1/3 + z$. $\text{O}(13)'$: $1 - x + y, 1 - x, z$.

radioactive americium, this structure offers the possibility of synthesizing new microporous lanthanide iodates with unique selectivity properties for ion-exchange, catalysis, and photochemical processes. From an academic perspective, structural characterization of transuranium complexes remains rare and only about a dozen single crystal structures of americium compounds are known. As demonstrated in $\text{K}_3\text{Am}_3(\text{IO}_3)_{12}\cdot\text{HIO}_3$, the rich coordination chemistry of americium may vary from its chemically analogue lanthanides and offers new insight into differences in bonding of 4f- and 5f-elements.

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Notes and references

† Hydrothermal reactions were performed in 10 mL PTFE-lined Parr autoclaves, which were loaded with 100 μL of $^{243}\text{Am}(\text{III})$ stock solution (0.12 M in 3 M HCl), 74 mg KIO_4 , 104 mg $\text{K}_2\text{S}_2\text{O}_8$ and 1 mL of deionized water. The vessels were heated at 180 °C for 3 days, then ramp cooled at 13 °C h^{-1} .

‡ *Crystal data* for $\text{KAm}(\text{IO}_3)_4\cdot\text{HIO}_3$: $\text{KHI}_5\text{O}_{15}\text{Am}$, $M = 3121.01$, trigonal, $R3c$, $a = b = 22.096(6)$, $c = 13.436(4)$ Å, $\gamma = 120^\circ$, $V = 5681(3)$ Å³, $T = 203$ K, $Z = 6$, $\lambda(\text{Mo}-\text{K}\alpha) = 1.6$ mm⁻¹, 8749 reflections measured, 1930 unique ($R_{\text{int}} = 0.0908$) which were used in all calculations. The final $wR(F^2)$ was 0.0695 (all data). CCDC 209298. See <http://www.rsc.org/suppdata/cc/b3/b304530g/> for crystallographic data in .cif or other electronic format.

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