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Synthesis and Characterization of *f*-Element Iodate Architectures with Variable Dimensionality, α- and β-$Am(IO_3)_3$

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Two americium(III) iodates, β-$Am(IO_3)_3$ (**I**) and α-$Am(IO_3)_3$ (**II**), have been prepared from the aqueous reactions of Am^{III} with KIO_4 at 180 °C and have been characterized by single-crystal X-ray diffraction, diffuse reflectance, and Raman spectroscopy. The α-form is consistent with the known structure type I of anhydrous lanthanide iodates. It consists of a three-dimensional network of pyramidal iodate groups bridging $[AmO_8]$ polyhedra where each of the americium ions are coordinated to eight iodate ligands. The β-form reveals a novel architecture that is unknown within the *f*-element iodate series. β-$Am(IO_3)_3$ exhibits a two-dimensional layered structure with nine-coordinate Am^{III} atoms. Three crystallographically unique pyramidal iodate anions link the Am atoms into corrugated sheets that interact with one another through intermolecular $IO_3^-\cdots IO_3^-$ interactions forming dimeric I_2O_{10} units. One of these anions utilizes all three O atoms to simultaneously bridge three Am atoms. The other two iodate ligands bridge only two Am atoms and have one terminal O atom. In contrast to α-$Am(IO_3)_3$, where the $[IO_3]$ ligands are solely corner-sharing with $[AmO_8]$ polyhedra, a complex arrangement of corner- and edge-sharing μ_2- and μ_3-$[IO_3]$ pyramids can be found in β-$Am(IO_3)_3$. Crystallographic data: **I**, monoclinic, space group $P2_1/n$, $a = 8.871(3)$ Å, $b = 5.933(2)$ Å, $c = 15.315(4)$ Å, $\beta = 96.948(4)°$, $V = 800.1(4)$ Å^3, $Z = 4$; **II**, monoclinic, space group $P2_1/c$, $a = 7.243(2)$ Å, $b = 8.538(3)$ Å, $c = 13.513(5)$ Å, $\beta = 100.123(6)°$, $V = 822.7(5)$ Å^3, $Z = 4$.

Introduction

The search for new materials with nonlinear optical and ferroelectric properties led to the synthesis of over 60 lanthanide(III) iodates.[1−11] However, only a handful of iodates have been prepared in sufficient crystal quality that allows a full structural characterization. On the basis of the analysis of IR, thermogravimetric, and X-ray diffraction data, 14 distinct structural families of the complexes $Ln(IO_3)_3\cdot xH_2O$ ($0 \leq x \leq 6$) have been suggested.[1] The largest structural diversity belongs to the anhydrous lanthanides, $Ln(IO_3)_3$, which were found to precipitate in six different structure types.[1,4,8−10] Only one structure type has been crystallographically characterized. Nearly all lanthanides crystallize in a centrosymmetric monoclinic structure with eight-coordinate lanthanide ions.[1,4,8] Type II polymorphs have a slightly increased unit cell volume and are obtained by precipitating anhydrous ytterbium and lutetium iodates from boiling HNO_3.[2] Four additional structure types for Ce, Pr, Nd, Sm (type III), La, Ce, Pr (type IV), Ce (type V), and La (type VI) are suggested to exist.[2] However, the polymorphs

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of types II−VI are reported to rapidly form the corresponding monohydrate[2] and are lacking complete structural characterization.

Despite early interest in 5*f* iodates for analytical and separation applications,[12,13] little quantitative information on the thermodynamic or structural properties of actinide(III) iodates is available to date. We expanded the structural variety of *f*-element iodates from the 4*f* series to the 5*f* series by the synthesis of a novel open-framework americium(III) iodate, $K_3Am_3(IO_3)_{12}\cdot HIO_3$.[14] Recently, the type I structure was also found in binary (α-form) americium(III)[3,15,20] and curium(III)[16] iodates. We report herein the synthesis and structural characterization of a new anhydrous americium(III) iodate, β-$Am(IO_3)_3$ (**I**), that exhibits a structure type unprecedented in the lanthanide series.

Experimental Section

KIO_4 (99.9%, Fisher) was used as received. A ^{243}Am(III) stock solution (0.1 M) was prepared by dissolution of $^{243}Am(OH)_3$ in 3 M HCl, followed by a subsequent precipitation with 1 M NaOH and dissolution of the washed precipitate in 0.5 M HCl. ***Warning!*** *Samples containing ^{243}Am or other transuranic elements must be handled with caution because of their high radioactivity and inhalation hazards.* Distilled and Millipore-filtered water with a resistance of 17.8 MΩ-cm was used in all reactions. The Raman spectra were collected on a Nicolet Magna 560 FT-IR/Raman spectrometer. Approximately 5-mg crystalline samples in doubly contained NMR tubes were used for Raman spectroscopy studies.

To prepare β-$Am(IO_3)_3$ (**I**), we reacted 0.19 mmol of KIO_4 (43.1 mg) with 1 mmol of $^{243}Am^{3+}$ in 1.6 mL of 0.1 M HCl in a polytetrafluoroethylene (PTFE)-lined autoclave at 180 °C for 72 h. The reaction vessel was ramp-cooled at 13 °C/h to room temperature. Light-orange crystals up to 0.2 mm in length were formed within a large amount of colorless salts, accompanied by nearly quantitative removal of Am from solution. The crystals were separated and analyzed by X-ray diffraction and Raman and diffuse-reflectance spectroscopies. X-ray crystal structure analysis revealed the light-orange product to be an anhydrous binary Am^{III} with a structure quite different from the well-described structure type I. Crystal data for β-$Am(IO_3)_3$: AmI_3O_9, $M = 767.70$, monoclinic, $P2_1/n$, $a = 8.871(3)$ Å, $b = 5.933(2)$ Å, $c = 15.315(4)$ Å, $\beta = 96.948(4)°$, $V = 800.1(4)$ Å^3, $Z = 4$, $T = 293$ K, R1 ($I > 2\sigma$) = 0.0307, and wR2 ($I > 2\sigma$) = 0.0786. The reflection data were collected on a Bruker P4/CCD using ϕ scans. The structure was solved using standard direct method techniques (SHELXS-97) and refined using full-matrix least squares based on F^2 (SHELXL-97). All atoms were refined anisotropically.

α-$Am(IO_3)_3$ (**II**) was obtained by reacting 0.18 mmol of KIO_4 (41.8 mg) with 0.9 mmol of $^{243}Am^{3+}$ in 2.1 mL of 0.1 M HCl in a PTFE-lined autoclave at 180 °C. After 72 h of reaction time, the autoclaves were ramp-cooled at 13 °C/h to room temperature. The product consisted of clear solutions over rectangular light-pink single crystals of up to 0.2 mm in length. The crystals were separated and analyzed by X-ray diffraction and Raman and diffuse-reflectance spectroscopies. Isostructural α-$Nd(IO_3)_3$ was prepared under analogous conditions.

Results and Discussion

Syntheses. The reaction of KIO_4 with $^{243}Am^{3+}$ in 0.1 M HCl at 180 °C produced either orange (**I**) or pink (**II**) crystals of anhydrous $Am(IO_3)_3$. As expected, the high oxidation potential of the periodate anion in acid [$E°(IO_4^-/IO_3^-) = 1.65$ V][13] is not sufficient to oxidize Am^{III} to Am^{VI} [$E°(Am^{3+}/AmO_2^{2+}) = 1.69$ V][17] but can oxidize chloride to chlorine [$E°(Cl^-/Cl_2) = 1.358$ V][13] or even hypochloric acid [$E°(Cl^-/HOCl) = 1.484$ V].[13] However, in 0.1 M HCl, HOCl is not stable and converts to Cl_2.

Structures. β-$Am(IO_3)_3$ (I). The type I anhydrous binary *f*-element iodates consist of a three-dimensional network of molecular $[MO_8]$ polyhedra that are solely connected by monodentate $[IO_3]^-$ groups. In contrast, the structure of **I** consists of corrugated $[Am(IO_3)_3]$ layers that are arranged along the crystallographic *b* axis (Figure 1).

Besides its lower dimensionality, the most significant structural differences from the type I *f*-element iodates are the higher coordination number of the Am ions and the more complex coordination modes of the iodate ligands in **I**. A combination of edge- and corner-sharing iodate groups permits the coordination of only seven ligands via nine O atoms to define a distorted tricapped trigonal prism around the Am center. The μ^2-$[I1O_3]$ group is bidentately coordinated to one Am atom via O1 and O7, with the terminal O8 atom pointing toward an adjacent layer. O7 is also coordinated to a second Am atom. The μ^3-$[I2O_3]$ group stabilizes the $[AmO_9]$ ribbon by sharing its three O atoms with three adjacent Am atoms. Through O4 and O5, the $[I2O_3]$ group is bidentately coordinated to one Am atom and linked through O5 and O9 to two other Am polyhedra. Thus, O5 and O7 are μ^3-O atoms shared between two Am atoms and one I atom. Both iodate atoms, I1 and I2, sustain a zigzag chain of $[AmO_9]$ polyhedra along the *b* axis. Selected bond lengths are given in Table 1.

The two-dimensionality of **I** is created by μ^2-$[I3O_3]$ groups that link two adjacent $[AmO_9]$ chains via O2 and O6 to form an extended layer along the *b* axis. The terminal O3 atom is arranged to point toward the neighboring $Am(IO_3)_3$ layer. All $[IO_3]$ groups exhibit the expected trigonal-pyramidal configuration of I^V with three short I−O bond distances between 1.81 and 1.84 Å. Each I atom has three further O atom neighbors at longer distances between 2.39 and 3.00 Å in a highly distorted octahedron. Interestingly, the I−O distance of 2.39 Å is distinctively short and has been only observed in δ-KIO_3−HIO_3,[18] while similar long-range I−O contacts have been found in many transition-metal and lanthanide iodates (ranging between 2.5 and 3.3 Å).[4,5,7,8,18−20]

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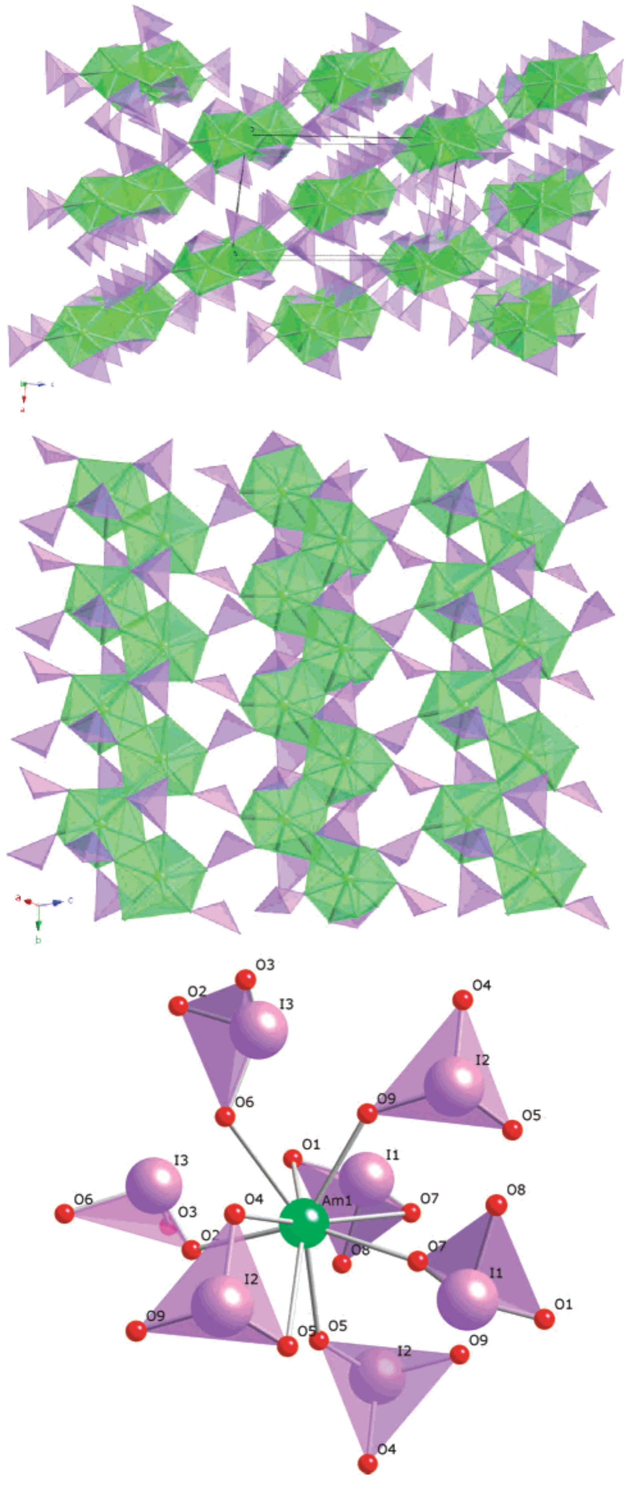

Figure 1. Polyhedral representation of the structural features in **I**. (top) Packing of the $Am(IO_3)_3$ layers along the *b* axis. (center) Illustration of $[I3O_3]$-connected zigzag chains of $[AmO_9]$ polyhedra in the $Am(IO_3)_3$ layer. (bottom) Mono- and bidentate coordination of IO_3^- ligands to the Am^{3+} ion in the $[AmO_9]$ polyhedra.

Table 1. Bond Lengths (Å) and Angles (deg) for β-$Am(IO_3)_3$

Am1−O1	2.530(8)	Am1−O6	2.482(8)
Am1−O2	2.459(8)	Am1−O7	2.676(8)
Am1−O4	2.483(8)	Am1−O7*	2.676(8)
Am1−O5	2.475(8)	Am1−O9	2.450(8)
Am1−O5′	2.823(8)	Am−Am	≥4.252
I−O	1.812(8)−1.839(8)	I1−O8′	2.390(8)
O−I−O	89.5(4)−100.5(4)		

The I2 and I3 octahedra are connected via O4 and O6, respectively, to form infinite chains of distorted $[IO_6]$ polyhedra along the *b* axis (figures illustrating the I2 and I3 chains are provided as Supporting Information). The $I1O_3$ groups, however, form $[I_2O_{10}]$ dimeric moieties with one short (1.839 Å) and one long (2.390 Å) distance between I1 and the μ^2-O8 atom (Figure 2). This close arrangement is unique within thus far reported *f*-element iodates and creates a pseudo-three-dimensional connection between the $Am(IO_3)_3$ layers.

The americium $[AmO_9]$ polyhedra are comprised of nine $[IO_3]$ oxygen atoms to complete a distorted tricapped trigonal-prismatic coordination (Figure 1, bottom). Eight Am−O distances range between 2.398(7) and 2.676(8) Å, which are similar to those observed in the type I americium(III) iodate compound (2.34−2.60 Å). In addition, one longer Am−O5 distance of 2.823(8) Å is observed, as was also found in the nine-coordination of Am in $K_3Am_3(IO_3)_{12}{\cdot}HIO_3$.[14] The triangular linkage of $[AmO_9]$ polyhedra by $[I1O_3]$ and $[I2O_3]$ groups creates close Am−Am distances of 4.252, 4.527, and 5.932 Å, which are significantly shorter than the Am−Am distances found in α-$Am(IO_3)_3$ (5.957, 6.057, and 7.243 Å)[15] and $K_3Am_3(IO_3)_{12}{\cdot}HIO_3$ (7.06 Å).[14]

α-$Am(IO_3)_3$ (II). In contrast to the β-form, the α-$Am(IO_3)_3$ consists of a three-dimensional network of molecular $[AmO_8]$ polyhedra that are solely connected by eight monodentate $[IO_3]$ groups (Figure 3). The eight Am−O distances range between 2.34(1) and 2.60(1) Å, which are slightly extended compared to the Ln^{III}−O distances in $Gd(IO_3)_3$[8] and $Tb(IO_3)_3$.[4]

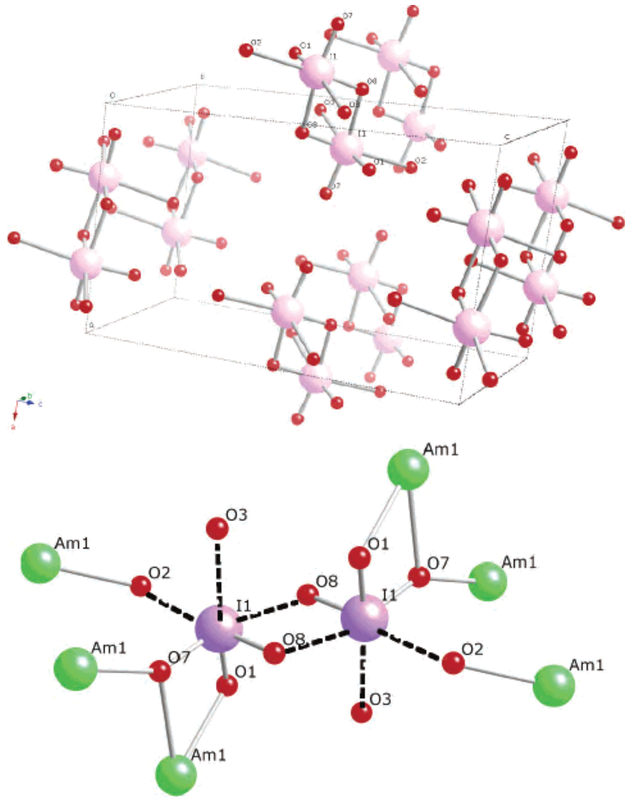

Figure 2. (top) View of the arrangement of $[I1O_3]$ groups from adjacent layers to form individual I_2O_{10} dimers in **I**. (bottom) Coordination environment of I1 within the I_2O_{10} dimers.

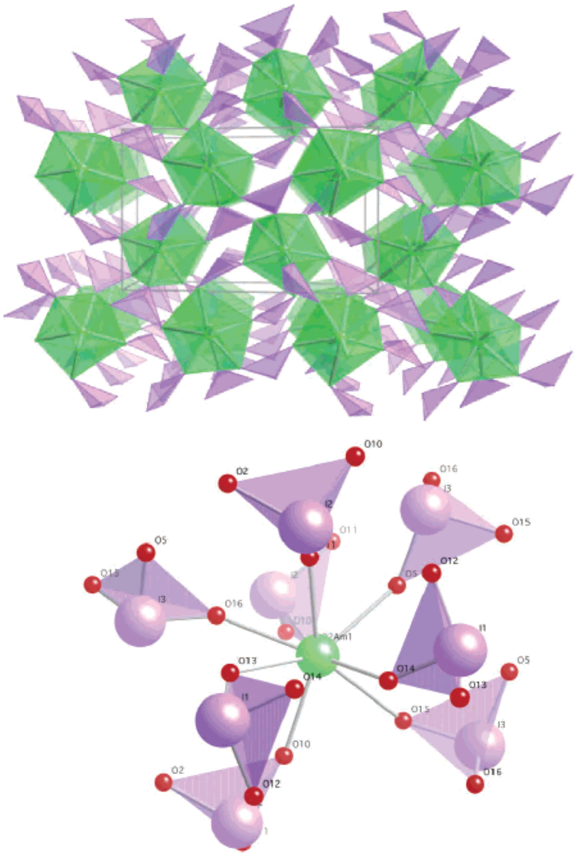

Figure 3. Polyhedral representation of the structural features in α-Am(IO_3)$_3$: (top) packing of the [AmO_8] polyhedra along the *a* axis; (bottom) monodentate coordination of IO_3^- ligands to the Am^{3+} ion.

The μ^3-[$I2O_3$] group with I2−O bond distances between 1.77 and 1.83 Å bridges three [AmO_8] polyhedra, forming zigzag layers in the *ab* plane, similar to those found in β-Am(IO_3)$_3$. Both [$I1O_3$] and [$I2O_3$] groups ensure a three-dimensional connection of the [AmO_8] polyhedra. The μ^3-[$I3O_3$] group also bridges three [AmO_8] polyhedra connecting Am atoms in the *bc* plane. The I−O distances in [$I3O_3$] range from 1.78(3) to 1.80(3) Å. The averaged I−O bond distance of 1.797 Å agrees well with the averaged I−O distance of 1.80 Å in Gd(IO_3)$_3$.[8] Each I atom shares two (I1−O = 3.02 and 3.04 Å) or three [I2 (I3)−O = 2.72−3.08 Å] additional O atoms from other [IO_3] groups, with the I−O distances significantly elongated compared to those in **I**.

Spectroscopy. We used conventional UV−vis−near-IR diffuse-reflectance spectroscopy to verify the oxidation state of the Am ion. The electronic absorbance spectrum for Am^{3+}(aq) is dominated by the well-known absorbance at 503 nm. This characteristic band is shifted slightly to about 508 nm with a shoulder at 516 nm in the diffuse-reflectance spectrum of Am(IO_3)$_3$, confirming the trivalent oxidation state of the Am ion. It is unclear why the absorbance shift of about 5 nm is less than shifts observed for other Am^{III} compounds with edge-sharing oxoanion ligands, such as $Am(CO_3)_3^{3-}$ (absorbance maximum at 509 nm). The Raman spectrum of the β-form is quite different from that of the α-form because of the inherently complex coordination modes of the iodate ligands. The most intense Raman frequencies of the β form (**I**; 737, 753, 784, and 814 cm^{-1}) can be assigned to the edge-sharing $I1O_3$ and $I2O_3$ groups. The less intense Raman frequencies at 765, 799, and 843 cm^{-1} can be assigned to $I3O_3$ and agree very well with the one symmetric and two asymmetric I−O stretching modes for the solely corner-sharing IO_3 ligands in α-Am(IO_3)$_3$ (761, 803, and 845 cm^{-1}),[15,20] α-Cm(IO_3)$_3$ (760, 804, and 846 cm^{-1}),[16] and in α-Nd(IO_3)$_3$ (764, 808, and 850 cm^{-1}).

Conclusion

Expanding the structural knowledge and spectroscopic characterization of transuranic compounds is a challenging task because of the difficult nature of handling highly radioactive material. The majority of synthetic studies of Am compounds resulted in the formation of rather amorphous or microcrystalline materials. Utilizing mild hydrothermal conditions enables us to approach the formation of crystalline materials and to unravel the largely unknown coordination chemistry of inorganic Am materials.

Despite the lower dimensionality, the cell volume of **I** (800.1 $Å^3$) is smaller than that of α-Am(IO_3)$_3$ (822.7 $Å^3$). The separation of the Am(IO_3)$_3$ layers in **I** increases the length of the *c* axis, while the connection of Am atoms via μ^3-O atoms enables a denser packing of [AmO_9] polyhedra along the *b* axis. Clearly, β-Am(IO_3)$_3$ is not representative of the structure type II, as suggested for Yb and Lu polymorphs.[1,9] It is apparent that this is the first architecture of its kind among the anhydrous binary f-element iodates with unexpected short Am−Am distances and multifaceted iodate binding modes. From an academic perspective, the rich coordination chemistry of Am surprisingly offered another novel architecture that is unknown from the chemically analogous lanthanides. However, it certainly will guide us in defining and further exploring the structural diversity of *f*-element iodates in the search for new materials for industrial applications.

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Supporting Information Available: Experimental (CIF) data and packing diagrams of $I2O_3$ and $I3O_3$ groups.[2] This material is available free of charge via the Internet at http://pubs.acs.org.

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