

First Structural Determination of a Trivalent Californium Compound with Oxygen Coordination

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Received September 28, 2005

Single crystals of Cf(IO₃)₃ (**1**) were synthesized by the hydrothermal reaction of CfCl₃ and H₅IO₆, and the structure was determined with single-crystal X-ray diffraction. This structural determination of **1** represents the first for a trivalent californium compound containing oxygen coordination. This compound has been further characterized with the use of Raman spectroscopy and emission spectroscopy. Crystallographic data: Cf(IO₃)₃, monoclinic, space group *P*2₁/*n*, *a* = 8.7994(10) Å, *b* = 5.9388(7) Å, *c* = 15.157(2) Å, β = 96.833(2)°, *V* = 786.43(16) Å³, *Z* = 4 (*T* = 295 K).

Californium is largely regarded as the most useful element in the second half of the actinide series; its main utility, specifically its short-lived ²⁵²Cf isotope, is used in the production of neutron sources, where it serves as the neutron emitter. This property has resulted in a variety of applications including neutron radiography, detection of explosives and land mines, treatment of cervical and brain cancers, and as a start-up source for nuclear reactors.^{1,2} Because of these many uses, reports on californium outnumber those of other transcurium elements. These reports primarily involve the nuclear aspects of californium as well as its applications; less has been reported about its fundamental structural chemistry.

The Transuranium Research Group at Oak Ridge National Laboratory has historically been focused on the basic solid-state properties of the transplutonium elements and, as such, has reported the only single-crystal diffraction studies on californium, for several trivalent halides³ and Cf(C₅H₅)₃.⁴

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However, the structural chemistry of californium compounds containing oxo ligands remains limited. Recently, it has been shown that microscale reactions can be carried out to prepare single crystals of both americium^{5,6} and curium⁷ iodates, and studies on these materials have extended the basic knowledge of the coordination chemistry, spectroscopic properties, and radiation resistance of 5f-element compounds. Iodate has been used to separate ²⁴⁹Cf from its parent ²⁴⁹Bk, using iodate precipitation from a homogeneous solution,⁸ which takes advantage of the ability to oxidize Bk³⁺ to Bk⁴⁺ in the presence of excess iodate, while retaining Cf³⁺. In those studies, the precipitated iodates were not structurally characterized. The work reported here was undertaken in an effort to provide fundamental knowledge about the structural environment of californium in compounds with oxo ligands.

Chemical studies with californium are complicated by its limited availability and the short half-lives of its isotopes. The studies reported here have made use of ²⁴⁹Cf (*t*_{1/2} = 351 years), the longest-lived isotope of californium that is available in quantities sufficient for chemical studies. The reaction of ~300 μg of Cf³⁺ with H₅IO₆⁹ resulted in the formation of pale-green, plate-shaped single crystals as the sole solid product. Raman spectroscopy was used initially to confirm the presence of iodate in the prepared compound.

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- (9) **1** was prepared by reacting aqueous CfCl₃ (100 μL, 0.013 M) and H₅IO₆ (2.5 mg, 11.0 μmol) in a 1-mL quartz tube. The tube was loaded, sealed, and subsequently heated at 180 °C for 70 h, after which time it was quenched to 22 °C. Pale-green, plate-shaped crystals of **1** were recovered as the sole crystalline product.

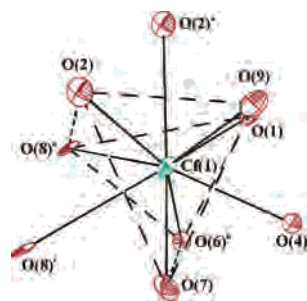


Figure 1. Coordination environment of Cf^{3+} in **1**. 50% displacement ellipsoids are shown. Dashed lines represent the edges of a distorted trigonal prism. Operations used to generate symmetry-equivalent atoms: (a) $1 - x, 1 - y, 2 - z$; (b) $1.5 - x, 0.5 + y, 1.5 - z$; (c) $x, 1 + y, z$.

Single-crystal X-ray diffraction experiments¹⁰ revealed the formula of this compound to be $\text{Cf}(\text{IO}_3)_3$ (**1**), representing the first single-crystal structural determination on a californium compound containing solely oxygen coordination. The emission of **1** shows sharp bands superimposed on a broad continuum extending from ~ 480 to 650 nm. The sharp bands are observed at 505.5 and 599.5 nm and correspond to $f-f$ transitions from the $J = 5/2$ and $7/2$ excited states to the ground $J = 15/2$ level of Cf^{3+} ,¹¹ and these therefore confirm the presence of trivalent californium in the structure.

1 crystallizes with the $\text{Bi}(\text{IO}_3)_3$ structure,¹² space group $P2_1/n$, a type that has not been seen previously in other actinide iodates, although very recently an isostructural analogue containing the larger Nd^{3+} cation has been reported.¹³ The structure of **1** is assembled from a combination of $[\text{CfO}_9]$ and $[\text{IO}_3]$ structural units. The coordination environment around the californium atom (Figure 1) is best described as a tricapped trigonal prism; however, significant distortions away from a regular prism are present. The six oxygen atoms that form the distorted trigonal prism and one capping oxygen atom, O(4), are significantly closer to the californium cation, with distances from 2.353(14) to 2.447(13) Å, than the remaining two capping oxygen atoms. These latter two oxygen positions, O(2)^a and O(8)^c, are situated 2.709(13) and 2.921(13) Å away from Cf(1), respectively. The structure contains three crystallographically unique IO_3^- anions, as determined by Raman and X-ray studies, with I–O bond distances and angles ranging from 1.801(15) to 1.825(14) Å and from 88.7(6) to 99.4(6)°, respectively. It is worth noting that the errors in the bond distances and angles

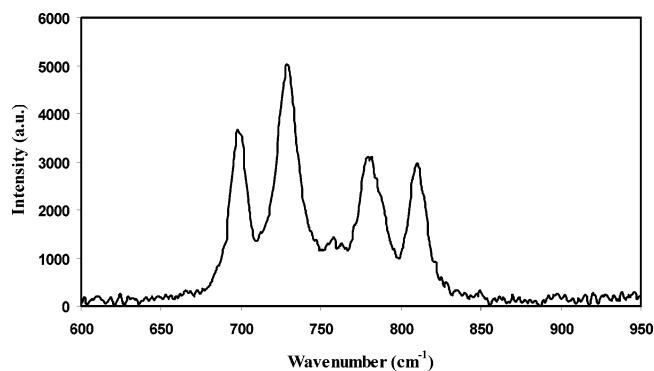


Figure 2. Raman spectrum of **1** covering the $\nu_{1-\text{O}}$ stretching region.

reported here for **1** are somewhat higher than those that often occur in similar materials, e.g., lanthanide or early actinide iodates. We attribute these effects to several factors, including the small crystal size, the required double containment procedure, and radiation effects.

One might expect that a trivalent californium iodate would be structurally similar to analogous trivalent americium or curium iodates,^{6,7} although this was not observed. All of the previously reported actinide(III) iodates contain three-dimensional structures, while **1** forms in a lower-dimensional, layered topology. The different structural topologies display distinctively different vibrational profiles.^{6,7} Hence, the Raman spectra were helpful as a rapid diagnostic tool to discern between these structural motifs. In the $\nu_{1-\text{O}}$ stretching region, **1** exhibits strong Raman bands at 697, 728, 782, and 810 cm^{-1} . The energy positions of these bands and the overall profile shown in Figure 2 are quite different from that reported for americium and curium iodates.^{6,7} A characteristic feature associated with the latter compounds is the appearance of a strong high-energy band at frequencies of > 840 cm^{-1} . This shift to higher energy, which was also observed in several lanthanide iodates¹⁴ that are isostructural with $\text{Am}(\text{IO}_3)_3$ and $\text{Cm}(\text{IO}_3)_3$, is significant when compared to either the ~ 770 - cm^{-1} average $\nu_{1-\text{O}}$ frequency reported for iodate salts of mono- and divalent cations¹⁵ or the ~ 785 - cm^{-1} frequency corresponding to the strongest symmetric stretching mode of actinyl iodates.¹⁶ In contrast, the highest $\nu_{1-\text{O}}$ stretching band in **1** is red-shifted by more than 30 cm^{-1} and appears at 810 cm^{-1} . An analogous red shift, albeit to a lesser degree, is also observed in trivalent lanthanide iodates¹⁴ with structural topologies similar to that of **1**. Hence, the Raman probe is adequately sensitive to distinguish between the two types of iodate structures.

As is the case with americium and curium iodates, the presence of three distinct iodate ions is also a feature in the **1** system. Moreover, the three unique IO_3^- ions in the structure show Raman bands at 728, 782, and 810 cm^{-1} , which indicates an absence of interionic vibronic coupling in the compound.¹⁷ The low-energy band at 697 cm^{-1} could

(10) Crystallographic data for **1**: pale-green plate, crystal dimensions 0.15 \times 0.05 \times 0.01 mm, monoclinic, $P2_1/n$, $Z = 4$, $a = 8.7994(10)$ Å, $b = 5.9388(7)$ Å, $c = 15.157(2)$ Å, $\beta = 96.833(2)^\circ$, $V = 786.43(16)$ Å³ ($T = 295$ K); Bruker APEX CCD diffractometer, $\theta_{\text{max}} = 51.34^\circ$, Mo $K\alpha$, $\lambda = 0.71073$ Å, $0.3^\circ \omega$ scans, 6261 reflections measured, 1493 independent reflections, all of which were included in the refinement. The data were corrected for Lorentz polarization effects and for absorption (SADABS), $\mu = 225.74$ cm^{-1} . The solution was solved by direct methods, anisotropic refinement of F^2 by full-matrix least squares with 114 parameters,²⁴ $R1 = 0.0401$ [$I > 2\sigma(I)$], $wR2 = 0.0694$.

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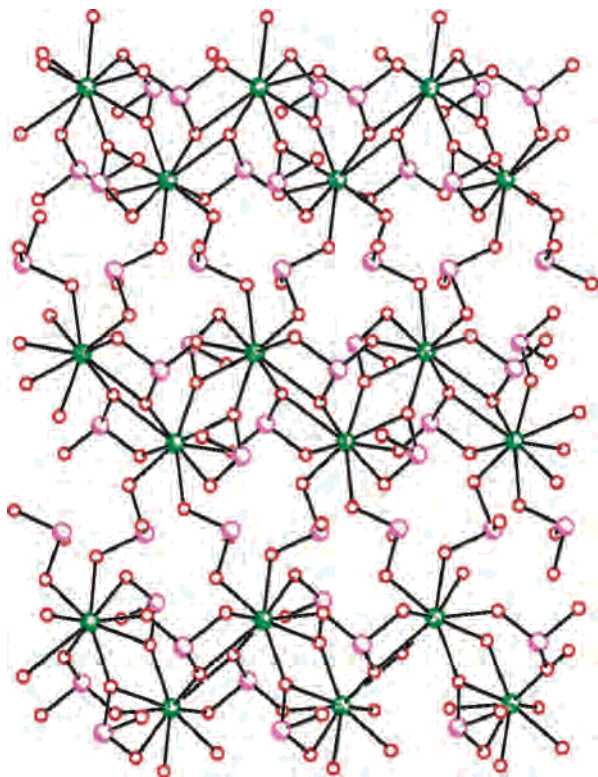


Figure 3. Ball-and-stick representation of a californium iodate layer found in **1**. Cf atoms are shown in green, I atoms are in purple, and O atoms are in red. The layer contains californium oxide chains built from edge-sharing $[\text{CfO}_9]$ polyhedra.

arise as a result of terminal I–O groups present in the structure or could be an asymmetric contribution of the 728-cm^{-1} band.

It is intriguing that **1** contains nine-coordinate $[\text{CfO}_9]$ polyhedra, while the reported curium iodate⁷ has $[\text{CmO}_8]$ distorted dodecahedral coordination. The smaller Cf^{3+} ion (0.949 \AA)¹⁸ would be expected to have equivalent or fewer inner-sphere atoms than the larger Cm^{3+} cation (0.979 \AA),¹⁸ on the basis of ionic radii arguments alone. An additional interesting feature in the structure of **1** is the presence of edge-sharing interactions between the $[\text{CfO}_9]$ polyhedra that lead to one-dimensional chains in the structure, shown in Figure 3, with alternating short–long Cf–Cf distances of 4.233 and 4.542 \AA . Therefore, this compound offers a unique opportunity to investigate the magnetism of the Cf^{3+} cations in a low-dimensional system. It would be of fundamental interest to search for the possibility of magnetic ordering or magnetic transitions in **1** and to study the role of the 5f electrons in the resultant magnetic behavior.

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The list of known compounds containing trivalent californium with solely oxo ligation is very short; only the binary oxides,¹⁹ an oxysulfate,²⁰ and the recently described pyrochlore, $\text{Cf}_2\text{Zr}_2\text{O}_7$,²¹ have been reported, while the face-centered-cubic CfO_2 ^{19d,22} and BaCfO_3 ²³ are the only examples with tetravalent californium. In the known compounds of Cf^{3+} , californium is assumed to contain coordination numbers of 4, 5, 6, and 8, analogous to isostructural compounds of other f elements. However, detailed structural information, including complete lists of oxygen positions, Cf–O bond distances, etc., is not known for any of these compounds, representing a major hindrance in fully understanding the structural chemistry of californium and not allowing informative comparisons of the californium coordination in **1** with these reported compounds.

Despite the use of the “long-lived” ^{249}Cf isotope, crystals of $^{249}\text{Cf}(\text{IO}_3)_3$ have been observed to lose crystallinity in a matter of weeks. A decrease in the Raman intensity of the iodate bands in **1**, as well as a gradual color change to a golden yellow, then orange, and finally to red, has also been observed. These effects are attributed to radiation damage associated with the α decay of ^{249}Cf .

Acknowledgment. Support for this work was provided by the Division of Chemical Sciences, Geosciences and Biosciences, OBES, U.S. Department of Energy, under Contract DE-AC05-00OR22725, with Oak Ridge National Laboratory (ORNL), managed by UT-Battelle, LLC, and by Grant DE-FG02-01ER15187 (to T.E.A.-S.). Dr. Radu Custelcean and Dr. Bruce Moyer are thanked for their generous allocation of X-ray diffractometer time. This research was supported in part by an appointment to the ORNL Postdoctoral Research Associates Program (to R.E.S.), administered jointly by the Oak Ridge Institute for Science and Education and ORNL.

Supporting Information Available: X-ray crystallographic file for **1** in CIF format and details of Raman and emission spectroscopic experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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