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Crystal Structures of the Trifluorides, Trichlorides, Tribromides, and Triiodides of Americium and Curium[1]

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Received February 22, 1965

The previously unreported lattice constants and crystal symmetries of the trifluoride, trichloride, tribromide, and triiodide of curium are given. Similar data for the isostructural trihalides of americium (except for the trifluoride) have been redetermined to a higher degree of precision. Correlations have been made between these actinide trihalides and the corresponding lanthanide trihalides. Curium trifluoride is hexagonal, LaF_3-type, space group $P6_3/mmc\text{-}D_{6h}^4$. Americium and curium trichlorides are hexagonal, UCl_3-type, space group $P6_3/m\text{-}C_{6h}^2$. The tribromides are orthorhombic, $PuBr_3$-type, space group $Cmcm\text{-}D_{2h}^{17}$. The triiodides are hexagonal, BiI_3-type, space group $R\bar{3}\text{-}C_{3i}^2$. When treated with hydrogen at elevated temperatures, no reduction of these trivalent americium or curium trihalides was observed.

Introduction

Since their discovery, there has been a continuing interest in the solid-state chemistry of the actinide elements. With the advent of macro (*i.e.*, multimilligram) amounts of the longer-lived isotopes, Am^{243} and Cm^{244}, it has been possible to carry out quite definitive experiments with these elements. More elegant purification schemes can be employed and the over-all handling difficulties are diminished due to the lower rate of γ emission. In general, such work confirmed the early tracer or microgram scale investigations. Occasionally, some of the early results could not be confirmed. In addition, the availability of modern computer programs for processing X-ray data has aided in the determination of more precise values for various crystal parameters.

Some values for the lattice constants of the trichloride, tribromide, and triiodide of americium were reported some time ago.[2] However, these results were based on work with Am^{241}, difficult to purify and to use for X-ray data because of its strong γ emission. The crystal properties of AmF_3 have been investigated more recently.[3] The purposes of the present work then were threefold: (1) to re-examine the trichloride, tribromide, and triiodide of americium using long-lived Am^{243}, (2) to prepare all the analogous trihalides of curium using Cm^{244}, and (3) to study the possible reduction of these trihalides by hydrogen at elevated temperatures.

Experimental

Unless otherwise stated, all chemicals were of A.R. grade. Americium as Am^{243} and curium as Cm^{244} were purified by conventional means.[4] Tank hydrogen was purified by passing it through a heated palladium alloy valve using a commercial apparatus.[5]

The insolubility of CmF_3 allowed its preparation directly from aqueous solution. Hydrofluoric acid was added to a solution of Cm(III); the resulting CmF_3 precipitate was washed with dilute HF, water, methyl alcohol, and acetone. The air-dried pellet of CmF_3 was treated with HF gas for 5 hr. at 400°. Hydrogen gas was mixed with HF gas for some experiments to study the effect of this reductant. X-Ray capillaries were loaded with the curium fluoride following such equilibrations.

The general technique used for preparing the other actinide halides has been described more fully elsewhere.[6] The trichloride starting material was formed by evaporation in air of an HCl solution of a 10:1 mole mixture of NH_4Cl and MCl_3. The ammonium chloride was sublimed from this material in a quartz capillary. The appropriate ammonium halide was then used to convert $AmCl_3$ or $CmCl_3$ to the desired halide at 400–450° in a stream of hydrogen. The conversion reaction yielding the desired halide salt was carried out in the same quartz capillary, from which a portion could be sealed for X-ray examination of the final product.

An attempt was made in all cases to reduce MX_3 to MX_2 by hydrogen at elevated temperatures. However, treatment of all of these trihalides with hydrogen (at *ca.* 3 p.s.i.g.) at temperatures up to 900° gave no evidence of reduction. Using samarium as a stand-in resulted in formation of samarium dihalides in good yield.

A Norelco X-ray unit was used with 114.6-mm. Debye–Scherrer cameras and Ilford "G" film. The X-ray films of the trihalide compounds were read three times and the results averaged.

A "proposed" powder pattern (using the information from ref. 2) was initially generated using the POWD[7] or ANIFAC[8] programs; this was used for preliminary indexing of lines. Lattice constants from the initial indexing were estimated by least-squares calculations using the MET-124[9] program. The constants were refined by two or three additional cycles between the programs until the over-all standard deviations and the individual variances of each line reached a satisfactory level.

Results and Discussion

In Table I are listed the values for the lattice constants of these halides. With the exception of the iodides, the actinide contraction is exhibited by all dimensions of the crystal lattices. The larger error for the iodides reflects the greater instability of the iodide compounds, possibly due to the disruptive effect of the α particles. Even using the relatively long-

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] W. H. Zachariasen, *Acta Cryst.*, **1**, 265 (1948).

[3] D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **75**, 4560 (1953).

[4] T. K. Keenan, *J. Inorg. Nucl. Chem.*, **20**, 185 (1961).

[5] Manufactured by The Milton Roy Co., Monterey Park, Calif.

[6] L. B. Asprey, T. K. Keenan, and F. H. Kruse, *Inorg. Chem.*, **3**, 1137 (1964).

[7] D. K. Smith, "A Fortran Program for Calculating X-ray Powder Diffractions," University of California Report UCRL-7196 (1963).

[8] A. C. Larson, Los Alamos Scientific Laboratory, unpublished work.

[9] M. H. Mueller and L. Heaton, "Determination of Lattice Parameters with the Aid of a Computer," Argonne National Laboratory Report ANL-6176 (1961).

lived Am^{243}, the iodide compound was more unstable than the other halides.

TABLE I

LATTICE CONSTANTS AND MOLECULAR VOLUMES FOR AMERICIUM AND CURIUM TRIHALIDES[a]

	a_0, Å.	b_0, Å.	c_0, Å.	Mol. vol., Å.^{3}
(A) Fluorides: hexagonal, LaF_3-type, space group $P6_3/mmc$-D_{6h}^4, $Z = 2$				
AmF_3	4.067 ± 0.001		7.225 ± 0.002	51.75
CmF_3	4.041 ± 0.001		7.179 ± 0.002	50.76
(B) Chlorides: hexagonal, UCl_3-type, space group $P6_3/m$-C_{6h}^2, $Z = 2$				
$AmCl_3$	7.390 ± 0.003		4.234 ± 0.002	100.1
$CmCl_3$	7.368 ± 0.006		4.228 ± 0.004	99.4
(C) Bromides: orthorhombic, $PuBr_3$-type, space group $Cmcm$-D_{2h}^{17}, $Z = 4$				
$AmBr_3$	4.064 ± 0.001	12.661 ± 0.006	9.144 ± 0.004	117.6
$CmBr_3$	4.048 ± 0.002	12.66 ± 0.01	9.124 ± 0.007	116.9
(D) Iodides: hexagonal, BiI_3-type, space group $R\bar{3}$-C_{3i}^2, $Z = 6$				
AmI_3	7.42 ± 0.04		20.55 ± 0.08	163.3
CmI_3	7.44 ± 0.09		20.4 ± 0.10	163.0

[a] Error limits are standard deviation.

No evidence could be obtained for an orthorhombic phase ($PuBr_3$-type) of AmI_3 as was reported some years ago.[2] Although a phase transition is known for the NdI_3 system,[10] orthorhombic AmI_3 was never obtained even though the conversion temperature was varied from 400 to 900°. Annealing of the hexagonal AmI_3 at various temperatures for as long as possible (considering the relative instability of the compound) showed no evidence for growth of an orthorhombic phase.

The failure of these compounds, particularly AmI_3, to form divalent salts is somewhat disappointing but does provide additional evidence for the stability of the trivalent state in the actinide series as compared to the lanthanides samarium and europium. Even with the thermodynamic advantage of flowing a stream of hydrogen over the triiodide, no evidence for reduction was obtained under conditions where SmI_2 was formed in good yield.

It will be of interest to observe whether the structure types exhibited by the americium and curium trihalides continue into the transcurium elements. Figure 1 shows a plot of molecular volume vs. atomic number for the known trivalent actinide trihalides. A change in structure type has already been observed for the bromides and iodides. In the lanthanide series, a change in structure type of all halides (including fluorides and chlorides) takes place at the approximate midpoint of the series.[2,6,11–14] In fact, terbium (the homolog of berkelium) trichloride exhibits a unique structure of its own[15] between the UCl_3 type of the first half of the lanthanides and the YCl_3 type of the second half. Since terbium is the transition point of the lanthanide chlorides, berkelium or californium may indeed show analogous behavior in the actinides.

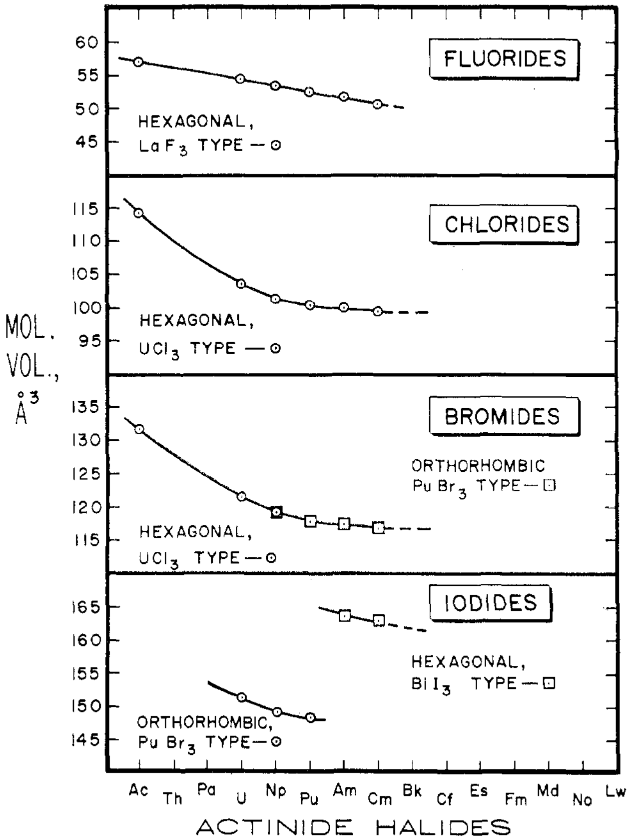

Figure 1.—Plot of molecular volume vs. atomic number for actinide halides.

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