

silica gel; 0.7 g. of 2,5-diphenylhexane was obtained, n_D^{20} 1.5385 (literature²³ n_D^{20} 1.5440).

Anal. Calcd. for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.36; H, 9.10.

(23) G. Dupont, *Compt. rend.*, **156**, 1623 (1913).

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COMMUNICATIONS TO THE EDITOR

EVIDENCE FOR QUADRIVALENT CURIUM. II. CURIUM TETRAFLUORIDE¹

Sir:

We wish to report the preparation and some properties of a new compound of curium, the tetrafluoride, in which curium has unequivocally the valence of four. Curium tetrafluoride was made by treatment of curium trifluoride with gaseous fluorine at elevated temperatures, and lattice constants have been measured for the monoclinic structure obtained.

Cm^{244} , an alpha emitter of 18.4 years² half-life, was used in this investigation and was a fraction of the same curium stock previously employed to prepare CmO_2 .³ The Cm^{242} content was only ~ 0.004 mass per cent.

TABLE I (Å. UNITS)

	a_0	b_0	c_0	β	Ionic radius (IV)
UF_4^5	12.82 ± 0.06	10.74 ± 0.05	8.41 ± 0.05	$126^\circ 10' \pm 30'$	0.93 ⁶
NpF_4^5	$12.70 \pm .06$	$10.64 \pm .05$	$8.33 \pm .05$	$126^\circ 10' \pm 30'$.92 ⁶
PuF_4^5	$12.62 \pm .06$	$10.57 \pm .05$	$8.28 \pm .05$	$126^\circ 10' \pm 30'$.90 ⁶
AmF_4^4	$12.49 \pm .06$	$10.47 \pm .05$	$8.20 \pm .05$	$126^\circ \pm 1^\circ$.89 ⁶
CmF_4	$12.45 \pm .06$	$10.45 \pm .05$	$8.16 \pm .05$	$126^\circ \pm 30'$.88

A 20–30 microgram pellet of air-dried curium trifluoride, precipitated from aqueous solution, was transferred into a sintered pre-fluorinated calcium fluoride crucible. The crucible was inserted into a nickel fluorinator⁴ and the fluorinator evacuated. Tank F_2 , which had been through a NaF trap to remove HF, was then used to fill the fluorinator to 1 atmosphere pressure. The fluorinator was heated to 400° over a one-half hour period, held at 400° for one hour, then at 300° for one hour, and finally cooled down to room temperature. A slow stream of fluorine was passed through the apparatus during this cycle. After the fluorine was displaced by helium gas, the curium compound was transferred to a Pyrex X-ray capillary and sealed off in air.

Initially, an exposure of 2 hours was made, using 114.6 mm. diameter camera with no-screen film and unfiltered copper radiation. This gave a good quality powder pattern of monoclinic CmF_4 . A 20-hour exposure of the same sample was made

(1) This work was sponsored by the U. S. Atomic Energy Commission. It is a joint project of the Argonne National Laboratory, the University of Chicago and the Los Alamos Scientific Laboratory.

(2) A. M. Friedman, A. L. Harkness, P. R. Fields, M. H. Studier, J. R. Huizenga, *Phys. Rev.*, **95**, 1501 (1954).

(3) L. B. Asprey, F. H. Ellinger, S. Fried and W. H. Zachariasen, *THIS JOURNAL*, **77**, 1707 (1955).

(4) L. B. Asprey, *ibid.*, **76**, 2019 (1954).

subsequently using the same camera, Eastman Type A film, and filtered copper radiation. The longer exposure gave a picture of generally poorer quality, due probably to radiation damage to the crystals.

In Table I are listed X-ray data for several tetrafluorides and their lattice constants in Å. units. All of these show the same monoclinic structure found for CmF_4 .

Under microscopic examination by Eugene Staritzky of this Laboratory, the curium tetrafluoride appeared as light greenish-tan aggregates with a crystal size of a few tenths of a micron. The mean refractive index was 1.62. The absorption spectrum, as viewed through a Zeiss prism spectrometer eyepiece, showed a single very

strong, narrow band at 452 millimicrons, which is not shown by $Cm(III)$.

The existence of the compound CmF_4 illustrates the difficulties of deriving chemical conclusions from the electronic configurations assigned to the "actinide elements."⁷ It is clear, and perhaps surprisingly so, that the stability of the $5f^7$ half-filled shell in curium is markedly less than the stability of the corresponding $4f^7$ half-filled shell in gadolinium. The present results re-enforce earlier observations that detailed predictions of the valence states of these elements may not be properly made on the basis of analogy to the lanthanide series.⁸

(5) W. H. Zachariasen, *Acta Cryst.*, **2**, 388 (1949).

(6) G. T. Seaborg, "The Actinide Elements," Chap. 18, National Nuclear Energy Series, IV-14A, McGraw-Hill Book Co., New York, N. Y., 1954.

(7) *Ibid.*, Chapter 17.

(8) R. A. Penneman and L. B. Asprey, Proc. International Conference on Peaceful Uses of Atomic Energy, Geneva, 1955, **7**, 355–362 (Pub. 1956).

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