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THE PREPARATION AND CRYSTAL STRUCTURE OF SOME BERKELIUM COMPOUNDS[†]

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The availability of microgram quantities of the trans-curium element ^{249}Bk has made it possible to study some aspects of the chemistry of this element.

A quantity of Bk was obtained by cycling 100 mg of ^{244}Cm in a nuclear reactor and isolating it from this irradiated material between cycles. More Bk was obtained from the U. S. Atomic Energy Commission. This letter reports on the preparation and crystal structure of $BkBr_3$, BkOBr, BkI_3, BkOI, and Bk_2S_3.

After preliminary gross separations from ^{244}Cm, fission products, etc., the Bk was purified using the following steps: extraction chromatography using a quaternary amine (Aliquat 336 nitrate[*]) (for Ce removal), solvent extraction using di-2-ethyl-hexyl ortho phosphoric acid, 2-ethyl-hexyl phenyl phosphonic acid (1), and a cation exchange column. Great care was used to prevent contamination of reagents and glassware. To check on the purity of the Bk, a sample was submitted for spectrographic analysis. No cerium (ordinarily the most ubiquitous impurity) could be detected; only traces of Al and Ca could be seen.

[†] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[*] General Mills, Inc., Kankakee, Illinois.

Compound preparations were carried out on the 1 to 3 microgram scale with the chemistry performed in quartz capillaries which also served as the container for the x-ray analysis.

All identifications were carried out by means of x-ray diffraction methods. Powder diffraction patterns were obtained with a Norelco camera (114.59 mm diameter) and CuKα radiation ($\lambda K\bar{\alpha}$ = 1.5417A). Some reduction in background arising from β-radiation was achieved by placing a 2 mil aluminum foil over the film.

Berkelium hydroxide was precipitated as a light green gelatinous mass in a quartz (100 λ) microcone by allowing a dilute HCl solution of Bk to stand in an atmosphere of NH_3. After centrifuging and washing cycles the Bk hydroxide was dried to form several fragments in the bottom of the cone. It was possible to fish a fragment from the cone with a tungsten needle and introduce it into a quartz capillary (0.10 mm diam., 0.010 mm wall thickness and about 15 cm long). The capillary was waxed to a 19/38 ground joint, attached to a vacuum system and evacuated. The vacuum system was arranged in such a manner that manipulation of various stopcocks made it possible to admit various gases or gas mixtures on to the Bk hydroxide. The end of the capillary was inserted into holes in a nickel bar which could be heated electrically up to temperatures of 1100°C.

$\underline{BkBr_3}$--Berkelium tribromide was prepared by the action of HBr gas (from liquid HBr) on Bk oxide at 800°C. The $BkBr_3$ sublimed out of the hot portion of the furnace and condensed as a yellow-green zone in the cool portion of the capillary. The tube was sealed off to a length of about 1 - 1.5 cm and submitted for x-ray diffraction analysis.

The $BkBr_3$ was produced as the β- or orthorhombic modification. Approximate cell dimensions are: a = 12.6A, b = 4.1A, and c = 9.1A. The space group for this structure type is reported as Ccmm-D_{2h}^{17} with 4 molecules in the cell (2). The pattern showed line splitting, and, in order to determine if this was unique to $BkBr_3$, preparations of the Cm, Pu, and Nd tri-bromides were re-examined. All show the splitting in a pronounced manner. The multiplicity of lines may indicate a change in cell dimensions or a change in symmetry. Although the general features of the diffraction patterns are similar, there are notable differences in line positions and intensities between these various patterns. This matter is being investigated further.

BkOBr--Berkelium oxybromide was prepared by partial hydrolysis of $BkBr_3$. A sample of $BkBr_3$ was opened and exposed to an atmosphere of H_2O - HBr from a saturated HBr solution at 450° for several hours. The capillary containing the white deposit was sealed off for x-ray analysis.

The pattern indicates that BkOBr belongs to the tetragonal PbFCl-type. The cell dimensions are: a = 3.95A, c = 8.1A. A CmOBr preparation, also isostructural, shows slightly larger dimensions.

BkI_3 - BkOI--Berkelium triiodide was formed by action of HI gas at 650°C on Bk oxide. A yellow volatile material sublimed out which was shown to be BkI_3. The remaining white non-volatile fraction was shown to be the berkelium oxyiodide, BkOI.

This compound, BkI_3 is isostructural with BiI_3, for which the space group is $R\overline{3}$ - C_{3i}^{2}. Approximate dimensions for the cell based on hexagonal axes are: a = 7.5A and c = 20.4A.

The cell of BkOI is tetragonal, with a PbFCl structure. The cell dimensions are close to those of PuOI (3), with a = 4.0A and c = 7.5A, approximately.

$\underline{Bk_2S_3}$--Action of a mixture of H_2S - CS_2 vapors on Bk oxide at 1100°C yielded the brownish black sulfide, Bk_2S_3.

The sulfide is isostructural with Ce_2S_3. Cell dimensions for the cubic cell are: a = 8.44A. A sample of Cm_2S_3 also has cell dimensions a = 8.44A. The cell constants are quite similar to those of Pu_2S_3 and Am_2S_3 (4).

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