former are probably obscured by the latter.

The lowest energy absorption of $[MoOCl_4]^-$ with an origin at ca. 15.0×10^3 cm^{-1} is assigned to the $d_{xy} \rightarrow d_{xz,yz}$ ($2b_2 \rightarrow 7e$) transition calculated to occur at 15.6×10^3 cm^{-1} (Table VI). The experimental information obtained for this transition[11] is fully consistent with this assignment. On the basis of these calculations, the second and third bands in the spectrum, with origins at ca. 21.6 and 26.4×10^3 cm^{-1} and intensities in *xy* polarization greater than *z*, are assigned to the chlorine to molybdenum charge-transfer ($^2B_2 \rightarrow {}^2E$) transitions $6e \rightarrow 2b_2$ and $5e \rightarrow 2b_2$, respectively. The intense absorptions to higher energy are also assigned to such transitions. The symmetry-forbidden $d_{xy} \rightarrow d_{x^2-y^2}$ and $\rightarrow d_{z^2}$ ($2b_2 \rightarrow 4b_1$ and $\rightarrow 8a_1$) transitions, calculated to occur in the same energy range as these symmetry-allowed chlorine to molybdenum charge-transfer transitions, are presumed to be obscured by them.

The situation for $[MoOBr_4]^-$ resembles that for $[CrOCl_4]^-$ and is further complicated by the rather poor spectral resolution so far achieved[34] for the former complex. The lowest energy band in the spectrum of $[MoOBr_4(H_2O)]^-$ is more intense in *xy* than in *z* polarization and shows some evidence for coupling with a vibrational mode of frequency ca. 900 cm^{-1}. Thus, in comparison to $[MoOCl_4]^-$, this band is assigned to the $d_{xy} \rightarrow d_{xz,yz}$ ($2b_2 \rightarrow 7e$) transition which is calculated to have an energy of 15.0×10^3 cm^{-1}. The lowest energy transition is calculated to be the $6e \rightarrow 2b_2$ bromine → molybdenum charge-transfer transition, and therefore the calculations are assumed to significantly underestimate the energies of these excitations. A series of reasonably intense bands dominate the visible and UV absorption spectrum of $[MoOBr_4(H_2O)]^-$ and are generally more intense in *xy* than in *z* polarization, and a tentative assignment of the lower energy transitions is included in Table VII. Once more, it is considered that the two symmetry-forbidden d → d transitions are not evident in the absorption spectrum.

Despite the simplistic approach adopted in these calculations, for example the neglect of spin–orbit coupling, multiplet structure and many-electron effects, they have provided a reasonable basis for the interpretation of the electronic spectra of $[CrOCl_4]^-$, $[MoOCl_4]^-$, and $[MoOBr_4]^-$. The principal debate concerning the assignments of these spectra is the location of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition and/or the origin of the second absorption band. The theoretical results described here clearly suggest that this band is due to a halogen → metal charge-transfer transition, in contrast to the oxygen → metal transition suggested by the ab initio calculation for $[CrOCl_4]^-$. The majority of the arguments advanced[10,11] in favor of the latter assignment vs. the $d_{xy} \rightarrow d_{x^2-y^2}$ promotion for the second band in the absorption spectra of $[CrOCl_4]^-$ and $[MoOCl_4]^-$ are equally applicable to the halogen → metal transition. However, it is recognized that more experimental and theoretical work is needed before the interpretation of the electronic spectrum of the oxotetrahalometalates of Cr(V) and Mo(V) can be regarded as settled.

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Registry No. $[CrOCl_4]^-$, 16737-27-2; $[MoOCl_4]^-$, 14874-89-6; $[MoOBr_4]^-$, 14874-88-5.

Supplementary Material Available: Tables II–IV (ground-state electronic structures of the complexes) (3 pages). Ordering information is given on any current masthead page.

Contribution from the Transuranium Research Laboratory, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830,
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Chemical Consequences of Radioactive Decay. 1. Study of ^{249}Cf Ingrowth into Crystalline $^{249}BkBr_3$: A New Crystalline Phase of $CfBr_3$[1]

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Spectrophotometric and X-ray powder diffraction methods have been applied to a study of the ingrowth of californium-249 by β^- decay of berkelium-249 in crystalline $^{249}BkBr_3$. It was found that the Cf daughter grows in with the same oxidation state and crystal structure as the parent. Thus, six-coordinate $BkBr_3$ ($AlCl_3$-type monoclinic structure) generates six-coordinate $CfBr_3$, and eight-coordinate $BkBr_3$ ($PuBr_3$-type orthorhombic structure) generates eight-coordinate $CfBr_3$, a previously unknown form of $CfBr_3$. It was also found that the daughter Cf(III) in the $BkBr_3$ parent compound can be reduced to Cf(II) by treatment with H_2, as it can in pure $CfBr_3$.

Introduction

The solid-state compounds of elements in the decay chain

$$^{253}\mathrm{Es} \xrightarrow[20.5\ \text{days}]{\alpha} {}^{249}\mathrm{Bk} \xrightarrow[314\ \text{days}]{\beta^-} {}^{249}\mathrm{Cf}\ \left(\xrightarrow[352\ \text{years}]{\alpha} {}^{245}\mathrm{Cm} \right)$$

provide a unique sample system in which a number of interesting and basic phenomena of nature can be examined. Transformation in the Es, Bk, Cf portion of this series occurs in a reasonable length of time, and studies of compounds of these elements are presently under way, utilizing both spectrophotometric and X-ray powder diffraction techniques to gain insight into the chemical consequences of α and β decay as these processes pertain to the generation of progeny compounds in the solid state. As an introduction to this broad area of study, we focus attention, first, on the consequences of β^- decay by a study of the behavior of Cf as it grows into a Bk compound.

Although other investigations have addressed the general area of chemical consequences of radioactive decay, such

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(2) (a) Analytical Chemistry Division, Oak Ridge National Laboratory. (b) Transuranium Research Laboratory, Oak Ridge National Laboratory. (c) University of Tennessee and Transuranium Research Laboratory, Oak Ridge National Laboratory.

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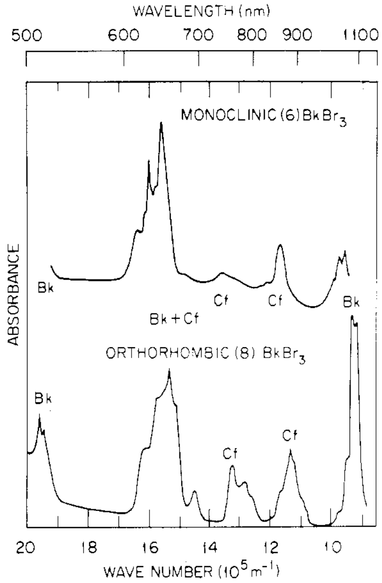

Figure 1. Absorption spectra of monoclinic and orthorhombic $^{249}BkBr_3$ showing daughter Cf absorption peaks.

studies have mainly involved dissolution steps and/or trace element techniques rather than a strictly bulk-phase study. An excellent summary of the previous work in this area has recently been published.[3a] In a study more nearly related to the present work, bulk-phase $^{147}Pm(OH)_3$ has been studied over a 1 half-life period (2.6 years) by X-ray and electron diffraction.[3b]

Both spectrophotometric and X-ray powder diffraction techniques were applied to follow the ingrowth of californium-249 into $^{249}BkBr_3$ over a period of 3 half-lives of berkelium-249. Experimental results demonstrating the independent nature of the chemical activity of the ingrown $CfBr_3$ are also described herein.

Experimental Section

With use of methods previously described,[3c] samples of monoclinic and orthorhombic $BkBr_3$,[4] monoclinic $CfBr_3$,[5] and tetragonal $CfBr_2$[6] were prepared from the respective oxides, in 2–10-μg sized samples, and characterized by absorption spectrophotometry and X-ray powder diffraction.[3c] The X-ray results were interpreted by comparison with published data.[4,5] All absorption spectra and X-ray diffraction patterns were obtained from the samples at room temperature without thermal annealing. A sample of monoclinic $BkBr_3$, 1 month old which contained about 4% $CfBr_3$, was treated with H_2[3c] and examined spectrophotometrically. Spectra of $BkBr_3$ compounds were obtained periodically for a time period of over 3 years. Two samples of aged berkelium oxide, which contained 45 and 58% californium daughter, respectively, were also converted to bromides; attempts were made to convert these mixed (Bk,Cf) tribromides to the orthorhombic form of $BkBr_3$ by the procedure established in an earlier study of that compound.[4] For a final experiment in this series, the thermal stability of a 3 year old sample of orthorhombic $BkBr_3$, containing 90% californium daughter, was investigated by heating the tribromide to a temperature of 360 °C while monitoring a Cf(III) absorption peak at 13×10^5 m^{-1} (773 nm).

Results and Discussion

Oxidation State of Daughter Californium-249 in $^{249}BkBr_3$. Portions of the spectra of orthorhombic and monoclinic $BkBr_3$ have been previously reported,[4] and it was pointed out that absorption peaks possibly due to daughter $CfBr_3$, present in concentrations as low as approximately 0.4%, could be observed in the spectral regions of 11 and 13×10^5 m^{-1}. Spectra of both forms of $BkBr_3$, containing 6% californium, are given in Figure 1. Note that two different sets of spectral peaks attributable to californium are seen.

A monoclinic, six-coordinate form of $CfBr_3$ has been reported.[5] Its absorption spectrum in the wavelength region of $(10–15) \times 10^5$ m^{-1} consists of a pronounced asymmetric peak in the region of 11×10^5 m^{-1} and a much weaker absorbance at 13×10^5 m^{-1}.[7] The spectrum of 6% californium in monoclinic $BkBr_3$ (Figure 1) is identical with that described earlier.[7] The spectrum of californium which was observed growing into the orthorhombic, eight-coordinate form of $BkBr_3$ exhibits a symmetrical peak near 11×10^5 m^{-1} and an almost equally intense peak at 13×10^5 m^{-1}. The fact that spectra of californium in both forms of $BkBr_3$, although differing in relative intensity, seem to arise from identical f–f manifolds and the fact that one spectrum has been identified as arising from $CfBr_3$ strongly suggest that the spectra of californium in both crystal forms of $BkBr_3$ arise from Cf(III). After a period of 3 years, 90% californium ingrowth, it has also been confirmed by both X-ray powder diffraction and absorption spectral analyses that $CfBr_3$, hence Cf(III), was the major constituent of the samples that were originally $BkBr_3$.

These results which show no oxidation state change between the parent and the daughter species produced by β^- decay are in contrast with those reporting the preparation of Cm(VI) from Am(V) by β^- decay.[8] The proof for the existence of Cm(VI) in that work is quite indirect; in our work the proof for no change in oxidation state is direct and is the result of in situ, bulk-phase absorption spectrophotometric and X-ray powder diffraction analyses. If one writes an atomic description of the β^- decay of Bk(III), one might write the expression

$$^{249}_{97}\mathrm{Bk}^{3+} \rightarrow {}^{249}_{98}\mathrm{Cf}^{4+} + {}^{0}_{-1}\mathrm{e}^{1-}$$

During the course of this study, no spectral evidence for Cf(IV) was seen (the spectrum of Cf(IV) is known from a study of CfF_4[9]). Since our results show that only Cf(III) is formed, we conclude that under our experimental conditions the end result of the β^- decay of Bk(III) is Cf(III).

Structure of Daughter Californium-249 in $^{249}BkBr_3$. As pointed out in the previous section, absorption peaks characteristic of Cf(III) in the region of $(10–15) \times 10^5$ m^{-1} grow into the spectrum of $BkBr_3$ as a function of time. The absorption peaks seen growing into the spectrum of orthorhombic, eight-coordinate $BkBr_3$ consisted of peaks in the same spectral region as those attributable to six-coordinate $CfBr_3$ but of altered intensity; see Figure 1. It could be reasoned that this latter, and somewhat more complex, spectrum arises from Cf(III) in some lower symmetry site than the essentially O_h site that californium has in monoclinic $CfBr_3$. After 4 months, X-ray diffraction studies of the then aged $BkBr_3$ samples could not confirm what seemed to be observed spectrally, i.e., that $CfBr_3$ was growing into $BkBr_3$ in either of two different forms that were dependent on the structure of the parent $BkBr_3$. Near the end of a year's time, the spectral peaks attributed

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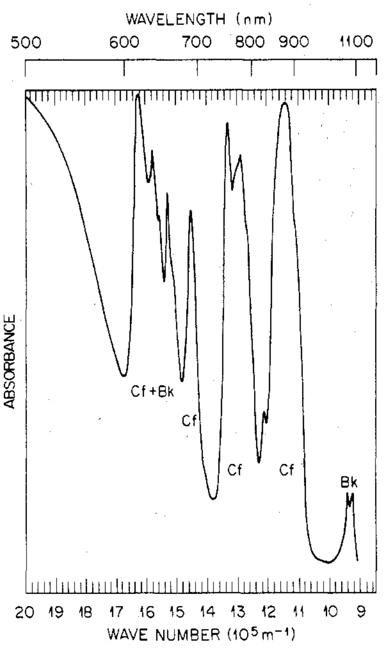

Figure 2. Absorption spectrum of orthorhombic ^{249}BkBr$_3$ after 1 year. Absorption peaks due to Cf(III) are identified.

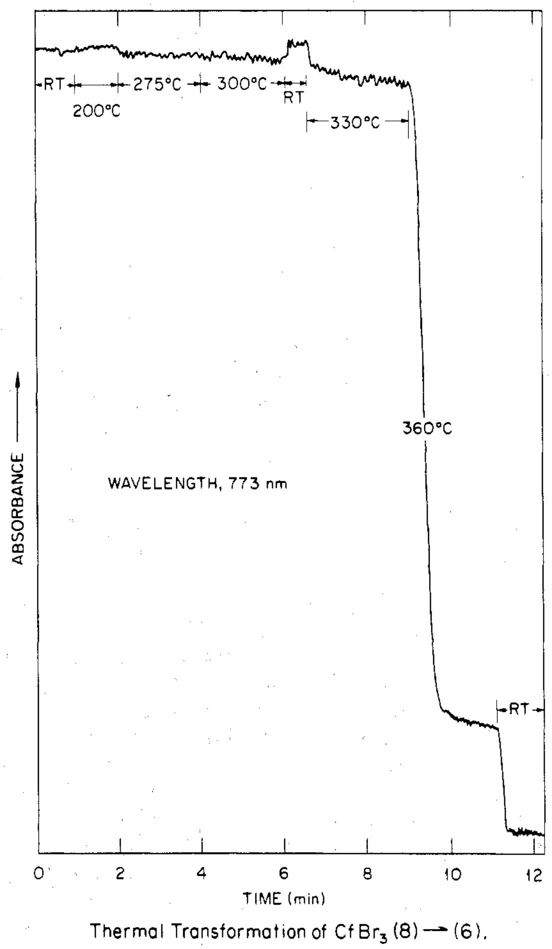

Figure 3. Effect of temperature on the absorbance of a peak (773 nm) associated with orthorhombic CfBr$_3$.

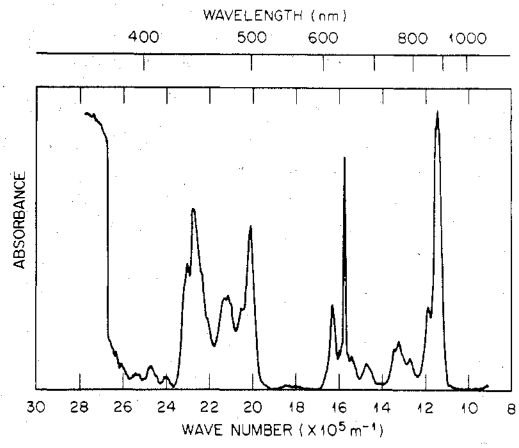

Figure 4. Absorption spectrum of monoclinic ^{249}CfBr$_3$ which resulted from the heating of orthorhombic CfBr$_3$. This latter form of CfBr$_3$ was generated by β^- decay of orthorhombic ^{249}BkBr$_3$.

to Cf(III) of lower symmetry continued to increase, and it was tempting to ascribe this spectrum to a new eight-coordinate form of CfBr$_3$.

Mixed (Bk,Cf)Br$_3$ samples were also prepared by standard HBr treatment[3c] of BkO$_2$ samples of various ages, which contained ingrown californium. With both the freshly separated BkO$_2$ and BkO$_2$ samples aged up to 1 month, it was found possible to prepare and transform the tribromide product into either of the known six- or eight-coordinate forms. With oxide samples approximately 1 year old (two samples containing 45 and 58% californium daughter, respectively), it was only possible to prepare the six-coordinate, monoclinic (Bk,Cf)Br$_3$. Attempts to synthesize or transform this product into the orthorhombic eight-coordinate structure failed, as evidenced by spectral and X-ray powder diffraction analyses. After 3 half-lives of berkelium-249, the spectrum of Cf(III) growing into the monoclinic BkBr$_3$ was as had been observed before,[7] a spectrum ascribable to six-coordinate monoclinic CfBr$_3$; the heretofore unknown spectrum of Cf(III) in orthorhombic BkBr$_3$ is shown in Figure 2.

Two old orthorhombic BkBr$_3$ samples were subjected to analysis by X-ray powder diffraction. There had been no thermal treatment (annealing) of the samples since their synthesis. From one sample containing 92% Cf, a weak diffraction pattern of 17 lines was observed, consistent with a PuBr$_3$-type orthorhombic structure, a new modification of CfBr$_3$. A second sample of BkBr$_3$ which initially exhibited the orthorhombic, eight-coordinate structure was also analyzed by X-ray powder diffraction when its daughter Cf content was 87%. Again, the 25 observed lines in the powder pattern were consistent with the PuBr$_3$-type orthorhombic structure. On the basis of these X-ray diffraction results, it is proven that the spectrum of Cf(III) shown in Figure 2 is that of Cf(III) in eight-coordinate orthorhombic CfBr$_3$, a new structural form of CfBr$_3$.

At 1050 days after the purification of berkelium-249 and its chemical conversion to BkBr$_3$, a sample of the orthorhombic product containing 90% CfBr$_3$ was heated in a stepwise fashion. During this heating the absorbance of the pronounced peak near 13 × 10^5 m^{-1}, attributable to eight-coordinate Cf(III), was monitored. The results are shown in Figure 3. Note that at the lower temperatures no significant change in absorbance of the monitored peak is seen. At a temperature of approximately 330 °C, a change in absorbance began to occur, and at 360 °C the absorbance of that peak decreased rapidly. (The further decrease in absorbance on cooling the sample to room temperature can be attributed to an optical artifact of movement of the sample on cooling.) The spectrum of this sample, which is essentially CfBr$_3$, after the heat treatment is shown in Figure 4 and is identical with that of six-coordinate monoclinic CfBr$_3$.[7] X-ray examination of this sample, when its californium daughter content was 91% and then again later at 94%, confirmed the transformation to the

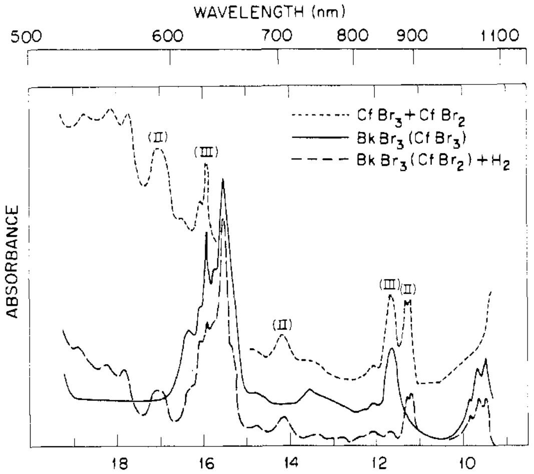

Figure 5. Absorption spectra of several californium and berkelium bromides showing the effect of H_2 reduction.

known $AlCl_3$-type monoclinic structure. In both cases the diffraction pattern exhibited about 20 lines.

The new orthorhombic $CfBr_3$ that was formed by nature via β^- decay of Bk in orthorhombic $BkBr_3$ was not thermally stable and was converted to the normal monoclinic form of $CfBr_3$ on heating. The observed temperature for the transformation of orthorhombic $CfBr_3$ to monoclinic $CfBr_3$ is similar to that for the transformation of orthorhombic to monoclinic $BkBr_3$ (350 °C).[4] It is not unexpected that californium might grow into solid-state compounds of berkelium without alteration of the crystal structure. The cation radii of Bk(III) and Cf(III) are quite similar, differing by approximately 0.01 Å.[10] The low-energy β^- decay of berkelium-249 (0.125 MeV maximum) results in such a low-energy (0.28 eV) recoil californium nucleus that it is not moved significantly within the lattice. One expects, then, that the atom-by-atom replacement of berkelium with californium should result in the daughter being trapped in the parent's lattice site. Thus, orthorhombic $CfBr_3$ might be a metastable system that exists only as a consequence of the β^- decay of $BkBr_3$. Another possibility is that the orthorhombic form is thermodynamically stable only at temperatures below about 330 °C, a temperature too low for its direct synthesis by our normal procedures.[3c]

We have demonstrated that the crystal structure of the daughter $CfBr_3$ depends on that of the parent $BkBr_3$. Whether these observations are to be expected generally for β^- decay processes in the solid state or are only valid for such processes with recoil energies less than chemical bond energies is presently under study.

Chemical Reactivity of Daughter Californium-249 in $^{249}BkBr_3$. It has not been possible to reduce $BkBr_3$ with H_2;[3c] however, $CfBr_3$ can be reduced by H_2 to form $CfBr_2$.[3c,6] It is also possible to carry out the H_2 reduction of the ingrown $CfBr_3$ daughter trapped in the parent $BkBr_3$ lattice. In fact, our first indication of the quantitative reduction of $CfBr_3$ with H_2, based on absorption spectrophotometric analysis, was observed with a sample of $BkBr_3$, containing 3.7% californium, treated with H_2 at a temperature of 695 °C. The results of this study are summarized in Figure 5. For comparison purposes, the uppermost spectrum is that of a mixed californium(III)–californium(II) bromide with the respective peaks noted by (III) or (II). The full-line spectrum is that of $CfBr_3$ in parent $BkBr_3$, and the dashed-line spectrum is that of $CfBr_2$ in the $BkBr_3$ parent that was observed after the mixed tribromide was treated with H_2 at elevated temperature.

Conclusions

In the β^- decay of $^{249}BkBr_3$, the daughter californium substitutes for its parent and maintains both the structure and the oxidation state of the parent. Thus, a new crystallographic form of $CfBr_3$, exhibiting the $PuBr_3$-type orthorhombic structure, was prepared by nature through a β^- decay process. This new modification of $CfBr_3$ was characterized by both X-ray powder diffraction and absorption spectrophotometric methods. Although daughter $CfBr_3$ substitutes for the parent $BkBr_3$ without alteration of oxidation state or structure, the daughter can undergo chemical reactions that are independent of the parent. Thus, Cf(III) in $BkBr_3$ can be reduced to Cf(II) quantitatively, as evidenced by absorption spectrophotometric measurement, by treatment with H_2 gas. Further studies are under way to determine if such behavior is unique with the Bk–Cf system or is generally descriptive of weak β^- decay processes in the solid state.

The present report is the first part of a general study of the chemical consequences of both α and β decay processes. In a separate publication, focus will be on the results of progeny growth in the α decay of ^{253}Es(II) and ^{253}Es(III) compounds where there is ingrowth of both berkelium daughter and californium granddaughter species.

Acknowledgment. We acknowledge the help of C. E. Bemis, Jr., in the calculation which showed that californium-249 would not move out of a berkelium-249 lattice site in recoiling from the β^- decay of the parent.

Registry No. ^{249}Cf, 15237-97-5; ^{249}Bk, 14900-25-5; $^{249}CfBr_3$, 24297-29-8.

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