

SPECTROSCOPIC AND X-RAY DIFFRACTION STUDIES OF THE BROMIDES  
OF CALIFORNIUM-249 AND EINSTEINIUM-253\*

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Spectral and X-ray diffraction studies of californium-249 and einsteinium-253 bromides have been undertaken to investigate the chemistry of these halides and to establish their composition under various thermal and/or chemical conditions. This report can best be considered a status report; there is much we have learned, but the information we have obtained has suggested, and is still suggesting, new experimental approaches that might help in the understanding of the chemical behavior of Cf and Es compounds. In earlier work describing these transuranic bromides, conclusions were generally drawn from either X-ray or spectral work, but never from experimental results in which both techniques were applied to the same sample. In the present work, both X-ray and spectral data were obtained on the same sample. The combination and application of these two investigative tools over a temperature range of 25 to 700°C permits a more complete characterization of these compounds.

Our initial study of the chemistry of these halides was a spectral and X-ray study of the effect of temperature on CfBr<sub>3</sub> [1]. A description of both a small radius, Debye-Scherrer type, powder diffraction camera and a microscope-spectrophotometer of local design modified for high temperature studies by the inclusion of a Pt wire heating coil surrounding each sample area has been given elsewhere ([2], [1], respectively). The microgram or submicrogram-sized samples are contained in quartz capillaries suitable for in situ analysis by either technique. The spectral apparatus has been limited to a wavelength range of 400 to 1350 nm because of the nature of the optical components. By the use of Cassegrainian reflecting microscope objective lenses and quartz field lenses, the ultraviolet range of this instrument has now been extended to 300 nm. In addition to these lenses, other changes were made including the use of quartz envelope-tungsten iodide or xenon high-intensity lamps and additional critical masks. A schematic diagram of the system is shown in Figure 1. We are still in the process of improving the useful wavelength range of the instrument; the problems now appear to be the result of stray light and/or higher order diffractions from the grating monochromator. This spectrophotometer is a single-beam instrument, and the data are recorded on a strip chart as amplified photomultiplier current readings. In

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the past, manual calculations have been used to analyze the data, but we presently are making use of a graphical data digitizer [3] and computer programs to convert the data to meaningful absorbance values.

We have already described the X-ray and spectral studies of CfBr<sub>3</sub> as a function of temperature over the range of 25 to 600°C [1]. The experimental work was carried out with the microscope-spectrophotometer prior to the modifications described above. In summary we found that Cf(III) in CfBr<sub>3</sub> was partially reduced to Cf(II) as the temperature was increased above 25°C, finally reaching a concentration of 15 to 30% at 600°C. The crystal lattice of the parent compound was retained, however, with only the expected thermal expansion up to 700°C. The spectral interpretation was based, in part, on predictions of Nugent *et al.* [4] as to the location of allowed transitions of Cf(III) and Cf(II). From our experimental work and earlier unpublished studies [5], we were able to identify the presence of Cf(II) by its predicted f-d transition in the region of 490 nm and the presence of f-f bands in the region of 900 nm.

With the knowledge gained from the thermal study of CfBr<sub>3</sub>, we re-investigated the reduction of CfBr<sub>3</sub> with H<sub>2</sub>. In an earlier paper, reporting the initial preparation of CfBr<sub>2</sub> based on X-ray data and describing the conditions for this reaction, it was noted that amber-colored CfBr<sub>2</sub> was obtained only with careful control of the temperature of reduction [6]. When the temperature was either too low or too high, the reaction product did not exhibit the CfBr<sub>2</sub> X-ray pattern. Visually, it was noted that at too low a temperature a green color persisted, indicative of CfBr<sub>3</sub>; at too high a temperature the amber-colored CfBr<sub>2</sub> changed to a green color, so the product was not studied further. Under certain conditions an unidentified green material formed, called an "intermediate", which was neither CfBr<sub>2</sub> nor CfBr<sub>3</sub>.

On the basis of the present X-ray and spectral data, we have identified CfBr<sub>3</sub>, CfBr<sub>2</sub>, and CfOBr as the compounds formed in SiO<sub>2</sub> capillaries by the high-temperature reduction of CfBr<sub>3</sub> with H<sub>2</sub>. Spectral characteristics that differentiate these various species are summarized in Table I.

Table I  
Spectral Characteristics of Some Californium Compounds

Wavelength, nm	Peak Description		
	CfBr <sub>2</sub>	CfBr <sub>3</sub>	CfOBr
905,910	sharp	*	*
875	?	intense	*
850	?	weak	intense-broad
640	*	very sharp	weak-broad
490	very intense f-d band	weak f-f	weak f-f

\*absent

Using these various absorbance peaks, which were exhibited by compounds that were identified by X-ray analysis, it was then possible to carry out spectral identification of the products of the reaction of  $H_2$  with heated  $CfBr_3$ . Our present understanding of the process indicates that when  $CfBr_3$  is treated with  $H_2$  below approximately  $650^\circ C$ , the rate of reduction is very slow. At slightly higher temperatures, approximately  $675^\circ C$ , the rate of reduction is increased and  $CfBr_2$  is formed. However, at the increased temperature, the rate of formation of  $CfOBr$  is likewise increased. The extent of reduction is therefore a compromise of both temperature and time of heating. With too high a temperature or too long a time,  $CfOBr$  is the final product. With the above competing reactions, it has not been possible for us to prepare pure  $CfBr_2$ , although the dibromide has been a major component of some samples. Various samples have been prepared which have shown either the spectra of  $CfBr_2$  and  $CfBr_3$ , or  $CfBr_2$  and  $CfOBr$ . It would be expected that we also have prepared samples which contained all three compounds. A spectral identification of low concentrations of  $CfOBr$  in such samples would be difficult, but X-ray data have confirmed that all three compounds are present in some samples. It seems probable that  $CfOBr$  is formed by a reaction of reduced Cf species with  $SiO_2$ . Whether it is a direct reaction of  $CfBr_2$  or a thermal disproportionation of  $CfBr_2$  followed by a reaction of Cf metal with  $SiO_2$  is not understood. Experimental work to elucidate the mechanism is presently underway. Based on earlier work [1], it appears that heating  $CfBr_3$  in  $SiO_2$ , in the presence of HBr gas, does not cause the formation of  $CfOBr$ . We have recently determined that heating  $CfBr_3$  in the presence of  $H_2$  in a  $SiO_2$  container does result in the formation of  $CfOBr$ . It seems unlikely that pure  $CfBr_2$  can be made from  $H_2$  reduction of  $CfBr_3$  in contact with  $SiO_2$ .

Chronologically, we examined the einsteinium bromide system and its response to  $H_2$  at elevated temperature prior to the re-examination of  $CfBr_3$  reduction with  $H_2$ . We re-examined the  $CfBr_3$  system because of our inability to observe spectrally the reduction of  $EsBr_3$  with  $H_2$ . Based on the work of Nugent *et al.* [4] and others [7], it is expected that the reduction potentials of  $Cf(III)-(II)$  and  $Es(III)-(II)$  are very similar. On a thermodynamic basis, and neglecting differences in radioactivity, similar thermal and/or  $H_2$  reduction behavior should be expected for  $Cf(III)$  and  $Es(III)$ . Evaluation of earlier experimental results led to the speculation that  $Es(III)$  might not even be stable and that  $EsBr_2$  could be the stable einsteinium bromide [8]. As more  $Es-253$  has become available in the past 8 months, we have synthesized einsteinium bromides in order to investigate further the chemistry of their compounds by X-ray and spectral means. Potentially, the spectral interpretation of  $Es(III)$  reduction is more difficult than that of  $CfBr_3$ , where the  $Cf(III)$  charge transfer (300 nm) and the  $Cf(II)$  f-d (500 nm) bands are well separated [1]. Six-coordinate  $Es(III)$ , as  $EsBr_6^{3-}$ , exhibits a charge transfer band at approximately 330 nm [4];  $Es(II)$  in  $CaF_2$  apparently exhibits an f-d band at approximately 360 nm [9,4]. On this basis a study of the reduction of  $Es(III)$  can best be undertaken by spectral examination in the ultraviolet region, and this is one reason why we modified the optical design of our microscope-spectrophotometer as described earlier in this paper.

The experimental work we have carried out with  $Es$  bromides has led to many interesting results. This work is the first to establish by spectral and X-ray methods, that  $EsBr_3$  does exist. The compound exhibits the  $AlCl_3$ -type monoclinic structure expected for  $EsBr_3$  and yields the expected absorption spectrum [10]. We have not clearly established that the  $EsBr_3$  charge transfer band is near 330 nm, but it is reasonably certain from our work that a very intense absorption band of  $EsBr_3$  is in this wavelength region. For clarification of the discussion to follow, the spectrum of  $EsBr_3$  that we reported [10] is shown in Figure 2.

We have found from the spectral study of  $EsBr_3$  and related compounds that the local environment of the  $Es$  ions is rapidly altered as a function of time following annealing. Both subtle and obvious changes occur in various f-f transitions

within 15 minutes after rapid cooling from a temperature of approximately 500-600°C. The changes are noted primarily in samples of Es(III) other than EsBr<sub>3</sub> and are observed in the regions of 10,500, 800, and 500 nm. The latter two wavelength regions include transitions that may be hypersensitive; however, the first region is not believed to be so [10,11]. In re-annealing the samples, the bands regenerate only to degrade with time. This kinetic behavior perhaps seems even more puzzling when one realizes that the einsteinium compounds are above room temperature as a result of heating from self-irradiation. The spectral changes are definitive proof of changes in the local environment of einsteinium cations. Whether these changes are also indicative of structural changes that could be seen by X-ray diffraction is an interesting yet unanswered question. It must be considered as a possibility, however.

A number of attempts to prepare EsBr<sub>2</sub> by the thermal reduction of EsBr<sub>3</sub> with H<sub>2</sub> have not seemed to yield the desired product as yet. Instead of the expected appearance of an f-d absorption and related gross alteration of the f-f transitions of Es(III), a new Es(III) compound is formed. Variations of band intensities within the f-f band system of Es(III) are seen, but it is obvious that these transitions are still those of trivalent einsteinium. The identity of this compound is not known. One possibility is EsOBr, but definitive data to support this conclusion are lacking. Based on the information we have obtained recently on the critical conditions necessary to maximize the reduction of EsBr<sub>3</sub> by treatments with H<sub>2</sub>, we will further investigate the H<sub>2</sub> reduction of EsBr<sub>3</sub> as more Es-253 becomes available. It should be remembered that X-ray studies of these compounds are difficult because of the extreme radioactivity associated with einsteinium. This element and its compounds generate a very interesting area of research, however. With sufficient experimental data, one can perhaps evaluate the interplay of radiation and chemical thermodynamics as a synthetic tool.

In the process of our spectral study of einsteinium bromides, we have also obtained their emission spectra. Again, we have seen unusual behavior. Preliminary data indicate that there may be, at least, two different emission spectra, one from EsBr<sub>3</sub> and one from an unidentified species. The emission spectra of einsteinium bromides are possibly due to transitions within the Es energy levels, but effects of impurities may also influence the emission. Recently the emission spectra of einsteinium compounds doped into SrCl<sub>2</sub> have been reported [12]. The emission spectra obtained in the present work bear no resemblance to those seen in the doped crystals. It is interesting to note that an unexpected but large increase in the intensity of an emission band system at 900 nm is seen as the external temperature of EsBr<sub>3</sub> is increased from its normal temperature to a temperature of about 325°C. A further increase in the temperature causes the emission peak system to decrease in intensity and ultimately to disappear when the temperature reaches 450°C. Of course, the actual temperature of the sample is a function of both the external heat input and the self-heating of the sample. The effect of temperature on the observed emission spectra, again, might indicate that we are observing the interplay of radiation and chemical forces. A possible explanation of the variation of intensity of the band system at 900 nm with temperature is that at normal temperatures, radiation damage allows radiationless processes to compete effectively in the de-excitation process. With the application of external heat, the radiation damage is removed by annealing and the emission process becomes more favorable. At higher temperatures, non-radiative processes again become important. It is important to note that no thermal broadening has been observed as this band system intensifies upon heating the sample.

Many interesting studies have yet to be made in order to understand fully the chemistry of einsteinium and californium and their compounds. What we have learned so far has pointed out further areas of study for the bromides of these elements and is leading us to spectral and X-ray diffraction studies of other Es and Cf halides. The results of these investigations should enhance our understanding of the chemistry of the heavier actinides, and of the effect of radioactivity on both the chemical and structural aspects of such compounds.

#### REFERENCES

1. J. P. Young, K. L. Vander Sluis, G. K. Werner, J. R. Peterson, and M. Noé J. Inorg. Nucl. Chem., In press.
2. J. N. Stevenson and J. R. Peterson, Microchem. J. 20 (1975).
3. Graphical Data Digitizer, Model E241, Elographics, Inc., Oak Ridge, Tenn., U.S.A.
4. L. J. Nugent, R. D. Baybarz, J. L. Burnett, and J. L. Ryan, J. Phys. Chem. 77 (1973) 1528.
5. R. D. Baybarz, G. K. Werner, L. J. Nugent, and J. R. Peterson, Oak Ridge National Laboratory, Oak Ridge, Tenn., unpublished results.
6. J. R. Peterson and R. D. Baybarz, Inorg. Nucl. Chem. Lett. 8 (1972) 423.
7. N. B. Mikheev, A. N. Kamenskaia, I. A. Rumer, V. I. Spitsyn, R. A. Diatchkova, and N. A. Rosenkevich, Radiochem. Radioanal. Lett. 9 (1972) 247.
8. R. D. Baybarz and L. J. Nugent, Oak Ridge National Laboratory, private communication, 1972. Reference 45 in J. R. Peterson, Proc., Tenth Rare Earth Res. Conf., 1 (1973) 4, Carefree, Arizona, April 30-May 3, 1973.
9. N. Edelstein, J. G. Conway, D. Fujita, W. Dolbe, and R. McLaughlin, J. Phys. Chem. 52 (1970) 6425.
10. R. L. Fellows, J. R. Peterson, M. Noé, J. P. Young, and R. G. Haire, Inorg. Nucl. Chem. Lett., In press.
11. W. T. Carnall, D. Cohen, P. R. Fields, R. K. Sjoblom, and R. F. Barnes, J. Chem. Phys. 59 (1973) 1785.
12. C. B. Finch and J. P. Young, J. Inorg. Nucl. Chem., In press.

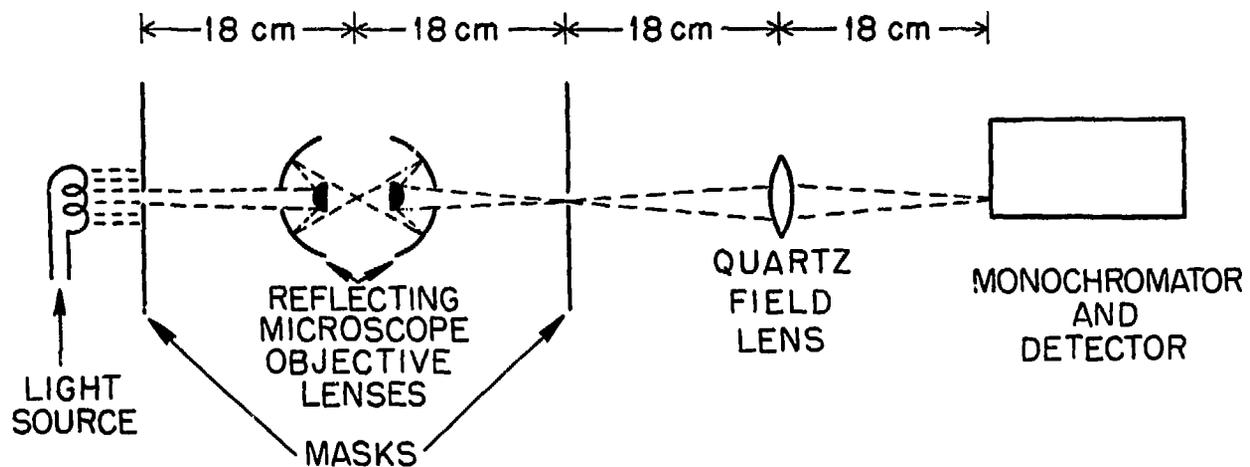


Figure 1. Schematic diagram of the optical components of the microscope-spectrophotometer.

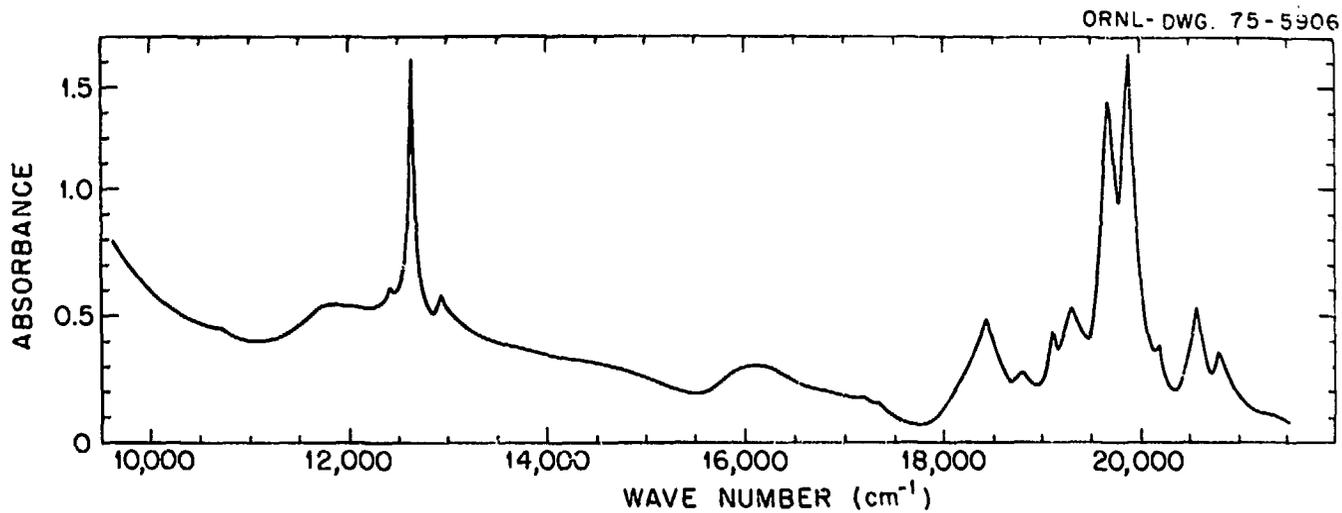


Figure 2. The absorption spectrum of  $\text{EsBr}_3$  after annealing at  $400^\circ\text{C}$ .