

Contribution from the Transuranium Research Laboratory (Chemistry Division), Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, and Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916

Chemical Consequences of Radioactive Decay. 2. Spectrophotometric Study of the Ingrowth of Berkelium-249 and Californium-249 into Halides of Einsteinium-253^{1a}

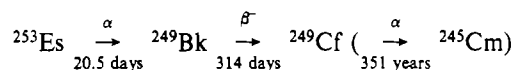
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The ingrowth of ²⁴⁹Bk daughter and ²⁴⁹Cf granddaughter into fluorides, chlorides, bromides, and iodides of parent ²⁵³Es was followed by spectrophotometric methods. In the case of trivalent Es halides, the oxidation state of the parent is maintained by its progeny. In the case of divalent Es halides, the oxidation state of the parent is retained by the granddaughter species. No other oxidation states or chemical species of the progeny ions are observed even though experimental conditions of storage such as physical state, temperature, or cover-gas composition were varied. These results are considered in terms of mechanisms that would allow such chemical stability.

Introduction

In a previous paper^{2a} the ingrowth of ²⁴⁹Cf into ²⁴⁹BkBr₃ was described as an introduction to a more general study of progeny growth into bulk-phase solid-state compounds derived from the radioactive decay scheme



Both X-ray diffraction and absorption spectrophotometric methods were applied to the Bk-Cf system. With Es compounds it is difficult to obtain X-ray powder diffraction patterns;^{2b} sample crystallinity, i.e., long-range repetitive order, required for X-ray diffraction is destroyed by the intense self-irradiation of ²⁵³Es. Short-range, local order is preserved, however, as is evident by the ability to obtain absorption spectra of Es compounds.^{3,4} In the present work absorption spectrophotometry has been applied to studies of the ingrowth of both Bk daughter and Cf granddaughter into einsteinium-(II) and -(III) fluorides, chlorides, bromides, and iodides.

Experimental Section

The general methods for preparing the chlorides, bromides, and iodides used in this study have been described elsewhere.⁵ The methods used for preparing the fluorides have also been reported.⁶ The samples, 1-10 μg in size, were characterized by absorption spectrophotometry and, where possible, by X-ray powder diffraction. The growth of the progeny was followed by absorption spectrophotometry. The procedures for carrying out these studies on such small samples have been described.⁷ Pure Bk halides and Cf di- and trihalides of various structures have also been characterized by both techniques,^{1,6-13} as have the pertinent oxyhalides,¹³ so that spectral

Table I. Conditions of Einsteinium Halide Time Studies

compd	cover gas	ambient temp, K
EsF ₃	He or air	300
EsCl ₃	HCl	873
	HCl or Ar	300
	HCl ^a	4
EsCl ₂	H ₂ or Ar	300
	H ₂ ^a	4
EsBr ₃	HBr, Ar, or H ₂	300
	HBr ^a	4
EsBr ₂	H ₂	300
EsI ₃	HI	300
EsI ₂	H ₂	300

^a Not in the gaseous state at the temperature of storage.

identification of a specific oxidation state, compound, and crystal structure can be made when these ions appear as progeny species in the parent, bulk-phase Es halide. With einsteinium compounds, it was found that better spectra were obtained if the compounds were annealed at 300-350 °C for several minutes immediately prior to spectral study. In some cases spectra were obtained both before and after annealing in order to evaluate this experimental parameter.

The Es compounds prepared for this study include EsF₃, EsCl₃, EsBr₃, EsI₃, EsCl₂, EsBr₂, and EsI₂. The individual compounds, sealed in silica capillary tubes, were stored under various conditions. Most of the Es trihalides were stored under a reduced pressure⁵ of the respective hydrogen halide at room temperature. EsCl₃ was also stored under HCl as a molten salt, at room temperature, and in liquid helium. EsBr₃ was maintained under HBr at both room temperature and in liquid helium and under hydrogen at room temperature. The dihalides were normally stored under a reduced pressure of hydrogen at room temperature. EsCl₂ was stored under H₂ or argon at room temperature, and one capillary containing this compound was stored in liquid helium. Some samples were stored under vacuum. A summary of the various experimental conditions of samples storage and einsteinium compounds studied spectrally, as a function of time, is shown in Table I.

In the process of these studies, over 80 samples, sealed in silica capillary tubing,⁵ have been stored for periods of time up to and exceeding 3 years. There have not been any capillary failures, i.e., cracking or breaking; storing anhydrous actinide halides in this manner seems to be quite satisfactory. All of the bulk-phase Es trihalides essentially retain their initial state of optical clarity as they age, although they do change color as the progeny cations grow in. In the case of Es dihalides, however, the samples generally darken after several months; the spectra become poorly resolved and remain so until the samples are 8-12 months old; after that time spectra become more resolvable.

- (1) (a) Research sponsored by the Division of Chemical Sciences, U.S. Department of Energy, under Contracts W-7405-eng-26 with Union Carbide Corp. and DE-AS05-76ER04447 with the University of Tennessee (Knoxville). (b) Analytical Chemistry Division, Oak Ridge National Laboratory. (c) Transuranium Research Laboratory, Oak Ridge National Laboratory. (d) University of Tennessee.
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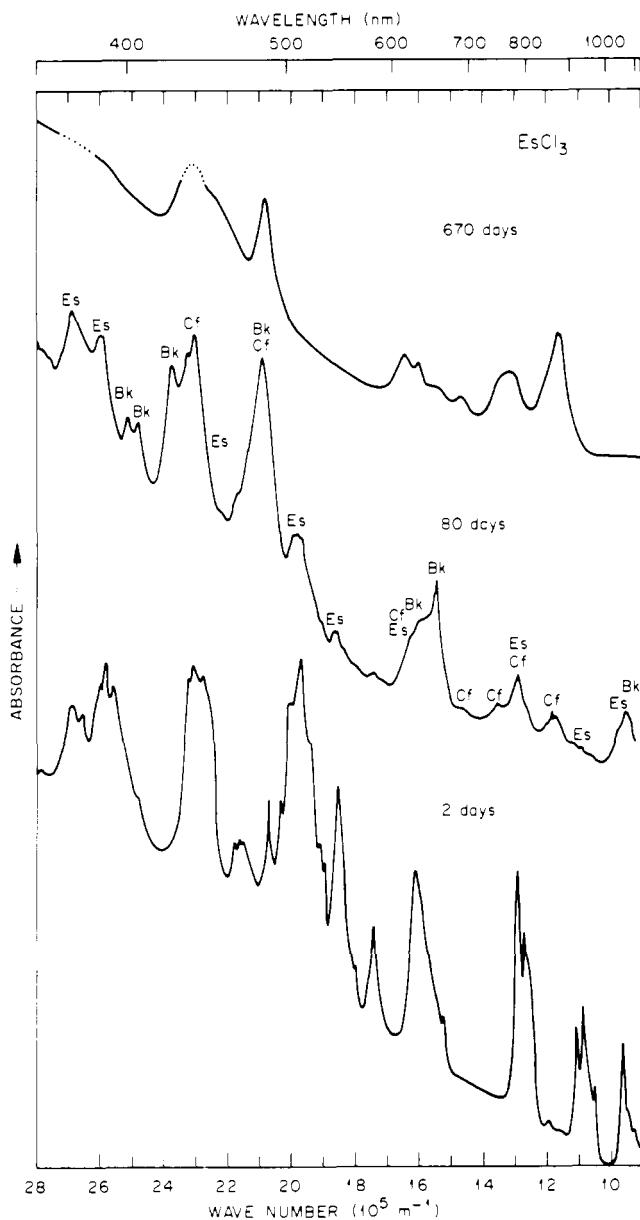


Figure 1. Change in the spectrum of EsCl_3 as a function of progeny ion ingrowth. Location of EsCl_3 , BkCl_3 , and CfCl_3 absorption peaks are designated by the respective atomic symbols at the appropriate energy locations.

Results and Discussion

Chemical Oxidation State. A typical set of spectra observed for EsCl_3 as a function of time, over a 2-year period, is shown in Figure 1; a similar set of spectra observed for EsBr_3 is shown in Figure 2. In both figures, the absorption peaks attributable to the trivalent oxidation states of the parent and progeny halides are identified by the respective chemical symbols. In both cases it can be noted that the spectrum of EsX_3 is altered, eventually leading to a spectrum of CfX_3 . In all our studies of Es trihalides we observe that the progeny compounds exhibit the same oxidation state as their parent, i.e., $\text{EsX}_3 \rightarrow \text{BkX}_3 \rightarrow \text{CfX}_3$, where X = F, Cl, Br, or I. Absorption peaks observed growing into EsX_3 as a function of time were always attributable to trivalent Bk or Cf species. No absorption peaks attributable to oxyhalides or other oxidation states of Bk or Cf were observed.

A typical spectrum observed for EsCl_2 as freshly prepared and again after 500 days is shown in Figure 3. Again it can be noted that the spectrum changes from that of EsCl_2 to that of CfCl_2 .¹¹ Similar spectral data for EsBr_2 is included in the

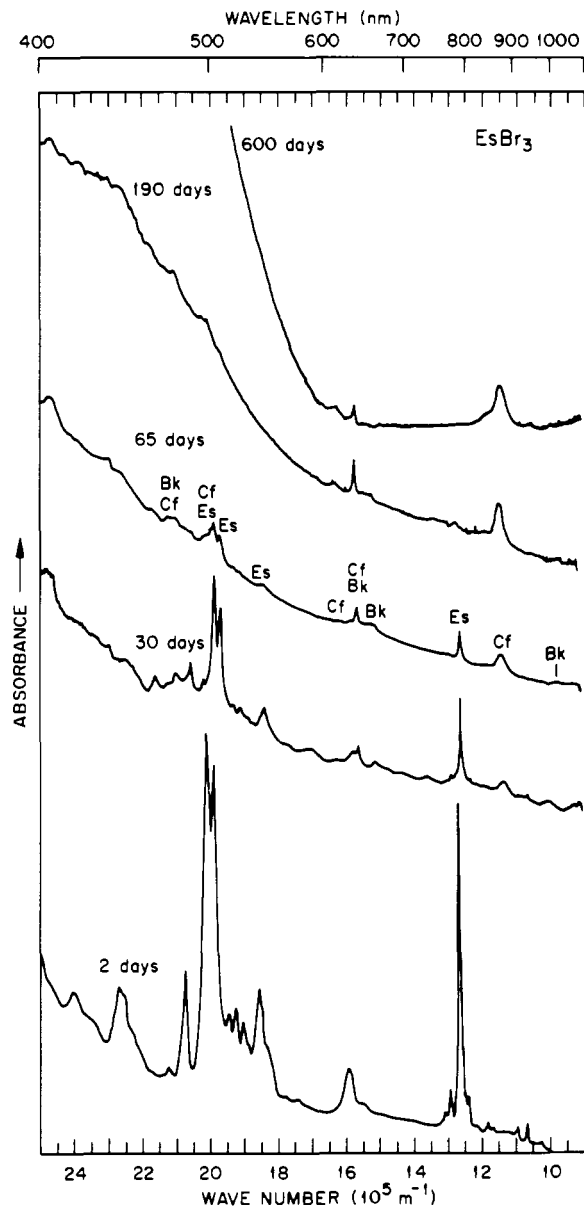


Figure 2. Change in the spectrum of EsBr_3 as a function of progeny ion ingrowth. Location of EsBr_3 , BkBr_3 , and CfBr_3 absorption peaks are designated by the respective atomic symbols at the appropriate energy locations.

supplemental material. In all the studies of einsteinium dihalides, the oxidation state of the parent is maintained by the granddaughter compound, i.e., $\text{EsX}_2 \rightarrow (\text{ }) \rightarrow \text{CfX}_2$, where X is Cl, Br, or I. However, no evidence of any spectral peaks attributable to Bk(II) has been observed. It should be recalled that divalent Bk halides have not yet been reported in the bulk-phase solid state. Efforts are presently under way in our laboratory to prepare BkBr_2 by reduction of BkBr_3 with Bk metal.¹³ The inability to observe BkX_2 may be caused by our inability to recognize the spectrum of this compound. The spectral peaks of Bk(II) may be weak and/or hidden by the peaks of Cf(II) and/or Es(II). It is tempting to assume that nature generated this compound in the transmutation of Es(II) to, ultimately, Cf(II). Evidence that supports this hypothesis comes from one sample of EsBr_2 , 11 weeks old, that was heated to melting and then cooled. Subsequent examination of the spectrum of this sample several years later showed spectral peaks of both Cf(II) and Cf(III). Other samples of EsBr_2 that have not been melted do not yield any spectral evidence for Cf(III) even after several years' storage. One could speculate

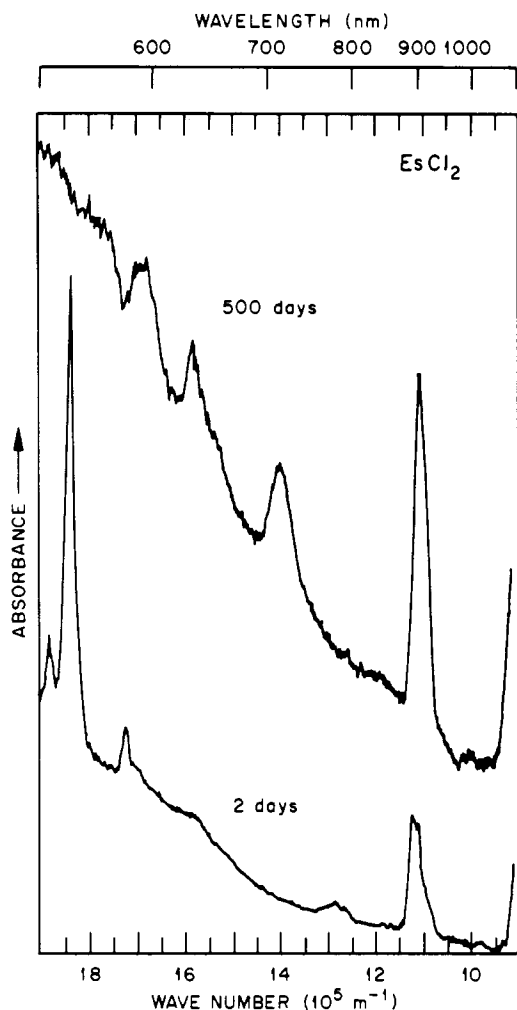


Figure 3. Spectrum of EsCl_2 as prepared compared to that of the same sample, now CfCl_2 , 500 days later.

that BkBr_2 , or more exactly the CfBr_2 precursor, present in the sample at the time of melting was demonstrated to be thermally unstable. The divalent state of Bk might well be thermally unstable.

The maintenance of oxidation state in the decay chain of Es di- and trihalides is independent of the methods used for storage of the samples. As noted in Table I, samples were stored in the respective hydrogen halide gas, inert gas, H_2 , and in some cases even vacuum, with no effect on the resultant maintenance of oxidation state of the Es parent by the spectrally observable progeny halides. For the investigation of the effects of recoil-ion mobility on the maintenance of oxidation state, separate samples of EsCl_3 were stored in liquid helium, at ambient temperature, and as a molten salt to impart a wide range of mobilities to all ions in the sample. Likewise, EsCl_2 samples were held in liquid helium and at room temperature. In all cases the oxidation state of the Es parent was retained by the progeny ions; as a matter of fact, excellent spectra were obtained from the samples stored in liquid helium where ion mobilities should have been minimal. The reader should be aware that Es is a heat source, generating $2.5 \times 10^2 \text{ kJ mol}^{-1} \text{ s}^{-1}$. Storage of an Es sample in liquid helium does not maintain the sample at 4 K but at some very low temperature. In any case, over the temperature range studied, which imparted very low to very high (liquid) mobilities to all ions in these compounds, the oxidation state of the parent was maintained by the progeny. In several samples where Es was purposefully added as a minor constituent in host compounds whose cation was not the same oxidation state as the Es, preliminary results suggest that the oxidation state of the parent Es is also retained

by the progeny. Two examples of the above can be cited: in one case the sample was a solid-state mixture of CaCl_2 with 15 mol % EsCl_3 , and the other a mixture of LaCl_3 with 20 mol % EsCl_2 .

When the spectrum of EsBr_3 is followed with time over a period of several half-lives of Es ($t_{1/2} = 20.5$ days), the first obviously new peak seen in the spectrum arises within 2 weeks at 875 nm and is a characteristic Cf(III) absorption peak; see Figure 2. Since our microscope-spectrophotometer is of single-beam design and the sample geometry is not reproducible within the instrument, our spectral data are not suitable for absolute measurement.⁵ Some assessment of relative intensities of spectral peaks of species can be inferred, however, and it seems that certain absorption peaks of CfBr_3 are much more intense than the absorption peaks associated with BkBr_3 . At longer periods of time, 3–4 weeks, peaks associated with BkBr_3 do appear in the sample spectrum. No other spectrally identifiable oxidation state or species of Bk, such as BkOBr , is observed. In the case of aged EsCl_3 samples, the daughter Bk(III) and granddaughter Cf(III) are clearly observed, spectrally, as they grow into the parent compound. The results of a study of progeny growth in EsF_3 are similar to those of the trichloride case; a detailed description of the fluoride study, part of a general spectrophotometric study of EsF_3 , is discussed elsewhere.¹⁴ Spectral data for EsI_3 and EsI_2 similar to those shown in Figures 1–3 are included in supplementary material. Although, as stated above, spectral data show that oxidation state is also preserved in Es iodide transformations, an insufficient number of samples have been studied to warrant an assessment of the relative sensitivities of progeny ion spectral peaks in these systems. Additional studies are presently under way that address the question of material balance of spectrally identifiable progeny compounds as a function of halide component.

Structural Assessments. X-ray powder diffraction patterns from Es compounds are very difficult to obtain and, if observed at all, are usually poor in quality.^{2b} As a result almost all of the progeny compound characterizations in these studies were made by spectral identification. In previous and related work, individually synthesized Bk and Cf compounds were characterized by both X-ray powder diffraction and spectrophotometric analyses.^{1,6–13} A particular absorption spectrum can therefore be associated not only with a particular oxidation state but also with a particular crystal structure of the Bk or Cf halide. It might be possible to gain information about the structure of Es halides from a knowledge of the structure of the ingrown progeny compounds. Any usefulness of such a method for obtaining information about the parent Es halide structure would seem to require the characterization of the structure of the first-generation Bk halide. In the case of the trihalides, however, it is known that the structure of BkX_3 , where X is Br^{2a} or Cl ,¹³ is preserved in its β^- decay to CfX_3 . Structural characterization by either Bk halide spectra or the more sensitive Cf halide spectra, or both, can therefore be used in this regard.

It has definitely been established by spectral characterization that only monoclinic CfBr_3 , the high-temperature six-coordinate form,⁸ grows into decaying EsBr_3 . The spectral insensitivity of the BkBr_3 daughter mentioned in the previous section might be associated with monoclinic BkBr_3 , as this is a six-coordinate centrosymmetric form whose spectrum is weak.^{2a} In the case of EsBr_3 , a limited X-ray powder diffraction study was possible on one particular sample. The pattern that was obtained, some 15 lines, was consistent with that expected for monoclinic EsBr_3 .³ Thus, in the decay of EsBr_3 to BkBr_3 to CfBr_3 only a six-coordinate, monoclinic

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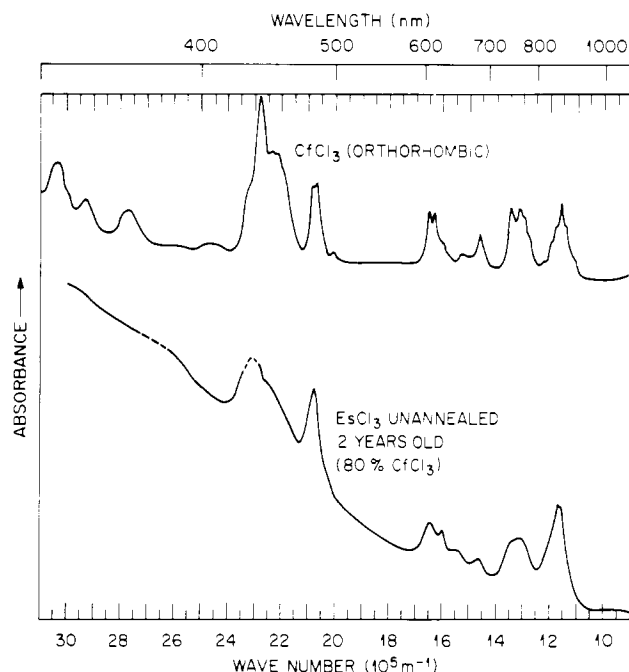


Figure 4. Spectrum of an unannealed 2 year old EsCl_3 sample containing 80% CfCl_3 and 20% BkCl_3 , compared with a spectrum of orthorhombic, eight-coordinate CfCl_3 .¹³

structure is observed, even though both BkBr_3 and CfBr_3 are known to exhibit other crystallographic forms.^{2a,8}

As a general rule all einsteinium compounds, of any age, are heated (annealed) at a temperature of 300–350 °C immediately prior to spectral study. This procedure might form a preferred structure of daughter BkX_3 and/or granddaughter CfX_3 . Examination of some spectral data obtained before and after annealing Es halide samples yields some interesting observations. In spectral studies of old samples of EsBr_3 , only the high-temperature, monoclinic, six-coordinate form of CfBr_3 ^{8,9} is seen, before or after annealing. The spectrum of an unannealed, 2 year old EsCl_3 sample is shown in Figure 4 and compared to the spectrum of the high-temperature, orthorhombic, eight-coordinate form of CfCl_3 . There are some similarities between the rather poor spectrum of the old EsCl_3 sample (now 80% CfCl_3) and that of the known form of CfCl_3 .¹³ Compare, particularly, the symmetric nature of the progeny Cf(III) peak at $11.5 \times 10^5 \text{ m}^{-1}$ to that of its counterpart in CfCl_3 ; compare also the flat, almost double-humped, broad peak of progeny Cf(III) at $13.25 \times 10^5 \text{ m}^{-1}$ with its counterpart in orthorhombic CfCl_3 . It is also interesting to note that there is only an extremely weak absorption in the $9.75 \times 10^5 \text{ m}^{-1}$ region; this is the energy of a BkCl_3 absorption peak, which is weak as an orthorhombic structure.¹³

After this EsCl_3 sample was annealed, its spectrum was altered as shown in Figure 5. It compares closely to that of the low-temperature, hexagonal, nine-coordinate form of CfCl_3 .¹³ Compare again the structural and asymmetric nature of the Cf(III) peak at $11.5 \times 10^5 \text{ m}^{-1}$ and the peak-shoulder configuration of the absorption at $13.5 \times 10^5 \text{ m}^{-1}$. Further note that a peak, attributable to Bk(III) in hexagonal BkCl_3 ,¹³ is observed at $9.75 \times 10^5 \text{ m}^{-1}$. In the case of EsF_3 , absorption spectra attributable to both trigonal BkF_3 ⁶ and trigonal CfF_3 ¹³ are observed¹⁴ as these progeny fluorides grow into the parent EsF_3 . The trigonal forms of BkF_3 and CfF_3 are their high-temperature forms.^{15,16} A case could be made, then, that

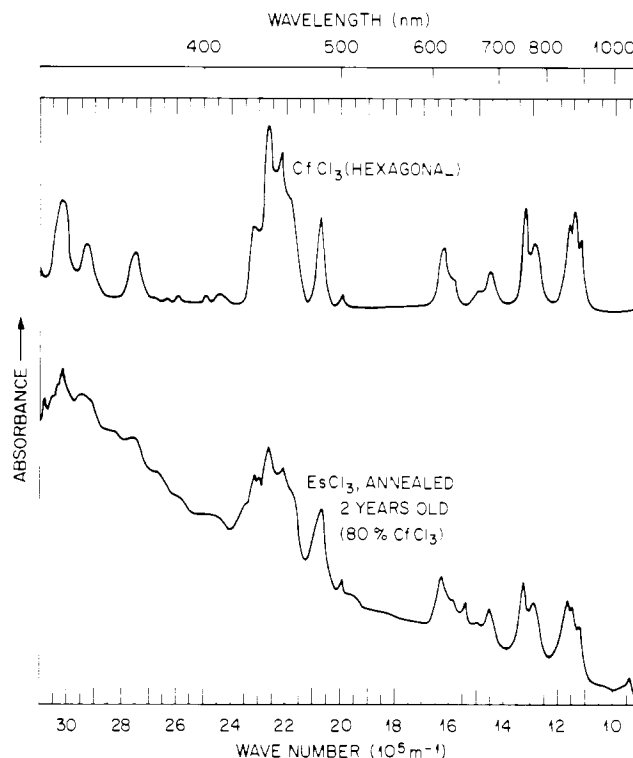
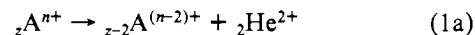


Figure 5. Spectrum of an annealed (see text) 2 year old EsCl_3 sample, containing 80% CfCl_3 and 20% BkCl_3 , compared with a spectrum of hexagonal, nine-coordinate CfCl_3 .¹³

EsX_3 , may well be in a form that, if not already in the BkX_3 high-temperature structure, leads to the high-temperature form of the daughter, which is retained by the granddaughter CfX_3 .^{2a,13} In considering these experimental results, it should be remembered that ^{253}Es is a source of heat, due to its radioactive decay. This thermal energy appears as highly localized, intense thermal spikes, of short duration. These thermal spikes also cause an increase in the average bulk-sample temperature, which slowly decreases as the Es is depleted. If it is correct to infer the structure of the parent EsX_3 from the structure of its progeny, then the spectral data indicate that EsF_3 is trigonal, EsBr_3 is monoclinic, and EsCl_3 is orthorhombic. Thus, it follows that the local order of the parent EsX_3 is maintained in α decay, a result previously observed in β decay of solid-state Bk halides.^{2a,13}

Mechanism of Progeny Growth. It is interesting to consider the mechanism by which oxidation state is preserved in the decay series, $\text{Es} \xrightarrow{\alpha} \text{Bk} \xrightarrow{\beta} \text{Cf}$. β decay has been considered traditionally to be an oxidative process, and in the gas phase, even decay of neutral species results in the generation of positively charged species.¹⁷ Consider, further, the violent upheaval of each recoil species that results from an α decay. Under the conditions of our studies, these processes, occurring in the bulk-phase solid state, do not yield the significant change in the chemical nature of the bulk phase that would be expected from the above consideration. In a totally enclosed system, all changes in oxidation state resulting from α decay could be balanced in the following way; first



Rearrangement of electronic charge, however, yields the products

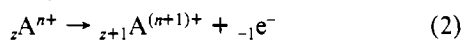


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Likewise, in β^- decay, one can write



Rearrangement of electronic charge then yields the product



The results of this study suggest that except for the α or β^- particles that escape the system permanently, such rearrangements generally occur resulting in the neutralization of excess or deficient charge. Thus, within the limits of our ability to observe such effects, the oxidation state of the parent is retained by the progeny.

Another view of the above mechanism has been suggested to explain our results^{2a} in β^- decay;¹⁸ it applies equally well to explain our observations of the effects of α decay. Even though the immediate oxidation state of a thermalized recoil species in a bulk-phase solid might be different from that of the parent cation, there is also a charge balance with anionic species present in that phase that must be considered. This balance promotes the maintenance of oxidation state.

The above hypothesis can explain the bulk-phase solid state system we describe here, i.e., Es $\xrightarrow{\alpha}$ Bk $\xrightarrow{\beta^-}$ Cf. We are not invoking any severe oxidation-state instabilities, with the possible exception of the status of Bk in the decay of solid-state,

divalent Es halides. In another study we have also observed that cation oxidation state is preserved in the α decay of ${}^{244}\text{CmBr}_3 \rightarrow {}^{240}\text{PuBr}_3$. Here again we are invoking no severe chemical instabilities to maintain oxidation state; i.e., both parent and daughter cations exhibit stable trivalent oxidation states.

In sharp contrast to the above results, very severe chemical instabilities could be created if oxidation states in bulk-phase solids are preserved in certain other α or β^- processes, such as Pa $\xrightarrow{\alpha}$ Ac, Th $\xrightarrow{\alpha}$ Ra, and Br $\xrightarrow{\beta^-}$ Kr. Further, if other radioactive decay schemes are considered such as ${}^7\text{Be}^{2+} \xrightarrow{\text{EC}} {}^7\text{Li}^{2+}$, various n,p reactions, etc., maintenance of oxidation state, or structure, does not seem possible. It would be worthwhile to establish the limits of such oxidation-state maintenance.

Expansion of the present work to other compounds and other decay systems is planned to elucidate more completely the chemical consequences of radioactive decay in the bulk-phase solid state. The results of such an expanded study should lead to a better understanding, for example, of the long-term, solid-state storage of nuclear materials.

Registry No. ${}^{253}\text{EsF}_3$, 78891-05-1; ${}^{253}\text{EsCl}_3$, 55484-87-2; ${}^{253}\text{EsBr}_3$, 57137-36-7; ${}^{253}\text{EsI}_3$, 78891-06-2; ${}^{253}\text{EsCl}_2$, 70420-31-4; ${}^{253}\text{EsBr}_2$, 60198-18-7; ${}^{253}\text{EsI}_2$, 70420-32-5; ${}^{249}\text{Bk}$, 14900-25-5; ${}^{249}\text{Cf}$, 15237-97-5; ${}^{253}\text{Es}$, 15840-02-5.

Supplementary Material Available: Spectra of EsBr_2 , EsI_3 , and EsI_2 as a function of time (3 pages). Ordering information is given on any current masthead page.

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Photophysics and Photochemistry of Polypyridyl Complexes of Chromium(III)¹

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The quantum yields of photoaquation (Φ_{rx}) and the lifetimes of the ${}^2T_1/{}^2E$ excited states (${}^2\tau$) have been determined in aqueous solution at 22 °C for 12 tris(polypyridyl) complexes of Cr(III), $\text{Cr}(\text{NN})_3^{3+}$ (where NN = bpy, 4,4'-Me₂bpy, 4,4'-Ph₂bpy, phen, 5-Cl(phen), 5-Br(phen), 5-Me(phen), 5-Ph(phen), 5,6-Me₂phen, 4,7-Me₂phen, 4,7-Ph₂phen, or 3,4,7,8-Me₄phen). Φ_{rx} was determined for deaerated solutions containing 1.0 M NaCl and 0.008 M Britton-Robinson buffer at pH 9.5; ${}^2\tau$ was determined under the same conditions of solution medium as well as in 1.0 M HCl (5.0 M HCl for NN = bpy, 4,4'-Me₂bpy, or 4,4'-Ph₂bpy). The values of ${}^2\tau$ for a given complex are dependent on [substrate]; increases in [substrate] result in a decrease in ${}^2\tau$ such that plots of $1/{}^2\tau$ vs. [substrate] are linear. The slopes of such plots yield values of 2k_g , the rate constant for the quenching of ${}^2T_1/{}^2E$ by the ground state (4A_2), that are in the range of 10^6 - 10^8 M⁻¹ s⁻¹. Ground-state quenching of ${}^2T_1/{}^2E$ is seen as a collisional phenomenon between the Cl⁻-associated ground and excited states; large substituents, especially phenyl groups, increase the value of 2k_g . The values of Φ_{rx} are low in acidic solution, rise in the mid-pH region, and reach a plateau at pH 9-10. Coupling the plateau values of Φ_{rx} with ${}^2\tau$, and assuming that the efficiency of ${}^4T_2 \rightarrow {}^2T_1/{}^2E$ intersystem crossing is ~ 1 for all the complexes, we have obtained values of ${}^2k_{\text{rx}}$ ($=\Phi_{\text{rx}}/{}^2\tau$), the rate constant of the reactive decay of ${}^2T_1/{}^2E$. Taking the values of ${}^2k_{\text{rx}}$ as reflecting the ease with which the seven-coordinate intermediate is formed upon interaction of solvent with ${}^2T_1/{}^2E$, we can see that the flexibility of the ligand structure and the degree of hydrophilicity in the vicinity of the interligand pockets are the determining factors. The rate constants of the nonradiative decay of ${}^2T_1/{}^2E$, ${}^2k_{\text{nr}}$, have also been evaluated.

Introduction

2,2'-Bipyridine (bpy), 1,10-phenanthroline (phen), and their substituted derivatives comprise an extensive series of tris-(polypyridyl) complexes of Cr(III), $\text{Cr}(\text{NN})_3^{3+}$, the photophysics and photochemistry of which can be examined under identical conditions in fluid solution at room temperature.

Determination of the lifetime of the thermally equilibrated excited states of lowest energy, ${}^2T_1/{}^2E$, by flash absorption and luminescence decay techniques reveals that ${}^2\tau$ for these metal-centered states is highly dependent on the nature of the ligands.³⁻⁸ Because of the long lifetimes of ${}^2T_1/{}^2E$ in fluid

- (1) Research supported by the Natural Sciences and Engineering Research Council of Canada (Grant No. A-5443), the National Science Foundation (Grant No. CHE79-18013), and the North Atlantic Treaty Organization (Grant No. 658). Presented in part at the 182nd National Meeting of the American Chemical Society, New York, Aug 1981; see Abstracts, No. INOR 244.
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