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Preparation, characterization, and decay of einsteinium(II) in the solid state (*)

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Résumé. — Pour la première fois, des échantillons de EsCl_2 , EsBr_2 et EsI_2 ont été préparés par réduction des trihalogénures d'einsteinium correspondants par de l'hydrogène à des températures élevées. Les trois dihalogénures ont été caractérisés principalement par leurs spectres d'absorption. Les produits de décroissance d'échantillons de EsX_2 maintenus à la température ambiante et à la température de l'hélium liquide ont été suivis par spectrophotométrie. Dans tous les cas, l'identification positive des espèces petit-fils, CfX_2 , a été faite. Aucune preuve spectrale définitive de la présence possible du produit fils BkX_2 n'a été obtenue.

Abstract. — Samples of EsCl_2 , EsBr_2 , and EsI_2 have been prepared for the first time by reduction of the corresponding einsteinium trihalides with hydrogen gas at elevated temperatures. The three dihalides were characterized primarily by their absorption spectra. The products of the decay of EsX_2 samples held at ambient and liquid helium temperatures have been monitored by spectrophotometry. In all cases positive identification of the granddaughter, CfX_2 , species has been made. No definite spectral evidence for the presence of the possible daughter products, BkX_2 , has been obtained.

1. Introduction. — Two factors severely limit the study of einsteinium chemistry in the solid state : (1) only several hundred micrograms of einsteinium become available twice a year ; and (2) the intense radiation associated with the decay of the predominant isotope Es-253 (9.3×10^8 dis/s · μg ; 2.5×10^2 kJ/mol · s). Both factors require that special microchemical techniques be used in such studies, and the second factor precludes the routine use of X-ray powder diffraction for the analysis of bulk phase einsteinium compounds.

Although the existence of Es(II) has been anticipated for some time [1-3] and actually demonstrated in two, tracer-level experiments [4, 5], the preparation of a bulk phase compound of Es(II) has been achieved only recently [6]. Since CfCl_2 [7], CfBr_2 [8], and CfI_2 [9] were prepared by hydrogen reduction of the corresponding trihalides, we expected that the corresponding Es(II) halides could be prepared in an analogous way. We report here the preparation of EsCl_2 , EsBr_2 , and EsI_2 , their characteristic absorption spectra, and the results of monitoring the products formed by the radioactive decay process



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2. Experimental. — A complete summary of the microscale preparative and spectrophotometric techniques employed in the present work is available in [10] and the references therein. The reactions $2 \text{EsX}_{3(s)} + \text{H}_{2(g)} \rightarrow 2 \text{EsX}_{2(s)} + 2 \text{HX}_{(g)}$ were carried out by repetitive treatments for 15-20 minutes with H_2 at temperatures in excess of 575 °C, 750 °C, and 800 °C, respectively, for the successively heavier halides, with intervening evacuations to remove HX . At any stage of the synthesis we could transfer [10] the sample-capillary unit (closed with a stopcock) to a microscope-spectrophotometer for analysis of the sample composition. Adjustment of the conditions of subsequent H_2 treatment could then be made, if necessary, to ensure essentially complete reduction to EsX_2 .

For monitoring the sample composition as a function of time, the sample capillary was flame sealed under reduced pressure of H_2 or Ar. Samples to be stored in liquid He were further encapsulated in a glass tube inside a copper tube before immersion. These samples were removed from the liquid He prior to spectral analysis. In all cases spectral data were obtained at ambient temperature without annealing the sample and then again immediately following several minutes' annealing at ~ 435 °C. The latter treatment generally yields spectral data of higher resolution than that obtained without annealing. However, the annealing process itself might effect a chemical change in the sample.

3. Results and discussion. — Spectra of EsCl_2 , EsBr_2 , and EsI_2 are presented in figure 1. A spec-

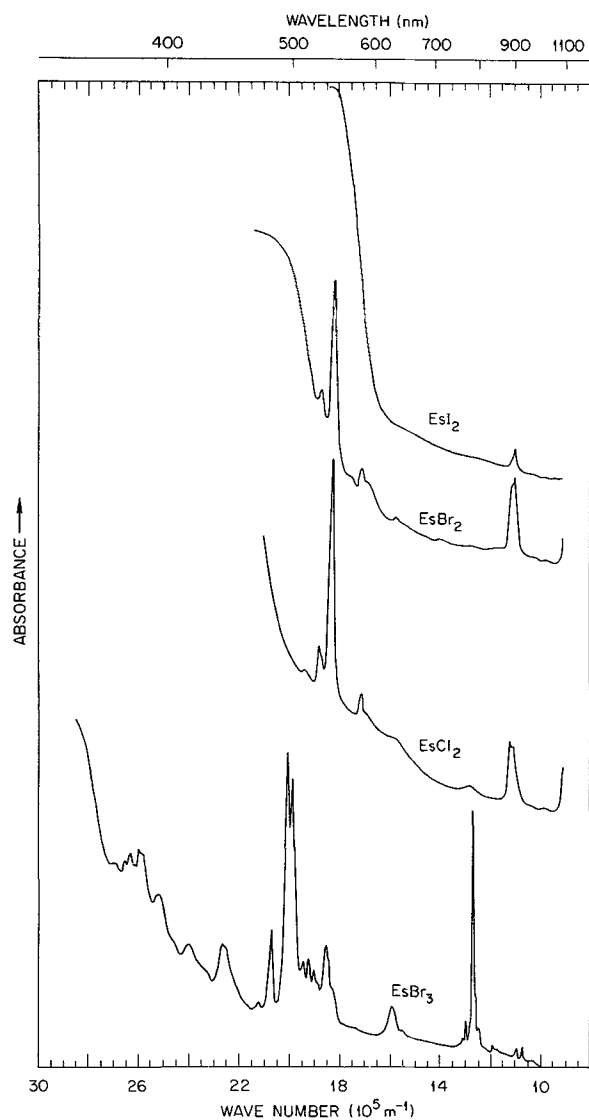
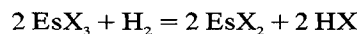


Fig. 1. — Absorption spectra of EsCl_2 , EsBr_2 , EsI_2 and EsBr_3 .

trum of EsBr_3 [11] is included for comparison. The dihalide absorption peak positions as well as the UV cutoffs shift to lower energy with the heavier halides. Some of the f-f absorption peaks of Es(II) are similar to those of Cf(II) [7, 9], a fact which compli-

cates the interpretation of spectral data obtained from aged EsX_2 samples.

The reversibility of the



reactions has been demonstrated. We determined through repetitive cycles of chemical synthesis/spectral analysis that high temperature (at or above the melting point of EsX_3) is required for complete reduction. Low-temperature reduction may lead only to mixed-valence compounds [12].

An interesting feature of our research has been the study of the chemical species that result from the radioactive decay of EsX_2 compounds. Is BkX_2 , unknown in bulk phase, produced through the alpha decay of EsX_2 ? Or more generally, are chemical oxidation states maintained through alpha and beta decay processes? Samples of the three einsteinium dihalides (and one each of $(\text{Es}, \text{Yb})\text{Cl}_2$ and Es(II) in LaCl_3) sealed in H_2 and stored at ambient temperature have been under study for various lengths of time. A sample of EsCl_2 , sealed in Ar and stored at ambient temperature, is under study as a companion sample to the above to test the influence of the sample's atmosphere. A sample of EsBr_2 sealed in H_2 was stored for 200 days in liquid He to minimize sample self-annealing.

Common to all the aged EsX_2 samples analysed so far is the presence of the corresponding grand-daughter CfX_2 species and the absence of new absorption peaks which might be attributed to BkX_2 species. One might speculate that since the parent and granddaughter species have been identified as dihalides, the intermediate, daughter species should also be a dihalide.

In two, aged samples of EsBr_2 , limited (< 5%) oxidation to the (III) state occurred, producing CfBr_3 in the sample stored at ambient temperature but producing CfOBr in the sample stored in liquid He. This result, which suggests the occurrence of different chemistry at the different temperatures, awaits confirmation. Continued study of the effects of time, storage temperature, and sample atmosphere on the chemical consequences of the radioactive decay of EsX_2 is planned or presently underway.

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