PREPARATION AND PROPERTIES OF SOME NEW CURIUM COMPOUNDS

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ABSTRACT. The following compounds of element 96, Curium, have been prepared and studied using ultramicrochemical techniques: CmPO₄·H₂O, Cm(ReO₄)₃·xH₂O, Cm(ReO₄)₃, Cm₂(MoO₄)₃, CmVO₄, CmCrO₄, CmAsO₄, CmScO₃, CmVO₃, CmCrO₃, CmFeO₃, Cm₂(C₂O₄)₃·10H₂O, Cm(HCOO)₃, CmOF, CmOCl, CmOBr. A new compound of tetravalent curium, Li₂CmO₃, and, what we believe to be the first representative of pentavalent curium, Na₃CmO₄, have also been prepared. A new synthesis for CmF₃ has been developed, and some thermodynamic properties of CmCl₃ have been studied.

1. INTRODUCTION

Even though element 96, Curium, was discovered no less than 40 years ago, in July 1944 (1)(2), and was isolated as the isotope $^{242}$Cm in 1948 (3)(4)(5), only relatively few solid compounds have been characterized to date. In the earliest time, when only short-lived $^{242}$Cm ($T_{1/2} = 162.5$ days, $S = 3320$ Ci/g = $7.4 \times 10^9$ dpm/μg) was available in sufficient quantities, it was possible only in a few exceptional cases to obtain X-ray data of curium compounds. Asprey and Ellinger (6) were the first ones to obtain lattice constants of CmF₃ and Cm₂O₃ using $^{242}$Cm in the preparation of these compounds.

The situation became somewhat better, when in August 1953, weighable quantities of $^{244}$Cm became available by irradiation of "napkin rings" in the MTR (7). $^{244}$Cm ($T_{1/2} = 17.9$ years, $S = 82$ Ci/g = $1.82 \times 10^8$ dpm/μg) was much better suited for chemical work than $^{242}$Cm, and a number of compounds were prepared and characterized by X-ray crystallography.

Besides the fluoride, CmF₃, which had been known from the earlier preparation (6), Asprey, Keenan, and Kruse (8) prepared the halides CmCl₃, CmBr₃, and CmI₃. The only oxyhalide known as early as 1955 was CmOCl₁, which was also obtained by Weigel et al (9) in a study of the vapor phase hydrolysis of CmCl₃. Asprey, Ellinger, Fried and Zachariasen (10) prepared CmO₄. Keenan reported the preparation of complex fluorides of

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tetravalent curium: LiCmF₆ (11), Na₇Cm₆F₃₁ (12), K₇Cm₆F₃₁ (13), and
Rb₂CmF₆ (14). Damien (15) prepared the chalcogenides, Charvillat et
al (17) the pnictides, Weigel et al (18) the silicides.

Quite a few papers deal with the curium oxygen system. The phase diagram
was established by Chikalla and Eyring (19)(20). Some phase transforma­
tions of this system were studied by Mosley (21), Haug (22), and by
Sudakov and Kapshukov (23). The melting point of Cm₂O₃ was determined by
Smith (24), the radiation-induced structural change of C - Cm₂O₃ into A­
Cm₂O₃ was reported by Wallmann (25), and by Noé (26).

Relatively few ternary compounds of Cm have been studied, using "⁴²⁴Cm.
These include CmPO₄ (27)(28)(29), CmNbO₄ (28), CmTaO₄ (28), and Cm₀.₅P₂O₅ (28).

A few papers have also been published using the rare isotope "⁴⁸Cm,
which is the daughter of "²⁵²Cf and is particularly well-suited for che­
chemical work because of its long half life (T₁/₂ = 3.5×10⁵ years, S =
4.24×10⁻³ Curies/g = 9.42×10³ dpm/µg). Compounds of "⁴⁸Cm, which have
been studied, include CmCl₃ (30), CmOCl (31), CmO₂ (32)(33), CmO₂·₂·₆ (34)
CmF₄ (35), BaCmO₃ (35), and Cm₂O₃ (36).

Because we have been supplied with a total of 40 mg of "⁴⁴Cm by courtesy
of the US Department of Energy, Isotopes Distribution Office, Oak Ridge,
TN, we decided to contribute to the solid state chemistry of curium by
synthesis and characterization of additional, hitherto unknown compounds,
and by restudying some of the known compounds using more advanced tech­
niques. This work is reported in this paper.

2. EXPERIMENTAL

2.1. Safety Precautions.

All work with "⁴⁴Cm was carried out in a Berkeley standard glove box,
which was shielded with 2 mm lead on its front side. Even though "⁴⁸Cm,
despite its short half life, has no serious radiation hazard due to
penetrating gamma radiation, and its fission yield is so small so that
even several milligrams pose no neutron hazard, we found it suitable to
use the well established techniques of Cunningham (37)(38), and those of
Fried and Davidson (39) because of their elegance, and because they
allow the preparation of individual compounds inside the X-ray capillary
or in its vicinity without difficult manipulation. The amount of "⁴⁴Cm
used in an individual preparation was limited to less than 100 µg, be­
cause such an amount still gives a good pattern without any film-fogging
due to radioactive background radiation.

2.2. Recovery and Purification of Curium.

The curium, which was used in this work had the isotope composition
shown in Table 1. It was supplied in two batches by the Isotope distri-