The relative intensities (in parentheses) were computed as $k = (100/PL) \log I_0/I$ for pressure P (reduced to 25°) and path L (both in cm.), from the literal record of per cent transmission I.

Attempts to compare the P–H and P–D bending modes for all six species failed because the pertinent bands proved too weak and complex; and CH_3 rocking and wagging interfered.

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CONTRIBUTION NO. 320 FROM THE DEPARTMENT OF CHEMISTRY, TUFTS UNIVERSITY, MEDFORD, MASSACHUSETTS

A Lithium Europium Hydride Inverse Perovskite Phase, $LiEuH_3$

BY CHARLES E. MESSER AND KENNETH HARDCASTLE

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An earlier note from this laboratory[1] described the preparation, and the characterization by X-ray powder diffraction, of the inverse perovskite phases of probable composition $LiSrH_3$ and $LiBaH_3$. With calcium only CaH_2 was found under similar conditions.

These studies have been extended to include europium and ytterbium, since the deuterides of these metals have been found[2] to have the orthorhombic structure of CaH_2, SrH_2, and BaH_2,[3] in contrast with the fluorite structures of the dihydride phases of the other rare earths.

Experimental

The europium metal, 99.9%, was obtained from the Cerium Metals and Alloys Division of Ronson Metals, Inc., Newark, N. J. The ytterbium metal (99.9%) was obtained from United Mineral and Chemicals Corporation.

The mixed hydrides were prepared, and their powder diffraction patterns taken, essentially by the procedures and under the conditions of the previous research.[1] Molybdenum boats were used as sample containers.

The principal europium preparation (I), with lowest europium content, was reddish orange and finely crystalline. Europium preparation II was reddish black before grinding, and reddish brown afterward. The ytterbium preparations were gray-black before and after grinding. All preparations except europium I, before grinding, had the gross shapes of the original metal lumps.

Preparation III, made from europium from a different source, had the appearance of preparation II. It was presumed impure because it could not be degassed under vacuum at 350° and because it took up so little hydrogen. It was briefly air exposed, but tested since its appearance was the same as that of sample II. It gave the same lattice constant with the same precision as sample I.

Table I gives information on the preparation and composition of the samples. The hydrogen contents were corrected for diffusion losses through the stainless steel outer bomb, because of the small size of the preparations—of the order of 0.1 g. of Li and 1–2 g. of rare earth metal.

TABLE I

PREPARATION AND COMPOSITION OF SAMPLES

Sample	Mole % Eu or Yb orig. alloy	% of theor. H_2 uptake	Hydride phase(s)	Other phase(s)
Eu I	32.9	94.7	$LiEuH_3$	Unidentified
Eu II	55.6	93.4	EuH_2, some $LiEuH_3$	None
Eu III	42.4	65.5	$LiEuH_3$, some EuH_2	Trace Eu_2O_3
Yb I	35.2	82.0	YbH_2	Trace Yb_2O_3 Unidentified
Yb II	44.4	94.7	YbH_2	Trace Yb_2O_3 Unidentified

Results and Discussion

For the hydrided lithium–europium samples I and III, 20 sharp, well-defined lines were found, which could be indexed on the basis of a primitive cubic unit cell. By analogy with the earlier research, these were interpreted in terms of a cubic inverse perovskite lattice of $LiEuH_3$. In the lithium–ytterbium samples, only ytterbium dihydride was found.

For $LiEuH_3$ sample I, five extraneous lines were found, all very weak, which could not be assigned to EuH_2 or to any other impurities which might reasonably be expected, including the recently reported $LiEuO_2$.[4] Several similar lines were also found in the LiH–YbH_2 system. These suggest the extraneous lines reported in the earlier paper[1] for Sr and Ca samples, which were attributed to residual unhydrided metallic phase. No information could be found in the literature on alloys of lithium with the rare earths.

The values of the lattice constant were determined, after correction for film shrinkage, by extrapolation, using the Nelson–Riley function.[5]

The lattice constant and density values for the perovskite phase from europium samples I and III were: $LiEuH_3$, $a_0 = 3.796 \pm 0.001$ Å., $\rho = 3.378$ g. cm.$^{-3}$. The lattice constant value from sample II, 3.794 ± 0.002 Å., was less accurate because of the smaller amount of perovskite phase present.

The amount of europium dihydride phase present in sample II was sufficient to enable an accurate determination of the lattice constants of orthorhombic EuH_2. These are shown in comparison with the europium dideuteride values of Warf and Korst.[2] The parameters were determined by the method of least squares, as adapted by Cohen[6] for use in X-ray powder diffrac-

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tion: EuH_2, this research, $a_0 = 6.262$, $b_0 = 3.799$, $c_0 = 7.213$ Å.; EuD_2, ref. 2, $a_0 = 6.21$, $b_0 = 3.77$, $c_0 = 7.16$ Å.

The formation of a perovskite by Eu^{2+} but not by Yb^{2+} is in accord with the closeness of the ionic radii to those of Sr^{2+} and Ca^{2+}, respectively. Table II shows the lithium–hydrogen and metal–hydrogen distances in the perovskites and related hydrides, and the ionic radii of the metal ions. The shortening of the Li–H distance, as compared with crystalline LiH, is even more striking in $LiEuH_3$ than in $LiSrH_3$.

TABLE II

Compd.	d_{Li-H}, Å.	d_{M-H}, Å.	$r_{M^{2+}}$, Å.[a]
LiH	2.04[b]	...	...
SrH_2	...	2.49[1]	1.10
EuH_2	...	2.45	1.09
$LiSrH_3$	1.92	2.71[1]	1.10
$LiEuH_3$	1.90	2.68	1.09
CaH_2	...	2.32	0.94
YbH_2	...	2.30	0.93

[a] W. T. Zachariasen in "The Actinide Elements," G. T. Seaborg and J. J. Katz, Ed., McGraw-Hill Book Co., New York, N. Y., 1954, Chapter 18. [b] E. Staritzsky and D. J. Walker, *Anal. Chem.*, **28**, 1055 (1956).

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CONTRIBUTION FROM THE LABORATORY OF GENERAL
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Another Preparation Method of Vanadium(III) and Uranium(IV) 1,3-Diketone Complexes

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Vanadyl(IV) and uranyl(VI) acetylacetonates as well as 1,3-diphenyl-1,3-propanedionates are reduced by zinc powder in a medium containing an excess of the appropriate diketone to the corresponding vanadium(III) and uranium(IV) complexes. The reduction is a convenient laboratory preparation of vanadium(III) and uranium(IV) acetylacetonates in practically quantitative yield from common chemicals. Otherwise, by using the methods hitherto described, vanadium(III) chloride[1] and uranium(IV) salts[2] are necessary.

The solutions of the reduced metal 1,3-diketonates were fairly stable; no sign of oxidation during the course of preparation was noticed. The by-product zinc complex can be easily separated from the vanadium(III) or the uranium(IV) complex owing to the difference in solubilities (petroleum ether) or vapor pressure (vacuum sublimation). The method, which is limited to only a few metals but is applicable to other complexes, is the subject of our further investigation. For instance, molybdenyl(VI) acetylacetonate is quantitatively reduced to a new molybdenum(IV) complex[3] which unexpectedly retains oxygen, as distinct from the vanadyl and uranyl 1,3-diketonates whose reduction by the same method is reported here.

Experimental

Tetrakis(2,4-pentanedionato)uranium(IV).—A mixture of anhydrous uranyl(VI) acetate (2 g.), obtained by drying commercial dihydrate (reagent grade, Merck—Darmstadt) at 110°, absolute ethanol (5 ml.), and dry acetylacetone (2 g.) was boiled under reflux for 1 hr.[4] The ethanol was then removed by distillation under reduced pressure and the residue heated (60–65°, 30 min.) with acetylacetone (45 ml.) and zinc powder (2 g.). The liquid, decanted from the remaining zinc powder, was diluted with an equal volume of petroleum ether (b.p. 40–70°) and left in a refrigerator overnight. The deposited crystals of the acetylacetonates were filtered off and washed with petroleum ether. Zinc acetylacetonate, being more volatile, was separated from the uranium complex by vacuum sublimation at 0.01 mm. pressure and 100°. The crude uranium(IV) acetylacetonate was purified by sublimation at 140° (0.01 mm.) or by recrystallization from acetylacetone–petroleum ether; this compound had m.p. 175°.

Anal. Calcd. for $U(C_5H_7O_2)_4$: U, 37.54. Found: U, 37.03.

Tetrakis(1,3-diphenyl-1,3-propanedione)uranium(IV).—A solution of uranyl(VI) dibenzoylmethane complex[5] (2 g.) and dibenzoylmethane (2.5 g.) in chloroform (25 ml.) was boiled with zinc powder (0.6 g.) under reflux for 15 min. in nitrogen atmosphere; the resulting mixture was filtered and the filtrate mixed with petroleum ether (30 ml.). The crystalline precipitate was thoroughly washed with ethyl ether to remove the zinc complex. The residue was recrystallized from a chloroform–petroleum ether mixture (1:1) in a dry nitrogen atmosphere; this compound had m.p. 180° dec.[6]

Anal. Calcd. for $U(C_{15}H_{11}O_2)_4$: U, 21.04. Found: U, 21.00.

Tris(2,4-pentanedionato)vanadium(III).—A solution of vanadyl(IV) acetylacetonate[7] (4 g.) in acetylacetone (25 ml.) was boiled with zinc powder (1 g.) for 5 min. in a dry nitrogen atmosphere, decanted from undissolved zinc powder, and cooled to room temperature. Zinc acetylacetonate was filtered off and the filtrate diluted with petroleum ether (20 ml.) in order to complete the separation of zinc complex. Pure vanadium(III) acetylacetonate crystallized out from the solution after several hours. The brown crystals had the same properties as described in the literature[2]; m.p. 184°.

Anal. Calcd. for $V(C_5H_7O_2)_3$: V, 14.66. Found: V, 14.95.

Bis(1,3-diphenyl-1,3-propanedione)oxovanadium(IV).—A different preparation of this compound has been reported.[8] A solution of vanadyl(IV) acetylacetonate (2 g.) and dibenzoylmethane (4 g.) in benzene (45 ml.) was refluxed until the color turned from blue to green (about 30 min.). The vanadyl(IV) complex formed as green crystals upon cooling the solution; m.p. 248° dec.

Anal. Calcd. for $VO(C_{15}H_{11}O_2)_2$: V, 9.92. Found: V, 9.93.

Tris(1,3-diphenyl-1,3-propanedione)vanadium(III).—Bis(1,3-diphenyl-1,3 propanedione)oxovanadium(IV) (2 g.), obtained by the foregoing method, was dissolved in benzene (30 ml.); dibenzoylmethane was added (3.5 g.) and reduction with zinc

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