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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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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powder (1.2 g.) carried out as described for the corresponding uranium(IV) compound. Dark brown crystals formed; m.p. 210° dec.

Anal. Calcd. for $V(C_{15}H_{11}O_2)_3$: V, 7.07. Found: V, 6.80.

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CONTRIBUTION FROM TEXACO EXPERIMENT,
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Hexahydroxylamminecobalt(III) Chloride and Fluoride

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Hexahydroxylamminecobalt(III) chloride has been prepared previously by Werner.[1] His procedure includes the reaction of free hydroxylamine with $(Co(en)_2Cl_2)Cl$. The method suffers from the disadvantage that small quantities of material must be used, and it involves the replacement of ethylenediamine, a strongly coordinated ligand, by hydroxylamine, a weaker, easily decomposed ligand. The method has been unreliable in our hands.

We have found that the general procedure of Bauer and Drinkard,[2] which uses $Na_3[Co(CO_3)_3]\cdot 3H_2O$ and amine hydrochlorides, can be adapted to the preparation of $[Co(NH_2OH)_6]Cl_3$. This procedure allows mild conditions to be used, which minimize the decomposition of free hydroxylamine. The preparation is best performed using small quantities of materials, and attempts to scale the reaction to larger quantities have been unsuccessful. However, the starting materials are widely available and the preparation is sufficiently rapid so that large amounts of the compound are readily accumulated.

The fluoride salt is obtained from the chloride by potentiometric titration with AgF. This is necessary in order to avoid an excess of silver ion, which decomposes the complex and is reduced to metallic silver.

The hexahydroxylamminecobalt(III) ion is relatively stable in acidic solution but rapidly decomposes in neutral or basic solution. The latter solutions are light-sensitive, and small amounts of impurities accelerate their decomposition. The pure compounds have been stored in the absence of light and moisture for periods of 2 years. It is interesting that the fluoride salt can be obtained quite readily free of hydrofluoric acid, whereas it is extremely difficult to obtain the amine salt in any form other than the acid salt.[3]

Experimental

Preparation of $[Co(NH_2OH)_6]Cl_3$.—Sodium triscarbonatocobaltate(III) trihydrate was prepared by the method of Bauer and Drinkard.[2] A solution of 4.2 g. of hydroxylamine hydrochloride dissolved in 20 ml. of 3 *N* HCl was added dropwise to a vigorously stirred slurry of 3.6 g. of the cobaltate in 10 ml. of water. The temperature was held between 0 and 5° during the addition. The cold mixture was stirred for 10 min., then cold concentrated HCl was added dropwise until leafy yellow crystals appeared. The mixture changed from muddy brown to blue-green when precipitation began. Filtration gave a crude brown product. Solution of this in the minimum amount of water and dropwise addition of concentrated HCl gave the pure hydroxylammine compound. Yields ranged from 10 to 15% of theoretical. The salt was extremely soluble, and unless the solutions were strongly acidic, severe decomposition resulted, with a corresponding decrease in yield. Concentrating the solution under vacuum gave slightly better yields.

Anal. Calcd. for $[Co(NH_2OH)_6]Cl_3$: H, 4.96; Co, 16.3; Cl, 29.3; N, 23.1. Found: H, 5.22; Co, 16.3; Cl, 27.9; N, 23.1.

Preparation of $[Co(NH_2OH)_6]F_3$.—A 3.5 *N* solution of AgF was prepared from Harshaw Spec. 101 grade material and was standardized against sodium chloride solution. A rapidly-stirred solution of 3.6 g. of $[Co(NH_2OH)_6]Cl_3$ in 30 ml. of 1 *N* HCl was titrated with 3.5 *N* AgF. The end point was determined potentiometrically, using a Beckman pH meter equipped with an Ag–AgCl and a calomel electrode. The observed end point agreed quite closely with the calculated amount of AgF required. It was necessary to avoid an excess of silver ion, as this appeared to promote decomposition of the complex. Filtration to remove AgCl gave a clear yellow solution, from which the fluoride salt was obtained by repeated addition of 2–3-ml. quantities of ethanol until precipitation was complete. The product was washed with alcohol and was dried over concentrated H_2SO_4. Yields averaged 50–60% of theoretical.

Anal. Calcd. for $[Co(NH_3OH)_6]F_3$: Co, 18.77; F, 18.15. Found: Co, 18.8; F, 18.2.

Analysis.—Cobalt was determined by an iodometric method similar to that outlined by McNabb for cobalt amines.[4] The sample was decomposed by heating in 6 *N* NaOH solution. Addition of 3% H_2O_2 to the cooled solution gave a precipitate of $Co(OH)_3$ which was filtered, washed, and dissolved in excess acidified KI solution. The liberated iodine was determined by titration with $Na_2S_2O_3$. Chloride was determined by potentiometric titration with $AgNO_3$. Fluoride was determined by precipitating as PbFCl.[5] This was separated by filtration, dissolved in 25% HNO_3, and chloride ion was determined by potentiometric titration with $AgNO_3$.[6]

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Spiro Silicon and Germanium Imidazolidines

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The reaction of germanium tetrachloride with ammonia[1] and various organic amines[1–4] has been known for over 30 years, but no studies of the action of difunctional organic amines have been reported. Ger-