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,
INCORPORATED, RICHMOND, VIRGINIA

Hexahydroxylamminecobalt(III) Chloride and Fluoride

BY RUDOLPH C. WHITE AND S. W. FINLEY

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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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CORNELL UNIVERSITY, ITHACA, NEW YORK

Spiro Silicon and Germanium Imidazolidines

BY C. H. YODER AND J. J. ZUCKERMAN

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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-