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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW HAMPSHIRE COLLEGE.]

NEW RARE EARTH COMPOUNDS.

BY L. A. PRATT AND C. JAMES.

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The salts given in this paper were prepared while searching for some crystallin compounds which might be useful for fractional crystallization of the yttria earths.

Yttrium Methylsulfonate, $Y(CH_3SO_2O)_3.4H_2O$.—In the preparation of this salt, yttrium oxide was dissolved in methylsulfonic acid and the solution evaporated. The residue was taken up in alcohol and precipitated by ether. The compound separated as a viscous mass, which rapidly became crystallin. It was separated from the liquid as far as possible with suction and air-dried. The salt was too soluble to be of value for fractional crystallization.

Calculated: Y, 19.93; S, 21.54. Found: Y, 19.72; S, 21.42.

Yttrium Methenedisulfonate, $Y_2(CH_2(SO_2O)_2)_3.(2^1/_2H_2O?)$.—This compound was prepared by dissolving yttrium oxide in methenedisulfonic acid. The solution was evaporated and treated with absolute alcohol and ether. The resulting precipitate was filtered, washed with ether, and air-dried. The salt is very soluble.

Calculated: Y, 23.87. Found: Y, 23.76.

Yttrium Methinetrisulfonate, $YCH(SO_2O)_3.3^1/_2H_2O$.—This salt was made by dissolving yttrium oxide in methinetrisulfonic acid and evaporating the solution. Upon the addition of alcohol to this liquid, the compound was completely precipitated. It was washed with alcohol with the aid of suction, and air-dried. The salt is insoluble in alcohol and in acetic acid and only slightly soluble in nitric acid.

Calculated: Y, 21.96; S, 23.73. Found: Y, 21.91; S, 24.04.

The methinetrisulfonic acid for this compound was prepared[1] by treating powdered acetanilide with fuming sulfuric acid.

Yttrium Ethylsulfonate, $Y(C_2H_5SO_2O)_3.4H_2O$.—Yttrium oxide was dissolved in ethylsulfonic acid and the solution evaporated. The residue was taken up in alcohol and upon treatment with ether the compound came down in a crystallin form. This was washed on a filter with ether and dried in the air. Like most of the other sulfonates, this compound was very soluble.

Calculated: Y, 18.23. Found: Y, 18.05.

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[1] *J. Chem. Soc.*, **75**, 280.

Yttrium Camphorsulfonate, $Y(C_{10}H_{15}OSO_2O)_3.7H_2O$.—In order to prepare this salt, yttrium oxide was treated with camphorsulfonic acid and the resulting solution evaporated. The residue was taken up with alcohol and precipitated by ether. The compound came down in a crystallin form, and was filtered off, and air-dried. This substance was found to be very soluble.

Calculated: Y, 9.80. Found: Y, 9.82.

Yttrium Methoxysulfonate.—In an attempt to make yttrium methoxysulfonate, yttrium oxide was dissolved in methoxysulfonic acid and the solution evaporated on the water bath. The residue was dissolved in alcohol treated with an excess of ether. A sticky mass was thrown out, which failed to crystallize under any conditions.

Yttrium Salicylate, $Y(C_6H_4(OH)COO)_3.3^1/_2H_2O$.—Since this salt is insoluble in water, it was advantageous in preparing it, to first make the yttrium oxide into the formate and to add to this the required amount of salicylic acid. This mass was boiled until all formic acid was volatilized. The precipitate was then filtered, washed with hot water and dried in the air. The compound was crystallin and very insoluble.

Calculated: Y, 15.81. Found: Y, 15.73.

Yttrium Phthalate, $Y_2(C_6H_4(COO)_2)_3.3H_2O$.—To prepare this compound, a known amount of yttrium oxide was dissolved in formic acid and the required amount of phthalic acid added. The resulting mass was boiled to expel all formic acid. The liquid was then decanted off, and the residue boiled for some time with water. It was filtered, further washed with water, and dried in the air. The compound was very insoluble.

Calculated: Y, 24.58; C, 39.77; H, 2.50. Found: Y, 24.55; C, 39.48; H, 2.46.

Yttrium Glycolate, $Y(CH_2OHCOO)_3.2H_2O$.—This compound was prepared by dissolving yttrium hydroxide in glycolic acid and heating, when the compound separated out. The precipitate was filtered, washed with water, and air-dried. This salt is practically insoluble.

Calculated: Y, 25.42; C, 20.56; H, 3.74. Found: Y, 25.41; C, 20.23; H, 3.78.

Yttrium Phenylacetate, $Y(C_6H_5.CH_2COO)_3.H_2O$.—An excess of phenylacetic acid was added to yttrium hydroxide and heated. The precipitate formed was filtered while the solution was hot, washed with water, and air-dried. This salt was insoluble.

Calculated: Y, 17.38; C, 56.22; H, 4.53. Found: Y, 17.42; C, 56.03; H, 4.42.

Yttrium Phenoxyacetate, $Y(C_6H_5OCH_2COO)_3.3^1/_2H_2O$.—For the preparation of this compound, a solution of yttrium chloride was treated with the sodium salt of phenoxyacetic acid and the precipitate washed thoroughly with cold water to separate sodium chloride. The product was further purified by recrystallization from hot water. This compound was only slightly soluble in cold water.

Calculated: Y, 14.71; C, 47.58: H, 4.66. Found: Y, 14.66; C, 47.80; H, 4.50.

The *phenoxyacetates of Sm, Nd, Pr, La* and *Ce* were prepared in exactly the same manner as the yttrium salt. They were, however, much more insoluble than the latter and therefore could not be recrystallized from water.

$Sm(C_6H_5OCH_2COO)_3.3^1/_2H_2O$.

Calculated: Sm, 22.57; C, 43.20; H, 4.23. Found: Sm, 22.61; C, 43.30; H, 4.03.

$Nd(C_6H_5OCH_2COO)_3.2^1/_2H_2O$.

Calculated: Nd, 22.47. Found: Nd, 22.51.

$Pr(C_6H_5OCH_2COO)_3.1^1/_2H_2O$.

Calculated: C, 46.38; H, 3.90. Found: C, 46.14; H, 4.03.

$La(C_6H_5OCH_2COO)_3.2^1/_2H_2O$.

Calculated: La, 21.82. Found: La, 21.83.

$Ce(C_6H_5OCH_2COO)_3$.

Calculated: Ce, 23.63. Found: Ce, 23.88.

Thorium Phenoxyacetate.—By working with a neutral solution of thorium, the authors found, on the addition of an excess of phenoxyacetic acid, that the thorium was almost quantitatively precipitated. On the other hand, the rare earths behave very differently and are not thrown out of solution, even though a great excess of the acid be added.

This reaction of phenoxyacetic acid on a *neutral thorium* solution affords a method for the separation of this element from the rare earths.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW HAMPSHIRE COLLEGE.]

THULIUM I.[1]

BY C. JAMES

Received June 11, 1911.

Thulium was discovered by Cleve[2] in 1879 while trying to separate the element that gives a rose color to the salts of "old erbium." The earths used for this investigation consisted of some material obtained by Nilson while working upon ytterbia. These residues were separated during the use of "the fusion of the nitrate method" and consisted of those portions which were less basic than yttrium but more basic than ytterbium.

Cleve submitted this crude erbia to another long series of fractionations by again fusing the nitrates. This work yielded more basic, intermediate and least basic portions. Thalen examined these fractions spectroscopically for Cleve and showed that old erbia consisted of at least three elements. To the more basic part, which accompanied yttria, Cleve gave the name holmium, and to the least basic, the name thulium, derived

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[1] Abstract given before the New York Section, March 10th.

[2] *Compt. rend.*, Sept. 1, 1879.