text-books on quantitative analysis, to this reaction, and believe the observation to be new. It is of interest, perhaps, to note certain observations which show that some investigators have probably had this phenomenon accompanying others, without, however, fully recognizing or explaining it. Thus, Scheuer[1] analyzed barium and other pervanadates by treating them in a flask with dilute sulfuric acid, boiling until no more oxygen was given off, and measuring the amount of oxygen evolved. Hydrogen peroxide is liberated under these conditions and if the concentration of sulfuric acid is right, some or all of the vanadium may be reduced to the quadrivalent condition. Speaking of the analysis of barium pervanadate, Scheuer says, concerning the operation of boiling the solution to expel oxygen: "Dies ist beendet wenn die anfangs rote Lösung (primary action of peroxide on vanadium, giving pervanadic acid) eine hellgrüne Färbung angenommen hat." The "hellgrüne" color must have been that of a mixture of V_2O_4 and of V_2O_5, due to a partial reduction of the V_2O_5 by hydrogen peroxide. However, Scheuer says "In die Filtrate fand sich noch die freie Vanadinsaure......," and then gives instructions for determining it by reducing with sulfur dioxide and titrating against permanganate. Also, Cammerer,[2] in preparing pervanadic acid by causing hydrogen peroxide to react with solid vanadium pentoxide, found that the aqueous solution of the reaction product, when evaporated on the steam-bath, deposited a greenish colored substance giving, in dilute sulfuric acid, a green solution which reduced permanganate. More recently, Trautmann,[3] in analyzing ferrovanadium, fuses it with sodium peroxide, extracts the fusion with water and filters. The solution, which contains the vanadium and an excess of hydrogen peroxide, is acidified with sulfuric acid, and Trautmann states that at this stage he often observed a reduction, after boiling off the hydrogen peroxide. It seems very likely that here, also, conditions are sometimes right for reduction of vanadic acid by hydrogen peroxide.

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

NEW COMPOUNDS OF SAMARIUM AND NEODYMIUM.

BY C. JAMES, F. M. HOBEN AND C. H. ROBINSON.

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The following compounds were prepared during a search for salts of the rare earths that might be useful for fractionating:

Samarium Ethylsulfonate $(C_2H_5SO_3)_6Sm_2.6H_2O$.—Ethylsulfonic acid was heated nearly to boiling and small quantities of samarium oxide added

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[1] *Z. anorg. Chem.*, 16, 289 (1898).

[2] *Chem. Ztg.*, 15, 958 (1891).

[3] *Z. anal. Chem.*, 50, 371 (1911).

until no more oxide would dissolve. Finally a little more acid was added, the whole boiled for a short time, filtered and evaporated down on the water bath. The compound gradually crystallized out upon standing. The crystals were freed from the mother liquor by suction and washed with acetone.

This salt formed pale yellow crystals, very soluble in water and alcohol, but insoluble in acetone and ether. Upon heating, this substance charred and gave off a strong garlic odor.

Samarium ethylsulfonate lost all its water of crystallization when heated to 100° for four hours.

Calculated: Sm_2O_3, 32.78; S, 18.09; H_2O, 10.16. Found: Sm_2O_3, 32.70; S, 18.17; H_2O, 10.14.

Samarium Methylsulfonate $(CH_3SO_3)_6Sm_2 \cdot 7H_2O$.—This substance was prepared in a similar manner to the former sulfonate. The solution, after filtering and evaporating was allowed to stand for a day and a half. The crystals were dried as much as possible by suction and washed with acetone.

This sulfonate formed pale yellow crystals, very soluble in water and alcohol, only slightly soluble in acetone, and insoluble in ether.

Samarium methylsulfonate lost six molecules of water of crystallization after heating to 100° for some time.

Calculated: Sm_2O_3, 34.97. Found: Sm_2O_3, 35.15.

Samarium Propylsulfonate $(C_3H_7SO_3)_6Sm_2 \cdot 9H_2O$.—Obtained like the ethylsulfonate.

This compound did not crystallize well. It was filtered from the mother liquor by suction and well washed with ether. The result of this treatment was a powder of small crystals, possessing a yellowish tint, soluble in water, alcohol and acetone but insoluble in ether.

The propylsulfonate, when heated for a long time at 100°, lost eight molecules of water of crystallization.

Calculated: Sm_2O_3, 29.04. Found: Sm_2O_3, 29.12.

Samarium Isobutylsulfonate, $(C_4H_9SO_3)_6Sm_2 \cdot 7H_2O$, was prepared by saturating isobutylsulfonic acid with samarium oxide, care being taken to have the solution acid before filtering and evaporating. The concentrated solution was allowed to stand over sulfuric acid for a few days. The crystals were separated and washed with ether.

Samarium isobutylsulfonate lost five molecules of water, when kept at 100° for two days.

Calculated: Sm_2O_3, 27.90. Found: Sm_2O_3, 27.97.

Samarium Camphorsulfonate, $(C_{10}H_{15}OSO_3)_6Sm_2 \cdot 10H_2O$.—This sulfonate was obtained as above. When sufficient of the salt had separated, the dish was removed from the desiccator, the crystals separated upon a small

Buchner funnel and washed with ether. The crystals were dissolved in alcohol and the solution allowed to crystallize, after which it was again well washed with ether.

Samarium camphorsulfonate formed a mass of very small crystals, white with only a faint yellow tint. It was very soluble in water, alcohol and acetone, but insoluble in ether.

This compound after heating for some time at 100° became nearly anhydrous.

Calculated: Sm_2O_3, 18.67. Found: Sm_2O_3, 18.61.

Samarium Methane-trisulfonate, $(CH(SO_3)_3)_2Sm_2.16H_2O$.—A slightly acid solution of samarium oxide in methane-trisulfonic acid was evaporated and set aside to crystallize. The samarium compound separated very well after standing for a day. The crystals were drained and well washed with alcohol. They were yellowish, transparent, soluble in water but insoluble in alcohol, acetone and ether. This salt is very stable since it can be heated to high temperatures, with fuming nitric acid in sealed tubes, without decomposition taking place.

Samarium methane-trisulfonate lost two molecules of water after prolonged heating to 100°.

Calculated: Sm_2O_3, 31.84. Found: Sm_2O_3, 31.88.

Samarium 1,3,4-Meta-xylenesulfonate, $(C_6H_3(CH_3)_2SO_3)_6Sm_2.7H_2O$.—A concentrated solution of samarium oxide in the xylenesulfonic acid crystallized after standing some time. The solid was drained and washed with acetone. It formed small, very pale yellow crystals, soluble in water and alcohol, insoluble in acetone and ether.

Calculated: Sm_2O_3, 22.69. Found: Sm_2O_3, 22.65.

Samarium Glycollate, $(CH_2.OH.COO)_6Sm_2$.—Samarium hydroxide was gradually added to cold glycollic acid. Upon heating the filtered solution the salt separated as a very dense precipitate which was almost insoluble in water.

Samarium glycollate differs from yttrium glycollate, inasmuch as the former is anhydrous while the latter contains two molecules of water of crystallization.[1]

Calculated: Sm_2O_3, 46.44. Found: Sm_2O_3, 46.54.

Samarium Cacodylate, $((CH_3)_2AsO_2)_6Sm_2.16H_2O$.—This substance was obtained by boiling a solution of cacodylic acid with samarium hydroxide. The last portions of samarium hydroxide were dissolved by the careful addition of more acid. Upon cooling, the solution crystallized. The whole was poured upon a Buchner funnel and the crystals washed with alcohol and dried.

The cacodylate forms white crystals which are soluble in hot water, insoluble in alcohol and acetone.

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[1] Pratt and James, THIS JOURNAL, **33**, 1330.

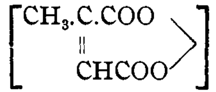
When kept at 100° for three hours all water of crystallization was lost.

Calculated: Sm_2O_3, 24.73; H_2O, 20.43. Found: Sm_2O_3, 24.81; H_2O, 20.43.

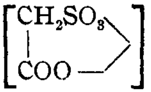
Samarium Ethylene-disulfonate, $(C_2H_4(SO_3)_2)_3Sm_2.4H_2O$, was prepared by saturating ethylene disulfonic acid with samarium hydroxide. The solution was made slightly acid, filtered and evaporated. The salt separated well. It formed yellow transparent crystals, soluble in water, slightly soluble in alcohol and insoluble in acetone.

Calculated: Sm_2O_3, 37.22. Found: Sm_2O_3, 37.04.

Samarium Ethylglycollate, $(C_2H_5O.CH_2COO)_6Sm_2.18H_2O$. — Separated from concentrated solution in large yellow transparent crystals which contained included mother liquor. An analysis showed the presence of eighteen molecules of water of crystallization. However, since there was doubt about mother liquor, the study of the rare earth ethylglycollates will be continued at an early opportunity, with larger amounts of material.

Samarium Citraconate,  $\left[\begin{array}{c}CH_3.C.COO \\ \| \\ CHCOO\end{array}>\right]_3Sm_2.12H_2O$.—Citraconic acid was saturated with samarium hydroxide, filtered and concentrated. The compound which separated out upon standing, was removed by suction and the mass of citraconate washed with alcohol and acetone.

Calculated: Sm_2O_3, 38.72. Found: Sm_2O_3, 38.88.

Samarium Sulfoacetate,  $\left[\begin{array}{l}CH_2SO_3 \\ | \\ COO\end{array}>\right]_3Sm_2$.—Samarium hydroxide rapidly dissolved in sulfoacetic acid. No crystals were obtained by evaporation and leaving over sulfuric acid. The solution merely formed a thick sticky mass.

Samarium Hydroxyethanesulfonate.—A concentrated solution of this compound would not crystallize when allowed to remain in a desiccator over sulfuric acid.

Neodymium Methylsulfonate, $(CH_3SO_3)_6Nd_2.7H_2O$.—Methylsulfonic acid was saturated with neodymium oxide and filtered. The concentrated solution solidified to a crystalline mass, when left in a desiccator, over sulfuric acid. The crystals were broken up and well washed with ether. They were very soluble in water, soluble in alcohol and slightly so in acetone, but insoluble in ether. It lost six molecules of water of crystallization at 100° similar to the samarium compound.

Calculated: Nd_2O_3, 34.17. Found: Nd_2O_3, 34.24.

Neodymium Ethylsulfonate, $(C_2H_5SO_3)_6Nd_2.6H_2O$.—The formation of this compound was brought about in the same manner as the preceding. It appeared to be less soluble than the methylsulfonate however, for it crystallized easily upon evaporation and being allowed to stand for a short time. The powdered salt was washed with ether. It possessed a pale amethyst color, was insoluble in acetone and ether, soluble in alcohol, and very soluble in water.

Calculated: Nd_2O_3, 32.02; H_2O, 10.28. Found: Nd_2O_3, 32.05; H_2O, 9.97.

Neodymium Propylsulfonate, $(C_3H_7SO_3)_6Nd_2.6H_2O$.—A solution of this substance gave upon evaporation a voluminous mass of small crystals. They were washed by ether and dried. The propylsulfonate is very soluble in water, soluble in acetone and alcohol. After heating for some time to 100°, one molecule of water remains.

Calculated: Nd_2O_3, 29.65. Found: Nd_2O_3, 29.63.

Neodymium Isobutylsulfonate, $(C_4H_9SO_3)_6Nd_2$.—Crystals of this compound formed with difficulty. They were voluminous, pale amethyst, soluble in alcohol and very soluble in water.

The estimation of Nd_2O_3 gave results corresponding to 8 H_2O, this being one molecule more than the samarium compound possessed. Moisture or efflorescence might be the cause of this difference. However, the salts did not seem to be of sufficient importance to make it worth while preparing again.

Calculated: Nd_2O_3, 26.81. Found: Nd_2O_3, 26.94.

Neodymium Ethylene-disulfonate, $(C_2H_4(SO_3)_2)_3Nd_2.10H_2O$.—The acid was carefully neutralized with neodymium oxide. The clear solution was evaporated, after which large amethyst crystals formed. They were insoluble in alcohol and acetone, but very soluble in water. When heated to 100° for a long time the salt gradually lost water until a hydrate containing 4 molecules of water remained.

Calculated: Nd_2O_3, 32.59. Found: Nd_2O_3, 32.58.

Neodymium Methane-trisulfonate, $(CH(SO_3)_3)_2Nd_2.14H_2O$.—Fairly large crystals of this substance were obtained by evaporating a solution of the oxide in the corresponding acid. They were of a pale amethyst color, insoluble in alcohol, acetone and acetic acid, but very soluble in water. Like most of the other sulfonates, there was very little difference between the solubilities at room temperature and 100°. This renders these compounds unsuitable for rapid fractionation.

The neodymium trisulfonate, similar to other salts of this acid, is very stable; it is not decomposed by fuming nitric acid, under pressure, until a high temperature is reached.

Calculated: Nd_2O_3, 32.15. Found: Nd_2O_3, 32.04.

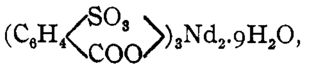
Neodymium Camphorsulfonate, $(C_{10}H_{15}OSO_3)_6Nd_2.17H_2O$.—A solution of this salt obtained in the usual way crystallized with difficulty, yielding a fluffy, very pale amethyst powder, soluble in alcohol and acetone, and very soluble in water.

Calculated: Nd_2O_3, 16.98. Found: Nd_2O_3, 17.02.

Several hydrates of the camphorsulfonates appear to exist.

Neodymium 1,3,4-Metaxylenesulfonate, $(C_6H_3(CH_3)_2SO_3)_6Nd_2.2H_2O$.—This sulfonate separated out, during the evaporation on a water bath, in crystalline form. It was of a very pale amethyst color, insoluble in acetone, slightly soluble in alcohol and soluble in water.

Calculated: Nd_2O_3, 22.46. Found: Nd_2O_3, 22.35.

Neodymium Metasulfobenzoate,  $(C_6H_4\left\langle\begin{smallmatrix}SO_3\\COO\end{smallmatrix}\right\rangle)_3Nd_2.9H_2O$, formed pale colored crystals soluble in alcohol and acetone, and very soluble in water.

Calculated: Nd_2O_3, 32.03. Found: Nd_2O_3, 32.19.

Neodymium Quinate, $(C_6H_7(OH)_4COO)_6Nd_2.11H_2O$.—Neodymium hydroxide was boiled with quinic acid; the solution filtered and evaporated. The quinate crystallized out upon cooling. Pale amethyst colored powder, slightly soluble in cold water.

Calculated: Nd_2O_3, 20.62. Found: Nd_2O_3, 20.61.

Neodymium Anisate, $(C_6H_4.CH_3O.COO)_6Nd_2$.—This compound was precipitated when a slightly acid solution of sodium anisate was added to a nearly neutral solution of neodymium chloride. Free anisic acid was removed from the precipitate by means of hot acetone. The pale colored precipitate was insoluble in water.

Calculated: Nd_2O_3, 28.16; H, 3.54; C, 48.19. Found: Nd_2O_3, 28.17; H, 3.31; C, 48.29.

Neodymium Oxanilate, $(C_6H_5NHOCCOO)_6Nd_2.5H_2O$.—When neodymium chloride was added to a hot, slightly acid solution of sodium oxanilate, a thick sticky mass separated, which rapidly became hard and crystalline upon cooling. The compound was insoluble.

Calculated: Nd_2O_3, 24.70. Found: Nd_2O_3, 24.69.

Neodymium Cacodylate, $((CH_3)_2AsO_2)_6Nd_2$.—Cacodylic acid was saturated with neodymium hydroxide. The liquid was filtered and evaporated. Upon cooling, the salt separated in very soft asbestos-like crystals. It was insoluble in alcohol and acetone, slightly soluble in cold water, and soluble in hot water.

Calculated: Nd_2O_3, 30.31. Found: Nd_2O_3, 30.40.

Neodymium Hydroxyethanesulfonate.—A solution containing this compound would not crystallize, so as to be workable.

DURHAM, NEW HAMPSHIRE.

A NEW METHOD FOR THE SEPARATION OF THORIUM.

BY T. O. SMITH AND C. JAMES.

Received January 13, 1912.

While working upon the separation of thorium from the rare earths the authors observed that sebacic acid gave a precipitate in a neutra solution which appeared to be quantitative.

Thorium sebacate is a voluminous, granular precipitate which settles