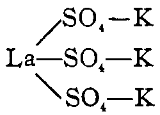

These specific properties of lanthanum render the formation of the alum more difficult.

UNIVERSITY OF NORTH CAROLINA.

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[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, UNIVERSITY OF NORTH CAROLINA.]

# CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS.

## ATTEMPTS TO PREPARE PRASEODYMIUM AND NEODYMIUM ALUMS —SOME NEW DOUBLE SULPHATES.[1]

BY CHARLES BASKERVILLE AND HAZEL HOLLAND.

Received November 9, 1903.

*Synopsis.*—Pure praseodymium and neodymium sulphates, *i. e.*, free from lanthanum, were prepared and attempts made to form alums by mixing with varying proportions of the alkaline sulphates. The four methods tried, *viz.*, concentration of solutions on the water-bath, in a vacuum desiccator, passing dry cold air over the solution kept at zero, and electrolysis (method of Piccini) failed to give an alum.

The following new double sulphates were prepared: $Pr_2(SO_4)_3.Cs_2SO_4.2H_2O$, $Pr_2(SO_4)_3.Cs_2SO_4.4H_2O$, and $Nd_2(SO_4)_3.Cs_2SO_4.3H_2O$, which may serve as types.

The methods of separation of lanthanum and the didymiums were not altogether satisfactory. It was thought, as these bodies are frequently classed together, that perhaps one might form an alum and serve as a method for separating them.

The alums decrease in stability with an increase in the atomic weight of the trivalent metal, while the heavier the univalent metal, the greater the stability. For instance, sodium enters into alums with the lightest of the trivalent metals, as aluminum, vanadium and chromium. On account of these characteristics and the statement made by Locke[2] that "if an alum cannot be formed with

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[1] Presented in abstract at the Cleveland meeting of the American Chemical Society.

[2] *Am. Chem. J.*, **27**, 281.

cesium, it cannot be formed at all," in most of our experiments cesium was used as the univalent element.

The praseodymium sulphate was prepared from oxide obtained according to the method of Baskerville and Turrentine.[1] The neodymium sulphate was prepared from the purest neodymium oxide obtained by the method of Baskerville and Stevenson.[2]

No lanthanum was present in either of these preparations, so we hoped to avoid the difficulties encountered in the former paper. In fact, it has been stated that lanthanum might be removed in part from praseodymium and neodymium by heating the sulphates, which will bring about the separation of the lanthanum almost entirely free from the other two bodies. Muthmann and Rölig[3] made a careful comparative study of the solubility of these sulphates. While both praseodymium and neodymium sulphates are precipitated from concentrated solutions by elevation of temperature, they do not come out so readily as the lanthanum. We did not push the method to such an extent to determine if it would serve as a successful method for the separation finally, but we did learn that it would be very slow.

The praseodymium sulphate was prepared by a solution of the oxide in concentrated sulphuric acid (1:1) in platinum, the excess of acid being evaporated off by heating upon a sand-bath. The pure green crystalline praseodymium sulphate was dissolved in cold water. This standard solution contained for each cubic centimeter 0.05 gram of the sulphate. The standard solution of cesium sulphate contained 0.039 gram of sulphate per cubic centimeter. Equivalent amounts of these solutions were mixed and placed in a glass evaporating dish in a vacuum desiccator; within twelve hours pretty green crystals separated out. The liquor was poured off, the crystals dried with alcohol and ether, finally, by pressing between folds of bibulous paper.

The crystals were analyzed according to the methods usually employed in the analysis of potash alums, namely, weighed portions were dissolved in cold water, acidified with concentrated hydrochloric acid, the praseodymium hydroxide being precipitated with ammonium hydroxide; the excess was removed by boiling, filtered, washed and the filtrate evaporated to dryness. Cesium was determined as normal sulphate. A small amount of pure ammo-

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[1] This Journal, **26**, 46.

[2] This Journal, **26**, 54.

[3] *Ber. d. chem. Ges.*, **31**, 1720.

nium carbonate was always added after the ammonium salts had been driven off to convert the cesium hydrogen sulphate into the normal sulphate. The praseodymium hydroxide was ignited in a platinum crucible and heated in the air with a blast-lamp to a constant weight. From a number of determinations and the amount of oxygen yielded by this greenish black residue when it was heated in hydrogen, its formula was taken as $Pr_4O_7$.

The first crystals obtained by the method outlined above gave, on analysis, the following:

| | Per cent. |
|---|---|
| Praseodymium sulphate | 61.07 |
| Cesium sulphate | 35.57 |
| Water of crystallization by difference | 3.36 |
| | 100.00 |

The body would, therefore, have the formula $Pr_2(SO_4)_3.Cs_2SO_4.2H_2O$. A new double salt corresponding to the type $Pr_2(SO_4)_3.K_2SO_4 2H_2O$ similar to Cleve's double lanthanum sulphate and Benedick's $Gd_2(SO_4)_3.K_2SO_4.2H_2O$;[1] but it is not an alum.

As the relationship of the two sulphates was correct, an attempt was made to increase the content of water of crystallization by mixing the sulphates at a reduced temperature; zero in the second experiment. When the mixture was kept at that temperature for sixteen hours with a rapid stream of dry air passing over it to facilitate evaporation, very soon exquisite green crystals separated out, which gave, on analysis:

| | |
|---|---|
| Praseodymium sulphate | 58.74 |
| Cesium sulphate | 37.64 |

or virtually the same compound.

The lowering of the temperature failing to raise the percentage of water, the third experiment was carried out at a temperature of 60° C. The beaker was maintained at this temperature by immersion in a carefully regulated water-bath. The crystals separated out very quickly and, like the others, possessed the characteristic green color. The analysis gave

| | |
|---|---|
| Praseodymium sulphate | 70.08 |
| Cesium sulphate | 26.99 |

While this body also contained 2 molecules of water of crystallization, the percentage of praseodymium sulphate obtained showed the presence of either a new sulphate or that the crystals analyzed

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[1] *Ztschr. anorg. Chem.*, **22**, 393.

constituted a mixture of those previously described and a sulphate probably resembling the nonahydrated lanthanum sulphate.

One experiment was made looking toward the preparation of the praseodymium potassium alum. Theoretical proportions of the sulphates were mixed in a glass evaporating dish and kept in a vacuum desiccator exhausted over night. Green crystals separated out. They were dried and analyzed and the compound was found to be a double sulphate containing 4 molecules of water of crystallization.

Failing to prepare the alum by simply mixing and evaporating the sulphates at different temperatures, Piccini's[1] method of electrolysis was applied to praseodymium and cesium sulphates. A description of the method is given in the previous paper. The experiment was interrupted at the end of forty-eight hours, a few crystals having separated out at the cathode. The solution was decanted and evaporated in a vacuum desiccator. The reduced pressure was continued for several days until sufficient of the crystals were obtained for analysis.

| | |
|---|---|
| Praseodymium sulphate | 58.14 |
| Cesium sulphate | 35.67 |
| Water of crystallization by difference | 6.19 |

The compounds, therefore, were double sulphates with 4 molecules of water of crystallization.

The crystals that separated out at the cathode were analyzed with the following result:

| | |
|---|---|
| Praseodymium sulphate | 56.73 |
| Cesium sulphate | 33.63 |

This is virtually the same double sulphate.

### ATTEMPT TO PREPARE NEODYMIUM ALUM.

Pure neodymium oxide obtained by the method of Baskerville and Stevenson[1] was converted into the sulphate in the same manner as described above for praseodymium. Standard solutions of this and cesium sulphate were prepared. Calculated quantities were evaporated *in vacuo*. Beautiful lavender crystals formed which were analyzed according to the same methods as given for praseodymium.

| | |
|---|---|
| Neodymium sulphate | 62.11 |
| Cesium sulphate | 32.34 |
| Water of crystallization by difference | 5.55 |

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[1] *Ztschr. anorg. Chem.*, **20**, 12 (1899).

[2] *Loc. cit.*

The compound was therefore a double cesium neodymium sulphate containing 3 molecules of water of crystallization, $Nd_2(SO_4)_3.Cs_2SO_4.3H_2O$.

Attempts were also made to prepare the potassium neodymium alum by electrolysis. The same method employed in preparing the praseodymium body was used. The crystals which separated out at the cathode gave, on analysis:

| | |
|---|---|
| Neodymium sulphate | 60.92 |
| Cesium sulphate | 33.08 |
| Water of crystallization by difference | 6.00 |

This body was also a double sulphate containing 3 molecules of water of crystallization.

Aluminum salts possess weak basicity, while the praseodymium and neodymium are, comparatively, basic.[1] This may account in part for our failure to prepare these alums. It is particularly interesting to note in considering these two so-called elements that the one gives a series of double salts with 2 and 4 molecules of water of crystallization, while the other gives one with 3.

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[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, UNIVERSITY OF NORTH CAROLINA.]

# CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS.

## LANTHANATES.

BY CHARLES BASKERVILLE AND GEORGE F. CATLETT.

Received November 9, 1903.

*Synopsis.*—The resemblance of lanthanum to aluminum was taken advantage of and the preparation of such bodies as the lanthanates and meta-lanthanates, hitherto not reported, described. The new substances are sodium tetra-lanthanate ($Na_2La_4O_7$) and meta-lanthanates of sodium, potassium, lithium and barium ($MH_9La_5O_{15}$). Two methods were used: Fusion of lanthanum oxide with alkaline carbonates, and prolonged digestion in a concentrated solution of the alkaline hydroxides at 100° C. These bodies do not serve as a means for the separation and purification of lanthanum.

Aluminum, which belongs to the third group in the periodic

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[1] *Am. Chem. J.*, **26**, 166.