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

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS.

ON LANTHAN-ALUMS—SOME NEW DOUBLE SULPHATES.

BY CHARLES BASKERVILLE AND EUGENE G. MOSS.

Received November 9, 1903.

Synopsis.—This paper gives an account of some attempts, not altogether successful, to prepare lanthan-alums. The characteristic properties of lanthanum sulphate, namely, ready formation of a comparatively insoluble hydrate and double salts, appear to interfere. The following new salts, belonging to known types, were prepared: $La_2(SO_4)_3.Rb_2SO_4.2H_2O$ and $La_2(SO_4)_3.Cs_2SO_4.2H_2O$, and $La_2(SO_4)_3.Rb_2SO_4$, as well as another model, *viz.*, $3La_2(SO_4)_3.2Rb_2SO_4$ and $3La_2(SO_4)_3.2Cs_2SO_4$.

It may be recalled that lanthanum was one of the elements whose atomic weight was corrected by Mendelêeff[1] in the enunciation of the periodic law. Lanthanum is now placed in the aluminum group. Many of the sulphates of elements which form sesquioxides, form the basis of the large class of bodies known as the alums. For these two reasons it is natural to expect lanthanum to form an alum.

Locke[2] has called attention to the fact that if an element will form an alum, it does so more readily with cesium sulphate than with any of the other alkaline sulphates. Experiments were therefore begun with lanthanum sulphate and cesium sulphate in an equimolecular mixture. In endeavoring to concentrate the solution to the crystallization point by heating, either directly or by evaporation upon the water-bath, there resulted almost immediately a precipitation of the nonahydrated lanthanum sulphate, $La_2(SO_4)_3.9H_2O$. It is well-known that lanthanum sulphate deports itself in this manner. We learn also that this body fails to go back into the solution in the same amount of water on cooling. Muthmann and Rölig,[3] in their investigation on the separation of the cerite metals through the solubility of their sulphates, state that the solubility of this nonahydrate varies but slightly with the temperature.

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[1] "Principles of Chemistry" (English translation). Vol. II, p. 88.

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

[3] *Ber. d. chem. Ges.*, **31**, 1723 (1898).

As it was impossible to bring about the proper concentration of the mixture by heating, it was placed in a vacuum desiccator and allowed to evaporate under diminished pressure. Beautiful large crystals, symmetrical in form, separated out. The analysis of these crystals, from which the mother-liquor was drained, gave the following percentages:

		Calculated for		
	Found.	$La_2(SO_4)_3Cs_2SO_4.24H_2O.$	$La_2(SO_4)_3.Cs_2SO_4.$	$3La_2(SO_4)_3.2Cs_2SO_4.$
Lanthanum oxide....	33.75	23.85	35.13	37.57
Cesium oxide........	21.72	20.76	30.39	21.60

Another experiment was carried out by placing a similar solution in a freezing-mixture of ice and salt, but no crystals were formed.

During the progress of these experiments, efforts were made to prepare lanthan-potash alum by electrolytic oxidation. Howe and O'Neal[1] prepared iron, cobalt and chromium alums and attempted to make manganese alums by electrolysis, but without success. Later Piccini[2] prepared the cesium manganese alum by that method. This method, varied in some respects, was used with lanthanum.

A saturated solution of lanthanum sulphate was prepared by saturating sulphuric acid with lanthanum hydroxide, which had been obtained by precipitation from lanthanum ammonium nitrate. The solution of lanthanum sulphate was placed within an unglazed porcelain annealing dish. This rested in a large beaker containing more than enough double sulphate of potassium and lanthanum to make a saturated solution. It is difficultly soluble in water, hence the excess of solid. A spiral platinum cathode was placed in the solution in the annealing dish while a sheet platinum anode rested in the outer liquid. Four Lalande-Edison cells were used, giving a current of about 0.16 ampere, and the process was allowed to continue sixteen hours. No perceptible change in either the outer or inner solution was noted. A few white, opaque crystals separated about the top of the annealing cup. The solution within the annealing cup was taken out and allowed to evaporate spontaneously. In a week's time a mixture of crystals formed. The larger ones were carefully removed by tweezers and analyzed.

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[1] This Journal, **20**, 764 (1898).

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

	Found.	Calculated for $La_2(SO_4)_3.K_2SO_4.24H_2O$.
Lanthanum oxide	27.24	27.69
Potassium oxide	8.47	8.03

This would indicate the formation of the alum. The amount obtained, 0.1868 gram, was used in the analysis. The remaining smaller crystals and some of the alums gave, on analysis, 47.37 per cent. lanthanum oxide. This indicates the coincident formation of the hexahydrate of Frerichs and Smith,[1] which carries 49.17 per cent. lanthanum oxide.

In hopes of repeating the above in another experiment with more dilute solutions the current was allowed to run for twenty-three hours. The crystals, a mixture, gave lanthanum oxide, 46.2 per cent., and potassium oxide, 9.71 per cent.

A third experiment was carried out on a larger scale, using 150 cc. of the double lanthanum potassium sulphate solution and 75 cc. of the lanthanum sulphate. The current, 0.1 ampere, was allowed to run for forty-eight hours. No crystallization took place, but four fractions were obtained in the concentration. None of them gave results on analysis worthy of mention.

Similar experiments were carried out with sodium sulphate and the current continued for fifty hours. The solutions obtained were evaporated under reduced pressure. The analysis of the crystals gave:

	Found.	Calculated for $La_2(SO_4)_3.2Na_2SO_4.18H_2O$.
Lanthanum oxide	27.40	27.41
Sodium oxide	9.78	10.47

This is doubtless a mixture and its study could not be of interest.

Another experiment with sodium sulphate was carried out with a larger current, 0.4 ampere, and continued for seventy hours. Some pretty needles separated contaminated with fine crystals. It was quite impossible to remove the former and free them from the mother-liquor—they were so soluble. The small crystals on analysis proved to be Cleve's[1] double sulphate.

	Found.	Calculated for $La_2(SO_4)_3.2Na_2SO_4+2H_2O$.
Lanthanum oxide	36.30	36.04
Sodium oxide	13.15	13.87

Experiments were carried out with rubidium sulphate. It may be remarked that it mattered not which one of the alkaline sul-

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[1] *Ann. Chem.* (Liebig), **191**, 460.

[2] *Ber. d. chem. Ges.*, **11**, 912.

phates was used in the mixture; any effort to concentrate by heating always caused a precipitation of the hydrated sulphate, some double salt, or both. In a solution made of rubidium and lanthanum sulphates in theoretical amounts and evaporated in a vacuum desiccator, thin, flat silky crystals formed which, on analysis, gave:

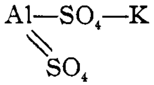
		Calculated for	
	Found.	$La_2(SO_4)_3.Rb_2SO_4.24H_2O$.	$3La_2(SO_3)_3.2Rb_2SO_4$.
Lanthanum oxide	43.10	25.77	43.62
Rubidium oxide	17.64	14.78	16.77

Lanthanum sulphate is, as remarked, much more soluble in cold than in hot water, the solubility, according to Mosander,[1] being 1 part in 115 of water at 100° and 1 in 6 parts at 13°. As one of us (M.) was forced to withdraw from the laboratory, an effort was made in closing up the work to concentrate the rubidium solution at the temperature 45°-50° C. The vessel was placed in an air-bath, the temperature regulated, and the evaporation facilitated by drawing a current of dry air over the liquid by means of a suction-pump. Crystals were obtained giving a percentage of 40.4 of lanthanum oxide which would indicate the formation $La_2(SO_4)_3.Rb_2SO_4$, where the percentage of lanthanum oxide is 39.13. The body belongs to the type $Di_2(SO_4)_3,K_2SO_4$ (Marignac)[2] and $Di_2(SO_4)_3,Tl_2SO_4$ (Zschiesche).[3]

Efforts were also made to prepare an ammonium alum, but with no more satisfactory results.

Perhaps under more suitable conditions, as spontaneous evaporation at low temperatures, the lanthan-alums may be prepared. Apparently, however, the property possessed by lanthanum sulphate of forming a stable compound with 9 molecules of water with slight elevations of temperature interferes materially with the formation of the alum. Muthmann and Rölig[4] have observed its formation at zero.

Attention has been directed by F. W. Clarke to the alum type



$$\begin{array}{l} Al{—}SO_4{—}K \\ \;\diagdown\!\!\diagdown \\ \quad SO_4 \end{array}$$

and the suggestion made that lanthanum, which readily gives $La_2(SO_4)_3.3K_2SO_4$, forms the model

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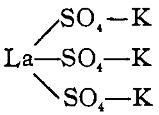
[1] *J. prakt. Chem.*, **30**, 380.

[2] *Ann. Chem.* (Liebig), **88**, 242.

[3] *J. prakt. Chem.*, **107**, 98.

[4] *Loc. cit.*



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

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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.