of double peroxidized compounds of those rare earths which have been shown by Cleve and others to form peroxides. If a number of such compounds could be prepared they would no doubt exhibit a variety in their chemistry sufficient to insure a comparatively rapid and easy separation of at least some members of the rare earth group.

In conclusion, the author wishes to thank Professor Victor Lenher for helpful suggestions and for the interest which he has taken in the above work.

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

SOME NEW RARE EARTH COMPOUNDS.

BY A. J. GRANT AND C. JAMES.

Received October 11, 1915.

The methods of separation of the rare earths, although greatly improved during recent years, still leave much to be desired. This is especially true of the terbium, dysprosium, holmium portion. Accordingly it seemed advisable to continue the search for suitable compounds either for crystallization or precipitation. Some of the more interesting salts which were prepared, are described below:

Terbium Pyromucate, $Tb(C_4H_3COO)_3.5H_2O$.—This salt was obtained by neutralizing an aqueous solution of the acid, heated upon the water bath, with terbium hydroxide. In preparing salts of terbium derived from weak acids, it was found necessary to use terbium hydroxide, for the common oxide of terbium is a heavy, dark brown, sometimes almost black, substance very difficultly soluble in acids. When boiled with hydrochloric acid, it showed no signs of dissolving for a long time, but suddenly the whole went into solution.

The solution of the pyromucate was filtered, evaporated and allowed to crystallize. The compound formed radiating crystals, which were very soluble in water.

For analysis, some of the compound was weighed out and ignited to the dark oxide. This dark oxide was then calculated to the white oxide by using a conversion factor, which had previously been determined by a series of experiments in which the dark oxide had been converted to the normal type of oxide by heating in a current of hydrogen. The amount of Tb_2O_3 found indicated that five molecules of water were present. After heating for twelve hours at 94° in a drying oven, nine-tenths of the water was lost.

Terbium 1,2,4-Bromonitrobenzenesulfonate, $Tb(C_6H_3Br.NO_2.SO_2O)_3.10H_2O$.—This salt was obtained in a similar manner to the pyromucate, with the exception that the solution was evaporated to dryness, the residue treated with alcohol and the remaining solid recrystallized from water.

It formed a heavy white compound, made up of very fine crystals. An analysis gave a mean of 15.59% of terbium oxide, while theory demands 15.49%.

The solubility of this bromonitrobenzenesulfonate did not appear to differ much from that of gadolinium. Though these compounds are well defined, they seem to be of no use for separating the rare earths.

Terbium Propionate, $Tb(C_2H_5COO)C.2H_2O$.—The hydroxide was dissolved in propionic acid until nearly neutral. The filtered solution was evaporated a little, and allowed to cool, when the salt crystallized out. It formed thin, white, powdery, voluminous crystals. The percentage of the normal oxide agreed fairly well with a formula containing two molecules of water of crystallization.

The citraconate and the quinate were found to be very soluble substances.

Caesium Ceric Chloride is a not very stable compound and is formed as follows: A solution of cerous nitrate was precipitated hot by sodium hydroxide and bromine. The ceric hydroxide which was formed was filtered off and carefully washed with water to remove all sodium salts. The ceric hydroxide was suspended in ethyl alcohol and dry HCl gas was passed in while the container was kept cool.[1] The reddish ceric chloride was filtered and mixed with caesium chloride in aqueous alcohol. A yellow precipitate formed immediately. This was separated upon a filter and washed with alcohol. It did not appear to be a definite compound. Ceric chloride also gives a similar derivative with tetramethyl ammonium chloride. This is apparently a little more stable. Ceric pyridine chloride described in the article referred to above is not very definite since the authors obtained material differing in composition by varying the amounts of the reacting salts.

Double Nitrates of the Rare Earths with Ferrous Nitrate.—In order to prepare these compounds, the writers first made a solution of ferrous nitrate by treating ferrous sulfide with nitric acid of a density less than 1.12. The liquid was evaporated below 60°, until green crystals of ferrous nitrate resulted. This very unstable nitrate was dissolved in water and a solution of the required rare earth nitrate added. In the case of the lanthanum double salt, the mixed solutions were placed in a desiccator over sodium hydroxide, and a vacuum maintained until a sufficient amount of lanthanum ferrous nitrate had collected. The flat, green hexagonal crystals were fairly stable in the absence of air. When exposed to the air they slowly turned reddish brown, owing to the formation of a basic ferric salt.

An analysis gave 20.02% La_2O_3 and 14.98% of iron in the form of Fe_2O_3. This corresponds well with the formula

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[1] *Z. anorg. Chem.*, 18, 305 (1898).

$$3Fe(NO_3)_2.2La(NO_3)_3.24H_2O,$$

or the general type,

$$3R(NO_3)_2.2X(NO_3)_3.24H_2O,$$

where R = Mg, Mn, Co, Ni, Zn or Fe''.

Lanthanum Pyromucate, $La(C_4H_3O.COO)_3.2H_2O$.—This lanthanum compound separated very easily in the form of crystals from solution in hot water. The results of the analysis of two different preparations indicated the presence of two molecules of water of crystallization.

Yttrium Pyromucate, $Yt(C_4H_3O.COO)_3.3H_2O$.—This was prepared in a similar manner to the above. An analysis showed the presence of three molecules of water of crystallization. Upon comparing the amounts of water of crystallization contained by the terbium and yttrium salts, it would seem that more than one state of hydration occurs. These compounds willl be studied more completely later on when the writers are able to obtain a larger amount of acid.

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AN AUTOMATIC VACUUM PUMP.

BY OTTO MAASS.

Received September 20, 1915.

The following is a description of a Töpler[1] vacuum pump which, in conjunction with an aspirator, works automatically. The arrangement does not involve the use of a mechanical spring or valve, is very simple to make, and can, with perfect safety, be allowed to run for an indefinite period.

The diagram shown below has been drawn to scale exhibiting the exact construction of a pump which has been in use for some time.

A is the body of the Töpler pump, tube P leads to the vessel which is to be exhausted, and B is the mercury reservoir. At the start, when the air throughout the apparatus is at atmospheric pressure, the mercury stands at level *a* in B and also in tubes M, E, L, and G. Tube K leads to the water pump. When the latter is set in action air is drawn out of A, P and R through one centimeter of mercury in bulb C and out at K. Simultaneously the pressure over the mercury in B is diminished, so that, since tubes E and M are open to the air pressure, the mercury level will be lowered in these. The volume of B being large compared to the volume of the tubing, the mercury gradually drops to the level *d* in tube E while the mercury rises to the top of tube L. A further decrease in the pressure and the mercury in the bottom of bulb D is forced through L and runs down H into B. Air now enters tube M into the water pump and into B and C, where the pressure is now that of the outside atmosphere. The mercury in bulb C rises in tube T so that the pressure in A remains equal

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[1] With Antropoff modification, *Chem. Ztg.*, 34, 979 (1910).