99. *Some Hydrated Nitrates of Rare-earth Elements.*

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Hexahydrates are yielded by crystallisation of the nitrates of the rare-earth elements from lanthanum to dysprosium in serial order. From erbium to lutecium pentahydrates are formed. Yttrium and dysprosium also give pentahydrates. Various other lower hydrates are formed by thulium, ytterbium, and lutecium nitrates. Desiccation over sulphuric acid is general.

ALTHOUGH it is well established that crystallisation from water of the nitrates of the cerium group of elements yields hexahydrated salts, yet more varied results have been recorded by different observers in the case of the earths of high atomic weight. In general, these salts are less hydrated than in the cerium group. The solubility falls from lanthanum nitrate to gadolinium nitrate and then starts to increase, but terbium nitrate is the last of the series for which a hexahydrate has been recorded. The next members of the series give pentahydrates, and thulium and ytterbium are said to give tetrahydrates.

The author has readily prepared hexahydrates of dysprosium and yttrium, and the pentahydrate appears to be the usual form for members of the series from dysprosium to lutecium at room temperature: all the crystals examined are obviously isomorphous with bismuth nitrate pentahydrate. The solubility at the lutecium end of the series is very high, and the salts are very hygroscopic though easily suffering dehydration over sulphuric acid. They are therefore difficult to prepare pure.

Ytterbium nitrate pentahydrate when heated to about 48° reaches a transition point at which water is liberated and a new hydrate formed which does not dissolve in the water until heated nearly to 100°. When a very concentrated warm solution of ytterbium nitrate is allowed to cool, the hydrate $2Yb(NO_3)_3,7H_2O$ crystallises and remains stable at room temperature, but the solvent water is absorbed as water of crystallisation and the final mother-liquor is a liquid ytterbium nitrate. On one occasion a crop of $Yb(NO_3)_3,4H_2O$ was obtained. This is the hydrate reported by Cleve (*Z. anorg. Chem.*, 1902, **32**, 129), and James (*J. Amer. Chem. Soc.*, 1911, **33**, 1332) found that thulium nitrate also gave a tetrahydrate, but in general a solution in the desiccator remains supersaturated until seeded with bismuth nitrate pentahydrate and thereupon it deposits the pentahydrate.

Yttrium nitrate pentahydrate was prepared by similarly seeding a concentrated solution. The mother-liquor from this crop was seeded with dysprosium nitrate hexahydrate, and a crop of yttrium nitrate hexahydrate grown in a desiccator. The pentahydrate crystallised unchanged from concentrated nitric acid. Löwenstein (*Z. anorg. Chem.*, 1909, **63**, 69) had prepared a pentahydrate by desiccating the hexahydrate over 60—70% sulphuric acid, but no direct preparation from solution has been recorded. He found that the hexahydrate passes into the pentahydrate at a vapour pressure less than that of 50% sulphuric acid.

EXPERIMENTAL.

As no acid nitrates are formed, the salts could be analysed with certainty by ignition to oxides. This was carried out in a small gas crucible furnace after preliminary baking at 130°, which removed most of the water.

Dysprosium Nitrate.—Hexahydrate. The oxide (containing 0·4% of holmium oxide) was dissolved in nitric acid, the solution evaporated to dryness, and the salt recrystallised from water over sulphuric acid; it formed large, prismatic, deliquescent crystals. A single clear crystal was analysed (Found : Dy_2O_3, 40·6. Calc. : Dy_2O_3, 40·8%).

Pentahydrate. The hexahydrate was warmed with nitric acid (*d* 1·3), and the solution cooled, the pentahydrate crystallising (Found : Dy_2O_3, 42·5. Calc. : Dy_2O_3, 42·5%). This hydrate was described by Urbain and Jantsch (*Compt. rend.*, 1908, **146**, 127) and is the more probable product of crystallisation from warm or acid solution. The penta- and hexahydrates were readily desiccated over sulphuric acid to a nearly white powder. The pentahydrate forms mixed crystals with that of bismuth nitrate.

Yttrium Nitrate.—Hexahydrate. The mother-liquor from a crop of pentahydrate was placed in a desiccator over sulphuric acid and seeded with dysprosium nitrate hexahydrate; the yttrium salt formed large, clear, deliquescent prisms (Found : Y_2O_3, 29·7. Calc., after correction for 2% of erbium nitrate : Y_2O_3, 29·7%).

Pentahydrate. A neutral nitrate solution was evaporated to a syrup and seeded with bismuth nitrate pentahydrate (Found : Y_2O_3, 31·0. Calc., after correction : Y_2O_3, 31·2%). After recrystallisation from nitric acid (*d* 1·42), the Y_2O_3 content was 30·8%.

Ytterbium Nitrate.—Pentahydrate. An aqueous solution was evaporated to a syrup over sulphuric acid. Either by seeding with bismuth nitrate pentahydrate or spontaneously, large, glass-clear, very deliquescent crystals were formed. They are readily dehydrated over sulphuric acid and are therefore difficult to prepare dry but fully hydrated. The m. p. is indefinite, the salt giving rise to a lower hydrate and water at *ca.* 48° (Found : Yb_2O_3, 43·85. Calc. : Yb_2O_3, 43·87%).

Tetrahydrate. On one occasion spontaneous crystals from dilute nitric acid gave this hydrate (Found : Yb_2O_3, 45·5. Calc. : Yb_2O_3, 45·71%). The crystals were clear prisms, but on removal from solution they quickly went dull and readily suffered dehydration over sulphuric acid.

3·5-*Hydrate.* A warm concentrated solution of the nitrate was crystallised. Crystals were inclined to be small and difficult to separate from viscous mother-liquor, but with care a crop of large crystals was obtained. Selected crystals were rapidly wiped free from mother-liquor, which was supercooled and tended to solidify suddenly (Found : Yb_2O_3, 46·68, 46·70. Calc. : Yb_2O_3, 46·69%). Incomplete removal of mother-liquor led to lower water content, indicating that this was a supercooled salt.

Trihydrate. Although Cleve reported this hydrate, the author has not been able to obtain it as a pure crystalline product.

Lutecium Nitrate.—Pentahydrate. By seeding a nitrate solution in a desiccator with bismuth nitrate this was obtained as exceedingly soluble, deliquescent crystals, two of which were used for analysis (Found : Lu_2O_3, 44·15. Calc. : Lu_2O_3, 44·13%).

4·5-*Hydrate.* This was obtained similarly to the pentahydrate, which it resembles in appearance, but by seeding with strontium nitrate tetrahydrate (Found : Lu_2O_3, 45·05, 45·07. Calc. : Lu_2O_3, 45·03%).

Owing to the scarcity of material, the very great solubility and deliquescence of the salts, and the viscosity of the solutions, the nitrates of lutecium are not easy to handle.

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