CCXXXIII.—*Neodymium Selenate.*

By John Albert Newton Friend and Albert Arthur Round.

Although selenates of lanthanum (Atomic No. 57), cerium (58), praseodymium (59) and samarium (62) have been described, *neodymium* (60) *selenate* does not appear to have been prepared hitherto. In the course of a search for the "missing" element, No. 61, some fairly pure neodymium magnesium nitrate was prepared by repeated fractionation from certain rare-earth residues. From this the oxalate was precipitated, ignited to oxide, and used in the preparation of the salts described below.

That the oxide thus obtained contained only traces of impurity was proved in several ways. (1) The visible absorption spectrum of a $N/16$-solution of the chloride prepared from the oxide showed close agreement with Rech's data (*Z. wiss. Photochem.*, 1905, **3**, 411). (2) An X-ray analysis was made by Messrs. Adam Hilger with a sample of the oxide on a copper target of a Shearer X-ray tube, using a Müller X-ray spectrograph with calcite crystal. The presence of traces of praseodymium, samarium, and gadolinium was ascertained. Traces of terbium were also present, as shown by the brown tint of

---

* A trace of a higher oxidation product separates if this residue is redissolved in a small volume of acetone.

the ignited oxide. (3) Chemical analysis was effected by converting a weighed quantity of oxide into sulphate, and pouring the solution into an excess of oxalic acid solution. After 24 hours, the precipitated oxalate was collected on an asbestos filter and estimated by titration with permanganate. This method, which was used by Gooch and Kobayashi (*Amer. J. Sci.*, 1918, **45**, 227) for thorium, appeared to work well with neodymium, the equivalent weight of which was found to be 48·17, 48·30; mean, 48·24, the accepted value for 1925 being 144·27 ÷ 3 or 48·09.

Neodymium Selenate Pentahydrate, $Nd_2(SeO_4)_3,5H_2O$.—Neodymia readily dissolves in aqueous selenic acid. A slight excess was added to the warm acid and, after filtration, the solution was concentrated on the water-bath until a good crop of pink crystals separated from the hot mother-liquor. These were dried between filter-paper and stored over sulphuric acid. Some of the dried salt was heated in a current of dry air, the evolved water being collected in a calcium chloride drying tube. If the heating was gentle, the loss in weight of the salt exactly equalled the gain of the drying tube, indicating that no reduction to selenite or change other than dehydration had taken place; but it was difficult to ensure complete desiccation without slight decomposition of the anhydrous salt [Found: H_2O, 11·47, 11·24; mean, 11·36. $Nd_2(SeO_4)_3,5H_2O$ requires H_2O, 11·15%]. Upon exposure to moist air the dry salt absorbed moisture.

Octahydrate, $Nd_2(SeO_4)_3,8H_2O$.—A solution of neodymium selenate saturated at about 15° was poured into excess of alcohol, whereupon a pink, viscous liquid separated. On agitation with a glass rod the liquid rapidly crystallised to a pink solid, which was coarsely crushed beneath the alcohol, drained, and washed with ether. After drying between filter-paper, the amount of combined water was determined as before [Found: H_2O, 17·19, 17·39, 17·26; mean, 17·28. $Nd_2(SeO_4)_3,8H_2O$ requires H_2O, 16·72. $Nd_2(SeO_4)_3,9H_2O$ requires H_2O, 18·42%]. This hydrate is also formed by prolonged exposure of the saturated solution over concentrated sulphuric acid.

Dodecahydrate, $Nd_2(SeO_4)_3,12H_2O$.—The previous salts readily absorbed moisture in a saturated atmosphere. When the semi-deliquescent mass thus obtained was dried over sulphuric acid, a break occurred in the dehydration–time curve at 23·37% H_2O, indicating the existence of a dodecahydrate (Theory: $12H_2O$, 23·14; $13H_2O$, 24·59%). This *hydrate* appears to be the one which first separates when a saturated solution is evaporated at room temperature over concentrated sulphuric acid. It rapidly loses water at the ordinary temperature, and prolonged exposure over concentrated sulphuric acid yields the octahydrate. When freed from adherent saturated solution by pressure between filter-paper, a sample had a water content of 22·2%. This was low for a dodecahydrate, as expected, but higher than the 21·6% required for an undecahydrate.

Neodymium Selenate, $Nd_2(SeO_4)_3$.—The pink *anhydrous* salt is readily obtained by gently heating any of the hydrates in a current of dry air, or at 170—180° for a more prolonged period [Found: Nd_2O_3, 47·29, 45·49; mean, 46·39. $Nd_2(SeO_4)_3$ requires Nd_2O_3, 46·86%]. Although the mean result is in fair agreement with theory, the individual results do not agree as well as one could desire. Probably the second specimen had been imperfectly dehydrated, and the first may have been slightly overheated (see above).

Selenates of all the elements of the cerium sub-group, save No. 61, are now therefore known. The neodymium salt is intermediate in hydrate formation between the praseodymium and samarium salts. For example, the former yields a penta- and an octa-hydrate (Scheele, *Z. anorg. Chem.*, 1898, **17**, 310), the latter yields an octa- and a dodeca-hydrate (Cleve, *Bull. Soc. chim.*, 1874, **21**, 196), and neodymium yields all three. A thorough study of the selenates of this group is in progress with a view to their possible use in the separation of rare-earth mixtures by fractional crystallisation.

THE TECHNICAL COLLEGE, BIRMINGHAM. [*Received, May* 23*rd*, 1928.]