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Abstract

Full Text

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On Double Salts of Lanthanum, Cerium, Praseodymium, and Neodymium with Triphenylbenzylarsonium Nitrate

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As was established earlier, tetraphenylphosphonium nitrate ([1]) and chloride ([2]) are capable of giving double salts with the nitrates or, respectively, chlorides of lanthanum, cerium, neodymium, and praseodymium. These salts crystallize well from ethanol and a number of other organic solvents. They are decomposed by water into their components. When such compounds are dissolved in organic solvents, partial dissociation of the complex ions occurs, which is intensified by the addition of chloroform, which forms crystallosolvates with tetraphenylphosphonium salts that are readily soluble in chloroform. This explains the increase in solubility of the above-mentioned double salts in ethanol after chloroform is added to it, despite the insolubility of these salts in the latter.

The difference in instability constants of complex ions of the type under consideration, the unequal tendency to undergo hydrolysis or cleavage in the presence of chloroform—all these factors, in combination, lead to the appearance of a substantial divergence in the solubility of double salts of rare-earth elements with salts of organic bases, even of elements that are very close to one another, for example praseodymium and neodymium. These considerations give special importance to the further study of such compounds.

As has been found, triphenylbenzylarsonium hydroxide nitrate is comparatively readily obtainable and at the same time is capable, upon interaction with nitrates of the rare-earth elements of the cerium group, of forming double salts which crystallize well from ethanol as plates, have different melting points, and are decomposed into their components by the action of water. These nitrates were isolated from 96° ethyl alcohol without water of crystallization or alcohol and had a composition corresponding to the formula:

$$E(NO_3)_3 \cdot 2[((C_6H_5)_3(C_6H_5 \cdot CH_2)As)NO_3],$$

where E is an atom of La, Ce, Pr, or Nd.

The solubility of such double salts in this solvent decreased from the lanthanum salt to the neodymium salt, i.e., together with an increase in the strength of

the complex ion $(E(NO_3)_5)^{-2}$. At the same time it was greater than that of the corresponding double salts of tetraphenylphosphonium hydroxide.

Double nitrate of lanthanum and triphenylbenzylarsonium

$$La(NO_3)_3 \cdot 2[(C_6H_5)_3(C_6H_5CH_2)As]NO_3.$$

Triphenylarsine was obtained by the method of Michaelis ([3]), modified by Popov and Terner ([4]). From it, by heating with benzyl bromide, triphenylbenzylarsonium bromide was prepared, and from the latter—the nitrate. The initial lanthanum nitrate contained a small impurity of neodymium and praseodymium.

0.68 g of $La(NO_3)_3 \cdot 6H_2O$ was dissolved in 2 ml of 96° ethanol, and 1.44 g of triphenylbenzylarsonium nitrate was added to the solution. Heating on a water bath then followed until the substance had dissolved completely. From the solution, on standing in a vacuum desiccator over sulfuric acid, large ···

transparent colorless short plates. After suction filtration of the mother liquor, washing with alcohol, drying, etc., 1.49 g of product with m.p. 158.2–159.5° was obtained. From the mother liquor a further 0.14 g of the double salt was isolated. The overall yield of crude salt was 84.2% of theory. After recrystallization from 0.7 ml of ethanol, 1.18 g of pure substance with m.p. 159.5° was isolated.

$$La(NO_3)_3 \cdot 2[(C_6H_5)_3(C_6H_5CH_2)As]NO_3.$$

Found, %: La 11.30; 11.33
Calculated, %: La 11.26

The lanthanum oxide obtained from this salt was almost colorless.

The double lanthanum salt was very readily soluble in 96° ethanol, especially when hot. It was practically insoluble in chloroform, ethyl ether, and hydrocarbons. It dissolved well in a mixture of 96° ethanol with chloroform.

Double nitrate of trivalent cerium and triphenylbenzylarsonium

$$Ce(NO_3)_3 \cdot 2[(C_6H_5)_3(C_6H_5CH_2)As]NO_3.$$

The starting material was cerium nitrate ($Ce(NO_3)_3 \cdot 3H_2O$), "pure."It contained an impurity of "didymium" salts.

A solution of 1.09 g of this nitrate in 5 ml of 96° ethanol was mixed with a solution of 2.3 g of triphenylbenzylarsonium nitrate in the same amount of alcohol, and the mixture was concentrated by evaporation to a total weight of 9 g. Crystallization from the slightly yellowish solution did not occur immediately upon cooling. It was completed on standing of the solution with the precipitated crystals in a desiccator over sulfuric acid. After suction filtration, washing of the crystals with alcohol, etc., 2.41 g of the double salt with m.p. 161.75–162.25° was isolated, and from the mother liquor, after its concentration, a further 0.21

g of the same substance with m.p. 162° with decomposition. The overall yield of crude cerium salt was 86.1% of theory. By recrystallization from 1.6 ml of hot ethanol, 2.2 g of pure salt with m.p. 163.75–164° was obtained.

$$Ce(NO_3)_3 \cdot 2[(C_6H_5)_3(C_6H_5CH_2)As]NO_3.$$

Found, %: Ce 11.24; N 5.59
Calculated, %: Ce 11.26; N 5.63

The double nitrate of trivalent cerium with triphenylbenzylarsonium nitrate crystallized from 96° ethanol in the form of slightly yellowish plates, and was less soluble in this solvent than the analogous lanthanum salt. It was practically insoluble in ethyl ether, chloroform, and hydrocarbons. It dissolved appreciably in boiling isoamyl alcohol. On heating above its melting point, decomposition occurred.

Double nitrate of praseodymium and triphenylbenzylarsonium

$$Pr(NO_3)_3 \cdot 2[(C_6H_5)_3(C_6H_5CH_2)As]NO_3.$$

0.69 g of hydrated praseodymium nitrate, containing an impurity of neodymium nitrate, after dissolution in 3.5 ml of hot 96° ethanol, was mixed with a hot solution of 1.67 g of triphenylbenzylarsonium nitrate in 3 ml of the same alcohol. In this operation the green color of the praseodymium salt changed to yellow. Concentration of the solution by evaporation on a water bath and crystallization on cooling then followed. Large lemon-yellow crystals were filtered under reduced pressure and washed with alcohol. The yield of salt after drying was 1.84 g, m.p. 164.25–164.5°. From the mother liquor a further 0.15 g of the double nitrate was isolated. The remaining solution had a noticeable pink color. The overall yield of crude substance was 83.5% of theory. As a result of its recrystallization from 3.3 ml of boiling alcohol, 1.56 g of pure compound with m.p. 165–165.25° was obtained.

$$Pr(NO_3)_3 \cdot 2[(C_6H_5)_3(C_6H_5CH_2)As]NO_3.$$

Found, %: N 5.57
Calculated, %: N 5.62

The double nitrate of praseodymium and triphenylbenzylarsonium crystallized from ethanol in the form of yellowish-green tablets and possessed lower solubility

solubility in alcohol than the analogous cerium salt. It is practically insoluble in ethyl ether, chloroform, and hydrocarbons.

Double nitrate of neodymium and triphenylbenzyl-arsonium $Nd(NO_3)_3 \cdot 2[(C_6H_5)_3(C_6H_5CH_2)As]NO_3$. To a solution of 1.23 g of $Nd(NO_3)_3 \cdot 6H_2O$ in 6 ml of hot 96% ethanol was added a solution of

2.78 g of triphenylbenzylarsonium nitrate in 5 ml of the same solvent, prepared with heating. The crystals that separated after removal of 7.8 g of alcohol by evaporation on a water bath and cooling were filtered off, washed with alcohol, and dried. Yield 3.11 g. From the mother liquor it was possible to extract only 0.04 g of the double salt and 0.13 g of the original triphenylbenzylarsonium nitrate. The total yield of the double salt was 89.9% of theoretical. By recrystallization from hot ethanol, 2.88 g of product with m.p. 165.75–166° was isolated. The pure product obtained after a second recrystallization melted at 166.25°.

$Nd(NO_3)_3 \cdot 2[(C_6H_5)_3(C_6H_5CH_2)As]NO_3$.

Found, %:	Nd 11.50
Calculated, %:	Nd 11.56

The double nitrate of neodymium and triphenylbenzylarsonium proved to be the least soluble in ethanol in comparison with the other double salts described above. It crystallized from ethanol, forming large violet crystals. It dissolved well in cold acetone, methanol, and a mixture of ethanol with chloroform, as well as in hot 96% ethanol. It is practically insoluble in ethyl ether, chloroform, benzene, toluene, and other hydrocarbons.

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Note: Figure translations are in progress. See original paper for figures.