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Abstract

Full Text

Chemistry

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ON DOUBLE CHLORIDES OF ELEMENTS OF THE CERIUM GROUP WITH TRIMETHYLAMINE CHLORIDE

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At one time, double chlorides (^1) and nitrites (^2) of the rare-earth elements of the cerium group with the corresponding salts of tetraphenylphosphonium were studied ([3-]5). Later, Maddock (^6) isolated double nitrates of lanthanum, cerium, praseodymium, and neodymium with triphenylbenzylphosphonium.

Double salts of this group with the indicated salts of organic bases were obtained from 96% ethyl alcohol; they decomposed under the action of water into the original components; they had characteristic melting points and unequal solubility in organic solvents and their mixtures.

Continuing work begun earlier on the study of double salts of rare-earth elements with salts of organic bases, we included methylamine, dimethylamine, and trimethylamine chlorides in our investigations, as more readily available substances. It seemed to us not without interest to determine how complex formation proceeds in the presence of water and in nonaqueous media for chlorides of rare-earth elements with the corresponding salts of the indicated amines, depending on the degree of their substitution.

The starting material for obtaining double chlorides of rare-earth elements with trimethylamine was lanthanum chloride (containing up to 1.6% praseodymium chloride), cerium chloride obtained from repeatedly recrystallized double ammonium nitrate salt of quadrivalent cerium, and chemically pure preparations of praseodymium and neodymium chlorides. Trimethylamine chloride had its characteristic melting point of 271°.

It was preliminarily established that lanthanum, cerium, praseodymium, and neodymium chlorides, when combined with trimethylamine chloride in the presence of 96% ethyl alcohol, give several compounds, the formation of which depends on the relative amounts of the substances entering into reaction and on the crystallization conditions. Thus, at a molecular ratio of the chlorides of the rare-earth elements (calculated as their anhydrous salts) to trimethylamine chloride of 1 : 8, i.e., with an excess of the latter, compounds are obtained in which four molecules of amine correspond to one atom of rare-earth metal.

To obtain these compounds, the chlorides of lanthanum, cerium, praseodymium, neodymium, and trimethylamine, taken in the ratio indicated above, were dissolved separately with gentle heating in the smallest possible quantities of ethyl alcohol (approximately 2 ml for each gram of starting substance). The resulting clear solutions of the rare-earth-element chlorides and trimethylamine were mixed together while warm. As the excess solvent was removed in a vacuum desiccator over calcium chloride and paraffin, after 1–2 days beautiful, well-formed crystals separated from the solution in the form of hexagonal plates, colorless in the case of lanthanum and cerium and colored green and violet in the case of praseodymium and neodymium. The crystals, which readily deliquesced in air, were quickly separated from the mother liquor and washed several times with cold ethanol.

with ethyl alcohol and dried under a vacuum bell at 50° and 4–5 mm, in the presence of calcium chloride and phosphorus anhydride.

In the dehydrated compounds, the content of the rare-earth metal was determined by the oxalate method, with subsequent conversion of the oxalate into the corresponding oxides (with the exception of praseodymium, which does not give an oxide of exact chemical composition), and also the contents of chlorine, nitrogen, carbon, and hydrogen.

Lanthanum double chloride with trimethylamine. Anhydrous salt.

$$LaCl_3 \cdot 4(CH_3)_3N \cdot HCl.$$

Found, %: La 22.48; 22.50; Cl 39.20, 39.40; C 22.64;
N 8.75, 9.03; H 6.70

Calculated, %: La 22.08; Cl 39.60; C 22.96;
N 8.93; H 6.43

Cerium double chloride with trimethylamine. Anhydrous salt.

$$CeCl_3 \cdot 4(CH_3)_3N \cdot HCl.$$

Found, %: Ce 22.32, 22.51; Cl 39.21, 39.30; N 8.68, 8.99;
C 22.81, 23.12; H 6.74, 6.95

Calculated, %: Ce 22.27; Cl 39.50; N 8.91;
C 22.92; H 6.40

Praseodymium double chloride with trimethylamine. Anhydrous salt.

$$PrCl_3 \cdot 4(CH_3)_3N \cdot HCl.$$

Found, %: Cl 39.48; 39.80; C 22.98; N 8.57; 8.89; H 6.80

Calculated, %: Cl 39.43; C 22.89; N 8.90; H 6.40

Neodymium double chloride with trimethylamine. Anhydrous salt.

$$NdCl_3 \cdot 4(CH_3)_3N \cdot HCl.$$

Found, %: Nd 22.86; 22.59; Cl 39.63, 39.58; N 8.99, 9.33;
C 23.04; H 6.99

Calculated, %: Nd 22.80; Cl 39.22; N 8.85;
C 22.80; H 6.71

The melting temperature of the double chlorides of rare-earth elements with trimethylamine proved to be 287° for the lanthanum salt and, for the analogous compounds of cerium, praseodymium, and neodymium, respectively 289, 295, and 296°. Double recrystallization of the double chlorides obtained, with the exception of the lanthanum salt, did not lead to a change in their melting temperatures. The lanthanum double chloride synthesized from a preparation containing up to 1.6% praseodymium chloride acquired a stable melting temperature only after triple recrystallization from 96% ethyl alcohol. The yield of the double chlorides obtained ranged from 80 to 90%.

The double chlorides of lanthanum, cerium, praseodymium, and neodymium with trimethylamine dissolved well only in water and methyl alcohol, and less well in ethyl alcohol; moreover, in the latter the solubility regularly decreased with increasing melting temperature from the lanthanum salt to the neodymium salt. They did not dissolve in ether, acetone, benzene, toluene, xylene, dichloroethane, chloroform, quinoline, pyridine, bromobenzene, isobutyl and isoamyl alcohols.

Thus, as a result of the work carried out, double chlorides of rare-earth elements with trimethylamine were obtained in the presence of 96% ethyl alcohol, corresponding to the general formula $MeCl_3 \cdot 4(CH_3)_3N \cdot HCl$, where Me = La, Ce, Pr, and Nd; the properties of these compounds were studied and their solubility in water and organic solvents was established.

The study of analogous double salts of the rare-earth elements of the cerium group with salts of aliphatic and aromatic amines in the presence of water and in nonaqueous media is being continued by us.

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