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N. N. SAKHAROVA

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Abstract

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N. N. SAKHAROVA

ON COMPLEX COMPOUNDS OF LANTHANUM, CERIUM, PRASEODYMIUM, AND NEODYMIUM WITH THIOUREA

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The ability of thiourea to form complex compounds with salts of various metals is very pronounced. Thus, as early as Reynolds (^1), who discovered thiourea in the isomeric transformation of ammonium thiocyanate, pointed out its ability to give compounds with metal salts. He obtained and described characteristic compounds with gold and platinum chlorides; subsequently a number of investigators ($^{2-}$7) obtained numerous compounds of thiourea with salts of lead, cadmium, mercury, tin, bismuth, thallium, tellurium, copper, cobalt, zinc, cadmium, iron, nickel, and other metals.

Extensive investigations in the field of complex compounds of silver, platinum, and palladium with thiourea, its alkyl-substituted derivatives, and other related sulfur-containing organic substances were carried out by N. S. Kurnakov (^8).

Later, compounds of this type were studied by L. N. Chugaev (^9), V. V. Lebedinskii with coauthors (^10), and others.

Taking into account the strongly expressed ability of thiourea to form complex compounds with metal salts, it is of some interest to undertake studies on the preparation and investigation of similar compounds with salts of the rare-earth elements of the cerium group.

The starting material for obtaining complex compounds of rare-earth elements with thiourea was their acetates in the anhydrous state and thiourea with m.p. 180–182°.

It was preliminarily established that the acetates of lanthanum, cerium, praseodymium, and neodymium, when combined with thiourea in an aqueous medium, give several products, the formation of which depends on the relative amounts and temperature of the reacting substances. The most stable complex compounds of these elements in an aqueous medium proved to be those in which, according to analytical data, one molecule of thiourea corresponded to one atom of the rare-earth element. These compounds were studied by us first of all.

The indicated complex compounds were obtained by mixing aqueous solutions of the acetates of the rare-earth elements with an excess of thiourea, namely at their molecular ratio of 1 : 2 (anhydrous metal acetate to thiourea), in a neutral or weakly acidic medium (several drops of acetic acid were added), followed by removal of the excess solvent.

For this purpose, a weighed portion of the anhydrous acetic acid salt of lanthanum, cerium, praseodymium, or neodymium was dissolved in the smallest possible amount of water heated to not above 30-40°, and into this solution was introduced a dry weighed portion of thiourea, calculated according to the ratio indicated above. Then the excess solvent was removed at room temperature in a vacuum desiccator over calcium chloride or by heating the solution to not above

55°. After some time, well-formed, large, lustrous crystals, strongly refracting light, separated from the solution in the form of thickened short prisms: colorless in the case of the lanthanum and cerium compounds, green in the case of praseodymium, and lilac in the case of neodymium. Separated from the mother liquor by filtration under reduced pressure, the crystals were quickly washed with a small amount of cold water and dried in air until they lost the ability to adhere to the walls of the beaker. Dehydration of the isolated compounds was then continued in a vacuum desiccator over calcium chloride and phosphorus anhydride, no loss in weight being observed. However, the compounds obtained contained water of crystallization, which was removed slowly and with difficulty in a thermostat.

Thus, the lanthanum and cerium compounds lost their water of crystallization at 105-110°, the analogous praseodymium compounds at 130-140°, and the neodymium compound at 155-160°.

The compounds obtained are stable in water and are readily and well recrystallized from it without any change in their chemical composition. They have definite melting temperatures, which proved to be 258-260° for the lanthanum complex and, for the analogous compounds of cerium, praseodymium, and neodymium, respectively, 225-226°, 292-293°, and 297-298°. At the stated temperatures the complex compounds of these elements melt with decomposition.

Repeated recrystallization of the compounds obtained from water did not lead to changes in their melting temperatures. The yield of the compounds obtained is almost theoretical: 98-99%.

The complex compounds of lanthanum, cerium, praseodymium, and neodymium with thiourea are readily soluble in cold and hot water, methyl alcohol, and aniline; less readily soluble in ethyl alcohol, pyridine, quinoline, and aniline; practically insoluble in ether, acetone, benzene, toluene, xylene, dichloroethane, chloroform, isoamyl and isobutyl alcohols. In addition to the organic solvents mentioned above, these compounds are readily soluble in dilute and 80% acetic acid, and in dilute hydrochloric and sulfuric acids; concentrated nitric acid, even in the cold, and dilute nitric acid on heating decompose them with evolution of nitrogen oxides.

Preliminary observations showed that, apparently, a study of the comparative solubility of these compounds in water, methyl and ethyl alcohols, pyridine, and quinoline should be of practical interest.

Analyses of the dehydrated complex compounds for the content of rare-earth elements, with the exception of praseodymium, were carried out by precipitating them as oxalates followed by conversion, by ignition, into the corresponding oxides. Sulfur was determined as barium sulfate. Nitrogen was determined by the Dumas method, and carbon and hydrogen by elementary organic analysis.

Complex lanthanum salt

Hydrated salt

$$La(C_2H_3O_2)_3 \cdot CS(NH_2)_2 \cdot 2H_2O.$$

Found, %: H_2O 8.53; 8.61
Calculated, %: H_2O 8.42

Anhydrous salt

Found, %: La 35.39; 35.55; S 8.02; 8.20; C 21.57; 21.34; H 3.27; 3.61; N 7.13; 7.04

$$La(C_2H_3O_2)_3 \cdot CS(NH_2)_2.$$

Calculated, %: La 35.42; S 8.17; C 21.44; H 3.33; N 7.14

Complex cerium salt

Hydrated salt

$$Ce(C_2H_3O_2)_3 \cdot CS(NH_2)_2 \cdot 2H_2O.$$

Found, %: H_2O 8.02; 8.29
Calculated, %: H_2O 8.29

Anhydrous salt

Found, %: Ce 35.5; 35.56; S 8.40; 8.69; C 21.98; 21.25; H 3.10; 3.40; N 7.30; 7.50
$Ce(C_2H_3O_2)_3 \cdot CS(NH_2)_2$. Calculated, %: Ce 35.56; S 8.14; C 21.33; H 3.30; N 7.12

Praseodymium complex salt

Hydrated salt

$Pr(C_2H_3O_2)_3 \cdot CS(NH_2)_2 \cdot H_2O$. Found, %: H_2O 4.46; 4.40
Calculated, %: H_2O 4.36

Anhydrous salt

Found, %: S 8.20; 8.50; C 21.68; 21.73; H 3.94; 3.54; N 7.55; 7.60
$Pr(C_2H_3O_2)_3 \cdot CS(NH_2)_2$. Calculated, %: S 8.10; C 21.28; H 3.40; N 7.13

Neodymium complex salt

Hydrated salt

$Nd(C_2H_3O_2)_3 \cdot CS(NH_2)_2 \cdot H_2O$. Found, %: H_2O 4.34; 4.51
Calculated, %: H_2O 4.33

Anhydrous salt

Found, %: Nd 36.10; 36.28; S 8.05; 8.52; C 21.33; 21.48; H 3.84; 3.52; N 7.41; 7.60
$Nd(C_2H_3O_2)_3 \cdot CS(NH_2)_2$. Calculated, %: Nd 36.22; S 8.059; C 21.02; H 3.26; N 7.04

The anhydrous complex compounds of lanthanum, cerium, praseodymium, and neodymium with thiourea show no differences in behavior or properties in comparison with their corresponding crystalline hydrates.

Saratov State University
named after N. G. Chernyshevsky

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