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Abstract

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CHEMISTRY

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ON THE PREPARATION OF HETERONIOBATES OF CERTAIN TRANSITION METALS

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The study of the nature of the interaction of the niobate ion with salts of metals, in particular transition metals, and the investigation of the chemical properties of the reaction products are of very great importance for understanding the technology of processing niobium-containing ores and minerals during their alkaline decomposition.

Up to the present time these reactions have been studied far from completely. The mechanism by which they proceed is insufficiently known, and the products of interaction of the niobate ion with metal salts have not been investigated (1-4). This served as the basis for carrying out the present work.

By methods of physicochemical analysis we studied the interaction of aqueous solutions of potassium metaniobate with salts of certain metals; for the first time the influence of an excess of the niobate ion was investigated. As a result of the study carried out, four groups of metal salts were identified, differing from one another in their relation to an excess of metaniobate ion and potassium hydroxide.

Group I comprises salts of copper(II), lead(II), and chromium(III), soluble in an excess of potassium niobate and potassium hydroxide; group II comprises salts of the alkaline-earth metals, cadmium, iron(III), lanthanum, cerium(IV), and thorium, insoluble in an excess of both precipitants; group III comprises salts of zinc and aluminum, soluble in the presence of an excess of potassium hydroxide but insoluble in an excess of potassium metaniobate; group IV comprises salts of manganese(II), iron(II), cobalt, nickel, and cerium(III), soluble only in an excess of potassium metaniobate but insoluble in potassium hydroxide.

The greatest theoretical and practical interest was presented by metal salts soluble in an excess of potassium metaniobate, i.e., the metal salts of the first and fourth groups. Studying the interaction of potassium metaniobate with salts of these metals in aqueous solutions by the nephelometric method, we established the general course of interaction of the reacting substances, characterized by precipitation of precipitates at the equivalence point. The precipitates formed dissolved in an excess of the precipitant; transparent colored solutions were obtained, the exception being lead compounds, the solutions of which are colorless.

We found that the break point on the transparency curve corresponds to a Me : Nb ratio approximately equal to 1 : 2 for divalent cations and 1 : 3 for trivalent cations. Further addition of potassium niobate leads to a rather sharp increase in the transparency of the solutions.

For points with minimal transparency, i.e., with the greatest amount of precipitate, two schemes of the interaction taking place may be considered probable:

$$x\,\mathrm{NbO}_3^- + \mathrm{Me}^{n+} \rightarrow \frac{x}{2}\,\mathrm{Nb}_2\mathrm{O}_5 + \mathrm{Me(OH)}_n, \tag{1}$$

$$n\,\mathrm{NbO}_3^- + \mathrm{Me}^{n+} \rightarrow \mathrm{Me(NbO}_3)_n. \tag{2}$$

Scheme (1) seemed implausible to us, since both niobium pentoxide and the hydroxides of the metals taken by us do not dissolve in an excess of potassium niobate.

On the basis of nephelometric studies it was possible to assume that the dissolution of the initially precipitated sediments upon addition of an excess of niobate ion is described by the following equation:

$$m\,\mathrm{NbO}_3^- + \mathrm{Me(NbO}_3)_n \rightarrow [\mathrm{Me(NbO}_3)_{n+m}]^{(n+m-2)-}. \tag{3}$$

For a more detailed study of the phenomenon observed by us, salts of iron(II), cobalt(II), nickel(II), copper(II), and cerium(III) were selected. The interaction was studied in isomolar series and in series with a constant metal concentration. In the systems studied, we determined electrical conductivity and pH. The break in the curves in the series also corresponds to a Me : Nb ratio approximately equal to 1 : 2 for divalent and 1 : 3 for trivalent cations. The pH data support reaction (2), since the hydroxides of the metals studied by us do not precipitate at pH 5–7 [2], i.e., the considerations expressed above are confirmed.

The optical spectra of aqueous solutions of the heteroniobates formed by the metals under study serve as one of the proofs of the formation of new compounds, since they differ markedly from the spectra of the starting substances. It is known that the niobate ion and the ion of trivalent cerium have a light-absorption region in the ultraviolet region of the spectrum, while the optical density of the initial salts of iron(II), cobalt(II), nickel(II), and copper(II), at concentrations on the order of 0.005 mol/l, is practically zero in the visible region of the spectrum.

Additional confirmation of the complex-formation reaction was provided by electrophoresis data for cerium(III) heteroniobate labeled with the cerium-144 isotope, as well as for the colored heteroniobates of cobalt(II), iron(II), and copper(II), showing that in all cases the ions of these metals move toward the anode, i.e., are part of negatively charged particles.

By the procedure developed by us, heteroniobates of iron(II), nickel(II), copper(II), and cerium(III) were isolated for the first time in solid form; in addition, two compounds (violet and green in color) containing cobalt as the central complex-forming atom were isolated.

The results of the analysis of air-dry salts are presented in Table 1.

Table 1

Composition of the synthesized heteroniobates

Ion-complex-forming agent	K_2O found	K_2O calc.	MeO (Ce_2O_3) found	MeO (Ce_2O_3) calc.	Nb_2O_5 found	Nb_2O_5 calc.	H_2O found	H_2O calc.	Proposed formula of the compound
Fe^{2+}	20.72	18.75	6.88	7.10	51	52.56	21.7	21.41	$K_4[Fe(NbO_3)_4(OH)_2] \cdot 11H_2O$
Co^{2+}	17.21	18.9	8.10	7.56	54.2	53.3	21.34	20.0	$K_4[Co(NbO_3)_4(OH)_2] \cdot 10H_2O$
Co^{2+}	16.73	17.3	14.20	13.80	49.3	49.0	20.0	20.0	$K_2[Co(NbO_3)_2(OH)_2] \cdot 5H_2O$
Ni^{2+}	43.56	42.63	17.90	17.0	29.44	30.15	8.9	10.2	$K_4[Ni(NbO_3)(OH)_5]$
Cu^{2+}	17.87	18.9	8.43	8.00	54.0	53.30	20.2	19.83	$K_4[Cu(NbO_3)_4(OH)_2] \cdot 10H_2O$
Ce^{3+}	21.06	20.23	24.00	23.53	38.0	38.16	17.64	18.07	$K_3[Ce(NbO_3)_2(OH)_4] \cdot 5H_2O$

The data obtained make it possible to assign to the heteroniobates the general formula $K_n[\mathrm{Me}(\mathrm{NbO}_3)_m(\mathrm{OH})_p] \cdot x\mathrm{H}_2\mathrm{O}$, where Me $=$ Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Ce^{3+}, $n = 2,\ 3,\ 4\ldots,\ m = 1,\ 2,\ 4\ldots,\ p = 2,\ 4,\ 5\ldots.$ The individuality of the compounds synthesized by us—their single-phase character—was established by a crystal-optical method.

We determined the electrical conductivity of solutions of the synthesized heteroniobates as a function of concentration. The measurements showed that the heteroniobates of iron, cobalt (the violet compound), and nickel in aqueous solutions are hydrolyzed to a considerable extent. For the complex niobates of copper, cerium, and cobalt (the green compound) were

the limiting molecular conductivities of their solutions were determined, and from the values found the mobilities and effective diameters of the anions were estimated (Table 2).

Table 2

Composition of the heteroniobate	Limiting electrical conductivity, ohm^{-1}	Anion mobility	Particle diameter, Å
$K_4[Cu(NbO_3)_4(OH)_2]\cdot 10H_2O$	478	45.5	3.1
$K_3[Ce(NbO_3)_2(OH)_4]\cdot 5H_2O$	376	52	2.2
$K_2[Co(NbO_3)_2(OH)_2]\cdot 5H_2O$	240	46.5	1.5

Thus, the existence—both in solutions and in the form of solid phases—of heteroniobates previously unknown in the literature has been demonstrated.

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