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Abstract

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CHEMISTRY

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INTERACTION OF RARE EARTHS WITH A CERIUM-MOLYBDENUM HETEROPOLY COMPOUND

A comparatively small number of heteropoly compounds are known in which the anion contains several atoms of complex formers ([1]). Such compounds include, in particular, a complex with two central cobalt atoms ([2]). The latter may have the same valence, equal to two, or may be in different valence states.

In the interaction of trivalent rare earths with a cerium–molybdenum heteropoly compound, we observed the formation of a new polynuclear complex. The initial reagents in the work were freshly prepared cerium–molybdic acid (CMA) $CeO_2 \cdot 12MoO_3 \cdot nH_2O$, obtained by the ion-exchange method ([3]), or its hexa-substituted ammonium salt (CMAS), synthesized by the method ([4]), of composition $3(NH_4)_2O \cdot CeO_2 \cdot 12MoO_3 \cdot 11H_2O$, as well as spectrally pure chlorides and nitrates of the trivalent rare earths lanthanum, cerium, praseodymium, samarium, yttrium, erbium, and ytterbium (E).

Table 1

Analysis of precipitates of cerium molybdates of rare-earth elements

Name of salt	Found, %	Found, %	Found, %	Found, %	Molecular ratio of oxides	Molecular ratio of oxides	Molecular ratio of oxides	Molecular ratio of oxides
	E_2O_3	CeO_2	MoO_3	H_2O	E_2O_3	CeO_2	MoO_3	H_2O
Lanthanum	18.11	6.58	66.00	9.30	1.45	1	12.06	13.51
Cerium	–	26.05	63.91	10.04	1.50	1	11.73	14.74
Praseodymium	16.60	6.27	61.96	15.17	1.38	1	11.82	23.15
Samarium	18.96	5.99	60.48	14.57	1.56	1	12.07	23.26

Addition of cerium–molybdic acid to a solution of trivalent rare earths showed

Fig. 1. Amperometric titration of cerimolybdic acid with LaCl3 solution. Amount of CMA 23.46 mg

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that the behavior of the cerium and yttrium groups is different. In the case of salts of lanthanum or trivalent elements of the cerium group, a yellow precipitate is formed, soluble in an excess of the heteropoly acid. Salts of elements of the yttrium group do not give precipitates with freshly prepared heteropoly acid at any ratio of the reagents; however, a clear weakening of the intensity of the coloration of the cerium–molybdic acid is observed visually.

The composition of the salt precipitates formed when a cerium-group element is added to the heteropoly acid or to its ammonium salt does not depend on the ratio of the initial reagents: $1.5E_2O_3 \cdot CeO_2 \cdot 12MoO_3 \cdot nH_2O$ (Table 1). The lanthanum and cerium salts are amorphous; the praseodymium and samarium compounds are crystalline.

To carry out chemical analysis, weighed portions of the obtained substances were decomposed on heating with an alkali solution (1 N). The precipitate of the hydroxides of the trivalent rare-earth element and Ce^{4+} was filtered off. Molybdenum was determined in the filtrate ([5]). In the case of analysis of lanthanum and samarium salts, the hydroxide precipitate was dissolved in 20% H_2SO_4. The content of Ce^{4+} was determined volumetrically from an aliquot portion. In another aliquot of the solution, the content of the sum of trivalent rare-earth ···

element and Ce^{4+} by the gravimetric method. The amounts of lanthanum and samarium were established from the difference between the content of the sum of the rare earths and Ce^{4+}. In the analysis of the Ce^{3+} salt, the total cerium content was determined. The amounts of Ce^{3+} and Ce^{4+} were found by calculation, taking into account that the ratio of Ce^{4+} to Mo in the salt being analyzed is 1:12. When determining the composition of the praseodymium salt, the mixture of rare-earth hydroxides was dissolved in HNO_3. Ce^{4+} was separated in the form of the iodate; praseodymium hydroxide was precipitated from the mother liquor. The water content in the isolated salts was found by dehydration at a temperature of 450°. The salt precipitates obtained when ammonium cerimolybdate and rare-earth-element nitrate were used were checked for nitrogen content. The analysis was carried out by the Kjeldahl method [6].

Fig. 1. Amperometric titration of cerimolybdic acid with $LaCl_3$ solution. Amount of CMA 23.46 mg

Fig. 2. Change in the absorption spectrum of an aqueous solution of cerimolybdic acid in the presence of $YbCl_3$.
1 –solution of cerimolybdic acid, 0.0496 mg/ml;
2 –the same in the presence of $YbCl_3$. Ratio $YbCl_3$:CMA = 2:1

Fig. 2. Change in the absorption spectrum of an aqueous solution of cerimolybdic acid in the presence of YbCl3.

Figure 2: Fig. 2. Change in the absorption spectrum of an aqueous solution of cerimolybdic acid in the presence of YbCl3.

The study of the process of interaction of the cerimolybdenum heteropoly compound with elements of the cerium and yttrium groups was carried out using a number of physicochemical methods. We established that cerimolybdic acid is reduced at the dropping mercury electrode in a single reduction wave, the height of which is proportional to the concentration. In this connection it proved possible to apply the method of amperometric titration with a voltage of 1 V imposed on the system. The background was 0.01 N and 0.1 N HCl. As a result of adding $LaCl_3$ or $CeCl_3$ solutions to cerimolybdic acid, a decrease in the wave height was observed until a salt precipitate began to form. On the titration curve this moment corresponds to the break (Fig. 1).

The decrease in the wave height is caused by a lowering, in the solution, of the concentration of free cerimolybdic acid as a result of its interaction with the rare-earth element. The compound formed in this process is characterized by a ratio of La(Ce^{3+}) to CMA equal to 2:1 and, unlike the heteropoly acid, is not reduced at the dropping mercury electrode. With further introduction into the solution of a rare-earth element of the cerium group, i.e., when the ratio La(Ce^{3+}) to CMA begins to exceed 2:1, a sparingly soluble salt of composition $1.5E_2O_3 \cdot CeO_2 \cdot 12MoO_3 \cdot nH_2O$ is formed. The solubility of the lanthanum salt $1.5La_2O_3 \cdot CeO_2 \cdot 12MoO_3 \cdot 13H_2O$ in water at 20° is 0.0937 g/l. In the series lanthanum–samarium, the solubility of the salts in water increases and for the samarium salt $1.5Sm_2O_3 \cdot CeO_2 \cdot 12MoO_3 \cdot 23H_2O$ is equal to 0.7290 g/l.

The absorption spectrum of a solution of cerimolybdic acid in the wavelength range 250–350 mμ has the form of a curve rising steeply toward the ultraviolet region. Upon addition of ions of a trivalent rare-earth element, the optical density of the heteropoly acid solution in the ultraviolet-

region increases noticeably (Fig. 2), although no fundamental changes in the character of the spectrum are observed.

Optical studies to determine the composition of the products formed in a series of experiments with a constant concentration of cerium molybdenum acid, using elements of the yttrium group as examples, also showed the formation of a compound at a ratio $Me^{3+} : CMA = 2 : 1$ (Fig. 3).

The formation of the new complex is accompanied by a decrease in the pH value. Investigation of the change in pH in a series of experiments with a constant concentration of ammonium cerium molybdate and an increasing concentration of yttrium nitrate confirmed the composition of the complex found. The curve in Fig. 4 has one inflection, corresponding to the ratio $Y^{3+} : CMA = 2 : 1$. The amount of gram-ions of hydrogen liberated on mixing solutions of ammonium

Figure 3 and Figure 4 graphs

Figure 3: Figure 3 and Figure 4 graphs

cerium molybdate

Fig. 3. Dependence of the optical density D at 350 mμ on the ratio YCl_3 to CMA. Concentration of CMA 0.340 mg/ml, cuvette 10 mm

Fig. 4. Change in pH in the system ammonium cerium molybdate–$Y(NO_3)_3$ –H_2O. Concentration of CMA 0.452 mg/ml

and yttrium nitrate with identical pH values of 3.50 was established by titration with alkali. It was found that the formation of the new complex is accompanied by the appearance in solution of 2 gram-ions of hydrogen per 1 gram-mole of hexasubstituted ammonium cerium molybdate. A decrease in pH was also observed by us when mixing solutions of ammonium cerium molybdate with nitrates of other rare earths.

By the electromigration method it was found that Ce^{3+} in a mixture with ammonium cerium molybdate moves toward the anode. The experiments were carried out in a U-shaped tube with an electric field applied. In the middle part of the tube a mixture of solutions of ammonium cerium molybdate and $CeCl_3$, labeled with trivalent Ce^{141}, was placed. The side parts of the tube were filled with 0.01 N HCl solution. The ratio Ce^{3+} : CMA was taken as 1:1 and 1.8:1. After completion of the experiment, the activity in the side and middle parts of the tube was determined. The movement of radioactive Ce^{3+} only toward the anode indicated the formation in the system under study of a new compound, whose anion contains Ce^{3+}.

Thus, the interaction of the cerium molybdenum heteropoly compound and ions of trivalent rare-earth elements proceeds with the formation in solution of a polynuclear complex, whose anion contains 12 molybdenum atoms, one atom of tetravalent cerium, and two atoms of a trivalent rare-earth element. This polynuclear complex, containing a trivalent element of the cerium group, gives a sparingly soluble salt with a third atom of the same element.

In all probability, the bonds in the polynuclear anion are effected through oxo bridges. For zirconium, for example, which is close in its complex-forming properties to Ce^{4+}, such compounds are well known (7). Hydroxyl groups are formed from water molecules present in the anion, with displacement into the outer sphere of the corresponding number of ions

hydrogen. The addends of the inner sphere evidently consist of molecules of H_2MoO_4, MoO_3, and ions MoO_4^{2-}, connected by hydrogen bonds and shared oxygen atoms ([8]). After the introduction of rare-earth-element atoms into the heteropolyanion, the molybdenum-containing addends are apparently redistributed, becoming arranged around all the indicated atoms.

Taking cerium molybdic acid to be octabasic, with two more strongly bound hydrogen atoms, the formula of the hexasubstituted ammonium salt may be represented as $(NH_4)_6H_2[Ce^{4+}Mo_{12}O_{42} \cdot nH_2O]$. Then the scheme of the reactions described above will be as follows:
$H_2[Ce^{4+}Mo_{12}O_{42} \cdot nH_2O]^{6-} + 2Me^{3+} \rightarrow H_2[Ce^{4+}(OH)Me^{3+}(OH)Me^{3+}Mo_{12}O_{42} \cdot (n-2)H_2O]^{2-} + 2H^+$;
the third atom* of a rare-earth element of the cerium group forms a sparingly soluble salt with the polynuclear anion:
$H_2[Ce^{4+}(OH)_2Me_2^{3+} \cdot Mo_{12}O_{42} \cdot (n-2)H_2O]^{2-} + Me^{3+} \rightarrow Me^{3+}H[Ce^{4+}(OH)_2 \cdot Me_2^{3+}Mo_{12}O_{42} \cdot (n-2)H_2O] +$

It is possible that the third atom of the rare-earth element, Me^{3+}, is also covalently bound through a tin bridge to the remaining atoms of the heteropolyanion, and then the entire molecule must acquire a nonionogenic character.

The investigation of the new class of polynuclear heteropoly compounds is continuing.

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