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Abstract

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MONOCITRATE COMPLEXES OF RARE-EARTH ELEMENTS

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The study of the interaction of alkali-metal citrates with salts of rare-earth elements (^{1}) was the first investigation to show that they are vigorous complex-forming agents. The reaction proceeds in equimolecular amounts, and at a ratio $Me : \text{cit} = 1 : 2$ a very stable complex compound is formed:

$$MeX_3 + 2K_3C_6H_5O_7 \rightarrow K_3[Me(C_6H_5O_7)_2] + 3KX,$$

where $Me = La—Lu$; $X = Cl^-$, NO_3^-, etc.

As was established (^{2}), rare-earth elements form a coordination bond with addends predominantly through oxygen atoms or tertiary nitrogen and exhibit a coordination capacity equal to six.

With the aid of a series of precipitants

$$PO_4^{3-} > F^- > C_2O_4^{2-} > OH^- > [Fe(CN)_6]^{4-}$$

it was possible to prove that the complex-forming ability of this group of elements with any of the addends increases as the ionic radius decreases, from lanthanum to lutetium. The stability of complex compounds of rare-earth elements depends sharply on the pH of the medium and, as a rule, decreases with increasing acidity. However, previously the products of interaction of rare-earth elements with alkali-metal citrates at the lower ratio $Me : \text{cit} = 1 : 1$ had not been studied in detail, since the precipitate initially formed was regarded as a simple citrate.

A subsequent, more detailed study of the precipitate separated at the ratio $Me : \text{cit} = 1 : 1$ showed that in this case as well a complex compound is formed. When it is dissolved in water, the ion of the rare-earth element is not detected by the action of $K_4[Fe(CN)_6]$; a precipitate appears only after acidification of the solution. It is very characteristic that, in the series of rare-earth elements, in this case also a general tendency toward an increase in the stability of their complexes is observed. Thus, for example, the reaction with potassium ferrocyanide is negative for all rare-earth elements; with oxalate it is observed for lanthanum, neodymium, and gadolinium, whereas with yttrium and erbium precipitates are no longer formed.

Particularly noteworthy is the fact that addition of caustic soda leads to dissolution of the complex, whereas alkali is one of the best precipitants of rare-earth elements. Although the addition of 1 mole of NaOH increases the pH of the solution to 9, the complex compound is noticeably strengthened: the lanthanum ion is not separated from the alkalized solution not only by potassium ferrocyanide, as described above, but even by such a vigorous precipitant as sodium fluoride.

Analytical data show that the precipitate formed at the ratio $Me : \text{cit} = 1 : 1$, in the case of lanthanum, has the composition $[LaC_6H_5O_7 \cdot 3H_2O]$. For this compound

$$\begin{aligned} \text{Found } \% : &\quad La\ 36.3; \quad H_2O\ 12.2 \\ \text{Calculated } \% : &\quad La\ 36; \quad H_2O\ 14.1 \end{aligned}$$

The indicated compound may be regarded as a nonelectrolyte in which six coordination sites of lanthanum are occupied by a citrate residue and by three water molecules. In aqueous solution the compound is converted into an electrolyte, with the metal becoming part of the anion, as is convincingly demonstrated by its quantitative transfer into the anode space. The experiments were carried out in the presence of the radioactive europium isotope $\mathrm{Eu}^{152,154}$.

This circumstance gives grounds for assuming that, in the process of dissolution of the substance, intrasphere dissociation of one water molecule occurs with formation of an electrolyte according to the reaction:

$$[\mathrm{LaC_6H_5O_7 \cdot 3H_2O}] \rightleftarrows \mathrm{H[LaC_6H_5O_7 \cdot 2H_2O \cdot OH]}.$$

When the precipitate of lanthanum tricitrate is dissolved in one mole of caustic soda, dissociation of one molecule of intrasphere water, as is evident, proceeds to completion with formation of the sodium salt of the complex lanthanum compound according to the reaction:

$$[\mathrm{LaC_6H_5O_7 \cdot 3H_2O}] + \mathrm{NaOH} \rightarrow \mathrm{Na[C_6H_5O_7 \cdot 2H_2O \cdot OH]}.$$

The precipitate isolated from the alkaline solution with alcohol, according to analysis, closely corresponds to the formula $\mathrm{Na[LaC_6H_5O_7 \cdot 2H_2O \cdot OH]}$.

$$\begin{aligned} \text{Found, \%:} &\quad \mathrm{La}\ 36.8; \quad \mathrm{H_2O}\ 13.9, \\ \text{Calculated, \%:} &\quad \mathrm{La}\ 34.4; \quad \mathrm{H_2O}\ 13.1. \end{aligned}$$

Sodium was determined indirectly with the aid of its radioactive isotope Na^{24}.

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CITED LITERATURE

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2. D. I. Ryabchikov, E. A. Terent' eva, Izv. AN SSSR, OKhN, 1949, No. 1, 44.

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

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