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Potentiometric Study of Reactions of Rare-Earth Elements with 3-Allylpentanedione in a Water–Dioxane Medium

N. V. Pashchevskaya, S. N. Bolotin, M. E. Sokolov, A. A. Sklyar, and V. T. Panyushkin

Kuban State University, ul Stavropol'skaya 149, Krasnodar, 350040 Russia
e-mail: epr_kb@chem.kubsu.ru

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Abstract—Reactions of the ions of La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, and Lu with 3-allylpentanedione (HL) in a water–dioxane (50 vol%) medium were studied by pH-metric titration. Stability constants of LnL^{2+} and LnL_2^+ complexes and pH range where these compounds are mainly formed were determined. The dependence of the stability constants on the atomic number of an element has a characteristic break on the gadolinium ion and shows that the stability of the complexes increases as the size of Ln^{3+} ions decreases.

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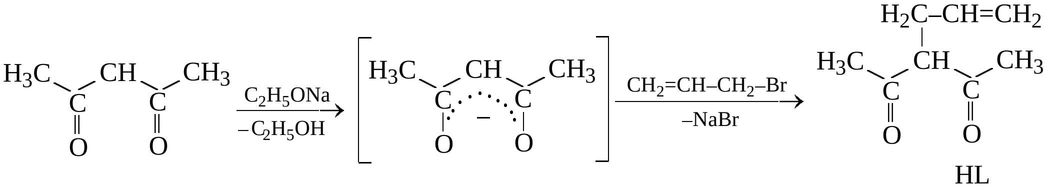
The synthesis and study of lanthanide-containing polymers based on β-dicarbonyl compounds allow obtaining composites capable of combining valuable properties of the lanthanides with processibility and availability of polymers. Possessing unique luminescent properties, the macromolecular complexes of rare-earth elements find wide application in high-sensitivity determination and isolation of these elements from several natural objects [1, 2] even in the presence of such strong luminescence quenchers as Ce, Pr, Nd, and Ho [3], and also are used as luminescent labels in immunofluorescent analysis [4–6] and light-absorbing and light-transforming materials in various industries [4–7]. Molar extinction coefficients, intensity, quantum yield, and life time of the luminescence of β-diketonates of the rare-earth elements entering into a polymeric matrix depend on the nature of substituents, namely on the distribution of charges in a chelated cycle, spatial structure, and hydrophobic properties of a ligand [5, 6, 8–10].

One way for obtaining polymeric compositions containing lanthanide ions is polymerization or copolymerization of the lanthanide-containing monomers, therefore it is actual to study physicochemical properties of the monomeric lanthanide complexes, in particular the study of their stability. Earlier we have studied the different-ligand lanthanide complexes containing acetylacetone and unsaturated carboxylic acids as ligands [10–12]. We have shown that introduction of a ligand containing a multiple bond to the composition of a complex makes it possible to use these complexes as monomers for the preparation of lanthanide-containing polymers.

The aim of the present work was to study stability of the lanthanide complexes with 3-allylpentanedione (HL), which can form compounds capable of forming polymers due to the presence of a double bond in side chain [13]. The study was carried out by the method of potentiometric titration, 3-allylpentanedione was obtained by the nucleophilic substitution of allyl bromide for a hydrogen atom in the acetylacetone α-position [13].



Mixing aqueous solutions of a lanthanide salt with a water–dioxane solution of a ligand (HL) results in a pH decrease that points to the formation of a complex with the deprotonated form of the ligand. The choice of the water–dioxane (50 vol%) solvent provides dissolution of the both ligand and complexes in

Stability constants[a] of the lanthanide (Ln) complexes with 3-allylpentanedione (25°C, 0.1 M KCl, 50 vol % of dioxane)

Ln^{3+}	$\log K_1$	$\log K_2$	$\log \beta_2$
La	4.98(3)	3.71(2)	8.69(5)
Pr	5.54(2)	4.67(2)	10.21(4)
Nd	5.79(4)	4.71(3)	10.50(7)
Sm	6.58(2)	5.47(1)	12.05(3)
Eu	6.43(2)	5.54(2)	11.97(4)
Gd	6.13(2)	5.53(2)	11.66(4)
Dy	6.44(3)	5.80(3)	12.24(6)
Ho	6.55(2)	5.96(3)	12.51(5)
Er	6.60(3)	5.62(4)	12.22(7)
Yb	6.82(2)	5.92(3)	12.74(5)
Lu	6.79(2)	6.04(3)	12.83(5)

[a] The error in the determination of the last figure is given in parentheses.

a sufficiently wide pH range. Curves of the HL titration in the presence of metal ions have a buffer zone in the range of pH 5–6, i.e. below the region of the titration of the ligand enol form. At pH > 8 a precipitate was formed, therefore we failed to obtain data for constructing portion of the curve corresponding to the formation of complexes with maximal average ligand numbers.

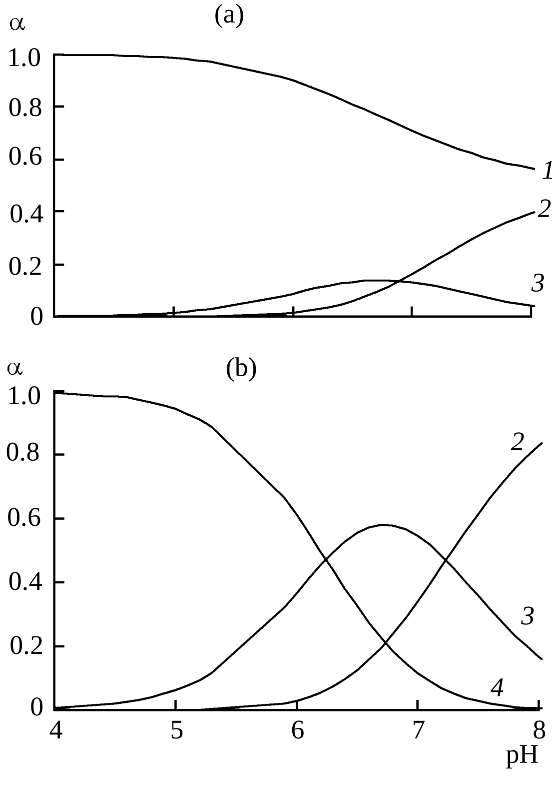


Fig. 1. Distribution of (a) ligand and (b) metal for the systems containing Eu^{3+} (0.005 M) and 3-allylpentanedion (HL) (0.02 M) in the mixed solvent (water–dioxane). (*1*) HL, (*2*) EuL_2^+, (*3*) EuL^{2+}, (*4*) Eu^{3+}.

$$Ln^{3+} + L^- \overset{K_1}{\rightleftarrows} LnL^{2+}, \qquad (1)$$

$$LnL^{2+} + L^- \overset{K_2}{\rightleftarrows} LnL_2^+. \qquad (2)$$

Thus, we determined only first two constants of the complex formation of lanthanide ions with 3-allylpentanedione corresponding to equilibria (1) and (2).

Nevertheless the data obtained are sufficient for their application to the chelating processes in polymers, because owing to steric difficulties the metal ions as a rule can be bound with no more than two macroligands [3].

In the calculation of stability constants of the complexes we used the constant of the ligand deprotonation 10.92±0.02 (25°C, 0.1 M KCl), which we determined by titration of its water–dioxane solution. Accounting for the opportunity of the participation of a lanthanide ion in the hydrolysis using the equilibrium constants of reaction (3) taken from [14] did not lead to essential changes in the constants of complex formation.

$$Ln^{3+} + H_2O \rightleftarrows LnOH^{2+} + H^+. \qquad (3)$$

The difference in the calculations of $\log K$ with the consideration of reaction (3) and without it is ~0.02–0.04 that does not exceed the error of the calculation (no more than ±0.05). Hence, the complex formation predominates while hydrolysis in the water–organic medium is suppressed.

The calculated values of stability constants are listed in the table. The plots of distribution of the metal ion and ligand forms as functions of pH calculated from the data obtained are given in Fig. 1. Even at a significant excess of the ligand (4 : 1) the complex LnL_2^+ prevails at low pH values, and only at pH > 7 a significant amount of the complex LnL_2^{2+} is formed.

The dependence of stability constants on the atomic number of an element presented in Fig. 2 shows that the stability increases as the atomic number increases, i.e. as the size of Ln^{3+} ions decreases. The dependence has a characteristic break on the gadolinium ion, which is clearly seen in the case of $\log K_1$. A similar dependence was detected for the complex formation of lanthanide ions with saturated [15] and unsaturated [16] β-diketones.

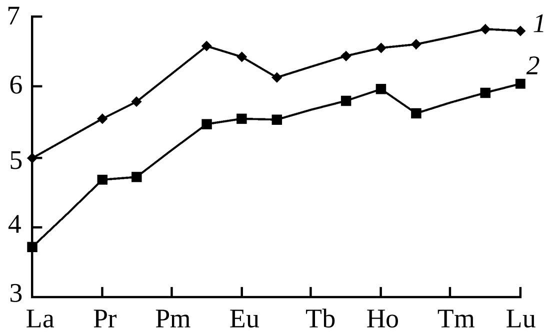


Fig. 2. Dependence of stability constants of lanthanide complexes with 3-allylpentanedione on the lanthanide atomic number. (*1*) $\log K_1$, (*2*) $\log K_2$.

Quantitative comparison of the resulting stability constants with the similar data for the lanthanide complexes with other β-diketones is complicated because of distinctions in the operating solvent composition, ionic strength, and temperature. Nevertheless, we can contend that the stability of 3-allylpentanedione complexes is comparable with the stability of acetylacetone complexes [11], which is attributable to the practical equality of the charges on oxygen atoms of enol form of the ligand, as calculated by quantum-chemical methods [17].

EXPERIMENTAL

Solutions of lanthanide chlorides were prepared by reactions of their oxides (chemically-pure grade) with concentrated hydrochloric acid (chemically-pure grade). Exact concentrations of the metals were determined by chelatometry [18]. As a solvent we used a solution of dioxane (50 vol%) purified by the technique [19] in twice-distilled water. Ionic strength of solutions (0.1 M) was maintained by adding KCl (special-purity grade) at their preparing. A free from carbonates ~0.1 M KOH solution was used as a titrating agent, its exact concentration was determined by the technique [20].

The values of pH were measured with the accuracy of 0.01 pH unit in a temperature-controlled cell at 25±0.5°C on an EV-74 measuring unit (ionomer) with an ESL-63-07 glass electrode and a silver chloride reference electrode. To determine the constant of the ligand deprotonation, its 0.02 M solution was titrated, and to study the complex formation, solutions containing a lanthanide ion and 3-allylpentanedione in the ratio 1:4 (c_{Ln} 0.005 M) was titrated.

A preliminary computation of stability constants was carried out by Irving-Rossoti [21] and Calvin–Melchior [22] methods, and then the data were refined using a computer program based on the standard procedure [23]. The error in the determination of equilibrium constants was established by the known technique [24]. In the calculations we took into account the variation in the water activity on adding the organic component, dioxane [25]. The ionic product of water $\mathrm{p}K_\mathrm{w}$ 15.18 for the mixed solvent has been calculated from the curves of titration of 0.1, 0.01, and 0.001 M HCl solutions. This value satisfactorily corresponds to the published data [26, 27].

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