

THE DIFFERENCE OF THE COMPLEX FORMATION OF THE RARE-EARTH ELEMENTS WITH THE L-MALIC ACID AT METAL ION EXCESS

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Abstract

The complex formation of the rare-earth ions (Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+}) with L-malic acid (H_3Mal) in the aqueous solutions was studied by pH-metric titration method in pH region 3.00 to 9.00 and constant ionic strength 0.1 M KCl. The ratios of the concentrations of the L-malic acid and the rare-earth elements (Ln) were 1:1 and 1:2. The compositions and the stability constants of the rare-earth element complexes with L-malic acid were calculated by SuperQuad program for complex equilibria. It was shown, that in addition to 1:1 complexes, the hydroxocomplexes, protonated and polynuclear complexes of the rare-earth elements are also formed.

Key words: complex formation, lanthanides, L-malic acid

Introduction

The malic acid is believed to be one of the best selective reagents for the industrial separation of the rare-earth elements and the transuranium elements¹ by the ion-exchange chromatography method.² The complex formation of the rare-earth ions with the malic acid was studied by potentiometric methods³⁻¹³ and spectroscopy method.¹⁴ At low pH values the $\text{LnH}_2\text{Mal}^{2+}$, LnHMal^+ and $\text{Ln}(\text{HMal})_2^-$ complexes only were found.⁵ Patnaik et al.⁷ reported that in the Ln - H_3Mal system the complexes of 1:1 and 1:2 compositions are formed at $\text{pH} < 7$, whereas at $\text{pH} > 7$ the formation of polynuclear complexes with the coordination of the oxy-group of the malic acid is observed. Yatzimirsky et al.⁴ assumed the existence of $\text{Ln}_2(\text{HMal})_3^0$, $\text{Ln}(\text{Mal})_2^{3-}$ and LnMal^0 complexes in the aqueous solutions. The isolation of $[\text{Ln}(\text{H}_2\text{Mal})(\text{HMal})]^0$ and $\text{Ln}_2(\text{HMal})_3^0$ complexes in the solid state was also reported by Patnaik et al.⁷ It should be noted that the complex formation with the racemic DL-malic acid was studied in most cases.

Thus, the complex formation of the rare-earth ions with the malic acid in the aqueous solutions at low pH values is rather well studied, though the data on the

composition and the stability constants of the complexes with malic acid formed in this pH range are contradictory (Table 1) and are not critically estimated. Table 1 data show the considerable dispersion of stability constant values. So there is the difference in 1.0–1.8 Lg K unit for LnHMal⁺ complexes. It should be noted that the most part of presented stability constant values (Table 1) are critically selected IUPAC SC-Database data.¹⁵

In the case of even the simplest malate complexes LnHMal⁺ and Ln(HMal)₂⁻ the considerable differences of stability constant values take place. The cause of that is *a priori* models of complex formation without statistic model assessment. For example, the results of the investigation⁵ are significant in this sense. There are some fatal contradictions in it though the authors used the method of mathematical modeling. For example at the concentration ratio C(Ln(NO₃)₃):C(H₃Mal) = 1:1 authors do not even take into account the formation of Ln(HMal)₂⁻ complexes whereas the modeling of equilibrium composition in the Ln(NO₃)₃ - H₃Mal system with malate stability constants of Sm and Nd, dissociation constants of malic acid of this article and pK_w value shows that the fraction of the accumulation of Ln(HMal)₂⁻ complexes is up to 10%. At the other concentration ratios C(Ln(NO₃)₃):C(H₃Mal) the stability constants values are also contradictory. The uncoordinated scheme of equilibrium of complex formation appears to be used by authors.⁵

Up to now, the stoichiometry and the stability constants of the complexes of the rare-earth ions with the malic acid formed at pH ≥ 7 and at metal ion excess have not been unequivocally determined.

In this work the results of a study of the complex formation of the complexes of the rare-earth ions with the L-malic acid by pH-metric titration method and mathematical modeling of complex equilibrium in solutions¹⁶ are presented. The ratios of the concentrations of the L-malic acid and the rare-earth elements were both 1:1 and 1:2. It was allowed to describe the studied equilibrium system more adequately. At that the hydrocomplexes and binuclear complexes were taken into account.

Results and discussion

The pH-metric titration data (Figure 1) were used for the calculations of the formation functions Z_{H^+} ,¹⁷ the protonation constants of ligand K_{oi} and the stability constants K of the malate complex species. The pH-metric titration data were treated by

Table 1. Logarithms of Apparent Stability Constants of Malate-Complexes of the Rare-Earth Ions.

Ref.	Medium	T, °C	CeHMal ⁺	PrH ₂ Mal ²⁺	PrHMAL ⁺	NdH ₂ Mal ²⁺	NdHMAL ⁺	SmH ₂ Mal ²⁺	SmHMAL ⁺
3	0.2 M KCl	25	4.11	-	4.28	-	4.45	-	4.41
5	0.1 M KNO ₃	20	-	1.80	4.41	2.09	4.59	2.23	4.76
6	0.2 M NaClO ₄	25	4.10	-	4.20	-	4.45	-	4.53
9	0.1 M NaClO ₄	25	-	-	4.65	-	4.77	-	4.89
10	0.1 M KCl	30	5.00	-	5.04	-	5.12	-	-
11	0.2 M NaClO ₄	25	5.23	-	5.04	-	5.66	-	5.42
12	0.1 M KNO ₃	20	-	3.18	-	3.57	-	4.36	-
13	0.1 M NaClO ₄	25	-	-	-	-	4.77	-	4.90
14	0.1 M KCl	20	-	-	-	-	4.65	-	-

the calculation procedure described in work,¹⁶ taking into account the recommendations given in works.¹⁷⁻¹⁸ The complex formation parameters were calculated using the SuperQuad program.¹⁹

Because literature data give mainly the dissociation constants for the racemic DL-malic acid, acid-base equilibria of L-malic acid at ionic strength of 0.1 M KCl were previously studied in pH 3.1-11.0 range. The number of experimental points for the each titration curve of L-malic acid (Figure 1) was 70-100 at 8 independent titrations. The calculated dissociation constants of L-malic acid given in Table 2 can be compared with the literature data displayed in the same table. It is no wonder that there is a difference between dissociation constants of L-malic acid we have calculated and the literature data, because in various works the form of the L-malic acid under study is not specified.

Besides, the pK_w value used for the calculation of the protonation constants was not indicated. The obtained dissociation constants of L-malic acid were used in further calculations of the stability constants of the complexes.

It should be noted that there are significantly different literature data on the dissociation constant pK_{α3} of the L-malic acid hydroxyl group. In the investigation²² 11.55 (0.1 M KNO₃, 293 K) value was used whereas Khalil et al.²³ used pK_{α3} value 15.46 (0.5 M NaNO₃, 298 K). These pK_{α3} values significantly differ from the one 14.3²⁴ used in series of works described in monograph.¹⁶ Therefore we carried out the additional experimental series of pH – titration up to pH 12.5 – 12.6. Our calculated pK_{α3} value was 12.34 ± 0.15.

Table 2. The Apparent Dissociation Constants of Malic Acid (298 K).

$\text{pK}\alpha_1$	3.24	3.26 ± 0.01^a	3.26	3.22	3.26
$\text{pK}\alpha_2$	4.68	4.78 ± 0.01^a	4.68	4.72	4.71
Ionic strength	0.1 (KCl)	0.1 (KCl)	0.2 (KCl)	0.1 (KNO ₃)	0.1 (KNO ₃)
Reference	20		3	21	5

^a The dissociation constants of L-malic acid were calculated in present work.

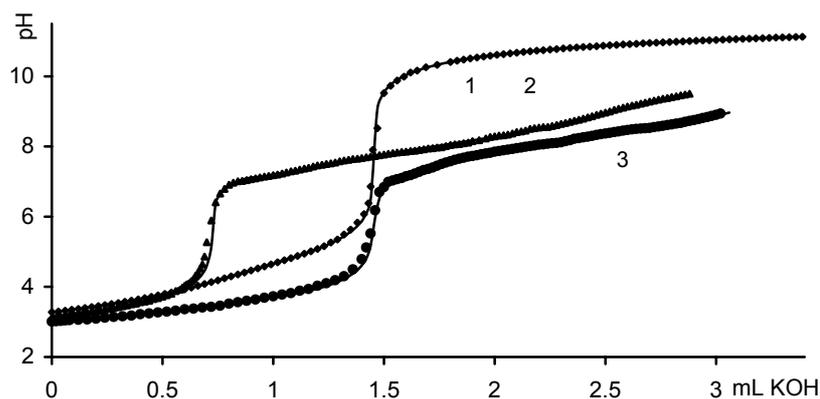


Figure 1. The pH-metric titration data: H₃Mal (1), SmCl₃ - H₃Mal 2:1(2), 1:1(3) (points - experiment, line - the best-fitted model function).

Since the formation of the α -hydroxycarboxylate chelate cycle is proved at the complex formation of the rare-earth elements with the L-malic acid at neutral region of pH,¹⁶ this may be an evidence in support of the lesser $\text{pK}\alpha_3$ value in comparison with the pK_w value. The pK_w value 13.78 was used.³⁰

The results of the titration of the L-malic acid - rare-earth element systems at 1:2 molar ratios and ionic strength of 0.1 M KCl are given in figures 1-2. The number of experimental points of the each curve of pH-metric titration was 80-90 at concentration ratios $C(\text{H}_3\text{Mal}):C(\text{LnCl}_3) = 1:2$ and $1:2$ for 5-6 independent titrations in the pH range 3.0-9.0. At $\text{pH} > 8.2$ the formation of a precipitate was observed.

The initial model for each system was that is in works.^{16,26} Salnikov et al. investigated the complex formation of DL-malic acid with heavy rare-earth metal by pH-metric titration and proton spin – lattice relaxation methods. We investigated the possible formation of the species ML, ML₂ and ML₃, the protonated and the hydrolysed species. The protonated species MH₂L and M(H₂L)₂ were introduced in our model because these species were observed that the titration curves had initial values of pH higher than expected. Assuming that hydrolysis begins with the loss of protons from

water molecules coordinated to the complex and that this is followed by dimerization and subsequent polymerization, it is then obvious that this process involves a complex equilibrium.¹⁷ On the other hand, it was of interest to evaluate the pH range where hydrolysis process initiated. Thus, using only the part of the titration curves where it was began the hydrolysis, it was possible to set up a model with the simplest hydrolysed species: $M(OH)$, $ML(OH)_2$, $M_2L_2(OH)$ and MOH , $M_2(OH)_2$, $M(OH)_2$ and $M(OH)_3$. The stability constants of the hydrocomplexes were previously calculated from the experimental data for $LnCl_3 - KOH$ systems.

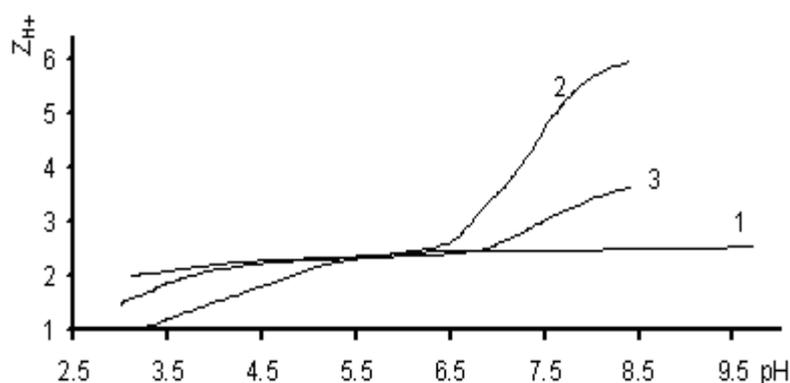


Figure 2. Formation functions: H_3Mal (1); $SmCl_3 - H_3Mal$ 2:1 (2), 1:1 (3).

The results of pH-metric titration were re-counted by equation (1) in order to obtain the functional dependence of Z_{H^+} vs. pH (Figure 2). The Z_{H^+} is a average degree of ligand titrate. The Z_{H^+} function is a formation function since it reflects the contribution of each complex species to the change of pH.²¹ Thus $Z_{H^+} = \sum \alpha_i Z_{(H^+)i}$, when α_i - equilibrium concentration of i - complex species

$$Z_{H^+} = \frac{10^{-pH}(V_{H_3Mal} + V_{OH}) + C_{OH} \cdot V_{OH} - 10^{(pH-pK_w)}(V_{H_3Mal} + V_{OH})}{C_{H_3Mal} \cdot (V_{H_3Mal} + V_{OH})} \quad (1)$$

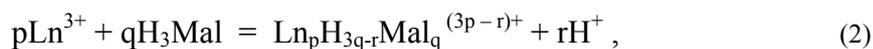
where C_{OH} is a concentration of titrant, C_{H_3Mal} is a concentration of L-malic acid, V_{OH} is a volume of titrant, V_{H_3Mal} is an initial volume of acid.

A comparison of the results of pH-metric titration of the free acid and in the presence of rare-earth elements shows that the complex formation starts at $pH < 2.5$. In the presence of the rare-earth elements the formation function Z_{H^+} reaches the value of 1.5 at pH 3.0-3.1, which points to the formation of complex species containing an

α -hydroxycarboxylate chelate ring according to the data of work.¹⁶ Further abrupt increase of Z_{H^+} at $pH > 6.5$ testifies to the formation of $LnMal^0$ complexes parallel with the hydroxocomplexes. At concentration ratio $C(LnCl_3):C(H_3Mal) = 2:1$ the Z_{H^+} value is > 3.5 , which may be an evidence of the formation of the mixed hydroxomalates.

The pH-metric titration data were treated using the SuperQuad program, which is successfully used for the treatment of the pH-metric titration data.¹⁹ The recommendations given in work¹⁷ were used during the development of models of complex formation and their validation for adequacy.

The formation of complexes with the composition $11X$ ($X = 1-5$) and $22Y$ ($Y = 2-9$) in the studied system was considered. These complexes correspond to the general equilibrium:



with equilibrium constant

$$K_p = \frac{[Ln_pH_{3q-r}Mal_q^{(3p-r)+}] \cdot [H^+]^r}{[Ln^{3+}]^p \cdot [H_3Mal]^q} \quad (3)$$

Calculated stability constants corresponding general equilibrium (2) were recounted to form presented in Table 3. Stability constant expressions presented in Table 3 do not include the acid-base equilibrium constants of ligand and water. It is possible to compare our data to the data of other authors (Table 1). Table 3 shows that, in addition to protonated and deprotonated complexes of compositions 1:1 $Ln(H_2Mal)^{2+}$, $Ln(HMal)^+$ the hydroxocomplexes $LnMalOH^-$ are also formed. It should be noted that there is a significant amount of hydroxocomplexes of the rare-earth elements. Calculated stability constants of hydroxocomplexes are satisfactorily agreed with data.³¹⁻³³ Binuclear complexes with various stoichiometry to a considerable amounts are not detected by us. Calculated stability constants of L-malate complexes are satisfactorily agreed with data.^{3,5,6,8,9-13} In works¹⁰⁻¹¹ calculated stability constants of monomalate complexes were probably overestimated. And it is possible to explain the use both of the uncoordinated scheme of equilibrium and the neglect of protonated complexes and hydroxocomplexes.

The distribution of complex species formed in the L-malic acid- $SmCl_3$ system and the L-malic acid- $NdCl_3$ system depending on pH is given in Figures 3a and Figures 3b.

Hyperquad simulation and speciation (HySS) program was used.³² The presented distribution diagrams testify to the formation of a significant amount of hydroxomalate and protonated complex species, which were ignored in previous works.³⁻⁷

The stability of the formed L-malate complexes of the rare-earth elements of cerium subgroup is $\text{Ce}(3+) < \text{Pr}(3+) < \text{Nd}(3+) < \text{Sm}(3+)$. This fact can be explained by strengthening of the spin-orbital coupling and a decrease of the ionic radii in this series of rare-earth elements.^{1,30-31} A difference of the coordination ability of the $\text{Sm}(3+)$ ion from that of $\text{Ce}(3+)$, $\text{Pr}(3+)$ and $\text{Nd}(3+)$ (coordination number 9) ions can be explained by the above reasons, because for the $\text{Sm}(3+)$ aqua ion in aqueous solutions an intermediate coordination number 8.50 ± 0.04 was established by the X-ray and neutron diffraction methods, and luminescent spectrophotometry as well.³³⁻³⁶ This coordination number shows the equilibrium between eight or nine coordination aqua ions. Consequently, the existence of two coordination polyhedron $\text{Sm}(\text{H}_2\text{O})_9$ and $\text{Sm}(\text{H}_2\text{O})_8$ is the cause of a greater variety of the composition of complexes of the $\text{Sm}(3+)$ ion as compared to the aqua ion with the constant coordination number (Ce^{3+} , Pr^{3+} , Nd^{3+}).

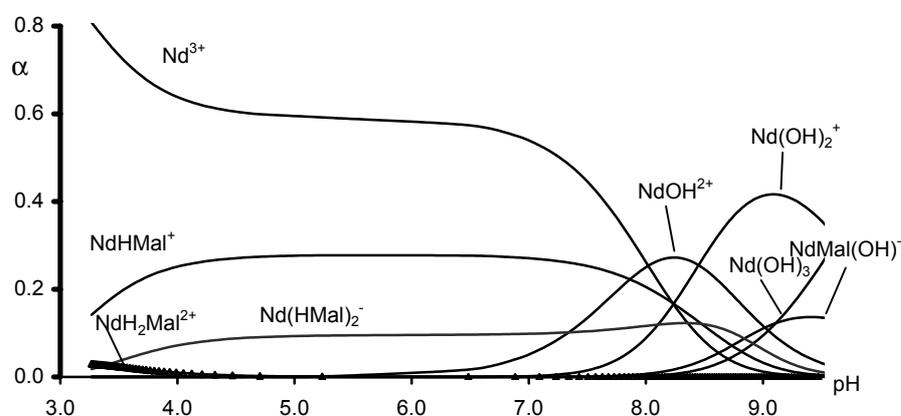


Figure 3a. Distribution of complex species in the NdCl_3 -L-malic acid system (2:1) depending on pH.

Conclusions

Thus the investigation we have carried out shows that not only 1:1 complexes are formed in the L-malic acid and the rare-earth elements of cerium subgroup (Ce, Pr, Nd, Sm) systems under study as described in literature, but also protonated, polynuclear and hydroxocomplexes, which should be taken into account when described equilibria with the participation of L-malic acid and 4f-elements.

Table 3. The Apparent Stability Constants of L-Malate Complexes (0.1 M KCl, 25±0.1 °C).

Coeff. of Eq. (2)			Expression of K	lg K			
q	p	r		Ce	Pr	Nd	Sm
1	1	1	$[\text{LnH}_2\text{Mal}^{2+}] [\text{Ln}^{3+}]^{-1} [\text{H}_2\text{Mal}^{-}]^{-1}$	2.09 ± 0.04	2.30 ± 0.03	2.40 ± 0.03	2.90 ± 0.04
1	1	2	$[\text{LnHMal}^+] [\text{Ln}^{3+}]^{-1} [\text{HMal}^{2-}]^{-1}$	4.32 ± 0.02	4.40 ± 0.02	4.60 ± 0.02	4.95 ± 0.02
1	1	3	$[\text{LnMal}] [\text{Ln}^{3+}]^{-1} [\text{Mal}^{3-}]^{-1}$	< 7.4 ^a	< 7.4 ^a	< 7.5 ^a	8.28 ± 0.15
1	1	4	$[\text{LnMal}(\text{OH})^-] [\text{Ln}^{3+}]^{-1} [\text{Mal}^{3-}]^{-1} [\text{OH}^-]^{-1}$	12.58 ^b ± 0.05	12.77 ^b ± 0.05	13.24 ^b ± 0.05	13.78 ^b ± 0.05
0	1	1	$[\text{LnOH}^{2+}] [\text{Ln}^{3+}]^{-1} [\text{OH}^-]^{-1}$	5.31 ± 0.05	5.39 ± 0.05	5.76 ± 0.03	5.88 ± 0.03
0	1	2	$[\text{Ln}(\text{OH})_2^+] [\text{Ln}^{3+}]^{-1} [\text{OH}^-]^{-2}$	10.43 ± 0.05	10.56 ± 0.05	11.09 ± 0.05	11.24 ± 0.05
0	2	2	$[\text{Ln}_2(\text{OH})_2^{4+}] [\text{Ln}^{3+}]^{-2} [\text{OH}^-]^{-2}$	12.75 ^b ± 0.12	12.96 ^b ± 0.11	13.39 ^b ± 0.09	13.68 ^b ± 0.08
0	1	3	$[\text{Ln}(\text{OH})_3] [\text{Ln}^{3+}]^{-1} [\text{OH}^-]^{-3}$	15.14 ± 0.08	15.12 ± 0.08	15.24 ± 0.08	15.86 ± 0.07

^a a reliable value of stability constant is not calculated because the fraction of LnMal complex is no more than 2 %. The approximate limit value is given in the table. ^b the fraction of LnMal(OH)⁻ and Ln₂(OH)₂⁴⁺ species is no more than 3%.

Experimental

Chemically pure L-malic acid, chemically pure CeCl₃, PrCl₃, NdCl₃, SmCl₃, chemically pure carbonate-free KOH, chemically pure KCl, and high-purity grade HCl were used. The Ln(3+) content was determined by complexometric titration with EDTA, and xylenol orange as the indicator.³⁷ A CO₂ free solution of 0.0275 M KOH solution was used as a titrant. The concentration of the titrant was determined by potentiometric titration with 0.1 M HCl solution. The solutions of the L-malic acid were prepared by the weighting means and then the concentration was précised by pH-metric titration method from equivalent points. Taking into account the low complex ability of the metals of the cerium subgroup of rare-earth elements with chloride ions,³⁸ KCl was used as a background electrolyte.

The L-malic acid concentration employed was 1×10⁻³ mol dm⁻³. Solutions containing rare-earth ions and L-malic acid were titrated in metal:ligand ratios 2:1 and 1:1.

pH-metric titration was carried out in an isolated thermostatically controlled (25±0.1) °C 40-mL cell at a variable volume and constant ionic strength (0.1 M KCl). The measurements were carried out on a Beckman digital pH-meter, Model 4500, using a glass-electrode combination Volta-pH-3002 (Saint-Petersburg, Saint-Petersburg State University). The estimated accuracy of titration system was ± 0.2 mV and ± 0.005 cm³ for e.m.f. and titrant volume reading, respectively. The certain amount of titrant was

added and the equilibrium potential values were measured while the e.m.f. was stable within 0.2 mV for 3 min. During the titration in titration cell, pure nitrogen was bubbled in order to avoid O₂ and CO₂ inside, and the solutions were magnetically stirred.

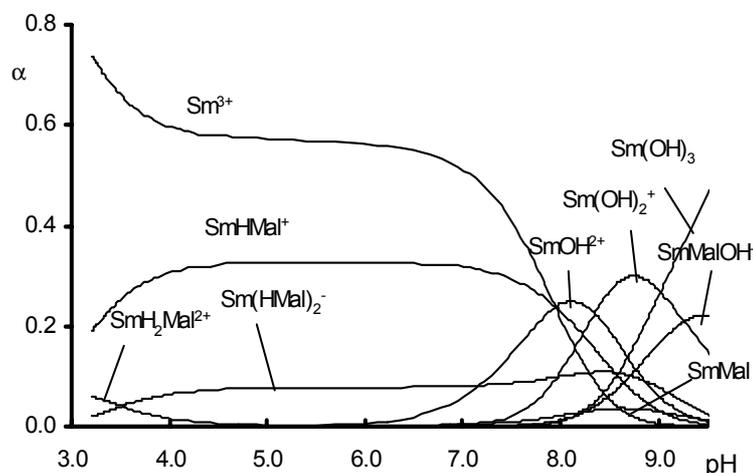


Figure 3b. Distribution of complex species in the SmCl₃-L-malic acid system (2:1) depending on pH.

Before the titration of each new series the electrode was calibrated by a titration of strong acid with strong base as a source of solutions with known hydrogen ion concentration.³⁹⁻⁴⁰ GLEE computer program for glass electrode calibration⁴¹ was used.

The initial volume of the solutions titrated was 25.00 mL. All solutions were prepared in deionized water (8 MΩ).

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Povzetek

S potenciometrično titracijo smo preučevali tvorbo koordinacijskih spojin med lantanoidi Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} in L-jabolčno kislino (H_3Mal) v vodnih raztopinah v območju pH med 3,00 in 9,00 pri ionski jakosti 0,1 M KCl. Razmerji koncentracij med L-jabolčno kislino in lantanoidom (Ln) sta bili 1:1 ali 1:2. Zgradbo in konstanto stabilnosti v zapletenih ravnotežjih smo ugotavljali s pomočjo programske opreme SuperQuad. Pokazali smo, da med L-jabolčno kislino in preučevanimi lantanoidi poleg koordinacijskih spojin v razmerju 1:1 nastajajo tudi hidroks-, protonirane in večjedrne koordinacijske spojine.