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Standard Enthalpies of Formation of Hydrated and Anhydrous Succinates of Some Rare-Earth Elements

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Abstract—Lanthanum, samarium, and holmium succinates were prepared and identified by chemical analysis, IR spectroscopy, thermal analysis, and X-ray diffraction. The enthalpies of solution of hydrated $[Ln_2(C_4H_4O_4)_3 \cdot nH_2O]$ and anhydrous succinates in hydrochloric acid ($HCl \cdot 100H_2O$) at 298.15 K were determined calorimetrically, and the standard enthalpies of formation were calculated.

Although data are available on synthesis, thermal behavior, and IR spectra of rare-earth succinates [1–3], systematic data on the thermodynamic characteristics and structure of these compounds are lacking. The constants and enthalpies of formation of $LnSuc^+$ complex species (Suc is succinate anion) were determined in [4] by calorimetric titration, and these data seem to be the only available thermodynamic data on rare-earth succinates.

Our goal was to prepare and identify succinates of some rare-earth elements and to determine their standard enthalpies of formation.

According to analytical data (Table 1), we prepared anhydrous lanthanum, samarium, and holmium succinates and their hydrates $La_2Suc_3 \cdot 5.70H_2O$, $Sm_2Suc_3 \cdot 5.94H_2O$, $Ho_2Suc_3 \cdot 6.06H_2O$, and $Ho_2Suc_3 \cdot 4.90H_2O$.

The analytical data are consistent with the IR spectra and thermogravimetric data. The IR spectra of the hydrated samples contain a broad band in the range 3300–3000 cm^{-1}, having a similar shape in the spectra of all the samples. This band, assignable to $\nu(H_2O)$, is appreciably shifted toward longer waves as compared to water of crystallization not involved in hydrogen bonding (3500–3600 cm^{-1}), which is apparently due to formation of hydrogen bonds. The dehydrated samples showed no absorption in this range. Identification of the bands at 1610–1600 cm^{-1} in the IR spectra of hydrated succinates was complicated by the overlap of the ranges of water bending and carboxylate stretching vibrations. The band at 1600 cm^{-1}, present in the IR spectra of anhydrous succinates, shows that the acid in complexation with $Ln^{3+}(aq)$ ions undergoes complete deprotonation, in agreement with published data [5]. Thus, synthesis of succinates was accompanied by complete substitution of acid protons in $C_4H_6O_4$ and formation of neutral salts.

The endoeffects in the heating curves of hydrated succinates (Table 2) corresponded to stepwise removal of energetically nonequivalent water molecules. Dehydration started at 40–50°C and was complete at 190, 250, and 160°C in lanthanum, samarium, and holmium succinates, respectively. Heating to 100–120°C caused continuous removal of weakly bound (apparently adsorbed) water. The major fraction of water

Table 1. Composition of rare-earth succinates, wt %

Ln	Ln_2Suc_3				$Ln_2Suc_3 \cdot nH_2O$		
	Ln^{3+}		Suc		Ln^{3+}	Suc	*n*, mol H_2O
	found	calculated	found	calculated			
La	44.32 ± 0.22	44.37	55.40 ± 0.22	55.63	38.12 ± 0.20	47.68 ± 0.06	5.70 ± 0.04
Sm	45.9 ± 10.28	46.33	53.78 ± 0.07	53.61	39.78 ± 0.36	46.54 ± 0.03	5.94 ± 0.06
Ho	48.25 ± 0.25	48.64	51.16 ± 0.05	51.36	41.72 ± 0.40	44.36 ± 0.04	6.06 ± 0.06
Ho					43.06 ± 0.22	45.85 ± 0.06	4.90 ± 0.03

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Table 2. Thermal analysis of $Ln_2Suc_3 \cdot nH_2O$

ΔT, °C	T_s, °C	ΔH	Δm, %
	$La_2Suc_3 \cdot 5.70H_2O$		
20–100	–	>0	1.43
100–160	120	>0	5.71
160–190	170	>0	7.14
20–190	–	>0	14.28
360–440	410	<0	7.86
440–480	450	<0	6.42
480–760	620	<0	21.42
760–860	810	<0	5.71
20–860	–		55.69
	$Sm_2Suc_3 \cdot 5.94H_2O$		
25–105	–	>0	5.74
210–250	230	>0	8.60
25–250	–	>0	14.34
380–410	395	<0	9.72
410–530	440	<0	20.82
530–700	610	<0	9.60
25–700	–		54.58
	$Ho_2Suc_3 \cdot 6.06H_2O$		
25–120	108	>0	5.84
120–160	150	>0	7.23
25–160	–	>0	13.07
440–490	440	<0	38.40
25–490	–		51.47

(apparently, coordinated water) was removed at temperatures above 120°C.

As judged from the DTA curves, the heat of dehydration increased with decreasing water content. The weight loss in dehydration of the hydrated samples agreed within the measurement error with the water content determined by chemical analysis.

Dehydration of holmium succinate, compared to lanthanum and samarium succinates, was characterized by better defined portions in the TG curves and sharp minima in the DTG curves, which may be due to the more perfect crystal lattice of this compound. Exothermic decomposition of holmium succinate started at 410°C, whereas lanthanum and samarium succinates started to decompose at lower temperatures (360 and 380°C).

The total weight loss corresponded to transformation of all the succinates into oxides Ln_2O_3.

Rare-earth succinates are sparingly soluble and are therefore precipitated as finely dispersed powders of imperfect structure. We failed to prepare single crystals of X-ray quality. Therefore, we analyzed powder patterns and made only qualitative conclusions. The mutual arrangement of reflections in the small-angle range suggests low symmetry of the samples. Dehydrated samples of freshly prepared samarium and lanthanum succinates appeared to be X-ray amorphous. Formation of X-ray amorphous products upon dehydration is a fairly common phenomenon [6, 7]. Presumably, a part of water molecules enter into the first coordination sphere of Ln^{3+} ions along with carboxylate groups. In dehydration under rigorous conditions, the structural rearrangement is incomplete, and an X-ray amorphous product is formed with the excess energy ranging from 10 to 30 kJ mol^{-1} depending on particular substance.

The X-ray diffraction patterns of hydrated samarium succinate, recorded a year after the synthesis, showed better ordering of the structure. Dehydration of this sample yielded a crystalline product, isostructural with holmium succinate, although in this case also the X-ray diffraction patterns of the dehydrated succinates were characterized by noticeably weakened and somewhat shifted reflections. This fact suggests that the dehydration occurs with preservation of the structure of the initial substance, though less perfect because of defects originating from dehydration, rather than with formation of new phases.

The X-ray diffraction pattern of hydrated lanthanum succinate appreciably differs from those of the samarium and holmium analogs, suggesting its different crystal lattice.

To calculate the standard enthalpies of formation of anhydrous succinates, we used the following thermochemical cycle:

$$Ln_2(C_4H_4O_4)_3(s) + k(HCl \cdot 100\,H_2O) = [2LnCl_3 \cdot 3C_4H_6O_4 \cdot (k - 6)HCl \cdot 100kH_2O] \text{ (solution I)}, \quad \Delta H_1; \quad (1)$$

$$2Ln(s) + k(HCl \cdot 100\,H_2O) = [2LnCl_3(k - 6)HCl \cdot 100kH_2O] \text{ (solution II)} + 3H_2(g), \quad \Delta H_2; \quad (2)$$

$$C_4H_6O_4(s) + [2LnCl_3 \cdot (k - 6)HCl \cdot 100kH_2O] \text{ (solution II)} = [2LnCl_3 \cdot 3C_4H_6O_4 \cdot (k - 6)HCl \cdot 100kH_2O] \text{ (solution I)}, \quad \Delta H_3; \quad (3)$$

$$12C(s) + 9H_2(g) + 6O_2(g) = 3C_4H_6O_4(s), \quad \Delta H_4; \quad (4)$$

$$2Ln(s) + 12C(s) + 6H_2(g) + 6O_2(g) = Ln_2(C_4H_4O_4)_3(s), \quad \Delta H_5 \quad (5)$$

$$\Delta H_5 = \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_1$$

Table 3, Standard enthalpies of formation of rare-earth succinates (ΔH, kJ mol^{-1}) and quantities used in their calculation

Compound	k[a]	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H_5$	$-\Delta H_6$
La_2Suc_3	85	160.57 ± 1.05	705.18 ± 0.60	3984.7 ± 2.3	
$La_2Suc_3 \cdot 5.70H_2O$		57.15 ± 0.86			4089.5 ± 2.2
Sm_2Suc_3	88	159.72 ± 0.92	688.19 ± 0.85	3951.8 ± 2.5	
$Sm_2Suc_3 \cdot 5.94H_2O$		58.80 ± 0.84			4053.9 ± 2.5
Ho_2Suc_3	43	163.79 ± 0.94	717.02 ± 1.46	4005.1 ± 3.5	
$Ho_2Suc_3 \cdot 4.90H_2O$		127.53 ± 0.80			4042.6 ± 3.4
$Ho_2Suc_3 \cdot 6.06H_2O$		85.64 ± 0.54			4084.7 ± 3.4

[a] (k) Molar ratio of hydrogen chloride and rare-earth succinate in calorimetric experiments, (ΔH_1) enthalpies of solution of succinates, (ΔH_2) enthalpies of solution of rare-earth metals in $HCl \cdot 100H_2O$, $\Delta H_5 = \Delta H_f^0[Ln_2(C_{H4}O_4)_3(s)]$, and ($\Delta H_6$) enthalpies of formation of hydrated succinates from the elements and liquid water.

Analysis of the complexation equilibria in the systems Ln^{3+}–$C_4H_4O_4^{2-}$ in HCl solutions, taking into account the stability constants of rare-earth succinate complexes [4] and the dissociation constants of succinic acid [8], suggests that the complexes fully decompose under the conditions of the calorimetric experiment and that the released succinic acid occurs mainly in the form of nondissociated molecules. As the most probable value of the standard enthalpy of formation of succinic acid (ΔH_4), we took the value of –940.88 ± 0.30 kJ mol^{-1}, based on data in [9, 10].

The enthalpies of reactions of rare-earth metals with asids were determined repeatedly, but, because of the low reaction rate, measurements were performed with considerably more concentrated acid solutions as compared to this study. At the same time, sufficiently reliable values are available for the standard enthalpies of formation of Ln^{3+}(soln; ∞H_2O) and for the enthalpies of formation of rare-earth chloride solutions and HCl solutions [11–13]. To bring the published data into correspondence with the experimental conditions of this study, we presented the reaction of a metal with an $HCl \cdot 100H_2O$ solution (enthalpy ΔH_2) as follows:

$$Ln(s) + k\,HCl(soln;\ HCl \cdot 100H_2O) = LnCl_3[soln;\ LnCl_3 \cdot (k - 3)HCl \cdot 100kH_2O] + (k - 3)HCl[soln;\ HCl \cdot 1/(k - 3)LnCl_3 \cdot 100k/(k - 3)H_2O] + 1.5H_2(g),\ \Delta H_r.$$

Considering that the standard enthalpy of formation of a substance in solution diluted with nH_2O is ΔH_f^0(soln; nH_2O) = ΔH_f^0(soln, H_2O, standard state) + φ_l, where φ_L is the relative apparent molar enthalpy of the substance, we calculated ΔH_r as follows:

$$\Delta H_r = \Delta H_r^0 + \varphi_L(LnCl_3 \cdot 100kH_2O) + (k - 3)\varphi_L''[HCl \cdot 100k/(k - 3)H_2O] - k\varphi_L'(HCl \cdot 100H_2O)$$

In this equation, ΔH_r^0 is the enthalpy of solution of rare-earth elements at zero ionic strength [ΔH_r^0 = $\Delta H_f^0(Ln^{3+}$, soln, H_2O, standard state)]. When calculating ΔH_r, we assumed that, within the concentration range studied, the relative partial enthalpy of water can be taken equal to zero, and the enthalpies of dilution of the solutions [$LnCl_3 \cdot (k - 3)HCl \cdot 100kH_2O$] and [$HCl \cdot 1/(k - 3)LnCl_3 \cdot 100k/(k - 3)H_2O$] can be replaced by the enthalpies of dilution of the solutions [$LnCl_3 \cdot 100kH_2O$] and [$HCl \cdot 100k/(k - 3)H_2O$]. The φ_L and φ_L'' values for HCl solutions were calculated from data in [11], and φ_L for solutions of lanthanum, samarium, and holmium chlorides was estimated from data in [12]. The resulting values of ΔH_2 and the standard enthalpies of formation of anhydrous succinates, $\Delta H_5 = \Delta H_f^0[Ln_2Suc_3(s)]$, are listed in Table 3.

Using a similar approach, we calculated the enthalpies of reactions (6) from the enthalpies of solution of hydrated succinates, taking into account the thermal effect of dilution of the solutions by water introduced with hydrated succinates:

$$2Ln(s) + 12C(s) + 6H_2(g) + 6O_2(g) + nH_2O(l) = Ln_2(C_4H_4O_4)_3 \cdot nH_2O(s),\ \Delta H_6. \quad (6)$$

Table 3 shows that the enthalpies of formation of anhydrous succinates are less negative and the enthalpies of formation of the hydrates decrease in the absolute value with decreasing water content (as shown for holmium succinate as example). This fact is consistent with the assumption, based on X-ray diffraction data, that dehydration of $Ln_2(C_4H_4O_4)_3 \cdot nH_2O$ yields disordered phases with excess energy.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-71 spectrometer (NaCl windows, mulls in mineral oil).

Thermal analysis was performed with a Paulik–Paulik–Erdey derivatograph using a Pt/Pt–Rh thermocouple (heating rate 10 deg min^{-1}, 20–50-mg samples, temperature range 20–950°C).

The diffraction patterns were taken with an HZG-4B diffractometer (CuK_α radiation, Fe filter).

Lanthanum, samarium, and holmium chlorides and succinic acid were of chemically pure grade, and hydrochloric acid, of ultrapure grade.

Hydrated rare-earth succinates were prepared by combining hot solutions of appropriate rare-earth chloride and succinic acid at 50–60°C; this was followed by neutralization with CO_2-free ammonia to pH 4.5–5.5. To provide complete precipitation of succinates, succinic acid was taken in a 1.5-fold excess. The precipitates were allowed to ripen under mother liquor for a day, filtered off, washed with hot (60°C) water acidified with succinic acid, and dried first in air and then in a vacuum desiccator (p 0.8–1.3 kPa) to constant weight.

The anhydrous samples were prepared by keeping hydrated succinates in a muffle furnace at the temperature gradually increased to the level corresponding to existence of the anhydrous phases. This level, specific for each substance, was preliminarily evaluated by thermal analysis. Dehydration at the maximal temperature was performed for 2–3 h. The process was additionally monitored gravimetrically. Anhydrous substances were stored in a desiccator over P_2O_5. All manipulations with anhydrous succinates (sample preparation for analysis, calorimetric experiments, and IR spectroscopy) were performed in a dry box.

The content of rare-earth elements in the succinates was determined by complexometric titration with Xylenol Orange indicator, after decomposition of the samples with HCl.

The procedure for determining succinate ion was based on ion exchange between rare-earth succinate and a cation exchanger (KU-2-8):

$$Ln_2Suc_3 + 6HKt = 2LnKt_3 + 3H_2Suc.$$

A succinate sample was finely ground. The resin after appropriate pretreatment was placed in a flask with distilled water, and a weighed portion of a succinate was added. The mixture was vigorously stirred for 3–4 h. Then the resin was separated by filtration and thoroughly washed with distilled water. The content of succinic acid in the filtrate was determined by titration with a standard 0.1 M KOH solution, with phenolphthalein as indicator. A blank run was performed in parallel. The water content in the succinate samples was calculated from the differences between the weights of hydrated samples and those of anhydrous samples, calculated from the analytical data.

The enthalpies of solution were determined in a variable-temperature microcalorimeter with an isothermal jacket. The working capacity of the calorimeter was 25 ml. The jacket temperature (298.15 K) was maintained with a ± 0.005 K accuracy. The temperature was measured with a copper resistivity thermometer wound around the calorimetric beaker (sensitivity 10^{-4} K per scale unit of the output device). The calorimeter was calibrated using electric current. The confidence interval of the mean thermal value of the calorimeter from a series of measurements was 0.08%. The absence of fixed errors in calorimetric measurements was confirmed by determination of the enthalpy of solution of KCl (17549 ± 41 J mol^{-1}, 0.278 m). The succinate sample weights in calorimetric experiments were 0.1–0.2 g. As solvent we used hydrochloric acid of the composition $HCl \cdot 100H_2O$.

The measurement errors were evaluated at 95% confidence level. The number of calorimetric experiments in each measurement series was no less than six. Additionally we determined the enthalpy of solution in $HCl \cdot 100H_2O$ of succinic acid (after recrystallization and drying in a vacuum desiccator; 29.17 ± 0.45 kJ mol^{-1}) and the enthalpy of dilution of solutions formed by dissolving anhydrous succinates in $HCl \cdot 100H_2O$. The latter quantity appeared to be equal, within the measurement error, for all the three rare-earth elements. In the calculations, we used the value of -0.196 ± 0.016 kJ mol^{-1} H_2O.

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