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Short communication

Synthesis, characterization and standard molar enthalpy of formation of $La(C_7H_5O_3)_2 \cdot (C_9H_6NO)$

Li Qiang-Guo [a,*], Li Xu [a], Huang Yi [a], Xiao Sheng-Xiong [a], Yang De-Jun [a],
Ye Li-Juan [a], Wei De-Liang [a], Liu Yi [a,b]

[a] Department of Chemistry and Life Science, Xiangnan University, Chenzhou, Hunan 423000, China
[b] College of Chemistry and Molecular Science, Wuhan University, Wuhan 430062, China

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Abstract

The product from reaction of lanthanum chloride seven-hydrate with salicylic acid and 8-hydroxyquinoline, $La(C_7H_5O_3)_2 \cdot (C_9H_6NO)$, was characterized by IR, elemental analysis, molar conductance, and thermogravimetric analysis. The standard molar enthalpies of solution of $[LaCl_3 \cdot 7H_2O\ (s)]$, $[2C_7H_6O_3\ (s)]$, $[C_9H_7NO\ (s)]$ and $[La(C_7H_5O_3)_2 \cdot (C_9H_6NO)\ (s)]$ in a mixed solvent of absolute ethyl alcohol, dimethyl formamide (DMF) and perchloric acid were determined by calorimetry to be $\Delta_s H_m^\ominus[LaCl_3 \cdot 7H_2O\ (s), 298.15\ K] = -96.45 \pm 0.18\ kJ\ mol^{-1}$, $\Delta_s H_m^\ominus[2C_7H_6O_3\ (s), 298.15\ K] = 14.99 \pm 0.17\ kJ\ mol^{-1}$, $\Delta_s H_m^\ominus[C_9H_7NO\ (s), 298.15\ K] = -3.86 \pm 0.06\ kJ\ mol^{-1}$ and $\Delta_s H_m^\ominus[La(C_7H_5O_3)_2 \cdot (C_9H_6NO)\ (s), 298.15\ K] = -117.78 \pm 0.11\ kJ\ mol^{-1}$. The enthalpy change of the reaction

$$LaCl_3 \cdot 7H_2O\,(s) + 2C_7H_6O_3\,(s) + C_9H_7NO\,(s) = La(C_7H_5O_3)_2 \cdot (C_9H_6NO)\,(s) + 3HCl\,(g) + 7H_2O\,(l) \tag{1}$$

was determined to be $\Delta_r H_m^\ominus = 91.57 \pm 0.34\ kJ\ mol^{-1}$. From data in the literature, through Hess' law, the standard molar enthalpy of formation of $La(C_7H_5O_3)_2 \cdot (C_9H_7NO)$ (s) was estimated to be $\Delta_f H_m^\ominus[La(C_7H_5O_3)_2 \cdot (C_9H_6NO)\ (s), 298.15\ K] = -\ 2076.5 \pm 3.9\ kJ\ mol^{-1}$.

Keywords: Lanthanum chloride seven-hydrate; Salicylic acid; 8-Hydroxyquinoline; Standard molar enthalpy of formation

1. Introduction

The synthesis and characterization of the complex of lanthanum with salicylic acid and 8-hydroxyquinoline, and the standard molar enthalpies of solution of $[LaCl_3 \cdot 7H_2O\ (s)]$, $[2C_7H_6O_3\ (s)]$, $[C_9H_7NO\ (s)]$ and $[La(C_7H_5O_3)_2 \cdot (C_9H_6NO)\ (s)]$ in a mixed solvent s of absolute ethyl alcohol, dimethyl formamide (DMF) and perchloric acid at 298.15 K are reported. By a thermochemical cycle, the molar enthalpy of the reaction:

$$LaCl_3 \cdot 7H_2O\,(s) + 2C_7H_6O_3\,(s) + C_9H_7NO\,(s) = La(C_7H_5O_3)_2 \cdot (C_9H_6NO)\,(s) + 3HCl\,(g) + 7H_2O\,(l) \tag{1}$$

and the standard molar enthalpy of formation of $La(C_7H_5O_3)_2 \cdot (C_9H_6NO)$ (s) are obtained.

2. Experimental

2.1. Chemicals and instruments

The chemicals $LaCl_3 \cdot 7H_2O$ (s) (>99%), $C_7H_6O_3$ (s) (>99.5%), C_9H_7NO (s) (>99.5%) and KCl of purity greater than 99.99% were obtained from Shanghai Reagent Company.

$LaCl_3 \cdot 7H_2O$ (s) was dried in a desiccator containing sulphuric acid (60%) [1] at room temperature and C_9H_7NO (s) and $C_7H_6O_3$ (s) was dried in a vacuum desiccator containing P_4O_{10} to constant mass. KCl (calorimetric primary standard) of purity greater than 99.99% was dried in a vacuum oven for 6 h at 135 °C.

Elemental analyzer (Perkin-Elmer 2400 CHN, USA), FT-IR spectrometer (Avatar 360, with KBr pellet, USA), thermogravimetrie analyzer (Perkin-Elmer TG6, at a heating

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* Corresponding author. Tel.: +86 735 2653129; fax: +86 735 2653013.
E-mail address: liqiangguo@163.com (Q.-G. Li).

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rate of 10 °C/min in flowing N_2, USA), Abbe refractometer (WAY, Shanghai, China), ultraviolet–visible spectrotometer (U-3010, HITACHI, Japan), solution-reaction isoperibol calorimeter (SRC 100, constructed by the thermochemical laboratory of Wuhan University, China), conductance (DDS-12A, Shanghai, China).

2.2. Preparations of $La(C_7H_5O_3)_2\cdot(C_9H_6NO)$ (s)

A mass of 0.02 mol of powdered $C_7H_6O_3$ (s) was dissolved in 40 cm^3 of absolute ethyl alcohol (solution A). Sodium salicylate solution was formed when an aqueous solution of 10% NaOH (a 0.02 mol of NaOH) was added into the solution A (solution B). A mass of 0.01 mol of powdered 8-hydroxyquinoline was dissolved in 40 cm^3 of absolute ethyl alcohol (solution C). A mixture solution was obtained when the solution B was added into the solution C (solution D). A mass of 0.01 mol of powdered $LaCl_3\cdot7H_2O$ was dissolved in 40 cm^3 of absolute ethyl alcohol (solution E). Primrose yellow crystals were separated out when the solution E was added slowly into the solution D at 37.5 °C after 3 h of magnetic stirring. The solution was left to settle at pH 6.5–7.0 during 12 h. Finally, the primrose yellow solid complex was obtained by filtration in vacuum, washed with several portions of distilled water, washed with absolute ethyl alcohol and washed with acetone. The product was put into a desiccator in vacuum at 37.5 °C for 24 h and kept until the mass of the crystals became constant. The chemical composition of the synthetic sample was determined by elemental analysis for C, H and N, by EDTA titration for La^{3+} [2], by mercury salt titration for Cl^- and by difference and TG-DTG curve for H_2O. The analysis results proved that the composition of the complex was $La(C_7H_5O_3)_2\cdot(C_9H_6NO)$ (s) and its purity was >99.5%.

2.3. The solution-reaction isoperibol calorimeter and calibration

The solution-reaction isoperibol calorimeter (SRC 100) is described in detail elsewhere [3]. A Dewar vessel with an internal volume of 100 ml, equipped with a twin-blade stirrer, was submerged in the water thermostat. The precision of temperature control and temperature measurement were ±0.001 and ±0.0001 K, respectively.

The calibration of the calorimeter was carried out by measuring the dissolution enthalpies of THAM (NBS 742a, USA) in 0.0001 mol cm^{-3} HCl and KCl (calorimetric primary standard) in water at 298.15 K. The mean dissolution enthalpies were -29776 ± 16 J mol^{-1} for THAM and 17597 ± 17 J mol^{-1} for KCl which agree with published data (-29766 ± 31.5 J mol^{-1} for THAM [4] and 17536 ± 9 J mol^{-1} for KCl [5]).

2.4. Determination of dissolution enthalpies

$La(C_7H_5O_3)_2\cdot(C_9H_6NO)$ (s) can be regarded as the product of the following Reaction (1), and the thermochemical cycle was designed as Fig. 1.

The chosen calorimetric solvent must dissolve the chemicals in the sample cell completely and very rapidly. The calorimetric solvent (S) of dimethyl formamide (DMF) and absolute ethyl alcohol and perchloric acid ($V_{DMF}:V_{EtOH}:V_{HClO4(71–72\%)} = 1:1:0.5$) is the most appropriate solvent for this experiment. Rigorous control of the stoichiometry was maintained through each series of experiments to ensure that the final solutions resulting from the dissolution of the reactants were of the same composition as those from the dissolution of the products.

A series of five experiments was performed for each of the dissolution reactions in Table 1.

The calorimetric results are listed in Table 1.

3. Results and discussion

3.1. Composition and electrolytic character of the complex

The elemental analysis (observed/% (calculated/%)): C 49.92 (49.57), H 2.69 (2.89), N 2.50 (2.51) and La 24.93 (24.92) showed that the complex has the stoichiometry of $La(C_7H_5O_3)_2\cdot(C_9H_6NO)$. It is insoluble in water, acetone, ether and benzene and slightly soluble in absolute ethyl alcohol. It is soluble in dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). The molar conductance of the complex is 0.00082 S m^2 mol^{-1} in DMF, indicating that the complex is a nonelectrolyte in DMF [6].

3.2. IR spectra

There are five characteristic bands observed for salicylic acid [7]: ν_{OH}^{COOH} (hydrogen bond intra-molecular, 3237 cm^{-1}, s), ν_{OH}^{COOH} (hydrogen bond intermolecular, 2857 cm^{-1}, s), $\nu_{O–H}$

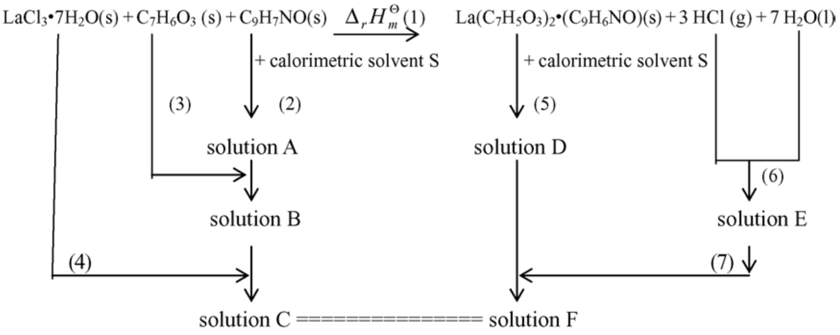

Fig. 1. Thermochemical cycle of the reaction (1).

Table 1
Dissolution enthalpies of [$2C_7H_6O_3$ (s)], [C_9H_7NO (s)], [$LaCl_3{\cdot}7H_2O$ (s)] and [$La(C_7H_5O_3)_2{\cdot}(C_9H_6NO)$ (s)] in the calorimetric solvent S at 298.15 K

System	$\Delta_s H_m^\Theta$ (kJ mol^{-1})
$2C_7H_6O_3$ (s) in S	$\Delta_s H_m^\Theta(2) = \Delta_s H_m^\Theta[2C_7H_6O_3$ (s), 298.15 K$] = 14.99 \pm 0.17$ kJ mol^{-1}[a]
C_9H_7NO (s) in the solution A	$\Delta_s H_m^\Theta(3) = \Delta_s H_m^\Theta[C_9H_7NO$ (s), 298.15 K$] = -3.86 \pm 0.06$ kJ mol^{-1}
$LaCl_3{\cdot}7H_2O$ (s) in the solution B	$\Delta_s H_m^\Theta(4) = \Delta_s H_m^\Theta[LaCl_3{\cdot}7H_2O$ (s), 298.15 K$] = -96.45 \pm 0.18$ kJ mol^{-1}
$La(C_7H_5O_3)_2{\cdot}(C_9H_6NO)$ (s) in S	$\Delta_s H_m^\Theta(5) = \Delta_s H_m^\Theta[La(C_7H_5O_3)_2{\cdot}(C_9H_6NO)$ (s), 298.15 K$] = -117.78 \pm 0.11$ kJ mol^{-1}
Solution D + solution E	$\Delta_s H_m^\Theta(7) = -5.78 \pm 0.19$ kJ mol^{-1}

[a] Uncertainty was estimated as twice the standard deviation of the mean of the results for five determinations.

(COOH, 2598 cm^{-1}, s), $\nu_{C\text{–}O}$ (COOH, 1663 cm^{-1}, vs) and $\delta_{O\text{–}H}$ (phenol, 1483 cm^{-1}, s). All these bands disappeared after complex formation except the band due to the angular deformation of the OH group. At the same time two new absorption bands due to the carboxylate group (COO$^-$), ν_{as} (1593 cm^{-1}, s) and ν_s (1387 cm^{-1}, s) appeared, indicating that the oxygen atoms of the carboxylate group are coordinated to the metal ion. These observed frequencies in the complex shifted to higher values when compared with the frequencies observed for the sodium salicylate salt but $\Delta\nu(\nu_{as} - \nu_s)$ staged the same (205 cm^{-1}). It can be concluded that the carboxylate group is coordinated to the metal ion through the two oxygen atoms, as a symmetrical bidentate group.

There are four characteristic absorption bands observed for 8-hydroxyquinoline: $\nu_{O\text{–}H}$ (3188 cm^{-1}, m), $\nu_{C\text{–}O}$ (1094 cm^{-1}, w), $\nu_{C{=}N}$ (1578 cm^{-1}, w) and $\delta_{O\text{–}H}$ (1223 cm^{-1}, s). After complex formation, both $\nu_{O\text{–}H}$ and $\delta_{O\text{–}H}$ disappeared and $\nu_{C\text{–}O}$ (1103 cm^{-1}, m) shifts to a higher frequency.

3.3. DTA-TG analysis

The thermal study was made in the temperature range between room temperature and 800 °C at a heating rate of 10 °C/min in flowing N_2. The results indicating that salicylic acid is melted at 158 °C and is gasified to decompose at 211 °C, 8-hydroxyquinoline is melted at 72 °C and is gasified to decompose at 207 °C. The complex showed one melting, endothermic weak peak at 198–280 °C and one or two decomposition, exothermic strong peaks at 350–500 °C.

3.4. Estimation of $\Delta_s H_m^\Theta$ (6)

According to the reaction (6)

$$1.5\,\text{mmol HCl (g)} + 3.5\,\text{mmol } H_2O\,\text{(l)} \rightarrow \text{solution E}$$

$$\begin{aligned}\Delta_s H_m^\Theta(6) &= \Delta_s H_m^\Theta(m = 0.0238\,\text{mol cm}^{-3}) \\ &= \Delta_s H_m^\Theta(m = 0.0010\,\text{mol cm}^{-3}) - \Delta_d H_m^\Theta(23.81 \\ &\quad \rightarrow 1.000) = [-74.843 - (-21.518)]\,\text{kJ mol}^{-1} \\ &= -53.33\,\text{kJ mol}^{-1}\end{aligned}$$

see ref. [8].

3.5. The molar enthalpy of reaction (1)

According to Hess' Law, the standard molar reaction enthalpy of reaction (1) is obtained:

$$\begin{aligned}&\Delta_r H_m^\Theta(1) \\ &\quad = \Delta_s H_m^\Theta(2) + \Delta_s H_m^\Theta(3) + \Delta_s H_m^\Theta(4) - \Delta_s H_m^\Theta(5) \\ &\qquad - \Delta_s H_m^\Theta(6) - \Delta_s H_m^\Theta(7) \\ &\quad = [14.99 - 3.86 - 96.45 + 117.78 + 53.33 + 5.78] \\ &\qquad \pm \left[\sqrt{0.17^2 + 0.06^2 + 0.18^2 + 0.11^2 + 0.19^2}\right] \\ &\quad = 91.57 \pm 0.34\,\text{kJ mol}^{-1}\end{aligned}$$

3.6. Evaluation of $\Delta_f H_m^\Theta[La(C_7H_5O_3)_2{\cdot}(C_9H_6NO)$ (s)]

According to Hess' law:

$$\begin{aligned}\Delta_r H_m^\Theta(1) = {} & \Delta_f H_m^\Theta[La(C_7H_5O_3)_2 \cdot (C_9H_6NO)\,(s), 298.15\,K] \\ & + 3\Delta_f H_m^\Theta[HCl\,(g), 298.15\,K] \\ & + 7\Delta_f H_m^\Theta[H_2O\,(l), 298.15\,K] \\ & - \Delta_f H_m^\Theta[LaCl_3 \cdot 7H_2O\,(s), 298.15\,K] \\ & - 2\Delta_f H_m^\Theta[C_7H_6O_3\,(s), 298.15\,K] \\ & - \Delta_f H_m^\Theta[(C_9H_7NO)\,(s), 298.15\,K]\end{aligned}$$

According to ref. [9]

$$\Delta_f H_m^\Theta[HCl\,(g), 298.15\,K] = -92.31 \pm 0.10\,\text{kJ mol}^{-1}.$$

$$\Delta_f H_m^\Theta[H_2O\,(l), 298.15\,K] = -285.830 \pm 0.040\,\text{kJ mol}^{-1}.$$

According to ref. [8]

$$\Delta_f H_m^\Theta[LaCl_3 \cdot 7H_2O\,(s), 298.15\,K] = -3178.6 \pm 2.5\,\text{kJ mol}^{-1}$$

where ±2.5 is calculated value according to the data in refs. [9] and [10].

According to ref. [11]

$$\Delta_f H_m^\Theta[C_7H_6O_3\,(s), 298.15\,K] = -592.1 \pm 1.3\,\text{kJ mol}^{-1}.$$

According to ref. [12]

$$\Delta_f H_m^\Theta[C_9H_7NO\,(s), 298.15\,K] = -83.0 \pm 1.5\,kJ\,mol^{-1}$$

and the above-calculated values of

$$\Delta_r H_m^\Theta = 91.57 \pm 0.34\,kJ\,mol^{-1}.$$

So that

$$\begin{aligned}
&\Delta_f H_m^\Theta[La(C_7H_5O_3)_2 \cdot (C_9H_6NO)\,(s), 298.15\,K] \\
&\quad = [91.57 - 3 \times (-92.31) - 7 \times (-285.830) + (-3178.6) \\
&\qquad +2 \times (-592.1) + (-83.0)] \\
&\qquad \pm \left[\sqrt{\begin{matrix}(0.34)^2 + (3 \times 0.10)^2 + (7 \times 0.040)^2 \\ +(2.5)^2 + (2 \times 1.3)^2 + (1.5)^2\end{matrix}}\right] \\
&\quad = -2076.5 \pm 3.9\,kJ\,mol^{-1}
\end{aligned}$$

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