

Short communication

Synthesis, characterization and standard molar enthalpy of formation of $\text{Sm}(\text{C}_7\text{H}_5\text{O}_3)_2 \cdot (\text{C}_9\text{H}_6\text{NO})$ [☆]

Li Xu^a, Li Qiangguo^{a,*}, Wei Deliang^a, Huang Yi^a, Ye Lijuan^a,
Xiao Shengxiong^a, Yang Dejun^a, Liu Yi^{a,b}

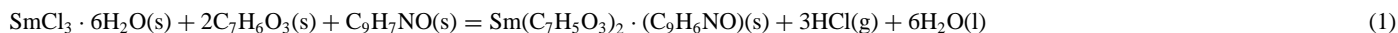
^a Department of Chemistry and Life Science, Xiangnan University, Chenzhou, Hunan 423000, China

^b College of Chemistry and Molecular Science, Wuhan University, Wuhan 430062, China

Available online 16 October 2007

Abstract

The complex of bis(salicylato)hydroxyquinolinosamarium(III), $\text{Sm}(\text{C}_7\text{H}_5\text{O}_3)_2 \cdot (\text{C}_9\text{H}_6\text{NO})$, was synthesized and characterized by IR, elemental analysis, molar conductance and thermogravimetric analysis. The standard molar enthalpies of solution of $[\text{SmCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})]$, $[\text{C}_7\text{H}_6\text{O}_3(\text{s})]$, $[\text{C}_9\text{H}_7\text{NO}(\text{s})]$ and $[\text{Sm}(\text{C}_7\text{H}_5\text{O}_3)_2 \cdot (\text{C}_9\text{H}_6\text{NO})(\text{s})]$ in the calorimetric solvent (a mixed solution consisting of absolute ethyl alcohol, dimethyl formamide (DMF) and perchloric acid) were determined by solution-reaction calorimetry at 298.15 K, respectively. The enthalpy of the reaction



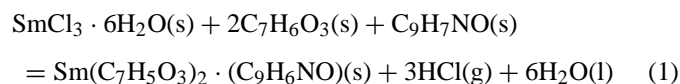
was determined to be $\Delta_f H_m^\circ = 89.59 \pm 0.18 \text{ kJ mol}^{-1}$. According to the above results and the data given in literature, through Hess' law, the standard molar enthalpy of formation of $\text{Sm}(\text{C}_7\text{H}_5\text{O}_3)_2 \cdot (\text{C}_9\text{H}_6\text{NO})(\text{s})$ was estimated to be $\Delta_f H_m^\circ[\text{Sm}(\text{C}_7\text{H}_5\text{O}_3)_2 \cdot (\text{C}_9\text{H}_6\text{NO})(\text{s}), 298.15 \text{ K}] = -2055.9 \pm 3.03 \text{ kJ mol}^{-1}$.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Bis(salicylato)hydroxyquinolinosamarium(III); Rare earths; Salicylic acid; 8-Hydroxyquinoline; Standard molar enthalpies of formation

1. Introduction

The synthesis and characterization of the complex of bis(salicylato)8-hydroxyquinolinosamarium(III), and molar enthalpies of solution of $[\text{SmCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})]$, $[\text{C}_7\text{H}_6\text{O}_3(\text{s})]$, $[\text{C}_9\text{H}_7\text{NO}(\text{s})]$ and $[\text{Sm}(\text{C}_7\text{H}_5\text{O}_3)_2 \cdot (\text{C}_9\text{H}_6\text{NO})(\text{s})]$ in a mixed solvent 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



and the standard molar enthalpy of formation of $\text{Sm}(\text{C}_7\text{H}_5\text{O}_3)_2 \cdot (\text{C}_9\text{H}_6\text{NO})(\text{s})$ are estimated.

[☆] This paper was submitted for publication in the Special Issue entitled Chemical Thermodynamics and Thermal analysis, from the 13th CCCTA symposium, which appeared in *Thermochimica Acta* 463/1–3.

* Corresponding author. Tel.: +86 735 2653129; fax: +86 735 2653013.

E-mail address: liqiangguo@163.com (L. Qiangguo).

2. Experimental

2.1. Chemicals and instruments

The chemicals $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})$ (>99%), $\text{C}_7\text{H}_6\text{O}_3(\text{s})$ (>99.5%), $\text{C}_9\text{H}_7\text{NO}(\text{s})$ (>99.5%) and KCl of purity greater than 99.99% were obtained from Shanghai Reagent Company.

$\text{SmCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})$ was dried in a desiccator containing sulphuric acid (60%) [1] at room temperature and $\text{C}_7\text{H}_6\text{O}_3(\text{s})$ and $\text{C}_9\text{H}_7\text{NO}(\text{s})$ were 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), thermogravimetry analyzer (Perkin-Elmer TG6, at a heating rate of 10 °C/min in flowing N_2 , USA), solution-reaction isoperibol calorimeter (SRC 100, constructed by the Thermochemical Laboratory of Wuhan University, China), conductance (DDS-12A, Shanghai, China).

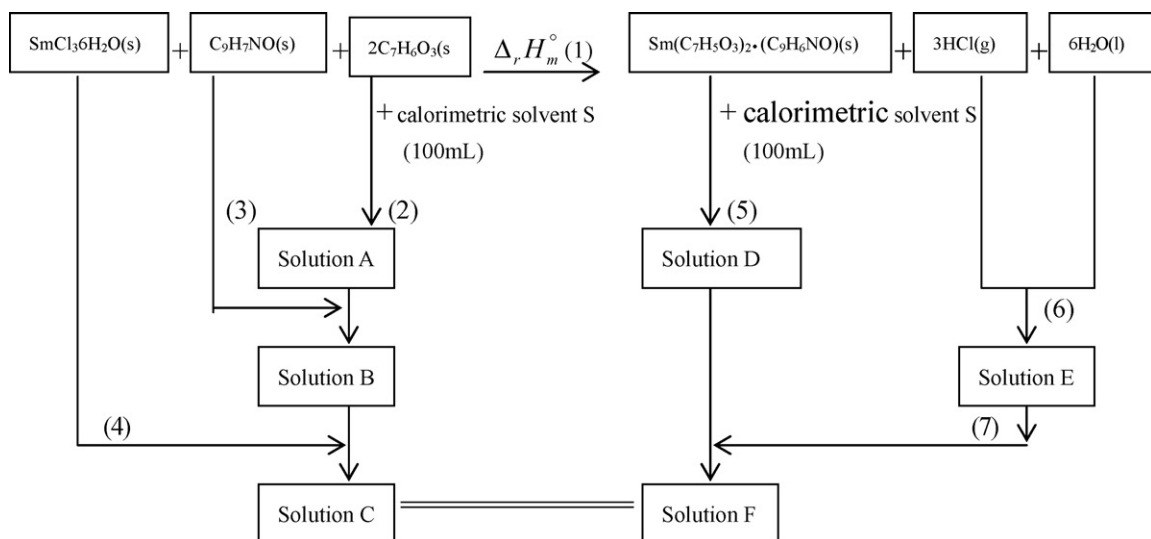


Fig. 1. Thermochemical cycle of the reaction (1).

2.2. Preparations of $\text{Sm}(\text{C}_7\text{H}_5\text{O}_3)_2 \cdot (\text{C}_9\text{H}_6\text{NO})(\text{s})$

A mass of 0.02 mol of powdered $\text{C}_7\text{H}_6\text{O}_3(\text{s})$ 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 $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ 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 down 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 many times, 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 a constant. The chemical composition of the synthetic sample was determined by elemental analysis for C, H and N, by EDTA titration for Sm^{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 $\text{Sm}(\text{C}_7\text{H}_5\text{O}_3)_2 \cdot (\text{C}_9\text{H}_6\text{NO})(\text{s})$ and its purity was $>99.5\%$.

2.3. The solution-reaction isoperibol calorimeter and calibration

The principle and structure of the calorimeter (SRC 100) are described in detail elsewhere [3]. Calibration of the calorimeter was carried out by measuring the dissolution enthalpies of THAM (NBS 742a, USA) (5 g) in 1 dm^3 $0.1000 \text{ mol dm}^{-3}$ HCl and KCl (calorimetric primary standard) in water ($n_{\text{KCl}} : n_{\text{H}_2\text{O}} \approx 1:1110$) at 298.15 K. The mean dissolution enthalpies were $-29,776 \pm 16 \text{ J mol}^{-1}$ for THAM and

$17,597 \pm 17 \text{ J mol}^{-1}$ for KCl which are in conformity, respectively, with the published data ($-29,766 \pm 31.5 \text{ J mol}^{-1}$ for THAM [4] and $17,536 \pm 9 \text{ J mol}^{-1}$ for KCl [5]). The uncertainties of both are less than 0.5%.

2.4. Determination of dissolution enthalpies

$\text{Sm}(\text{C}_7\text{H}_5\text{O}_3)_2 \cdot (\text{C}_9\text{H}_6\text{NO})(\text{s})$ can be regarded as the product of 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. 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. The calorimetric solvent (S) of dimethyl formamide (DMF) and absolute ethyl alcohol and perchloric acid ($V_{\text{DMF}}:V_{\text{EtOH}}:V_{\text{HClO}_4} = 1:1:0.5$) is the solvent in the experiment.

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 data (observed/% (calculated/%)): C 47.59(48.56), H 2.48(2.84), N 2.77(2.46) and Sm 26.47(26.44) show that the complex has the stoichiometry of $\text{Sm}(\text{C}_7\text{H}_5\text{O}_3)_2 \cdot (\text{C}_9\text{H}_6\text{NO})$. The complex is obtained as a yellow solid. It cannot be dissolved in water, acetone, ether and benzene. It dissolves very few in absolute ethyl alcohol. It can be dissolved in dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). The molar conductance of the complex is $0.00041 \text{ S m}^2 \text{ mol}^{-1}$ in DMF, indicating that the complex is non-electrolyte and exists as neutral molecule in DMF [6].

Table 1

Dissolution enthalpies of [2C₇H₆O₃(s)], [C₉H₇NO(s)], [SmCl₃·6H₂O(s)] and [Sm(C₇H₅O₃)₂·(C₉H₆NO)(s)] in the calorimetric solvent S at 298.15 K

2C ₇ H ₆ O ₃ (s) in S	$\Delta_s H_m^\circ[2C_7H_6O_3(s), 298.15\text{ K}] = 16.35 \pm 0.14\text{ kJ mol}^{-1a}$
C ₉ H ₇ NO(s) in the solution A	$\Delta_s H_m^\circ[C_9H_7NO(s), 298.15\text{ K}] = -6.11 \pm 0.08\text{ kJ mol}^{-1}$
SmCl ₃ ·6H ₂ O(s) in the solution B	$\Delta_s H_m^\circ[SmCl_3 \cdot 6H_2O(s), 298.15\text{ K}] = -103.98 \pm 0.04\text{ kJ mol}^{-1}$
Sm(C ₇ H ₅ O ₃) ₂ ·(C ₉ H ₆ NO)(s) in S	$\Delta_s H_m^\circ[Sm(C_7H_5O_3)_2 \cdot (C_9H_6NO)(s), 298.15\text{ K}] = -130.08 \pm 0.04\text{ kJ mol}^{-1}$
Solution D + solution E	$-3.79 \pm 0.04\text{ kJ mol}^{-1}$

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

3.2. IR spectra

There are five characteristic bands that are observed for the salicylic acid [7]: ν_{OH}^{COOH} (hydrogen bond intramolecular, 3237 cm⁻¹, s), ν_{OH}^{COOH} (hydrogen bond intermolecular, 2857 cm⁻¹, s), $\nu_{O-H}(COOH)$, 2598 cm⁻¹, s), $\nu_{C-O}(COOH)$, 1663 cm⁻¹, vs) and $\delta_{O-H}(\text{phenol})$, 1476 cm⁻¹, s). All these bands disappeared after complex formation except by 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 (1389 cm⁻¹, s) appeared, indicating that the oxygen atoms of the carboxylate group are coordinated to the metal ion. These are observed frequencies in the complex shifted to higher values when compared with the frequencies observed for the sodium salicylate salt but, $\Delta\nu(\nu_{as} - \nu_s)$ stated the same (204 cm⁻¹). According to these results 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 that are observed for 8-hydroxyquinoline: ν_{O-H} (3188 cm⁻¹, m), ν_{C-O} (1094 cm⁻¹, w), $\nu_{C=N}$ (1578 cm⁻¹, w) and δ_{O-H} (1223 cm⁻¹, s). After complex formation, both ν_{O-H} and δ_{O-H} disappeared and ν_{C-O} (1103 cm⁻¹, m) shifts towards higher frequencies.

3.3. DTA-TG analysis

The thermal study is made in the temperature range between room temperature and 800 °C at a heating rate of 10 °C/min in flowing N₂. The results indicate 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 and the complex shows one melting, endothermic weak peak at 224 °C and one or two decomposition oxidative exothermic strong peaks at 380–628 °C, respectively, and at one time with association of a mass loss.

3.4. Estimation of $\Delta_s H_m^\circ$, reaction (6)

$$\Delta_s H_m^\circ(6) = -49.46\text{ kJ mol}^{-1} [8].$$

3.5. The molar enthalpy of reaction (1)

$$\Delta_f H_m^\circ(1) = \Delta_s H_m^\circ(2) + \Delta_s H_m^\circ(3) + \Delta_s H_m^\circ(4) - \Delta_s H_m^\circ(5) - \Delta_s H_m^\circ(6) - \Delta_s H_m^\circ(7) = 89.59 \pm 0.18\text{ kJ mol}^{-1}$$

3.6. Evaluation of $\Delta_f H_m^\circ[Sm(C_7H_5O_3)_2 \cdot (C_9H_6NO)(s)]$

- $\Delta_f H_m^\circ(1) = \Delta_f H_m^\circ[Sm(C_7H_5O_3)_2 \cdot (C_9H_6NO)(s), 298.15\text{ K}] + 3\Delta_f H_m^\circ[HCl(g), 298.15\text{ K}] + 6\Delta_f H_m^\circ[H_2O(l), 298.15\text{ K}] - \Delta_f H_m^\circ[SmCl_3 \cdot 6H_2O(s), 298.15\text{ K}] - 2\Delta_f H_m^\circ[C_7H_6O_3(s), 298.15\text{ K}] - \Delta_f H_m^\circ[(C_9H_7NO)(s), 298.15\text{ K}]$
- $\Delta_f H_m^\circ[HCl(g), 298.15\text{ K}] = -92.31 \pm 0.10\text{ kJ mol}^{-1a} [9]$
- $\Delta_f H_m^\circ[H_2O(l), 298.15\text{ K}] = -285.830 \pm 0.040\text{ kJ mol}^{-1a} [9]$
- $\Delta_f H_m^\circ[SmCl_3 \cdot 6H_2O(s), 298.15\text{ K}] = -2870.2\text{ kJ mol}^{-1} [8]$
- $\Delta_f H_m^\circ[C_7H_6O_3(s), 298.15\text{ K}] = -592.1 \pm 1.3\text{ kJ mol}^{-1} [10]$
- $\Delta_f H_m^\circ[C_9H_7NO(s), 298.15\text{ K}] = -83.0 \pm 1.5\text{ kJ mol}^{-1} [11]$

So that

$$\Delta_f H_m^\circ[Sm(C_7H_5O_3)_2 \cdot (C_9H_6NO)(s), 298.15\text{ K}] = -2055.9 \pm 3.03\text{ kJ mol}^{-1}$$

Acknowledgements

This work was financially supported by the Hunan Provincial Natural Sciences Foundation (No. 03JJY3019) and the Hunan Educational Ministry Foundation (04C635) of China.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2007.10.003.

References

- [1] Q.G. Li, S.S. Qu, Y. Liu, Thermochim. Acta 376 (2001) 101.
- [2] Z.Q. Xie, J. Wuhan Univ. 2 (1985) 116.
- [3] H.G. Yu, Y. Liu, Z.C. Tan, et al., Thermochim. Acta 401 (2003) 217.
- [4] R. Rychly, V. Pekarek, J. Chem. Thermodyn. 9 (4) (1977) 391.
- [5] R.A. Melaugh, C.C. Lau, et al., J. Chem. Thermodyn. 9 (10) (1977) 915.
- [6] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.
- [7] K.K. Rohatgi, S.K. Sen Gupta, J. Inorg. Nucl. Chem. 32 (1970) 2247.
- [8] R.C. Weast, CRC Handbook of Chemistry and Physics, 69th ed., CRC Press Inc., Florida, 1988/1989, D-63, D-69.
- [9] J.D. Cox, D.D. Wagman, V.A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere Publishing Corp., New York, 1984, p. 1.
- [10] R. Sabbah, T.H.D. Le. Can. J. Chem. 71 (1993) 1378.
- [11] M.A.V. Ribeiro Da Silva, M.J.S. Monte, M.A.R. Matos, J. Chem. Thermodyn. 21 (1989) 159.