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THERMOCHEMICAL STUDY OF $[Sm(C_7H_5O_3)_2{\cdot}(C_4H_6NO_2S)]{\cdot}2H_2O$

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The product from reaction of samarium chloride hexahydrate with salicylic acid and Thioproline, $[Sm(C_7H_5O_3)_2{\cdot}(C_4H_6NO_2S)]{\cdot}2H_2O$, was synthesized and characterized by IR, elemental analysis, molar conductance, and thermogravimetric analysis. The standard molar enthalpies of solution of $[SmCl_3{\cdot}6H_2O(s)]$, $[2C_7H_6O_3(s)]$, $[C_4H_7NO_2S(s)]$ and $[Sm(C_7H_5O_3)_2{\cdot}(C_4H_7NO_2S){\cdot}H_2O(s)]$ in a mixed solvent of absolute ethyl alcohol, dimethyl sulfoxide(DMSO) and 3 mol L^{-1} HCl were determined by calorimetry to be $\Delta_s H_m^{\ominus}[SmCl_3{\cdot}6H_2O\ (s), 298.15\ K]=-46.68\pm0.15\ kJ\ mol^{-1}$, $\Delta_s H_m^{\ominus}[2C_7H_6O_3\ (s), 298.15\ K]=25.19\pm0.02\ kJ\ mol^{-1}$, $\Delta_s H_m^{\ominus}[C_4H_7NO_2S\ (s), 298.15\ K]=16.20\pm0.17\ kJ\ mol^{-1}$ and $\Delta_s H_m^{\ominus}[Sm(C_7H_5O_3)_2{\cdot}(C_4H_6NO_2S)]{\cdot}2H_2O\ (s), 298.15\ K]=-81.24\pm0.67\ kJ\ mol^{-1}$. The enthalpy change of the reaction

$$SmCl_3{\cdot}6H_2O(s)+2C_7H_6O_3(s)+C_4H_7NO_2S\ (s)=Sm(C_7H_5O_3)_2{\cdot}(C_4H_6NO_2S){\cdot}2H_2O\ (s)+3HCl(g)+4H_2O(l) \qquad (1)$$

was determined to be $\Delta_r H_m^{\ominus}=123.45\pm0.71\ kJ\ mol^{-1}$. From date in the literature, through Hess' law, the standard molar enthalpy of formation of $Sm(C_7H_5O_3)_2(C_4H_6NO_2S){\cdot}2H_2O(s)$ was estimated to be $\Delta_f H_m^{\ominus}[Sm(C_7H_5O_3)_2{\cdot}(C_4H_6NO_2S)]{\cdot}2H_2O(s), 298.15\ K]=-2912.03\pm3.10\ kJ\ mol^{-1}$.

Keywords: *salicylic acid, samarium chloride hexahydrate, standard molar enthalpies of formation, thioproline*

Introduction

It is known that rare earth ions and salicylic acid are antibacterial [1–7]. Thioproline possesses some special functions as prolonging body life, controlling medicament toxicity and catalyzing plant growth, and in particular, function as anticancer drugs, which can make cancer cell reverse to normal cell [8–10]. The synthesis and characterization of the rare earth complexes with thioproline and salicylic acid were reported and their application research experiments were carried out on *Escherichia coli*, indicating that the catalysis of the ternary complexes of rare earth ions against *Escherichia coli* was more significant than that of their ligand, thioproline and salicylic acid. Obviously, it is very important to carry out research on the rare earth complex of thioproline and salicylic acid. The standard molar enthalpy of formation of the complex has not yet been reported. As everyone knows, it is necessary to obtain their basic thermodynamics property as the gist and basis for theoretical researches and industrial designing when they are synthesized and developed industrially.

In the paper, the standard molar enthalpies of solution of $[SmCl_3{\cdot}6H_2O\ (s)]$, $[2C_7H_6O_3\ (s)]$, $[C_4H_7NO_2S(s)]$ and $[Sm(C_7H_5O_3)_2{\cdot}(C_4H_6NO_2S)(s)]$ in a mixed solvents of absolute ethyl alcohol, dimethyl sulfoxide (DMSO) and 3 mol L^{-1} HCl at 298.15 K are reported. By a thermochemical cycle, the molar enthalpy of the reaction:

$$SmCl_3{\cdot}6H_2O(s)+2C_7H_6O_3(s)+C_4H_7NO_2S(s)= \\ =Sm(C_7H_5O_3)_2{\cdot}(C_4H_6NO_2S){\cdot}2H_2O(s)+3HCl(g)+ \\ +4H_2O(l) \qquad (1)$$

and the standard molar enthalpy of formation of $[Sm(C_7H_5O_3)_2{\cdot}(C_4H_6NO_2S)]{\cdot}2H_2O(s)$ was obtained.

Experimental

Materials

Chemicals

The chemicals $SmCl_3{\cdot}6H_2O(s)$ (>99%), $C_7H_6O_3(s)$ (>99.5%) and KCl of purity greater than 99.99% were obtained from Shanghai Reagent Company. The *L*-Thioproline ($C_4H_7NO_2S$,s) (>99.5%) was from Wuhan University Hoyo Co., Ltd.

$SmCl_3{\cdot}6H_2O(s)$ was dried in a desiccator containing sulphuric acid (60%) [1] at room temperature and $C_7H_6O_3(s)$ and $C_4H_7NO_2S$ (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.

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Preparations of $[Sm(C_7H_5O_3)_2\cdot(C_4H_6NO_2S)]\cdot 2H_2O$ (s)

A mass of 0.04 mol of powdered $C_7H_6O_3$ (s) was dissolved in 30 cm^3 of absolute ethyl alcohol (solution I). Sodium salicylate solution was formed when an aqueous solution of 10% NaOH (0.04 mol of NaOH) was added into the solution I (solution II). A mass of 0.02 mol of powdered thioproline was dissolved in 50 cm^3 of distilled water (solution III) at 333.15 K in water-bath. A mixture solution was obtained when the solution II was added into the solution III (solution IV). A mass of 0.02 mol of powdered $SmCl_3\cdot 6H_2O$ was dissolved in 40 cm^3 of distilled water (solution V). White crystals were separated out when the solution IV was added slowly into the solution V at 333.15 K in water-bath after 11 h of magnetic stirring. The solution was left to settle down at pH=5.0–6.0 during 12 h. Finally the white solid complex was obtained by filtration in vacuum, washed with absolute ethyl alcohol three times, and several portions of hot distilled water many times at 343.15 K. The product was put into desiccator in vacuum at 333.15 K 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+} [11], 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 $Sm(C_7H_5O_3)_2\cdot(C_4H_6NO_2S)\cdot 2H_2O$(s) and its purity was >99.0%.

Methods

Instrumental methods

An elemental analyzer (PerkinElmer 2400 CHN, USA), an FTIR spectrometer (Avatar 360, with KBr pellet, USA), a thermogravimetry analyzer (PerkinElmer TG6, at a heating rate of 10°C min^{-1} in flowing N_2, USA), an Abbe refractometer (WAY, Shanghai, China), an ultraviolet-visible spectrotometer (U-3010,HITACHI, Japan), a solution-reaction isoperibol calorimeter (SRC 100, constructed by the thermochemical laboratory of Wuhan University, China), and a conductance (DDS-12A, Shanghai, China) were used.

The solution-reaction isoperibol calorimeter and calibration

The solution-reaction isoperibol calorimeter (SRC 100) was detail elsewhere [12]. A Dewar vessel with an internal volume of 100 mL, equipped with a twin-blade stirrer, was submerged in the water thermostat. The precisions 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 [13] and 17536±9 J mol^{-1} for KCl [14]).

Determination of dissolution enthalpies

$Sm(C_7H_5O_3)_2\cdot(C_4H_6NO_2S)\cdot 2H_2O$(s) can be regarded as the product of the following reaction (1),

$$\begin{aligned}&SmCl_3\cdot 6H_2O(s)+2C_7H_6O_3(s)+C_4H_7NO_2S\,(s)=\\&=Sm(C_7H_5O_3)_2(C_4H_6NO_2S)\cdot 2H_2O(s)+\\&+3HCl(g)+4H_2O(l)\end{aligned}\qquad(1)$$

and the thermochemical cycle was designed as Fig. 1.

The UV spectra and refractive indexes of the final solution of the reactants and the final solution of the products can be used to determine if they have the same thermodynamic state. In the present experiments, we determined the spectrum and refractive indexes of solution C and solution F in Fig. 1, and found for both of them the same UV spectrum (Fig. 2)

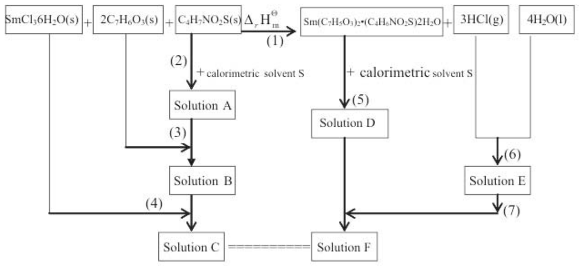

Fig. 1 Thermochemical cycle of the reaction (1)

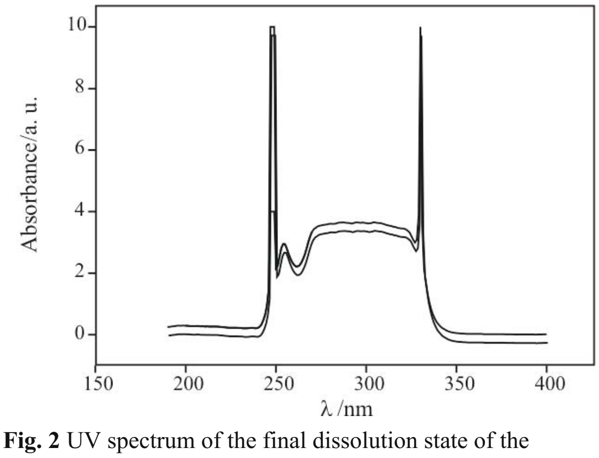

Fig. 2 UV spectrum of the final dissolution state of the reactants and products

and equal refractive index ($\eta_{25°C}$=1.4134), which proves that both have the same thermodynamics state and that the thermochemical cycle of the reaction (1) is reliable.

The chosen calorimetric solvent must dissolve the chemicals in the sample cell completely and very rapidly. The calorimetric solvent (S) of dimethyl sulfoxide (DMSO) and absolute ethyl alcohol and 3 mol L^{-1} HCl (V_{DMSO}:V_{EtOH}:V_{HCl}=1:1:1) 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.

The $C_4H_7NO_2S$ (s) was grinded in an agate mortar and a sample (0.06 g) was placed into a sample cell in calorimeter. The calorimetric solvent (100 cm^3) was added into the reaction vessel. The calorimeter was adjusted to a constant temperature of 298.15 K and the dissolution enthalpy was determined. A series of five experiments were performed.

$$C_4H_7NO_2S\ (s) + S \rightarrow \text{solution A} \qquad (2)$$

where S is the calorimetric solvent (100 cm^3). The solution A above was kept in the reaction vessel. Powdered $C_7H_6O_3$(s) (0.13 g) was put into the sample cell. A series of five experiments were performed.

$$2C_7H_6O_3(s) + \text{solution A} \rightarrow \text{solution B} \qquad (3)$$

The solution B above was kept in the reaction vessel. Powdered $SmCl_3{\cdot}6H_2O$ (s) (0.18 g) was put into the sample cell. A series of five experiments were performed.

$$SmCl_3{\cdot}6H_2O\ (s) + \text{solution B} \rightarrow \text{solution C} \qquad (4)$$

Powdered $Sm(C_7H_5O_3)_2(C_4H_7NO_2S){\cdot}2H_2O(s)$ (0.29 g) was put into the sample cell in the calorimeter, and the calorimeter solvent (100 cm^3) was added into the reaction vessel. The calorimeter was adjusted to a constant temperature of 298.15 K and the dissolution enthalpy was determined. A series of five experiments were performed.

$$Sm(C_7H_5O_3)_2{\cdot}(C_4H_6NO_2S){\cdot}2H_2O(s)+ \\ +S \rightarrow \text{solution D} \qquad (5)$$

where S is the calorimetric solvent (100 cm^3). A mass of 1.5 mmol HCl (g) was dissolved into 2.0 mmol H_2O (l).

$$1.5\text{ mmol HCl (g)}+2.0\text{ mmol }H_2O(l) \rightarrow \\ \text{solution E} \qquad (6)$$

The solution D above was kept in the reaction vessel. The solution E was put into the sample cell. A series of five experiments were performed.

$$\text{solution D+solution E} \rightarrow \text{solution F} \qquad (7)$$

The calorimetric results of Reactions (2), (3), (4), (5) and (7) are listed in Table 1.

Results and discussion

Elemental analyses and infrared spectra

Analytical results for the complex and proposed formula are given in Table 2. The determined results coincide with the theoretical ones very well.

Frequencies of characteristic absorption bands in IR spectra (cm^{-1}) for ligands and complex are given in Table 3.

There are five characteristic bands observed for the salicylic acid [15]: ν_{OH}^{COOH}(hydrogen bond intramolecular, 3237cm^{-1}, s), ν_{OH}^{COOH}(hydrogen bond intermolecular, 2857cm^{-1}, s), $\nu_{O–H}$(COOH, 2598 cm^{-1}, s), $\nu_{C–O}$(COOH, 1663 cm^{-1}, vs) and $\delta_{O–H}$(phenol, 1475 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 $\nu_{as}^{COO^-}$ (1594 cm^{-1}, s) and $\nu_{s}^{COO^-}$ (1387 cm^{-1}, s) appeared, indicating that the oxygen atoms of the carboxylate group are coordinated to the metal ion. The values of the splitting for the absorption bands of the valency vibration $\nu_{as}^{COO^-}$ and $\nu_{s}^{COO^-}$ is Δν(νas–νs)= 207 cm^{-1}. This Δν with the Δν of the sodium salicylate salt is equivalent. According with 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 observed for thioproline [16]: $\nu_{N–H}$(3058 cm^{-1}, s,sh), $\delta_{N–H}$(1632 cm^{-1}, sb), $\nu_{as}^{COO^-}$ (1556 cm^{-1}, s) and $\nu_{s}^{COO^-}$ (1434 cm^{-1}, s). After complex formation, both $\nu_{N–H}$ and $\nu_{s}^{COO^-}$ shift towards higher frequencies $\nu_{N–H}$(3066 cm^{-1}, m) and $\nu_{s}^{COO^-}$ (1462 cm^{-1}, s), both $\delta_{N–H}$ and $\nu_{as}^{COO^-}$ shift towards less frequencies $\delta_{N–H}$(1622 cm^{-1}) and $\nu_{as}^{COO^-}$ (1548 cm^{-1}). According with these results it can be concluded that the lanthanum ion is coordination with N atoms of imine group and O atoms of the carboxylate group in Thioproline, as an antisymmetric bidentate group.

Thermal decomposition of the complex

TG and DTG curves of $[Sm(C_7H_5O_3)_2{\cdot}(C_4H_6NO_2S)]{\cdot}2H_2O$, at a heating rate of 10°C min^{-1} in flowing N_2 are shown in Fig. 3. The thermal decomposition

Table 1 Dissolution enthalpies of [$2C_7H_6O_3(s)$], [$C_4H_7NO_2S(s)$], [$SmCl_3\cdot 6H_2O(s)$] and [Sm $C_7H_5O_3)_2\cdot(C_4H_6NO_2S)\cdot 2H_2O$ (s)] in the calorimetric solvent S at 298.15 K

System	No.	*m*/g	*t*/s	$\Delta_s H_m^\Theta$/kJ mol^{-1}
$C_4H_7NSO_2$(s) in S	1	0.0666	85.24	16.2326
	2	0.0668	79.96	16.3346
	3	0.0666	80.40	16.1109
	4	0.0667	81.52	16.3824
	5	0.0665	84.32	15.9574
$\Delta_s H_m^\Theta(2)=\Delta_s H_m^\Theta[C_4H_7NSO_2(s), 298.15\ K]=16.20\pm0.17\ mol^{-1a}$				
$2C_7H_6O_3$(s) in the solution A	1	0.1379	138.83	25.2177
	2	0.1382	160.87	25.1418
	3	0.1379	140.68	25.1501
	4	0.1383	146.19	25.2264
	5	0.1382	161.65	25.1924
$\Delta_s H_m^\Theta(3)=\Delta_s H_m^\Theta[2C_7H_6O_3(s), 298.15\ K]=25.19\pm0.02\ kJ\ mol^{-1}$				
$SmCl_3\cdot 6H_2O$(s) in the solution B	1	0.1826	102.03	–46.9002
	2	0.1826	107.19	–46.3189
	3	0.1823	97.10	–46.3047
	4	0.1822	99.25	–46.8715
	5	0.1823	100.21	–47.0021
$\Delta_s H_m^\Theta(4)=\Delta_s H_m^\Theta[SmCl_3\cdot 6H_2O(s), 298.15\ K]=-46.68\pm0.15\ kJ\ mol^{-1}$				
$Sm(C_7H_5O_3)_2(C_4H_6NO_2S)\cdot 2H_2O$(s) in S	1	0.2920	144.20	–81.2287
	2	0.2977	144.56	–80.3169
	3	0.2949	170.64	–81.8766
	4	0.2949	154.65	–81.8738
	5	0.2954	169.58	–80.9046
$\Delta_s H_m^\Theta(5)=\Delta_s H_m^\Theta[Sm(C_7H_5O_3)_2\cdot(C_4H_6NO_2S)\cdot 2H_2O(s), 298.15\ K]=-81.24\pm0.67\ kJ\ mol^{-1}$				
Solution D+solution E	1	0.0551	63.26	–7.6806
	2	0.0553	73.44	–7.6703
	3	0.0541	68.59	–7.5056
	4	0.0551	71.01	–7.4924
	5	0.0555	65.24	–7.5647
$\Delta_s H_m^\Theta(7)=-7.58\pm0.09\ kJ\ mol^{-1}$				

n: molar number of sample; *t*: heating period of electrical calibration; [a]uncertainty was estimated as twice the standard deviation of the mean of the results

Table 2 Analytical results of the complex/%

Complex	C	H	S	N	Sm
[$Sm(C_7H_5O_3)_2\cdot(C_4H_6NO_2S)]\cdot 2H_2O$					
Theoretical values	36.47	3.38	5.50	2.36	25.36
Experimental data	36.35	3.26	5.85	2.51	25.85

process of [$Sm(C_7H_5O_3)_2\cdot(C_4H_6NO_2S)]\cdot 2H_2O$ can be divided into three stages. The first stage is at 84–134°C. The TG curve shows that the mass loss corresponding to this temperature range is 6.17%, which roughly coincides with the value of 6.07%, calculated for the loss of 2 mol H_2O from the complex. The second stage starts from 260–580°C with the mass loss of 47.36%, which corresponds to the loss of 2 mol $C_7H_5O_3^-$. The theoretical mass loss is 46.26%. The third stage degradation temperature is in the range of 580–641°C with the mass loss of 54.14%, which corresponds to the loss of 1 mol $C_4H_7NO_2S^-$.

Table 3 IR absorption for ligands and complex/ cm^{-1}

Compounds	ν_{O-H}	ν_{C-O}	ν_{N-H}	$\nu_{as}^{COO^-}$	$\nu_{s}^{COO^-}$	δ_{N-H}	δ_{O-H}
$C_7H_6O_3$	2598	1663					1475
$C_4H_7NO_2S$			3048	1555	1461	1627	
$[Sm(C_7H_5O_3)_2\cdot(C_4H_6NO_2S)\cdot 2H_2O$	3418		2922	1593 (1595)	1462 (1387)	1461	

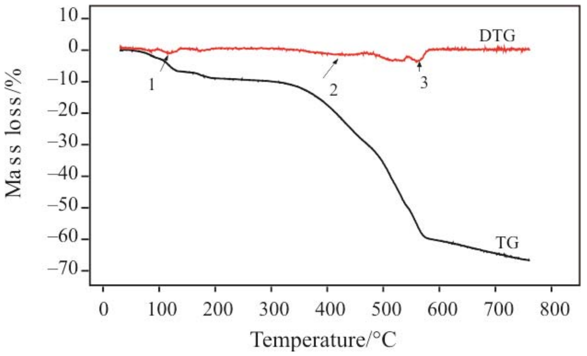

Fig. 3 TG-DTG curves of $Sm(C_7H_5O_2)\cdot(C_4H_7NO_2S)\cdot 2H_2O$

The theoretical mass loss is 53.84%. On the bases of experimental and calculated results, the thermal decomposition of $[Sm(C_7H_5O_3)_2\cdot(C_4H_7NO_2S)]\cdot 2H_2O$ was postulated as follows:

$$[Sm(C_7H_5O_3)_2\cdot(C_4H_6NO_2S)]\cdot 2H_2O \xrightarrow{84-134℃}$$

$$Sm(C_7H_5O_3)_2\cdot(C_4H_6NO_2S) \xrightarrow{260-580℃}$$

$$Sm(C_4H_6NO_2S)O \xrightarrow{580-641℃} 1/2Sm_2O_3$$

Results of calorimetric experiment

The results of the calorimetric measurements are given in Table 1.

Estimation of $\Delta_s H_m^\ominus$ *(6)*

According to the reaction (6)

1.5 mmol HCl (g)+2.0 mmol H_2O (l) → solution E

$$\Delta_s H_m^\ominus (6)=\Delta_s H_m^\ominus (m=0.0417 \text{ mol cm}^{-3})=$$

$$=\Delta_s H_m^\ominus (m=0.0010 \text{ mol cm}^{-3})-$$

$$-\Delta_d H_m^\ominus (41.66\rightarrow 1.000)=$$

$$=[-74.843-(-34.923)] \text{ kJ mol}^{-1}= -39.92 \text{ kJ mol}^{-1}$$

See ref. [17].

The molar enthalpy of reaction (1)

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

$$\Delta_r H_m^\ominus(1)=\Delta_f H_m^\ominus(2)+\Delta_s H_m^\ominus(3)+$$

$$+\Delta_s H_m^\ominus(4)-\Delta_s H_m^\ominus(5)-\Delta_s H_m^\ominus(6)-\Delta_s H_m^\ominus(7)=$$

$$=[16.20+25.19-46.68+81.24+39.92+7.58]$$

$$\pm[\sqrt{0.17^2+0.02^2+0.15^2+0.67^2+0.09^2}]=$$

$$=123.45\pm 0.71 \text{ kJ mol}^{-1}$$

Evaluation of $\Delta_f H_m^\ominus$ *$[Sm(C_7H_5O_3)_2\cdot(C_4H_6NO_2S)\cdot 2H_2O(s)]$*

According to Hess' law:

$$\Delta_f H_m^\ominus(1)=\Delta_f H_m^\ominus[Sm(C_7H_5O_3)_2\cdot(C_4H_6NO_2S)\cdot$$

$$2H_2O(s), 298.15 \text{ K}]+3\Delta_f H_m^\ominus[HCl(g), 298.15 \text{ K}]+$$

$$+4\Delta_f H_m^\ominus[H_2O \text{ (l)}, 298.15 \text{ K}]-$$

$$-\Delta_f H_m^\ominus[SmCl_3\cdot 6H_2O(s), 298.15 \text{ K}]-$$

$$-2\Delta_f H_m^\ominus[C_7H_6O_3(s), 298.15 \text{ K}]-$$

$$-\Delta_f H_m^\ominus[(C_4H_7NO_2S) \text{ (s)}, 298.15 \text{ K}]$$

According to reference [18]

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

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

According to reference [17]

$$\Delta_f H_m^\ominus[SmCl_3\cdot 6H_2O(s), 298.15 \text{ K}]= -2870.2 \text{ kJ mol}^{-1}$$

According to reference [18]

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

According to reference [19]

$$\Delta_f H_m^\ominus[C_4H_7NO_2S \text{ (s)}, 298.15 \text{ K}]=$$

$$-401.33\pm 1.54 \text{ kJ mol}^{-1}$$

And the above-calculated values of

$$\Delta_f H_m^\ominus=123.\ 45\pm 0.71 \text{ kJ mol}^{-1}$$

So that

$$\Delta_f H_m^\ominus[Sm(C_7H_5O_3)_2\cdot(C_4H_6NO_2S)\cdot$$

$$2H_2O \text{ (s)},298.15 \text{ K}]=[123.45-3\cdot(-92.31)-$$

$$-4\cdot(-285.830)+(-2870.2)+2\cdot(-592.1)+(-401.33)]$$

$$\pm\left[\sqrt{0.71^2+(3\cdot0.10)^2+(4\cdot0.040^2+(2\cdot1.3)^2+(1.5)^2}\right]=$$

$$=-2912.03\pm3.10\ \mathrm{kJ\ mol^{-1}}$$

Acknowledgements

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