

Short communication

Enthalpies of reaction of lanthanide trifluoroacetate trihydrate with 2-azacyclononanone to form lanthanide trifluoroacetate-tris 2-azacyclononanone

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Received 3 October 2006; received in revised form 12 December 2006; accepted 19 December 2006

Available online 3 January 2007

Abstract

The condensed phase, acid–base reaction enthalpy for $\text{Ln}(\text{tfa})_3 \cdot 3\text{H}_2\text{O} (\text{s}) + 3\text{aza} (\text{s}) \rightarrow \text{Ln}(\text{tfa})_3 \cdot 3\text{aza} (\text{s}) + 3\text{H}_2\text{O}$; $\Delta_r H_m^\theta$ (kJ mol^{-1}) = -33.90 ± 1.54 , -2.10 ± 1.25 , -9.40 ± 2.10 , 0.05 ± 2.27 and 2.46 ± 1.45 for the Pr, Nd, Sm, Eu and Tb compounds, respectively, where tfa, the trifluoroacetate, and aza, the 2-azacyclononanone, were measured by calorimetry.

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Keywords: Cycloazanonanone; Lanthanides; Enthalpy

1. Introduction

Due to their possible use as light conversion molecular devices (LCMD), lanthanide complexes with organic ligands are important in coordination chemistry [1,2]. However, there are relatively few thermochemical data for such compounds. Lanthanide 2,2,6,6-tetramethyl-3,5-heptanedione [3] and lanthanide trifluoromethanesulfonate [4] compounds are among these few.

This publication reports the results of a calorimetric study of $\text{Ln}(\text{tfa})_3 \cdot 3\text{aza}$ where Ln = Pr, Nd, Sm, Eu and Tb and tfa = trifluoroacetate and aza = 2-azacyclononanone [5–7].

2. Experimental

All reagents were of analytical grade (Aldrich or Merck) and were employed without further purification.

The lanthanide fluoroacetates were synthesized as follows: the respective oxides were treated with a 6.0 mol dm^{-3} HCl aqueous solution until complete dissolution. Then urea

was added until pH 7.0 and the solution was heated for 3 days until complete precipitation of the basic carbonates: $\text{Ln}(\text{OH})\text{CO}_3 \cdot x\text{H}_2\text{O}$. The carbonates were filtered off, washed with distilled water (until complete removal of Cl^- ion) and then dried at 80°C in a water bath. The carbonates were suspended in water and trifluoroacetic acid added to dissolve the carbonates (a small amount of the carbonate was not dissolved in order to guarantee that all acid had been consumed). The solution was then filtered and evaporated in a water bath. The crystals of lanthanide fluoroacetates were ground and stored over calcium chloride.

The compounds with 2-azacyclononanone (aza) were prepared by reaction of lanthanide trifluoroacetate and aza, both in ethanolic solution. The resulting solution was then aged for 20–30 days until the precipitation of the compounds. After crystallization, the compounds were washed with carbon tetrachloride and dried under vacuum over calcium chloride.

Lanthanide, carbon, hydrogen and nitrogen elemental analyses and FTIR data have been published [5–7]. Melting point measurements were performed in a MQAPF-301 equipment from Microquímica.

The calorimetric experiments (ampoule break procedure) were performed in a model LKB 8700-1 calorimeter. Ethanol

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Table 1
Dissolution enthalpies (kJ mol^{-1}) for lanthanide trifluoroacetate compounds with aza

aza	$\Delta H_1 = 19.27 \pm 0.25$
Pr	$\Delta H_2 = -56.99 \pm 0.77$
	$\Delta H_3 = 36.38 \pm 1.31$
	$\Delta H_4 = -1.66 \pm 0.01$
Nd	$\Delta H_2 = -31.84 \pm 1.18$
	$\Delta H_3 = 29.68 \pm 0.34$
	$\Delta H_4 = -1.61 \pm 0.01$
Sm	$\Delta H_2 = -32.42 \pm 1.47$
	$\Delta H_3 = 36.51 \pm 1.48$
	$\Delta H_4 = -1.72 \pm 0.10$
Eu	$\Delta H_2 = -32.64 \pm 0.59$
	$\Delta H_3 = 26.05 \pm 2.18$
	$\Delta H_4 = -0.93 \pm 0.11$
Tb	$\Delta H_2 = -29.11 \pm 1.22$
	$\Delta H_3 = 27.89 \pm 0.74$
	$\Delta H_4 = -1.64 \pm 0.06$

was employed as the calorimetric solvent. All calorimetric measurements were performed at 1 atm and 298 K.

3. Results and discussion

The melting temperatures are 100–112, 90–95, 79–101, 65–70 and 64–76 °C for the Pr, Nd, Sm, Eu and Tb compounds, respectively. A decrease of the melting temperature is associated with the increase of the lanthanide atomic number.

The infrared data have been published [5–7] and are in agreement with coordination through oxygen for aza.

The condensed phase, acid–base reaction enthalpy ($\Delta_r H_m^\theta$) associated with the process $\text{Ln}(\text{tfa})_3 \cdot 3\text{H}_2\text{O}(\text{s}) + 3\text{aza}(\text{s}) \rightarrow \text{Ln}(\text{tfa})_3 \cdot 3\text{aza}(\text{s}) + 3\text{H}_2\text{O}$ was calculated by the cycle [8]:

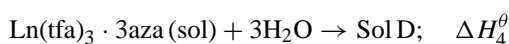
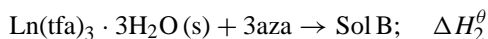
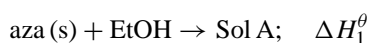
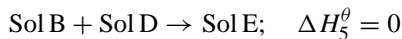


Table 2
Condensed phase reaction enthalpies (kJ mol^{-1}) for lanthanide fluoroacetate compounds with aza

Ln	Z	$\Delta_r H_m^\theta$ (kJ mol^{-1})
Pr	59	-33.90 ± 1.54
Nd	60	-2.10 ± 1.25
Sm	62	-9.40 ± 2.10
Eu	63	0.05 ± 2.27
Tb	65	2.46 ± 1.45



Hence,

$$\Delta_r H_m^\theta = (3\Delta H_1^\theta) + \Delta H_2^\theta - \Delta H_3^\theta - \Delta H_4^\theta + \Delta H_5^\theta \quad (1)$$

The measured ΔH_1^θ , ΔH_2^θ , ΔH_3^θ and ΔH_4^θ values are reported in Table 1. By using Eq. (1) and Table 1, the $\Delta_r H_m^\theta$ values reported in Table 2 were calculated. The $\Delta_r H_m^\theta$ values for Pr, Nd and Sm are exothermic, whereas for Eu it is about zero and endothermic for Tb. The Lewis acidity sequence based on $\Delta_r H_m^\theta$ values [9] is: Pr » Sm > Nd > Eu > Tb.

The ΔH_3^θ values as a function of the atomic number (Z) follow the “inclined W symmetry” proposed by Sinha [10,11].

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