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Thermochemical properties of rare-earth chloride with DL–alanine

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Abstract

Combustion energies have been determined for the 24 solid complexes of rare-earth chlorides with DL–alanine: RE(Ala)Cl_3·6H_2O (I) (RE=Eu–Ho, Yb, Y), RE$(Ala)_2Cl_3$·nH_2O (II) (RE=La–Nd, Sm, n=3; RE=Ho, Yb, Y, n=4) and RE$(Ala)_3Cl_3$·3H_2O (III) (RE=La–Nd, Sm–Dy). The standard enthalpies of combustion, $\Delta_{c,coor}H^0$, and standard enthalpies of formation, $\Delta_{f,coor}H^0$, have been calculated for these complexes. The relationship of $\Delta_{f,coor}H^0$ with the ionic radius of rare-earth cations has been examined. The results show that a certain amount of covalence is present in the chemical bond between the rare-earth cation and DL–alanine.

Keywords: DL–Alanine; Rare-earth chloride; Solid complexes; Standard enthalpy of formation

1. Introduction

Gao et al., [1] have investigated the $RECl_3$–Ala–H_2O ternary systems, using the semimicro-method of phase equilibrium study. The resultant of phase equilibrium indicated: there are three kinds of complexes of molecule ratio, $RECl_3$/Ala, formed in these investigated systems, RE(Ala)Cl_3·6H_2O(I)(RE=Eu–Ho, Yb, Y; Ala the DL–Alanine in this paper); RE$(Ala)_2Cl_3$·nH_2O(II) (RE=La–Nd, Sm; n=3; RE=Ho, Yb, Y; n=4) and RE$(Ala)_3Cl_3$·3H_2O(III) (RE is La-Nd, Sm-Dy). However, complexes of rare-earth chloride with amino acids have not yet been investigated by thermochemical methods. Therefore, the standard enthalpies of combustion and standard enthalpies of formation of the complexes have not yet been reported in the literature.

In this paper, combustion energies have been determined for twenty four solid complexes mentioned above using a rotating-bomb calorimeter. The standard enthalpies of combustion, $\Delta_{c,coor}H^0$ and standard enthalpies of formation, $\Delta_{f,coor}H^0$ have been calculated for these complexes. Meanwhile, we still have to determine the combustion energies of Ala. The standard enthalpies of combustion, $\Delta_{c,Ala(s)}H^0$, and the standard enthalpies of formation, $\Delta_{f,Ala(s)}H^0$, have been calculated. The relationship of $\Delta_{f,coor}H^0$ with the ionic radius of rare-earth cation has been examined.

2. Experimental

2.1. Preparation and composition of the complexes

Based on phase-equilibrium data, solid complexes were prepared and put into a desiccator containing

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P_2O_5 until the weight of the crystals became constant. Chemical analysis proved that the compositions of the complexes are $RE(Ala)Cl0_3\cdot 6H_2O$(I), $RE(Ala)_2Cl_3\cdot nH_2O$(II) and $RE(Ala)_3Cl_3\cdot 3H_2O$(III), respectively. The purity of all complexes determined by chemical analysis is greater than 99.9% (analytical error, $\leq$0.2%).

2.2. Apparatus and experimental procedure

The precision rotating-bomb calorimeter (RBC-type 1) and the basic experimental procedures used in this investigation have already been described [2]. The initial temperature was $(25.000\pm 0.0005)^\circ$C, and the initial oxygen pressure was 2533.125 kPa. The procedures for analyzing the final products of the bomb were the same as in Ref. [3]. Analytical data of the final products show that the combustion reaction is complete, without carbon deposits or carbon monoxide being formed during the combustion reaction. The final products were shown to be RE_2O_3 or CeO_2 by IR spectroscopy and chemical analysis. The calorimetric system was calibrated by benzoic acid of standard calorific value prior to use. The energy equivalent of the RBC-type 1 calorimeter was calculated according to the equation

$$W=\frac{Qa+Gb+5.983v}{\Delta T} \tag{1}$$

Where W is the energy equivalent of the RBC-type 1 calorimeter (in J K^{-1}), Q the combustion enthalpy of benzoic acid (in J g^{-1}), a the mass of determined benzoic acid (in g), G the combustion enthalpy of Ni–Cr wire for ignition (0.9 J cm^{-1}), b the length of actual Ni–Cr wire consumed (in cm), 5.983 is the formation enthalpy and solution enthalpy of nitric acid corresponding to 1 cm^{-3} of 0.1000 mol dm^{-3} solution of NaOH (in J cm^{-3}), v the volume (in cm^{-3}) of consumed 0.1000 mol dm^{-3} solution of NaOH and ΔT the correct value of the temperature rise. The average energy equivalent of the RBC-type 1 calorimeter, W (obtained from nine runs) is equal to (17.94 ± 0.63)kJ K^{-1}.

2.3. Correction of heat exchange

The method of correction used in this investigation has already been described [4].

3. Results and discussion

3.1. Combustion energy of Ala

The method of combustion energy determination for Ala is the same as that for the calibration of the calorimeter with benzoic acid. The sample weights were determined in vacuo. The combustion energies of the samples of Ala were calculated by the formula

$$\Delta_{c,\mathrm{Ala(s)}}E=\frac{W\Delta T-Gb-5.983v}{m} \tag{2}$$

where $\Delta_{c,\mathrm{Ala(s)}}E$ (in J g^{-1}) denotes the constant-volume combustion energy of the sample, and m the mass (in g) of the determined sample. The other symbols are the same as in Eq. (1). The results of calculations are given in Table 1.

3.2. Standard combustion enthalpy of Ala

The standard combustion enthalpy of Ala, $\Delta_{c,\mathrm{Ala(s)}}H^0$, refers to the combustion enthalpy change

Table 1
Combustion energy, standard combustion enthalpy and standard enthalpy of formation of Ala (in kJ mol^{-1})

No.	Mass of Ala a/g	ΔT/K	Heat of q_N/J	Heat of q_c/J	$-\Delta_{c,\mathrm{Ala(s)}}E$	$-\Delta_{c,\mathrm{Ala(s)}}H^0$	$-\Delta_{f,\mathrm{Ala(s)}}H^0$
1	1.17763	1.1577	251.20	12.78	1568.4	1569.09	611.85
2	1.22565	1.2078	268.32	10.35	1570.30	1570.92	610.02
3	1.20239	1.1826	260.40	10.80	1569.15	1569.77	611.17
4	1.21508	1.1965	260.52	11.25	1569.43	1570.05	610.89
5	1.18250	1.1612	255.65	9.90	1568.46	1569.08	611.86
6	1.21006	1.1895	258.82	9.45	1568.63	1569.25	611.69
average					1569.4±1.5	1569.7±1.5	611.2±1.6

of the following ideal combustion reaction at 298.15 K and 100 kPa

$$CH_3CHNH_2COOH_{(s)} + \frac{15}{4}O_{2(g)} \rightarrow 3CO_{2(g)} + \frac{1}{2}N_{2(g)} + \frac{7}{2}H_2O_{(l)} \tag{3}$$

The standard combustion enthalpy of the Ala was calculated from the combustion energy by the equation

$$\Delta_{c,Ala(s)}H^0 = \Delta_{c,Ala(s)}E + \Delta nRT \tag{4}$$

The results of the calculations are also given in Table 1.

3.3. Standard formation enthalpy of Ala

The standard formation enthalpy of Ala was calculated by Hess's law according to the thermochemical equation

$$\Delta_{f,Ala(s)}H^0 = 3\Delta_{f,CO_2(g)}H^0 + \frac{7}{2}\Delta_{f,H_2O(l)}H^0 - \Delta_{c,Ala(s)}H^0 \tag{5}$$

The results of the calculations are also given in Table 1. Our data of $\Delta_{f,Ala(s)}H^0$ is greater than one of $\Delta_{f,Ala(s)}H^0$ in Ref. [5]. This probably is owing to the fact that the purity of Ala and the precision of calorimeter used are different.

3.4. Combustion energy of sample of the complexes (in solid)

The method of determining the combustion energy for samples is the same as for the calibration of the calorimeter with benzoic acid. The sample weights were determined in vacuo. The combustion energies of the sample were calculated according to the formula

$$\Delta_{c,coor}E = \frac{W\Delta T - Gb - 5.983v}{m'} \tag{6}$$

Where $\Delta_{c,coor}E$ (in J g^{-1}) denotes the constant-volume combustion energy of the sample, and m' the mass (in g) of the determined sample. The other symbols are as in Eq. (1). The results of the calculations are given in Tables 2–4, respectively.

Table 2
Combustion energy, standard combustion enthalpy and standard enthalpy of formation of RE(Ala)Cl$_3$·6H$_2$O (I) (in kJ mol^{-1})

Complex	No. of experiments	$-\Delta_{c,coor(I)}E$	$\Delta_{c,coor(I)}H^0$	$-\Delta_{c,coor(I)}H^0$
Eu(Ala)Cl$_3$·6H$_2$O	6	2593.4±3.1	2586.5±3.1	1989.1±3.2
Gd(Ala)Cl$_3$·6H$_2$O	6	2133.4±2.8	2126.6±2.8	2525.2±3.3
Tb(Ala)Cl$_3$·6H$_2$O	6	1381.2±1.9	1374.4±1.9	3283.5±2.1
Dy(Ala)Cl$_3$·6H$_2$O	6	656.2±1.0	649.4±1.0	4027.3±2.2
Ho(Ala)Cl$_3$·6H$_2$O	6	110.2±0.2	103.4±0.2	4581.1±2.6
Yb(Ala)Cl$_3$·6H$_2$O	6	2516.2±2.8	2509.5±2.8	2431.4±3.0
Y(Ala)Cl$_3$·6H$_2$O	6	1620.9±2.1	1614.1±2.1	3082.9±2.4

Table 3
Combustion energy, standard combustion enthalpy and standard enthalpy of formation of RE(Ala)$_2$Cl$_3$·nH$_2$O (II) (in kJ mol^{-1})

Complex	No. of experiments	$-\Delta_{c,coor(II)}E$	$\Delta_{c,coor(II)}H^0$	$-\Delta_{f,coor(II)}H^0$
La(Ala)$_2$Cl$_3$·3H$_2$O	6	3573.2±3.2	3527.0±3.2	2437.2±3.3
Ce(Ala)$_2$Cl$_3$·3H$_2$O	6	2982.8±3.0	2977.3±3	3178.9±3.4
Pr(Ala)$_2$Cl$_3$·3H$_2$O	6	3239.8±3.6	3233.6±3.6	2747.7±3.7
Nd(Ala)$_2$Cl$_3$·3H$_2$O	6	3507.3±3.5	3501.1±3.5	2470.4±3.6
Sm(Ala)$_2$Cl$_3$·3H$_2$O	6	3112.2±3.5	3105.4±3.5	2869.3±3.7
Ho(Ala)$_2$Cl$_3$·4H$_2$O	6	2410.6±3.1	2404.4±3.1	3889.3±4.1
Yb(Ala)$_2$Cl$_3$·4H$_2$O	6	2415.2±3.4	3409.0±3.4	2851.7±3.7
Y(Ala)$_2$Cl$_3$·4H$_2$O	6	3184.1±3.5	3177.9±3.5	3078.4±3.8

Table 4
Combustion energy, standard combustion enthalpy and standard enthalpy of formation of $RE(Ala)_3Cl_3 \cdot 3H_2O$ (III) (in kJ mol^{-1})

Complex	No. of experiments	$-\Delta_{c,coor(III)}E$	$-\Delta_{c,coor(III)}H^0$	$-\Delta_{f,coor(III)}H^0$
$La(Ala)_3Cl_3 \cdot 3H_2O$	6	4869.5±6.3	4863.9±6.3	3281.±6.5
$Ce(Ala)_3Cl_3 \cdot 3H_2O$	6	5107.0±5.6	5102.0±5.6	3235.0±5.9
$Pr(Ala)_3Cl_3 \cdot 3H_2O$	6	5618.6±6.2	5613.0±6.2	2549.3±6.4
$Nd(Ala)_3Cl_3 \cdot 3H_2O$	6	6051.8±5.4	6046.2±5.4	2106.2±5.6
$Sm(Ala)_3Cl_3 \cdot 3H_2O$	6	5031.8±6.0	5026.2±6.0	3130.0±6.2
$Eu(Ala)_3Cl_3 \cdot 3H_2O$	6	5287.2±6.3	5281.6±6.3	2798.4±6.5
$Gd(Ala)_3Cl_3 \cdot 3H_2O$	6	5567.2±6.1	5561.7±6.1	2594.5±6.5
$Tb(Ala)_3Cl_3 \cdot 3H_2O$	6	5395.9±5.4	5390.2±5.4	2772.0±5.6
$Dy(Ala)_3Cl_3 \cdot 3H_2O$	6	4694.9±6.6	4689.3±6.6	3491.7±7

3.5. Standard combustion enthalpy of the complexes

3.5.1. Standard combustion enthalpy of the RE(Ala)Cl$_3$·6H$_2$O (I)

Standard combustion enthalpy of $RE(Ala)Cl_3 \cdot 6H_2O$ (I) $\Delta_{c,coor(I)}H^0$, refers to the change in combustion enthalpy of the following ideal combustion reaction at 298.15 K and 100 kPa

$$\begin{aligned} &RE(Ala)Cl_3 \cdot 6H_2O_{(s)} + \frac{15}{4}O_{2(g)} \\ &\rightarrow \frac{1}{2}RE_2O_{3(s)} + 3CO_{2(g)} \\ &+3HCl_{(g)} + 8H_2O_{(l)} + \frac{1}{2}N_{2(g)} \end{aligned} \tag{7}$$

The standard combustion enthalpies of the complexe (I) were calculated from the combustion energy by the equation

$$\Delta_{c,coor}H^0 = \Delta_{c,coor}E + \Delta nRT \tag{8}$$

The results of the calculations are also given in Table 2.

3.5.2. Standard combustion enthalpy of RE(Ala)$_2$Cl$_3$·nH$_2$O (II)

The standard combustion enthalpy of $RE(Ala)_2Cl_3 \cdot nH_2O$ (II), $\Delta_{c,coor(II)}H^0$, refers to the change in combustion enthalpy of the following ideal combustion reaction at 298.15 K and 100 kPa

$$\begin{aligned} &RE(Ala)_2Cl_3 \cdot nH_2O_{(s)} + \frac{15}{2}O_{2(g)} \\ &\rightarrow \frac{1}{2}RE_2O_{3(s)} + 6CO_{2(g)} + 3HCl_{(g)} \\ &+ \left(n + \frac{11}{2}\right)H_2O_{(l)} + N_{2(g)} \end{aligned} \tag{9}$$

$$\begin{aligned} &Ce(Ala)_2Cl_3 \cdot 3H_2O_{(s)} + \frac{31}{4}O_{2(g)} \\ &\rightarrow CeO_{2(s)} + 6CO_{2(g)} + 3HCl_{(g)} \\ &+\frac{17}{2}H_2O_{(l)} + N_{2(g)} \end{aligned} \tag{10}$$

The standard combustion enthalpies of the complexes (II), $\Delta_{c,coor(II)}H^0$, were calculated from the combustion energies from Eq. (8). The results of the calculations are also given in Table 3.

3.5.3. Standard combustion enthalpy of the RE(Ala)$_3$Cl$_3$·3H$_2$O (III)

The standard combustion enthalpy of the $RE(Ala)_3Cl_3 \cdot 3H_2O$ (III), $\Delta_{c,coor(III)}H^0$, refers to the change in combustion enthalpy of the following ideal combustion reaction at 298.15 K and 100 kPa

$$\begin{aligned} &RE(Ala)_3Cl_3 \cdot 3H_2O_{(s)} + \frac{45}{2}O_{2(g)} \\ &\rightarrow \frac{1}{2}RE_2O_{3(s)} + 9CO_{2(g)} + 3HCl_{(g)} \\ &+12H_2O_{(l)} + \frac{3}{2}N_{2(g)} \end{aligned} \tag{11}$$

$$\begin{aligned} &Ce(Ala)_3Cl_3 \cdot 3H_2O_{(s)} + \frac{21}{2}O_{2(g)} \\ &\rightarrow CeO_{2(s)} + 9CO_{2(g)} + 3HCl_{(g)} \\ &+12H_2O_{(l)} + \frac{3}{2}N_{2(g)} \end{aligned} \tag{12}$$

The standard combustion enthalpies of the complexes (III), $\Delta_{c,coor(III)}H^0$, were calculated from the combustion energies by Eq. (8). The results of the calculations are also given in Table 4.

3.6. Standard formation enthalpies of the complexes

3.6.1. Standard formation enthalpies of RE(Ala)Cl$_3$·6H$_2$O (I)

The standard formation enthalpies of RE(Ala)Cl$_3$·6H$_2$O (I), $\Delta_{f,coor(I)}H^0$, were calculated by Hess's law according to the following thermochemical equation

$$\Delta_{f,coor(I)}H^0 = \frac{1}{2}\Delta_{f,RE_2O_3(s)}H^0 + 3\Delta_{f,CO_2(g)}H^0 + 3\Delta_{f,HCl(g)}H^0 + 8\Delta_{f,H_2O(l)}H^0 - \Delta_{c,coor(I)}H^0 \tag{13}$$

3.6.2. Standard formation enthalpies of RE(Ala)$_2$Cl$_3$·nH$_2$O (II)

The standard formation enthalpies of RE(Ala)$_2$Cl$_3$·nH$_2$O (II), $\Delta_{f,coor(II)}H^0$, were calculated by Hess's law according to the thermochemical equation

$$\Delta_{f,coor(II)}H^0 = \frac{1}{2}\Delta_{f,RE_2O_3(s)}H^0 + 6\Delta_{f,CO_2(g)}H^0 + 3\Delta_{f,HCl(g)}H^0 + \left(n + \frac{11}{2}\right) \times \Delta_{f,H_2O(l)}H^0 - \Delta_{c,coor(II)}H^0 \tag{14}$$

$$\Delta_{f,Ce(Ala)_2Cl_3\cdot 3H_2O}H^0 = \Delta_{f,CeO_2(s)}H^0 + 6\Delta_{f,CO_2(g)}H^0 + 3\Delta_{f,HCl(g)}H^0 + \frac{17}{2}\Delta_{f,H_2O(l)}H^0 - \Delta_{c,Ce(Ala)_2Cl_3\cdot 3H_2O}H^0 \tag{15}$$

3.6.3. Standard formation enthalpies of RE(Ala)$_3$Cl$_3$·3H$_2$O (III)

The standard formation enthalpies of RE(Ala)$_3$Cl$_3$·3H$_2$O (III), $\Delta_{f,coor(III)}H^0$, were calculated by Hess's law according to the following thermochemical equation

$$\Delta_{f,coor(III)}H^0 = \frac{1}{2}\Delta_{f,RE_2O_3(s)}H^0 + 9\Delta_{f,Co_2(g)}H^0 + 3\Delta_{f,HCl(g)}H^0 + 12\Delta_{f,H_2O(l)}H^0 - \Delta_{c,coor(III)}H^0 \tag{16}$$

$$\Delta_{f,ce(Ala)_3Cl_3\cdot 3H_2O}H^0 = \Delta_{f,CeO_2(s)}H^0 + 9\Delta_{f,CO_2(g)}H^0 + 3\Delta_{f,HCl(g)} + 12\Delta_{f,H_2O(l)}H^0 - \Delta_{c,Ce(Ala)_3Cl_3\cdot 3H_2O}H^0 \tag{17}$$

Where (in Eqs. (13)–(17): $\Delta_{f,RE_2O_3(s)} = -1793.14\pm 0.79$(La), -1827.60 ± 1.52(Pr), -1808.12 ± 1.00 (Nd),

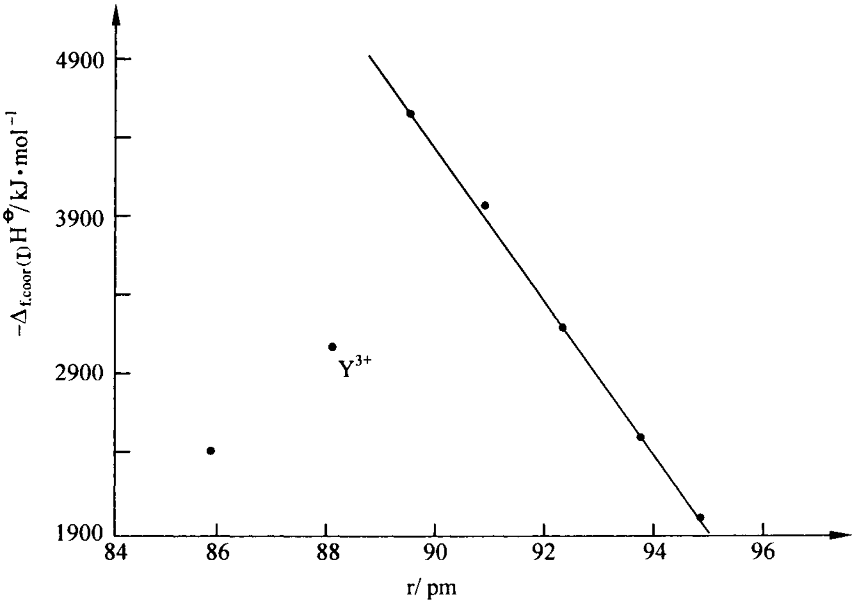

Fig. 1. Plot of $-\Delta_{f,coor(I)}H^0$ values against the ionic radius of RE^{3+}.

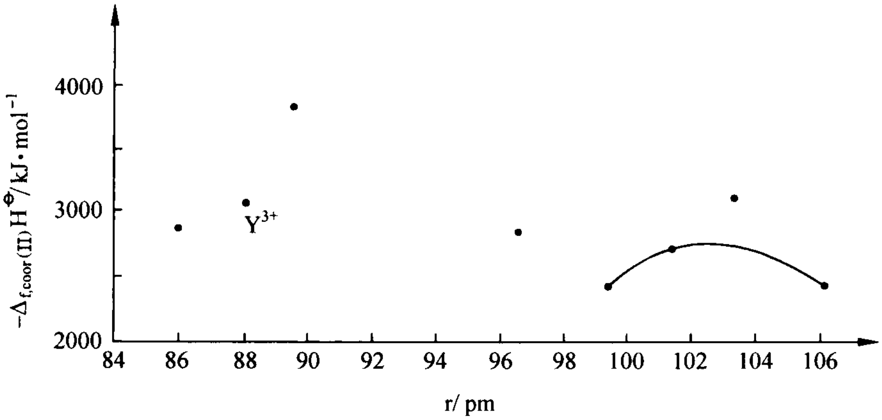

Fig. 2. Plot of $-\Delta_{f,coor(II)}H^0$ values against the ionic radius of RE^{3+}.

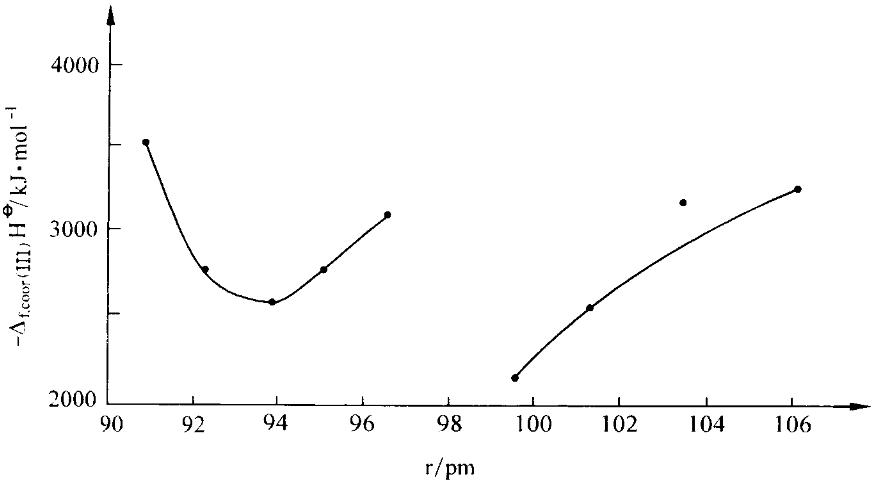

Fig. 3. Plot of $-\Delta_{f,coor(III)}H^0$ values against the ionic radius of RE^{3+}.

-1815.40 ± 2.01(Sm), -1663.00 ± 1.62 (Eu), -1815.60 ± 3.60 (Gd), -1827.60 ± 1.48 (Tb), -1865.39 ± 3.89 (Dy), -1881.13 ± 5.02 (Ho), -1814.52 ± 2.22 (Yb) and -1905.60 ± 2.26 (Y) kJ mol^{-1} [6], $\Delta_{f,H_2O(l)} = -285.83\pm0.04$ kJ mol^{-1} [7]; $\Delta_{f,CeO_2(s)}H^0 = 1088.59 \pm 1.38$ kJ mol^{-1} [6], and $\Delta_{f,HCl(g)}H^0 = -92.31\pm0.03$ kJ mol^{-1} [7].

These results of the calculations of the $\Delta_{f,coor}H^0$ are also given in Tables 2–4, respectively.

$\Delta_{f,coor}H^0$ values of the above complexes: I, II, III are plotted against the ionic radius of rare-earth cations by us. It is found from these plots (Figs. 1–3), that the change of $\Delta_{f,coor}H^0$ with the ionic radius of rare-earth cations is neither showing a regular pattern nor is there a unidirectional increase or decrease. Since these changes with the ionic radius of rare-earth cations would be unidirectional increases or decreases, when the chemical bond between the rare-earth cations and Ala is a purely ionic bond; Therefore, the results show that a certain amount of covalence is present for the chemical bond between the rare-earth cations and Ala.

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