Chapter 5

Thermodynamic Property Study on the Complexes of Rare-Earth Elements with Amino Aids

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Additional information is available at the end of the chapter

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Abstract

In this chapter, the following three rare-earth complexes with amino acids, Eu(Glu)(Im)₅(ClO₄)₃·C₁₃HClO₄·C₁₆H₂O, Nd(Gly)₂Cl₃·C₁₃H₂O, and La(Glu)(Im)₆(ClO₄)₃·C₁₄HClO₄·C₁₄H₂O, are synthesized and characterized by element analysis, infrared (IR) spectrum, and x-ray diffraction (XRD) analysis. The thermodynamic property studies on these complexes are performed. For the first one, Eu(Glu)(Im)₅(ClO₄)₃·C₁₃HClO₄·C₁₆H₂O, the low temperature heat capacity, phase transition, and thermodynamic functions are determined by adiabatic calorimetry. For the second one, Nd(Gly)₂Cl₃·C₁₃H₂O, the molar dissolution enthalpy and standard molar enthalpy of formation are determined by isoperibol solution reaction calorimetry. For the third one, La(Glu)(Im)₆(ClO₄)₃·C₁₄HClO₄·C₁₄H₂O, the microcalorimetry is used to investigate the interaction between the complex and the Escherichia coli DH5α to elucidate the biological effects of the complex.

Keywords: complexes of rare-earth elements, amino acids, adiabatic calorimetry (AC), solution reaction calorimetry, microcalorimetry, thermal analysis, thermodynamic properties, heat capacity, phase transition

1. Introduction

Rare-earth (RE) elements and their compounds have been extensively investigated in last several decades, because of their important significance in sciences and the growing practical applications in industries. New frontiers concerned with RE science and technology are increasingly and rapidly developed.

It is well know that China is the country richest in RE minerals all over the world. In order to sufficiently develop and effectively utilize the RE resources, the industries concerned were in urgent need of huge numbers of basic data of RE compounds. Undoubtedly, the thermodynamic property data are absolutely necessary for the study and application of rare-earth
compounds. As one part of Chinese national research projects for rare-earth science and technology, in the period of 1990–2006, our Thermochemistry Laboratory in cooperation with Microcalorimetry Research Center of Osaka University well successfully completed the research project “low temperature heat capacity and thermodynamic properties of a series of rare-earth isothiocyanate hydrates, RE(NCS)$_3$·nH$_2$O (RE = La, Ce, Pr, Nd, Sm, Gd, Yb, Y).” The research results concerned were published in international journals [1–4].

Rare-earth elements have found their applications in many areas nowadays; because of their unique properties, they have been introduced into microfertilizer, pesticide, and antibacterial agent. Accompanying these applications, rare-earth elements inevitably spread into the food chain, the biological chain, and then into the bodies of human beings. This leads people to care about and study the influence and the long-term effect of rare-earth elements on themselves. Rare-earth complexes formed with amino acid were then synthesized for this purpose, because amino acid is the basic unit comprising protein and enzyme, the fundamental and functional materials in the bodies of human beings and animals. In the last 30 years, more than 200 kinds of these complexes were synthesized, and about 50 kinds among them had their own crystallograms. However, the thermodynamic property data of these complexes were seldom reported. As we all well know, only with these data we can quantitatively describe their characteristics in terms of the energetics, for example, stable forms in different temperature range, melting process, thermal anomaly, and so on. Comparisons of these data for a series of complexes comprised by the same RE (or ligands) with different ligands (or RE) may enable us to have a deeper understanding of their properties.

Rare-earth complex coordinated with amino acids possesses many unique physiological and biochemical effects. In 1975, Anghileri et al. reported for the first time that La(Gly)$_3$Cl$_3$·3H$_2$O was antineoplastic [5]. Since then, the rare-earth complexes coordinated with amino acids have been synthesized and studied intensively by a variety of methods [6–10]. Nowadays, the applications of rare-earth complexes with amino acids have expanded into the fields of medicine, biology, and agriculture more widely. However, the fundamental thermodynamic property data of these complexes have rarely been reported yet, especially the data of low temperature heat capacity and standard thermodynamic functions, and standard enthalpy of formation, although these data are significant for the further applications of the rare-earth complex with amino acids.

Based on previous work about thermodynamic study of rare-earth isothiocyanate hydrates, our thermochemistry laboratory in cooperation with several national academic groups has intensively contributed to this effort for thermodynamic property studies on rare-earth complexes with amino acids, and 28 academic papers concerned with this research project have been published [11–38].

In this chapter, we present the following three papers to report our recent research results and describe in detail the modern advanced experimental calorimetric techniques used for thermodynamic property studies of rare-earth complexes.

1. Thermodynamic properties of rare-earth complex with amino acid: Eu(Glu)(Im)$_5$(ClO$_4$)$_3$·3HClO$_4$·6H$_2$O
2. Thermodynamic study on rare-earth complex of neodymium with glycine: Nd(Gly)_2Cl_3·3H_2O

3. Microcalorimetric study on biological effect of rare-earth complex with amino acid: La(Glu)(Im)_6(ClO_4)_3·4HClO_4·4H_2O

2. Thermodynamic properties of rare-earth complex with amino acid: Eu(Glu)(Im)_5(ClO_4)_3·3HClO_4·6H_2O

2.1. Experiment

2.1.1. Synthesis and characterization of the complex

The complex, Eu(Glu)(Im)_5(ClO_4)_3·3HClO_4·6H_2O, was synthesized according to the procedures mentioned below. All starting materials used for the synthesis are the analytical reagents purchased from the Beijing Chemical Reagent Co. The rare-earth oxide (Eu_2O_3) was dissolved in an excess amount of perchloric acid (1:1), and the concentration of the solution was determined by ethylene diamine tetraacetic acid (EDTA) titration analysis. Then, solid L-Glutamic acid was added to the solution in molar ratio of Eu^{3+}:Glu = 1:1. After the pH value of the reaction mixture was carefully adjusted to about 4.0 by slow addition of NaOH solution, imidazole was added in molar ratio of Eu^{3+}:Glu:Im = 1:1:5. The solution was stirred for a further 2 h in flask. The solution was transferred to the culture dish, and the culture dish was sealed using preservative film with many tiny holes stabbed using needle. The culture dish was placed in a desiccator using phosphorus pentoxide as the desiccant. The complex formed slowly in the solution and was taken out of the solution for analysis.

An elemental analysis apparatus (Model PE-2400 II, USA) was used to measure the C, H, N of the complex, and Eu was determined by EDTA titration analysis. The Cl amount in ClO_4^- of the complex was determined by the ion chromatography (Waters Alliance® 2695 System with the Waters Conductivity Detector and Waters Micromass® Quattro micro™ Mass Spectrometer). The experimental values are: Eu (11.60%) (mass fraction), C (17.794%), N (11.4093%), H (3.304%), and Cl (15.665%), which are close to the theoretical values, Eu (11.2792%), C (17.8293%), N (11.4358%), H (3.2917%), and Cl (15.789%). The sample formula was determined to be Eu(Glu)(Im)_5(ClO_4)_3·3HClO_4·6H_2O.

Infrared spectra of the complex and L-Glutamic acid were obtained through KBr pellets at room temperature using a Bruker Tensor 27-IR spectrophotometer. The infrared spectrum of the complex was shown in Figure 1. Compared with the IR spectrum of L-Glutamic acid, the νs (carboxyl) band of the complex shifted from 1410 cm\(^{-1}\) to higher wave numbers (1431 cm\(^{-1}\)), which shows that the carboxyl groups of the ligand have been coordinated to the metal ion [39]. The special absorptions of -NH\(_2\) shifted from 3050 to 3240 cm\(^{-1}\) (ν -NH), from 2750 to 2740 cm\(^{-1}\) (ν -NH), and from 1560 to 1562 cm\(^{-1}\) (δNH\(_2\)), because a hydrogen bond formed in the complex. The spectrum also shows the wide peak symmetrical resonance frequencies, νs (N-H), shifted from 3286 to 3425 cm\(^{-1}\) down to 3166 to 3098 cm\(^{-1}\), which is evidence of the
coordination of imidazole molecules [40]. A broad absorption band for $\nu$ (hydroxyl) appearing at 3400 cm$^{-1}$ shows the presence of water molecules in the complex.

Powder X-ray diffraction (XRD) patterns were recorded using Rigaku D/Max 3400 X with Cu Kα radiation at 0.02 steps per second in angle range $2\theta = 5$–90, and the results were shown in Figure 2. Judging from the shape and number of the peak in the patterns, the sample was a kind of complex with single phase.

Figure 1. Infrared spectrum of the complex.

Figure 2. Powder X-ray diffraction patterns of complex.
2.1.2. Adiabatic calorimetry

Adiabatic calorimetry is the most accurate approach to obtain the heat capacity data. In the present study, heat capacity measurements were carried out by a high-precision automatic adiabatic calorimeter over the temperature range of 80–350 K. The adiabatic calorimeter was established by Thermochemistry Laboratory of Dalian Institute of Chemical Physics, Chinese Academy of Sciences in PR China. The structure and principle of the adiabatic calorimeter have been described in detail elsewhere [41]. The schematic diagram of the adiabatic calorimeter is shown in Figure 3. Briefly, the automatic adiabatic calorimeter is mainly composed of a sample cell, a miniature platinum resistance thermometer, an electric heater, the inner and outer adiabatic shields, two sets of six-junction chromel-constantan thermopiles installed between the calorimetric cell and the inner shield and between the inner and the outer shields, respectively, and a high vacuum can. The working temperature range is 78–400 K and, if necessary, it can be cooled by liquid nitrogen. The heat capacity measurements were conducted by the standard procedure of intermittently heating the sample and alternately measuring the temperature. The heating rate and the temperature increments of the experimental points were generally controlled at 0.1–0.4 K-min⁻¹ and at 1–4 K, respectively, during the whole experimental process. The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were kept within 10⁻³–10⁻⁴ K-min⁻¹ during the acquisition of heat capacity data. In order to verify the reliability of the adiabatic calorimeter, the molar heat capacities $C_p, m$ of the Standard Reference Material (SRM-720) (α-Al₂O₃) were measured in the range of 78–400 K. The deviation of our calibration data from those of NIST [42] was within ±0.1% (standard uncertainty). In the present study, the mass of the complex, Eu(Glu)(Im)₅(ClO₄)₃·3HClO₄·6H₂O, used for heat capacity measurement was 2.0352 g.

The result of heat capacity measurement of the complex was listed in Table 1 and shown in Figure 4.

2.1.3. Other thermal analysis

A differential scanning calorimeter (DSC–141, SETARAM, France) was used to perform the thermal analysis of Eu(Glu)(Im)₅(ClO₄)₃·3HClO₄·6H₂O. In the range 100–300 K, liquid nitrogen was used as cryogen. In the range 300–700 K, nitrogen gas was taken as protective gas with flow rate of 50 cm³·min⁻¹, at the heating rate of 10 K-min⁻¹. The masses of the samples used in the above two experiments were 4.03 and 4.26 mg, respectively.

Two aluminum crucibles were used and the reference crucible was empty. The calibrations for the temperature and heat flux of the calorimeter were performed prior to the experimental measurements of the sample. The temperature scale was calibrated by measuring the melting points of Hg, In, Sn, Pb, and Zn, at different heating rates, and the heat flux was calibrated by the Joule effect. Measurements of the melting temperature and the enthalpy of fusion of benzoic acid (NIST, Standard Reference Material 39i) were performed in the laboratory to check the accuracy of the instrument.

The result of DSC measurement was shown in Figure 5.
Figure 3. (A) Schematic diagram of main body of the adiabatic calorimeter. (B) Schematic diagram of sample cell of the adiabatic calorimeter.
| T/K    | $C_{p,m}$ /kJ mol$^{-1}$ | T/K    | $C_{p,m}$ /kJ mol$^{-1}$ |
|--------|--------------------------|--------|--------------------------|
| 80.809 | 919.23                   | 216.99 | 2245.5                   |
| 85.210 | 937.21                   | 220.72 | 2147.5                   |
| 89.334 | 959.77                   | 224.63 | 2043.8                   |
| 92.891 | 985.26                   | 228.55 | 1900.4                   |
| 96.695 | 999.58                   | 232.60 | 2160.4                   |
| 100.86 | 1023.5                   | 236.58 | 2483.0                   |
| 103.43 | 1041.7                   | 240.60 | 2787.8                   |
| 107.12 | 1059.7                   | 244.18 | 4772.0                   |
| 112.49 | 1090.3                   | 246.08 | 1180.8                   |
| 116.85 | 1120.2                   | 252.57 | 2262.7                   |
| 120.68 | 1140.2                   | 258.60 | 2282.7                   |
| 124.34 | 1163.4                   | 262.37 | 2297.0                   |
| 128.48 | 1187.6                   | 266.06 | 2302.0                   |
| 132.40 | 1209.4                   | 269.69 | 2305.4                   |
| 136.47 | 1242.6                   | 273.60 | 2316.5                   |
| 140.42 | 1263.1                   | 277.58 | 2330.1                   |
| 144.39 | 1284.7                   | 281.39 | 2336.3                   |
| 148.49 | 1308.0                   | 285.46 | 2355.6                   |
| 152.58 | 1334.7                   | 289.26 | 2377.3                   |
| 156.48 | 1359.5                   | 293.34 | 2416.1                   |
| 160.77 | 1383.9                   | 297.43 | 2444.2                   |
| 164.78 | 1412.6                   | 301.37 | 2490.8                   |
| 168.80 | 1439.5                   | 305.18 | 2526.2                   |
| 172.87 | 1465.4                   | 309.23 | 2571.8                   |
| 176.80 | 1488.0                   | 313.12 | 2611.6                   |
| 180.71 | 1512.7                   | 316.85 | 2661.0                   |
| 184.90 | 1542.9                   | 319.85 | 2721.8                   |
| 188.89 | 1577.1                   | 324.82 | 2779.0                   |
| 192.76 | 1610.9                   | 328.77 | 2842.9                   |
| 196.79 | 1644.1                   | 332.78 | 2906.9                   |
| 200.75 | 1681.2                   | 336.67 | 2974.1                   |
| 204.67 | 1728.7                   | 340.52 | 3051.9                   |
| 208.78 | 1788.1                   | 344.52 | 3126.9                   |
| 212.99 | 2025.9                   | 348.77 | 3209.9                   |

**Table 1.** Experimental molar heat capacity of the complex from 80 to 350 K at pressure $p = 0.1$ MPa.
The thermogravimetric (TG) measurement of the complex was carried out by a TG analyzer (Model: setsys 16/18 from Setaram Company, France) at the heating rate of 10 K/min under nitrogen atmosphere (99.999%), with flow rate of 65 cm$^3$/min. The mass of the sample used in the experiment was 6.3 mg. Two Al$_2$O$_3$ crucibles with capacity of 100 μL were used for sample and empty cell, respectively. The calibration of TG analyzer was performed by the SRM in thermal analysis, CaC$_2$O$_4$·H$_2$O(s).

The result of TG measurement of the complex was shown in Figures 6 and 7, respectively.
2.2. Results and discussion

2.2.1. Phase transitions

From the view of phase temperature of the process, Yukawa et al. [43] found a phase transition of the first order and a glass transition of crystalline (TMA)$_2$[Sm(Ni-Pro)$_2$)$_6$[ClO$_4$]$_4$ at $T = (190 \pm 1)$ K and $T = (162 \pm 2)$ K. They contributed the phase transition to orientational order/disorder process of perchlorate ions ClO$_4^-$ and the glass transition to a freezing-in phenomenon of the reorientational motion of perchlorate ions ClO$_4^-$. They discussed that the cooperative interaction between the orientations of the ClO$_4^-$ ions operates through the orientational
and positional shifts of TMA ions, and thus the lattice deformation in the relevant region, associated with the orientational change of the ClO$_4^-$ ions. The position of the ClO$_4^-$ ions itself would shift to form preferable ionic interaction.

It can be seen from Figure 4 that there are two thermal events in the range 80–350 K on the $C_{p,m}$-T curve. The heat capacity of the sample increases with increasing temperature in a smooth and continuous manner in the temperature range from 80 to 208 K. A little peak occurs at $T = 216.98$ K on the $C_{p,m}$-T curve, which is consistent with the peak ($T_{trs} = 217.30$ K) on the DSC curve (Figure 5). Such thermal event is deduced to be the phase transition of the complex. The second peak is at 246.08 K, which is also deduced to be the phase transition consistent with the peak ($T_{trs} = 245.06$ K) on the DSC curve.

It can be proved from Figure 4 that there are two endothermic processes in the temperature range 100–300 K. One is at 217.30 K, and the other is at 245.06 K, which confirms the results of the heat capacity measurements (216.98 and 246.08 K). The temperature ranges and peak values of the endothermic processes correspond to those of the phase transitions in the $C_{p,m}$-T curve obtained from the heat capacity measurements. It is also verified that there are two phase transitions in the temperature range 100–350 K.

From the view of energy accompanying the process, Yukawa et al. [43] estimated the entropy of the phase transition was to be from 20 to 45 J·K$^{-1}$·mol$^{-1}$ in the range. The present work calculated that the molar entropy $\Delta_{trans} S_m$ of the first-phase transition is $27.86 \pm 0.08$ J·mol$^{-1}$·K$^{-1}$, which was in the range of entropy of the phase transition estimated by Yukawa et al.

The combined consideration based on the results of AC (adiabatic calorimetric) and DSC (differential scanning calorimetric) measurements, the values of thermodynamic functions, and the report of former documents leads to a conclusion that the phase transition was interpreted as a freezing-in phenomenon of the reorientational motion of perchlorate ions ClO$_4^-$. The endothermic process at $T = 246.86$ K was deduced to be the orientational order/disorder process of ClO$_4^-$ ion [43–46].

### 2.2.2. Molar heat capacity, molar enthalpies, and entropies

Experimental molar heat capacities, $C_{p,m}$ against temperature $T$ in the range 80–350 K, were listed in Table 1 and plotted in Figure 4. It can be seen from the figure that no phase change or thermal decomposition was found before 206 K and after 258 K.

None-phase transitions process:

Before the solid-solid phase transitions process (from 80 to 208 K):

$$
H_T - H_{298.15} = \int_{298.15}^{T} C_{p,m}(s) dT
$$

(1)

$$
S_T - S_{298.15} = \int_{298.15}^{T} [C_{p,m}(s)/T] dT
$$

(2)

After the solid-solid phase transitions process (from 258 to 350 K):
where $C_{p,m}(s)$ is the molar heat capacity of the solid state, $T_i$ is the temperature at which the solid-solid phase transition started, and $T_f$ is the temperature at which the solid-solid phase transition ended.

The values of the experimental heat capacities except the phase change regions were fitted. One polynomial Eq. (5) was obtained by least squares fitting using the experimental molar heat capacities ($C_p,m$) and the reduced temperatures ($x$).

$$C_{p,m}/(J \cdot K \cdot mol^{-1}) = 1838 + 1240x - 136.0x^2 - 806.7x^3 + 376.3x^4 + 765.5x^5$$

where $x = [(T/K) - 215]/135$, $x$ is the reduced temperature, and $T$ is the experimental temperature. Correlation coefficient of the least squares fitting, $R^2$, is 0.9989 ($T_i = 80$ K and $T_f = 350$ K).

Phase transitions process (from 206 to 258 K):

In the solid-solid phase transitions process (from 206 to 258 K), the temperature $T_{trans}$, molar enthalpies $\Delta_{trans}H_m$ and molar entropies $\Delta_{trans}S_m$ of the first two-phase transitions are determined according to Eqs. (6)-(10) and listed in Table 3.

$$\Delta_{trans}H_m = \sum_{k=1}^{f} [C_{p,m}(trans)(T_{k+1} - T_k)]$$

$$\Delta_{trans}S_m = \sum_{k=1}^{f} \left[ \frac{C_{p,m}(trans)}{T_{trans}}(T_{k+1} - T_k) \right]$$

where $C_{p,m}(trans)$ is the molar heat capacity during the solid-solid phase transitions process:

$$C_{p,m}(trans) = [C_{p,m}(k) + C_{p,m}(k+1)]/2$$

$T_{trans}$ can be seen as follows:

$$T_{trans} = [(T_k + T_{k+1})]/2$$

From Eqs. (6) to (9), molar enthalpies, $\Delta_{trans}H_m$, and molar entropies, $\Delta_{trans}S_m$, of the two solid-solid phase transition processes from 208 to 228 K and from 228 to 252 K were calculated as follows:

$$\Delta_{trans}H_m = \sum_{k=1}^{f} [C_{p,m}(trans, 1)(T_{k+1} - T_k)]$$

The values of the experimental heat capacities except the phase change regions were fitted. One polynomial Eq. (5) was obtained by least squares fitting using the experimental molar heat capacities ($C_p,m$) and the reduced temperatures ($x$).
\[ \Delta_{\text{trans}} S_m = \sum_{k=1}^{f} \left[ \frac{C_{p,m}(\text{trans}, 1)}{T_{\text{trans}}}(T_{k+1} - T_k) \right] \]  

(11)

\[ C_{p,m}(\text{trans}, 1) = C_{p,m}(\text{trans}) - C_{p,m}(\text{trans}, 2) \]  

(12)

where \( C_{p,m}(\text{trans}, 1) \) is the molar heat capacity caused by solid-solid phase transitions. \( C_{p,m}(\text{trans}) \) is the total molar heat capacity. \( C_{p,m}(\text{trans}, 2) \) is the molar heat capacity induced by temperature change of substance, and its polynomial equation was obtained by least squares analysis using the experimental molar heat capacities in the non-phase transition regions from 80 to 350 K as in Eq. (5).

The molar enthalpy of the first-phase transition was calculated from 208 to 228 K as follows:

\[ \Delta_{\text{trans}} H_{m,1} = \sum_{k=1}^{f} \left[ \frac{C_{p,m}(\text{trans}, 1)}{T_{\text{trans}}}(T_{k+1} - T_k) \right] = (3.896 \pm 0.011) \text{kJ} \cdot \text{mol}^{-1} \]  

(13)

(Standard uncertainty), where \( T_1 = 208.86 \text{K} \) and \( T_f = 228.55 \text{K} \).

The molar enthalpy of the second-phase transition was calculated from 228 to 252 K, at 0.1 MPa as follows:

\[ \Delta_{\text{trans}} H_{m,2} = \sum_{k=1}^{f} \left[ \frac{C_{p,m}(\text{trans}, 1)}{T_{\text{trans}}}(T_{k+1} - T_k) \right] = (53.763 \pm 0.160) \text{kJ} \cdot \text{mol}^{-1} \]  

(15)

(Standard uncertainty), where \( T_1 = 228.55 \text{K} \) and \( T_f = 252.57 \text{K} \). The thermodynamic functions relative to the reference temperature 298.15 K, \( (H_{T} - H_{298.15}) \), and \( (S_{T} - S_{298.15}) \) were calculated in the temperature range from 80 to 350 K with an interval of 5 K at pressure 0.1 MPa, and listed in Table 2, using the above thermodynamic polynomial Eqs. (1)–(12).

2.2.3. Thermal decomposition properties

It can be seen from Figure 6 that there are two peaks on the DSC curve from 300 to 700 K. One is a little endothermic peak \( (T_{\text{trans}} = 485.57 \text{K}) \), which was caused by decomposition of amino, and the other is a wide exothermic peak from 530 to 600 K, which was contributed to decomposition of the complex. It was consistent with the results of TG analysis.

The result of TG analysis was showed in Figure 7. It can be seen from the TG curve that mass loss of Eu(Glu)(Im)$_3$(ClO$_4$)$_3$·3HClO$_4$·6H$_2$O began at about 298 K and ended at about 900 K. The whole process was divided into three stages. The mechanism of the decomposition was deduced as following:
The value in the parentheses is theoretical calculation result.

| T/K  | \(C_{p,m}/\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\) | \(\langle H - H_{298.15} \rangle/\text{kJ} \cdot \text{mol}^{-1}\) | \(\langle S - S_{298.15} \rangle/\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\) |
|------|-------------------------------------------------|---------------------------------|---------------------------------|
| 80   | 879.70                                          | -417.61                         | -2182.7                         |
| 85   | 928.49                                          | -413.09                         | -2127.0                         |
| 90   | 970.11                                          | -408.34                         | -2072.6                         |
| 95   | 1006.0                                          | -403.39                         | -2019.4                         |
| 100  | 1037.4                                          | -398.28                         | -1967.5                         |
| 105  | 1065.6                                          | -393.02                         | -1916.6                         |
| 110  | 1091.5                                          | -387.63                         | -1866.9                         |
| 115  | 1116.0                                          | -382.10                         | -1818.1                         |
| 120  | 1139.9                                          | -376.46                         | -1770.3                         |
| 125  | 1163.8                                          | -370.70                         | -1723.4                         |
| 130  | 1188.3                                          | -364.82                         | -1677.2                         |
| 135  | 1213.9                                          | -358.81                         | -1631.8                         |
| 140  | 1240.8                                          | -352.67                         | -1587.0                         |
| 145  | 1269.4                                          | -346.40                         | -1542.7                         |
| 150  | 1299.9                                          | -339.97                         | -1498.9                         |
| 155  | 1332.3                                          | -333.39                         | -1455.5                         |
| 160  | 1366.7                                          | -326.64                         | -1412.4                         |
| 165  | 1403.1                                          | -319.72                         | -1369.6                         |
| 170  | 1441.4                                          | -312.61                         | -1327.0                         |
| 175  | 1481.5                                          | -305.30                         | -1284.5                         |
| 180  | 1523.2                                          | -297.79                         | -1242.1                         |
| 185  | 1566.3                                          | -290.07                         | -1199.7                         |
| 190  | 1610.6                                          | -282.12                         | -1157.3                         |
| 195  | 1655.9                                          | -273.96                         | -1114.9                         |
| 200  | 1701.8                                          | -265.56                         | -1072.4                         |
| 205  | 1748.2                                          | -256.94                         | -1029.9                         |
| 210–250| Phase transitions | \[ \] | \[ \] |
| 255  | 2180.7                                          | -100.65                         | -365.32                         |
3.1. Experiment

3.1.1. Sample preparation and characterization

The complex, Nd(Gly)_2Cl_3·3H_2O, was synthesized according to the following procedure. Firstly, rare-earth oxide (Nd_2O_3, purity 99.18%) was dissolved in chloride acid to obtain an aqueous solution of the rare-earth chloride. Following that, the aqueous solution was mixed...
with glycine in the molar ratio of 1:2 at about pH = 2.5 for 7–8 h. After that, the mixed solution was concentrated in a thermostat bath at 323 K until most of the water was evaporated, and then the concentrated solution was dried in a vacuum desiccator over phosphorus pentoxide for several weeks until lavender crystals appeared.

The actual amount of C, H, and N in the as-prepared sample was confirmed by elemental analysis instrument (model PE-2400 II, USA). The contents of Cl and Nd were determined by the EDTA titration and Mohr method, respectively. The experimental values are: C(10.66%), N (2.97%), H(2.49%), Cl(23.13%) and Nd(31.65%), which are close to the theoretical values of C (10.56%), N(3.08%), H(2.42%), Cl(23.39%) and Nd(31.72%). The sample formula was determined to be Nd(Gly)\(_2\)Cl\(_3\)·3H\(_2\)O, and the purity obtained from the EDTA titration under the same conditions was found to be 99.78%, which was high enough to meet the requirements of the present calorimetric study. Infrared spectra of the complex Nd(Gly)\(_2\)Cl\(_3\)·3H\(_2\)O, Pr(Gly)\(_2\)Cl\(_3\)·3H\(_2\)O, Er(Gly)\(_2\)Cl\(_3\)·3H\(_2\)O and glycine were obtained from KBr pellets at room temperature using an IR spectrophotometer (model AVATAR 370 NICOLET USA).

Infrared spectra of Nd(Gly)\(_2\)Cl\(_3\)·3H\(_2\)O, Pr(Gly)\(_2\)Cl\(_3\)·3H\(_2\)O, Er(Gly)\(_2\)Cl\(_3\)·3H\(_2\)O, and glycine are demonstrated in Figure 8. Compared with the IR spectrum of glycine, the vs(carboxyl) band of Nd(Gly)\(_2\)Cl\(_3\)·3H\(_2\)O shifted from 1394 cm\(^{-1}\) to higher wave numbers (1418 cm\(^{-1}\)), which reveals that the carboxyl groups of the ligand have been coordinated to the metal ion. The special absorption of NH\(_2\) shifted from 3105 cm\(^{-1}\) to 3420 cm\(^{-1}\) (\(\nu\)N-H), from 2604 to 2580 cm\(^{-1}\) (\(\nu\)N-H), and from 1500 to 1477 cm\(^{-1}\) (\(\nu\)NH\(_2\)) indicates a hydrogen bond formed in the complex. A broad absorption band for vs(hydroxyl) appearing at 3400 cm\(^{-1}\) suggests the presence of water molecules in the complex. Meanwhile, it can be observed that main diffraction peaks of Nd

![Figure 8](image_url)
(Gly)$_2$Cl$_3$·3H$_2$O are in good agreement with that of Pr(Gly)$_2$Cl$_3$·3H$_2$O and Er(Gly)$_2$Cl$_3$·3H$_2$O. The above results suggest that the structure of as-synthesized complex is similar to that of Pr(Gly)$_2$Cl$_3$·3H$_2$O and Er(Gly)$_2$Cl$_3$·3H$_2$O.

3.1.2. DSC and TG measurements

Thermal analysis of Nd(Gly)$_2$Cl$_3$·3H$_2$O was performed using a differential scanning calorimeter (DSC-141, SETARAM, France) and a thermogravimetric analyzer (model DT-20B, Shimadzu, Japan). The DSC measurement was carried out with a heating rate of 10 K$^{-1}$ min$^{-1}$ under high-purity nitrogen with a flow rate of 50 mL min$^{-1}$. The mass of the sample used in the experiment was 3.36 mg. The calibrations for the temperature and heat flux of the calorimeter were performed prior to the experiment. The temperature scale was calibrated by measuring the melting points of Hg, In, Sn, Pb, and Zn at different heating rates, and the heat flux was calibrated using the Joule effect. Measurement of the melting temperature and the enthalpy of fusion of benzoic acid (NIST, SRM 39i) were carried out in this laboratory to check the accuracy of the instrument. The TG measurement of the complex was conducted at a heating rate of 10 K$^{-1}$ min$^{-1}$ under high-purity nitrogen with a flow rate of 120 mL min$^{-1}$. The mass of the sample used in the experiment was 9.47 mg. The reference crucible was filled with $\alpha$-Al$_2$O$_3$. The TG-DTG equipment was calibrated by the thermal analysis of the SRM, CaC$_2$O$_4$·H$_2$O(s).

3.1.3. Dissolution enthalpy measurements

3.1.3.1. Isoperibol solution reaction calorimeter

The Isoperibol solution reaction calorimeter (SRC-100) used for this study was constructed in our thermochemistry laboratory and has been used for measuring enthalpies of solid-liquid, liquid-liquid dissolution reactions enthalpies of the reactant, and the product to obtain the formation enthalpies of the complex. The principle and structure of the instrument were described elsewhere [47]. The schematic diagram of the calorimeter is shown in Figure 9. The calorimeter mainly consisted of a water thermostat, a pyrex-glass Dewar with volume of 100 mL, a glass sample cell with volume of 2 mL, a heater for calibration and equilibration purposes, a glass-sheathed thermistor probe, an amplifier, a circuit used as an A/D converter, and a personal computer for data acquisition and processing. The Dewar vessel, equipped with a twin-blade stirrer, served as a mixing chamber, was submerged in the water thermostat. The precisions of controlling and measuring the temperature of the calorimeter are ±0.001 and ±0.0001 K, respectively. The measurements of solution-reaction enthalpy of samples were conducted under atmospheric pressure. The calorimeter was tested by measuring the dissolution enthalpies of the KCl (calorimetric primary standard) in water at 298.15 K. The mean dissolution enthalpies obtained from five experiments are 17515 ± 12 J mol$^{-1}$, which are in conformity with the reported data (17536 ± 9 J mol$^{-1}$) [48].

3.1.3.2. Dissolution and formation enthalpy measurements

The dissolution enthalpies of reactants and the products, and standard molar enthalpy of formation of Nd(Gly)$_2$Cl$_3$·3H$_2$O were determined through the proposed Hess thermochemical cycle, which is demonstrated in Figure 10. The dissolution enthalpy of H$_2$O (l), $\Delta_dH$, as one of
the products in above cycle under the same condition was within the range of experimental error and may be omitted because the amount of H₂O (l) was very small according to the stoichiometric number of H₂O (l) in above cycle.

As illustrated in Figure 10, the molar enthalpy of formation of Nd(Gly)₂Cl₃·3H₂O(s) is given as:

\[
\Delta_s H_1 + 100\text{ml} \ 2\text{mol·L}^{-1} \ \text{HCl} + 0.027\text{mLH}_2\text{O} \rightarrow \Delta_s H_2
\]

Figure 9. The schematic diagram of isoperibol solution-reaction calorimeter.

Figure 10. Hess thermochemical cycle.
\[ \Delta_r H_m^\theta = \Delta_l H_m^\theta \left[ \text{Nd(Gly)}_2\text{Cl}_3 \cdot 3\text{H}_2\text{O}, \text{s} \right] + 3\Delta_l H_m^\theta (\text{H}_2\text{O}, \text{l}) + \Delta_l H_m^\theta (\text{NdCl}_3 \cdot 6\text{H}_2\text{O}, \text{s}) \\
+ 2\Delta_l H_m^\theta (\text{Gly}, \text{s}) = \Delta sH_1 - \Delta sH_2 - \Delta H = \Delta sH_1 \Delta sH_2 \]  

where \( \Delta_l H_m^\theta \left[ \text{Nd(Gly)}_2\text{Cl}_3 \cdot 3\text{H}_2\text{O}, \text{s} \right] \), \( \Delta_l H_m^\theta (\text{NdCl}_3 \cdot 6\text{H}_2\text{O}, \text{s}) \), and \( \Delta_l H_m^\theta (\text{Gly}, \text{s}) \) are the molar enthalpy of formation of the corresponding compounds. \( \Delta_l H_m^\theta \left[ \text{Nd(Gly)}_2\text{Cl}_3 \cdot 3\text{H}_2\text{O}, \text{s} \right] \) could be calculated from the following equation:

\[ \Delta_l H_m^\theta \left[ \text{Nd(Gly)}_2\text{Cl}_3 \cdot 3\text{H}_2\text{O}, \text{s} \right] = \Delta sH_1 - \Delta sH_2 + \Delta_l H_m^\theta (\text{NdCl}_3 \cdot 6\text{H}_2\text{O}, \text{s}) \\
+ 2\Delta_l H_m^\theta (\text{Gly}, \text{s}) - 3\Delta_l H_m^\theta (\text{H}_2\text{O}, \text{l}) \]  

The mixture of \( \text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s}) \) and \( \text{Gly}(\text{s}) \) at mole ratio of \( n(\text{NdCl}_3 \cdot 6\text{H}_2\text{O})/n(\text{Gly}) = 1:2 \) was dissolved in 100 mL of 2 mol-L\(^{-1}\) hydrochloric acid at 298.15 K. The final solution obtained was named as Solution A. Dissolution enthalpy of 1 mol \( \text{Nd(Gly)}_2\text{Cl}_3 \cdot 3\text{H}_2\text{O}(\text{s}) \) in 100 mL of 2 mol-L\(^{-1}\) hydrochloric acid was determined under the same condition as above. The final solution obtained was named as Solution A’. Finally, UV–vis spectroscopy and the data of the refrangibility were applied to confirm whether Solution A was in the same thermodynamic state as that of Solution A’. These results mentioned above indicated that chemical components and physical-chemistry properties of Solution A obtained agreed with those of Solution A’. In this chapter, UV–vis spectrum and the data of the refrangibility of Solution A obtained agreed with those of Solution A’. These results demonstrated that the designed thermochemical cycle is reasonable and reliable, hence can be used to calculate the standard molar enthalpy of formation of \( \text{Nd(Gly)}_2\text{Cl}_3 \cdot 3\text{H}_2\text{O}(\text{s}) \).

### 3.2. Results and discussion

#### 3.2.1. Thermal analysis

The thermal analysis results of \( \text{Nd(Gly)}_2\text{Cl}_3 \cdot 3\text{H}_2\text{O} \) are shown in Figures 11 and 12, respectively. The DSC curve (Figure 11) reveals that the two endothermic peaks appear at 146.68 and 282.21°C, which are in agreement with those obtained from the TG-DTG (thermogravimetric-differential thermogravimetric) experiments at 147.5 and 283.0°C.

The mass loss of \( \text{Nd(Gly)}_2\text{Cl}_3 \cdot 3\text{H}_2\text{O} \) was mainly divided to two steps. Based on the TG curve and the structure of \( \text{Nd(Gly)}_2\text{Cl}_3 \cdot 3\text{H}_2\text{O} \), the conclusion can be drawn that from 59 to 188°C the three coordinating water molecules break away from the complex. The experimental mass loss (%) of the first step was found to be 8.9%. The result is consistent with the theoretical mass loss, 11.9%, of the three water molecules. The second step of the mass loss from 262 to 904°C should be due to the glycine being separated from the \( \text{Nd}^{3+} \) cations, and the residue of the TG experiment should be \( \text{NdCl}_3 \) and \( \text{Nd} \). The experimental mass loss (%) of the decomposition is 52.8%, which is in accord with the theoretical mass loss, 48.6%. The possible mechanism of the thermal decompositions was deduced as

\[
\text{3Nd(Gly)}_2\text{Cl}_3 \cdot 3\text{H}_2\text{O} \xrightarrow{59–188°C, 8.9\% (11.9\%)} \text{3Nd(Gly)}_2\text{Cl}_3 \xrightarrow{262–904°C, 52.8\% (48.6\%)} \text{NdCl}_3 + 2\text{Nd}
\]
3.2.2. The standard molar enthalpy of formation of the complex Nd(Gly)$_2$Cl$_3$·3H$_2$O

The experimental values of the dissolution enthalpies of the mixture prepared at the mole ratio of the reactants were measured. Dissolution enthalpies $\Delta H_1$ and $\Delta H_2$ were determined by the dissolution process tested. The experiment was repeated five times in the same condition, and
The results were listed in Table 4. The enthalpy change \( \Delta r H^\theta_m \) could be calculated in accordance with expression (19) as follows:

\[
\Delta r H^\theta_m = \Delta s H_1 - \Delta s H_2 = -4.4718 - 10.3707 = (-14.8425 \pm 0.1512) \text{kJ} \cdot \text{mol}^{-1}
\]

The experimental values of the dissolution enthalpies of the reactants and products in the thermochemical cycle are combined with the following auxiliary thermodynamic data:

\[
\Delta f H^\theta_m (\text{NdCl}_3 \cdot 6\text{H}_2\text{O}, s) = -2867.5 \text{kJ} \cdot \text{mol}^{-1} \quad [49]
\]

\[
\Delta f H^\theta_m (\text{H}_2\text{O}, l) = -285.8 \text{kJ} \cdot \text{mol}^{-1} \quad [49]
\]

\[
\Delta f H^\theta_m (\text{Gly}, s) = -528.5 \text{kJ} \cdot \text{mol}^{-1} \quad [50]
\]

According to the expression (20), the standard molar enthalpy of formation of the complex \( \text{Nd(Gly)}^2\text{Cl}_3\cdot3\text{H}_2\text{O} \) (s) at 298.15 K can be calculated as follows:

\[
\Delta f H^\theta_m [\text{Nd(Gly)}^2\text{Cl}_3\cdot3\text{H}_2\text{O}, s] = (-3081.3 \pm 1.08) \text{kJ} \cdot \text{mol}^{-1}
\]

4. Microcalorimetric study on biological effect of rare-earth complex with amino acid: \( \text{La(Glu)(Im)}_6(\text{ClO}_4)_3\cdot4\text{HClO}_4\cdot4\text{H}_2\text{O} \)

4.1. Experiment

4.1.1. Synthesis and characterization of the complex

The complex, \( \text{La(Glu)(Im)}_6(\text{ClO}_4)_3\cdot4\text{HClO}_4\cdot4\text{H}_2\text{O} \), was synthesized in water solution. All the starting materials were analytical reagents from the Beijing Chemical Reagent Co. Rare-earth oxide (La\(_2\)O\(_3\)) was dissolved in an excess amount of perchloric acid, and the concentration of the solution was determined by EDTA (ethylene diamine tetraacetic acid) titrimetric analysis. Then solid glutamic acid was added to the solution of La\(^{3+}\) in molar ratio of La\(^{3+}\):Glu = 1:1. After the pH value of the reaction mixture was carefully adjusted to 6.0 by adding 0.1 mol\(\cdot\)L\(^{-1}\) NaOH slowly, imidazole was added as the same molar as glutamic acid. The reaction was performed at \(60^\circ\text{C}\) in water bath for 5 h. Then the solution was condensed at \(80^\circ\text{C}\) for 5 h and put into desiccator in the fridge at \(-4^\circ\text{C}\). The crystal was obtained after about one month.

An elemental analysis apparatus (Model PE-2400 II, USA) was used to measure the ratio of C, H, and N in the complex. Content of La % was determined by EDTA titration. The experimental values are: La, (9.423%), C (18.363%), N (12.964%) and H (2.736%), which are close to the theoretical values, La (9.057%), C (18.883%), N (12.452%) and H (2.805%). The sample formula

| No. | \( \Delta f H_1 \) | \( \Delta f H_2 \) |
|-----|---------------------|---------------------|
| 1   | 4.5298              | 10.3709             |
| 2   | -4.7254             | 10.3722             |
| 3   | -4.3564             | 10.3699             |
| 4   | -4.4486             | 10.3678             |
| 5   | -4.2986             | 10.3731             |
| Mean value | -4.4718 | 10.3707 |

Table 4. The determination results of the \( \Delta s H_1 \) and \( \Delta s H_2 \) at 298.15 K.
was determined to be La(Glu)(Im)₆(ClO₄)₃·4HClO₄·4H₂O, and the purity obtained from the EDTA titration under the same conditions was found to be 99.79%.

IR spectra were obtained using KBr pellets with a Tensor 27 (Bruker) spectrometer. It can be seen from the IR spectra of the complex that the symmetrical resonance frequencies, νₛ(COO⁻), shifted from 1431 to 1413 cm⁻¹, which suggests that the carboxyl group of Glu has coordinated to the metal ions.

4.1.2. The Escherichia coli (E. coli) DH5α

The E. coli DH5α was provided by Biomass Conversion Technology Group, Dalian Institute of Chemical Physics, CAS, Dalian 116023, PR China. The strain of E. coli DH5α was stored in 10% glycerol solution at −20°C.

The E. coli DH5α used in the present research was prepared as follows. A single colony of E. coli DH5α from LB (Luria-Bertani) plates was inoculated into a 10 mL LB culture medium and cultivated at 37°C in a rotary shaker (220 rpm) for 12 h under aerobic condition. Then, 200 μL of the above suspension was inoculated into 10 mL LB culture medium at 37°C in a rotary shaker (220 rpm) for 2.5 h once again. The value of optical density (OD) of the E. coli DH5α suspension was measured to be about 0.6 by spectrophotometry at λ = 600 nm. Per 200 mL of LB culture medium contained 2 g tryptone, 1 g yeast extract powder, 2 g and NaCl (pH 7.0–7.2). It was sterilized in high-pressure steam at 120°C for 20 min before experiment.

4.1.3. Microcalorimeter

Thermal Analysis Microcalorimeter (TAM) Air is a type of eight-channel twin isothermal microcalorimeters that originally was developed for the study of the hydration process of cement and concrete. TAM represents an ultra-sensitive heat flow measurement which is complementary to TA instruments differential scanning calorimeters (DSC). “Air” means the thermostat type. However, the high sensitivity and excellent long-term stability make TAM Air useful also for other applications such as stability testing of energetic materials, determining the shelf life of food and monitoring biological processes [51].

A TAM Air Isothermal Microcalorimeter (see Figure 13) manufactured by Thermometric AB Company of Sweden (incorporated by TA Instruments in 2006) was used to measure the power-time curves of the metabolism of E. coli DH5α at 37°C. The main structure of the instrument is eight channels, each of which consists of aluminum heat sink, vessel holder, and thermocouple plate, and each two of them are twin. Glass reaction vessel of 20 mL was used in each channel. The working temperature in the instrument was 5–60°C controlled by air thermostat. The deviation of the controlled temperature is within ±0.02°C. A computer was employed to record the voltage-time signals continuously which were converted to power-time signals through calibration. Thermal power detection limit was stated to be ±2 μW. The development and theory of many kinds of multi-channel isothermal microcalorimeters have been studied by Wadsö [52, 53].

The ampoule method was used for the microcalorimetric measurement in this work. Luria-Bertani (LB) culture medium (10 mL) containing object compound with different concentrations
was put into eight sample ampoules, which had been cleaned and sterilized. Then, the *E. coli* DH5α suspension was inoculated into the above eight ampoules. At last, the ampoules were sealed with ampulla cap by ampoule filler. The working temperatures of the calorimeter were set and controlled at 37°C. The power-time signals were recorded at intervals of 1 min.

The ampoule method was used for the microcalorimetric measurement in this work. LB culture medium (10 mL) containing object compound with different concentrations was put into eight sample ampoules, which had been cleaned and sterilized. Then, the *E. coli* DH5α suspension was inoculated into the above eight ampoules. At last the ampoules were sealed with ampulla cap by ampoule filler. The working temperatures of the calorimeter were set and controlled at 37°C. The power-time signals were recorded at intervals of 1 min.

4.2. Results and discussion

4.2.1. Thermokinetics

In the log phase of growth, the growth of *E. coli* DH5α cells is exponential [54]. It can be expressed as follows:

\[ n_t = n_0 \exp(kt) \]  \hspace{1cm} (21)

Where \( t \) is the incubation time, \( n_t \) is the cell number at time \( t \), \( n_0 \) is the initial cell number, and \( k \) is the constant of cell growth rate. If the power output of each cell is denoted as \( P_w \), then

\[ n_t P_w = n_0 P_w \exp(kt) \]  \hspace{1cm} (22)

We define \( P_0 \) as the initiative power output and \( P_t \) as the power output at time \( t \), then Eq. (2) can be rewritten as follows:
\[ P_t = P_0 \exp (kt) \]  \hspace{1cm} \text{(23)}

or

\[ \ln P_t = \ln P_0 + kt \]  \hspace{1cm} \text{(24)}

For thermokinetic parameters, inhibitory ratio \((I)\) is defined as:

\[ I = \frac{(k_0 - k_c)}{k_0}/100\% \]  \hspace{1cm} \text{(25)}

Where \(k_0\) is the rate constant of the control, and \(k_c\) is the rate constant of \(E. coli\) DH5α growth inhibited by the complex with a concentration of \(C\).

4.2.2. Thermokinetic parameters

Figures 14 and 15 show the growth power-time curves of \(E. coli\) DH5α under various concentrations (0–5.0 \(\mu\)g·mL\(^{-1}\)) of the complex at 37°C. It can be seen from the figures that growth curve of \(E. coli\) DH5α can be divided into four typical phases, which are lag phase, log phase, stationary phase, and decline phase. The thermokinetic parameters of growth, growth rate constants \((k/10^{-3}\text{·min}^{-1})\), the maximum heat power \((P_m/\mu\text{W})\), and the time of the maximum heat power \((t_m/\text{min})\) are derived from the curves by using Eqs. (1)–(5), and the results are listed in Tables 5 and 6.

The relationships among the concentration \((C)\), the rate constant \((k)\), and the maximum heat power \((P_m)\) were plotted in Figure 16 at different concentrations (0, 0.1, 0.5, and 1.0 \(\mu\)g·mL\(^{-1}\)) based on the data of Table 5. It can be seen from Figure 16 that the rate constant \((k)\) and the maximum heat power \((P_m)\) were both increasing with the increase of the concentration from

---

Figure 14. Growth curves of \(E. coli\) DH5α at different concentrations (0, 0.1, 0.5, and 1.0 \(\mu\)g·mL\(^{-1}\)) of the complex at 37°C.
0 to 0.5 μg mL⁻¹, which indicated that the complex could speed up the growth of *E. coli* DH5α. When the concentration (C) reached 0.5 μg mL⁻¹, the value of rate constant (k) showed a highest value. It demonstrated that the complex could promote clearly the growth of *E. coli*
DH5α at this time. At the concentration (C) from 0.5 to 1.0 μg mL⁻¹, the line decreased, which was consistent with Figure 17.

Figure 17 was plotted from the data of Table 6, when the concentration (C) was from 0.5 to 5.0 μg mL⁻¹. It showed that the rate constant (k) and the maximum heat power (Pₘ) were both decreasing with the increase of the concentration (C), which indicated that the complex inhibited the growth of E. coli DH5α at this range of concentrations (C). When the concentration reached 5.0 μg mL⁻¹, E. coli DH5α almost could not grow.
5. Conclusions

In this chapter, the following three rare-earth complexes with amino acids were synthesized and characterized by element analysis, infrared (IR) spectrum, and x-ray diffraction (XRD) analysis. The thermodynamic property studies on these complexes were performed. For the first rare-earth complex, Eu(Glu)(Im)₅(ClO₄)₃/Cl₆HClO₄/Cl₆H₂O, the low-temperature molar heat capacity was measured by adiabatic calorimetry. Two thermal abnormalities interpreted as phase transitions were discovered at 216.18 and 246.86 K by the AC technique, and proved by DSC. The thermodynamic functions \([H_T-H_{298.15}]\) and \([S_T-S_{298.15}]\) were derived in the temperature range from 80 to 320 K. The mechanism of thermal decomposition was deduced in terms of the results of TG. For the second rare-earth complex, Nd(Gly)₂Cl₃·3H₂O, the standard molar enthalpy of formation was determined to be \((−3081.3 \pm 1.08)\) kJ·mol⁻¹ by an isoperibol solution-reaction calorimeter in terms of a designed thermochemical cycle. For the third rare-earth complex, Eu(Glu)(Im)₅(ClO₄)₃·3HClO₄·6H₂O, the microcalorimetry was used to investigate the interaction between the complex and the Escherichia coli DH5α to elucidate the biological effects of the complex. The thermokinetic parameters of growth of the E. coli DH5α were obtained. The results show that the complex has a stimulatory effect on the growth of E. coli DH5α below the concentration 0.5 μg mL⁻¹, and the complex could inhibit its growth in the concentration range between 0.5 and 5.0 μg mL⁻¹.

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