

## MOLAR HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF CRYSTALLINE $\text{Ho}(\text{Asp})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$

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The molar heat capacity,  $C_{p,m}$ , of a complex of holmium chloride coordinated with *L*-aspartic acid,  $\text{Ho}(\text{Asp})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ , was measured from 80 to 397 K with an automated adiabatic calorimeter. The thermodynamic functions  $H_T - H_{298.15}$  and  $S_T - S_{298.15}$  were derived from 80 to 395 K with temperature interval of 5 K. The thermal stability of the complex was investigated by differential scanning calorimeter (DSC) and thermogravimetric (TG) technique, and the mechanism of thermal decomposing of the complex was determined based on the structure and the thermal analysis experiment.

**Keywords:** adiabatic calorimetry, *L*-aspartic acid, DSC, heat capacity,  $\text{Ho}(\text{Asp})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ , TG-DTG, thermal analysis

### Introduction

Rare earth elements have many unique properties and have been used in many areas, such as fertilizer, pesticide and antibacterial agent and so on. With these applications, rare earth elements are inevitably spread into food chain, and then into the bodies of human beings. In order to obtain information about the long-term effect of rare earth elements on people, the complexes of lanthanide ions with amino acids as ligands have been synthesised and extensively studied by a variety of methods [1–5], but only a few publications deal with thermodynamic investigation [6, 7].

As we know, the molar heat capacities  $C_{p,m}$  of compound at different temperature are basic physical data, from which many other thermodynamic properties such as enthalpy, entropy and Gibbs free energy which are important to both theoretical and practical purposes, can be calculated [8, 9]. Only with thermodynamic data we can quantitatively describe their properties of energetics, such as thermal stability and stable forms in different temperature, melting point and energy changing in different processes and so on.

In the present work, a complex of holmium aspartate chloride,  $\text{Ho}(\text{Asp})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ , was synthesised [10]. A self-made-adiabatic calorimeter was used to measure the molar heat capacity,  $C_{p,m}$ , of the complex from 80 to 397 K. Moreover, the thermodynamic functions,  $H_T - H_{298.15}$  and  $S_T - S_{298.15}$  were derived. The thermal stability of the complex was studied by DSC and TG analysis, and the mechanism of thermal decomposition was given on the base of its structure and the thermal analysis.

### Experimental

#### Sample preparation

The complex was synthesized according to [10]. The  $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$  was crystallized from a solution of holmium oxide in hydrochloric acid. The holmium aspartate chloride complex was prepared by dissolving  $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$  in excess in an acidic solution ( $1.4 < \text{pH} < 3.3$ ) of *L*-aspartic acid.

An element analysis apparatus (Model PE-2400 II, USA) was used to measure the C, H, N of the complex and Ho was determined by EDTA titration. Found: Ho (34.45%), C (10.10%), N (2.90%) and H (4.05%), close to the theoretical value: Ho (34.57%), C (10.07%), N (2.94%) and H (4.01%). The IR spectra of the complex which proved the formation of the chemical bond between the ions and atoms of  $\text{Ho}(\text{Asp})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ , were obtained from KBr pellets at room temperature using a Tensor 27 (Bruker) spectrophotometer. Combining with the IR spectrum of the complex, the sample formula was determined to be  $\text{Ho}(\text{Asp})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  and the purity was known as 99.65% obtained from EDTA titration in the same condition.

#### Methods

##### Adiabatic calorimetry

A precision automatic adiabatic calorimeter was used to measure the heat capacities of the compound over the temperature range between 78 and 400 K. The calorimeter was established in Thermochemistry

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Laboratory of Dalian Institute of Chemical Physics, Chinese Academy of Sciences, The structure and operation principle of the calorimeter have been described in detail elsewhere [11–13].

The adiabatic calorimeter mainly consisted of a sample cell with electric heater, a miniature platinum resistance thermometer, an inner and outer adiabatic shields with electric heater; two sets of six-junctions chromel-constantan thermopiles and a high vacuum can [14–16].

The sample cell was made of gold-plated copper with an inner volume of 6 cm<sup>3</sup>. The heater wire was bifilarly wound on the outside wall of the cell, in which there were four gold-plated copper vanes of 0.2 mm in thickness with X-shape to promote heat distribution. The thermometer (IPRT No. 2, fabricated by Shanghai Institute of Industrial Automatic Meters, 16 mm in length, 1.6 mm in diameter and a nominal resistance of 100  $\Omega$ , at 275.15 K) was inserted into a horizontal copper sheath soldered on the bottom of the sample cell. The thermometer was calibrated in terms of ITS-90 by the Station of Low-temperature Metrology and Measurements, Academia Sinica. The resistance of the thermometer was measured by a 7 1/2 Digit NanoVolt/Micro Ohm Meter, (Model 34420, Agilent, USA). The two sets of thermopiles were installed between the sample cell and the inner shield and between the inner and the outer shields, respectively. After the sample cell was loaded, sealed and evacuated, a little helium gas (0.1 MPa) was introduced into the cell through a capillary on the lid of the cell to enhance the heat transfer. Then, the capillary was pinched off and soldered from the end.

First, the vacuum can was evacuated to about 10<sup>-3</sup> Pa, then the sample cell was heated and the temperature difference between the cell and the inner shield was monitored by a set of differential thermocouples. The signal from the thermocouples was used to control the heating current through the heating wires distributed on the walls of the inner shields. The temperature difference between inner and outer shield was monitored by another set of thermocouples. Both shields were heated under the control of a Temperature Controller (Model 340, Lakeshore, USA) and kept at the same temperatures as that of the sample cell. The electrical energy introduced into the sample cell and the subsequent equilibrium temperature of the cell were automatically measured by a Data Acquisition/Switch Unit (Model 34970A, Agilent, USA) and the 7 1/2 Digit Nano Volt/Micro Ohm Meter, respectively. Both energy and temperature data were processed on line by a computer.

The heat capacity measurements were performed by the standard procedure of intermittently heating the sample and alternately measuring the temperature.

The heating rate was 0.1 to 0.4 K min<sup>-1</sup>; the temperature increments of each experimental point were between 1 and 4 K; the heating duration was 10 min and the temperature drift rates of the sample cell, which was measured in an equilibrium period, were kept within 10<sup>-3</sup> to 10<sup>-4</sup> K min<sup>-1</sup>.

Prior to the heat capacity measurement of the sample, the molar heat capacities of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (NIST, Standard Reference Material 720) were measured from 78 to 400 K to verify the reliability of the adiabatic calorimeter. The results showed that the deviation of our calibration data from those recommended by NIST [14] was within  $\pm 0.3\%$ .

In the present paper, the mass of Ho(Asp)Cl<sub>2</sub>·6H<sub>2</sub>O used for the heat capacity measurement was 0.7826 g, which was equivalent to 0.0016 mol on the base of its molar mass  $M=477.06$  g mol<sup>-1</sup>.

### Thermal analysis

Thermal analysis of Ho(Asp)Cl<sub>2</sub>·6H<sub>2</sub>O was performed using a Differential Scanning Calorimeter (DSC-141, Setaram, France) and a thermogravimetric analyzer (Model: DT-20B, Shimadzu, Japan).

The DSC test was carried out at the heating rate of 10 K min<sup>-1</sup> under high purity nitrogen with flowing rate of 50 mL min<sup>-1</sup>. The mass of the sample used in the experiment was 2.9 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 by the Joule effect. Measurement of the melting temperature and the enthalpy of fusion of benzoic acid (NIST, Standard Reference Material 39i) were made in our laboratory to check the accuracy of the instrument.

The TG measurement of the complex was conducted at the heating rate of 10 K min<sup>-1</sup> under high purity nitrogen with flow rate of 30 mL min<sup>-1</sup>. The mass of the sample used in the experiment was 9.9 mg. The reference crucible was filled with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The TG-DTG equipment was calibrated by the SRM in the thermal analysis, CaC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O(s).

## Results and discussion

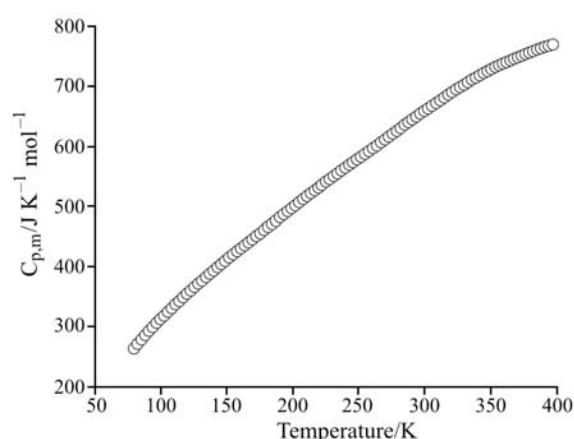
### *Heat capacity and thermodynamic functions*

The experimental molar heat capacities,  $C_{p,m}$ , and temperature,  $T$  of Ho(Asp)Cl<sub>2</sub>·6H<sub>2</sub>O, from 80 to 400 K were listed in Table 1 and plotted in Fig. 1.

From the figure it can be seen that the  $C_{p,m}-T$  curve is smooth and continuous; no any thermal anomaly occurred in the entire experimental temperature

**Table 1** The experimental molar heat capacities of Ho(Asp)Cl<sub>2</sub>·6H<sub>2</sub>O

| <i>T</i> /K | <i>C</i> <sub>p,m</sub> /J mol <sup>-1</sup> K <sup>-1</sup> | <i>T</i> /K | <i>C</i> <sub>p,m</sub> /J mol <sup>-1</sup> K <sup>-1</sup> | <i>T</i> /K | <i>C</i> <sub>p,m</sub> /J mol <sup>-1</sup> K <sup>-1</sup> | <i>T</i> /K | <i>C</i> <sub>p,m</sub> /J mol <sup>-1</sup> K <sup>-1</sup> |
|-------------|--|-------------|--|-------------|--|-------------|--|
| 81.991      | 270.39   | 160.390     | 431.36   | 239.671     | 565.27   | 320.758     | 691.85   |
| 84.935      | 277.77   | 163.279     | 436.16   | 242.706     | 570.25   | 323.805     | 696.34   |
| 87.792      | 285.35   | 166.136     | 441.17   | 245.519     | 574.49   | 326.788     | 700.12   |
| 90.563      | 292.35   | 169.071     | 445.96   | 248.550     | 579.18   | 329.827     | 704.16   |
| 93.420      | 298.63   | 172.056     | 451.70   | 251.602     | 583.60   | 332.781     | 708.07   |
| 96.320      | 305.66   | 175.108     | 456.22   | 254.567     | 588.29   | 335.820     | 712.64   |
| 99.144      | 311.92   | 178.074     | 461.93   | 257.597     | 593.00   | 338.775     | 716.06   |
| 102.043     | 318.50   | 181.108     | 466.88   | 260.645     | 597.77   | 341.745     | 719.71   |
| 105.011     | 325.18   | 184.069     | 471.80   | 263.688     | 602.17   | 344.712     | 723.53   |
| 107.905     | 331.24   | 187.035     | 476.95   | 266.732     | 607.61   | 347.667     | 726.91   |
| 110.779     | 337.67   | 190.000     | 482.49   | 269.775     | 612.36   | 350.545     | 730.25   |
| 113.580     | 343.19   | 192.944     | 487.45   | 272.736     | 617.28   | 353.519     | 733.89   |
| 116.450     | 349.53   | 195.909     | 492.46   | 275.693     | 622.00   | 356.390     | 736.66   |
| 119.416     | 355.46   | 198.788     | 497.38   | 278.740     | 626.76   | 359.344     | 739.39   |
| 122.294     | 360.72   | 201.671     | 502.37   | 281.619     | 631.68   | 362.130     | 742.11   |
| 125.173     | 366.79   | 204.545     | 507.67   | 284.654     | 637.11   | 365.028     | 744.92   |
| 128.009     | 372.11   | 207.597     | 512.83   | 287.532     | 641.30   | 367.814     | 747.47   |
| 130.923     | 377.32   | 210.563     | 517.60   | 290.498     | 646.06   | 370.697     | 749.93   |
| 133.896     | 383.27   | 213.506     | 522.81   | 293.463     | 650.66   | 373.636     | 752.50   |
| 136.861     | 388.74   | 216.472     | 527.35   | 296.580     | 655.80   | 376.494     | 755.14   |
| 139.762     | 394.23   | 219.264     | 531.95   | 299.632     | 659.99   | 379.385     | 757.69   |
| 142.657     | 399.58   | 221.667     | 536.25   | 302.511     | 664.14   | 382.294     | 760.38   |
| 145.518     | 405.02   | 224.957     | 541.96   | 305.563     | 668.86   | 385.338     | 762.93   |
| 148.463     | 410.13   | 227.836     | 546.21   | 308.680     | 673.43   | 388.216     | 765.21   |
| 151.472     | 416.11   | 230.866     | 551.13   | 311.732     | 678.04   | 391.177     | 767.58   |
| 154.459     | 421.22   | 233.745     | 555.72   | 314.762     | 682.57   | 394.139     | 769.43   |
| 157.468     | 426.31   | 236.710     | 560.67   | 317.812     | 687.55   | 397.264     | 771.36   |

**Fig. 1** Experimental molar heat capacity of Ho(Asp)Cl<sub>2</sub>·6H<sub>2</sub>O as a function of temperature

range, which indicates that the structure of the complex is stable from 80 to 400 K. On polynomial equations to describe the heat capacity as a function of temperature was obtained by the least-squares fitting from the experimental molar heat capacities (*C*<sub>p,m</sub>) and the experimental temperature (*T*),

$$C_{p,m} [\text{J K}^{-1} \text{mol}^{-1}] = 565.4 + 262.1x - 13.104x^2 - 13.995x^3 - 24.895x^4 + 5.1084x^5 - 9.3848x^6 \quad (1)$$

where *x* is the reduced temperature,  $x = (T [\text{K}] - 240)/160$ , *T* is the experimental temperature, 240 is obtained from polynomial  $(T_{\text{max}} + T_{\text{min}})/2$ , 160 is obtained from polynomial  $(T_{\text{max}} - T_{\text{min}})/2$ , *T*<sub>max</sub> and *T*<sub>min</sub> is the upper limit (400 K) and lower limit (80 K) of the above experimental temperature region. Correlation coefficient *R*<sup>2</sup> of least square fitting is 0.9999.

The deviations of the experiment heat capacities from the smoothed values were plotted in Fig. 2. From the figure it can be seen that the deviations were all within ±0.3%.

Thermodynamic functions *H*<sub>*T*</sub>–*H*<sub>298.15</sub> and *S*<sub>*T*</sub>–*S*<sub>298.15</sub> of the complex were calculated in the temperature range from 80 to 395 K with a temperature interval of 5 K in terms of the polynomials of heat capacity and the thermodynamic relationship, and listed in Table 2.

*Thermal analysis*

On the DSC curve (Fig. 3), an endothermal peak occurred from about 480 to 535 K, and another smaller endothermal peak appeared from about 619 to 667 K. At the same time, the TG curve (Fig. 4) showed that the complex lost its mass in two sequential stages: one was from about 480 to 538 K, the other began at about 600 K and ended at about 660 K. Seen from the DTG curve, the fastest rate of the two stages were at 514 and 637 K, respectively.

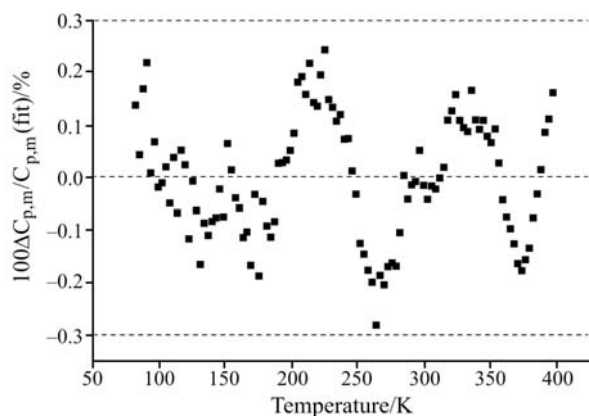
The structure of  $\text{Ho}(\text{Asp})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  has been reported in [10]. The structural model was refined to a final linear  $R$  value of 0.035 for 2582 reflections. The

$\text{Ho}^{3+}$  cations are eight-coordinated by five water oxygens and three carboxyl oxygens of three different aspartate moieties. The crystal structure consists of parallel polymeric chains of holmium-*L*-aspartate-hydrate. The chloride anions and the sixth, non-coordinating water molecule reside in the cavities between the chains, and stabilize the crystal packing by forming hydrogen bonds.

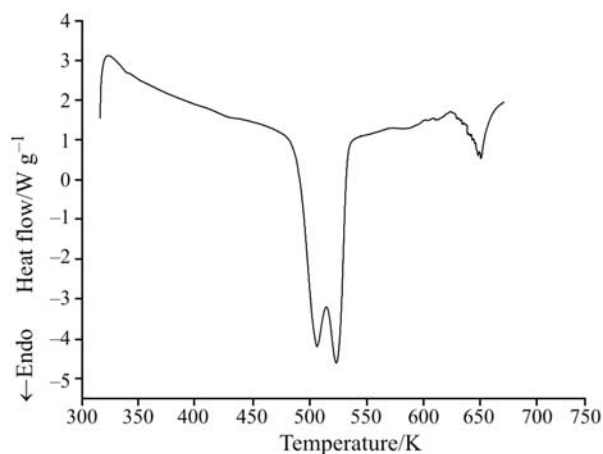
Associating the TG curve with the DSC curve and based on the structure of  $\text{Ho}(\text{Asp})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ , the conclusion can be drawn that from 480 to 538 K the six – non-coordinating water molecule, residing in the cavities between the chains, broke away from the complex. Since the experimental mass loss (%) of the first

**Table 2** The thermodynamic functions  $H_T - H_{298.15}$  and  $S_T - S_{298.15}$  of  $\text{Ho}(\text{Asp})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$

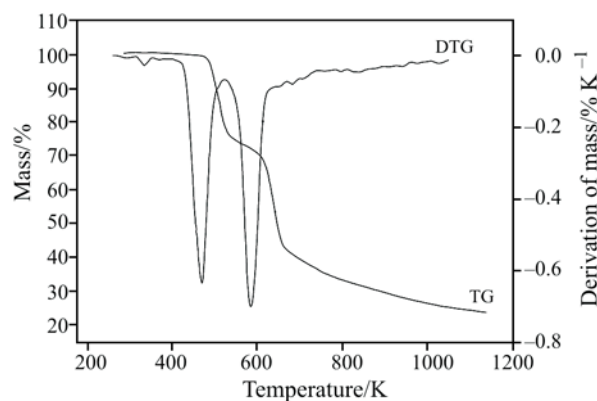
| $T/\text{K}$ | $C_{p,m}/\text{J mol}^{-1} \text{K}^{-1}$ | $H_T - H_{298.15}/\text{kJ mol}^{-1}$ | $S_T - S_{298.15}/\text{J mol}^{-1} \text{K}^{-1}$ | $T/\text{K}$ | $C_{p,m}/\text{J mol}^{-1} \text{K}^{-1}$ | $H_T - H_{298.15}/\text{kJ mol}^{-1}$ | $S_T - S_{298.15}/\text{J mol}^{-1} \text{K}^{-1}$ |
|--------------|---|---------------------------------------|--|--------------|---|---------------------------------------|--|
| 80           | 264.74                                    | -103.81                               | -571.58  | 245          | 573.58                                    | -32.753                               | -120.71  |
| 85           | 277.82                                    | -102.45                               | -555.03  | 250          | 581.73                                    | -29.865                               | -109.04  |
| 90           | 290.34                                    | -101.03                               | -538.73  | 255          | 589.85                                    | -26.936                               | -97.441  |
| 95           | 302.36                                    | -99.551                               | -522.68  | 260          | 597.93                                    | -23.966                               | -85.908  |
| 100          | 313.93                                    | -98.009                               | -506.86  | 265          | 605.97                                    | -20.956                               | -74.442  |
| 105          | 325.09                                    | -96.411                               | -491.26  | 270          | 613.97                                    | -17.906                               | -63.040  |
| 110          | 335.89                                    | -94.758                               | -475.90  | 275          | 621.92                                    | -14.817                               | -51.702  |
| 115          | 346.37                                    | -93.052                               | -460.74  | 280          | 629.81                                    | -11.687                               | -40.425  |
| 120          | 356.55                                    | -91.294                               | -445.80  | 285          | 637.63                                    | -8.5186                               | -29.210  |
| 125          | 366.48                                    | -89.486                               | -431.06  | 290          | 645.39                                    | -5.3110                               | -18.055  |
| 130          | 376.18                                    | -87.629                               | -416.51  | 295          | 653.06                                    | -2.0647                               | -6.9599  |
| 135          | 385.68                                    | -85.724                               | -402.15  | 298.15       | 657.85                                    | 0.0000                                | 0.0000   |
| 140          | 395.00                                    | -83.772                               | -387.96  | 300          | 660.65                                    | 1.2197                                | 4.0768   |
| 145          | 404.17                                    | -81.774                               | -373.95  | 305          | 668.14                                    | 4.5418                                | 15.055   |
| 150          | 413.20                                    | -79.730                               | -360.11  | 310          | 675.52                                    | 7.9011                                | 25.975   |
| 155          | 422.12                                    | -77.642                               | -346.42  | 315          | 682.78                                    | 11.297                                | 36.837   |
| 160          | 430.93                                    | -75.509                               | -332.89  | 320          | 689.91                                    | 14.729                                | 47.641   |
| 165          | 439.66                                    | -73.332                               | -319.50  | 325          | 696.90                                    | 18.196                                | 58.386   |
| 170          | 448.31                                    | -71.112                               | -306.25  | 330          | 703.73                                    | 21.698                                | 69.073   |
| 175          | 456.90                                    | -68.849                               | -293.13  | 335          | 710.38                                    | 25.234                                | 79.700   |
| 180          | 465.43                                    | -66.543                               | -280.14  | 340          | 716.84                                    | 28.802                                | 90.266   |
| 185          | 473.91                                    | -64.195                               | -267.27  | 345          | 723.10                                    | 32.402                                | 100.77   |
| 190          | 482.36                                    | -61.804                               | -254.52  | 350          | 729.13                                    | 36.033                                | 111.21   |
| 195          | 490.77                                    | -59.371                               | -241.89  | 355          | 734.90                                    | 39.694                                | 121.59   |
| 200          | 499.16                                    | -56.896                               | -229.35  | 360          | 740.41                                    | 43.382                                | 131.90   |
| 205          | 507.51                                    | -54.379                               | -216.92  | 365          | 745.62                                    | 47.098                                | 142.15   |
| 210          | 515.84                                    | -51.821                               | -204.59  | 370          | 750.51                                    | 50.839                                | 152.32   |
| 215          | 524.16                                    | -49.221                               | -192.36  | 375          | 755.04                                    | 54.603                                | 162.42   |
| 220          | 532.45                                    | -46.579                               | -180.21  | 380          | 759.20                                    | 58.390                                | 172.44   |
| 225          | 540.72                                    | -43.896                               | -168.15  | 385          | 762.94                                    | 62.196                                | 182.38   |
| 230          | 548.97                                    | -41.172                               | -156.17  | 390          | 766.22                                    | 66.019                                | 192.23   |
| 235          | 557.20                                    | -38.407                               | -144.28  | 395          | 769.02                                    | 69.858                                | 202.00   |
| 240          | 565.40                                    | -35.600                               | -132.46  |              |   |                                       |  |



**Fig. 2** The plot of relative deviations of the experimental molar heat capacity values  $C_{p,m}(\text{exp})$  from the fitted molar heat capacity values  $C_{p,m}(\text{fit})$  vs. temperature ( $T$ ).  
 $\{\Delta C_{p,m} = C_{p,m}(\text{exp}) - C_{p,m}(\text{fit})\}$



**Fig. 3** DSC curve of Ho(Asp)Cl<sub>2</sub>·6H<sub>2</sub>O

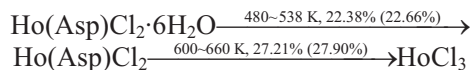


**Fig. 4** TG-DTG curve of Ho(Asp)Cl<sub>2</sub>·6H<sub>2</sub>O

step was 22.38 %, which was consistent with the theoretical mass loss (22.60%) of the six water molecules. The second step of the mass loss from 600 to 660 K should be due to the *L*-aspartate separated from the Ho<sup>3+</sup> cations, and the residue of the TG experiment

should be HoCl<sub>3</sub>, because the experimental mass loss (%) of the decomposition is 27.21%, which is in accord with the theoretical mass loss (27.90%).

In conclusion, the possible stoichiometry of the thermal decompositions should be as follows:



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