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Synthesis, Crystal Structure, and Thermal Decomposition Kinetics of the Complex of Ho 2,4-Dichlorobenzoic Acid and 2,2′-Bipyridine

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The complex $[Ho(2,4\text{-DClBA})_3bipy]_2$ (2,4-DClBA = 2,4-dichlorobenzoate; bipy = 2,2′-bipyridine) was synthesized and characterized by elemental analysis, infrared spectra, ultraviolet spectra, single-crystal X-ray diffraction, thermogravimetry, and differential thermogravimetry (TG-DTG) techniques. The crystal is monoclinic with space group $P2(1)/n$. The coordination number of the Ho^{3+} ion is nine. Two Ho^{3+} ions are connected via two bidentate bridging and two bidentate chelating−bridging modes. The thermal decomposition behavior of the title complex under a nitrogenous atmosphere was studied using the TG-DTG and IR techniques. The nonisothermal kinetics was investigated by using the Popescu method and the integral isoconversional nonlinear method (NL-INT). The mechanism function of the first decomposition step was determined. The thermodynamic parameters ($\Delta G^‡$, $\Delta H^‡$, and $\Delta S^‡$) were also calculated, and kinetic parameters (activation energy E and the pre-exponential factor A) were also obtained.

Introduction

Because thermal analysis plays an important role in several metallurgical materials and chemical processes,[1−3] many scholars and researchers have been investigating the thermal decomposition behavior and nonisothermal kinetics[4,5] recently. The results will provide some valuable information for the choice of the functional materials of rare-earth complexes. In particular, lanthanide complexes were used as photo/electroluminescent devices,[6] optical signal amplifiers,[7] and so on. Furthermore, special structures have also attracted great attention,[8−10] including monodentate, bidentate chelating, bidentate bridging, bidentate chelating−bridging, etc. In this work, a Ho(III) complex with 2,4-dichlorobenzoate and 2,2′-bipyridine was prepared. The propetries of the complex were investigated via elemental analysis, molar conductance, infrared spectra, ultraviolet spectra, single-crystal X-ray diffraction, and thermogravimetry (TG-DTG). On the basis of the studies of the thermal decomposition process, the nonisothermal kinetics of the complex $[Ho(2,4\text{-DClBA})_3bipy]_2$ has been investigated by the Popescu method[11] and the integral isoconversional nonlinear method (NL-INT).[12]

Experimental Section

Preparation of the Title Complex. The complex $[Ho(2,4\text{-DClBA})_3bipy]_2$ (2,4-DClBA = 2,4-dichlorobenzoate; bipy = 2,2′-bipyridine) was synthesized, and a single crystal was obtained according to our previous studies.[13−17] The element analysis is as follows: Anal. Calcd (%) for $Ho(2,4\text{-DClBA})_3bipy$: C, 41.74; H, 2.06; N, 3.16; Ho, 19.04. Found: C, 41.78; H, 1.92; N, 3.14; Ho, 18.51.

Chemicals and Apparatus. All the other reagents were used as received without further purification. Analysis of C, H, and N was carried out with a Vario-EL III element analyzer, while the metal content was assayed using an EDTA titration method. The IR spectra were recorded with a Perkin-Elmer FTIR-1730 spectrometer using the KBr pellet technique at room temperature in the range of (4000 to 400) cm^{-1}. The UV spectra were recorded on a Shimadzu 2501 spectrophotometer in DMSO (DMSO = dimethylsulfoxide). The molar conductance was determined with a Shanghai DDS-307 conductivity meter. The single-crystal X-ray diffraction data were obtained by an AFC10/Saturn724+ diffractometer at 293 K. Semiempirical absorption corrections were applied using the SADABS program. The structure was solved by direct methods using the SHELXS-97 program[18] and refined by full-matrix least-squares on F^2 using the SHELXL-97 program.[19] TG and DTG experiments for the title complex were performed using a Perkin-Elmer TGA7 thermogravimetric analyzer. The heating rate used was (3, 5, 7, 10, and 15) $K\cdot min^{-1}$ from ambient to 1173 K under a static air atmosphere.

Table 1. IR Absorption of the Ligands and the Complex (cm^{-1})

compounds	ν_{CN}	δ_{CC}	δ_{CH}	ν_{CO}	ν_{as} (COO^-)	ν_s (COO^-)	ν(RE−O)
bipy	1578	992	757	-	-	-	-
2,4-HDClBA					1699		
$[Ho(2,4\text{-DClBA})_3bipy]_2$	1588	1015	787	-	1619	1413	417

Results and Discussion

Infrared Spectra. The IR absorptions of the ligands and the complex are listed in Table 1. The characteristic band of the carboxylate group at 1699 cm^{-1} of the free ligand 2,4-DClBA disappears in the complex $[Ho(2,4\text{-DClBA})_3bipy]_2$. Asymmetric and symmetric absorption peaks at 1619 cm^{-1} and 1413 cm^{-1} appear in the spectra of the title complex. These facts indicate that the oxygen atoms of 2,4-dichlorobenzoic acid take part in coordination to the Ho^{3+} ion.[20] In addition, the appearance of the band of ν(Ho−O) at 417 cm^{-1} also indicates the oxygen atoms are coordinated to the Ho(III) ion. In a free bipy ligand, the bands of ν_{CN}, δ_{CC}, and δ_{CH} are at around 1578 cm^{-1}, 992

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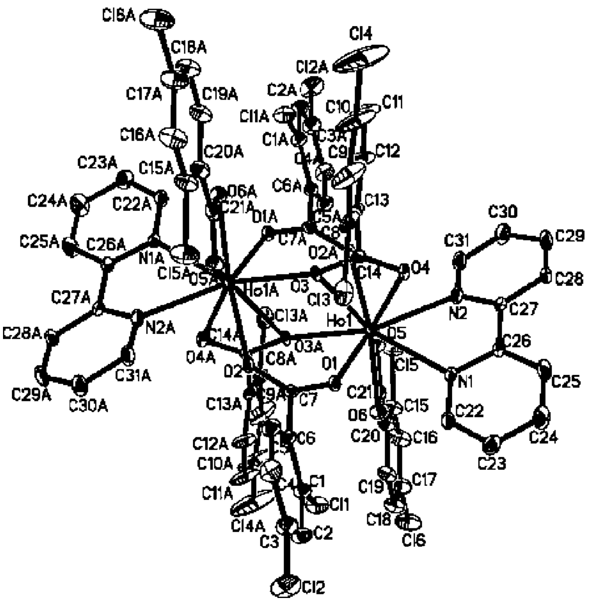

Figure 1. Molecular structure of the title complex.

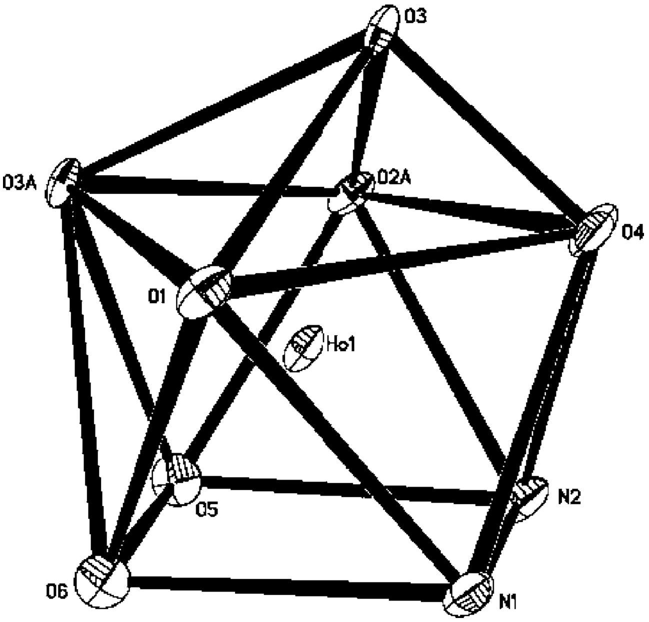

Figure 2. Coordination geometry of the Ho^{3+} ion.

cm^{-1}, and 757 cm^{-1} respectively. However, in the spectra of the complex, the characteristic absorptions of ν_{CN}, δ_{CC}, and δ_{CH} are at around 1588 cm^{-1}, 1015 cm^{-1}, and 787 cm^{-1}. Obviously, the characteristic absorption of the ligand shifts to higher wavenumbers, indicating that the nitrogen atoms of a bipy ligand are coordinated to the Ho^{3+} ion.[21]

Ultraviolet Spectra. The title complex and two ligands were dissolved in DMSO solution, with DMSO as a reference. The maximum peak of the free ligand 2,4-HDClBA is 260 nm, and the molar extinction coefficient is 0.02; the main absorption of the complex $[Ho(2,4\text{-}DClBA)_3bipy]_2$ is 285 nm. This fact can be explained by the fact that the free ligand was coordinated to the metal ion, and a π-conjugated system was formed.[22] Moreover, compared with the title complex, the maximum peak of bipy at 280 nm is similar to that in the complex $[Ho(2,4\text{-}DClBA)_3bipy]_2$, but the molar extinction coefficient is enhanced from 0.28 to 0.35, suggesting a bigger chelating ring is formed.

Crystal Structure Determination. Figure 1 shows the molecular structure of the complex $[Ho(2,4\text{-}DClBA)_3bipy]_2$. The title complex is a symmetrical dinuclear unit. Each Ho^{3+} ion is nine-coordinated by seven oxygen atoms, five from 2,4-dichlorobenzoate and two nitrogen atoms from 2,2′-bipyridine. Two Ho^{3+} ions were connected via two bridging bidentate carboxyl and two bidentate chelating−bridging groups. The coordination geometry of the Ho^{3+} ion has a capped square antiprism geometry, and the capping donor atom is the oxygen atom as shown in Figure 2.

The crystal and its associated refinement data are listed in Table 2. The selected bond distances and angles are given in Table 3. The distance of Ho−O is from 2.303(3) Å to 2.457(9) Å, and the average distance of Ho−O is 2.360 Å. The length of Ho−N bonds is in the range of (2.510(4) to 2.528(3)) Å with a mean bond length of 2.519 Å. Comparing the two distances, the bond energy of Ho−O is stronger than the Ho−N bond, which can be proved well by the thermal decomposition process.

Compared with $[Eu(2,4\text{-}DClBA)_3bipy]_2$,[23] they are both binuclear molecules and have the same crystal structure and ion coordination geometry. However, the average distance of the Ho−O and the mean bond distance of Ho−N in the title complex is slightly shorter than the corresponding average distance of the complex $[Eu(2,4\text{-}DClBA)_3bipy]_2$, which may be explained by the fact that the radius of Eu^{3+} is larger than that of Ho^{3+}.

Table 2. Crystal Data and Structure Refinement for the Title Complex

empirical formula	$C_{62}H_{34}Cl_{12}Ho_2N_4O_{12}$
formula weight	1782.19
temperature	293 K
wavelength	0.71073 Å
crystal system, space group	monoclinic, *P*2(1)/*n*
unit cell dimensions	$a = 11.791(4)$ Å, $b = 17.117(5)$ Å, $\beta = 107.173(7)°$, $c = 16.679(6)$ Å
volume	3216.2(19) Å^{-3}
Z, calculated density	2, 1.840 Mg·m Å^{-3}
absorption coefficient	3.006 mm^{-1}
F(000)	1736
crystal size	(0.27 × 0.23 × 0.20) mm
θ range for data collection	(3.03 to 27.51)°
limiting indices	$-15 \leqslant h \leqslant 14$, $-22 \leqslant k \leqslant 22$, $-21 \leqslant l \leqslant 17$
reflections collected/unique	26145/7338 [*R*(int) = 0.0499]
completeness to $\theta = 27.51$	99.2 %
absorption correction	empirical
max. and min. transmission	0.5847 and 0.5008
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	7338/5/456
goodness-of-fit on F^2	1.000
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0362$, w$R_2 = 0.0683$
R indices (all data)	$R_1 = 0.0460$, w$R_2 = 0.0726$
largest diff. peak and hole	1.511 and −1.286 e·Å^{-3}

Table 3. Selected Bond Lengths (Å) and Angles (deg) of the Title Complex[a]

Ho(1)−O(1)	2.303(3)	Ho(1)−N(2)	2.510(4)
Ho(1)−O(3)#1	2.315(9)	Ho(1)−N(1)	2.528(3)
Ho(1)−O(2)#1	2.338(3)	Ho(1)−O(3)	2.567(7)
Ho(1)−O(5)	2.366(3)	O(2)−C(7)	1.258(5)
Ho(1)−O(6)	2.380(3)	O(1)−C(7)	1.253(5)
Ho(1)−O(4)	2.457(9)	O(5)−Ho(1)−N(1)	106.20(11)
O(1)−Ho(1)−N(1)	76.00(11)	O(6)−Ho(1)−N(1)	73.61(11)
O(3)#1−Ho(1)−N(1)	146.2(2)	O(4)−Ho(1)−N(1)	71.6(3)
O(2)#1−Ho(1)−N(1)	137.91(11)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z + 1$.

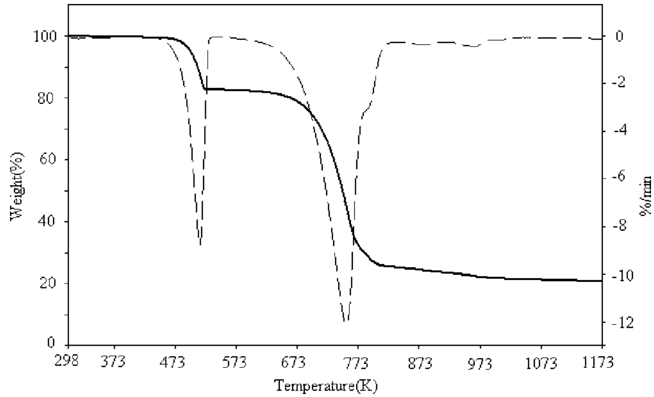

Figure 3. TG-DTG curves of the title complex at a heating rate of 15 K·min^{-1}.

Thermal Decomposition Process of the Title Complex. Figure 3 shows the TG-DTG curves of the title complex with a heating rate of 15 K·min^{-1}. The data of the thermal decomposition are listed in Table 4. As seen from the DTG curve, the thermal decomposition process of the title complex took place by two stages. In the temperature range of (417.41 to 575.49) K, a mass loss of 17.07 % (theoretical mass loss is 17.53 %) is equivalent to the loss of two 2,2′-bipyridines. The IR spectra of the intermediate residue at 575.49 K show the disappearance of the absorption band of C═N at 1588 cm^{-1}. The second stage occurs between (575.49 and 1058.75) K, which accounts for the loss of $C_{42}H_9Cl_{12}O_9$. As shown in the IR spectra of the residue, the bands of the asymmetric vibrations $\nu_{as}(COO^-)$ at 1619 cm^{-1} and symmetric vibrations $\nu_s(COO^-)$ at 1413 cm^{-1} disappear. Obviously, the temperature of loss of the bipy ligand is lower than that of the 2,4-dichlorobenzoate ligand, which can be proven by the bond distances of the complex. As mentioned above, the Ho−N (2.519 Å) bond distance is obviously longer than the Ho−O (2.360 Å) bond. The characteristic absorption band of the final residue is similar to the standard sample spectra of Ho_2O_3 in the IR spectra.[24] So the final residue is Ho_2O_3 with the total weight loss of 78.23 % (theoretical mass loss is 78.80 %). On the basis of the studies above, the thermal decomposition process of $[Ho(2,4\text{-}DClBA)_3bipy]_2$ can be expressed in the following way: $[Ho(2,4\text{-}DClBA)_3bipy]_2 \rightarrow [Ho(2,4\text{-}DClBA)_3]_2 \rightarrow Ho_2O_3$

Kinetics of the First Decomposition Stage. Popescu Method. Determination of f(α) and G(α). The relationship of the activation energy E and conversion α of the first decomposition stage for the title complex $[Ho(2,4\text{-}DClBA)_3bipy]_2$ is displayed in Figure 4. As seen from Figure 4, the E values keep change slightly with different conversion α. It can be concluded that the first decomposition process is a single-step reaction.[25] The probable mechanism function can be calculated using the Popescu method.

The main equations are given as follows

$$G(\alpha)_{mn} = \int_{\alpha_m}^{\alpha_n} \frac{d\alpha}{f(\alpha)} \tag{1}$$

$$I(T)_{mn} = \int_{T_m}^{T_n} K(T)\, dT \tag{2}$$

$$G(\alpha)_{mn} = \frac{1}{\beta} I(T)_{mn} \tag{3}$$

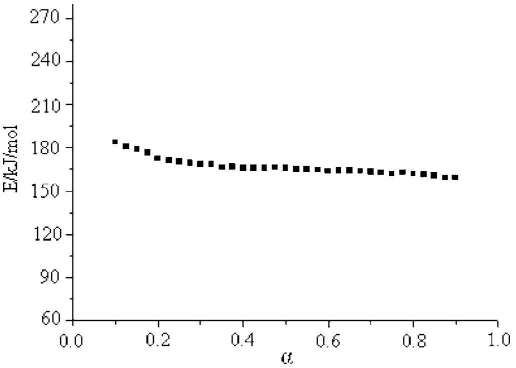

Figure 4. Relationship of E and conversion α of the first decomposition stage for the title complex.

Table 5. Conversion Degrees at the Same Temperature and at Various Heating Rates for the Complex $[Ho(2,4\text{-}DClBA)_3bipy]_2$ (Stage I)

	α				
T/K	$\beta = 3$ K·min^{-1}	$\beta = 5$ K·min^{-1}	$\beta = 7$ K·min^{-1}	$\beta = 10$ K·min^{-1}	$\beta = 15$ K·min^{-1}
475.04	0.1809	0.1299	0.1000	0.0988	0.0720
480.20	0.2719	0.1960	0.1500	0.1336	0.0780
484.14	0.3659	0.2654	0.2000	0.1696	0.1057
487.09	0.4500	0.3308	0.2500	0.2019	0.1286
489.64	0.5390	0.3990	0.3000	0.2359	0.1517

Table 6. Partial Results From the Popescu Method at Different Temperatures for the Complex $[Ho(2,4\text{-}DClBA)_3bipy]_2$ (Stage I)

T/K	function no.[a]	a	b	r
475.04 to 480.20	**1**	**−0.008116**	**0.148085**	**0.998458**
	6	−0.001331	0.021556	0.998000
	26	−0.007297	0.223047	0.988902
	37	−0.014238	0.516347	0.986730
	41	−0.053052	1.36773	0.994234
480.20 to 484.14	**1**	**−0.010120**	**0.208909**	**0.998195**
	6	−0.002129	0.034948	0.994842
	26	−0.003935	0.254047	0.997833
	37	−0.013802	0.649314	0.998636
	41	−0.084038	2.01391	0.995690
484.14 to 487.09	**1**	**−0.011158**	**0.241164**	**0.998866**
	6	−0.002931	0.046445	0.996856
	26	−0.003374	0.259984	0.992859
487.09 to 489.64	**1**	**−0.015217**	**0.311724**	**0.998512**
	6	−0.004855	0.070246	0.994149
	26	−0.005259	0.306172	0.993969

[a] The function no. is from Tables 6−10 in ref 26.

where α_m and α_n are two different degrees of conversion and T_m and T_n are their corresponding temperatures. The method assumes that the kinetics of the reaction does not change over certain ranges of α and β values. According to the experimental data, a pair of values of α, that is, $(\alpha_{m1}, \alpha_{n1})$, $(\alpha_{m2}, \alpha_{n2})$, ..., $(\alpha_{mi}, \alpha_{ni})$, will be determined, when $T = T_m$ and $T = T_n$, under different heating rates β. The conversion degrees at the same temperature and at various heating rates for the title complex are listed in Table 5.

By substituting α and β in Table 5 and various conversion functions[26] into eqs 1, 2, and 3 using the Popescu method, the intercept a, the slope b, and the linear correlation coefficient r were collected, and the partial results are listed in Table 6.

As shown in Table 6, the linear correlation coefficient r of the No. 1 function approaches 1, and the intercept a is close to zero. So, the No. 1 function is best. Then, the probable

Table 4. Thermal Decomposition Data for the Complex $[Ho(2,4\text{-}DClBA)_3bipy]_2$ (β = 15 K·min^{-1})

		mass loss rate/%			
temperature range (K)	DTG peak temperature (K)	TG	theory	probable composition of removed groups	intermediate
417.41 to 575.49	514.64	17.07	17.53	$2C_{10}H_8N_2$	$[Ho(2\text{-}Cl\text{-}4\text{-}FBA)_3]_2$
575.49 to 1058.75	753.80	61.16	61.27	$C_{42}H_9Cl_{12}O_9$	Ho_2O_3

Table 7. Temperatures of the Same Degree of Conversion at Different Heating Rates for the Complex [Ho(2,4-DClBA)$_3$bipy]$_2$ (Stage I)

	T (K)				
α	$\beta = 3$ K·min^{-1}	$\beta = 5$ K·min^{-1}	$\beta = 7$ K·min^{-1}	$\beta = 10$ K·min^{-1}	$\beta = 15$ K·min^{-1}
0.100	467.76	474.27	475.04	474.76	483.30
0.150	472.71	479.81	480.20	482.08	489.51
0.200	476.18	483.68	484.14	486.94	493.93
0.250	479.15	486.78	487.09	490.61	497.27
0.300	481.51	489.34	489.64	493.53	499.97
0.350	483.45	491.59	491.82	496.03	502.26
0.400	485.30	493.50	493.72	498.21	504.25
0.450	487.10	495.22	495.44	500.15	506.09
0.500	488.53	496.75	496.96	501.89	507.62
0.550	489.95	498.14	498.36	503.49	509.23
0.600	491.25	499.51	499.68	504.94	510.74
0.650	492.54	500.77	500.89	506.34	512.03
0.700	493.74	501.93	502.10	507.73	513.36
0.750	494.87	503.06	503.24	509.02	514.71
0.800	495.98	504.20	504.42	510.32	515.87
0.850	497.14	505.29	505.51	511.63	517.27
0.900	498.36	506.39	506.59	513.02	518.61

Table 8. Values of the Kinetic Parameters Computed by the Iterative Method for the Complex [Ho(2,4-DClBA)$_3$bipy]$_2$

$\alpha_n - \alpha_m$	E (kJ·mol^{-1})	E^a (kJ·mol^{-1})	A ·10^{13} min	A^a ·10^{13} min	r
0.4 to 0.15	159.93	160.76	941.81	1647.67	−0.995791
0.3 to 0.15	159.38		679.17		−0.994826
0.3 to 0.2	161.33		1173.94		−0.994116
0.5 to 0.2	162.69		2206.99		−0.995306
0.6 to 0.3	160.26		1420.21		−0.993774
0.7 to 0.4	161.44		2095.61		−0.991160
0.7 to 0.5	159.48		1351.96		−0.989241
0.7 to 0.6	162.37		2776.66		−0.988360
0.65 to 0.45	160.71		1767.51		−0.991860
0.8 to 0.6	159.21		1327.55		−0.989895
0.8 to 0.75	161.64		2382.98		−0.993040

[a] Average value of E and A.

mechanism function of the first decomposition stage is $g(\alpha) = a^2$, $f(\alpha) = a^{-1}/2$.

Calculation of E and A. The equation for the calculation of E and A is as follows

$$\ln\left[\frac{\beta}{T_n - T_m}\right] = \ln\left[\frac{A}{G(\alpha)_{mn}}\right] - \frac{E}{RT_\xi} \quad \left(T_\xi = \frac{T_m + T_n}{2}\right) \tag{4}$$

The values of temperature of the same conversion degree at different heating rates for the complex [Ho(2,4-DClBA)$_3$bipy]$_2$ are presented in Table 7.

By substituting all values and the mechanism function No. 1 into eq 4 and using the Popescu method with $\ln[\beta/(T_n - T_m)]$ versus $1/T_\xi$, on the basis of the value of the slope, the activation energy E was calculated, and the pre-exponential A was also obtained from the value of the intercept. The partial results are presented in Table 8.

The thermodynamic parameters of activation can be calculated from the equations[27,28]

$$A \exp(-E/RT) = \nu \exp(\Delta G^{\ddagger}/RT) \tag{5}$$

$$\Delta H^{\ddagger} = E - RT \tag{6}$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{7}$$

where ν is the Einstein vibration frequency; $\Delta G^{\ddagger}$ is the Gibbs energy of activation; $\Delta H^{\ddagger}$ is the enthalpy of activation; $\Delta S^{\ddagger}$ is the entropy of activation. The values of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ at the peak temperature of the first step reaction obtained based on eqs 5 to 7 are given in Table 9. Clearly, the values of $\Delta G^{\ddagger}$ are more than 0, indicating that the thermal decomposition reaction of the first stage for the title complex does not belong to a spontaneous reaction. The values of $\Delta H^{\ddagger}$ are more than 0, suggesting that the reaction is endothermic.

Table 9. Thermodynamic Parameters of the Title Complex

complex	β K·min^{-1}	$\Delta G^{\ddagger}$ kJ·mol^{-1}	$\Delta H^{\ddagger}$ kJ·mol^{-1}	$\Delta S^{\ddagger}$ J·mol^{-1}·K^{-1}	T_P K
[Ho(2,4-DClBA)$_3$bipy]$_2$	3	130.35	156.63	52.99	496.13
	5	130.27	156.62	52.96	497.62
	7	129.84	156.55	52.83	505.75
	10	129.62	156.52	52.76	509.90
	15	129.37	156.48	52.69	514.64
	an average value	129.89	156.56	52.85	504.81

Conclusions

The complex was synthesized by the reaction of HoCl$_3$·6H$_2$O, 2,4-dichlorobenzoic acid, and 2,2′-bipyridine. The crystal structure of the [Ho(2,4-DClBA)$_3$bipy]$_2$ shows that the carboxylic groups are coordinated to the Ho^{3+} ion with bidentate bridging and bidentate chelating−bridging. The coordination number is nine. The mechanism function of the first step for the complex [Ho(2,4-DClBA)$_3$(bipy)]$_2$ is $g(\alpha) = a^2$, $f(\alpha) = a^{-1}/2$. The activation energy E, the pre-exponential factor A, the enthalpy of activation $\Delta H^{\ddagger}$, the Gibbs energy of activation $\Delta G^{\ddagger}$, and the entropy of activation $\Delta S^{\ddagger}$ were also calculated.

Appendix

CCDC 748634 is the number of the Ho^{3+} complex, which contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_ request/cif.

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