SYNTHESIS, CRYSTAL STRUCTURE, AND THERMAL DECOMPOSITION KINETICS OF HOLMIUM WITH BENZOATE AND 2, 2'-BIPYRIDINE COMPLEX

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ABSTRACT

The complex [Ho(BA)₃bipy]₂ (BA=benzoate; 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 *P*2₁/*n*. The unit cell parameters are: *a*=14.1114(8) Å, *b*=15.3743(9) Å, *c*=25.8887(14) Å, β =103.555(2)°. Two Ho³⁺ ions are connected by four carboxylic groups through a bridging bidentate mode. The thermal decomposition behavior of the title complex under nitrogenous atmosphere was studied using the TG-DTG, and IR techniques. The non-isothermal kinetics was investigated by using the Popescu method and the integral iso-conversional non-linear method (NL-INT). The mechanism function of the first decomposition step was determined. The thermodynamic parameters ($\Delta G^\ddagger$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$) were also calculated, and kinetic parameters (activation energy *E* and the pre-exponential factor *A*) were also obtained.

Keywords: Ho(III) complex, Crystal structure, Thermal decomposition mechanism, Non-isothermal kinetics

INTRODUCTION

In recent years, the lanthanide carboxylic acid complexes have been attracting more and more attention due to their fascinating architectures and potential applications as luminescence, magnetism, catalysis, and gas separation.¹⁻⁵ Aromatic carboxylic acids and their derivatives have the multifunctional coordination sites with chelating and bridging ability. 1,10-phenanthroline(1,10-phen) and 2,2'-bipyridine(2,2'-bipy) are good nitrogen-containing ligands for lanthanide ions, which can enhance the stability of polymers and luminescent properties of resulting complexes. A survey of literature shows that crystal structures and luminescent properties on ternary lanthanide complexes (Ln= Sm, Eu, Tb, Dy, Nd, Gd, Er) containing benzoic and its derivatives and 1,10-phen or 2,2'-bipy have been investigated extensively.⁶⁻¹⁷ However thermal behaviour and non-isothermal kinetics of these complexes are rare in literatures. In material science, the investigation of thermal analysis for lanthanide aromatic carboxylic acids complexes is an important field. The study can get the relationship between the structures and stability, which can promote the coordination development structure.

In our previous works, a series of lanthanide carboxylate complexes were synthesized and characterized.¹⁵⁻¹⁹ Herein, the synthesis, crystal structure, thermal stability of the Ho(III) complex based on benzoic and 2,2'-bipy were reported. And The kinetic parameters such as activation energy *E* and the pre-exponential factor *A* have been calculated using both Popescu method²⁰ and the integral iso-conversional non-linear (NL-INT) method.²¹ The thermodynamic parameters $\Delta G^\ddagger$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of activation on the peak temperature were also calculated.

EXPERIMENTAL

Materials and apparatus

All the reagents were used from commercial sources without further purification. HoCl₃·6H₂O was prepared from Ho₂O₃ by treatment with concentrated hydrochloric acid.

Analyses of C, H, and N were performed on a Vario-EL III element analyzer, while the metal content was assayed using an EDTA titration method. The infrared spectra were recorded at room temperature in the range of 4000–400 cm⁻¹ using a Perkin-Elmer FTIR-1730 spectrometer with KBr disk technique. The ultraviolet spectra were recorded on a Shimadzu 2501 spectrophotometer in DMSO (DMSO= dimethylsulfoxide). TG and DTG experiments for the title complex were performed using a Perkin-Elmer TGA7 thermogravimetric analyzer with the heating rate of (3, 5, 10, and 15) K·min⁻¹ from ambient to 1173 K under nitrogenous atmosphere at a flow rate of 35 cm³min⁻¹.

The single crystal X-ray diffraction data were obtained by a FC10/Saturn724+ diffractometer at 293 K. Semi-empirical absorption corrections were applied using SADABS program. The structure was solved by direct

methods using SHELXS-97 program and refined by Full-matrix least-squares on *F*² using SHELXL-97 program. A semiempirical absorption correction with SADABS was applied.

Synthesis

The molar ratio of HoCl₃·6H₂O/HBA/bipy was 1:3:1. HoCl₃·6H₂O was dissolved in distilled water, and benzoic acid and 2,2'-bipyridine were dissolved in ethanol solution. The pH of the mixed ligands solution was controlled in a range of 6-7 with 1 mol·L⁻¹ NaOH solution. The complex was prepared by adding slowly the solution of the ligand to the solution of HoCl₃·6H₂O, with continuous stirring. The precipitates were washed with distilled water and ethanol solution, and dried in a desiccator. The single crystals were obtained by slow evaporation of the mother solution at room temperature after about two weeks. For C₆₂H₄₆Ho₂N₄O₁₂ anal. calcd, %: C 54.40, H 3.39, N 4.09; Ho 24.11; found, %: C 53.93, H 3.45, N 3.93, Ho 24.50

RESULTS AND DISCUSSION

IR spectra

The IR spectra of the free ligand HBA shows a strong absorption band at 1688 cm⁻¹, which are assigned to the stretch vibration of the carboxylate group. The antisymmetric and symmetric absorption peaks about at 1640 cm⁻¹ and 1416 cm⁻¹ appear in the spectra of the complex, indicating that only the oxygen atoms of ligand were involved in coordination to Ho³⁺ ion.¹⁵ In addition, the appearance of the band of ν(Ho-O) at 428 cm⁻¹ also indicates the conclusions above. The characteristic absorption bands of the free bipy ligand due to ν(CN) and δ(CH) appear at 1578, 992 and 757 cm⁻¹, respectively, which shift to long wave numbers (1599, 1013 and 774 cm⁻¹) after the formation of the title complex. The results clearly show that the nitrogen atoms of bipy ligand participate in the coordination to Ho³⁺ ion.¹⁶

UV spectra

The UV spectra of the title complex and two ligands were depicted with DMSO as a reference at room temperature. The maximum absorption peak of HBA ligand at 260 nm shifts to 280 nm after coordination. It may be caused by the π-conjugated system due to metal coordination.²² In addition, the maximum absorption peak of the title complex at 280 nm is the same as that of free bipy ligand, but the molar extinction coefficient in the same wavelength is greatly enhanced, suggesting a bigger chelating ring has been formed.

Crystallographic study

Crystal data and structure refinement details for the title complex are summarized in Table 1, and selected bond lengths and angles are shown in Table 2. The structure of the complex [Ho(BA)₃bipy]₂ is shown in Fig. 1. The molecular structure shows a center-related dinuclear unit. Each Ho³⁺ ion is eight-coordinated to two oxygen atoms from one bidentate chelating carboxyl group, four oxygen atoms from four bridging bidentate carboxyl groups, and two nitrogen atoms from one bipy molecule. It is similar to the reported isomorphous complexes [Ln(BA)₃bipy]₂ (Ln= Nd, Sm, Eu, Tb, Dy, Er).¹¹⁻¹⁶ The

coordination geometry of the Ho(III) center is a trigonal dodecahedron (Fig. 2.) consisting of O(4), O(6), O(8), O(10), O(11), O(12), N(3) and N(4). It is the same to the coordination geometries of complexes [Ln(BA)₃bipy]₂ (Ln= Nd, Sm, Eu, Tb, Dy). But the coordination geometry of complex [Er(BA)₃bipy]₂ is distorted square antiprisms due to the different symmetry.

The bond distances of Ho-O are in the range 2.267(2)-2.431(2) Å , while those of Ho-N are in the range 2.542(3)-2.592(3) Å. The average distance of Ho-O (the chelated carboxyl group, 2.397 Å) is longer than that of Ho-O (the bridging carboxyl group, 2.294 Å), maybe four-membered ring of chelating coordination has larger tension. Obviously, the distance between Ho and O atom is shorter than the length of Ho-N bond. So, the bond energy of Ho-O is stronger than Ho-N bond, which is in good agreement with the results of thermal decomposition process. Compared with the length of Ln-O and Ln-N in the complexes of [Ln(BA)₃bipy]₂ (Ln= Nd, Sm, Eu, Tb, Dy, Ho, Er), the Ln-O and Ln-N bond distances are shrinking From Nd to Er. This may be related to the shorter radius with the increment of atomic number caused by the result of lanthanide contraction. The average distances of Ho-O and Ho -N in this work are somewhat shorter than those of [Ho(BA)₃phen]₂¹⁸ due to stronger steric hindrance effect of phen than that of bipy.

Parameter	Data
Empirical formula	C ₆₂ H ₄₆ Ho ₂ N ₄ O ₁₂
Formula weight	1368.89
Temperature	293 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2₁/n
Unit cell dimensions	$a=14.0771(16)\text{\AA}$, $\alpha=90^\circ$ $b=15.1839(16)\text{\AA}$, $\beta=103.555(2)^\circ$ $c=25.672(3)\text{\AA}$, $\gamma=90^\circ$
Volume	$5334.5(10)\text{\AA}^3$
Z, Calculated density	4, 1.704 Mg/m $\text{\AA}^3$
Absorption coefficient	3.015 mm^{-1}
F(000)	2704
Crystal size	$0.30\times0.27\times0.23\text{ mm}$
Theta range for data collection	$(3.04\text{ to }27.50)^\circ$
Limiting indices	$-18\leq h\leq18$, $-16\leq k\leq19$, $-32\leq l\leq33$
Reflections collected / unique	43296 / 12169 [R(int) = 0.0335]
Completeness to $\theta=27.50$	99.3 %
Absorption correction	Empirical
Max. and min. transmission	0.5401 and 0.4649
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	12169 / 0 / 721
Goodness-of-fit on F ²	1.006
Final R indices [I>2 σ (I)]	$R_1=0.0298$, $wR_2=0.0675$
R indices (all data)	$R_1=0.0320$, $wR_2=0.0691$
Largest diff. peak and hole	0.953 and -0.645 e. $\text{\AA}^{-3}$

Table 2. Selected bond lengths (Å) and angles(°) of the title complex

Ho(1)-O(4)	2.267(2)	Ho(1)-N(4)	2.542(3)
Ho(1)-O(8)	2.268(2)	Ho(1)-N(3)	2.592(3)
Ho(1)-O(10)	2.308(2)	O(2)-C(7)	1.271(4)
Ho(1)-O(6)	2.332(2)	O(1)-C(7)	1.254(4)
Ho(1)-O(11)	2.362(2)	Ho(1)-O(12)	2.431(2)
O(4)-Ho(1)-N(4)	93.92(8)	O(8)-Ho(1)-O(10)	78.98(8)
O(8)-Ho(1)-N(4)	141.88(8)	O(4)-Ho(1)-O(6)	78.09(8)
O(10)-Ho(1)-N(4)	75.68(8)	O(8)-Ho(1)-O(6)	77.48(7)
O(6)-Ho(1)-N(4)	139.02(8)	O(10)-Ho(1)-O(6)	138.14(7)
O(11)-Ho(1)-N(4)	85.06(8)	O(4)-Ho(1)-O(11)	147.37(8)
O(12)-Ho(1)-N(4)	73.03(8)	O(8)-Ho(1)-O(11)	92.51(8)
O(10)-Ho(1)-O(12)	79.33(8)	O(10)-Ho(1)-O(11)	133.75(8)
O(6)-Ho(1)-O(12)	125.82(7)	O(6)-Ho(1)-O(11)	81.49(7)
O(11)-Ho(1)-O(12)	54.75(7)	O(4)-Ho(1)-O(12)	154.87(8)

Figure 1. The molecular structure of the title complex

Figure 2. Coordination geometry of Ho³⁺ ion

Thermogravimetric analysis
Fig.3 shows the thermoanalytical curves of the title complex at a heating

rate of $15 \text{ K} \cdot \text{min}^{-1}$ under nitrogenous atmosphere. As shown from the DTG curve, in the temperature range 413.84–508.26 K, the experimental loss weight ($w=23.17\%$) was in good agreement with the loss of 2 bipy molecules. The second step took place between 508.26 K and 750.28 K, and a part of $\text{C}_6\text{H}_5\text{COO}^-$ was lost. The third stage began at 750.28 K and ended at 1020.22 K, which was the loss of residual $\text{C}_6\text{H}_5\text{COO}^-$. Obviously, the loss of bipy ligand is earlier than that of benzoic acid ligand, which can be demonstrated by the bonds distance of the complex. The IR spectra of the intermediate residue at 573 K shows the disappearance of absorption band of $\text{C}=\text{N}$ at 1599 cm^{-1} . The characteristic absorption band of the final residue is similar to the standard sample spectra of Ho_2O_3 . Therefore, by 1020.22 K, complex $[\text{Ho}(\text{BA})_3\text{bipy}]_2$ is completely degraded into Ho_2O_3 with the total weight loss of 72.53% (the theoretical mass loss is 72.40%). Based on the analysis above, the thermal decomposition process of $[\text{Ho}(\text{BA})_3\text{bipy}]_2$ can be expressed in the following ways:

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

Non-isothermal thermoanalysis kinetics

The dependence of the activation energy E on conversion α of the first decomposition stage by using integral isoconversional non-linear method is displayed in Fig. 4. As shown in Fig. 4, the values of the activation energy E remain almost constant with different conversion α . It can be concluded that the first decomposition process is a single step reaction.²³ So the probable mechanism function can be obtained by means of Popescu method.

Figure 4. The relationship of E and α of the first decomposition stage of the complex

Popescu Method

The determination of $f(\alpha)$ and $G(\alpha)$

The Popescu method was applied to study the kinetics of the thermal decomposition process of the title complex. The main equations are described as follows

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

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

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

Where α_m, α_n are two different degrees of conversion and T_m, 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, $(\alpha_{m1}, \alpha_{n1}), (\alpha_{m2}, \alpha_{n2}), \dots, (\alpha_{mi}, \alpha_{ni})$ will be determined, when $T=T_m$ and $T=T_n$, under different heating rates β . The values of conversion degrees at the same temperature on four TG curves at different heating rates for the title complex are shown in Table 3. By substituting the values of α and β in Table 3, and 41 mechanism functions²⁴ into Eqs(1,2,3), then the intercept a , the slope b and the linear correlation coefficient r were obtained by Popescu method. The partial results are listed in Table 4.

Table 3. Conversion degrees at the same temperature and at various heating rates of the complex (Stage I)

T/K	α			
	$\beta=3 \text{ K} \cdot \text{min}^{-1}$	$\beta=5 \text{ K} \cdot \text{min}^{-1}$	$\beta=10 \text{ K} \cdot \text{min}^{-1}$	$\beta=15 \text{ K} \cdot \text{min}^{-1}$
455.04	0.2529	0.1795	0.0949	0.0703
459.35	0.3776	0.2662	0.1376	0.1021
462.53	0.4995	0.3519	0.1821	0.1325
465.02	0.6038	0.4357	0.2257	0.1654
467.23	0.7078	0.5200	0.2714	0.1961

Table 4. Partial results by Popescu method at different temperatures of the complex (Stage I)

T/K	Function No*	a	b	r
	1	-0.015910	0.287309	0.997704
	5	0.022364	0.173980	0.992889
455.02-459.33	15	0.157280	0.492387	0.997632
	17	-0.029100	0.600640	0.997585
	27	-0.015910	0.280480	0.997704
	1	-0.021400	0.390332	0.998325
	5	0.018195	0.166440	0.994438
459.33-462.51	15	0.008144	0.551827	0.999535
	17	-0.050290	0.899769	0.995401
	27	-0.021400	0.381215	0.998325
	1	-0.018860	0.405867	0.997641
462.51-465.00	15	0.010107	0.950669	0.997219
	17	-0.064270	1.116903	0.996024
	1	-0.027350	0.492473	0.983438
465.00-467.21	15	-0.004560	0.688856	0.999798
	17	-0.112980	1.708084	0.991990

*The function No. is from Tables 6-10 in ref 24

As seen from Table 4, the intercept a and the linear correlation coefficient r of the function No.15 is best. Then the probable mechanism function of the first decomposition stage is $g(\alpha)=[-\ln(1-\alpha)]^{3/4}$, $f(\alpha)=3/4(1-\alpha)[-\ln(1-\alpha)]^{1/4}$.

The calculation of E and A

The equation is as follow

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

The values of temperature at the same degree of conversion for the different heating rates are listed in Table 5. By substituting of the values and the corresponding mechanism function into Eq.(4). Via the Popescu method with $\ln\left[\frac{\beta}{T_n - T_m}\right]$ versus $1/T_\xi$, the activation E was obtained based on the value

of the slope and the pre-exponential A was also calculated from the value of the intercept. The partial results are presented in Table 6, which are approached to the values of the activation energy by NL-INT method as shown in Fig. 4.

Table 5. Temperatures of the same degree of conversion at different heating rates of the complex (Stage I)

α	$T(K)$			
	$\beta=3 \text{ K}\cdot\text{min}^{-1}$	$\beta=5 \text{ K}\cdot\text{min}^{-1}$	$\beta=10 \text{ K}\cdot\text{min}^{-1}$	$\beta=15 \text{ K}\cdot\text{min}^{-1}$
0.100	445.44	448.60	455.69	459.21
0.150	449.69	453.16	460.32	463.96
0.200	452.53	456.21	463.61	467.38
0.250	454.89	458.65	466.28	469.98
0.300	456.79	460.69	468.50	472.16
0.350	458.49	462.46	470.36	473.83
0.400	459.98	464.06	472.05	475.82
0.450	461.34	465.43	473.55	477.43
0.500	462.58	466.78	474.99	478.85
0.550	463.8	467.97	476.42	480.28
0.600	464.93	469.15	477.74	481.45
0.650	465.98	470.26	478.95	482.75
0.700	467.04	471.35	480.09	484.03
0.750	468.07	472.44	481.28	485.03
0.800	469.19	473.59	482.58	486.35
0.850	470.36	474.78	483.92	487.79
0.900	471.54	476.09	485.42	489.28

Table 6. The values of the kinetic parameters obtained by the Popescu method of the complex

$\alpha_n - \alpha_m$	$E/$ (kJ·mol ⁻¹)	$E^a/$ (kJ·mol ⁻¹)	$A/\times 10^{15}$ min	$A^a/\times 10^{15}$ min	r
0.2-0.1	170.39	164.58	4161.61	1522.53	-0.99797
0.3-0.1	170.22		3918.02		-0.99741
0.4-0.2	167.23		1627.46		-0.99760
0.8-0.2	162.02		476.33		-0.99641
0.5-0.3	163.10		546.04		-0.99794
0.4-0.3	165.48		997.00		-0.99828
0.5-0.4	160.67		290.29		-0.99760
0.6-0.4	160.52		282.77		-0.99509
0.6-0.5	160.29		266.22		-0.99186
0.75-0.7	170.20		3874.48		-0.98897
0.8-0.7	160.29		307.66		-0.99336

^a Average value of E and A .

The thermodynamic parameters of activation can be calculated from the equations:²⁵⁻²⁶

$$A \exp(-E/RT) = \exp(-\Delta G^\ddagger/RT) \quad (5)$$

$$\Delta H^\ddagger = E - RT \quad (6)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (7)$$

Where n is the Einstein Vibration frequency, $\Delta G^\ddagger$ is the Gibbs free enthalpy of activation, $\Delta H^\ddagger$ is the enthalpy of activation, $\Delta S^\ddagger$ is entropy of activation. The values of $\Delta G^\ddagger$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ at the peak temperature obtained based on the Eqs. (5)-(7) are given in Table 7. The values of $\Delta G^\ddagger$ are more than 0, suggesting that the thermal decomposition reaction of the first step for the title complex is not spontaneous. The values of $\Delta H^\ddagger$ are more than 0, indicating that the reaction belongs to endothermic reaction.

Table 7. The thermodynamic parameters of the complex

Complex	$\beta/\text{K}\cdot\text{min}^{-1}$	$\Delta G^\ddagger/$ kJ·mol ⁻¹	$\Delta H^\ddagger/$ kJ·mol ⁻¹	$\Delta S^\ddagger/$ J·mol ⁻¹ ·K ⁻¹	T_p/K
[Ho(BA) ₃ bipy] ₂	3	118.04	160.69	91.14	467.95
	5	117.66	160.65	91.07	472.13
	10	116.90	160.58	90.92	480.44
	15	116.61	160.56	90.87	483.68
	Average value	117.30	160.62	91.00	476.05

CONCLUSION

In summary, the complex [Ho(BA)₃(bipy)]₂ was synthesized and characterized. The crystal structure shows that the carboxylic groups coordinated to Ho³⁺ ion with bidentate bridging and bidentate chelating modes. The coordination number is eight. The mechanism function of the first step for the complex is $g(\alpha)=[-\ln(1-\alpha)]^{3/4}$, $f(\alpha)=3/4(1-\alpha)[-\ln(1-\alpha)]^{1/4}$. The activation energy E , the pre-exponential factor A , the enthalpy of activation $\Delta H^\ddagger$, the Gibbs free energy of activation $\Delta G^\ddagger$ and the entropy of activation $\Delta S^\ddagger$ were also calculated.

Supplementary Information

CCDC 711417 is number of Ho³⁺ 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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