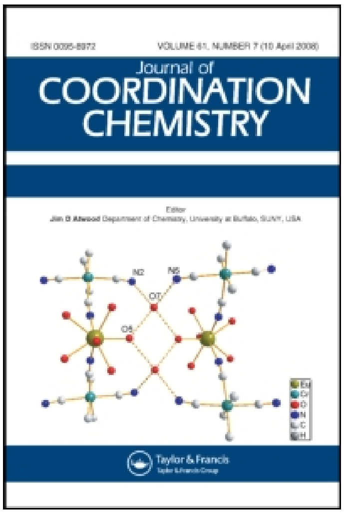

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Synthesis and thermal decomposition kinetics of Er(III) complex with unsymmetrical Schiff-base ligand

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A new unsymmetrical, solid, Schiff base (H_2LLi) was synthesized using L-lysine, o-vanillin and salicylaldehyde. An Er(III) complex of this ligand $[Er(H_2L)(NO_3)](NO_3)\cdot 2H_2O$ was prepared and characterized by elemental analysis, IR, UV and molar conductance. The thermal decomposition kinetics of the complex for the second stage was studied under non-isothermal conditions by TG and DTG methods. The kinetic equation may be expressed as, $d\alpha/dt = A\cdot e^{-E/RT}\cdot 1/2(1-\alpha)[-\ln(1-\alpha)]^{-1}$. The kinetic parameters (E, A), activation entropy $S^{\neq}$ and activation free-energy $G^{\neq}$ were also determined.

1. Introduction

Some Schiffbase complexes derived from amino acids are particularly active in biology. Studies of such metal complexes of mono-Schiff bases have been reported [1–4]. To continue the investigation, a new unsymmetrical Schiff-base ligand has been synthesized starting from L-lysine, o-vanillin and salicylaldehyde by a new method. This article deals with the preparation and characterization of the complex formed from this Schiff-base ligand with Er(III). The thermal decomposition of $[Er(H_2L)(NO_3)](NO_3)\cdot 2H_2O$ by TG-DTG is described in this article and the corresponding non-isothermal kinetics are discussed. The kinetic equation of thermal decomposition for the complex and the corresponding kinetic parameters were determined. This article offers a new method to prepare unsymmetrical Schiff bases of significance in the fields of biology and catalysis.

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2. Experimental

2.1. *Reagents*

All reagents used in this work were analytical grade.

2.2. *Preparation of the ligand*

Mono-Schiff base (HR): L-lysine (2.193 g, 15 mmol) was dissolved in 230 mL anhydrous ethanol and methanol in the proportion of 1 : 1 (v/v) and heated for 1.5 h at 55–50°C, and then filtered. o-Vanillin (2.282 g, 15 mmol) dissolved in 40 mL of hot ethanol was added dropwise to the filtered solution and stirred for 2 h at 50–55°C to give a light yellow precipitate. The precipitate was collected by filtration, washed with ethanol and dried in vacuum. Yield, 2.943 g (70%); m.p. 232–234°C.

Unsymmetrical Schiff base (H_2LLi): HR (1.402 g, 5.0 mmol) and lithium hydroxide (0.120 g, 5.0 mmol) were dissolved in 60 mL anhydrous methanol and isopropanol in the proportion of 1 : 5 (v/v) and stirred for 1 h at 50–55°C. Salicylaldehyde (0.6 mL, 5.0 mmol) dissolved in 10 mL isopropanol was added dropwise to the above solution and stirred for 4 h at 50–55°C to give a yellow precipitate. The precipitate was collected by filtration, washed with ethanol and dried in vacuum. The yield of the Schiff base (H_2LLi) was 1.405 g (72%) and the purity was higher than 99%. Calculated for $C_{21}H_{23}N_2O_5Li$ (390.4): C, 64.59; H, 5.04; N, 7.18, Found: C, 63.18; H, 5.91; N, 7.20%.

2.3. *Preparation of the complex*

The unsymmetrical Schiff base (1.717 g, 3.0 mmol) dissolved in 65 mL anhydrous methanol and isopropanol in the proportion of 1 : 5 (v/v) was mixed with Er $(NO_3)_3 \cdot 6H_2O$ (1.384 g, 3.0 mmol) dissolved in 15 mL anhydrous ethanol and stirred for 3 h at 50–55°C to give yellow precipitate. The precipitate was filtered, recrystallized with anhydrous methanol and isopropanol in the proportion of 1 : 5 (v/v), and dried in vacuum. The yield of the complex was 1.745 g (68%) and the purity was higher than 99%. Calculated for $C_{21}H_{27}N_4O_{13}Er$ (710.8): C, 35.48; H, 3.83; N, 7.88; Er, 23.54, Found: C, 35.97; H, 3.75; N, 7.73; Er, 23.59%.

2.4. Physical measurement

Elemental analyses were carried out with a model 2400 Perkin-Elmer analyzer. The metal content was determined gravimetrically. The ultraviolet spectra were recorded on a Shimadzu UV-3000 spctrophotometer in DMSO. The molar conductance was measured with a Shanghai DDS-11A conductivity meter. Infrared spectra of the ligand and complex were recorded in KBr pellets using a Bio-Rad FTS 165 spectrophotometer. Thermogravimetric measurements were made using a Perkin-Elmer TGA7 instrument. The heating rate was programmed to be $10\,C\,min^{-1}$ with a protecting stream of N_2 flowing at a rate of $40\,mL\,min^{-1}$. The mass spectrogram of the ligand was recorded on a Finnegan MAT-212 mass spectrometer.

3. Results and discussion

The reaction activity and steric hindrance of the two $-NH_2$ in L-lysine is different with the $-NH_2$ in α seat having higher activity than the $-NH_2$ in ε seat because of the induced effect of $-COO^-$ in L-lysine. When the molar ratio of L-lysine and o-vanillin was 1 : 1, the o-vanillin reacted with the $-NH_2$ in α seat first forming the mono-Schiff base. Then the mono-Schiff base reacted with salicylaldehyde forming the unsymmetrical di-Schiff base. The synthesis reactions of the ligand are shown in figure 1. The synthesis of the complex may be represented as:

$$Er(NO_3)_3 \cdot xH_2O + H_2LLi = [Er(H_2L)(NO_3)](NO_3) \cdot 2H_2O + LiNO_3 + (x-2)H_2O$$

The molar conductance value of the complex determined in DMSO is $73.4\,S \cdot cm^2 \cdot mol^{-1}$, which is expected for 1 : 1 electrolytes [5]. This suggests that one nitrate ion is within the coordination sphere and the second is ionic and not coordinated. The complexes are stable in air and soluble in DMSO and DMF; however they are insoluble in diethyl ether, benzene, and acetone.

3.1. *Mass spectrum*

The mass spectrum of H_2LLi is shown in figure 2. The molecular weight of H_2LLi is 390, which indicates that the reaction product of L-lysine with o-vanillin and salicylaldehyde is an unsymmetrical di-Schiff base.

3.2. *IR spectra*

The shift of $\nu(C{=}N)$ from $1635.3\,cm^{-1}$ in the ligand to $1647.2\,cm^{-1}$ in the complex, suggests formation of a C=N–Er bond. The $\nu(Ar{-}O)$ of H_2LLi occurs at $1229.7\,cm^{-1}$; the shift to lower frequency (about $10\,cm^{-1}$) in the complex indicates the coordination

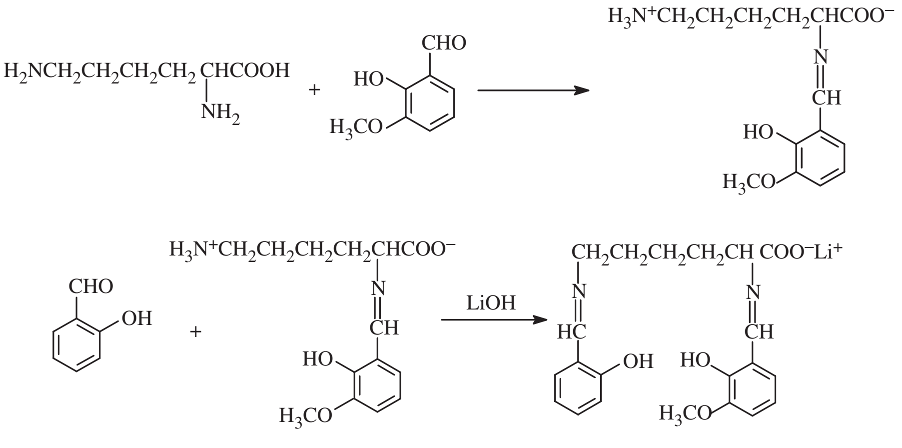

Figure 1. Preparation of the ligand.

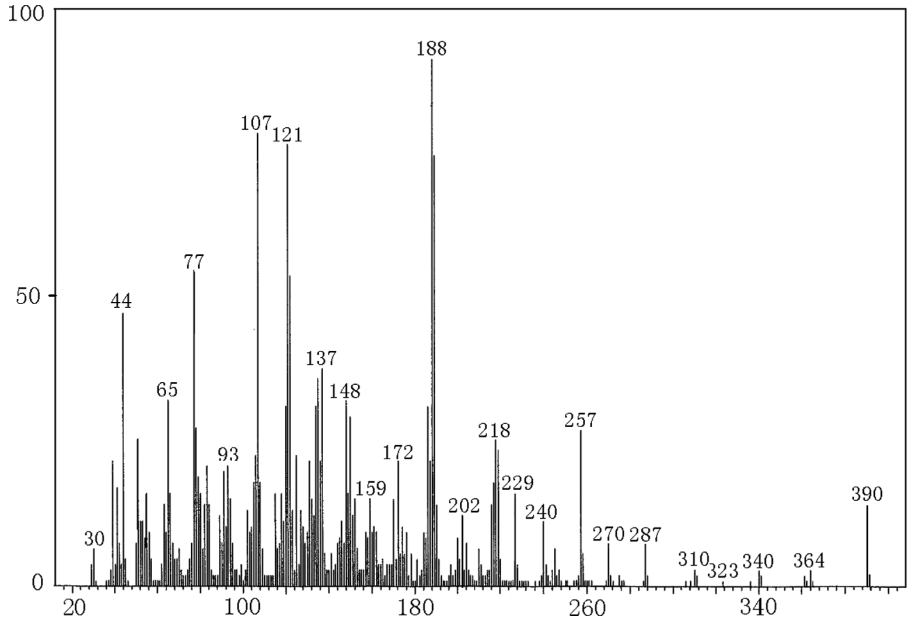

Figure 2. Mass spectrum of H_2LLi.

of hydroxyl oxygen to metal. The shift of ν(C–O–C) from 1150.2 cm^{-1} in the ligand to 1124.7 cm^{-1} in the complex, indicates coordination of the oxygen in the methoxy to metal. In the spectrum of the complex, five additional bands, which are not present in the spectrum of the ligand, were observed. Of these, the bond at 1030.5 cm^{-1} is assigned to the ν_2 mode of the nitrate group. The bands of 1481.7 and 1290.2 cm^{-1} in the complex are the two split bands ν_4 and ν_1, respectively, of the coordinated nitrate group. The magnitude of $\nu_4 - \nu_1$ is more than 180 cm^{-1} for the complex, indicating that the nitrate group is coordinated to the metal ion bidentate. The bands at 1393.4 and 813.3 cm^{-1} are assigned to the non-coordinated nitrate [6]. The shifts of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ from 1635.3 and 1399.8 cm^{-1} in the ligand to 1647.2 and 1410.8 cm^{-1} in the complex, respectively, suggest coordination of the oxygen in the carboxylate group to the Er^{3+}. The magnitude of $\nu_{as}(COO^-) - \nu_s(COO^-)$ is more than 200 cm^{-1} in the complex, indicating monodentate –COO^- [7]. The broad band at 3072.8 cm^{-1} in the complex is attributed to ν(O–H) of phenol and water molecules.

3.3. *Electronic spectra*

The electronic spectrum of the complex in DMSO exhibits two spectral bands at 266 and 320 nm, having molar extinction coefficients $\varepsilon = 1.32 \times 10^4$ and 5.67×10^5 L mol^{-1} cm^{-1}, respectively. These bands occur at 266, 324 nm ($\varepsilon = 1.73 \times 10^4$ and 6.42×10^5 L mol^{-1} cm^{-1}) in the spectrum of the ligand. The change in molar absorptivity suggests the ligand is coordinated to the metal.

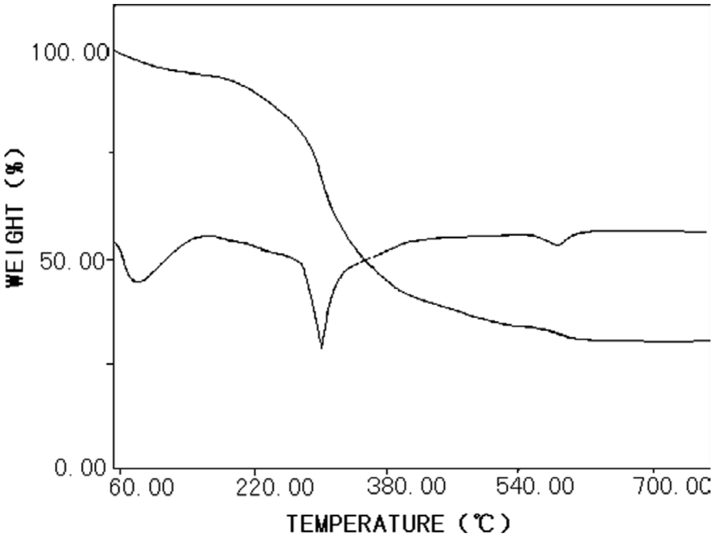

Figure 3. TG-DTG curves of the complex.

3.4. *Thermal decomposition studies*

The TG and DTG curves of the complex, shown in figure 3, indicate that the complex decomposes in three steps. The first weight loss stage has a decomposition temperature range of 60–140°C, with a weight loss of 5.74%, which corresponds to the loss of two molecules of water (Calcd 5.07%). That the water was lost at low temperature suggests that the water is crystal water. The second weight loss stage showed a continuous weight loss between 140 and 422°C, with a weight loss of 53.96%, which corresponds to the loss of unsymmetrical Schiff base ligand (Calcd 53.94%). The third stage showed a continuous weight loss between 422 and 770°C, and 27.13% of the original sample remained. With its calculated weight percentage of 26.91%, Er_2O_3 is the final product.

On the basis of 30 kinetic functions in both differential and integral forms commonly used [8], the non-isothermal kinetics of the steps were investigated using the Achar differential method [9] and the Coats–Redfern integral method [10].

The original kinetic data for the second step obtained form the TG and DTG curves are listed in table 1, in which T_i is the temperature at any point i on the TG and DTG curves, and α_i is the corresponding decomposition rate, $(\mathrm{d}\alpha/\mathrm{d}t)_i = [\beta/(W_0 - W_1)](\mathrm{d}W/\mathrm{d}T)_i$ in which $(\mathrm{d}W/\mathrm{d}T)_i$ is the height of the peak in the DTG curve, β is the heating rate, and W_0 and W_1 are the initial and final weight at that stage, respectively. The calculated kinetic parameters (E, A) and correlation coefficients (r) of step (2) are listed in table 2.

The results obtained from the two different methods are approximately the same when based on function No. 21. The kinetic equation is expressed as: $\mathrm{d}\alpha/\mathrm{d}t = \mathrm{A} \cdot \mathrm{e}^{-E/RT} \cdot 1/2(1-\alpha)[\text{-}\ln(1-\alpha)]^{-1}$, $E = 265.6\,\mathrm{kJ\,mol^{-1}}$, $\ln A = 90.49$ and $r = 0.9938$.

The activation entropy $S^{\neq}$ and activation free-energy $G^{\neq}$ are calculated by the following equations [11]: $A = kT_s/h \exp(S^{\neq}/R)$, $\mathrm{A} \cdot \mathrm{e}^{-E/RT} = kT_s/h \exp(S^{\neq}/R) \exp(-H^{\neq}/RT)$,

Table 1. Data for step (2) of the thermodecomposition of $[Er(H_2L)(NO_3)](NO_3) \cdot 2H_2O$ obtained from TG and DTG of curves.

T_i (K)	α_i	$(d\alpha/dt)_i$
563	0.2544	0.0819
568	0.3287	0.1086
569	0.3661	0.1143
570	0.4029	0.1205
571	0.4393	0.1257
572	0.4683	0.1314
573	0.5047	0.1367
574	0.5348	0.1305
575	0.5779	0.1248
576	0.6137	0.1171
577	0.6480	0.1129
579	0.6999	0.1019
581	0.7513	0.0911

Table 2. Results of analysis of the data for step (2) in table 1 by Achar differential method and Coats–Redfern integral method.

No.	E (kJ mol^{-1})	ln A	r	E (kJ mol^{-1})	ln A	r
1	184.1	36.44	0.8812	340.3	57.30	0.9916
2	260.8	52.22	0.9512	384.2	66.05	0.9935
3	291.6	57.3	0.9659	401.9	68.32	0.9941
4	350.5	69.92	0.9822	437.5	75.96	0.9948
5	127.2	21.89	0.7865	300.3	46.42	0.9904
6	527.2	107.8	0.9959	555.2	101.2	0.9947
7	185.5	37.53	0.9726	242.1	37.76	0.9949
8	101.5	19.61	0.9190	158.2	20.27	0.9947
9	59.48	10.56	0.8060	116.3	11.53	0.9945
10	17.47	1.400	0.3675	74.36	2.790	0.994
11	−3.530	−3.270	0.0789	53.39	−1.590	0.9934
12	97.15	17.91	0.8378	200.9	28.23	0.994
13	126.6	23.81	0.9126	214.0	30.63	0.9945
14	8.780	−0.3300	0.1041	165.4	21.30	0.9911
15	−78.87	−19.06	0.7122	77.94	3.300	0.9900
16	−108.1	−25.48	0.8182	48.79	−2.700	0.9887
17	−122.7	−28.77	0.8529	34.21	−5.700	0.987
18	362.2	75.39	0.9969	342.0	59.13	0.9922
19	273.9	55.77	0.994	78.79	4.220	0.9625
20	−49.65	−12.76	0.5289	107.1	9.300	0.9906
21*	237.6	90.77	0.9924	293.5	90.21	0.9951
22	689.6	143.7	0.9947	745.4	142.7	0.9951
23	941.7	196.6	0.9953	997.0	195.1	0.9952
24	539.0	113.9	0.9938	343.7	60.97	0.9681
25	141.3	26.68	0.9352	220.8	31.80	0.9947
26	−167.9	−37.50	0.7985	110.1	10.08	0.9776
27	−344.7	−74.95	0.8967	71.85	2.26	0.9524
28	−521.4	−112.5	0.9251	46.03	−3.14	0.9142
29	14.65	0.41	0.2606	102.2	7.97	0.994
30	53.32	8.19	0.6661	95.68	6.76	0.9934

$G^{\neq} = H^{\neq} - TS^{\neq}$, in which T_p is the temperature at the top of peak (2), k is Boltzmann constant, R is gas constant, h is Plank constant. The activation entropy $S^{\neq}$ and activation free-energy $G^{\neq}$ for the second thermal decomposition stage were determined as $S^{\neq} = 502.1\ \mathrm{J\,mol\,K^{-1}}$ and $G^{\neq} = -22.21\ \mathrm{kJ\,mol^{-1}}$.

4. Conclusions

The results presented here indicate that L-lysine can react with o-vanillin and salicylaldehyde forming an unsymmetrical Schiff base H_2LLi; erbium nitrate forms a stable complex with this ligand. The compositions of the complex is confirmed to be $[Er(H_2L)(NO_3)](NO_3) \cdot 2H_2O$. The kinetic equation for second decomposition step may be expressed as: $d\alpha/dt = A \cdot e^{-E/RT} \cdot 1/2(1-\alpha)[-\ln(1-\alpha)]^{-1}$, $E = 265.6\,\mathrm{kJ\,mol^{-1}}$, $\ln A = 90.49$, $S^{\neq} = 502.1\,\mathrm{J\,mol\,K^{-1}}$ and $G^{\neq} = -22.21\,\mathrm{kJ\,mol^{-1}}$.

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