

SYNTHESIS AND THERMAL DECOMPOSITION KINETICS OF La(III) COMPLEX WITH UNSYMMETRICAL SCHIFF BASE LIGAND

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A new unsymmetrical solid Schiff base (LLi) was synthesized using *L*-lysine, *o*-vanillin and 2-hydroxy-1-naphthaldehyde. Solid lanthanum(III) complex of this ligand [LaL(NO₃)]NO₃·2H₂O have been prepared and characterized by elemental analyses, IR, UV and molar conductance. The thermal decomposition kinetics of the complex for the second stage was studied under non-isothermal condition by TG and DTG methods. The kinetic equation may be expressed as: $d\alpha/dt = Ae^{-E/RT}(1-\alpha)^2$. The kinetic parameters (*E*, *A*), activation entropy ΔS^\ddagger and activation free-energy ΔG^\ddagger were also gained.

Keywords: La(III) complex, non-isothermal kinetics, thermal decomposition, unsymmetrical Schiff base

Introduction

Some Schiff base complexes derived from amino acid are particularly active in biology. Recently, studies of such metal complexes of mono-Schiff bases have been reported [1–6]. To continue the investigation in this area, a new unsymmetrical Schiff base ligand has been synthesized starting from *L*-lysine, *o*-vanillin and 2-hydroxy-1-naphthaldehyde by a new method. Since this ligand does not exist in literature, this paper deals with the preparation and characterization of the complex formed from this Schiff base ligand with La(III). As thermal aspects are essential to the complex, the thermal decomposition process of [LaL(NO₃)]NO₃·2H₂O by TG-DTG is described in this paper and the corresponding non-isothermal kinetics are discussed. The kinetic equation of thermal decomposition for the complex and the corresponding kinetic parameters were gained. This paper offered a new method preparing this kind of unsymmetrical Schiff base and its complexes. It is of important significance in the fields of biology and catalysis.

Experimental

Materials

Reagents

All reagents used in this work were of analytical grade. Hydrated lanthanum(III) nitrate was prepared by the reaction of lanthanum(III) oxide with nitric acid.

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, filtered. *o*-vanillin (2.282 g, 15 mmol) dissolved in 40 mL of hot ethanol was added dropwise to the above 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 (LLi): 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. 2-Hydroxy-1-naphthaldehyde (0.861 g, 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 (LLi) was 1.563 g (71%) and the purity was higher than 99%. Calculated for C₂₅H₂₅N₂O₅Li (440.4): C, 68.18; H, 5.72; N, 6.36, found: C, 67.24; H, 5.77; N, 6.34%.

Preparation of the complex

The unsymmetrical Schiff base (1.321 g, 3.0 mmol) dissolved in 65 mL anhydrous methanol and isopropanol in the proportion of 1:5 (v/v) was mixed with La(NO₃)₃·6H₂O (1.300 g, 3.0 mmol) dissolved in 15 mL anhydrous ethanol and stirred for 3 h at 50–55°C to

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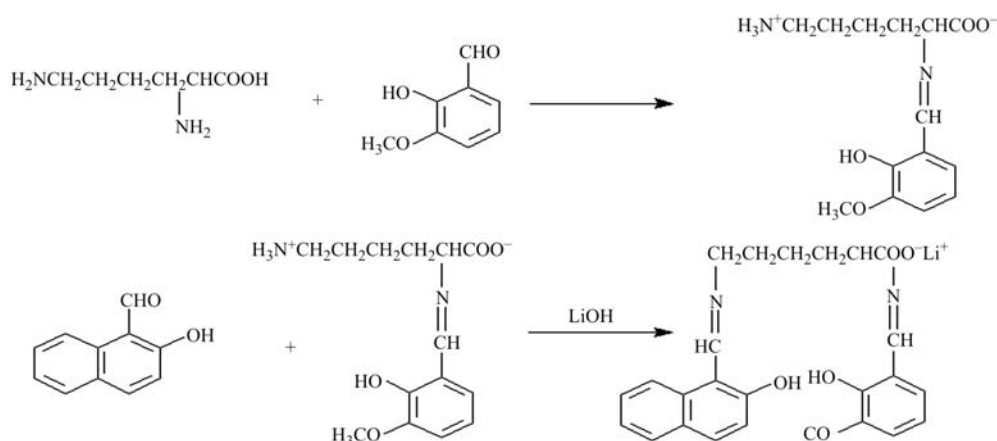


Fig. 1 Preparation of the ligand

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 1.516 g (69%) and the purity was higher than 99%. Calculated for $C_{25}H_{29}N_4O_{13}La$ (732.4): C, 41.00; H, 3.99; N, 7.65; La, 18.97, found: C, 41.10; H, 3.98; N, 7.73; La, 19.03%.

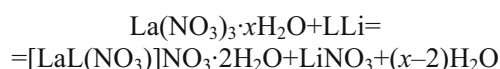
Instrumental measurements

Perkin-Elmer analyzer. The metal content was determined gravimetrically. The ultraviolet spectra were recorded on elemental analyses were carried out with a model 2400 a Shimadzu UV-3000 spectrophotometer 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 $10^{\circ}\text{C min}^{-1}$ 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.

Results and discussion

The reaction activity and steric hindrance of the two $-\text{NH}_2$ in *L*-lysine is different and the $-\text{NH}_2$ in α seat have higher activity than the $-\text{NH}_2$ in ϵ seat because of the induced effect of $-\text{COO}^-$ in *L*-lysine. When the molar ratio of *L*-lysine and *o*-vanillin was 1:1, the *o*-vanillin reacted with the $-\text{NH}_2$ in α seat first forming the mono-Schiff base. Then the mono-Schiff base reacted with 2-hydroxy-1-naphthaldehyde forming the unsymmetrical di-Schiff base. The synthesis reactions of the ligand are shown in Fig. 1. The synthesis of the complex may be represented as:



The molar conductance value of the complex determined in DMSO is $53.7 \text{ S cm}^2 \text{ mol}^{-1}$, which is expected for 1:1 electrolyte [7]. This suggests that one nitrate ion is within the coordination sphere and the second is ionic and not coordinated. The complex is stable in air and soluble in DMSO and DMF; however insoluble in diethyl ether, acetone or benzene.

Mass spectrum

The mass spectrum of LLi is shown in Fig. 2. The molecular mass of LLi is 440, which indicates that the reaction product of *L*-lysine with *o*-vanillin and 2-hydroxy-1-naphthaldehyde is an unsymmetrical di-Schiff base.

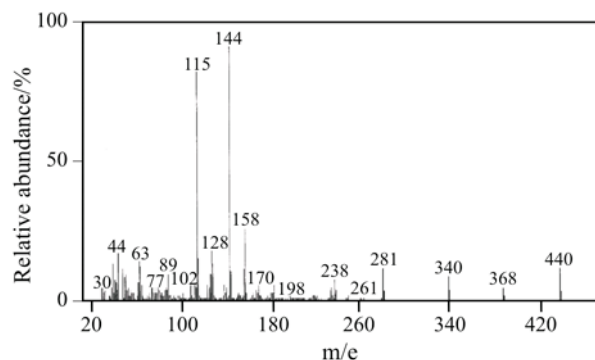


Fig. 2 Mass spectrum of LLi

IR spectra

The shift of $\nu_{\text{C}=\text{N}}$ from 1633.5 cm^{-1} in the ligand to 1644.4 cm^{-1} in the complex, suggests the formation of a $\text{C}=\text{N}-\text{La}$ bond system. The vibration $\nu_{\text{Ar}-\text{O}}$ of LLi occurs at 1228.5 cm^{-1} and the shift to lower frequency about 11 cm^{-1} in the complex indicates the coordination of

hydroxyl oxygen to metal ion. The shift of ν_{C-O-C} from 1093.3 cm^{-1} in the ligand to 1081.1 cm^{-1} in the complex, which indicates the coordination of the oxygen in the methoxyl to metal ion. 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 of 1036.7 cm^{-1} is assigned to the ν_2 mode of the nitrate group. The bands of 1492.7 and 1270.7 cm^{-1} in the complex are the two split bands of 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, which indicates that the nitrate group in coordinated to the metal ion in a bidentate fashion. The bands at 1396.2 and 817.4 cm^{-1} are assigned to the non-coordinated nitrate group [8, 9]. The shift of $\nu_{as(COO^-)}$ and $\nu_{s(COO^-)}$ from 1633.5 and 1398.1 cm^{-1} in the ligand to 1644.4 and 1396.1 cm^{-1} in the complex, respectively, suggests the coordination of the oxygen in the carboxylate group to the metal ion. The magnitude of $\nu_{as(COO^-)}-\nu_{s(COO^-)}$ is more than 200 cm^{-1} in the complex, which indicates that the $-COO^-$ group is coordinated to the metal ion in a monodentate fashion [9, 10]. The broad bands at 3114.4 cm^{-1} in the complex is attributed to ν_{O-H} of phenol and water molecules.

Electronic spectra

The electronic spectrum of the complex in DMSO exhibits two spectral bands at 266 and 380 nm, having the molar extinction coefficients $\epsilon=2.43\cdot 10^4$, $6.42\cdot 10^3\text{ L mol}^{-1}\text{ cm}^{-1}$, respectively. These bands occur at 270, 375 nm ($\epsilon=3.65\cdot 10^4$, $9.33\cdot 10^3\text{ L mol}^{-1}\text{ cm}^{-1}$) in the spectrum of the ligand. The change of the molar extinction coefficients suggests that the ligand is coordinated to the metal.

Thermal decomposition studies

The TG and DTG curves of the complex are shown in Fig. 3, which indicates that the complex decomposes in three steps. The first mass loss stage has a decomposition temperature range of 60–141°C, with a mass loss of 5.24%, which corresponds to the loss of two molecules of water (calcd. 4.92%). The fact that the water molecule was lost at a low temperature suggests that the water is crystal water. The second mass loss stage showed a continuous mass loss between 141 and 427°C, with a mass loss of 59.34%, which corresponds to the loss of unsymmetrical Schiff base ligand (calcd. 59.19%). The third stage showed a continuous mass loss between 427 and 770°C, and 22.87% of the original sample remained. With its calculated mass percentage of 22.24%, La_2O_3 is the final product.

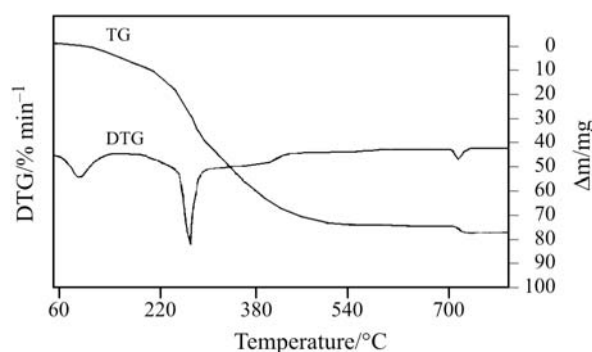


Fig. 3 TG-DTG curves of the complex

On the basis of 30 kinetic functions in both differential and integral forms commonly used in recent reviews [11], the non-isothermal kinetics of the steps were investigated using the Achar differential method [12] and the Coats–Redfern integral method [13].

The original kinetic data for the second step obtained from 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, α_i is the corresponding decomposition rate. $(d\alpha/dt)_i = [\beta/(W_0 - W_1)](dW/dT)_i$ in which $(dW/dT)_i$ 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 mass at that stage, respectively. The calculated kinetic parameters (E , A) and correlation coefficients (r) of steps (2) are listed in Table 2.

The results obtained from the two different methods are approximately the same when based on function No. 18. The kinetic equation is expressed as: $d\alpha/dt = Ae^{-E/RT}(1-\alpha)^2$, $E=274.3\text{ kJ mol}^{-1}$, $\ln A=52.99$, $r=0.9877$.

Table 1 Data for step (2) of the thermodecomposition of $[\text{LaL}(\text{NO}_3)]\text{NO}_3\cdot 2\text{H}_2\text{O}$ obtained from TG and DTG curves

T_i/K	α_i	$(d\alpha/dt)_i$
543	0.2342	0.0918
547	0.3092	0.1210
549	0.3223	0.1354
550	0.3861	0.1422
551	0.4064	0.1497
552	0.4882	0.1585
553	0.4950	0.1667
554	0.5258	0.1592
555	0.5479	0.1510
556	0.5660	0.1449
557	0.5787	0.1347
559	0.6293	0.1204
563	0.7288	0.0912

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

No.	$E/\text{kJ mol}^{-1}$	$\ln A$	r	$E/\text{kJ mol}^{-1}$	$\ln A$	r
1	152.54	31.08	0.7747	294.25	49.81	0.9717
2	211.94	43.63	0.8695	328.75	56.82	0.9763
3	235.37	47.34	0.8937	342.37	58.35	0.9779
4	280.40	54.36	0.9257	369.84	64.47	0.9806
5	105.50	18.26	0.66	261.18	40.15	0.9689
6	415.50	87.43	0.9679	459.91	84.52	0.9862
7	135.92	28.24	0.8647	201.92	30.83	0.9831
8	65.54	12.68	0.6851	131.55	15.68	0.9823
9	30.36	4.82	0.4207	96.37	8.10	0.9814
10	-4.83	-3.17	0.0782	61.18	0.520	0.9796
11	-22.42	-7.24	0.3511	43.59	-3.27	0.9774
12	68.37	12.51	0.6234	170.21	23.07	0.9776
13	90.88	17.12	0.7372	180.32	24.92	0.9797
14	0.820	-1.83	0.0087	142.53	17.59	0.9699
15	-75.04	-18.64	0.6819	66.67	1.48	0.9657
16	-100.33	-24.41	0.7957	41.38	-3.89	0.9607
17	-112.97	-27.39	0.8352	28.74	-6.58	0.9545
18	271.01	58.31	0.9869	277.62	47.66	0.9885
19	203.46	42.58	0.9396	58.35	0.410	0.9737
20	-49.75	-12.98	0.5058	91.96	6.85	0.9679
21	347.03	74.39	0.9527	413.04	76.29	0.9838
22	558.15	120.26	0.9677	624.16	121.75	0.984
23	769.27	166.01	0.9734	835.28	167.21	0.9842
24	406.11	89.08	0.9837	261.00	45.51	0.9787
25	102.14	19.33	0.7792	185.55	25.80	0.9806
26	-134.27	-31.21	0.7627	98.34	8.39	0.9475
27	-269.37	-60.88	0.8923	66.67	1.67	0.9158
28	-404.46	-90.66	0.9297	44.42	-3.09	0.8745
29	-3.87	-3.35	0.0555	85.57	5.15	0.9774
30	30.44	3.76	0.3626	80.51	4.22	0.975

The activation entropy ΔS^\ddagger and activation free-energy ΔG^\ddagger are calculated by the following equations [14]:

$$A = kT_s \exp(\Delta S^\ddagger/R)/h,$$

$$Ae^{-E/RT} = kT_s \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT)/h,$$

$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$, in which T_s is the temperature at the top of peak (2), k is Boltzmann constant, R is gas constant, h is Plank constant. The activation entropy ΔS^\ddagger and activation free-energy ΔG^\ddagger for second thermal decomposition stage were gained, $\Delta S^\ddagger = 190.5 \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta G^\ddagger = 169.6 \text{ kJ mol}^{-1}$.

Conclusions

The results presented here indicate that *L*-lysine can react with *o*-vanillin and 2-hydroxy-1-naphthaldehyde forming unsymmetrical Schiff base LLi and lanthanum nitrate can form stable solid complex with this ligand. The composition of the complex is confirmed to be $[\text{LaL}(\text{NO}_3)]\text{NO}_3 \cdot 2\text{H}_2\text{O}$. The kinetic equation for second decomposition step may be expressed as: $d\alpha/dt = Ae^{-E/RT}(1-\alpha)^2$, $E = 274.3 \text{ kJ mol}^{-1}$, $\ln A = 52.99$, $r = 0.9877$, $\Delta S^\ddagger = 190.5 \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta G^\ddagger = 169.6 \text{ kJ mol}^{-1}$.

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