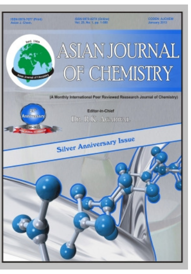
Asian Journal of Chemistry; Vol. 25, No. 6 (2013), 3267-3270

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13624



Synthesis and Thermal Decomposition Kinetics of Gd(III) Complex with Unsymmetrical Schiff Base Ligand

SHUANGYU BI[1], JIAN ZUO[2], NAN ZHANG[2], PENGFEI ZHANG[2], ZHEN ZHANG[2] and YUHUA FAN[2,*]

[1]Center for Theoretical Biology, Academy for Advanced Interdisciplinary Studies, Peking University, Haidian District, Beijing 100871, P.R. China
[2]Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, P.R. China

*Corresponding author: E-mail: fanyuhua301@163.com

(*Received*: 18 February 2012; *Accepted*: 17 December 2012) AJC-12563

A new unsymmetrical solid Schiff base (LLi) was synthesized using L-lysine, *o*-vanillin and 2-hydroxy-l-naphthaldehyde. Solid gadolinium(III) complex of this ligand [GdL(NO_3)]NO_3·$2H_2O$ has been prepared and characterized by elemental analyses, IR spectra, ^{1}H NMR spectra, UV spectra 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 $\Delta S^{\neq}$ and activation free-energy $\Delta G^{\neq}$ were also gained.

Key Words: Unsymmetrical Schiff base, Gd(III) complex, Thermal decomposition.

INTRODUCTION

Some Schiff base complexes derived from amino acids are particularly active in biology. Recently, studies of such metal complexes of mono-Schiff bases have been reported[1-4]. In this study, a new unsymmetrical Schiff base ligand has been synthesized starting from L-lysine, *o*-vanillin and 2-hydroxy-l-naphthaldehyde by a new method. Since this ligand dose not exist in literature, this paper deals with the preparation and characterization of the complex formed from this Schiff base ligand with Gd(III). As thermal aspects are essential in the complex, the thermal decomposition process of [GdL(NO_3)]NO_3·$2H_2O$ by TG-DTG is described in this paper and the corresponding non-isothermal kinetics are discussed.

EXPERIMENTAL

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

Mono-Schiff base (HR): L-lysine (2.193 g, 15 mmol) was dissolved in 230 mL of anhydrous ethanol and methanol in the proportion of 1:1 (v/v) and heated for 1.5 h at 55-50 ºC, filtered. *o*-Vanillin (2.282 g, 15 mmol) dissolved in 40 mL of hot ethanol was added drop-wise to the above filtered solution and stirred for 2 h at 50-55 ºC 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 ºC.

Unsymmetrical Schiff base (LLi): Mono-Schiff base (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 ºC. 2-Hydroxy-l-naphthaldehyde (0.861 g, 5.0 mmol) dissolved in 10 mL isopropanol was added drop-wise to the above solution and stirred for 4 h at 50-55 ºC 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 %. Calcd. (%) for $C_{25}H_{25}N_2O_5Li$ (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 Gd(NO_3)$_3$·$6H_2O$ (1.355 g, 3.0 mmol) dissolved in 15 mL anhydrous ethanol and stirred for 3 h at 50-55 ºC 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 1.532 g (68 %) and the purity was higher than 99 %. Calcd. (%) for $C_{25}H_{29}N_4O_{13}Gd$ (750.8): C, 39.99; H, 3.89; N, 7.46; Gd, 20.95, found (%): C, 40.09; H, 3.76; N, 7.52; Gd, 21.96.

Elemental analyses were carried out with a model 2400 Perkin-Elmer analyzer. The metal content was determined gravimetrically. Infrared spectra of the ligand and complex were recorded in KBr pellets using a Bio-Rad FTS 165 spctrophotometer. The ultraviolet spectra were recorded on a Shimadzu UV-3000 spctrophotometer in DMSO. The molar conductance was measured with a Shanghai DDSJ-308A conductivity meter. ^{1}H NMR spectra were recorded in DMSO-d_6 as the solvent at 600 MHz with a JNM ECP-600 spectrometer using tetramethylsilane (TMS) as an internal reference. Thermogravimetric measurements were made using a Perkin-Elmer TGA7 instrument. The heating rate was programmed to be 10 ºC/min with a protecting stream of N_2 flowing at a rate of 40 mL/min. 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 -NH_2 in L-lysine is different and the -NH_2 in a seat have higher activity than the -NH_2 in e 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 a seat first forming the mono-Schiff base. Then the mono-Schiff base reacted with 2-hydroxy-l-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:

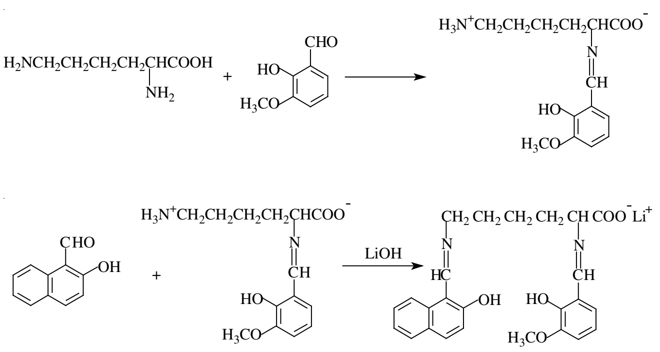


Fig. 1. Preparation of the ligand

$$Gd(NO_3)_3{\cdot}xH_2O + LLi = [GdL(NO_3)]NO_3{\cdot}2H_2O + LiNO_3 + (x\text{-}2)H_2O$$

The molar conductance value of the complex determined in DMSO is 50.8 S cm^2 mol^{-1}, which is expected for 1:1 electrolyte[5]. 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 benzene, acetone or diethyl ether.

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

IR Spectra: The shift of ν(C=N) from 1633 cm^{-1} in the ligand to 1644 cm^{-1} in the complex, suggests the formation of a C=N-La bond system. The vibration ν(Ar-O) of LLi occurs at 1228 cm^{-1} and the shift to lower frequency *ca.* 13 cm^{-1} in the complex indicates the coordination of hydroxyl oxygen to metal ion. The shift of ν(C-O-C) from 1093 cm^{-1} in the ligand to 1085.8 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 1035 cm^{-1} is assigned to the ν_2 mode of the nitrate group. The bands of 1489 and 1270 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 ν_4-ν_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 1387 and 819 cm^{-1} are assigned to the non-coordinated nitrate group[6]. The shift of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ from 1633 and 1398 cm^{-1} in the ligand to 1644 and 1398 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[7]. The broad bands at 3144 cm^{-1} in the complex is attributed to ν(O-H) of phenol and water molecules.

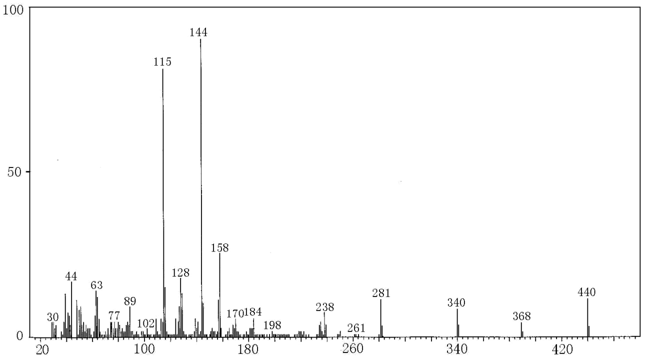


Fig. 2. Mass spectrum of LLi

Electronic spectra: The electronic spectrum of the complex in DMSO exhibits two spectral bands at 262 and 382 nm, having the molar extinction coefficients $\varepsilon = 2.77 \times 10^4$, 7.21×10^3 L mol^{-1} cm^{-1}, respectively. These bands occur at 270, 375 nm ($\varepsilon = 3.65 \times 10^4$, 9.33×10^3 L mol^{-1} cm^{-1}) in the spectrum of the ligand. The change of the molar extinction coefficients suggests that the ligand is coordinated to the metal.

^{1}H NMR spectra: The ^{1}H NMR spectra of the ligand and complex $[GdL(NO_3)]NO_3{\cdot}2H_2O$ were recorded in DMSO-d_6. In the spectrum of the ligand the phenolic OH proton appears at 14.21 ppm. This signal shifts to 12.68 ppm in the complex spectrum, which indicates that the coordination of phenolic oxygen to metal ions. The peak at 9.37 ppm in the ligand can be assigned to CH=N proton. It shifts to 8.74 ppm in the spectrum of the complex, which confirms the coordination of azomethine group to metal ion. In the spectrum of the complex the multisignals within the 7.36-7.58 ppm range were assigned to aromatic H protons. In the spectrum of the ligand the -OCH_3 proton appears at 3.36 ppm and it appears at 3.34 ppm in the complex spectrum, which indicates the -OCH_3 is not bound to metal ion.

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 weight loss stage has a decomposition temperature range of 61-141 ºC, with a weight loss of 5.12 %, which corresponds to the loss of two molecules of water (calcd. 4.80 %). The fact that the water molecule was lost at a low temperature suggests that

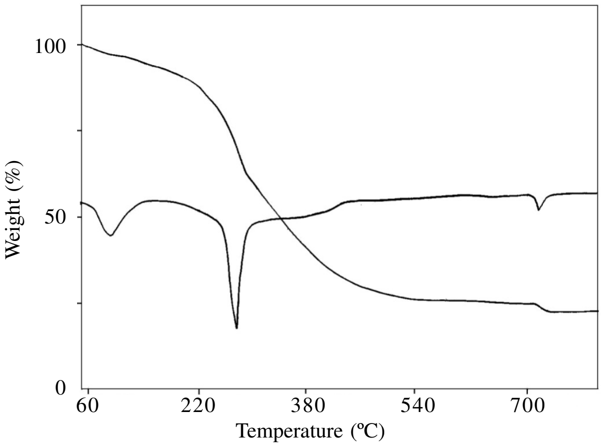


Fig. 3. TG-DTG curves of the complex

the water is crystal water. The second weight loss stage showed a continuous weight loss between 141 and 429 ºC, with a weight loss of 58.26 %, which corresponds to the loss of unsymmetrical Schiff base ligand (calcd. 57.74 %). The third stage showed a continuous weight loss between 429 and 770 ºC and 23.88 % of the original sample remained. With its calculated weight percentage of 24.15 %, Gd_2O_3 is the final product.

On the basis of 30 kinetic functions in both differential and integral forms commonly used in recent reviews[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, α_i is the corresponding decomposition rate. $(d\alpha/dt)_i = [\beta/(W_0 - W_1)] \times (dW/dT)_i$ 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 weight at that stage, respectively. The calculated kinetic parameters (E, A) and correlation coefficients (r) of steps (2) are listed in Table-2.

TABLE-1
DATA FOR STEP (2) OF THE THERMODECOMPOSITION OF $[GdL(NO_3)]NO_3{\cdot}2H_2O$ OBTAINED FROM TG AND DTG OF 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 (kJ/mol)	ln (A/s^{-1})	r	E (kJ/mol)	ln (A/s^{-1})	r
1	153.5	31.08	0.7747	294.3	49.81	0.9717
2	211.9	43.63	0.8695	328.8	56.82	0.9763
3	235.4	47.34	0.8937	342.4	58.35	0.9779
4	280.4	54.36	0.9257	369.8	64.47	0.9806
5	105.5	18.26	0.66	261.18	40.15	0.9689
6	415.5	87.43	0.9679	459.9	84.52	0.9862
7	135.9	28.24	0.8647	201.9	30.83	0.9831
8	65.54	12.68	0.6851	131.6	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	170.2	23.07	0.9776
13	90.88	17.12	0.7372	180.3	24.92	0.9797
14	0.820	-1.83	0.0087	142.5	17.59	0.9699
15	-75.04	-18.64	0.6819	66.67	1.48	0.9657
16	-100.3	-24.41	0.7957	41.38	-3.89	0.9607
17	-113.0	-27.39	0.8352	28.74	-6.58	0.9545
18	270.0	58.30	0.9879	275.6	49.69	0.9886
19	203.5	42.58	0.9396	58.35	0.410	0.9737
20	-49.75	-12.98	0.5058	91.96	6.85	0.9679
21	347.0	74.39	0.9527	413.0	76.29	0.9838
22	558.2	120.26	0.9677	624.2	121.75	0.984
23	769.3	166.01	0.9734	835.3	167.21	0.9842
24	406.1	89.08	0.9837	261	45.51	0.9787
25	102.1	19.33	0.7792	185.6	25.8	0.9806
26	-134.3	-31.21	0.7627	98.34	8.39	0.9475
27	-269.4	-60.88	0.8923	66.67	1.67	0.9158
28	-404.5	-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	0.9750

The results obtained from the two different methods are approximately the same when based on function No. 18. The kinetic equation is expressed as: $d\alpha/dt = A\ e^{-E/RT}\ (1-\alpha)^2$, E = 272.8 kJ/mol, ln A = 54.00, r = 0.9883.

The activation entropy $\Delta S^{\neq}$ and activation free-energy $\Delta G^{\neq}$ are calculated by the following equations[11]: $A = kT_s \exp(\Delta S^{\neq}/R)/h$, $A^{e-E/RT} = kT_s \exp(\Delta S^{\neq}/R) \exp(-\Delta H^{\neq}/RT)/h$, $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$, 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 $\Delta S^{\neq}$ and activation free-energy $\Delta G^{\neq}$ for second thermal decomposition stage were gained, $\Delta S^{\neq}$ = 198.9 J/mol K, $\Delta G^{\neq}$ = 162.8 kJ/mol.

Conclusion

The results presented here indicate that L-lysine can react with *o*-vanillin and 2-hydroxy-l-naphthaldehyde forming unsymmetrical Schiff base LLi and gadolinium nitrate can form stable solid complex with this ligand. The composition of the complex is confirmed to be $[GdL(NO_3)]NO_3\cdot 2H_2O$. The kinetic equation for second decomposition step may be expressed as: $d\alpha/dt = A\ e^{-E/RT}(1-\alpha)^2$, E = 272.8 kJ/mol, ln A = 54.00, r = 0.9883, $\Delta S^{\neq}$ = 198.9 J/mol K, $\Delta G^{\neq}$ = 162.8 kJ/mol.

ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation of China (No. 20971115 and No. 21071134).

REFERENCES

1. Q. Wang, C.F. Bi, Y.H. Fan, X. Zhang, J. Zuo and S.B. Liu, *Russ. J. Coord. Chem.*, **37**, 228 (2011).
2. X. Zhang, C.F. Bi, Y.H. Fan, Q.Z. Cui, D. Chen, Y. Xiao and Q.P. Dou, *Int. J. Mol. Med.*, **22**, 677 (2008).
3. Y. Xiao, C.F. Bi, Y.H. Fan, C. Cui, X. Zhang and Q.P. Dou, *Int. J. Oncol.*, **33**, 1073 (2008).
4. Y.H. Fan, S.Y. Bi, Y.Y. Li, C.F. Bi and S.T. Xie, *Russ. J. Coord. Chem.*, **34**, 772 (2008).
5. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
6. N.F. Curtis and Y.M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).
7. Q.L. Xu, L.J. Sun, H. Li, R.J. Wu and H.G. Wang, *Appl. Organomet. Chem.*, **8**, 57 (1994).
8. Y.Z. Li, Thermal Analysis, Qinghua University Press, Beijing, p. 94 (1987).
9. B.N. Achar, Proceeding International Clay Conference, Jerusalem, Book 1, p. 67 (1966).
10. A.W. Coats and J.P. Redfern, *Nature*, **201**, 68 (1964).
11. R.Z. Hu and Q.Z. Shi, Thermal Analysis Kinetics, Science Press, Beijing, p. 206 (2001).