研究简报

水杨醛缩乙醇胺及 8-羟基喹啉氧钒三元配合物的合成、晶体结构及热分解研究

李连之* 许 涛 陶绪泉 杜茂喜 刘 颖 杜凌云
(聊城大学化学化工学院,聊城 252059)

关键词: 氧钒三元配合物 合成 晶体结构 热分解
分类号: O614

Synthesis, Crystal Structure and Thermal Decomposition of Oxovanadium(Ⅴ) Ternary Complex with N-salicylidene-N′-aminoethanol and 8-hydroxy Quinoline

LI Lian-Zhi* XU Tao TAO Xu-Quan DU Mao-Xi LIU Ying DU Ling-Yun
(*School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng* 252059)

A new oxovanadium(Ⅴ) ternary complex, VO(L)(hq) [H_2L: N-salicylidene-N′-aminoethanol; hq: 8-hydroxy quinoline], was synthesized by the reaction of salicyaldehyde, aminoethanol and 8-hydroxy quinoline with vanadyl sulfate. It was characterized by elemental analysis, IR and X-ray diffraction analysis. The crystal of the title complex ($C_{18}H_{15}N_2O_4V$, M_r=374.26) belongs to monoclinic, space group $P2_1/n$ with the following crystallographic parameters: a=1.543 5(5) nm, b=0.662 0(2) nm, c=1.648 9(6) nm, β=105.043(7)°, V=1.627 3(10) nm^3, Z=4, D_c=1.528 g·cm^{-3}, μ(Mo$K\alpha$)=0.636 mm^{-1}, F(000)=768, and final R_1=0.056 8, wR_2=0.106 7 for observed reflections 957 ($I>2\sigma(I)$). The complex is six-coordinate in distorted octahedral geometry. The thermal decomposition for the complex was studied by TG-DTG curves and the apparent activation energy was obtained by the Kissinger formula. CCDC: 218497.

Keywords: oxovanadium(Ⅴ) ternary complex synthesis crystal structure thermal decomposition

The insulin-mimetic property of vanadium complexes is the most noteworthy finding and the relationship between vanadium and diabetes mellitus has been extensively studied in the past decades[1~5]. Vanadium complexes have been shown to increase glucose transport and inhibit gluconeogenesis, i. e. vanadium is able to mimic most of the biological effects of insulin in various cell types. Great efforts have been devoted to design and synthesize vanadium complexes of high biological activity and low toxicity which are readily absorbed in place of insulin[6~8]. The vanadium-bound alkoxides complexes are receiving considerable attention in view of their insulin-mimetic property[9], the implications in vanadium-bromoperoxidase[10], potential utility as selective oxidants[11], bioinorganic linkages to process as phosphorylation[12]. In the present

收稿日期:2003-12-15。收修改稿日期:2004-04-15。
聊城大学科研基金资助项目(No.X031017)。
*通讯联系人。E-mail:lilianzhi1963 @ 163.com
第一作者:李连之,男,40 岁,博士,教授,研究方向:生物无机化学和配位化学。

paper, we reported syntheses and crystal structure of VO(Ⅴ) ternary complex: VO(L)(hq) [H_2L: N-salicylidene-N′-aminoethanol; hq: 8-hydroxy quinoline]. In order to study the thermal stability of the complex, the thermal decomposition for the complex was investigated by TG-DTG curves and the apparent activation energy was obtained by the Kissinger formula.

1 Experimental

1.1 Materials and Instruments

All reagents were of A.R. grade and were used without further purification. Elemental analyses for C, H, N were performed on a Perkin-Elmer 2400 analyzer. IR spectra were obtained for KBr pellets on a Nicolet-460 spectrophotometer in the 4 000~400 cm^{-1}. X-ray diffraction data were collected on a Bruker Smart-1000 CCD diffractometer. Thermal decomposition was measured on Pyris 1 thermogravimetric analyzer. Melting point was gained by way of XT_4 melting point microdetector.

1.2 Synthesis of VO(L)(hq)

VO(L): To a solution of aminoethanol (0.305 g, 5 mmol) in ethanol (5 mL) were added successively a solution of salicylaldehyde (0.525 mL, 5 mmol) in ethanol (7.5 mL) and a solution of sodium acetate (0.82 g, 10 mmol) in water(10 mL). An aqueous solution of vanadyl sulfate hydrate (1.127 g, 5 mmol) in water (4 mL) was then added dropwise to the stirring mixture. A deep brown coloured solution initially formed and immediately turned to a heavy gray precipitate, and it was filtered after stirring the solution for one and half hour at room temperature. It was washed thoroughly with water, 50% ethanol and diethyl ether and dried in desiccator.

VO(L)(hq): To a methanolic solution (30 mL) of VO (L) (0.253 g, 1.1 mmol) was added 8-hydroxy quinoline (0.160 g, 1.1 mmol). After stirring the reaction mixture for some time a deep coloured solution was formed. The black precipitate was obtained after 4h with continuous stirring, which was filtered and dried in desiccator. m.p.: 220 ℃; IR (KBr, cm^{-1}): 1 633 ν(C=N), 958 ν(V=O); Found(%): C, 57.46; H, 4.13; N 7.68 for $C_{18}H_{15}N_2O_4V$ calcd.(%): C, 57.77; H, 4.04; N, 7.49.

1.3 X-ray Single Crystal Structure Determination

Single crystal of VO(L)(hq) (0.25 mm × 0.20 mm × 0.03 mm) grown by slow evaporation of a methanolic solution was placed on Bruker Smart-1000 CCD diffractometer. Intensity data were collected with a graphite monochromated Mo$K\alpha$ radiation (λ=0.071 073 nm) at 298(2) K. A total of 2 850 independent reflections (R_{int}=0.129 2) were collected in the range of $1.61° \leqslant \theta \leqslant 25.03°$ by ω-2θ scan technique, of which 957 reflections with $I>2\sigma(I)$ were considered to be observed and used in structural analysis. The structure was solved by direct methods, the position of the rest nonhydrogen atoms were determined from successive Fourier syntheses. The position and anisotropic parameters of all nonhydrogen atoms were refined on F^2 by full-matrix least-squares method using the SHELXL-97 program package. The final refinements converged at R_1=0.056 8, wR_2=0.106 7 with $w=1/[\sigma^2(F_o^2)+(0.068\ 8P)^2]$, where $P=(F_o^2+2F_c^2)/3$. The maximum shift-to-error ratio $(\Delta/\sigma)_{max}$=0.000 and the goodness of fit S=0.800. The maximum and minimum peaks on the Fourier map are corresponding to 291 e·nm^{-3} and −285 e·nm^{-3}, respectively. Crystal data and data collection parameters are summarized in Table 1.

CCDC: 218497.

2 Results and Discussion

2.1 Crystal Structure

Selected bond distances and angles are listed in Table 2. The molecular structure and packing diagram of the complex are shown in Fig.1 and Fig.2.

The molecular structure of Fig.1 demonstrates that V(Ⅴ) ion is six-coordinated in distorted octahedral geometry containing one oxo ligand, two phenolic oxygen atoms, one alkoxidic oxygen atom, one imine nitrogen atom and one azomethine nitrogen atom. The coordination type $V^{V}O$ (ONO)(ON) of the complex is based on tridentate schiff base ligand and bidentate 8-hydroxy quinoline ligand.

The V=O[V(1)-O(4)] bond length, 0.157 5(5) nm,

Table 1　Crystallographic Data of Title Complex

crystal data	complex
formula	$C_{18}H_{15}N_2O_4V$
M_r	374.26
T / K	293(2)
λ / nm	0.071 073
crystal system	monoclinic
space group	$P2_1/n$
a / nm	1.543 5(5)
b / nm	0.662 0(2)
c / nm	1.648 9(6)
β / (°)	105.043(7)
V / nm^3	1.627 3(10)
Z	4
D_c / (g·cm^{-3})	1.528
F(000)	768
μ / mm^{-1}	0.636
reflections collected	8 217
independent reflections	2 850
scan range θ / (°)	1.61~25.03
R_1	0.056 8
wR_2	0.106 7
largest diff. peak and hole / (e·nm^{-3})	291/−285

Table 2　Selected Bond Lengths (nm) and Angles (°) of Title Complex

V(1)-O(4)	0.157 5(5)	V(1)-O(2)	0.182 6(5)
V(1)-O(3)	0.186 7(5)	V(1)-O(1)	0.187 7(5)
V(1)-N(1)	0.207 4(6)	V(1)-N(2)	0.243 9(7)
O(4)-V(1)-O(2)	99.5(2)	O(4)-V(1)-O(3)	99.8(2)
O(2)-V(1)-O(3)	96.6(2)	O(4)-V(1)-O(1)	97.1(2)
O(2)-V(1)-O(1)	158.4(2)	O(3)-V(1)-O(1)	94.1(2)
O(4)-V(1)-N(1)	103.0(3)	O(2)-V(1)-N(1)	79.1(2)
O(3)-V(1)-N(1)	157.2(2)	O(1)-V(1)-N(1)	83.8(2)
O(4)-V(1)-N(2)	174.4(3)	O(2)-V(1)-N(2)	82.5(2)
O(3)-V(1)-N(2)	74.8(2)	O(1)-V(1)-N(2)	82.3(2)
N(1)-V(1)-N(2)	82.5(2)		

is unexceptional and the N(hq) atom lies trans to the oxo oxygen O(4) as in other cases, and a possible reason for this is that, if O(hq) was placed in this position it would have competed with O(4) in O → V π-donation. The angles of O(4)-V(1)-O(1), O(4)-V(1)-N(1), O(4)-V(1)-O(2) and O(4)-V(1)-O(3) are 97.1(2)°, 103.0(3)°, 99.5(2)°, 99.8(2)°, and the angle of O(4)-V(1)-N(2) is 174.4(3)°. Thus, the central atom V(Ⅴ) and six coordinated atoms form a significantly distorted octahedral structure. O(4) and N(1) are situated in axial situation, O(1), N(1), O(2), O(3) are in equator, which is similar with the previous report[13]. These angles also show that the four atoms of the equator are apart from vanadyl oxygen because of the repelling effect of V=O bond [V(1)-O(4)]. In the equator, the angles of O(1)-V(1)-N(1), N(1)-V(1)-O(2), O(2)-V(1)-O(3) and O(3)-V(1)-O(1) are 83.8(2)°, 79.1(2)°, 96.6(2)°, 94.1(2)°. The sum of these angles is 353.6°, which is close to 360°. The mean deviation of the four coordinated atoms in the equatorial plane is 0.006 41 nm, and the distances of O(4), N(2) in the axial situation from the equatorial plane are 0.189 74 nm, 0.211 14 nm, respectively. The central vanadium atom is displaced by 0.032 36 nm from the equatorial plane towards the oxo oxygen.

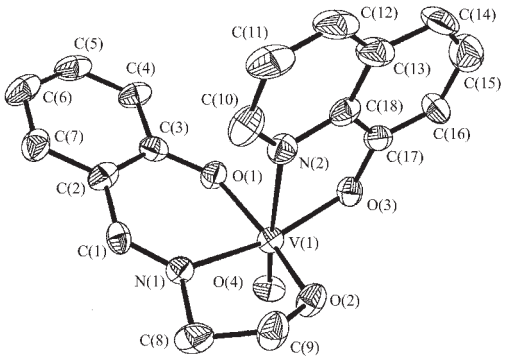

Fig.1　Molecular structure of title complex

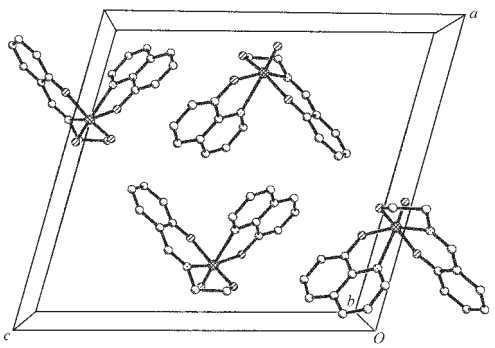

Fig.2　Molecular packing of the title complex in a unit cell

The complex forms three chelate rings that are six-membered or five-membered. One six-membered ring (Plane Ⅰ) is formed by V(1), O(1), C(3), C(2), C(1) and N(1), the rest two rings are five-membered [Plane

Ⅱ is formed by V(1), N(1), C(8), C(9) and O(2), Plane Ⅲ is formed by V(1), O(3), C(17), C(18) and N(2)]. In the three planes, Plane Ⅲ are highly planar with the mean deviation of 0.000 73 nm. Plane Ⅰ and Plane Ⅲ are inclined to each other by 100.7° to minimize steric interaction. The dihedral angle between Plane Ⅰ and Plane Ⅱ is 22.3°, and the angle between Plane Ⅱ and Plane Ⅲ is 80.5°. The three chelate rings increase the stability of the complex.

2.2 Thermal Decomposition of VO(L)(hq)

We make thermal analysis of three rates (5 ℃·min^{-1}, 10 ℃·min^{-1}, 15 ℃·min^{-1}) to title complex under a N_2 atmosphere by using the method of unequal thermal weight. Fig.3 is TG-DTG curves at a heating rate of 5 ℃·min^{-1}, which is very similar to those of the other two rates. It can be observed that there are two different decomposition stages. The first decomposition stage which occurs in the temperature ranges 186~259 ℃, was observed as mass loss 12% corresponding to that the losing of -CH_2CH_2O- group (calculated value 11.76%), and the melting point was also observed in the course; The second stage is corresponding to the slow decomposition of the remainder, and the complex still decompose slowly even it is heated to the temperature of 900 ℃ at the rate of 15 ℃·min^{-1}.

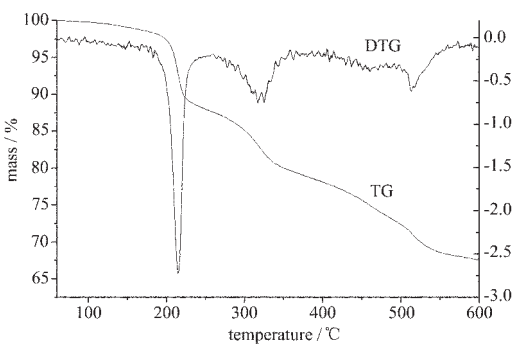

Fig.3 TG-DTG curve of title complex

The method of Kissinger[14] is used to calculate the reaction kinetics parameter of the first step.

$\ln(\beta/T_p^2)=-E_a/RT_p+C$

(β: the different heating rate; T_p: the different peak temperature of DTG curves).

The left of the equation construct to $-1/RT_p$, the slope of the line is E_a, which is the activation energy of the stage. The data are managed by EXCEL and the data β, T_p and E_a of this stage are listed in Table 3.

Table 3 Decomposition Peak Temperature and Apparent Activation Energy of the First Decomposition Stage for Title Complex

sample	β / (K·min^{-1})	T_p / K	E_a / (kJ·mol^{-1})
complex	5	487	290
	10	495	
	15	502	

References

[1] Heyliger C. E., Tahiliani A. G., McNeill J. H. *Science*., **1985**,**227**,1474.

[2] Thompson K. H., McNeil J. H., Orvig C. *Chem. Rev*., **1999**, **99**,2561.

[3] Crans D. C., Keramidas A. D., Hoover L. H., Anderson O. P., Miler M. M., Lemoine L. M., Pleasin W. S., Vandenberg M., Rossomando A. J., Sweet L. J. *J. Am. Chem. Soc*., **1997**, **119**,5447.

[4] Yuen V. G., Caravan P., Gelmini L., Glover L., Mcneil J. H., Setyawatti I. A., Zhou Y. C., Orvig J. *J. Inorg. Biochem*., **1997**,**68**,109.

[5] Schechter Y., Karlish S. J. *Nature*., **1980**,**284**,556.

[6] Wikksky G. R., Goldfine A. B., Kostyniak P. J., McNeill J. H., Yang L. Q., Khan H. R., Crans D. C. *J. Inorg. Biochem*., **2001**,**85**,33.

[7] Shaver A., Hall D. A., Ng J. B., Lebuis A. M., Hynes R. C., Posner B. I. *Inorg. Chim. Acta*, **1995**,**229**,253.

[8] Caravan P., Gelmini L., Glover N., Herring F. G., Li H. L., Mcneill J. H., Rettig S. J., Setyawati I. A., Shuter E., Sun Y., Tracey A. S., Yuen V. G., Orvig C. *J. Am. Chem. Soc*., **1995**,**117**,12759.

[9] Crans D. C., Simone C. M., Blanchard J. S. *J. Am. Chem. Soc*., **1992**,**114**,4926.

[10]Arber J. M., de Boer E., Garner C. D., Hasnain S. S., Wever R. *Biochemistry*., **1989**,**28**,7968.

[11]Hirao T., Mori M., Ohshiro Y. *J. Org. Chem*., **1990**,**55**,358.

[12]Crans D. C., Felty R. A., Miller M. M. *J. Am. Chem. Soc*., **1991**,**113**,265.

[13]Rath S. P., Ghosh T., Mondal S. *Polyhedron*., **1997**,**16**,4179.

[14]Kissinger H. E. *Anal. Chem*., **1957**,**29**,1702.