研究简报

一种新型不对称三足四胺席夫碱锌(Ⅱ)配合物的合成、结构及杀菌性能研究

高 健[1] 陈 军[2] 许兴友[1,2] 李树安[2] 杨绪杰[1] 陆路德*,[1] 汪 信[1]
([1]南京理工大学材料化学实验室,南京 210094)
([2]淮海工学院化学工程系,连云港 222005)

关键词: Zn(Ⅱ)配合物 不对称三足四胺 晶体结构 抗微生物活性
分类号: O614

Synthesis, Crystal Structure and Biocidal Study of a New Schiff-base Zn(Ⅱ) Complex Derived from Asymmetrical Tripodal Tetraamine

GAO Jian[1] CHEN Jun[2] XU Xing-You[1,2] LI Shu-An[2] YANG Xu-Jie[1] LU Lu-De*,[1] WANG Xin[1]
([1]*Materials Chemistry Laboratory, Nanjing University of Science and Technology, Nanjing* 210094)
([2]*Dept. of Chemical Engineering, Huaihai Institute of Technology, Lianyungang* 222005)

A new tripodal complex $[ZnL](ClO_4)_2$ ($C_{26}H_{31}Cl_2N_7O_8Zn$) was synthesized by Schiff base condensation of 2-aminoethyl-bi (3-aminopropyl)amine with 2-pyridinecarbaldehyde in the presence of Zn^{2+} and characterized by X-ray diffraction and ES mass spectral analysis. It crystallized in the Monoclinic system, space group $P2_1/c$ with a= 1.088 5(4) nm, b=1.614 6(6) nm, c=1.783 0(5) nm, β=94.405(2)°. Z=4, R_1=0.092 9, wR_2=0.175 8. Zn atom rendered six-coordinate in a trigonal antiprism geometry. The complex was valued for its antimicrobial activity against bacterial strands using the agar diffusion method. It was found to be active against the four test bacterial organisms. CCDC: 231275.

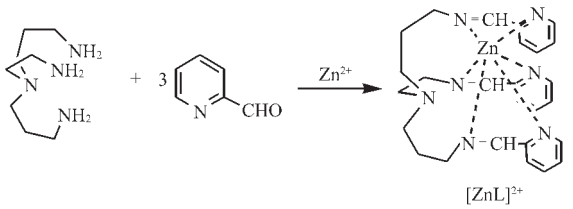
Keywords: **Zn(Ⅱ) complex** **asymmetrical tripodal tetraamine** **crystal structure** **antimicrobial activity**

0 Introduction

The study of tripodal Schiff-base complexes derived from tetraamine has, for many years, been an active area of research, growing interest in which continues to expand due to the ligands' strong coordination ability, recognition functions and structural variety for transition metal ions[1~5]. Structures and properties of these complexes condensed from the symmetrical tetraamines and aromatic aldehydes or ketones have been reported[6~12], but few reports on which of asymmetrical tetraamine[13], and much less biocidal studies on it. In this paper, we will report the synthesis, crystal structure and biocidal study of a new fully

收稿日期:2004-03-10。收修改稿日期:2004-07-15。
国家自然科学基金资助项目(No.50372028)。
*通讯联系人。E-mail:lulude@mail.njust.edu.cn
第一作者:高 健,女,34 岁,博士生;研究方向:配位化学。

condensed Schiff-base Zn(Ⅱ) complex obtained from the condensation of 2-aminoethyl-bi (3-aminopropyl) amine and 2-pyridinecarbaldehyde in the presence of Zn^{2+}. The synthesis of the complex is shown in Scheme 1.



Scheme 1

1 Experimental

1.1 Materials and Instruments

2-aminoethyl-bi (3-aminopropyl)amine was prepared according to the literature[14]. All other starting materials and solvents were of analytical purity.

Elemental analysis was determined with a Perkin-Elmer 240C instrument. Solution electrical conductivity was measured by a BSD-A numerical conductometer (Jiangsu, China) with solution concentration of ~1.0×10^{-3} mol·dm^{-3} in methanol at 279 K. IR spectrum was measured as KBr discs using a Nicolet 5DX FT-IR spectrophotometer. The ES mass spectral measurement of the complex was carried out on a LCQ System (Finngann MAT, USA) using methanol as mobile phase. The spray mass spectrum and capillary temperature were set at 5 kV and 200 ℃, respectively. The quoted *m/z* values represent the major peaks in the isotopic distribution. Thermogravimetric and differential analyzer were under flowing N_2 with a heating rate of 10 ℃·min^{-1}.

1.2 Synthesis of the Complex

To a stirred solution of 2-pyridinecarbaldehyde (1.5 mmol) and $Zn(ClO_4)_2\cdot6H_2O$ (0.5 mmol) in 20 cm^3 absolute methanol was added dropwise a solution of 2-aminoethyl-bi(3-aminopropyl)amine (0.5 mmol) in 10 cm^3 absolute methanol. After stirring for 3 h at 45 ℃, white microcrystals of the complex was precipitated and filtered off, washed with methanol and dried in vacuo. Yield 66%, m. p. >252 ℃(dec.). Anal. Calc. for $C_{26}H_{31}Cl_2N_7O_8Zn$ (%): C, 44.20; H, 4.39; N, 13.88; Found (%): C, 44.18; H, 4.21; N, 13.75. ES-MS: *m/z* (%): 252.6(100), 504.2(8), 606.1(7). IR (cm^{-1}): 1 644s, ν(C=N); 1 596s, ν(C=N, py); 1 094s, $\nu(ClO_4^-)$. Λ_M (CH_3OH, 279 K): 236 S·cm^2·mol^{-1}. A brown single crystal suitable for X-ray structure determination was obtained by slow evaporation of the filtrate for about twenty days at ambient temperature. Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with caution.

1.3 Crystallographic Measurements

A brown block single crystal of dimensions 0.60 mm × 0.58 mm × 0.50 mm was mounted on a glass fiber. The crystal data were collected at 293(2) K on a Siemens Smart/CCD area-detector diffractometer with Mo$K\alpha$ radiation (λ=0.071 073 nm) over the range $2.29°\leqslant\theta\leqslant25.11°$ with a ω scan mode. Data reductions and cell refinements were performed with Smart-CCD software. An absorption correction by using SADABS software was applied. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXL-97[15]. All H atoms were placed in calculated position. Table 1 lists relevant crystallographic data.

CCDC: 231275.

1.4 Antimicrobial Activity Determination

As a preliminary screening for antimicrobial activity, complex $[ZnL](ClO_4)_2$ was tested against standard strains of Candida albicans CMCC (F) 98001, Staphylococcus aureus CMCC (B) 26003, Bacillus pumilus CMCC (B) 63202, Klebosiella pneumoniae CMCC (B) 46 117 using the agar diffusion method as described in the literature[16]. For the comparison, the antimicrobial activity of $Zn(ClO_4)_2\cdot6H_2O$ are also tested. $[ZnL](ClO_4)_2$ and $Zn(ClO_4)_2\cdot6H_2O$ were dissolved in DMF. Nutrient agar thawed by heating in water bath was transferred to plates and froze at 37 ℃. After test strains were spread on the solid nutrient agar surface, stainless steel tubes (7.8 mm × 6 mm × 10 mm) were placed vertically on the surface. 0.04 mL compound with certain concentration were injected to the steel

Table 1 Crystallographic Data for the Complex

empirical formula	$C_{36}H_{31}Cl_2N_7O_8Zn$
formula weight	705.85
crystal system	monoclinic
space group	$P2_1/c$
a / nm	1.088 5(4)
b / nm	1.614 6(6)
c / nm	1.7830(5)
β / (°)	94.405(2)
V / nm^3	3.124 3(2)
Z	4
μ / mm^{-1}	1.015
θ range / (°)	$2.29 \leqslant \theta \leqslant 25.11$
D_{cal} / (g·cm^{-3})	1.501
F(000)	1 456
reflections measured / unique	9 096 / 5 480 [R_{int}=0.035 2]
observed / cut-off	4 185 / $2\sigma(I)$
goodness of fit on F^2	1.292
R_1 / wR_2	0.092 9 / 0.175 8
largest difference peak and hole / (e·nm^{-3})	668 / −494

tubes. They were allowed to incubate at 37 °C for 24 hours. The inhibition zone around the disc was calculated as zone diameter in millimeters. Blank tests showed that DMF in the preparation of the test solutions does not affect the test organisms. All tests were repeated three times and average data were taken as the final results.

2 Results and Discussion

2.1 Crystal Structure of Complex

The crystal structure of the Zn(Ⅱ) complex consists of cationic unit of $[ZnL]^{2+}$ and noncoordinated perchlorate ions. The structure of $[ZnL]^{2+}$ showing the atomic numbering scheme is indicated in Fig.1. The cation has a similar helical structure with three propeller blades when it is observed along the Zn(1)-N(1) direction. Zn(1) locates in a N6 coordination environment composed of three imino N and three N atoms from the pyridine ring with a moderately distorted trigonal antiprism geometry. Selected bond distances and bond angles, together with some TAP structural model parameters[14], are given in Table 2. Three imino N of N(2), N(4), N(6) and three pyridine N of N(3), N(5), N(7) form two approximate equilateral triangles between which the metal atom is located. The triangles, which parallel each other with dihedral angle 2.9° and centroid-centroid distance 0.213 2 nm, are mutually staggered by 52.2°, similar to those analogous Zn^{2+} ($3d^{10}$) complex ([Zn(py$_3$tren)][11]) and Cd^{2+} ($4d^{10}$) complexes ([Cd(py$_3$tren)][12] and [Cd(py$_3$trpn)][13]). The three arms of tripodal tetramine in $[ZnL]^{2+}$, with total bond length of 0.591 1, 0.591 1 and 0.446 9 nm, respectively, are approximately equal to the distance (0.282 7, 0.307 5 and 0.297 8 nm), which may be convenient for the formation of stable coordination geometry. The three pyridine rings are approximately vertical each other with centroid-centroid distances 0.533 5 nm, 0.526 8 nm and 0.540 3 nm, respectively, indicating no interaction among them. Zn(1)-N(imino) distances, being in the range 0.213 2~0.213 8 nm, are similar to the previous report[10]. The distance between Zn(1) and bridging nitrogen N(1) is 0.308 7 nm, which is greater than the van der Waals contact distance, and indicates no coordination reaction between them.

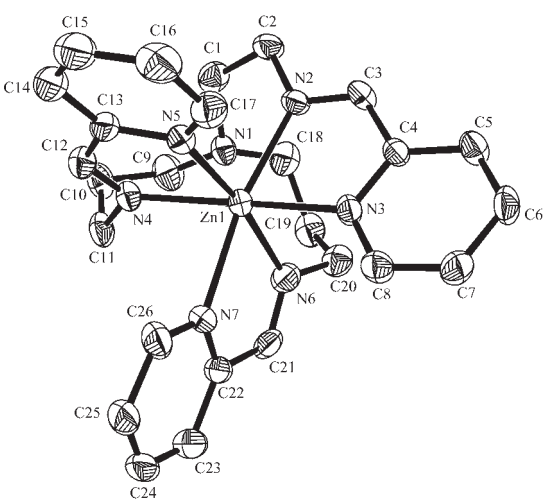


Fig.1 A stereoview of [ZnL] with the atom numbering scheme (ellipsoids at 30% probability)

2.2 Spectral Characteristics

The structure of the title complex was further confirmed by spectral characteristics. Condensation of all primary amine groups and carbonyl groups is confirmed by the lack of N-H double stretching bands in

Table 2　Selected Bond Lengths(nm) and Bond Angles(°) and Some TAP Structure Parameters

Zn(1)-N(2)	0.213 2(4)	Zn(1)-N(3)	0.220 5(4)	Zn(1)-N(6)	0.213 7(5)
Zn(1)-N(5)	0.222 8(4)	Zn(1)-N(4)	0.213 8(4)	Zn(1)-N(7)	0.225 2(5)
N(2)-Zn(1)-N(6)	101.59(18)	N(4)-Zn(1)-N(5)	76.61(17)	N(2)-Zn(1)-N(4)	109.09(18)
N(3)-Zn(1)-N(5)	90.48(17)	N(6)-Zn(1)-N(4)	103.07(18)	N(2)-Zn(1)-N(7)	167.93(17)
N(2)-Zn(1)-N(3)	77.10(17)	N(6)-Zn(1)-N(7)	76.37(19)	N(6)-Zn(1)-N(3)	88.11(18)
N(4)-Zn(1)-N(7)	82.89(18)	N(4)-Zn(1)-N(3)	165.45(17)	N(3)-Zn(1)-N(7)	90.90(17)
N(2)-Zn(1)-N(5)	89.82(17)	N(5)-Zn(1)-N(7)	91.61(17)	N(6)-Zn(1)-N(5)	167.87(18)

coordination polyhedron model values[a]	$[ZnL]^{2+}$ [this work]	$[Zn(py_3tren)]^{2+}$ (see ref.[11])	$[Cd(py_3tren)]^{2+}$ (see ref.[12])	$[Cd(py_3trpn)]^{2+}$ (see ref.[13])
twist angle ϕ / (°)	52.2	45.9	47	52
M-N (bridging nitrogen) / nm	0.3088	0.3013	0.2778	0.2486
M-N_6 / nm	0.2182	0.2180	0.2412	0.2425
a	0.338	0.329	0.336	0.401
c	0.318	0.314	0.329	0.373
a / *c*	1.06	1.05	1.02	1.07
b (bite)	0.271	0.264	0.279	0.289

a: For the definition of model, see ref.[11]

Table 3　Diameter of Inhibition Zone (mm)

compound	concentration / ($mg \cdot mL^{-1}$)	diameter of inhibition zone / mm			
		candida albicans	staphylococcus aureus	bacillus pumilus	klebosiella pneumoniae
$[Zn_2L]$	20.0	24.1	28.6	29.3	27.6
	10.0	22.3	21.3	25.6	24.3
	5.0	18.9	18.9	20.3	20.1
	2.5	15.2	16.8	15.8	16.7
$Zn(ClO_4)_2$	15.0	16.4	20.4	20.8	20.5
	7.5	14.3	16.7	17.4	18.0
	3.8	11.9	11.9	13.2	14.3
	1.9	8.2	9.1	11.0	9.4
tetracycline[b]	(30 μg)	22	22	16	

b: adapted from ref.[17]

the IR region 3 150~3 450 cm^{-1} and the presence of strong C=N stretching bands at 1 644 cm^{-1}. The main peaks at *m/z* 252.6, 504.2 and 606.1 are observed in the ES mass spectrum, corresponding the species of $[ZnL\text{-}2H\cdot]^{2+}$, $[ZnL\text{-}H]^{+}$ and $[[ZnL](ClO_4)]^{+}$, respectively. The three species were confirmed by good agreements between the observed and calculated isotopic distributions.

2.3　Antimicrobial Activity

From the data of Table 3 it is observed that $[ZnL](ClO_4)_2$ and $Zn(ClO_4)_2\cdot 6H_2O$ exhibited antibacterial activity against all the test bacterial organisms, but are less effective than Tetracycline[17]. In the test range, these compounds were more active against the strains with the increase of concentration. Complex $[ZnL](ClO_4)_2$ show higher activity against bacteria as compared to metal salt $Zn(ClO_4)_2\cdot 6H_2O$. The reason may be attributed to the formation of Schiff-base structure and the present of pyridine ring, which can increase the antimicrobial activity due to their active antibacterial and antitumor function[18~23].

References

[1] Keypour H., Stotter D. A. *Inorg. Chim. Acta*, **1979**,**33**,141.

[2] Kirchner R. M., Mealli C., Bailey M., Howe N., Torre L. P., Wilson L. J., Andrews L. C., Rose N. J., Lingafelter E. C. *Coord. Chem. Rev.*, **1987**,**77**,89.

[3] Keypour H., Pritchard R. G., Parish R. V. *Transition Met. Chem.*, **1998**,**23**,609.

[4] Keypour H., Salehzadeh S. *Transition Met. Chem.*, **2000**,**25**, 205.

[5] CHANG Jia-Gui(常加贵), WU Ling(吴 琳), NI Jun(倪钧), WANG Zhi-Lin(王志林), LUO Qin-Hui(罗勤慧) *Wuji Huaxue Xuebao*(*Chinese J. Inorg. Chem.*), **2001**,**17**(6),826.

[6] GONG Yan(龚 雁), SHI Qing-Fang(史清芳), HE Ling(贺玲), HUANG Xiang(黄 翔), GOU Shao-Hua(苟少华) *Wuji Huaxue Xuebao*(*Chinese J. Inorg. Chem.*), **1998**,**14**(2),241.

[7] Alcock N. W., Cook D. F., Mckenzie E. D., Worthington J. M. *Inorg. Chim. Acta*, **1980**,**38**,107.

[8] Wilson L. J., Rose N. J. *J. Am. Chem. Soc.*, **1968**,**90**,6041.

[9] Mealli C., Lingafelter L. C. *J. Chem. Soc., Chem. Commun.*, **1970**,885.

[10]Guo S. H., You X. Z., Yu K. B., Lu J. P. *Inorg. Chem.*, **1993**, **32**,1883.

[11]Kirchner R. M., Mealli C., Bailey M., Howe N., Torre L. P., Wilson L. J., Andrews L. C., Rose N. J., Lingafelter E. C. *Coord. Chem. Rev.*, **1987**,**77**,89.

[12]Jantti A., Wagner M., Suontamo R., Kolehmainen E., Rissanen K. *Eur. J. Inorg. Chem.*, **1998**,1555.

[13]Keypour H., Salehzadeh S., Pritchard R. G., Parish R. V. *Polyhedron*, **2000**,**19**,1633.

[14]Dittler-Klingemann A., Hahn F. E. *Inorg. Chem.*, **1996**,**35**, 1996.

[15]Sheldrick G. M. *SHELXL*-97, University of Göttingen, Germany, **1997**.

[16]LU Kui-Shan(吕奎山), XU Yuan-Chun(徐远春), YU Hong(于 宏), SHI Yan(史 彦) *Zhongguo Huanjing Jiance* (*Environmental Monitoring in China*), **1991**,**7**(5),9.

[17]Patel. M., Patel. N., Patel. K., Dholakiya. P., Patel. D. *Synth. React. Inorg. Met. -Org. Chem.*, **2003**,**33**(1),51.

[18]ZHU Xin-De(祝心德), DANG Yuan-Lin(党元林), WANG Cheng-Gang(王成刚), LE Zhi-Feng(乐芝凤), WU Zhi-Shen(吴自慎) *Wuji Huaxue Xuebao*(*Chinese J. Inorg. Chem.*), **1997**,**13**(1),68.

[19]BI Si-Wei(毕思玮), LI Gui-Zhi(李桂芝), LIU Shu-Xiang(刘树祥) *Wuji Huaxue Xuebao*(*Chinese J. Inorg. Chem.*), **1998**, **14**(2),153.

[20]ZHOU Yu-Ping(周毓萍), YU Hong-Juan(于红娟), YANG Zheng-Yin(杨正银), YANG Ru-Dong(杨汝栋) *Wuji Huaxue Xuebao*(*Chinese J. Inorg. Chem.*), **1998**,**14**(2),153.

[21]ZHANG Jian-Ming(张建民), LI Rui-Fang(李瑞芳), LIU Shu-Xiang(刘树祥) *Wuji Huaxue Xuebao*(*Chinese J. Inorg. Chem.*), **1999**,**15**(4),493.

[22]MA Jun-An(马军安), HUANG Run-Qiu(黄润秋) *Gaodeng Xuexiao Huaxue Xuebao*(*Chem. J. Chin. Uni.*), **2003**,**24**(4), 654.

[23]LIU Chang-Ling(刘长令), WANG Can-Ming(汪灿明), YU Chun-Rui(于春睿), SHE Yong-Hong(佘永红) *Nongyao*(*Pesticide*), **1999**,**38**(6),1.