



N-亚水杨基苄胺过渡金属配合物的合成、结构与抑菌性能研究

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关键词: N-亚水杨基苄胺配合物; 合成; 晶体结构; 抑菌性

中图分类号: O614.24⁺1

文献标识码: A

文章编号: 1001-4861(2005)05-0767-04

Synthesis, Structure and Antimicrobial Study of N-salicylidene-benzylamineato Transition Metal Complexes

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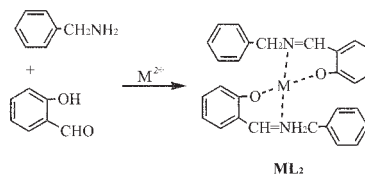
Abstract: N-salicylidene-benzylamineato M(II) complexes (ZnL₂, CuL₂ and CdL₂) were synthesized, characterized and valued for antimicrobial activities against bacterial strands using the agar diffusion method. The crystal of ZnL₂ was determined by X-ray diffraction. It crystallizes in the Monoclinic system, space group C2/c with *a*=2.269 1(3), *b*=0.918 2(1), *c*=1.239 5(2) nm, β =117.89(2), *Z*=4, *R*₁=0.049 4, *wR*₂=0.138 2. The complexes were found to be active against *Staphylococcus aureus* and *Escherichia Coli*. CCDC: 249474.

Key words: N-salicylidene-benzylamineato; M(II) complex; synthesis; crystal structure; antimicrobial activity

0 Introduction

In the past decades, Schiff bases complexes derived from the condensation of salicylaldehyde with primary amines have received a great deal of interests due to their important bioactivities such as catalysis^[1,2], antimicrobial and antifungal activities^[3-6]. As a part of our studies on the relationship between structure and antimicrobial activity of the compounds with biologically active units, we have taken up investigations on N-salicylidene-benzylamineato M(II) complexes (ML₂, M=Zn, Cu and Cd), and these results are presented in

this paper. The synthesis of ML₂ is shown in Scheme 1.



Scheme 1

1 Experimental

1.1 Materials and instruments

All the starting materials and solvents were of analytical purity.

收稿日期: 2004-10-10. 收修改稿日期: 2004-12-31。

江苏省海洋生物技术重点建设实验室资助。

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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 $\sim 1.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ in methanol at 279 K. IR spectrum was measured as KBr discs using a Nicolet 5DX FTIR spectrophotometer. The ES mass spectral measurement of the complex was carried out on a LCQ System (Finnigan MAT, USA) using methanol as mobile phase. Thermogravimetric and differential analyzer were under flowing N_2 with a heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$.

1.2 Synthesis of the complexes

The title complexes were synthesized by the procedure as follows: To a stirred solution of salicylaldehyde (10 mmol) and $\text{M}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (5 mmol) in 20 cm^3 absolute methanol was added dropwise a solution of benzylamine (10 mmol) in 15 cm^3 absolute methanol. After stirring for 3 h at $45 \text{ }^\circ\text{C}$, microcrystals of the complexes was precipitated and filtered off, washed with methanol and dried in vacuo. Yellow single crystal of ZnL_2 suitable for X-ray structure determination was obtained by slow evaporation of the filtrate for about four days at ambient temperature. Table 1 lists analytical data of the complexes.

Table 1 Analytical data for the complexes

Complexes	Yield / %	A_M / ($\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$)	Melt. / Dec. / $^\circ\text{C}$	Empirical formula	Anal. found (calc.) / %		
					C	H	N
ZnL_2	35	26	223	$\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_2\text{Zn}$	69.46(69.15)	4.98(4.94)	5.69(5.76)
CuL_2	34	24	219	$\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_2\text{Cu}$	69.50(69.41)	4.98(4.96)	5.82(5.78)
CdL_2	41	21	229	$\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_2\text{Cd}$	62.95(62.91)	4.42(4.49)	5.28(5.24)

1.3 Structure determination

A yellow block single crystal of dimensions $0.20 \text{ mm} \times 0.20 \text{ mm} \times 0.30 \text{ mm}$ 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 ($\lambda = 0.071\,073 \text{ nm}$) over the range $2.03^\circ \leq \theta \leq 25.00^\circ$ with a φ - ω scan mode. Data reductions and cell refinements were performed with saint

and Smart program, respectively. An absorption correction was applied by using SADABS software. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELX-97 [7]. All H atoms were placed in calculated position. Table 2 lists relevant crystallographic data.

CCDC: 249474.

Table 2 Crystallographic data for the complex

Empirical formula	$\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_2\text{Zn}$	μ / mm^{-1}	1.104
Formula weight	485.86	θ range / $^\circ$	$2.03 \leq \theta \leq 25.00$
Crystal system	Monoclinic	$D_{\text{calc}} / (\text{g} \cdot \text{cm}^{-3})$	1.414
Space group	$C2/c$	$F(000)$	1 008
a / nm	2.269 1(3)	Reflections measured / unique	5 682 / 2 017 ($R_{\text{int}} = 0.022$)
b / nm	0.918 2 (1)	Observed / cut-off	1 762 / $2\sigma(I)$
c / nm	1.239 5(2)	Goodness of fit on F^2	1.03
$\beta / (^\circ)$	117.89(2)	R_1 / wR_2	0.049 4 / 0.138 2
V / nm^3	2.282 5(5)	Largest difference peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	990 / -710
Z	4		

1.4 Antimicrobial activity determination

As a preliminary screening for antimicrobial activity, using agar diffusion method described in the previous paper [8]. ZnL_2 , CuL_2 and CdL_2 dissolved in DMF were tested against standard strains of *Staphylococcus aureus* CMCC (B) 26 003 and *Escherichia*

Coli CMCC (B) 44 102, which belong to Gram-positive bacteria and Gram-negative bacteria, respectively. Nutrient agar thawed by heating in water bath was transferred to glass plates and froze at about $37 \text{ }^\circ\text{C}$. After test strains were spread on the solid nutrient agar surface, stainless steel tubes ($7.8 \times 6 \times 10 \text{ mm}$)

were placed vertically on the surface. 0.04 ml samples with certain concentration were injected to the steel tubes. They were allowed to incubate at 37 °C for 24 hour. 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 result.

2 Results and discussion

2.1 Crystal structure of complex ZnL_2

Crystal structure of the centro-symmetrical $\text{Zn}(\text{II})$ complex consists of an isolated molecule unit, in which two hydrogen atoms of hydroxyl were lost during the formation of coordinate bond for the charge balance. The structure of ZnL_2 showing the atomic numbering scheme is indicated in Fig.1. $\text{Zn}(1)$ locates in a N_2O_2 coordination environment with a distorted tetrahedral geometry. Selected bond distances and bond angles are given in Table 3. The bond lengths of $\text{Zn}(1)\text{-O}(1)$ and $\text{Zn}(1)\text{-N}(1)$, being 0.191 7(3) and 0.200 7(3) nm, respectively, are basically similar to the previous report^[9,10], but somewhat shorter than the corresponding distances in the complex $[\text{Zn}_2\text{L}_3(\text{OAC})(\text{OH}_2)](\text{BF}_4) \cdot 2\text{MeOH} \cdot \text{H}_2\text{O}$ ^[11]. The six bond angles formed by $\text{Zn}(1)$ and coordination atoms are 96.11(11)°, 114.75(12)°, 113.21(12)°, 113.21(12)°, 124.69(11)° and 96.11(11)°, respectively, having great departure from which of perfectly tetrahedron. The chelating ring plane 1 (composed of atoms $\text{Zn}(1)$, $\text{N}(1)$, $\text{C}(7)$, $\text{C}(6)$, $\text{C}(1)$ and $\text{O}(1)$) and chelating ring plane 2 (composed of atoms $\text{Zn}(1)$, $\text{N}(1\text{A})$, $\text{C}(7\text{A})$, $\text{C}(6\text{A})$, $\text{C}(1\text{A})$ and $\text{O}(1\text{A})$) are approximately vertical each other with dihedral angle of

81.5°. The dihedral angle between the aromatic ring (composed of atoms $\text{C}(1)$, $\text{C}(2)$, $\text{C}(3)$, $\text{C}(4)$, $\text{C}(5)$ and $\text{C}(6)$) and plane 1 is 8.1°, and therefore a approximately coplanar conjugation system was formed. Most of the bond lengths in the system are in the range of single bond to double bond.

Table 3 Selected bond lengths (nm) and bond angles (°) of ZnL_2

$\text{Zn}(1)\text{-O}(1)$	0.191 7(3)	$\text{Zn}(1)\text{-N}(1)$	0.200 7(3)
$\text{O}(1)\text{-C}(1)$	0.130 5(4)	$\text{C}(1)\text{-C}(2)$	0.141 0(6)
$\text{N}(1)\text{-C}(7)$	0.127 8(4)	$\text{C}(1)\text{-C}(6)$	0.141 5(5)
$\text{N}(1)\text{-C}(8)$	0.147 6(5)	$\text{C}(2)\text{-C}(3)$	0.137 6(6)
$\text{C}(3)\text{-C}(4)$	0.138 0(7)	$\text{C}(9)\text{-C}(14)$	0.138 2(5)
$\text{C}(4)\text{-C}(5)$	0.135 8(7)	$\text{C}(10)\text{-C}(11)$	0.138 6(6)
$\text{C}(5)\text{-C}(6)$	0.140 7(5)	$\text{C}(11)\text{-C}(12)$	0.135 8(6)
$\text{C}(6)\text{-C}(7)$	0.144 2(5)	$\text{C}(12)\text{-C}(13)$	0.136 9(7)
$\text{C}(8)\text{-C}(9)$	0.149 7(5)	$\text{C}(13)\text{-C}(14)$	0.136 7(6)
$\text{C}(9)\text{-C}(10)$	0.137 5(5)		
$\text{N}(1)\text{-Zn}(1)\text{-O}(1)$	96.11(11)	$\text{O}(1)\text{-Zn}(1)\text{-O}(1\text{A})$	114.75(12)
$\text{N}(1\text{A})\text{-Zn}(1)\text{-O}(1)$	113.21(12)	$\text{N}(1)\text{-Zn}(1)\text{-O}(1\text{A})$	113.21(12)
$\text{N}(1\text{A})\text{-Zn}(1)\text{-N}(1)$	124.69(11)	$\text{N}(1\text{A})\text{-Zn}(1)\text{-O}(1\text{A})$	96.11(11)
$\text{Zn}(1)\text{-O}(1)\text{-C}(1)$	123.7(2)	$\text{C}(1)\text{-C}(6)\text{-C}(7)$	124.5(3)
$\text{Zn}(1)\text{-N}(1)\text{-C}(7)$	119.7(2)	$\text{C}(5)\text{-C}(6)\text{-C}(7)$	116.2(3)
$\text{Zn}(1)\text{-N}(1)\text{-C}(8)$	122.53(19)	$\text{N}(1)\text{-C}(7)\text{-C}(6)$	128.2(3)
$\text{C}(7)\text{-N}(1)\text{-C}(8)$	117.7(3)	$\text{N}(1)\text{-C}(8)\text{-C}(9)$	112.5(3)
$\text{O}(1)\text{-C}(1)\text{-C}(2)$	118.6(3)	$\text{C}(8)\text{-C}(9)\text{-C}(10)$	121.5(3)
$\text{O}(1)\text{-C}(1)\text{-C}(6)$	124.2(3)	$\text{C}(8)\text{-C}(9)\text{-C}(14)$	120.2(3)
$\text{C}(2)\text{-C}(1)\text{-C}(6)$	117.2(3)	$\text{C}(10)\text{-C}(9)\text{-C}(14)$	118.2(3)
$\text{C}(1)\text{-C}(2)\text{-C}(3)$	121.5(4)	$\text{C}(9)\text{-C}(10)\text{-C}(11)$	120.6(4)
$\text{C}(2)\text{-C}(3)\text{-C}(4)$	120.7(4)	$\text{C}(10)\text{-C}(11)\text{-C}(12)$	120.2(4)
$\text{C}(3)\text{-C}(4)\text{-C}(5)$	119.3(4)	$\text{C}(11)\text{-C}(12)\text{-C}(13)$	119.8(4)
$\text{C}(4)\text{-C}(5)\text{-C}(6)$	121.9(4)	$\text{C}(12)\text{-C}(13)\text{-C}(14)$	120.4(4)
$\text{C}(1)\text{-C}(6)\text{-C}(5)$	119.3(4)	$\text{C}(9)\text{-C}(14)\text{-C}(13)$	120.9(4)

2.2 Spectra characterization

The IR and ES-MS spectra of the three complexes resemble each other indicating a similar structural relationship (see Table 4). Condensation of all primary amine groups and carbonyl groups is confirmed by the lack of N-H double stretching bands in the IR region 3 150~3 450 cm^{-1} and the presence of strong $\text{C}=\text{N}$ stretching bands at 1 630~1 690 cm^{-1} . The $\nu(\text{O-H})$ band originally found in the ligand salicylaldehyde disappeared on complexation indicating deprotonation of the phenolic hydroxyl group and coordination of phenolic oxygen to the metal ion. This is in agreement

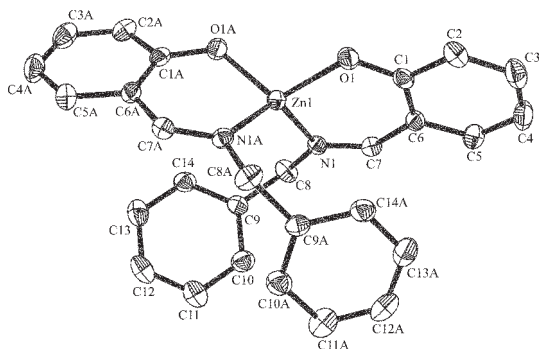


Fig.1 A stereoview of ZnL_2 with the atom numbering scheme (ellipsoids at 30% probability)

Table 4 IR and ES-MS spectra

Complex	$\nu(\text{C}=\text{N})$	$\nu(\text{furan ring})$	$\nu(\text{CH})$	$m/z/\%$	
				$[\text{ML}_2+\text{H}]^+$	$[\text{ML}_2+2\text{H}]^{2+}$
ZnL_2	1 638	1 586~1 435	2 857, 2 900	486.9(100%)	244.1(25%)
CuL_2	1 643	1 597~1 432	2 856, 2 900	484.9(24%)	243.1(100%)
CdL_2	1 641	1 569~1 431	2 849, 2 889	535.1(100%)	268.3(21%)

with molar conductivity of the complexes ($\Lambda_{\text{M}}(\text{CH}_3\text{OH}, 289 \text{ K})=21\sim 26 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$), which is attributable to non-electrolyte and molecular complex^[12]. The main peaks at m/z 486.9 and 244.1 in ZnL_2 are assigned to $[\text{ZnL}_2+\text{H}]^+$ and $[\text{ZnL}_2+2\text{H}]^{2+}$, respectively. Similarly, the peaks at m/z 484.9 and 243.1 in CuL_2 are corresponding to $[\text{CuL}_2+\text{H}]^+$ and $[\text{CuL}_2+2\text{H}]^{2+}$; peaks at m/z 535.1 and 268.3 in CdL_2 are corresponding to $[\text{CdL}_2+\text{H}]^+$ and $[\text{CdL}_2+2\text{H}]^{2+}$.

2.3 Antimicrobial activity

From the data of Table 5 it is observed that all the complexes exhibited antibacterial activity against

Staphylococcus aureus and *Escherichia Coli*. In the test range, the compounds were more active against the strains with the increase of concentration. CdL_2 show higher activity against bacteria as compared to complexes CuL_2 and ZnL_2 , especially in the activity against *Staphylococcus aureus*. Compared CuL_2 with ZnL_2 , the activities were basically similar but somewhat different with respect to the activities against *Escherichia Coli* in the concentration of 24.0 and 12.0 $\text{mg}\cdot\text{mL}^{-1}$. This fact may indicate that the metal center is an essential factor to the antibacterial value.

Table 5 Diameter of inhibition zone

(mm)

Compound	Concentration / ($\text{mg}\cdot\text{mL}^{-1}$)	Diameter of inhibition zone / mm	
		<i>Staphylococcus aureus</i>	<i>Escherichia Coli</i>
ZnL_2	24.0	20.6	17.6
	12.0	16.3	15.9
	6.0	10.9	12.3
	3.0	9.5	8.6
CuL_2	24.0	21.1	24.1
	12.0	16.5	20.4
	6.0	11.3	12.5
	3.0	9.3	10.7
CdL_2	24.0	40.4	29.1
	12.0	34.7	21.4
	6.0	28.9	16.5
	3.0	20.1	13.7

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