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Synthesis, Crystal Structures, and Antimicrobial Activities of Zinc Complexes Derived from Methyl Substituted 2-(Pyridin-2-yliminomethyl)phenols

San-Jun Peng^a, Liu-Bin Song^a, Jin-Heng Ning^a & Zhong-Liang Xiao^a ^a College of Chemistry and Biological Engineering, Changsha University of Science and Technology, Hunan, Changsha, P. R. China Published online: 16 Feb 2010.

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San-Jun Peng, Liu-Bin Song, Jin-Heng Ning, and Zhong-Liang Xiao

College of Chemistry and Biological Engineering, Changsha University of Science and Technology, Hunan, Changsha, P. R. China

A new mononuclear zinc(II) complex [ZnL1(MPA)I] (1) (HL1 = 2-[(4-methylpyridin-2-ylimino)methyl]phenol, MPA = 4methylpyridin-2-ylamine), and a new centrosymmetric dinuclear zinc(II) complex $[Zn_2L2_2I_2]$ (2) (HL2 = 2-[(5-methylpyridin-2ylimino)methyl]phenol), have been synthesized and structurally characterized by elemental analysis and X-ray diffraction. In 1, the Zn atom is four-coordinate in a tetrahedral coordination, while those in 2 are five-coordinate in severely distorted square pyramidal coordinations. The complexes, as well as the two Schiff bases, have been screened and evaluated for their antimicrobial activities.

Keywords antimicrobial, crystal structure, schiff base, X-ray crystallography, zinc complex

INTRODUCTION

Schiff bases are very easily synthesized by the condensation reaction of aldehydes with primary amines.^[1-3] Zinc complexes derived from Schiff base ligands have been studied extensively due to their interesting structures and wide applications.^[4-6] Recently, we have reported a few Schiff base zinc complexes with halide ligands;^[7,8] however, the Schiff base zinc(II) complexes containing the iodide ligands have seldom been reported so far. As a continuation of our work on such complexes, we report herein the synthesis, crystal structures and antimicrobial activities of two new zinc complexes [ZnL1(MPA)I] (1) and [Zn₂L2₂I₂] (2) (HL1 = 2-[(4-methylpyridin-2-ylimino)methyl]phenol, MPA = 4-methylpyridin-2-ylamine, HL2 = 2-[(5-methylpyridin-2ylimino)methyl]phenol).



EXPERIMENTAL

Materials and Methods

All chemicals and reagents were obtained from commercial sources and used as received. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240C elemental analyzer.

HL1 and HL2 were synthesized by the reaction of equimolar quantities of salicylaldehyde with 4-methylpyridin-2-ylamine and 5-methylpyridin-2-ylamine, respectively, in methanol, as that described in the literature.^[9] The Schiff bases were used without purification.

Synthesis of the Complex 1

A methanol solution (2 mL) of ZnI₂ (30.8 mg, 0.1 mmol) was added dropwise to a methanol solution (10 mL) of freshly produced HL1 (21.2 mg, 0.1 mmol) that might contain small amount of starting materials. The mixture was stirred at room temperature for 30 min and filtered. Colorless block crystals were formed when slow evaporation of the filtrate in air for a few days. Yield: 32.7 mg (64%). Anal. calcd. for C₁₉H₁₉IN₄OZn: C, 44.6; H, 3.7; N, 10.9%. Found: C, 44.3; H, 3.8; N, 11.1%.

Synthesis of the Complex 2

Complex **2** was prepared by a similar method as that for **1**, with HL1 replaced by HL2. Colorless block crystals of **2** were formed after a few days. Yield: 35.0 mg (87%). Anal. calcd. for $C_{26}H_{22}I_2N_4O_2Zn_2$: C, 38.7; H, 2.7; N, 6.9%. Found: C, 38.4; H, 2.9; N, 6.7%.

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Address correspondence to Dr. San-Jun Peng, College of Chemistry and Biological Engineering, Changsha, 410014, China. E-mail: sanjunpeng@163.com

Complex	1	2
Formula	C ₁₉ H ₁₉ IN ₄ OZn	$C_{26}H_{22}I_2N_4O_2Zn_2$
FW	511.6	807.0
Crystal color/shape	Colorless/block	Colorless/block
Crystal size/(mm ³)	$0.20 \times 0.18 \times$	$0.20 \times 0.17 \times$
-	0.17	0.15
Crystal system	Monoclinic	Triclinic
Space group	$P2_{1}/c$	P-1
a (Å)	10.625(2)	7.840(2)
<i>b</i> (Å)	21.716(3)	8.741(2)
$c(\dot{A})$	8.454(2)	10.514(2)
α (/°)	90	84.557(3)
β (/°)	94.74(3)	80.605(3)
γ (/°)	90	72.598(3)
V (Å ³)	1943.9(7)	677.5(2)
Z	4	1
T (K)	298(2)	298(2)
$\mu \text{ (mm}^{-1}) \text{ (Mo K}\alpha)$	2.867	4.079
$D_c ({ m g}{ m cm}^{-3})$	1.748	1.978
Unique reflections	4373	2757
Independent reflections	2930	1893
Parameters	243	164
Restraints	3	0
<i>F</i> (000)	944	388
Index range (h, k, l)	-13/13, -27/28,	-9/9, -10/10,
	-10/10	-13/13
T_{\min}	0.598	0.496
$T_{\rm max}$	0.641	0.580
Goodness of fit on F^2	1.029	1.049
$R_1, wR_2 [I \ge 2\sigma (I)]^a$	0.0490, 0.0948	0.0510, 0.0934
R_1 , wR_2 (all data) ^{<i>a</i>}	0.0818, 0.1064	0.0827, 0.1039
$aR_{1} = \sum_{v \in F_{o}^{2}} F_{o} - F_{o} - F_{o} $	$ F_c /\sum F_o , wR_2 =$	$\sum \overline{w(F_o^2 - F_c^2)^2}/$

TABLE 1 Crystal data for the complexes **1** and **2**

DATA COLLECTION, STRUCTURAL DETERMINATION, AND REFINEMENT

Crystal Structure Determination

Single crystals of both complexes were selected and mounted on the top of glass fibers. The data were collected on a Bruker SMART 1000 CCD area diffractometer at 298(2) K. Graphitemonochromatized Mo K α radiation ($\lambda = 0.71073$ Å) and the ω scan technique were used to collect the data sets. Absorption corrections were applied using SADABS.^[10] The crystal structures were solved with direct methods and refined with a full-matrix least-squares technique using SHELXTL package.^[11] Anisotropic thermal parameters were applied to all non-hydrogen atoms. The two amino H atoms in **1** were located from a difference Fourier map and refined isotropically, with N—H and H···H distances restrained to 0.90(1) and 1.43(2) Å,

 TABLE 2

 Selected bond lengths (Å) and bond angles (°) for the complexes 1 and 2

L						
1						
Zn1–O1	1.988(3)	Zn1-N3	2.029(4)			
Zn1–N1	2.021(4)	Zn1–I1	2.5623(9)			
O1–Zn1–N1	91.72(14)	O1–Zn1–I1	112.76(11)			
O1–Zn1–N3	107.48(14)	N1-Zn1-I1	120.10(11)			
N1-Zn1-N3	116.46(15)	N3–Zn1–I1	107.02(11)			
		2				
Zn1–O1	2.082(4)	Zn1-N2	2.518(5)			
Zn1–O1 ⁱ	1.975(4)	Zn1–I1	2.5413(10)			
Zn1–N1	2.003(5)					
O1 ⁱ –Zn1–N1	125.8(2)	O1–Zn1–N2	140.51(18)			
O1 ⁱ –Zn1–O1	81.41(19)	O1 ⁱ –Zn1–I1	113.94(14)			
N1–Zn1–O1	86.29(19)	N1-Zn1-I1	119.55(15)			
O1 ⁱ -Zn1-N2	104.85(19)	O1–Zn1–I1	112.17(14)			
N1-Zn1-N2	58.0(2)	N2-Zn1-I1	100.89(13)			

Symmetry code: (i) 1 - x, -y, 2 - z.

respectively. Other H atoms were generated geometrically. The crystallographic data as well as details of the data collection and refinement for the complexes are listed in Table 1. Selected bond lengths and angles are given in Table 2.

RESULTS AND DISCUSSION

Structure Description of the Complexes

Figures 1 and 2 give perspective views of the complexes 1 and 2 together with the atomic labeling systems. Complex 1 is a mononuclear zinc(II) compound, while complex 2 is a phenolic O-bridged centrosymmetric dinuclear zinc(II) compound.

The Zn atom in **1** is four coordinated by one O and one N atoms of HL1, one pyridine N atom of a MPA, and one I atom, forming a distorted tetrahedral coordination. The Zn–I bond is much longer than the other three bonds. The dihedral angle between the HL1 and MPA planes is $73.3(2)^\circ$, which can decrease the steric effects between them. Except for the linkage of the Zn1 atom between the HL1 and MPA molecules, there exists an intramolecular N4–H4B···O1 hydrogen bond. The molecules are further linked through intermolecular N–H··O hydrogen bonds, forming chains running along the *c* axis, as shown in Figure 3.

The inversion center of complex **2** lies at the midpoint of the two Zn atoms. Each Zn atom is five-coordinate in a distorted square pyramidal geometry, with one imine N, one pyridine N, and two phenolic O atoms from two Schiff base ligands defining the base plane, and with one I atom occupying the apical position. The square pyramidal coordination is distorted, which can be found from the coordinate bond angles. The N1–Zn1–N2 and O1–Zn1–O1ⁱ (symmetry code: i) 1 - x, -y, 2 - z) bond angles largely deviate from the ideal values of 90° for a square



FIG. 1. The structure of 1 showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Intramolecular hydrogen bond is drawn as a dashed line.

pyramidal geometry, and are caused by the strain created by the four-membered chelate rings Zn1-N1-C8-N2 and Zn1-O1-Zn1ⁱ-O1ⁱ. The Zn1–N2 bond is much longer than those of the other bonds in the base plane, indicating the coordination between them is very weak. Each Schiff base ligand is nearly coplanar with the dihedral angle of $3.1(2)^\circ$ between the benzene and the pyridine rings. The dihedral angle between the perfectly planar Zn1–O1–Zn1ⁱ–O1ⁱ and the least-squares plane of the Schiff base ligand is $44.6(2)^\circ$. The distance between the two Zn atoms is 3.076(2) Å. In the crystal structure of **2**, molecules are stack



FIG. 2. The structure of **2** showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labeled with the suffix A or unlabeled are at the symmetry position (-x, y, 1/2 - z).



FIG. 3. The molecular packing of 1, viewed along the *a* axis. Intermolecular hydrogen bonds are shown as dashed lines.

along the a axis, with no obvious short contacts, as shown in Figure 4.

The corresponding bond lengths in the two complexes are comparable to each other, and also comparable to the similar Schiff base zinc complexes with I atoms.^[12]

IR Spectra

The IR spectra of HL1, HL2, and the two complexes provide information about the metal-ligand bonding. The assignments are based on the typical group frequencies. The middle and broad bands centered at about 3420-3450 cm⁻¹ in the two Schiff bases are due to the phenolic OH groups, which are absent in the two complexes. The strong absorption bands at 1627 cm^{-1} in the spectra of both Schiff bases are assigned to the azomethine groups, ν (C=N). The bands are shifted to lower wave numbers in the two complexes (1613 cm^{-1} for **1** and 1615 cm^{-1} for **2**), which may be attributed to the coordination of the nitrogen atom of the azomethine group to the Zn atoms. The middle absorption bands at about 1200 cm⁻¹ in the spectra of the Schiff bases are assigned to the phenolic groups, $\nu(Ar-O)$. The bands are also shifted to lower wave numbers in the two complexes (1187 cm⁻¹ for 1 and 1172 cm^{-1} for 2), indicating the coordination of the phenolic O to the Zn atoms.



FIG. 4. The molecular packing of 2, viewed along the a axis.

Antimicrobial Activities

The antimicrobial activities of the complexes were estimated by minimum inhibitory concentration (MIC: $\mu g m L^{-1}$), according to the literature method.^[13]

The anitimicrobial activities of the complexes and the corresponding Schiff bases are listed in Table 3, as estimated by MIC. Antimicrobial activities of the free Schiff bases, HL1 and HL2, were estimated as >100 μ g mL⁻¹ for *B. subtilis* and *S. aureus*, but show weak activities against *E. coli* and *P. aeruginosa*. The two complexes show stronger activities agaist all the bacteria than the two Schiff bases. The activities of complex 1 are a little superior than those of **2**, which might be caused by the amino groups in the complex, which readily forms intermolecular hydrogen bonds.

CONCLUSIONS

In the above study, two new zinc(II) complexes with Schiff bases HL1 and HL2 are discussed. X-ray crystallography indicates that the Schiff bases coordinate to the Zn atoms through the phenolic O and imine N atoms. The pyridine N atoms of the Schiff bases are not or weak coordinate to the Zn atoms due to

TABLE 3 Antimicrobial activities (MIC: μ g mL⁻¹)

	E. coli	B. subtilis	S. aureus	P. aeruginosa
HL1	52.3	> 100	> 100	37.2
HL2	61.2	> 100	> 100	35.0
1	8.5	15.8	13.2	4.5
2	11.2	27.6	19.0	8.7

the large steric effects of the four-membered chelated rings. The antimicrobial tests indicate that both complexes show remarkable activities against the bacteria.

Supplementary Data

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre with the Cambridge Crystallographic Data Centre (The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk; website: http://www.ccdc.cam.ac.uk; fax: +44 1223 336033) and are available free of charge on request, quoting the Deposition No. CCDC 729551 & 729552.

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