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Synthesis, Crystal Structure and Antibacterial Evaluation of Di- μ -chlorido-bis({2-[(4-methoxyphenyl)- iminomethyl]pyridine- κ^2 N,N'})Mercury(II)

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Abstract

New coordination polymer of $[\text{HgLCl}_2]_n$ (**1**) with HgCl_2 and Schiff base bidentate ligand (4-methoxyphenyl) pyridine-2yl methyleneamine (L) was prepared and structurally characterized. In the 1D network structure of **1**, the mercury (II) ion adopts an HgN_2Cl_3 distorted square pyramid geometry. In this complex, one of the chlorine acts as bridging ligand connecting two adjacent mercury(II) ions while, the L ligand is coordinated to mercury(II)ion in a cyclic-bidentate fashion forming an five-membered metallocyclic ring. Coordination compounds **1** has been characterized by infrared spectroscopy, UV-visible spectroscopy, elemental analyses and single-crystal X-ray diffraction. The compound crystallizes in the monoclinic space group $P 2_1/c$ with $a = 9.3053(17)$, $b = 7.1125(13)$, $c = 20.708(4)$, and $\beta = 80.208(4)^\circ$. The antibacterial activities of the complex, ligand and metal salt were tested against Gram-positive bacteria *Staphylococcus aureus* and Gram-negative bacteria *Escherichia coli* studied by disk diffusion method.

Keywords: *Coordination polymers, Mercury (II) compounds, Nitrogen-donor ligands, Schiff bases, Crystal structure, Antibacterial activities.*

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Introduction

Transition metals with oxidation state +2 react with the nitrogen donor ligands to form various complexes with fascinating structures and desirable properties. Most of the recent work in this area has concentrated on the coordination complexes formed by the rigid and flexible nitrogen donor ligands. Up to now, many attempts have been made to synthesize a variety of transitional metal (II) complexes by using different ligands with different coordination ability to design coordination compounds with fascinating structures and desirable physically and chemically properties. In contrast to the coordination complexes of 3d (or 4d) transition metal ions, the formation of compounds with heavy metal ions such as mercury (II) is unreasonably sparse. Mercury (II) in some of its complexes has a remarkable ability to self-assemble in different manners through the coordination bridges between the metal ions or non-classical bonds such as π - π stacking and hydrogen bonds to form structures with 0D, 1D, 2D and 3D frameworks [1–7]. In these structures, Hg (II) ion exhibits a range of coordination configurations such as trigonal-planar, square-planar, tetrahedral and octahedral environment [8, 9]. Mercury (II) compounds attractive properties in terms of their potential applications such as paper industry, paints, thermometers, manometers, fluorescent lamps and mercury batteries [10].

The development in the field of biological inorganic chemistry has increased [11,12]. A large number of Schiff bases and their metal complexes have been investigated due to their interesting biological properties such as their ability to reversibly bind oxygen, biological modeling applications and antibacterial, anticancer, antifungal, and herbicidal activities [13–15]. In many cases, when Schiff bases administered as their metal complexes, the biological activity of these complexes is enhanced in comparison to the free ligand [16–18]. As an extension of our investigation, herein we report synthesis, characterization, and antibacterial activities of Hg(II) complexes with (4-methoxyphenyl) pyridine-2yl methyleneamine ligand.

Experimental

Instrumentation

All experiments were carried out in air atmosphere. Starting materials were purchased from commercial sources and used without further purification. The ligands (4-methoxyphenyl) pyridine-2-ylmethyleneamine was prepared according to the published method [19]. Infrared spectra (4000-400 cm^{-1}) and Electronic absorption spectra were recorded using KBr pellets with a Bruker Tensor 27 and JASCO V-570 spectrophotometer, respectively. Elemental analyses for C, H and N were performed on a Thermo Finigan Flash EA 1120 CHN analyzer.

Synthesis of HgLCl_2 (1)

An aqueous solution of HgCl_2 (0.027g, 0.1 mmol) was added while stirring to an ethanol solution of L (0.0212g, 0.1 mmol). The solution was filtered and allowed to evaporate slowly in air. Light yellow crystals of 1 (Figure 1) suitable for single crystal X-ray diffraction were isolated directly from the solution after a few days. Yield 75%. IR (KBr; v/cm^{-1}): $\nu(\text{C}=\text{N})$, 1605. UV-Vis: (DMSO; $\log \epsilon$): 232 (4.11), 277 (3.86), 293 (3.63). Anal. Calc. for $\text{C}_{13}\text{H}_{12}(\text{Cl})_2\text{N}_2\text{OHg}$: C,(28.87);H,(2.20);N,(6.12), %. Found: C,(28.76);H,(2.25)N,(6.21)% .

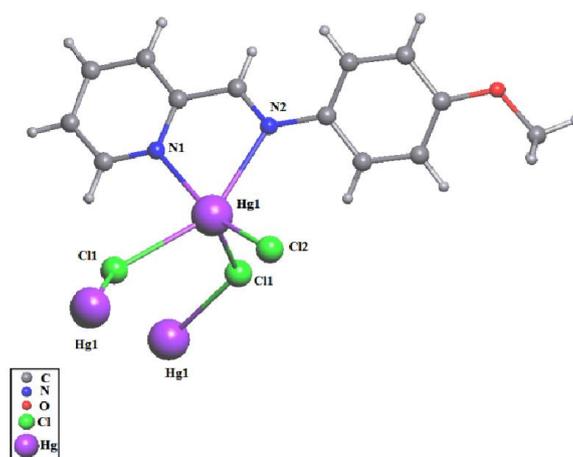


Figure 1. The coordination environment in $[\text{HgLCl}_2]_n$ with atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

X-ray Diffraction Analysis

Crystals of the complexes suitable for X-ray diffraction analysis were obtained as described above. A summary of the key crystallographic information is listed in Tables 1 and 2. Diffraction data for this compound was collected on a Bruker–Nonius Kappa-CCD diffractometer using a monochromated $\text{MoK}\alpha$ radiation and measured using a combination of φ scans and ω scans with κ offsets to fill the Ewald sphere. The data was processed using the Denzo-SMN package [20]. Absorption corrections were carried out using SORTAV [21]. The structure was solved and refined using SHELXTL, version 6.1 [22], for full-matrix least squares refinement based on F^2 . All H atoms were included in calculated positions and allowed to refine structure in a riding-motion approximation with Uiso tied to the carrier atom. CCDC 1526131 contains the supplementary crystallographic data for 1.

Table 1. Crystal data and single-crystal X-ray diffraction refinement details for the title compound.

Complex	data
Formula	C ₁₃ H ₁₂ Cl ₂ HgN ₂ O
Formula weight (gr/mol)	483.74
Temperature (K)	150(1)
Wavelength(Å)	0.71073
Crystal system	Monoclinic
Space group	P 2 ₁ /c
a(Å)	9.3053(17)
b (Å)	7.1125(13)
c (Å)	20.708(4)
β (°)	80.208(4)°.
Volume(Å ³)	1365.2 (4)
Z	4
Calculated density (mg/m ³)	2.354
Absorption coefficient (mm ⁻¹)	11.657
F(000)	904
Crystal size (mm ³)	0.25×0.20×0.15
Theta range for data collection (°)	1.97 to 27.51
Index ranges	-12<h<12, -9<k<8, -26<l<26
Reflections collected	11904
Completeness to theta = 27.51°	99.4
Max. and min. transmission	0.7456 and 0.5232
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3114 / 0 / 173
Goodness-of-fit on F ²	1.047
Final R indices [I>2σ(I)]	R1 = 0.0198, wR2 = 0.0418
R indices (all data)	R1 = 0.0241, wR2 = 0.0431
Largest diff. peak and hole (e.Å ⁻³)	0.973 and -0.960

Crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/datarequest/cif>. or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Table 2. Selected bond lengths [Å] and bond angles [°] for the title compound.

Bond lengths (Å)		Bond Angles (°)	
Hg(1)-N(1)	2.270(3)	Cl(1)-Hg(1)-Cl(2)	106.56(3)
Hg(1)-N(2)	2.561(3)	Cl(1)-Hg(1)-N(1)	98.98(7)
Hg(1)-Cl(1)	2.5642(9)	Cl(1)-Hg(1)-N(2)	100.24(6)
Hg(1)-Cl(2)	2.4116(9)	Cl(1)-Hg(1)-Cl(1)	100.58(2)
Hg(1)-Cl(1)	2.7873(8)	Cl(2)-Hg(1)-N(1)	153.06(7)
Cl(2)-Hg(1)-Cl(1)	95.12(3)	Cl(2)-Hg(1)-N(2)	96.73(7)
N(1)-Hg(1)-N(2)	69.93(9)		
N(1)-Hg(1)-Cl(1)	88.28(7)		
N(2)-Hg(1)-Cl(1)	151.70(6)		

Antibacterial activities

The antibacterial activity of the complex, ligand and metal salt was studied against Gram-positive bacteria *Staphylococcus aureus* and Gram-negative bacteria *Escherichiacoli*. Each of the compounds dissolved in dimethylsulfoxide with a concentration of 37 mg/ml was prepared. Filter Paper discs of 10 mm in size prepared by using Whatman filter paper no.1 were sterilized by autoclave. Antibacterial activities of each compound were evaluated by the agar disc-diffusion method [23, 24]. The paper discs were saturated with 37 mg/ml of the compound dissolved in dimethyl sulfoxid solution and were place aseptically in the Petri dishes containing Nutrient agar media inoculated with the above mentioned two bacteria separately. The petri dishes were incubated at 37°C and the inhibition zones were recorded after 24h of incubation. The inhibition zones were measured in mm and results are shown in Table 3. The results of table 3 showed that zone of inhibition growth for $HgCl_2$ is more than Hg(II) complex. Also antibacterial effects for each of compounds in comparative with *Escherichia coli* and is bigger than *Staphylococcus aureus*.

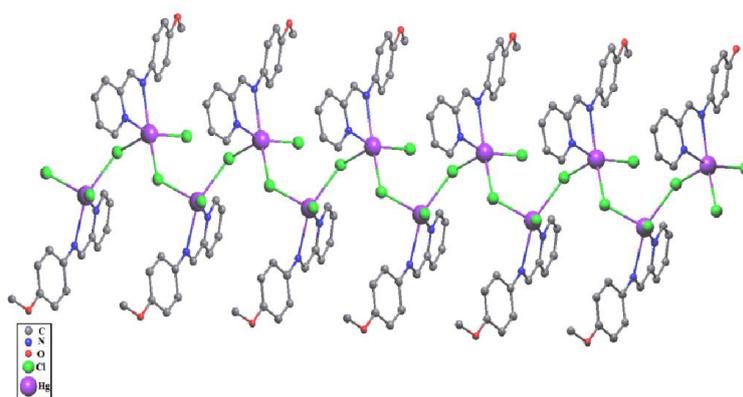
Table 3 . Growth inhibition zone bacterial in mm.

Compounds	<i>Escherichiacoli</i>	<i>Staphylococcus aureus</i>
$HgCl_2$	4.4	4
Schiff base	5	2.8
Hg(II) Complex	3.8	2.6

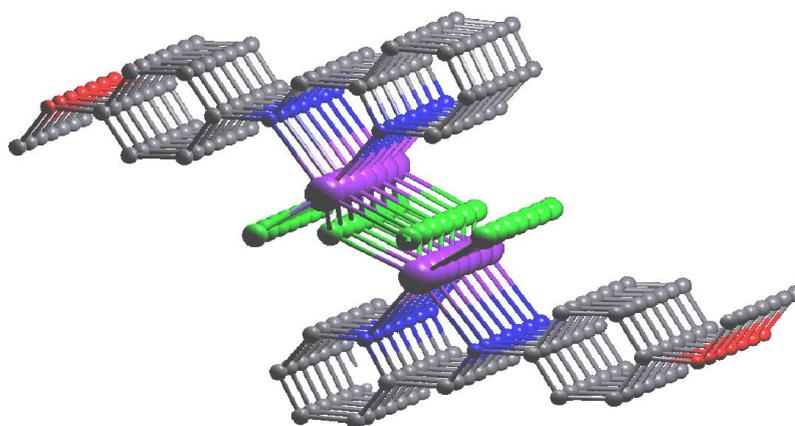
Results and Discussion

The atom labeling scheme and molecular view of **1** is shown in Figure 1. This compound crystallizes in the monoclinic space group $P 2_1/c$ with $Z = 4$ (Table 1). Selected bond distances and

angles are listed in Table 2. The Hg(II) atom is in a distorted CuN_2Cl_3 square pyramidal ($\tau = 0.022$), based on the Addison analysis [25], where $\tau = 0.00$ describes a perfect square pyramid and $\tau = 1.00$ shows a trigonal bipyramidal. The basal plane of the square pyramidal is defined by the two imine nitrogen atoms of the chelating bidentate L ligand with bond lengths of 2.270(3), 2.561(3), and two chlorine atoms with bond lengths of 2.5643(9), 2.7873(9). The axial position of this structure is occupied by a chlorine atom with bond lengths of 2.4116(9). In the crystal structure, the chlorine act as a bridging ligand, linking the Hg(II) centers into a one-dimensional zigzag chain structure running along the crystallographic b and c -axis (Figure 2).



(a)



(b)

Figure 2. a) View of a portion of the 1D net in $[\text{HgLCl}_2]_n$ along the b -axis. b) along the c -axis.

Structural comparison between the $[\text{Hg}_2\text{Cl}_4(\text{dip})_2]$ (dip= (E)-4-ethyl-*N*-(pyridine-2-ylmethylene)benzeneamine) [26] and compound 1 shows that the replacement of the dip by the (4-methoxyphenyl) pyridine-2-yl methyleneamine ligand change the structure from dimer to polymer. Accordingly, the ligands are responsible for directing the structure of these compounds.

Conclusion

In summary, by using Schiff base bidentate ligand (4-methoxyphenyl) pyridine-2-yl methyleneamine (L) and appropriate metal salt of mercury (II), we successfully obtained new coordination polymer. This compound has a polymeric structure with 1D network. These observations clearly attributed to the effects of the Schiff base ligands on the final structure of the complexes. The results of antibacterial screening, indicate that each of the compounds show more activity for Escherichia coli than Staphylococcus aureus. On the other hand, experiments showed that inhibition zone of mercury(II) complex is fewer than mercury(II) salt, So we can say toxicity of complex is lower than mercury(II) salt.

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