Research Article

Synthesis, characterization and 2,5-pyridinedicarboxylic acid interaction of Zinc(II) complexes with N-(4-X-phenyl)pyridine-2-yl-methanimine ligands (X= -Cl and -N(CH_3)$_2$)

Nicole Dinamarca[a], Pedro Levín[a], Hugo Muñoz[a], Francesco Caruso[b], Miriam Rossi[b], Juan Guerrero[a] and Manuel Ignacio Azócar[a]*.

[a]*Departamento de Química de los Materiales, Facultad de Química y Biología, Universidad de Santiago de Chile, Av. L. B. O`Higgins 3363, Casilla 40, Correo 33, Santiago Chile.* [b]*Vassar College, Department of Chemistry, Poughkeepsie, NY 12604, USA.* *e-mail: manuel.azocar@usach.cl

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Abstract: Two new Zn(II) N-(4-X-phenyl)pyridine-2-yl-methanimine complexes, [Zn(NN´-Cl)Cl_2](**1**) and [Zn(NN´-N(CH_3)$_2$)Cl_2](**2**), have been synthesized and characterized by elemental analysis, FT-IR and NMR-^{1}H spectra. The crystal structure of complex **1** was determined by X-ray single crystal diffraction. Experiments performed by Benesi-Hilderbrand method indicate that zinc complexes interact with 2,5-pyridinedicarboxyc acid.

Supporting information: CIF file.

Keywords: *Zinc(II) complex; X-ray crystal structure; 2,5-pyridinedicarboxylic acid; Benesi-Hilderbrand.*

1. INTRODUCTION

Zinc is one of the most important trace elements in biological systems and plays an important role in hundreds of metalloenzymes [1]. Zinc complexes possess diverse biological activity, such as anticancer[2], antioxidant[3], antimicrobial activity,[4] and other complexes have been tested for the treatment of Alzheimer disease [5].

Recently, N-(4-nitrophenyl)pyridine-2-yl-methanimine ligand has been used for the synthesis of copper (I) complexes and their studies of the self-association in solution and solid phase [6]. Investigations of molecular structures of N-(phenyl substituted)-pyridine-2-aldimines, have indicated that changes in substituents in both aniline and benzylidene rings largely affect the overall electronic distribution and conformation of the molecules [7,8].

Even the biological of N-(phenyl substituted)pyridine-2-, -3-, and -4-aldimines have been studied in detail, demonstrating their antileishmanial and antioxidant activities [9].

However, zinc complexes with N-(phenyl substituted)pyridine-2-aldimines have not been synthezised in order to study their chemical and biological properties or even the interaction with other molecules.

Herein we report two zinc compounds formed with N-(4-X-phenyl)pyridine-2-yl-methanimine ligands (X= -Cl, -N(CH_3)$_2$, Figure 1).

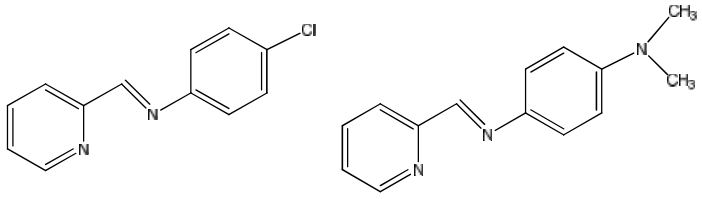

Figure 1: N-(4-Cl-phenyl)pyridine-2-yl-methanimine and N-(4-N(CH_3)$_2$-phenyl)pyridine-2-yl-methanimine ligands.

Structural characterization of Zinc(II) complex with N-(4-Cl-phenyl)pyridine-2-yl-methanimine ligand was carried out by X-ray diffraction analysis. Interaction of the new Zn(II) complexes with 2,5-pyridinedicarboxylic acid was tested by Uv-Vis Benesi-Hildebrand method [10].

2. EXPERIMENTAL

2.1 Material and physical measurements

All chemicals were analytical grade of Merck and Aldrich and used without purification. The methods used for preparing all the new Zn(II) complexes was quite similar to previously reported procedures [6]. C, H, and N were analyzed with a CE elemental analyzer (EA 1108 model). IR spectra (KBr discs) were recorded on a FT-IR spectrometer Shimadzu IR-Tracer 100. NMR Spectra were recorder in a Bruker 400 Mhz spectrometer in DMSO-d^6. The crystal structure was determined by X-ray diffraction, using a low temperature data set collected with a BRUKER Apex II diffractometer at 125 K, with SMART as a driving software and SAINT for data reduction.

The structure was solved by direct methods using SHELXS-97

and refined on F2 by full-matrix least-squares with SHELXL-97. The molecular representations shown in the figure 2 were generated using XP in the SHELXTL package and Mercury. The interaction of the zinc complexes with 2,5-pyridinedicarboxylic acid was studied by Benesi-Hildebrand method[10].

[Zn(NN´-Cl)Cl_2]: Red powder, 77,3% Yield, m.p.: 270ºC, Anal. Calculated for $C_{12}H_9N_2Cl_3Zn$: C, 40.84; N, 7,94; H, 2.57. Anal. Found: C, 41.02; N, 8,04 H, 2.47, FT-IR: 2909 (w, pyridine ring), 1621(s, imine), cm^{-1}. ^{1}H-NMR: 7.38(d, Ar-H), 7,45 (d, Ar-H), 7.75(m, Ar-H), 8.11(d, Ar-H), 8.16(t, Ar-H), 8.72(s, CH=N), 8.90(s, CH=N), ppm. λmax= 235 nm (ε = 26,473 M^{-1} cm^{-1}).

[Zn(NN´-N(CH_3)$_2$)Cl_2]: Orange powder, 86% Yield, m.p.: 240ºC, Anal. Calculated for $ZnC_{14}H_{15}N_3Cl_2$: C, 46.50; N, 11,62, H, 4.18,. Anal. Found: C, 46.68; N, 11.93, H, 4.05, FT-IR: 2924 (w, pyridine ring), 1616(s, imine), cm^{-1}. ^{1}H-NMR: 8.80 (d, Ar-H), 8,78 (s, CH=N), 8,10 (d, Ar-H), 8,10 (t, Ar-H), 7,66 (m, Ar-H), 7,45 (d, Ar-H), 6,76 (d, Ar-H), 2,97 (s, 6H, -N-CH_3), ppm. λMax = 247nm (ε = 11,769 M^{-1} cm^{-1}).

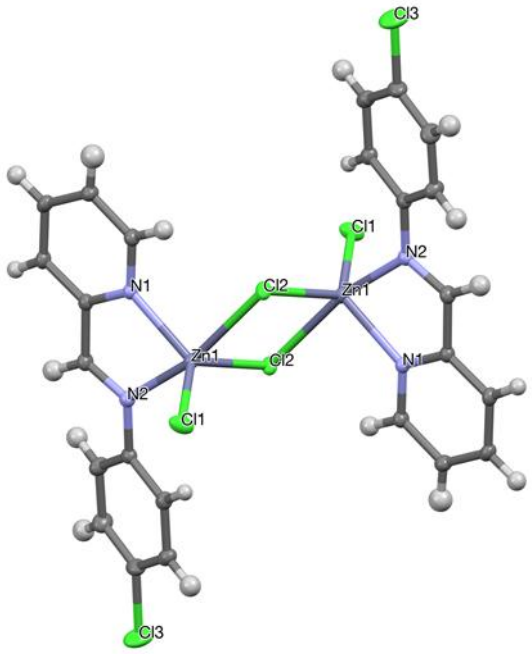

Figure 2: The molecular structure of **1**

3. RESULTS AND DISCUSSION

The complex was prepared by reaction of equimolar amounts of $ZnCl_2$ and the ligands (N-(4-X-phenyl)pyridine-2-yl-methanimine (X: -Cl_2 and -N(CH_3)$_2$) in acetone at room temperature and stirring by 1 hour. The products were obtained as a dark red solid and crystallized by slow ether diffusion into a dichloromethane solution of the complex. The ^{1}H-NMR spectrum of the complex is consistent with the presence of NN´-NO_2 and NN´-N(CH_3)$_2$ coordinated to the metal center.

Crystallographic and structural data for the five-coordinate zinc compound (**1**) is found in Table 1. The geometry is a distorted trigonal-bipyramidal, which is common for this type of zinc complexes[11]. The apical positions are ocupied by chlorine and the nitrogen of the imine group(N(2)-Zn(1)-Cl(2)) with an angle of 166.17º.

The Zn-Cl_{eq} (2.2285 and 2.2807 Å) bond distance is shorter than that of Zn-Cl_{ap}(2.6820 and Å) and the zinc complex is dimeric with two zinc atoms bridging through two chlorine atoms.

The angles for an idealized trigonal bipyramid are 90º, 120º and 180º. By contrast, the observed angles range from 78.35º (N_{eq}-Zn-Cl_{ap}) to 119.53º(N_{eq}-Zn-Cl_{eq}), and 166.17º (N_{ap}-Zn-Cl_{ap}) respectively. Chelate ligand spanning the apical and equatorial positions appear primarily responsible for these distortions[11, 12].

For the six-membered rings, the L-Zn-L angles are all within the range 82º to 94º, but in the complex 1, the imine group played a role in decreased the angle to a value of 78.35º [11].

The square-pyramidal zinc(II) compounds are mostly purple or violet in colour by electron withdrawing of the ligands and the

Table 1: Selected bond length[Å] and angles[º] for complex **1**

Cl(2)-Zn(1)-Cl(1)	122.73(1)	N(1)-Zn(1)-Cl(2)	90.37(3)
Cl(2)-Zn(1)-N(1)	117.63(3)	N(2)-Zn(1)-Cl(2)	166.17(3)
Cl(2)-Zn(1)-N(2)	92.64(3)	Zn(1)-Cl(2)-Zn(1)	94.53(1)
Cl(2)-Zn(1)-Cl(2)	85.47(1)	Zn(1)-Cl(1)	2.2285(7)
Cl(1)-Zn(1)-N(1)	119.53(3)	Zn(1)-Cl(2)	2.2807(10)
Cl(1)-Zn(1)-N(2)	101.56(3)	Zn(1)-Cl(2)	2.6820(9)
Cl(1)-Zn(1)-Cl(2)	90.92(1)	Zn(1)-N(1)	2.0760(10)
N(1)-Zn(1)-N(2)	78.35(3)	Zn(1)-N(2)	2.2100(12)

Space Group: P21/n, Cell: a 7.433(3)Å b 14.338(6)Å c 12.705(6),Å, α 90° β 97.378(7)° γ 90°. cell_volume 1342.82. 1 x,y,z 2 1/2-x,1/2+y,1/2-z 3 -x,-y,-z 4 1/2+x,1/2-y,1/2+z

trigonal bipyramidal compounds are mostly colourless[11]. However, the complexes obtained are colored because the imine ligands absorb in the Uv-vis region of the spectra.

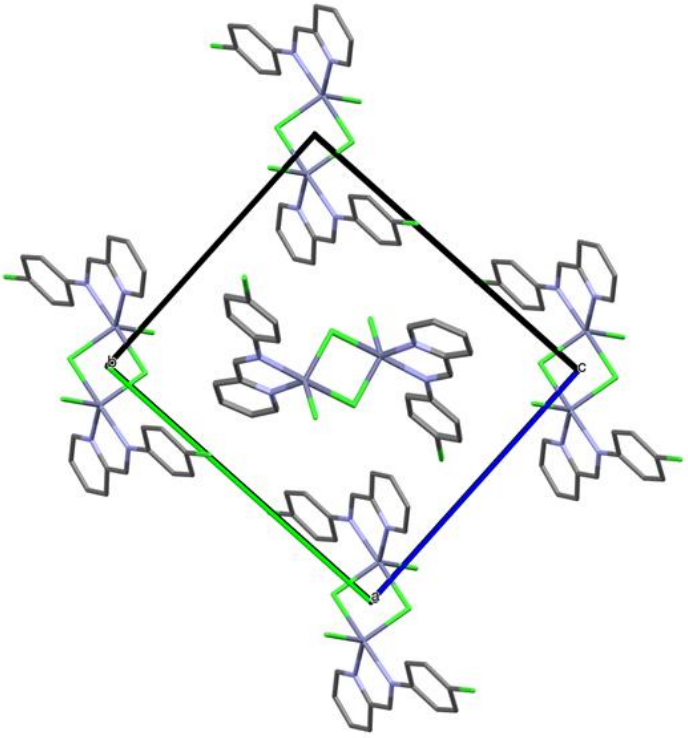

Figure 3: View of the 2D framework of the complex 1.

Subsequently, the interaction between the complex and the 2,5-pyridinecarboxylic(2,5) ligand was studied, by varying the absorbance at 235 nm of complex **1**(Figure 4).

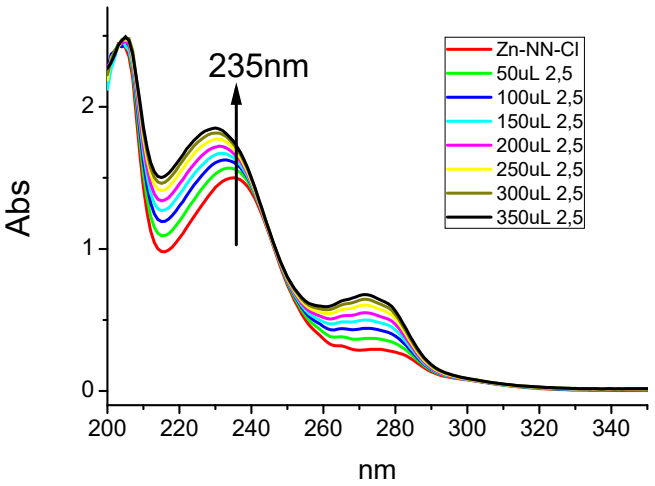

Figure 4: Effect of the increase in the concentration of 2,5-pyridinecarboxylate in the absorption spectrum of the [Zn-(NN'-Cl)Cl_2] complex. The concentration of 2,5-pyridinecarboxylate in water increased from 0 to 6.205x10^{-5} M.

From plot 1(Figure 5), the affinity constant (Kb) was calculated between the complex and the 2,5-pyridinecarboxylic ligand. This calculation was performed using the Benesi-Hildebrand equation (1), which establishes a linear relationship between the inverse of the absorbance difference and the inverse of the concentration of the added ligand (applicable for 1:1 interactions). Data were recorded in figure 5.

$$\frac{1}{\Delta Abs} = \frac{1}{\Delta\varepsilon[2,5]} + \frac{1}{K_b(\Delta\varepsilon[2,5])}\frac{1}{[2,5]} \quad (1)$$

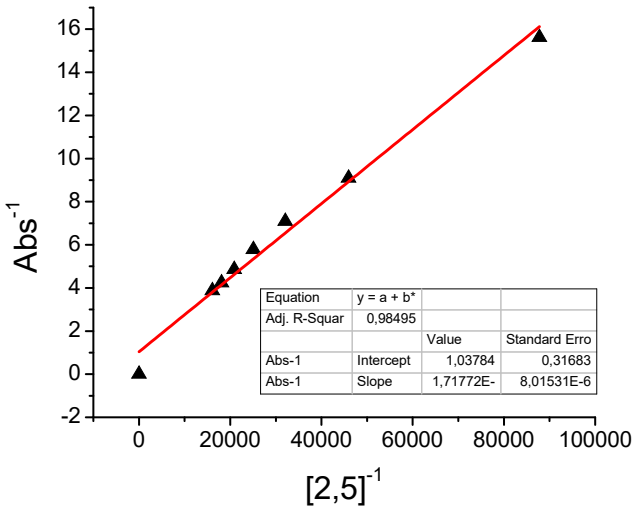

Figure 5. Graph of the Benesi-Hildebrand equation at 235nm according to equation (1) to calculate the affinity constant between the complex [Zn-(NN'-Cl)Cl_2] and the 2,5-pyridinecarboxylic ligand.

From the graph the affinity constant (Kb = 6.062) was determined for the Zn- (NN'-Cl)Cl_2 complex.

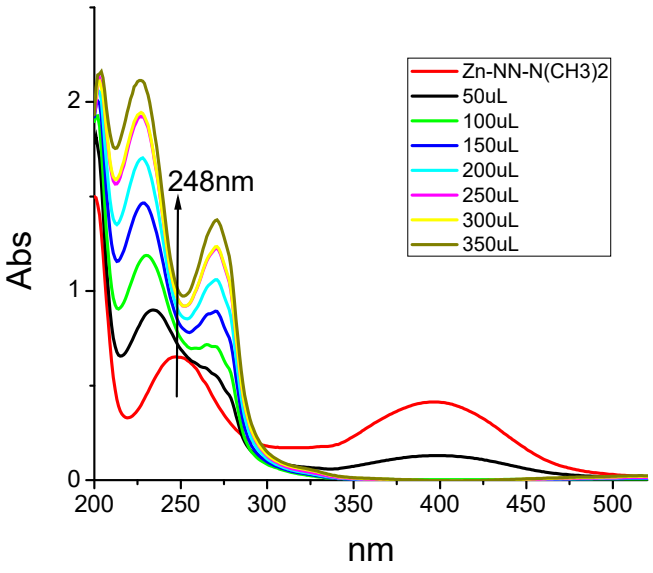

Figure 6: Effect of the increase in the concentration of 2,5-pyridinecarboxylate in the absorption spectrum of the [Zn-(NN'- $N(CH_3)_2$)Cl_2] complex. The concentration of 2,5-pyridinecarboxyc acid in water increased from 0 to 6.205x10^{-5}

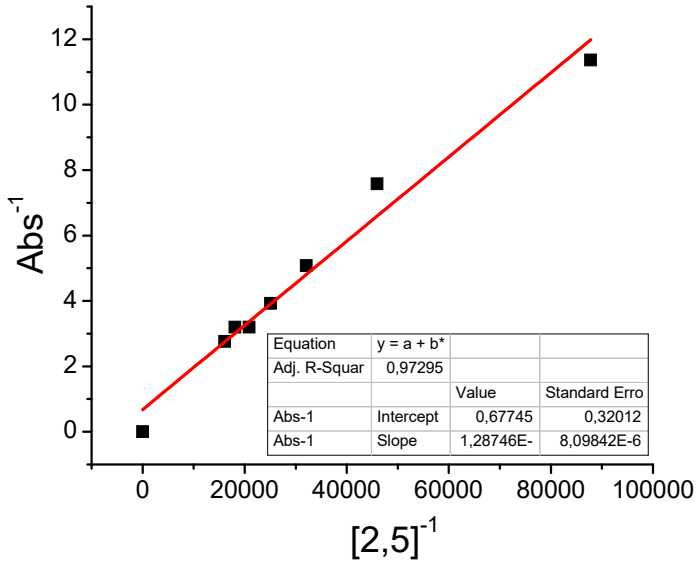

Figure 7: Graph of the Benesi-Hildebrand equation at 248nm according to equation (1) to calculate the affinity constant between the complex [Zn-(NN'-$(CH_3)_2$)Cl_2] and the 2,5-pyridinecarboxylic ligand.

From the graph, the affinity constant Kb (5,261) was determined for the complex [Zn-NN'-N $(CH_3)_2$)Cl_2]. These constants suggest that interaction occurs between the pyridinecarboxylic ligand and both zinc (II) complexes.

These results could be a first approximation to use this type of ligand as potential inhibitors of zinc metalloproteins[13].

Supplementary materials

CCDC 1526035 contains the supplementary crystallographic data. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre. e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

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