Synthesis of Zn compounds derived from *1H*-benzimidazol-2-ylmethanamine

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Dedicated to Professor Rosalinda Contreras on the occasion of her 60th anniversary

Abstract

The influence of the pH on the synthesis of Zn(II) complexes derived from *1H*-benzimidazol-2-ylmethanamine (HL) has been investigated with X-ray crystallography, FAB mass spectrometry, NMR, infrared and Raman spectroscopy. The crystal structures of (*1H*-benzimidazol-2-ylmethanamine)tetrachlorozincate(2-) dihydrogen $[H_3LZnCl_4]$ **(2)**, (*1H*-benzimidazol-2-ylmethanamine-κN^3)trichlorozincate(1-) hydrogen hydrate $[H_2LZnCl_3]\bullet H_2O$ **(3)**, (*1H*-benzimidazol-2-ylmethanamine-κ^2N^2,N^3)dichlorozinc(II) $[HLZnCl_2]$ **(4)** and Bis[*1H*-benzimidazol-2-ylmethanamine-k^2N^2,N^3]chlorozinc(II) chloride hydrate $[(HL)_2ZnCl]Cl\bullet H_2O$ (**5**) are reported. Compounds **2**-**4** exhibit a distorted tetrahedral environment around the metal center. Complex **5** has distorted trigonal bipyramidal geometry. The crystalline structures of **2**-**5** show the presence of strong intermolecular hydrogen bond interactions that produces graph sets with pseudo-macrocyclic network. The NMR studies show the dynamic behavior of compounds **3**-**5** due to break-formation phenomena of N→Zn bonds.

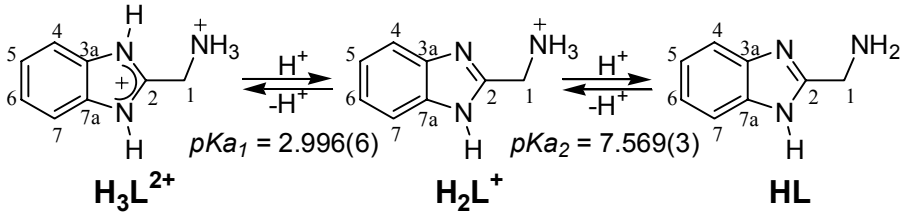
Keywords: Benzimidazole, zinc, X-ray, Raman, infrared, NMR

Introduction

The Zn(II) has a relevant role in chemical and biological systems.[1-5] For example, in the active site of zinc-metalloenzymes there is present a Zn(II) ion coordinated principally to histidine, cysteine, aspartic acid, or H_2O.[4,6-8] The interaction of Zn(II) ion with the environment of the

active site has a significant impact on the catalytic activity of these enzymes.[4,6-8] Normally, the Zn(II) ion has a tetrahedral geometry in the active site, however, the coordination and geometry of this ion depend on the acid-base properties of the histidine residues.[4,6,9] The presence of imidazolic-histidine residues, that can donate or accept various protons, allows different types of Zn coordination in the active site. Thus, the activity of the zinc-metalloenzymes has a delicate and sensitive dependence of pH values.[6]

Polyligand derived from imidazole and benzimidazole are used as working models to understanding the role of the Zn(II) ions in biological systems because they can mimic the histidine side chain.[4,7-9] In our ongoing research on benzimidazole derivatives we are interested in the coordinating acid and behavior of *1H*-benzimidazol-2-ylmethanamine (HL) **1**.[10-13] Compound **1** has three pKa values (Scheme 1); at pH below 2.9 the three nitrogen atoms are blocked by protons (H_3L^{2+}) and apparently this benzimidazole could not coordinate to Zn(II).[11] When the pH values increase **1** could act as a mono- or bidentate ligand. In any of three cases, the coordinated form of the metallic ion will be different. On the other hand, it is known that Zn(II) is selective for coordination of chloride ions because they are small and hydrophilic species.[14,15] In the presence of Cl^- ions the formation of Zn(II) complexes is favored because of the existence of intermolecular hydrogen bonds.[14] In this paper we studied the synthesis of four complexes at different pH, concentration and reaction times in order to analyze the factors that determine the coordination of Zn(II) ions to *1H*-benzimidazol-2-ylmethanamine. These compounds were also characterized using NMR, X-ray crystallography, infrared and Raman spectroscopies.



Scheme 1. Acid-base behavior of *1H*-benzimidazol-2-ylmethanamine **1**.[11]

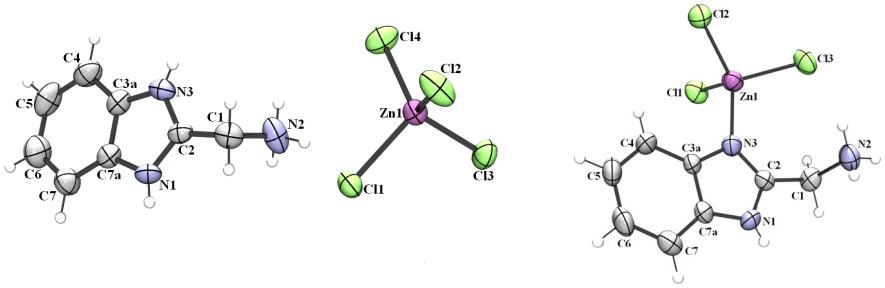
Results and Discussion

In aqueous solution, Zn(II) presents a set of chemical equilibria that basically depend on the ion concentration and pH. The predominance-existence diagrams show that Zn(II) species can only occur in acid solutions.[16,17] In basic solutions, insoluble $Zn(OH)_2$ is formed and this limits the reactivity of Zn(II). However, it is possible to reduce the formation of insoluble hydroxy-compounds through the addition of liganting agents.[16] The presence of the chloride ion (for which Zn(II) has great affinity[14]) in the reaction environment is specially important because it allows the formation of soluble chemical species ($ZnCl^+$, $ZnCl_2$, $ZnCl_3^-$) able to react with

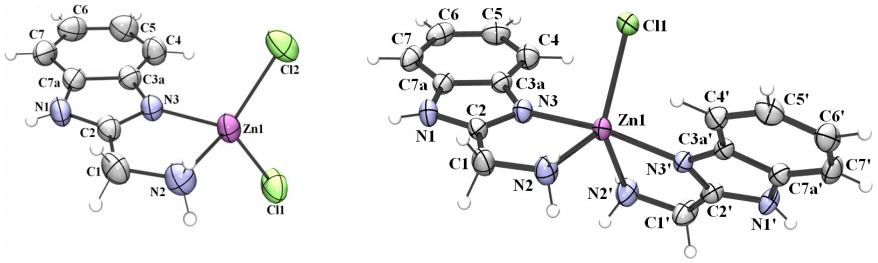
polydentate ligands. Thus, we performed the treatment of **1** with Zn(II) in aqueous media and effected scanning reactions by two means: 1) At constant concentration (0.1 M), the reaction of **1** with $ZnCl_2$ was performed at different values of pH (from 1 to 7); and 2) At variable concentrations (from 0.06 to 0.12 M), H_3L^{2+} dihydrochloride was made to interact with $3Zn(OH)_2 \bullet 2ZnCO_3$.

Reaction of 1 with $ZnCl_2$ at variable pH

At constant concentration, we scanned, the reaction of **1** with $ZnCl_2$ every 0.5 units of pH through the use of infrared spectroscopy and X-Ray diffraction (Figure 1). We found that the action of Zn(II) ion changes the pKa values of **1**. Thus, in the range of pH from 0 to 2.4 compound **2** is present. The ligand in **2** features the entire coordination center blocked by N-H bonds. In these reaction conditions, the Zn(II) ion assumes the form of tetrachlorozincate(2-).[18] At pH 2.4, compounds **2** and **3** are present in solution, but at higher pH's, **2** disappears and **3** predominates. Formation of **3** is due to the first deprotonation of **1** ($H_3L^{2+} \rightleftarrows H_2L^{+} + H^{+}$) and the formation of the N→Zn bond on the imidazolic N atom.



Compound **2** Compound **3**



Compound **4** Compound **5**

Figure 1. Ortep representation of compounds $[H_3LZnCl_4]$ **2**; $[H_2LZnCl_3] \bullet H_2O$ **3**; $[HLZnCl_2]$ **4** and $[(HL)_2ZnCl]Cl \bullet H_2O$ **5**, where HL is *1H*-benzimidazol-2-ylmethanamine.

In absence of any metallic ion, the neutral species of **1** ($H_2L^{+} \rightleftarrows HL + H^{+}$) must predominate after pH 7.[11] However, we determine the existence of compound **5** at more acidic values of pH (4.5 to 6.4). The presence of the bidentate form of the ligand **1** in solution and its chelate coordination with the Zn(II) ion perhaps favor the formation of compound **5** in these acid

conditions. However, total evaporation of the solutions at pH 5.6 - 6.4 leads only to compound **4**. Presumably, the slow evaporation causes the increase of the chloride concentration and instead of compound **5**, the complex **4** is obtained.

Reaction of H_3L^{2+} with $3Zn(OH)_2•2ZnCO_3$ at concentration variable

Although the $3Zn(OH)_2•2ZnCO_3$ salt is practically insoluble in water, the presence of **1** in the form of H_3L^{2+} makes it possible the reaction of Zn(II). A slow acid-base reaction leads to produce the neutral form of **1** (HL) and makes Zn(II) become soluble. Thus, the concentration of Zn(II) in solution is always small and the ligand is in excess. We effected a set of reactions of H_3L^{2+} with $3Zn(OH)_2•2ZnCO_3$ at different concentrations of benzimidazole (from 0.06 to 0.12 M). In all cases, when the mixture was stirred for 24 hours, compound **4** was obtained. On the other hand, when the mixture was stirred for 30 minutes, the reaction yielded instead compound **5**. Moreover, we found that the best conditions of reaction (good yields and excellent quality of crystallization) were achieved at benzimidazole concentrations of 0.08 M.

Infrared and Raman studies

The infrared and Raman studies confirm the presence of the Zn-compounds **2**-**5**. Thus, the in plane mode vibrations in benzimidazoles are present between 419 and 1620 cm^{-1} [19] and the characteristic signal for the in-plane vibration of the imidazole N-H is localized near 1590 cm^{-1}. The in-plane N-H vibrations for **2** are shifted toward smaller frequencies ($\Delta\delta$ = 25 cm^{-1}) compared to compounds **3**-**5** (δ = 1588 cm^{-1}) and this makes evident the presence of strong hydrogen bond interactions.[19] In contrast to complexes **2**-**4**, where the C=N stretching vibration appears as a lone signal in the region of 1617-1624 cm^{-1}, compound **5** shows two signals (1624 and 1651 cm^{-1}) that support the Zn penta-coordination. On the other hand, IR spectra of **1** and **3** show a signal at 1598 cm^{-1} attributed to in-plane bending vibrations of the NH_3 group,[20] while the absence of this signal in compounds **4** and **5** suggests the chelate coordination of HL ligand to Zn. Moreover, the typical NH_2 wagging vibrations for compounds **4** and **5** are found at 680 and 673 cm^{-1}, respectively, and support the chelate coordination in these compounds.[20,21] The set of signals for the aromatic C-H and imidazolic N-H out-plane mode vibrations are characteristic for each of the Zn compounds **3**-**5** in the infrared spectra and therefore are useful to differentiate one another. Thus, for **3** the out-plane mode vibrations are grouped next to 751 cm^{-1} as strong, thin signals, in the case of **4**-**5** the corresponding signals are strong and coarse and are distributed in the region form 535 to 768 cm^{-1}. Nevertheless, the double coordination of **1** with the Zn atom and its minor symmetry causes a larger number of these signals for **5** (546, 609, 640, 711, 756, 771 cm^{-1}) than for **4** (533, 627, 758, 769 cm^{-1})**.**

In Raman spectra the Zn-Cl stretching vibrations for **2** and **3** are observed as single signals (286, and 284 cm^{-1} respectively) and are evidence that in these molecules the Zn-Cl bonds are symmetrically equivalent.[22] For compound **4** the two Zn-Cl stretching vibrations are observed in 310 and 235 cm^{-1} and confirm the presence of two chlorine atoms bonded to Zn. On the one hand, for compound **5** the Zn-Cl stretching vibration (230 cm^{-1}) appears at a lower frequency

than in the case of **2-4.** This result is in agreement with the penta-coordination of compound **5** and a longer Zn-Cl bond distance. Furthermore, two Zn-N stretching vibrations are observed in compounds **4** and **5** (424 and 490 cm^{-1}) that make evident the chelate coordination of ligand HL in these compounds.[23]

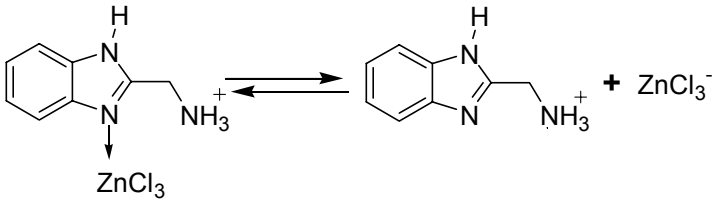
NMR studies in solution

The ^{13}C NMR spectra of compounds **2-5** have a symmetric behavior and only one set of signals were found for all aromatic carbons (Table 1). Thus, in all cases C5 and C6 have the same resonance. Compared to **1**, the presence of N→Zn coordination bond on the imidazole nitrogen in compounds **3-4** causes a shift toward lower frequencies for C5 and C6 ($\Delta\delta$ = 3.7-3.1 ppm). However, in compounds **4** and **5**, C4 and C7 have broad signals that are evidence of a dynamic behavior. It is known that the Zn complexes are characterized by a high coordinate flexibility due to presence of bond-breaking phenomena ($Zn \leftarrow L \rightleftarrows Zn + L$).[24-27] Therefore, it is probable that in aqueous solution, compounds **3-5** undergo N→Zn bond-breaking phenomena at aromatic nitrogen atoms (Scheme 2). On the other hand, it is known that in diazoles the interconversion between tautomers is very fast due to the employ of a third molecule.[28-34] Thus, in compounds **3-5**, it is possible that the free benzimidazole groups present an intermolecular proton transfer mechanism with the solvent (D_2O) and this fact perhaps explains the high symmetry of their NMR spectra. When the solvent is evaporated of the NMR tubes with **3** or **5** complexes, the infrared spectra and X-ray diffraction of the solid residues show that these compounds have once more the original crystalline structure where the aromatic nitrogen atoms present the N→Zn coordination**.** This information corroborates the existence of N→Zn bond-breaking equilibrium of **3** and **5** in aqueous solutions. On the other hand, in ^{1}H NMR the methylene hydrogens (H1) resonances of compounds **4** and **5** are displaced toward lower frequencies ($\Delta\delta$ = 0.54-0.2 ppm) with respect to compounds **2** and **3.** This result confirms the coordination of the amine group with the Zn(II) ion in **4** and **5**.

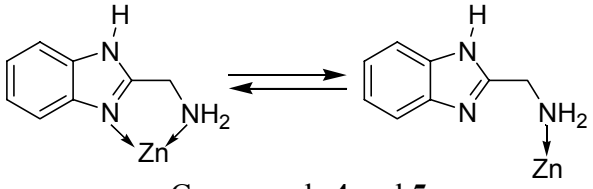
Table 1. ^{13}C and ^{1}H NMR (δ in ppm) of **1-5** in D_2O

Compound	C1	C2	C3a C7a	C4 C7	C5 C6	H1	H4 H7	H5 H6
1[a]	34.5	143.51	131.0	114.5	127.4	4.84	7.81	7.60
2	34.4	143.7	131.4	114.6	127.2	4.81	7.82(m)	7.62(m)
3	36.3		136.5	115.2	124.3	4.48	7.39(m)	7.67(m)
4	36.3			115.0(b)	123.7	4.28	7.36(m)	7.67(s,b)
5	36.6			115.6(b)	123.7	4.27	7.27(s,b)	7.50(b)

[a] Reference 11



Compound **3**



Compounds **4** and **5**

Scheme 2. N→Zn bond-breaking equilibrium in $[H_2LZnCl_3]•H_2O$ **3**, $[HLZnCl_2]$ **4** and $[(HL)_2ZnCl]Cl•H_2O$ **5** compounds.

X-Ray crystallography

The X-ray crystallography corroborates the molecular structure of **2**-**5** (Table 2) and shows the presence of strong intermolecular hydrogen bonds. Molecule **2** is not a coordination compound because all the coordinated centers in the *1H*-benzimidazol-2-ylmethanamine are blocked by N-H bonds. However, the $ZnCl_4^{2-}$ anion takes part in the hydrogen bond network. It is interesting that only three Cl atoms in $ZnCl_4^{2-}$ anion are acceptors of H atoms (Figure 2) and this fact is reflected in the Zn-Cl bond length. Thus, Zn1-Cl1 and Zn1-Cl2 statistically have (e.s.d.) the same bond lengths [2.317(1) and 2.297(1) Å respectively] and these are longer than Zn1-Cl3 [2.258(1) Å]. These differences can be attributed to Cl1 and Cl2 having stronger intermolecular hydrogen bonds with N2-H2B and N1-H1 than the one Cl3 has with N3-H3. Finally, Cl4 does not act as acceptor of hydrogen atoms and the bond length Zn1-Cl4 is the shortest [2.233(1) Å]. The H atoms are donated by ammonia and imidazole groups, and in the hydrogen bond pattern, three graph sets with pseudo-macrocyclic structure can be distinguished: $\mathbf{R}_4^4$**(18)** involving atoms (-Zn1-Cl2···H1-N1-C2-C1-N2-H2B···Cl1-)$_2$, $\mathbf{R}_2^2$**(9)** involving atoms (-Zn1-Cl1···H2A-N2-C1-C2-N3-H3···Cl3-), and $\mathbf{R}_4^2$**(8)** involving atoms (Cl1···H2B-N2-H2A···Cl1-)$_2$.[35]

Table 2. Crystal data of **2-5**

	2	**3**	**4**	**5**
Formula	$C_8H_{11}Cl_4N_3Zn$	$C_{16}H_{22}Cl_6N_6OZn_2$	$C_8H_9Cl_2N_3Zn$	$C_{16}H_{20}Cl_2N_6OZn$
Fw	356.37	657.84	283.45	448.65
Space group	P2(1)/c	P2(1)/n	P2(1)/n	P2(1)/n
		Cell parameters		
a (Å)	15.516(3)	14.205(3)	7.670(2)	9.719(2)
b (Å)	9.441(2)	7.422(2)	14.931(3)	10.685(2)
c (Å)	9.662(2)	24.538(5)	9.519(2)	18.193(4)
α (°)	90	90	90	90
β (°)	107.19(3)	104.99(3)	91.05(3)	102.17(3)
γ (°)	90	90	90	90
V($Å^3$)	1352.2(5)	2499.3(9)	1089.9(4)	1847.0(6)
Z	4	4	4	4
μ (mm^{-1})	2.582	2.582	2.706	1.638
ρ_{calcd} (g cm^{-3})	1.751	1.748	1.727	1.613
		Data Collection		
θ limits (º)	1.37<θ< 25.50	1.51<θ<25.00	2.54<θ<25.00	2.21<θ<25.00
hkl limits	-16, 16; -10, 10; -10, 9	-16,16; -8, 8; -29, 24	-9,9; -17, 17; -10, 11	-9, 11; -12, 12: -21, 21
no. Collected refl.	6360	14622	6548	11064
no. of Indep reflns (R_{int})	1770	4399 (0.0507)	1919 (0.0282)	3254 (0.0234)
No. of obsed reflns	1770	4399	1919	3254
		Refinement		
R	0.0271	0.0398	0.0273	0.0267
R_w	0.0757	0.0964	0.0689	0.0702
No. of params	154	298	163	315
Goodness-of-fit on F^2	1.167	1.079	1.048	1.086
$\Delta\rho_{min}$ (e $Å^{-3}$)	-0.328	-0.403	-0.225	-0.387
$\Delta\rho_{max}$(e $Å^{-3}$)	0.327	0.685	0.335	0.370

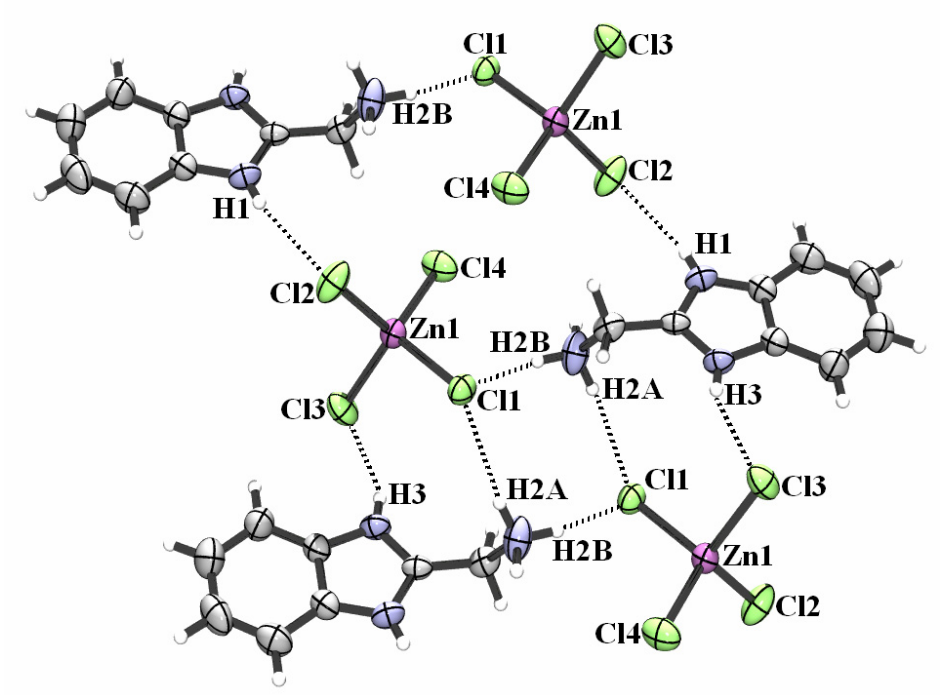


Figure 2. Crystal structure of $[H_3LZnCl_4]$ **2** showing the hydrogen bond patterns: $\mathbf{R}_4^4\mathbf{(18)}$, $\mathbf{R}_2^2\mathbf{(9)}$ and $\mathbf{R}_4^2\mathbf{(8)}$.

Compound **3** is mono-coordinated, the metal atom is bonded to an imidazolic nitrogen atom. In the unit cell there are two Zn complexes that are not symmetrically equivalent (Figure 3). Furthermore, **3a** and **3b** have different geometry parameters because they have different intermolecular interactions. Whereas, the imidazole hydrogen H1 of **3a** has a strong intermolecular hydrogen bond with a water molecule [N1···O1 = 2.779(7), Å], the imidazole hydrogen H1' of **3b** has a weak hydrogen bond with Cl2 [N1' ···Cl2 = 3.285(10) Å]. The strong interaction of H1 with O1 is reflected in the bond length of C2-N1 [1.357(6) Å] that is statistically larger than C2'-N1' [1.3261(6) Å]. All Cl atoms in **3a** and **3b** are acceptors of H atoms (Figure 3), but they present different intermolecular interactions and the bond lengths Zn-Cl are not the same. Four graph sets with pseudo-macrocyclic structure can be distinguished: The hydrogen bond of Cl1 with H2C' [Cl1···N2' = 3.304(5) Å] and Cl2 with H1' [Cl2···N1' = 3.230(5) Å] produce graph set $\mathbf{R}_2^2\mathbf{(9)}$ involving atoms (-Cl1···H2C'-N2'-C1'-C2'-N1'-H1'···Cl2-Zn1-) (Figure 3), The interactions of Cl2' with H2B' [Cl2'···N2' = 3.239(4) Å] and Cl3' with H2A' [Cl3'···N2' = 3.215(5) Å] cause the graph set $\mathbf{R}_2^2\mathbf{(6)}$ involving atoms (-Zn1'-Cl2'···H4B'-N2'-H2A'···Cl3'-). Likewise, these interactions produce the graph set $\mathbf{R}_2^2\mathbf{(14)}$ involving two possible set of atoms $(\cdots H2A'\text{-}N2'\text{-}C1'\text{-}C2'\text{-}N3'\text{-}Zn1'\text{-}Cl3'\cdots)_2$ or $(\cdots H2B'\text{-}N2'\text{-}C1'\text{-}C2'\text{-}N3'\text{-}Zn1'\text{-}Cl2'\cdots)_2$. Finally, the Hydrogen bonds Cl1···H2C'-N2' and Cl3'···H2A'-N2' with the interaction Cl1'···H2A-N2 [Cl5···N1 = 3.285(5) Å] lead to a pseudo-macrocyclic estructure with a graph set $\mathbf{R}_{10}^3\mathbf{(70)}$ involving (-Cl3'···H2A'-N2'-C1'-C2'-N3'-Zn1'-Cl1'···H2A-N2-C1-C2-N3-

Zn1-Cl1···H2C'-N2'-C1'-C2'-N3'-Zn1'-Cl1'···H2A-N2-C1-C2-N3-Zn1-Cl1···H2C'-N2'-C1'-C2'-N3'-Zn1'-)$_2$.

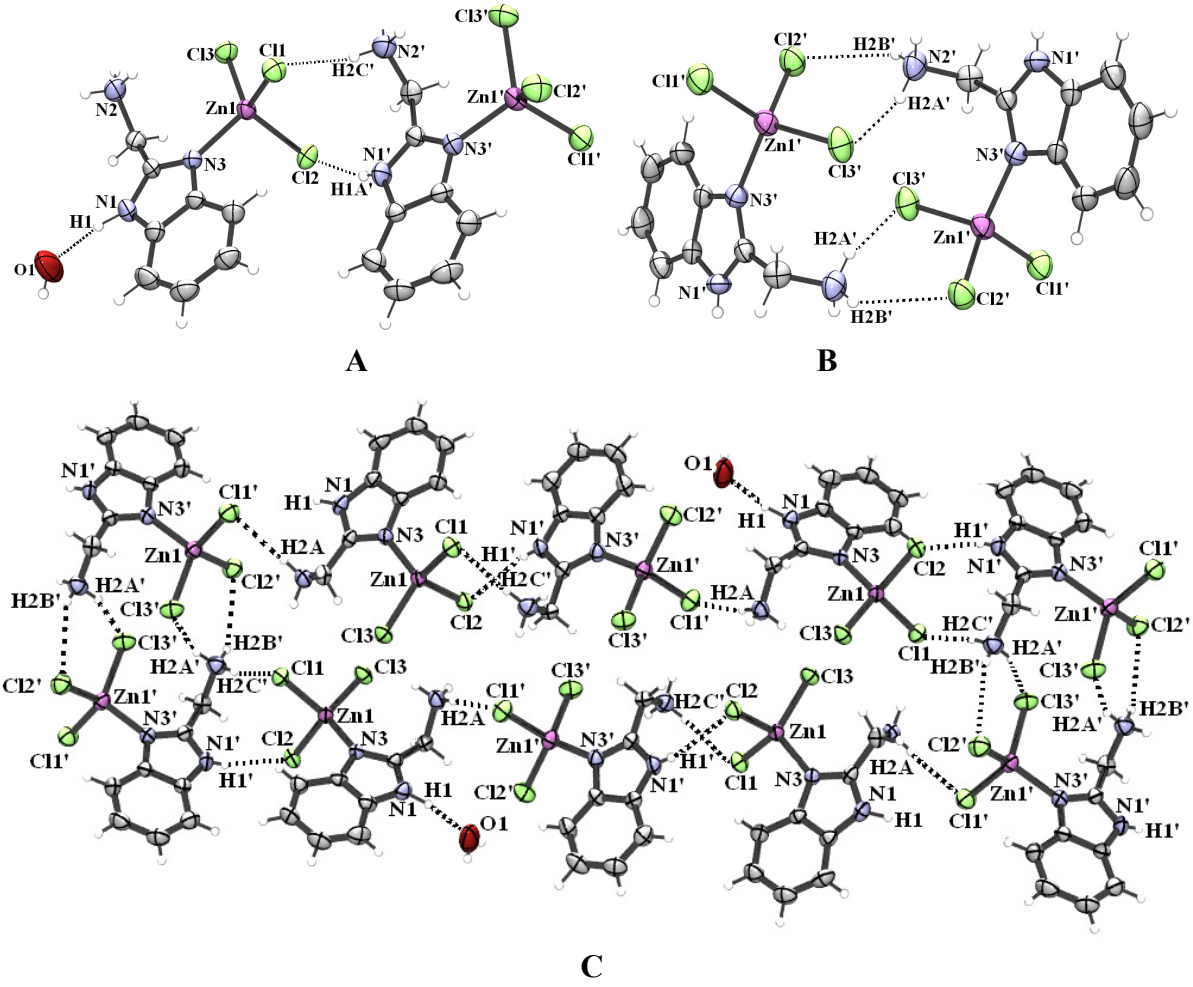


Figure 3. Crystal structure of [H_2LZnCl_3]•H_2O **3** showing the hydrogen bond patterns: A) $\mathbf{R_2^2(9)}$, B) $\mathbf{R_2^2(6)}$ and $\mathbf{R_2^2(14)}$, C) $\mathbf{R_{10}^3(70)}$.

In compound **4** the benzimidazole ligand is coordinated to Zn in chelate form. The Zn atom has a deformed tetrahedral geometry where the bond length Zn1-Cl1 [2.240(1) Å] is statistically longer than Zn1-Cl2 [2.235(1) Å] (Figure 4). This fact is due to Cl1 having two intermolecular hydrogen bonds with H1 and H22 [Cl1···N3 = 3.410(3) and Cl1···N2 = 3.501(3) Å respectively] while Cl2 only presents one hydrogen bond with H21 [Cl2···N2 = 3.306(4) Å]. Four graph sets with pseudo-macrocyclic structure can be distinguished: $\mathbf{R_4^2(14)}$ involving atoms (···Cl1···H1-N1-C2-C1-N2-H22···)$_2$ and $\mathbf{R_4^4(18)}$ involving atoms (-H1···Cl1-Zn1-Cl2···H21-N2-C1-C2-N1-)$_2$.

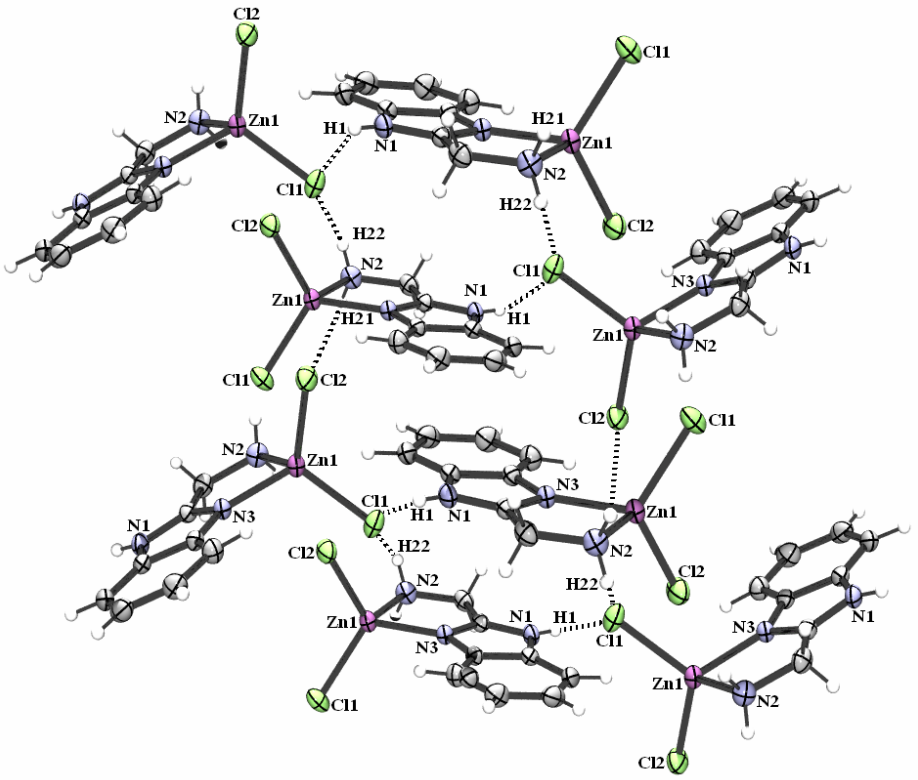


Figure 4. Crystal structure of [$HLZnCl_2$] **4** showing the hydrogen bond patterns: $\mathbf{R_4^2(14)}$ and $\mathbf{R_4^4(18)}$.

In compound **5** two *1H*-benzimidazol-2-ylmethanamine ligands are coordinated to Zn atom in chelate form (Figure 5). The Zn atom has a deformed trigonal bipyramidal geometry where the chlorine Cl1 and amine nitrogen (N2 and N2') atoms are disposed in equatorial positions. The imidazole nitrogen atoms (N3 and N3') are located in apical positions and statistically have the same bond lengths [Zn1-N3 = 2.113(2) Å] and [Zn1-N3' = 2.111(2) Å]. However, the Zn1-N2' bond length [2.200(2) Å] is statistically bigger than Zn1-N2 [2.114(2) Å] and therefore, the N2'-Zn1-N3' bond angle [77.25(7)º] is shorter than N2-Zn1-N3 [80.41(7)º]. Thus, in compound **5** the two HL are not equivalently coordinated to Zn. This fact is reflected in the supramolecular arrangement that **5** adopt (Figure 5). For example, the two hydrogen atoms bonded to N2 have a intermolecular hydrogen bond with Cl2 [N2···Cl2 = 3.393(2) Å for H2A and 3.474(2) Å for H2B] and, only one hydrogen atom (H2B') bonded to N2' presents hydrogen interactions [N2'···Cl2 = 3.489(3) Å]. Moreover, the imidazole hydrogen atoms H1 and H1' have different interactions: whereas H1 atom interacts with O1 [N1···O1 = 2.908(3) Å], H1' presents an intermolecular interaction with Cl1 [N1'···Cl1 = 3.337(2) Å]. The presence of the Cl2 anion and water molecules is important because they take part in of the hydrogen bond network and likely stabilize the crystalline structure. Three graph sets with pseudo-cyclic structure can be distinguished: $\mathbf{R_2^1(6)}$ motif involving (-Zn1-N2'-H2B'···Cl2···H2B-N2-), $\mathbf{R_5^4(18)}$ motif

involving (-N2-H2B···Cl2···H1F-O1···H1-N1-C2-C1-)$_2$, and $\mathbf{R}_4^4\mathbf{(16)}$ motif involving (···H1-N1-C2-N3-Zn1-Cl1···H1E-O1···)$_2$.[35]

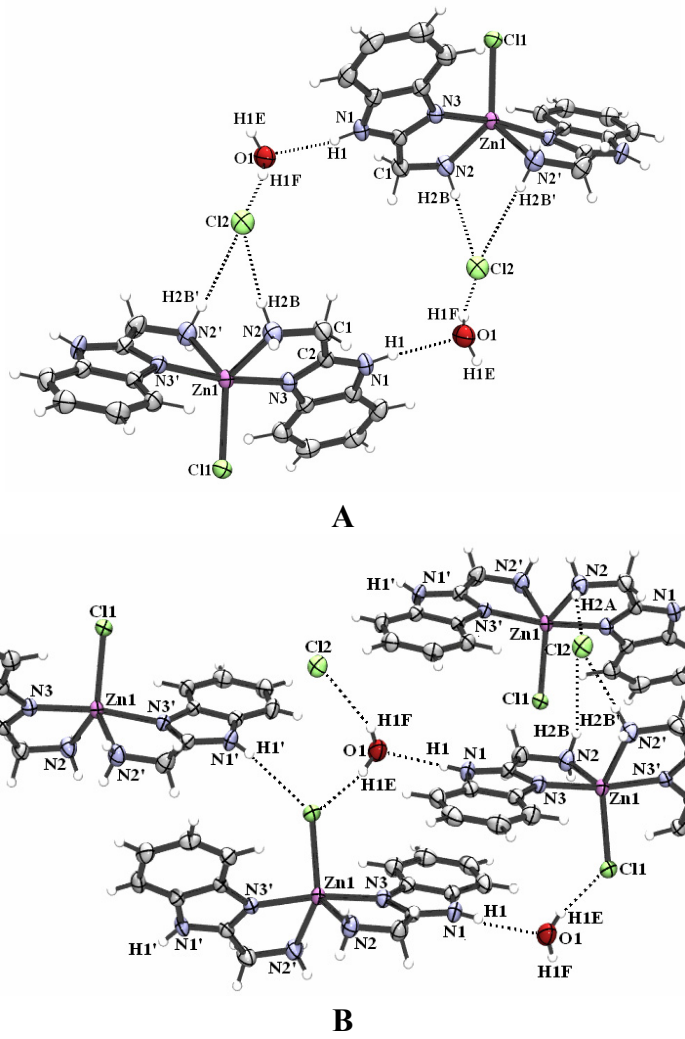


Figure 5. Crystal structure of [(HL)$_2$ZnCl]Cl•H$_2$O **5** showing the hydrogen bond patterns: A) $\mathbf{R}_2^1\mathbf{(6)}$ and $\mathbf{R}_5^4\mathbf{(18)}$, B) $\mathbf{R}_4^4\mathbf{(16)}$.

In conclusion, the synthesis of compounds **2-5** has strong dependence on pH and concentration of the reactants. The coordination modes of Zn(II) with *1H*-benzimidazol-2-ylmethanamine depend on the acid-base behavior of the ligand and the existence of the metallic ion in solution. The X-ray crystallography of **2-5** shows the presence of strong hydrogen bonds that produce pseudo-macrocyclic networks. The presence of the chloride ion in the crystalline structures is important since it maximizes the hydrogen bond interactions. The NMR studies suggest that compounds **3-5** have fluxional behavior in aqueous solution, where the N→Zn bonds present breaking phenomena.

Experimental Section

General Procedures. Water was freshly distilled and de-ionized before use. Melting points were measured on a Mel-Temp II apparatus and are uncorrected. The IR spectra and Raman were recorded on a Perkin-Elmer System Spectrum GX spectrophotometer. Mass spectra were recorded on JEOL MStation JMS-700 with FAB method and 3-nitrobenzyl alcohol (NBA) as matrix. Elemental analyses were determined on a Perkin-Elmer Series II CHNS/O analyzer 2400 instrument. NMR spectra were obtained on a JEOL GXS-400 MHz spectrometer in D_2O solution. Chemical shifts (ppm) are relative to MeOH as external reference for ^1H and ^{13}C. pH measurements were obtained using a Radiometer-Copenhagen PHM 250 pH-meter equipped with an ORION combined ROSS pH-electrode. Calibration of the electrode system was performed with Radiometer-Copenhagen IUPAC standard buffers of pH 4.005, 7.000 and 10.012.

Data was collected on a Bruker Smart 6000 diffractometer equipped with a CCD area detector ($\lambda_{Mok\alpha}$ = 0.71073 Å, monochromar: graphite). Frames were collected via ω/ϕ-rotation (Δ/ω = 0.3º) at 10 s per frame (program SMART).[36] The measured intensities were reduced to F^2 without absorption correction (program SAINT-NT [37]). Structure solution, refinement and data output were carried out with the SHELXTL-NT program package.[38] The non-hydrogen atoms were refined anisotropically. All H atoms in compounds **4** and **5** were located in a difference Fourier map and refined isotropically. In compounds **2** (except H1, H3) and **3** (except H1, H16, H17, H1'), the H atoms were placed in geometrically calculated positions using a riding model.

Although we examined the yield of compounds **2-5** varying concentration of the reagents or pH, we only show the best experimental procedure that we found for each Zn(II) compound.

(*1H*-Benzimidazol-2-ylmethanamine)tetrachlorozincate(2-) dihydrogen (2)

A mixture of 0.0261 g (0.4 mmol) of Zn and 100 μL of concentrated HCl was diluted up to 2 mL with de-ionized water. Then, 2 mL of a 0.2 M solution (0.4 mmol) of *1H*-benzimidazol-2-ylmethanamine hydrate **1** were added. The mixture was stirred at room temperature for 5 minutes. Slow evaporation of the solvent yielded 0.0796 g (56 %) of **2** as colorless crystals. Mp 293-295 °C. Found: C, 26.9; H, 3.1; N, 11.1; $C_8H_{11}N_3Cl_4Zn•0.4H_2O$ requires C, 26.4, H, 3.3, N, 11.6. m/z (FAB, 10 eV, NBA) no (M^+), 281(M^+-2HCl).

(*1H*-benzimidazol-2-ylmethanamine-κN^3)trichlorozincate(1-) hydrogen hydrate (3)

A mixture of 0.0261 g (0.4 mmol) of Zn and 78.7 μL of concentrated HCl was diluted up to 2 mL with de-ionized water. Then, 2 mL of a 0.2 N solution (0.4 mmol) of *1H*-benzimidazol-2-ylmethanamine dihydrochloride hydrate **1** were added. The pH was adjusted to 3.5 with NaOH 1 M and the mixture was stirred at room temperature for 5 minutes. Slow evaporation of the solvent yielded 0.0665 g (51 %) of **3** as orange crystals. Mp 269-271 °C. Found: C, 26.9; H, 3.3; N, 11.3; $C_8H_{10}N_3Cl_3Zn•2.1H_2O$ requires C, 26.9, H, 4.0, N, 11.8. m/z (FAB, 10 eV, NBA) no (M^+), 289(M^+-C_2H_4Cl).

(*1H*-Benzimidazol-2-ylmethanamine-κ^2N^2,N^3)dichlorozinc(II) (4)

A mixture of 0.1321 g (0.6 mmol) of *1H*-benzimidazol-2-ylmethanamine dihydrochloride hydrate **1** diluted in 5 mL of de-ionized water and 0.3293 g (0.6 mmol) of $3Zn(OH)_2•2ZnCO_3$ was stirred at room temperature for 24 hours. Then, the resulting mixture was filtered and slow evaporation of dissolvent yielded 0.0122 g (7 %) of **4** as orange crystals. Mp 249-251 °C. Found: C, 33.9; H, 3.2; N, 14.1; $C_8H_9N_3Cl_2Zn$ requires C, 33.9, H, 3.2, N, 14.8. m/z (FAB, 10 eV, NBA) no M^+, 279(M^+-H_2), 246(M^+-Cl).

Bis[*1H*-Benzimidazol-2-ylmethanamine-k^{2}N^2,N^3]chlorozinc(II) chloride hydrate (5).

A mixture of 0.0880 g (0.4 mmol) of *1H*-benzimidazol-2-ylmethanamine dihydrochloride hydrate **1** diluted in 5 mL of de-ionized water and 0.2196 g (0.4 mmol) of $3Zn(OH)_2•2ZnCO_3$ was stirred at room temperature for 30 minutes. Then, the result mixture was filtered and slow evaporation of the solvent yielded 0.0362 g (23 %) of **5** as amber crystals. Mp 210-212 °C. Found: C, 41.9; H, 4.6; N, 17.8; $C_{16}H_{18}N_6Cl_2Zn•1.7H_2O$ requires C, 41.7, H, 4.7, N, 18.2. m/z (FAB, 10 eV, NBA) 393(M^+), 357(M^+-HCl), 246(M^+-$C_8H_9N_3$).

Supplementary Information Available

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as CCDD 651136, 651137, 651138 and 651139. Copies of the data can be obtained free of charge on application to: The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by CONACYT-México (832240-E and J33279-E). AR T-B thanks Alejandro Álvarez for reading the manuscript and for his helpful comments.

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