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## Synthesis and characterization of Zn(II), Cd(II) and Hg(II) complexes with imidazole derivatives. Crystal structure of dichloro-bis(5-amino-4-carboethoxy-1-*p*-methoxyphenylimidazole)zinc(II)

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## Abstract

Two imidazole-derivative ligands, 5-amino-4-carboethoxy-1-*p*-methoxyphenyl-imidazole (L) and 5-amino-4-nitrile-1-*p*-methoxyphenylimidazole (L'), have been prepared and their interactions with Zn(II), Cd(II) and Hg(II) reported. For the L ligand a series of complexes of general formulae MCl<sub>2</sub>L<sub>x</sub>, where x = 1 or 2, has been obtained while for the L' ligand only the Cd(II) complex fits with the general formulae. For this latter ligand the corresponding Hg(II) complexes were not isolated and a Zn(II) complex obtained with the ligand in the protonated form. All the complexes have been characterized by spectroscopic and thermal techniques. In addition, the crystal structure of the ZnCl<sub>2</sub>L<sub>2</sub> complex is reported. The compound crystallized in the monoclinic system, space group *P*-1, with cell constants a = 8.7328(18), b = 10.5494(21) and c = 17.3269(24) Å,  $\alpha = 75.265(10)$ ,  $\beta = 81.094(17)$  and  $\gamma = 70.399(1)^{\circ}$  and Z = 2. The structure was solved and refined to R = 0.056 ( $R_w = 0.031$ ). The structure consists of discrete neutral ZnCl<sub>2</sub>L<sub>2</sub> entities in which the L ligand coordinates through the N atom belonging to the imidazole ring, the Zn(II) ion exhibiting a distorted tetrahedral geometry.

Keywords: Crystal structures; Zinc complexes; Cadmium complexes; Mercury complexes; Imidazole complexes

## 1. Introduction

The imidazole ring is present in living systems [1-3] where it plays a variety of roles [4]. Bonding between metal (II) ions and imidazole ligands is very common in nature and many examples of metals 'n metalloproteins coordinated by imidazole side-chains of histidyl residues have been reported [5-10], these types of compounds being of considerable interest. In previous papers, we have reported the synthesis, characterization and biological activities of metal complexes with imidazolic derivatives [11–13]. In the present paper we extend the work reporting on the preparation of complexes of two imidazole derivatives, 5-amino-4-carboethoxy-1-p-methoxyphenyl-imidazole (L) and 5-amino-4-nitrile-1-p-methoxyphenyl-imidazole (L') (see Fig. 1), with Zn(II), Cd(II), and Hg(II) ions. The complexes were characterized by elemental analysis, IR, 'H and 'a'C NMR spectroscopic and thermal techniques. The crystal structure of the complex  $2nCl_2L_2$  has been solved by X-ray diffraction methods.

## 2. Experimental

## 2.1. Preparation of the ligands

## 2.1.1. 5-Amino-4-carboethoxy-1-p-methoxyphenylimidazole (L)

To a solution of ethyl-2-amine-2-cyanoacetate (0.04 mol) in acetonitrile (50 ml) was added triethyl orthoformate (0.05 mol) and the mixture was heated under reflux for 1 h. Then, p-anisidine (0.04 mol) in acetonitrile (10 ml) was added and the heating continued for another 30 min (Scheme 1). After cooling, the solid product obtained was filtered off, washed with cold ethanol, dried and crystallized from n-butanol to give L (41%), m.p. 220-222°C.

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Fig. 1. Structures of (a) 5-amino-4-carboethoxy-1-p-methoxyphenyl-imidacole (L) and (b) 5-amino-4-nitrile-1-p-methoxyphenyl-imidazole (L').

## 2.1.2. 5-Amino-4-nitrile-1-p-methoxyphenyl-imidazole(L')

To an ice cold solution of dimethylformamide/phosphorus oxychloride (15 ml DMF, 2.5 ml POCl<sub>3</sub>) was added 5amino-4-carbamoyl-1-p-methoxyphenyl-imidazole [14] (0.01 mol) in four portions over 20 min duration. The resulting solution was stirred for 30 min before being warmed and stirred another hour at room temperature. Then the mixture was poured onto crushed ice (50 g) and adjusted to pH 6 using aqueous ammonia solution. The solid product obtained was collected, washed with cold water, dried and crystallized from methanol to give 5-(dimethylamino)methyleneamino-1-p-methoxyphenyl-4-nitrile-imidazole (1) (63%), m.p. 144-146°C.

The ligand (1) was hydrolysed as follows: a suspension of I (0.01 mol) in hydrochloric acid solution (150 ml, 2%) was warmed on a steam bath for 1 h. After cooling, the reaction mixture was treated with aqueous ammonia solution to pH 3.5 (Scheme 2). The solid product precipitated was filtered off, washed with cold water, dried and crystallized from aqueous ethanol to give L' (84%), m.p. 212–214°C.

## 2.2. Preparation of the complexes

HgCl<sub>2</sub>L was prepared by mixing L and HgCl<sub>2</sub> in a 1/10 molar ratio, in a minimum amount of water. The complex precipitated almost immediately.

The remaining complexes were obtained by dissolving the corresponding ligand and the metallic salt (CdCl<sub>2</sub> and ZnCl<sub>2</sub>), in a molar ratio of 1/40 ligand to metal, in a minimum amount of water. The resulting solutions were then evaporated on a water bath at 50°C for 1 day to give crystals of ZnCl<sub>2</sub>L<sub>2</sub> and CdCl<sub>2</sub>L, while complexes ZnCl<sub>4</sub>(HL')<sub>2</sub>·H<sub>2</sub>O and CdCl<sub>2</sub>L'<sub>2</sub> precipitated after two days. Only the crystals of ZnCl<sub>2</sub>L<sub>2</sub> were found to be suitable for X-ray analysis. All the attempts to obtain solids from the Hg(II)/L' system were unsuccessful.

#### 2.3. Physical measurements

Microanalyses of C, H, and N and IR spectra were obtained as described previously [15]. <sup>1</sup>I and <sup>13</sup>C NMR spectra were recorded on a Bruker AM-300 spectrometer, using DMSOd<sub>6</sub> as solvent and TMS as internal standard. The TG, DTG and DSC diagrams were obtained with a Mettler TG-50 thermobalance in a dynamic pure air atmosphere (100 ml min<sup>-1</sup>) with heating rate of 20°C min<sup>-1</sup>.

#### 2.4. X-ray data collection and structure determination

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Single crystal data collection was performed at 293 K with a Siemens R3m/V diffractometer using graphite monochromatized Mo K $\alpha$  ( $\lambda = 0.71065$  Å) radiation. A prismatic crystal was used with dimensions  $0.19 \times 0.30 \times 0.27$  mm. The complex crystallizes in the triclinic system, space group  $P_{-1}$  (No. 2) with cell constants: a=8.7328(18), b=



#### Scheme 1. Reaction to prepare ligand L.



Scheme 2. Reactions to prepare ligand L'.

10.5494(21) and c = 17.3269(34) Å,  $\alpha = 75.265(10)$ ,  $\beta = 81.094(17)$  and  $\gamma = 70.939(11)^\circ$ , V = 1454.6(1) Å<sup>3</sup>, Z = 2,  $D_c = 1.504$  g cm<sup>-3</sup>, F(000) = 680.0,  $\mu$ (Mo K $\alpha$ ) = 1.079 mm<sup>-1</sup>.

The unit cell parameters were calculated by least-squares refinement of 25 well centred reflections in the range  $15^{\circ} < 20 < 45^{\circ}$ . The data were collected by  $\omega/2\theta$  scan mode in the range  $3^{\circ} < 2\theta < 55^{\circ}$ . Intensities of three check reflections measured after every 120 min showed no significant variation. A total of 4107 reflections was considered as observed with  $l^{\sim} 2\sigma(l_{o})$ . The data were corrected for Lorentz and polarization effects and for absorption.

The structure was solved by Patterson methods and subsequent Fourier syntheses with the SHELXTL PLUS program [16]. All non-hydrogen atoms were refined anisotropically in the final refinements. The positions of the hydrogen atoms were calculated with isotropic temperature factors (U=0.08) and were not refined. Neutral atomic scattering and dispersion factors were those included in the SHELXTL package. The function minimized was  $\Sigma w (\Delta F)^2 (1/w = \sigma^2(F_o))$ , resulting in a final  $R = \Sigma |F_o - F_o| |\Sigma| |F_o|$  value of 0.056 and  $R_w = [(\Sigma w |F - F_o|)^2 / \Sigma w |F_o|^2]^{1/2}$  value of 0.031, with S = 2.38 for 370 parameters. Maximum and minimum transmission factors were 0.7746 and 0.6716, respectively.

#### 3. Results and discussion

## 3.1. X-ray structure of ZnCl<sub>2</sub>L<sub>2</sub>

The structure of the complex consists of discrete neutral  $2nCl_{2}L_{2}$  molecules. The 2n(11) ion is tetraccordinated by two chloride ions and two neutral ligands giving rise to a distorted tetrahedral arrangement. A perspective view of the asymmetric unit together with the atomic labelling scheme is giving in Fig. 2. A three-dimensional view of the packing is shown in Fig. 3. Selected bond distances and angles are listed in Table 1.



Fig. 2. Labelling scheme of the asymmetric unit of the structure.



Fig. 3. Three-dimensional view of the packing in ZnCl<sub>2</sub>L<sub>2</sub>.

Table 1 Selected bond distances (Å) and angles (°) for  $Z{=}Cl_2L_2$ 

Zn(1)Cl(1)	2.251(2)	Zn(1)-Cl(2)	2.283(2)
Zn(1)-N(1)	2.029(4)	Zn(1)-N(1A)	2.049(3)
Cl(1)-Zn(1)-Cl(2)	108.2(1)	Cl(1)-Zn(1)-N(1)	113.9(1)
Cl(1)-Zn(1)-N(1A)	105.1(1)	Cl(2)-Zn(1)-N(1)	99.7(1)
Cl(2)-Zn(1)-N(1A)	109.0(1)	N(1)-Zn(1)-N(1A)	120.4(1)

Table 2

Analytical data	(t	heoretica	I va	lues	in	parentheses
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Compound	с	н	N		
ZnCl <sub>2</sub> L <sub>2</sub>	47.11(47.40)	4.59(4.56)	12.82(12.76)		
CdCl <sub>2</sub> L	35.28(35.11)	3.28(3.38)	9.82(9.45)		
HgCl <sub>3</sub> L	28.60(29.30)	2.56(2.82)	8.33(7.89)		
ZnCl <sub>4</sub> (HL'), 2H <sub>2</sub> O	38.66(39.22)	3.63(3.86)	16.63(16.64)		
CdCl <sub>2</sub> L' <sub>2</sub>	43.10(43.18)	3.75(3.27)	18.93(18.32)		

Within each ZnN<sub>2</sub>Cl<sub>2</sub> core the chloride ions and the nitrogen atoms are not equivalent. Two long bonds of 2.251 and 2.283 Å are formed with the chloride ions while the Zn–N distances are 2.029 and 2.049 Å, all distances being similar to those reported for ZnN<sub>2</sub>Cl<sub>2</sub> cores of imidazole derivatives [17–21].

The ligand is monocoordinated to the Zn(II) ion through the N(1) atom. This is the expected donor atom since the other imidazolic nitrogen atom is blocked by the bulky methoxyphenyl group and the amino group remains protonated. Within the bulky ligands the two six- and five-membered rings are not coplanar but twisted by 135.7(2) and  $64.0(3)^{\circ}$ for N(1) and N(1A) ligands, respectively. All the rings are planar within the experimental errors, the maximum deviation being 0.0113 Å for C(35).

The angles in the coordination polyhedron range from 99.7 to  $120.4^{\circ}$  (Table 1). The larger value corresponds to the N(1)-Zn-N(1A) angle and is likely a consequence of the steric requirements of these bulky ligands, while the smaller one reduces the interactions between the C(2) and the carboethyl chain belonging to the C(5A) of the imidazole ring. The remaining angles are close to those found in a tetrahedral arrangement, so the chromophore can be described as a distorted tetrahedron. Finally the three-dimensional packing is achieved by stacking of the monomers parallel to the *a* axis, resulting in all the rings being parallel to each other.

# 3.2. Spectroscopic and thermal characterization of the complexes

Analytical, IR and <sup>13</sup>C-NMR data of the complexes are summarized in Tables 2-4, respectively. The assignments of the IR bands for L and L' were made on the basis of literature data [22,23].

The three complexes obtained with the L ligand and the Zn(II), Cd(II) and Hg(II) ions can be formulated as  $MCl_2L_x$  (Table 2), where x = 1 or 2 and the L ligand coordinates in a neutral molecular fashion. Their anhydrous character has been confirmed by the thermal analyses.

The IR spectra of the MCl<sub>2</sub>L<sub>x</sub> complexes in the 4000– 600 cm<sup>-1</sup> range show a main feature when compared to the corresponding spectrum of the free L ligand. Thus, in all the spectra the intensities of the  $\nu$ (C=C) and  $\nu$ (C=N) stretching vibration bands decrease with regard to the free ligand (Table 3). Having in mind the X-ray diffraction data, these changes have been attributed to the M-N<sub>ring</sub> interaction. Besides this, the spectra of the Zn(II) and Hg(II) complexes show no shifts for the  $\nu$ (C=O) bands, while in the Cd(II) spectrum this band is significantly shifted to lower wavenumber. Since this complex is anhydrous and no hydrogen bonds between C=O and water molecules can be responsible of this effect, the observed shift might be a consequence of a Cd-O interaction.

In the low frequency range,  $600-180 \text{ cm}^{-1}$ , the spectrum of the Cd(II) complex exhibits two new bands centred at 237 and 183 cm<sup>-1</sup>. The former band has been assigned to  $\nu$  (Cd-N) stretching vibration by comparison with the spectra of L and the Zn(II) complex. The latter band, centred at 183 cm<sup>-1</sup>, corresponds to a bridging chloride ion [23,24].

As for the Hg(II) complex, its 600–180 cm<sup>-1</sup> spectrum shows two new strong bands at 320 and 180 cm<sup>-1</sup>. Both bands have been assigned to  $\nu$ (Hg–Cl) stretching vibrations of terminal and bridging chloride ions [23], respectively. It should be noted that no band attributable to  $\nu$ (Hg–N) is found in the 600–180 cm<sup>-1</sup> range, likely because it is masked by the ligand absorption bands.

On the other hand, the <sup>13</sup>C-NMR data (Table 4) of these compounds were assigned on the basis of similar reported compounds [25]. The data show that the coordination of the L ligand, via the N<sub>ring</sub>, to the metal ion causes little deshielding of the C2 atom in the imidazole ring while C4, C5, and the C atom of the (C=O) group are slightly shielded.

Table 3 IR data for L and L' ligands and their isolated complexes  $(cm^{-1})$ 

Compound	ν(C≡N)	ν(C=O)	$\nu$ (C=C) + $\nu$ (C=N)	ν(M-Cl)	ν(M-N)
L		1672s	1555s, 1512s		
ZnCl <sub>2</sub> L <sub>2</sub>		1673s	1550s, 1510s	274s	105m
CdCl <sub>2</sub> L		1654s	1558m, 1512s	1835	237m
HgCl <sub>2</sub> L		1670s	1565vw, 1503s	320s 180s	25711
L'	2216s		1578s, 1518s	5203, 1003	
ZnCl <sub>4</sub> (HL') <sub>2</sub> ·2H <sub>2</sub> O	2200vw		1600s, 1540s, 1504s	2810	
CdCl <sub>2</sub> L' <sub>2</sub>	2220vw		1609s, 1549s, 1514s	226s, 200s	

Table 4			
13C NMR	data	(δin	ppm)

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Compound	-COO	C4′	C1'	C2	C5	C≕N	C3′	C2′	C4	CH <sub>2</sub>	OCH3	CH3
L	163.79	159.08	146.01	131.30	126.72		126.61	114.83	109.28	58.40	55.40	14.48
ZnCl <sub>2</sub> L <sub>2</sub>	162.78	159.56	145.83	132.73	125.97		127.17	114.95	107.64	59.05	55.51	14.40
CdCl <sub>2</sub> L	163.51	159.52	145.81	132.56	126.05		127.12	114.98	107.84	59.40	55.54	14.47
HgCl <sub>2</sub> L	162.96	159.55	145.81	132.80	125,92		127.18	114.94	107.53	59.24	55.47	14.42
Ľ		159.26	147.44	132.64	126.38	117.06	126.94	114.83	90.62		55.41	• · · · ·
ZnCl <sub>4</sub> (HL') <sub>2</sub> ·2H <sub>2</sub> O		159.34	142.08	130.99	126.42	165.82	126.95	114.91	111.09		55.52	
CdCl <sub>2</sub> L' <sub>2</sub>		158.95	142.58	129.95	127.03	166.45	126.35	114.80	112.35		55.42	

From all the above data, we propose the following tentative structures for the Cd(II) and Hg(II) complexes with the L ligand. For the CdCl<sub>2</sub>L complex, we propose a polynuclear structure in which the Cd(II) ion might be in an octahedral arrangement with the chloride ions bridging metal atoms and the ligand acting in a chelating bidentate form, through the N<sub>ring</sub> and the (C=O) group. The complex HgCl<sub>2</sub>L has a probable dimeric structure in which the Hg(II) ions are in a tetrahedral environment, with two bridging chloride ions, a terminal chloride ion and the L ligand coordinating through the N<sub>ring</sub>. The structure is likely very similar to that reported for the HgCl<sub>2</sub>(HL)<sub>2</sub> complex, where HL is 4-amino-2-methylthio-6-methoxy pyrimidine [26].

For the L' ligand only the Cd(II) complex fits the general formulae MCl<sub>2</sub>L<sub>x</sub>, since the Zn(II) complex is formulated as  $ZnCl_4(HL')_2 \cdot 2H_2O$ , with the ligand acting in the protonated form, and the corresponding Hg(II) complex could not be isolated.

Comparison of the IR spectrum (Table 3) of the CdCl<sub>2</sub>L'<sub>2</sub> complex with the free ligand reveals the loss of the  $\nu$ (C=N) band and the appearance of new bands in the region of the  $\nu$ (C=C) and  $\nu$ (C=N) vibrations. In the <sup>13</sup>C-NMR spectrum (Table 4), the signals due to C=N and the C4 of the imidazolic ring are shifted to lower field with regard to the free ligand, 49.39 and 21.73 ppm, respectively. All these data would suggest that the coordination of the L' ligand to the Cd(II) ion takes likely place through the  $\pi$  electrons of the (C=N) group [27]. The IR bands of CdCl<sub>2</sub>(L')<sub>2</sub> in the low frequency range, at 200 and 226 cm<sup>-1</sup>, are assigned to terminal  $\nu$ (Cd-Cl). These values are consistent with those reported for terminal Cl-Cd bonds in complexes of the type MX<sub>2</sub>L<sub>2</sub> with a tetrahedral structure [28].

On the other hand, the TG plot of the  $ZnCl_4(HL')_2 \cdot 2H_2O$ complex shows an abrupt weight loss (16.3%) in the 250– 275°C temperature range, while in the DSC plot this effect appears as an asymmetric endothermic process. The energy of this latter could not be obtained accurately since overlaps with an exothermic effect due to the onset of the combustion of the ligand. This effect corresponds to the loss of two water molecules together with two HCI molecules (16.19% calc.), in accordance with the following reaction:

## $ZnCl_4(HL')_2 \cdot 2H_2O \rightarrow ZnCl_2L'_2 + 2HCl + 2H_2O$

This process was confirmed by bubbling the gas evolved during the start of the pyrolysis through an aqueous AgNO<sub>3</sub> solution and the precipitation of AgCl, as expected. The remaining  $ZnCl_2L'_2$  compound decomposes steadily similarly to its homologous  $CdCl_2L'_2$  complex.

The analytical and thermal data for ZnCl<sub>4</sub>(HL')<sub>2</sub>·2H<sub>2</sub>O show that in this complex the ligand is in the protonated form. IR and <sup>13</sup>C-NMR data are very similar to the CdCl<sub>2</sub>L'<sub>2</sub> complex, indicating that protonation of L' probably takes place on the carbon-nitrogen triple bond of the (C=N) group. This is not surprising given the low basicity of the N atom of the NH<sub>2</sub> group directly attached to an aromatic pyrrolic imidazolic ring [29,30]. In the low frequency range IR spectrum of the ZnCl<sub>4</sub>(HL')<sub>2</sub>·2H<sub>2</sub>O complex, the strong band at 281 cm<sup>-1</sup> is typical of a Zn(II) ion in a tetrahedral environment with chloride ions [23]. Thus the data point to an ionic structure consisting of ZnCl<sub>2</sub><sup>2-</sup> and HL'<sup>+</sup> units, as found in other Zn(II) chloride complexes of protonated heterocyclic bases [31,32].

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