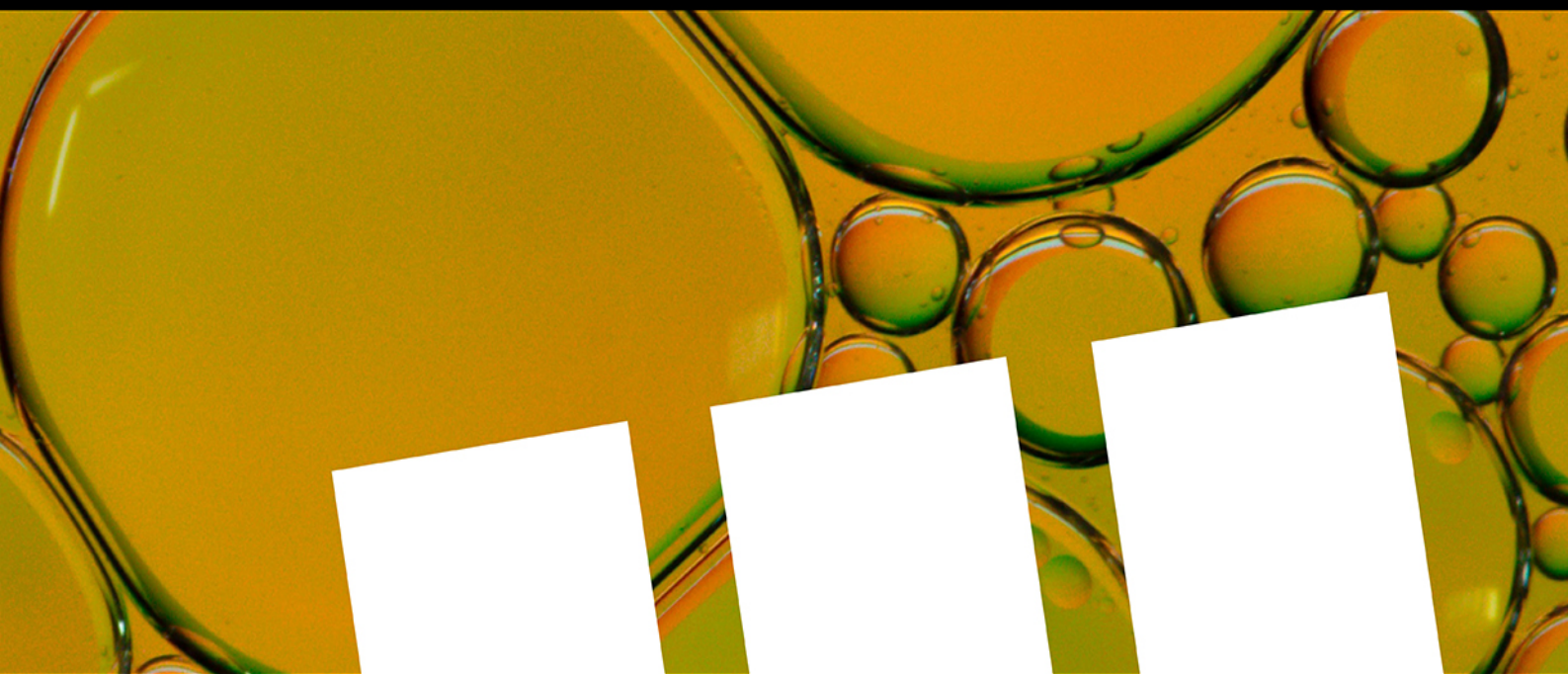


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Gem-diol generation in copper and zinc *N*-methyl-2-imidazolecarboxaldehyde complexes: *solid-state* NMR, EPR and single-crystal X-ray studies

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Abstract: Novel coordination compounds, mono- (**1**) and binuclear copper complexes (**2**) and a zinc complex (**3**) were synthesized and studied through single-crystal X-ray crystallography, *solid-state* NMR and EPR techniques to determine the chemical functionalization of the carbonyl group in *N*-methyl-2-imidazolecarboxaldehyde ligand. Particularly, molecules containing carbonyl groups are versatile ligands that give rise to a wide range of new materials due to the high reactivity of the carbonyl group. However, the chemical identification of the functional group present in these coordination compounds is a challenge because the copper ion affects the NMR signals. In this sense, X-ray crystallography becomes an indispensable tool for the analysis. The imidazole ligands in copper complexes **1** and **2** were found to be the aldehyde and the *gem*-diol forms, respectively. Furthermore, the *gem*-diol and carboxylate moieties were detected in the crystal lattice for the zinc complex **3** and studied by *solution*- and *solid-state* NMR.

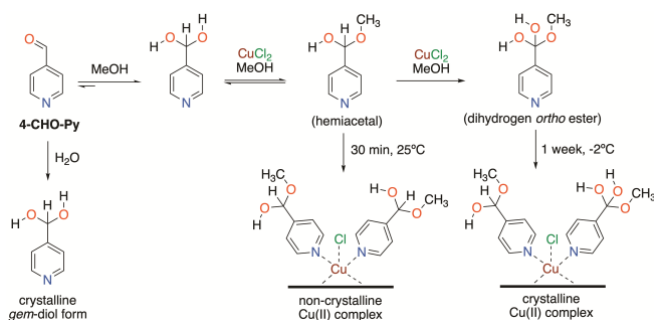
Introduction

The versatility of the metal–ligand bond has allowed the field of coordination chemistry to grow from strength to strength. Metal complexes are still playing a vital role in many areas of Chemistry, ranging from homogeneous catalysis to material science.^[1–3] Generally, heterocyclic compounds like azoles and pyridine derivatives are widely used as ligands because of their electron-donor characteristic.^[4] *N*-heterocyclic carbenes used in copper, zinc, and cobalt complexes have been reported to have a wide range of applications.^[5–7] Based onazole derivatives with antifungal activity, Azevedo-França *et al.* reported the synthesis

and characterization of a series of new metal complexes containing Zn(II) and Cu(II).^[8] Catalano *et al.* studied the behavior of different pyridine/imidazole-bridged triangular copper(I) complexes in which all the systems exhibited an intense blue photoluminescence in solution.^[9] Besides, Teyssot *et al.* reported the antitumor activity of a copper(I) complex derived from 1,3-bis-[2,4,6-trimethylphenyl]imidazolin-2-ylidene.^[10] Particularly, imidazole and pyridine compounds containing carbonyl groups of aldehydes and/or ketones directly bound to the ring are versatile ligands that give rise to a wide range of new materials. This is possible because of the high reactivity of the carbonyl group, which allows to obtain different chemical functionalities as *gem*-diol and hemiacetals.^[11–13] In a recent study, Wan *et al.* synthesized a copper complex obtained from 2-pyridinyl-2-pyrazinylmethanone and Cu(BF₄)₂·6H₂O in which the functional group of the metal complex was a *gem*-diol coordinating the metal ion.^[14] Moreover, Patel *et al.* reported two alkoxo-bridged complexes synthesized by metal-assisted hydrolysis of *N*-[(E)-phenyl(pyridin-2-yl)methylidene]furan-2-carbohydrazide and *N*-[(E)-phenyl(pyridin-2-yl)methylidene]aceto-hydrazide.^[15] The isolation of *gem*-diol derivatives is challenging because they quickly tend to revert to the carbonyl form, except in compounds where the loss of a water molecule is hindered by the electron withdrawing effect of the surrounding functional groups.^[16] Furthermore, some of these *gem*-diol forms can coexist with their carbonyl forms in solution depending on the degree of hydration and the characteristics of the solvent and pH.^[11,13,17] A particular case is that of 4-pyridinecarboxaldehyde which can be easily hydrated rendering single-crystals in minutes due to the high tendency of the *gem*-diol moiety to crystallize (Scheme 1).^[11] Interestingly, the coordination with metal ions can

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either have a stabilizing effect on the *gem*-diol^[18,19] or catalyze the chemical modification of functional groups present in the ligands.^[20] The aldehyde group of copper and cobalt complexes obtained from 4-pyridinecarboxaldehyde has been reported to undergo an unusual chemical transformation to dihydrogen *ortho* ester and hemiacetal groups in the same complex (Scheme 1).^[21] However, in 3-pyridinecarboxaldehyde copper and cobalt complexes, the aldehyde group remained unchanged. In this context, there are no reports of single-crystal X-ray structures for metal complexes containing ligands derived from *N*-methyl-2-imidazolecarboxaldehydes bearing *gem*-diol moieties, except for a related imidazole structure in a silver complex.^[22] The coordination of different metal ions in *N*-propyl-2-imidazolecarboxaldehyde were studied by Barszcz *et al.* In these studies, solution-state NMR experiments demonstrated that in Zn(II) complexes the aldehyde group was hydrated.^[23] Furthermore, Elliott *et al.* studied the generation of *gem*-diol moieties in 2-imidazolecarboxaldehyde ligands in Ru(II/III) complexes by UV-Visible and NMR spectroscopies.^[24]



Scheme 1. Chemical transformations reported for 4-pyridinecarboxaldehyde (4-CHO-Py) copper complexes.

Even though imidazole derivatives have been reported as ligands for different metal ions, studies carried out on 2-imidazolecarboxaldehyde are scarce, with most of them focusing only on their Schiff bases.^[25]

Studying the functionalization in metal complexes is vital, since the structure usually determines the application.^[26,27] Solid-state NMR (ss-NMR) has proved to be a promising and well-established tool to investigate the structure of different types of transition metal complexes including copper, and zinc metal ions, even in amorphous or crystalline states.^[28–30] However, the study of paramagnetic systems by NMR requires, in most cases, complementation with techniques like Electronic Paramagnetic Resonance (EPR) and X-ray crystallography or even theoretical calculations.^[31–34]

The aim of this work is to report novel single-crystal X-ray structures for three coordination compounds derived from *N*-methyl-2-imidazolecarboxaldehyde. Two of the complexes were obtained from Cu(II) and the other one from Zn(II). In addition, the chemical characterization of each sample was supported with solution- and ss-NMR and EPR techniques.

Results and Discussion

Single-Crystal X-Ray Studies

(*N*-CH₃-2-CHO-Im)₂-CuCl₂ (**1**) and (*N*-CH₃-2-CH(OH)₂-Im)₂-CuCl₂ (**2**) complexes

The incubation of an aqueous solution containing *N*-methyl-2-imidazolecarboxaldehyde with CuCl₂ gave rise to two different single crystals, one of them blue and the other green. The asymmetric unit of both coordination compounds contained one independent molecule and crystallized in the monoclinic P 2₁/c space group. The bluish crystals corresponded to the aldehyde form of the ligand ((*N*-CH₃-2-CHO-Im)₂-CuCl₂, compound **1**). The crystalline structure of this form consisted of a mononuclear copper center with two *N*-methyl-2-imidazolecarboxaldehyde molecules and two chloride atoms, with the oxygen atoms of the aldehyde group also contributing to the coordination of the copper complex with the nitrogen atoms (Figure 1).

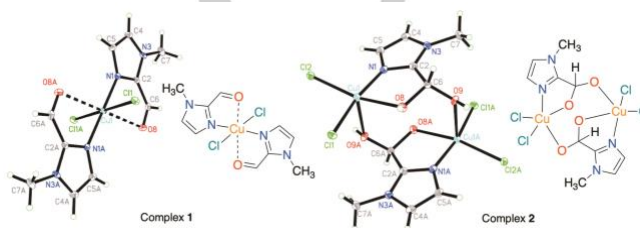


Figure 1. Single-crystal X-ray structures and their chemical representations for the copper complexes **1** and **2**. For complex **2** the hydrogen atoms of the hydroxyl groups were omitted for a clearer representation.

The greenish crystals corresponded to the *gem*-diol form ((*N*-CH₃-2-CH(OH)₂-Im)₂-CuCl₂, compound **2**) where each copper ion was coordinated with an oxygen atom from two different *gem*-diol groups, two chloride ions, and one nitrogen from the imidazole ring. Interestingly, compound **2** was the majority product in the synthesis of the copper complex (Figure 1). Noteworthy, although the *gem*-diol was isolated as the major form in the crystal lattice, ¹H solution-state NMR experiments did not show the presence of the *gem*-diol form in D₂O (Figure S7 and S8). The transformation of the aldehyde group into the *gem*-diol form was mediated and stabilized by the copper ions giving rise to a novel dimeric binuclear structure. The stabilizing effect can also be observed in the intermolecular hydrogen bonds between chloride ions and oxygen atoms of the *gem*-diol group linking two independent molecules to form a chain (Figure S4). Remarkably, this is the first binuclear Cu(II) complex to be synthesized from *N*-methyl-2-imidazolecarboxaldehyde. Compared with different isomers of pyridinecarboxaldehyde and acetylpyridine ligands evaluated in previous works,^[21,35] imidazolecarboxaldehyde ligands demonstrated to be less reactive to the nucleophilic addition of water, considering that both the aldehyde and *gem*-diol single-crystals were isolated in the same CuCl₂ solution.

(*N*-CH₃-2-CH(OH)₂-Im)-(N-CH₃-2-CO₂-Im)-ZnCl complex (**3**)

Furthermore, single crystal materials for the Zn(II) complex with *N*-methyl-2-imidazolecarboxaldehyde (**3**) were isolated (Figure 2). In this complex, both the *gem*-diol and carboxylate moieties were detected in the crystal lattice. Probably, the Zn(II) ions mediated the addition of water to the aldehyde group and the oxidation to the carboxylic acid in the same complex. As compounds **1** and **2**, the asymmetric unit of compound **3** contained one molecule, and crystallized in the monoclinic P 2₁/n space group. In this case, the metal ion was coordinated by two nitrogen atoms from two *N*-methyl-2-imidazolecarboxaldehyde ligands, two oxygen atoms from the *gem*-diol and the carboxylate moieties together with one

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chloride ion in a distorted tetrahedral geometry (Figure 2). In this case, no hydrogen bond interactions were observed between the oxygen atoms of the *gem*-diol group and chloride atoms.

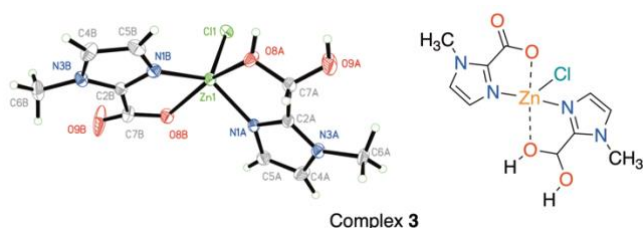


Figure 2. Single-crystal X-ray structure and its chemical representation for the zinc complex **3**.

Considering that the chemical functionalization of the *N*-methyl-2-imidazolecarboxaldehyde ligand was completely different for both the copper and zinc complexes, the X-ray crystallography studies were complemented with *solid-state* NMR and EPR.

EPR Studies

While X-ray crystallography studies were performed on single crystals taken from the mother liquor, EPR experiments were done on a polycrystalline material obtained after complete solvent evaporation. This strategy was chosen because single crystals could not be analyzed by EPR due to their small size. The X-band EPR spectrum obtained with this powder sample is shown in Figure 3. This spectrum, centered at $g \sim 2.09$, showed the typical features of a dinuclear species of Cu(II), with low zero field splitting (ZFS) with nearly axial symmetry, indicating that the contribution of compound **1** to the spectrum was negligible (less than 5%) in concordance with the powder X-ray diffraction (XRD) results (See supporting information). The absence of a hyperfine structure with the copper nucleus ($I=3/2$) together with the presence of a slight broadening of the resonance line indicated the presence of magnetic interactions between neighboring dinuclear units of the crystal lattice that partially caused resonance lines to merge into a single line.^[36,37]

The X-ray data showed that the link between copper atoms in the dinuclear unit involved an equatorial-apical chemical path, suggesting that the J coupling between the Cu(II) ions is very weak. For systems with low interdimer J values, what produces the typical dimer signal is the dipolar interaction between the copper atoms since all other anisotropic exchanges can be considered negligible.

Under the point dipole approximation, the separation of the two most intense lines of the spectrum should be ~ 48 mT. The fact that this separation was smaller (~ 20 mT) indicated the existence of exchange interactions between neighboring dimers in the crystal lattice.

It can be concluded that the dinuclear structure is undoubtedly reflected in the EPR spectrum and therefore the monomer resonances do not have a significant contribution in the spectrum.

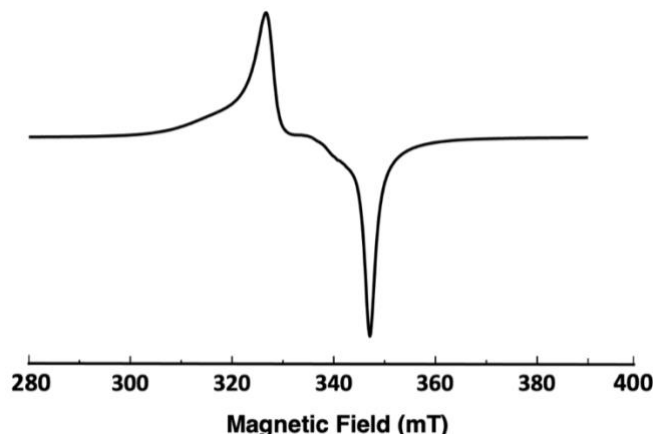


Figure 3. X-band (9.875 GHz) EPR spectrum of a crystalline sample obtained for the polycrystalline material containing both the copper complexes **1** and **2** at room temperature.

NMR studies

Copper complex **1** (*N*-CH₃-2-CH(OH)₂-Im)₂-(CuCl₂)₂

As the copper complexes were obtained in water, the *N*-methyl-2-imidazolecarboxaldehyde compound was first analyzed by *solution-state* NMR in D₂O and D₂O/CuCl₂ to determine if the carbonyl group was either in the *gem*-diol or the aldehyde form during the synthesis of the metal complexes. The ¹H-NMR spectra showed only the presence of the aldehyde form at a proton chemical shift ($\delta^1\text{H}$) of 9.47 ppm, even after the addition of 8 μmol of copper chloride (Figure 4A and 4C). The generation of copper complexes in methanol was also evaluated since the percentage of the *gem*-diol form in such solvent was 39% (Figure 4B). Noteworthy, the *gem*-diol generation was enhanced when deuterated methanol with residual water molecules ($\leq 0.05\%$ water) was used in comparison with water, where the *gem*-diol form cannot be obtained (Figure 4). However, it was not possible to obtain a solid copper complex in methanol to be analyzed.

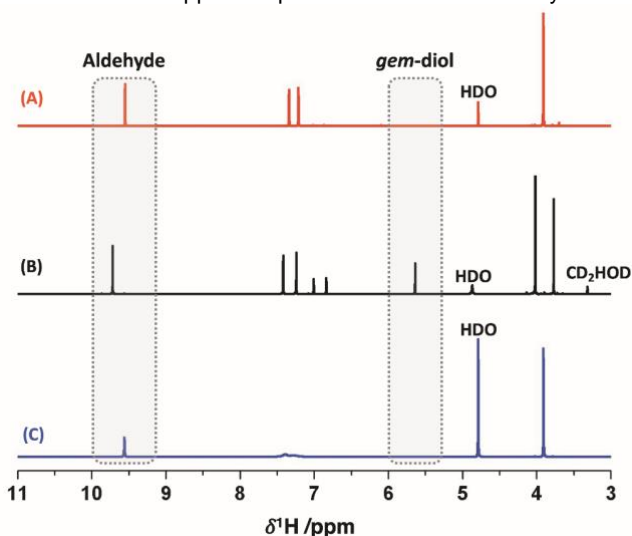


Figure 4. ¹H NMR results obtained for *N*-methyl-2-imidazolecarboxaldehyde in D₂O (A), CD₃OD (B) and D₂O with de addition of 8 μmol of CuCl₂ (C).

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Considering the results of EPR and powder XRD measurements which showed that complex **2** was the majority one (~95%), ss-NMR studies were performed to obtain chemical information related with the functionalization of the aldehyde group in the copper complex. The ^{13}C CP-MAS and ^1H -MAS spectra for compound **2** are shown in Figure 5. The three resonance signals observed in the ^{13}C spectra seemed to be diamagnetic, as evidenced by their chemical shift. This could have indicated the presence of a free uncoordinated ligand. However, the signal belonging to the methyl group at $\delta^{13}\text{C}=40$ ppm was not present. Similarly, the rotational band observed at $\delta^{13}\text{C}=95$ ppm was analyzed to ensure that it was not the *gem*-diol form of the free ligand, which is usually observed at a $\delta^{13}\text{C}$ around 70-100 ppm.^[11,12,16,17] However, the ^1H -MAS spectrum clearly showed a paramagnetic effect, as determined by the $\delta^1\text{H}$ values around 35-50 ppm (Figure 5B).

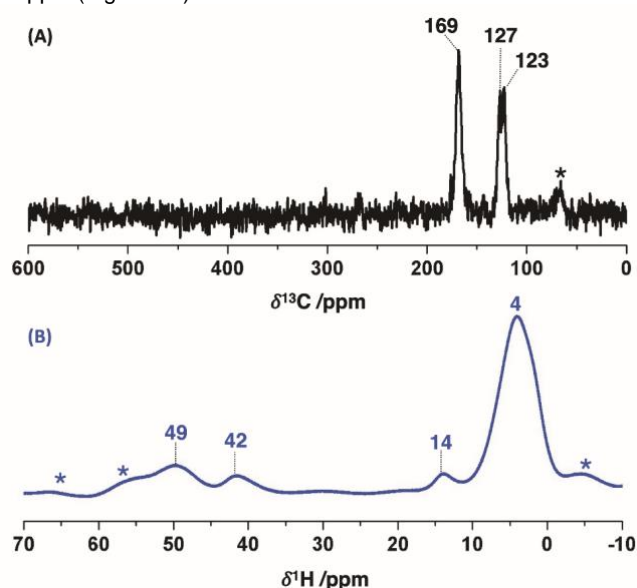


Figure 5. Solid-state NMR results for the crystalline powder **2**. ^{13}C CP-MAS (MAS rate: 15 kHz) (A) and ^1H -MAS spectra (MAS rate: 32 kHz) (B). Rotational bands are indicated with an asterisk.

Moreover, 2D ^1H - ^{13}C HETCOR experiments were carried out using two different contact times (CT) of 100 and 500 μs . Figure 6 shows the results obtained using a CT=500 μs . First, the correlations present in the 2D spectrum showed that the three resonance signals visualized in the ^{13}C CP-MAS belonged to proton-bound carbon atoms, since the same correlations were observed even when a CT of 50 μs was employed. Second, two populations of carbon atoms were detected under the resonance signal at a $\delta^{13}\text{C}=169$ ppm, given the correlation depicted as "C". In turn, the broad proton signal observed at 4 ppm in the ^1H -MAS spectrum was resolved into more signals, evidencing the presence of three type of protons at a $\delta^1\text{H}$ of 1, 4 and 6 ppm. These ^1H signals were bound directly to the carbon atoms at $\delta^{13}\text{C}=123$, 169 and 127 ppm, respectively.

The homonuclear interactions of the copper complex **2** were studied by 2D ^1H - ^1H PSD and ^1H - ^1H SQ/DQ. The ^1H - ^1H DQ-NMR experiment (Figure S10) showed only one correlation, depicted as "a-c", which evidenced proximity between protons at a $\delta^1\text{H}=2$ and 14 ppm. Likewise, in the 2D ^1H - ^1H PSD spectrum (Figure 7),

three correlations were observed, depicted as D, E, and F, which notably corresponded to three different interactions involving the proton signal at a $\delta^1\text{H}$ of 2 ppm. This was indicative that this proton signal belonged to the methyl group since, according to its position and bond distances, it is the only one capable of presenting this type of interactions. Taking this evidence into account, a preliminary assignment was performed (Table 1).

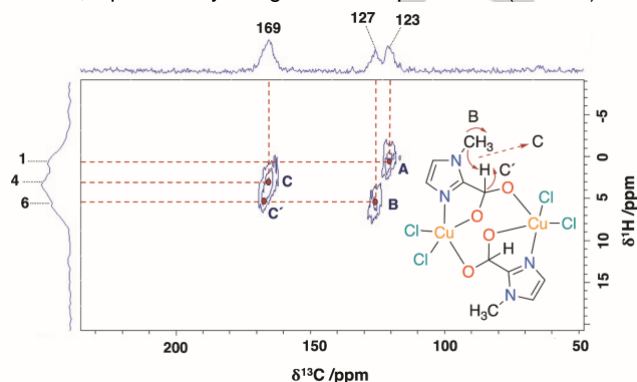


Figure 6. 2D ^1H - ^{13}C HETCOR ss-NMR spectrum of compound **2** acquired using a CT of 500 μs (MAS rate: 15 kHz).

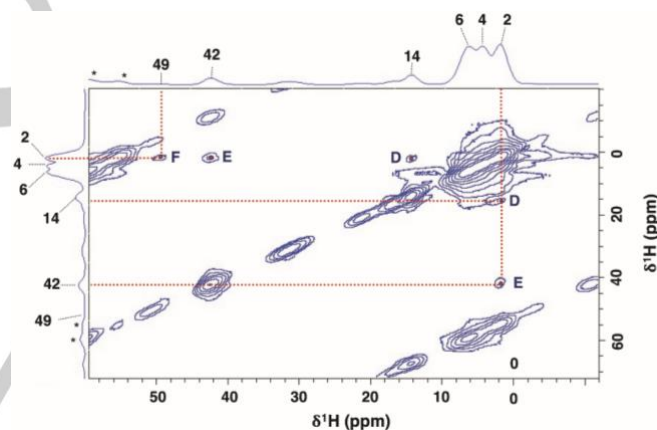


Figure 7. 2D ^1H - ^1H PSD ss-NMR spectra for compound **2** acquired with a mixing time (MT) of 5 ms (MAS rate: 32 kHz).

Table 1. NMR assignment of the Cu(II) complex (*N*-CH₃-2-CH(OH)₂-Im)₂-(CuCl₂)₂.

Chemical shift $^1\text{H}/^{13}\text{C}$ (ppm)	Evidence for $^1\text{H}/^{13}\text{C}$ assignment	Site
~4/169	Peak C in 2D ^1H - ^{13}C HETCOR exp.	-CH=CH
6/127	Peak B in 2D ^1H - ^{13}C HETCOR exp.	-CH=CH
2/123	Peak A in 2D ^1H - ^{13}C HETCOR exp.	-CH ₃
14/-	Peak D in 2D ^1H - ^1H PSD exp. Peak a-c in 2D ^1H - ^1H SQ/DQ exp.	-CH(OH) ₂
42-49/-	Peak E/F in 2D ^1H - ^1H PSD exp.	-OH

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Zinc Complex 3 (*(N-CH₃-2-CH(OH)₂-Im)-(N-CH₃-2-CO₂-Im)-ZnCl*) To analyze the chemical composition of the crystalline powder of the Zn(II) complex, ss-NMR experiments were performed, and the results are shown in Figure 8. Even when the Zn(II) complex is diamagnetic, some structural features needed to be addressed for the assignment of the NMR signals in comparison with previous solution- and ss-NMR studies carried out with *N*-methyl-2-imidazolecarboxaldehyde. As for X-ray results, two distinctive ligands were evidenced by ¹³C CP-MAS. The *gem*-diol form was identified by its characteristic resonance signal at $\delta^{13}\text{C}=84$ ppm as well as the carboxylate group at $\delta^{13}\text{C}=181$ ppm with no direct evidence of the aldehyde moiety. Furthermore, carbons of the imidazole ring were tentatively assigned to the resonance signals at a $\delta^{13}\text{C}$ of 141, 131 and 128 ppm, respectively, as well as the ¹³C of the methyl groups at $\delta^{13}\text{C}=39$ and 37 ppm ascribed to different ligands within the Zn(II) complex.

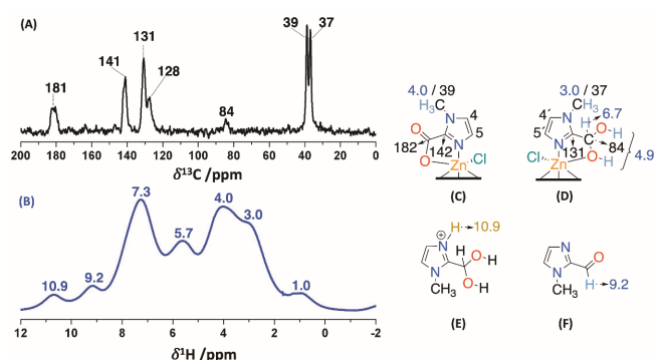


Figure 8. ss-NMR results for the crystalline powder **3**. ¹³C CP-MAS (MAS rate: 15 kHz) (A) and ¹H-MAS spectra (MAS rate: 32 kHz) (B). NMR assignment for the Zn(II) complex **3** (C and D), the *gem*-diol in its protonated form (E), and the aldehyde form (*N*-CH₃-2-CHO-Im) (F) in the residual polycrystalline residue. All chemical shift values are expressed in ppm. For structures E and F only their characteristic resonance signals are indicated. Positions 4/4' and 5/5' were assigned to $\delta^1\text{H}=7.6\text{--}8.4$ ppm and $\delta^{13}\text{C}=126\text{--}129$ ppm respectively.

The 2D ¹H-¹³C HETCOR experiments provided a good resolution of correlations between carbon atoms and their neighboring protons (Figure S11). First, the ¹³C resonance signals present in the imidazole ring (C₂ and C_{4,5}) for each of the ligand of the zinc complex were discriminated. At the same time, their associated protons were identified within a chemical shift range of 7.6–8.4 ppm (correlations O, P, Q and T). Moreover, in the ¹H indirect dimension, two resonances were observed corresponding to the methyl protons of the metal complex depicted as correlations I and J.

Remarkably, the ¹H-MAS spectrum presented resonances belonging not only to the metal complex but also to different chemical forms of the imidazole ligand. Consequently, 2D ¹H-¹H SQ/DQ experiments were done (Figure 9). The Zn(II) complex **3** showed three strong autocorrelation peaks observed at $\omega_{\text{DQ}}=6.8$, 9.8 and 16 ppm corresponding to the methyl groups (-CH₃), the hydroxyl groups of the *gem*-diol (-CH(OH)₂) and the aromatic protons (=CH-), respectively. Besides, these protons exhibited four mutual interactions depicted as correlations a-b, a-c, a-d, and b-d indicating their spatial proximity.

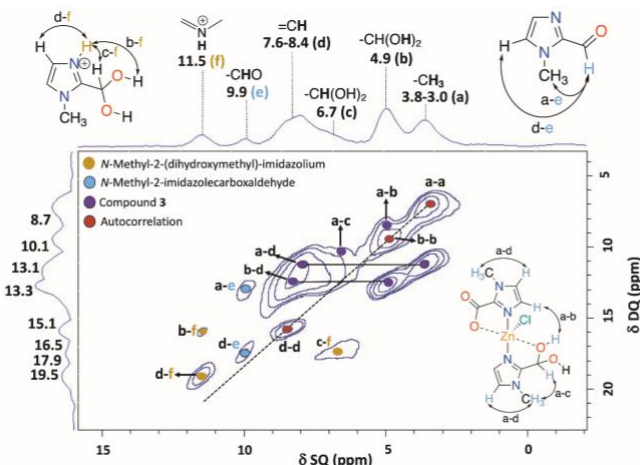


Figure 9. 2D ¹H-¹H SQ/DQ ss-NMR spectrum of compound **3** (MAS rate: 32 kHz) acquired with two rotor periods of DQ recoupling. The DQ values of autocorrelations (a-a, b-b, and d-d) are not included.

Furthermore, five extra correlation peaks were observed, which provided direct evidence of the presence of different chemical forms of the *N*-methyl-2-imidazolecarboxaldehyde molecule in the solid sample. Two of these correlations depicted as a-e and d-e corresponded to the aldehyde form. The DQ signal d-e observed at $\omega_{\text{DQ}}=17.9$ ppm (9.9 + 8.0 ppm) resulted from a DQ coherence between the aromatic proton site H₅ and the hydrogen of the aldehyde group. The latter is also in close spatial proximity to the methyl group evidenced by the DQ signal a-e observed at $\omega_{\text{DQ}}=13.3$ ppm (9.9 + 3.4 ppm). The remaining three interactions corresponded to the *gem*-diol form in which the pyridinic nitrogen of the imidazole ring was protonated (correlations b-f, c-f, and d-f).

Even when the ¹H-MAS and 2D ¹H-¹H SQ/DQ spectra showed the presence of residual aldehyde groups ($\delta^1\text{H}=9.9$ ppm) in the polycrystalline sample, the C-H correlation of this group (-CHO) was not detected in the 2D ¹H-¹³C HETCOR experiments using both short and long contact times due to the low concentration of the aldehyde form in the powder sample. In this sense, the 2D ¹H-¹³C HETCOR experiments did not show any correlation between the ¹³C signal at 181 ppm and the aldehyde hydrogen at 9.9 ppm, indicating that only the carboxylate group was present.^[17]

Density functional theory-based calculations of NMR chemical shifts were carried out employing GIAO-B3LYP method. In Tables 2 and 3 experimental and theoretical results are detailed. As it can be observed, chemical shifts were accurately reproduced by DFT calculations for the proposed structures present in the solid sample.

To determine if the aldehyde or the carboxylic acid forms were in their protonated forms, the minimization of these structures and the calculation of the NMR chemical shift values were carried out. The results obtained allowed ruling out the presence of these species in the solid sample (See supporting information).

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Table 2. Calculated (calc.) and experimental (exp.) ^{13}C and ^1H chemical shifts for compound **3** (expressed in ppm relative to TMS) and difference between experimental and calculated shifts (Δ).

Position	$\delta^{13}\text{C}_{\text{calc.}}/\delta^{13}\text{C}_{\text{exp.}}$ (ppm)	Δ	$\delta^1\text{H}_{\text{calc.}}/\delta^1\text{H}_{\text{exp.}}$ (ppm)	Δ
gem-diol ligand				
2'	144.9/141.0	3.9	-	-
4'	124.4/129.0	-4.6	7.9/7.3	0.6
5'	122.1/127.0	-4.9	6.8/7.3	-0.5
-CH(OH) ₂	90.1/84.0	6.1	6.0/6.7	-0.7
-OH	-	-	4.5/4.9	-0.4
-CH ₃	33.9/37.0	-3.1	3.8/3.0	-0.8
carboxylate ligand				
2	142.0/141.0	1.0	-	-
4	126.4/129.0	-2.6	7.2/7.3	-0.1
5	124.3/127.0	-2.7	6.9/7.3	-0.4
-CO ₂ ⁻	178.4/184.0	-5.6	-	-
-CH ₃	34.8/39.0	-4.2	4.4/4.0	0.4

Table 3. Calculated (calc.) and experimental (exp.) ^1H chemical shifts for *N*-methyl-2-imidazolecarboxaldehyde and *N*-methyl-2-(dihydroxymethyl)imidazolium compounds (expressed in ppm relative to TMS) and difference between experimental and calculated shifts (Δ).

Position	$\delta^1\text{H}_{\text{calc.}}/\delta^1\text{H}_{\text{exp.}}$ (ppm)	Δ
<i>N</i>-methyl-2-imidazolecarboxaldehyde		
5	7.9/7.3	0.6
-CHO	8.9/9.9	-1.0
-CH ₃	3.7/3.4	0.3
<i>N</i>-methyl-2-(dihydroxymethyl)imidazolium		
4/5	7.6/7.3	0.3
-OH	3.9/4.9	-1.0
NH ⁺ /NH	10.9/11.5	-0.6

Conclusion

In this work, three metal complexes were obtained by employing *N*-methyl-2-imidazolecarboxaldehyde as ligand. Particularly, two of them were synthesized from copper(II) and the other from zinc(II). The three metal complexes were studied in detail using spectroscopic techniques as single-crystal X-ray crystallography, *solution*- and *ss*-NMR, and EPR. Interestingly, the chemical behavior of the carbonyl group of the ligand depended on the metal ion involved in the coordination compounds, demonstrating

that even working under the same experimental conditions, either the aldehyde, the *gem*-diol or the carboxylate moiety can be obtained. Moreover, the metal:ligand stoichiometry differed even when the same metal ion was employed to generate the complex. In this sense, two different copper complexes were isolated with the same CuCl₂ solution, being one of them a mononuclear copper complex bearing the aldehyde and the other a binuclear copper complex having the *gem*-diol moieties.

The *ss*-NMR experiments for the binuclear copper complex showed that even when the presence of copper ions induce a strong source of relaxation in the entire complex as well as a paramagnetic shift of the NMR signals, some structural interactions can be obtained if the acquisition parameters in the heteronuclear and homonuclear experiments assisting in the assignment of the NMR signals are adapted.

The structural analysis of compound **3** was carried out in combination with theoretical calculations. All the *ss*-NMR chemical shifts were assigned with a good approximation based on GIAO/B3LYP/6-31++G(d,p) method.

Experimental Section

Materials. *N*-methyl-2-imidazolecarboxaldehyde (*N*-CH₃-2-CHO-Im, 98%), copper(II) chloride (CuCl₂·2H₂O, 99.95%), zinc(II) chloride (ZnCl₂, ≥ 98%) deuterium oxide (D₂O, 99.9 atom %D) and methanol-*d*₄ (CD₃OD, >99.8 atom %D) were purchased from Sigma Aldrich and used without further purification.

General procedure for the synthesis of copper (1** and **2**) and zinc (**3**) complexes with *N*-methyl-2-imidazolecarboxaldehyde.** Copper(II) chloride (0.292 mmol) was dissolved in 4.0 mL of water and 0.450 mmol of *N*-methyl-2-imidazolecarboxaldehyde were added with stirring. The reaction mixture turned dark green and was stored at room temperature until two different crystals appeared (green and blue). After that, crystals were filtered, washed with 3 mL of water and vacuum-dried. The chemical composition of the polycrystalline sample was estimated by EPR experiments, being the binuclear copper complex **2** the major component in the mixture (95%).

For the synthesis of complex **3**, zinc(II) chloride (0.292 mmol) was dissolved in 4.0 mL of water and 0.400 mmol of *N*-methyl-2-imidazolecarboxaldehyde were added with stirring. The reaction mixture was stored at room temperature until colorless crystals appeared. After that, crystals were filtered, washed with 3 mL of water and vacuum-dried. The reaction yield was 45 % (32 mg, 0.0901 mmol).

Single-crystal X-ray crystallography studies. Single crystals were isolated by slow evaporation of each solution containing the compound of interest obtained as described above. Single-crystal X-ray diffraction data were collected at 100 K, using a Quest ECO diffractometer. The strategy employed for the collection and reduction of data followed the standard procedures implemented in the APEX3 Control Software. Different reflections were collected for each sample (specified in the Supporting Information). Deposition Numbers 2217294 (for copper complex **1**), 2217295 (for copper complex **2**) and 2217296 (for zinc complex **3**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

EPR measurements. X-band CW-EPR measurements were performed at room temperature on a Bruker EMX-Plus spectrometer equipped a rectangular cavity at a field modulation frequency of 100 kHz. Powder sample for EPR spectroscopy was placed inside 4 mm inner diameter EPR quartz tube.

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NMR studies. Solid- and solution-state Nuclear Magnetic Resonance data were acquired with a Bruker Avance-III HD spectrometer equipped with a 14.1 T narrow bore magnet operating at Larmor frequencies of 600.09 MHz and 150.91 MHz for ^1H and ^{13}C , respectively. Powdered samples were packed into 3.2 and 2.5 mm ZrO_2 rotors and rotated at room temperature at magic angle spinning (MAS) rates of 15 or 32 kHz, respectively. ^{13}C CP-MAS (cross-polarization and magic angle spinning) experiments were done in a 3.2 mm MAS probe. Different contact times during CP step were used (0.05–2.0 ms) to obtain the highest signal-to-noise ratio in each scan and in the total time of the experiments, with number of scans between 2000 and 10000. Glycine was used as external reference for the ^{13}C spectra and to set the Hartmann–Hahn matching condition in the cross-polarization experiments in ^{13}C spectra.^[38] The SPINAL64 sequence was used for heteronuclear decoupling during acquisition.^[39] The 2D ^1H – ^{13}C HETCOR experiment with frequency-switched Lee–Goldberg irradiation during the dipolar proton evolution in the solid state was recorded varying the contact time from 50 μs to 2 ms to sense interactions between ^{13}C and ^1H , respectively (MAS rate: 15 kHz).^[40] ^1H -MAS and 2D homonuclear correlation experiments were recorded in a 2.5 mm MAS probe at a MAS rate of 32 kHz. The 2D ^1H – ^1H Proton Spin Diffusion (PSD) experiments were acquired using mixing times from 10 μs to 20 ms and the 2D ^1H – ^1H Single Quantum/Double Quantum (SQ/DQ) experiment was acquired with the back-to-back (BaBa) pulse sequence with excitation and reconversion times of two rotor period.^[41] Chemical shifts for ^{13}C and ^1H (expressed in ppm) are relative to glycine and $(\text{CH}_3)_4\text{Si}$, respectively.

DFT calculations. The structure calculations were performed at the level of the Kohn–Sham Density Functional Theory (DFT) with the Becke’s three-parameter hybrid exchange functional^[42] and the Lee–Yang–Parr correlation functional^[43] (together denoted as B3LYP). The basis set employed was 6-31++G(d,p).^[44] The crystal structures determined by X-ray crystallography were used as the starting structure for geometry optimization, in which the positions of all the atoms were relaxed. The GIAO method was applied for calculations of the ^1H and ^{13}C chemical shifts (δ) and were reported relative to the reference compound, typically TMS, according to Equation 1:

$$\delta = \sigma_{\text{iso}(\text{orb})}(\text{TMS}) - \sigma_{\text{iso}(\text{orb})} \quad (1)$$

All calculations were performed with the Gaussian09 software.^[45]

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Biography

Juan M. Lázaro-Martínez studied Biochemistry at the University of Buenos Aires (UBA, 2005), Argentina. Afterwards, he reached his PhD degree in Organic Chemistry under the supervision of Prof. G. Buldain and V. Campodall’Orto (UBA, 2011). After that,

he had a postdoctoral training at the University of Córdoba (Argentina) working in ss-NMR with Prof. G. Monti and A. Chattah (2011–2013). Nowadays, he is Assistant Professor (UBA) and Independent Researcher from CONICET. His research group focuses on the synthesis and structural characterization of a broad kind of organic/inorganic materials and copper/cobalt complexes and their applications for advanced oxidation processes.



Keywords: copper • *N*-methyl-2-imidazolecarboxaldehyde • single-crystal X-ray • solid-state NMR • zinc

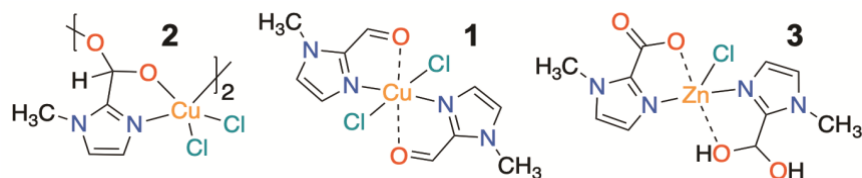
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Mono- (1) and binuclear copper complexes (2) and a zinc complex (3) were synthesized and studied through X-ray crystallography, *solid-state* NMR and EPR techniques to determine the chemical functionalization of the aldehyde group in *N*-methyl-2-imidazolecarboxaldehyde. The ligands in the complexes 1, 2 and 3 were found to be the aldehyde, the *gem*-diol, and both the *gem*-diol and carboxylate moieties, respectively.

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