Theoretical Approach by DFT in the characterization of the Zn(II) Benzoate

Abordagem Teórica por DFT na Caracterização do Benzoato de Zn(II)

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Resumo
A reação de condensação entre o bicarbonato de aminoguanidina e o ácido benzoico produziu 1,2,4-triazol que, após reação com cloreto de zinco(II), levou à formação de um complexo, Zn(II)-1,2,4-triazol. Este complexo se decompõe em clorofórmio levando à formação de um subproduto identificado por RMN multinuclear (^{13}C e ^{1}H) como benzoato de zinco(II). Posteriormente, um estudo teórico, utilizando os métodos de Hartree-Fock e DFT, foi aplicado para validar o benzoato de zinco(II) como subproduto da decomposição através do cálculo do tensor de blindagem magnética (RMN), bem como abordar algumas características estruturais deste composto uma vez que compostos de zinco apresentam uma variedade de arranjos geométricos e números de coordenação. O resultado teórico mostrou que o Benzoato de Zn(II) é o subproduto da reação e que o mesmo dimeriza em solução de clorofórmio.
Palavras-chave: Zinco(II). Geometria. Espectroscopia. DFT. Hartree-Fock.

Abstract
The condensation reaction between aminoguanidine bicarbonate and benzoic acid produced 1,2,4-triazole which, after reaction with zinc(II) chloride, led to the formation of a complex, Zn(II)-1,2,4-triazole. This complex decomposes into chloroform leading to the formation of a by-product identified by multinuclear NMR (^{13}C and ^{1}H) as zinc(II) benzoate. Subsequently, a theoretical study, using the Hartree-Fock and DFT methods, was applied to validate zinc(II) benzoate as a byproduct of decomposition through the calculation of the magnetic shielding tensor (NMR), as well as to address some structural characteristics of this compound since zinc compounds present a variety of geometric arrangements and coordination numbers. The theoretical result showed that Zn(II) benzoate is the by-product of the reaction and that it dimerizes in chloroform solution.
Keywords: Zinc(II). Geometry. Spectroscopy. DFT. Hartree-Fock.

1. Introduction

Zinc(II) compounds are acknowledged regarding its biological activities against several microorganisms such as *P. aerugonisa* and *C. albanians* (Arjmand *et al*., 2011; Bagihalli *et al*., 2009; Dhahagani *et al*., 2014). Although the Zinc(II) benzoate can be prepared by various reaction path, for instance, direct reaction between Zinc(II) hydroxide and benzoic acid in aqueous medium or by grinding ZnO with benzoic acid, this compound has been isolated as a by-product from decomposition reaction of a complex produced in our laboratory by the reaction between 3-fenil-*1H*-1,2,4-triazole-5-amine and Zn(II) chloride (Almeida, Maia, Falqueto, & Oliveira, 2022; Ming-cai *et al*., 2004; Skorsepa *et al*., 2004). The practical amount of by-product separated in this decomposition reaction does not correspond to the 2% excess of benzoic acid used to prepare the 3-fenil-*1H*-1,2,4-triazole-5-amine, which indeed has been eliminated after washing this final product with the proper solvent. In addition, the signals of the NMR spectrum of the by-product does not correspond to those expected for the final product, 3-fenil-*1H*-1,2,4-triazole-5-amine (Almeida, Maia, Souza, & Pacheco, 2022).

Coordination compounds of Zinc metal has a variety of geometrical arrangements and coordination number (CN) concerning the chemistry of its metal ion. The most common are the bipyramidal trigonal, tetrahedral and the octahedral arrangements where the Zn(II) ion bonds to a diversity of ligands such as Schiff bases, 1,2,4-trizoles, trimethylenepyridine, among others (Almeida, Maia, Falqueto, & Oliveira, 2022; Maia *et al*., 2018; Tella *et al*., 2020). The characterisation of Zinc compounds by X-ray diffraction analysis shows these typical geometric arrangements as for the tetrahedral Zn(II)-trimethylenepyridine polymer (Tella *et al*., 2020). This potent technique can not only determine the crystal structures but point out unknown stereochemistry as in the case of the compound of Zn(II)-tetrakis[methyl(diphenylphosphoryla-ted)] in which the number of coordination is equal to eight (Tsebrikova *et al*., 2018).

Density functional theory (DFT) is an electronic structure calculation method which is considerably used in the field of physical chemistry, material science, and condensed matter physics. The Gaussian program is the most frequently used computational chemistry packages for DFT calculations. Performing DFT calculations using Gaussian program starts by setting up an input file with the appropriate level of theory, followed by running the job of Gaussian calculation, and analyzing the output file (James & F., 2015).

Although spectroscopic methods are fundamental to envisage the properties and structural features of compounds in general, DFT calculations has also been showing significance in the experimental data interpretation in the field of inorganic chemistry (Almeida, Maia, Souza, & Pacheco, 2022; Jin *et al*., 2014; Phalgune *et al*., 2013; Tella *et al*., 2020; Thomas *et al*., 2005). Stable octahedral complex of Zn(II)-histidine was explored by the B3LYP/6-311G(d) level of theory where the calculation of the free energy shows that the complex is formed spontaneously only with two coordinated histidine to the metal (Franklin *et al*., 2020). The catalytic effect of complexes derived from tridentate hydrazone ligands were explored by TD-DFT/B3LYP/6-31G and B3LYP/6-311G(d,p) level of theory where it was found that the higher catalytic effect is correlated to lower kinetic stability (Adejumo *et al*., 2020). The NMR calculation of Zn(II) complexes derived from Schiff bases have been reported by DFT using the M06-2X functional and the triple-zeta basis set 6-311+G(d,p) as well as the basis set LanL2DZ for the Zn(II) metal ion. The computational data for these complexes has indicated the formation of tautomeric species because of the discrepancy relative to the calculated NH signal (Omidinia *et al*., 2022).

The objective of this work is, therefore, to use the Density Functional Theory (DFT) to validate Zn(II) benzoate as a by-product from the decomposition reaction of the complex Zn(II)-3-fenil-*1H*-1,2,4-triazole-5-amine in chloroform as well as point out some of its structural features. A theoretical approach was established based on the magnetic shielding tensor of the proposed structures computed by DFT at the B3LYP/6-31G+, B3LYP/6-31G++, B3LYP/GEN6-311G+(2d,p)/6-31G+ level of theory. The experimental datum of the by-product was obtained by multinuclear NMR techniques.

2. Results and discussion

The infrared, carbon 13 and hydrogen NMR of the by-product, Zn(II) benzoate, has been previously characterised by our group (Almeida, Maia, Falqueto, & Oliveira, 2022). The Inorganic Chemistry field classify ligands according to the number of available pair of electrons that can bind to a metal ion. The benzoate ion is, therefore, a tetradentate ligand since each of the oxygen atom has two pairs of electrons to bind to a metallic centre. The first attempt to envisage its coordination mode to a metal ion is through two pair of electrons, each one from a distinct oxygen atom, which leads to a chelating bidentate coordination mode and, consequently, to a possible tetrahedral arrangement with two benzoate ligands at the coordination sphere of the metal. Nevertheless, the most likely coordination mode is correlated to intrinsic thermodynamic parameters of the reaction which means that not necessarily a polydentate ligand would bind to a metal in a bidentate coordination mode as it was observed for the tetrakis[methyl(diphenyl phosphorylated)] ligand (Franklin *et al.*, 2020; Tsebrikova *et al.*, 2018).

The crystallographic datum of the compound [$Zn_2(BA)_4(NA)_2$].(BAH) (BAH – benzoic acid; NA – nicotinamide) is reported having the benzoate anion (BA) performing both bridging bidentate and chelating coordination modes where one Zn(II) is at the centre of a tetrahedron and the other at the centre of a square pyramidal arrangement. The tetrahedral arrangement has the benzoate anion acting in a monodentate coordination mode and the square pyramidal in the chelating mode (Aycan, 2021). Complexes of Zn(II) having the benzoate anion in the latter mentioned coordination modes are reported as possible catalysts (Kwak *et al.*, 2008). The structure of a tetranuclear complex of Zn benzoate, of molecular composition $Zn_4O(C_6H_5CO_2)_6$, is also known by X-ray diffraction analysis. This compound has been prepared by thermal decomposition of the Zinc(II) benzoate at 300 °C under argon atmosphere where the benzoate anion in the crystal structure is performing in a bridging bidentate coordination mode between two Zn atoms (Ming-cai *et al.*, 2004).

2.1. Theoretical NMR Approach

The use of computational studies to complement and even confirm structure and properties of materials in general have been widely used in the chemistry field. Basis set such as 6-311G++(2d,p) and 6-31G* were used in the calculation of the LUMO and HOMO in the Zn(II) derivatives complexes with α-diketimine and 5-bromo-2-((allylimino)methyl)phenol Schiff-based ligand (Abhijith *et al.*, 2022; Deilami *et al.*, 2018). The Level of theory such as B3LYP/Def2-TZVP were also conducted by DFT and TD-DFT computational studies in the calculation of DNA binding to substrates and molecular docking in addition to the electronic structure of Zn(II) derivative complexes (Eroshin *et al.*, 2022; Kargar *et al.*, 2021).

Geometry optimization has also been reported on the B3LYP/6-31G+(d,p) level of theory in Zn(II) derivatives complexes with 2-((thiophene-2-ylmethylene)amino)benzamide to calculate the energy of the HOMO and LUMO orbitals of these compounds (Tyagi *et al.*, 2015). Theoretical approach on the NMR chemical shifts calculation have been reported in several levels of theory for organic and organometallic compounds and even to paramagnetic substances (Di Micco *et al.*, 2019; Johnston *et al.*, 2013; Kaupp, 1996; Kaupp *et al.*, 1996; Rastrelli & Bagno, 2009).

Exploration of the coordination modes on tetranuclear complexes of Ag and Au derived from tetra-NHC ligand revealed at the low-temperature by NMR techniques strong influences on the vibrational behaviour of the ligand confirmed by DFT/M06L/TZVP calculations (Altmann *et al.*, 2016). DFT calculations combined with infrared spectroscopy revealed furthermore to be an important tool in the structural estimation of palladium complexes for which the crystallographic data was unknown. The geometry optimizations for these palladium complexes were carried out with ORCA 3.02 software applying the density theory functionals BP86 and B97-D. The computational data were obtained on the basis set def2-TZVP for all elements, except for Pd where the effective-core-potential was used, employing "ECP {def2-TZVP, def2-TZVP/J} def2-TZVP def2-TZVP/J" (Popović *et al.*, 2021).

The ORCA 3.0.3 software package has also been used to predict hydrogen chemical shift in Zn(II) complexes derived from 2-acetylthiophenyl-thiosemicarbazone, using the functional B3LYP to perform the geometry optimizations with the 6-31G(d,p) basis set. The results were in good agreement with the experimental data providing evidence for the NH group in the structure of the complexes (Şen Yüksel, 2021).

In this work the proposed Zinc(II) by-products were optimized by the Hartree-Fock method using the basis set 6-31G++, 6-31G+ and GEN6-311G+(2d,p)/6-31G+. Subsequently, the magnetic shielding tensor was calculated by the DFT/B3LYP method using the corresponding basis set as described in Tables 1, 2 and 3. The Tables show the experimental NMR data for the by-products having number of coordination two (C and D) and four (B and E). Several attempts to achieve the best optimized structure was carried out applying the Hartree-Fock and DFT/B3LYP methodologies to dimeric structures having bridging and chelate benzoate anion bonded to the metal. The geometry optimization by frequency analyses of the proposed Zinc compounds showed no imaginary frequency in the calculation.

The accuracy of the results was evaluated by linear regression as well as percentage relative error. The percentage error between the experimental and the calculated chemical shift of the carboxylic group, C=O, using 6-31G++ basis set, as shown in Table 1, was 0.08 % for B, 0.24% for C, 0.34% for D and 7.30 % for E.

Table 1 - Experimental and calculated NMR data*#.

NMR	B	C†	D‡	E
	δ exp.	$\delta\,^{13}$C calc.		
C=O	172.49	172.3422	172.0797	171.9064	185.0849
C-COO	133.65	130.7396	130.4771	129.8835	125.4624
Ph	130.23	126.9588	127.5946	128.1318	128.7170
	129.68	125.3784	125.3719	125.3157	125.8316
	128.41	128.8674	128.9719	129.0584	130.6832
		$\delta\,^{1}$H calc.		
Ph	8.13	8.4935	8.4835	8.5014	8.5939
	7.61	7.5329	7.6854	7.6855	7.7747
	7.47	7.6280	7.7001	7.8089	7.9421
CDCl$_3$	7.26				

Opt+Freq: *HF/6-31G++. NMR: # B3LYP/6-31G++; C, D – Zinc(II) Benzoate, NC = 2;
B, E - Zinc(II) Benzoate NC = 4; Bond Angle (O-Zn-O): † - 162.09923°; ‡ - 161.81831°

The tetrahedral Zn(II) compound, E, has two O-Zn-O bond angles, an acute less than 70° and an obtuse higher than 100° that leads to a distorted tetrahedral structure, showing a calculated chemical shift of δ 185.0849 for the carbon atom of the carboxylic group. This chemical shift is too far to correspond the experimental data. However, the calculated chemical shift for C and D relative to this group did not change much by using different O-Zn-O bond angles.

Equivalent results have been observed considering the less polarizable basis set 6-31G+, as shown in the Table 2. The percentage error for the carboxylic group was 0.43 % for B, 1.57 % for C, 1.56 % for D and 7.69 % for E. The result for the calculated chemical shift of compound E is equivalent of that in Table 1 which presumably is correlated to the bond angles O-Zn-O for the distorted tetrahedral structure. The calculated chemical shift for this compound reinforces the influence from the magnetic chemical environment in NMR techniques which correlates to the structural features of compounds leading to distinct chemical shift to certain groups.

The Table 3 shows the calculated NMR data for the same substances as described previously in Tables 1 and 2. However, the basis set 6-311G+(2d,p) was used for carbon, hydrogen and oxygen atoms, except for the Zinc atom which was 6-31G+. The percentage error relative of the carboxylic group was 0.21 % for B, 1.08 % for C, 0.49 % for D and 5.09 % for E.

Table 2 - Experimental and calculated NMR data*#.

NMR	δ exp.	B	C[†]	D[⚌]	E
			$\delta\,^{13}$**C** calc.		
C=O	172.49	171.7319	169.7762	169.7954	185.7716
C-COO	133.65	131.4306	130.1706	130.2119	125.4080
Ph	130.23	127.5239	128.3418	128.3141	130.0906
	129.68	126.4462	126.0379	126.0875	125.2847
	128.41	129.2487	130.1721	130.1637	133.1325
			$\delta\,^{1}$**H** calc.		
Ph	8.13	8.5008	8.4550	8.4859	8.6189
	7.61	7.5004	7.6247	7.6231	7.7814
	7.47	7.6140	7.7059	7.7133	7.8375
CDCl₃	7.26				

Opt+Freq: *HF/6-31G+; NMR: # B3LYP/6-31G+; C, D – Zinc(II) Benzoate, NC = 2;
B, E - Zinc(II) Benzoate NC = 4; Bond Angle (O-Zn-O): † - 162.49382°, ⚌ - 161.86478°

Table 3 - Experimental and calculated NMR data. #‡

NMR	δ exp.	B	[†]C	[⚌]D	E
			$\delta\,^{1}$**C** calc.		
C=O	172.49	172.1416	170.6243	171.6426	181.2660
C-COO	133.65	139.1780	136.1091	135.6102	132.1724
Ph	130.23	134.3833	134.8451	135.0036	135.5902
	129.68	131.5847	132.0420	132.0766	132.3150
	128.41	135.9024	136.2258	136.4172	138.0748
			$\delta\,^{1}$**H** calc.		
Ph	8.13	7.8890	7.9316	7.9398	8.0423
	7.61	7.2234	7.3215	7.3328	7.3913
	7.47	7.2744	7.4036	7.4157	7.4622
CDCl₃	7.26				

Opt+Freq: # HF/GEN B3LYP/6-311G+(2d,p)/6-31G+. NMR: ‡ GEN B3LYP/6-311G+(2d,p)/6-31G+;
C, D – Zinc(II) Benzoate, NC = 2; B, E - Zinc(II) Benzoate NC = 4;
Bond Angle (O-Zn-O): † - 162.94260 °; ⚌ - 160.66985°

Three different basis set were used to calculate the magnetic shielding tensor of the proposed zinc benzoate structures. In general, the calculated data presented on all three Tables show that compound B, C or D may represent the by-product by comparison between the calculated chemical shifts with the experimental data, despite the slight differences in the bond angle O-Zn-O between the latter two compounds. The correlation coefficient between the experimental and the calculated

data as well as the standard error, obtained by simple linear regression, are shown in Table 4. Good correlation coefficient (R^2) is clearly showed for all the basis set used for the magnetic shielding tensor calculation. However, the standard error indicates that among the basis sets used in the calculation better statistic results were achieved for B, C and D structures using 6-31G++ and 6-31G+ bases set. Compound E shows higher standard error to all the basis set used in the calculation. The less percentage relative error for the carboxylic group of B, C or D is corroborated by the statistical results. The theoretical optimized structures of these compounds are shown in Figure 1 and 2. Therefore, the by-product must have coplanar benzoate ions bonded to the metallic centre consistent with the planar bent structure I as shown in Figure 1 or a dimeric tetracoordinated Zn(II) bonded to the bridging benzoate ions (IIIa or IIIb) as shown in Figure 2. However, the calculated data indicates that structure I may dimerizes in chloroform to the structure III which is reasonable assuming the proximity of the statistical results among them.

Table 4. Statistical analysis for the computational NMR.

Basis set	B		C		D		E	
	R^2	SE	R^2	SE	R^2	SE	R^2	SE
	Carbon data							
T1	0.99939	1.84441	0.99943	1.77833	0.99939	1.84693	0.99308	6.23267
T2	0.99963	1.43378	0.99942	1.79177	0.99943	1.77445	0.99238	6.54016
T3	0.99864	2.76224	0.99828	3.10661	0.99847	2.92370	0.99793	3.40513

R^2 – Correlation coefficient between experimental and calculated data; SE - Standard Error.
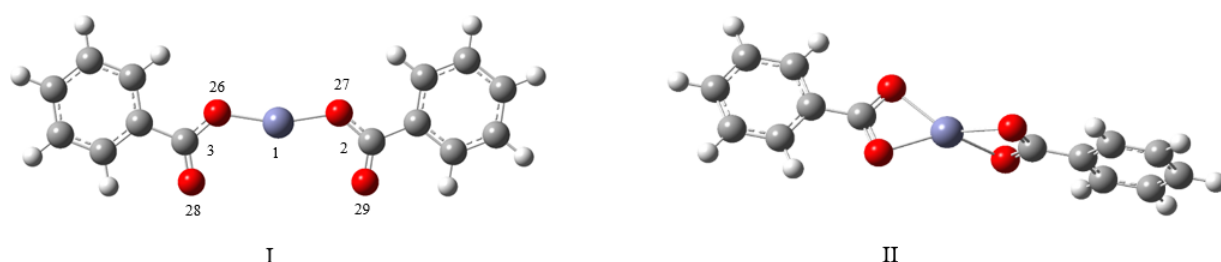T1 – 6-31G++; T2 – 6-31G+; T3 – GEN/6-311G+(2d,p)/6-31G+

Figure 1. Optimized structures of the Zn(II) benzoate showing two possible coordination modes of the benzoate ion: monodentate I (C or D) and chelating bidentate II (E).
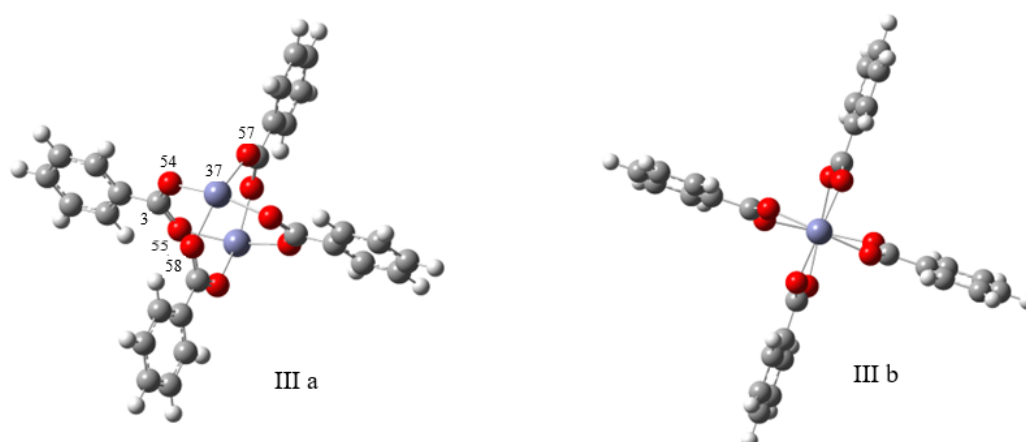

Figure 2. Optimized structure B (IIIa and IIIb) in perspective for the dimeric Zn(II) benzoate.

The Zn(II) benzoate was obtained unexpectedly by attempting of purifying a Zn(II) complex (8a and/or 8b) derived of the rection between Zn(II) chloride and 3-fenil-*1H*-1,2,4-triazole-5-amine in chloroform. Two substances were separated in the process as Zn(II) Benzoate and a Zn(II) complex derivative of aminoguanidine (*amgu*) which is not soluble in chloroform. The general reaction pathway of the decomposition is shown in Figure 3 (Almeida, Maia, Falqueto, & Oliveira, 2022)
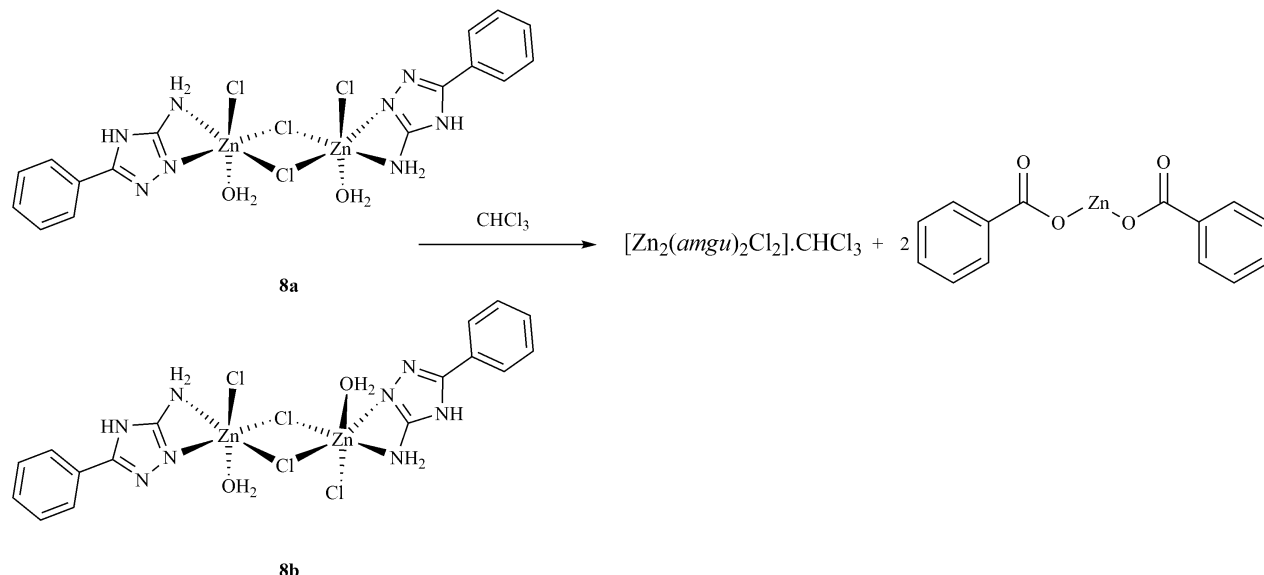

Figure 3. Reaction pathway for the decomposition of 8a and/or 8b in Chloroform.

Some datum of bond angles (°) and bond lengths (Å) for the structure D and B are shown in Table 5 according to the label of the atoms in Figure 1 and 2.

Table 5. Selected bond angles and bond lengths from structure D an B.

Structure D			
Bond Angles (°)		Bond Lengths (Å)	
O(26)-Zn(1)-O(27)	161.81831	Zn(1)-O(26)	1.86515
Zn(1)-O(27)-C(2)	129.46571	Zn(1)-O(27)	1.86515
Zn(1)-O(26)-C(3)	129.46641	C(3)-O(26)	1.31025
O(28)-C(3)-O(26)	122.09232	C(2)-O(27)	1.31026
O(29)-C(2)-(27)	122.09084	C(3)-O(28)	1.23719
O(26)-Zn(1)-O(27)-C(2)	179.98065	C(2)-O(29)	1.23719
Zn(1)-O(27)-C(2)-C(15)	179.99283		
Structure B			
O(53)-Zn(37)-O(58)	87.90779	Zn(37)-O(57)	2.05436
O(57)-Zn(37)-O(58)	157.97751	Zn(37)-O(58)	2.05445
O(55)-C(3)-O(54)-Zn(37)	-9.32742		

3. Materials and methods

3.1. Density Functional Theory (DFT)

The Gaussian 09 software was used to execute all the calculations in chloroform. The compounds were submitted to geometrical optimization (Opt+Freq) by means of the Hartree-Fock

method using 6-31G+, 6-31G++ and GEN/6-311G+(2d,p)/6-31G+ basis set. Subsequently the magnetic shielding tensor (NMR) values were calculated by DFT/B3LYP functional applying each of the basis set and the results compared to the experimental data. The TMS was the shielding tensor reference calculated for each level of theory applied (M. J. Frisch *et al.*, 2009). The Microsoft Excel was used for the statistical analyses by simple linear regression (Microsoft® Excel® para-Microsoft 365 MSO (Version 2401 Build 16.0.17231.20194) 64 bits).

3.2. The by-product Zn(II) benzoate

This compound was obtained from a decomposition reaction of the complex Zn(II)-3-fenil-*1H*-1,2,4-triazole-5-amine which was prepared by the reaction between Zn(II) chloride and 3-fenil-*1H*-1,2,4-triazole-5-amine (Almeida, Maia, Falqueto, & Oliveira, 2022). The experimental NMR data of ^{13}C and hydrogen for this compound in chloroform has been used in this work for comparison with the calculated NMR data.

[Zn(PhCOO)$_2$]: IR (Nujol, CsI, $v_{máx}$ / cm^{-1}): 1689 v(CO); 1454 v_{as}(COO), 1402 v_s(COO); 709 v(CH, Ph); 497 v(Zn-O). ^{1}H NMR (CDCl$_3$, 300 MHz, δ): 8.13 (d, *J(H-H)* = 6.0 Hz, Ph), 7.61 (t, *J(H-H)* = 6.0 Hz, Ph), 7.47 (t, *J(H-H)* = 9.0 Hz, Ph). ^{13}C NMR (CDCl$_3$, 75 MHz, δ): 172.4 (C=O), 133.6, 130.2, 129.6, 128.4 (Ph).

4. Conclusion

The calculated NMR data by DFT/B3LYP method show chemical shifts that, when in comparison to the experimental data, indicates the Zinc(II) benzoate is indeed the by-product from decomposition of the Zn(II)-3-fenil-*1H*-1,2,4-triazole-5-amine complex in chloroform. To the best of our knowledge the X-ray diffraction analysis of Zn(II) benzoate salt is unknown. Nevertheless, the result of the theoretical calculation points out possible structures, suggesting dimerization in this solvent. The coplanar bent structure with an angular geometry surrounding the metallic centre would be the precursor of the dimerization into two tetracoordinated metallic centre having the benzoate ions bonded to the metal centre at the bridging bidentate coordination mode.

Acknowledgements

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