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Research Article

A Novel Zn^{II} Complex Bearing Two Monodentate (4-Methoxyphenyl)[(1E, 2E)-3-phenylprop-2-en-1-ilidene] Schiff Bases: Crystal Structure and DFT Study

Giuliano M. Cordeiro,[1] Emanoel Hottes,[1] Andressa Esteves-Souza,[1] Guilherme P. Guedes,[2] Carlos Maurício R. de Sant'Anna,[1] and Marcelo H. Herbst[1]

[1] *Instituto de Química, Universidade Federal Rural do Rio de Janeiro, Seropédica, RJ 23890-000, Brazil*
[2] *Instituto de Química, Universidade Federal Fluminense, Niterói, RJ 24020-150, Brazil*

Correspondence should be addressed to Marcelo H. Herbst; herbst_marcelo@yahoo.com.br

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A novel Zn^{II} complex bearing two monodentate (4-methoxyphenyl)[(1E, 2E)-3-phenylprop-2-en-1-ilidene] Schiff bases was synthesized and investigated both in the solid state by single-crystal X-ray diffraction, elemental analysis, and FTIR and in solution by ^1H NMR spectroscopy. The complex crystallizes in the $P2_1/c$ monoclinic space group. The asymmetric unit contains one Zn^{II} ion coordinated to two Schiff base ligands and two chloride ions, in a distorted tetrahedral geometry. The title complex was also investigated by DFT, using the hybrid functional B3LYP with basis set 6-31G++, which reproduced the geometry and structural features of the complex in the crystal, and was used to assign the main bands in the FTIR spectrum. In solution, the complex maintains its integrity against decomposition to the parent reagents.

1. Introduction

Schiff bases are important intermediates in many enzymatic reactions involving interactions between an enzyme and a substrate carbonyl group. They are generally prepared by the condensation of primary amines with carbonyl compounds, for instance, aldehydes. The IUPAC classifies Schiff bases as compounds that present an imino (C=N) moiety, in which a nonhydrogen radical is directly bonded to the nitrogen atom, given the $R_2C{=}NR$ formula. According to the literature, Schiff bases and many of their metal complexes have presented significant biological activities, such as antifungal, antimicrobial, and antitumor activities [1–5]. The imine employed in this work has been used for several purposes. For instance, Bhalla et al. [6] reported the synthesis of novel trans- and cis-3-methylseleno substituted β-lactams through Staudinger cycloaddition reaction between the Schiff's bases and ketene generated from 2-methylselenoethanoic acid. Cai et al. [7] designed and synthesized some 50 N-benzylideneaniline compounds and carried out in vitro studies on the inhibitory activity in human HEK-Blue TLR2 cells. Chigurupati et al. [8] synthesized a new series of azomethine derivatives of β-phenyl acrolein. The imine used in this work, dubbed 4-methoxy-N-(3-phenylallylidene)benzamine, synthesized by that new route, was also screened for antibacterial activity against Gram-positive and Gram-negative bacteria, being active against *P. aeruginosa* and *S. aureus*. Barta et al. [9] found that the selective iron catalyzed direct monoalkylation of p-methoxyaniline with 2-phenyl-ethane-1-ol generated as an intermediate the imine used in this work. Bekdemir and Efil [10] developed a simple microwave-assisted solvent-free method for the synthesis of imines, including the BS-4-OCH_3, using a wetting reagent (β-ethoxyethanol). Chen et al. [11] investigated bridge carbon ^{13}C NMR shifts of a wide set of substituted cinnamyl anilines of the general type p-$XC_6H_4CH@CHCH@NC_6H_4Yp$, using those compounds as a probe to study the change of substituent effect in the conjugated system. They found that the change of the inductive effect and the conjugative effect on different bridge carbons is related to the bond number (*m*) from the substituent to the corresponding carbon. Bidentate imines are important ligands in coordination chemistry. For example, the salen ligand and its analogues are widely used [12]. However, unlike the Schiff bases derived from salicylic aldehyde, which are bidentate ligands, the complexation reactions of monodentate Schiff bases derived from cinnamic aldehyde are not known in great detail. In this work, our objective was to investigate, both theoretically and experimentally, the coordination of the monodentate Schiff base (4-methoxyphenyl)[(1E, 2E)-3-phenylprop-2-en-1-ilidene] (Figure 1), for complexation with Zn^{II}.

Recently, Kürşat and Yunus [13] used ab initio HF and DFT methods (B3LYP with 6-31G∗ basis set) and investigated the optimized geometrical structure, vibrational frequencies, and NMR shifts of (4-methoxyphenyl)[(1E, 2E)-3-phenylprop-2-en-1-ilidene], based on the crystal structure of the molecule, previously reported by Li et al. [14]. The reactivity of the (4-methoxyphenyl)[(1E, 2E)-3-phenylprop-2-en-1-ilidene] molecule to transition metals was also previously investigated by Knölker et al. [15], Mashima et al. [16], and Zhang et al. [17], who obtained organometallic compounds of iron, titanium, and zirconium, respectively. However, to our knowledge, there is no report about coordination compounds of Zn^{II} of that molecule.

2. Materials and Methods

The Schiff base (4-methoxyphenyl)[(1E, 2E)-3-phenylprop-2-en-1-ilidene] (BS-4-OCH_3) was prepared by the solvent-free reaction of equimolar amounts of cinnamic aldehyde (7.83 g, 0.06 mol) and 4-methoxyaniline (123.20 g, 0.06 mol), in the presence of silica gel, through manual maceration with a mortar and pestle for one hour. Thin-layer chromatography ($CHCl_3$ as eluent) was used to check the formation of the product, and after dissolving the mixture in ethanol and filtering, the product was recrystallized from hot ethanol (95% yield). The Zn^{II} complex was prepared by dissolving 0.050 g (2.10×10^{-4} mol) of BS-4-OCH_3 in 15 mL of anhydrous ethanol, followed by the slow addition of an ethanol solution (5 mL) of anhydrous $ZnCl_2$ (0.0537 g, 4.20×10^{-4} mol) to the solution containing the Schiff base. The mixture was kept under agitation at 50°C for approximately 2 hours, when the solution turned from pale yellow to dark brown. The solution was concentrated in a rotary evaporator at ~50°C until less than 10% of the initial volume remained, and after that, it was kept at room temperature for some days, until a brown crystalline solid precipitated. The solid was filtered (0.036 g, 91% yield), washed with cold ethanol, air-dried, and single crystals were separated. Elemental analysis (Central Analítica–USP–Brazil) of the single crystals gave the following % calculated (found) results: C 62.92 (61.51), H 4.95 (4.95), and N 4.58 (4.46) for $ZnCl_2C_{32}H_{30}N_2O_2$. The calculation method applied to the structure of the BS-4-OCH_3 Zn^{II} complex was the DFT, using the hybrid functional B3LYP with basis set 6-31G++. The optimization of the geometry and the vibrational frequencies and chemical shifts were carried out by the Spartan 14 package. The structure used for the computations was based on the crystal structure obtained by single-crystal X-ray diffraction on an Enraf-Nonius Kappa CCD diffractometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. DIRAX program was used to determine the final unit cell parameters, while the integration of the collected reflections was performed using EVALCCD program. The absorption correction was performed with SADABS. The structure solutions and full-matrix least-squares refinements based on F^2 were performed with the SHELXS-97 and SHELXL-97 packages, respectively [18–21]. The ^1H NMR spectra for the (4-methoxyphenyl)[(1E, 2E)-3-phenylprop-2-en-1-ilidene] and the BS-4-OCH_3 Zn^{II} complex were measured with a Bruker 400 AVII spectrometer and are expressed in the usual ppm scale. FTIR spectra were obtained in the 4000–400 cm^{-1} range in ATR mode, with a Bruker Vertex-70 spectrometer. The FAR-IR spectra were measured with a PerkinElmer spectrometer, in polyethylene pellets, in the 600–30 cm^{-1}

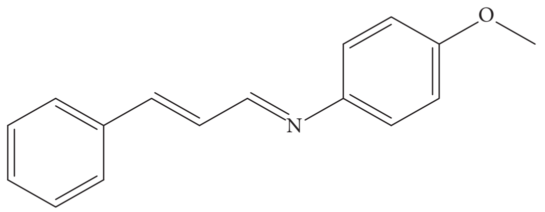

Figure 1: Structure of the monodentate Schiff base (4-methoxyphenyl)[(1E, 2E)-3-phenylprop-2-en-1-ilidene].

Table 1: Summary of crystal, data collection, and refinement of the [$ZnCl_2$(BS-4-OCH_3)$_2$] complex.

Empirical formula	$C_{32}H_{30}Cl_2N_2O_2Zn$
Molecular mass	610.87
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 16.793(3)$ Å $\alpha = 90°$ $b = 8.2170(16)$ Å $\beta = 111.07(3)°$ $c = 22.941(5)$ Å $\gamma = 90°$
Volume	2953.9(12) $Å^3$
Z	4
Density (calculated)	1.374 Mg/m^3
Absorption coefficient	1.04 mm^{-1}
F(000)	1264
Theta range for data collection	3.6 to 25.4°
Reflections collected	18257
Independent reflections	5412 (R(int) = 0.062)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5349/0/352
Goodness-of-fit on F^2	1.04
Final *R* indices ($I > 2$sigma(I))	$R_1 = 0.056$, $wR_2 = 0.119$
R indices (all data)	$R_1 = 0.097$, $wR_2 = 0.138$

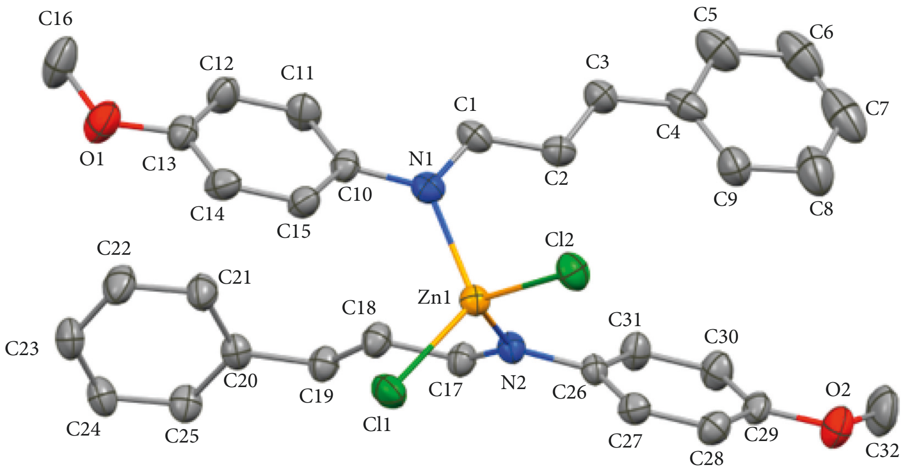

Figure 2: Asymmetric unit of the compound [$ZnCl_2(BS\text{-}4\text{-}OCH_3)_2$]. Ellipsoids at 30% probability. Hydrogen atoms were omitted for clarity (gray (carbon), red (oxygen), blue (nitrogen), green (chloride), and yellow (zinc)).

range. Data treatment was carried out by the ACD I-Lab software package.

3. Results and Discussion

3.1. X-Ray Crystallography and DFT. The single-crystal X-ray diffraction data were collected at room temperature. The title complex crystallizes in the $P2_1/c$ monoclinic space group. A summary of crystal, data collection, and refinement are gathered in Table 1. The asymmetric unit is shown in Figure 2 and contains one Zn^{II} ion coordinated to two BS-4-OCH_3 molecules and two chloride ions in a distorted tetrahedral geometry. The Zn1-N1 and Zn1-N2 bond lengths are 2.1098 (8) Å and 2.0757 (3) Å, respectively. On the other hand, the Zn1-Cl1 e Zn1-Cl2 bond distances are 2.2348 (3) Å and 2.2386 (5) Å. Because of the coordination with the Zn^{II}, the dihedral angles between the 4-methoxyphenyl and imine groups in the two ligands are not planar, with angles of 27.4(7)° (C1-N1-C10-C11) and 44.9(6)° (C17-N2-C26-C31). The crystalline packing is stabilized by a network of $Csp^2H\text{---}O$, $Csp^2\text{-}H\text{---}Csp^2$, and $Csp^2\text{-}H\text{---}Cl$ weak intermolecular interactions involving the imine and chloro ligands.

Tables 2–4 present the results selected for bonding distances and bonding angles as well as dihedral angles obtained from single-crystal X-ray diffraction as well as a comparison with theoretical values as calculated by DFT.

The inspection of the data in Tables 2–4 shows that, in general, the calculated structural parameters (bond distances and bond angles) are in good agreement with the experimental data. This observation can be confirmed by analyzing the determination coefficient (R^2), a parameter that measures the deviation of the theoretically calculated values from the experimental ones, where we obtained R^2 of 0.986104 and 0.87703, respectively, for bond lengths and bond angles. Calculations performed for both the free ligand as well as similar complexes found in the literature showed R^2 patterns which are in agreement with those observed for the compound under study [13]. However, in the case of dihedral angles, large discrepancies between theoretical and experimental values were observed, with R^2 of 0.567535. As the uncomplexed BS-4-OCH_3 molecule is free to rotate, but not when complexed to the metallic center, such discrepancies in the dihedral angles are expected. Another crucial factor that leads to the distancing of the experimental parameters is associated with the conditions adopted in each system; since in the complex, the theoretical data were obtained in a vacuum, not taking into account the actual intermolecular interactions in the molecule. However, the values obtained mainly for angles and bond distances indicate that the calculation method was quite satisfactory [13].

Table 2: Selected bond lengths (experimental and calculated) for the [$ZnCl_2(BS\text{-}4\text{-}OCH_3)_2$] complex.

Bond	X-ray (Å)	B3LYP/6-31G++ (Å)
Zn1-Cl1	2.238(2)	2.2529
Zn1-Cl2	2.235(2)	2.2493
Zn1-N1	2.108(4)	2.1193
Zn1-N2	2.075(3)	2.1192
N1-C1	1.284(7)	1.3002
C1-C2	1.454(8)	1.4352
C2-C3	1.340(7)	1.3552
C1-H1	0.930	1.0950
N2-C17	1.290(6)	1.3006
C17-C18	1.444(7)	1.4349
C18-C19	1.339(7)	1.4349
C17-H17	0.931	1.0948
$R^2 = 0.986104$		

In order to understand the effect of coordination on the ligand, we compared our calculated data for the complex with the previously reported data for BS-4-OCH_3 [13, 14]. In doing so, we observed that the experimental values for N1-C1 (1.284(7) Å), C1-C2 (1.454(8) Å), C2-C3 (1.340(7) Å), N2-C17 (1.290(6) Å), C17-C18 (1.444(7) Å), and the C18-C19 bonds (1.339(7) Å) in the Zn complex are quite similar to the ligand (N1-C1 = 1.275 Å, C1-C2 = 1.442 Å, and

Table 3: Selected bond angles (experimental and calculated) for the $[ZnCl_2(BS\text{-}4\text{-}OCH_3)_2]$ complex.

Bond angle	X-ray (°)	B3LYP/6-31G++ (°)
Cl1-Zn1-Cl2	111.49(5)	118.31
Cl1-Zn1-N1	117.8(1)	111.47
Cl1-Zn1-N2	104.9(1)	107.85
Cl2-Zn1-N1	104.2(1)	107.70
Cl2-Zn1-N2	116.1(1)	111.92
N2-Zn1-N1	102.5(2)	97.67
N1-C1-C2	124.4(4)	124.48
C1-C2-C3	120.2(4)	120.99
N1-C1-H1	117.8	118.59
N2-C17-C18	123.2(4)	124.44
C17-C18-C19	122.1(5)	121.14
N2-C17-H17	118.3	118.64
Zn1-N1-C1	119.4(3)	122.29
Zn1-N2-C17	122.0(3)	122.00
Zn1-N1-C10	122.7(3)	120.14
Zn1-N2-C26	119.7(3)	120.46
N2-C17-C18	123.2(4)	124.44
C17-C18-C19	122.1(5)	121.14
N2-C17-H17	118.3	118.64
Zn1-N1-C1	119.4(3)	122.29
Zn1-N2-C17	122.0(3)	122.00
Zn1-N1-C10	122.7(3)	120.14
Zn1-N2-C26	119.7(3)	120.46
$R^2 = 0.807703$		

Table 4: Selected dihedral angles (experimental and calculated) for the $[ZnCl_2(BS\text{-}4\text{-}OCH_3)_2]$ complex.

Dihedral angle	X-ray (°)	B3LYP/6-31G++ (°)
N1-C1-C2-C3	174.4(5)	177.85
N2-C17-C18-C19	−169.4(5)	177.08
H1-C1-C2-C3	−5.5	−2.82
H17-C17-C18-C19	10.8	−3.64
C17-N2-Zn1-N1	−60.26	−66.95
C26-N2-Zn1-N1	120.9(3)	108.06
C10-N1-Zn1-N2	118.0(4)	108.41
C1-N1-Zn1-N2	−60.4(4)	−66.20
Cl1-Zn1-N1-C1	−179.9(3)	−178.86
Cl1-Zn1-N1-C10	3.5(4)	−4.25
Cl1-Zn1-N2-C17	63.3(4)	48.61
Cl1-Zn1-N2-C26	−115.4(3)	−136.39
Cl2-Zn1-N1-C1	61.0(4)	49.80
Cl2-Zn1-N1-C10	−120.6(3)	−135.59
Cl2-Zn1-N2-C17	−173.2(3)	−179.58
Cl2-Zn1-N2-C26	8.1(3)	−4.48
C10-N1-C1-C2	−177.2(4)	−177.34
C26-N2-C17-C18	−179.9(4)	−177.64
$R^2 = 0.567535$		

C2-C3 = 1.329 Å). This indicates that the coordination did not affect the electronic density in that region, a result that is corroborated by the DFT calculations, as shown in Tables 2 and 3. However, the coordination affected the dihedral angles, also shown in Table 4, and this characteristic was not reproduced by the DFT calculations, which as previously mentioned is due to the isolated molecule method [13, 14]. The bond distances of the complex obtained in this work were compared with data in the literature for analogous molecules. We observed that the Zn1-N1 binding length values of 2.108(4) Å and Zn1-N2 of 2.075(3) Å in the compound of the present work are in agreement with the observed values of similar bonds, which are in the range of 1.923–2.072 Å. The distorted tetrahedral geometry was confirmed for the $[ZnCl_2(BS\text{-}4\text{-}OCH_3)_2]$ since the bond angles around the metal ion are in the range 102.5(2)° to 117.8(1)° (Table 3), similar for analogous compounds that presented values between 96° and 117°. The reported values in the literature for the angles and distances also presented a good agreement with the obtained data for the compound described in this work. In the case of the $[ZnCl_2(BS\text{-}4\text{-}OCH_3)_2]$ complex, the theoretical values for Zn-N and N-Zn-N were 2.1193 Å and 97.67°, respectively, and values for the same angles and bonding lengths were obtained in the ranges of 1.94 to 2.18 Å and 82.7° to 135.9°, showing again that the method used in the present work performed well, considering that the calculations reported in the literature are obtained by simulating conditions closer to the experimental one [22–24].

3.2. ^1H NMR.

The ^1H NMR spectra of the BS-4-OCH_3 and of its Zn^{II} complex (Figure 3) did not show significant differences in the chemical shifts. However, the coordination stoichiometry was confirmed in solution by the alteration of the signal assigned to the iminic hydrogen at 8.43 ppm. In the spectrum of the free BS-4-OCH_3, that signal is a doublet integrating one hydrogen atom, but in the Zn^{II} complex that signal is a singlet, integrating two hydrogens (H1 and H17). We also observed that the integration of all other signals (Figure 3) in the spectra of the Zn^{II} complex was twice that of the uncomplexed BS-4-OCH_3 [13].

Therefore, the integrity of the title complex in solution was confirmed by NMR.

3.3. FTIR Spectroscopy.

According to the literature [25], the conformation of a molecule such as BS-4-OCH_3 may lead to the coupling of C=C and C=N bonds, that is, both stretching vibrations may appear as a single band in the FTIR spectrum. In the spectrum of the uncomplexed BS-4-OCH_3, the strong and broad band centered at 1513 cm^{-1} was assigned to the aliphatic C=C stretching vibrations. In turn, the shoulder at 1590–1600 cm^{-1} was assigned to both the C=N and the C=C stretching of the aromatic rings [13].

Upon coordination with Zn(II), presumably the C=N bond is softened, giving origin to two bands in the FTIR spectrum. Based on our calculations, the 1619 cm^{-1} band was assigned to the $\nu C{=}N + \nu C{=}C$ ring and the band at 1686 cm^{-1} was assigned to the aliphatic C=C stretching, although it is not possible to discard a contribution of the aromatic ring stretching to those bands. Assuming a C_{2v} local symmetry around the Zn^{II} center, that is, a tetrahedral coordination of the Zn^{II}, two bands are expected, which can be assigned to the Zn-Cl stretching and another two bands assigned to the Zn-N stretching [26]. Indeed, in the region below 600 cm^{-1}, new bands appeared at 517 and 507 cm^{-1}, assigned to the Zn-N stretching, and at 317 and 303 cm^{-1}, assigned to the Zn-Cl stretching. Our calculations gave 448

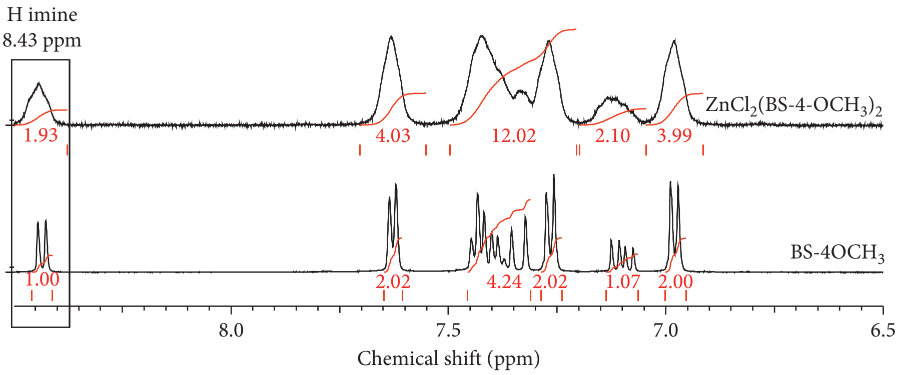

FIGURE 3: ^1H NMR spectra of the uncomplexed BS-4-OCH$_3$ and of its Zn^{II} complex.

and 364 cm^{-1} for the νZn-N stretching, and 336 and 319 cm^{-1} for the νZn-Cl stretching. The other regions of the FTIR spectrum of the Zn^{II} complex show no significant alteration when compared to the uncomplexed Schiff base.

4. Conclusions

We synthesized and characterized a novel Zn^{II} complex bearing two monodentate Schiff bases (4-methoxyphenyl) [(1E, 2E)-3-phenylprop-2-en-1-ilidene] and two chlorides as ligands. The single-crystal X-ray diffraction showed that there are few structural modifications in the Schiff base upon coordination. The Zn^{II} complex was characterized by elemental analysis, confirming the formula encountered for the single-crystal, and by solid-state FTIR, which presented new bands assigned to the coordination of the imine nitrogen, as well as modifications in bands previously present in the spectrum of the uncomplexed Schiff base. The title complex was also investigated by DFT, using the hybrid functional B3LYP with basis set 6-31G++, which reproduced the geometry and structural features of the complex in the crystal, and was used do assign the main bands in the FTIR spectrum. Solution ^1H NMR measurements confirmed the integrity of the title complex against decomposition to the uncomplexed reagents.

Data Availability

Crystallographic data for the structure reported in this article have been deposited at the Cambridge Crystallographic Data Centre under CCDC number 1021645. Copies of these data can be obtained free of charge from http://www.ccdc.cam.ac.uk/data_request/cif.

Conflicts of Interest

The authors declare there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

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