Design, synthesis, characterization, and antimicrobial activity of the new 2-{(*E*)-[(4-aminophenyl)imino]methyl}-4,6-dichlorophenol and its complexes with Co(II), Ni(II), Cu(II) and Zn(II): An experimental and DFT study

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Abstract: In this study, the complexes of Co(II), Ni(II), Cu(II) and Zn(II) with 2-{(*E*)-[(4-aminophenyl)imino]methyl}-4,6-dichlorophenol were prepared and characterized by physical, spectral and analytical data. The metal:ligand stoichiometric ratio was 1:2 in all the complexes. The results suggested that the Schiff bases were coordinated to the metal ions through the phenolic oxygens and the azomethine nitrogen to give mononuclear complexes. Their structures were elucidated based on elemental analysis, IR, ^{1}H- and ^{13}C-NMR, UV–Vis, and magnetic susceptibility measurements and thermogravimetric analyses. Both the antibacterial and antifungal activities and the minimum inhibitory concentration (*MIC*) values of compounds are reported. Among the tested compounds, the most effective compound providing an *MIC* value of 64 μg mL^{-1} was Zn(L)$_2$ against *Candida tropicalis* and *Bacillus subtilis*. The theoretically optimized geometries of the complexes were tetrahedral structures. The computed stretching frequencies of the C=N, C–O and N–H bonds were in good agreement with the experimental data. All the calculated frequencies fell within about 5 % of the experimental frequency regions.

Keywords: Schiff base; transition metal complex; antibacterial and antifungal activities; DFT.

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INTRODUCTION

Several Schiff base metal complexes have been studied in the past because of their wide applicability.[1] Schiff bases have often been used as chelating ligands in the field of coordinatiation chemistry for obtaining thermotropic liquid crystalline polymers and their metal complexes have been used as radio-pharmaceuticals for cancer targeting, dioxygen carriers and model systems for biological macromolecules.[2–6] The presence of transition metals in human blood plasma indicates their importance in the mechanisms for the accumulation, storage and transport of transition metals in living organisms.[7]

The synthesis and characterization of various transition metal complexes with novel Schiff bases were experimentally investigated.[8–19] In a previous theoretical study, 2-{(*E*)-[(4-aminophenyl)imino]methyl}-6-bromo-4-chlorophenol as Schiff base ligand and its complexes with Co, Ni, Cu and Zn metals were examined.[19] In the present study, the synthesis and characterization of cobalt(II), nickel(II), copper(II) and zinc(II) complexes with 2-{(*E*)-[(4-aminophenyl)-imino]methyl}-4,6-dichlorophenol (LH) were investigated. All compounds were characterized by elemental analyses, UV–Vis, IR, and ^{1}H- and ^{13}C-NMR spectroscopy, magnetic susceptibility measurements and thermogravimetric analyses (TGA). Moreover, density functional theory (DFT) calculations were performed to examine the parameters of the optimized structure and to calculate the IR spectra of the ligand and its complexes with Co, Ni, Cu and Zn metals in order to compare them with the experimental data obtained in this study. Additionally, all the complexes were assayed for their antibacterial activities against two Gram-positive bacterial strains (*Bacillus subtilis* and *Staphylococcus aureus*) and two Gram-negative bacterial strains (*Escherichia coli* and *Salmonella enterica* subsp. *enterica* serovar Typhimurium) by the minimum inhibitory concentration (*MIC*) method.

EXPERIMENTAL

Methods

Elemental analyses (C, H and N) were realized using a LECO-932 CHNSO analyzer by the Technical and Scientific Research Council of Turkey (TUBITAK). The IR spectra were recorded on a Mattson 1000 FT-IR spectrometer as KBr pellets. The NMR spectra were recorded on a Bruker Dpx-400 MHz high performance digital FT-NMR spectrometer. The electronic spectra were obtained on a Shimadzu UV probe 2.1 spectrometer at the Firat University. Magnetic susceptibilities were determined on a Sherwood scientific magnetic susceptibility balance (Model MK1) at room temperature using Hg[Co(SCN)$_4$] as the calibrant; diamagnetic corrections were calculated from Pascal's constants. The TG curves were recorded on a Shimadzu TG-50 thermo-balance.

Preparation of the ligand and its complexes

*2-{(*E*)-[(4-Aminophenyl)imino]methyl}-4,6-dichlorophenol (LH).* A solution of 2.16 g (20 mmol) 1,4-phenylendiamine dissolved in 25 mL absolute ethanol was added dropwise to 1.81 g (10 mmol) 3,5-dichlorosalicylaldehyde and 0.01 g *p*-toluenesulfonic acid dissolved in

25 mL absolute ethanol under reflux at 60 °C under continuous stirring for 1 h. After over-night stirring, the precipitate was filtered off, washed several times with hot water, cold ethanol and diethyl ether and dried under vacuum.

Bis(2-{(E)-[(4-aminophenyl)imino]methyl}-4,6-dichlorophenolato)cobalt(II), Co(L)$_2$. The ligand (0.28 g, 1.00 mmol) was dissolved in 25 mL absolute ethanol. A solution of Co(AcO)$_2$·4H$_2$O (0.13 g, 0.50 mmol) in 25 mL of absolute ethanol was added dropwise over 1 h to the ligand solution under reflux at 60 °C under continuous stirring. After stirring overnight, the precipitated complex was filtered off, washed several times with hot H$_2$O, cold EtOH and cold Et$_2$O and dried under vacuum.

Bis(2-{(E)-[(4-aminophenyl)imino]methyl}-4,6-dichlorophenolato)nickel(II), Ni(L)$_2$. Ni(L)$_2$ was prepared following the same procedure as described for Co(L)$_2$, starting with LH (0.28 g, 1.00 mmol) and Ni(AcO)$_2$·4H$_2$O (0.12 g, 0.50 mmol).

Bis(2-{(E)-[(4-aminophenyl)imino]methyl}-4,6-dichlorophenolato)copper(II), Cu(L)$_2$. Cu(L)$_2$ was prepared following the same procedure as described for Co(L)$_2$, starting with LH (0.28 g, 1.00 mmol) and Cu(AcO)$_2$·H$_2$O (0.10 g, 0.50 mmol).

Bis(2-{(E)-[(4-aminophenyl)imino]methyl}-4,6-dichlorophenolato)zinc(II) Zn(L)$_2$. Zn(L)$_2$ was prepared following the same procedure as described for Co(L)$_2$, starting with LH (0.28 g, 1,00 mmol) and Zn(AcO)$_2$·2H$_2$O (0.11 g, 0.50 mmol).

Microbiology

The tested microorganisms were the gram-positive *Staphylococcus aureus* ATCC 6538P and *Bacillus subtilis* ATCC 6633, the gram-negative *Escherichia coli* ATCC 25922 and *Salmonella enterica* subsp. *enterica* serovar Typhimurium NRRL B 4420, and the yeast-like fungi, *Candida glabrata* ATCC 66032 and *Candida tropicalis* ATCC 13803. Ampicillin (Mustafa Nevzat) and fluconazole (Pfizer) were used as antibiotic references for the bacteria and yeasts, respectively (obtained from the Department of Biology, Fırat University, Turkey).

Antibacterial and antifungal assays. The bacterial cultures were obtained in Mueller––Hinton broth (Difco) for all the bacterial strains after 24 h incubation at 37±0.1 °C. The yeasts were propagated in Sabouraud dextrose broth (Difco) by incubation for 24 h at 25±0.1 °C. Testing was performed in Mueller–Hinton broth and Sabouraud dextrose broth at pH 7.4 for the bacteria and yeast, respectively. The final inoculum size for the bacteria and fungi was 10^5 CFU mL^{-1}. The test compounds were dissolved in DMSO at an initial concentration of 1024 µg mL^{-1} and then serially diluted in culture medium to 1 µg mL^{-1}. A set of tubes containing only inoculated broth was kept as the control. The antibacterial activity was determined after incubation for 24 h at 37 °C for the bacteria and after incubation for 48 h at 25 °C for the yeasts. The *MIC* was defined as the lowest concentration of the compounds that inhibited the visible growth of a microorganism. All experiments in the antibacterial and antifungal assays to define the *MIC* values were performed in duplicate.
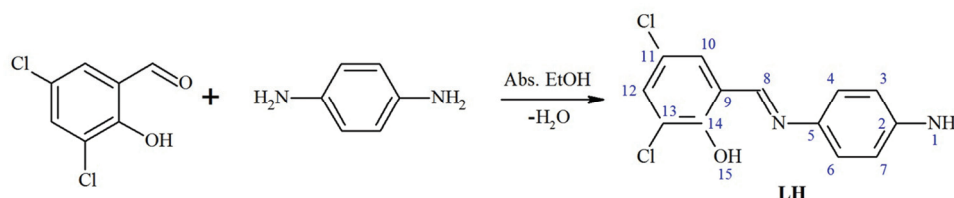
Computational methods

In the present work, the theoretical calculations were based on DFT[20] implemented in Gaussian 09 software.[21] The B3LYP hybrid formalism [22-24] was used for the calculations. The hybrid method of B3LYP is a high-quality DFT technique for theoretical calculations in organic chemistry.[25] The theoretical approach applied in this study was presented in previous studies.[18,19] The spin contamination value must be very small (less than 10 %).[26] The <S2> values were negligible in this study. Vibrational analysis was also performed to obtain vibrational frequencies. All vibrational frequencies were obtained for the 6-31g(d,p) method. All frequency values were scaled using a factor of 0.9613 to reproduce the experimental

fundamentals.[27] Mulliken population analysis[28] was utilized to obtain spin density values (showing where unpaired electrons of the system are located) of the metal atoms. Natural bond orbital (NBO)[29] analysis was employed to obtain the NBO charge values and the electronic configurations of the metal atoms. The criteria of convergence in the calculations were 12×10^{-4}, 18×10^{-4}, 3×10^{-4} and 45×10^{-5} for gradients of the root-mean-square (rms) displacement, the max. displacement, the rms of the force and the max. force, respectively.

RESULTS AND DISCUSSION

The ligand (LH) was prepared by reacting equimolar amounts of 1,4-phenylendiamine with 3,5-dichlorosalicylaldehyde in absolute ethanol (Scheme 1). The structures of the ligand and the complexes were established by the use of their IR, ^{1}H-NMR and electronic spectra, elemental analyses, magnetic susceptibility measurements and thermogravimetric analyses.

Scheme 1. Preparation of the ligand.

All the metal complexes with LH were prepared by the stoichiometric reaction of the corresponding metal(II) acetate with LH in the mole ratio M:L = 1:2. The complexes are stable intensely colored solids. A summary of the elemental analysis data for ligand and the complexes are given in the Supplementary material to this paper.

The elemental analysis results agree with the calculated values showing that the complexes had 1:2 metal/ligand rations. The elemental analysis also confirmed the composition of the above-synthesized compounds.

The characteristic IR bands of the ligand and its complexes are given in Table S-I of the Supplementary material. In the IR spectrum of the ligand, ν(O–H) (phenolic), ν(C=N) (azomethine), ν(C–O) (phenolic) and ν(N–H) stretching vibrations were observed at 3350–3200, 1609, 1290 and 3315 and 3190 cm^{-1}, respectively. These values are in agreement with those observed for similar compounds.[14,15] The ν(O–H) band of the phenolic group appeared at *ca.* 3350–3200 cm^{-1}; its low value was due to the formation of intramolecular hydrogen bonds.[4,30] This band was absent in the spectra of all the complex, indicating the deprotonation of Schiff base prior to coordination through its oxygen atom.[31,32] The azomethine vibration of the ligand at 1609 cm^{-1} was shifted to lower frequencies after complexation, appearing at 1608, 1607, 1602 and 1608 cm^{-1} for cobalt(II), nickel(II), copper(II) and zinc(II) complexes, respectively. This clearly indicates the coordination of the Schiff base through the azomethine nitro-

gen.[31,32] This is also supported by an increase in the absorption frequency of the phenolic ν(C–O) band from 1290 cm^{-1} in the spectrum of the free ligand to values in the range 1323–1293 cm^{-1} in the spectra of the complexes, indicating that the other coordination site of the Schiff base is the phenolic oxygen atom.[32]

^{1}H- and ^{13}C-NMR spectra of the ligand (LH) were recorded in CDCl$_3$. The NMR assignments are given in detail in Table S-II of the Supplementary material. Characteristic ^{1}H-NMR peaks of the ligand occurred at 15.30 (OH), 7.60 (CH=N) and 5.60–8.90 ppm (Ar-H). The OH (phenolic) signal at 15.30 ppm disappeared upon addition of D$_2$O to the solution, indicating that it is an acidic proton.[15,16,33] The zinc(II) complex did not dissolve in DMSO-d_6 and therefore, the NMR spectra of the zinc (II) complex could not be obtained.

The magnetic susceptibility data of the complexes are given in Table S-III of the Supplementary material. The Co(II), Ni(II) and Cu(II) complexes were paramagnetic, while the Zn(II) complex was diamagnetic, as expected for a d^{10} configuration. According to the magnetic moment calculations, Co(II), Ni(II) and Cu(II) have three, two and one unpaired electrons, respectively. The magnetic moments of the Co(II), Ni(II) and Cu(II) complexes at room temperature were 4.45, 2.82 and 1.77 μ_B, respectively, which are characteristic for mononuclear, tetrahedral complexes.[34,35] In the Zn (II) complex, a tetrahedral structure was proposed and the diamagnetic behavior was confirmed.[36]

The electronic spectra of the ligand and the Co(II), Ni(II), Cu(II) and Zn(II) complexes were recorded in DMSO at room temperature. The aromatic band of the ligand at 260 nm was attributed to benzene $\pi{\to}\pi^*$ transitions. The band around 400 nm is due to the n$\to\pi^*$ transition of the non-bonding electrons present on the nitrogen of the azomethine group in the Schiff base. All the complexes showed an intense band near 380–435 nm, which was assigned to n$\to\pi^*$ transitions associated with the azomethine linkage.[33] The spectra of all the complexes show intense band at *ca.* 386–450 nm, which can be assigned to charge transfer transition of the tetrahedral geometry.[37]

The thermal behaviors of the ligand and all the complexes were investigated by thermogravimetry in the temperature range from ambient to 600 °C at a heating rate of 10 °C min^{-1}. Thermogravimetric studies of all the complexes showed no weight loss up to 230 °C, indicating the absence of lattice/coordinated water molecules in the complexes.[1,38] All these complexes underwent complete decomposition to the corresponding metal oxides, CoO, NiO, CuO and ZnO.[39–43] Based on the experimental results, the suggested structure of the complexes, where M = Co(II), Ni(II) Cu(II) and Zn(II), is shown in Fig. 1.

A comparative study of *MIC* values of the Schiff base LH and its complexes indicated that the metal complexes in general had a better activity than the free ligand. Such increased activity of the metal chelates could be explained on the basis of the chelating theory.[32] The synthesized Schiff base compounds had com-

parable and similar inhibitory effects (low to moderate *MIC* values ranging from 64 to 512 μg mL^{-1}) on the growth of tested strains (Table I). The antibacterial results evidently showed that the activity of the Schiff base became more pronounced when coordinated to the metal ions. Thus, all the complexes show high bactericidal activities against *S. enterica, S. aureus and E. coli* (*MIC* = 128 μg mL^{-1}) and *B. subtilis* (*MIC* = 64 μg mL^{-1}) as compared to corresponding Schiff base. The structure of the tested compounds seemed to be the principal factor influencing the antimicrobial activity. The present investigations of the antimicrobial screening data revealed that all of the newly synthesized compounds exhibited poor activities compared to those of the control drugs.
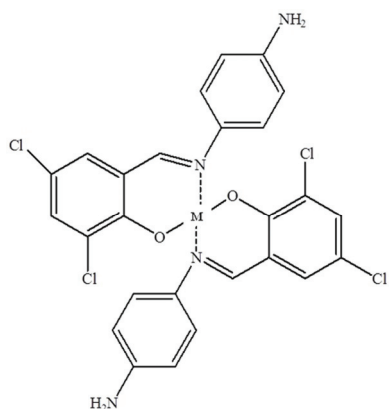

Fig. 1. Experimentally suggested structural formula of the complexes of the ligand (where M = Co(II), Ni(II) Cu(II) or Zn(II)).

TABLE I. The *in vitro* activities of the compounds and the reference drugs (the *MIC* values are in μg mL^{-1})

Sample	*S. enterica*	*S. aureus*	*E. coli*	*B. subtilis*	*C. tropicalis*	*C. glabrata*
LH	256	512	512	128	256	256
Co(L)$_2$	128	128	128	512	256	256
Ni(L)$_2$	128	256	256	128	256	256
Cu(L)$_2$	256	256	256	256	128	256
Zn(L)$_2$	256	256	128	64	64	128
Ampicillin	2	2	2	2	–	–
Fluconazole	–	–	–	–	8	8

Theoretical

Geometries of the ligand and its complexes with metals were constructed using the structures experimentally suggested in this study. Initially, the ligand was optimized by means of equilibrium geometry (EG) calculations. The optimized geometry of the ligand is presented in Fig. 2.

The spin multiplicity (SM) numbers determined for the complexes of the ligand with Zn, Cu, Ni and Co metals were 1, 2, 3 and 4, respectively. The optimized geometry of the 2-{(*E*)-[(4-aminophenyl)imino]methyl}-6-bromo-4-chloro-

phenol complexes with Zn is shown as an example in Fig. 3. In this optimization calculation, the computed $\langle S2 \rangle$ values confirmed that the spin contamination was very small (max 0.5 % after annihilation).
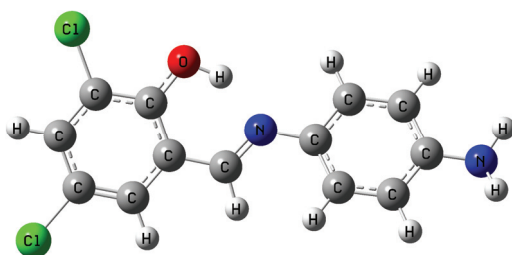

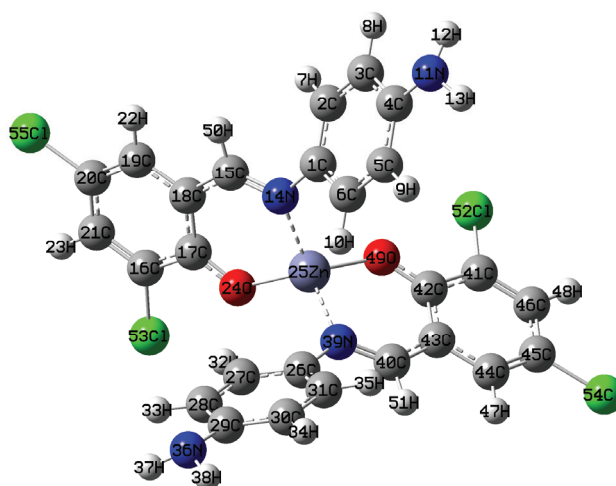Fig. 2. Optimized geometry of the ligand.

Fig. 3. Optimized geometry of the Zn complex with 6-bromo analogue of L⁻.

NBO charges with color representation for the optimized complexes are shown in Fig. 4. The NBO charges, spin density values and electron configuration of metal atoms for the optimized complexes with Zn, Cu, Ni and Co metals are presented in Table II, from which it can be seen that the metal atoms have a high spin density, which indicates that the unpaired electrons are localized on the metal atoms. The optimized complexes with Cu, Ni and Co atoms have distorted tetrahedral structures, while the complex with a Zn atom has a normal tetrahedral structure. The reason for this might be that metal atoms in the optimized complexes with Cu, Ni and Co atoms have some spin density whereas the Zn atom has no spin density in its optimized complex. Additionally, according to Fig. 4, the atomic charges of the metal atoms in the complexes are higher than those of the other atoms of the ligands, which show that the metal atoms have the highest positive character.
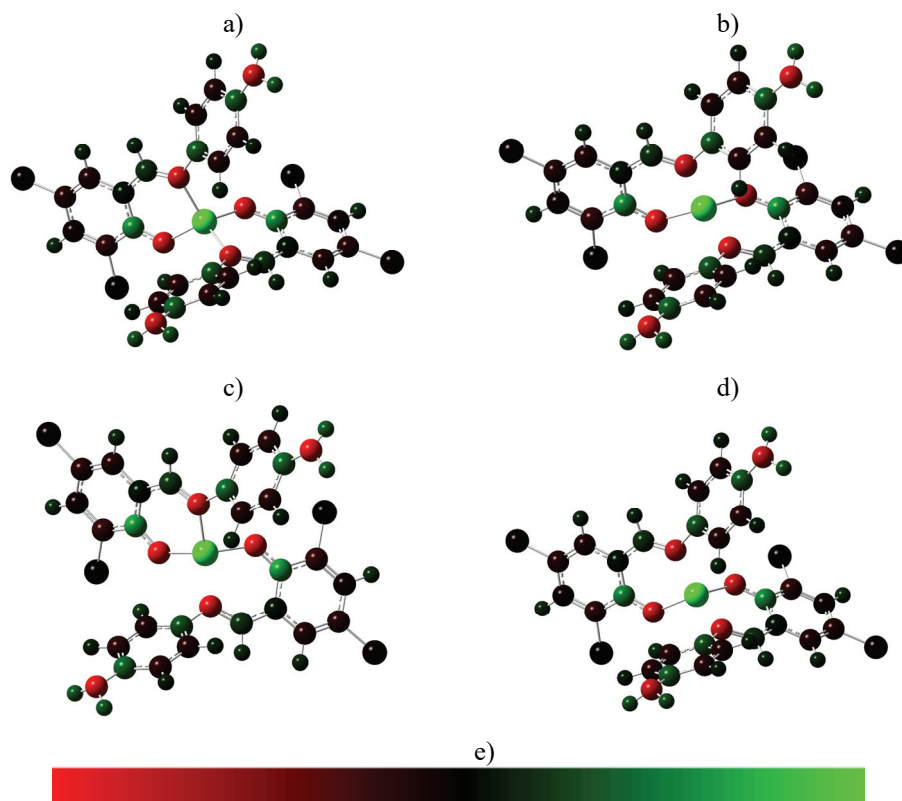
Fig. 4. NBO charges with color representation for optimized: a) Zn-complex, b) Ni-complex, c) Cu-complex and d) Co-complex; e) scale for charges (left side: lowest charge (–) and right side: highest charge (+)).

TABLE II. NBO charges, spin density values and electron configurations of the metal atoms of the optimized Zn, Cu, Ni and Co complexes

Metal	NBO charge	Spin density	Electron configuration
Zn	1.297	–	[core]4s(0.37)3d(9.91)4p(0.42)5p(0.01)
Cu	1.123	0.683	[core]4s(0.35)3d(9.15)4p(0.37)
Ni	1.162	1.710	[core]4s(0.29)3d(8.16)4p(0.39)
Co	1.229	2.776	[core]4s(0.29)3d(7.13)4p(0.35)

The vibrational frequencies obtained in a previous study for 2-{(*E*)-[(4--aminophenyl)imino]methyl}-6-methoxy-4-nitrophenol and its complexes with Co, Ni, Cu and Zn metals using the 6-31g(d,p), DGDZVP and CEP-121G basis sets were relatively similar.[18] Thus, in the present study, the vibrational frequencies were obtained by the 6-31g(d,p) method. The calculated vibrational frequency values of the C=N, C–O and N–H stretching modes for the optimized

complexes are tabulated in Table III, from which it could be seen that the calculated values of the C=N, C–O and N–H stretching frequencies were in good agreement with experimental frequency data given in Table S-I for the ligand and its Zn, Cu, Ni and Co complexes. The calculated C=N stretching frequencies for the ligand and its metal complexes (Zn, Cu, Ni and Co) were 1621, 1574 (1575), 1572 (1575), 1569 (1572) and 1568 (1571) cm^{-1}, respectively. The experimental frequencies were 1609, 1608, 1602, 1607 and 1608 cm^{-1}, respectively. The stretching frequencies of the C–O mode were computed as 1272, 1304 (1306), 1305 (1307), 1304 (1307) and 1303 (1304) cm^{-1} for the ligand and its Zn, Cu, Ni and Co complexes, respectively. The corresponding experimental frequency values were 1290, 1293, 1323, 1295 and 1294 cm^{-1}, respectively. The N–H stretching frequencies were also similar to the corresponding experimental IR bands. Consequently, all calculated frequencies fell within 5.1 % of the experimental frequency region reported in this study. This is a reasonable error region as pointed out in the literature.[44]

TABLE III. The calculated vibrational frequency values (cm^{-1}) for the optimized ligand and its complexes

Frequency type		Ligand	Complex			
			Zn	Cu	Ni	Co
C=N stretching	15C=14N	1621	1574	1572	1569	1568
	40C=39N		1575	1575	1572	1571
C–O stretching	16C–27O	1272	1304	1305	1304	1303
	49C–60O		1306	1307	1307	1304
N–H symmetrical stretching	11N–12H, 13H	3440	3438	3436	3437	3438
	36N–37H, 38H		3440	3438	3440	3440
N–H anti-symmetrical stretching	11N–12H, 13H	3546	3541	3539	3540	3541
	36N–37H, 38H		3545	3542	3545	3544

CONCLUSIONS

Many Schiff-base derivatives containing a substituted aromatic amine have been synthesized, characterized and used for complexation of transition metals. Functional groups, such as amines are very far removed from the pendants participating in the complexation and have no effect on the complexes. TGA and elemental analysis indicated no lattice/coordinated water molecules in the complexes. The satisfactory analytical data and all of the physicochemical studies suggested that these complexes might be formulated as M(L)$_2$. DFT calculations with the B3LYP method/6-31g(d,p) basis set were performed on the optimized structures and the vibrational IR spectra of the ligand and its Co, Ni, Cu and Zn complexes. The optimized geometries of complexes were tetrahedral structures. The calculated stretching frequency values of the C=N, C–O and N–H bonds were in good agreement with experimental frequency data reported in this study

for the ligand and its Zn, Cu, Ni and Co complexes. All the calculated frequencies fell within about 5 % of the experimental frequency regions. The antibacterial data given for the compounds presented in this paper indicated that the antimicrobial activity of metal complexes depended on the structure of the tested compound. The sensitivity spectrum of the microbial strains towards the ligand and the corresponding complexes was determined by qualitative and quantitative methods. The quantitative antimicrobial activity test results proved that both the ligand and complex combinations have specific antimicrobial activity, depending on the microbial species tested. Although none of the presented compounds was as effective against the tested microorganisms as the used reference drugs, the determination of their antibacterial activity against other Gram-negative and Gram-positive strains is in progress.

SUPPLEMENTARY MATERIAL

Detailed physical, analytical and spectral data for the ligand and its Zn, Cu, Ni and Co complexes are available electronically from http://www.sbd.org.rs/JSCS/ or from the corresponding author on request.

ИЗВОД
СИНТЕЗА, КАРАКТЕРИЗАЦИЈА, АНТИБАКТЕРИЈСКА И АНТИФУНГАЛНА АКТИВНОСТ 2-{(*E*)-[(4-АМИНОФЕНИЛ)ИМИНО]МЕТИЛ}-4,6-ДИХЛОРОФЕНОЛА И ОДГОВАРАЈУЋИХ Co(II), Ni(II), Cu(II) И Zn(II) КОМПЛЕКСА: ЕКСПЕРИМЕНТАЛНО И DFT ИСПИТИВАЊЕ

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У овом раду су синтетисани и окарактерисани физичкохемијским методама комплекси Co(II), Ni(II), Cu(II) и Zn(II) са 2-{(*E*)-[(4-аминофенил)имино]метил}-4,6-дихлорофенолом. Стехиометријски однос метала и лиганда у свим комплексима је 1:2. На основу добијених резултата, може се претпоставити да се Шифова база координује за јоне метала преко фенолног атома кисеоника и азометинског атома азота, при чему настају мононуклеарни комплекси. Структуре комплекса су одређене применом елементалне микроанализе, IR, ^{1}H- и ^{13}C-NMR спектроскопије, UV–Vis спектрофотометрије, мерењем магнетне сусцептибилности и термогравиметријском анализом. Применом DFT методе нађено је да комплекси имају тетраедарску структуру. Теоријски израчунате вредности за фреквенције C=N, C–O и N–H веза су у сагласности са експерименталним подацима, при чему израчунате вредности одступају до 5 % од експериментално одређених фреквенција. Испитивана је антибактеријска и антифунгална активност синтетисаних једињења и добијени резултати су приказани у облику *MIC* вредности. Од свих испитиваних једињења, Zn(L)$_2$ комплекс показује највећу активност

према микроорганизмима *Candida tropicalis* and *Bacillus subtilis,* при чему је *MIC* вредност 64 µg mL^{-1}.

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