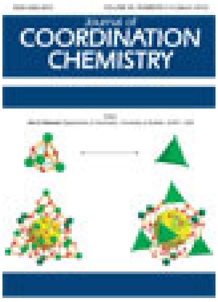

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Synthesis, characterization, and X-ray crystal structures of metal complexes with new Schiff-base ligands and their antibacterial activities

Hassan Keypour [a] , Maryam Shayesteh [a] , Reza Golbedaghi [b] , Abdolkarim Chehregani [c] & Allan G. Blackman [d]

[a] Faculty of Chemistry , Bu-Ali Sina University , Hamedan 65174 , Iran

[b] Chemistry Department , Payame Noor University , Tehran 19395-4697 , Iran

[c] Department of Biology , Bu-Ali Sina University , Hamedan 65178-38683 , Iran

[d] Department of Chemistry , University of Otago , P.O. Box 56, Dunedin , New Zealand

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Synthesis, characterization, and X-ray crystal structures of metal complexes with new Schiff-base ligands and their antibacterial activities

HASSAN KEYPOUR*†, MARYAM SHAYESTEH†, REZA GOLBEDAGHI‡,
ABDOLKARIM CHEHREGANI§ and ALLAN G. BLACKMAN¶

†Faculty of Chemistry, Bu-Ali Sina University, Hamedan 65174, Iran
‡Chemistry Department, Payame Noor University, Tehran 19395-4697, Iran
§Department of Biology, Bu-Ali Sina University, Hamedan 65178-38683, Iran
¶Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand

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Two new potentially hexadentate Schiff bases, $[H_2L^1]$ and $[H_2L^2]$, were prepared by condensation of 2-(3-(2-aminophenoxy)naphthalen-2-yloxy)benzenamine with 3,5-di-tert-butyl-2-hydroxy benzaldehyde and *o*-vanillin, respectively. Reaction of these ligands with cobalt(II) chloride, copper(II) perchlorate, and zinc(II) nitrate gave complexes ML. The ligands and their complexes have been characterized by a variety of physico-chemical techniques. The solid and solution state investigations show that the complexes are neutral. Molecular structures of $[CuL^1]$, $[CoL^1]\cdot C_7H_8$, and $[ZnL^2]\cdot CH_3CN$, which have been determined by single-crystal X-ray diffraction, indicate that $[CuL^1]$ and $[ZnL^2]\cdot CH_3CN$ display distorted square planar and distorted trigonal-bipyramidal geometry, respectively; the geometry around cobalt in $[CoL^1]\cdot C_7H_8$ is almost exactly between trigonal bipyramidal and square pyramidal. The synthesized ligands and their complexes were screened for their antibacterial activities against eight bacterial strains and the ligands and complexes have antibacterial effects. The most effective ones are $[CuL^2]$ against *Proteus vulgaris, Serratia marcescens, Staphylococcus subtilis,* $[H^2L^1]$ against *S. subtilis,* and $[H_2L^2]$ against *S. subtilis.*

Keywords: Schiff-base complexes; X-ray structures; Antibacterial effects

1. Introduction

Transition-metal complexes of Schiff bases have been used as molecular ferromagnets, catalysts for many organic reactions, models for the active sites in metalloenzymes, optical and luminescent materials, and DNA cleavage reagents [1–5]. Some Schiff-base complexes have also been used as models for biological oxygen carrier systems [6–9] and in analysis [10]. Salen-type ligands are tetradentate with rich coordination chemistry [11–15], offering versatile electronic, steric, and lipophilic properties. They may be easily prepared by condensation of an aromatic *o*-hydroxyaldehyde and a diamine. The hydrophilic–lipophilic balance can be easily tuned by choosing the appropriate amine

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*Corresponding author. Email: haskey1@yahoo.com

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precursors and ring substituents of the aromatic aldehyde. Salen complexes of various metal ions are widely used as catalysts for organic transformations [15–17] such as polymerizations, epoxidations, and aziridinations, and have attracted attention as building blocks for supramolecular chemistry [18–20]. In this article, we report the synthesis and characterization of two new potentially hexadentate (H_2L^1) and octadentate (H_2L^2) Schiff bases (figure 1) containing three different types of donors (imine N, phenol O, and ether O), their complexation reactions with various transition-metal salts and characterizations of the products formed. We also explored the antibacterial activities of synthesized ligands and their complexes against *Citrobacter amalonaticus* (Lio), *Enterobacter aerogenes* (PTCC 10009), *Serratia marcescens* (PTCC 1330), *Proteus vulgaris* (Lio), *Bacillus cereus* (ATCC 7064), *Bacillus megaterium* (PTCC 1672), *Staphylococcus subtilis* (Lio), and *Staphylococcus aureus* (ATCC 6633).

2. Experimental

2.1. *Starting materials*

3,5-Di-tert-butyl-2-hydroxy benzaldehyde [21] and 2-(3-(2-aminophenoxy)naphthalen-2-yloxy)benzenamine were synthesized according to literature procedures [22–26]. Solvents, naphthalene-2,3-diol, *o*-vanillin, 1-fluoro-2-nitrobenzene, and metal salts were purchased from Merck and used without purification.

2.2. *Synthesis*

2.2.1. H_2L^1. 2-(3-(2-Aminophenoxy)naphthalen-2-yloxy)benzenamine (0.342 g, 1 mmol) in methanol (20 mL) was added dropwise with stirring to a solution of 3,5-di-tert-butyl-2-hydroxy benzaldehyde (0.468 g, 2 mmol) in methanol (30 mL). The mixture was

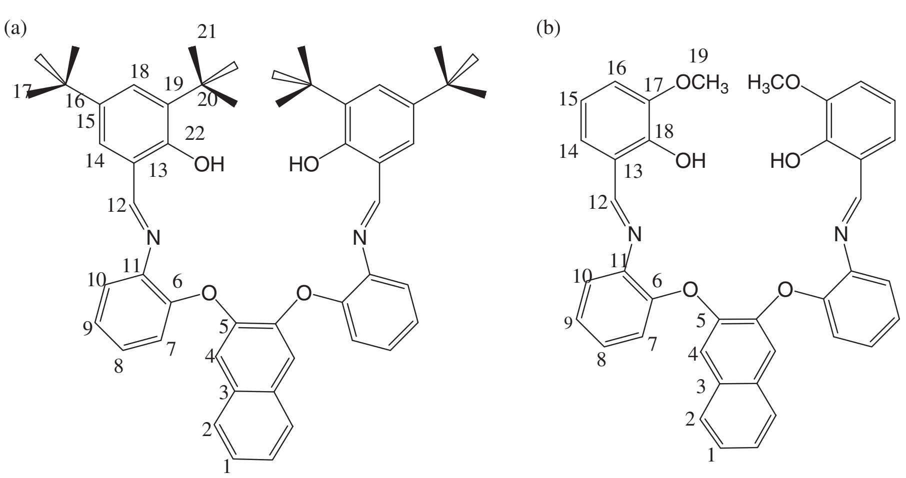

Figure 1. Structures of (a) H_2L^1 and (b) H_2L^2, along with atom numbering.

stirred and heated to reflux for 4 h. A yellow precipitate was obtained that was filtered off, washed with cold methanol, and dried *in vacuo*. Yield: 0.6 g (77.4%); m.p. 135°C. Anal. Calcd for $C_{52}H_{58}N_2O_4$: C, 80.6; H, 7.5; N, 3.6. Found (%): C, 80.3; H, 7.3; N, 3.9. IR (cm^{-1}, KBr): 1620 (s, νC=N). UV-Vis [λ (nm), ε (($mol\,L^{-1})^{-1}cm^{-1}$)]: 280(30,500), 370(14,700).

2.2.2. H_2L^2. In a manner similar to the above, a methanol solution (20 mL) of 2-(3-(2-aminophenoxy)naphthalen-2-yloxy)benzenamine (0.342 g, 1 mmol) was added dropwise with stirring to a solution of *o*-vanillin (0.304 g, 2 mmol) in methanol (30 mL). The mixture was stirred and heated to reflux for 4 h. A red solid was formed that was filtered off, washed with cold methanol, and dried *in vacuo*. Yield: 0.5 g (81.9%); m.p. 132°C. Anal. Calcd for $C_{38}H_{30}N_2O_6$: C, 74.7; H, 4.9; N, 4.6. Found (%): C, 74.8; H, 4.7; N, 4.8. IR (cm^{-1}, KBr): 1617 (s, νC=N). UV-Vis [λ (nm), ε (($mol\,L^{-1})^{-1}cm^{-1}$)]: 282(44,400), 332(33,300).

2.2.3. [CuL^1]. A methanol solution (15 mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.3704 g, 1 mmol) and a moderate excess of NEt_3 were added to a warm solution of [H_2L^1] (0.775 g, 1 mmol) in methanol (50 mL). The mixture was stirred and heated to reflux for 4 h. The resulting green solid was collected by filtration and washed with cold methanol. Green crystals of [CuL^1] were obtained by liquid diffusion of acetonitrile into a solution of the complex in toluene. Yield: 0.7 g (83.7%); m.p. 339°C. Anal. Calcd for $C_{52}H_{56}CuN_2O_4$: C, 74.7; H, 6.8; N, 3.4. Found (%): C, 74.2; H, 6.4; N, 3.2. IR (cm^{-1}, KBr): 1612 (s, νC=N), 445–479 (M–O), 539 (M–N). UV-Vis [λ (nm), ε(($mol\,L^{-1})^{-1}cm^{-1}$)]: 298 (38,000), 332(sh), 432(13,700), 694 (116). $\Lambda_m = 3\,cm^2\,\Omega^{-1}\,mol^{-1}$.

2.2.4. [CoL^1] · C_7H_8. Similar to the above, a methanol solution (15 mL) of $CoCl_2 \cdot 6H_2O$ (0.2378 g, 1 mmol) and a moderate excess of NEt_3 were added to a warm solution of [H_2L^1] (0.775 g, 1 mmol) in methanol (50 mL). The resulting red solid was collected by filtration and washed with cold methanol. Red crystals of [CoL^1] · C_7H_8 were obtained by liquid diffusion of acetonitrile into a solution of the complex in toluene. Yield: 0.6 g (64.9%); m.p. 312°C. Anal. Calcd for $C_{59}H_{64}CoN_2O_4$: C, 76.7; H, 7.0; N, 3.0. Found (%): C, 76.4; H, 6.8; N, 3.2. IR (cm^{-1}, KBr): 1614 (s, νC=N), 441–475 (M–O), 540 (M–N). UV-Vis [λ (nm), ε (($mol\,L^{-1})^{-1}cm^{-1}$)]: 295(26,400), 344(15,300), 416(8300), 655(sh), 704(90), 825(66). $\Lambda_m = 1.5\,cm^2\,\Omega^{-1}\,mol^{-1}$.

2.2.5. [CuL^2]. Following the above procedure, [H_2L^2] (0.610, 1 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ yielded the product as green crystals. Yield: 0.5 g (74.2%); m.p. 302°C. Anal. Calcd for $C_{38}H_{28}CuN_2O_6$: C, 67.7; H, 4.2; N, 4.2. Found (%): C, 67.5; H, 4.2; N, 4.0. IR (cm^{-1}, KBr): 1610 (s, νC=N), 524–559 (M–O), 442–473 (M–N). UV-Vis [λ (nm), ε (($mol\,L^{-1})^{-1}cm^{-1}$)]: 300(25,400), 326(sh), 418(7400), 658(128). $\Lambda_m = 5\,cm^2\,\Omega^{-1}\,mol^{-1}$.

2.2.6. [ZnL^2] · CH_3CN. A methanol solution (15 mL) of $Zn(NO_3)_2 \cdot 6H_2O$ (0.297 g, 1 mmol) and a moderate excess of NEt_3 were added to a warm solution of H_2L^2 (0.610 g, 1 mmol) in methanol (50 mL). The resulting yellow solid was collected by filtration and washed with cold methanol. $[ZnL^2]\cdot CH_3CN$ was recrystallized by slow evaporation over several days from acetonitrile solution. Yield: 0.4 g (56.0%); m.p. 315°C. Anal. Calcd for $C_{40}H_{31}ZnN_3O_6$: C, 67.2; H, 4.4; N, 5.9. Found (%): C, 67.1; H, 4.3; N, 5.8. IR (cm^{-1}, KBr): 1608 (s, νC=N), 530–555 (M–O), 435–470 (M–N). UV-Vis [λ (nm), ε ($(mol\,L^{-1})^{-1}cm^{-1}$)]: 296(19,700), 334(16,200), 422(7300). $\Lambda_M = 9\ \Omega^{-1}\,cm^2\,mol^{-1}$.

2.3. *Physical measurements*

Infrared (IR) spectra were collected using KBr pellets on a BIO-RAD FTS-40A spectrophotometer (400–4000 cm^{-1}). A Perkin-Elmer, Lambda 45 (UV-Vis) spectrophotometer was used to record the electronic spectra. CHN analyses were carried out using a Perkin-Elmer, CHNS/O elemental analyzer model 2400. Conductance measurements were performed using a Hanna HI 8820 conductivity meter. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance 400 MHz and Jeol 90 MHz spectrometers using $Si(CH_3)_4$ as internal standard.

2.4. *X-ray crystallography*

Single-crystal X-ray diffraction analyses were performed on a Bruker Kappa APEX-II system at 91(2) K using graphite monochromated Mo-Kα X-ray radiation ($\lambda = 0.71069$ nm) with exposures over 0.5°. They were corrected for Lorentz and polarization effects using SAINT [27] and for absorption using SADABS. All structures were solved using SIR-97 [28] within the WinGX [29] package and weighted full-matrix refinement on F^2 was carried out using SHELXL-97 [30]. Hydrogen atoms were included in calculated positions and refined as riding with individual (or group, if appropriate) isotropic displacement parameters. Details of the X-ray experiments and crystal data are summarized in table 1.

2.5. *Antibacterial study*

2.5.1. Materials and methods

2.5.1.1. *Test organisms for antibacterial assay.* The standard strains of the following microorganisms were used as test organisms: *C. amalonaticus* (Lio), *E. aerogenes* (PTCC 10009), *S. marcescens* (PTCC 1330), *P. vulgaris* (Lio), *B. cereus* (ATCC 7064), *B. megaterium* (PTCC 1672), *S. subtilis* (Lio), *St. aureus* (ATCC 6633). Some microorganisms were obtained from Persian Type Culture Collection, Tehran, Iran and others locally isolated (Lio). The organisms were sub-cultured in nutrient broth and nutrient agar (Oxiod Ltd.) for use in experiments, while diagnostic sensitivity test (DST) agar (Oxoid Ltd.) was used in antibiotic sensitivity testing.

2.5.1.2. *Sensitivity testing.* For bioassays, a suspension of approximately 1.5×10^8 cells per mL in sterile normal saline was prepared as described by Forbes *et al.* [31]. The sensitivity testing was determined using the agar-gel diffusion method [32, 33]. In each disc 20 µL of a solution containing 10 µg of each compound in DMSO were loaded.

Table 1. Crystal data and structure refinement for [CuL^1], [CoL^1] · C_7H_8, and [ZnL^2] · CH_3CN.

Empirical formula	$C_{52}H_{56}CuN_2O_4$	$C_{59}H_{64}CoN_2O_4$	$C_{40}H_{31}N_3O_6Zn$
Formula weight	836.53	924.05	715.05
Temperature (K)	91(2)	91(2)	91(2)
Wavelength (Å)	0.71069	0.71069	0.71069
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*P2(1)/c*	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)			
a	17.3621(18)	13.6278(4)	10.8764(6)
b	15.1981(16)	13.7519(4)	11.0897(6)
c	18.4353(21)	15.5082(4)	15.8040(9)
α	90.000	69.126(2)	102.977(3)
β	115.710(5)	74.933(2)	105.986(3)
γ	90.000	68.468(2)	104.512(3)
Volume (Å^3), *Z*	4383.0(8), 4	2498.1(1), 2	1683.4(2), 2
Calculated density (Mg m^{-3})	1.268	1.228	1.411
Absorption coefficient (mm^{-1})	0.546	0.392	0.783
F(000)	1772	982	740
Crystal size (mm^3)	$0.28 \times 0.28 \times 0.06$	$0.38 \times 0.25 \times 0.25$	$0.27 \times 0.19 \times 0.10$
θ range for data collection (°)	1.30–26.40	1.85–26.12	2.00–27.12
Limiting indices	$-21 \le h \le 20$; $-18 \le k \le 18$; $-21 \le l \le 23$	$-16 \le h \le 16$; $-17 \le k \le 17$; $-19 \le l \le 19$	$-13 \le h \le 13$; $-14 \le k \le 14$; $-20 \le l \le 20$
Reflections collected/unique	50,821/8944 [R(int) = 0.0724]	59,250/9860 [R(int) = 0.0535]	42,551/7365 [R(int) = 0.0549]
Completeness to $\theta = 25.00$ (%)	99.9	99.8	99.4
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.000000 and 0.782835	1.000000 and 0.888110	1.000000 and 0.889512
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8944/0/544	9860/0/608	7365/0/454
Goodness-of-fit on F^2	1.080	1.054	1.067
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0424$, $wR_2 = 0.1085$	$R_1 = 0.0419$, $wR_2 = 0.1023$	$R_1 = 0.0384$, $wR_2 = 0.0748$
R indices (all data)	$R_1 = 0.0724$, $wR_2 = 0.1246$	$R_1 = 0.0519$, $wR_2 = 0.1097$	$R_1 = 0.0497$, $wR_2 = 0.0811$
Largest difference peak and hole (e Å^{-3})	0.482 and −0.693	0.327 and −0.455	0.598 and −0.452

The minimum inhibitory concentration (MIC) of the compounds was also determined using a two-fold dilution method [34]. The isolated bacterial strains were first grown in nutrient broth for 18 h before use. The inoculum suspensions were standardized and then tested against the effect of the compounds at 20 µL for each disc in DST medium. The plates were later incubated at 37 ± 0.5°C for 24 h after which were observed for zones of inhibition. The effects were compared with the standard antibiotic chloramphenicol at 1 mg mL^{-1} [35]. The MICs of the chemicals were also determined by tube dilution techniques in Mueller-Hinton broth (Merck) according to National Committee for Clinical Laboratory Standards (NCCLS) [34]. The experiments were repeated at least three times for each organism and the data were presented as the mean ± SE of 3–5 samples.

3. Results and discussion

Two new potentially hexadentate N_2O_4 and octadentate N_2O_6 Schiff bases (H_2L^1 and H_2L^2, respectively) have been prepared from the reaction of 2-(3-(2-aminophenoxy)naphthalen-2-yloxy)benzenamine with 3,5-di-tert-butyl-2-hydroxy benzaldehyde or *o*-vanillin, respectively. The analytical and spectral data are consistent with the proposed formulation. The Cu(II), Co(II), and Zn(II) complexes of these ligands were also synthesized. All complexes were characterized by IR spectra, elemental analysis, molar conductance (Λ_m), UV-Vis spectra and in the case of [CuL^1], [CoL^1]$\cdot C_7H_8$, and [ZnL^2]$\cdot CH_3CN$, by X-ray diffraction.

3.1. *IR spectra*

The IR spectra of H_2L^1 and H_2L^2 from 4000 to 400 cm^{-1} contain a strong absorption at 1620 and 1617 cm^{-1}, respectively, assigned to a C=N stretch, confirming formation of the Schiff base. This observation is supported by the absence of aldehyde C=O and amine N–H stretching vibrations in spectra of the ligands. The reactions of Cu(II), Co(II), or Zn(II) salts with H_2L^1 and H_2L^2 yield [CuL^1], [CoL^1]$\cdot C_7H_8$, [CuL^2], and [ZnL^2]$\cdot CH_3CN$. Deprotonation of all phenolic functions is confirmed by the lack of O–H stretching bands at 3300–3400 cm^{-1} for the complexes [36, 37]. IR spectra provide some information about the bonding in these complexes. The strong ν(C=N) bands shift to lower frequencies compared with free imine bands, indicating coordination of the ligands to Cu(II), Co(II), and Zn(II) *via* the azomethine nitrogen atoms. The bands at 1167 cm^{-1} and 1188 cm^{-1} for H_2L^1 and H_2L^2, respectively, are ascribed to phenolic C–O stretch. These bands shift to lower frequencies in the complexes due to O-metal coordination. Conclusive evidence for metal binding is given by new bands in the IR spectra of the complexes at 441–559 and 435–540 cm^{-1}, assigned to ν(M–O) and ν(M–N) stretches [38–45].

3.2. *NMR spectra*

^{1}H and ^{13}C NMR data for H_2L^1 and H_2L^2 and [ZnL^2]$\cdot CH_3CN$ are listed in "Supplementary material" (table S1) while the atom numbering is shown in figure 1.

Both ^{1}H and ^{13}C NMR spectra of H_2L^1 and H_2L^2 show only a single imine resonance (^{1}H: 8.550 ppm (H_2L^1), 8.475 ppm (H_2L^2); ^{13}C: 165.015 ppm (H_2L^1), 163.057 ppm (H_2L^2)), demonstrating the equivalence of the two imine environments. Seventeen peaks are observed in the aromatic region of the ^{13}C NMR spectra (117.159–158.464 ppm for [H_2L^1]; 114.577–151.603 ppm for [H_2L^2]), as expected. The ^{1}H spectrum of [ZnL^2] · CH_3CN shows loss of the phenolic-OH signal observed at 13.697 ppm in free H_2L^2, indicating deprotonation of OH on coordination of Zn^{2+}. Also a downfield shift of the imine proton resonance of 0.3 ppm was observed in [ZnL^2] · CH_3CN.

3.3. *Electronic absorption spectroscopy*

The electronic spectra of the ligands and their complexes were recorded in $CHCl_3$. Bands below 370 nm are attributable to intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. In the electronic spectra, intraligand transitions are slightly shifted as a result of coordination.

Co(II) and Cu(II) complexes show low intensity shoulders at *ca* 655–825 nm, assigned as d−d transitions. For [CoL^1] · C_7H_8, three bands in the visible region at 655, 704, and 825 nm are typical for high spin cobalt(II) in a trigonal-bipyramidal field [46]. Electronic spectra of the Cu(II) complexes show an absorption at 658–694 nm attributed to $^{2}E_g \rightarrow {}^{2}T_{2g}$ transition, characteristic of distorted octahedral geometry [47, 48]. The energy of the band assigned to d–d transitions provides a rough estimate of the ligand field strength, since one of the electronic transitions contained in the band envelope is $d_{x^2-y^2}$–d_{xy} and the energy associated with this transition is $10D_q$-C [39, 47, 48]. All spectra of the Co(II), Zn(II), and Cu(II) complexes show an intense band at *ca* 416–432 nm, due to a charge transfer transition [49–52]. The electronic spectral details of the complexes are given in table 2.

3.4. *Molar conductivity*

The molar conductivities (Λ_M) of the Cu(II), Co(II), and Zn(II) complexes in $CHCl_3$ at 10^{-3} mol L^{-1} were 1.5–9 Ω^{-1} cm^2 mol^{-1}. These low values indicate that all their complexes are nonelectrolytes [53, 54]. The molar conductances indicate that [H_2L^1] and [H_2L^2] are coordinated as doubly negatively charged anions, suggesting deprotonation of the two phenolic OH groups on coordination [55].

Table 2. Electronic spectroscopy data (nm) for H_2L^{1-2} and complexes.

	λ_{max}(nm) (ε)[a]					
Compound	Intraligand (LL)		CT	d–d		
[H_2L^1]	280 (30,500)	370 (14,700)				
[H_2L^2]	282 (44,400)	332 (33,300)				
[CuL^1]	298 (38,000)	332 (sh)	432 (13,700)	694 (116)[b]		
[CuL^2]	300 (25,400)	326 (sh)	418 (7400)	658 (128)[b]		
[CoL^1]	295 (26,400)	344 (15,300)	416 (8300)	655 (sh)	704 (90)[b]	825 (66)
[ZnL^2]	296 (19,700)	334 (16,200)	422 (7300)			

[a] Mol^{-1} cm^{-1}.

[b] Shoulder.

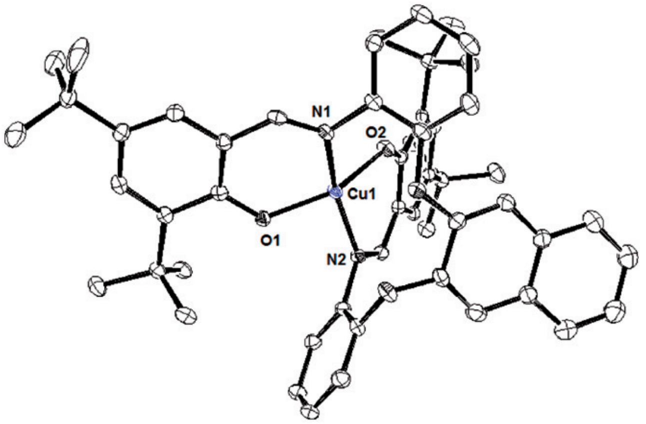

Figure 2. ORTEP diagram of [CuL[1]] showing 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

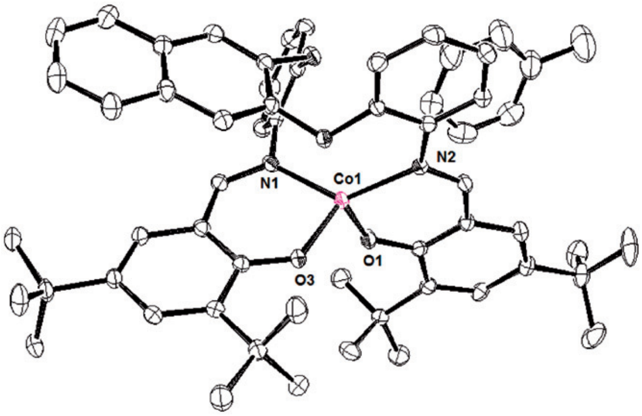

Figure 3. ORTEP diagram of [CoL[1]] $\cdot$ C_7H_8 showing 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

3.5. *X-ray structures*

Suitable crystals of [CuL^1] and [CoL^1] $\cdot$ C_7H_8 were obtained from a toluene solution on slow diffusion of acetonitrile. Crystals of [ZnL^2] $\cdot$ CH_3CN were obtained by slow evaporation from acetonitrile over several days. The ORTEP views of the complexes are shown in figures 2–4. Crystallographic data and structure refinement parameters are given in table 1 and selected bond distances and angles are given in table 3. [CuL^1] displays a distorted square planar geometry about the metal ion ($\tau_4 = 0.32$) [56], with the two N and two O donors adopting a mutually pseudo *trans* arrangement (O–Cu–O and N–Cu–N bond angles of 151.58(7)° and 163.57(8)°, respectively). The Cu–O(1) and Cu–O(2) distances to phenol are 1.9057(17) and 1.9148(17) Å. Such distances are consistent with deprotonation and formal coordination as phenoxide [57]. The ether

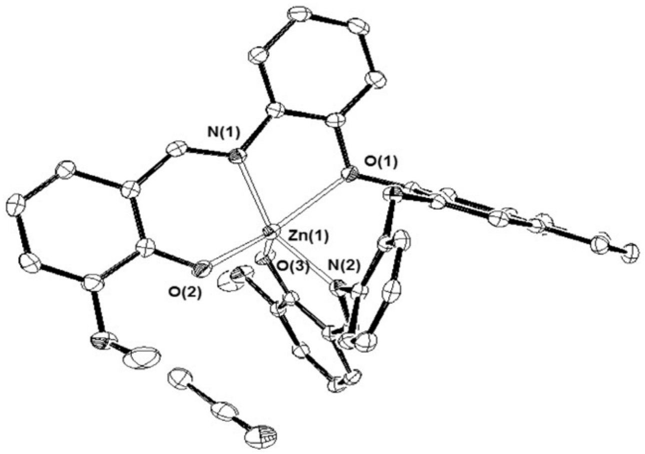

Figure 4. ORTEP diagram of $[\mathrm{ZnL}^2]\cdot\mathrm{CH_3CN}$ showing 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Table 3. Selected bond lengths (Å) and angles (°) for $[\mathrm{CuL}^1]$, $[\mathrm{CoL}^1]\cdot\mathrm{C_7H_8}$, and $[\mathrm{ZnL}^2]\cdot\mathrm{CH_3CN}$.

$[\mathrm{CuL}^1]$		$[\mathrm{CoL}^1]\cdot\mathrm{C_7H_8}$		$[\mathrm{ZnL}^2]\cdot\mathrm{CH_3CN}$	
Cu(1)–O(1)	1.9057(17)	Co(1)–O(1)	1.9161(14)	Zn(1)–O(3)	1.9343(16)
Cu(1)–O(2)	1.9148(17)	Co(1)–O(3)	1.9258(14)	Zn(1)–O(2)	1.9576(15)
Cu(1)–N(1)	1.959(2)	Co(1)–N(2)	2.0165(16)	Zn(1)–N(1)	2.0157(17)
Cu(1)–N(2)	1.9761(19)	Co(1)–N(1)	2.0202(18)	Zn(1)–N(2)	2.0355(17)
		Co(1)–O(2)	2.3697(14)	Zn(1)–O(1)	2.3417(15)
O(1)–Cu(1)–O(2)	151.58(7)	O(1)–Co(1)–O(3)	105.45(6)	O(3)–Zn(1)–O(2)	105.84(7)
O(1)–Cu(1)–N(1)	93.40(8)	O(1)–Co(1)–N(2)	93.97(6)	O(3)–Zn(1)–N(1)	116.54(6)
O(2)–Cu(1)–N(1)	90.32(8)	O(3)–Co(1)–N(2)	126.85(6)	O(2)–Zn(1)–N(1)	94.15(7)
O(1)–Cu(1)–N(2)	92.51(8)	O(1)–Co(1)–N(1)	100.34(6)	O(3)–Zn(1)–N(2)	94.68(7)
O(2)–Cu(1)–N(2)	91.75(8)	O(3)–Co(1)–N(1)	94.10(6)	O(2)–Zn(1)–N(2)	93.02(7)
N(1)–Cu(1)–N(2)	163.57(8)	N(2)–Co(1)–N(1)	130.84(6)	N(1)–Zn(1)–N(2)	144.46(7)
		O(1)–Co(1)–O(2)	168.33(5)	O(3)–Zn(1)–O(1)	87.16(6)
		O(3)–Co(1)–O(2)	84.31(6)	O(2)–Zn(1)–O(1)	166.00(6)
		N(2)–Co(1)–O(2)	74.82(6)	N(1)–Zn(1)–O(1)	75.00(6)
		N(1)–Co(1)–O(2)	85.05(6)	N(2)–Zn(1)–O(1)	91.02(6)

O(3) and O(4) are not coordinated, lying 2.831 Å and 3.174 Å, respectively, from Cu. Most of them are within normal values for Schiff-base copper(II) [58–63] or other [64–70] complexes.

$[\mathrm{CoL}^1]\cdot\mathrm{C_7H_8}$ displays a very different coordination geometry to the Cu(II) analog. Co(II) is five-coordinate, binding to phenoxide oxygen atoms O(1) and O(3), the azomethine nitrogen atoms N(1) and N(2), and one ether oxygen atom O(2) in a geometry almost exactly between trigonal bipyramidal and square pyramidal ($\tau_5 = 0.62$) [71]. The Co–N bond lengths are nearly identical (Co(1)–N(1) 2.0202(18) Å, Co(1)–N(2) 2.0165(16) Å) with a N(1)–Co(1)–N(2) bond angle of 130.84(6)°. The Co(1)–O(1) (1.9161(14) Å) and Co(1)–O(3) (1.9258(14) Å) bond lengths are again consistent with coordination of phenoxide, rather than neutral phenol [72], while the Co–O(2) distance

Table 4. Antibacterial activity of the studied chemicals as diameter of inhibition zone (mm) and MIC.

Chemicals bacterial strains	ZnL^2	CuL^2	H_2L^1	CuL^1	CoL^1	H_2L^2	Chloramphenicol	MIC	
								CM[a] ($\mu g\,mL^{-1}$)	STD[b] ($\mu g\,mL^{-1}$)
C. amalonaticus	12 ± 3	12.5 ± 2	14 ± 3.5	12 ± 6	14.4 ± 2	12 ± 4	13 ± 4	20–25	8
P. vulgaris	15 ± 4	18 ± 5	17 ± 4	14 ± 4	12 ± 5	13 ± 5	35 ± 8	18–20	4
S. marcescens	14 ± 2	18 ± 4	13 ± 2	12 ± 3	12 ± 5	14 ± 6	22 ± 5	22–25	4
E. aerogenes	13 ± 3	12 ± 4	13 ± 4	12 ± 2	12 ± 4	14 ± 7	22 ± 3	30–36	4
St. aureus	12 ± 2.5	16 ± 4	14 ± 4	12 ± 6	13 ± 4	12 ± 3	25 ± 3.5	8–11	2
S. subtilis	12 ± 2	18 ± 4.4	18 ± 3	14 ± 2	16 ± 5	18 ± 6	25 ± 4	6–10	4
B. cereus	12 ± 3	14 ± 6	15 ± 4	15 ± 4	14 ± 5	11 ± 3	18 ± 2.5	14–20	1
B. megaterium	12 ± 2	11 ± 2	12 ± 4	15 ± 3	12 ± 3	14 ± 4	17 ± 3	11–16	1

Each datum represented the means ± SE of 3–5 samples.
[a] The ranges for the chemicals.
[b] Chloramphenicol standard.

(2.3697(14) Å) indicates a somewhat weak bond to the ether oxygen [73]. The other ether oxygen atom, O(4), lies 3.422 Å from the metal ion and is not coordinated.

In $[ZnL^2]\cdot CH_3CN$, the Zn(II) has five-coordinate geometry, with the same donor atom set (two phenoxide O atoms, two azomethine N atoms, and an ether O atom) as found in $[CoL^1]\cdot C_7H_8$. In this case, however, the coordination geometry tends more toward square pyramidal ($\tau_5 = 0.36$). The bond lengths involving the metal ion are similar to those of $[CoL^1]\cdot C_7H_8$, with the Zn(1)–O(2) and Zn(1)–O(3) distances (1.9576 Å and 1.9343 Å, respectively) again consistent with coordination of phenoxide [74]. The Zn(1)–O(1) distance of 2.3417 Å also confirms coordination of one ether [75].

The three crystal structures reported herein display significant differences in geometry about the metal ion, despite the ligands having the same donor set and broadly similar structures. Four-coordination in $[CuL^1]$ arises from the inability of the ether O(3) to be positioned at a suitable distance from the Cu(II) ion for bonding. Comparison with the structures of $[CoL^1]\cdot C_7H_8$ and $[ZnL^2]\cdot CH_3CN$ suggests that this may arise due to the orientation of the phenyl ring to which the imine nitrogen is attached; when this is close to coplanar with the neighboring phenoxide, as in $[CoL^1]\cdot C_7H_8$ and $[ZnL^2]\cdot CH_3CN$ (mean plane angles between the two rings of 1.74° and 14.69°, respectively), binding of the ether O(3) at a distance of ~2.3 Å is facilitated. However, in $[CuL^1]$ the mean plane angle between the two rings is 37.94°, which leads to a Cu(1)–O(3) distance of over 2.8 Å. The origin of the, albeit small, difference in geometry between $[CoL^1]\cdot C_7H_8$ and $[ZnL^2]\cdot CH_3CN$ is less obvious. However, the O(3)–Zn(1)–N(1) angle in the latter complex (116.54°) allows expansion of the opposite N(1)–Zn(1)–N(2) angle (144.46°) to better accommodate a square-pyramidal geometry in comparison to the corresponding angles in the more trigonal bipyramidal $[CoL^1]\cdot C_7H_8$ (O(3)–Co(1)–N(2) = 126.85° and N(2)–Co(1)–N(1) = 130.84°).

3.6. *Antibacterial activities*

Antibacterial activities of the compounds were studied against four Gram positive and four Gram negative bacterial strains (table 4). All compounds inhibited the growth of bacterial strains producing zone of inhibition diameters from 11.0 to 18.0 mm, depending on the susceptibility of the tested bacteria. The most effective compounds are CuL^2 against *P. vulgaris, S. marcescens, S. subtilis,* H_2L^1 against *S. subtilis,* and H_2L^2 against *S. subtilis*. For the *C. amalonaticus,* the inhibition zones of all compounds were near those of chloramphenicol and showed inhibition zones at very low concentrations. Since comparison of the size of inhibition zones is not trustworthy, the MICs of the compounds were also determined according to the method of NCCLS [34]. Results indicate that the MIC of the compounds against the tested organisms varies between 6 and $10\,\mu g\,mL^{-1}$ against *S. subtilis* and 30 and $36\,\mu g\,mL^{-1}$ against *E. aerogenes*. The standard chloramphenicol had MIC values varying between 1 and $8\,\mu g\,mL^{-1}$. The results indicated that standard antibiotic chloramphenicol had stronger activity than the compounds against some bacterial strains. The antibacterial effect of the compounds is notable. The lowest MICs ($6–10\,\mu g\,mL^{-1}$) were detected for all compounds against *S. subtilis* and for other bacterial strains were 8–11 (*St. aureus*), 14–20 (*B. cereus*), and 11–19 (*B. megaterium*) $\mu g\,mL^{-1}$.

4. Conclusion

Copper(II), cobalt(II), and zinc(II) complexes $[CuL^1]$, $[CoL^1]\cdot C_7H_8$, $[ZnL^2]\cdot CH_3CN$, and $[CuL^2]$ have been synthesized and characterized. Molecular structures for $[CuL^1]$, $[CoL^1]\cdot C_7H_8$, and $[ZnL^2]\cdot CH_3CN$ reveal quite different geometries. All the compounds have antibacterial effects against the studied bacterial strains, with the most effective being $[CuL^2]$, $[H_2L^1]$, and $[H_2L^2]$; these can be considered as new antibacterial compounds. In general, comparison of the microbial activity of N_2O_2 Schiff bases and their related complexes show that the majority of such complexes are more active than their respective Schiff-base ligands [76–88]. However, the ligands reported in this article have higher antibacterial activity than their respective complexes. The remarkable activity of the H_2L^1 and H_2L^2 arise from existence of two hydroxyl groups in these ligands, which may play an important role in antibacterial activity. The higher antimicrobial activity of the $[CuL^2]$ complex relative to the other complexes in this work may be related to the stronger copper(II)–ligand bond in this complex relative to the M(II)–ligand bonds in other complexes, and this in turn increases the lipophilic character of the copper(II) complex compared to the other complexes [82]. The variation in the activity of the metal complexes against different organisms depends on the impermeability of the microorganism cells or on differences in the ribosome of microbial cells [89].

Supplementary material

CCDC nos 808225, 808226, and 808227 contain the supplementary crystallographic data of $[ZnL^2]\cdot CH_3CN$, $[CoL^1]\cdot C_7H_8$, and $[CuL^1]$ complexes, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ica.2009.12.009.

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