APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2004; **18**: 149–155
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.608

Synthesis, characterization, and antimicrobial activity of cobalt(II), nickel(II), copper(II) and zinc(II) complexes with ferrocenyl Schiff bases containing a phenol moiety

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Received 13 August 2003; Accepted 31 December 2003

Three ferrocenyl Schiff bases containing a phenol moiety have been formed by 1 : 1 molar condensation of acetylferrocene with 2-aminophenol, 2-amino-5-picoline or 2-amino-5-chlorophenol. These ligands form 2 : 1 complexs with cobalt(II), copper(II), nickel(II), and zinc(II) ions. From the different spectral data, it was found that coordination of the ligands with the metal ions takes place via the azomethine nitrogen atoms and the deprotonated oxygen of the phenol groups. These ligands and their complexes have been characterized by IR, ^{1}H NMR, ^{13}C NMR, UV–Vis spectra, and elemental analysis. The spectral data of the ligands and their complexes are discussed in connection with the structural changes due to complexation. The complexes prepared showed good antimicrobial activity against *Escherichia coli*, *Bacillus subtilus*, and *Candida albicans*. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: acetylferrocene; Schiff bases; phenol moiety; characterization; antimicrobial activity

INTRODUCTION

A large number of papers has been published on the characterization of mono- and di-substituted derivatives of ferrocene as typical organometallic species.[1–4] Part of this work was directed to ferrocene-containing metal chelates complexes, which, in themselves, can be considered as polynuclear metal complexes involving various aspects of both organometallic and coordination chemistry.[1,2,5,6] The presence of these systems may affect the interactions of these metals, giving wide applications in catalysis,[7–9] organic synthesis,[1,10] nonlinear optics,[11] and as biologically active compounds.[12–17]

In this study, three ferrocenyl Schiff bases containing a phenol moiety have been prepared from the condensation of acetylferrocene with 2-aminophenol, 2-amino-5-picoline or 2-amino-5-chlorophenol (HL1, HL2 and HL3 respectively; Fig. 1). These compounds act as (N, O) bidentate ligands, and so the study was extended to the investigation of the prepared ligands towards some metal(II) chlorides (MCl_2, where M = Co, Ni, Cu, and Zn) in order to obtain the heterobimetallic species. These ligands and their complexes have been characterized by IR, ^{1}H NMR, ^{13}C NMR, UV–Vis spectra, and elemental analysis.

EXPERIMENTAL

All chemicals and solvents were obtained from Merck except 2-amino-5-picoline and 2-amino-5-chlorophenol were obtained from Acros Organics. Acetylferrocene was prepared by a literature method.[18] The yields refer to analytically pure compounds and were not optimized. ^{1}H NMR and ^{13}C NMR

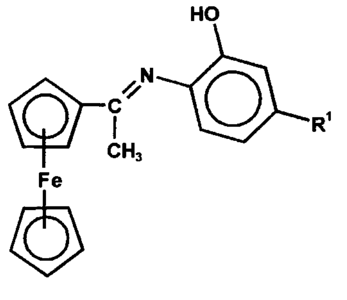

Figure 1. Structure of the ligands: R^1 = H (L1); CH_3(L2); Cl (L3).

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Table 1. Physical and analytical data of the ligands and their complexes

Ligand/complex	Formula (formula weight)	Melting point (°C)	Yield (%)	Analysis found (calc) (%)		
				C	H	N
HL1	$C_{18}H_{17}FeNO$ (319.19)	174	72	67.61	5.12	4.15
				(67.73)	(5.37)	(4.39)
$Co(L1)_2\cdot 2H_2O$	$C_{36}H_{36}CoFe_2N_2O_4$ (731.32)	222	73	58.98	4.76	3.71
				(59.13)	(4.96)	(3.83)
$Ni(L1)_2\cdot 2H_2O$	$C_{36}H_{36}Fe_2N_2NiO_4$ (731.08)	214	71	59.00	4.86	3.51
				(59.15)	(4.96)	(3.83)
$Cu(L1)_2$	$C_{36}H_{32}CuFe_2N_2O_2$ (699.90)	212	74	61.83	4.66	3.93
				(61.78)	(4.61)	(4.00)
$Zn(L1)_2\cdot 2H_2O$	$C_{36}H_{36}Fe_2N_2O_4Zn$ (737.77)	216	70	58.74	4.98	3.73
				(58.61)	(4.92)	(3.80)
HL2	$C_{19}H_{19}FeNO$ (333.21)	176	68	68.53	5.87	4.11
				(68.49)	(5.75)	(4.20)
$Co(L2)_2\cdot 2H_2O$	$C_{38}H_{40}CoFe_2N_2O_4$ (759.37)	222	72	60.01	5.11	3.48
				(60.10)	(5.31)	(3.69)
$Ni(L2)_2\cdot 2H_2O$	$C_{38}H_{40}Fe_2N_2NiO_4$ (759.13)	228	69	60.28	5.21	3.53
				(60.12)	(5.31)	(3.69)
$Cu(L2)_2$	$C_{38}H_{36}CuFe_2N_2O_2$ (727.96)	226	71	63.01	4.87	3.76
				(62.70)	(4.98)	(3.85)
$Zn(L2)_2\cdot 2H_2O$	$C_{38}H_{40}Fe_2N_2O_4Zn$ (765.82)	221	69	59.64	5.34	3.53
				(59.60)	(5.26)	(3.66)
HL3	$C_{18}H_{16}ClFeNO$ (353.63)	177	68	61.18	4.61	3.84
				(61.14)	(4.56)	(3.96)
$Co(L3)_2\cdot 2H_2O$	$C_{36}H_{34}Cl_2CoFe_2N_2O_4$ (800.21)	226	69	54.24	4.36	3.41
				(54.04)	(4.28)	(3.50)
$Ni(L3)_2\cdot 2H_2O$	$C_{36}H_{34}Cl_2Fe_2N_2NiO_4$ (799.97)	228	68	54.17	4.37	3.44
				(54.05)	(4.28)	(3.50)
$Cu(L3)_2$	$C_{36}H_{30}Cl_2CuFe_2N_2O_2$ (768.79)	224	70	56.38	3.88	3.49
				(56.24)	(3.93)	(3.64)
$Zn(L3)_2\cdot 2H_2O$	$C_{36}H_{34}Cl_2Fe_2N_2O_4Zn$ (806.66)	227	69	53.72	4.35	3.39
				(53.60)	(4.25)	(3.47)

spectra were recorded with a Bruker AC 250 spectrometer in deuterated dimethylsulforide (DMSO-d_6) as a solvent and were reported relative to tetramethylsilane (TMS) as internal standard. IR spectra were recorded on a Perkin Elmer (Spectrum 1000) FT-IR spectrometer, using KBr pellets. Elemental analyses were determined using a Heraeus CHN-O-RAPID analyser. Electronic absorptions were recorded on a Shimadzu UV240 automatic spectrophotometer in DMSO.

General procedure for the synthesis of the ligands HL1, HL2, and HL3

2-Aminophenol (1.09 g, 10 mmol), dissolved in about 20 ml absolute ethanol, was added slowly to a magnetically stirred solution of acetylferrocene (2.28 g, 10 mmol) in 20 ml ethanol. The mixture was refluxed for 2 h. Concentration of the solution to the appropriate volume and cooling at 5 °C yielded HL1, which was filtered, washed with cold ethanol, and dried. The product obtained was recrystallized from 10–15 ml hot ethanol to give HL1.

A similar method was used for preparation of HL2 and HL3 from condensation of acetylferrocene with 2-amino-5-picoline and 2-amino-5-chlorophenol respectively.

General procedure for the synthesis of the complexes

The different complexes were prepared by the addition of 2.0 mmol of $CoCl_2\cdot 6H_2O$, $NiCl_2\cdot 6H_2O$, $CuCl_2\cdot 2H_2O$, or $ZnCl_2$ (dissolved in *ca* 20 ml water) into a warmed solution of the ligand (4.0 mmol of HL1, HL2, or HL3) in ethanol (20 ml). The mixture was refluxed for 2.0 h. The complex that separated out on cooling at 5 °C, was filtered, washed twice with cold ethanol, and dried.

Antimicrobial studies

Preparation of the discs

The ligand/complex (60 µg) in $CHCl_3$ (0.01 ml) was mounted on a paper disc (prepared from blotting paper (5 mm diameter)) with the help of a micropipette. The discs were left at room temperature until dry and then applied on the microorganisms grown on agar plates.

Preparation of agar plates

Minimal agar was used for the growth of specific microbial species. For the preparation of agar plates for *Escherichia coli* and *Bacillus subtilus*, nutrient agar (2.30 g) obtained from Panreac Quimica SA (Spain) was suspended in freshly distilled water (100 ml). For *Candida albicans* (yeast), potato dextrose agar medium (3.9 g/100 ml) was obtained from Merck. The agar was allowed to soak for 15 min and then boiled on a water bath until completely dissolved. The mixture was autoclaved for 15 min at 120 °C and then poured into previously washed and sterilized Petri dishes and stored at 30 °C for inoculation.

Inoculation procedure

Inoculation was done via a platinum wire loop. The loop was heated to red-heat in a flame, cooled, and then used for the application of the microbial strains.

Application of the discs

Sterilized forceps were used for the application of the paper disc on previously inoculated agar plates. When the discs were applied, they were incubated at 37 °C for 24 h. The zone of inhibition around the disc was then measured in millimetres.

RESULTS AND DISCUSSION

The ligands HL1, HL2, and HL3 were formed by 1 : 1 molar condensation of acetylferrocene with 2-aminophenol, 2-amino-5-picoline or 2-amino-5-chlorophenol respectively (Fig. 1). The ligands are 1-[1-(2-hydroxyphenyl-2-imino)ethyl]-ferrocene (HL1), 1-[1-(2-hydroxy-4-methyl-phenyl-2-imino)ethyl]-ferrocene (HL2), and 1-[1-(4-chloro-2-hydroxyphenyl-2-imino)ethyl]-ferrocene (HL3). The ligands HL1–HL3 are soluble in methanol, DMSO, dichloromethane, and ethanol. They are potential N, O donor ligands containing ferrocenyl groups. They react easily with the cobalt(II), copper(II), nickel(II) and zinc(II) ions to give stable complexes. All of the complexes were prepared in good yield from 2 : 1 equimolar reaction of the ligands and the corresponding metal(II) chloride. The elemental analysis data of the Schiff bases and their complexes are consistent with the calculated results from the empirical formula of each compound (Table 1).

IR spectra

The important IR frequencies of the ligands and their complexes with cobalt, copper, nickel, and zinc, and their assignments, are presented in Table 2. The disappearance of two bands was observed in the preparation of the ligands. The first is the characteristic carbonyl (C=O) group band at 1714 cm^{-1} in acetylferrocene. The second band is the stretching vibration band at 3417 cm^{-1} due to the $\mathrm{NH_2}$ group. These two bands were replaced by a new band in the spectra of the ligands observed at *ca* 1624 cm^{-1} and assigned to the azomethine linkage (C=N).[19,20] This result demonstrated the formation of the Schiff bases HL1–HL3 from the condensation of the amino group of the phenol moiety with the carbonyl group of the acetylferrocene.

In general, the ligands prepared exhibited similar IR features (Table 2). Two strong ligand bands were observed at *ca* 1280 cm^{-1} and 909 cm^{-1}. These bands are assigned to

Table 2. Important IR spectral data of the ligands and their metal(II) complexes

	$\nu(\mathrm{cm}^{-1})$				
Ligand/complex	(OH) in phenol moiety or H_2O	C–O phenolic	($CH_3C{=}N$)	(M–N)	(M–O)
HL1	3433 br	1298 m	1622 s		
$Co(L1)_2{\cdot}2H_2O$	3445 br	1330 m	1631 s	370 w	465 m
$Ni(L1)_2{\cdot}2H_2O$	3450 br	1329 m	1635 s	371 w	463 w
$Cu(L1)_2$		1334 m	1634 s	372 w	462 m
$Zn(L1)_2{\cdot}2H_2O$	3448 br	1329 m	1635 s	372 w	465 m
HL2	3435 br	1304 m	1625 s		
$Co(L2)_2{\cdot}2H_2O$	3450 br	1319 m	1634 s	373 w	465 m
$Ni(L2)_2{\cdot}2H_2O$	3444 br	1328 m	1636 s	372 w	465 w
$Cu(L2)_2$		1324 m	1635 s	373 w	463 m
$Zn(L2)_2{\cdot}2H_2O$	3454 br	1326 m	1634 s	370 w	464 w
HL3	3430 br	1302 m	1624 s		
$Co(L3)_2{\cdot}2H_2O$	3447 br	1336 m	1632 s	371 w	464 m
$Ni(L3)_2{\cdot}2H_2O$	3452 br	1329 m	1636 s	374 w	465 w
$Cu(L3)_2$		1337 m	1635 s	373 w	464 m
$Zn(L3)_2{\cdot}2H_2O$	3451 br	1334 m	1634 s	372 w	465 w

the hydrogen-bonded O–H in-plane and out-of-plane bending vibrations respectively. The spectra of the ligands also showed a broad weak band in the region 2800–2700 $\mathrm{cm^{-1}}$, which confirms an intramolecular hydrogen-bonded OH.[21] These bands were not found in the spectra of the complexes, indicating that the coordination with the different metal ions takes place via the deprotonated OH group of the phenol moiety. This result was confirmed from the shift

Table 3. ^{1}H NMR and ^{13}C NMR data of the ligands and their metal(II) complexes

Ligand/complex	^{1}H NMR (DMSO-d_6), δ (ppm)	^{13}C NMR (DMSO-d_6), δ (ppm)
HL1	2.32 (s, 3H, CH_3), 4.21 (s, 5H, C_5H_5), 4.51 (m, 2H, C_5H_4), 4.74 (m, 2H, C_5H_4), 7.08–7.93 (m, 4H, Ph), 9.74 (s, 1H, OH)	20.6 (CH_3), 68.6 (C_5H_5), 69.4, 73.3, 78.6 (C_5H_4), 146.3 (C=N), 119.2, 127.4, 131.2, 153.5 (Ph)
$Co(L1)_2\cdot 2H_2O$	2.37 (s, 6H, CH_3), 4.30 (s, 10H, C_5H_5), 4.58 (m, 4H, C_5H_4), 4.80 (m, 4H, C_5H_4), 7.10–7.99 (m, 8H, Ph)	21.0 (CH_3), 68.9 (C_5H_5), 69.7, 73.6, 78.8 (C_5H_4), 146.8 (C=N), 119.4, 127.6, 131.4, 153.7 (Ph)
$Ni(L1)_2\cdot 2H_2O$	2.39 (s, 6H, CH_3), 4.29 (s, 10H, C_5H_5), 4.59 (m, 4H, C_5H_4), 4.81 (m, 4H, C_5H_4), 7.11–7.99 (m, 8H, Ph)	21.1 (CH_3), 68.9 (C_5H_5), 69.8, 73.6, 78.8 (C_5H_4), 146.9 (C=N), 119.4, 127.7, 131.5, 153.8 (Ph)
$Cu(L1)_2$	2.38 (s, 6H, CH_3), 4.31 (s, 10H, C_5H_5), 4.58 (m, 4H, C_5H_4), 4.80 (m, 4H, C_5H_4), 7.11–7.98 (m, 8H, Ph)	21.1 (CH_3), 68.9 (C_5H_5), 69.7, 73.6, 78.8 (C_5H_4), 146.9 (C=N), 119.4, 127.6, 131.4, 153.7 (Ph)
$Zn(L1)_2\cdot 2H_2O$	2.39 (s, 6H, CH_3), 4.29 (s, 10H, C_5H_5), 4.59 (m, 4H, C_5H_4), 4.81 (m, 4H, C_5H_4), 7.12–7.99 (m, 8H, Ph)	21.2 (CH_3), 68.9 (C_5H_5), 69.8, 73.6, 78.9 (C_5H_4), 146.8 (C=N), 119.5, 127.6, 131.5, 153.8 (Ph)
HL2	2.21 (s, 3H, CH_3 in Ph), 2.32 (s, 3H, CH_3), 4.20 (s, 5H, C_5H_5), 4.50 (m, 2H, C_5H_4), 4.72 (m, 2H, C_5H_4), 7.09–7.94 (m, 3H, Ph), 9.71 (s, 1H, OH)	20.5 (CH_3), 68.5 (C_5H_5), 69.3, 73.2, 78.6 (C_5H_4), 146.2 (C=N), 119.1, 127.3, 131.1, 153.4 (Ph)
$Co(L2)_2\cdot 2H_2O$	2.24 (s, 6H, CH_3 in Ph), 2.39 (s, 6H, CH_3), 4.27 (s, 10H, C_5H_5), 4.57 (m, 4H, C_5H_4), 4.77 (m, 4H, C_5H_4), 7.13–8.01 (m, 6H, Ph).	21.0 (CH_3), 68.8 (C_5H_5), 69.7, 73.5, 78.9 (C_5H_4), 146.7 (C=N), 119.3, 127.6, 131.4, 153.7 (Ph)
$Ni(L2)_2\cdot 2H_2O$	2.23 (s, 6H, CH_3 in Ph), 2.39 (s, 6H, CH_3), 4.29 (s, 10H, C_5H_5), 4.57 (m, 4H, C_5H_4), 4.78 (m, 4H, C_5H_4), 7.13–8.03 (m, 6H, Ph)	20.9 (CH_3), 68.9 (C_5H_5), 69.7, 73.5, 78.9 (C_5H_4), 146.6 (C=N), 119.3, 127.5, 131.5, 153.6 (Ph)
$Cu(L2)_2$	2.23 (s, 6H, CH_3 in Ph), 2.38 (s, 6H, CH_3), 4.28 (s, 10H, C_5H_5), 4.56 (m, 4H, C_5H_4), 4.78 (m, 4H, C_5H_4), 7.13–8.02 (m, 6H, Ph)	20.9 (CH_3), 68.8 (C_5H_5), 69.7, 73.5, 78.8 (C_5H_4), 146.7 (C=N), 119.3, 127.6, 131.4, 153.7 (Ph)
$Zn(L2)_2\cdot 2H_2O$	2.25 (s, 6H, CH_3 in Ph), 2.38 (s, 6H, CH_3), 4.28 (s, 10H, C_5H_5), 4.57 (m, 4H, C_5H_4), 4.78 (m, 4H, C_5H_4), 7.13–8.03 (m, 6H, Ph)	21.0 (CH_3), 68.9 (C_5H_5), 69.7, 73.5, 78.8 (C_5H_4), 146.7 (C=N), 119.3, 127.5, 131.5, 153.6 (Ph)
HL3	2.32 (s, 3H, CH_3), 4.23 (s, 5H, C_5H_5), 4.53 (m, 2H, C_5H_4), 4.75 (m, 2H, C_5H_4), 7.12–7.96 (m, 3H, Ph), 9.78 (s, 1H, OH)	20.7 (CH_3), 68.6 (C_5H_5), 69.5, 73.4, 78.6 (C_5H_4), 146.3 (C=N), 119.3, 127.6, 131.3, 153.6 (Ph)
$Co(L3)_2\cdot 2H_2O$	2.39 (s, 6H, CH_3), 4.30 (s, 10H, C_5H_5), 4.58 (m, 4H, C_5H_4), 4.81 (m, 4H, C_5H_4), 7.15–8.06 (m, 6H, Ph)	21.1 (CH_3), 69.0 (C_5H_5), 69.9, 73.6, 78.8 (C_5H_4), 146.8 (C=N), 119.6, 127.8, 131.5, 153.8 (Ph)
$Ni(L3)_2\cdot 2H_2O$	2.39 (s, 6H, CH_3), 4.30 (s, 10H, C_5H_5), 4.59 (m, 4H, C_5H_4), 4.80 (m, 4H, C_5H_4), 7.16–8.07 (m, 6H, Ph)	21.1 (CH_3), 68.9 (C_5H_5), 69.9, 73.6, 78.8 (C_5H_4), 146.9 (C=N), 119.7, 127.9, 131.6, 153.9 (Ph)
$Cu(L3)_2$	2.38 (s, 6H, CH_3), 4.31 (s, 10H, C_5H_5), 4.59 (m, 4H, C_5H_4), 4.81 (m, 4H, C_5H_4), 7.15–8.07 (m, 6H, Ph)	21.2 (CH_3), 69.0 (C_5H_5), 69.9, 73.6, 78.8 (C_5H_4), 146.8 (C=N), 119.6, 127.9, 131.6, 153.9 (Ph)
$Zn(L3)_2\cdot 2H_2O$	2.38 (s, 6H, CH_3), 4.30 (s, 10H, C_5H_5), 4.59 (m, 4H, C_5H_4), 4.80 (m, 4H, C_5H_4), 7.15–8.08 (m, 6H, Ph)	21.2 (CH_3), 68.9 (C_5H_5), 69.9, 73.6, 78.8 (C_5H_4), 146.8 (C=N), 119.7, 127.8, 131.6, 153.9 (Ph)

of the C–O stretching vibration (*ca* 1298 cm^{-1} in the ligands) towards higher frequencies (1324–1337 cm^{-1}) in the complexes.[21] The band located at 3450 cm^{-1} in the spectra of the cobalt, nickel, and zinc complexes was assigned to the ν(OH) frequency of the coordinated water molecules associated with these complexes.

The frequency of the (C=N) band in the ligands was shifted to higher frequency (10–15 cm^{-1}) in the complexes, indicating that the coordination of the ligands with the metal ions takes place via the azomethine nitrogen.[21]

In the low-frequency region, two bands were observed for all the complexes at *ca* 370 cm^{-1} and 465 cm^{-1}, which were attributed to ν(M–N) and ν(M–O) respectively. These bands were not found in the spectra of the ligands, suggesting that the coordination of the ligands with the metal ions takes place via the azomethine nitrogen atoms and also via the deprotonated oxygen of the phenol groups.[17,22,23]

The characteristic frequencies of the ferrocenyl moiety in the spectra of the ligands were observed at 3081 cm^{-1}, 1442 cm^{-1}, 1105 cm^{-1}, 830 cm^{-1}, 503 cm^{-1}, and 482 cm^{-1}. These bands were attributed to ν(C–H), ν(C–C), δ(C–H), π(C–H), and δ(Fe–ring) respectively.[24,25] The corresponding frequencies of the complexes appeared at nearly the same position, which indicates that the cyclopentadienyl ring of the ferrocene is not directly coordinated to the metal ion.[24,25]

^{1}H and ^{13}C NMR spectra

The NMR spectra of the ligands (HL1, HL2 and HL3) and their metal(II) chelates were carried out in DMSO-d_6 at room temperature using TMS as internal standard (Table 3). The ^{1}H NMR spectra of the ligands and of the complexes showed two multiplets for the α- and β-protons for the substituted cyclopentadienyl ring, appearing at *ca* 4.7 and 4.5 ppm, and a singlet for the unsubstituted cyclopentadienyl ring at *ca* 4.2 ppm.[24] The signals of the methyl group bonded to the azomethine linkage (C=N) was observed at *ca* 2.3 ppm in the free ligands. These signals were shifted slightly downfield in the spectra of the complexes, which may be due to complexation of the azomethine nitrogen with the metal ion.

The signal observed for the OH protons of the ligands (*ca* 9.7 ppm) was not observed in any of the complexes (Table 3), which confirms the bonding of the phenolic oxygen to the metal ions (C–O–M).[17,21,24] The other signals of the phenyl group in the free ligands and the complexes were found in the expected regions (Table 3). Also, the broad signal at *ca* 1.7 ppm in the cobalt(II), nickel(II), and zinc(II) complexes was assigned to the water of crystallization.

In the ^{13}C NMR spectra, the ligands display a signal at *ca* 20.6 ppm due to the methyl group bonded to the azomethine group, a signal at *ca* 68.6 ppm assigned to the unsubstituted cyclopentadienyl ring, and three signals at 69.4, 73.3 and 78.6 ppm due to the substituted ring. The signal that appeared at *ca* 146.5 ppm was assigned to C=N,[17] and the signals of the phenyl group were found in the expected region at *ca* 119.2, 127.4, 131.2, and 153.5 ppm. These signals were shifted slightly downfield in the spectra of the metal(II) chelates due to complexation and conjugation with the metal ion (Table 3).

Table 4. Electronic spectral data of the prepared metal(II) complexes

Ligand/complex	λ_{max} (nm)			
$Co(L1)_2 \cdot 2H_2O$	578	484		443
$Ni(L1)_2 \cdot 2H_2O$	640	383		448
$Cu(L1)_2$	659	510	329	446
$Zn(L1)_2 \cdot 2H_2O$	350			444
$Co(L2)_2 \cdot 2H_2O$	579	486		447
$Ni(L2)_2 \cdot 2H_2O$	642	385		443
$Cu(L2)_2$	655	512	330	448
$Zn(L2)_2 \cdot 2H_2O$	351			444
$Co(L3)_2 \cdot 2H_2O$	579	485		447
$Ni(L3)_2 \cdot 2H_2O$	640	381		446
$Cu(L3)_2$	658	511	329	448
$Zn(L3)_2 \cdot 2H_2O$	350			445

Electronic spectra

The important electronic spectra of the Schiff bases and their complexes are summarized in Table 4. The electronic spectra of the copper(II) complexes showed three bands at *ca* 659 nm, 510 nm, and 329 nm. The first two bands are assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions respectively.[17,26] The third band is assigned to a metal–ligand charge transfer. These bands are typically characteristic for square-planar[17,26] configuration for copper(II) complexes (Fig. 2a).

The electronic spectra of the cobalt(II) complexes (Table 4) consist of two bands *ca* 579 nm and 485 nm. These bands are assigned to the transitions $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ respectively, and they are characteristic for high-spin octahedral[17,27] geometry for the cobalt(II) complexes (Fig. 2b). The electronic spectra of the nickel(II) complexes also showed two bands at *ca* 640 nm and 383 nm. These bands are assigned[17,26,27] to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ respectively, which are characteristic for octahedral geometry[17,26,27] for the nickel(II) complexes (Fig. 2b). The electronic spectra of the zinc(II) complexes showed one high-intensity band at 350 nm, which was assigned to ligand–metal charge transfer.[17]

Moreover, a broad band at 446 nm observed for each complex was assigned to the transition $^1A_{1g} \rightarrow {}^1E_{1g}$ in the iron atom of the ferrocenyl group, which indicated[28] that there is no magnetic interaction between the cobalt(II), nickel(II), copper(II), and zinc(II) ions and the iron(II) ion of the ferrocenyl group.

On the basis of the physical and spectral data of the complexes discussed above, one can deduce that the metal ions are bonded to the Schiff bases via the deprotonated oxygen atom and the imino nitrogen atom, as illustrated in Fig. 2.

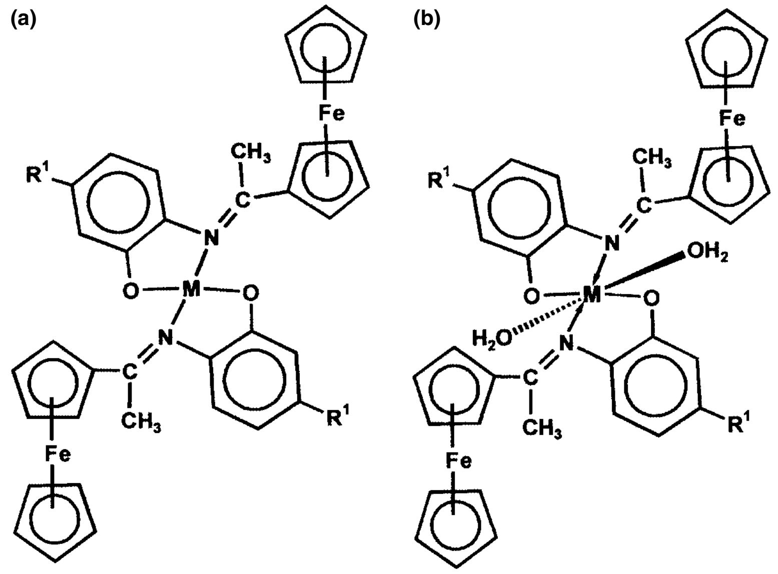

Figure 2. Structure representation of the complexes: (a) M = Cu; (b) M = Co(II), Ni(II) or Zn(II); R^1 = H (L1); CH_3(L2); Cl (L3).

Table 5. Antimicrobial activity data for the ligands and complexes investigated

	Inhibition zone[a]		
Ligand/complex	*Escherichia coli*	*Bacillus subtilis*	*Candida albicans*
HL1	–	–	–
$Co(L1)_2 \cdot 2H_2O$	+	+	++
$Ni(L1)_2 \cdot 2H_2O$	+	++	++
$Cu(L1)_2$	+++	+++	++++
$Zn(L1)_2 \cdot 2H_2O$	+++	+++	++++
HL2	–	–	–
$Co(L2)_2 \cdot 2H_2O$	+++	++	++++
$Ni(L2)_2 \cdot 2H_2O$	++	+++	++++
$Cu(L2)_2$	+++	+++	++++
$Zn(L2)_2 \cdot 2H_2O$	+++	+++	++++
HL3	–	–	–
$Co(L3)_2 \cdot 2H_2O$	+++	+++	+++
$Ni(L3)_2 \cdot 2H_2O$	++	++	+++
$Cu(L3)_2$	+++	+++	+++
$Zn(L3)_2 \cdot 2H_2O$	+++	+++	+++

[a] Inhibition zone diameter (percentage inhibition): +, 6–12 mm (20–43%); ++, 13–19 mm (44–63%); +++, 20–26 mm (64–86%); ++++, 27–30 mm (87–100%). Percentage inhibition values were relative to inhibition zone (30 mm) with 100% inhibition.

Antimicrobial properties

The title Schiff bases and their metal(II) complexes were evaluated for their antimicrobial activity against *E. coli*, *B. subtilus*, and *C. albicans*. The compounds were tested at a concentration of 60 μg ml in $CHCl_3$ solution using the paper disc diffusion method.[2,29] The diameter of the susceptibility zones was measured in millimeters and the results are given in Table 5. The susceptibility zones measured were the clear zones around the discs inhibiting the microbial growth. All the ligands were found to be microbially inactive, but the complexes showed significant antimicrobial activity. It is known that chelation tends to make the ligands act as more powerful and potent bactericidal agents, than the parent Schiff bases. A possible explanation[2,30] is that, in the chelated complex, the positive charge of the metal is partially shared with the donor atoms in the ligands and there is π-electron delocalization over the whole chelate ring. This, in turn, increases the lipophilic character of the metal chelate and favours its permeation through the lipoid layers of the microorganism membranes. Apart from this, factors such as solubility, conductivity, and dipole moment (influenced by the presence of metal ions) may also be possible reasons for this increased activity.[2,30]

Acknowledgment

I would like to thank Professor H. Fischer for providing laboratory facilities at Constance University (Germany), and thank Mr Ahmed A. El-Beih, Chemistry of Natural and Microbial Products Department, NRC, for his help in undertaking the antimicrobial studies.

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