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Synthesis, characterization and antibacterial properties of symmetric 1,1′-ferrocene derived Schiff-base ligands and their Co(II), Cu(II), Ni(II) and Zn(II) chelates

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Symmetric 1,1′-dimethylferrocene derived Schiff-base ligands have been prepared by the condensation reaction of 1,1′-diacetylferrocene with 2-aminopyrazine, 2-aminopyridine and 2-aminothiazole respectively. Their transition metal chelates, of the type $[M(L)]Cl_2$ [M = Cu(II)] and $[M(L)(Cl_2)]$ [M = Co(II), Ni(II) and Zn(II)] have been prepared. The synthesized Schiff-base ligands and their metal(II) chelates have been characterized by their physical, analytical and spectral data. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: ferrocene derivatives; Schiff-base ligands; metal chelates; coordination; antibacterial

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INTRODUCTION

In the past few years a number of studies[1,2] have highlighted the use and extensive substituent chemistry[3–5] of ferrocene. The heterocyclic system based chalcogens, (O, N or S) and their various Schiff-base compounds have widespread applications[6–8] as key precursors in contemporary organic chemistry. The possibility of combining the chemistry of organometallics and heterocyclic systems has previously gained less attention. Only a few reports have indicated[9,10] that replacement of aromatic groups by the ferrocenyl moiety in penicillin and cephalosporin antibiotics improves their antibacterial properties. These considerations attracted our attention and we have previously reported[11] monosubstituted ferrocene derived pyrazinoyl and nicotinoyl Schiff bases and their application as antibacterial agents. We now thought it worthwhile to use both cyclopentadienyl ring systems to prepare symmetric 1,1′-ferrocene derived Schiff-base ligands (Fig. 1) and study their ligational and antibacterial behavior with Co(II), Cu(II), Ni(II) and Zn(II) species. These studies would make it possible to design and prepare useful multifunctional organometallic-based antibacterial agents.

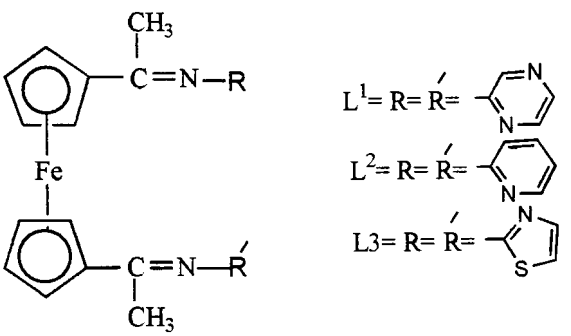

Figure 1 Structure of the symmetric 1,1′-ferrocene derived Schiff-base ligands.

EXPERIMENTAL

Methods and materials

All solvents used were Analar grade, 1,1′-Diacetylferrocene, 2-aminopyrazine, 2-aminopyridine and 2-aminothiazole were obtained from Merck. All metals were used as chlorides. IR, ^{1}H NMR and ^{13}C NMR spectra were recorded on Perkin-Elmer 283B and 300 MHz Varian XL-300 instruments.

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UV–visible spectra were obtained on a Baush and Lomb Spectronic 1001. Conductance of the metal complexes was determined in DMF using a YSI-32 model conductometer. Magnetic measurements were performed on solid complexes by the Gouy method. Microanalyses were carried out by Butterworth Laboratories Ltd. Melting points were recorded on a Gallenkamp apparatus and are uncorrected.

Antibacterial studies were carried out with the help of Microbiology Department, Qaid-e-Azam Medical College, Bahawalpur, Pakistan. These studies were done on wild pathogenic bacterial species collected from urine and blood samples of infected patients admitted to Bahawal Victoria Hospital, Bahawalpur.

Synthesis of ligands L^1, L^2 and L^3

For the preparation of L^1, a solution of 2-aminopyrazine (0.89 g, 10 mmol) in ethanol (30 cm^3) was added to a magnetically stirred solution of 1,1′-diacetylferrocene (1.35 g, 5 mmol) in ethanol (20 cm^3). The mixture was refluxed for 2 h. The dark orange precipitated product formed during reflux was cooled to room temperature. It was filtered, washed with cold ethanol and dried. The product thus obtained was recrystallized from a mixture of hot ethanol and chloroform to give L^1. A similar method was used for the preparation of L^2 and L^3.

Synthesis of metal complexes

To a magnetically stirred and warmed solution of ligand (1.0 mmol) in ethanol (30 cm^3) was added a solution of metal(II) chloride (1.0 mmol) in ethanol (20 cm^3). The mixture was refluxed for 2.5 h. During this time, a complex was precipitated which, upon cooling, was filtered, washed several times with warm ethanol and diethyl ether and then dried over anhydrous $CaCl_2$. All other complexes were prepared similarly using the same method.

Preparation of disc

The ligand/complex (30 μg) in DMF (0.01 cm^3) was applied to a paper disc [prepared from blotting paper (3 mm diameter)] with the help of a micropipette. The discs were left in an incubator for 48 h at 37 °C and then applied to the bacteria grown agar plates.

Preparation of agar plates

Minimal agar was used for the growth of specific bacterial species. For the preparation of agar plates for *Escherichia coli*, MacConkey agar (50 g), obtained from Merck Chemical Co., was suspended in freshly distilled water (1 litre). It was allowed to soak for 15 min and then boiled on a water bath until the agar was 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 40 °C for inoculation.

Inoculation procedure

Inoculation was done via a platinum wire loop which was made red hot in a flame, cooled and then used for the application of bacterial strains.

Application of discs

Sterilized forceps were used for the application of the paper discs to the already-inoculated agar plates. The discs were then incubated at 37 °C for 24 h. The diameter of the zone of inhibition was measured around the disc.

Table 1 Physical, spectral and analytical data of the ligands

Ligand	Mol. formula	M.p. (°C)	IR, (νcm^{-1})	Analysis (%): Calcd (Found) C	H	N	Yield (%)
L^1	$C_{22}H_{20}FeN_6$	423.85	188	1625 (C=N), 1575, 1515, 1170, 955	62.3 (62.5)	4.7 (4.4)	19.8 (20.1)	80
L^2	$C_{24}H_{22}FeN_4$	421.85	176	1620 (C=N), 1580, 1525, 1175, 1065, 955	68.3 (68.5)	5.2 (5.0)	13.3 (13.6)	78
L^3	$C_{20}H_{18}FeN_4S_2$	433.97	183	1625 (C=N), 1580, 1525, 1325, 1170, 955	55.3 (55.6)	4.1 (4.5)	12.9 (13.2)	82

Table 2 Physical, analytical and spectral data of metal complexes

Complex	Mol. formula	M.p. (°C)	IR: (νcm^{-1})	λ_{max}(cm^{-1})	Magnetic moment (B.M)	Analysis (%): Calcd (Found) C	H	N
1 $[Co(L^1)(Cl_2)]$	553.68	232–234	1630 (C=N), 372 (M—N), 305 (M—Cl)	7545, 17 255, 20 530, 22 415	3.9	47.7 (47.9)	3.6 (3.3)	15.2 (15.5)
2 $[Cu(L^1)]Cl_2$	558.29	241–243	1635 (C=N), 370 (M—N)	15 170, 19 605, 22 415, 30 345	1.7	47.3 (47.7)	3.6 (3.2)	15.0 (15.3)
3 $[Ni(L^1)(Cl_2)]$	553.44	218–220	1630 (C=N), 372 (M—N) 305 (M—Cl),	10 210, 15 565 22 415, 26 245,	3.2	47.7 (48.0)	3.6 (3.5)	15.2 (15.5)
4 $[Zn(L^1)(Cl_2)]$	560.13	220–222	1630 (C=N), 372 (M—N) 305 (M—Cl),	22 415, 28 255	Dia[a]	47.1 (47.2)	3.6 (3.8)	15.0 (15.2)
5 $[Co(L^2)(Cl_2)]$	551.68	215–217	1630 (C=N), 372 (M—N) 305 (M—Cl),	7615, 17 290, 20 765, 22 415	4.1	52.2 (52.5)	4.0 (4.3)	10.2 (9.8)
6 $[Cu(L^2)]Cl_2$	556.29	224–226	1635 (C=N), 370 (M—N),	15 190, 19 585, 22 415, 30 425	1.9	51.8 (51.5)	4.0 (3.8)	10.1 (10.5)
7 $[Ni(L^2)(Cl_2)]$	551.44	220–222	1630 (C=N), 372 (M—N) 305 (M—Cl),	10 865, 15 715, 22 415, 26 550	2.9	52.2 (52.4)	4.0 (4.3)	10.2 (10.6)
8 $[Zn(L^2)(Cl_2)]$	558.13	212–214	1630 (C=N), 372 (M—N), 305 (M—Cl)	22 415, 29 115	Dia[a]	51.6 (51.3)	4.0 (4.2)	10.0 (10.4)
9 $[Co(L^3)(Cl_2]$	563.8	215–217	1630 (C=N), 372 (M—N), 305 (M—Cl)	7585, 17 275, 22 415, 20 680	4.0	42.6 (42.8)	3.2 (3.3)	10.0 (9.9)
10 $[Cu(L^3)]Cl_2$	568.41	224–226	1635 (C=N), 370 (M—N),	15 185, 19 600, 22 415, 30 390	1.8	42.2 (42.5)	3.2 (3.0)	9.9 (9.6)
11 $[Ni(L^3)(Cl_2)]$	563.56	220–222	1630 (C=N), 372 (M—N), 305 (M—Cl)	10 615, 15 610, 22 415, 26 345	3.1	42.6 (42.8)	3.2 (3.5)	10.0 (10.4)
12 $[Zn(L^3)(Cl_2)]$	570.25	218–220	1630 (C=N), 372 (M—N), 305 (M—Cl)	22 415, 28 870	Dia[a]	42.1 (42.2)	3.2 (3.1)	9.8 (9.5)

[a] Diamagnetic.

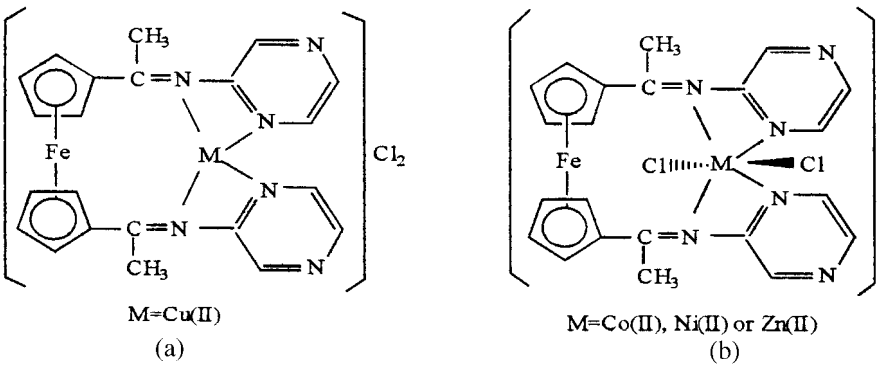

Figure 2 Proposed structures for the metal(II) chelates of L^1–L^3.

RESULTS AND DISCUSSION

The ligands were soluble in methanol and ethanol. All the metal complexes dissolved only in DMF and DMSO. All of them were amorphous solid. The molar conductances of the metal complexes (12.2–13.5 $\Omega\,cm^2\,mol^{-1}$) in DMF solution showed all the complexes to be non-electrolytes.[12]

IR spectra

The important IR frequencies of the ligands and their complexes along with their assignments are given in Tables 1 and 2. The IR spectrum of the ligand is almost identical to those of its metal complexes in the 650–1500 cm^{-1} region, except that the bands due to pyrazine, pyridine and thiazole ring vibrations at 1565–1580 cm^{-1} in the ligand moves to slightly higher frequency (5–10 cm^{-1}) in the spectra of the metal complexes. This in turn suggests that coordination take place through the pyrazine, pyridine and thiazole ring nitrogens to the metal atom. Also, disappearance of a band at 3150 cm^{-1} due to $\nu(NH_2)$ in the spectrum of the ligand and appearance instead of a new band due to an azomethine linkage (C=N) at 1620–1625 cm^{-1} clearly suggests[13,14] the formation of the proposed Schiff-base compounds (L^1–L^3). The shifting of the azomethine band to higher frequency (10–15 cm^{-1}) provides further support for the involvement of the azomethine nitrogen with the metal atom. Moreover for all the complexes, in the far-infrared region a band at ~370 cm^{-1} attributed to (ν M-N) is observed (Table 2) which is not found in the spectrum of the free ligand. However, this suggests[15] that ring nitrogen and azomethine nitrogen atoms are involved in complex formation.

Also, a weak band at 305 cm^{-1} was found in the spectra of the Co(II), Ni(II) and Zn(II) complexes due to the ν(M—Cl) mode, but was not observed in the spectrum of the Cu(II) complex. This suggests[16] a square-planar geometry for the Cu(II) complex (Fig. 2a) and an octahedral geometry for the Co(II), Ni(II) and Zn(II) complexes (Fig. 2b).

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

The ^{1}H NMR and ^{13}C NMR spectra of the free ligands and their metal(II) chelates were determined in DMSO-d_6. The ^{1}H NMR spectra of the free ligand (Table 3) exhibited signals due to the methyl group bonded to the azomethine (C=N) linkage and other substituted ferrocenyl and heteroaromatic groups (Table 3).

The protons due to the pyrazine, pyridine and thiazole rings were found to be in the expected region. The protons due to the ferrocenyl moiety were also found in the same expected region as reported[17] earlier. The protons shifted downfield due to increased conjugation and coordination to the metal atoms. The ^{13}C NMR spectra of the ligand and its metal complexes (Table 3) indicate the same behavior. All the carbons were found to be shifted downfield in the spectra of their metal complexes. However all the carbons were found in their expected region, which by comparison with the reported[18] values helped in establishing these structures.

It was also observed that DMSO did not have any coordinating effect either on the ligands or on their complexes.

Table 3 ^{1}H NMR and ^{13}H 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)
L^1	2.4 (s, 6H, CH_3), 4.5–4.6 (m, 4H ferrocenyl), 4.7–4.9 (m, 4H ferrocenyl), 8.3–8.4 (m, 2H, pyrazine), 8.5–8.6 (m. 4H, pyrazine)	22.6 (CH_3), 68.7, 69.5, 83.7 (ferrocenyl), 141.3 (C=N), 145.6, 147.5, 149.2, 153.3 (pyrazine)
L^2	2.3 (s, 6H, CH_3), 4.5–4.6 (m, 4H ferrocenyl), 4.6–4.8 (m, 4H, ferrocenyl), 7.8–7.9 (m, 2H, pyridine), 8.1–8.3 (m, 1H, pyridine), 8.5–8.7 (m, 1H, pyridine)	22.4 (CH_3), 68.6, 69.5, 83.3 (ferrocenyl), 141.1 (C=N), 144.1, 145.7, 147.5, 149.6 (pyridine), 153.3 (HC=N)
L^3	2.5 (s, 6H, CH_3), 4.5–4.9 (m, 4H, ferrocenyl), 4.7–4.8 (m, 4H, ferrocenyl), 8.8–9.0 (m, 2H, thiazole)	22.6 (CH_3), 68.7, 69.5, 83.4 (ferrocenyl), 118.5 (thiazole), 141.3 (C=N), 143.3 (thiazole), 152.7 (thiazole), 153.3 (HC=N)
1	2.5 (s, 6H, CH_3), 4.5–4.8 (m, 4H, ferrocenyl), 4.9–5.1 (m, 4H, ferrocenyl), 8.6–8.8 (m, 2H, pyrazine), 8.8–8.9 (m, 4H, pyrazine)	22.8 (CH_3), 68.9, 69.8, 83.9 (ferrocenyl), 141.5 (C=N), 145.8, 147.7, 149.5, 153.8 (pyrazine)
2	2.5 (s, 6H, CH_3), 4.5–4.7 (m, 4H, ferrocenyl), 4.8–4.9 (m, 4H, ferrocenyl), 8.8–8.8 (m, 2H, pyrazine), 9.0–9.1 (m, 4H, pyrazine)	22.9 (CH_3), 68.9, 69.9, 84.0 (ferrocenyl), 141.5 (C=N), 145.8, 147.7, 149.5, 153.6 (pyrazine)
3	2.4 (s, 6H, CH_3), 4.5–4.7 (m, 4H, ferrocenyl), 4.8–4.9 (m, 4H, ferrocenyl), 8.9–9.0 (m, 2H, pyrazine), 9.0–9.2 (m, 4H, pyrazine)	22.8 (CH_3), 68.9, 69.8, 83.9 (ferrocenyl), 141.5 (C=N), 145.8, 147.9, 149.7, 153.6 (pyrazine)
4	2.5 (s, 6H, CH_3), 4.5–4.7 (m, 4H, ferrocenyl), 4.8–5.0 (m, 4H, ferrocenyl), 8.7–8.9 (m, 2H, pyrazine), 9.0–9.2 (m, 4H, pyrazine)	22.8 (CH_3), 68.9, 69.9, 83.8 (ferrocenyl), 141.5 (C=N), 145.8, 147.9, 149.6, 153.7 (pyrazine)
5	2.4 (s, 6H, CH_3), 4.5–4.7 (m, 4H, ferrocenyl), 4.8–4.9 (m, 4H, ferrocenyl), 7.9–8.1 (m, 2H, pyridine), 8.3–8.5 (m, 1H, pyridine), 8.6–8.9 (m, 1H, pyridine)	22.9 (CH_3), 69.0, 69.7, 83.8 (ferrocenyl), 141.3 (C=N), 144.6, 145.9, 147.8, 149.9, (pyridine), 153.8 (HC=N).
6	2.4 (s, 6H, CH_3), 4.5–4.7 (m, 4H, ferrocenyl), 4.8–4.9 (m, 4H, ferrocenyl), 8.0–8.2 (m, 2H, pyridine), 8.3–8.5 (m, 1H, pyridine), 8.6–8.8 (m, 1H, pyridine)	22.8 (CH_3), 68.9, 69.6, 83.8 (ferrocenyl), 141.4 (C=N), 144.4, 145.9, 147.9, 149.8, (pyridine), 153.9 (HC=N)
7	2.4 (s, 6H, CH_3), 4.5–4.8 (m, 4H, ferrocenyl), 4.6–4.7 (m, 4H, ferrocenyl), 8.1–8.2 (m, 2H, pyridine), 8.4–8.7 (m, 1H, pyridine), 8.8–9.0 (m, 1H, pyridine)	22.9 (CH_3), 68.8, 69.9, 83.8 (ferrocenyl), 141.3 (C=N), 144.5, 145.8, 147.9, 149.9, (pyridine), 153.8 (HC=N)
8	2.4 (s, 6H, CH_3), 4.6–4.7 (m, 4H, ferrocenyl), 4.8–4.9 (m, 4H, ferrocenyl), 8.0–8.2 (m, 2H, pyridine), 8.4–8.8 (m, 1H, pyridine), 9.0–9.2 (m, 1H, pyridine)	22.9 (CH_3), 68.9, 69.8, 83.7 (ferrocenyl), 141.3 (C=N), 144.5, 145.8, 147.9, 149.8, (pyridine), 153.7 (HO=N)
9	2.6 (s, 6H, CH_3), 4.8–4.9 (m, 4H, ferrocenyl), 4.8–5.0 (m, 4H, ferrocenyl), 9.0–9.2 (m, 2H, thiazole)	22.8 (CH_3), 68.9, 69.8, 83.9 (ferrocenyl), 118.8 (thiazole), 141.5 (C=N), 143.8 (thiazole), 153.0 (thiazole), 153.8 (HC=N)
10	2.6 (s, 6H, CH_3), 4.7–4.8 (m, 4H, ferrocenyl), 4.9–5.0 (m, 4H, ferrocenyl), 9.1–9.3 (m, 2H, thiazole)	22.9 (CH_3), 69.0, 69.8, 83.7 (ferrocenyl), 118.9 (thiazole), 141.6 (C=N), 143.8 (thiazole), 153.1 (thiazole), 153.7 (HC=N)
11	2.6 (s, 6H, CH_3), 4.6–4.7 (m, 4H, ferrocenyl), 4.8–4.9 (m, 4H, ferrocenyl), 9.1–9.2 (m, 2H, thiazole)	22.8 (CH_3), 68.8, 69.9, 83.8 (ferrocenyl), 118.8 (thiazole), 141.5 (C=N), 143.7 (thiazole), 153.1 (thiazole), 153.6 (HC=N)
12	2.6 (s, 6H, CH_3), 4.7–4.9 (m, 4H, ferrocenyl), 4.9–5.0 (m, 4H, ferrocenyl), 9.1–9.3 (m, 2H, thiazole)	22.8 (CH_3), 68.9, 69.7, 83.9 (ferrocenyl), 118.8 (thiazole), 141.6 (C=N), 143.7 (thiazole), 153.0 (thiazole), 153.7 (HC=N)

Table 4 Antibacterial activity[a] of the ligands and their complexes

Ligand/ complex	Microbial species			
	E. coli	*S. aureus*	*P. aeruginosa*	*K. pneumonae*
L^1	+++	++	++	++
L^2	+	++	−	++
L^3	+++	++	+++	++
1	+++	+++	++	+++
2	++	+++	++	++
3	++++	++	+++	+++
4	+++	++	+++	++
5	++	++	++	++
6	++	++	+	++
7	+++	+++	++	++
8	++	++	++	+++
9	++++	++	+++	+++
10	++	+++	++	+++
11	++	++	++	+++
12	++	+++	+++	+++

[a] Inhibition zone diameter (mm) [% inhibition]: +, 6–10 (27–45%); ++ 10–14 [45–64%]; +++, 14–18 [64–82%]; ++++, 18–22 [82–100%]. Percentage inhibition values are relative to the inhibition zone (22 mm) of the most active compound with 100% inhibition.

Electronic spectra and magnetic moments

The electronic spectra of the Cu(II) complexes (Table 2) showed two low-energy weak bands at 15 170–15 190 and 19 585–19 605 cm^{-1} and a strong high-energy band at 30 345–30 425 cm^{-1}. The low-energy bands in this position typically are expected for its square-planar configuration and may be assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively.[19,20] The strong high-energy band, in turn is assigned to a metal → ligand charge transfer. Also, the magnetic moments (1.7–1.9 B.M) of Cu(II) complexes were found to be consistent with the proposed square-planar structure of Cu(II) complexes (Fig. 2a).

The Co(II) complexes exhibited well-resolved low-energy bands at 7545–7615 and 17 255–17 290 cm^{-1} and a strong high-energy band at 20 530–20 765 cm^{-1} assigned to the transitions $T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ for high-spin octahedral geometry.[21,22] The magnetic susceptibility measurements (3.9–4.2 B.M) for the Co(II) solid complexes are also indicative of three unpaired electrons per Co(II) ion, suggesting[23] consistency for their octahedral environment (Fig. 2b).

The electronic spectra of the Ni(II) complexes showed *d–d* bands in the 26 245–26 550, 15 565–15 715 and 10 210–10 865 cm^{-1} regions. These are assigned[24] to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(P)$ respectively, consistently with their well-defined octahedral configuration. The magnetic measurements (2.9–3.2 B.M) showed two unpaired electrons per Ni(II) ion, also suggesting[25] an octahedral geometry for the Ni(II) complexes (Fig 2b).

The electronic spectra of the Zn(II) complexes exhibited only a high-intensity band at 28 255–29 115 cm^{-1} assigned[23] to ligand–metal charge transfer.

Furthermore, a broad band centered at 22415 cm^{-1} observed for every complex was assigned to the transition $^1A_{1g} \rightarrow {}^1E_{1g}$ in the iron atom of the ferrocenyl group, which indicated[20] that there is no magnetic interaction between the Cu(II), Co(II), Ni(II) and Zn(II) ions and the diamagnetic Fe(II) ion of the ferrocenyl group.

Similar structures were proposed for the metal(II) cheletes of L^2 and L^3, as shown in Fig. 2.

Antibacterial properties

The antibacterial properties of the ligands and their metal complexes were studied against the bacterial species *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Klebsiella pneumonae*. These were tested at a concentration of 30 μg/0.01 cm^3 in DMF solution using a paper-disc

diffusion method devised and reported[26,27] earlier. The results of these studies, reproduced in Table 4, indicated that both the Schiff-base ligands and their metal complexes showed variable activity against one or more bacterial strains. In comparison with the ligands, the metal complexes were found to be more biologically active. These studies however, provided useful information about the biological activity of ferrocene-containing compounds with the possibility that this activity could become more pronounced when more potent compounds were coupled with ferrocene molecules thereby introducing a new class of biologically active compounds.

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