APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 911–916
Published online 17 June 2005 in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.927

Synthesis, characterization and biological studies of ferrocenyl complexes containing thiophene moiety

Mokhles M. Abd-Elzaher[1]*, Wael H. Hegazy[2] and Alaa El-Din M. Gaafar[3]

[1]Inorganic Chemistry Department, National Research Centre, PO 12622 Dokki, Cairo, Egypt
[2]Ministry of Education, College of Education for Girls (Scientific Departments), Chemistry Department, Al-Ahsa, Saudi Arabia
[3]Photochemistry Department, National Research Centre, PO 12622 Dokki, Cairo, Egypt

Received 20 February 2005; Accepted 21 March 2005

A new ferrocenyl ligand was prepared from the condensation of 1,1′-diacetylferrocene dihydrazone with 2-thiophenealdehyde. The ligand, 1,1′-bis[(2-thienylmethylidene)hydrazono-1-ethyl]ferrocene, forms 1 : 1 complexes with cobalt(II), nickel(II), copper(II) and zinc(II) in good yield. Characterization of the ligand and complexes was carried out using IR, ^{1}H NMR, electronic absorption and elemental analysis. Biological activity of the ligand and its complexes was assessed against *Bacillus subtilis* (+ve), *Staphylococcus aureus* (+ve), *Candida albicans* (yeast), *Esherichia coli* (−ve), *Salmonella typhi* (−ve), *Aspergillus niger* (fungi), and *Fusarium solani* (fungi). The biological results indicated that the complexes prepared are more active than the ligand. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: diacetylferrocene dihydrazone; thiophenealdehyde; complexes; characterization; biological activity

INTRODUCTION

The chemistry of ferrocene attracted a great interest in the last decade.[1–8] This interest may be due to the wide application of ferrocenyl compounds in catalysis,[9–12] in the design of new nonlinear optics materials,[13,14] or in the preparation of new biologically active compounds.[15,16] In medicine, ferrocene derivatives have shown good activity against several types of cancer.[17–25] The best example of these derivatives is ferrocifen, which is biologically active against some types of cancer and expected to enter phase I clinical trials very soon.[1,24,25] An excellent review has recently been published, summarizing the important bioorganometallic compounds (including ferrocene) and their pharmaceutical application.[1]

These interesting applications of the ferrocenyl compounds attracted us to continue our previous studies[26,27] on the heterobimetallic complexes since some ferrocenyl complexes show more biological activity than the parent ligand. The aim of this article is to prepare and characterize a new ferrocenyl ligand derived from condensation of 1,1′-diacetylferrocene dihydrazone with 2-thiophenealdehyde. The study have been extended to prepare and characterize the cobalt(II), nickel(II), copper(II) and zinc(II) complexes with the ligand mentioned in order to obtain the heterobimetallic complexes. The ligand and its complexes prepared have been characterized by IR, ^{1}H NMR, UV–Vis spectra and elemental analysis. The complexes prepared showed good antimicrobial activity against *Bacillus subtilis* (+ve), *Staphylococcus aureus* (+ve), *Candida albicans* (yeast), *Esherichia coli* (−ve), *Salmonella typhi* (−ve), *Aspergillus niger* (fungus), and *Fusarium solani* (fungus).

*Correspondence to: Mokhles M. Abd-Elzaher, Inorganic Chemistry Department, National Research Centre, PO Box 12622, Dokki, Cairo, Egypt.
E-mail: mokhlesm20@yahoo.com
Contract/grant sponsor: Alexander von Humboldt Foundation.

EXPERIMENTAL

All chemicals and solvents are obtained from Merck. 1,1′-Diacetylferrocene was prepared by the literature method.[28] The yields refer to analytically pure compounds and were not optimized. Melting points were taken on a capillary melting-point apparatus and are uncorrected. ^{1}H NMR spectra were recorded with a JEOL EX-270 MHz FT NMR spectrometer in $CDCl_3$ as a solvent. IR spectra were recorded on a Perkin Elmer (Spectrum 1000) FT-IR spectrometer, using KBr pellets. Elemental analyses were determined at the Microanalytical Centre, Cairo University. Electronic absorptions were recorded on a Shimadzu UV240 automatic spectrophotometer in $CHCl_3$.

Synthesis of the 1,1′-diacetylferrocene dihydrazone

2.16 g of 1,1′-diacetylferrocene (8.0 mmol) was dissolved in small amount of dry ethanol and stirred in hydrazine hydrate

(70 ml) for about 48 h at room temperature under nitrogen. The colour begins to change from reddish brown to orange within 6 h and the stirring continued for 48 h. The orange product was filtered, washed with cold ethanol and dried under vacuum. Yield: 2.19 g (92%). Anal. Found: C, 56.4; H, 6.1; N, 18.0. Calc.: C, 56.3; H, 6.2; N, 18.1%. M.p. 184 °C. IR (cm^{-1}): 3340, 3205 (–NH_2), 1590 (–C═N). ^1H NMR (δ ppm, $CDCl_3$): 1.97 (s, 6H, $2CH_3$), 4.25 (m, 4H, Cp ring), 4.50 (m, 4H, Cp ring), 5.08 (br-s, 4H, NH_2). UV–Vis (MeOH): 448 nm.

Synthesis of the ligand L

2.03 ml (22 mmol) of 2-thiophenealdehyde was slowly added to a magnetically stirred solution of 1,1′-diacetylferrocene dihydrazone (2.98 g, 10 mmol) in 30 ml methanol. The mixture was refluxed for 2 h. Concentration of the solution to the appropriate volume and cooling at 5 °C yield the ligand L, which was filtered, washed with cold methanol and dried.

The ligand, 1,1′-bis[(2-thienylmethylidene)hydrazono-1-ethyl]ferrocene

$C_{24}H_{22}FeN_4S_2$ (486.45), Yield: 64%. Anal. Found: C, 59.08; H, 4.67; N, 11.43. Calc.: C, 59.26; H, 4.56; N, 11.52%. M.p. 89 °C. IR (cm^{-1}): 1659 s (–C═N), 1520 s (–C═C thiophene); 854 m (C–S–C ring); 1043 m (N–N). ^1H NMR (δ ppm, $CDCl_3$): 2.21 (s, 6H, $2CH_3$), 4.21 (m 4H, C_5H_4), 4.43 (m, 4H, C_5H_4), 6.71–7.55 (m, 6H thiophene ring), 8.36 (s, 2H, H–C═N). UV–Vis ($CHCl_3$): 456 nm.

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 ethanol, to a warmed solution of the ligand (2.0 mmol of L) in methanol (20 ml). The mixture was refluxed for 2.0 h. The complex, which separated out with cooling at 5 °C, was filtered, washed twice with cold ethanol and dried.

1,1′-Bis[(2-thienylmethylidene)hydrazono-1-ethyl] ferrocene dichlorocobalt(II)

$C_{24}H_{22}Cl_2CoFeN_4S_2$ (616.28). Yield: 67%. Anal. Found: C, 46.86; H, 3.63; N, 8.94. Calc.: C, 46.77; H, 3.60; N, 9.09%. M.p. 203 °C. IR (cm^{-1}): 1632 s (–C═N), 1506 s (–C═C thiophene); 842 m (C–S–C ring); 1060 m (N–N); 421 w (Co–N); 592 w (Co–S). ^1H NMR (δ ppm, $CDCl_3$): 2.27 (s, 6H, $2CH_3$), 4.30 (m 4H, C_5H_4), 4.49 (m, 4H, C_5H_4), 6.78–7.64 (m, 6H thiophene ring), 8.45 (s, 2H, H–C═N). UV–Vis ($CHCl_3$): 560, 486, 450 nm.

1,1′-Bis[(2-thienylmethylidene)hydrazono-1-ethyl] ferrocene dichloronickel(II)

$C_{24}H_{22}Cl_2FeN_4NiS_2$ (616.04). Yield: 61%. Anal. Found: C, 46.93; H, 3.72; N, 8.88. Calc.: C, 46.79; H, 3.60; N, 9.09%. M.p. 208 °C. IR (cm^{-1}): 1638 s (–C═N), 1508 s (–C═C thiophene); 843 m (C–S–C ring); 1056 m (N–N); 418 w (Ni–N); 588 w (Ni–S). ^1H NMR (δ ppm, $CDCl_3$): 2.25 (s, 6H, $2CH_3$), 4.31 (m 4H, C_5H_4), 4.50 (m, 4H, C_5H_4), 6.79–7.64 (m, 6H thiophene ring), 8.47 (s, 2H, H–C═N). UV–Vis ($CHCl_3$): 531, 490, 452 nm.

1,1′-Bis[(2-thienylmethylidene)hydrazono-1-ethyl] ferrocene dichlorocopper(II)

$C_{24}H_{22}Cl_2CuFeN_4S_2$ (620.90). Yield: 65%. Anal. Found: C, 46.68; H, 3.65; N, 8.75. Calc.: C, 46.43; H, 3.57; N, 9.02%. M.p. 198 °C. IR (cm^{-1}): 1622 s (–C═N), 1508 s (–C═C thiophene); 845 m (C–S–C ring); 1056 m (N–N); 415 w (Cu–N); 582 w (Cu–S). ^1H NMR (δ ppm, $CDCl_3$): 2.27 (s, 6H, $2CH_3$), 4.27 (m 4H, C_5H_4), 4.49 (m, 4H, C_5H_4), 6.78–7.66 (m, 6H thiophene ring), 8.45 (s, 2H, H–C═N). UV–Vis ($CHCl_3$): 647, 513, 450, 332 nm.

1,1′-Bis[(2-thienylmethylidene)hydrazono-1-ethyl] ferrocene dichlorozinc(II)

$C_{24}H_{22}Cl_2FeN_4S_2Zn$ (737.77). Yield: 63%. Anal. Found: C, 46.42; H, 3.42; N, 8.77. Calc.: C, 46.29; H, 3.56; N, 9.00%. M.p. 235 °C. IR (cm^{-1}): 1626 s (–C═N), 1510 s (–C═C thiophene); 841 m (C–S–C ring); 1054 m (N–N); 418 w (Zn–N); 586 w (Zn–S). ^1H NMR (δ ppm, $CDCl_3$): 2.26 (s, 6H, $2CH_3$), 4.27 (m 4H, C_5H_4), 4.49 (m, 4H, C_5H_4), 6.78–7.68 (m, 6H thiophene ring), 8.47 (s, 2H, H–C═N). UV–Vis ($CHCl_3$): 354, 447 nm.

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 till dryness and then applied on the microorganism-grown agar plates.

Preparation of agar plates

Minimal agar was used for the growth of specific microbial species. The preparation of agar plates for *B. subtilis*, *S. aureus*, *E. coli* and *S. typhi* (bacteria) utilized nutrient agar (2.30 g; obtained from Panreac Quimica SA, Spain) suspended in freshly distilled water (100 ml), and potato dextrose agar medium (3.9 g/100 ml; obtained from Merck) for *C. albicans* (yeast), *A. niger* and *F. solani* (fungi). This 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 30 °C for inoculation.

Procedure of inoculation

Inoculation was done with the help of a platinum wire loop, which was heated to red-hot 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 for bacteria

and yeast, and at 28 °C for 48 h for fungi. The zone of inhibition around the disc was then measured in millimetres.[27]

RESULTS AND DISCUSSION

Synthesis and characterization of the ligand

1,1′-Diacetylferrocene dihydrazone was prepared by dissolving 1,1′-diacetylferrocene in small amount of dry ethanol and in presence of excess of hydrazine hydrate while stirring under nitrogen atmosphere (Fig. 1). The IR spectra of the dihydrazone prepared showed a medium band at 1659 cm^{-1}, which was assigned to the formation of the C═N group. In addition, the frequency of the two NH_2 groups appeared as a broad band in the IR spectra at about 3340 to 3205 cm^{-1}.[29] This result was confirmed from the broad band appearing in the ^1H NMR spectrum at 5.08 ppm, which was assigned to the NH_2 group. 1,1′-Diacetylferrocene dihydrazone was prepared previously by reflux in ethanol,[29] and by Casey *et al*.[30] at room temperature.

The ligand L, 1,1′-bis[(2-thienylmethylidene)hydrazono-1-ethyl]ferrocene (Fig. 1), was prepared by addition of 2-thiophenealdehyde to 1,1′-diacetylferrocene dihydrazone in ~2:1 molar ratio in ethanol with reflux for 2 h. Characterization of the ligand was confirmed from the IR spectra; it was found that the band at 1659 cm^{-1} due to N═C became stronger and broader. This may be due to the formation of another two N═C bonds in the ligand. It was also noted that new bands appeared in the ^1H NMR spectrum at 7.3–7.8 ppm, which were assigned to the thiophene ring protons (Fig. 1). The proton in the H–C═N group appeared at 8.3 ppm in the ^1H NMR spectrum. This band was confirmed from other ^1H NMR spectra of similar Schiff bases.[31] In the UV–Vis spectra, a broad band centred at 456 nm was noted for the ligand. This band was attributed to charge transfer in the ferrocenyl group (transition of the 3d electrons on iron to either the nonbonding or the antibonding orbitals of the cyclopentadienyl ring).[4] The ligand is red in colour, soluble in MeOH, dimethylformamide (DMF), CH_2Cl_2 and $CHCl_3$ and it was purified by crystallization from $CHCl_3$.

Synthesis and characterization of the complexes

The complexes of cobalt(II), copper(II), nickel(II) and zinc(II) ions were prepared easily and in good yields from the equimolar ratio of the ligand and the corresponding metal(II) chloride in methanol with reflux. All the complexes are deep red, stable in air and light, and are soluble in MeOH, DMF, dimethylsulfoxide and $CHCl_3$. The elemental analysis data of the ligand and its complexes are consistent with the calculated results from the empirical formula of each compound.

The IR spectra of the free ligand and its metal(II) complexes were recorded in KBr and are given with their assignments in

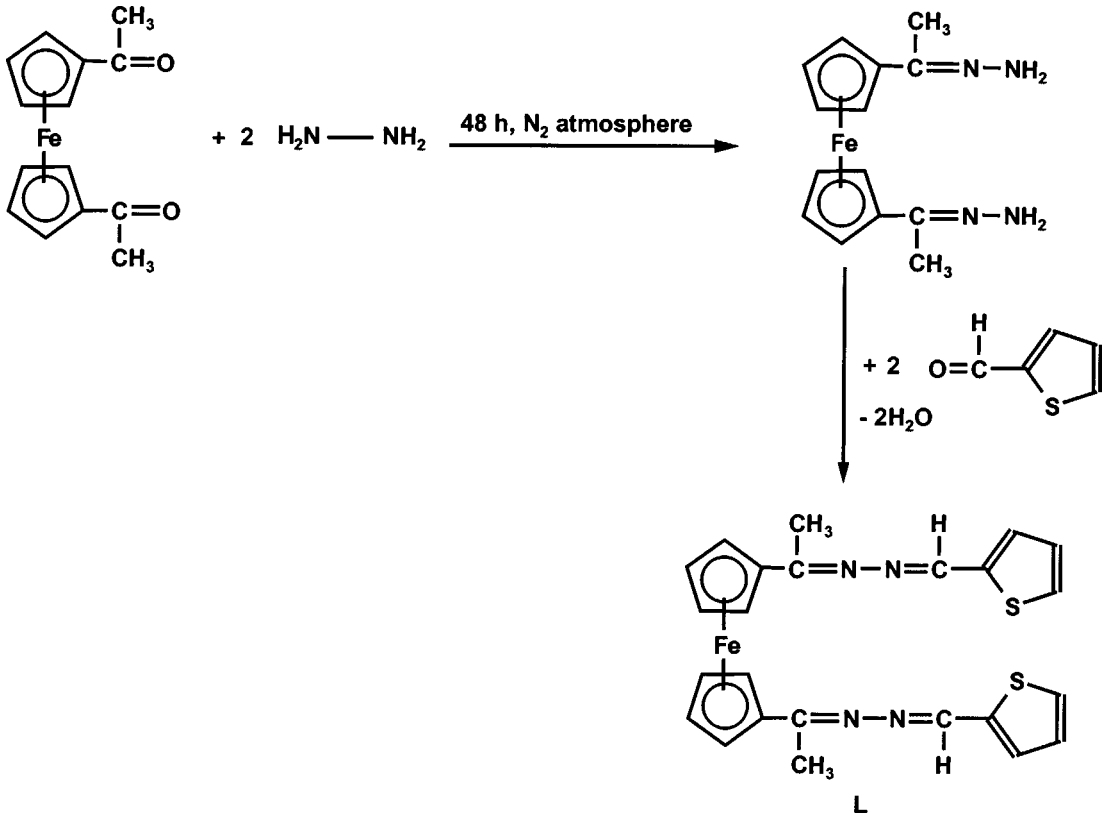

Figure 1. Preparation of the ligand.

the Experimental section. It was found that the characteristic band of the C=N group in the free ligand (at 1659 cm^{-1}) was shifted to a lower frequency (1622–1638 cm^{-1}) in the complexes.[32] This shift indicates coordination of the azomethine nitrogen to the metals in the complexes. It was also found that the medium band due to N–N in the free ligand (at 1043 cm^{-1}) was shifted to lower frequency (by 11–17 cm^{-1}) in the complexes.[32] This shift indicates the bonding in the complexes were through the nitrogen atom. The medium intensity band at 854 cm^{-1} observed in the free ligand assigned to C–S–C (ring) stretching vibration.[33] This band shifted to lower values by 11–13 cm^{-1} for all complexes which indicates the involvement of the sulphur atom in the bonding with the metal ions.[33]

Two new bands at 582–592 and 415–421 cm^{-1}, were also observed. These two bands were observed in the complexes and not found in the free ligand and they are attributed to M–S and M–N bonds in the complexes (M=Co, Cu, Ni, Zn).[32,34]

The characteristic frequencies of the ferrocenyl moiety in the spectra of the ligands were observed at 3073 cm^{-1}, 1451 cm^{-1}, 1101 cm^{-1}, 822 cm^{-1}, 509 cm^{-1}, and 482 cm^{-1}. These bands were attributed to ν(C=C) after ν(C–H) and before ν(C–C) respectively.[35,36] The corresponding frequencies of the complexes appeared nearly at the same position, which indicates that the cyclopentadienyl ring of the ferrocene is not directly coordinated to the metal ion.[35,36]

The ^{1}H NMR spectra of the ligand and complexes were recorded at room temperature in $CDCl_3$; they showed two multiplets for the α- and β-protons for the substituted cyclopentadienyl rings appearing at ca 4.43 and 4.21 ppm.[26] The signals of the methyl bonded to the azomethine linkage (CH_3C=N) was observed at ca 2.21 ppm in the free ligands. The signal appearing at 8.3 ppm in the ligand was assigned to HC=N. The other signals of the thiophene group appeared in the expected region. These signals were shifted slightly downfield in the spectra of the complexes, which may be due to complexation of the azomethine nitrogen and sulfur atoms with the metal ion.[26,27]

The important electronic spectral data of the ligand and its complexes were measured in $CHCl_3$. The electronic spectra of the cobalt(II) complex consists of two shoulder bands at 560 nm and 486 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 geometry for the cobalt(II) complexes (Fig. 2b).[4,37] On the other hand, the spectrum of the nickel(II) complex consists of two bands at 531 and 490 nm. These bands are attributed to the $b_{2g} \rightarrow b_{1g}$ and $a_{1g} \rightarrow b_{1g}$ transitions, which is compatible with the complexes having a square-planar structure.[38,39] In the spectra of the copper(II) complex, three bands were found at 647 nm, 513 nm and 332 nm. The first two bands are assigned to the $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions respectively.[4,40] These bands are typically characteristic for a square-planar configuration. The third band is assigned to a metal → ligand charge transfer (Fig. 2a). The electronic spectra of the zinc(II) complexes showed one high-intensity band at 354 nm, which assigned to ligand–metal charge transfer.[4,27]

A weak broad band was also observed for every complex at 447–452 nm. This band was assigned to the transition $^1A_{1g} \rightarrow {}^1E_{1g}$ in the iron atom of the ferrocenyl group, which indicates 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.[41]

On the basis of the physical and spectral data of the complexes discussed above, and also by comparison with other ferrocenyl dihydrazone complexes,[29] one can assume that the metal ions are bonded to the ligand via one of the azomethine nitrogen atoms and the thiophene-sulfur atom in all complexes. Moreover, the chloride ion bonds directly with the cobalt(II) and zinc(II) complexes to form an octahedral structure, whereas the nickel(II) and copper(II) complexes have a square-planar structure. Both structures are illustrated in Fig. 2a and b.

Antimicrobial properties

The title ligand and its metal(II) complexes were evaluated for their antimicrobial activity against *B. subtilis*, *S. aureus*, *E. coli*, *S. typhi* (bacterium), *C. albicans* (yeast), *A. niger* and *F. solani* (fungi). The compounds were tested at a concentration of 60 μg ml^{-1} in $CHCl_3$ solution using the paper

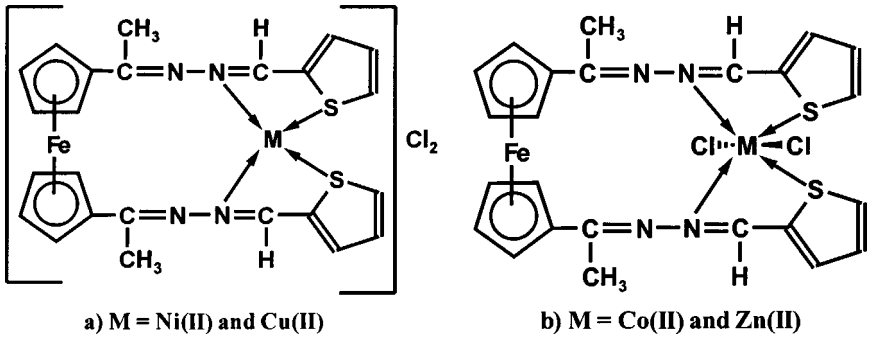

Figure 2. Structure representation of the complexes.

Table 1. Antimicrobial activity data for the ligand and its complexes[a]

Ligand/complex	*B. subtilis*	*S. aureus*	*C. albicans*	*E. coli*	*S. typhi*	*A. niger*	*F. solani*
L	—	—	—	—	—	—	+++
$Co(L)Cl_2$	—	+	+	++	+	—	—
$Ni(L)Cl_2$	+++	+++	++++	+++	+	+	+
$Cu(L)Cl_2$	++	+++	++++	++	++++	+	++
$Zn(L)Cl_2$	++	++	++++	++	+++	+	+

[a] Inhibition zone diameter (% inhibition): +, 6–9 mm (33–50%); ++, 10–12 mm (55–67%); +++, 13–15 mm (72–83%); ++++, 16–18 mm (89–100%). Percentage inhibition values were relative to inhibition zone (18 mm) with 100% inhibition.

disc diffusion method.[27,34] The diameter of the susceptibility zones was measured and the results are given in Table 1. The susceptibility zones measured were the clear zones around the discs inhibiting the microbial growth. The ligand was found to be microbially inactive except against *F. solani*, but the complexes showed significantly antimicrobial activity. It is clear that the complexes of nickel(II), copper(II) and zinc(II) are more active towards *C. albicans* than the cobalt(II) complex (Table 1). It is known that, compared with the parent Schiff bases, chelation tends to make the ligands act as more powerful and potent bactericidal agents, thus killing the microorganisms. A possible explanation is that, in the chelated complex, the positive charge of the metal is partially shared with the donor atoms present in the ligands and there is π-electron delocalization over the whole chelate ring.[34,42] 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, other factors, such as solubility, conductivity and dipole moment (influenced by the presence of metal ions), may also be the possible reasons for increasing this activity.[34,42]

Acknowledgements

M. M. A. would like to thank the Alexander von Humboldt Foundation for providing the equipment, and thank Mr Ahmed A. El-Beih, Chemistry of Natural and Microbial Products Department, NRC, for his help in undertaking the antimicrobial studies.

REFERENCES

1. Allardyce CS, Dorcier A, Scolaro C, Dyson PJ. *Appl. Organometal. Chem.* 2005; **19**: 1.
2. Fish RH, Jaouen G. *Organometallics* 2003; **22**: 2166.
3. Jaouen G, Vessieres A, Butler IS. *Acc. Chem. Res.* 1993; **26**: 361.
4. Chohan ZH, Praveen M. *Appl. Organometal. Chem.* 2001; **15**: 617.
5. Chen L, Wang Q, Huang R, Mao C, Shang J, Song H. *Appl. Organometal. Chem.* 2005; **19**: 45.
6. Lobbia GG, Pellei M, Pettinari C, Santini C, Skelton BW, White AH. *Polyhedron* 2005; **24**: 181.
7. Hatten X, Weyhermueller T, Metzler-Nolte N. *J. Organometal. Chem.* 2004; **689**: 4856.
8. Steffen W, Laskoski M, Morton JGM, Bunz UHF. *J. Organometal. Chem.* 2004; **689**: 4345.
9. Hu X, Bai C, Dai H, Chen H, Zheng Z. *J. Mol. Catal. A: Chem.* 2004; **218**: 107.
10. Murata M, Buchwald SL. *Tetrahedron* 2004; **60**: 7397.
11. Ojani R, Raoof JB, Alinezhad A. *Electroanalysis* 2002; **14**: 1197.
12. Tarraga A, Molina A, Curiel D, Bautista D. *Tetrahedron-Asymm.* 2002; **13**: 1621.
13. Mang C, Wu K, Zhang M, Hong T, Wei Y. *J. Mol. Struct.: THEOCHEM* 2004; **674**: 77.
14. Tsuboya N, Lamrani M, Hamasaki R, Ito M, Mitsuishi M, Miyashita T, Yamamoto Y. *J. Mater. Chem.* 2002; **12**: 2701.
15. Bohm L, Rensburg C, Swarts J. *Eur. J. Cancer Suppl.* 2004; **2**: 68.
16. Casas JS, Castano MV, Cifuentes MC, Garcia-Monteagudo JC, Sanchez A, Sordo J, Abram U. *J. Inorg. Biochem.* 2004; **98**: 1009.
17. Popova LV, Babin VN, Belousov YA, Nekrasov YS, Snegireva AE, Borodina NP, Shaposhnikova GM, Bychenko OB, Raevskii PM. *Appl. Organometal. Chem.* 1993; **7**: 85.
18. Koepf-Maier P, Koepf H, Neuse EW. *J. Cancer Res. Clin.* 1984; **108**: 336.
19. Koepf-Maier P, Koepf H. *Chem. Rev.* 1987; **87**: 1137.
20. Henderson W, Alley SR. *Inorg. Chim. Acta* 2001; **322**: 106.
21. Rosenfeld A, Blum J, Gibson D, Ramu A. *Inorg. Chim. Acta* 1992; **201**: 219.
22. Viotte M, Gautheron B, Kubicki MM, Nifant'ev IE, Fricker SP. *Metal-Based Drugs* 1995; **2**: 311.
23. Liu R-C, Ma Y-Q, Yu L, Li J-S, Cui J-R, Wang R-Q. *Appl. Organometal. Chem.* 2003; **17**: 662.
24. Top S, Vessieres A, Cabestaing C, Laios I, Leclercq G, Provot C, Jaouen G. *J. Organometal. Chem.* 2001; **637–639**: 500.
25. Jaouen G, Top S, Vessieres A, Leclercq G, Quivy J, Jin L, Croisy A. *C. R. Acad. Sci. IIc* 2000; **3**: 89.
26. Abd-Elzaher MM. *J. Chinese Chem. Soc.* 2004; **51**: 499.
27. Abd-Elzaher MM. *Appl. Organometal. Chem.* 2004; **18**: 149.
28. Rosenblum M, Woodward RB. *J. Am. Chem. Soc.* 1958; **80**: 5443.
29. Fang CJ, Duan CY, Mo H, He C, Meng QJ, Liu YJ, Mei YH, Wang ZM. *Organometallics* 2001; **20**: 2525.
30. Casey RMT, Guinan P, Canavan A, McCann M, Cardin C, Kelly NB. *Polyhedron* 1991; **10**: 483.
31. Zhang H, Lei J, Chen Y, Lin L, Wu Q, Zhang H. *Synth. React. Inorg. Met. Org. Chem.* 2001; **31**: 1053.
32. Zhou X, Liang Y, Nan F, Ma Y. *Polyhedron* 1992; **11**: 447.
33. Mohapatra SC, Rao DVR. *J. Indian Chem. Soc.* 1980; **57**: 262.
34. Chohan ZH, Farooq MA. *Synth. React. Inorg. Met. Org. Chem.* 2001; **31**: 1853.
35. Patil SR, Kantank UN, Sen DN. *Inorg. Chim. Acta* 1982; **63**: 261.
36. Wang G, Chang JC. *Synth. React. Inorg. Met. Org. Chem.* 1994; **24**: 1091.
37. Chohan ZH, Pervez H, Kausar S, Supuran CT. *Synth. React. Inorg. Met. Org. Chem.* 2002; **32**: 529.

38. Atkins R, Breweg G, Kakot E, Mockler GM, Sinn E. *Inorg. Chem.* 1985; **24**: 127.
39. Mockler GM, Chaffey GW, Sin E, Wong H. *Inorg. Chem.* 1972; **11**: 1308.
40. Lever ABP. *Inorganic Electronic Spectroscopy*. Elsevier: Amsterdam, 1984; 555–572.
41. Li P, Scowen IJ, Davies JE, Halcrow MA. *J. Chem. Soc. Dalton Trans.* 1998; 3791.
42. Chohan ZH, Kausar S. *Metal-Based Drugs* 2000; **7**: 17.