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Synthesis, characterization and biocidal studies of new ferrocenyl thiadiazolo-triazinone complexes

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One-pot synthesis of ferrocenyl ligand, 1,1′-bis[1,5-methyl-4H-(1,3,4)-thiadiazolo(2,3-c)(1,2,4)triazin-4-one]ferrocene was prepared from the reaction of 1,1′-diacetylferrocene with 4-amino-2,3-dihydro-6-methyl-3-thioxo[1,2,4]triazin-5(4H)one. The ligand, L, forms 1 : 1 complexes with Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) in good yield. Characterization of the ligand and its complexes was carried out using IR, ^{1}H NMR, magnetic susceptibility as well as elemental analysis. Biocidal activity of the ligand and its complexes were determined against the standard fungal strains of *Aspergillus niger, Cladosporium herbarum* and *Fusarium moniliforme* using the paper disc diffusion method; and against bacterial strains of *Escherichia coli* and *Staphylococcus aureus* using viable cell counting technique. The results indicated that the complexes are biologically more active than the free ligand. The biocidal activity depends on the metal ion, concentration as well as the tested fungi and bacteria.

KEYWORDS: diacetylferrocene; thiadiazolo-triazinone; magnetic properties; biocidal activity

INTRODUCTION

Ferrocene compounds are characterized by their ability to make metal-centred redox systems, so they have wide applications in various fields such as molecular recognition as sensors and biosensors,[1,2] in homogenous and asymmetric catalysis,[3–5] in polymer science as red-ox active polymers and dendrimers,[6] in synthesis of photochemical complexes[7] or in the design of new nonlinear optical materials,[8,9] new materials such as liquid crystals[10] and supramolecular chemistry.[11] Ferrocene is often incorporated into some organic molecules in order to obtain newly compounds which have higher biological activity due to unique structure, different membrane-permeation properties and anomalous metabolism.[12,13] A successful example is the application of platinum ferrocene complexes as antitumour agents.[14] Therefore, ferrocene compounds, such as ferrocifen[15–18] and 7-chloro-4[2-(*N*′,*N*′-dimethylaminomethyl)-*N*-ferrocenyl-methylamino]quinoline,[19–21] have good activities as medicals and chemotherapy agents.

On the other hand, several reports have indicated that (1,3,4)thiadiazolo(2,3-c)(1,2,4)triazin-4-one derivatives have significant biological activities against *Aspergillus niger* and *Fusarium oxysporium*.[22–24] It was found also that some thiadiazole derivatives have wide applications as antitumour agents, pesticides, dyes lubricants, herbicides and analytical reagents.[25–27]

In continuation of our previous studies,[28–30] a new ligand has been prepared from the reaction of 1,1′-diacetylferrocene with 4-amino-2,3-dihydro-6-methyl-3-thioxo[1,2,4]triazin-5(4H)one. The ligand has high potential to react with various ions to form stable complexes. Therefore, the aim of the article was extended to prepare and characterize the Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes with the mentioned ligand in order to obtain the heterobimetallic complexes. The prepared ligand and its complexes have been characterized by IR and ^{1}H NMR spectra as well as elemental analysis and magnetic susceptibility. These compounds were evaluated for their biocidal activity against *Aspergillus niger, Cladosporium herbarum, Fusarium moniliforme, Escherichia coli* and *Staphylococcus aureus*.

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EXPERIMENTAL

All chemicals and solvents were obtained from Merck.The starting materials, 4-amino-2,3-dihydro-6-methyl-3-thioxo [1,2,4]triazin-5(4H)one[31] and 1,1′-diacetylferrocene,[32] were prepared by the method described in the literature. The yields refer to analytically pure compounds and were not optimized. ^{1}H NMR was recorded on a Varian Gemini spectrometer in DMSO as a solvent. IR spectra were recorded on a Pye–Unicam SP300 FT-IR spectrometer, using KBr pellets. Elemental analyses were determined at the microanalytical centre, Cairo University. Magnetic susceptibilities were measured at 20 °C by the Gouy method at the Faculty of Science, Cairo University.

Synthesis of the ligand L

A 1.35 g (5.0 mmol) aliquot of 1,1′-diacetylferrocene was dissolved in small amount of dry pyridine (30 ml) and slowly added to a solution of 4-amino-2,3-dihydro-6-methyl-3-thioxo[1,2,4]triazin-5(4H)one (10.0 mmol dissolved in 30 ml pyridine). The mixture was refluxed with stirring for about 2 h. The colour began to change from reddish brown to brown within 30 min and the reflux continued to 2 h. The brown product was filtered, washed with cold ethanol and recrystallized from DMF to give needles.

General procedure for the synthesis of the complexes

The different complexes were prepared by the addition of 2.0 mmol of the corresponding metal acetate dissolved in ca. 30 ml DMF, into a warmed solution of the ligand (2.0 mmol/l) in DMF (30 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.

BIOCIDAL STUDIES

Materials and methods

Microorganisms and culture conditions

All strains of fungi and bacteria used in this study were obtained from the Northern Regional Research Laboratory (NRRL) and American Type Culture Collection (ATCC), and maintained as pure cultures. The fungi *Aspergillus niger, Cladosporium herbarum* and *Fusarium moniliforme* were maintained on Czapek–Dox agar. The bacteria *Escherichia coli* and *Staphylococcus aureus* were maintained on nutrient agar.

Bioassay for antifungal activity

The susceptibilities of the test fungal spores (*Aspergillus niger, Cladosporium herbarum* and *Fusarium moniliforme*) as seeded in Dox's medium on filter paper discs (6 mm diameter) soaked with 0.5 mg/ml of each sample (dissolved in 2-propanol), were determined.[33] The soaked and completely dried filter paper discs were placed on the surface of the seeded Dox medium in triplicate tests for each sample. Plates were allowed to stand for 2 h to allow diffusion. Then, the plates were incubated at 28 °C for 48 h, after which the susceptibility of each organism to each sample was estimated by measuring the diameter of the zones of inhibition.

Minimum inhibitory concentration of the antifungal samples

The minimum inhibitory concentrations (MICs) of the ligand and its complexes on *Aspergillus niger, Cladosporium herbarum* and *Fusarium moniliforme* were determined by the dilution method described by Nair *et al.*[34]

Antibacterial assessment

Bactericidal activity was evaluated based on the killing rate by the viable cell counting technique according to the method described by Park *et al.*[35]

Statistics

All measurements are the means of three replicates; the results obtained were processed by analysis of variance and the significance was determined as the least significant difference (LSD) levels of 1 and 5%.

RESULTS AND DISCUSSION

Synthesis and characterization of the ligand

The ferrocenyl ligand, 1,1′-bis[(1,5-methyl-4H-(1,3,4)-thiadiazolo(2,3-c)(1,2,4)triazin-4-one)]ferrocene (L) was prepared from the reaction of 1,1′-diacetylferrocene with 4-amino-2,3-dihydro-6-methyl-3-thioxo[1,2,4]triazin-5(4H)one in good yield (Fig. 1) (79% referred to diacetylferrocene) using 1 : 2 molar ratio. The elemental analysis of the ferrocenyl ligand is given in Table 1 and is consistent with the calculated result.

The ligand, L, was characterized using different spectroscopic tools. In IR spectra, no bands were found due to the ferrocenyl–C=N or SH groups, which confirmed the conversion of the intermediate i to the ligand L. A new broad band centred at 3436 cm^{-1} was found in the spectra of the ligand. This band was assigned to the N–H bond.[36] Further evidence for the conversion of the i to L is the medium band at 852 cm^{-1} assigned to C–S–C (ring) stretching vibration.[29] A broad band centred at 1033 was also observed with medium to strong intensity, which was assigned to the N–N groups in the triazinone moiety ligand.[37] The band of the C=O group in the triazinone moiety appeared at 1654 cm^{-1}. The characteristic peaks of the ferrocenyl moiety appeared in the expected region (Table 2).

In the ^{1}H NMR spectra (Table 3), the signal of the two methyl groups in the diacetylferrocene was observed at 1.12 ppm and the signal of the two methyl groups in the triazinone moiety appeared at 1.94 ppm. The spectra showed a broad band at 7.46 ppm, which was assigned to the N–H group (Fig. 1). The protons of the ferrocenyl moiety appeared as two multiplets at 4.56 and 4.76 ppm. These bands were assigned to the α- and β-protons for the substituted

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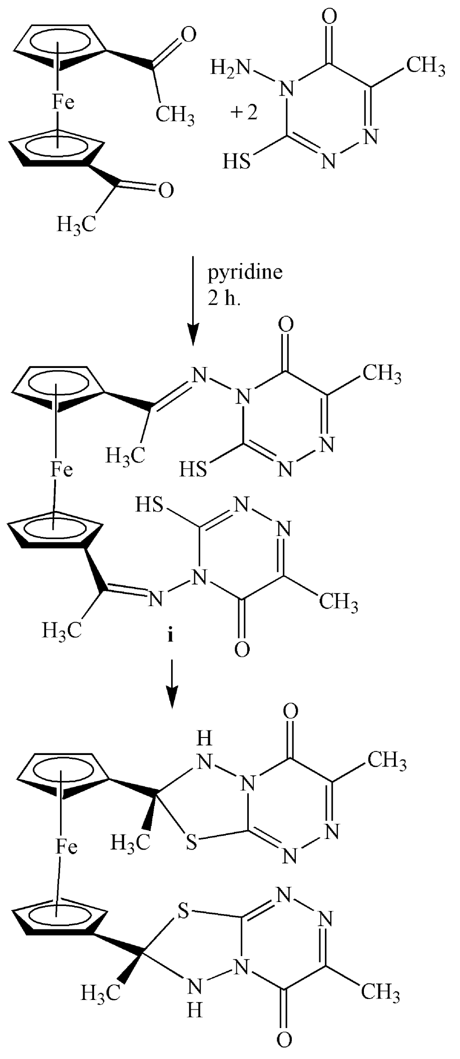

Figure 1. Preparation of the ligand.

cyclopentadienyl rings.[36,38] The absence of N–NH$_2$ and SH protons signals of the starting compound was also noticed, which appeared at 5.2 and 10–12 ppm, respectively.[31]

From the above spectral data, it was confirmed that the ligand was formed via the intermediate (i) in Fig. 1, which could not be separated from the reaction mixture. This is may be due to the high activity of SH group in triazinone ring. Thus it is suggested that the reaction of diacetylferrocene with 4-amino-2,3-dihydro-6-methyl-3-thioxo[1,2,4]triazin-5(4H)one proceeded through two steps: the first is the condensation of the amino group of triazinone with C=O of diacetylferrocene to give (i), whereas the second step is the addition of thiol group of triazinone to C=N as soon as it is formed with concurrent Michael type addition.[26,27] All attempts to separate the intermediate were unsuccessful; presumably, such an intermediate was converted under the conditions used to give the ligand L.[27] The elemental analysis of the ligand is consistent with the calculated results (Table 1).

Synthesis and characterization of the complexes

The complexes of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) ions were prepared easily and in good yield from the equimolar ratio of the ligand and the corresponding metal salts in DMF with reflux for 2 h (Figs 2 and 3). All the complexes are deep brown, stable in air and light. They are slightly soluble in DMF and soluble in warm DMSO. The elemental analysis data of the ligand and its complexes are consistent with the calculated results from the empirical formula of each compound (Table 1).

The IR spectra of the free ligand and its metal complexes were recorded in KBr and are represented in Table 2. It was found that the characteristic band of the N–H bond in the free ligand at 3436 cm^{-1} was shifted to a lower frequency to ca. 3420 cm^{-1} in the complexes.[39] Also, it was found that the band due to the N–N bond in the triazinone moiety, which appeared at 1033 in the free ligand, was shifted to ca. 1022 cm^{-1}. This shift indicates that the nitrogen atom coordinates to the metal ions in the complexes (Fig. 2). The medium band at 852 cm^{-1}, observed in the free ligand, was assigned to C–S–C (ring) stretching vibration.[29] This band shifted to lower values with 7–11 cm^{-1} for all complexes, which indicates the involvement of the sulfur atom in the bonding with the metal ions.[29]

Further conclusive evidence of the coordination of the ligand with the metal ions was the appearance of new two weak bands at ca. 573 and 448 cm^{-1} assigned to metal–sulfur

Table 1. Physical and analytical data of the ligand and its complexes

Ligand/complex	Formula (F.W.)	Yield (%)	%C found (calcd)	%H found (calcd)	%N found (calcd)
L	$C_{22}H_{22}FeN_8O_2S_2$ (550.45)	79	47.84 (48.00)	3.91 (4.03)	20.20 (20.36)
Mn(L)(OAc)$_2$	$C_{26}H_{28}FeMnN_8O_6S_2$ (723.48)	72	43.01 (43.16)	3.64 (3.90)	15.26 (15.49)
Fe(L)(OAc)$_3$	$C_{28}H_{31}Fe_2N_8O_8S_2$ (783.43)	74	42.74 (42.93)	3.77 (3.99)	14.23 (14.30)
Co(L)(OAc)$_2$	$C_{26}H_{28}CoFeN_8O_6S_2$ (727.47)	73	42.66 (42.93)	3.73 (3.88)	15.28 (15.40)
Ni(L)(OAc)$_2$	$C_{26}H_{28}FeN_8NiO_6S_2$ (727.23)	67	42.64 (42.94)	3.81 (3.88)	15.29 (15.41)
Cu(L)(OAc)$_2$	$C_{26}H_{28}CuFeN_8O_6S_2$ (732.08)	69	42.32 (42.66)	3.59 (3.86)	15.38 (15.31)
Zn(L)(OAc)$_2$	$C_{26}H_{28}FeN_8O_6S_2Zn$ (733.92)	71	42.42 (42.55)	3.62 (3.85)	15.19 (15.27)

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Table 2. The important IR spectral data of the ligand and their metal(II) complexes (νcm^{-1})

Ligand/ complex	(N–H)	N–N	(C=O)	(Fc moiety)	C–S–C in ring	(M–O)	(M–S)	(M–N)
L	3436 br	1033 br, s	1654 s	3061 m, 1443 w, 1105 m, 1002 m, 804 m, 469 m	852 m			
$Mn(L)(OAc)_2$	3425 br	1018 br, s	1652 s	3062 m, 1444 w, 1103 m, 1006 m, 803 m, 469 m	845 m	432 m	560 w	455 w
$Fe(L)(OAc)_3$	3421 br	1022 br, m	1655 s	3066 w, 1441 w, 1112 m, 1006 m, 805 m, 467 m	841 m	438 w	555 s	454 m
$Co(L)(OAc)_2$	3417 br	1018 br, m	1656 s	3061 w, 1442 w, 1103 m, 1009 m, 803 m, 465 m	844 m	440 m	573 s	451 m
$Ni(L)(OAc)_2$	3422 br	1028 br, m	1659 s	3062 w, 1444 w, 1107 m, 1006 m, 804 m, 467 m	845 m	440 m	583 s	455 m
$Cu(L)(OAc)_2$	3429 br	1014 br, s	1654 s	3064 w, 1442 w, 1103 m, 1006 m, 805 m, 468 m	845 m		579 s	434 w
$Zn(L)(OAc)_2$	3421 br	1026 br, m	1655 s	3062 w, 1441 w, 1107 m, 1006 m, 807 m, 468 m	844 w	432 w	582 s	442 s

Fc = ferrocene.

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

Ligand/ complex	^{1}H NMR (DMSO-d6), δ in ppm
L	1.12 (s, 6H, $2CH_3$ in Fc), 1.94 (s, 6H, $2CH_3$ in Tz), 4.56 (m, 4H, C_5H_4), 4.76 (m, 4H, C_5H_4), 7.46 (s, 2H, NH).
$Ni(L)(OAc)_2$	1.80 (s, 6H, $2CH_3$ in Fc), 2.32 (s, 6H, $2CH_3$ in Tz), 2.75 (s, 3H, CH_3 in Oac), 4.59 (m, 4H, C_5H_4), 4. 80 (m, 4H, C_5H_4), 7.83 (s, 2H, NH).
$Cu(L)(OAc)_2$	1.75 (s, 6H, $2CH_3$ in Fc), 2.25 (s, 6H, $2CH_3$ in Tz), 2.78 (s, 3H, CH_3 in Oac), 4.60 (m, 4H, C_5H_4), 4. 82 (m, 4H, C_5H_4), 7.89 (s, 2H, NH).
$Zn(L)(OAc)_2$	1.77 (s, 6H, $2CH_3$ in Fc), 2.36 (s, 6H, $2CH_3$ in Tz), 2.74 (s, 3 H, CH_3 in Oac), 4.59 (m, 4H, C_5H_4), 4.83 (m, 4H, C_5H_4), 7.80 (s, 2H, NH).

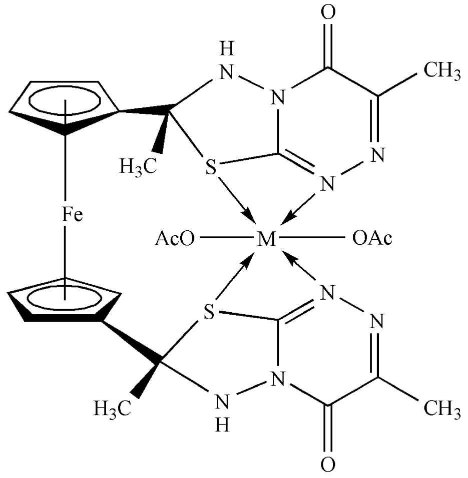

Figure 2. Structural representation of the octahedral complexes.

(M–S) and metal–nitrogen (M–N) stretching, respectively. These new bands were observable only in the spectra of the metal complexes and not in the spectra of the ligand, thus confirming the participation of the sulfur and nitrogen atoms in the complexation.[40,41] In the low frequency region, it was observed a band in the spectra of Mn(II), Fe(III), Co(II), Ni(II) and Zn(II) at ca. 432 cm^{-1}, which was attributed to ν(M–O). This band suggested that the acetate group bonded directly with the Mn(II), Fe(III), Co(II), Ni(II) and Zn(II) complexes, forming octahedral structure (Fig. 2).[28] The latter band was not found in the spectra of the Cu(II) complex, suggesting that it has square planar geometry of the Cu(II) complex (Fig. 3).[28]

The characteristic frequencies of the ferrocenyl moiety in the spectra of the ligands were observed at 3061, 1443, 1105, 1002, 804 and 469 cm^{-1}. These bands were attributed to ν(C–H), ν(C=C), ν(C–C), δ(C-H), π(C-H) and δ(Fe-ring), respectively.[42,43] 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.[42,43]

The ^{1}H NMR spectra of the complexes were recorded at room temperature using DMSO as a solvent (Table 3). The signal of the N–H group appeared at ca. 7.84 ppm in the complexes compared with 7.46 ppm in the ligand. The spectra also showed two multiplets for the α- and β- protons for the substituted cyclopentadienyl rings appeared at ca. 4.6 and 4.8 ppm.[37] Three signals were observed at 1.77, 2.30 and 2.75 ppm for the three methyl groups in the complexes (Table 3). These signals were shifted slightly downfield in the spectra of the complexes compared with the ligand. This shift confirmed the complexation of the sulphur and nitrogen atoms with the metal ions.[29,40,41]

Magnetic moment and electronic spectra

The magnetic moments and the electronic spectra of the ligand and its complexes with Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) are represented in Table 4. The magnetic moments were calculated from the corrected magnetic susceptibilities. The effective magnetic moment (μ_{eff}) of the Mn(II) complex is 5.96 B.M., which is within the limits of the spin-free value (5.92 B.M.), for five unpaired electrons. The electronic absorption of the complex showed two d–d transition bands at 553 and 586 nm attributed to the $^2A_1 \rightarrow {}^4T_1$ transition. These bands are

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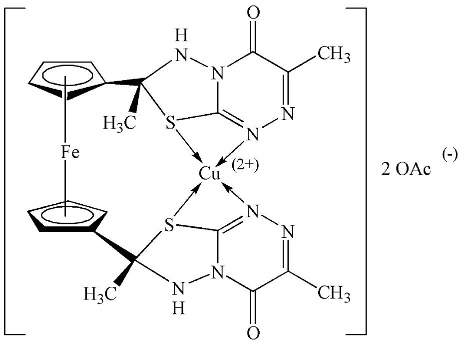

Figure 3. Structural representation of the Cu(II) complex.

Table 4. Magnetic and electronic data of the ligand and its metal(II) complexes

Ligand/ complex	λ_{max} (nm)				Magnetic moment, μ_{eff} (B.M.)
L				445	Dia
$Mn(L)(OAc)_2$	553	586		446	5.96
$Fe(L)(OAc)_3$	405	553		446	5.87
$Co(L)(OAc)_2$	484	579		444	4.56
$Ni(L)(OAc)_2$	379	639		445	2.92
$Cu(L)(OAc)_2$	325	506	656	446	1.94
$Zn(L)(OAc)_2$	336			448	dia

characteristic for octahedral geometry of the Mn(II) complex (Fig. 2).[44]

The effective magnetic moment of the Fe(III) complex measured at room temperature is 5.87 B.M. This value falls within the range reported for high-spin octahedral Fe(III) complexes. The electronic spectra showed two bands at 405 and 584 nm which assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transitions respectively. The magnetic moment and the electronic spectra of the Fe(III) indicated that the complex may be in octahedral structure (Fig. 2).[45]

The effective magnetic values of the Co(II) complex with the ligand was found to be 4.56 B.M. The electronic spectra of the Co(II) complexes (Table 4) consist of two bands at 579 and 484 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 Co(II) complexes (Fig. 2).[28] Furthermore, the Ni(II) complex was proposed to have octahedral geometry. This result was based on the basis of its magnetic moments (2.92 B.M.) and its electronic absorption in which two bands are observed at 639 and 379 nm. These bands are assigned to the transitions ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ respectively,[28] which are characteristic for octahedral geometry for the Ni(II) complexes (Fig. 2). On the other hand, the magnetic moment of the Cu(II) complex was observed at 1.94 B.M. This value is consistent with the proposed square-planar structure of Cu(II) complexes (Fig. 3). The electronic spectra of the Cu(II) complex showed three bands at 656, 506 and 325 nm. The first two bands are assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively.[28] The third band is assigned to a metal → ligand charge transfer. These bands are typically characteristic for square-planar[28] configuration for Cu(II) complexes (Fig. 3).

The electronic spectra of the Zn(II) complexes showed one high-intensity band at 336 nm, which was assigned to ligand-metal charge transfer.[28]

A weak broad band centred at ca. 446 nm was also observed for the ligand and every complex. This band was assigned to the transition ${}^1A_{1g} \rightarrow {}^1E_{1g}$ in the iron atom of the ferrocenyl group, which indicates[28] that there is no magnetic interaction between the Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) ions and the Fe(II) ion of the ferrocenyl group.

Biocidal studies

The ligand and its metal complexes were evaluated for their biocidal activity against the standard fungal strains of *Aspergillus niger, Cladosporium herbarum* and *Fusarium moniliforme* using the paper disc diffusion method;[33] and against bacterial strains of *Escherichia coli* and *Staphylococcus aureus* using viable cell counting technique.[35]

Table 5. Antifungal activity data of the ligand and its complexes (inhibition zone diameter in mm)

Complex	*Aspergillus niger*	*Cladosporium herbarum*	*Fusarium moniliforme*
L	17.0	14.9	18.7
$Mn(L)(OAc)_2$	20.2	19.4	22.4
$Fe(L)(OAc)_3$	18.1	15.4	19.5
$Co(L)(Oac)_2$	19.3	18.7	20.1
$Ni(L)(Oac)_2$	18.7	16.5	19.6
$Cu(L)(Oac)_2$	25.1	23.2	26.2
$Zn(L)(Oac)_2$	26.3	25.6	31.0
LSD 5%	1.5	1.4	1.3
1%	3.1	2.7	2.8

Table 6. The MIC of the ligand and its complexes on the tested fungi (µg/ml)

Complex	*Aspergillus niger*	*Cladosporium herbarum*	*Fusarium moniliforme*
L	175	125	100
$Mn(L)(OAc)_2$	40	30	10
$Fe(L)(OAc)_3$	75	25	15
$Co(L)(Oac)_2$	40	25	10
$Ni(L)(Oac)_2$	50	40	10
$Cu(L)(Oac)_2$	25	20	15
$Zn(L)(Oac)_2$	25	25	10
LSD 5%	1.4	1.6	1.5
1%	2.9	3.3	3.2

The inhibition zones of the tested fungi were measured in mm and the results are represented in Tables 5 and 6. The inhibition zones are the clear zones around the discs. It was found that the complexes have higher fungicidal activity than the free ligand. The MIC values of the ligand and different complexes are given in Table 6. The results also revealed the trend of growth inhibition of the complexes in the order Zn(II) > Cu(II) > Mn(II) > Co(II) > Ni(II) > Fe(III).

Figures 4 and 5 show the log plots of viable cell number of the *Escherichia coli* and *Staphylococcus aureus* as a function of time after adding the ligand or its complexes. All the ligands and its complexes exhibited a bactericidal effect in killing about 10^5 cells/ml of the bacteria within 23 h. The results show that the *Staphylococcus aureus* tend to tolerate better than *Escherichia coli* the ligand and its complexes.

The results show that the biocidal activity depends on the nature of the metal ion and its concentration as well as the tested fungi and bacteria. It is known[28–30] that the complexation tends to make the ligands more potent bactericidal agents, thus killing more of the bacteria than the parent ligand. A possible explanation is that 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 chelated ring.[28,29] This, in turn, increases the lipophilic character of the metal complex and favours its permeation through the lipid layers of the microorganism membranes. Furthermore, other factors, such as solubility,

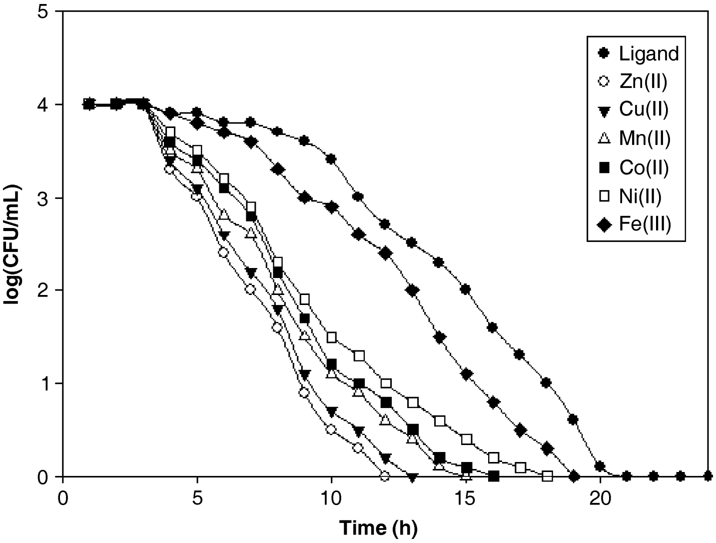

Figure 4. Viable cell number of *E. coli* as a function of time of the ligand and its complexes.

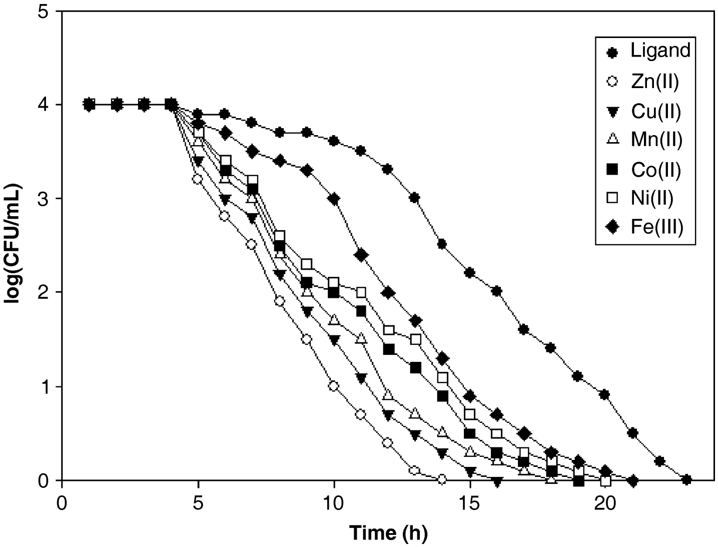

Figure 5. Viable cell number of *S. aureus* as a function of time of the ligand and its complexes.

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conductivity and dipole moment (influenced by the presence of metal ions) also may be reasons for this increased activity.[28,29] On the other hand, the inhibition of the growth of the microorganisms may be due to the inhibition of the glucose uptake,[46] inhibition of RNA and protein synthesis.[47]

By comparison with the results[23,24] obtained on the commercial antifungal dithane m-45 [a mixture of manganous and zinc salt of *N*,*N*′-ethylenebis(dithiocarbamic acid)] against *Aspergillus niger* and *Fusarium oxysborum*, we can conclude that the synthesized Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes have a good antifugal activity.

CONCLUSION

From the results discussed above, we can conclude that:

1. The metal ions are bonded to the ligand via the nitrogen and sulfur atoms in all complexes. Moreover the acetate group bonded directly with the Mn(II), Fe(III), Co(II), Ni(II) and Zn(II) complexes to form octahedral structure, whereas Cu(II) complexes have a square-planar structure (Figs 2 and 3).
2. The biocidal results indicated that the complexes are more active than the free ligand and this activity depends on the metal ion concentration as well as the tested fungi and bacteria.

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