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New lanthanide complexes of 1,1`-*bis*[(2-thienylmethylidene)hydrazono-1-ethyl]-ferrocene and 1,1`-*bis*(2,3-dihydro-2-methylbenzo[*d*]thiazol-2-yl) ferrocene: Synthesis, characterization and antimicrobial properties

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ABSTRACT

In this paper; synthesis, characterization and biocidal properties of new prepared Sc(III), Y(III), La(III) and Ce(III) complexes with the two ferrocenyl ligands of 1,1`-*bis*[(2-thienylmethylidene)hydrazono-1-ethyl]ferrocene and 1,1`-*bis*(2,3-dihydro-2-methylbenzo[*d*] thiazol-2-yl)ferrocene are reported. These organometallic compounds are potential ligands for lanthanide metal ions. The composition of these complexes is discussed on the basis of elemental analysis, IR, NMR, magnetic moments, electronic absorption spectra and conductivity measurements. In vitro antimicrobial activity of the prepared complexes was screened. All complexes showed remarkable antibiotic activity. Scandium complexes are very effective towards *Salmonella spp*. Sc-L^2 complex found to have inhibition activity against *B. subtilis* more than the standard drugs.

1. Introduction

In the past few years, the versatile chemistry of ferrocene has attracted the attention of many researchers [1-13]. It has been used as a precursor for the preparation of coordination and biologically active compounds. Ferrocene is nontoxic and has a unique structure as well as an excellent redox property, allowing wide applications in medicinal chemistry. These interesting applications of ferrocenyl compounds resulted in several reports of hetero-bimetallic complexes [14-17], since some ferrocenyl complexes showed enhanced biological activity compared to parent ligand. The aim of this work is to prepare a series of lanthanide complexes with two ferrocenyl ligands and to characterize the structure of these complexes. The antibacterial activities of the prepared complexes were assessed against Gram-positive bacteria *B. subtilis* and *S. aureus* and Gram-negative bacteria *E. coli*, *S. typhi* and *Salmonella spp.*

2. Experimental

All chemicals and solvents (AR) were obtained from Merck except absolute ethanol was (Sigma-Aldrich). $Sc(NO_3)_3 \cdot xH_2O$ 99%, $Y(NO_3)_3 \cdot 6H_2O$ 99%, $Ce(NO_3)_3 \cdot 6H_2O$ 99%, and $La(NO_3)_3 \cdot 6H_2O$ 97% were purchased from BDH (England). 1,1`-Diacetyl-ferrocene was prepared according to Rosenblum and Woodward method [18]. 1,1`-*Bis*[(2-thienylmethylidene) hydrazono-1-ethyl]-ferrocene (**L^1**) and 1,1`-*bis*(2,3-dihydro-2-methylbenzo[*d*]thiazol-2-yl)ferrocene (**L^2**) were synthesized and characterized as described in the literature [15,19]. Yields refer to analytically pure compounds and were not optimized. ^{1}H and ^{13}C NMR was recorded on Perkin Elmer 283B and 300 MHz Varian XL-300 instruments. IR spectra were recorded on a Perkin Elmer (Spectrum 1000) Fourier-transform infrared (FT-IR) spectrometer, using KBr pellets. Elemental analyses were determined at the College of Science, King Saud University, and the results are in agreement with calculated values. Electronic absorptions were recorded on a Shimadzu UV-1800 automatic spectrophotometer. Molar Conductance Λ_m, (Ω^{-1} cm^2 mol^{-1}), at 25 °C of freshly prepared (0.001 mol.dm^{-3}) metal chelates in DMF was determined using a YSI-32 model conductometer. The magnetic susceptibilities were measured using a Sherwood Scientific Ltd. Magnetic susceptibility balance (England).

2.1. Preparation of the complexes

A solution of 3 mmol of ligand was refluxed with 4 mmol of Sc(III), Y(III), La(III) or Ce(III) nitrates in 50 cm^3 dry absolute ethanol with **L^1** and in methanol with **L^2** for about 5 h, cooled to room temperature, filtered, washed and dried. The separated complexes recrystallized from dry ethanol, and dried. The physical properties of the prepared complexes are stable under ordinary conditions (Figure 1 and 2).

1,1`-Bis[(2-thienylmethylidene)hydrazono-1-ethyl]-ferrocene (**L^1**): $C_{24}H_{22}FeN_4S_2$. Yield: 67%. M.p.: 89 °C. FT-IR (KBr, ν, cm^{-1}): 1659 (s -C=N), 1520 (s -C=C thiophene), 1043 (m N-N), 854 (m C-S-C ring). ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 2.21 (s, 6H, 2CH$_3$), 4.21 (m 4H, C$_5$H$_4$), 4.43 (m, 4H, C$_5$H$_4$), 6.71-7.55 (m, 6H thiophene ring), 8.36 (s, 2H, H-C=N). ^{13}C NMR (75 MHz, DMSO-*d$_6$*, δ, ppm): 22.9, 68.8, 69.6, 73.1, 146.6, 121.3, 124.8, 139.8, 144.5. UV/Vis (CHCl$_3$, λ$_{max}$, nm): 456. Anal. calcd. for $C_{24}H_{22}FeN_4S_2$: C, 59.26; H, 4.56; N, 11.52. Found: C, 59.29; H, 4.49; N, 11.51 %.

1,1`-Bis[(2-thienylmethylidene)hydrazono-1-ethyl]ferrocene scandium nitrate (**Sc-L^1**): $C_{24}H_{22}FeScN_7O_9S_2$. Yield: 63%. M.p.: >360 °C. FT-IR (KBr, ν, cm^{-1}): 1642 (s -C=N), 1630, 1310 (m -NO$_3$), 1511 (s -C=C thiophene), 1026 (m N-N), 821 (m C-S-C

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ring), 422 (w Sc-N), 369 (w Sc-S). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.32 (s, 6H, $2CH_3$), 4.42 (m 4H, C_5H_4), 4.61 (m, 4H, C_5H_4), 6.82-7.81 (m, 6H thiophene ring), 8.49 (s, 2H, H-C=N). ^{13}C NMR (75 MHz, DMSO-*d*$_6$, δ, ppm): 23.3, 69.1, 70.4, 73.6, 146.9, 122.1, 124.9, 140.3, 144.8. UV/Vis (CHCl$_3$, λ_{max}, nm): 239, 456. Anal. calcd. for $C_{24}H_{22}FeScN_7O_9S_2$: C, 40.18; H, 3.09; N, 13.67. Found: C, 40.31; H, 3.21; N, 13.71 %. $Λ_M$ ($Ω^{-1}$ cm^2 mol^{-1}): 84.32. μ_{eff} = diamagnetic.

1,1`-Bis[(2-thienylmethylidene)hydrazono-1-ethyl]ferrocene yttrium nitrate (**Y-L^1**): $C_{24}H_{22}FeYN_7O_9S_2$. Yield: 54%. M.p.: >360 °C. IR (KBr, ν, cm^{-1}): 1638 (s -C=N), 1561, 1342 (m -NO_3), 1494 (s -C=C thiophene), 1032 (m N-N), 834 (m C-S-C ring), 415 (w Y-N), 374 (w Y-S). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.31 (s, 6H, $2CH_3$), 4.44 (m 4H, C_5H_4), 4.58 (m, 4H, C_5H_4), 6.84-7.80 (m, 6H thiophene ring), 8.53 (s, 2H, H–C=N). ^{13}C NMR (75 MHz, DMSO-d$_6$, δ, ppm): 23.4, 68.9, 70.6, 74.5, 147.3, 123.1, 125.5, 141.2, 145.3. UV/Vis (CHCl$_3$, λ_{max}, nm): 247, 456. Anal. calcd. for $C_{24}H_{22}FeYN_7O_9S_2$: C, 37.86; H, 2.91; N, 12.88. Found: C, 37.21; H, 3.05; N, 12.91 %. $Λ_M$ ($Ω^{-1}$ cm^2 mol^{-1}): 2.41. μ_{eff} = diamagnetic.

1,1`-Bis[(2-thienylmethylidene)hydrazono-1-ethyl]ferrocene lanthanum nitrate (**La-L^1**): $C_{24}H_{22}FeLaN_7O_9S_2$. Yield: 59%. M.p.: >360 °C. IR (KBr, ν, cm^{-1}): 1643 (s -C=N), 1587, 1296 (m -NO_3), 1502 (s -C=C thiophene), 1041 (m N-N), 831 (m C-S-C ring), 426 (w La-N), 377 (w La-S). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.29 (s, 6H, $2CH_3$), 4.51 (m 4H, C_5H_4), 4.54 (m, 4H, C_5H_4), 6.79-7.72 (m, 6H thiophene ring), 8.57 (s, 2H, H–C=N). ^{13}C NMR (75 MHz, DMSO-d$_6$, δ, ppm): 23.3, 69.3, 71.2, 73.8, 147.1, 122.4, 125.2, 140.6, 145.2. UV/Vis (CHCl$_3$, λ_{max}, nm): 221, 456. Anal. calcd. for $C_{24}H_{22}FeLaN_7O_9S_2$: C, 35.53; H, 2.73; N, 12.08. Found: C, 34.98; H, 2.75; N, 12.52 %. $Λ_M$ ($Ω^{-1}$ cm^2 mol^{-1}): 3.57. μ_{eff} = diamagnetic.

1,1`-Bis[(2-thienylmethylidene)hydrazono-1-ethyl]ferrocene cerium nitrate (**Ce-L^1**): $C_{24}H_{22}FeCeN_7O_9S_2$. Yield: 58%. M.p.: >360 °C. IR (KBr, ν, cm^{-1}): 1650 (s -C=N), 1576, 1322 (m -NO_3), 1496 (s -C=C thiophene), 1033 (m N-N), 835 (m C-S-C ring), 432 (w Ce-N), 364 (w Ce-S). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.31 (s, 6H, $2CH_3$), 4.46 (m 4H, C_5H_4), 4.56 (m, 4H, C_5H_4), 6.83-7.84 (m, 6H thiophene ring), 8.54 (s, 2H, H–C=N). ^{13}C NMR (75 MHz, DMSO-d$_6$, δ, ppm): 23.0, 69.2, 71.3, 74.2, 147.3, 122.6, 125.3, 140.4, 145. UV/Vis (CHCl$_3$, λ_{max}, nm): 358, 371, 456. Anal. calcd. for $C_{24}H_{22}FeCeN_7O_9S_2$: C, 35.47; H, 2.73; N, 12.11. Found: C, 35.57; H, 2.81; N, 12.11 %. $Λ_M$ ($Ω^{-1}$ cm^2 mol^{-1}): 2.13. μ_{eff} = 2.51 μ_B.

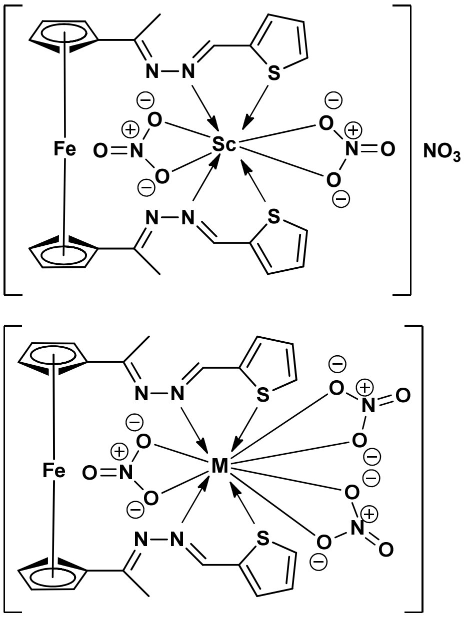

Figure 1. Suggested structure of L^1 complexes, M= Y, La or Ce.

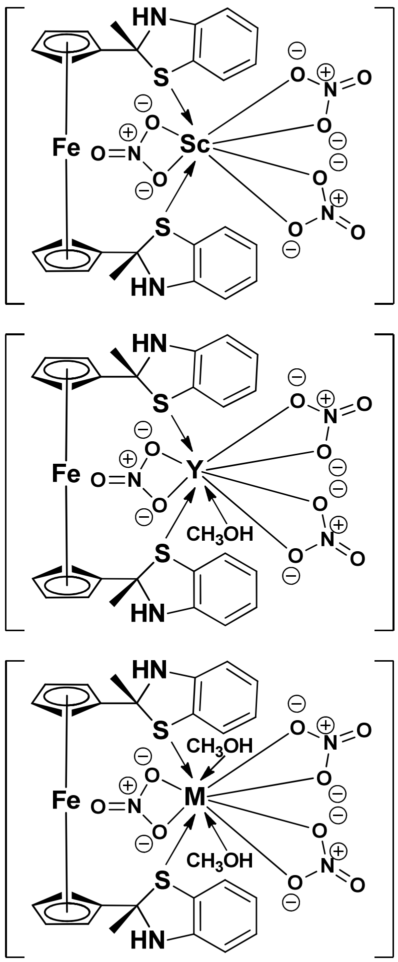

Figure 2. Suggested structure of L^2 complexes, M: La or Ce.

1,1`-Bis(2,3-dihydro-2-methylbenzo[d]-thiazol-2-yl)-ferrocene (**L^2**): $C_{26}H_{24}FeN_2S_2$. Yield: 84%. M.p.: 63-65 °C. IR (KBr, ν, cm^{-1}): 3,294 (N-H), 1,455 (C=C, Fc moiety), 1,112 (C–C, Fc moiety), 1,028 (δ C-H, Fc moiety), 844 (C-S-C), 806 (π C-H, Fc moiety), 487 (δ Fe-ring). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.11 (s, 6H, $2CH_3$ in Fc), 4.80 (m, 4H, C_5H_4), 5.00 (m, 4H, C_5H_4), 5.63 (s, 2H, NH), 6.62-7.32 (m, 8H, Ph). ^{13}C NMR (75 MHz, DMSO-d$_6$, δ, ppm): 24.8, 68.4, 69.6, 72.7, 78.9, 118.8, 127.5, 138.3, 146.5. UV/Vis (CHCl$_3$, λ_{max}, nm): 454. Anal. calcd. for $C_{26}H_{24}FeScN_5O_9S_2$: C, 64.46; H, 4.99; N, 5.78. Found: C, 64.52; H, 4.82; N, 5.67%.

1,1`-Bis(2,3-dihydro-2-methylbenzo[d]-thiazol-2-yl)-ferrocene scandium nitrate (**Sc-L^2**): $C_{26}H_{24}FeScN_5O_9S_2$. Yield: 67%. M.p.: >360 °C. IR (KBr, ν, cm^{-1}): 3287 (N-H), 1588, 1289 (m -NO_3), 1456 (C=C, Fc moiety), 1121 (C-C, Fc moiety), 1027 (δ C-H, Fc moiety), 822(C-S-C), 804 (π C-H, Fc moiety), 480 (δ Fe-ring), 384 (w Sc-S). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.32 (s, 6H, $2CH_3$ in Fc), 4.85 (m, 4H, C_5H_4), 5.08 (m, 4H, C_5H_4), 5.82 (s, 2H, NH), 6.82-7.61(m, 8H, Ph). ^{13}C NMR (75 MHz, DMSO-d$_6$, δ, ppm): 25.2, 68.9, 70.6, 73.2, 79.4, 120.3, 128.6, 140.3, 148.5. UV/Vis (CHCl$_3$, λ_{max}, nm): 248, 454. Anal. calcd. for $C_{26}H_{24}FeScN_5O_9S_2$: C, 43.65; H, 3.59; N, 9.88. Found: C, 43.38; H, 3.59; N, 9.88 %. $Λ_M$ ($Ω^{-1}$ cm^2 mol^{-1}): 3.68. μ_{eff} = diamagnetic.

1,1`-Bis(2,3-dihydro-2-methylbenzo[d]-thiazol-2-yl)-ferrocene yttrium nitrate (**Y-L^2**): $C_{27}H_{28}FeYN_5O_{10}S_2$. Yield: 52%. M.p.: >360 °C. IR (KBr, ν, cm^{-1}): 3585 (OH methanol), 3282 (N-H), 1611, 1324 (m-NO_3), 1457 (C=C, Fc moiety), 1116 (C-C, Fc moiety), 1027 (δ C-H, Fc moiety), 833 (C-S-C), 808 (π C-H, Fc moiety), 478 (δ Fe-ring) 391 (w Y-S). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.34 (s, 6H, $2CH_3$ in Fc), 3.38 (s, 3H, methanol CH_3), 1.12 (s, 1H methanol OH), 4.91 (m, 4H, C_5H_4), 5.11(m, 4H, C_5H_4), 5.84 (s, 2H, NH), 6.84-7.62 (m, 8H, Ph). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 25.1, 47.2, 68.6, 70.2, 72.9, 79.3, 123.1, 127.9, 140.6, 147.3. UV/Vis ($CHCl_3$, λ_{max}, nm): 262, 454. Anal. calcd. for $C_{27}H_{28}FeYN_5O_{10}S_2$: C, 41.92; H, 3.65; N, 9.05. Found: C, 42.16; H, 3.51; N, 9.17 %. Λ_M (Ω^{-1} cm^2 mol^{-1}): 3.09. μ_{eff} = diamagnetic.

1,1`-Bis(2,3-dihydro-2-methylbenzo[d]-thiazol-2-yl)-ferrocene lanthanum nitrate (**La-L^2**): $C_{28}H_{32}FeLaN_5O_{11}S_2$. Yield: 61%. M.p.: >360 °C. IR (KBr, ν, cm^{-1}): 3592 (OH methanol), 3301 (N-H), 1628, 1275 (m-NO_3), 1460 (C=C, Fc moiety), 1119 (C-C, Fc moiety), 1029 (δ C-H, Fc moiety), 834 (C-S-C), 805 (π C-H, Fc moiety), 476 (δ Fe-ring) 389 (w La-S). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.29 (s, 6H, 2CH_3 in Fc), 3.40 (s, 3H, methanol CH_3), 1.15 (s, 1H, methanol OH), 4.87 (m, 4H, C_5H_4), 5.06 (m, 4H, C_5H_4), 5.79 (s, 2H, NH), 6.86-7.64 (m, 8H, Ph). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 24.9, 47.1, 68.7, 70.4, 73.2, 79.6, 119.5, 128.1, 139.7, 147.9. UV/Vis ($CHCl_3$, λ_{max}, nm): 232, 454. Anal. calcd. for $C_{28}H_{32}FeLaN_5O_{11}S_2$: C, 38.49; H, 3.69; N, 8.02. Found: C, 38.53; H, 3.70; N, 7.99 %. Λ_M (Ω^{-1} cm^2 mol^{-1}): 2.73. μ_{eff} = Diamagnetic.

1,1`-Bis(2,3-dihydro-2-methylbenzo[d]-thiazol-2-yl)-ferrocene cerium nitrate (**Ce-L^2**): $C_{28}H_{32}FeCeN_5O_{11}S_2$. Yield: 56%. M.p.: >360 °C. IR (KBr, ν, cm^{-1}): 3479 (OH methanol), 3285 (N-H), 1572, 1309 (m-NO_3), 1454 (C=C, Fc moiety), 1114 (C-C, Fc moiety), 1023 (δ C-H, Fc moiety), 829 (C-S-C), 806 (π C-H, Fc moiety), 484 (δ Fe-ring) 388 (w Ce-S). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.32 (s, 6H, 2CH_3 in Fc), 3.38 (s, 3H, methanol CH_3), 1.07 (s, 1H, methanol OH), 4.83 (m, 4H, C_5H_4), 5.04 (m, 4H, C_5H_4), 5.90 (s, 2H, NH), 6.87-7.62 (m, 8H, Ph). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 25.1, 47.1, 69.3, 70.5, 73.1, 79.5, 120.7, 128, 140.2, 148.4. UV/Vis ($CHCl_3$, λ_{max}, nm): 375, 387, 454. Anal. calcd. for $C_{28}H_{32}FeCeN_5O_{11}S_2$: C, 38.44; H, 3.69; N, 8.01. Found: C, 38.21; H, 3.43; N, 7.54%. Λ_M (Ω^{-1} cm^2 mol^{-1}): 2.54. μ_{eff} = 2.46 μ_B.

2.2. Antimicrobial activity

2.2.1. Preparation of the discs

The complex (30 μg) in DMF (0.01 cm^3) was mounted on a paper disc (prepared from blotting paper (5 mm diameter)) with the help of micropipette. The discs were left at room temperature till dryness and then applied on the microorganism-grown agar plates.

2.2.2. 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*, *S. typhi* and *Salmonella spp.* utilized nutrient agar (2.30 g; obtained from Panreac Quimica SA, Spain).

2.2.3. 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 millimeters [20].

3. Results and discussion

3.1. Synthesis and characterization of the ligands

1,1`-Diacetylferrocene dihydrazone was prepared by dissolving 1,1`-diacetyl-ferrocene in small amount of dry ethanol and in presence of excess of hydrazine hydrate while stirring under nitrogen atmosphere. The ligand **L^1**, 1,1`-*bis*[(2-thienylmethylidene)hydrazono-1-ethyl]ferrocene was prepared by addition of 2-thiophenealdehyde to 1,1`-diacetylferrocene dihydrazone in ~2:1 molar ratio in ethanol with reflux for 2h [15]. Characterization of the ligand L^1 was confirmed from the elemental analysis, IR, ^1H NMR and ^{13}C NMR spectra. It was found that the band at 1659 cm^{-1} due to -C=N became stronger and broader than that of the dihydrazone. This may be due to the formation of another two -C=N bonds in the ligand. It was also noted that new bands appeared in the ^1H NMR spectrum at 6.71-7.55 ppm, which were assigned to the thiophene ring protons. The proton in the H–C=N group appeared at 8.36 ppm in the ^1H NMR spectrum. ^{13}C NMR spectrum (in ppm) is at 22.9, 68.8, 69.6, 73.1 (ferrocenyl), 146.6 (C=N), 121.3, 124.8, 139.8, 144.5 ppm (thiophene). In the UV-Vis spectra, a broad band centered at 456 nm was noted for the ligand. This band was attributed to charge transfer $^1A_{1g} \rightarrow {}^1E_{1g}$ in the ferrocenyl group (transition of the 3*d* electrons on iron to either the nonbonding or the antibonding orbitals of the cyclopentadienyl ring) [21]. The ligand is red in color, soluble in MeOH, C_2H_5OH, dimethylformamide, CH_2Cl_2 and $CHCl_3$ and it was purified by crystallization from $CHCl_3$.

The ligand **L^2**, 1,1`-*bis*(2,3-dihydro-2-methylbenzo[*d*] thiazol-2-yl)ferrocene was prepared from the reaction of 1,1`-diacetylferrocene with 2-aminothiophenol using 1:2 molar ratio [19]. The ligand **L^2** was characterized from the elemental analysis, IR, ^1H NMR and ^{13}C NMR spectra. In the IR spectra, no bands were found due to the ferrocenyl -C=N or -SH groups. A new broad band centered at 3294 cm^{-1} was found in the spectra of ligand, this band was assigned to the N–H bond. Another medium band appeared at 844 cm^{-1} which was assigned to the C-S-C (ring) stretching vibration. The characteristic peaks of the ferrocenyl moiety occurred at about 1112, 1028, 806, and 487 cm^{-1}. These bands were attributed to ν(C–C), δ(C–H), π(C–H), and δ (Fe-ring), respectively. In the ^1H NMR spectra of ligand **L^2**, the signal of the two methyl groups occurred at 2.11 ppm and the spectra showed a peak at 5.63 ppm, which was assigned to the N–H group. The protons of the ferrocenyl moiety appeared as two multiplets at 4.80 and 5.00 ppm. These signals were assigned to the *α*- and *β*-protons of the substituted cyclopentadienyl rings. The signals of the phenyl protons occurred at (6.62-7.32) ppm. The spectra showed that no signal at 3.5 ppm was found due to the proton of SH groups. ^{13}C NMR spectrum (in ppm) is at 24.8 (2 CH_3), 68.4 (tert. carbon), 69.6, 72.7, 78.9 (ferrocenyl), 118.8, 127.5, 138.3, 146.5 (aromatic). In the UV–Vis spectra, a weak broad band centered at 454 nm were noted for the ligand. This band was attributed to charge transfer $^1A_{1g} \rightarrow {}^1E_{1g}$ in the ferrocenyl group. The ligand is deep orange in color, soluble in CH_3OH, C_2H_5OH, dimethylformamide and dimethylsulphoxide and it was purified by crystallization from ethanol.

3.2. Synthesis and characterization of the complexes

Reactions of $Sc(NO_3)_3.xH_2O$, $Y(NO_3)_3.6H_2O$, $La(NO_3)_3.6H_2O$ and $Ce(NO_3)_3.6H_2O$ with **L^1**, were performed in dry absolute ethanol while with **L^2** were performed in methanol. The complexes show 1:1, metal:ligand ratio as indicated by their analyses.

The IR spectra of the complexes of **L^1** exhibit strong bands at (1638-1643) cm^{-1} assigned to -C=N and are shifted to lower frequencies than that of the free ligand 1659 cm^{-1}. This shift indicates that the azomethine nitrogens are involving in coordination. 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 10-17 cm^{-1} in the complexes. 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 [22] was shifted to lower frequencies by (18-33) cm^{-1} for all complexes that indicates the participation of the sulfur atom in the bonding with the metal ions.

Table 1. Antimicrobial activity data for the complexes *.

Compound	**Diameter of the inhibition zone**				
	B. subtilis	***S. aureus***	***E. coli***	***S. typhi***	***Salmonella spp.***
L^1	11.5	10.4	12.4	10.3	7.4
Sc-L^1	16.4	15.3	15.3	14.8	18.6
Y-L^1	15.7	16.2	14.6	13.1	14.8
La-L^1	17.1	16.1	16.1	14.8	15.4
Ce-L^1	16.0	15.8	15.8	13.9	13.7
L^2	10.2	11.7	9.5	7.6	6.8
Sc-L^2	19.4	17.2	15.7	15.6	19.3
Y-L^2	18.2	18.7	14.5	14.5	15.2
La-L^2	18.1	17.1	14.8	14.4	14.1
Ce-L^2	18.0	15.9	14.6	13.5	13.3
Ampicillin	18.2	16.7	14.0	15.4	14.5
Tetracycline	16.5	15.1	17.4	17.6	19.2
Chloramphenicol	18.8	19.8	18.3	16.5	20.1

* Inhibition zone diameter mm (% inhibition): 6-10 (27-45%); 10-14 (45-64%); 14-18 (64-82%); 18-22 (82–100%). Percent inhibition values are relative to inhibition zone (22 mm) of the most active compound with 100% inhibition.

Two new sets of bands are observed at 1561, 1587, 1576 cm^{-1} and 1342, 1296, 1322 cm^{-1} for the **Y-L^1**, **La-L^1** and **Ce-L^1**, respectively. These bands are assigned to symmetric and asymmetric stretching modes of NO_3 as ligands under C_{2V} symmetry. The separation of the two sets is large (219, 291, 254 cm^{-1}) confirming the bidentate character of the nitrate as a ligand. In the low IR wavenumbers region, two new weak bands at 415-432 and 364-377 cm^{-1}, were also observed in the complexes and not found in the free ligand and they are attributed to M-N and M-S bonds in the complexes.

The ^1H 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 (4.43 and 4.21 ppm) for the ligand and 4.61-4.54 and 4.51-4.42 ppm for the complexes. The signal appearing at 8.36 ppm (H-C=N) in the ligand was shifted down field to (8.57-8.49) ppm for the complexes confirming the coordination through the azomethine nitrogen's and sulfur atoms [20,23].

The ^{13}C NMR spectra of the complexes showed the same signals of the ligand slightly shifted downfield which may be due to coordination.

On the other hand, comparing the IR frequencies (given in the experimental section) of L^2 with its complexes, we cannot observe remarkable shifts except for the C-S-C stretching frequency where there is shifting to lower frequencies by 10-22 cm^{-1}. This shift indicates the bonding in the complexes were through the sulfur atoms. Two new sets of bands are observed at 1588, 1611, 1628, 1572 cm^{-1} and 1289, 1324, 1275, 1309 cm^{-1} for the **Sc-L^2**, **Y-L^2**, **La-L^2** and **Ce-L^2**, respectively. These bands are assigned to ν_4 and ν_1 modes of NO_3 as ligands under C_{2V} symmetry, which suggest that the nitrate anions in the complexes are covalently bonded and are present inside the coordination sphere [24]. As noted above, the separation of the two sets are large (299, 287, 253, 263 cm^{-1}) confirming the bidentate character of the nitrate as a ligand [25]. One new week band attributed to M-S vibrations also created in the complexes spectra at 384-391 cm^{-1}. New bands are observed at 3585, 3582, 3479 cm^{-1} for **Y-L^2**, **La-L^2** and **Ce-L^2**, respectively, representing the OH stretching vibrations of the methanol ligand.

The ^1H and ^{13}C NMR spectra of complexes (**Sc-L^2**, **Y-L^2**, **La-L^2** and **Ce-L^2**) were recorded at room temperature using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent. The spectra of the complexes showed slight downfield shift compared with the spectra of **L^2**, which may be due to coordination of sulfur atoms to the metal ion.

New chemical shifts are observed in NMR spectra at 3.38, 1.12 pm; 3.40, 1.15 ppm and 3.38, 1.07 ppm and at 47.2 pm; 47.1 ppm; and 46.8 ppm in **Y-L^2**, **La-L^2** and **Ce-L^2**, respectively. These ^1H and ^{13}C NMR shifts are characteristic for methanol inside the coordination sphere.

Magnetic moment data show that Sc(III), Y(III) and La(III) complexes are diamagnetic, while Ce(III) complexes have magnetic moments 2.51 and 2.46 BM for **Ce-L^1** and **Ce-L^2**, respectively which agree well with the expected values of Ce(III) complexes due to the presence of 4f electrons whose effectively shielded by $5s^25p^66s^2$ electrons.

The molar conductivity of the complexes (0.001 mol dm^{-3} in DMF) were measured at 25 °C using YSI-32 model conductometer. The results for all complexes except **Sc-L^1** were in the range 2.13-3.57 Ω^{-1} cm^2 mol^{-1}, which means that these complexes are neutral, whilst the molar conductance of complex **Sc-L^1** was 84.3 Ω^{-1} cm^2 mol^{-1} suggesting the presence of nitrate anion.

The electronic spectra of ligands and their corresponding lanthanide (III) complexes are recorded in in the region 200-900 nm. The ligands **L^1** and **L^2** Show weak bands at 456 and 454 nm, respectively. The broad bands observed at (239 for **Sc-L^1** and 248 nm for **Sc-L^2**), (247 nm for **Y-L^1**, 262 nm for **Y-L^2**) and (221 nm for **La-L^1**, and 232 nm for **La-L^2**) complexes are attributed to ligand to metal charge transfer (LMCT). Although the *f-f* transition is forbidden by the Laporte rule, the electronic spectra of **Ce-L^1** and **Ce-L^2** show high intensity bands in the near UV region at (358, 371 nm for **Ce-L^1**) and (375, 387 nm for **Ce-L^2**) which are due to 4f→5d transition [18,26].

On the basis of the physical and spectral data of the complexes, one can assume that **L^1** bonded to the metal(III) ions through one of the azomethine nitrogen atoms and the thiophene sulfur atom and they complete their coordination number 8, 10, 10 and 10 (**Sc-L^1**, **Y-L^1**, **La-L^1** and **Ce-L^1**, respectively) by nitrate anions as represented in Figure 1, while **L^2** bonded to the metal(III) ions as represented in Figure 2 with coordination numbers 8, 9, 10 and 10 for **Sc-L^2**, **Y-L^2**, **La-L^2** and **Ce-L^2**, respectively. In the last three complexes methanol molecule appears as a monodentate ligand, which is elucidated by elemental analysis, IR and NMR. Many disappointing unsuccessful trials are made to prepare single crystal for X-ray analysis.

3.3. Antimicrobial activity

In vitro antibacterial screening activity of the prepared ligands and their lanthanide complexes with trivalent Sc, Y, La and Ce were carried out successfully with *B. subtilis, S. aureus, E. coli, S. typhi and Salmonella spp.*, (obtained from microbial genetics department, National Research Center, Giza, EGYPT), using paper disc method on appropriate nutrient medium. The results included in Table 1 revealed that the complexes are more effective than their parent ligands. Complexes of **L^2** show great efficiency towards *B. subtilis and S. aureus* to the extent that **Sc-L^2** has inhibition activity against *B. subtilis* more than the standard drugs. Scandium complexes are very effective towards *Salmonella spp.* All complexes showed remarkable antibiotic activity compared with the standard drugs (Ampicillin, tetracycline and chloramphenicol).

4. Conclusion

The present work reported the preparation and characterization of new organometallic lanthanide complexes using physical and spectral techniques. The new complexes are screened in vitro as antibiotics for some Gram-positive and Gram-negative bacteria. The results reveal that the complexes possess significant antibacterial activity compared with standard antibiotics, ampicillin, tetracycline and chloramphenicol. Scandium complexes are very effective towards *Salmonella spp.* **Sc-L^2** complex found to have inhibition activity against *B. subtilis* more than the given standard drugs.

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