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Synthesis, crystal structure and antibacterial activity of a group of mononuclear manganese(II) Schiff base complexes

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ABSTRACT

Five mononuclear complexes of manganese(II) of a group of the general formula, $[MnL(NCS)_2]$ where the Schiff base L = *N*,*N*′-bis[(pyridin-2-yl)ethylidene]ethane-1,2-diamine (L^1), (**1**); *N*,*N*′-bis[(pyridin-2-yl)benzylidene]ethane-1,2-diamine (L^2), (**2**); *N*,*N*′-bis[(pyridin-2-yl)methylidene]propane-1,2-diamine (L^3), (**3**); *N*,*N*′-bis[(pyridin-2-yl)ethylidene]propane-1,2-diamine (L^4), (**4**) and *N*,*N*′-bis[(pyridin-2-yl)benzylidene]propane-1,2-diamine (L^5), (**5**) have been prepared. The syntheses have been achieved by reacting manganese chloride with the corresponding tetradentate Schiff bases in presence of thiocyanate in the molar ratio of 1:1:2. The complexes have been characterized by IR spectroscopy, elemental analysis and other physicochemical studies, including crystal structure determination of **1**, **2** and **4**. Structural studies reveal that the complexes **1**, **2** and **4** adopt highly distorted octahedral geometry. The antibacterial activity of all the complexes and their respective Schiff bases has been tested against Gram(+) and Gram(−) bacteria.

1. Introduction

The coordination chemistry of manganese has long been a subject of considerable interest in inorganic biochemistry [1]. Enhanced interest in synthesis and characterization of Schiff base complexes of manganese in various oxidation states is due to their important roles in metalloenzymes, redox and non-redox proteins [2,3]. In addition to the biological importance, diverse catalytic and magnetic properties of such compounds are now being explored [4–6]. Designing a suitable polydentate Schiff base ligand to combine with a metal ion along with pseudohalide anions has opened a new era of synthesizing metal complexes of particular choice [7]. Although a plenty of Schiff bases have been extensively used to synthesize complexes of manganese(II), simple mononuclear complexes with Schiff bases derived from diamines like ethane-1,2-diamine or propane-1,2-diamine and pyridine-2-al or its derivatives are lacking. A report on the preparation and characterization of two such complexes containing Schiff base of 1,3-diaminopropane as the amine counterpart along with thiocyanate anion has appeared earlier [8]. However, the investigation of biological properties of such Schiff bases or their complexes of Mn(II) have not received adequate attention. Only a few reports on the antimicrobial activity of Mn(II) complexes have been reported recently [9–13].

In the present work, we describe the synthesis of a group of five new mononuclear complexes of manganese(II), *viz.* $[MnL^1(NCS)_2]$ (**1**), $[MnL^2(NCS)_2]$ (**2**), $[MnL^3(NCS)_2]$ (**3**), $[MnL^4(NCS)_2]$ (**4**) and $[MnL^5(NCS)_2]$ (**5**) containing the corresponding N-donor Schiff base ligand (L = L^1–L^5). These ligands were prepared by the condensation of ethylenediamine with 2-acetyl pyridine (L^1) or 2-benzoyl pyridine (L^2), 1,2-diaminopropane with pyridine 2-carboxaldehyde (L^3) or 2-acetyl pyridine (L^4) or 2-benzoyl pyridine (L^5). All the complexes have been characterized by microanalytical, spectroscopic, magnetic and other physicochemical studies, including single crystal X-ray structural analysis of **1**, **2** and **4**. The complexes and the constituent Schiff base ligands have also been tested *in vitro* to assess their antibacterial activities against some common reference bacteria and the results were compared with similar doses of commercial antibiotics *viz.* Gattifloxacin and Ciprofloxacin.

2. Experimental

2.1. Physical measurements

Elemental analyses for carbon, hydrogen and nitrogen were carried out using a Perkin–Elmer 2400-II elemental analyzer. Manganese content was determined using the titrimetric method. Sulphur contents of **3** and **5** were determined gravimetrically by converting it to barium sulphate. The infrared spectra were

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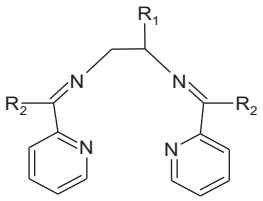
recorded on a Perkin–Elmer FT-IR spectrophotometer with KBr discs (4000–300 cm^{-1}). Room temperature solid phase magnetic susceptibilities were measured at 298 K with a PAR 155 vibrating sample magnetometer with $Hg[Co(NCS)_4]$ as the calibrant. The diamagnetic corrections were calculated from Pascal's constants. Molar conductances of the complexes in dry DMF were measured using a direct reading conductivity meter of Systronics (Type 304).

2.2. Materials

Reagent grade ethylenediamine, 1,2-diaminopropane, pyridine 2-carboxaldehyde, 2-acetyl pyridine, 2-benzoyl pyridine, ammonium thiocyanate and manganese(II) chloride tetrahydrate were purchased from reputed manufacturers and used as received. All other chemicals and solvents were of analytical grade. The tetradentate ligands *N*,*N*′-bis[(pyridin-2-yl)ethylidene]ethane-1,2-diamine (L^1), *N*,*N*′-bis[(pyridin-2-yl)benzylidene]ethane-1,2-diamine (L^2), *N*,*N*′-bis[(pyridin-2-yl)methylidene]propane-1,2-diamine (L^3), *N*,*N*′-bis[(pyridin-2-yl)ethylidene]propane-1,2-diamine (L^4) and *N*,*N*′-bis[(pyridin-2-yl)benzylidene]propane-1,2-diamine (L^5) were prepared by the condensation of the respective carbonyl compounds and amines using similar methods as described earlier [14].



Structure of L: $R_1 = H$, $R_2 = CH_3$ for **1**; $R_1 = H$, $R_2 = C_6H_5$ for **2**; $R_1 = CH_3$, $R_2 = H$ for **3**; $R_1 = CH_3$, $R_2 = CH_3$ for **4** and $R_1 = CH_3$, $R_2 = C_6H_5$ for **5**.

2.3. Synthesis of compounds *1*–*5*

All the complexes **1**–**5** were prepared by a general method *viz*. mixing $MnCl_2{\cdot}4H_2O$, the respective Schiff base ligand and ammonium thiocyanate in a 1:1:2 M ratio in methanol solvent followed by slow evaporation. In case of compound **1**, a methanolic solution (10 ml) of Schiff base ligand, L^1 (0.13 g, 0.5 mmol) was added dropwise to a methanolic solution (5 ml) of $MnCl_2{\cdot}4H_2O$ (0.1 g, 0.5 mmol) with constant stirring at room temperature. To the resulting light yellow solution, a methanolic solution (5 ml) of ammonium thiocyanate (0.08 g, 1.0 mmol) was added slowly. Stirring was continued for 15 min and the solution was left for slow evaporation at room temperature in a beaker open to the atmosphere. After 3–5 days, yellow brown crystals of compound **1** appeared. The crystals were collected by filtration, washed with methanol and finally dried. Yield: 0.15 g (68%). The synthetic route described for **1** was followed in the preparation of other four compounds **2**, **3**, **4** and **5**, except that 10 ml methanolic solution of the Schiff base ligand, L^2 (0.2 g, 0.5 mmol), L^3 (0.13 g, 0.5 mmol), L^4 (0.14 g, 0.5 mmol) and L^5 (0.20 g, 0.5 mmol) respectively was used instead of L^1 in each case. Yields of **2**, **3**, **4** and **5** starting from 0.1 g of $MnCl_2{\cdot}4H_2O$ are 0.16 g (57%), 0.13 g (61%), 0.15 g (66%) and 0.18 g (62%), respectively. Although all the complexes are crystalline in nature, crystals suitable for X-ray structural analysis could only be collected for **1**, **2** and **4**. *Anal*. Calc. for $C_{18}H_{18}MnN_6S_2$ (**1**): C, 49.42; H, 4.15; N, 19.21; Mn, 12.56. Found: C, 49.98; H, 4.18; N, 18.92; Mn, 12.44%. FTIR (KBr, cm^{-1}): Λ_M (DMF, Ω^{-1} cm^2 mol^{-1}): 5. μ_{eff} (RT, BM): 5.88. *Anal*. Calc. for $C_{28}H_{22}MnN_6S_2$ (**2**): C, 59.88; H, 3.95; N, 14.96; Mn, 9.78. Found: C, 59.75; H, 4.02; N, 14.92; Mn, 9.69%. FTIR (KBr, cm^{-1}): 2934(m), 2058(s), 1643(s), 1590(s), 1442(m), 1348(m), 1318(m), 1258(w), 1105(m), 1008(m), 955(w), 804(m), 705(m), 632(w). Λ_M (DMF, Ω^{-1} cm^2 mol^{-1}): 7. μ_{eff} (RT, BM): 5.92. *Anal*. Calc. for $C_{17}H_{16}MnN_6S_2$ (**3**): C, 48.22; H, 3.81; N, 19.85; Mn, 12.97; S, 15.15. Found: C, 48.35; H, 3.85; N, 19.82; Mn, 12.95; S, 15.22%. FTIR (KBr, cm^{-1}): 2959(s), 2066(s), 1651(s), 1593(s), 1474(w), 1441(w), 1383(w), 1297(w), 1153(w), 1090(w), 1005(m), 889(w), 776(m), 703(s), 627(w). Λ_M (DMF, Ω^{-1} cm^2 mol^{-1}): 6. μ_{eff} (RT, BM): 5.93. *Anal*. Calc. for $C_{19}H_{20}MnN_6S_2$ (**4**): C, 50.55; H, 4.47; N, 18.61; Mn, 12.17. Found: C, 50.35; H, 4.29; N, 18.62; Mn, 12.12%. FTIR (KBr, cm^{-1}): 2917(m), 2339(m), 2067(s), 1642(s), 1590(s), 1476(w), 1434(s), 1379(s), 1248(w), 1139(w), 1007(m), 802(w), 781(s), 631(w). Λ_M (DMF, Ω^{-1} cm^2 mol^{-1}): 5. μ_{eff} (RT, BM): 5.87. *Anal*. Calc. for $C_{29}H_{24}MnN_6S_2$ (**5**): C, 60.51; H, 4.20; N, 14.60; Mn, 9.54; S, 11.14. Found: C, 60.65; H, 4.15; N, 14.72; Mn, 9.59; S, 11.02%. FTIR (KBr, cm^{-1}): 2971(s), 2350(m), 2063(s), 1628(s), 1589(s), 1466(w), 1440(s), 1328(m), 1256(m), 1155(w), 1007(m), 803(m), 751(m), 703(s), 664(w). Λ_M (DMF, Ω^{-1} cm^2 mol^{-1}): 6. μ_{eff} (RT, BM): 5.91.

2.4. Crystal structure determination and refinement

Suitable single crystals of **1**, **2** and **4** with dimensions of $0.06 \times 0.04 \times 0.03$, $0.06 \times 0.05 \times 0.04$ and $0.04 \times 0.04 \times 0.04$ mm^3, respectively, were collected on a Bruker APEX-II diffractometer, equipped with CCD area detector and graphite-monochromated Mo Kα radiation. The intensity data were processed with the Bruker-Nonius program suite SAINT-PLUS and corrected for Lorentz, polarization, background and absorption effects [15,16]. The structures were solved by direct methods and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-square refinements on F^2 using the program SHELX [17]. Scattering factors for neutral atoms were employed in the refinements.

In the refinement process of **1** and **2**, all hydrogen atoms were located from the difference Fourier maps and refined freely, except for the methyl hydrogen atoms in **1** where displacement parameters were constrained to 1.2 times that of the parent atoms. For **4**, the hydrogen atoms were placed at geometrically calculated positions and then treated as riding on their parent atoms, with free refinement of the isotropic displacement parameters (except for H atoms attached to C7, C9, C10 and C12 which were constrained like that in **1**). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms isotropically. The final *R*-values of the refinements for $F_o > 4\sigma(F_o)$ were 0.046, 0.047 and 0.064 respectively for **1**, **2** and **4**. A summary of the crystallographic data, structural parameters and refinement details is presented in Table 1.

2.5. Antimicrobial activity – minimum inhibitory concentration

Antibiograms of the compounds **1**–**5** and two reference commercial antibiotics *viz*. Gattifloxacin and Ciprofloxacin (purchased in powder form from Span Diagnostic Limited, Surat, India) were prepared against two Gram positive bacteria, *viz*. *Staphylococcus aureus* MTCC 2940 and *Bacillus subtilis* MTCC 441 and two Gram negative bacteria *viz*. *Pseudomonas aeruginosa* MTCC 2453 and *Escherichia coli* MTCC 739 using the agar well diffusion method on nutrient agar medium with necessary modifications [18]. During the experiment, the test microbes were removed from the slant aseptically with inoculating loops and transferred to separate test tubes containing 5.0 ml of saline solution (0.85% NaCl). Sufficient inoculum was then added to adjust the turbidity to 0.5 McFarland (10^8 CFU ml^{-1}), as recorded in a digital colony counter. For each bacterium, 1.0 ml of the suspension was added to 15–20 ml of nutrient agar and transferred to an agar plate of 9.0 cm diameter. The antibacterial activities of the compounds were tested after cooling the inoculated agars at room temperature for 25 min. The

Table 1
Crystal data and structure refinement for **1**, **2** and **4**.

Parameters	**1**	**2**	**4**
Formula	$C_{18}H_{18}MnN_6S_2$	$C_{28}H_{22}MnN_6S_2$	$C_{19}H_{20}MnN_6S_2$
Formula weight (g mol^{-1})	437.44	561.58	451.47
Crystal size (mm^3)	0.06 × 0.04 × 0.03	0.06 × 0.05 × 0.04	0.05 × 0.04 × 0.04
Crystal system	monoclinic	monoclinic	triclinic
Space group	*C*2/*c*	$P2_1/c$	$P\bar{1}$
a (Å)	12.549(1)	8.1917(3)	8.658(1)
b (Å)	16.370(2)	16.7332(6)	9.142(2)
c (Å)	9.944(1)	20.6123(7)	14.582(3)
α (°)	90	90	84.481(7)
β (°)	90.805(5)	98.252(2)	79.330(6)
γ (°)	90	90	70.642(5)
V (Å^3)	2042.7(4)	2796.1(2)	1069.4(3)
Z	4	4	1
D_{calc} (g cm^{-3})	1.422	1.334	1.402
μ (mm^{-1})	0.865	0.649	0.829
F(0 0 0)	900	1156	466
hkl range	−18/17, ±24, ±14	−10/12, −24/21, −30/23	±12, −13/12, −18/21
T (K)	293(2)	293(2)	293(2)
Reflections measured	12580	34740	12416
Reflections unique	3432	9361	6906
Data with $F_o > 4\sigma(F_o)$	2254	7285	4842
R_{int}	0.045	0.016	0.014
Parameters refined	147	422	289
R^a, $F_o > 4\sigma(F_o)$	0.0459	0.0472	0.0635
wR^b	0.1396	0.1344	0.1847
Weighting parameters *a*/*b*	0.050/1.775	0.057/1.117	0.071/0.882
S	1.06	1.05	1.021
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.42/−0.54	0.72/−0.62	0.65/−0.37

[a] $R = \Sigma||F_o| - |F_c||\Sigma|F_o|$.
[b] $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (a \times P)^2 + b \times P]$, $P = (F_o^2 + 2F_c^2)/3$.

antibacterial activities of the five constituent Schiff bases L^1–L^5 were also evaluated during the same experiment. All the compounds including the antibiotics were dissolved in dimethylsulphoxide (DMSO) to prepare five different concentrations (0.5, 1.0, 2.0, 3.0 and 4.0 mg ml^{-1}) for evaluation of limiting doses. Wells of 0.6 cm diameter were punched in the agar and filled with the test compounds of varied concentrations and incubated for 24 h at 303 K for *B. subtilis* and at 310 K for all other bacteria. Antibacterial activities were evaluated by measuring the inhibition zone diameters (IZD) and their minimum inhibitory concentrations (MIC). The MIC values of the test compounds were determined by serial dilution technique adopted by the National Committee for Clinical Laboratory Standards [19]. Each of the above experiments was repeated thrice along with a control set using DMSO.

3. Results and discussion

3.1. Synthesis

The one-pot reaction of the respective tetradentate Schiff base ligand with manganese chloride and thiocyanate in the mole ratio Mn(II):L:SCN^- = 1:1:2 in methanol solvent resulted in the formation of the complexes **1**–**5**. All the complexes have been characterized by elemental analysis, IR spectroscopy, electrical conductivity and magnetic susceptibility measurements as well as by single crystal X-ray structural analysis for **1**, **2** and **4**. In DMF solvent, all of these compounds behave as non-electrolytes as is evident from their Λ_M values (*ca.* 5–7 Ω^{-1} cm^2 mol^{-1} respectively). Room temperature magnetic susceptibility measurements indicate that the complexes have magnetic moments (5.87–5.93 B.M.) close to the spin-only value of Mn(II). This is indicative of the presence in each, a high spin idealized $t_{2g}^3e_g^2$, $S = 5/2$ electronic configuration with five unpaired electrons as expected for a Mn(II) species [3]. All these results along with the X-ray structural analysis of **1**, **2** and **4** are consistent with the proposed mononuclear formulae of the Mn(II) complexes. Although determination of structures of **3** and **5** was not possible due to non-availability of good quality single crystals, all other studies support that these two complexes also belong to the same series of Mn(II) complexes.

3.2. FTIR spectra

The infrared spectra of the compounds **1**–**5** are similar in some respects as expected. They all show sharp and distinct absorption bands in the region 2058–2070 cm^{-1}, assignable to the asymmetric stretching vibrations of N-bonded terminal thiocyanate. Strong absorption bands in the regions 1628–1651 and 1589–1593 exhibited by **1**–**5** correspond to the ν_{CN} stretches of the ligands. Few other characteristic vibrations of the metal-bound Schiff bases are located in the range 600–1600 cm^{-1}. Thus, the infrared spectra of the compounds are in good agreement [20] with their respective structural features.

3.3. Crystal structure of the complexes *1*, *2* and *4*

The molecular structures of the complexes **1**, **2** and **4** are displayed in Fig. 1 and some selected bond lengths and angles are listed in Table 2. These three compounds are structurally similar as is evident from insignificant variations in their bond lengths and angles. In each of these complexes, the central Mn(II) ion is a member of three five-membered rings and adopts a highly distorted octahedral (MnN_6) geometry. The irregular hexacoordination environment around Mn(II) comprises four nitrogen atoms (N1, N1, N2, N2 in **1** and N1, N2, N3, N4 in **2** and **4**, respectively) from the tetradentate Schiff base ligand and two nitrogen atoms (N1A, N1A in **1** and N1A, N1B in **2** and **4** respectively) from the thiocyanate anion.

The Mn–N distances ranging from 2.116 to 2.379 Å in **1**, **2** and **4** are comparable to each other and with other analogous complexes containing MnN_6 chromophores [8]. The two Mn–NCS distances in

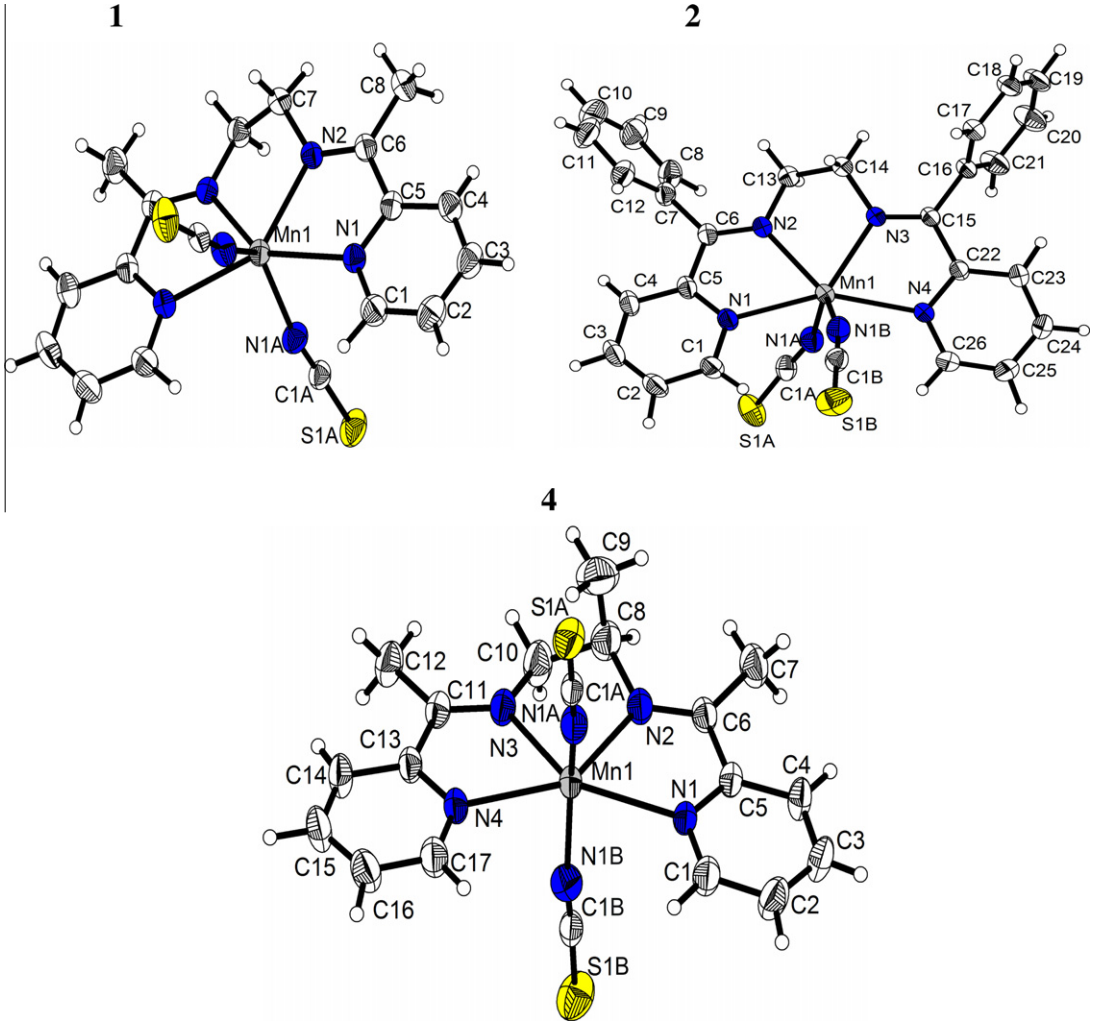


Fig. 1. Molecular structures of **1**, **2** and **4** with atom numbering scheme [21] and 30% probability ellipsoids. For clarity, hydrogen labels are omitted.

each complex are considerably shorter than the Mn–N(L) counterparts due to the stronger ability of thiocyanate ion to bind the Mn(II) ion in comparison to the neutral polydentate ligand [22].

Table 2
Selected bond lengths [Å] and bond angles [°] for compounds **1**, **2** and **4**.

1	**2**	**4**
Mn1–N1A 2.121(2)	Mn1–N1B 2.116(4)	Mn1–N1B 2.119(3)
Mn1–N1A 2.121(2)	Mn1–N1A 2.135(4)	Mn1–N1A 2.138(4)
Mn1–N2 2.266(2)	Mn1–N3 2.268(5)	Mn1–N3 2.262(3)
Mn1–N2 2.266(2)	Mn1–N2 2.290(3)	Mn1–N2 2.267(3)
Mn1–N1 2.379(2)	Mn1–N4 2.364(3)	Mn1–N4 2.346(2)
Mn1–N1 2.379(2)	Mn1–N1 2.378(3)	Mn1–N1 2.355(2)
N1A–Mn1–N1A 128.30(9)	N1B–Mn1–N1A 122.91(8)	N1B–Mn1–N1A 152.23(1)
N1A–Mn1–N2 114.15(8)	N1B–Mn1–N3 110.60(7)	N1B–Mn1–N3 98.55(1)
N1A–Mn1–N2 106.84(8)	N1A–Mn1–N3 117.42(7)	N1A–Mn1–N3 103.67(1)
N1A–Mn1–N2 106.84(8)	N1B–Mn1–N2 129.29(7)	N1B–Mn1–N2 102.09(1)
N1A–Mn1–N2 114.15(8)	N1A–Mn1–N2 94.44(7)	N1A–Mn1–N2 100.18(1)
N2–Mn1–N2 73.48(7)	N3–Mn1–N2 72.28(5)	N3–Mn1–N2 73.01(1)
N1A–Mn1–N1 84.53(8)	N1B–Mn1–N4 83.50(7)	N1B–Mn1–N4 86.27(1)
N1A–Mn1–N1 82.04(8)	N1A–Mn1–N4 86.02(6)	N1A–Mn1–N4 85.93(1)
N2–Mn1–N1 141.80(7)	N2–Mn1–N4 136.72(5)	N2–Mn1–N4 142.84(1)
N2–Mn1–N1 69.14(7)	N3–Mn1–N4 69.36(5)	N3–Mn1–N4 69.94(1)
N1A–Mn1–N1 82.04(8)	N1B–Mn1–N1 82.91(7)	N1B–Mn1–N1 83.32(1)
N1A–Mn1–N1 84.53(8)	N1A–Mn1–N1 82.05(6)	N1A–Mn1–N1 89.13(1)
N2–Mn1–N1 141.80(7)	N3–Mn1–N1 137.43(5)	N3–Mn1–N1 142.09(1)
N2–Mn1–N1 69.14(7)	N2–Mn1–N1 68.56(5)	N2–Mn1–N1 69.63(9)
N1–Mn1–N1 148.89(7)	N4–Mn1–N1 153.07(5)	N4–Mn1–N1 147.49(9)

In these molecules, the distortions in the coordination spheres are too large as is evident from the wider ranges of the cisoid and transoid angles. As noted earlier [23–25], these substantial distortions are due to the structural constraints imposed by the polydentate ligand framework around the Mn(II) ion. In each of **1**, **2** and **4**, the Schiff base nitrogen atoms form a non-planar trapezoid around the central Mn(II) ion and therefore, the thiocyanato nitrogens move far away from the apical positions to give rise to an irregular coordination polyhedron.

3.4. Antibacterial activity

The antibacterial potentiality of all the tested compounds and their MIC values against the four chosen bacteria are presented in Tables 3 and 4, respectively. The results of the antibacterial screening indicate that all the compounds exhibit broad spectrum antibacterial activity against the reference bacteria. However, they possess rather high MIC and low IZD values. The antibacterial activity was found to be highest at a concentration of 4 mg ml^{-1} for each of the tested compounds. Among all of the tested compounds, the highest IZD and lowest MIC values of similar magnitude are observed in compounds **2** and **5**. This suggests that these two compounds are the most active against all the reference bacteria. In this case, the corresponding Schiff bases L^2 and L^5, however, lack any bacterial growth retardation activity. For the

Table 3
Antibacterial activities of **1**–**5** and their constituent Schiff bases compared to control (DMSO) and standard antibiotics.

Compounds	Dose (mg ml^{-1})	Inhibition zone diameter (mean ± standard error) in cm			
		Gram positive bacteria		Gram negative bacteria	
		S. aureus MTCC 2940	*B. subtilis* MTCC 441	*P. aeruginosa* MTCC 2453	*E. coli* MTCC 739
1	4	1.267 ± 0.333	1.267 ± 0.333	1.400 ± 0.577	1.367 ± 0.333
	3	–	–	1.133 ± 0.333	1.067 ± 0.333
	2, 1, 0.5	–	–	–	–
2	4	2.100 ± 0.000	2.267 ± 0.333	2.533 ± 0.333	2.267 ± 0.333
	3	1.533 ± 0.333	1.633 ± 0.333	2.133 ± 0.333	1.600 ± 0.000
	2	1.233 ± 0.333	1.300 ± 0.577	1.667 ± 0.333	1.300 ± 0.577
	1	1.033 ± 0.333	1.067 ± 0.333	1.433 ± 0.333	1.100 ± 0.000
	0.5	–	–	1.133 ± 0.333	–
3	4	1.000 ± 0.000	1.233 ± 0.333	1.133 ± 0.333	1.633 ± 0.333
	3	–	–	–	1.233 ± 0.333
	2	–	–	–	1.033 ± 0.333
	1, 0.5	–	–	–	–
4	4	1.133 ± 0.333	1.167 ± 0.333	1.267 ± 0.333	1.233 ± 0.333
	3	1.067 ± 0.333	1.000 ± 0.000	1.167 ± 0.333	1.033 ± 0.333
	2, 1, 0.5	–	–	–	–
5	4	2.400 ± 0.577	2.233 ± 0.333	2.633 ± 0.333	2.433 ± 0.333
	3	1.700 ± 0.577	1.633 ± 0.333	2.233 ± 0.333	1.767 ± 0.667
	2	1.433 ± 0.333	1.433 ± 0.333	1.700 ± 0.577	1.633 ± 0.333
	1	1.167 ± 0.333	1.133 ± 0.333	1.433 ± 0.333	1.367 ± 0.333
	0.5	–	–	1.133 ± 0.333	1.067 ± 0.333
L^1	4	1.367 ± 0.333	1.533 ± 0.333	1.533 ± 0.333	1.433 ± 0.333
	3	1.133 ± 0.333	1.133 ± 0.333	1.000 ± 0.000	1.167 ± 0.333
	2, 1, 0.5	–	–	–	–
L^2	4	1.000 ± 0.000	1.067 ± 0.333	1.033 ± 0.333	1.033 ± 0.333
	3, 2, 1, 0.5	–	–	–	–
L^3	4	1.967 ± 0.333	1.667 ± 0.333	1.767 ± 0.333	1.967 ± 0.667
	3	1.667 ± 0.333	1.200 ± 0.577	1.433 ± 0.333	1.667 ± 0.333
	2	1.300 ± 0.577	0.967 ± 0.667	1.133 ± 0.333	1.200 ± 0.577
	1	1.033 ± 0.333	–	–	1.033 ± 0.333
	0.5	–	–	–	–
L^4	4	1.633 ± 0.333	1.967 ± 0.667	1.767 ± 0.667	1.533 ± 0.333
	3	1.133 ± 0.333	1.033 ± 0.333	1.067 ± 0.333	1.167 ± 0.333
	2, 1, 0.5	–	–	–	–
L^5	4	–	1.066 ± 0.333	–	–
	3, 2, 1, 0.5	–	–	–	–
Gattifloxacin	4	3.133 ± 0.333	3.433 ± 0.333	3.333 ± 0.333	3.667 ± 0.333
	3	2.633 ± 0.577	3.133 ± 0.333	3.233 ± 0.577	3.133 ± 0.577
	2	2.233 ± 0.333	2.333 ± 0.333	2.433 ± 0.667	2.633 ± 0.333
	1	1.867 ± 0.667	2.167 ± 0.667	1.933 ± 0.667	2.433 ± 0.667
	0.5	1.433 ± 0.667	1.333 ± 0.333	1.433 ± 0.333	1.633 ± 0.333
Ciprofloxacin	4	2.667 ± 0.577	2.833 ± 0.333	2.333 ± 0.333	2.667 ± 0.333
	3	2.433 ± 0.577	2.333 ± 0.333	1.967 ± 0.667	2.133 ± 0.333
	2	2.133 ± 0.667	2.167 ± 0.333	1.633 ± 0.333	1.967 ± 0.333
	1	1.833 ± 0.667	1.833 ± 0.333	1.433 ± 0.333	1.433 ± 0.667
	0.5	1.533 ± 0.333	1.433 ± 0.667	1.133 ± 0.667	1.133 ± 0.333
Control (DMSO)	4–0.5	–	–	–	–

Table 4
MIC[a] values (mg ml^{-1}) of **1**–**5**, related Schiff bases and antibiotics.

Compounds	*S. aureus*	*B. subtilis*	*P. aeruginosa*	*E. coli*
1 (L^1)	<4 (<3)	<4 (<3)	<3 (<3)	<3 (<3)
2 (L^2)	<1 (<4)	<1 (<4)	<0.5 (<4)	<1 (<4)
3 (L^3)	<4 (<1)	<4 (<2)	<4 (<2)	<2 (<1)
4 (L^4)	<3 (<3)	<3 (<3)	<3 (<3)	<3 (<3)
5 (L^5)	<1 (>4)	<1 (<4)	<0.5 (>4)	<0.5 (>4)
Gattifloxacin	<0.5	<0.5	<0.5	<0.5
Ciprofloxacin	<0.5	<0.5	<0.5	<0.5

[a] MIC was the lowest concentration of a compound extracted in DMSO that exhibited no visual growth of the organisms during culture.

complexes **1**, **3** and **4**, the MIC values are higher and the metal complexes exhibit less antibacterial activity than their respective Schiff bases unlike **2** and **5**. Among all the bacteria, *P. aeruginosa* is found to be the most susceptible one against all the compounds except **3**. From the *in vitro* antibacterial assay, it is thus found that all the tested compounds possess antibacterial activities to some extent, but the activities are much lower than those of the tested commercial antibiotics at similar concentrations.

4. Conclusion

Synthesis and characterization of a series of five new mononuclear Mn(II) complexes containing N-donor tetradentate Schiff base ligands and terminal thiocyanate anion have been described in this paper. Three representative complexes of the series have been studied by X-ray diffraction and found to possess severely distorted hexacoordination around the Mn(II) ions. The results of the antibacterial screening of the test compounds indicate mild to moderate bactericidal activities. In addition to the synthetic and structural investigations, this study helps to evaluate the potentiality and effectiveness of newer Schiff base complexes of Mn(II) to use as antibacterial agents.

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Appendix A. Supplementary data

CCDC 763039, 763038 and 781567 contains the supplementary crystallographic data for **1**, **2** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] V.L. Pecoraro, W.-Y. Hsieh, in: A. Sigel, H. Sigel (Eds.), Metal Ions in Biological Systems: Manganese and its Role in Biological Processes, vol. 37, Marcel Dekker, New York, 2000, pp. 431–444.
[2] J.J.R. Fraústo da Silva, R.J.P. Williams, The Biological Chemistry of the Elements, Oxford University Press, 2001.
[3] V.L. Pecoraro (Ed.), Manganese Redox Enzymes, VCH, New York, 1992.
[4] E.M. McGarrigle, D.G. Gilheany, Chem. Rev. 105 (5) (2005) 1563.
[5] Reviews: O. Kahn, Molecular Magnetism, VCH, Weinheim, Germany, 1993.
[6] S. Mandal, A.K. Rout, M. Fleck, G. Pilet, J. Ribas, D. Bandyopadhyay, Inorg. Chim. Acta 363 (2010) 2250.
[7] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, sixth ed., John Wiley and Sons, Inc., New York, 1999.
[8] T.K. Karmakar, B.K. Ghosh, S.K. Chandra, Ind. J. Chem. 45A (2006) 1121.
[9] P. Dorkov, I.N. Pantcheva, W.S. Sheldrick, H. Mayer-Figge, R. Petrova, M. Mitewa, J. Inorg. Biochem. 102 (2008) 26.
[10] M. Geraghty, J.F. Cronin, M. Devereux, M. McCann, BioMetals 13 (2000) 1.
[11] M. Patil, R. Hunoor, K. Gudasi, Eur. J. Med. Chem. 45 (2010) 2981.
[12] G.G. Mohamed, M.M. Omar, A.A. Ibrahim, Spectrochim. Acta A, Mol. Biomol. Spectrosc. 75 (2010) 678.
[13] N. Nishat, Rahis-Ud-Din, S. Dhyani, J. Coord. Chem. 62 (2009) 996.
[14] T.K. Karmakar, B.K. Ghosh, A. Usman, H.-K. Fun, E. Rivière, T. Mallah, G. Aromi, S.K. Chandra, Inorg. Chem. 44 (2005) 2391.
[15] Bruker-Nonius, Apex-II and SAINT-PLUS (Version 7.06a), Bruker AXS Inc., Madison, Wisconsin, USA, 2004.
[16] Z. Otwinowski, W. Minor, Methods Enzymol. A 276 (1997) 307.
[17] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
[18] C. Perez, M. Paul, P. Bazerque, Acta Biol. Med. Exp. 15 (1990) 113.
[19] National Committee for Clinical Laboratory Standards, Performance Standards for Antimicrobial Disc Susceptibility Tests. Approved Standard NCCLS Publications. M2-A5, Villanova, 1993.
[20] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fourth ed., Wiley Interscience, New York, 1986.
[21] G. Bergerhoff, M. Berndt, K. Brandenburg, J. Res. NIST 101 (1997) 221.
[22] S. Deoghoria, G. Mostafa, T.H. Lu, S.K. Chandra, Ind. J. Chem. 43A (2004) 329.
[23] S. Collinson, N.W. Alcock, A. Raghunathan, P.K. Kahol, D.H. Busch, Inorg. Chem. 39 (2000) 757.
[24] M.G. Barandika, M.L. Hernandez-Pino, M.K. Urtiaga, R. Cortes, L. Lezama, M.I. Arriortua, T. Rojo, J. Chem. Soc., Dalton Trans. (2000) 1469.
[25] E.V. Rybak-Akimova, N.W. Alcock, D.H. Busch, Inorg. Chem. 37 (1998) 1563.