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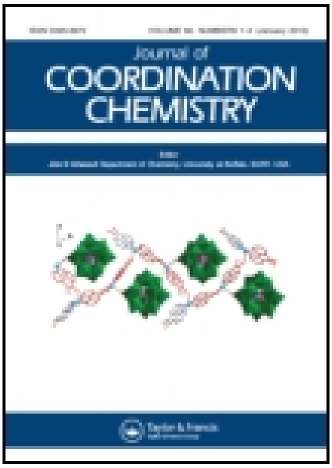

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Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, crystal structure, and antibacterial activity of two new mononuclear nickel(II) complexes of a NNS Schiff base

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Accepted author version posted online: 01 Sep 2014.Published online: 23 Sep 2014.

To cite this article: Manas Layek, Mahendra Ghosh, Michel Fleck, Rajat Saha & Debasis Bandyopadhyay (2014) Synthesis, crystal structure, and antibacterial activity of two new mononuclear nickel(II) complexes of a NNS Schiff base, Journal of Coordination Chemistry, 67:20, 3371-3379, DOI: 10.1080/00958972.2014.960861

To link to this article: http://dx.doi.org/10.1080/00958972.2014.960861

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Journal of Coordination Chemistry, 2014
Vol. 67, No. 20, 3371–3379, http://dx.doi.org/10.1080/00958972.2014.960861

Synthesis, crystal structure, and antibacterial activity of two new mononuclear nickel(II) complexes of a NNS Schiff base

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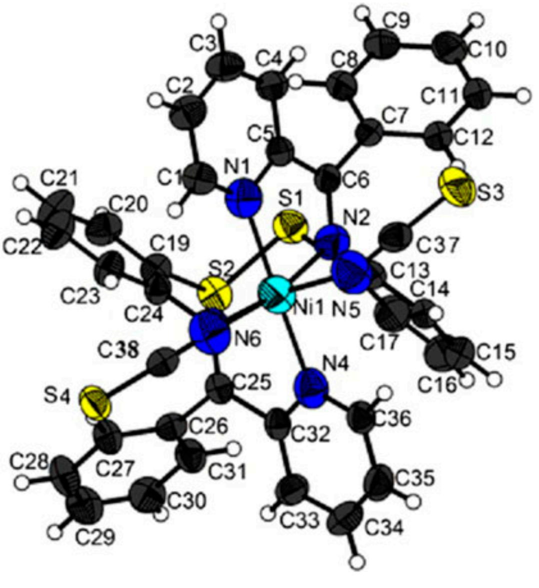
(*Received 7 April 2014; accepted 16 August 2014*)



Two new mononuclear nickel(II) complexes, $[Ni(L)(N_3)]$ (**1**) and $[Ni(L)_2(NCS)_2]$ (**2**), where HL = 2-{[phenyl(pyridin-2-yl)methylidene]amino}benzenethiol, a tridentate Schiff base derived from 2-aminothiophenol and 2-benzoylpyridine, have been prepared and characterized. The syntheses of **1** and **2** have been achieved by the reaction of equimolar amounts of nickel perchlorate and HL in the presence of azide and thiocyanate, respectively. The complexes have been characterized by microanalytical, spectroscopic, single-crystal X-ray diffraction, and other physicochemical studies. Structural studies reveal that **1** and **2** adopt two different geometries, distorted square planar in **1** and octahedral in **2**. The two mononuclear complex units are held together by $\pi \ldots \pi$ or C–H…π weak intermolecular interactions to develop supramolecular networks in their solid states.

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The antibacterial activity of **1**, **2** and their constituent Schiff base has been tested against some gram (+) and gram(−) bacteria.

Keywords: Nickel(II); Schiff base; Crystal structure; Antibacterial activity

1. Introduction

Coordination chemistry of nickel has been subject of much attention due to its diverse nature, with enhanced interest in the synthesis and characterization of nickel(II) complexes of Schiff base ligands due to their important catalytic and magnetic properties [1–5]. The structural diversity leading to supramolecular architecture through various non-covalent intermolecular interactions in the solid state gives further impetus to study of such complexes [5–7]. A sulfur-rich coordination environment has been identified in some biologically active nickel centers [8]. Therefore, biological properties of Schiff bases containing sulfur and their nickel(II) complexes are still being investigated [9–17]. Although numerous Schiff base ligands have been used to synthesize such complexes, reports on complexes of nickel(II) containing the tridentate Schiff base derived from 2-aminothiophenol and 2-benzoylpyridine, along with a pseudohalide, are lacking.

In the present work, we describe the synthesis of two new mixed-ligand complexes of nickel(II) containing a tridentate (NNS) Schiff base ligand (HL). The complexes have been characterized by microanalytical, spectroscopic, and single-crystal X-ray diffraction studies. The same synthetic system has given two non-electrolytic mononuclear Ni(II) complexes of different geometries in the presence of different pseudohalides, viz. square planar $[Ni(L)(N_3)]$ (**1**) in the presence of azide and octahedral $[Ni(L)_2(NCS)_2]$ (**2**) in the presence of thiocyanate. The complex units in **1** and **2** are linked by weak intermolecular $\pi\ldots\pi$ or C–H$\ldots\pi$ interactions in the solid state. In addition to the physicochemical studies, the complexes and other relevant compounds have been tested *in vitro* to assess their antibacterial activities against some common reference bacteria. The results were compared with similar doses of a commercial antibiotic Ciprofloxacin.

2. Experimental

2.1. *Physical measurements*

Elemental analyses for carbon, hydrogen, and nitrogen were carried out using a PerkinElmer 2400-II elemental analyzer. Infrared spectra were recorded on a PerkinElmer Spectrum 65 FTIR spectrophotometer with KBr disks (4000–400 cm^{-1}). Room-temperature solid-phase magnetic susceptibilities were measured by Gouy's method using $Hg[Co(NCS)_4]$ as the calibrant. The diamagnetic corrections were calculated from Pascal's constants.

2.2. *Materials*

Commercially available reagent-grade 2-aminothiophenol, 2-benzoylpyridine, nickel(II) perchlorate hexahydrate, sodium azide, and ammonium thiocyanate were used without purification. All other chemicals and solvents were of analytical grade. The tridentate Schiff base (HL) was obtained by the usual method of condensation of 2-aminothiophenol with 2-benzoylpyridine in 1 : 1 M ratio.

Caution! Although no problems were encountered in the present work, compounds containing perchlorate and azide are potentially explosive. Therefore, only a small amount of the materials should be used at a time and handled with proper care.

2.3. *Syntheses of compounds*

2.3.1. Synthesis of [Ni(L)(N_3] (1). Ten milliliters of a methanolic solution of Ni $(ClO_4)_2 \cdot 6H_2O$ (0.18 g, 0.5 mM) was added with constant stirring to same volume of HL (0.15 g, 0.5 mM) solution in methanol. To the resulting green solution, an aqueous solution of NaN_3 (0.03 g, 0.5 mM) was added and the total volume was made up to 40 mL by adding methanol. Stirring was continued for half an hour, and the solution was left for slow evaporation at room temperature. After a week, dark green crystals of **1** appeared. The crystals were collected by filtration, washed with methanol, and finally dried. Yield: 0.12 g, 62%. Anal. Calcd for $C_{18}H_{13}N_5NiS$ (%): C, 55.42; H, 3.36; N, 17.95. Found: C, 55.46; H, 3.38; N, 17.92. FTIR (KBr, strong peaks, cm^{-1}): 2080, 1615, 1595, 759. Diamagnetic.

2.3.2. Synthesis of [Ni(L)$_2$(NCS)$_2$] (2). The synthetic route described above for **1** was followed in the preparation of **2** also, except that a solution of NH_4SCN (0.04 g, 0.5 mM) in 10 mL methanol was used instead of sodium azide. Green crystals of **2** appeared after 10–12 days in this case. Yield: 0.2 g (53%). Anal. Calcd for $C_{38}H_{26}N_6NiS_4$ (%) C, 60.56; H, 3.48; N, 11.15. Found: C, 60.53; H, 3.46; N, 11.12. FTIR (KBr, strong peaks, cm^{-1}): 2052, 1612, 1595, 758. μ_{eff} (RT, BM): 2.98.

2.4. *Crystal structure determination and refinement*

X-ray diffraction data were collected at ambient conditions on a Bruker APEX II diffractometer, equipped with a CCD area detector and graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) using suitable single-crystals of **1** and **2** with dimensions of 0.20 × 0.16 × 0.14 and 0.60 × 0.40 × 0.35 mm^3, respectively. In the case of **2**, the crystal quality was not optimal, but enough reflections could be collected and integrated to perform the structure analysis satisfactorily. In the measurements, multiple sets of φ- and ω-scans were used. The intensity data were processed with the Bruker-Nonius program suite SaintPlus and corrected for Lorentz, polarization, background, and absorption effects [18, 19]. The crystal structures were determined by direct methods and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-squares refinements on F^2 [20]. Scattering factors for neutral atoms were employed in the refinements. In **1**, all atoms were refined freely. All non-hydrogen atoms were refined anisotropically and all hydrogens isotropically. In the refinement of **2**, the hydrogens were placed geometrically and refined as riding. The final $R1$-values of the refinements were 0.051 for both **1** and **2**. The crystallographic data, structural parameters, and refinement details of **1** and **2** are presented in table 1. The molecular structure and packing diagrams of the complexes are presented in figures 1 and 2, respectively. A few selected bond parameters including those relevant to intermolecular attractions are presented in table 2.

Table 1. Crystallographic data and refinement parameters for **1** and **2**.

Parameters	**1**	**2**
Formula	$C_{18}H_{13}N_5NiS$	$C_{38}H_{26}N_6NiS_4$
Formula weight ($g\,M^{-1}$)	390.10	753.60
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	10.8338(4)	19.390(4)
b (Å)	15.6872(6)	10.351(2)
c (Å)	9.8111(3)	18.454(4)
β (°)	97.892(2)	96.42(3)
V (Å^3)	1651.6(1)	3680.6(1)
Z	4	4
D ($g\,cm^{-3}$)	1.569	1.360
μ (mm^{-1})	1.311	0.790
$F(0\,0\,0)$	800	1552
hkl range	±16, ±23, –9/14	±21, −8/10, ±19
T (K)	293(2)	296(2)
Reflections collected	21,289	5992
Reflections unique	5604	3873
Data with $F_o > 4\sigma(F_o)$	4023	2385
R_{int}	0.027	0.040
Parameters refined	262	442
R^a	0.051	0.051
wR^b	0.1325	0.1238
S	1.026	1.072
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.076, −0.481	0.233, −0.251

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

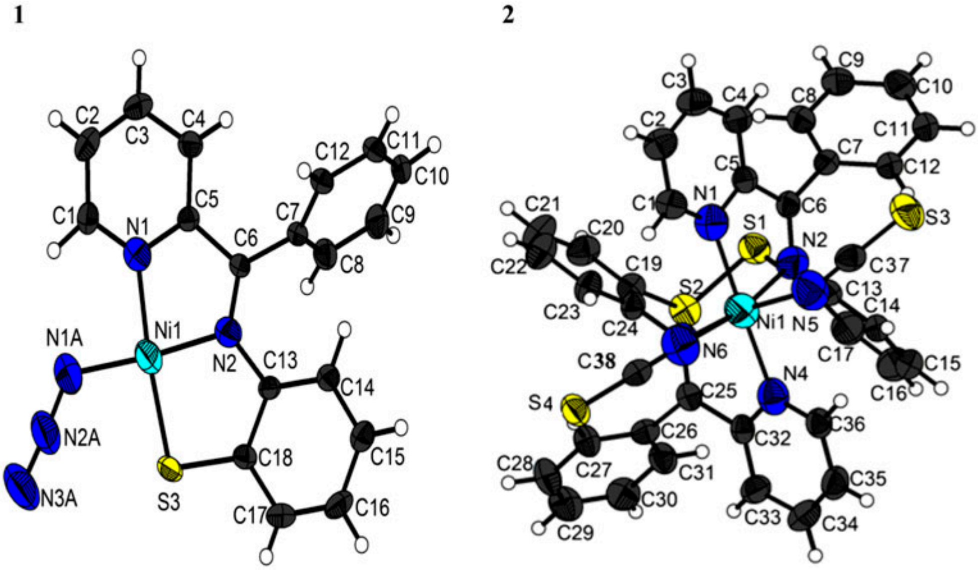


Figure 1. Molecular structures of **1** and **2**.

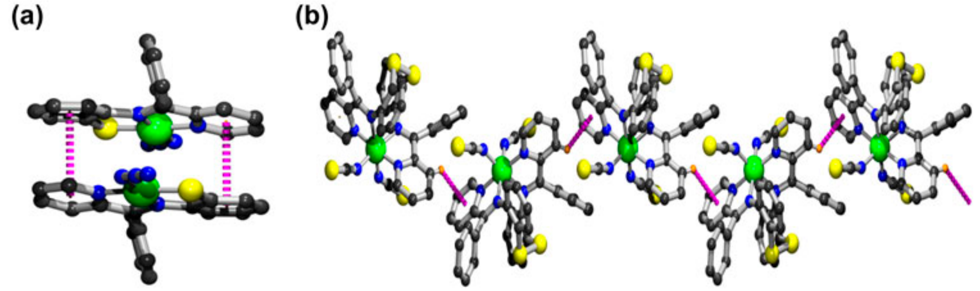


Figure 2. Formation of supramolecular (a) dimers through $\pi\cdots\pi$ interactions in **1** and (b) 1-D chains along the *c*-axis through C–H$\cdots\pi$ interactions in **2**.

Table 2. Selected bond parameters for **1** and **2**.

Bond lengths (Å) and angles (°) in **1**

Ni1–S3	2.130(8)	S3–Ni1–N1A	94.28(9)	N1A–Ni1–N1	91.3(1)
Ni1–N1A	1.876(2)	S3–Ni1–N1	173.98(7)	N1A–Ni1–N2	175.4(1)
Ni1–N1	1.932(2)	S3–Ni1–N2	90.22(7)	N1–Ni1–N2	84.16(9)
Ni1–N2	1.888(2)				

$\pi\cdots\pi$ interactions in **1**

R*i*…R*j*	Distance (Å)	Dihedral angle, α (°)	Symmetry
R1…R2	3.6851	11.17	$1-x, -y, 1-z$
R2…R1	3.6850	11.17	$1-x, -y, 1-z$

Bond lengths (Å) and angles (°) in **2**

Ni1–N6	2.052(5)	N6–Ni1–N5	97.7(2)	N5–Ni1–N4	93.6(2)
Ni1–N5	2.075(6)	N6–Ni1–N1	93.7(2)	N1–Ni1–N2	77.4(2)
Ni1–N1	2.068(6)	N6–Ni1–N2	169.6(2)	N1–Ni1–N3	100.5(2)
Ni1–N2	2.115(4)	N6–Ni1–N3	87.1(2)	N1–Ni1–N4	176.5(2)
Ni1–N3	2.124(4)	N6–Ni1–N4	89.3(2)	N2–Ni1–N3	89.1(2)
Ni1–N4	2.055(5)	N5–Ni1–N1	87.6(2)	N2–Ni1–N4	99.4(2)
		N5–Ni1–N2	87.5(2)	N3–Ni1–N4	77.9(2)
		N5–Ni1–N3	170.3(2)		

C–H…π interactions in **2**

C–H…R*i*	H…R*i* (Å)	X–H…R*i* (°)	Symmetry
C4–H4…R1	2.96	129	$x, 1/2-y, -1/2+z$

[R1 = N1–C1–C2–C3–C4–C5, R2 = C13–C14–C15–C16–C17–C18 for **1**; R1 = N4–C32–C33–C34–C35–C36 for **2**].

2.5. *Antibacterial screening – materials and methods*

Complexes **1**, **2**, and Ciprofloxacin were tested *in vitro* to assess their growth inhibitory activity against two gram-positive bacteria (*Staphylococcus aureus* MTCC 2940 and *Bacillus subtilis* MTCC 441) and two gram-negative bacteria (*Pseudomonas aeruginosa* MTCC 2453 and *Escherichia coli* MTCC 739) by Kirby-Bauer method with necessary modifications [21]. The bacterial strains grown on nutrient agar at 37 °C for 18 h were suspended in a saline solution (0.85%) and adjusted to a turbidity of 0.5 McFarland standards (10^8 CFU mL^{-1}). The suspension was used to inoculate sterile Petri plates of 9.0 cm diameter in which the test organisms were grown. After solidification, a hole of diameter 0.6 cm was pierced by a sterile cork borer. Complexes **1**, **2**, and Ciprofloxacin were dissolved in DMSO to prepare five different concentrations (0.2, 0.4, 0.6, 0.8, and 1.0 mg mL^{-1}) for evaluation of dose response.

The disks were placed on the holes of previously seeded plates and incubated at 303 K for *B. subtilis* and at 310 K for all other bacteria. Antibacterial activities of the compounds were evaluated by measuring the inhibition zone diameters (IZD). Each of the above experiments was repeated thrice along with a control set using DMSO, and the mean value was taken for comparison.

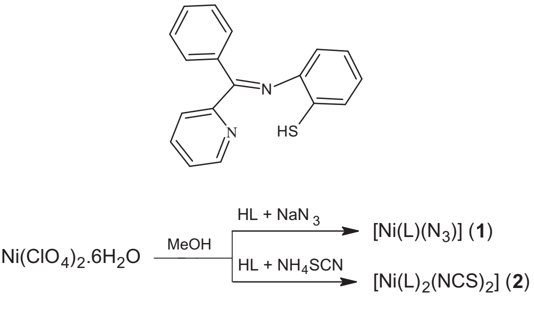
3. Results and discussion

3.1. *Synthesis and characterization*

The non-electrolytic nickel(II) complexes **1** and **2** were obtained as green crystalline solids by reacting nickel perchlorate with HL and sodium azide (for **1**) and ammonium thiocyanate (for **2**) in 1 : 1 : 1 M ratio in methanol. The same synthetic system and equimolar ratio of reactants yielded complexes of two different geometries in the presence of two different pseudohalides. The structure of the ligand and relevant equations for the formation of the complexes are presented in scheme 1. The complexes have been characterized by elemental analysis, IR spectroscopy, magnetic susceptibility measurements, and also by single-crystal X-ray diffraction studies. Room-temperature magnetic susceptibility measurements show that **1** is diamagnetic, indicating the absence of unpaired electrons. In contrast, **2** has a magnetic moment of 2.94 BM, close to the spin-only value of Ni(II), indicating the presence of two unpaired electrons. The μ_{eff} values are in conformity with the presence of a square planar low-spin 3d^8 system in **1** and an idealized $t_{2g}{}^6e_g{}^2$, $S = 1$ electronic state in **2**. All these results including the X-ray structural analysis are consistent with the proposed mononuclear formulas of **1** and **2**.

3.2. *FTIR spectra*

The infrared spectra of **1** and **2** exhibit strong absorptions at 1595–1615 cm^{-1} corresponding to the stretch of C=N [ν_{CN}] of the Schiff base ligand. They also show sharp and distinct absorptions between 2080 and 2052 cm^{-1}, which are attributable to the asymmetric stretch of terminal azide and N-bonded thiocyanate, respectively. Several other bands at 2900–3340 cm^{-1} are assigned to characteristic absorptions of CH groups present in **1** and **2**. All other characteristic vibrations including the thiophenolate C–S stretch of the metal-bound



Scheme 1. Structure of HL and formation of **1** and **2**.

Schiff bases are at 600–1600 cm^{-1}. Thus, IR spectra of the compounds agree well [22] with the respective structural features of **1** and **2**.

3.3. *Crystal structures of 1 and 2*

X-ray diffraction studies reveal that both **1** and **2** crystallize in the monoclinic system with $P2_1/c$ space groups. Complex **1** is comprised of a non-electrolytic mononuclear unit (figure 1) with slightly distorted square planar geometry. The central Ni(II) is surrounded by N1, N2, and N1A of the pyridine ring, the imine nitrogen of the Schiff base, and the terminal azide ion in the basal plane. The fourth coordination is completed by the thiophenolate sulfur (S3) of the tridentate ligand. The Ni–N bond distances vary from 1.876 to 1.923 Å, while the Ni–S bond distance is 2.13 Å. The *cis* and *trans* angles in **1**, of 84.16–94.28° and 174–175°, respectively, indicate some distortions from ideal square planar geometry. In its solid state, discrete molecules of **1** are connected to each other by $\pi\ldots\pi$ interactions to form supramolecular dimeric units [figure 2(a)]. The phenyl ring (R1) of one molecular unit interacts with a phenyl ring (R2) of another unit at $1-x$, $-y$, and $1-z$ symmetry positions and *vice versa* to form such dimers (table 2).

X-ray diffraction studies show that each mononuclear unit of **2** (figure 1) contains NiN_6 chromophore with a distorted octahedral geometry. The six-coordinate environment is maintained by two imino nitrogens (N2 and N3), two pyridine nitrogens (N1 and N4) of the tridentate Schiff base, and two nitrogens (N5 and N6) of two thiocyanates. The two thiocyanate groups are *cis* to each other. The Ni–N bond distances in **2** are 2.052–2.124 Å. The distortions in the coordination sphere of the metal ion from ideal geometries are due to the structural constraints imposed by the polydentate ligand framework. The *cis* and *trans* angles involving Ni(II) in **2**, of 77.4°–100.5° and 169.6°–176.5°, respectively, support the fact. All bond parameters of **1** and **2** agree well with analogous Schiff base complexes of Ni(II) containing NiN_6 chromophores [23, 24]. In contrast to **1**, sulfurs of the thiophenolic groups in **2** do not coordinate to Ni(II). Rather, the two sulfurs of two different Schiff base units are close enough (S1–S2 distance = 2.055 Å) to form a covalent bond. In the structural packing diagram of **2** [figure 2(b)], the molecular units are involved in weak intermolecular C–H…π interactions. Metal–organic moieties are linked through C4–H4…R1 (R1 is the centroid of the pyridine ring N4–C32–C33–C34–C35–C36) interactions (table 2) to form 1-D supramolecular chains along the crystallographic *c*-axis.

3.4. *Antibacterial activity of the compounds*

The antibacterial activities of all of the tested compounds are presented as their IZD values in table 3. The data of antibacterial screening indicate that the Ni(II) complexes exhibit broad spectrum antibacterial activity against the reference bacteria. However, **2** exhibits rather less bactericidal properties than **1** in lower concentrations. The study reveals that the constituent Schiff base HL itself is moderately active toward all the bacteria, but the bactericidal property is greatly enhanced on complexation with nickel, particularly in **1**. The activity of **1** is very high against the gram(+) bacteria reflected from the comparable IZD values of Ciprofloxacin and those of **1** at higher doses. Complex **2** is moderately active against all the bacteria, more than the Schiff base at higher doses. Among all the bacteria, *B. subtilis* is most susceptible against the nickel(II) complexes. The overall antibacterial screening indicates that the bactericidal activities of the complexes are mild to high, depending on the

Table 3. Antibacterial activities of **1**, **2,** and related compounds compared to control (DMSO) and Ciprofloxacin.

		Inhibition zone diameter in mm			
		Gram positive bacteria		Gram negative bacteria	
Compounds	Dose (mg mL^{-1})	*S. aureus*	*B. subtilis*	*P. aeruginosa*	*E. coli*
1	0.2	17	18	16	18
	0.4	20	21	18	19
	0.6	22	24	18	20
	0.8	25	25	20	22
	1.0	26	26	20	23
2	0.2	16	18	16	16
	0.4	18	20	17	18
	0.6	19	22	18	19
	0.8	21	23	20	20
	1.0	22	24	20	20
HL	0.2	12	14	14	10
	0.4	14	14	16	12
	0.6	17	16	16	12
	0.8	19	17	17	14
	1.0	20	18	18	15
Ciprofloxacin	0.2	18	20	16	18
	0.4	21	22	18	20
	0.6	23	25	20	22
	0.8	26	26	22	25
	1.0	28	28	25	28
DMSO	0.2–1	–	–	–	–

dose. Nevertheless, none of tested compounds are as potent as Ciprofloxacin as far as the bactericidal properties are concerned. These observations are similar to earlier reports [9–17] of biological activities of similar Schiff base complexes of nickel(II).

4. Conclusion

Synthesis and characterization of two new mononuclear complexes of nickel(II) with a tridentate Schiff base containing sulfur have been described in this paper. The reaction of nickel(II) perchlorate with the Schiff base in the presence of azide ions yielded a square planar complex containing a Ni–S bond. However, the same synthetic system in the presence of thiocyanate yielded an octahedral complex with no such metal–sulfur link. The complex units in **1** and **2** are linked by weak intermolecular $\pi \ldots \pi$ or C–H…π interactions in their solid state. Antibacterial screening of the compounds indicates moderate to strong bactericidal activities.

Supplementary material

CCDC 988966 and 988967 contain the supplementary crystallographic data of **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336 033; or E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

The authors (DB and ML) gratefully acknowledge the financial support under Minor Research Project No. PSW-002/12-13(ERO) from UGC, Eastern region, Kolkata, India.

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