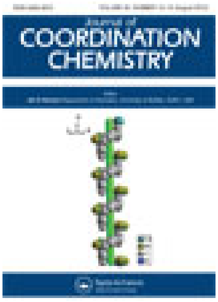

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Synthesis, crystal structure, and antibacterial activity of mononuclear nickel(II) and cobalt(III) Schiff-base complexes

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Four new mononuclear complexes, $[Ni(L^1)(NCS)_2]$ (**1**), $[Ni(L^2)(NCS)_2]$ (**2**), $[Co(L^1)(N_3)_2]ClO_4$ (**3**), and $[Co(L^2)(N_3)_2]ClO_4$ (**4**), where L^1 and L^2 are *N*,*N′*-bis[(pyridin-2-yl)methylidene]butane-1,4-diamine and *N*,*N′*-bis[(pyridin-2-yl)benzylidene]butane-1,4-diamine, respectively, have been prepared. The syntheses have been achieved by reaction of the respective metal perchlorate with the tetradentate Schiff bases, L^1 and L^2, in presence of thiocyanate (for **1** and **2**) or azide (for **3** and **4**). The complexes have been characterized by microanalytical, spectroscopic, single crystal X-ray diffraction and other physicochemical studies. Structural studies reveal that **1**–**4** are distorted octahedral geometries. The antibacterial activity of all the complexes and their constituent Schiff bases have been tested against Gram-positive and Gram-negative bacteria.

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

1. Introduction

Nickel and cobalt complexes containing Schiff bases have received attention due to their important catalytic, magnetic, and biological properties [1–8]. Complexes containing Schiff bases derived from butane-1,4-diamine and pyridine-2-al or its derivatives have been synthesized and characterized [9–13]. However, simple mononuclear complexes of nickel(II) and cobalt(III) containing these tetradentate ligands along with azide or thiocyanate anions are rare and studies on their biological properties are being continued [12–14].

Here, we describe the synthesis of four mononuclear complexes of nickel(II) and cobalt(III), $[Ni(L^1)(NCS)_2]$ (**1**), $[Ni(L^2)(NCS)_2]$ (**2**), $[Co(L^1)(N_3)_2]ClO_4$ (**3**), and $[Co(L^2)(N_3)_2]ClO_4$ (**4**). L^1 and L^2 were prepared by condensation of butane-1,4-diamine with pyridine-2-al and 2-benzoyl pyridine, respectively. The complexes were

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characterized by microanalytical, spectroscopic, and single crystal X-ray diffraction studies. The complexes and Schiff bases were tested *in vitro* to assess their antibacterial activities against some common reference bacteria and the results were compared with a commercial antibiotic, Gattifloxacin.

2. Experimental

2.1. *Physical measurements*

Elemental analyses for carbon, hydrogen, and nitrogen were carried out using a Perkin-Elmer 2400-II elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer Spectrum 65 FT-IR spectrophotometer with KBr discs (4000–400 cm^{-1}). Electronic spectra were obtained on a Systronics 2202 spectrophotometer using DMF at $10^{-4}\,\mathrm{mol\,L}^{1}$ concentration. Room temperature solid phase magnetic susceptibilities were measured at 298 K with a PAR 155 vibrating sample magnetometer with $\mathrm{Hg[Co(NCS)_4]}$ as the calibrant. Diamagnetic corrections were calculated from Pascal's constants. Molar conductances of the complexes in dry methanol were measured using a direct reading conductivity meter, Systronics (Type 304).

2.2. *Materials*

Reagent grade 1,4-diaminobutane, pyridine 2-carboxaldehyde, 2-benzoyl pyridine, ammonium thiocyanate, sodium azide, nickel(II) perchlorate hexahydrate, and cobalt(II) perchlorate hexahydrate were purchased and used as received. All other chemicals and solvents were of analytical grade. The tetradentate ligands *N*,*N*′-bis[(pyridin-2-yl)methylidene]butane-1,4-diamine (L^1) and *N*,*N*′-bis[(pyridin-2-yl)benzylidene]butane-1,4-diamine (L^2) were prepared by condensation of the respective carbonyl compound with butane-1,4-diamine using similar methods as described earlier [15].

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 $[\mathrm{Ni(L^1)(NCS)_2}]$ (1) and $[\mathrm{Ni(L^2)(NCS)_2}]$ (2). The nickel(II) complexes **1** and **2** were prepared by mixing nickel(II) perchlorate, the Schiff base L^1 or L^2 and ammonium thiocyanate in 1 : 1 : 2 molar ratio in acetonitrile followed by slow evaporation. For **1**, an acetonitrile solution (10 mL) of Schiff base L^1 (0.13 g, 0.5 mmol) was added dropwise to an acetonitrile solution (5 mL) of $\mathrm{Ni(ClO_4)_2 \cdot 6H_2O}$ (0.18 g, 0.5 mmol) with constant stirring at room temperature. To the resulting yellow solution, $\mathrm{NH_4SCN}$ (0.08 g, 1.0 mmol) dissolved in 5 mL acetonitrile 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 7–10 days, yellow brown crystals of **1** appeared. The crystals were collected by filtration, washed with a little acetonitrile and finally dried. Yield: 0.15 g (69%). Complex **2** was synthesized in the same manner except that L^2 (0.21 g, 0.5 mmol) was used instead of L^1. Yield: 0.18 g (62%). Anal. Calcd for $C_{18}H_{18}N_6NiS_2$ (**1**): C, 49.00; H, 4.11; N, 19.05%. Found: C, 49.12; H, 4.18; N, 19.12%. Anal. Calcd for $C_{30}H_{26}N_6NiS_2$ (**2**): C, 60.72; H, 4.42; N, 14.16%. Found: C, 60.55; H, 4.35; N, 13.98%.

2.3.2. Synthesis of [Co(L^1)(N_3)$_2$]ClO_4 (3) and [Co(L^2)(N_3)$_2$]ClO_4 (4). The cobalt(III) complexes **3** and **4** were prepared by the same synthetic procedure as described above for **1** and **2** but in methanol. A methanolic solution (10 mL) of 0.5 mmol of L^1 (for **3**) or L^2 (for **4**) was mixed with methanolic solution of $Co(ClO_4)_2 \cdot 6H_2O$ (0.18 g, 0.5 mmol) followed by addition of an aqueous solution of NaN_3 (0.07 g, 1.0 mmol) in each case. Crystals of **3** and **4** were grown and then collected by the same method as adopted in **1** and **2**. Yields of **3** and **4** were 0.12 g (48%) and 0.20 g (62%), respectively. Anal. Calcd for $C_{16}H_{18}ClCoN_{10}O_4$ (**3**): C, 37.77; H, 3.57; N, 27.53%. Found: C, 37.75; H, 3.59; N, 27.58%. Anal. Calcd for $C_{28}H_{26}ClCoN_{10}O_4$ (**4**): C, 50.88; H, 3.96; N, 21.19%. Found: C, 50.85; H, 3.92; N, 21.12%.

2.4. *Crystal structure determination and refinement*

For X-ray diffraction studies, suitable single crystals of **1**–**4** with dimensions of $0.15 \times 0.36 \times 0.70$, $0.08 \times 0.06 \times 0.06$, $0.24 \times 0.29 \times 0.60$, and $0.09 \times 0.06 \times 0.06\,\text{mm}^3$, respectively, were mounted on glass needles with laboratory grease. An Oxford Diffraction Gemini diffractometer (for **1** and **3**) and a Bruker-Nonius APEX-II diffractometer (for **2** and **4**), both equipped with a CCD area detector and graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), were used for the measurements. Reflection data were collected and processed using the Oxford Diffraction CrysAlis RED (for **1** and **3**), the Bruker-Nonius program suites COLLECT, DENZO-SMN (for **2** and **4**) and related analysis software [16–18]. 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 programs SIR97, CRYSTALS, and SHELX [19–21]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were partially located from difference Fourier maps, partially placed geometrically, and refined keeping restraints (riding mode). Crystallographic data and details of the refinement processes are summarized in table 1.

2.5. *Antibacterial activity – materials and methods*

Complexes **1**–**4** and a reference commercial antibiotic, Gattifloxacin (purchased in powder form from Span Diagnostic Limited, Surat, India), 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 [22]. The antibacterial activities of 1,4-diaminobutane (dab), pyridine 2-carboxaldehyde (pyal), 2-benzoyl pyridine (bzpy), L^1 and L^2 were also evaluated during the same experiment. The bacterial strains grown on

Table 1. Crystal data and details of refinement for **1–4**.

Parameters	**1**	**2**	**3**	**4**
Empirical formula	$C_{18}H_{18}N_6NiS_2$	$C_{30}H_{26}N_6NiS_2$	$C_{16}H_{18}ClCoN_{10}O_4$	$C_{28}H_{26}ClCoN_{10}O_4$
Formula weight	441.22	593.40	508.77	660.97
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)				
a	7.916(1)	8.650(2)	10.2636(7)	8.956(1)
b	8.470(1)	10.333(2)	11.2191(8)	13.085(2)
c	16.109(2)	18.089(3)	11.698(1)	13.520(2)
α	95.838(9)	105.528(6)	66.419(8)	92.523(3)
β	99.628(9)	96.032(5)	66.005(8)	97.565(3)
γ	113.436(10)	92.254(5)	83.505(6)	109.711(3)
Volume (Å^3), Z	960.0(2), 2	1545.3(5), 2	1125.8(2), 2	1471.9(4), 2
D_{Calcd} (g cm^{-3})	1.527	1.275	1.501	1.491
Absorption coefficient (mm^{-1})	1.244	0.791	0.925	0.727
$F(000)$	456	616	520	680
Limiting indices	$-10 \le h \le 10$; $-11 \le k \le 11$; $-20 \le l \le 20$	$-12 \le h \le 9$; $-15 \le k \le 15$; $-26 \le l \le 26$	$-11 \le h \le 13$; $-14 \le k \le 13$; $-15 \le l \le 15$	$-11 \le h \le 9$; $-15 \le k \le 16$; $-17 \le l \le 15$
Temperature (K)	110(2)	296(2)	293(2)	296(2)
Reflections collected	8283	13,561	9003	9602
Independent reflection	4511 [R(int) = 0.041]	10,013 [R(int) = 0.037]	5161 [R(int) = 0.028]	6358 [R(int) = 0.071]
Data with $F_o > 4\sigma(F_o)$	3730	5020	4082	3941
Parameters refined	244	353	217	397
R^a [for $F_o > 4\sigma(F_o)$]	0.041	0.070	0.049	0.057
wR^a	0.130	0.188	0.060	0.145
S	1.00	1.277	1.044	1.027
Largest difference peak and hole (e Å^{-3})	0.72 and −0.51	1.43 and −0.52	1.18 and −0.31	0.61 and −0.44

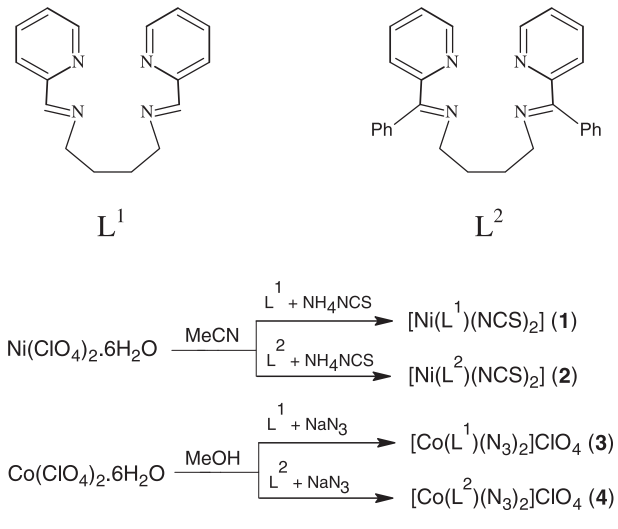
[a] $R = \Sigma||F_o| - |F_c||/\Sigma F_o|$, $wR = [\Sigma\, w(F_o^2 - F_c^2)^2/\Sigma\, wF_o^4]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (a \times P)^2 + b \times P]$, $P = (F_o^2 + 2F_c^2)/3$.

nutrient agar at 37°C for 18 h were suspended in a saline solution (0.85%) and adjusted to a turbidity of 0.5 MacFarland 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 of 0.6 cm was pierced by a sterile cork borer. All the compounds and the antibiotic 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 discs 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*

One-pot reactions of L^1 and L^2 with nickel(II) perchlorate and thiocyanate in acetonitrile or with cobalt(II) perchlorate and azide in methanol resulted in the formation of **1**–**4**. The structures of the ligands and relevant equations for formation of the complexes are presented in scheme 1. The same reactions were performed with the pseudohalides in reverse order to obtain the respective azido complexes of nickel(II) and thiocyanato complexes of cobalt(III). However, no crystal suitable for X-ray structural analysis could be collected from the products. Therefore, only **1**–**4** have been characterized in addition to the single crystal X-ray structural analysis. In methanol, **1** and **2** are non-electrolytes while **3** and **4** are 1 : 1 electrolytes, as evident from their Λ_M values. Room temperature magnetic susceptibility measurements indicate (table 2) that **1** and **2** possess magnetic moments of 2.92 and 2.88 BM, respectively, indicating $t_{2g}^6e_g^2$



Scheme 1. Structures of the ligands and formation of **1**–**4**.

Table 2. Important analytical data of **1–4**.

Compound	FTIR (KBr, cm^{-1})	UV-Vis (λ, nm)	Λ_M (MeOH, Ω^{-1} cm^2 mol^{-1})	μ_{eff} (RT, BM)
1	2936, 2086, 1643, 1595, 786, 705	358, 394, 562	6	2.92
2	2942, 2080, 1628, 1592, 705	360, 388, 560	7	2.88
3	2017, 1601, 1091, 774	330, 382, 508	120	Diamagnetic
4	2942, 2006, 1628, 1091, 705	332, 396, 510	110	Diamagnetic

electronic configuration with two unpaired electrons in an octahedral Ni(II) species. Complexes **3** and **4** are diamagnetic showing singlet ground state with $t_{2g}^6e_g^0$ configurations as expected for low-spin octahedral Co(III) complexes. Co^{II} underwent aerial oxidation to Co^{III} during the formation of **3** and **4** to accommodate ligands with harder donors. All the results along with the X-ray structural analysis of **1–4** are consistent with the proposed mononuclear formulas of the Ni(II) and Co(III) complexes.

3.2. *FTIR and electronic spectra*

Infrared spectra of **1–4** are similar with distinct absorptions (table 2) at 1600 cm^{-1}, assignable to ν_{CN} of the Schiff-base ligands. Strong and sharp absorptions at 2086, 2080, 2017, and 2006 cm^{-1} for **1–4**, respectively, are attributed to asymmetric stretch of terminal thiocyanate (for **1** and **2**) and azide (for **3** and **4**). The asymmetric single and sharp band expected for ClO_4^- is observed at 1091 cm^{-1} in **3** and **4**. Other vibrations of the metal-bound Schiff bases are located in the range 600–1600 cm^{-1}. Thus, infrared spectra of **1–4** are in agreement [23] with their respective structural features.

The electronic spectra of **1–4** in DMF show several intense absorptions (table 2) in the 200–900 nm range. Bands at λ_{max} of 560–562 and 358–360 nm in **1** and **2** are assigned to spin allowed transitions in octahedral nickel(II) complexes. In **3** and **4**, the spectral patterns reflect the presence of six-coordinate cobalt(III). High intensity bands at λ_{max} of 508 and 510 nm in **3** and **4**, respectively, may be attributed to LMCT transitions. Intense bands at λ_{max} 382–396 nm in **1–4** are attributable to transitions of C = N groups. Other high intensity bands observed in the UV region of all compounds are assigned to intraligand n–π^*/π–π^* transitions [24].

3.3. *Crystal structures of 1–4*

Molecular structures of **1–4** are displayed in figure 1 and selected bond lengths and angles are listed in table 3. Compounds **1** and **2** differ from **3** and **4** in that nickel(II) complexes are non-electrolytes, while the cobalt(III) complexes contain cationic units along with a perchlorate. Nevertheless, these four complexes are structurally very similar, evident from insignificant variations in their bond lengths and angles. Each Ni(II) or Co(III) ion is a member of one seven-membered and two five-membered rings in a distorted octahedron (NiN_6 in **1**, **2**; CoN_6 in **3**, **4**). Two pyridine nitrogen atoms (N1, N20 in **1**, **3**; N1, N4 in **2** and **4**) and two imine nitrogen atoms (N8, N13 in **1**, **3**; N2, N3 in **2**, **4**) of the tetradentate Schiff bases (L^1 in **1**, **3**; L^2 in **2**, **4**) along with

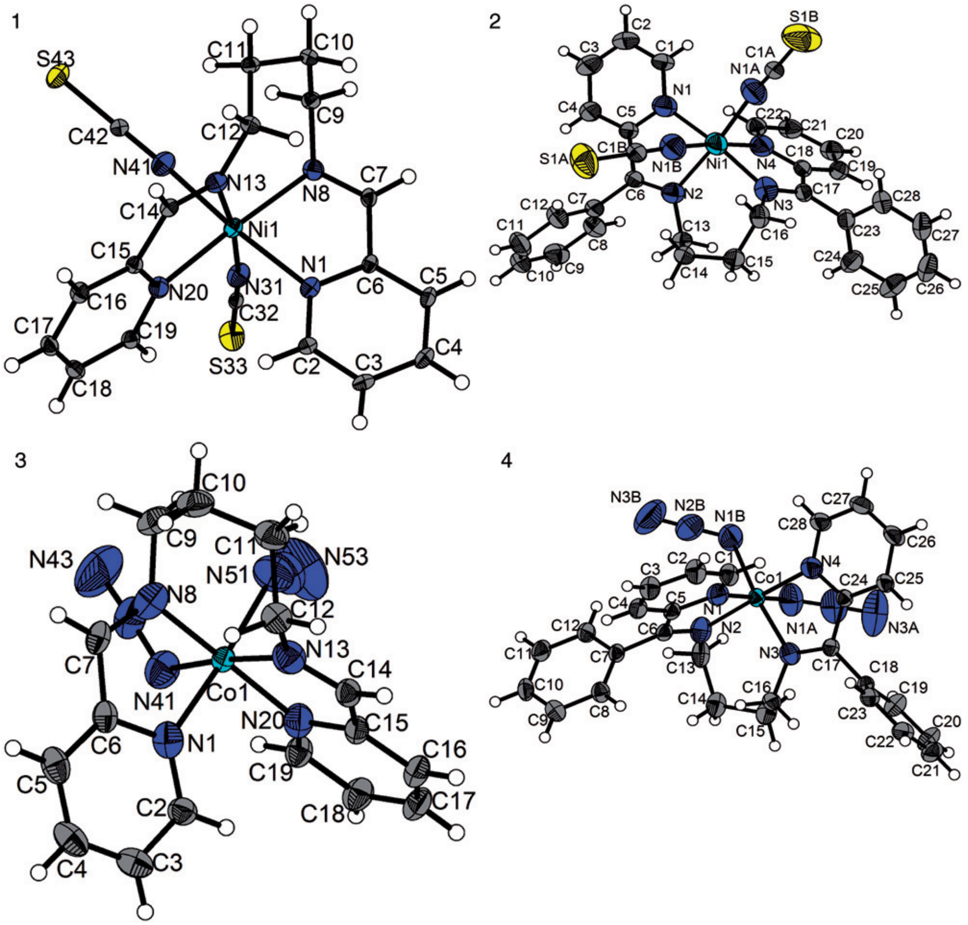


Figure 1. Molecular structures of **1–4**.

another two nitrogen atoms (N31, N41 in **1**, N41, N51 in **3**, and N1A, N1B in **2**, **4**) of the thiocyanate (for **1**, **2**), or the azide (for **3**, **4**) constitute the irregular six-coordinate structure around each metal. The two pseudohalides are *cis* in all complexes. The Ni–N distances from 2.027–2.121 Å in **1** and **2** are comparable to each other and analogous complexes containing NiN_6 chromophores [25]. The Co–N distances in **3** and **4** from 1.918–1.959 Å are comparatively shorter than the corresponding Ni–N distances of **1** and **2** but agree well with similar cobalt(III) complexes [14, 26]. Distortion in the coordination sphere of the central metal ions from ideal is obvious due to structural constraints imposed by a polydentate ligand framework. However, the distortion is small in these complexes as reflected by *cis* and *trans* angles being close to ideal.

Heterocyclic rings of L^1 and L^2 in **1**–**4** are nearly at 90° to each other. Additional aromatic rings in **2** and **4** are also oriented perpendicular to their neighboring pyridine rings giving loosely packed arrangements, stabilized by weak π–π interactions. The azides and thiocyanates are almost linear and extend into the interstices of the lattice like those of the perchlorate anions in **3** and **4**. These pseudohalides face away from the

Table 3. Selected bond parameters for **1–4**.

1		**2**		**3**		**4**	
Bond lengths (Å)							
Ni1–N1	2.121(2)	Ni1–N1A	2.057(3)	Co1–N1	1.956(2)	Co1–N4	1.918(3)
Ni1–N8	2.046(2)	Ni1–N3	2.063(3)	Co1–N8	1.919(2)	Co1–N2	1.926(3)
Ni1–N13	2.089(2)	Ni1–N2	2.077(2)	Co1–N13	1.934(2)	Co1–N1	1.936(3)
Ni1–N20	2.078(2)	Ni1–N1	2.078(3)	Co1–N20	1.932(2)	Co1–N3	1.936(2)
Ni1–N31	2.027(2)	Ni1–N1B	2.079(3)	Co1–N41	1.934(2)	Co1–N1B	1.955(3)
Ni1–N41	2.072(2)	Ni1–N4	2.089(3)	Co1–N51	1.949(2)	Co1–N1A	1.959(4)
Bond angles (°)							
N1–Ni1–N8	78.33(7)	N1A–Ni1–N1	96.8(1)	N1–Co1–N8	82.63(9)	N1A–Co1–N1B	86.7(2)
N1–Ni1–N13	93.89(8)	N1A–Ni1–N2	175.1(1)	N1–Co1–N13	90.81(9)	N1A–Co1–N1	175.1(1)
N1–Ni1–N20	94.48(8)	N1A–Ni1–N3	92.5(1)	N1–Co1–N20	95.15(9)	N1A–Co1–N2	94.0(1)
N1–Ni1–N31	89.52(8)	N1A–Ni1–N4	90.3(1)	N1–Co1–N41	87.75(9)	N1A–Co1–N3	89.1(1)
N1–Ni1–N41	175.42(8)	N1A–Ni1–N1B	91.9(1)	N1–Co1–N51	175.9(1)	N1A–Co1–N4	89.7(1)
N8–Ni1–N13	91.33(7)	N1–Ni1–N2	78.9(1)	N8–Co1–N13	92.95(9)	N1B–Co1–N1	90.4(1)
N8–Ni1–N20	168.13(7)	N1–Ni1–N3	168.4(1)	N8–Co1–N20	175.75(9)	N1B–Co1–N2	91.3(1)
N8–Ni1–N31	94.82(8)	N1–Ni1–N4	94.9(1)	N8–Co1–N41	92.11(9)	N1B–Co1–N3	173.3(1)
N8–Ni1–N41	97.09(7)	N1–Ni1–N1B	89.1(1)	N8–Co1–N51	93.3(1)	N1B–Co1–N4	92.0(1)
N13–Ni1–N20	79.65(8)	N2–Ni1–N3	92.0(1)	N13–Co1–N20	83.44(9)	N1–Co1–N2	82.2(1)
N13–Ni1–N31	173.46(9)	N2–Ni1–N4	92.5(1)	N13–Co1–N41	174.52(9)	N1–Co1–N3	94.2(1)
N13–Ni1–N41	86.29(8)	N2–Ni1–N1B	85.6(1)	N13–Co1–N51	89.3(1)	N1–Co1–N4	94.2(1)
N20–Ni1–N31	94.54(9)	N3–Ni1–N4	78.1(1)	N20–Co1–N41	91.43(9)	N2–Co1–N3	94.2(1)
N20–Ni1–N41	90.06(8)	N3–Ni1–N1B	97.5(1)	N20–Co1–N51	89.0(1)	N2–Co1–N4	175.1(1)
N31–Ni1–N41	90.74(9)	N4–Ni1–N1B	175.2(1)	N41–Co1–N51	92.5(1)	N3–Co1–N4	82.7(1)

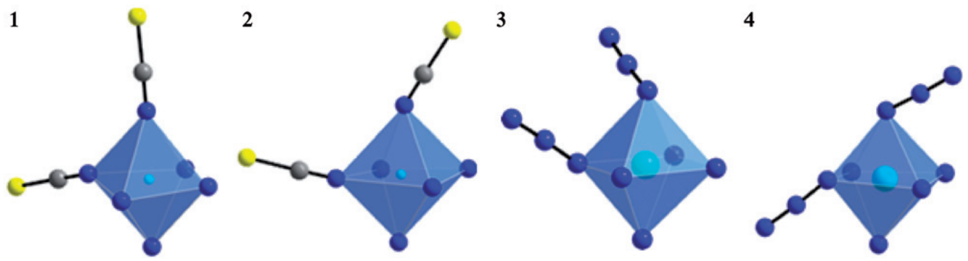


Figure 2. Coordination polyhedra in **1–4**.

metal cations with appreciable difference in the relevant angles. For example, the thiocyanates face outward (∠Ni–N–C being 164.2° and 173.8° in **1**; 150.7° and 161.6° in **2**) and are straighter than azides (∠Co–N–N being 120.0° and 118.0° in **3**; 119.9° and 119.2° in **4**), as shown in figure 2. These differences arise due to the presence of a lone pair in azide unlike thiocyanate.

3.4. *Antibacterial activity of the compounds*

The antibacterial activities as IZD are presented in table 4. Complexes **1–4** exhibit broad spectrum antibacterial activity against the four chosen bacteria. Although, Schiff bases are mildly active against some of these bacteria, the constituents of the Schiff bases lack bactericidal property. The IZD data show that L^1 is mildly active against *S. aureus* and *E. coli* but inactive against *B. subtilis* or *P. aeruginosa* whereas the reverse

Table 4. Antibacterial activities of **1–4** and related compounds compared to control (dmso) and Gattifloxacin.

	Mean IZD in cm (dose in mg mL^{-1})			
	Gram-positive bacteria		Gram-negative bacteria	
Compounds	*S. aureus*	*B. subtilis*	*P. aeruginosa*	*E. coli*
1	1.2 (0.2), 1.4 (0.4), 1.5 (0.6), 1.6 (0.8), 1.6 (1.0)	1.2 (0.2), 1.4 (0.4), 1.5 (0.6), 2.0 (0.8), 2.2 (1.0)	1.2 (0.2), 1.4 (0.4), 1.5 (0.6), 1.6 (0.8), 1.7 (1.0)	1.2 (0.2), 1.4 (0.4), 1.5 (0.6), 1.9 (0.8), 2.3 (1.0)
2	1.2 (0.2), 1.4 (0.4), 1.5 (0.6), 1.6 (0.8), 1.8 (1.0)	1.2 (0.2), 1.4 (0.4), 1.5 (0.6), 1.9 (0.8), 2.2 (1.0)	1.0 (0.2), 1.2 (0.4), 1.4 (0.6), 1.6 (0.8), 1.7 (1.0)	1.2 (0.2), 1.4 (0.4), 1.5 (0.6), 1.8 (0.8), 2.0 (1.0)
3	1.4 (0.2), 1.5 (0.4), 1.6 (0.6), 1.8 (0.8), 2.1 (1.0)	1.2 (0.2), 1.5 (0.4), 1.7 (0.6), 1.9 (0.8), 2.2 (1.0)	1.3 (0.2), 1.4 (0.4), 1.6 (0.6), 1.8 (0.8), 2.1 (1.0)	1.5 (0.2), 1.4 (0.4), 1.5 (0.6), 1.9 (0.8), 2.4 (1.0)
4	1.7 (0.2), 1.9 (0.4), 2.1 (0.6), 2.2 (0.8), 2.4 (1.0)	1.3 (0.2), 1.5 (0.4), 1.8 (0.6), 1.9 (0.8), 2.2 (1.0)	1.2 (0.2), 1.4 (0.4), 1.6 (0.6), 1.8 (0.8), 2.0 (1.0)	1.3 (0.2), 1.6 (0.4), 1.9 (0.6), 2.2 (0.8), 2.4 (1.0)
L^1	0.6 (0.2), 0.6 (0.4), 0.8 (0.6), 1.2 (0.8), 1.4 (1.0)	–	–	0.8 (0.2), 0.8 (0.4), 1.0 (0.6), 1.2 (0.8), 1.5 (1.0)
L^2	–	0.8 (0.2), 1.0 (0.4), 1.0 (0.6), 1.3 (0.8), 1.4 (1.0)	1.0 (0.2), 1.1 (0.4), 1.2 (0.6), 1.2 (0.8), 1.4 (1.0)	–
Gattifloxacin	1.7 (0.2), 1.9 (0.4), 2.2 (0.6), 2.6 (0.8), 2.8 (1.0)	1.4 (0.2), 1.6 (0.4), 1.8 (0.6), 2.2 (0.8), 2.7 (1.0)	1.3 (0.2), 1.5 (0.4), 1.8 (0.6), 2.2 (0.8), 2.5 (1.0)	1.3 (0.2), 1.6 (0.4), 1.9 (0.6), 2.3 (0.8), 2.8 (1.0)
dab, pyal, bzpy, dmso	–	–	–	–

is seen for L^2. Nickel(II) compounds **1** and **2** are more active against *B. subtilis* and *E. coli* but less active against the other two bacteria. Cobalt(III) compounds **3** and **4** are, however, susceptible to all the bacteria at even lower doses. Among the bacteria, *E. coli* is most susceptible to **1**–**4**. Compound **4** is best among all compounds for bactericidal property. From the *in vitro* antibacterial assay, thus, it may be concluded that all the metal complexes and their Schiff bases possess mild to moderate antibacterial activities against bacteria and such antibacterial activities increase with dose in most cases. However, the activities are much lower than those of the tested commercial antibiotic (Gattifloxacin) at similar concentrations. All these observations are similar to earlier reports [12–14, 27–30] of bioactivities of analogous nickel(II) and cobalt(III) Schiff-base complexes.

4. Conclusions

Synthesis and characterization of four mononuclear Ni(II) and Co(III) complexes containing N-donor tetradentate Schiff bases with terminal thiocyanate or azide anions have been described. The complexes have been studied by X-ray diffraction, possessing slightly distorted octahedral geometry around the metal. Antibacterial screening indicates mild to moderate bactericidal activities which are comparable to those of the analogous Ni(II) and Co(III) Schiff-base complexes reported earlier. In addition to the synthetic and structural investigations, this study helps to evaluate the effectiveness of new Schiff bases and their metal complexes for use as antibacterial agents.

Supplementary material

The crystallographic data (excluding structure factors) for all the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 864929–864932 for **1**–**4**, respectively. 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

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References

[1] J.J.R. Fraústo da Silva, R.J.P. Williams. *The Biological Chemistry of the Elements*, Oxford University Press, Oxford (2001).
[2] P.G. Cozzi. *Chem. Soc. Rev.*, **33**, 410 (2004).
[3] E.M. McGarrigle, D.G. Gilheany. *Chem. Rev.*, **105**, 1563 (2005).
[4] O. Kahn. *Molecular Magnetism*, VCH, Weinheim, Germany (1993).
[5] J.R. Lancaster (Ed.). *The Bioinorganic Chemistry of Nickel*, VCH, New York, 1988.
[6] E.I. Solomon, U.M. Sundaram, T.E. Machokin. *Chem. Rev.*, **96**, 2563 (1996).
[7] G. Wilkinson. *Comprehensive Coordination Chemistry*, Vol. 5, p. 775, Pergamon Press, Oxford (1987).
[8] T.K. Karmakar, B.K. Ghosh, A. Usman, H.-K. Fun, E. Rivière, T. Mallah, G. Aromí, S.K. Chandra. *Inorg. Chem.*, **44**, 2391 (2005).
[9] H. Temel, Ü. Çakir, B. Otludil, H.İ. Uğraş. *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 1323 (2001).
[10] H. Chowdhury, S.H. Rahaman, R. Ghosh, T.-H. Lu, B.K. Ghosh. *Ind. J. Chem.*, **44A**, 1565 (2005).
[11] T.K. Karmakar, S.K. Chandra, J. Ribas, G. Mostafa, T.H. Lu, B.K. Ghosh. *Chem. Commun.*, 2364 (2002).
[12] B. Samanta, J. Chakraborty, C. Choudhury, S. Dey, D. Dey, S. Batten, P. Jensen, G. Yap, S. Mitra. *Struct. Chem.*, **18**, 33 (2007).
[13] M. Shakir, M. Azam, Y. Azim, S. Parveen, A.U. Khan. *Polyhedron*, **26**, 5513 (2007).
[14] M. Fleck, D. Karmakar, M. Ghosh, A. Ghosh, R. Saha, D. Bandyopadhyay. *Polyhedron*, **34**, 157 (2012).
[15] S. Mandal, G. Rosair, J. Ribas, D. Bandyopadhyay. *Inorg. Chim. Acta*, **362**, 2200 (2009).
[16] *CrysAlis RED*, Oxford Diffraction (2002); *Gemini User Manual*, Oxford Diffraction (2006).
[17] NONIUS. *Kappa CCD Program Package: COLLECT, DENZO, SCALEPACK, SORTAV*, Nonius BV, Delft, The Netherlands (1999).
[18] Z. Otwinowski, W. Minor. *Methods Enzymol. A*, **276**, 307 (1997).

[19] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna. *J. Appl. Cryst.*, **32**, 115 (1999).

[20] P.W. Betteridge, J.R. Carruthers, R.I. Cooper, K. Prout, D.J. Watkin. *J. Appl. Cryst.*, **36**, 1487 (2003).

[21] G.M. Sheldrick. *Acta Crystallogr. Sect. A*, **64**, 112 (2008).

[22] A.W. Bauer, W.M. Kirby, J.C. Sheris, M. Turck. *Am. J. Clin. Pathol.*, **45**, 149 (1966).

[23] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 6th Edn, John Wiley & Sons, Inc., New Jersey (2009).

[24] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, 2nd Edn, Elsevier Science, New York (1984).

[25] S. Deoghoria, S. Sain, B. Moulton, M.J. Zaworotko, S.K. Bera, S.K. Chandra. *Polyhedron*, **21**, 2457 (2002).

[26] Y. Song, Z. Xu, Q. Sun, B. Su, Q. Gao, H. Liu, J. Zhao. *J. Coord. Chem.*, **61**, 1212 (2008).

[27] A.A. Nejo, G.A. Kolawole, A.O. Nejo. *J. Coord. Chem.*, **63**, 4398 (2010).

[28] D.P. Singh, K. Kumar. *J. Coord. Chem.*, **63**, 4007 (2010).

[29] D.P. Singh, M. Kamboj, K. Kumar, K. Jain, C. Sharma. *J. Coord. Chem.*, **64**, 502 (2011).

[30] D.-C. Zhong, Z.-F. Chen, Y.-C. Liu, X.-J. Luo, C. Barta, H. Liang. *J. Coord. Chem.*, **63**, 3146 (2010).