

**SYNTHESES, CHARACTERIZATION,
AND CRYSTAL STRUCTURES OF COBALT(III)
COMPLEXES DERIVED FROM 2-(((2-
(PYRROLIDIN-1-YL)ETHYL)IMINO)METHYL)
PHENOL WITH THE ANTIBACTERIAL ACTIVITY**

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A mononuclear cobalt(III) complex [CoL(NCS)₂(OH₂)] (**1**) and a trinuclear cobalt(III–II–III) complex [Co{CoLN₃(μ_{1,1}-N₃)₂(CH₃OH)}₂] (**2**), derived from the Schiff base ligand 2-(((2-(pyrrolidin-1-yl)ethyl)imino)methyl)phenol (HL), are synthesized and characterized by IR and electronic spectra. The structures of both complexes are studied in detail by single crystal X-ray diffraction. In complex **1**, the Co(III) atom is coordinated by three donor atoms of the Schiff base ligand, two thiocyanate N atoms, and one water O atom, forming an octahedral geometry. In complex **2**, the terminal Co(III) atom is coordinated by three donor atoms of the Schiff base ligand, two end-on azide N atoms, and one terminal azide N atom, forming an octahedral geometry. The central Co(II) atom is coordinated by four end-on azide N atoms and two methanol O atoms, forming an octahedral geometry. The complexes exhibit interesting antibacterial activities against *B. subtilis* and *E. coli*.

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Keywords: Schiff base, cobalt complex, crystal structure, antibacterial property.

INTRODUCTION

In bioinorganic and coordination chemistry, Schiff bases are the most extensively studied ligands due to their facile synthesis, versatile coordination modes, and interesting biological activities [1-4]. In recent years, a great number of Schiff base complexes have been prepared and characterized because of their wide applications in magnetic, catalytic, and biological fields [5-10]. The Schiff complexes of cobalt are very important in these respects. Schiff base cobalt complexes are considered as an important class of compounds in pharmaceutical and medicinal fields since they have been reported to be biologically active [11-15]. They show potential activities and applications such as antibacterial, antifungal, antioxidant, anticancer, and antitumor agents [16-20]. In addition, thiocyanate and azide anions are interesting building blocks in the construction of new Schiff base complexes [21-24]. Compounds bearing the pyrrolidine group are reported to have interesting antibacterial activities [25-32]. Although numerous Schiff base complexes with versatile structures have been reported, studies on the complexes derived from Schiff bases containing a terminal pyrrolidine group are scanty. In pursuit of

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efficient antibacterial drugs, two new Schiff base cobalt complexes $[\text{CoL}(\text{NCS})_2(\text{OH}_2)]$ (**1**) and $[\text{Co}\{\text{CoLN}_3(\mu_{1,1}\text{-N}_3)_2(\text{CH}_3\text{OH})\}_2]$ (**2**), where L is the deprotonated form of the Schiff base 2-(((2-(pyrrolidin-1-yl)ethyl)imino)methyl)phenol (HL), are reported in this work.

EXPERIMENTAL

Materials and methods. Commercially available salicylaldehyde, *N*-(2-aminoethyl)pyrrolidine, cobalt(II) acetate tetrahydrate, ammonium thiocyanate, and sodium azide (all of reagent grade) were used without further purification. All the other chemicals and solvents were of analytical grade. The Schiff base was synthesized by condensation of salicylaldehyde and *N*-(2-aminoethyl)pyrrolidine in a 1:1 molar ratio in methanol. The product was distilled to remove the excess solvent to get a semisolid and used as such without further purification.

Elemental analyses were performed on a PerkinElmer 2400 CHNS/O elemental analyzer. IR spectra (KBr discs, 4000-400 cm^{-1}) were recorded using a PerkinElmer FTIR model RX1 spectrometer. The electronic spectra (800-200 nm) were recorded on a PerkinElmer LAMBDA 35 spectrometer using $1 \cdot 10^{-5}$ M solutions of the complexes in HPLC grade acetonitrile. Single crystal X-ray diffraction (XRD) was carried out on a Bruker APEX II CCD diffractometer.

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

Synthesis of $[\text{CoL}(\text{NCS})_2(\text{OH}_2)]$ (1**).** Cobalt acetate tetrahydrate (0.015 mol, 3.7 g) dissolved in methanol (30 mL) was added to a solution of HL (0.010 mol, 2.2 g) in methanol (20 mL). The color of the solution changed to dark red. The mixture was stirred at room temperature for 30 min. Then, ammonium thiocyanate (0.030 mol, 2.3 g) was added to the mixture. The mixture was further stirred at room temperature for 30 min to give a deep brown solution. Brown block-shaped single crystals suitable for XRD were obtained from the filtrate after slow evaporation for 3 days. Yield: 1.7 g (41%). Anal. calc. for $\text{C}_{15}\text{H}_{19}\text{CoN}_4\text{O}_2\text{S}_2$ (%): C 43.90, H 4.67, N 13.65. Found (%): C 43.72, H 4.81, N 13.82. FTIR (KBr disc) (cm^{-1}): 3436 br, 2112 vs, 1639 s, 1599 s, 1537 m, 1450 s, 1349 w, 1310 m, 1280 m, 1198 m, 1146 m, 1129 m, 1085 m, 1021 m, 926 w, 900 m, 827 w, 959 s, 611 w, 568 w, 530 w, 472 w (br is broad; w is weak; m is medium; s is strong; vs is very strong). UV-Vis (λ , nm (ϵ , $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)): 252 ($6.77 \cdot 10^3$), 375 ($9.23 \cdot 10^2$).

Synthesis of $[\text{Co}\{\text{CoLN}_3(\mu_{1,1}\text{-N}_3)_2(\text{CH}_3\text{OH})\}_2]$ (2**).** Cobalt acetate tetrahydrate (0.015 mol, 3.7 g) dissolved in methanol (30 mL) was added to a solution of HL (0.010 mol, 2.2 g) in methanol (20 mL). The color of the solution changed to dark red. The mixture was stirred at room temperature for 30 min. Then, sodium azide (0.030 mol, 2.0 g) was added to the mixture. The mixture was further stirred at room temperature for 30 min to give a deep brown solution. Brown block-shaped single crystals suitable for XRD were obtained from the filtrate after slow evaporation for 5 days. Yield: 1.5 g (48%). Anal. calc. for $\text{C}_{28}\text{H}_{42}\text{Co}_3\text{N}_{22}\text{O}_4$ (%): C 36.26, H 4.56, N 33.22. Found (%): C 36.40, H 4.71, N 33.05. FTIR (KBr disc) (cm^{-1}): 3432 br, 2065 vs, 2016 vs, 1633 s, 1600 s, 1545 w, 1470 m, 1450 s, 1289 s, 1204 w, 1152 w, 1131 m, 1080 w, 1031 w, 927 w, 898 m, 765 s, 612 w, 587 w, 470 w, 438 w. UV-Vis (λ , nm (ϵ , $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)): 250 ($7.16 \cdot 10^3$), 340 ($2.05 \cdot 10^3$).

X-ray crystallography. Brown block-shaped single crystals of the complexes with suitable dimensions were selected and mounted on a Bruker APEX II CCD diffractometer. Graphite-monochromatized MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) and the ω scan technique were used at 298(2) K to collect the intensity data. Data collection and unit cell refinement were carried out using Bruker XSCANS [33]. No significant loss of intensity was observed. A multi-scan absorption correction was empirically applied to the intensity values using SADABS [34]. Data reductions were performed using Bruker SHELXTL [35]. The crystal structures were solved by direct methods using SHELXS [36], combined with the Fourier difference synthesis, and refined with the full matrix least square technique based on F^2 using SHELXL [36]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located from the difference Fourier map and treated with suitable riding models with isotropic displacement parameters derived from their carrier atoms. The C8–C9 and C23–C24 moieties of complex **1** are disordered over two sites, with occupancies of 0.39(1) \AA and 0.61(1) \AA , and 0.62(1) \AA and 0.38(1) \AA , respectively. Molecular graphics and crystallographic illustrations were prepared using SHELXTL.

Crystallographic data and refinement parameters are given in Table 1, and important interatomic distances and angles are given in Table 2.

Antibacterial assay. The antibacterial activity of the complexes was tested against *B. subtilis*, *S. aureus*, *S. faecalis*, *P. aeruginosa*, *E. coli*, and *E. cloacae* using the MTT medium. The minimum inhibitory concentrations (MICs) of the compounds were determined by a colorimetric method using MTT dye [37]. A stock solution of the compounds (50 µg/mL) in DMSO was prepared and quantities of the compounds were incorporated in a specified quantity of the sterilized liquid medium. A specified quantity of the medium containing the compounds was poured into microtitration plates. A suspension of the microorganism was prepared to contain approximately 10⁵ cfu/mL and applied to microtitration plates with serially diluted compounds in DMSO to be tested, and incubated at 37 °C for 24 h for bacteria. After MICs were visually determined on each microtitration plate, 50 µL of phosphate-buffered saline (PBS 0.01 mol/L, pH 7.4: Na₂HPO₄·12H₂O 2.9 g, KH₂PO₄ 0.2 g, NaCl 8.0 g, KCl 0.2 g, distilled water 1000 mL) containing 2 mg/mL of MTT was added to each well. Incubation was continued at room temperature for 4-5 h. The content of each well was removed, and 100 µL of isopropanol containing 5% 1 mol/L HCl was added to extract the dye. After 12 h of incubation at room temperature, the optical density (OD) was measured with a microplate reader at 570 nm.

RESULTS AND DISCUSSION

Chemistry. The Schiff base HL was synthesized by the literature method [38] via the the condensation of salicylaldehyde with *N*-(2-aminoethyl)pyrrolidine in methanol without isolation, purification, or characterization. In situ prepared HL has been coordinated with cobalt(II) acetate, followed by the addition of ammonium thiocyanate for **1** and sodium azide for **2**, in the presence of air, which allowed spontaneous oxidation to cobalt(III) complex **1** and cobalt(III)–cobalt(II)–cobalt(III) complex **2**. It is well known that thiocyanate and azide anions are the preferred building blocks in the

TABLE 1. Crystallographic Data for the Complexes

Parameter	1	2
Empirical formula	C ₁₅ H ₁₉ CoN ₄ O ₂ S ₂	C ₂₈ H ₄₂ Co ₃ N ₂₂ O ₄
Formula weight	410.39	927.62
Temperature, K	298(2)	298(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
Crystal size, mm	0.25×0.23×0.23	0.23×0.22×0.20
<i>a</i> , <i>b</i> , <i>c</i> , Å	9.1676(13), 10.3257(15), 17.8784(15)	19.1740(3), 11.3540(2), 18.3294(3)
α , β , γ , deg	90.182(1), 92.073(1), 90.061(1)	90, 96.806(1), 90
<i>V</i> , Å ³	1691.3(4)	3962.2(1)
<i>Z</i>	4	4
μ (MoK α), mm ⁻¹	1.278	1.306
<i>T</i> _{min} / <i>T</i> _{max}	0.741 / 0.758	0.753 / 0.780
ρ _{calcd.} , g/cm ³	1.612	1.555
Collected / unique reflections	9165 / 6255	21098 / 3692
Observed reflections (<i>I</i> ≥ 2σ(<i>I</i>))	4039	3107
<i>R</i> _{int}	0.0276	0.0235
Parameters / restraints	473 / 12	262 / 1
<i>GOOF</i> on <i>F</i> ²	0.983	1.039
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> ≥ 2σ(<i>I</i>))	0.0785, 0.2157	0.0345, 0.0891
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1109, 0.2458	0.0441, 0.0963

TABLE 2. Selected Bond Distances (Å) and Angles (deg) for the Complexes

Bond length	Distance, Å	Bond angle	Value, deg	Bond angle	Value, deg
1	2	3	4	5	6
1					
Co1–N1	1.814(5)	N1–Co1–O1	94.8(2)	O4–Co2–N6	96.0(2)
Co1–N2	1.956(5)	O1–Co1–N3	90.6(2)	N1–Co1–N3	89.2(3)
Co1–N3	1.836(7)	O1–Co1–N4	87.3(2)	N1–Co1–N4	89.1(3)
Co2–N5	1.812(5)	N1–Co1–O2	177.5(2)	N3–Co1–N4	177.2(3)
Co2–N6	1.954(5)	N3–Co1–O2	92.0(2)	O1–Co1–O2	82.99(19)
Co2–N7	1.853(7)	N1–Co1–N2	85.9(2)	N4–Co1–O2	89.6(2)
Co1–O1	1.823(4)	N3–Co1–N2	90.3(2)	O1–Co1–N2	178.83(19)
Co1–O2	1.911(4)	O2–Co1–N2	96.2(2)	N4–Co1–N2	91.8(2)
Co1–N4	1.845(6)	N5–Co2–O3	95.0(2)	N5–Co2–N8	89.4(3)
Co2–O3	1.826(4)	O3–Co2–N8	90.1(2)	N5–Co2–N7	89.1(3)
Co2–O4	1.909(4)	O3–Co2–N7	88.1(2)	N8–Co2–N7	177.5(3)
Co2–N8	1.837(7)	N5–Co2–O4	178.0(2)	O3–Co2–O4	83.3(2)
		N8–Co2–O4	91.7(2)	N7–Co2–O4	89.8(2)
		N5–Co2–N6	85.6(2)	O3–Co2–N6	179.0(2)
		N8–Co2–N6	90.7(2)	N7–Co2–N6	91.2(2)
2					
Co1–O1	1.9123(19)	N1–Co1–O1	93.84(10)	N1–Co1–N6	93.51(10)
Co1–N6	1.930(2)	O1–Co1–N6	89.25(10)	N1–Co1–N9	172.08(9)
Co1–N2	2.019(2)	O1–Co1–N9	89.61(8)	N6–Co1–N9	93.66(9)
Co2–O2	2.092(2)	N1–Co1–N3	93.51(9)	O1–Co1–N3	87.73(9)
Co2–N3	2.140(2)	N6–Co1–N3	172.52(10)	N9–Co1–N3	79.49(8)
Co1–N1	1.890(2)	N1–Co1–N2	85.84(10)	O1–Co1–N2	176.19(8)
Co1–N9	1.9758(19)	N6–Co1–N2	86.98(10)	N9–Co1–N2	91.19(9)
Co1–N3	1.997(2)	N3–Co1–N2	96.08(9)	O2–Co2–O2A	84.80(18)
Co2–N9	2.114(2)	O2–Co2–N9A	163.55(9)	O2–Co2–N9	84.14(10)
		N9–Co2–N9A	109.06(11)	O2–Co2–N3A	95.98(10)
		O2–Co2–N3	96.80(10)	N9–Co2–N3A	96.44(8)
		N9–Co2–N3	73.32(8)	O2–Co2–N3A	95.98(10)
		N9–Co2–N3A	96.44(8)	N3–Co2–N3A	162.66(13)

Symmetry code for A: $1-x, y, 1/2-z$.

construction of polymeric complexes. However, the thiocyanate anions coordinate to the Co atom through the terminal mode. Interestingly, the azide anions coordinate to the Co atom through terminal and end-on bridging modes.

Crystal structure description of complex 1. The molecular structure of complex **1** is shown in Fig. 1. The asymmetric unit of the compound contains two independent molecules. The Co atom is hexacoordinated with an octahedral geometry, with the axial positions being occupied by two thiocyanate N atoms. The equatorial plane is defined by phenolate O, imino N, and pyrrolidine N atoms of the Schiff base ligand, and one O atom of the water ligand. The bond angles in the equatorial planes vary from $83.0(2)^\circ$ to $96.2(2)^\circ$ for Co1 and $83.3(2)^\circ$ to $96.0(2)^\circ$ for Co2, and those between the axial and the equatorial donor atoms vary from $87.3(2)^\circ$ to $94.8(2)^\circ$ for Co1 and from $88.1(2)^\circ$ to $91.7(2)^\circ$ for Co2, indicating that the octahedral coordination is distorted. The distortion can also be observed from the bond lengths among the donor and Co atoms. The Co–O and Co–N bond lengths are in the range of 1.814(5)-1.956(5) Å, which are comparable to those observed in

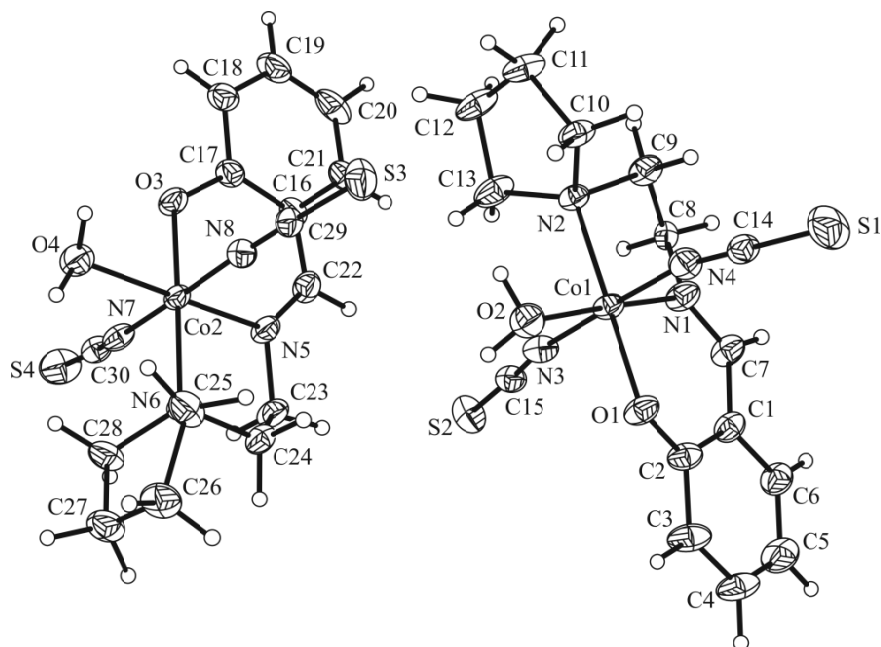


Fig. 1. A perspective view of the molecular structure of complex **1** with the atom labeling scheme; thermal ellipsoids are drawn at the 30% probability level.

cobalt complexes with Schiff bases [39, 40]. The molecules of the complex are linked through intermolecular O–H···S hydrogen bonds (Table 3) to form a two-dimensional network along the *bc* plane (Fig. 2).

Crystal structure description of complex 2. The molecular structure of complex **2** is shown in Fig. 3. The molecule possesses a crystallographic twofold rotation axis symmetry. The terminal Co atoms are in the 3+ oxidation state and are hexacoordinated in an octahedral geometry, with the axial positions being occupied by one terminal azide N atom and one end-on bridging azide N atom. The equatorial plane is defined by phenolate O, imino N, and pyrrolidine N atoms of the Schiff base ligand, and one end-on azide N atom. The *cis* bond angles in the equatorial plane vary from 85.8(1)° to 93.8(1)°, and those between the axial and the equatorial donor atoms vary from 79.49(8)° to 96.08(9)°, indicating that the octahedral coordination is distorted. The distortion can also be observed from the bond lengths among the donor and Co atoms. The Co–O and Co–N bond lengths are in the range of 1.890(2)–2.019(2) Å, which are comparable to those observed in azide coordinated cobalt(III) complexes with Schiff bases [41, 42].

The central Co atom is in the 2+ oxidation state and is hexacoordinated by four end-on azide N atoms and two methanol O atoms, forming an octahedral geometry. The *cis* and *trans* bond angles vary from 73.32(8)° to 96.80(10)° and

TABLE 3. Hydrogen Bonding Geometry for the Complexes

<i>D</i> –H··· <i>A</i>	<i>D</i> –H, Å	H··· <i>A</i> , Å	<i>D</i> ··· <i>A</i> , Å	<i>D</i> –H··· <i>A</i> , deg
1				
O2–H2A····S1 ^{#1}	0.87	2.87	3.555(6)	137(5)
O2–H2B···S3	0.87	2.68	3.480(5)	154(5)
O4–H4A···S4 ^{#2}	0.88	2.75	3.554(6)	152(5)
O4–H4B···S2 ^{#3}	0.88	2.64	3.479(5)	158(5)
2				
O2–H2···O1	0.84(1)	1.80(1)	2.617(3)	165(4)

Symmetry codes: ^{#1} 1–*x*, 1–*y*, 2–*z*; ^{#2} 1–*x*, –*y*, 1–*z*; ^{#3} *x*, –1+*y*, *z*.

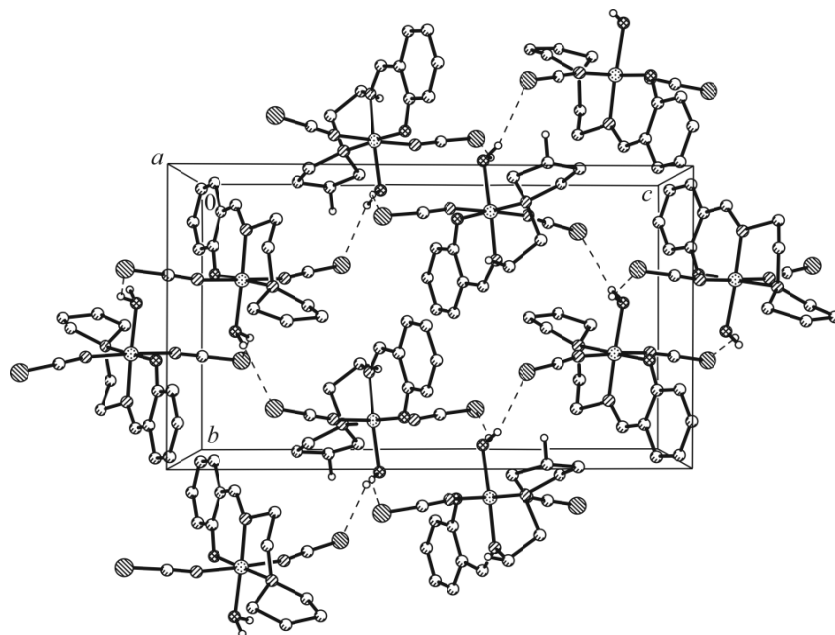


Fig. 2. Hydrogen bonds (dashed lines) linking the two-dimensional network of complex **1**, viewed along the *a* axis; the H atoms not related to hydrogen bonds are omitted for clarity.

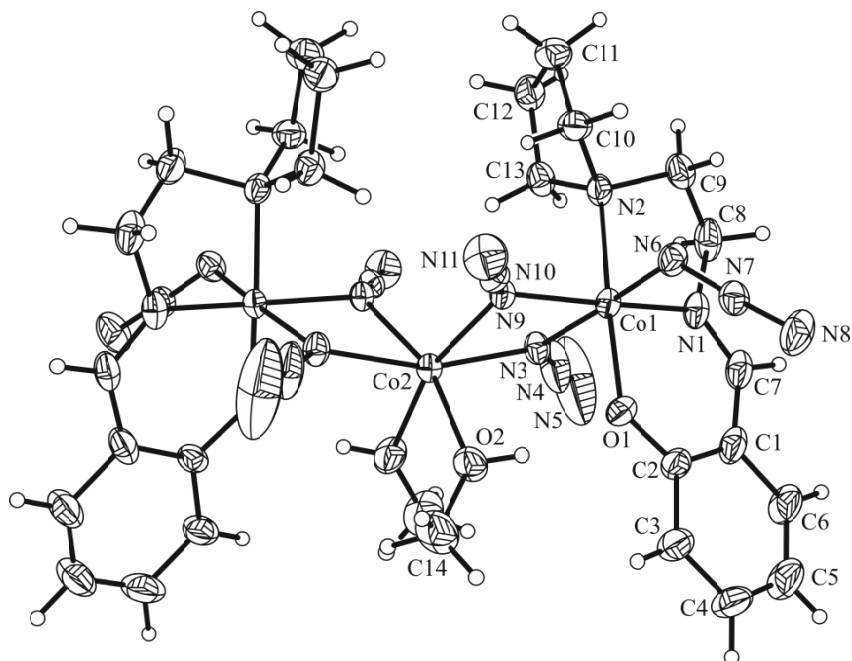


Fig. 3. A perspective view of the molecular structure of complex **2** with the atom labeling scheme; thermal ellipsoids are drawn at the 30% probability level; unlabelled atoms are at the symmetry position $1-x$, $1-y$, $1-z$.

from $162.66(13)^\circ$ to $163.55(9)^\circ$, respectively, indicating that the octahedral coordination is distorted. The distortion can also be observed from the bond lengths among the donor and Co atoms. The Co–O and Co–N bond lengths are in the range of $2.092(2)$ – $2.140(2)$ Å, which are longer than those of the Co(III) coordination and comparable to those observed in azide coordinated cobalt(II) complexes with the methanol ligand [43, 44].

The molecules of the complex are linked through intermolecular O–H···O hydrogen bonds (Table 3) to form a two-dimensional network along the *ac* plane (Fig. 4).

The experimental powder XRD patterns of the bulk samples of the complexes agree well with the simulated patterns calculated from the single crystal XRD data (Figs. 5 and 6). The results prove the purity of the bulk samples.

IR and UV spectra. The broad and weak absorption bands centered at about 3430–3440 cm^{-1} in the spectra of the complexes substantiate the presence of O–H groups. The very strong absorption band at 2112 cm^{-1} in the spectrum of **1** can be assigned to the thiocyanate ligand [45], and those observed at 2065 cm^{-1} and 2016 cm^{-1} in the spectrum of **2** can be assigned to the bridging and terminal azide ligands [46]. The intense absorption bands at 1639 cm^{-1} for **1** and 1633 cm^{-1} for **2** are assigned to the azomethine groups, $\nu(\text{C}=\text{N})$ [47, 48]. Several weak bands corresponding to aromatic and aliphatic C–H stretchings are in the range of 2815–3010 cm^{-1} . The C–O stretching bands are located at 1280–1289 cm^{-1} [49]. The weak bands at 600–400 cm^{-1} can be assigned to $\nu(\text{Co–O/N})$ [50].

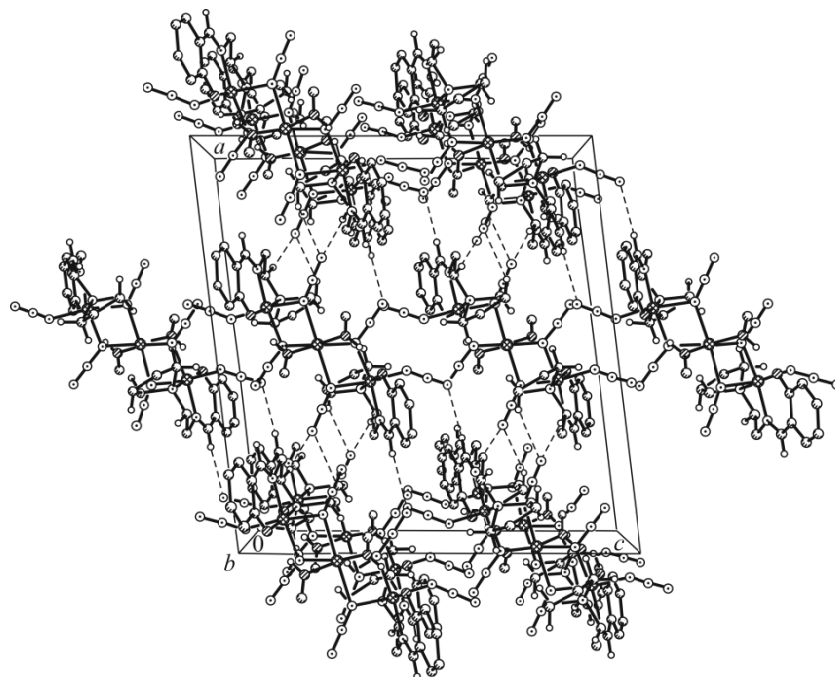


Fig. 4. Hydrogen bonds (dashed lines) linking the one dimensional chain structure of complex **2**, viewed along the *b* axis; the H atoms not related to hydrogen bonds are omitted for clarity.

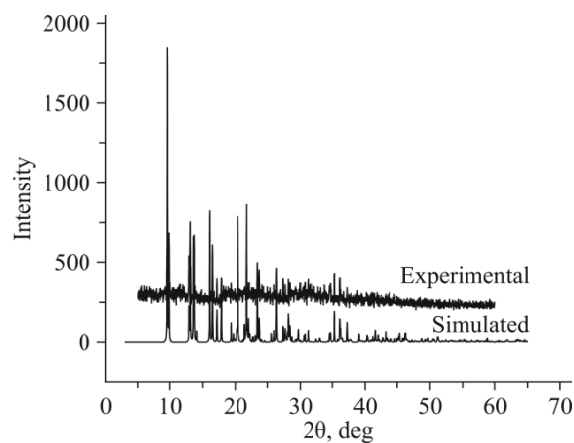


Fig. 5. Experimental and simulated powder XRD patterns of complex **1**.

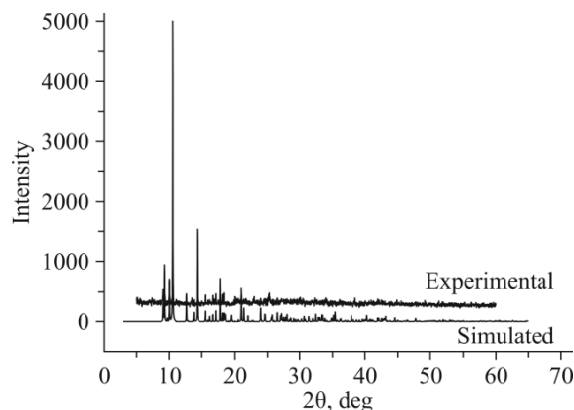


Fig. 6. Experimental and simulated powder XRD patterns of complex **2**.

The electronic spectra of both complexes exhibit very similar features. One can observe bands at 250-252 nm that belong to intraligand $\pi-\pi^*$ transitions of the Schiff base ligand. The charge transfer transitions appear in range of 340-375 nm [51, 52].

Antibacterial activity. The two complexes and HL were assayed for antibacterial activities against three Gram-positive bacterial strains (*B. subtilis*, *S. aureus*, and *St. faecalis*) and three Gram-negative bacterial strains (*E. coli*, *P. aeruginosa*, and *E. cloacae*) by the MTT method. MICs of the tested materials are presented in Table 4. Penicillin and kanamycin were used as references. Thiocyanate coordinated complex **1** shows a strong activity against *B. subtilis* and *E. coli*, a medium activity against *S. aureus* and *E. cloacae*, and no or weak activity against the remaining bacteria. Azide-coordinated complex **2** shows a strong activity against *B. subtilis*, *S. aureus*, and *E. coli*, a medium activity against *E. cloacae*, and a weak activity against the remaining bacteria. Obviously, both complexes have a better activity against the bacteria than free Schiff base HL. Notably, both complexes are more active than or similar to penicillin and kanamycin for *B. subtilis* and *E. coli*. In comparison with the related complexes in the literature, the presented complexes have a better activity against *B. subtilis* and *E. coli*, but a lower activity against *S. aureus* than copper and cobalt complexes with 2-[(3-chloropyridinium-2-yl)hydrazonomethyl]-6-methoxyphenol [53]. Obviously, the presented cobalt complexes bearing pyrrolidine groups have a higher activity against *S. aureus* and *E. coli* than the similar cobalt complex with 2-((2-(dimethylamino)ethylimino)methyl)-4-fluorophenol [54].

CONCLUSIONS

Two new cobalt complexes with the Schiff base ligand 2-((2-(pyrrolidin-1-yl)ethyl)imino)methyl)phenol, and with the secondary thiocyanate or azide ligands were prepared and characterized. The structures of the complexes have been further confirmed by single crystal XRD. The Co atoms in the complexes are in the octahedral coordination. Both complexes

TABLE 4. MICs ($\mu\text{g/mL}$) of the Tested Compounds

Tested material	Gram-positive			Gram-negative		
	<i>B. subtilis</i>	<i>S. aureus</i>	<i>St. faecalis</i>	<i>P. aeruginosa</i>	<i>E. coli</i>	<i>E. cloacae</i>
HL	12.5	> 50	> 50	> 50	> 50	> 50
1	1.56	12.5	> 50	25	3.12	12.5
2	0.78	6.25	25	25	1.56	12.5
Penicillin	1.56	1.56	1.56	6.25	6.25	3.12
Kanamycin	0.39	1.56	3.12	3.12	3.12	1.56

have efficient antibacterial activities against *B. subtilis* and *E. coli* and might be used as antibacterial drugs after the evaluation of their cytotoxicity.

ADDITIONAL INFORMATION

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 2090162 for **1** and 2090163 for **2**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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CONFLICT OF INTERESTS

The authors declare that they have no conflict of interests.

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