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1 **Synthesis, crystal structure and antibacterial activity of azido complexes of**
2 **cobalt(III) containing heteroaromatic Schiff bases**

3
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10
11 A B S T R A C T

12 Three new Schiff base complexes of cobalt(III) viz. $[\text{Co}(\text{L}^1)(\text{N}_3)]_2$ (**1**), $[\text{Co}(\text{L}^2)_2(\text{N}_3)_2]\text{NO}_3$ (**2**)
13 and $[\text{Co}(\text{L}^3)_2(\text{N}_3)_2]\text{ClO}_4$ (**3**), where $\text{H}_2\text{L}^1 = N,N'$ -propane-1,3-diylbis[1-(pyrrol-2-
14 yl)methanimine], $\text{L}^2 = 1$ -[(thiophen-2-ylmethylidene)amino]propan-2-amine and $\text{L}^3 = 1$ -[(3-
15 methylthiophen-2-ylmethylidene)amino]propan-2-amine, have been prepared and characterized.
16 The syntheses have been achieved by the reaction of cobalt(II) nitrate or perchlorate with the
17 tetradentate Schiff base (H_2L^1) or the bidentate ligands L^2 and L^3 in presence of azide. All the
18 complexes **1-3** have been characterized by microanalytical, spectroscopic, single crystal X-ray
19 diffraction and other physicochemical studies. Structural studies reveal that all the complexes
20 contain CoN_6 chromophore in which the central Co(III) ions adopt distorted octahedral
21 geometry. While **1** is a binuclear end-on bis(μ -azido) complex, both of **2** and **3** are mononuclear
22 with two terminal azide ions disposed in *cis* positions. Structural studies reveal that weak
23 intermolecular H-bonding or $\pi \dots \pi$ interactions are operative to bind the complex units or the
24 anions in the solid state. The antibacterial activity of all the complexes and their constituent
25 Schiff base ligands has been tested against some Gram(+) and Gram(-) bacteria.

26 *Keywords:* Cobalt(III); Schiff base; Crystal structure; Azido bridge; Antibacterial activity

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30 **1. Introduction**

31 Schiff bases have long been used as multidentate ligands in the synthesis of transition metal
32 complexes. In recent years, there has been enhanced interest in the preparation and
33 characterization of such complexes due to their wide application and uses. A good number of
34 Schiff base complexes of first row transition metals possess interesting catalytic, magnetic and
35 biological properties. Such complexes of cobalt in different oxidation states including +3 are
36 very important in these respects [1-8]. Although numerous cobalt complexes of organic chelating
37 ligands are known, reports on synthesis of cobalt(III) complexes with heteroaromatic Schiff
38 bases are scanty [9-11]. Until now, a limited number of such complexes have been structurally
39 characterized. Report on mixed ligand complexes containing such ligands along with any
40 pseudohalide is also lacking. Significance of this type of complexes in bioinorganic chemistry
41 gives further impetus to the extensive study of these complexes. Some cobalt complexes are
42 already known to exhibit higher antiviral and antimicrobial activities in comparison to other
43 transition metals. Therefore, investigation of biological properties of various Schiff bases and
44 their metal complexes are being continued by many research groups including ours [12-19].

45 In the present communication, we describe the synthesis of three new complexes of
46 cobalt(III) by using a tetradentate Schiff base, H_2L^1 and the bidentate ligands L^2 and L^3 in
47 presence of azide. All the compounds have been characterized by microanalytical, spectroscopic
48 and single crystal X-ray diffraction studies. In addition to the physicochemical studies, the
49 complexes have been tested *in vitro* to assess their antibacterial activity against some common
50 reference bacteria and the results were compared with similar doses of Ciprofloxacin.

51 **2. Experimental**

52 *2.1. Physical measurements*

53 Elemental analyses for carbon, hydrogen and nitrogen were carried out using a Perkin-Elmer
54 2400-II elemental analyzer. The infrared spectra were recorded on a Perkin-Elmer Spectrum 65
55 FT-IR spectrophotometer with KBr discs (4000–400 cm^{-1}). The electronic spectra were obtained
56 on a Systronics 2202 spectrophotometer using DMF as the solvent at 10^{-4} M concentration.
57 Room temperature solid phase magnetic susceptibilities were measured by Gouy's method using
58 $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant. The diamagnetic corrections were calculated from Pascal's
59 constants. Molar conductance of the complexes in dry methanol were measured using a
60 Systronics (Type 304) direct reading conductivity meter.

61 2.2. Materials

62 Commercially available reagent grade propane-1,2-diamine, propane-1,3-diamine, pyrrole-2-
63 carboxaldehyde, thiophene-2- carboxaldehyde, 3-methyl-thiophene-2- carboxaldehyde, cobalt(II)
64 perchlorate hexahydrate, cobalt(II) nitrate hexahydrate and sodium azide were used without
65 further purification. All other chemicals and solvents were of analytical grade. The heterocyclic
66 Schiff base ligands were obtained by the usual method of condensation between propane-1,3-
67 diamine and pyrrole-2-carboxaldehyde (H_2L^1), propane-1,2-diamine and thiophene-2-
68 carboxaldehyde (L^2) or 3-methyl-thiophene-2-carboxaldehyde (L^3) in 1:2 molar ratio in each
69 case. In each case, the product was evaporated on water bath to remove the excess solvent to get
70 a semisolid and used as such without further purification.

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

74 2.3. Synthesis of the complexes

75 2.3.1. Synthesis of $[\text{Co}(\text{L}^1)(\text{N}_3)]_2$ (**I**)

76 A solution of H_2L^1 (0.12 g, 0.5 mmol) in methanol (20 mL) was added dropwise with
77 constant stirring to $Co(NO_3)_2 \cdot 6H_2O$ (0.15 g, 0.5 mmol) dissolved in same volume of methanol.
78 To the resulting brown solution, an aqueous solution of NaN_3 (0.03 g, 0.5 mmol) was added.
79 Stirring was continued for half an hour and the solution was left for slow evaporation at room
80 temperature. After 4-5 days, dark brown crystals of compound **1** appeared. The crystals were
81 collected by filtration, washed with a little methanol and finally dried. Yield 0.12 g (71%). *Anal.*
82 Calc. for $C_{26}H_{28}Co_2N_{14}$ (**1**): C, 47.72; H, 4.31; N, 29.96. Found: C, 47.46; H, 4.22; N, 29.52%.
83 FTIR (KBr, cm^{-1}): 2024(s), 1607(s). UV-Vis (λ , nm): 256, 290, 508. Λ_M (MeOH, $\Omega^{-1}cm^2$
84 mol^{-1}): 5. Diamagnetic.

85 2.3.2. Synthesis of $[Co(L^2)_2(N_3)_2]NO_3$ (**2**) and $[Co(L^3)_2(N_3)_2]ClO_4$ (**3**)

86 The complexes **2** and **3** were prepared by the same synthetic procedure as described above for
87 **1**. While equal volumes of methanolic solution (20 mL) of L^2 (0.09 g, 0.5 mmol) and
88 $Co(NO_3)_2 \cdot 6H_2O$ (0.15 g, 0.5 mmol) were mixed for **2**, same amount of L^3 (0.5 mmol) was added
89 to $Co(ClO_4)_2 \cdot 6H_2O$ (0.18 g, 0.5 mmol) in the same medium for **3**. Resultant solutions obtained in
90 both the cases were treated with NaN_3 (0.03 g, 0.5 mmol) with constant stirring as before.
91 Crystals of **2** and **3** were then allowed to grow and finally collected within 5-8 days. Yields of **2**
92 and **3** were 0.18 g (64%) and 0.16 g (52%), respectively. *Anal.* Calc. for $C_{16}H_{24}Co N_{11}O_3S_2$ (**2**):
93 C, 35.49; H, 4.47; N, 28.45. Found: C, 35.46; H, 4.42; N, 28.32%. FTIR (KBr, cm^{-1}): 3350(s),
94 2036(s), 1600(s), 1385(s), 852(m). UV-Vis (λ , nm): 210, 324, 520. Λ_M (MeOH, $\Omega^{-1}cm^2$ mol^{-1}):
95 120. Diamagnetic.

96 *Anal.* Calc. for $C_{18}H_{28}ClCoN_{10}O_4S_2$ (**3**): C, 35.62; H, 4.65; N, 23.08. Found: C, 35.46; H, 4.52;
97 N, 22.82%. FTIR (KBr, cm^{-1}): 3352(s), 2032(s), 1630(s), 1100(s), 848(m). UV-Vis (λ , nm): 280,
98 312, 580. Λ_M (MeOH, $\Omega^{-1}cm^2$ mol^{-1}): 110. Diamagnetic.

99 2.4. Crystal structure determination and refinement

100 For X-ray diffraction studies, suitable single crystals of **1**, **2** and **3** with dimensions of $0.18 \times$
101 0.16×0.10 , $0.28 \times 0.18 \times 0.15$ and $0.20 \times 0.16 \times 0.12$ mm³, respectively, were mounted on a
102 Bruker SMART or a Bruker APEX-II CCD diffractometer equipped with graphite
103 monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The reflection data were collected and
104 processed using the program suites BrukerAPEX2, Bruker SAINT, COLLECT, DENZO-SMN
105 and related analysis software [20-22]. The structures were solved by direct methods using the
106 program SHELXS97 or SHELXT and refined with full-matrix least-squares based on F^2 using
107 program SHELXL-2014/7 [23-25]. All H atoms were placed geometrically and refined using a
108 riding atom approximation. In **1**, large solvent accessible voids presumably filled with severely
109 disordered solvent molecules were present and could not be modeled. In **2**, the S2/C13-C16
110 thiophene ring was found to be disordered about two sets of sites approximately rotated by 180°
111 about the C12-C13 bond with refined occupancy ratio of 0.703(5):0.297(5). One azido
112 (N5/N6/N7) and the nitrate anions were also found to be disordered over two orientations with
113 refined occupancy ratio of 0.686(8):0.314(8). During the refinement, the bond lengths involving
114 the disordered atoms were restrained to be similar (SADI instruction in SHELXL-2014/7) and
115 the ADP's isotropic (ISOR instruction). The thiophene ring was modeled with geometric (FLAT
116 instruction) and displacement parameter (DELU instruction) restraints in order to reduce the
117 components of the ADP's along the C-C and C-S bonds. EADP constraints were also applied to
118 corresponding pairs of disordered atoms. In **1-3**, subsequent difference Fourier synthesis and
119 least-square refinement revealed the positions of the remaining non-hydrogen atoms. Non-
120 hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen
121 atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2

122 times larger than those of the parent atom. Successful convergence was indicated by the
123 maximum shift/error of 0.001 for the last cycle of the least squares refinement. All calculations
124 were carried out using SHELXS 97, SHELXL 97, PLATON 99, ORTEP-32 and WinGX system
125 Ver-1.64 [20-25]. Crystallographic data and refinement details for the compounds are
126 summarized in Table 1. The molecular structures of **1-3** are presented in Fig. 1 and a few
127 selected bond parameters are collected in Tables 2 and 3.

128 2.5. Antibacterial screening – materials and methods

129 The Schiff base ligands H_2L^1 , L^2 , L^3 and the respective Co(III) complexes **1-3** were subjected
130 to screening for antimicrobial activity by using agar disc diffusion assay [26]. The antimicrobial
131 activity of each compound under experiment was evaluated against two Gram-positive bacteria,
132 viz. *Staphylococcus aureus* MTCC 2940 and *Bacillus subtilis* MTCC 441 and two Gram-
133 negative bacteria viz. *Pseudomonas aeruginosa* MTCC 2453 and *Escherichia coli* MTCC 739.
134 The samples were dissolved in dimethyl sulphoxide solvent, which itself did not show any
135 inhibition against the tested organisms. Solutions of four different concentrations (250, 500, 750
136 and 1000 $\mu\text{g mL}^{-1}$) of each compound were prepared for evaluation of limiting doses. A
137 suspension of the tested microorganism (500 μL of 10^8 CFU/mL) was spread on the solid media
138 plates and then filter paper discs (6 mm in diameter) were soaked with 20 μL of the stock
139 solutions and placed on the inoculated plates. After keeping at 2°C for 2 h, they were incubated
140 at 37°C for 24 h for all the bacteria. Antibacterial activities of the compounds were then
141 evaluated by measuring the inhibition zone diameters (IZD) in millimeter as well as by minimum
142 inhibitory concentrations (MIC). Each test was carried out in triplicate and the average inhibition
143 zone diameters were calculated. The activities of the Co(III) complexes and the parent ligands

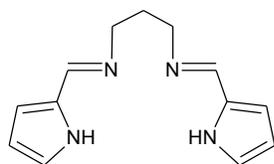
144 were then compared with the activity of a standard antibiotic viz. ciprofloxacin at similar
145 concentrations.

146 **3. Results and discussion**

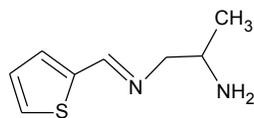
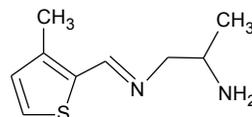
147 *3.1. Synthesis and characterization*

148 Similar synthetic routes were followed to obtain cobalt complexes containing different
149 heterocyclic Schiff bases. The reaction of cobalt(II) nitrate, Schiff base (H_2L^1) and azide in the
150 molar ratio of 1:1:1 in methanol yielded **1**, a binuclear end-on bis(μ -azido) cobalt(III) complex.
151 The same molar ratio of reactants as in H_2L^1 was maintained to prepare similar Schiff bases L^2
152 and L^3 . However, the reactions of cobalt(II) nitrate or perchlorate with those Schiff bases
153 formed mononuclear and isostructural cobalt(III) complexes, **2** and **3**. It was noticed that during
154 the synthesis of either the Schiff bases or the complexes, single amine group of the diamine was
155 involved in the condensation process with thiophene-2-al and the other remained as free donor
156 center. Again, all the complexes were prepared using cobalt(II) salts as the starting material but,
157 as usual, Co^{II} underwent aerial oxidation to Co^{III} during the formation of **1-3** to accommodate
158 ligands with harder donor atoms and to gain higher CFSE. The structure of the ligands and
159 relevant equations for the formation of the complexes are presented in Scheme 1. The complexes
160 **1-3** have been characterized by microanalytical, spectroscopic and single crystal X-ray
161 diffraction studies. In methanol solvent, complex **1** behaves as a non-electrolyte while **2** and **3**
162 behave as 1:1 electrolytes as it is evident from their Λ_M values. Room temperature magnetic
163 susceptibility measurements show that **1-3** are diamagnetic, indicating the absence of unpaired
164 electrons in them. This is in conformity with the presence of singlet ground state with $t_{2g}^6e_g^0$
165 configuration in all the low spin octahedral Co(III) complexes. All these results including those
166 of X- ray structural analysis are consistent with the proposed formulae of **1-3**.

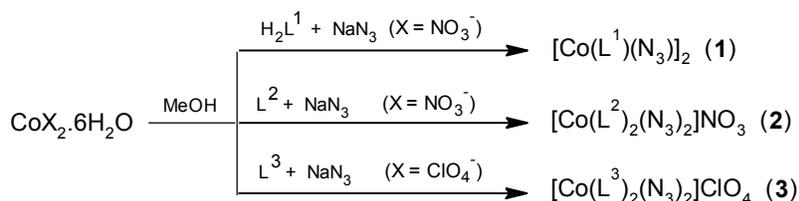
167



168

 H_2L^1  L^2  L^3

169

170 **Scheme 1.** Structures of the ligands and formation of the complexes **1-3**.171 *3.2. FTIR and electronic spectra*

172 The infrared spectra of the compounds **1-3** exhibit strong absorption bands in the region
 173 1600-1630 cm^{-1} corresponding to the $\nu(\text{C}=\text{N})$ stretching frequency. These values are
 174 considerably lower than those of the precursor Schiff bases (1620-1635 cm^{-1}) and indicate the
 175 coordination of the azomethine N-atoms of the respective Schiff bases to the central cobalt(III)
 176 ion. Complexes **1-3** also show a sharp and distinct absorption band each in the range 2024-2036
 177 cm^{-1} , attributable to the stretching vibrations of the bridging or terminal azides. The N-H
 178 stretching vibration invariably found in pyrrole or its derivatives at around 3265-3321 cm^{-1} is
 179 missing in compound **1**. This suggests coordination of deprotonated N-atom of pyrrole ring of
 180 H_2L^1 to the metal ion. However, bands in nearly the same frequency region are observed both in
 181 **2** and **3** indicating presence of N-H bond. This is justified because single amine group out of the
 182 two only participated in the formation of L^2 and L^3 . An intense band observed at 1385 cm^{-1} in **2**
 183 is due to the presence of NO_3^- ion. A strong bifurcated band in the range 1090-1108 cm^{-1} is
 184 suggestive of the presence of ClO_4^- in **3**. The sharp bands observed around 850 cm^{-1} due to $\nu(\text{C}-$
 185 S-C) of the thiophene moiety in L^2 and L^3 do not shift appreciably after complexation. This

186 supports that the S atoms in these ligands do not take part in coordination. All other
187 characteristic vibrations of the metal-bound Schiff bases including the C-N and C-S stretches are
188 located in the range 600-1500 cm^{-1} . Thus, the IR spectral data of the compounds are fairly
189 consistent [27] with the respective structural features of **1-3**.

190 The electronic spectra of the complexes **1-3** in DMF solution reflect the presence of six-
191 coordinate octahedral geometry around each of the cobalt(III) ion. The spectra exhibit several
192 intense absorption bands in the range 210-280 nm, corresponding to π - π^* transitions of the
193 heterocyclic rings. Other bands at 290–324 nm were assigned to the n - π^* transitions of the non-
194 bonding electrons present on the nitrogen of the azomethine group of the Schiff base. The high
195 intensity bands at λ_{max} values in the region 508 - 580 nm in **1-3** may be attributed to the LMCT
196 transitions in these complexes. The other high intensity bands observed in the UV region of all
197 the compounds are assignable to intraligand n - π^* / π - π^* transitions.

198 3.3. Crystal structure of **1**

199 X-ray diffraction studies reveal that the structure of **1** comprises a neutral and discrete
200 binuclear complex unit $[\text{Co}_2(\text{L}^1)_2(\text{N}_3)_2]$ (Fig. 1a) in which two slightly dissimilar $[\text{Co}(\text{L}^1)]$ units
201 are connected through two end-on bridging azide ligands (Fig.1b). The intramolecular Co-Co
202 separation in this bis(μ -azido) complex is 3.082 Å. Each Co(III) ion in **1** adopts a distorted
203 octahedral geometry with CoN_6 chromophore. While two *cis* positions around each cobalt ion are
204 occupied by N-atoms (N1C, N1D) of the bridging azides, the other four are due to the nitrogens
205 of the deprotonated Schiff base. Two imine nitrogens (N2A, N3A in Co1 and N2B, N3B in Co2)
206 and two pyrrole nitrogens (N1A, N4A in Co1 and N1B, N4B in Co2) also dispose in the *cis* sites
207 to complete the six coordination environment around the cobalt(III) ions. The Co–N bond
208 distances in **1** vary from 1.894–1.983 Å, the Co–N(azide) being the longer ones. Distortion in

209 the coordination sphere of Co(III) ion from ideal geometry is obvious due to structural
210 constraints imposed by the polydentate ligand framework. It is evident from the rather wide
211 spread of the *cisoid* and *transoid* angles, being 77.73–96.74° and 167.49–172.43°, respectively.
212 However, all the bond parameters of **1** are comparable with similar other Co(III) complexes
213 reported earlier [11-15].

214 3.4. Crystal structures of **2** and **3**

215 Both **2** and **3** contain mononuclear cationic units of Co(III) along with a nitrate and a
216 perchlorate ion, respectively to maintain their electroneutrality (Fig. 1c and 1d). Nevertheless,
217 these two complexes are structurally very similar which is evident from insignificant variations
218 in their bond lengths and angles. In these complexes, the central Co(III) ion is a member of two
219 five-membered rings and adopts a distorted octahedral (CoN₆) geometry. Two imine nitrogens
220 (N2, N4 in **2**; N1A, N1B in **3**), two nitrogen atoms (N1, N3 in **2**; N2A, N2B in **3**) of the
221 remaining free amine of the Schiff base along with other two azide nitrogen atoms (N5, N8 in **2**;
222 N1C, N1D in **3**) constitute the irregular hexacoordinated structure around the central Co(III) ion.
223 Furthermore, the two azide ions are disposed in *cis* positions with respect to each other in both
224 the complexes. The Co–N bond lengths in **2** and **3** range from 1.938–1.964 Å and are
225 comparable with each other as well as other analogous complexes containing CoN₆
226 chromophores [11-15]. The Co–N(imine) distances are, however, somewhat shorter than other
227 Co–N distances. Distortion in the coordination sphere of these complexes is inevitable due to the
228 presence of asymmetric polydentate ligand framework. The *cisoid* and *transoid* angles around
229 the Co(III) ion in the range of 84.1–94.2° and 172.9–177.8°, respectively, support the fact.

230 3.5. Supramolecular structures of **1-3**

231 The supramolecular interactions involved in **1-3** are displayed in Fig. 2 and the relevant data
232 are listed in Table 3. In **1**, the binuclear complex units are connected by very weak
233 intermolecular C-H...N hydrogen bonding interactions to form 1D supramolecular chain along
234 the crystallographic *b*-axis (Fig. 2a). In **2**, the monomeric $[\text{Co}(\text{L}^2)_2(\text{N}_3)_2]^+$ units are similarly
235 connected by nitrate mediated N-H...O hydrogen bonding interactions (Table 3) to form
236 supramolecular 1D chain parallel to the *c*-axis (Fig. 2b). These 1D supramolecular chains are
237 further connected by C-H...S, C-H...N hydrogen bond as well as π ... π interactions to form 2D
238 supramolecular architecture (Fig. 2c) in the crystallographic *ac*-plane. In **3**, stronger N-H...O
239 hydrogen bonding interactions are operative between the free amine group and the perchlorate
240 ions to constitute 1D supramolecular chain (Fig. 2d). These 1D supramolecular chains are further
241 connected by hydrogen bonding, C-H... π and Cl-O... π interactions to form 3D supramolecular
242 network (Fig. 2e). Thus, all the perchlorate ions outside the coordination sphere of **3** participate
243 actively in various weak intermolecular interactions.

244 3.6. Antibacterial activity of the compounds

245 The results of the antibacterial screening of the tested compounds are presented as IZD and
246 MIC values in Tables 4 and 5, respectively. The study reveals that the Schiff bases (H_2L^1 , L^2 and
247 L^3) are mildly active against all of the reference bacteria even at higher doses. But, the
248 bactericidal property is greatly enhanced on complexation with the cobalt(III) ion, particularly in
249 **2** and **3**. The IZD data indicate that the antibacterial activities of **2** and **3** are comparable to each
250 other and to similar other cobalt(III) complexes [12-19]. It also demonstrate that **2** and **3** are
251 more susceptible to the Gram(+) bacteria than to the Gram(-) bacteria. Among all the bacteria,
252 *B. subtilis* is found to be the most susceptible against these two complexes. It has been noticed
253 that all the tested compounds possess rather low IZD and high MIC values in comparison to

254 ciprofloxacin. While the MIC values of **1** are invariably higher, those of **2** and **3** are comparable
255 to ciprofloxacin at higher doses in some cases. All these observations are more or less similar to
256 the earlier reports [12-19] of bioactivities of analogous cobalt(III) Schiff base complexes.

257 From the *in vitro* antibacterial assay, it can be concluded that the tested compounds possess
258 mild to strong bactericidal properties which increase with dose to some extent. But, none of the
259 compounds is as potent as the commercial antibiotic like ciprofloxacin at similar concentrations.
260 Although no correlation could be made, the results of the study certainly suggest that the
261 antibacterial activity of the complexes is dictated by the nature of the constituent ligands.

262 **4. Conclusions**

263 Synthesis and characterization of three new cobalt(III) complexes of Schiff bases with
264 different heterocyclic rings have been described in this paper. Reaction of cobalt(II) salt with a
265 tetradentate ligand derived from pyrrole-2-al and propane-1,3-diamine plus azide yielded a
266 binuclear end-on bis(μ -azido) complex of cobalt(III). In contrast, same reaction with the Schiff
267 base of thiophene-2-al or its derivative with propane-1,2-diamine resulted in the formation of
268 two isostructural mononuclear complexes with two terminal azide ions disposed in *cis* positions.
269 All the complexes adopt distorted octahedral arrangement around the central Co(III) ions which
270 are held together by weak intermolecular H-bonding and/or π -interactions in their solid state.
271 Results of antibacterial screening indicate that the complexes possess quite strong bactericidal
272 properties. In addition to the synthetic and structural investigations, this study also demonstrates
273 the higher antibacterial potential of some cobalt(III) complexes in comparison to their constituent
274 Schiff bases.

275 **Acknowledgements**

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277 constant encouragement and support in the progress of the work.

278 **Appendix A. Supplementary data**

279 CCDC 988965, 1510663 and 1510662 contain the supplementary crystallographic data of **1-3**.
280 These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>,
281 or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK;
282 fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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