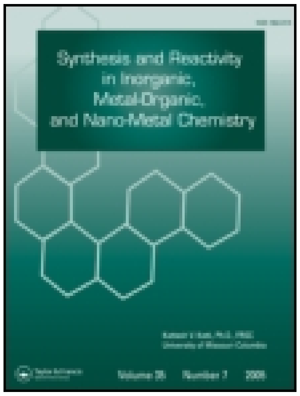

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

Synthesis, Structures, and Antimicrobial Activity of Schiff Base Cobalt Complexes $[Co(HL^1)_2(N_3)_2]\cdot H_2O$ and $[CoL^2{}_2]\cdot ClO_4$

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To cite this article: Ling-Wei Xue, Yong-Jun Han, Gan-Qing Zhao & Yun-Xiao Feng (2012): Synthesis, Structures, and Antimicrobial Activity of Schiff Base Cobalt Complexes $[Co(HL^1)_2(N_3)_2]\cdot H_2O$ and $[CoL^2{}_2]\cdot ClO_4$, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 42:2, 154-159

To link to this article: http://dx.doi.org/10.1080/15533174.2011.609510

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 42:154–159, 2012

ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2011.609510

Synthesis, Structures, and Antimicrobial Activity of Schiff Base Cobalt Complexes $[Co(HL^1)_2(N_3)_2]\cdot H_2O$ and $[CoL^2{}_2]\cdot ClO_4$

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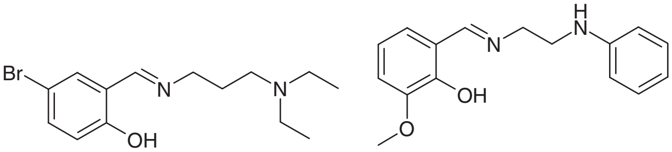
The new Schiff bases 4-bromo-2-[(3-diethylaminopropylimino) methyl]phenol (HL^1) and 2-methoxy-6-[(2-phenylaminoethylimino) methyl]phenol (HL^2) derived from 5-bromosalicylaldehyde with *N,N*- diethylpropane -1,3- diamine and 3- methoxysalicylaldehyde with *N*-phenylethane-1,2-diamine, respectively, and their cobalt complexes, $[Co(HL^1)_2(N_3)_2]\cdot H_2O$ and $[CoL^2{}_2]\cdot ClO_4$, have been prepared and characterized by elemental analyses, infrared, and single crystal X-ray crystallographic determination. The HL^1 coordinates to the Co atom through the phenolic O and imino N atoms with a zwitterionic form, while the HL^2 coordinates to the Co atom through the phenolic O, imino N, and amino N atoms with a deprotonated form. Each Co atom in the complexes adopts an octahedral coordination. The effect of the Schiff bases and the complexes on the antimicrobial activity against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans* were studied.

Keywords antimicrobial, cobalt complex, crystal structure, Schiff base, synthesis

INTRODUCTION

Schiff bases are a kind of versatile ligands in coordination chemistry.[1–3] In recent years, metal complexes of Schiff bases have attracted considerable attention due to their remarkable biological activity, such as antifungal, antibacterial and antitumor.[4–6] It has been shown that the Schiff base complexes derived from salicylaldehyde and its derivatives with primary amines, bearing the N_2O, N_2S, NO_2, or NSO donor sets, have interesting biological activity.[6–8] Furthermore, mono- and multinuclear complexes of cobalt in its varied oxidation states have become a central theme of current research because of their potentially useful properties in the realm of relevant scientific and technological fields. The search in the Cambridge Crystallographic Database (version 5.31 with addenda up to August 2010)[9] has revealed that there are no complexes with the Schiff bases 4-bromo-2-[(3-diethylaminopropylimino)methyl]phenol (HL^1) and 2-methoxy-6-[(2-phenylaminoethylimino)methyl]phenol (HL^2; Chart 1). In the present article, the preparation, characterization and antimicrobial activity of two new cobalt complexes with the Schiff bases are reported.



SCH. 1.

EXPERIMENTAL

Material and Methods

5-Bromosalicylaldehyde, 3-methoxysalicylaldehyde, *N,N*-diethylpropane-1,3-diamine, and *N*-phenylethane-1,2-diamine were purchased from Fluka. Other reagents and solvents were analytical grade and were used without further purification. Elemental (C, H, and N) analyses were made on a PerkinElmer Model 240B automatic analyzer. Cobalt analysis was carried out by EDTA titration. Infrared (IR) spectra were recorded on an IR-408 Shimadzu 568 spectrophotometer. X-ray diffraction was carried out on a Bruker SMART 1000 CCD area diffractometer.

Preparation of HL^1

The Schiff base ligand HL^1 was prepared by the condensation of equimolar quantities of 5-bromosalicylaldehyde (0.20 g, 1 mmol) with *N,N*-diethylpropane-1,3-diamine (0.13 g, 1 mmol) in methanol (30 ml) at ambient temperature for 1 h. Then the methanol was evaporated by distillation, yielding yellow oil of the Schiff base, which was used for the preparation of the complexes without purification. Elemental analysis found: C,

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Received 17 February 2011; accepted 28 July 2011.

This research was supported by the National Sciences Foundation of China (No. 20676057 and 20877036) and Top-class foundation of Pingdingshan University (No. 2008010).

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53.5; H, 6.7; N, 9.0%; $C_{14}H_{21}BrN_2O$ Anal. Calcd.: C, 53.7; H, 6.8; N, 8.9%.

Preparation of HL^2

The Schiff base ligand HL^2 was prepared by the condensation of equimolar quantities of 3-methoxysalicylaldehyde (0.15 g, 1 mmol) with *N*-phenylethane-1,2-diamine (0.14 g, 1 mmol) in methanol (30 ml) at ambient temperature for 1 h. Then the methanol was evaporated by distillation, yielding yellow oil of the Schiff base, which was used for the preparation of the complexes without purification. Elemental analysis found: C, 71.2; H, 6.8; N, 10.2%; $C_{16}H_{18}N_2O_2$ Anal. Calcd.: C, 71.1; H, 6.7; N, 10.4%.

Preparation of $[Co(HL^1)_2(N_3)_2]\cdot H_2O$ (1)

The Schiff base HL^1 (0.31 g, 1 mmol) was diluted by methanol (20 ml), to which was added with stirring a methanol solution (10 ml) of $Co(ClO_4)_2\cdot 6H_2O$ (0.36 g, 1 mmol) and an aqueous solution (10 ml) of NaN_3 (0.07 g, 1 mmol). The mixture was stirred for 1 h at ambient temperature to give a red solution. Red block-shaped single crystals suitable for X-ray diffraction were formed by slow evaporation of the solution in air for about a week. Yield: 37%. Elemental analysis found: C, 42.6; H, 5.6; N, 17.9; Co, 7.7%; $C_{28}H_{44}Br_2CoN_{10}O_3$ Anal. Calcd.: C, 42.7; H, 5.6; N, 17.8; Co, 7.5%.

Preparation of $[CoL^2{}_2]\cdot ClO_4$ (2)

The Schiff base HL^2 (0.27 g, 1 mmol) was diluted by methanol (20 ml), to which was added with stirring a methanol solution (10 ml) of $Co(ClO_4)_2\cdot 6H_2O$ (0.36 g, 1 mmol) and an aqueous solution (10 ml) of NaN_3 (0.07 g, 1 mmol). The mixture was stirred for 1 h at ambient temperature to give a red solution. Red block-shaped single crystals suitable for X-ray diffraction were formed by slow evaporation of the solution in air for 5 d. Yield: 45%. Elemental analysis found: C, 54.9; H, 5.0; N, 8.1; Co, 8.6%, $C_{32}H_{34}ClCoN_4O_8$ Calcd: C, 55.1; H, 4.9; N, 8.0; Co, 8.5%.

X-Ray Diffraction

Data were collected from selected crystals mounted on glass fibers. The data for the two complexes were processed with SAINT[10] and corrected for absorption using SADABS.[11] Semi-empirical absorption corrections were applied with ψ-scans.[12] The structures were solved by direct methods using the program SHELXS-97, and were refined by full-matrix least-squares techniques on F^2 using anisotropic displacement parameters.[13] H2 and H4A atoms in (**2**) were located from a difference Fourier map and refined isotropically, with N–H distances restrained to 0.90(1) Å. The remaining hydrogen atoms were placed at the calculated positions. Idealized H atoms were refined with isotropic displacement parameters set to 1.2 (1.5 for O and methyl C atoms) times the equivalent isotropic *U* values of the parent atoms. The crystallographic data for the complexes are listed in Table 1.

RESULTS AND DISCUSSION

Two new Schiff bases and their cobalt complexes have been prepared. The Schiff bases prepared in this way are formed in nearly quantitative yields and are of high purity. The reaction involving the Schiff bases, $Co(ClO_4)_2\cdot 6H_2O$, and sodium azide in the molar ratio of 1:1:1 generates beautiful red colored block-shaped single crystals of the complexes. The results of the elemental analyses are in accord with the composition suggested for the ligands and the complexes. The sodium azide was used in the preparation of both complexes, however, it coordinates to the Co atom of (**1**), but does not coordinate to the Co atom of (**2**). This might be caused by the larger hindrance effect of the

TABLE 1
Crystal and structure refinement data for (**1**) and (**2**)

	(**1**)	(**2**)
Empirical formula	$C_{28}H_{44}Br_2CoN_{10}O_3$	$C_{32}H_{34}ClCoN_4O_8$
Color; habit	Block, red	Block, red
Formula weight	787.5	697.0
Temperature (K)	298(2)	298(2)
Crystal size (mm)	0.20 × 0.20 × 0.17	0.27 × 0.25 × 0.23
Radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
Unit cell dimensions		
a (Å)	12.679(2)	10.869(1)
b (Å)	9.269(1)	11.375(1)
c (Å)	28.627(4)	14.370(1)
α (°)	90	99.874(1)
β (°)	101.913(2)	111.284(1)
γ (°)	90	103.512(1)
V (Å^3)	3291.8(7)	1543.9(1)
Z	4	2
Density (g cm^{-3})	1.589	1.499
Absorption coefficient (mm^{-1})	2.996	0.702
θ range for data collection (°)	2.64–27.00	1.59–27.00
Index ranges (h, k, l)	–16, 15; –11, 11; –36, 36	–13, 13; –14, 10; –17, 18
Reflections collected	26640	9263
Independent reflections	7144	6476
Data/parameters	3005/404	5461/423
Final R indices [$I > 2\sigma(I)$]	0.0783	0.0375
R indices (all data)	0.1406	0.0879
Goodness-of-fit on F^2	0.970	1.026

N,N-diethyl groups in (**1**) than that of the phenyl groups in (**2**). It is notable that the oxidation numbers of the Co atoms are +2 for (**1**) and +3 for (**2**). The air-stable Schiff bases and the cobalt complexes are soluble in DMF, methanol, ethanol, chloroform, and acetonitrile.

IR Spectra

Complexes (**1**) and (**2**) exhibit similar IR absorption. Both complexes exhibit strong and sharp bands at 1627 and 1633 cm^{-1}, respectively, which can be assigned to the C = N stretching frequency of the coordinated Schiff base ligands.[14,15] The shift of these bands toward lower frequencies compared to those of the free Schiff bases indicates the coordination of the imino N atoms to the metal centers. For the complexes, the phenolic C–O stretching is obtained at about 1273 cm^{-1}. The sharp bands in both spectra of the complexes at 3272 and 3253 cm^{-1} can be attributed to the N–H vibrations. The bands at about 2935 cm^{-1} can be correlated to the alkyl C–H bond stretching. Several weak peaks observed in the range 3180–3000 cm^{-1} are likely to be due to the aromatic stretches. For (**1**), a very strong single sharp band is obtained at 2037 cm^{-1} characteristic of the azide ligands,[16] whereas complex (**2**) exhibits a very strong splitted band centered at 1091 cm^{-1} for the perchlorate anion. The bands in the region 560–410 cm^{-1} are assigned to the Co-N and Co-O vibrations.[17]

Crystal Structure Description of Complex (1)

The molecular structure of complex (**1**) is in Figure 1. Selected bond distances and angles are listed in Table 2.

The complex contains a mononuclear cobalt(II) complex moiety and a water molecule. The Co atom has an octahedral geometry and coordinated by two zwitterionic Schiff base ligands HL^1 and two azide groups. The Schiff bases act as bidentate ligands and coordinate to the Co atom through the phenolic O and imino N atoms. The azide groups are monodentate ligands and coordinate to the Co atom through the terminal N atoms. For the octahedral coordination, the three *trans* angles are in the range 177.3(3)–178.0(2)°, and the other angles are in the range 86.7(2)–93.5(2)°, indicating a slightly distorted octahedral geometry. The distances of the Co–O and Co–N bonds are comparable to the values observed in other cobalt(II) complexes with Schiff bases.[18,19] In the crystal structure, the molecules are connected by intermolecular hydrogen bonds O–H···N, N–H···O, and N–H···N, forming 2D layered structure along the *ab* plane, as shown by Figure 2. The corresponding hydrogen bonding parameters are listed in Table 3.

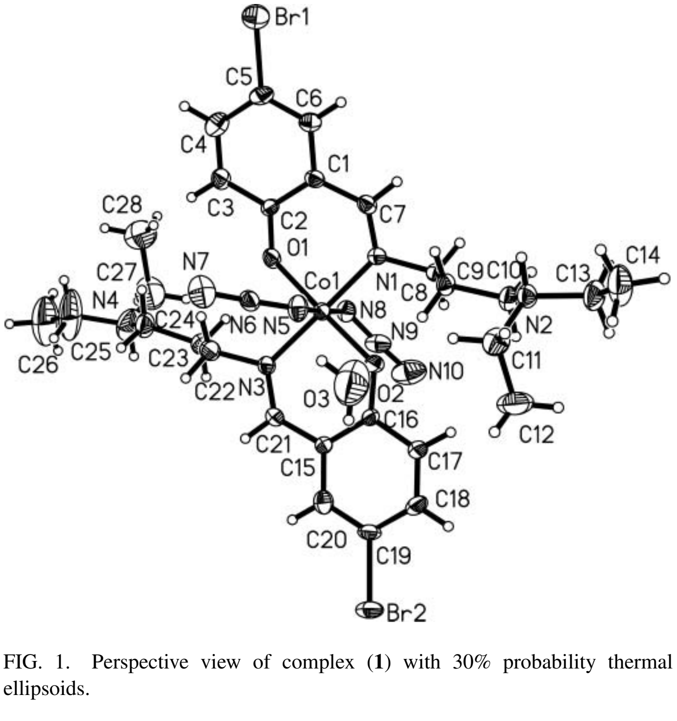

FIG. 1. Perspective view of complex (**1**) with 30% probability thermal ellipsoids.

TABLE 2
Coordinate bond distances (Å) and angles (°) for (**1**) and (**2**)

(1)			
Co1-O1	1.877(5)	Co1-O2	1.866(5)
Co1-N1	1.949(6)	Co1-N3	1.949(6)
Co1-N5	1.957(7)	Co1-N8	1.971(7)
O2-Co1-O1	178.0(2)	O2-Co1-N3	93.5(2)
O1-Co1-N3	88.1(2)	O2-Co1-N1	86.7(2)
O1-Co1-N1	91.7(2)	N3-Co1-N1	177.9(3)
O2-Co1-N5	88.8(3)	O1-Co1-N5	92.3(3)
N3-Co1-N5	90.5(3)	N1-Co1-N5	87.4(3)
O2-Co1-N8	91.8(3)	O1-Co1-N8	87.0(3)
N3-Co1-N8	92.1(3)	N1-Co1-N8	89.9(3)
N5-Co1-N8	177.3(3)		
(2)			
Co1-O1	1.868(1)	Co1-O2	1.893(1)
Co1-N1	1.906(2)	Co1-N2	2.046(2)
Co1-N3	1.904(2)	Co1-N4	2.032(2)
O1-Co1-O2	90.7(1)	O1-Co1-N3	85.7(1)
O2-Co1-N3	92.8(1)	O1-Co1-N1	94.4(1)
O2-Co1-N1	84.8(1)	N3-Co1-N1	177.6(1)
O1-Co1-N4	87.7(1)	O2-Co1-N4	176.6(1)
N3-Co1-N4	84.2(1)	N1-Co1-N4	98.3(1)
O1-Co1-N2	178.2(1)	O2-Co1-N2	90.2(1)
N3-Co1-N2	95.8(1)	N1-Co1-N2	84.2(1)
N4-Co1-N2	91.5(1)		

Crystal Structure Description of Complex (2)

The molecular structure of the complex (2) is in Figure 3. Selected bond distances and angles are listed in Table 2.

The complex contains one [CoL$^2{}_2$]$^+$ cation and one perchlorate anion. The hexa-coordinated cobalt(III) center is bonded to two tridentate Schiff base ligands L^2 in an octahedral geometry. Each Schiff base ligand offers deprotonated phenolic O, imino N, and amino N atoms as the coordination sites

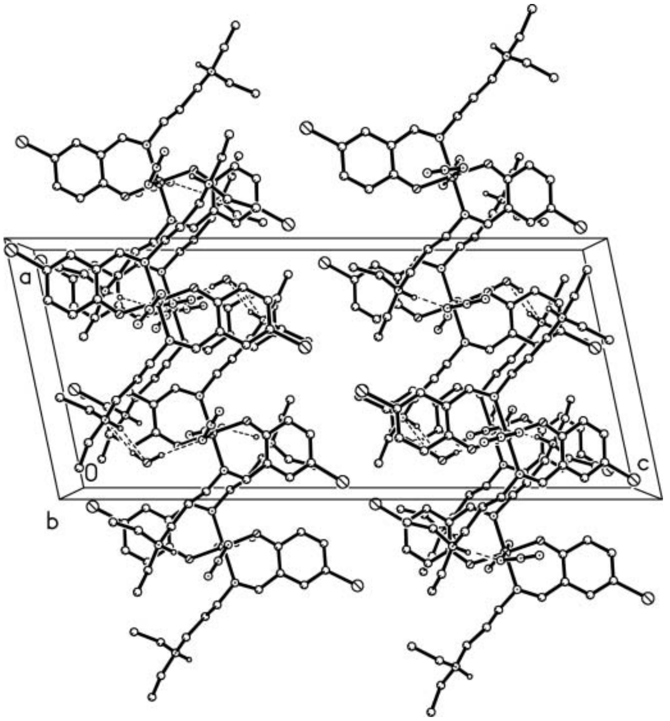

FIG. 2. Molecular packing of complex (**1**), viewed along the *b* axis.

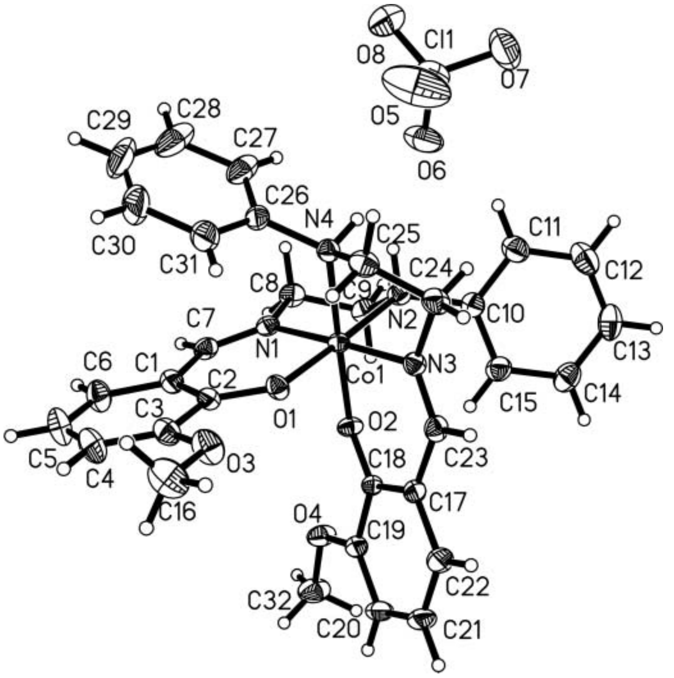

FIG. 3. Perspective view of complex (**2**) with 30% probability thermal ellipsoids.

providing a CoN_4O_2 chromophore. The fact that Co–N_{amino} bonds are longer than Co–N_{imino} bonds is quite evident from the difference in hybridization states (sp^2 for imino N and sp^3 for amino N). For the octahedral coordination, the three *trans* angles are in the range 176.6(1)–178.2(1)°, and the other angles are in the range 84.2(1)–98.3(1)°, indicating a slightly distorted octahedral geometry. The distances of the Co–O and Co–N bonds are consistent with corresponding values of analogous CoN_4O_2 chromophores.[20,21] The perchlorate anion plays a significant role in hydrogen bonding interactions leading to the formation of 1D chain along the *c* axis, as shown by Figure 4. The corresponding hydrogen bonding parameters are listed in Table 3.

TABLE 3
Hydrogen bonding parameters for (**1**) and (**2**)

D–H···*A*	*d*(*D*–H) (Å)	*d*(H···*A*) (Å)	d(*D*···*A*) (Å)	□(*D*–H···*A*) (°)
(**1**)				
O3–H3A···N4[a]	0.85	2.30	2.98(1)	137
O3–H3B···N5	0.85	2.40	2.98(1)	126
N4–H4A···O3[b]	0.91	2.13	2.98(1)	154
N2–H2···N8[c]	0.90(1)	2.05(2)	2.94(1)	169 (8)
N2–H2···N9[c]	0.90(1)	2.63(4)	3.48(1)	158 (7)
(**2**)				
N4–H4A···O6	0.90(3)	2.00(3)	2.87(1)	163 (3)
N2–H2···O6	0.90(3)	2.65(2)	3.41(1)	142 (3)
N2–H2···O8[d]	0.90(3)	2.52(2)	3.24(1)	137 (3)

Symmetry transformations used to generate equivalent atoms: (a) 1 – *x*, 1/2 + *y*, 1/2 – *z*; (b) 1 – *x*, –1/2 + *y*, 1/2 – *z*; (c) 2 – *x*, 1/2 + *y*, 1/2 – *z*; (d) 2 – *x*, 2 – *y*, 1 – *z*.

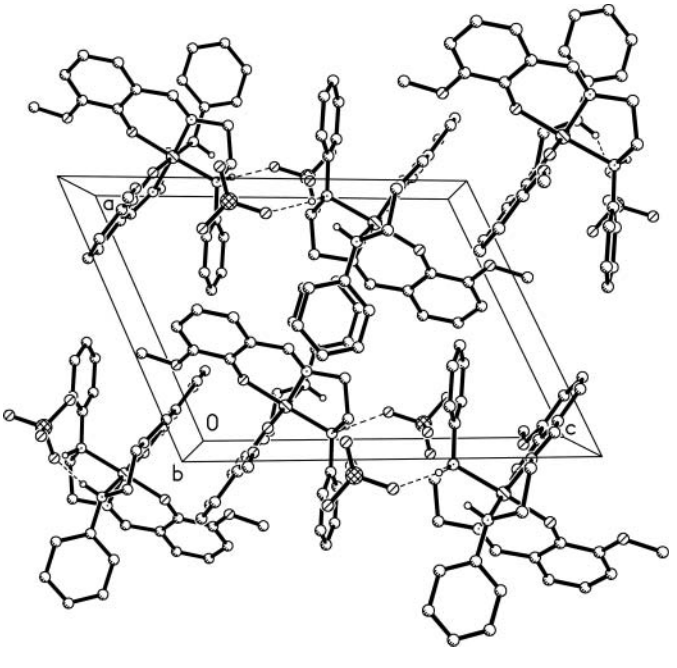

FIG. 4. Molecular packing of complex (**2**), viewed along the *b* axis.

TABLE 4
Minimum inhibitory concentration values (μg/mL) for the antimicrobial activities of the tested compounds

	Staphylococcus aureus	*Escherichia coli*	*Candida albicans*
HL^1	512	512	> 1024
HL^2	128	256	> 1024
(**1**)	16	64	512
(**2**)	2	16	256
Tetracycline	0.32	2.12	> 1024

Antimicrobial Activity

Qualitative determination of antimicrobial activity was done using the disk diffusion method.[22,23] The results are summarized in Table 4. A comparative study of minimum inhibitory concentration values of the Schiff bases and the two complexes indicate that the cobalt complexes have better activity than the free Schiff bases. Generally, this is caused by the greater lipophilic nature of the complexes than the ligand. Such increased activity of the metal chelates can be explained on the basis of chelating theory.[24] On chelating, the polarity of the metal atoms will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of the metal atoms with donor atoms. Further, it increases the delocalization of *p*-electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and blocks the metal binding sites on enzymes of micro-organisms.

From Table 4, it is obvious that the cobalt complexes show greater antimicrobial and antifungi activities against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans* when compared with the Schiff bases. The structures of the tested compounds seem to be the principal factor influencing the antimicrobial activity. The activity of (**2**) is stronger than (**1**). For *Staphylococcus aureus* and *Escherichia coli*, even though the activities of the cobalt complexes are stronger than those of the Schiff bases, it is still much less than the control drug Tetracycline. But for *Candida albicans*, both complexes show stronger activity than the Schiff bases and Tetracycline.

CONCLUSION

The new Schiff bases The new Schiff bases 4-bromo-2-[(3-diethylaminopropylimino)methyl]phenol and 2-methoxy-6-[(2-phenylaminoethylimino)methyl]phenol and their cobalt complexes were prepared and characterized. The crystal structures of both complexes were confirmed by X-ray single crystal structure determination. The antimicrobial test shows that both complexes have potential activity against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans*.

SUPPLEMENTARY MATERIALS

The crystallographic data of the structures described in this paper were deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC- 812229 for (**1**) and 763167 for (**2**). Copies of these data are available free of charge from http://www.ccdc.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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