ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2014, Vol. 40, No. 2, pp. 120–124. © Pleiades Publishing, Ltd., 2014.

Synthesis, Structures, and Antibacterial Activity of Schiff-Base Cobalt(III) Complexes[1]

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Received January 4, 2013

Abstract—Two new Schiff-base cobalt(III) complexes, $[CoL^1(En)N_3]Cl$ (**I**) and $[CoL^2N_3(OH_2)]$ (**II**), where L^1, L^2, and En are 2-[1-(2-aminoethylimino)ethyl]phenolate, bis(5-chlorosalicylidene)ethane-1,2-diamine, and 1,2-ethylenediamine, respectively, have been prepared and characterized by physicochemical methods and single crystal X-ray determination. Complex **I** crystallizes in monoclinic system space group $P2_1/n$ with $a = 7.113(1)$, $b = 21.385(1)$, $c = 10.599(1)$ Å, $\beta = 106.067(2)°$, $V = 1549.2(3)$ Å^3, $Z = 4$, $R_1 = 0.0322$, and $wR_2 = 0.0800$. Complex **II** crystallizes in monoclinic system space group $P2_1/c$ with $a = 1.679(1)$, $b = 11.145(1)$, $c = 12.493(1)$ Å, $\beta = 110.553(2)°$, $V = 1783.5(2)$ Å^3, $Z = 4$, $R_1 = 0.0360$, and $wR_2 = 0.0838$. Single crystal X-ray diffraction analysis reveals that the Co atoms in the complexes are six-coordinated in octahedral geometry. The complexes were screened in vitro for their antibacterial activity against *Bacillus subtillis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas aeruginosa*.

DOI: 10.1134/S107032841402002X

INTRODUCTION

In recent years, considerable attention has been focused on Schiff bases and their complexes in the fields of coordination chemistry and biological chemistry [1–3]. A number of Schiff bases were reported to possess antibacterial, antifungal and antitumor activities [4–6]. Cobalt complexes have been proved to participate in various biological processes [7–10]. Recently, we have reported some Schiff base complexes [11]. As a further study of such complexes, this work deals with the synthesis and antibacterial activity of two new cobalt(III) complexes, $[CoL^1(En)N_3]Cl$ (**I**) and $[CoL^2N_3(OH_2)]$ (**II**), where L^1, L^2, and En are 2-[1-(2-aminoethylimino)ethyl]phenolate, bis(5-chlorosalicylidene)ethane-1,2-diamine, and 1,2-ethylenediamine, respectively. The coordination behavior of the ligands toward cobalt ion was investigated via the single crystal X-ray determination.

EXPERIMENTAL

Materials and methods. 2-Acetylphenol, 5-chlorosalicylaldehyde, and 1,2-ethylenediamine with AR grade were available from Alfa Aesar Company. Sodium azide, cobalt salts and other chemicals with AR grade were purchased from Beijing Chemical Reagent Company and used without further purification. Carbon, hydrogen, and nitrogen were determined on a PerkinElmer 240C microanalyser. The metal contents were determined by complexometric titration with EDTA. IR spectra (4000–400 cm^{-1}), as KBr pellets, were recorded on a Nicolet FT-IR 170X spectrophotometer.

Synthesis of I. 2-Acetylphenol (0.136 g, 1 mmol), 1,2-ethylenediamine (0.122 g, 2 mmol), sodium azide (0.065 g, 1 mmol), and cobalt chloride (0.238 g, 1 mmol) were mixed in methanol (20 mL). The mixture was stirred at room temperature for 2 h. The insoluble impurities were removed by filtration. Block and brown crystals, suitable for single crystal X-ray diffraction, were formed by slow evaporation of the filtrate in air for a few days. The yield was 51%.

For $C_{12}H_{21}ClN_7OCo$

anal. calcd., %:	C, 38.57;	H, 5.66;	N, 26.23;	Co, 15.77.
Found, %:	C, 38.43;	H, 5.59;	N, 26.32;	Co, 15.95.

IR data (ν, cm^{-1}): 3189 (N–H), 2021 (N_3), 1595 (CH=N).

Synthesis of II. 5-Chlorosalicylaldehyde (0.313 g, 2 mmol), 1,2-ethylenediamine (0.061 g, 1 mmol), sodium azide (0.065 g, 1 mmol), and cobalt nitrate (0.291 g, 1 mmol) were mixed in methanol (20 mL). The mixture was stirred at room temperature for 2 h. The insoluble impurities were removed by filtration.

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Table 1. Crystallographic data and refinement parameters for complexes **I** and **II**

Parameter	Value	
	I	**II**
F_w	373.7	454.2
T, K	298(2)	298(2)
Crystal shape/color	Block/brown	Block/brown
Crystal size, mm	0.27 × 0.23 × 0.23	0.30 × 0.27 × 0.23
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a, Å	7.113(1)	13.679(1)
b, Å	21.385(1)	11.145(1)
c, Å	10.599(1)	12.493(1)
β, deg	106.067(2)	110.553(2)
V, Å^3	1549.2(3)	1783.5(2)
Z	4	4
ρ_c, g/cm^3	1.602	1.691
μ(MoK_α), cm^{-1}	1.293	1.291
F(000)	776	920
Index ranges, h, k, l	−8/8, −26/26, −11/12	−16/16, −13/13, −15/15
Measured reflections	13792	15424
Independent reflections	2956	3382
Observed reflections, $I \geq 2\sigma(I)$	2647	2811
Parameters	200	252
Restraints	0	3
T_{min}/T_{max}	0.7215/0.7552	0.6981/0.7556
Goodness of fit on F^2	1.109	1.041
R_1, wR_2 ($I \geq 2\sigma(I)$)*	0.0322, 0.0800	0.0360, 0.0838
R_1, wR_2 (all data)*	0.0369, 0.0822	0.0483, 0.0907
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.508, −0.241	0.354, −0.320

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Block and brown crystals, suitable for single crystal X-ray diffraction, were formed by slow evaporation of the filtrate in air for a few days. The yield was 45%.

For $C_{16}H_{14}Cl_2N_5O_3Co$

anal. calcd., %:	C, 42.31;	H, 3.11;	N, 15.42;	Co, 12.98.
Found, %:	C, 42.22;	H, 3.07;	N, 15.56;	Co, 13.17.

IR data (ν, cm^{-1}): 3410 (N–H), 2017 (N_3), 1606 (CH=N).

Table 2. Selected bond lengths (Å) and bond angles (deg) for the complexes

Bond	d, Å	Bond	d, Å
		I	
Co(1)–O(1)	1.8795(16)	Co(1)–N(1)	1.9120(18)
Co(1)–N(2)	1.9445(18)	Co(1)–N(3)	1.9742(19)
Co(1)–N(4)	1.9703(19)	Co(1)–N(5)	1.960(2)
		II	
Co(1)–N(1)	1.890(2)	Co(1)–N(2)	1.887(2)
Co(1)–O(1)	1.9055(18)	Co(1)–O(2)	1.9038(17)
Co(1)–N(3)	1.920(2)	Co(1)–O(3)	1.9922(18)
Angle	ω, deg	Angle	ω, deg
		I	
O(1)Co(1)N(1)	95.59(7)	O(1)Co(1)N(2)	178.04(8)
N(1)Co(1)N(2)	85.36(8)	O(1)Co(1)N(5)	90.77(9)
N(1)Co(1)N(5)	91.89(9)	N(2)Co(1)N(5)	87.49(9)
O(1)Co(1)N(4)	87.91(8)	N(1)Co(1)N(4)	93.21(8)
N(2)Co(1)N(4)	93.74(8)	N(5)Co(1)N(4)	174.83(8)
O(1)Co(1)N(3)	87.06(7)	N(1)Co(1)N(3)	176.57(8)
N(2)Co(1)N(3)	92.05(8)	N(5)Co(1)N(3)	90.25(9)
N(4)Co(1)N(3)	84.69(8)		
		II	
N(2)Co(1)N(1)	85.72(10)	N(2)Co(1)O(2)	94.50(9)
N(1)Co(1)O(2)	179.11(9)	N(2)Co(1)O(1)	177.40(9)
N(1)Co(1)O(1)	92.59(9)	O(2)Co(1)O(1)	87.15(7)
N(2)Co(1)N(3)	91.66(10)	N(1)Co(1)N(3)	88.47(10)
O(2)Co(1)N(3)	92.39(9)	O(1)Co(1)N(3)	90.27(9)
N(2)Co(1)O(3)	89.36(9)	N(1)Co(1)O(3)	89.23(8)
O(2)Co(1)O(3)	89.91(8)	O(1)Co(1)O(3)	88.64(8)
N(3)Co(1)O(3)	177.41(10)		

X-ray crystallography. Single crystals of complexes **I** and **II** suitable for X-ray diffraction were mounted on thin-walled glass fibers and aligned on the Bruker SMART 1000 CCD area diffractometer, equippted with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The θ ranges for data collection are 1.90°–5.75° for **I** and 2.42°–25.69° for **II**. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structures were solved by the direct method and refined by least-square cycles. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the water ligand in **II** were located from a difference Fourier map and refined isotropically, with O–H and H···H distances restrained to 0.85 and 1.37 Å, respectively. The remaining hydrogen were located as riding atoms and not refined. All calculations were performed using SHELXTL-97 [12]. The data collection and refinement parameters are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Crystallographic data for the complexes have been deposited with the Cambridge Crystallographic Data Centre

Table 3. Geometric parameters of hydrogen bonds for complexes **I** and **II***

D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
		I		
N(2)–H(2*A*)···Cl(1)^{a}	0.90	2.59	3.373(2)	146
N(2)–H(2*B*)···Cl(1)^{b}	0.90	2.38	3.173(2)	147
N(3)–H(3*A*)···Cl(1)^{b}	0.90	2.52	3.367(2)	158
N(3)–H(3*B*)···O(1)^{b}	0.90	2.29	3.118(2)	153
N(4)–H(4*A*)···N(6)^{c}	0.90	2.62	3.412(3)	147
N(4)–H(4*B*)···Cl(1)^{d}	0.90	2.49	3.283(2)	147
		II		
O(3)–H(3*A*)···O(2)^{e}	0.85(1)	2.12(2)	2.778(3)	135(3)
O(3)–H(3*B*)···O(1)^{e}	0.85(1)	1.88(2)	2.658(2)	152(3)

* Symmetry codes: $^{a}\,x, y, -1 + z$; $^{b}\,1 - x, -y, 1 - z$; $^{c}\,-1 + x, y, z$; $^{d}\,-1 + x, y, -1 + z$; $^{e}\,-x, 1 - y, -z$.

Table 4. Inhibition zone (mm) of the antibacteiral activities

Compound	*Bacillus subtilis*	*Staphylococcus aureus*	*Escherichia coli*	*Pseudomonas aeruginosa*
$\mathrm{L^1}$	9	6		5
$\mathrm{L^2}$	15	17	9	13
$[\mathrm{CoL^1(En)N_3}]\mathrm{Cl}$	22	25	18	23
$[\mathrm{CoL^2N_3(OH_2)}]$	26	29	26	24

(nos. 931207 (**I**) and 931208 (**II**); deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Microbiological test. For the microbiological test the filter paper disc method was applied according to the method reported by Gupta and co-workers [13]. The investigated isolates of bacteria were seeded in tubes with nutrient broth. The seeded nutrient broth (1 cm^3) was homogenized in the tubes with 9 cm^3 of melted (45°C) nutrient agar. The homogeneous suspensions were poured into Petri dishes. The discs of filter paper (diameter 4 mm) were ranged on the cool medium. After cooling on the formed solid medium, 2×10^{-5} dm^3 of the investigated compounds were applied using a micropipette. After incubation for 24 h in a thermostat at 25–27°C, the inhibition (sterile) zone diameters were measured and expressed in mm. An inhibition zone diameter over 7 mm indicates that the tested compound is active against the bacteria under investigation. The antibacterial activities of the compounds were tested against *Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis*, and *Staphylococcus aureus*, respectively. The concentration of each solution was 1.0×10^{-3} mol/L.

RESULTS AND DISCUSSION

ORTEP plots with atom numbering schemes for the complexes **I** and **II** are shown in Fig. 1. Complex **I** contains a mononuclear $[\mathrm{CoL^1(En)N_3}]$ cation and a chloride anion. Complex **II** is a neutral mononuclear complex. The coordination around the Co atoms in the complexes are best described as distorted octahedra. The equatorial plane of the Co coordination of **I** is defined by O(1), N(1), and N(2) atoms of L^1 and N(3) atom of En. The two axial positions are occupied by N(4) atom of En and N(5) atom of the azide ligand. The equatorial plane of the Co coordination of **II** is defined by O(1), O(2), N(1), and N(2) atoms of L^2. The two axial positions are occupied by O(3) atom of the water ligand and N(3) atom of the azide ligand. Distortion from the ideal octahedral geometry is due to the strain created by the five-membered chelate rings Co(1)–N(1)–C(9)–C(10)–N(2) and Co(1)–N(3)–C(11)–C(12)–N(3) in **I** and Co(1)–N(1)–C(8)–C(9)–N(2) in **II**. The Co atoms are displaced from the mean planes containing the equatorial atoms by 0.004(1) Å in **I** and 0.024(1) Å in **II**. The bond lengths related to the Co atoms are comparable to each other and also comparable to those reported in the cobalt(III) complexes with octahedral coordination [14–16]. The linear (N(5)N(6)N(7) angle of 176.4(3)° for **I**, and N(3)N(4)N(5) angle of 175.5(3)° for **II**) terminal azide ligands are coordinated to the Co atoms in a bent fashion, as evident from the CoNN bond angles of 118.5(2)° for **I** and 116.7(2)° for **II**.

In the molecular packing structure of complex **I**, molecules are linked via intermolecular N–H···O,

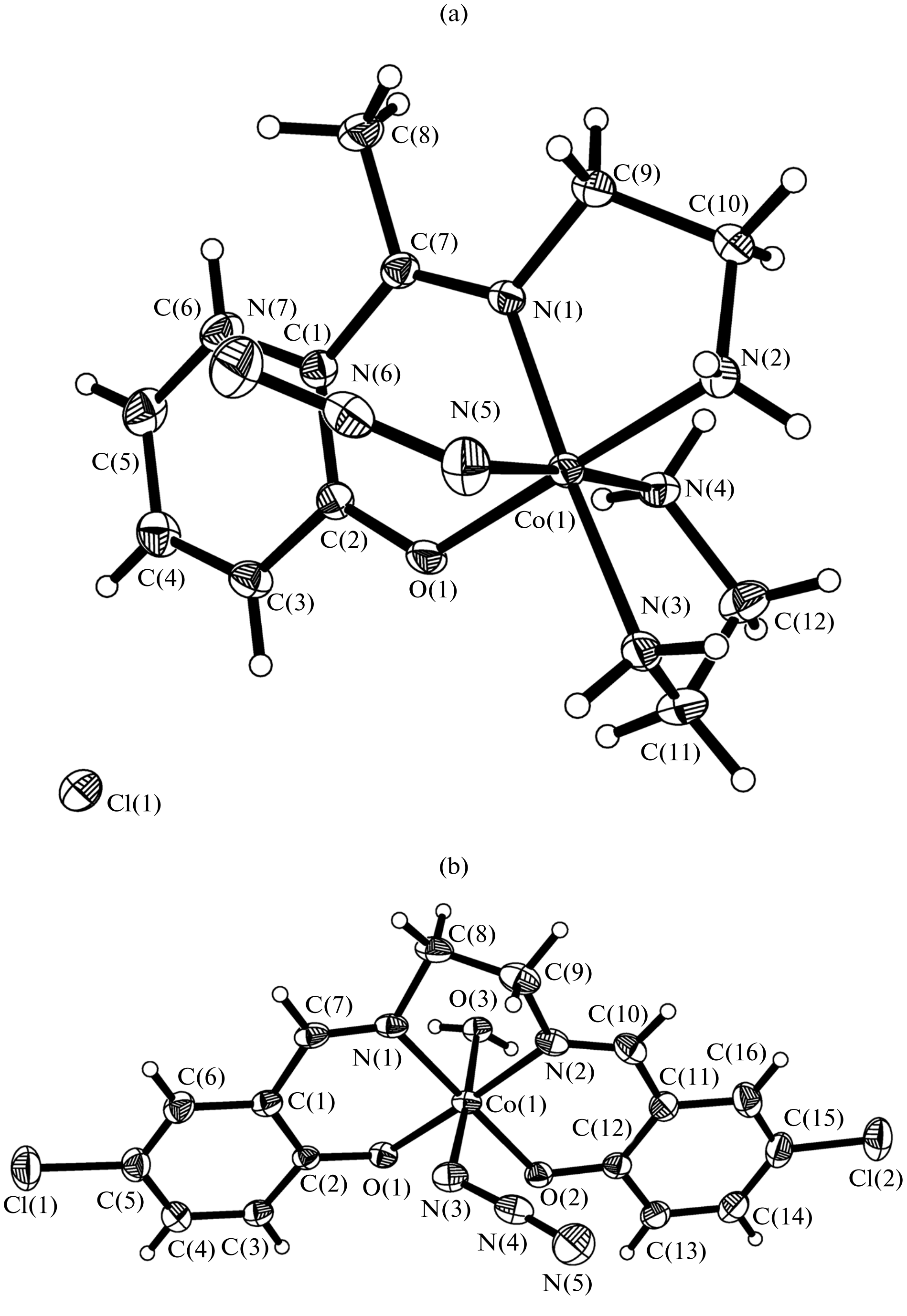

Fig. 1. Molecular structure of complex **I** (a) and **II** (b) with 30% probability thermal ellipsoids.

N–H···N, and N–H···Cl hydrogen bonds (Table 3) to form a 3D network, as shown in Fig. 2a. In the molecular packing structure of complex **II**, molecules are linked via intermolecular O–H···O hydrogen bonds (Table 3) to form dimers, as shown in Fig. 2b.

The biological activities of the free Schiff-bases and the cobalt(III) complexes were tested against the bacteria *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas aeruginosa*. The results are recorded in Table 4. The data revealed that the cobalt(III) complexes have stronger activities than the free ligands. This enhancement of the activity of ligands on complexation can be explained by Overtone's Concept and Chelation Theory [17]. The theory states that chelation reduces the polarity of the metal atom by the partial sharing of its positive charge with donor groups and possible π-electron delocalization over the whole ring. This results with increasing of the lipophilic character of the complex and favor the permeation of the complex through the lipid layer of cell membrane. The complexes block the metal binding sites in the enzymes of microorganisms. Consequently, the complexes disturb the metabolism pathways in cell and as a result microorganisms die.

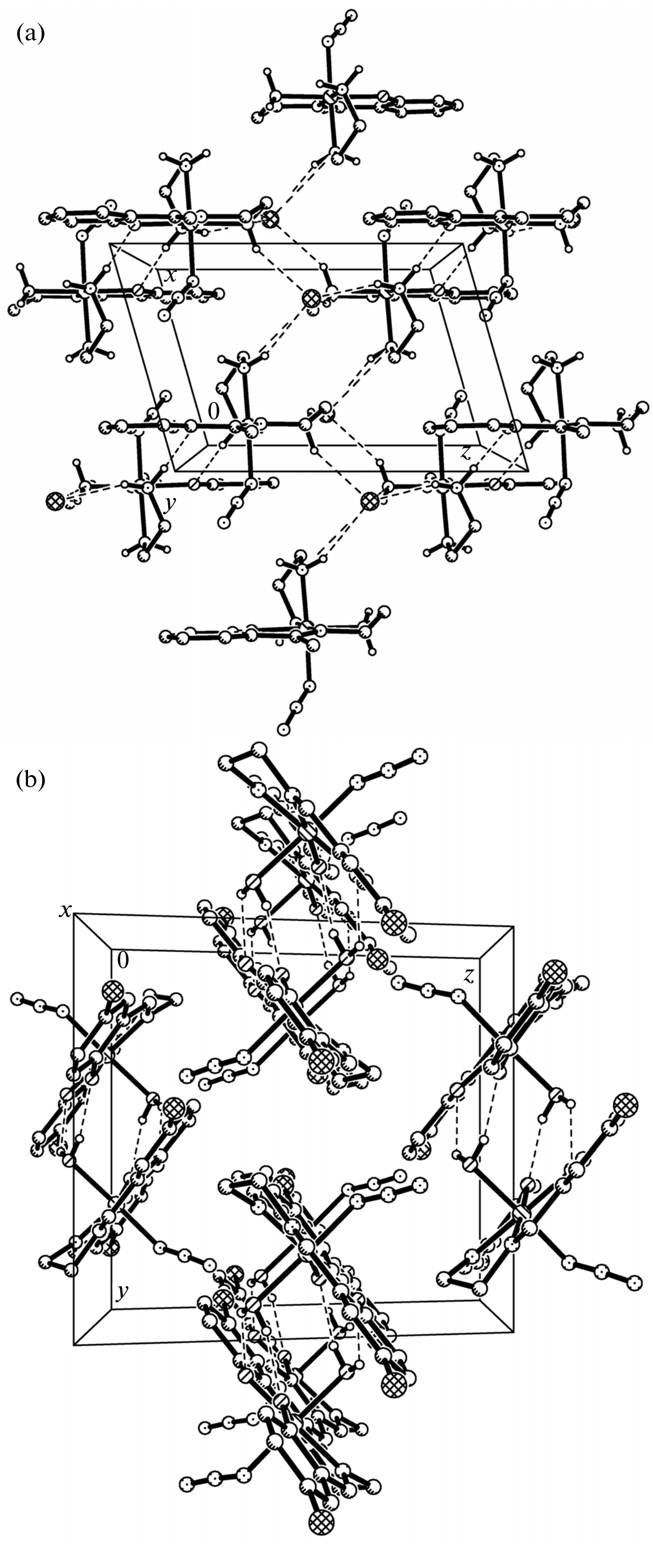

Fig. 2. The molecular packing diagram of complexes **I** (a) viewed along the *y* axis and **II** (b) viewed along the *x* axis). Intermolecular hydrogen bonds are drawn as dotted lines.

ACKNOWLEDGMENTS

We acknowledge the Yancheng Teachers University for a financial support.

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