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Synthesis, characterization, and crystal structure of three cobalt(II) complexes with Schiff bases derived from rimantadine

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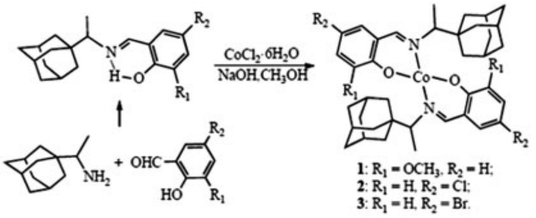

By condensation of rimantadine and substituted salicylaldehyde, three new Schiff bases, **HL^1**, **HL^2** and **HL^3**, were synthesized. Then, a mixture of one of the new ligands and cobalt(II) chloride hexahydrate in ethanol led to **1**, **2**, and **3**, respectively. These complexes were characterized by melting point, elemental analysis, infrared spectra, molar conductance, thermal analysis, and single-crystal X-ray diffraction analysis. X-ray diffraction analysis reveals that **1** crystallizes in the orthorhombic system, *Pbcn* space group; each asymmetric unit consists of one cobalt(II) ion, two deprotonated ligands, and one lattice water. The central cobalt is four coordinate via two nitrogens and two oxygens from the corresponding Schiff base ligand, forming a distorted tetrahedral geometry. Complexes **2** and **3** crystallize in the monoclinic system, $P2_1/c$ space group; each asymmetric unit consists of one cobalt(II), two corresponding deprotonated ligands, one lattice water, and one methanol. The central cobalt is also four-coordinate via two nitrogens and two oxygens from the corresponding Schiff base ligand, forming a distorted tetrahedral geometry.

Keywords: Cobalt(II) complexes; Rimantadine; Schiff bases; Synthesis; Crystal structures

1. Introduction

Metal Schiff base complexes have been studied as reagents for oxygen separation and transport [1], as models for biological dioxygen carriers [2], metalloenzymes [3], or used in catalytic reactions [4]. In particular, Schiff bases and complexes containing sulfur and nitrogen

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*Corresponding author. Email: hgxy@lnu.edu.cn donors have demonstrated significant antifungal [5], antibacterial, anticancer, and catalytic activities [6–11]. Cobalt is a vital element in organisms with important enzyme active sites; it can stimulate the hematopoietic system, prompting the synthesis of hemoglobin and red blood cells [12–15]. In many countries, amantadine (Symmetrel™) and rimantadine (Flumadine™) have been widely used to treat or prevent seasonal influenza as efficacious remedies [16–19]. However, the incidence of side effects to the central nervous system was higher with amantadine [20]. Salicylaldehyde and its derivatives, especially with one or more halogens in the aromatic ring, have antibacterial and antiviral activity and were used to produce efficient herbicides, insecticides and fungicides [21–23]. As an extension of our previous work on zinc(II) complexes with a Schiff base derived from amantadine, we designed and synthesized three cobalt(II) complexes with three different Schiff bases derived from rimantadine and three substituted salicylaldehydes (*o*-vanillin-salicylaldehyde, 5-chloro-salicylaldehyde, and 5-bromo-salicylaldehyde). The coordination behaviors of the ligands towards cobalt(II) were investigated and their absolute structures were determined by single-crystal X-ray diffraction analyses.

2. Experimental

2.1. *Materials and methods*

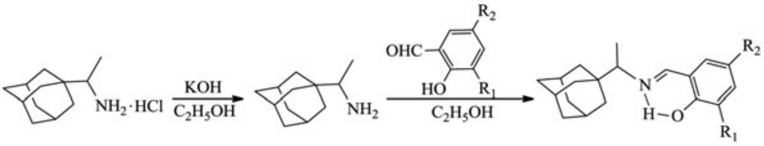
All chemicals and solvents were analytical grade and used as received. Elemental analyses for ligands and complexes were carried out on a Perkin Elmer Flash EA 1112. Infrared spectra (IR) were scanned from 4000 to 400 cm^{-1} with KBr pellets on a Nicolet NEXUS FT-IR 5700 spectrophotometer. Thermal analyses were carried out on a METTLER TOLEDO TGA/SDTA851e. Melting points were measured on a WRS-1B micro-melting point apparatus and are not corrected. The molar conductance of the complexes in DMF (1.0×10^{-3} M L^{-1}) was measured on a DDS-11A conductometer.

2.2. *Synthesis of the ligands*

Three ligands (figure 1) were prepared by an improved method based on the literature [24]. Rimantadine hydrochloride (432 mg, 2.0 mM) and KOH (112 mg, 2.0 mM) in 50 mL anhydrous ethanol were stirred for 1 h. White precipitate (KCl) was filtered out and the transparent liquid was added dropwise to a solution of substituted salicylaldehyde (2.0 mM) in 20 mL anhydrous ethanol. The resulting solution was refluxed for 1 h at 60 °C and cooled to room temperature; a yellow Schiff base precipitate was obtained after one week under slow solvent evaporation.

HL^1: 420 mg, yield 67%. Yellowish powder. m.p. 98.5–99.6 °C. IR (KBr): 3442(w), 2993(w), 2930(s), 2848(m), 1633(s), 1589(w), 1466(s), 1420(m), 1383(w), 1360(w), 1348(w), 1330(w), 1312(w), 1273(m), 1246(s), 1189(w), 1171(w), 1154(w), 1117(w), 1084(w), 1026(w), 973(m), 934(w) 920(w), 876(w), 827(m), 779(w), 737(s), 705(w), 634(w), 557(w), 520(w). Anal. Calcd for $C_{20}H_{27}NO_2$ (313.43):C, 76.64; H, 8.68; N, 4.47. Found: C, 76.12; H, 8.59; N, 4.57.

HL^2: 445 mg, yield 70%. Yellow powder. m.p. 74.9–75.5 °C. IR (KBr): 3433(m), 2905(s), 2849(m), 1632(m), 1578(w), 1481(m), 1450(w), 1380(w), 1346(w), 1317(w), 1279(w), 1193(w), 1151(w), 1094(w), 973(w), 823(m), 787(w), 721(w), 686(w), 647(w), 625(w),



HL^1: $R_1 = OCH_3$, R_2 = H; **HL**^{2}: R_1 = H, R_2 = Cl; **HL**^{3}: R_1 = H, R_2 = Br.

Figure 1. The formation of the Schiff bases.

569(w), 551(w), 530(w), 511(w), 492(w), 471(w), 450(w). Anal. Calcd for $C_{19}H_{24}ClNO$ (317.85):C, 71.80; H, 7.61; N, 4.41. Found: C, 71.64; H, 7.65; N, 4.43.

HL^3: 565 mg, yield 78%. Yellowish powder. m.p. 102.9–103.4 °C. IR (KBr): 3441(m), 2973(m), 2908(s), 2849(m), 1630(m), 1571(m), 1477(m), 1377(m), 1279(m), 1191(w), 1086(w), 976(w), 921(w), 821(m), 681(w), 624(m). Anal. Calcd for $C_{19}H_{24}BrNO$ (362.30): C, 62.99; H, 6.68; N, 3.87. Found: C, 62.95; H, 6.65; N, 4.90.

2.3. *Synthesis of the complexes*

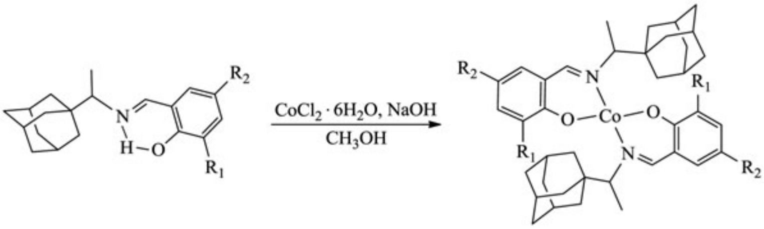
Complexes **1–3** were prepared in a similar procedure starting from their corresponding Schiff base, NaOH, and cobalt(II) chloride hexahydrate in anhydrous methanol (figure 2).

To a solution of ligand (2.0 mM) in anhydrous methanol (20 mL) was added a solution of NaOH (80 mg, 2.0 mM) in anhydrous methanol (20 mL) followed by addition of cobalt(II) chloride hexahydrate (238 mg, 1.0 mM) in anhydrous methanol (20 mL). The mixture was refluxed for 2 h and then concentrated until a large amount of precipitate was observed. The red solid was suction filtered, washed with cold water, and dried to afford a complex.

Complex **1**: 424 mg, yield 62%. Bright red powder. m.p. 244.3–246.1 °C. IR (KBr): 3465(m), 3053(w), 2972(w), 2901(s), 2845(m), 1655(w), 1603(s), 1547(m), 1465(s), 1448 (s), 1420(m), 1381(w), 1341(m), 1243(s), 1215(s), 1169(w), 1153(w), 1083(m), 1003(w), 982(w), 856(w), 742(m), 635(w), 586(w). Anal. Calcd for $C_{40}H_{52}CoN_2O_4$ (683.79):C, 70.20; H, 7.60; N, 4.09. Found: C, 70.26; H, 7.67; N, 4.10.

Complex **2**: 402 mg, yield 58%. Bright red powder. m.p. 258.3–260.7 °C. IR (KBr): 3438(m), 2899(s), 2847(m), 1600(s), 1520(m), 1453(s), 1391(s), 1314(m), 1169(m), 1083 (m), 979(w), 870(w), 815(w), 708(m), 657(w), 498(m), 456(m). Anal. Calcd for $C_{38}H_{46}Cl_2CoN_2O_2$ (692.60):C, 65.90; H, 6.64; N, 4.04. Found: C, 65.85; H, 6.65; N, 4.00.

Complex **3**: 508 mg, yield 65%. Bright red powder. m.p. 264.3–265.6 °C. IR (KBr): 3428 (m), 2902(s), 2847(m), 1599(s), 1518(m), 1455(s), 1391(s), 1310(m), 1170(m), 1133(w),



1: $R_1 = OCH_3$, R_2 = H; **2**: R_1 = H, R_2 = Cl; **3**: R_1 = H, R_2 = Br.

Figure 2. Proposed structures of **1–3**.

1080(w), 975(w), 871(w), 824(w), 799(w), 684(m), 648(m), 496(m), 460(m). Anal. Calcd for $C_{38}H_{46}Br_2CoN_2O_2$ (781.52):C, 58.35; H, 5.89; N, 3.58. Found: C, 58.40; H, 5.87; N, 3.55.

2.4. *X-ray crystallography*

Crystals of the complexes suitable for X-ray analysis developed from a solution of CH_3OH/CH_2Cl_2/H_2O (4 : 4 : 1 *v*/*v*/*v*) through slow evaporation. The crystallographic data collections were conducted on a Bruker Smart Apex II CCD with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at 298(2) K using the ω-scan technique. The data were integrated using SAINT, which also corrected the intensities for Lorentz and polarization effects [25]. An empirical absorption correction was applied using SADABS [26]. The structures were solved by direct methods using SHELXS-97 and all non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares using the SHELXL-97 crystallographic software package [27]. Hydrogens were generated geometrically. All calculations were performed on a personal computer with the SHELXL-97 crystallographic software package. The crystal parameters, data collection, and refinement are summarized in table 1. Selected bond lengths and angles with their estimated standard deviations are given in table 2.

Table 1. Crystallographic data for **1–3**.

Empirical formula	$C_{40}H_{52}CoN_2O_4{\cdot}H_2O$ **(1)**	$C_{38}H_{46}Cl_2CoN_2O_2{\cdot}H_2O{\cdot}CH_3OH$ **(2)**	$C_{38}H_{46}Br_2CoN_2O_2{\cdot}H_2O{\cdot}CH_3OH$ **(3)**
Formula weight (g M^{-1})	701.78	742.60	831.52
Crystal size (mm)	0.33 × 0.27 × 0.19	0.40 × 0.30 × 0.20	0.30 × 0.20 × 0.10
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Color	Bright red	Bright red	Bright red
Space group	*Pbcn*	$P2_1/c$	$P2_1/c$
a (Å)	10.9176(18)	9.2609(3)	9.3452(6)
b (Å)	13.088(2)	19.2802(5)	19.3896(14)
c (Å)	25.228(4)	21.3356(6)	21.2518(17)
α (°)	90.00	90	90.00
β (°)	90.00	98.987(3)	99.125(6)
γ (°)	90.00	90	90.00
V(Å^3)	3604.8(10)	3762.75(19)	3802.1(5)
Z	4	4	4
θ Range (°)	1.26–28	2.35–24.2	2.56–26.47
Index ranges	$-14 \le h \le 12$, $-16 \le k \le 14$, $-30 \le l \le 32$	$-11 \le h \le 9$, $-22 \le k \le 22$, $-25 \le l \le 25$	$-11 \le h \le 11$, $-23 \le k \le 14$, $-25 \le l \le 23$
ρ (g cm^{-3})	1.293	1.223	1.365
μ (mm^{-1})	0.522	0.631	2.586
Reflections collected/ unique	12792/4113 [R(int) = 0.0575]	14275/6600 [R(int) = 0.0252]	14904/6680 [R(int) = 0.0521]
Data/restraints/ parameters	4133/186/339	6600/0/408	6680/0/406
Goodness-of-fit (GoF)	1.001	1.058	0.924
F (0 0 0)	1500	1460	1604
T/K	298(2)	298(2)	298(2)
R_1[a]/wR_2[b]($I > 2\sigma(I)$)	0.0540/0.1254	0.0413/0.1002	0.0551/0.1011
R_1/wR_2 (all data)	0.1233/0.1563	0.0589/0.1081	0.1183/0.1205

[a] $R_1 = \Sigma||F_o| - |F_c||/|F_o|$.

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

Hydrogen bond geometry of **1** is listed in table 3. The molecular structures of **1–3** are shown in figures 3–5, as visualized by Diamond [28].

3. Results and discussion

3.1. *Elemental analysis and molar conductance*

From the analysis, the C, H, and N contents suggest that **1–3** consist of one cobalt(II) and two deprotonated ligands. Although all compounds are soluble in dichloromethane and

Table 2. Selected bond lengths (Å) and angles (°) in **1–3**.

1			
Co1–O1	1.910(2)	Co1–N1	1.856(9)
Co1–O1^{i}	1.910(2)	Co1–N1^{i}	1.856(9)
N1–C8	1.457(9)	N1–C9	1.547(13)
O1–C1	1.305(4)	O2–C7	1.427(4)
O1–Co1–O1^{i}	98.68(12)	O1–Co1–N1	99.80(2)
O1^{i}–Co1–N1	122.45(4)	O1–Co1–N1^{i}	122.45(4)
O1^{i} –Co1–N1^{i}	99.80(4)	N1–Co1–N1^{i}	114.30(8)
O1–C1–C6	118.99(3)	O1–C1–C2	124.13(3)
N1–C8–C2	125.71(6)	N1–C9–C10	109.71(10)
C8–N1–C9	93.97(6)	C8–N1–Co1	119.22(14)
C1–O1–Co1	125.79(19)	C9–N1–Co1	146.36(6)
2			
Co1–O1	1.907(17)	Co1–N1	2.016(18)
Co1–O2	1.915(16)	Co1–N2	2.019(19)
N1–C7	1.280(3)	N1–C8	1.489(3)
N2–C26	1.287(3)	N2–C28	1.497(3)
O1–C1	1.309(3)	O2–C20	1.312(3)
O1–Co1–O2	108.25(7)	O2–Co1–N2	95.28(7)
O1–Co1–N1	94.16(7)	O2–Co1–N1	117.79(7)
O1–Co1–N2	120.30(7)	N2–Co1–N1	122.03(8)
O1–C1–C6	123.6(2)	O1–C1–C2	119.16(7)
O2–C20–C25	123.8(2)	O2–C20–C21	118.9(2)
N1–C7–C6	128.1(2)	N1–C8–C10	111.50(18)
N1–C8–C9	108.67(19)	N2–C28–C29	108.73(9)
N2–C27–C28	108.2(6)	N2–C28–C30	112.21(18)
C1–O1–Co1	124.1(5)	C20–O2–Co1	125.02(15)
C7–N1–Co1	119.23(15)	C8–N1–Co1	123.97(15)
C26–N2–Co1	119.49(15)	C28–N2–Co1	124.43(15)
3			
Co1–O1	1.915(3)	Co1–N1	2.005(4)
Co1–O2	1.912(3)	Co1–N2	2.006 (4)
N1–C7	1.304(6)	N1–C8	1.489(6)
N2–C26	1.281(5)	N2–C27	1.480(6)
O1–C1	1.320(5)	O2–C20	1.302(5)
O1–Co1–O2	107.27(15)	O1–Co1–N2	117.16 (15)
O1–Co1–N1	95.63(15)	O2–Co1–N2	94.42(15)
O2–Co1–N1	120.62(15)	N2–Co1–N1	122.43(16)
O1–C1–C2	118.7(4)	O1–C1–C6	123.5(5)
O2–C20–C25	123.9(4)	O2–C20–C21	119. 1(5)
N1–C7–C6	128.0(5)	N1–C8–C9	107.4(4)
N1–C8–C10	113.3(4)	N2–C27–C29	112.0(4)
N2–C26–C25	127.5(5)	N2–C27–C28	108.7(4)
C1–O1–Co1	125.0(3)	C20–O2–Co1	124.5(3)
C7–N1–Co1	119.5(3)	C8–N1–Co1	125.6(3)
C26–N2–Co1	119.1(3)	C27–N2–Co1	124.6(3)

Symmetry code: (i) $-x+1$, y, $-z+1/2$.

Table 3. Hydrogen bond geometry (Å, °) in **1**.

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
O1w–H1w···O1	0.851	2.302	2.892	126.73
O1w–H2w···O1^{i}	0.849	2.231	2.892	134.67

Symmetry code: (i) $-x+1, y, -z+1/2$.

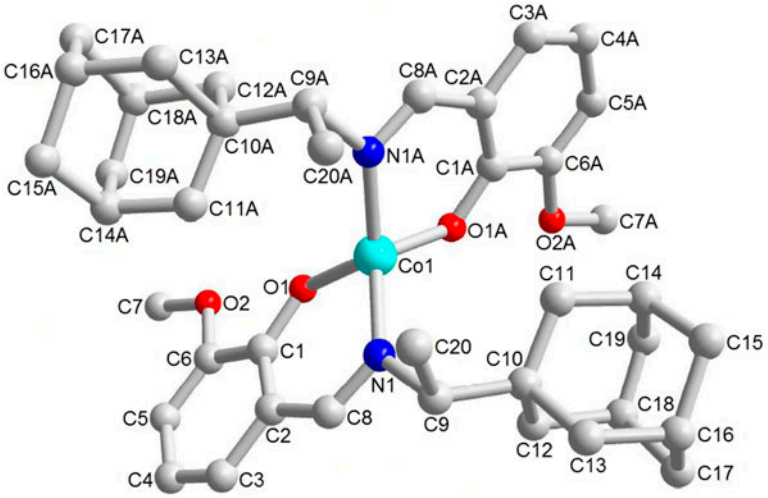


Figure 3. Molecular structure of **1**. Hydrogens are omitted for clarity.

chloroform, the complexes are less soluble than the ligands in other solvents such as ethanol, THF, benzene, and ethyl acetate. The molar conductance values (Λ_M) for **1–3** are 2.26, 2.08, and 2.56 S cm^2 M^{-1}, indicating non-electrolytes [29].

3.2. *IR spectra*

The main IR data for **1–3** are presented in table 4, with data for ligands provided for comparison. IR spectra of ligands show bands at 3442, 3443, and 3441 cm^{-1} attributed to OH stretch. Free OH stretching vibrations are generally at 3500–3600 cm^{-1}; the observed lower value is due to intramolecular hydrogen bonding. These bands are absent in complexes, indicating deprotonated phenolic OH. Bands at 1633, 1632, and 1629 cm^{-1} in ligands are assigned to C=N stretches, shifted to lower wave number (1603, 1600, and 1599 cm^{-1}) in **1–3**, implying coordination of azomethine nitrogen to Co(II). The spectra of ligands display strong bands at 1246–1279 cm^{-1}, which are C–O stretches; these bands occur in complexes at 1169–1243 cm^{-1}. In the low frequency region, absorptions at 456–586 cm^{-1} for complexes reveals Co–O vibration, indicating that oxygen of the Schiff base is coordinated to Co(II).

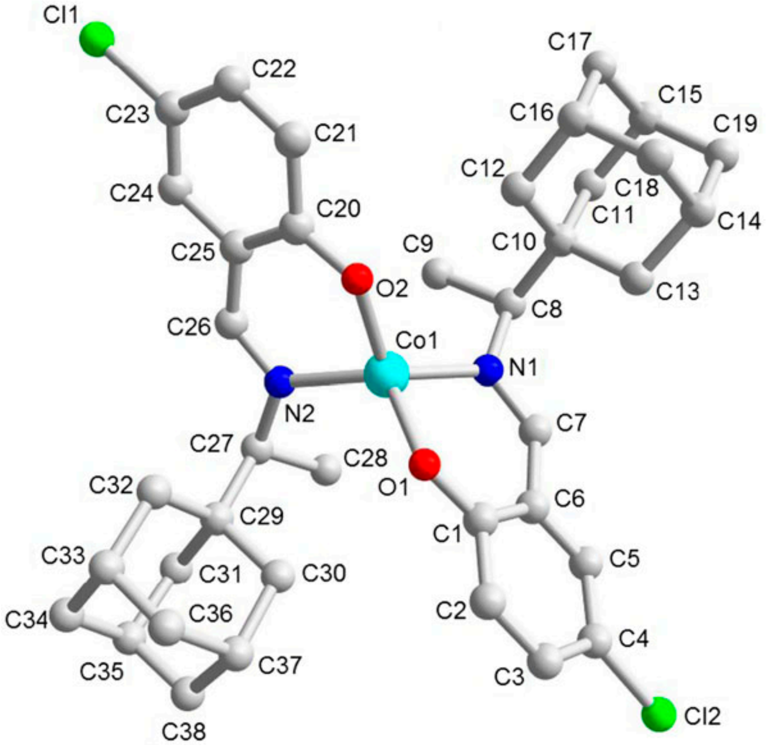


Figure 4. Molecular structure of **2**. Hydrogens are omitted for clarity.

3.3. *Crystal structures of complexes*

The crystallographic analysis reveals that **1** crystallizes in the orthorhombic system, *Pbcn* space group; each asymmetric unit comprises one cobalt(II) complex and one lattice water. Complexes **2** and **3** crystallize in the monoclinic system, $P2_1/c$ space group; each asymmetric unit comprises one cobalt(II) complex, one lattice water, and one lattice methanol. The central cobalt(II) in **1–3** lies on a twofold rotation axis and is bonded to oxygen and nitrogen donors of the two bidentate ligands in a *trans*-arrangement. In general, the coordination of these cobalt(II) complexes is close to a zinc(II) complex we reported [30]. The geometry around cobalt(II) in **1–3** is intermediate between square planar and tetrahedral, where the dihedral angle between the two coordination planes defined by O1–Co1–N1 and $O1^i$–Co1–$N1^i$ is 76.55° for **1**, by O1–Co1–N1 and O2–Co1–N2 is 86.01° for **2**, and by O1–Co1–N1 and O2–Co1–N2 is 85.76° for **3** [31]. The two phenyl rings are in intersecting planes with a dihedral angle of 83.07° for **1**, 85.11° for **2**, and 83.90° for **3**. Bond angles also show that the coordination geometry of cobalt in **1** is distorted tetrahedral ($\tau_4 = [360 - (\alpha + \beta)]/141° = 0.82$) [32], with N1–Co1–$O1^i$ (α) and O1–Co1–$N1^i$ (β) angles of 122.45(4)° and 122.45(4)°, respectively. Complex **2** is a distorted tetrahedral ($\tau_4 = [360 - (\alpha + \beta)]/141° = 0.83$), with N1–Co1–N2 ($\alpha$) and O1–Co1–N2 ($\beta$) angles of 122.03(8)° and 120.30(7)°, respectively. Complex **3** is also a distorted tetrahedral ($\tau_4 = [360 - (\alpha + \beta)]/141° = 0.83$), with N1–Co1–N2 ($\alpha$) and O2–Co1–N1 ($\beta$) angles of 122.43(16)° and 120.62(15)°, respectively. The τ_4 parameters for these complexes are close to 1.00 and the distances between two adamantane cages from two ligands in **1–3** are relatively far, which

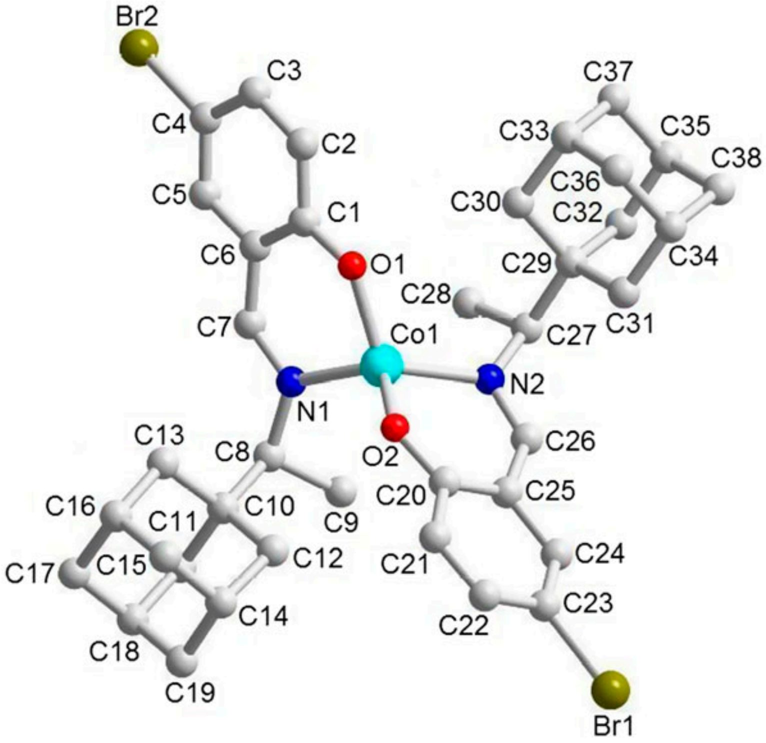


Figure 5. Molecular structure of **3**. Hydrogens are omitted for clarity.

Table 4. Main IR data for ligands and complexes (cm^{-1}).

Compound	$\upsilon_{C=N}$	$\upsilon_{C–O}$	υCH_2	$\upsilon_{O–H}$	$\upsilon_{M–O}$
HL^1	1633(s)	1246(s)	2848(s)	3442(w)	–
1	1603(s)	1243(s)	2845(m)	–	586(w)
HL^2	1632(m)	1279(w)	2849(m)	3433(m)	–
2	1600(s)	1169(m)	2847(m)	–	456(m)
HL^3	1629(m)	1279(m)	2849(m)	3441(m)	
3	1599(s)	1170(m)	2902(s)	–	460(m)

Notes: s – strong; m – medium; and w – weak.

suggests a *trans*-coordination of two ligands to cobalt, expected for a typical Schiff base ligand (containing a short C=N bond distance of 1.297 Å for **1**, 1.287 Å for **2**, and 1.304 Å for **3**) coordinated to a metal center, where the imine form is predominant. The distinctly shortened Co1–O1 and Co1–N1 bonds in **1** are 1.910 and 1.857 Å, respectively (the normal bond lengths are 1.940 and 1.960 Å), so the coordination geometry around the Co(II) ion reflects the Jahn–Teller effect [33]. The distinctly shortened Co1–O1 and slightly elongated Co1–N1 bonds in **2** and **3** are 1.907 Å/1.915 Å and 2.015 Å/2.005 Å, respectively, which also reflects the Jahn–Teller effect. The distances of two neighboring cobalt along the *b*-axis are 8.522 Å in **1**, 10.636 Å in **2**, and 13.080 Å in **3**. The bidentate coordination inhibits forming intramolecular hydrogen bonds because of the deprotonated ligands, but there also exist two six-membered rings through a cobalt ion, two oxygens, and two nitrogens in **1–3** [34]. The organic molecules alternate with crystallization water molecules forming O–H···O intermolecular hydrogen bonds between water and two phenol oxygens from two ligands in **1** (figure 6). The distances between two O are 2.892 Å and the hydrogen bond angles O–H···O are 126.73° and 134.67° (see table 3). The same number and configuration of lattice water and methanol were found in crystals of **2** and **3**, which occupied the interspaces of the organic molecules, implying that **2** has the similar spatial arrangement as **3** (figures 7 and 8).

Specifically, in complex **1**, C9 and C9A are chiral centers, however, the centrosymmetric crystal represents a racemate, with the other stereoisomer being within the lattice. The situations of C8 and C27 for **2** and **3** are similar.

3.4. *Thermal analyses of 1–3*

Thermal stability and the mechanism of decomposition for **1–3** were investigated by TG–DTG measurements and with a heating rate of 20 °C min^{-1} under N_2 from 25 to 900 °C. The TG–DTG curves are provided in Supplementary material (see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.885509). The thermal decompositions were observed with three stages for **1–3**. The starting decomposition and weight losses for **1–3** were approximately 100 °C corresponding to loss of one lattice water for **1,** and one lattice water and one lattice methanol for **2** and **3**, indicating that solvents were not coordinated. The second rapid weight loss stages took place at 330 °C and the third degradation stages occurred at 400 °C. When the complexes were heated above 700 °C for **1** and 900 °C for **2** and **3**, the residues were deduced as oxides.

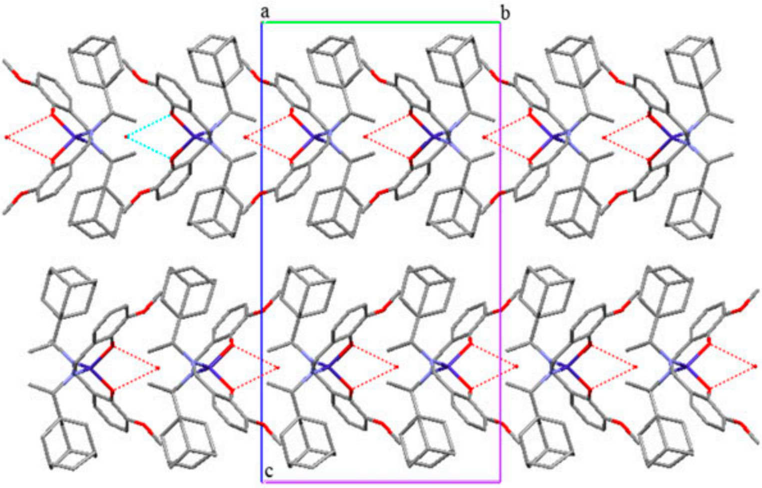


Figure 6. The packing diagram of **1** viewed along the *a*-axis.

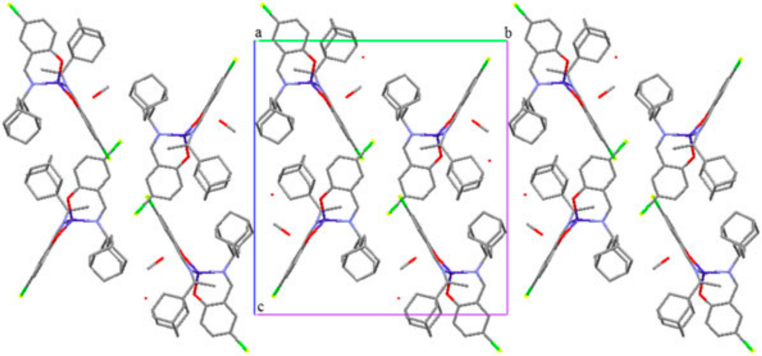


Figure 7. The packing diagram of **2** viewed along the *a*-axis.

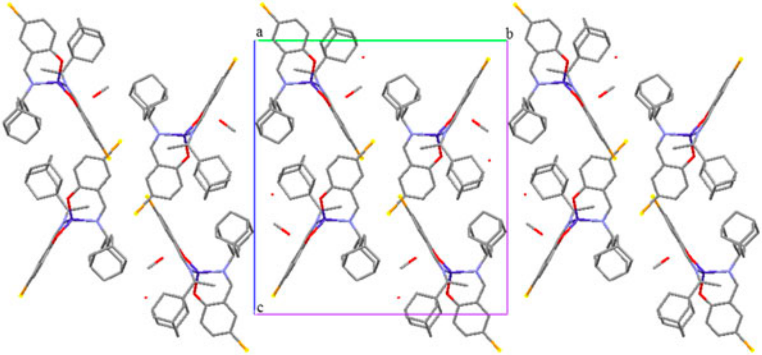


Figure 8. The packing diagram of **3** viewed along the *a*-axis.

4. Conclusion

Three Schiff base ligands and their corresponding cobalt(II) complexes have been prepared and characterized by melting point, elemental analysis, IR, molar conductance, thermal analysis, and single-crystal X-ray diffraction analysis. Their single-crystal structures reveal that in **1–3** each Schiff base serves as a bidentate ligand coordinating through an oxygen and nitrogen. The geometry around cobalt is intermediate between square planar and tetrahedral.

Supplementary material

Supplementary X-ray crystallographic data for **1** (CCDC 893305), **2** (CCDC 969173), and **3** (CCDC 969172) can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033 or E-mail: deposit@ccdc.cam.ac.uk).

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