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一种不对称 Salamo-型螯合配体及其钴(Ⅱ)配合物：合成、表征与晶体结构

董文魁* 李 刚 李 翔 杨成娟 赵萌萌 董秀延
（兰州交通大学化学与生物工程学院，兰州 730070）

摘要：合成了一种不对称 Salamo-型螯合配体 4-氯-6′-甲氧基-2,2′-[乙二氧双(氮次甲基)]二酚(H_2L)及其钴(Ⅱ)配合物[Co(L)(H_2O)]，并通过元素分析、红外光谱、紫外-可见吸收光谱及 X-射线单晶衍射方法对配体 H_2L 及其配合物进行了表征。结果表明：配体属单斜晶系，$P2_1/n$ 空间群，配合物属正交晶系，$Iba2$ 空间群。配合物为单核结构，由 1 个 Co(Ⅱ)离子和 1 个四齿的 L^{2-}配体单元和 1 个配位水分子组成，中心 Co(Ⅱ)原子的配位数是 5，且具有稍微扭曲的三角双锥几何结构，而配合物分子通过分子间 C8-H8···Cl1 氢键组装成 1D 链状的超分子结构。

关键词：Salamo-型螯合配体；钴(Ⅱ)配合物；合成；晶体结构；超分子作用
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An Asymmetrical Salamo-Type Chelating Ligand with Its Cobalt(Ⅱ) Complex: Syntheses, Characterizations and Crystal Structures

DONG Wen-Kui* LI Gang LI Xiang YANG Cheng-Juan
ZHAO Meng-Meng DONG Xiu-Yan
(*School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou* 730070, *China*)

Abstract: A salamo-type chelating ligand 4-chloro-6′-methoxy-2,2′-[ethylenediyldioxybis (nitrilomethylidyne)] diphenol (H_2L) and its complex [Co(L)(H_2O)], have been synthesized and characterized by elemental analyses, IR spectra, UV-Vis spectra and X-ray single crystal diffraction method. The ligand crystallizes in the monoclinic system, space group $P2_1/n$ with cell parameters: a=1.555 54(17) nm, b=0.470 55(5) nm, c=2.423 3(2) nm, β=106.108(2)°, Z=4, V=1.704 1 (3) nm^3, R_1=0.055 3, wR_2=0.063 3, and the Co(Ⅱ) complex crystallizes in the orthorhombic system, space group $Iba2$ with cell parameters: a=1.934 27(14) nm, b=2.497 20(19) nm, c=0.752 96(5) nm, Z=8, V=3.637 0(5) nm^3, R_1=0.045 4, wR_2=0.083 9, the Co(Ⅱ) complex is mono-nuclear structure. The five-coordinated Co(Ⅱ) atom of the complex lies in the N_2O_2 coordination sphere of one bis-oxime ligand, and the Co(Ⅱ) atom of the complex has a slightly distorted trigonal bipyramid geometry, while the molecules also assemble to a 1D infinite chain-like supramolecular structure by intermolecular C8-H8···Cl1 hydrogen bond. CCDC: 940101,H_2L; 940100, Co(Ⅱ) complex.

Key words: salamo-type ligand; Co(Ⅱ) complex; synthesis; crystal structure; supramolecular interaction

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*通讯联系人。E-mail：dongwk@126.com

Salen-type compounds have long been a research focus of coordination chemistry because of their potential application in catalysis[1-2], bioscience[3-4], new materials [5], magnetic properties [6-9] and constructing supramolecular structures[10-11]. Now, some researchers have tried many approaches to change the (-CH=N-$(CH_2)_n$-N=CH-) instead of (-CH=N-O-$(CH_2)_n$-O-N=CH-) unit in order to make the exchange reaction and hydrolysis reaction rate of the compounds greatly reduced and the balance level raised to a very great extent, so the Salamo-type compounds is more stable than the Salen-type compounds[12-15]. The Salamo-type compounds can easily coordinate with transition metal ions to form mononuclear, multinuclear and hetero-polynuclear complexes which have novel structures and excellent performance[16-17]. And these complexes often form supramolecular systems which have unique structure, novel bonding way, specific microstructure and excellent macroscopic properties by the intermolecular association of the weak non-covalent bonding[18]. These intermolecular weak forces can occur in-cooperation and synergistic action with each other under certain conditions to form a strong force with strong directivity and selectivity, which can be the main forces of the supramolecular formation, molecular recognition and molecular assembly [19-21]. Herein, in order to further study the supramolecular structures of the transition metal complexes with the Salamo-type ligands, the syntheses, characterizations, crystal structures of an asymmetrical Salamo-type ligand, 4-chloro-6′-methoxy-2,2′-[ethylenediyldioxybis(nitrilomethylidyne)]diphenol (H_2L) and its Co(Ⅱ) complex have been reported.

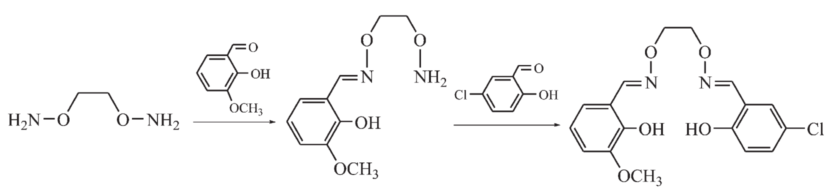
1 Experimental

1.1 Reagents and physical measurements

Commercially available 3-methoxysalicylaldehyde, 5-chlorosalicylaldehyde were purchased from Aladdin Chemistry, other solvents from Tianjin Chemical Reagent Factory were analytical grade and used without further purification. Elemental analysis for Co was detected by IRIS ER/S·WP-1ICP atomic emission spectrometer. C, H, and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. FTIR spectra were recorded on a VERTEX70 FTIR spectrophotometer, with samples prepared as KBr (400~4 000 cm^{-1}) and CsI (100~500 cm^{-1}) pellets. UV-Vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. ^{1}H NMR spectra were recorded on a Mercury-400BB spectrometer at room temperature. X-Ray single crystal structures were determined on a Bruker Smart 1 000 CCD area detector. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company, and the thermometer was uncorrected.

1.2 Synthesis and characterization of H_2L

The major reaction steps involved in the synthesis of H_2L are given in Scheme 1.



Scheme 1 Synthetic route to the asymmetrical Salamo-type ligand H_2L

1,2-Bis (aminooxy)ethane: It was synthesized by a similar method [22-23]. Yield: 52.7% . Anal. Calcd. for $C_2H_8N_2O_2$ (%): C, 26.08; H, 8.76; N, 30.42. Found (%): C, 25.92; H, 8.87; N, 30.39. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.79 (s, 4H), 5.52 (s, 4H).

2-[*O*-(1-ethyloxyamide)]oxime-6-methoxyphenol: It was synthesized according to an analogous method reported previously in the literature[24]. A solution of 1,2-bis(aminooxy)ethane (875.3 mg, 9.45 mmol) in ethanol (20 mL) was added to a solution of 3-methoxysalicylaldehyde (745.0 mg, 4.85 mmol) in ethanol (20 mL) and the mixture was stirred at 55~

57 ℃ for 4 h. The solution was concentrated in vacuo and the residue was purified by column chromatography (SiO_2, $V_{chloroform}:V_{ethyl\ acetate}$=20 :1) to afford 897.5 mg colourless crystals of 2-[*O*-(1-ethyloxyamide)]oxime-6-methoxyphenol. Yield, 81.8 %, m.p. 96~97 °C. Anal. Calcd. for $C_{10}H_{14}N_2O_4$ (%): C, 53.09; H, 6.24; N, 12.38. Found: C, 52.94; H, 6.31; N, 12.32. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.91 (s, 3H), 3.97 (t, *J*=4.4 Hz, 2H), 4.37 (t, *J*=4.4 Hz, 2H), 5.52 (brs, 2H), 6.81 (dd, *J*=7.7, 1.6 Hz, 1H), 6.86 (t, *J*=7.7 Hz, 1H), 6.91 (dd, *J*=7.7 Hz, 1.6 Hz, 1H), 8.23 (s, 1H), 9.87 (s, 1H).

4-Chloro-6′-methoxy-2,2′-[ethylenediyldioxybis(nitrilomethylidyne)]diphenol: a solution of 2-[*O*-(1-ethyloxyamide)]oxime-6-methoxyphenol (225.0 mg, 0.99 mmol) in ethanol (20 mL) was added to a solution of 5-chlorosalicylaldehyde (154.1 mg, 0.98 mmol) in ethanol (20 mL), and the mixture was stirred at 55~57 ℃ for 6 h. The formed precipitate was separated by filtration, and washed successively with ethanol and n-hexane, respectively. The product was dried under vacuum to yield 625.0 mg of H_2L. Yield, 80.38 %, m.p. 108~109 ℃. Anal. Calcd. for $C_{17}H_{17}ClN_2O_5$ (%): C, 55.97; H, 4.70; N, 7.68. Found: C, 56.02; H, 4.57; N, 7.79. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.91 (s, 3H), 4.47~4.49 (m, 4H, CH_2), 6.89 (d, *J*=8.6 Hz, 1H), 6.91 (t, *J*=7.8 Hz, 1H), 6.97 (d, *J*=7.8 Hz, 1H), 7.15 (dd, *J*=7.8 Hz, 1.5 Hz, 1H), 7.27 (d, *J*=2.5 Hz, 1H), 7.34 (dd, *J*=8.6 Hz, 2.5 Hz, 1H), 8.15 (s, 1H), 8.21 (s, 1H), 9.70 (s, 1H), 9.74 (s, 1H), 10.38 (s, 1H).

Pale-yellow prismatical single crystals suitable for X-ray diffraction studies were obtained by slow evaporation from a solution of ethanol at room temperature for about four weeks.

1.3 Synthesis of the Co(Ⅱ) complex

A pale-pink ethanol solution (2 mL) of Co(Ⅱ) acetate tetrahydrate (2.17 mg, 0.009 mmol) was added dropwise to a color-less ethanol solution (2 mL) of H_2L (3.70 mg, 0.010 mmol) at room temperature. The color of the mixing solution turned to yellow immediately, and then turned to brown slowly and the filtrate was allowed to stand at room temperature for about three weeks. Reddish-brown prismatical single crystals suitable for X-ray structural determination were obtained by the slow evaporation from ethanol solution. Anal. Calcd. for $C_{17}H_{17}ClCoN_2O_6$ (%): C, 46.22; H, 4.34; N, 6.34; Co, 13.34. Found: C, 46.39; H, 4.24; N, 6.51; Co, 13.25.

1.4 X-ray crystallography

The single crystals of H_2L and its Co(Ⅱ) complex with approximate dimensions of 0.48 × 0.24 × 0.09 and 0.45 × 0.16 × 0.10 mm were placed on a Bruker Smart 1000 CCD area detector. The diffraction data of H_2L and its Co(Ⅱ) complex were collected using a graphite monochromated Mo $K\alpha$ radiation (λ = 0.071 073 nm) using φ-ω scan technique at 298(2) K. The data integration and empirical absorption corrections were carried out by SAINT programs[25]. An empirical absorption correction was applied using the SADABS program[26]. The structures were solved by direct methods using the program SHELXS-97[27] and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package[28]. The hydrogen atoms of water molecules in the Co(Ⅱ) complex were located from difference Fourier maps, and the other hydrogen atoms were generated geometrically. All calculations were performed on a personal computer with the SHELXL-97 crystallographic software package. Details of the crystal parameters, data collection and refinements for H_2L and its Co(Ⅱ) complex are summarized in Table 1.

CCDC: 940101, H_2L; 940100, Co(Ⅱ) complex.

Table 1 Crystal data and structure refinement for H_2L and its Co(Ⅱ) complex

Compound	H_2L	$[Co(L)(H_2O)]$
Empirical formula	$C_{17}H_{17}ClN_2O_5$	$C_{17}H_{17}ClCoN_2O_6$
Formula weight	364.78	439.71
Temperature / K	298(2)	298(2)
Wavelength / nm	0.071 073	0.071 073

Continued Table 1

Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Iba2$
Unit cell dimensions		
a / nm	1.555 54(17)	1.934 27(14)
b / nm	0.470 55(5)	2.497 20(19)
c / nm	2.423 3(2)	0.752 96(5)
α / (°)	90.00	90.00
β / (°)	106.108(2)	90.00
γ / (°)	90.00	90.00
V / nm^3	1.704 1(3)	3.637 0(5)
Z	4	8
D_c / (g·cm^{-3})	1.422	1.606
μ / mm^{-1}	0.255	1.128
F(000)	760	1800
Crystal size / mm	0.48×0.24×0.09	0.45×0.16×0.10
θ range / (°)	3.494 to 20.584	2.664 to 26.29
Limiting indices	$-16 \leqslant h \leqslant 18$; $-5 \leqslant k \leqslant 5$; $-28 \leqslant l \leqslant 28$	$-22 \leqslant h \leqslant 23$; $-29 \leqslant k \leqslant 19$; $-8 \leqslant l \leqslant 8$
Reflections collected / unique	6 031 / 3 017 (R_{int}=0.052 2)	8 887 / 3 138 (R_{int}=0.050 7)
Completeness to θ / %	99.9(25.02)	99.7(25.01)
Max. & min. transmission	0.977 4, 0.887 4	0.895 6, 0.630 8
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3 017/0/238	3 138/1/245
GOF on F^2	1.038	1.062
R_1, wR_2 [$I>2\sigma(I)$]	R_1=0.055 3, wR_2=0.063 3	R_1=0.045 4, wR_2=0.083 9
R indices (all data)	R_1=0.155 2, wR_2=0.098 1	R_1=0.067 6, wR_2=0.093 9
Largest diff. peak and hole / (e·nm^{-3})	232 and −214	359 and −364

2 Results and discussion

2.1 FTIR spectra

Main IR bands of H_2L and its Co(Ⅱ) complex are listed in Table 2. IR spectra of H_2L and its corresponding Co (Ⅱ) complex show several distinguishable resonances in the 100~4 000 cm^{-1} region consistent with the coordination geometry, revealed from structure determination.

The O-H stretching frequency of the free ligand H_2L is expected in the 3 300~3 800 cm^{-1} region, but this frequency is displaced to 3 437 cm^{-1} because of the intramolecular hydrogen bond OH···N=C[10-11]. The characteristic C=N stretching band of the free ligand H_2L appears at 1 620 cm^{-1}, while the C=N stretching band of the Co(Ⅱ) complex is observed at 1 606 cm^{-1}, which indicates the stretching vibration absorption center shifts to the lower wave numbers because of the coordination of the Co(Ⅱ) and the N atoms from oxime section lowered the C=N bond energy[29-30]. The Ar-O stretching frequencies appear within 1 263~1 193 cm^{-1} as reported for similar Salamo-type ligands [11-13].

Table 2 Infrared absorption spectra of H_2L and its Co(Ⅱ) complex (cm^{-1})

Compound	ν(O-H)	ν(C=N)	ν(Ar-O)	δ(H_2O)	ρ(O-H)	ν(Co-N)	ν(Co-O)
H_2L	3 437	1 620	1 261	–	–	–	–
[Co(L)(H_2O)]	3 423	1 606	1 255	1 628	536	446	422

Meanwhile, a bending vibration of phenolic alcohol in H_2L at 1 182 cm^{-1}, which disappears in the Co(Ⅱ) complex, indicating the oxygen in the phenolic alcohol of the Co(Ⅱ) complex has been protonated and coordinated to the Co(Ⅱ) ions. The infrared spectrum of the Co(Ⅱ) complex shows the expected absorption bands at ca. 3 423, 1 628 and 536 cm^{-1}, assigned to the effect of the coordinated water molecule, as is substantiated by the crystal structure[10,31].

The weaker bands at 446 and 422 cm^{-1} for the Co(Ⅱ) complex are assigned to the stretching bands of Co-N and Co-O, these assignments are consistent with the literature frequency values[32]. These bands are not observed in the spectra of corresponding free ligand H_2L.

2.2 UV-Vis absorption spectra

The absorption spectra of H_2L and its corresponding Co(Ⅱ) complex in diluted DMF solution are shown in Table 3. UV-Vis spectrum of the free ligand H_2L exhibits two absorption peaks at ca. 280 and 319 nm. The former is assigned to the π-π^* transition of the benzene rings, which is shifted to low energy region by 11 nm in the Co(Ⅱ) complex, indicating the Co(Ⅱ) ion coordinated with the O and N atoms of the deprotonated L^{2-} unit[13] .The absorption peak at 319 nm in H_2L was attributed to the intra-ligand π-π^* transition of the C =N bonds, which is absent in the Co(Ⅱ) complex[33]. While, a new absorption peak is observed at 364 nm in the Co(Ⅱ) complex is assigned to the n-π^* charge transfer transition from the filled $p\pi$ orbital of the bridging ketonic oxygen to the unsaturated d-orbital of Co(Ⅱ) ions[34].

Table 3 UV-Vis absorption spectra of H_2L and its Co(Ⅱ) complex in DMF

Compound	C / (μmol·L^{-1})	λ_{max} / nm	λ_{max} / nm
H_2L	50.0	280	319
[Co(L)(H_2O)]	50.0	291	364

2.3 Crystal and supramolecular structure

2.3.1 Crystal and supramolecular structure of H_2L

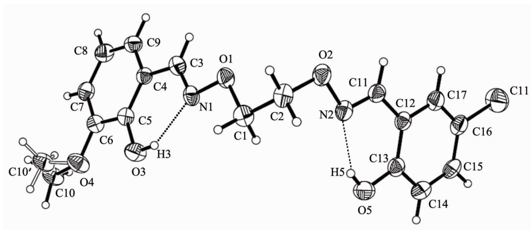
X-ray crystallographic analysis reveals the crystal structure of H_2L. Selected bond lengths and bond angles are summarized in Table 4. The ORTEP representation of the title compound is shown in Fig.1. The ligand H_2L crystallizes in the monoclinic system, space group $P2_1/n$, and Z=4. The unit cell consists of two benzene rings and a (-CH=N-O-$(CH_2)_2$-O-N=CH-) segment, etc. The dihedral angle between the two benzene rings (C4-C9 and C12-C17) is 84.60(4)°.

Table 4 Selected bond distances (nm) and bond angles (°) for H_2L

Cl1-C16	0.174 2(5)	O4-C10′	0.146(5)	C8-C9	0.138 3(5)
N1-C3	0.128 0(5)	O5-C13	0.135 9(5)	C11-C12	0.146 3(5)
N1-O1	0.142 0(3)	C1-C2	0.150 1(5)	C12-C17	0.138 6(5)
N2-O2	0.140 8(4)	C3-C4	0.146 5(5)	C12-C13	0.139 7(6)
O1-C1	0.143 4(5)	C4-C5	0.138 5(6)	C13-C14	0.139 3(5)
O2-C2	0.143 6(4)	C4-C9	0.139 8(5)	C4-C10′	0.146 0(5)
O3-C5	0.136 3(5)	C5-C6	0.140 8(5)	O14-C15	0.137 5(6)
O4-C6	0.135 5(5)	C6-C7	0.138 3(6)	C15-C16	0.137 8(6)
O4-C10	0.145 0(4)	C7-C8	0.137 5(6)	C16-C17	0.137 4(5)
C3-N1-O1	111.4(4)	C9-C4-C3	119.0(4)	C17-C12-C11	118.6(4)
C11-N2-O2	110.0(4)	O3-C5-C4	123.8(4)	C13-C12-C11	122.2(4)
N1-O1-C1	108.3(3)	O3-C5-C6	115.6(4)	O5-C13-C14	117.2(5)
N2-O2-C2	109.4(3)	C4-C5-C6	120.6(4)	O5-C13-C12	122.2(4)

Continued Table 4

C6-O4-C10	122.0(0)	O4-C6-C7	125.9(4)	C14-C13-C12	120.6(5)
C6-O4-C10′	109.0(2)	O4-C6-C5	115.5(4)	C15-C14-C13	119.0(5)
C10-O4-C10′	123.0(2)	C9-C4-C3	119.0(4)	C14-C15-C16	120.4(4)
O2-C2-C1	114.7(3)	C8-C7-C6	121.3(4)	C17-C16-Cl1	119.6(4)
N1-C3-C4	121.5(4)	C7-C8-C9	119.8(4)	C15-C16-Cl1	119.4(4)
C5-C4-C9	119.1(4)	C8-C9-C4	120.5(4)	C16-C17-C12	119.8(5)
C5-C4-C3	121.9(4)	N2-C11-C12	121.4(4)	C17-C12-C11	118.6(4)



Displacement ellipsoids for non-H atoms are drawn at the 30% probability level

Fig.1　Molecular structure and intramolecular hydrogen bonds of H_2L with atom numbering

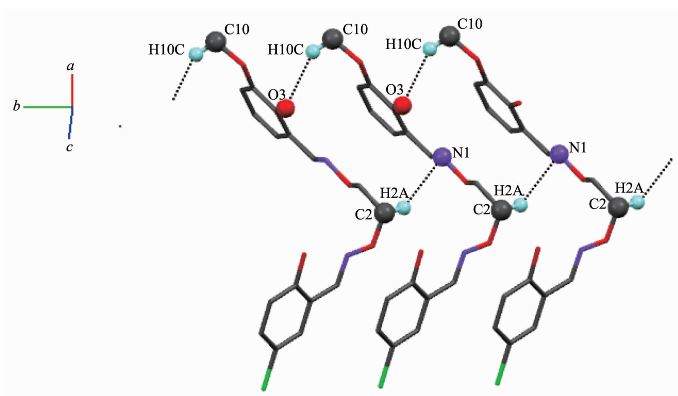
In the crystal structure, there are two strong intramolecular O3-H3···N1 and O5-H5···N2 hydrogen bonds between the (-CH=N-O-$(CH_2)_2$-O-N=CH-) group and oxygen atoms of phenolic oxygen group, which generate two six-membered S (6) ring motifs (Fig.1, Table 5). Each molecule interlinks two neighboring molecules into a 1D infinite chain along *b* axis through two intermolecular C2-H2A···N1 and C10-H4C···O3 hydrogen bonds (Fig.2).

2.3.2　Crystal and supramolecular structure of the Co(Ⅱ) complex

X-ray crystallographic analysis of [Co(L)(H_2O)]

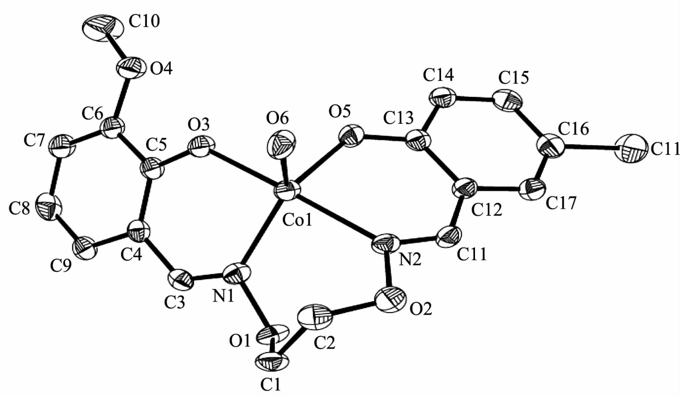
Table 5　Intramolecular and intermolecular hydrogen bonds of H_2L

D-H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠D-H···A / (°)
O3-H3···N1	0.082	0.195	0.266 0(3)	145
O5-H5···N2	0.082	0.192	0.263 9(3)	146
C10-H10···O3	0.096	0.267	0.342 8(3)	136
C2-H2A···N1	0.097	0.267	0.348 8(3)	142



Hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity

Fig.2　Part of the infinite 1D chain motif of H_2L along *b* axis reveals formation of a mononuclear structure. The Co(Ⅱ) complex crystallizes in the orthorhombic system, space group *Iba*2, and *Z* =8. The Co(Ⅱ) complex consists of one cobalt(Ⅱ) ion, one quadridentate L^{2-} unit and one coordinated H_2O molecule, as expected from the analytical data. The molecular structure of the Co(Ⅱ) complex is shown in Fig.3, and selected bond lengths and angles are listed in Table 6.



Hydrogen atoms are omitted for clarity; Displacement ellipsoids for non-H atoms are drawn at the 30% probability level

Fig.3 Molecular structure of the Co(Ⅱ) complex with atom numbering

Table 6 Selected bond distances (nm) and bond angles (°) of the Co(Ⅱ) complex

Co1-O5	0.196 0(4)	Co1-O6	0.201 8(3)	Co1-N2	0.214 0(4)
Co1-O3	0.200 2(3)	Co1-N1	0.204 3(4)		
O5-Co1-O3	90.50(16)	O6-Co1-N1	124.19(16)	C3-N1-Co1	128.3(3)
O5-Co1-O6	103.33(15)	O5-Co1-N2	86.62(16)	O1-N1-Co1	126.3(4)
O3-Co1-O6	95.79(14)	O3-Co1-N2	172.33(16)	C11-N2-Co1	124.6(3)
O5-Co1-N1	132.43(16)	O6-Co1-N2	91.79(15)	O2-N2-Co1	130.4(3)
O3-Co1-N1	87.18(15)	N1-Co1-N2	89.53(15)	C13-O5-Co1	133.1(3)

In the molecule structure of the Co(Ⅱ) complex, the Co(Ⅱ) center is penta-coordinated by two phenoic O and two oxime N atoms from one deprotonated L^{2-} unit and one O atom from one coordinated water molecule. The distances from five coordinated atoms (O3, O5, N2, N1 and O6) to the centre Co(Ⅱ) atom are 0.200 2(3), 0.196 0(3), 0.214 0(3), 0.204 3(3) and 0.201 8(3) nm, respectively. The Co1-N1 bond (0.204 3(4) nm) is slightly shorter than Co1-N2 bond (0.214 0(4) nm), and Co1-O5 bond (0.196 0(4) nm) is also shorter than Co1-O3 bond (0.200 2(3) nm), which can attributed to the introduction of the asymmetric groups to the two benzene rings. In accordance with the Addision distortion parameters τ ($\tau=|\beta-\alpha|/60$), as $\tau=0.665$, the centre Co(Ⅱ) atom adopts a slightly distorted trigonal biyramid geometric configuration (Fig.4).

The introduction of one coordinated water molecule in the Co(Ⅱ) complex successfully leads to the assembly of those monomeric units by intermolecular hydrogen bonds. As illustrated in Fig. 5, two intermolecular O6-H6B···O4 and O6-H6C···O5 hydrogen bonds are formed, and each molecule interlinks two neighboring molecules by those two intermolecular hydrogen bonds along *c* axis into a 1D infinite chain-like supramolecular structure. Furthermore, along *b* axis the molecules also assemble to a 1D infinite chain-like supramolecular structure by another intermolecular C8-H8 ··· Cl1 hydrogen bond (Fig.6). Hydrogen-bonding data for the Co(Ⅱ) complex is listed in Table 7.

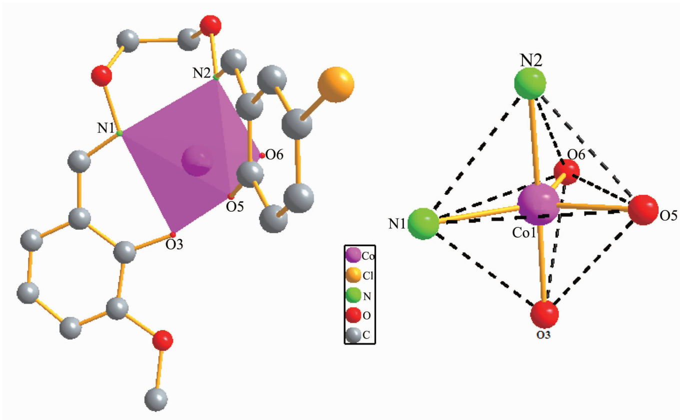
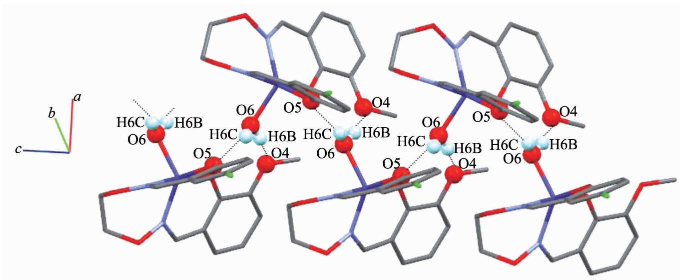
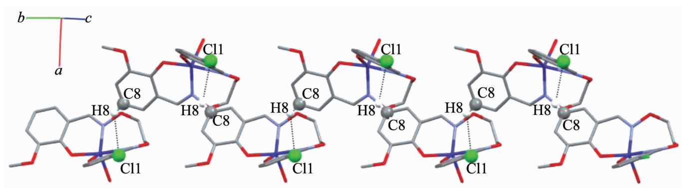


Fig.4 Coordination configuration of the Co(Ⅱ) complex



Hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity

Fig.5 Part of the 1D chain-like supramolecular interactions of the Co(Ⅱ) complex along c axis



Hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity

Fig.6 Part of the 1D chain-like supermolecular interactions of the Co(Ⅱ) complex along b axis

Table 7 Intermolecular hydrogen bonds of the Co(Ⅱ) complex

D-H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠D-H···A / (°)
O6-H6C···O5	0.085	0.196	0.271 3(3)	147
O6-H6B···O4	0.085	0.221	0.300 0(3)	156
C8-H8···Cl1	0.093	0.289	0.3563(3)	131

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