

超分子钴(II)配合物 $[\text{CoL}(\text{H}_2\text{O})_2]_n$ 的合成与结构表征

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关键词: 4,4',6,6'-四溴-2,2'-[乙二氧双(氮次甲基)]二酚; 钴(II)配合物; 合成; 晶体结构

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Synthesis and Structural Characterization of Supramolecular Cobalt(II) Complex: $[\text{CoL}(\text{H}_2\text{O})_2]_n$

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Abstract: A mononuclear Cobalt(II) complex $[\text{CoL}(\text{H}_2\text{O})_2]_n$ (H_2L : 4,4',6,6'-Tetrabromo-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol), has been synthesized and structurally characterized by elemental analysis, IR and X-ray diffraction single crystal structure analysis. The crystal of the complex belongs to monoclinic space group $P2_1/c$ with $a=2.516\ 8(3)$ nm, $b=1.023\ 43(18)$ nm, $c=0.789\ 17(14)$ nm, $\beta=91.375(2)^\circ$, $V=2.032\ 1(5)$ nm³, $Z=4$, $D_c=2.317$ Mg·m⁻³, $\mu(\text{Mo } K\alpha)=8.747$ mm⁻¹, $F(000)=1\ 356$, $R_1=0.049\ 7$, $wR_2=0.110\ 4$. The crystal structure of $[\text{CoL}(\text{H}_2\text{O})_2]_n$ indicates that the complex consists of one cobalt(II) atom, one L^{2-} unit and two coordinated water molecules, and the coordination number of the cobalt(II) atom is six. One-dimensional chain supramolecular structure is formed by intermolecular hydrogen bonds and π - π stacking of neighboring benzene rings. CCDC: 652649.

Key words: 4,4',6,6'-tetrabromo-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol; cobalt(II) complex; synthesis; crystal structure

Recently, transition metal complexes with salen and its analogues have been widely used as catalysts for a number of organic redox reactions and electrochemical reduction processes^[1~5], in addition, they are also used as models of reaction centers of metalloenzymes^[6], nonlinear optical materials^[7,8], and exhibit interesting magnetic properties^[9,10]. Here, in continuation of our previous studies on characterization of transition metal complexes^[11,12], we synthesized a novel salen-type ligand, 4,4',6,6'-tetrabromo-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol (H_2L) and its corresponding

cobalt(II) complex $[\text{CoL}(\text{H}_2\text{O})_2]_n$, the latter was structurally characterized by X-ray single crystal diffraction.

1 Experimental

1.1 Materials and instruments

All chemicals were of analytical reagent grade and were used without further purification. C, H, and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument. Elemental analysis for Co was detected by an IRIS ER/S·WP-1 ICP atomic emission spectrometer. The IR spectra in

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the range of 400~4 000 cm^{-1} were recorded with a VERTEX70 FTIR spectrophotometer using KBr pellets. ^1H NMR spectrum was determined by German Bruker AVANCE DRX-400 spectroscopy. X-ray single crystal structure determination was carried out on a Bruker Smart Apex CCD diffractometer. Melting points were obtained by use of a X4 microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and were uncorrected.

1.2 Preparation of cobalt(II) complex

1.2.1 Synthesis of H_2L

4,4',6,6'-Tetrabromo-2,2'-[ethylenedioxybis(nitri-lomethylidyne)]diphenol (Chart 1) was synthesized according to an analogous method reported earlier^[13,14]. To an ethanol solution (10 mL) of 3,5-dibromo-2-hydroxybenzaldehyde (559.86 mg, 2.00 mmol) was added an ethanol solution (5 mL) of 1,2-bis(aminooxy) ethane (92.12 mg, 1.0 mmol). After the solution had been stirred at 55 $^{\circ}\text{C}$ for 3 h, the mixture was filtered, washed successively with ethanol and hexane, respectively. The product was dried under reduced pressure and purified with recrystallization from ethanol to yield 479.1 mg of colorless crystalline solid. Yield, 78.6%.

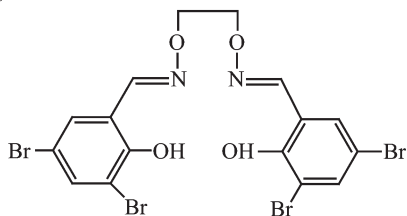


Chart 1

m.p. 189~189.5 $^{\circ}\text{C}$. Anal. Calc. for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_4\text{Br}_4$ (%): C, 31.20; H, 1.96; N, 4.55. Found: C, 31.18; H, 1.94; N, 4.58. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ , ppm) 4.49 (s, 4H, CH_2), 7.68 (d, $J=2.4$ Hz, 2H, Ar-H), 7.82 (d, $J=2.4$ Hz, 2H, Ar-H), 8.47 (s, 2H, $=\text{C}-\text{H}$), 10.43 (s, 2H, OH).

1.2.2 Synthesis of complex

A solution of Co(II) acetate tetrahydrate (0.012 5 g, 0.05 mmol) in methanol (18 mL) was added dropwise to a solution of H_2L (0.030 8 g, 0.05 mmol) in acetonitrile/tetrahydrofuran (1:1) (40 mL) at room temperature. The color of the mixed solution turned to yellow immediately, the mixture was filtered and the filtrate was allowed to stand at room temperature for about one month. The solvent was partially evaporated and several reddish-orange-colored block-shaped single crystals which suitable for X-ray crystallographic analysis were obtained. Anal. Calc. for $\text{C}_{16}\text{H}_{14}\text{Br}_4\text{CoN}_2\text{O}_6$ (%): C, 27.11; H, 1.99; N, 3.95; Co, 8.31. Found: C, 27.08; H, 1.94; N, 3.99; Co, 8.33.

1.3 Crystal structure determination

X-ray diffraction data (Table 1) were collected on a Bruker Smart Apex CCD diffractometer at (298 ± 2) K using graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm). Unit cell parameters were determined by least squares analysis. The LP factor and Semi-empirical absorption corrections were applied to the intensity data. The structure was solved by the direct methods (SHELXS-97^[15]) and subsequent difference-fourier map revealed the positions of the remaining

Table 1 Crystal data and structural refinements for $[\text{CoL}(\text{H}_2\text{O})_2]_n$

Empirical formula	$\text{C}_{16}\text{H}_{14}\text{Br}_4\text{CoN}_2\text{O}_6$	$\mu(\text{Mo } K\alpha) / \text{mm}^{-1}$	8.747
Formula weight	708.86	$F(000)$	1 356
T / K	298(2)	Crystal size / mm	$0.30 \times 0.11 \times 0.09$
Wavelength / nm	0.071073	θ range for data collection / $^{\circ}$	1.62~25.01
Crystal system	Monoclinic	Index ranges	$-21 \leq h \leq 29, -11 \leq k \leq 12, -9 \leq l \leq 8$
Space group	$P2_1/c$	Completeness to $\theta=25.01^{\circ}$	99.5%
a / nm	2.516 8(3)	Reflections collected	9 859
b / nm	1.0234 3(18)	Independent reflections	3 567 ($R_{\text{int}}=0.062\ 2$)
c / nm	0.789 17(14)	Reflections observed [$I>2\sigma(I)$]	2273
$\beta / ^{\circ}$	91.375(2)	Data / restraints / parameters	3 567 / 0 / 262
V / nm^3	2.032 1(5)	Goodness-of-fit on F^2	1.033
Z	4	Final R Indices [$I>2\sigma(I)$]	$R_1=0.049\ 7, wR_2=0.110\ 4$
$D_c / (\text{Mg}\cdot\text{m}^{-3})$	2.317	R Indices (all data)	$R_1=0.089\ 8, wR_2=0.124\ 3$

atoms, and all hydrogen atoms were added theoretically. All non-hydrogen atoms were refined anisotropically using a full-matrix least-squares procedure on F^2 with SHELXL-97^[16].

CCDC: 652649.

2 Results and discussion

IR spectra of H_2L and $\text{Co}(\text{II})$ complex are shown that the bands due to $\nu_{\text{C}=\text{N}}$ and $\nu_{\text{Ar-O}}$ of the complex were lowered by 4 and 58 cm^{-1} respectively, as compared to H_2L values ($\nu_{\text{C}=\text{N}}$ and $\nu_{\text{Ar-O}}$ appear at $1\,604$ and $1\,269\text{ cm}^{-1}$ respectively). It provides evidence for the coordination of H_2L with $\text{Co}(\text{II})$ ions. Meanwhile, a bending vibration of phenolic alcohol in H_2L at $1\,269\text{ cm}^{-1}$, which disappears in the complex, indicates the oxygen in the phenolic alcohol of the complex has been deprotonated and coordinated to the metal.

The crystal structure and atom numbering of the title complex, three-dimensional packing diagram of the title complex are shown in Fig.1 and Fig.2, respectively. The selected bond lengths and bond angles are listed in Table 2.

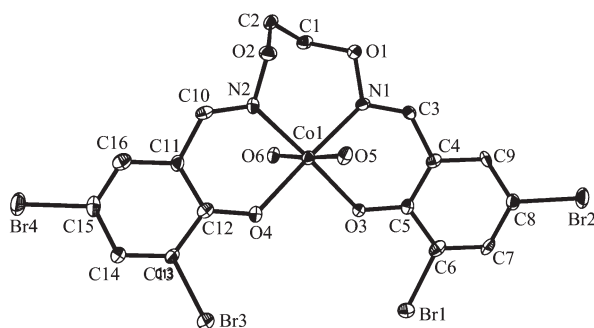


Fig.1 Crystal structure and atom numbering of the title complex

The crystal structure of the complex reveals formation of a mononuclear structure, which consists of

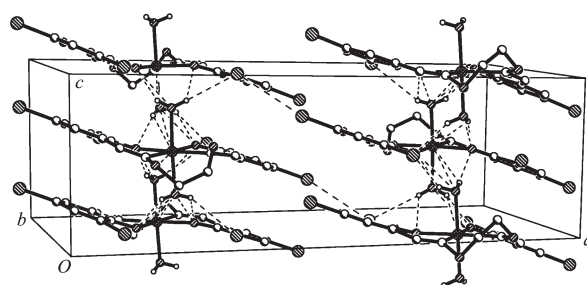


Fig.2 Three-dimensional packing diagram of the title complex

one cobalt(II) atom, one L^{2-} unit and two coordinated water molecules. The cobalt(II) atom is six-coordinated by the nitrogen (N(1), N(2)) atoms and the oxygen atoms (O(3), O(4)) of L^{2-} unit and two oxygen atoms (O(5), O(6)) of water molecules. The dihedral angle between the coordination plane of N(2)-Co(1)-O(4) and that of N(1)-Co(1)-O(3) is $1.78(6)^\circ$, indicating slight distortion from the square planar structure toward tetrahedral geometry. The distances between Co1 and O5, Co1 and O6 are $0.214\,3(5)\text{ nm}$ and $0.211\,7(5)\text{ nm}$, respectively, which are correspondingly longer than the distance between Co1 and O3 ($0.206\,4(5)\text{ nm}$), Co1 and O4 ($0.208\,7(5)\text{ nm}$).

In the crystal structure of the title compound, there exist a strong $\text{O5-H5A} \cdots \text{O3}$ and a weak $\text{O5-H5B} \cdots \text{Br3}$ intermolecular hydrogen bonds, the hydrogen bond data are summarized in Table 3. It is interesting to note that there are strong intermolecular π - π stacking interactions between the nearest benzene rings. Two benzene planes of the crystal cell form π - π stacking interaction at a distance of $0.375\,7\text{ nm}$. One-dimensional chain supramolecular structure is formed by hydrogen bonds and π - π stacking of neighboring benzene rings.

Table 2 Selected bond distances (nm) and angles ($^\circ$) for the title complex

Co(1)-O(3)	0.206 4(5)	Co(1)-N(2)	0.208 6(6)	Co(1)-O(4)	0.208 7(5)
Co(1)-O(6)	0.211 7(5)	Co(1)-N(1)	0.213 4(6)	Co(1)-O(5)	0.214 3(5)
O(3)-Co(1)-N(2)	176.7(2)	O(3)-Co(1)-O(4)	92.4(2)	N(2)-Co(1)-O(4)	84.5(2)
O(3)-Co(1)-O(6)	92.6(2)	N(2)-Co(1)-O(6)	88.6(2)	O(4)-Co(1)-O(6)	88.9(2)
O(3)-Co(1)-N(1)	85.5(2)	N(2)-Co(1)-N(1)	97.5(2)	O(4)-Co(1)-N(1)	177.6(2)
O(6)-Co(1)-N(1)	92.5(2)	O(3)-Co(1)-O(5)	91.3(2)	N(2)-Co(1)-O(5)	87.6(2)
O(4)-Co(1)-O(5)	92.0(2)	O(6)-Co(1)-O(5)	176.0(2)	N(1)-Co(1)-O(5)	86.8(2)

Table 3 Hydrogen-bonding geometry

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$	$d(\text{D}\cdots\text{A}) / \text{nm}$	Symmetry
O5-H5A...O3	0.085	0.203	152.6	0.281 6	$x, 3/2-y, z+1/2$
O5-H5B...O4	0.085	0.246	132.0	0.308 9	$x, 3/2-y, z+1/2$
O5-H5B...Br3	0.085	0.281	148.6	0.356 4	$x, 3/2-y, z+1/2$
O6-H6A...O3	0.085	0.206	152.0	0.283 7	$x, 3/2-y, z-1/2$
O6-H6A...O5	0.085	0.261	123.8	0.316 0	$x, 3/2-y, z-1/2$
O6-H6B...O4	0.085	0.219	124.1	0.275 5	$x, 3/2-y, z-1/2$
O6-H6B...Br3	0.085	0.293	136.0	0.359 5	$x, 3/2-y, z-1/2$

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