

3-羧基甲氧基-2-萘甲酸钴配合物的水热合成、 晶体结构和电化学研究

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摘要: 标题化合物 $[\text{Co}(\text{L})(\text{H}_2\text{O})]_n$ 是由 $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ 、3-羧基甲氧基-2-萘甲酸(H_2L)、 NaOH 经水热反应得到。采用元素分析、IR及X-射线衍射法表征了该配合物。晶体结构表明: 晶体属于单斜晶系, 空间群 $P2_1$, Flack参数值为0.026(13)。晶胞参数: $a=0.50587(7)$ nm, $b=0.94288(12)$ nm, $c=1.23403(16)$ nm, $\beta=95.015(9)^\circ$, $V=0.58635(13)$ nm³, $Z=2$, $M_r=321.14$, $D_c=1.819$ g·cm⁻³, $\mu=1.487$ mm⁻¹, $F(000)=326$, $R_{\text{int}}=0.0238$, $R_1=0.0228$, $wR_2=0.0532$ 。配合物的中心钴离子是六配位稍变形的八面体结构, 3-羧基甲氧基-2-萘甲酸将配合物桥联成二维层状结构。对配合物的电化学行为进行了研究。

关键词: 钴配合物; 晶体结构; 3-羧基甲氧基-2-萘甲酸; 水热合成

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Hydrothermal Synthesis, Crystal Structure and Electrochemical Properties of a Cobalt(II) Complex Constructed by 3-(carboxymethoxy)-2-naphthoic Acid

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Abstract: The title complex, $[\text{Co}(\text{L})(\text{H}_2\text{O})]_n$, **1**, where H_2L =3-(carboxymethoxy)-2-naphthoic acid, was synthesized through hydrothermal synthesis and its crystal structure was determined by X-ray diffraction analysis. The crystal is monoclinic, space group $P2_1$ with $a=0.50587(7)$ nm, $b=0.94288(12)$ nm, $c=1.23403(16)$ nm, $\beta=95.015(9)^\circ$, $V=0.58635(13)$ nm³, $Z=2$, $M_r=321.14$, $D_c=1.819$ g·cm⁻³, $\mu=1.487$ mm⁻¹, $F(000)=326$, $R_{\text{int}}=0.0238$, $R_1=0.0228$, $wR_2=0.0532$, and the Flack parameter is 0.026(13). In the complex, the cobalt atom is six-coordinated by six oxygen atoms, completing an octahedral geometry. The molecules are connected to form a 2D layer structure bridged by 3-(carboxymethoxy)-2-naphthoic acid. The cyclic voltammetric behavior of the complex was also studied. CCDC: 826094.

Key words: Co(II) complex; crystal structure; 3-(carboxymethoxy)-2-naphthoic acid; hydrothermal synthesis

In recent years, metal-organic frameworks (MOFs) have been a hot research field through assembly of suitable metal salts with designed organic ligands, not

only due to their intriguing structural and topological diversity^[1-8], but also owing to their potential application as functional materials, such as magnetism, optical, ion

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exchange, catalysis, and gas storage, ferroelectric, etc. However, precise supramolecular design or “crystal engineering” of a solid-state structure is not an easy task^[9-11]. An effective and facile approach to control crystal structure is the consideration of robust and flexible organic molecules with exodentate functionality such as carboxylate or their derivatives. In this context, 3-(carboxymethoxy)-2-naphthoic acid is rarely chosen as an effective building unit for the formation of extended robust aggregates. Therefore, in this work, we incorporate 2,2'-bipyridine into the reaction system of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and 3-(carboxymethoxy)-2-naphthoic acid (H_2L), and a new cobalt coordination complex $[\text{Co}(\text{L})(\text{H}_2\text{O})]_n$, **1** is correspondingly synthesized. Moreover, the spectra characterization, and crystal structure of **1** are also discussed.

1 Experimental

1.1 Materials and instruments

All the reagents and solvents were used as commercial sources without further purification. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. The IR spectra were recorded on Shimadzu FTIR-8700 spectrophotometer using KBr discs. TG curves was recorded on a Perkin-Elmer Pyris Diamond thermoanalyser in flow of N_2 , in the temperature range from 20 to 800 °C, with a heating rate of 10 °C·min⁻¹.

1.2 Synthesis of the title complex

The compound was hydrothermal synthesized

under autogenous pressure. A mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.249 g, 1.0 mmol), 3-(carboxymethoxy)-2-naphthoic acid (0.246 g, 1.0 mmol), 2,2'-bipyridine (0.155 g, 1.0 mmol) NaOH (0.041 g, 1.0 mmol) and $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (9 mL, 2:1) was heated in a 25 mL capacity Teflon-lined autoclave at 120 °C for 3 d, the reaction mixture was cooled to room temperature over a period of 24 h. The product was collected by filtration, washed with H_2O and air-dried, Yields based on Co: 37% . Molecular formula is $\text{C}_{13}\text{H}_{10}\text{CoO}_6$. Elemental analysis: Calcd.(%): C, 48.58; H, 3.11. Found (%): C, 48.55; H, 3.16. Main IR bands (cm⁻¹): 3 381s, 1 597s, 1 541s, 1 419ms, 1 114s, 1 084m, 841ms, 760m, 472w.

1.3 X-ray crystallography

A pink block crystal with dimension of 0.20 mm×0.20 mm×0.10 mm was selected for the measurement. The diffraction data were collected at 296(2) K on a Bruker Smart Apex II CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.071\,073\text{ nm}$). A total of 4 016 reflections were collected in the range of $1.66^\circ \leq \theta \leq 27.65^\circ$ by using an ω -scan mode, of which 2 184 were unique and 2 109 ($I > 2\sigma(I)$) were used in the succeeding structure calculations. The structure was solved by direct methods and difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. All calculations were performed with SHELXTL-2000 package^[12-13]. Crystal data and structure refinement parameters are listed in Table 1.

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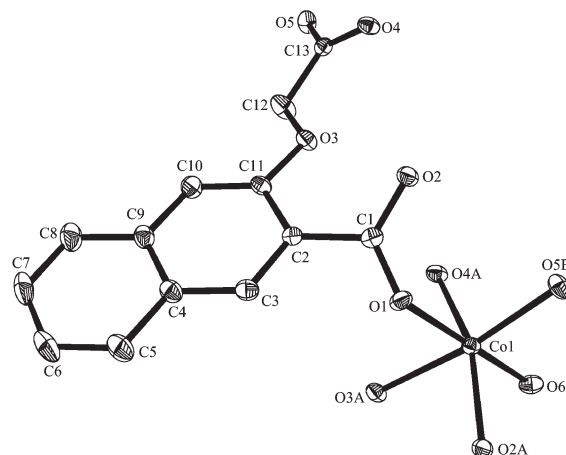
Table 1 Crystal data and structure parameters for the title complex

Empirical formula	$\text{C}_{13}\text{H}_{10}\text{CoO}_6$	Z	2
Formula weight	321.14	Absorption coefficient / mm ⁻¹	1.487
Temperature / K	296(2)	$F(000)$	326
Crystal system	Monoclinic	Crystal size / mm	0.20×0.20×0.10
Space group	$P2_1$	$\theta / (^\circ)$	1.66 to 27.65
a / nm	0.505 87(7)	Limiting indices	$-6 \leq h \leq 6, -12 \leq k \leq 9, -15 \leq l \leq 16$
b / nm	0.942 88(12)	Reflections collected / unique (R_{int})	4 016 (0.023 8)
c / nm	1.234 03(16)	Data / restraints / parameters	2 184 / 1 / 175
$\beta / (^\circ)$	95.015(9)	Goodness of fit on F^2	1.036
V / nm^3	0.58635(13)	Final R indices [$I > 2\sigma(I)$]	$R1=0.022\,8, wR2=0.053\,2$
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.819	Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	247 and -242
Flack parameter	0.026(13)		

2 Results and discussion

2.1 Crystal structure of the title complex

The asymmetric unit and metal coordination environment of **1** is shown in Fig.1, and the selected bond lengths and bond angle are given in Table 2.

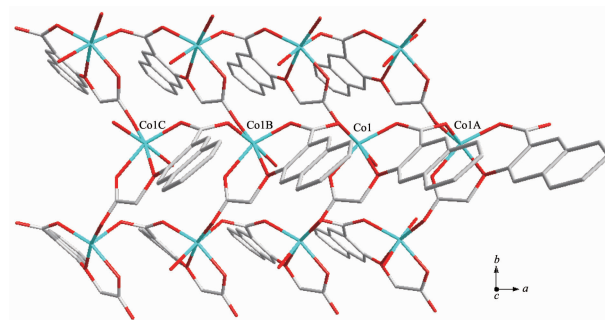


All hydrogen atoms are omitted for clarity; symmetry code: A: $1+x, y, z$; B: $1-x, 1/2+y, -z$

Fig.1 Ortep plot of the title complex showing the local coordination environment with displacement ellipsoids at 30% probability

X-ray analyses revealed that the complex has an infinite 2D layer structure paralleling *ab* plane. The asymmetric unit and metal coordination environment of **1** is shown in Fig.1. Each Co(II) atom is six-coordinated and exhibits a little distorted octahedral geometry. Five oxygen atoms O1, O2A, O3A, O4A and O5B from three L^{2-} ligands and one coordinated water molecule O(6) with the Co-O bond distances fall in the region 0.202 52~0.223 75 nm (symmetry code A: $1+x, y, z$; B: $1-x, 1/2+y, -z$). We can presume that the equatorial plane is composed of O2A, O3A, O4A and O5B, which

the sum of bond angles O(2A)-Co(1)-O(3A) ($82.75(5)^\circ$), O(3A)-Co(1)-O(4A) ($75.63(7)^\circ$), O(4A)-Co(1)-O(5B) ($94.91(7)^\circ$) and O(5B)-Co(1)-O(2A) ($106.62(6)^\circ$) is 359.91° , and the angle O(1)-Co(1)-O(6) being in axial place is $175.56(6)^\circ$, these data indicate that the Co1 atom of the complex is in distorted octahedron configuration. It is noteworthy that the two carboxylate groups of each L^{2-} ligand the same coordination modes, they act as $\mu_2-\eta^1:\eta^1$ -bridging modes, and the O atom of methoxyl group also coordinates to central atom. Therefore, the coordination interactions between the L^{2-} ligand and six-coordinated Co(II) atom as described above make **1** a 2D network (Fig.2).



Symmetry code: A: $1+x, y, z$; B: $1-x, 1/2+y, -z$; C: $-2+x, y, z$

Fig.2 2D infinite network constructed by L^{2-}

An interesting feature of this structure is the presence of intramolecular hydrogen bonds which are observed between the coordinated water O-H groups and carboxylate oxygen atoms, such as O6-H6A...O4A and O6-H6B...O2A with D...A separations in the 0.277 37(19)~0.283 38 nm region and the D-H-A angles range from 163° to 168° . These hydrogen bonds thus appear to stabilize the asymmetry molecular disposition around the Co center. The detailed data of hydrogen bonds for **1** are shown in Table 3.

Table 2 Selected bond lengths (nm) and bond angles ($^\circ$)

Co(1)-O(1)	0.208 60(16)	Co(1)-O(2A)	0.202 52(11)	Co(1)-O(3A)	0.223 75(17)
Co(1)-O(6)	0.211 85(11)	Co(1)-O(4A)	0.207 53(17)	Co(1)-O(5B)	0.202 72(18)
O(1)-Co(1)-O(6)	175.56(6)	O(2A)-Co(1)-O(3A)	82.75(5)	O(5B)-Co(1)-O(6)	87.90(6)
O(1)-Co(1)-O(3A)	85.93(7)	O(2A)-Co(1)-O(1)	96.16(5)	O(5B)-Co(1)-O(3A)	170.54(7)
O(2A)-Co(1)-O(5B)	106.62(6)	O(6)-Co(1)-O(3A)	91.38(6)	O(4A)-Co(1)-O(1)	90.37(7)
O(2A)-Co(1)-O(4A)	156.91(6)	O(5B)-Co(1)-O(4A)	94.91(7)	O(4A)-Co(1)-O(6)	85.53(6)
O(2A)-Co(1)-O(6)	86.99(4)	O(5B)-Co(1)-O(1)	94.17(7)	O(4A)-Co(1)-O(3A)	75.63(7)

Symmetry code: A: $1+x, y, z$; B: $1-x, 1/2+y, -z$.

Table 3 Parameters of hydrogen bonds for complex 1

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H-A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
O(6)-H(3A)···O(4) ^D	0.077	0.203	0.277 37(19)	163
O(6)-H(3B)···O(2) ^E	0.084	0.201	0.283 38	168

Symmetry codes: ^D 2+x, y, z; ^E 2-x, -1/2+y, -z.

2.2 Spectra characteristics and cyclic voltammetry

The infrared spectrum of the title complex has been recorded and some important assignments are shown in experimental section. One feature of the IR data is the separation between $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$, which have often been used to diagnose the coordination modes in the carboxylate ligands. The separation for monodentate carboxylate groups is $>200\text{ cm}^{-1}$, whereas it is $<200\text{ cm}^{-1}$ in bidentate groups^[14]. The separation ($\Delta\nu$) between $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ is 178 cm^{-1} for **1**, indicating bidentate coordinating modes for the coordinated carboxylate groups, these IR results are coincident with the crystallographic structural analyses. In the IR spectrum, the band at 3381 cm^{-1} is due to the $\nu(\text{O-H})$ absorptions of water molecules. The results of thermo-gravimetric analyses (TGA) illustrates that complex **1** loses its one coordinated water molecule in the temperature range of $30\sim110\text{ }^\circ\text{C}$. The weight loss of 5.47% is consistent with calculated one of 5.61%. After the loss of the coordinated water molecule, the 2D framework is stable up to $380\text{ }^\circ\text{C}$, followed by another weight loss at high temperature.

In the CV measurement, tri-electrode system was used with glass/C as working electrode, Pt as auxiliary

electrode and SCE as reference electrode. The solvent is the mixture of methanol and water with complex condensation of $1.5\times10^{-5}\text{ mol}\cdot\text{L}^{-1}$. KCl was used as the supporting electrolyte and HAc-NaAc buffer solution was adopted. The scanning range is $0\sim1.500\text{ V}$ and scanning rate $100\text{ mV}\cdot\text{s}^{-1}$ and the transfer in the electrode reaction is irreversible. The peak potential of our complex could be comparable with that of Co(II)/Co ($E=-0.42\text{ V}$) under standard conditions, as shown in Fig.3, so we can deduce that the oxidizability of Co(II) in the title complex has been strengthened.

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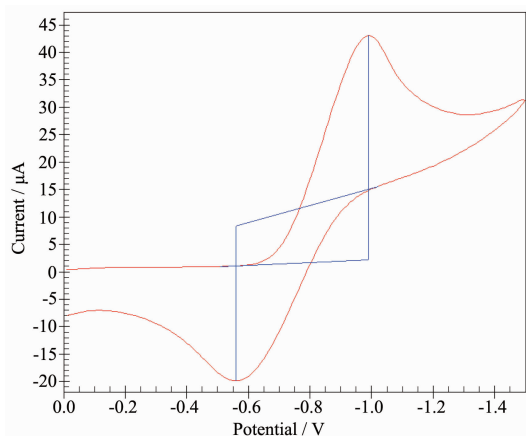


Fig.3 Cyclic voltammograms of complex 1