

一维链状钴配位聚合物 $\{[\text{Co}(\text{C}_4\text{H}_4\text{O}_5)(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}\}_n$ 的合成与晶体结构

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Synthesis and Crystal Structures of 1D Chain-Like Cobalt(II) Complex $\{[\text{Co}(\text{C}_4\text{H}_4\text{O}_5)(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}\}_n$

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Abstract: One dimensional chain cobalt coordination polymer has been synthesized with malic acid and cobalt(II) chloride anhydrous, and characterized by the element analysis, IR, TGA and single crystal X-ray diffraction structure analysis. The title complex crystallizes in monoclinic system with space group $P2_1$, $a=0.575\ 61(9)$ nm, $b=0.905\ 86(14)$ nm, $c=0.841\ 02(13)$ nm, $\beta=105.350(2)^\circ$; $V=0.422\ 88(11)$ nm³, $Z=2$, $D_c=1.924$ Mg·m⁻³, $\mu=2.044$ mm⁻¹, $F(000)=250$, and final $R_1=0.029\ 3$, $wR_2=0.074\ 2$. The crystal structure shows that the cobalt ion is coordinated with four oxygen atoms from two different malate molecules and two oxygen atoms from two water molecules respectively, forming a distorted octahedral coordination geometry. Two adjacent cobalt(II) atoms are bridged by one malate groups in bis-monodentate mode, constructing a one dimensional chain structure along b axis, with the adjacent Co...Co distance being 0.530 9 nm. Moreover, the molecules are packed in three-dimensional supramolecular network through the intermolecular hydrogen bonds. CCDC: 704441.

Key words: malic acid; crystal structure; cobalt(II) complex

Considerable attention has been paid to the design and synthesis of metal coordination polymers not only because these polymers may possess intriguing variety of architectures and topologies^[1,2] but also owing to their potential applications in the fields of catalysis,

molecular-based magnets, electrical conductivity, and zeolite-like materials^[3,4]. Among these metal coordination polymers, polycarboxylate systems have received special interest due to their fascinating structural frameworks, physical and chemical properties, and

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potential applications in many fields. Hydroxypolycarboxylic acids as polycarboxylate ligands have drawn particular attention of materials chemists and inorganic chemists to date owing to their unique features. For example, hydroxypolycarboxylic acids possess terminal carboxylic acid and hydroxyl groups which may be completely or partially deprotonated which leads to a versatile coordination behavior towards metal cations such as nonchelating, chelating, and bridging modes^[5]. In addition, Hydroxypolycarboxylic acids can act not only as hydrogen-bond acceptors, but also as hydrogen-bond donors, depending on the number of deprotonated carboxyl groups. Malate as hydroxypolycarboxylic acids which is present in fruits and living cells is a suitable candidate for assembling such metal coordination polymers. However, only a few examples of metal-malate coordination polymers have recently been reported^[6-8]. In this paper, we report on synthesis, crystal structure and thermal properties of the coordination compound of cobalt(II) chloride with polydentate malate ligand.

1 Experimental

1.1 General procedures

All chemicals were reagent grade and used as received. All solvents were of analytical grade and used directly. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 2400 analyzer. The IR spectra were taken on a Vector22 Bruker Spectrophotometer (400~4 000 cm^{-1}) with KBr pellets. The thermal analysis experiment was performed on Perkin-Elmer TG/D600 analyzer. Thermogravimetric analysis was determined on a TA/Q600 in the 40~700 $^{\circ}\text{C}$ (20 $^{\circ}\text{C} \cdot \text{min}^{-1}$) range under nitrogen atmosphere.

1.2 Synthesis of the complex $\{[\text{Co}(\text{C}_4\text{H}_4\text{O}_5)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$

Na_2CO_3 (0.64 g, 6 mmol) was added to a solution of

L-2-hydroxysuccinic acid (0.804 g, 6 mmol) in water (10 mL). The mixture was then stirred until the evolution of CO_2 ceased and then added to a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.42 g, 6 mmol) in water (15 mL). The resulting solution was stirred for 30 minutes and kept at room temperature overnight. The red crystals of complex **1** suitable for X-ray analysis was obtained. Elemental analysis calculated for $\text{C}_4\text{H}_{10}\text{CoO}_8$ (%): C, 25.34; H, 4.25. Found(%): C, 25.11; H, 4.51. IR (KBr): 3 377, 1 610, 1 440, 1 396, 1 330 cm^{-1} .

1.3 Crystal structure determination

A red single crystal with dimensions of 0.18 mm \times 0.20 mm \times 0.25 mm was selected for X-ray structure analysis. The data were collected on a Rigaku SCX Mini CCD diffractometer using a graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\,073\,\text{nm}$) at 293 K. A total of 2 250 reflections were collected in the range of $2.5^{\circ} \leq \theta \leq 26.0^{\circ}$ by using an ω - 2θ scan mode, of which 1 255 were unique with $R_{\text{int}}=0.039$. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques using the SHELXS-97 and SHELXL-97 program^[9,10]. The H atoms attached to C3 were positioned geometrically and treated as riding, with C-H=0.097 nm (methylene) and with $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$. Other H atoms were positioned geometrically and refined using a riding model with C-H=0.097, O (hydroxy)-H=0.090, O (water)-H=0.085 nm and with $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$ or $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{O})$. All of the non-hydrogen atoms were refined by full-matrix least-squares techniques for 1 228 observed reflections with $I>2\sigma(I)$ to give the final $R=0.029\,3$, $wR=0.074\,2$ ($w=1/[\sigma^2(F_o^2)+(0.052\,7P)^2]$, where $P=(F_o^2+2F_c^2)/3$, $S=1.06$). The highest peak and deepest hole in the final difference Fourier map are 320 and $-380\,\text{e} \cdot \text{nm}^{-3}$, respectively. Crystal data and structure refinement for the title complex are listed in Table 1.

CCDC: 704441.

Table 1 Crysta data amd structure refinement parameters for the title complex

Empirical formula	$\text{C}_4\text{H}_{10}\text{CoO}_8$	$F(000)$	250
Formular weight	245.05	Crystal size / mm	0.18 \times 0.20 \times 0.25
T / K	293	θ range for data collection / ($^{\circ}$)	2.5~26.0
Crystal system	Monoclinic	Index ranges	$-6 \leq h \leq 7, -7 \leq k \leq 11, -10 \leq l \leq 10$
Space group	$P2_1$	Reflections collected / unique (R_{int})	2 250 / 1 255 (0.038)

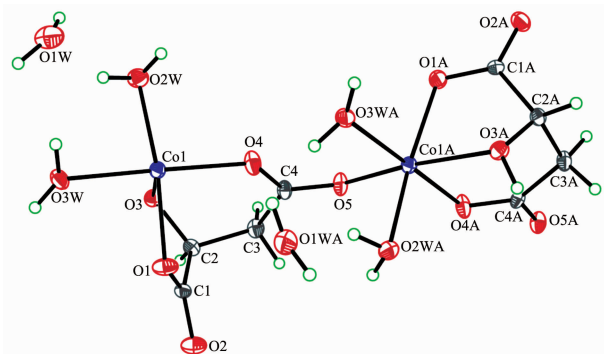
Continued Table 1

a / nm	0.575 61(9)	Refinement method	Full-matrix least-squares on F^2
b / nm	0.905 86(14)	Data / restraints / parameters	1 255 / 1 / 118
c / nm	0.841 02(13)	Goodness-of-fit on F^2	1.06
$\beta / (^\circ)$	105.350(2)	R_1 (on F) [$I > 2\sigma(I)$]	0.0293
Z	2	wR_2 (on F^2)	0.0742
$\rho_{\text{calc}} / (\text{g} \cdot \text{cm}^{-3})$	1.924	Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	380 and -320
μ / mm^{-1}	2.044	Absorption correction	Multi-scan
Flack parameter	0.01(2)		

2 Results and discussion

2.1 Structural analysis

An ORTEP drawing of the structure with atomic numbering are shown in Fig.1. Analysis of the structures X-ray crystallography reveals that the complex consists of two Co atom, two malic ligand, four coordination water molecules and two lattice water molecules in each independent crystallographic unit. The selected bond lengths and angles of this compound are listed in Table 2.



Displacement ellipsoids are drawn at the 30% probability level, symmetry code: (A) $1-x, -y+1/2, -z+2$

Fig.1 A view of the title compound with the atomic numbering scheme

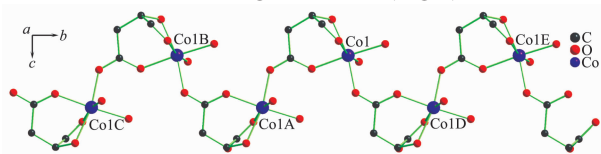
The Co(II) atom is six-coordinated by two malate dianion and two water molecules with a slightly distorted octahedral geometry (Table 2). The structure is similar to that found in the Co(II) complex^[11]. Two water molecules coordinate to the Co(II) atom in a cis configuration with anormal O2w-Co-O3w bond angle $[87.24(11)^\circ]$. The O2w-Co1 band distance is almost equivalent to the value of O3w-Co. Two malate dianions chelate to the Co(II) atom with an unusual coordination mode; the hydroxyl oxygen atom and one oxygen atom of the carboxyl group are involved in the chelate bonding but the other O atom of the carboxyl group is uncoordinated. Thus, the carboxyl group coordinates in a monodentate mode to the Co atom. The carboxyl groups and the hydroxy group of the malate coordinates to the Co^{II} atom to form one five-membered and one six-membered chelate ring. The five-membered ring displays an envelope conformation, with the Co(II) atom in the flap position and deviating from the mean plane formed by the other four atoms by 0.085 4 nm. In the five-membered chelate ring, the Co-O_{hydroxy} bond distance (0.212 7(3) nm) is longer than the Co-O_{carboxyl} distance (0.205 0(3) nm) which indicates that the hydroxyl

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

Co1-O1	0.205 0(3)	Co1-O5(A)	0.207 5(2)	Co1-O3	0.212 7(3)
Co1-O2W	0.207 0(3)	Co1-O3W	0.208 6(3)	C1-O2	0.122 7(5)
Co1-O4	0.207 0(3)				
O1-Co1-O3	76.43(10)	O2W-Co1-O3	92.82(10)	O4-Co1-O3W	175.65(11)
O1-Co1-O2W	167.51(11)	O2W-Co1-O3W	87.24(11)	O4-Co1-O5(A)	82.95(11)
O1-Co1-O3W	88.22(12)	O2W-Co1-O5(A)	90.41(11)	O5(A)-Co1-O3	167.23(11)
O1-Co1-O4	90.39(13)	O3W-Co1-O3	99.20(10)	O5-Co1-O3W	93.29(10)
O1-Co1-O5(A)	101.47(11)	O4-Co1-O3	84.47(10)		

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

group of the complex is protonated, this is also found in many other α -hydroxycarboxylate complexes [12]. However, the two Co-O_{carboxyl} distances are nearly identical in the six-membered ring. In addition, the O3-Co1-O5(A) (symmetry code: (A) $1-x, 0.5+y, 2-z$) angle of $167.23(11)^\circ$ shows the degree of distortion of the octahedral coordination geometry. The two carboxyl planes of the malate anion are nearly perpendicular to each other, the dihedral angle being $83.75(0.11)^\circ$. Cobalt atoms are binded by the carboxylate groups of malate ligand in bridging mode into one dimensional chain, with Co \cdots Co ($1-x, 0.5+y, 2-z$) distance of about 0.5309 nm viewed along the b axis (Fig.2).

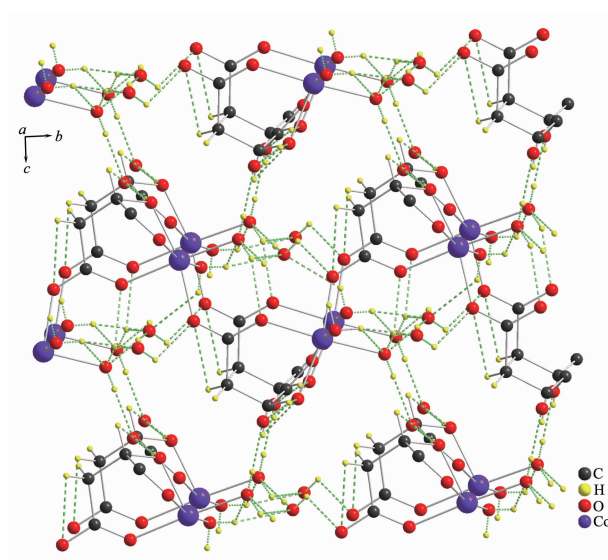


Hydrogen atoms are omitted for clarity, symmetry code: (A) $1-x, y-0.5, -z+2$; (B) $x, -1+y, z$; (C) $1-x, -1.5+y, 2-z$; (D) $1-x, 0.5+y, 2-z$; (E) $x, 1+y, z$

Fig.2 One-dimensional chain structure of the title complex

Extensive intermolecular hydrogen bonding occurs in the crystal structure (Table 3). Each mononuclear unit bears both proton donors (water molecules and hydrogen group) and acceptors (water molecules and carboxylate groups), thus it can act as a good building unit for hydrogen-bonded networks. It is notable that intermolecular hydrogen-bond contacts involve the

hydroxy groups and the coordinated O atoms of the carboxylate groups or the water molecules, as well as the hydroxy group and non-coordinated O atoms of the carboxylate groups or the water molecules. As shown in Fig.3, the hydrogen bonds connect the one dimension $[\text{Co}(\text{mal})(\text{H}_2\text{O})_3]_n$ chains into a novel three-dimensional supramolecular network. Hydrogen bond interactions are usually important in the synthesis of supramolecular architectures, undoubtedly they play an important role in the stabilization of compound **1**.



Hydrogen atoms are omitted for clarity

Fig.3 A view of the unit-cell packing in (I), showing the 3D supramolecular network formed by the hydrogen-bond network (dashed lines) along a axis

Table 3 Hydrogen-bond geometry

D-H \cdots A	D-H / nm	H \cdots A / nm	D \cdots A / nm	D-H \cdots A / ($^\circ$)
O1W-H1WA \cdots O3W ⁱ	0.085	0.253	0.338 1(4)	179.7
O3-H3C \cdots O2 ⁱ	0.090	0.181	0.268 7(4)	164.5
O1W-H1WB \cdots O5 ⁱⁱ	0.085	0.238	0.291 1(4)	121.0
O2W-H2WA \cdots O1W ⁱⁱⁱ	0.085	0.228	0.294 2(4)	135.4
O2W-H2WB \cdots O1W	0.085	0.199	0.272 9(5)	144.7
O2W-H2WB \cdots O3W	0.085	0.238	0.286 7(4)	116.9
O3W-H3WA \cdots O4 ^{iv}	0.085	0.209	0.272 7(4)	131.0
O3W-H3WA \cdots O1W	0.085	0.254	0.311 9(4)	126.4
O3W-H3WB \cdots O2 ^v	0.085	0.186	2.710(4)	179.5

Symmetry codes: ⁱ $x+1, y, z$; ⁱⁱ $x, y+1, z$; ⁱⁱⁱ $-x+2, y-1/2, -z+2$; ^{iv} $-x+1, y+1/2, -z+2$; ^v $-x, y+1/2, -z+1$.

2.2 IR spectroscopy

The IR spectra of the title compound exhibit a broad band centered at *ca.* $3\,377\text{ cm}^{-1}$ that is due to the

hydroxyl group stretching vibration of the water molecules involved in extensive hydrogen-bonding interactions^[5]. Furthermore, The title Compounds shows

one intense absorptions at $1\,610\text{ cm}^{-1}$ for the antisymmetric stretching of carboxyl group and three signals at $1\,440$, $1\,396$, and $1\,330\text{ cm}^{-1}$ corresponding to the symmetric stretching of carboxyl group. The separations (Δ) between $\nu_{\text{as}(\text{OCO})}$ and $\nu_{\text{s}(\text{OCO})}$ indicate that the malate ligand is monodenate and bidentate coordination mode in the compound **1**^[6] which is consistent with the crystal structure of **1**.

2.3 Thermal analysis

The thermal analysis experiment was performed on samples consisting of numerous single crystals of the complex under N_2 atmosphere. The sample of the complex was heated to $700\text{ }^\circ\text{C}$. The first weight loss of 21.96% (calcd 22.04%) between 102 and $205\text{ }^\circ\text{C}$ corresponds to the loss of lattice and coordinated water molecules in the complex. The further decomposition occurred in the range of $210\sim 591\text{ }^\circ\text{C}$, which may be attributed to the elimination of the malate ligands. The remaining products may be CoO (obsd 29.56% , calcd 30.57%).

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