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配位聚合物$[Co(ip)(Eim)_2]_n$的合成和晶体结构

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摘要:本文用氯化钴、间苯二甲酸钠、1-乙基咪唑在乙醇和水的混合溶剂中反应得到了配位聚合物$[Co(ip)(Eim)2]_n$(其中 ip^{2-}为间苯二甲酸二价阴离子,Eim 为 1-乙基咪唑),用 X 单晶衍射方法测定了其晶体结构。晶体属单斜晶系,$P2_1/c$ 空间群。配合物结构中含有沿着 b 轴延伸的"zigzag"链,每个 Cu 原子分别与 2 个 N 原子、2 个 O 原子进行配位,形成了一个扭曲的四面体结构。热重分析表明配合物的分解经历了 3 个阶段。电化学研究显示配合物中的 Co^{2+}/Co^{3+}氧化还原是一个准可逆的过程。

关键词:间苯二甲酸配合物;羧酸钴(Ⅱ)盐;晶体结构;循环伏安法
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Synthesis and Crystal Structure of Catena-Poly([bis(1-ethyl-1*H*-imidazole-κN^3)cobalt(Ⅱ)]-μ-isophthalato-$\kappa^2O:O'$)

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Abstract: The reation of $CoCl_2$, disodium isophthalate and Eim in ethanol and distilled water affords coordination polymer $[Co(ip)(Eim)_2]_n$ (where ip^{2-}=isophthalate dianion, Eim=1-ethyl-1*H*-imidazole), which has been characterized by X-ray single crystal structure analysis and elemental analysis. It crystallizes in monoclinic system, $P2_1/c$ space group with the cell parameters of a=1.517 4(3) nm, b=0.966 50(19) nm, c=1.318 3(3) nm, β=104.63(3)°, and V=1.870 7(6) nm^3, Z=4, and D_c=1.475 $g\cdot cm^{-3}$. With 2 711 reflections observed [$I>2\sigma(I)$], final R indices are: R_1=0.056 9, wR_2=0.137 0 while R indices for all data R_1=0.071 9, wR_2=0.151 7. The structure of the title complex contains polymeric zigzag chains extended along b axis. Each Co(Ⅱ) ion is located at a crystallographic center being coordinated by two N and two O atoms in a distorted tetrahedral geometry. The thermal gravity data indicate the complex undergoes three decomposition stages. The electrochemical studies reveal that redox of Co^{2+}/Co^{3+} in the complex is a quasi-reversible process. CCDC: 724304.

Key words: isophthalate complex; Co(Ⅱ) carboxylate; crystal structure; cyclic voltammetry

0 Introduction

The metal-ion-directed assembly of organic molecular building blocks in the construction of suprmolecule has attracted increased interest, not only because of the novel framework structures of the resulted compounds, but the potential applications as new functional materials, such as catalysis, optics, sensors, magnetism, and molecular recognition[1~11]. Metals and ligands are self-assembly organized by covalent or no covalent interactions in such suprmoleculars. During the design of new suprmolecular frameworks, some bi-

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or multidentate O- or N- donors are always used as building blocks to bind metal centers to form covalent orderly and high- dimensional arrangement. Additionally, the no covalent suprmolecular frameworks are also self-assembled by H-bonding, π-π stacking, van der waals interactions. Recently, some novel coordination polymers have been constructured successfully by using phthalate as building block and Imidazole or its 1-H substituted derivatives as the second ligand[12~19]. In these compounds, imidaole or its derivatives can donate hydrogen bonds, and the geometry of hydrogen bonds is different from each other. As an extension of these research, herein we synthesize and report a new one-dimensional chain complex $[Co(ip)(Eim)_2]_n$ (where ip^{2-}=isophthalate dianion, and Eim=1-ethyl-1*H*-imidazole).

1 Experimental

1.1 Materials and instruments

All the chemical reagents for synthesizing the title compound were purchased commercially and used without further purification. Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 1400C analyzer. Voltammetry was performed by using a CHI 832B electrochemical analysis system (China) with a three-electrode system consisting of a glass carbon (GC) electrode (U=3 mm) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the auxiliary electrode. All the electrochemical measurements were carried out in a 10 mL electrolyte cell with 0.01 mol·L^{-1} pH 6.86 KH_2PO_4-Na_2HPO_4 buffer solution as electrolyte. IR spectra were recorded in the range of 400~4 000 cm^{-1} on a Nicolet 170SX spectrometer with pressed KBr pellets. TG curve was recorded on a NETZSCH-TG209 GmbH thermoanalyser in flow of N_2, in the temperature range from 20~900 ℃, with a heating rate of 10 ℃·min^{-1}.

1.2 Preparation

The title compound was prepared as follows. To a solution of Eim (0.75 g, 8 mmol) in 10 mL of distilled water and 40 mL of ethanol was added $CoCl_2·6H_2O$ (1.12 g, 4 mmol). The resulting solution was added to a solution of disodium isophthalate (0.84 g, 4 mmol) in 10 mL of distilled water and 100 mL of ethanol (under continuous stirring at room temperature), and the mixture was refluxed for 7 h. The powder precipitate formed was filtered off, and the purple filtrate was allowed to stay at ambient temperature for a period of about 3 weeks, gave 0.42 g (25% yields) of purple single crystals suitable for structural determinations. Anal. Calcd. for $C_{18}H_{20}CoN_4O_4$ (%): C 52.08, H 4.82, N 13.49; found(%): C 51.99, H 4.71, N 13.42. IR (KBr) ν: 3 118 (m), 1 604 (s), 1 570 (s), 1 529 (m), 1 432 (w), 1 382(s), 1 340(s), 1 245(m), 1 106(s), 962(w), 852(w), 838(m), 750(s), 717(m), 655(m), 630(w), 490(w),461(w).

1.3 Crystal structure determination

A block shaped purple crystal with dimensions of 0.20 mm×0.10 mm×0.10 mm was mounted on a Bruker SMART 1000 CCD area detector X-ray single crystal diffractometer with graphite-monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) and a φ/ω scanning mode at 293 (2) K. Intensities was corrected for Lorentz and polarization effects and empirical absorption.

The structure was solved by direct methods by using SHELXS-97 program[20] and refined by full-matrix least squares on F^2 with SHELXL-97 program[21]. Some of non-hydrogen atoms were located from the difference Fourier map. All non-hydrogen atoms were refined anisotropically. H atoms were positioned geometrically (C-H=0.093, 0.096 or 0.097 nm) and allowed to ride on their parent atoms with U_{iso} (H)=1.2 times U_{eq}(C) during the refinement. Crystalographic data for the title complex are listed in Table 1.

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Table 1　Crystal and structure refinement data for the title complex

Empiricalformula	$C_{18}H_{20}CoN_4O_4$	F(000)	860
Formula weight	415.31	Crystal size / mm	0.20×0.10×0.10
Temperature / K	293(2)	θ range for data collection / (°)	1.39~25.16
Crystalsystem	Monoclinic	Limiting indices	$-18 \leqslant h \leqslant 17, 0 \leqslant k \leqslant 11, 0 \leqslant l \leqslant 15$
Space group	$P2_1/c$	Reflections collected	3 522

Continued Table 1

a / nm	1.517 4(3)	Unique reflections (R_{int})	3 360 (0.028 8)
b / nm	0.966 5(19)	Refinement method	Full-matrix least-squares on F^2
c / nm	1.318 3(3)	Data / restraints / parameters	3 360 / 40 / 233
β / (°)	104.63(3)	Goodness-of-fit on F^2	1.020
V / nm^3	1.8707(6)	Final R_1, wR_2 [$I>2\sigma(I)$]	0.056 9, 0.137 0
Z	4	R_1, wR_2 (all data)	0.071 9, 0.151 7
D_c / (Mg·m^{-3})	1.475	Largest diff. peak and hole / (e·nm^{-3})	729 and −1494
μ / mm^{-1}	0.949		

2 Result and discussion

2.1 Explanations to the crystal structure

Selected bond lengths and bond angles are presented in Table 2. Selected hydrogen-bonds are presented in Table 3. Fig.1 shows a portion of the polymeric chain of the title complex, showing 30% probability displacement ellipsoids and the atom-numbering scheme, and Fig.2 shows a perspective view of the crystal packing in the unit cell.

The crystal structure of the title complex consists of [Co(Eim)$_2$] units linked by 1,3-bridging isophthalate anions into a polymeric zigzag chain. Each distorted tetrahedron Co atom center is bonded by two N atoms from two Eim molecules and two O atoms of different ip ligands. The Co-N distances are 0.200 8(4) and 0.203 5 (3) nm, and the Co-O are 0.195 6 (3), 2.008 (3) nm. These bond lengths are comparable to those of the structurally analogous complex [Co(ip)(Him)$_2$]$_n$ (Co-N= 0.202 3(0) and 0.203 1(3) nm, Co-O=0.197 3(5) and 0.201 6(2) nm)[22]. In the bridged isophthalate anions with amphimonodentate coordination mode the C-O distance for the coordinated oxygen atom(0.128 1(5) nm) is slightly longer than for uncoordinated ones (0.123 9(5) nm). There is the normal difference of 0.004 2 nm between the two C-O distances, implying a partial double bond character of the C(17)-O(2) bond.

In the title compound, the polymer backbone propagates along the crystallographic b-axis. The metal-

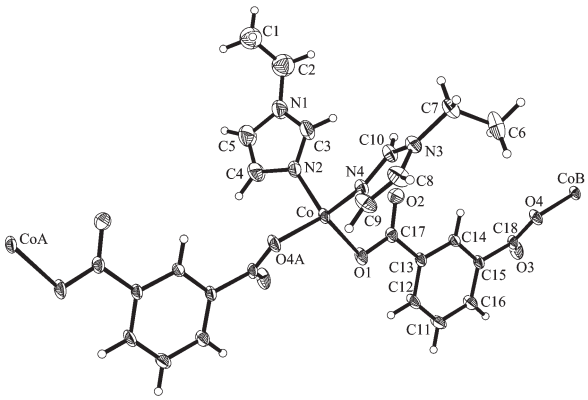
Table 2 Selected bond lengths (nm) and bond angles (°) for the complex

Co-O(1)	0.195 6(3)	O(1)-C(17)	0.128 1(5)	N(1)-C(3)	0.133 7(7)
Co-N(2)	0.200 8(4)	O(2)-C(17)	0.123 9(5)	N(1)-C(5)	0.135 8(7)
Co-N(4)	0.203 5(3)	N(2)-C(3)	0.130 3(6)	N(1)-C(2)	0.148 1(8)
Co-O(4)^{ii}	0.200 8(3)	N(2)-C(4)	0.136 6(6)	C(13)-C(17)	0.150 5(5)
O(1)-Co-N(2)	118.23(14)	C(4)-N(2)-Co	127.0(3)	C(5)-N(1)-C(2)	126.2(5)
O(1)-Co-N(4)	108.77(13)	C(9)-N(4)-Co	126.8(3)	C(4)-C(5)-N(1)	105.1(5)
N(2)-Co-N(4)	109.39(15)	C(10)-N(4)-Co	128.3(3)	O(2)-C(17)-O(1)	123.3(3)
O(1)-Co-O(4)^{ii}	115.92(12)	N(2)-C(3)-N(1)	112.1(4)	O(2)-C(17)-C(13)	120.5(3)
N(2)-Co-O(4)^{ii}	104.31(13)	C(8)-C(9)-N(4)	109.9(4)	O(1)-C(17)-C(13)	116.2(3)
O(4)^{ii}-Co-N(4)	98.31(13)	N(4)-C(10)-N(3)	111.8(4)	C(12)-C(13)-C(14)	119.5(3)
C(17)-O(1)-Co	108.5(2)	C(3)-N(1)-C(5)	107.5(5)	C(12)-C(13)-C(17)	120.3(3)
C(3)-N(2)-Co	128.4(3)	C(3)-N(1)-C(2)	126.2(5)	C(14)-C(13)-C(17)	120.3(3)

Symmetry transformations used to generate equivalent atoms: ^{i} x, y+1, z; ^{ii} x, y−1, z.

Table 3 Hydrogen bonds of the complex

D–H···A	Symmetry codes	d(H···A) / nm	d(D···A) / nm	∠(DHA) / (°)
C(3)–H(3A)···O(3)	x, −1/2−y, −1/2+z	0.240	0.325 92	154
C(5)–H(5A)···O(3)	−x, −y, 1−z	0.241	0.332 77	168
C(12)–H(12A)···O(1)		0.245	0.276 77	100



Symmetry codes: (A) x, y+1, z; (B) x, y−1, z

Fig.1　A portion of the polymeric chain in the title compound showing atomic numbering and 30% probability displacement ellipsoids

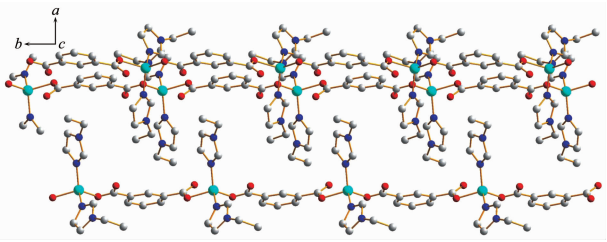


Fig.2　Packing of the title compound, viewed down the c axis

metal distances across each polymer backbone are 0.966 5(6) nm, which are longer than those found in $[Co(ip)(Him)_2]_n$ (0.931 7(2) nm)[22], whereas the closest metal-metal distances between neighboring strands are 0.668 6(2) nm, which are shorter than those of 0.862 3(2) nm in $[Co(ip)(Him)_2]_n$[22].

The dihedral angle between the two carboxylate groups is 46.07(2)°, which is 7.74(2)° in $[Co(ip)(Eim)_2]_n$[22]. The dihedral angles of the plane of the carboxylate group with benzene ring is 41.34(3)°. Distances and angles in the Eim ligand are normal.

Some potentially weak (C–H⋯O) intramolecular and intermolecular interactions exist in the lattice[23,24], which control the packing between the adjacent chains (Table 3).

The O(3) and C(3), C(5) atoms form potentially weak C–H⋯O intermolecular interactions, and the donor and acceptor distances are 0.325 92 nm for C(3)⋯O(3), 0.332 77 nm for C(5)⋯O(3), respectively. The O(1) and C(12) atoms form potentially weak C–H⋯O intramolecular interactions, with the donor and acceptor distance of 0.276 77 nm.

2.2　IR spectra

The main features in the IR spectra of the title compound are related to ligands ip and Eim. The absorption bands are assigned as follows: a medium intensity absorption at 3 118 cm^{-1} was ascribed to the stretching vibration of the aromatic C-H. The skeleton vibration frequencies of the benzene ring appeared at 1 520~1 430 cm^{-1}. The 1 604~1 570 and 1 387~1 382 cm^{-1} characteristic strong and broad bands were assigned to the symmetric and asymmetric stretching vibration of the coordinated COO groups, respectively. And the separation of 188~222 cm^{-1} between these stretching frequencies range indicates the carboxylate groups adopt monodentate coordination mode[25,26]. The stretching vibration absorption associated with the C-O bond was at 1 245 cm^{-1}. The band at 1 340 cm^{-1} was attributed to the out of plane bending vibration of methyl groups. The band at 490 and 461 cm^{-1} was ascribed to ν(Co-N).

2.3　Thermal properties

Thermal analyses of the title complex reveal that the polymeric networks retain stability below 180 ℃. On further heating the compound underwent three weight loss processes in a temperature range of 180~900 ℃. The first weight loss of 45.51% around 180~330 ℃ via two unidentified steps corresponds to the loss of two Eim molecules (calculated 46.25%). In the temperature range of 330~510 ℃ weight loss of 33.21% was ascribed to the release of ip ligand (calculated 35.66%), to give expected oxides CoO (observed 19.15%, calculated 18.09%).

2.4　Electrochemistry

Cyclic voltammetry curve for the title complex in 0.01 $mol\cdot L^{-1}$ pH 6.86 KH_2PO_4-Na_2HPO_4 buffer solution at scan rate 0.1 $V\cdot s^{-1}$ is shown in Fig.3 and the results at different scan rates are summarized in Table 4.

The complex at 0.1 $V\cdot s^{-1}$ has a anodic peak at 0.823 V and an cathodic peak at 0.710V, corresponding to the electrochemical process of Co^{2+}/Co^{3+} [27]. The separation of the cathodic and anodic peak potential, ΔE= 0.113 V, indicates that the electrochemical behavior of the cobalt complex on the glass carbon electrode is an

Table 4 Redox potential, ΔE_p, i_{pa}/i_{pc} and other calculated parameters from the CV data

v / (V·s^{-1})	E_{pc} / V[a]	E_{pa} / V	ΔE_p / V	i_{pa}/i_{pc}	α	k / s^{-1}
0.04	0.718	0.808	0.090	1.21		
0.06	0.715	0.814	0.099	1.25		
0.08	0.713	0.815	0.102	1.28		
0.10	0.710	0.823	0.113	1.33	0.61	226.04[b]
0.12	0.701	0.829	0.128	1.41		
0.15	0.697	0.836	0.139	1.46		
0.20	0.685	0.842	0.157	1.54		

[a] Data versus an SCE reference electrode; [b] Data obtained at scan rate 0.1 V·s^{-1}.

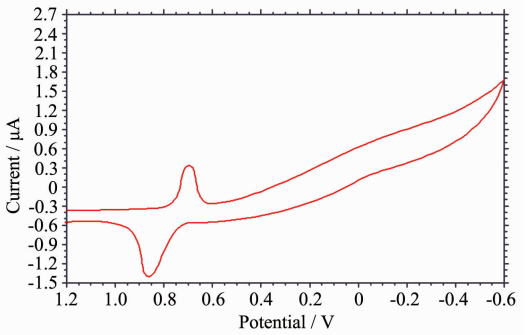


Fig.3 Cyclic voltammetry of 3.00×10^{-4} mol·L^{-1} cobalt(Ⅱ) complex in 0.01 mol·L^{-1} pH 6.86 KH_2PO_4-Na_2HPO_4 buffer solution, at a scan rate: 0.1 V·s^{-1}

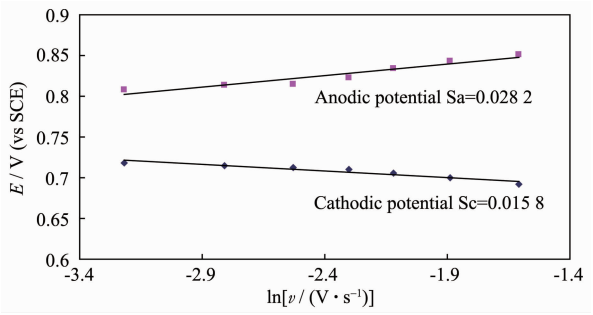


Fig.4 Variations of ln$v$ versus E_p for both the anodic peaks and the cathodic peaks

quasi-reversible process.

Lavirons approach, which is valid for quasi-reversible reactions for an electroactive species[28], was used to determine the energy transfer coefficient α and the rate constant k. The anodic (E_{pa}) and the cathodic (E_{pc}) peak potentials are expressed by this approach as follows:

$$E_{pc}=E^{\circ\prime}-\frac{RT}{\alpha nF}\left(\ln\frac{\alpha nF}{kRT}+\ln v\right) \quad (1)$$

$$E_{pa}=E^{\circ\prime}+\frac{RT}{(1-\alpha)nF}\left[\ln\frac{(1-\alpha)nF}{kRT}+\ln v\right] \quad (2)$$

where $E^{\circ\prime}$(V) is the formal potential, F Faraday constant (96 487 Coulombs mol^{-1}), R universal gas constant (8.314 J·K^{-1}·mol^{-1}), and T Kelvin temperature. So, plots of E_{pc} and E_{pa} versus ln$v$ should have two straight lines with slopes s_c and s_a as $-\frac{RT}{\alpha nF}$ and $\frac{RT}{(1-\alpha)nF}$, respectively (see Data in Fig.4). Then the α value can be calculated by the following relationships:

$$\alpha=\frac{s_a}{s_a-s_c} \quad (3)$$

k can be calculated with the help of the equation when $n\Delta E_p<200$ mV[28].

$$\frac{1}{m}=1.459\times10^{-2}+(2.335\times10^{-2})\Delta E_p+(1.323\times10^{-4})\Delta E_p^2+\cdots \quad (4)$$

where: $m=\frac{RT}{F}\cdot\frac{k}{nv}$ and n=1.

Finally, an energy transfer coefficient α value of 0.64 for this electrochemical process can be obtained by the equtation (**3**). When a scan rate is 0.1 V·s^{-1}, and ΔE_p=113 mV, k was estimated to be 226.04 s^{-1} by the equation (**4**).

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