

2,2'-联喹啉-4,4'-二羧酸构筑的一维钴(II)配位聚合物

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摘要: 利用 2,2'-联喹啉-4,4'-二羧酸钠 (Na_2bqdc), 2,2'-联吡啶与硫酸钴在溶剂热作用下合成了 1 个一维配位聚合物 $[\text{Co}(\text{bqdc})(\text{bipy})(\text{H}_2\text{O})]_n$ (**1**)。通过元素分析、粉末衍射、红外、紫外光谱对配合物进行了表征, 利用 X 射线单晶衍射仪测定了其晶体结构。中心 Co^{II} 离子分别与 2 个来自 2,2'-联喹啉-4,4'-二羧酸钠配体的双齿羧基氧原子和 1 个来自配体的单齿羧基氧原子、辅助配体 2,2'-联吡啶上的 2 个 N 原子和 1 个水分子的氧原子配位, 形成了 1 个稍微扭曲的八面体配位构型。紫外光谱实验表明, 相对 2,2'-联喹啉-4,4'-二羧酸钠配体, 配合物的紫外光谱发生了少量的蓝移。对该配合物多晶样品的差热分析(TGA)表明该化合物在 217 °C 后开始分解。

关键词: 2,2'-联喹啉-4,4'-二羧酸钠; 钴配合物; 晶体结构; 紫外光谱

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A One Dimensional Co(II) Coordination Polymer Constructed from 2,2'-Biquinoline-4,4-dicarboxylic Acid

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Abstract: Utilizing 2,2'-biquinoline-4,4-dicarboxylate ligand (Na_2bqdc) and CoSO_4 with 2,2'-bipyridine as auxiliary ligand under hydrothermal condition produces a novel coordination polymer $[\text{Co}(\text{bqdc})(\text{bipy})(\text{H}_2\text{O})]_n$ (**1**). The coordination geometry around central metal Co^{II} ion can be best described as a distorted octahedron which constructed by one bidentate chelating carboxylic group, one monodentate carboxylic group, two nitrogen atoms from the chelating bipyridine ligand and one water molecules. Crystal data for **1**, $P2_1/c$, $a=1.3671(15)$, $b=0.9996(11)$, $c=1.9948(16)$ nm, $\beta=113.555(6)^\circ$, $V=2.4989(4)$ nm³, $Z=4$, $R_1=0.0388$, $wR_2=0.0851$. The UV absorption spectrum of title compound show a small blue shifts corresponding to the free ligand probably be due to the formation of coordination polymer and supramolecular hydrogen-bonding interactions thus increasing the rigidity of **1**. Thermogravimetric analysis (TGA) of the polycrystalline sample shows that the compound is stable up to 217 °C. CCDC: 847230.

Key words: 2,2'-biquinoline-4,4-dicarboxylate; cobalt(II) complex; crystal structure; Ultra-Violet

0 Introduction

Recently, metallic supramolecular chemistry dealing with the design of highly organized architectures based upon metal-ion-directed self-assembly

processes have been received much interest^[1-6]. Especially, constructing metal-organic framework (MOF) with peculiar configuration structure and powerful photoelectric functional properties have become one of the hot topic in coordination chemistry^[6-8]. It's well

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known, there are two necessary components for constructing the inorganic supramolecular architectures: the suitably designed organic ligand and the metal ion. Because of the versatile coordination modes and potential properties in catalysis, magnetism, electrochemistry and ion exchange, N-containing and polybasic carboxylic acid ligands have afforded great success in this field. Considerable research efforts have been focused on the studies of polymeric frameworks with these kinds of ligands^[3-10]. As a new kind of N-containing and polybasic carboxylic acid ligands, Na₂bqdc (Na₂bqdc=2,2'-biquinoline-4,4-dicarboxylate disodium salt) possesses several advantages for constructing metal-organic frameworks (MOFs). Firstly, the biquinoline dicarboxylate ligand contains both nitrogen atoms and oxygen atoms, it may be used to constructed d-f heterometallic complexes^[3-5]; Secondly, the biquinoline dicarboxylate ligand possesses rigid and conjugated structure, its metal complex maybe obtain some interesting optical properties such as luminescent properties; Lastly, Ligand have multiple coordination sites can make the center atom links in different locus on thereby forming a high-dimension structure. During the past few years, a serial of metal complexes with biquinoline dicarboxylate ligand such as Cu, Zn, Mn, Ni and Co have been reported before^[11-15], however, the metal complexes with second ligand 2,2'-bipyridine have not been reported yet. Under hydrothermal condition, utilizing 2,2'-biquinoline-4,4-dicarboxylate ligand (Na₂bqdc) and CoSO₄ with 2,2'-bipyridine as auxiliary ligand, we synthesized a coordination polymer [Co (bqdc)(bipy)(H₂O)]_n, **1**. To our surprised, the crystal structure analysis shows that the coordination mode of biquinoline dicarboxylate ligand in title complex is

different from other reported bqdc complexes such as Dai^[14] and Luo's work^[15]. Here we report its synthesis, characterization and solid state structure as well as thermal stability.

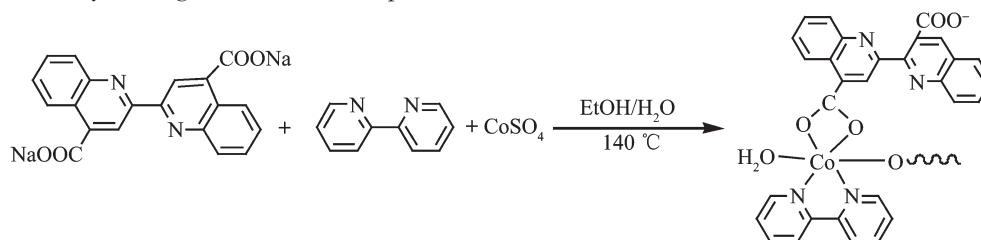
1 Experimental

1.1 Materials and measurements

All the starting materials were purchased commercially and used without further purification. IR spectrum was recorded on an FTIR-8700 spectrometer with KBr pellets in the range of 4 000 ~400 cm⁻¹. Elemental analysis was performed on a EuroEA3000 elemental analyzer. Single-crystal X-ray diffraction measurement was carried out on a Bruker SMART APXE II diffractometer with Mo K α radiation (λ = 0.071 073 nm). (TG) was performed on a TGA Q500 thermal analyzer under nitrogen atmosphere at a scan rate of 10 °C · min⁻¹.

1.2 Synthesis of [Co(bqdc)(bipy)(H₂O)]_n (**1**)

The synthetic of the title compound is shown in Scheme 1. A mixture of Na₂bqdc (0.077 6 g, 0.2 mmol) and CoSO₄ · 7H₂O (0.056 2 g, 0.2 mmol), 2,2-pyridine (0.031 2 g, 0.2 mmol) were placed in a thick Pyrex tube (ca. 20 cm). After addition of 1.5 mL water and 0.8 mL ethanol, the tube was frozen with liquid N₂, evacuated under vacuum and sealed with a torch. The tube was then placed in an oven and heated at 140 °C for two days to give red block crystals in 53% yield based on Na₂bqdc. Elemental analysis calcd. (%): C 52.56, H 3.48, N 9.73; found (%): C 52.67, H 3.38, N 9.68. IR, (KBr, cm⁻¹): 3 313(m), 1 631(s), 1 596(s), 1 548(vs), 1 521(w), 1 468(s), 1 452(vs), 1 323(m), 1 247(m), 1 197(m), 1 119(w), 921(w), 843(s), 799(w), 734(m), 671(m), 599(m), 536(w), 451(w).



Scheme 1 Preparation of compound **1**

1.3 Single crystal structure determination

A red block-like crystal of **1** with dimensions of

0.25 mm × 0.20 mm × 0.16 mm was selected for data collection. The data were collected on a Bruker P4

diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at 292 K using the φ - ω scan technique. The reflection intensities were corrected for Lp and absorption effects. The crystal structure was solved using direct methods with the SHELXS-97 program^[16]. Subsequent difference Fourier syntheses enabled all non-hydrogen atoms to be located. All non hydrogen atoms were refined with anisotropic displacement parameters by full-matrix least-squares techni-

ques^[17]. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms for the refinement. Detailed information about the crystal data and structure determination for title compound are summarized in Table 1. Its selected atomic distances and bond angles are given in Table 2.

CCDC: 847230.

Table 1 Crystal data and structure refinement for 1

Empirical formula	C ₃₀ H ₂₀ CoN ₄ O ₅	$\mu(\text{Mo } K\alpha) / \text{mm}^{-1}$	0.738
Formula weight	575.43	$F(000)$	1180
T / K	296(2)	Crystal size / mm	0.25×0.20×0.16
Wavelength / nm	0.071 073	Orange for data collection / (°)	2.17~25.00
Crystal system	Monoclinic	Index ranges	$-16 \leq h \leq 16, -11 \leq k \leq 11, -23 \leq l \leq 23$
Space group	$P2_1/c$	Reflections collected	14 291
a / nm	1.367 1(15)	Independent reflections (R_{int})	4 353 (0.047 6)
b / nm	0.999 6(11)	Refinement method	Full-matrix least-squares on F^2
c / nm	1.994 8(16)	Data / restraints / parameters	4 353 / 0 / 361
$\beta / (^\circ)$	113.555(6)	Final R indices ($I > 2\sigma(I)$)	$R_1=0.038\ 8, wR_2=0.077\ 4$
V / nm^3	2.498 9(4)	Rindices (all data)	$R_1=0.068\ 3, wR_2=0.085\ 1$
Z	4	$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$	318, -329
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.530		

Table 2 Selected bond distances (nm) and angles (°) for 1

Co(1)-O(3)#1	0.198 8(18)	Co(1)-N(2)	0.208 9(2)	Co(1)-O(1)	0.210 5(18)
Co(1)-O(1W)	0.210 8(19)	Co(1)-N(1)	0.212 9(2)	Co(1)-O(2)	0.232 4(2)
O(3)#1-Co(1)-N(2)	93.82(9)	O(3)#1-Co(1)-O(1)	173.63(8)	N(2)-Co(1)-O(1)	92.49(8)
O(3)#1-Co(1)-O(1W)	90.89(8)	N(2)-Co(1)-O(1W)	98.00(8)	O(1)-Co(1)-O(1W)	89.08(7)
O(3)#1-Co(1)-N(1)	94.61(9)	N(2)-Co(1)-N(1)	77.39(9)	O(1)-Co(1)-N(1)	85.93(8)
O(1W)-Co(1)-N(1)	173.03(8)	O(3)#1-Co(1)-O(2)	114.72(8)	N(2)-Co(1)-O(2)	149.70(8)
O(1)-Co(1)-O(2)	58.92(7)	O(1W)-Co(1)-O(2)	91.80(7)	N(1)-Co(1)-O(2)	89.79(8)

2 Results and discussion

2.1 Synthesis and IR spectra

The IR spectrum of complex **1** shows three very strong peaks at 1 631(s), 1 596(s), 1 548(vs) cm^{-1} combined with two moderately strong peaks at 1 468(s) and 1 452(s) cm^{-1} suggesting that the carboxylic acid group of bqdc ligands have been deprotonated in **1**^[18]. In addition, a broad peak at 3 300~3 500 cm^{-1} suggests that there is coordinated or crystalline water in title compound.

2.2 Crystal structures

The one-dimensional structure of **1** was revealed by the X-ray single-crystal structure analysis. Crystallographic data of **1** (as shown in Table 1) indicates the crystal belongs to monoclinic system, space group $P2_1/c$ and $Z=4$. Fig.1 presents the local coordination environments around the cobalt atoms. It can be best described as a distorted octahedral polyhedron which connected by one water molecule, one bidentate chelating carboxylic group, one monodentate carboxylic group and two nitrogen atoms from the chelating bipyridine

ligand through forming a five-membered ring. The Co(1)-O(2) distance (0.232 4(2) nm) is longer than that of Co(1)-O(3)#1 (0.198 8(18) nm) suggesting that the Co center in **1** lies in a highly unsymmetrical fashion. All the bond distances of Co-O and Co(1)-N varied from 0.198 8 nm to 0.232 4(2) nm and 0.208 9(2) to 0.212 9(2) nm respectively, and well agree with their normal distances^[18]. Compared by **1**, Dai et al.^[14] have ever reported a compound [Co(bqdc)(phen)₂(H₂O)]_n (**2**) by hydrothermal reaction of Co(OAc)₂·4H₂O, phen and H₂bqdc in a higher temperature^[14]. However, the structure of **2** contains double coordinated water molecules while **1** contains only one water molecule.

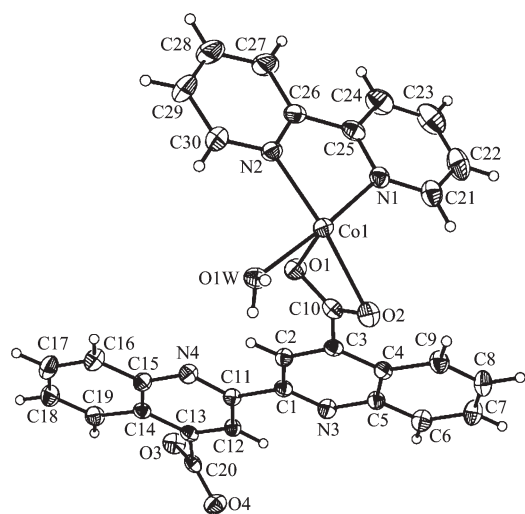


Fig.1 Coordination environment of Co atom in compound **1**

Each bqdc²⁻ ligand in **1** acting as tridentate bridging spacer link two different cobalt metals, thus resulting in the formation of one dimensional zigzag structure. All the auxiliary ligands 2,2'-bipyridine stand in the vertex of the catenarian structure (Fig.2). As we can see, for **1**, two carboxylate groups of the bqdc²⁻ ligand exhibit different coordination modes, namely one carboxylate group coordinated with a Co atom by bidentate chelating mode and the other one by monodentate mode (Scheme 1). Totally different from **1**, in compound **2**^[14], all the carboxylic group of bqdc²⁻

ligand adopt the same monodentate coordination modes by bonding two different cobalt metal, and on the contrary, in Luo et al's work^[15], both two carboxylate groups of each bqdc²⁻ ligand coordinated with two metal atoms by bidentate chelating fashion to form helix-like chain. To our knowledge, all these kind of coordination modes of bqdc²⁻ ligand have been well summarized by Zhang et al.^[11].

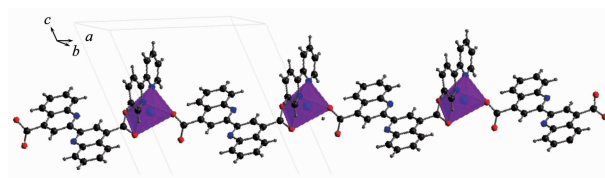
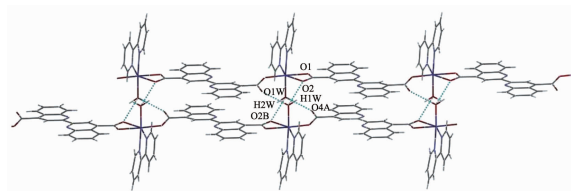


Fig.2 Zigzag structure in compound **1** viewed from *b* axis

As shown in Fig.3 and Table 3, there exist two kinds of strong H-bonds (O-H...O) in the crystal structure such as between oxygen atom of carboxylate and hydrogen atoms of water (O(1W)-H(1W)...O(4)#1 0.185 7 nm, O(1W)-H(2W)...O(2)#2 0.192 1 nm). The molecular skeleton is bonded by bridging Na₂bqdc ligands to form a one-dimensional linear structure, and then double neighboring linear structures are further linked by hydrogen bonds resulting in the formation of an interesting one-dimensional ladder structure^[19]. In addition, if we defined the centroid gravity (Cg) of aromatic rings N(1)-C(21)-C(22)-C(23)-C(24)-C(25), N(2)-C(26)-C(27)-C(28)-C(29)-C(30), N(3)-C(1)-C(2)-C(3)-C(4)-C(5), N(4)-C(11)-C(12)-C(13)-C(14)-C(15), C(4)-C(5)-C(6)-C(7)-C(8)-C(9), C(14)-C(15)-C(16)-C(17)-C(18)-C(19) are Cg(3), Cg(4), Cg(5), Cg(6), Cg(7) and Cg(8), the distance between Cg(3) and Cg(4),



Symmetry codes: A: 1-x, 2-y, 1-z; B: 2-x, 2-y, 1-z

Fig.3 Ladder structure of **1** along *c* axis

Table 3 Intermolecular hydrogen bonds lengths and bond angles for **1**

Bond (D-H...A)	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
O(1W)-H(1W)...O(4)A	0.82	0.185 7	0.267 0	171.03
O(1W)-H(2W)...O(2)B	0.977	0.192 1	0.276 8	143.44

Symmetry codes: A: 1-x, 2-y, 1-z; B: 2-x, 2-y, 1-z.

Cg(5) and Cg(6), Cg(5) and Cg(8), Cg(7) and Cg(8) are 0.399 0, 0.358 8, 0.363 5 and 0.369 1 nm respectively, also the vertical distance between above rings are 0.346 1, 0.342 2, 0.342 6 and 0.342 5 nm respectively, indicating another form of strong supramolecular interactions π - π stacking lie in title structure. They are speculated to hold together the molecules into a three layer structure (Fig.4)^[20].

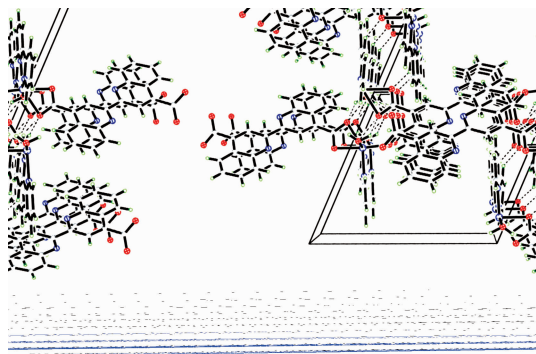


Fig.4 π - π stacking in compound **1**

2.3 Thermogravimetric properties

To study the thermal stability of compound **1**, thermogravimetric analysis (TGA) was performed on its polycrystalline sample. The compound is stable up to 314 °C. One strikingly clean weight loss step 220 °C occurred at ca. 220~230 °C (2.98% loss) corresponding to the removal of one coordinated water molecule per subunit (calcd. 3.13%). The framework is stable at 332~424 °C. Beyond this temperature, decomposition of the network was observed.

2.4 Ultraviolet spectrometry

The UV absorption spectrum of Na₂bqdc ligand and complex **1** in solid state are shown in Fig.5. As we can see, there are two distinct absorption bands at 248,

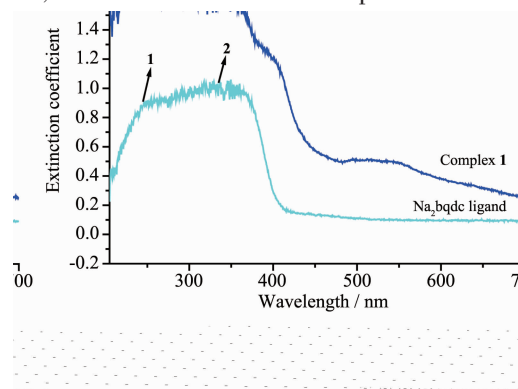


Fig.5 UV-Vis absorption spectrum of complex **1** and Na₂bqdc ligand in solid state

346 for Na₂bqdc ligand and 242, 340 nm for complex **1** respectively, which can be attribute to the $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transition of the benzene, pyridine and CO₂⁻ group. A small blue shifts corresponding to the free ligand probably be due to the formation of coordination polymer and supramolecular hydrogen-bonding interactions thus increasing the rigidity of **1**^[21].

2.5 Powder X-ray diffraction

As shown in Fig.6, powder X-ray diffraction showed the product to be highly crystalline, and also revealed that the reaction was quantitative, since no starting materials were detected in crystallizing product. Their stimulated PXRD pattern based on the crystal structure analysis allowed unambiguous identification via a comparison of the experimental and computed powder diffraction patterns.

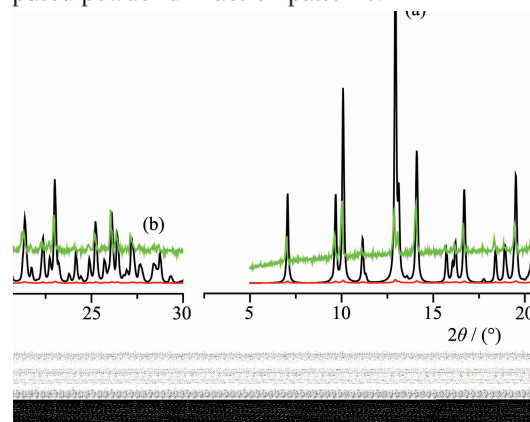


Fig.6 Powder XRD patterns of (a) the simulation based on the single-crystal analysis of **1**, (b) as-synthesized sample by grinding

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