研究简报

DBBD 及其 Cu(I)配位聚合物$[CuI(DBBD)_2]_n$的合成

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关键词:一价铜;配位聚合物;合成;晶体结构
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Synthesis of DBBD and Copper(I) Coordination Polymer $[CuI(DBBD)_2]_n$

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Abstract: In this article we report the synthesis of (*R*,*S*)-4,4′-biquinoline-6,6′-dimethyl-3,3′-dicarboxylate (DBBD) (**1**) and the formation of copper(I) coordination polymer $[CuI(DBBD)_2]_n$ (**2**) by inducing a bidentate organic ligand (DBBD). The crystal **1** belongs to monoclinic system with space group $P2_1$, and a=0.881 30(19) nm, b=1.966 0(6) nm, c=1.478 1(4) nm, β=119.429(12)°, V=2.230 5(10) nm^3, D_c=1.276 g·cm^{-3}. The crystal **2** belongs to orthogonal system with space group *Fmm*2, and a=2.044 41 (17) nm, b=1.543 06 (13) nm, c=1.652 45 (13) nm, V=5.212 9(7) nm^3, D_c=1.669 g·cm^{-3}, Z=8. CCDC: 292931, **1**; 292934, **2**.

Key words: Cu(I); coordination polymer; synthesis; crystal structure

0 Introduction

Polynuclear complexes with d^{10} metal have been achieving a lot of attention and developing rapidly since diversiform pyridine, phosphine, arsine and sulfide complex of d^{10} metal center appeared and were investigated in last thirty years[1-6]. Our group have been interested in preparation of copper(I) coordination involving the bidentate organic ligand[7]. In this article we mainly discuss the effect of anion of the salts CuX (X=Cl, I) on the structure of $[CuX(DBBD)_2]_n$ and report the formation of 2D sheet copper(I) coordination polymer $[CuI(DBBD)_2]_n$ (**2**) by inducing a bidentate organic ligand (*R*,*S*)-4,4′-biquinoline-6,6′-dimethyl-3,3′-dicarboxylate (DBBD) (**1**).

1 Experimental

1.1 Preparation of dimethyl (*R*,*S*)-4,4′-biquinoline-6,6′-dimethyl-3,3′-dicarboxylate (1)

As shown in Scheme 1, racemic (**1**) was prepared following literature methods[8]. This involved heating 4-methyl-aniline with diethylethoxymethylene malonate (EMME) at 100 ℃ until no further alcohol could be volatilized, followed by rising the reaction temperature to 250 ℃ to force compound cyclization and formation of ethyl 6-methyl-4-hydroxy-3-quinolinecarboxylate. Chlorination of this newly formed heterocyclic intermediate with $POCl_3$ gave ethyl 6-methyl-4-chloro-3-quinolinecarboxylate[9,10], which was subsequently shown to readily undergo homocoupling when treated with

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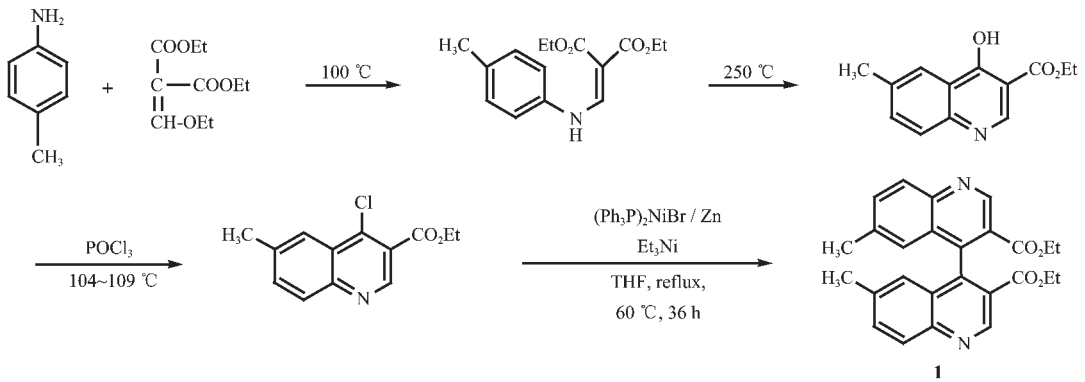


Scheme 1

$(Ph_3P)_2NiBr_2$, powdered Zn and Et_4NI to give (**1**) as a racemate in 55% yield. The structure of (**1**) was determined on the basis of mass spectrometric and IR spectroscopic analysis and is soluble in most common organic solvents such as Et_2O, CH_2Cl_2 and MeOH and can be re-crystallized under ambient conditions to give a single crystal (see Fig.1 for the solid-state structure of (**1**)). It is interesting to note that, the C-C, C-N, C-O and C=O distances in (**1**) are comparable to literature values and the dihedral angle between the planes occupied by the two quinoline rings is *ca.* 88.3° . We attribute this near right angle spacial arrangement to be due unfavorable steric interactions between the bulky substituents in 3,3′, 4,4′ and 6,6′ positions restricting free-rotation.

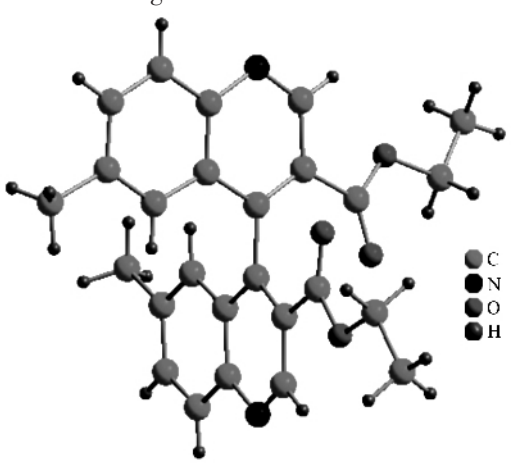
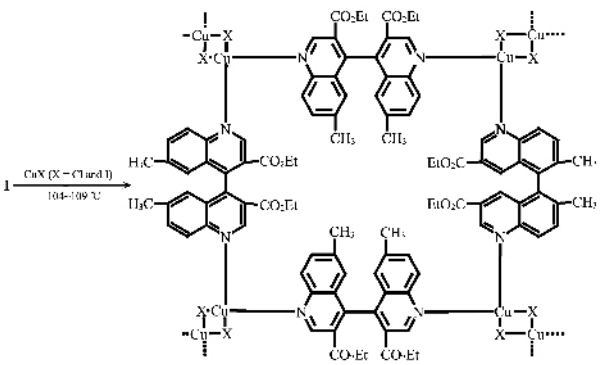


Fig.1 Molecular structure of compound **1**

1.2 Preparation and analysis of compound (2)

Hydrothermal treatment of CuI (2 mmol), dimethyl (*R*,*S*)-4,4′-biquinoline-6,6′-dimethyl-3,3′-dicarboxylate (1 mmol), H_2O (1 mL) and C_2H_5OH (2 mL) over 4 day at 100 ℃ yielded colorless block crystal 2 (Scheme 2). IR (KBr, cm^{-1}): 3 447(s), 3 043(w), 2 918 (w), 1 714(v, s), 1 624(m), 1 577(s), 1 505(s), 1 433(m), 1 370(s), 1 320(s), 1 237(m), 1 184(m), 1 129(s), 1 031(w), 828(s), 765(w), 646(w), 586(w).

CCDC: 292931, **1**; 292934, **2**.



Scheme 2

2 Results and discussion

As shown in Fig.2, the coordination environment around the Cu(I) center can be best described as a

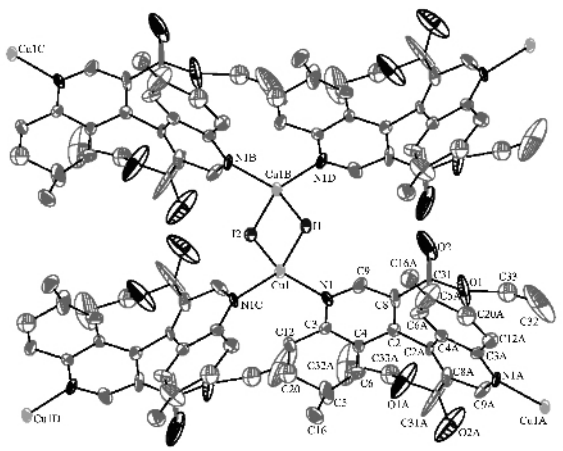
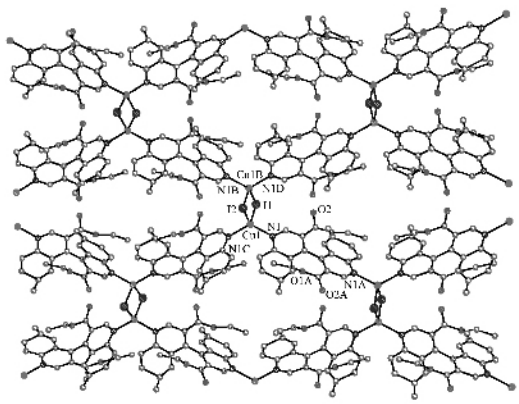


Fig.2 An Asymmetric ORTEP of (**2**) drawn with ellipsoids at 30% of probability and hydrogen atoms are omitted for clarity

slightly distorted tetrahedron. The Cu ion is coordinated to two iodide atoms and two nitrogen atoms from two independent ligands; the iodide anion act as a μ_2-bridging ligand that coordinates to two Cu atoms, and two Cu centers connected by two bridging iodide ligands.

IR spectroscopic measurements of (**2**) showed diagnostic peaks at *ca.* 1 500 cm^{-1} and 1 715 cm^{-1} assignable to ν(C=C) and ν(C=O), respectively. The presence of a strong peak at 3 447 cm^{-1} indicates water could be also coordinated in (**2**).

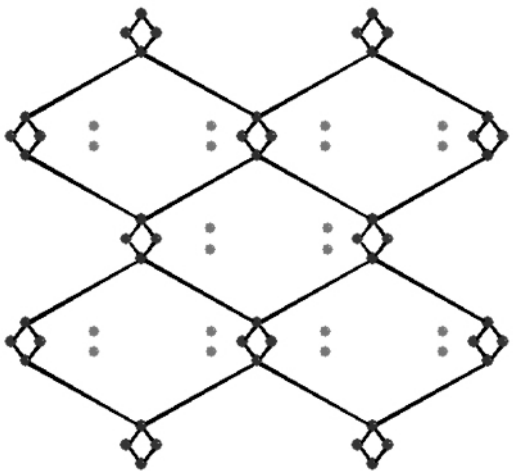
As seen from packing structure of (**2**), the coordination polymers possess a 2D layered structure that are stack together in an ABAB …… sequence that extend in three dimensions (Fig.3~5) that is the same as the compound $[CuCl(DBBD)_2]_n$ (**3**). Water is found to occupy the interspaces of the 2D (4,4) net sheets in (**2**) (Fig.4), which we postulate to be one possible reason for (**2**) crystallizing in the space group *Fmm*2. But **3** crystallizes in the space group *C*2/*c*. On the other hands, the distances of two adjacent nodal are separately 1.132 0 nm and 1.114 4 nm for **2** and **3**.



Water molecules have been omitted for clarity

Fig.3　A perspective view of the 2D coordination polymeric sheet in (**2**)

With the size of the bridging halogen atoms increases along the sequence Cl < I, the bond distance between Cu and halides and the angles of X-Cu-X (100.52(4)° for **3** and 115.68(3)° for **2**) increase too while the angles of Cu-X-Cu (79.48 (4)° for 3, and 64.45 (5)° and 64.14 (6)° for 2) decrease gradually. Compared to the angle of ideal tetrahedron is 109.28, the coordination geometry around Cu centers in the



Blue balls represent copper atoms, purple balls represent iodine atoms and red balls represent oxygen atoms of water, The Cu-Cu distances are 1.132 0 nm for (**2**)

Fig.4　Non-interpenetrating (4,4) net of (**2**)

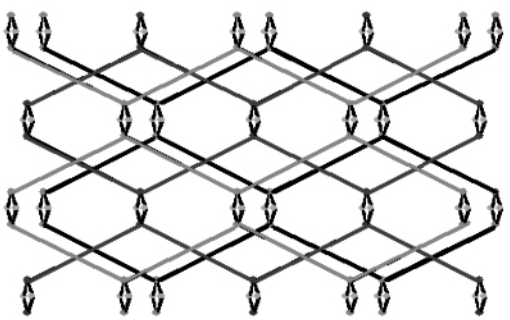


Fig.5　A packing view of (**2**) in which the red sheet is the top layer, the blue sheet is the middle layer and the black sheet is the bottom layer that stacks together in a 2D layered structure with ABAB sequence extending in three-dimension direction (along the *c*-axis)

compounds **3** almost display a perfect tetrahedron (107° ~111°), while the coordination environment around Cu center in the compound 2 significantly deviates from an ideal tetrahedron with a angle of 102° ~124° . The stereochemical changes with the halide anions in the above-mentioned two structures, to some extent, are probably due to the size effects of the different halide anions on the dinuclear frameworks and intramolecular non-bonding Cu-Cu and X-X interactions.

From the luminescent spectrum in solid state at room temperature, compounds **2** and **3** have almost identical maximum emission (~650 nm) (Fig.6). This emission energy may be attributed to halide to copper

charge transfer (XMCT), ligand to copper charge transfer (LMCT) and copper to ligand charge transfer (MLCT). And there is no cluster centered (CC) and metal centered *d* to *s* (MC) excited states for the long distance of two copper atoms.

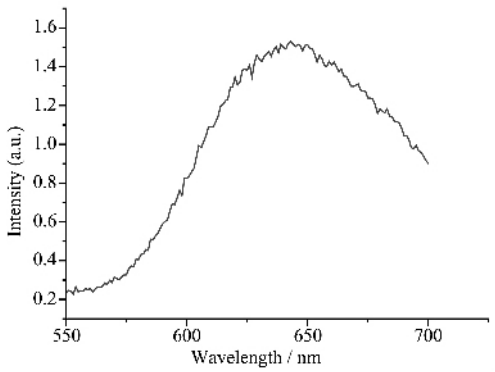


Fig.6 Solid-state emission spectrum of 2 at room temperature

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