4,4′-联喹啉酸铅(Ⅱ)配位聚合物

王 威
(东南大学化学化工学院,南京 210096)

摘要: 消旋轴手性配体(*R*,*S*)-4,4′-联二喹啉-3,3′-二甲酸乙酯(DBD) (**1**)与 $Pb(OAc)_2$ 在吡啶催化水热 140 ℃合成条件下合成一新颖的配位聚合物$[Pb(BD)(pyridine)]_n$ (**3**),荧光测量表明,该配位聚合物与有机配体一样,在 390 nm 附近展现紫色荧光。

关键词: 铅(Ⅱ); 配位聚合物; 4,4′-喹啉酸; 晶体结构; 荧光性质
中图分类号: O614.43+3 **文献标识码**: A **文章编号**: 1001-4861(2007)06-1040-05

Lead(Ⅱ) Coordination Polymer with 4,4′-biquinoline Ligand

WANG Wei
(*College of Chemistry and Chemical Engineering, Southeast University, Nanjing* 210096)

Abstract: Hydrothermal treatment of racemic atropisomeric ligand diethyl(*R*,*S*)-4,4′-biquinoline-3,3′-dicarboxylate (DBD) (**1**) with $Pb(OAc)_2$, in the presence of pyridine over 4 days at 140 ℃, offers the coordination polymer $[Pb(BD)(pyridine)]_n$ (**3**), which displays purple luminescent spectrum at about 390 nm without much transfer comparing to that of the free ligand. CCDC: 631004, **1**; 631005, **2**; 631006, **3**.

Key words: lead(Ⅱ); coordination polymer; 4,4′-biquinoline acid; crystal structure; fluorescence

Since the first example of isomers due to restricted rotation, 2,2′-dinitro-6,6′ diphennic acid, was resolved in 1922, many biaryl derivatives have been discussed. While 4,4′-quinolines were prepared by Stang till 1996[1,2]. Such 4,4′-biquinoline organic compound may be used as good bridging ligands to form novel organic-inorganic frameworks for it integrates carboxylate and quinoline. Herein, we would like to report the synthesis of the Pb (Ⅱ) coordination polymer with such a organic ligand, It can be predicted that the situation is more complicated when ligands containing two different types of binding units (carboxylate and quinoline) are employed, especially, when the nitrogen atoms from quinoline ring coordinate to metal cation, the other units (carboxylate) display a high degree of variability in their coordination.

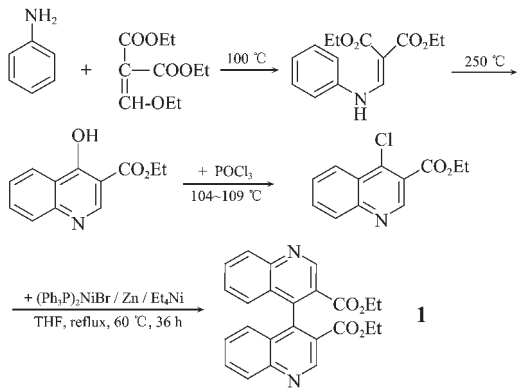
1 Experimental

1.1 Preparation and analysis of diethyl (*R*,*S*)-4,4′-biquinoline-3,3′-dicarboxylate (DBD) (1)

Aniline and EMME react at 100 ℃ until no alcohol was volatilized, then rise the reaction temperature to 250 ℃ to make the compound cyclolize to 5-hydroxy-3-carboxylateme-thylester quinoline. Chlorinate it with $POCl_3$ to afford 5-chloro-3-carboxylatemethylester quinoline. In a 50 mL Schlenk flask containing a magnetic stirring bar was charge with $(Ph_3P)_2NiBr_2$ (1.12 g, 1.5 mmol), Zn (490 mg, 7.5 mmol) and Et_4NI (1.29 g, 5 mmol). The flask was

收稿日期:2007-04-03。收修改稿日期:2007-05-24。
东南大学启动基金资助项目。
E-mail:chem_wangw@seu.edu.cn
作者:王 威,男,28 岁,副教授;研究方向:手性配合物分子电子学。

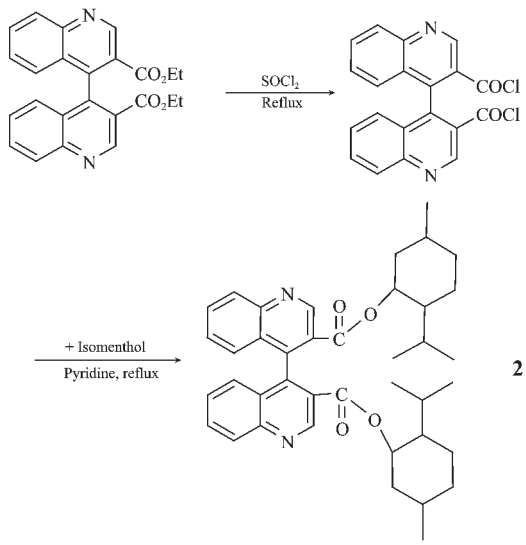
evacuated and filled with N_2 several times (vacuum line). Anhydrous THF (15 mL) was added via syringe. The mixture was stirred at r.t. After the dark brown catalyst had formed (30 min), a nitrogen-purged solution of the 5-chloro-3-carboxylatemethylester quinoline (1.2 g, 5 mmol) in THF (10 mL) was added via syringe to mixture. After stirring at 60 ℃ for 36 h the mixture was pouring into 2 mol·L^{-1} aq NH_3 (30 mL) and $CHCl_3$ (150 mL) was added and the precipitates were filtered. The aqueous layer was extracted with $CHCl_3$ (2 × 50 mL), the combined organic layers were washed with H_2O (100 mL) and brine (100 mL). Dried ($MgSO_4$) and evaporated in vacuo, the residue was recrystallized in alcohol to get the light yellow block crystals. Yield: 55%~60% based on aniline ((3 or 4)-methyl-aniline) the IR spectrum and MS agree with culture (Scheme 1).



Scheme 1

1.2 Preparation of compound 2

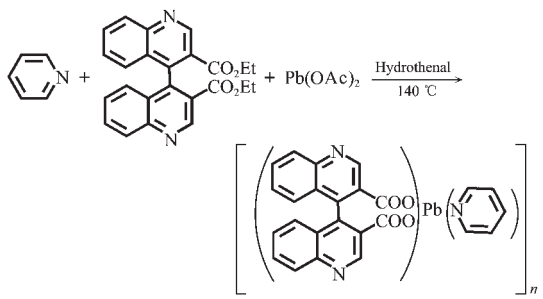
Diethyl (*R*,*S*)-4,4′-biquinoline-3,3′-dicarboxylate (10 mmol) refluxed in sulfinyl cloride (20 mL) 4 h, and then evaporated in vacuo to make the sulfinyl chloride clean and get the pale yellow residue. Added the solution of (+) isomenthol (20 mmol) in dry pyridine (25 mL) to the residue and refluxed. 2 h later, TLC was used to decide whether the reaction is complete. Then extracted with $CHCl_3$ (2 × 50 mL), the combined organic layers were washed with H_2O (100 mL). Dried ($MgSO_4$) and evaporated in vacuo, the residue was recrystallized in alcohol to get colorless block crystals **2**. Yield: 46%~52% based on diethyl-(*R*,*S*)-4,4′-biquinoline-3,3′-dicarboxylate. $C_{40}H_{48}N_2O_4$ (620.80) cacld (%): C 77.31, H 7.73, N 4.51, O 10.31. IR (KBr, cm^{-1}): 3 439(w), 3 069(w), 2 954(s), 2 932(s), 1 710(s), 1 697(s), 1 637(w), 1 577(m), 1 367(w), 1 315(m), 1 236(m), 1 167(m), 985(w), 846(w), 768(m) (Scheme 2).



Scheme 2

1.3 Preparation of compound 3

Hydrothermal treatment of $Pb(OAc)_2$ (1 mmol), diethyl (*R*,*S*)-4,4′-biquinoline-3,3′-dicarboxylate (1 mmol), H_2O (1 mL), pyridine (1 mL) and C_2H_5OH (2 mL) over 4 days at 140 ℃ yielded colorless block crystal **3** (Scheme 3) $C_{25}H_{15}PbN_3O_4$ (628.59) cacld(%). C 47.73, H 2.39, N 6.68, O 10.18, Pb 32.96. IR (KBr, cm^{-1}): 3 420(m), 3 036(s), 1 624(s), 1 587(s), 1 571(s) 1 536(s), 1 506(m), 1 496(m), 1 462(m), 1 443(s), 1 378(s), 1 335(s), 1 268(s), 1 212(m), 1 134(m), 1 064(m), 1 005(m), 810(s), 771(s), 758(s), 701(s), 613(m), 421(m).



Scheme 3

CCDC: 631004, **1**; 631005, **2**; 631006, **3**.

2 Results and discussion

According to the culture of diethyl 4,4′-biquind-

Table 1 Crystallographic data for compounds 1, 2 and 3

	1	2	3
Chemical formula	$C_{24}H_{20}N_2O_4$	$C_{40}H_{48}N_2O_4$	$C_{25}H_{15}PbN_3O_4$
Fornula weight	400.42	620.80	628.59
Space group	$P2_1/n$	$P2_1$	$P2_1/c$
a / nm	0.823 82(8)	1.475 0(4)	1.517 76(12)
b / nm	2.495 2(2)	0.824 3(2)	0.865 18(6)
c / nm	1.012 70(9)	1.478 6(4)	1.684 01(12)
β / (°)	103.629(2)	98.522(6)	109.966(2)
V / nm^3	2.023 1(3)	1.777 9(8)	2.078 4(3)
Z	4	2	4
T / K	296(2)	296(2)	296(2)
λ / nm	0.071 073	0.071 073	0.710 73
ρ_{calcd} / (g·cm^{-3})	1.315	1.160	2.009
μ / cm^{-1}	0.90	7.4	81.51
R, wR_2 [$I>2\sigma(I)$]	0.087 3, 0.188 6	0.053 0, 0.119 9	0.036 6, 0.082 7

$R=\sum||F_o|-|F_c||/\sum|F_o|$, $wR_2=\{[\sum w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

ine-3,3′-dicarboxyl acid (DBD) (**1**) which Stang and his coworkers have done, We succeeded in synthesizing such ligand. And Mass spectrums and IR spectrums of the products certified the synthesis of the final lignds. At the same time, the compound (**1**) (R =H) is soluble in common organic solvents and volatilized in air to afford the single crystal. Through the X-ray single crystal diffraction characterizing, we can be easy to find that the bond distances of C-H, C-C, C-N, C-O, C=O are usual, and the angle of two quinoline rings is about 85.0° for the existence of carboxylate increase the space resistance. In other words, DBD is restricted rotation due to the bulky substituents in 3,3′ and 4,4′ exsition. Since compound (**1**) (R =H) is racemic, then use the homochiral compound (+) isomenthol to resolute it after compound (**1**) changes to dicarboxylic acid (Scheme 2), and we got the crystal structure of the ester as shown in Fig.2. But unfortunately we haven′t got the crystal structure of the homochiral coordination compounds with the chiral organic ligand (**1**), maybe the homochiral compound of (**1**) has been racemized under hydrothermal condition at high temperatures.

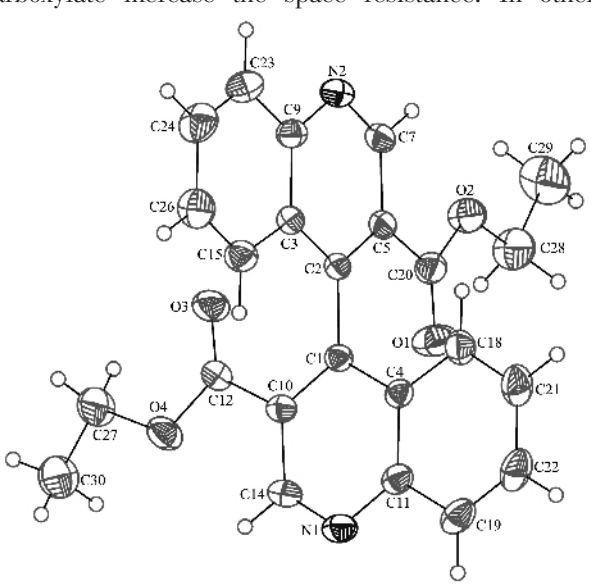


Fig.1 Crystal structure of ligand **1** at 30% ellipsoids

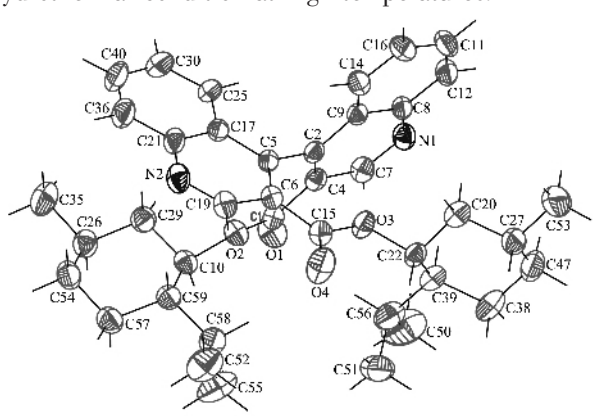


Fig.2 Crystal structure of **2** at 30% ellipsoids

Introducing above-mentioned ligand, the reaction of diethyl 4,4′-biquindine-3,3′-dicarboxylate (DBD) (**1**) with $Pb(OAc)_2$ in the presence of pyridine under hydrothermal conditions offers a lead(Ⅱ) coordination polymer $[Pb(BD)(pyridine)]_n$ (**3**) (Scheme 3). There are

diagnostic peaks (1 624 cm^{-1}) of the carbonyl groups and some peaks (about 1 500 cm^{-1}) of the quinoline ring π-π double bonds system existing in IR spectrums of the product (**3**). Fig.3 shows the solid state structure of (**3**), in which the geometry of Pb center can be best described as a distorted tetragonal pyramid. The Pb atom coordinates to one pyridine and three ligands through three oxygen atoms from carboxylic acid groups of ligand (**1**), one nitrogen atom from quinoline ring of ligand (**1**) and one nitrogen atom from pyridine ring. Evidently, in such hydrothermal treatment, the ligand was occurred in-situ hydrolyzing reaction through presenting pyridine as base catalyst. Every ligand as a quadridentate compound coordinate to three lead atom, in which one carboxylic acid group chelated to lead atom, to result in the formation of 1D chain lead(Ⅱ) polymer (Fig.4). Interestingly, the chain was constructed by a lot of sharing side dimmers those are composed of two lead atoms and two bridging ligands. And such two ligands and two lead atoms come into being a fifteen-membered ring rectangle framework, while the pyridine ligand just take up this space to coordinate to lead atom. Seen from the space filling diagram of $[Pb(BD)(pyridine)]_n$, there is no interspaces in such one dimension chain (shown in Fig.5). All of the angles of two quinoline rings of ligand (**1**) in this polymer are about 91.3° which is closer to rectangle compared with that of free ligand. Seen from Table 2, the bond lengths of Pb-N (0.261 0(6) nm, 0.278 9(6) nm) of compound

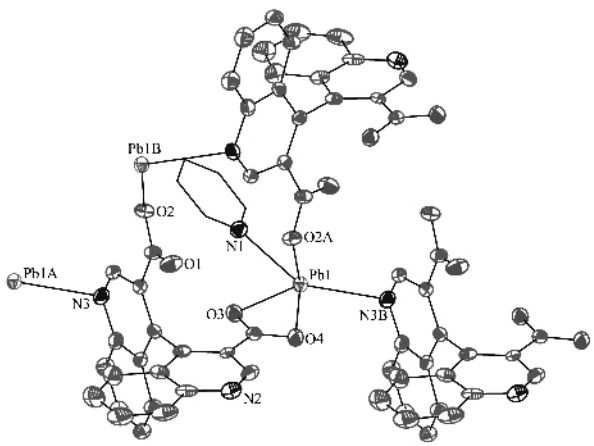


Fig.3　Crystal structure of **3** at 30% ellipsoids

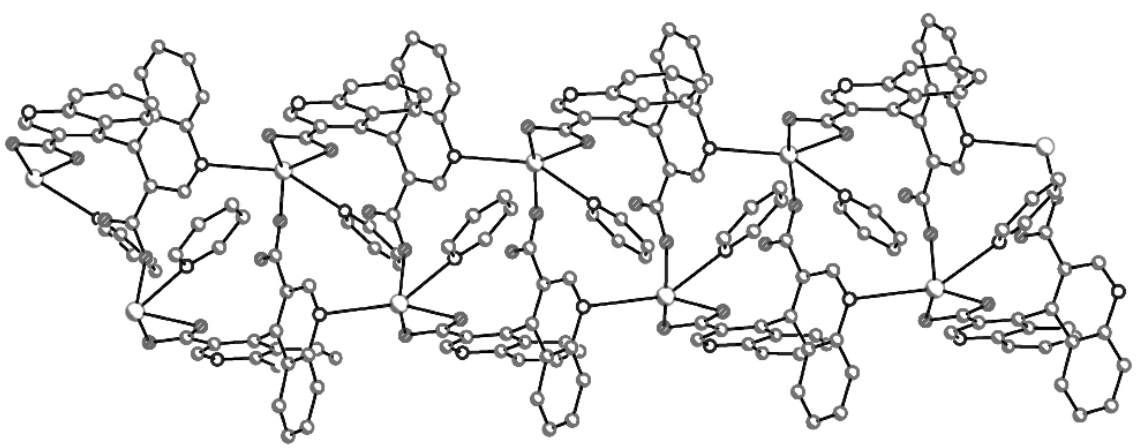


Fig.4　1D chain of coordination polymer $[Pb(BD)(pyridine)]_n$ (**3**)

Table 2　Bond distance (nm) and angle (°) of coordination polymer 3

Pb1-O2A	0.223 5(5)	Pb1-O3	0.239 6(5)	Pb1-O4	0.254 1(5)
Pb1-N1	0.261 0(6)	Pb1-N3B	0.278 9(6)		
O2A-Pb1-O3	77.57(17)	O2A-Pb1-O4	75.36(17)	O3-Pb1-O4	52.79(15)
O2A-Pb1-N1	79.32(18)	O3-Pb1-N1	77.32(18)	O4-Pb1-N1	127.50(17)
O2A-Pb1-N3B	87.82(17)	O3-Pb1-N3B	126.47(16)	O4-Pb1-N3B	73.74(16)
N1-Pb1-N3B	149.90(18)	O2A-Pb1-C2	72.76(18)	O3-Pb1-C2	26.57(16)
O4-Pb1-C2	26.37(15)	N1-Pb1-C2	102.01(19)	N3B-Pb1-C2	99.91(19)

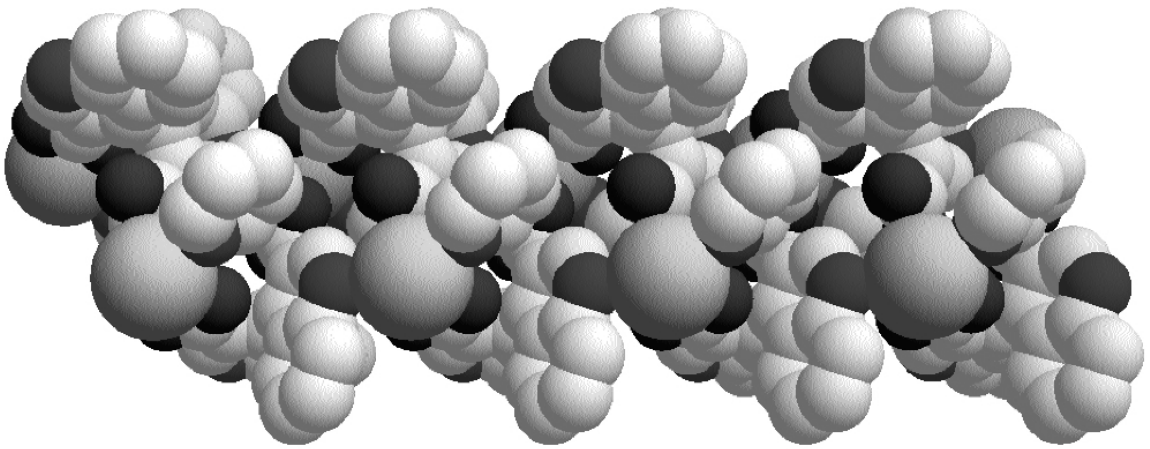


Fig.5 Space filling picture of 1D chain of coordination polymer $[Pb(BD)(pyridine)]_n$ (**3**)

(**3**) are comparable to those found in (1,3-bis(3-(2-pyridyl)pyrazoly) propane)-bis-(nitratol-O,O′) lead (Ⅱ) (0.268 8 nm, 0.275 0 nm) and fall in those of tetrakis (μ_2-4,6-bis(2,2′-bipyridin-6-yl)pyridine)(μ_2-trifluoromethanesulfonato) lead (Ⅱ) trifluoro methane sulfonate (0.250 4~0.278 4 nm). While the bond distances of Pb-O (0.223 5(5), 0.239 6(5) and 0.254 1(5) nm) are similar to those of [Pb(3,5-dinitrotyrosine)(0.5H_2O)] (0.230 5~0.245 4 nm)[3~5]. Finally, the bond distances of other bonds are normal and the bond angles are unexceptional too.

From the Fig.6, it is easy to find that **3** displays purple luminescent spectrum at about 390 nm without much transfer comparing to that of the free ligand.

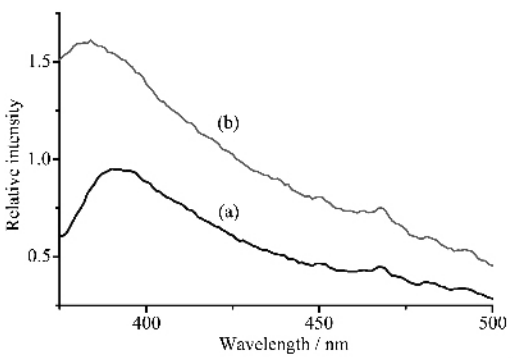


Fig.6 Solid-state emission spectrum of **3** (a) and the ligand (b) at room temperature

References:

[1] Stang P J, Olenyuk B. *Acc. Chem. Res.*, **1997**,**30**:502~518

[2] Leininger S, Olenyuk B, Stang P J. *Chem. Rev.*, **2000**,**100**: 853~903

[3] Sattistazzi G, Borsari M L, Menbue M, et al. *Inorg. Chem.*, **1996**,**35**:4239~4241

[4] Mann K L V, Jeffery J C, Mcdeverty J A, et al. *Dalton Trans.*, **1998**:89~97

[5] Garcia A M, Romero-Salguero F J, Bassani D M, et al. *Chem. Eur. Journal*, **1999**,**5**:1803~1808