Hydrothermal Synthesis, Structure and Property of a Zinc Coordination Polymer Based on Aromatic Polycarboxylate and Phenanthroline Ligands

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Abstract. A zinc coordination polymer $[Zn(\mu_2-H_2bta)_{1/2}(\mu_4-H_2bta)_{1/2}(phen)(H_2O)]_n$ (1) $(H_4bta = benzene-1,2,4,5-tetra$ carboxylic acid, phen = 1, 10-phenanthroline) has been hydrothermally synthesized and characterized by elemental analysis, IR spectroscopy, thermogravimetric and single-crystal X-ray diffractionanalyses. Compound 1 displays pucker layer structure formed from $<math>Zn^{2+}$ ions and μ_2 -H₂bta²⁻ and μ_4 -H₂bta²⁻ bridging ligands, and it

Introduction

The design and synthesis of new coordination polymers have received much attention recently owing to their interesting crystal structures and potential application in magnetism, electrical conductivity, luminescence, biology and catalysis etc. [1]. To date, a variety of coordination polymers with different structures based on different bridging ligands especially aromatic polycarboxylate ligands have been synthesized [2]. Among these ligands, benzene-1,2,4,5-tetracarboxylic acid (H₄bta) possesses several interesting characteristics. Firstly, it has four carboxyl groups inducing multiple coordination modes with transition metal centers and providing abundant structural motifs; Secondly, it can act not only as hydrogen bond donors but also as acceptors because of the existence of deprotonated and/or protonated carboxyl groups [2(h)-2(m), 3]. So it is regarded as an excellent candidate of bridging ligands to build different kinds of coordination polymers, including one dimensional (1D) chain [2(i), 2(k), 2(o), 3(a), 4(b)], two dimensional (2D) layer [2(h), 2(l), 4(a), 4(d)] and three dimensional (3D) network compounds [2(i), 3(d), 4(c)]. Furthermore, the introduction of a second aromatic organonitrogen ligands such as 1, 10-phenanthroline (phen) and 2, 2'-bipyridine are aslo important in the syntheses of coordination polymers and may provide potential supramolecular recognition sites for is linked into three dimensional (3D) supramolecular frameworks through the hydrogen bonds and π - π interactions. It exhibits strong blue fluorescence at room temperature in the solid state.

Keywords: Zinc; Coordination polymer; Benzene-1,2,4,5-tetracarboxylic acid; Hydrothermal synthesis; fluorescence

 π - π aromatic stacking interactions to form interesting structures [2(h), 5].

On the other hand, d^{10} metal coordination polymers are noted extensively because they exhibit not only intriguing structures but also photoluminescent properties [6]. One of our research interests is focused on a systematic study of the preparation of coordination polymers by using multicarboxylate bridging ligands and azacyclo terminal ligands and d^{10} metal. In this paper, we report a d^{10} metal coordination polymers $[Zn(\mu_2-H_2bta)_{1/2}(\mu_4-H_2bta)_{1/2}(phen)-(H_2O)]_n$ (1) which shows strong blue fluorescent emission at room temperature in the solid state.

Experimental Section

Materials and general methods

All chemicals were obtained commercially and used without further purification. Infrared spectrum was recorded as KBr pellets by using a Perkin-Elmer Spectrum One FT-IR spectrometer in the 4000-400 cm⁻¹ region. Elemental analyses for C, H and N were performed on a Perkin-Elmer 2400 element analyzer. Fluorescent data were obtained from an Edingburgh FS900 instrument at room temperature. Thermogravimetric analysis was performed on a Perkin-Elmer TGA-7 instrument with a heating rate of 20 °C·min⁻¹ in air.

Synthesis

 $[Zn(\mu_2-H_2bta)_{1/2}(\mu_4-H_2bta)_{1/2}(phen)(H_2O)]_n(1)$: A mixture of ZnCl₂ (0.14 g, 1.0 mmol), H₄bta (0.38 g, 1.5 mmol), 1,10-phen (0.12 g, 0.6 mmol) and H₂O (20 ml) was continuously stirred for 2 h in air at room temperature and the pH was adjusted to 3.0 with sodium hydroxide aqueous solution. The resulting solution was sealed in a 30 ml Teflon-lined stainless steel vessel and heated at 170 °C for 4



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days under autogenous pressure. After slowly cooling to ambient temperature, light yellow columnar crystals were obtained and washed with distilled water. The yield based on Zinc is approximately 48 %. Anal. Calc. (Found) for $C_{22}H_{14}N_2O_9Zn$ (%), C: 51.24 (51.07), H: 2.74 (2.63); N: 5.43 (5.45).

IR (KBr, pellet): $\delta(OH)$ 3258 s; $\delta(COOH)$ 1706 s; $v_{asym}(COO^{-})$ 1564 vs; $v(C-C)_{skeletal}$ 1518 m, 1494 m, 1426 m; $v_{sym}(COO^{-})$ 1358 s; $\delta(CH_{aromatic})_{in-plane}$ 1289 w, 1226 s, 1130 w, 1112 m; $\delta(CH_{aromatic})_{out-of-plane}$ 923 m, 850 s, 801 m, 776 w, 724 s cm⁻¹.

X-ray single-crystal structure determinations

Suitable single crystal of as-synthesized compound with the dimensions of $0.25 \times 0.15 \times 0.05$ mm for **1** was carefully selected and glued to thin glass fibers with epoxy resin. Data for compound **1** were collected on a Siemens SMART CCD diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å) at room temperature. The structure was solved by using the direct methods with SHELXL program and refined by full-matrix leastsquares technique. All of the non-hydrogen atoms were refined anisotropic parameters. All the hydrogen atoms were located from difference Fourier map and refined with isotropic temperature factors. The structure was then refined on F^2 with SHELXL-97. Details of the final refinements, the selected parameters of bond lengths, angles and hydrogen bonds of compound **1** are given in Table 1 and 2, respectively.

Crystal refinement data of 1

$$\begin{split} &[Zn(\mu_2-H_2bta)_{1/2}(\mu_4-H_2bta)_{1/2}(\text{phen})(H_2O)]_n &\equiv C_{22}H_{14}N_2O_9Zn, \\ &M = 515.72, \text{ triclinic, space group } P\overline{1}. \ a = 9.6922(9), \ b = \\ &10.2132(9), \ c = 11.3887(10) \text{ Å}, \ \alpha = 87.345(1)^\circ, \ \beta = 72.154(1)^\circ, \ \gamma = \\ &65.327(1)^\circ. \ V = 970.79(15) \text{ Å}^3. \ Z = 2. \ \rho_{calc} = 1.764 \text{ g/cm}^3. \\ &F(000) = 524. \ R(wR) = 0.0382(0.0896) \text{ for } 3865 \text{ reflections with} \\ &I>2\sigma(I). \end{split}$$

Results and Discussion

Synthesis

Compound 1 was synthesized under mid-temperature hydrothermal conditions and pH value of reaction system being 3.0. The pH value of reaction system and the reaction temperature are important factors effecting formation of compound 1. When pH value of reaction system being 6.0 and other reaction conditions being unchanged, compound $[Zn(\mu_4-bta)_{1/2}(phen)(H_2O)]_n$ (2) was got, in which benzene-1,2,4,5-tetracarboxylate ligands are fully deprotonated¹,



Fig. 1 Perspective view of crystal structure of 1, showing the coordination environments of Zn^{II} atoms and two kinds of coordination modes of μ_2 -H₂bta²⁻.

Table 1 Selected bond lengths /Å and bond angles $/^{\circ}$ for compound 1.

Zn(1)-OW1	2.0686(18)	OW1-Zn(1)-O(3)	95.98(7)
Zn(1)-O(3)	2.0957(15)	OW1-Zn(1)-N(1)	173.45(7)
Zn(1)-N(1)	2.1107(19)	O(3)-Zn(1)-N(1)	90.56(7)
Zn(1)-N(2)	2.1188(18)	OW1-Zn(1)-N(2)	94.33(8)
Zn(1)-O(2)	2.1303(15)	O(3)-Zn(1)-N(2)	169.65(7)
Zn(1)-O(1)	2.2110(16)	OW1-Zn(1)-O(2)	88.23(7)
O(1)-C(15)	1.292(3)	O(3)-Zn(1)-O(2)	94.67(6)
O(5)-C(15)	1.222(3)	N(1)-Zn(1)-O(2)	90.90(7)
O(2)-C(18)	1.251(3)	N(2)-Zn(1)-O(2)	86.49(7)
O(4)-C(18)	1.252(3)	OW1-Zn(1)-O(1)	84.90(8)
O(3B)-C(22)	1.233(3)	O(3)-Zn(1)-O(1)	84.65(6)
O(8)-C(22)	1.289(3)	N(1)-Zn(1)-O(1)	96.08(7)
O(6)-C(17)	1.315(3)	N(2)-Zn(1)-O(1)	95.43(6)
O(7)-C(17)	1.207(3)	O(2)-Zn(1)-O(1)	172.99(6)

Symmetry code: (B) 1+x, y, z;

while when pH value being larger than 7, only powder product was obtained. It can be explained that the compounds obtained under different pH value contain multicarboxylate ligands with different extent of deprotonation. In fact, when different metals react with the same multicarboxylic acid, different pH values of reaction system are required for getting the compound with multicarboxylate ligands possessing the same extent of deprotonation. For example, when pH value of reaction system being 7.0, the compound $\{[Fe(OH)(H_2bta)](H_2O)\}_n$ with partly deprotonated benzene-1,2,4,5-tetracarboxylate ligands rather than the compound with fully deprotonated one was obtained [8].

Additionally, reaction temperature and time are also important factors for the synthesis of compound **1**. When the reaction temperature was lower than 150 °C or the crystallization time was longer than 6 days, no perfect crystal product was obtained.

Structure description of 1

In the crystal structure of 1, which is isostructural with $[Co(C_{10}H_4O_8)(C_{12}H_8N_2)(H_2O)]$ [10], as shown in Figure 1, the Zn^{II} atom displaying distorted octahedral coordination

¹⁾ [Zn(μ_4 -bta)_{1/2}(phen)(H₂O)]_n (2) Compound 2 was obtained using procedure similar to that of 1, except that the pH was adjust to 6.0 with sodium hydroxide solution. Yellow crystals of 2 were obtained. The yield of crystal material was based on Zn^{II} is approximately 57 %, Anal. Calcd. (Found) for C₁₇H₁₁N₂O₅Zn (%), C: 52.53(52.63), H: 2.85(3.04); N: 7.21(7.05); Crystal data for 2: Monoclinic, *P*2₁/*n*, *a* = 7.9585(4), *b* = 11.7976(5), *c* = 15.3951(7), β = 99.6080, *V* = 100.416(2), *Z* = 4, λ (Mo K α) = 0.71073, *R*1 = 0.0331, *wR*2 = 0.0945 [*I*>2 σ (*I*)]; *R* indices (all data): *R*1 = 0.0346, *wR*2 = 0.0955; Reflections collected: 7843; Independent reflection (*R*_{int}): 2796 [*R*_{int} = 0.0424]. The result of single crystal structure determination indicates that compound 2 and the compound reported in ref. [7] are the same one. CCDC NO. 60797 for 2

Table 2	Hydrogen	bonds of	complex 1
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D-H···A···	d(D-H)/ Å	d(HA)/ Å	d(DA)/ Å	
				∠DHA/°
06-H10····O4A	0.907	1.710	2.593	163.58
O8-H12…O1B	1.056	1.457	2.484	162.30
OW1-H13O4	0.915	1.802	2.667	156.71
OW1-H14…O5 C	0.845	1.976	2.721	146.37
C20-H11O8	0.899	2.464	2.756	99.31
C13-H9…O6	0.881	2.362	2.693	102.45
C5-H5…O5 D	0.909	2.766	3.112	103.87

Symmetry code: (A) x-1, y+1, z; (B) x+1, y, z; (C) 1-x, 1-y, 1-z; (D) -x+1, -y+1, -z+1.

Table 3 Sum of bond-valences of oxygen atoms in compound 1^{a)}

Oi	O1	02	O3	O4	O5	O6 (b)	O7	O8 (t
Vi	1.77	1.77	2.00	1.64	1.63	1.24	1.64	1.32

^{a)} The valences of hydrogen bonds have been included in sum of bond-valences of oxygen atoms in the table; ^{b)} The valences of O-H bond do not have been included.

is coordinated by two nitrogen atoms N1, N2 from phen ligand, one water molecule Ow1, two oxygen atoms O2, O3 from two $\mu_4\text{-}H_2\text{bta}^{2-}$ groups and one oxygen atom O1 from μ_2 -H₂bta²⁻ group. H₂bta²⁻ ligands exhibit two kinds of coordination modes in compound 1, μ_4 -H₂bta²⁻ and μ_2 - H_2bta^{2-} . In μ_4 - H_2bta^{2-} bridging ligand the two carboxyl groups in para positions, O3B-C22-O8-H12 and O3A-C22A-O8A-H12A, are undeprotonated and this has been proved by sum of bond-valence being 1.32 for O8 [13] (Table 3). The other two carboxyl groups in μ_4 -H₂bta²⁻ are deprotonated and it has been justified by bond-valence sum being 1.77 and 1.64 for O2 and O4, respectively. It has been similarly justified that in μ_2 -H₂bta²⁻ ligand there are also two carboxyl groups, O7-C17-O6-H10 and O7A-C17A-O6A-H10A, being undeprotonated and the other two carboxyl groups being deprotonated. The located positions of hydrogen for undeprotonated carboxyl groups through sum of bond-valence of relevant oxygen atoms are in agreement with those found from difference Fourier map.

As shown in Figure 2, Zn^{II} atoms are connected into 1D ribbons along *a* axis by μ_4 -H₂bta²⁻ ligands through four monodentate-coordinated carboxyl groups, and two deprotonated carboxyl groups in para position of μ_2 -H₂bta²⁻ adopt monodentate-coordinated mode to bridge the 1D ribbons into 2D layer in [111] plane. In the layer there exist 14-membered A ring *ca*. (5.872(3) Å × 4.779(3) Å) and 34-membered B ring *ca*. (13.813(7) Å × 7.156(4) Å), in which coordinated phen are filled. There are π - π interactions between phen and μ_2 -H₂bta²⁻ which made the architecture more stable.

The adjacent 2D layers are connected through hydrogen bonding (Table 2) to form a 3D supramolecular network. Within the layer, the coordinated water molecule Ow1 as hydrogen donor bonds to O4 of μ_4 -H₂bta²⁻ as hydrogen acceptor, and O1B of coordinated carboxyl group of μ_2 -



Fig. 2 View of the 2D layer structure of 1.



Fig. 3 View of the hydrogen bonded network structure along the *a*-axis (phen ligands are omitted for clarity).

 H_2bta^{2-} as hydrogen acceptor bonds to O8 of undeprotonated carboxyl group from μ_4 - H_2bta^{2-} . The 2D layer structure becomes more stable because of the effect of the intralayer hydrogen bonding (Fig. 2). There are also interlayer hydrogen bonds which link 2D layers into 3D supramolecular structure in which channels with different size exist (Fig. 3). O5C of coordinated carboxyl group of μ_2 - H_2bta^{2-} as hydrogen acceptor bonds to water molecule Ow1; O6 of uncoordinated carboxyl group of μ_2 - H_2bta^{2-} as hydrogen donor bonds to O4A from μ_4 - H_2bta^{2-} . In addition, there exist also C-H···O hydrogen bonds in the supramolecular net work of compound 1.

Fluorescence properties

Solid-state fluorescence spectra of 1 and 2 at room temperature are depicted in Figure 4. The main peaks of 1 and 2 locate at the nearly same positions: 388(shoulder), 422(423),



Fig. 4 Solid-state fluorescence emission spectrum of 1 (a) and 2 (b) at room temperature.

460 and 486 nm upon excitation at 270 nm. According to the previously reported observation, intense fluorescence emission band with an emission maximum at 422 (423) nm may be assigned to the emission of ligand-to-metal charge transfer (LMCT) [6b]. The emission at 388 nm may be ascribed to intraligands charge transfer of coordinated phen because of its similarity to the emission of free phen·H₂O [11]. The emission bands at 460 and 486 nm are neither LMCT nor metal-to-ligand charge transfer (MLCT) in nature, but rather are assigned to intraligand emission, as reported for other zinc(II) complexes with *N*-donor ligands [12]. These research results reveal that compounds 1 and 2 may be potential intense blue light emitting materials due to their good thermal stability and non-solubility in water and common organic solvents.

Thermogravimetric analysis

The thermal properties of complexes 1 and 2 were measured between 30-800 °C. The results show that both compounds possess very similar thermal behavior. These two compounds are thermally stable until around 140 °C. Weightloss is ca. 3.21 % (calc. 3.49 %) for 1 and 5.02 % (calc. 4.63 %) for 2 between 140-170 °C, corresponding to loss of one coordinated H₂O per formula unit. Compounds 1 and 2 after losing coordination water are still stable until 380 °C. Both weight-loss of 35.07 % (calc. 34.90 %) for 1 and 46.54 % (calc. 46.31 %) for 2 correspond to losing phen ligands. The final weight-loss steps from 470 to 660 °C for 1 and from 500 to 590 °C for 2 are corresponding to releasing benzene-1,2,4,5-carboxylate ligands and give ZnO as final decomposition product about equalling to 16.31 % (calc. 15.71 %) and 20.56 % (calc. 20.84 %) of weights of measured samples for 1 and 2, respectively. Above-mentioned results indicate both compounds 1 and 2 have good thermal stability.

Conclusions

Through controlling pH value of reaction systems two structurally different zinc complexes involving benzene1,2,4,5-tetracarboxylate as bridging ligands were hydrothermally synthesized in which compound **1** has a covalent layer structure and compound **2** has a covalent chain structure although the structure of compound **2** has been reported already [7]. Both compounds exhibit good thermal stability and intense blue photoluminescence in the solid state.

CCDC 607896 (1) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conta/retrieving.html or form the Cambridge Crystallographic Data Center, 12, Union Rood Cambridge. CB2 1EZ, UK; fax: (internat.) +44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk

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