

以 3, 5-二甲基-1*H*-1, 2, 4-三氮唑及对苯二甲酸根构筑的三维锌配位聚合物的合成、晶体结构及荧光性质

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摘要: 水热法合成了 1 个新颖的锌配位聚合物 $\{[\text{Zn}_3(\text{Hdmtrz})_2(1,4\text{-bdc})_3] \cdot 2\text{H}_2\text{O}\}_n$ (**1**, Hdmtrz =3,5-二甲基-1-*H*-1,2,4-三氮唑, 1,4-bdc=对苯二甲酸根), 对其进行了红外光谱、元素分析、X 射线粉末衍射和热重分析等表征, 并用 X-射线单晶衍射法测定了配合物的单晶结构。该配合物属三斜晶系, $P\bar{1}$ 空间群, 晶胞参数为 $a=0.917\ 97(18)\ \text{nm}$, $b=0.983\ 3(2)\ \text{nm}$, $c=1.071\ 7(2)\ \text{nm}$, $\alpha=100.81(3)^\circ$, $\beta=102.589(3)^\circ$, $\gamma=106.90(3)^\circ$, $V=0.8418(3)\ \text{nm}^3$, $Z=1$ 。该化合物为三维框架结构, 拓扑类型为 $pcu\ \alpha\text{-Po}$ 简单立方格子, Schläfli 符号记为 $\{4^{12}\cdot 6^3\}$ 。室温固态荧光测试显示, 配合物在 471 nm (λ_{max}) 具有强的荧光吸收。

关键词: 锌配合物; 晶体结构; 拓扑结构; 荧光性质

中图分类号: O614.24[†]

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Synthesis, Structures and Luminescence Property of a 3D Zinc Coordination Polymer Based on 3, 5-Dimethyl-1*H*-1, 2, 4-triazole and 1,4-Benzenedicarboxylate Dianion

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Abstract: A new zinc(II) coordination polymer $\{[\text{Zn}_3(\text{Hdmtrz})_2(1,4\text{-bdc})_3] \cdot 2\text{H}_2\text{O}\}_n$ (**1**), where Hdmtrz =3,5-dimethyl-1-*H*-1,2,4-triazole and 1,4-bdc=1,4-benzenedicarboxylate dianion, has been prepared by hydrothermal method and structurally characterized by elemental analysis, infrared spectra, X-ray powder diffraction, thermogravimetric analysis and single-crystal X-ray diffraction. The title compound crystallizes in triclinic, space group $P\bar{1}$ with $a=0.917\ 97(18)\ \text{nm}$, $b=0.983\ 3(2)\ \text{nm}$, $c=1.071\ 7(2)\ \text{nm}$, $\alpha=100.81(3)^\circ$, $\beta=102.589(3)^\circ$, $\gamma=106.90(3)^\circ$, $V=0.841\ 8(3)\ \text{nm}^3$, $Z=1$, and compound **1** shows a 3D framework with Schläfli symbols of $\{4^{12}\cdot 6^3\}$ which is a typical $pcu(\alpha\text{-Po})$ structure. The zinc(II) complex exhibits strong fluorescence absorption at 471 nm (λ_{max}) in the solid state at room temperature. CCDC: 771399.

Key words: Zn(II) coordination polymer; crystal structure; topology; luminescence

The design and synthesis of novel functional metal-organic frameworks (MOFs) have been spotlighted because of their diverse structural topologies and potential applications in gas storage,

magnetism, catalysis, and luminescence^[1-7]. Regardless, rationally preparing and controlling the structures and composition of target products in crystal engineering remain challenging. The construction of MOFs is

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influenced by both structural and experimental factors, such as organic ligands, pH values, temperature, solvents etc.^[8-9]. In practice, choosing or designing a suitable ligand is the most important strategy in constructing the MOFs with targeted structures and properties.

Unsubstituted or substituted 1,2,4-triazole (trz), which is a small five-membered heterocyclic simple molecule, acts as a neutral bridging ligand for two metal sites or for three metal centers in the anionic form in $\mu_{1,2}$, $\mu_{2,4}$ or $\mu_{1,2,4}$ modes^[10-11]. Aromatic carboxylate, as one of the functional ligands displaying various coordination modes, has been introduced into trz-based metal complexes as coligands by hydrothermal method, and a series of novel 3-D topological frameworks have been produced unexpectedly. Aromatic polycarboxylate coligand dominates in tuning the nuclearity of metal-trz clusters and the connectivity of a specific network^[12-13]. Despite the exciting progress, only limited trz-based complexes with aromatic acid as coligand have been reported hitherto probably owing to the insoluble and intractable polycrystalline powders during the preparation^[14].

Therefore, it is necessary to systematically explore the coordination behaviors of aromatic acid/trz/metal system. In this work, a novel dmtrz-based complexes, $\{[\text{Zn}_3(\text{Hdmtrz})_2(1,4\text{-bdc})_3] \cdot 2\text{H}_2\text{O}\}_n$ (**1**), was successfully isolated by incorporating 1,4-benzenedicarboxylate dianion (1,4-bdc) as coligand through hydrothermal synthesis.

1 Experimental

1.1 Materials and measurements

All commercially available chemicals were of reagent grade and were used as received without further purification. Elemental analysis of C, H and N was performed on a Perkin-Elmer 240 elemental analyzer. Infrared (IR) spectra were recorded on a Bruker Vector22 FTIR spectro-photometer by using KBr pellets. X-ray powder diffraction (XRPD) data were obtained on a Rigaku X-ray powder diffractometer D/MAX 2000/PC. Luminescence

spectra for the powdered solid samples were recorded at room temperature on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. Emission and excitation spectra were measured with the pass width of 5 nm. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with a simultaneous NETZSCH STA 449F3 thermal analyzer underflowing N_2 ($20 \text{ mL} \cdot \text{min}^{-1}$) from 50 to 900°C at the heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$.

1.2 Synthesis of $\{[\text{Zn}_3(\text{Hdmtrz})_2(1,4\text{-bdc})_3] \cdot 2\text{H}_2\text{O}\}_n$ (**1**)

1.2.1 Synthesis of **1**

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol), 1,4-H₂bdc (0.5 mmol), Hdmtrz (0.5 mmol), and water (10 mL) was placed in a Teflon reactor (23 mL). After adjusting the pH to 6.0 by adding triethylamine, the mixture was heated at 165°C for three days, and then it was cooled to room temperature at the rate of $10^\circ\text{C} \cdot \text{h}^{-1}$. Colorless crystals of **1** were obtained in 38% yield (based on Zn). Elemental Analysis (%) Calcd.: C 41.84, H 3.29, N 9.15; Found: C 41.68, H 3.49, N 9.03; IR (cm^{-1} , KBr): 3 454 (w), 3 168(w), 3 057(w), 2 967 (w), 2 923 (w), 1 595 (s), 1 503 (m), 1 392(s), 1 370 (s), 1 341 (s), 1 142 (w), 1 092 (w), 1 052(w), 1 015(w), 888(w), 820(w), 747(s), 548(w), 515(w).

1.2.2 Single-crystal X-ray diffraction measurements

Single-crystal data were collected at 293(2) K on a Rigaku SCXmini CCD diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation. The structure was solved using direct methods and successive Fourier difference synthesis (SHELXS-97)^[15], and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all nonhydrogen atoms (SHELXL-97)^[16]. Hydrogen atoms bonded to the carbon atoms were placed in calculated positions and refined as riding mode, with C-H 0.093 nm and $U_{\text{eq}}(\text{H})=1.2 U_{\text{eq}}(\text{C})$. Water hydrogen atoms were located in the difference Fourier maps and refined with an OH distance restraint (0.090 nm) and $U_{\text{eq}}(\text{H})=1.5 U_{\text{eq}}(\text{O})$. The crystal data, details on the data collection and refinement of **1** are summarized in Table 1.

CCDC: 771399.

Table 1 Crystal data and refinement results for complex **1**

Empirical formular	C ₃₂ H ₃₀ N ₆ O ₁₄ Zn ₃	<i>Z</i>	1
Formula weight	918.73	<i>T</i> / K	293(2)
Crystal system	triclinic	<i>D_c</i> / (g·cm ⁻³)	1.812
Space group	<i>P</i> $\bar{1}$	μ / mm ⁻¹	2.202
<i>a</i> / nm	0.917 97(18)	<i>F</i> (000)	466
<i>b</i> / nm	0.983 3(2)	Collected reflections	8 666/3 827 (<i>R_{int}</i> =0.052 0)
<i>c</i> / nm	1.071 7(2)	<i>R</i> ₁ ^[a] , <i>wR</i> ₂ ^[b] (<i>I</i> >2σ(<i>I</i>))	<i>R</i> ₁ =0.061 8, <i>wR</i> ₂ =0.172 6
α / (°)	100.81(3)	<i>R</i> ₁ ^[a] , <i>wR</i> ₂ ^[b] [all data]	<i>R</i> ₁ =0.087 1, <i>wR</i> ₂ =0.188 4
β / (°)	107.49(3)	Largest diff. peak and hole / (e·nm ⁻³)	1 007 and -1 927
γ / (°)	106.90(3)	GOF	1.169
<i>V</i> / nm ³	0.841 8(3)		

$$^{[a]} R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; ^{[b]} wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w[(F_o^2)^2]]^{1/2}$$

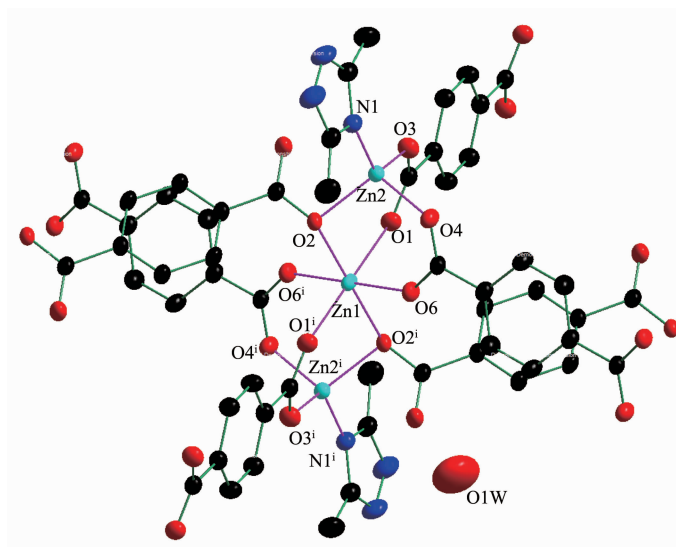
2 Results and discussion

2.1 Crystal structure of {[Zn₃(Hdmtrz)₂(1,4-bdc)₃·2H₂O]_n (**1**)}

The complex crystallizes in the triclinic space group *P* $\bar{1}$ and shows a dense 3D framework structure comprising a centrosymmetric linear array of three zinc ions, which are coordinated by three 1,4-bdc and two neutral Hdmtrz ligands. The middle zinc atom, which occupies a special position and lies on the crystallographic inversion centre, is octahedrally coordinated by six oxygen atoms from six 1,4-bdc. Each of the two terminal zinc ions is coordinated

tetrahedrally by three oxygen atoms from 1,4-bdc and nitrogen (N3) atom from the Hdmtrz molecule (Fig.1).

There are two types of carboxylate coordination in this complex. two 1,4-bdc are bidentate-coordinated by both oxygen atoms of carboxylate, forming synsyn bridges between central and terminal zinc ions. The other one is monodentate-coordinated and function as monatomic Zn-O-Zn bridges with one oxygen atom which remains uncoordinated and involved only in a weak interaction with the zinc atom (Zn2 ... O5 0.268 24(39) nm). The lengths of ZnO bonds in the carboxylate ligands of complex **1** range from 0.190 9(4) to 0.222 8(3) nm (Table 2). Since the shortest distance



Displacement ellipsoids are drawn at 30% probability level; H atoms are omitted for clarity; Symmetry code: ⁱ -3-*x*, -2-*y*, 2-*z*

Fig.1 Coordination environment of Zn(II) in complex **1**

Table 2 Selected bond lengths (nm) and angles ($^{\circ}$) of **1**

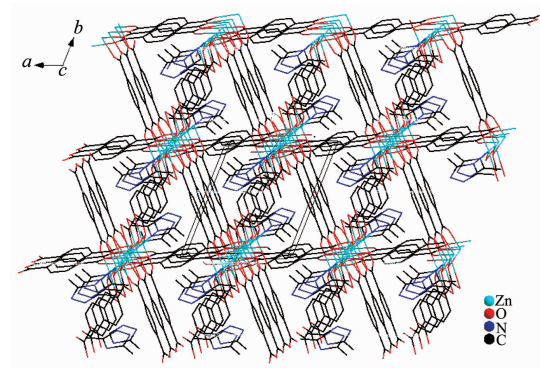
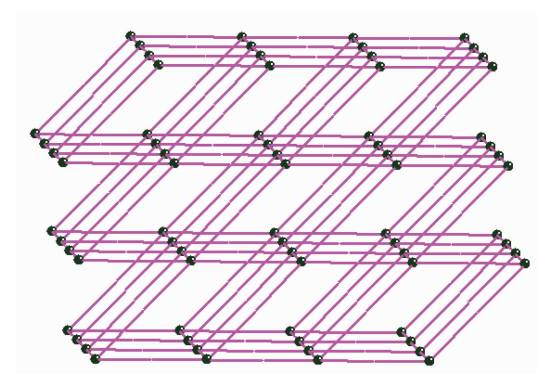
Zn1-O6	0.202 0(3)	Zn1-O6 ⁱ	0.202 0(3)	Zn1-O2	0.214 7(3)
Zn1-O2 ⁱ	0.214 7(3)	Zn1-O1 ⁱ	0.222 8(3)	Zn1-O1	0.222 8(3)
Zn2-O3	0.190 9(4)	Zn2 ⁱ -O4	0.196 9(4)	Zn2-N1	0.197 3(4)
Zn2 ⁱ -O2	0.201 4(3)				
O6-Zn1-O6 ⁱ	180.000(1)	O6-Zn1-O2	93.54(13)	O6 ⁱ -Zn1-O2	86.46(13)
O6-Zn1-O2 ⁱ	86.46(13)	O6 ⁱ -Zn1-O2 ⁱ	93.54(13)	O6-Zn1-O1 ⁱ	87.73(14)
O2-Zn1-O2 ⁱ	180.000(1)	O6 ⁱ -Zn1-O1 ⁱ	92.27(14)	O2-Zn1-O1 ⁱ	90.62(13)
O2 ⁱ -Zn1-O1 ⁱ	89.38(13)	O6-Zn1-O1	92.27(14)	O6 ⁱ -Zn1-O1	87.73(14)
O2-Zn1-O1	89.38(13)	O2 ⁱ -Zn1-O1	90.62(13)	O1 ⁱ -Zn1-O1	180.000(1)
O3-Zn2-O4	105.47(16)	O3-Zn2-N1	118.99(17)	O4-Zn2-N1	106.48(16)
O3-Zn2-O2	114.33(15)	O4-Zn2-O2	104.79(15)	N1-Zn2-O2	105.66(15)

Symmetry codes: ⁱ $-3-x, -2-y, -2-z$

from the host atom (N2) to the water oxygen atom (O1W) is 0.300 2(12) nm, the guest H₂O molecules are stabilized by hydrogen bonding interactions.

On average, the bond lengths and angles are slightly larger than those of similar zinc 1,4-bdc complexes. Four oxygen atoms of the 1,4-bdc groups form an equatorial plane of the octahedron around Zn1, with the distances of 0.202 0 (3), 0.202 0(3), 0.214 7 (3) and 0.2147 (3) nm, respectively. Apical positions of the octahedron are occupied by oxygen atoms (O1) (Zn1-O1 distances 0.222 8 (3) nm). The bond angles around Zn1 vary from 86.46(13) $^{\circ}$ to 180.000(1) $^{\circ}$. Zn2 is four-coordinated by three O atoms from symmetrically related 1,4-bdc ligands and one N atom from one neutral Hdmtrz molecule. The distance of Zn2-N1 is 0.197 3 (4) nm, and those of Zn2-O are in the range of 0.190 9 (4)~0.201 4 (3) nm. The bond angles around Zn2 vary from 104.79(15) $^{\circ}$ to 118.99(17) $^{\circ}$. In other words, 1,4-bdc ligands construct the 3D framework structure of complex **1** by connecting zinc ions (Fig.2).

The intricate framework structure of **1** was further investigated by topological analysis^[17-18]. As discussed above, each metal trinuclear unit can be defined as a six-connecting node, and each 1,4-bdc ligand is regarded as connection by only linking two metal trinuclear units. Consequently, the 3D net with $\{4^{12} \cdot$

Fig.2 3D network structure of complex **1**

The red lines represent the bdc ligands, and the black spheres show the connection of trimer Zn₃ units

Fig.3 Schematic plot of the 3D network of **1**

$6^3\}$ topology shows a typical *pcu* (α -Po) structure (Fig.3).

2.2 XRPD patterns of complex **1**

Complex **1** was characterized by XRPD at room temperature. As shown in Fig.4, the patterns

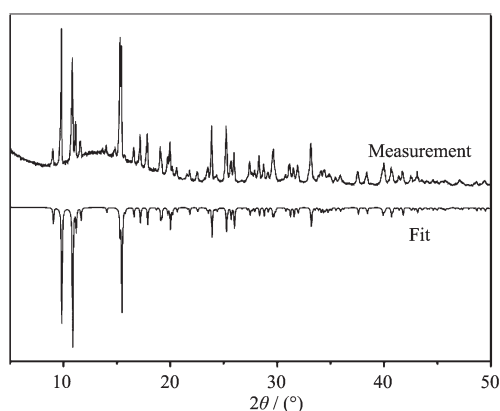


Fig.4 Experimental and simulated XRPD patterns of **1**

calculated from the single-crystal X-ray data of **1** well accord with the observed ones in almost identical peak position but with different peak intensities.

2.3 Photoluminescent property study

Fluorescence properties of coordination polymers of **1** have been investigated for potential applications as fluorescence-emitting materials [19]. Due to the influence of organic materials on emission wavelength, novel luminescent materials based on inorganic-organic coordination polymers can feasibly be fabricated by the rationally selecting organic spacers and metal centers [20-21]. It is well known that metal-organic polymeric complexes with a d^{10} closed-shell electronic configuration are fluorescent. The solid-state fluorescence spectra of **1** at room temperature are presented in Fig.5 to examine the luminescent properties. Complex **1** emits emission at 471 nm upon excitation at 390 nm, which can be attributed to the ligand chelation to the metal center, and the deprotonation of aromatic acid [22-23].

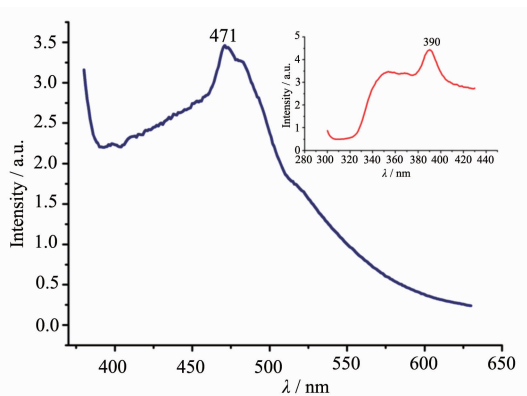


Fig.5 Emission spectra of complex **1** in the solid state

2.4 TGA

TGA of the crystalline sample (3.187 mg) of **1** was performed in flowing N_2 at the heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. As displayed in Fig.5, one can see that one consecutive weight loss occurs under $400\text{ }^\circ\text{C}$, which is corresponded to the loss of two water molecules per formula (Calcd. 3.92%). An abrupt weight loss occurs from 400 to $800\text{ }^\circ\text{C}$ corresponding to the complete framework decomposition of **1**, which associated with two endothermic peaks at $445\text{ }^\circ\text{C}$, $860\text{ }^\circ\text{C}$ and an exothermic peak at $596\text{ }^\circ\text{C}$ in its DSC curve.

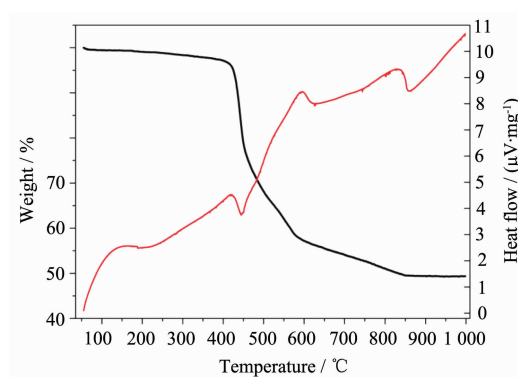


Fig.6 TGA/DSC curves of the complex **1**

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