5-取代-1-氢四唑合成中捕获的一个新奇的三维镉配聚物

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摘要: 在水热条件下,1,4-对二氰基苯,氯化镉以及叠氮化纳反应,成功地组装了一个三维网状镉四唑配位聚合物[monoaqua-4-tetrazolyl-benzenecarboxylate cadmium(Ⅱ) (**1**)],该化合物并不是预期的双四唑镉配位聚合物,而是其中一个氰基水解成羧基形成了单四唑镉配位聚合物。晶体结构分析表明,化合物 **1** 具有 PtS 的拓扑结构,室温下,化合物 **1** 显示强的蓝色荧光。

关键词: 镉; 水热合成; 配位聚合物; 荧光
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An Unexpected Intermediate or Precipitate——Novel 3D Cd-Coordination Polymer Formed in the Preparation of 5-Substituted 1H-Tetrazoles from Nitrile in Water

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Abstract: The hydrothermal reaction of 1,4-dicyanobenzene with NaN_3 in the presence of H_2O and Lewis acid ($CdCl_2$) unexpectedly affords a novel mono-tetrazole Cd coordination polymer, monoaqua-4-tetrazolyl-benzenecarboxylate cadmium(Ⅱ) (Te-Ph-CA)Cd(H_2O) (**1**) , rather than an expected Sharpless′s precipitate product with bis(tetrazolyl)benzene ligand. 3D Network of **1** with a PtS topology highlights the importance in construction novel supramolecular motifs through in situ ligand-synthesis. Its strong blue fluorescent property is also reported. CCDC: 215388.

Key words: Cd; hydrothermal reaction; coordination polymer; fluorescent

0 Introduction

Tetrazole ligand can be formed by the reaction of cyano group with NaN_3 in the presence of $ZnBr_2$ (Lewis acid) as a catalyst and water under reflux or hydrothermal reaction condition[1,2]. Due to the formation of tetrazole ligand through a decomposition of solid precipitate or intermediate, the nature (composition and structure) of the intermediate is very important for one to synthesize tetrazole ligand and optimize reaction condition. Recently, we have successfully trapped and structurally characterized many intermediates in which organic part contains one cyano group or two cyano groups, and they competely formed mono-tetrazolyl or bi-tetrazolyl organic ligand although the intermediates are quite different and complicate (Scheme 1). The results supports Sharpless′s proposed mechanism[1]. To this end, we extend this method to the preparation of bi-tetrazole ligand by the hydrothermal reaction of 1,4-dicyanoaromatic compound and NaN_3 with $CdCl_2$ (Scheme 2). To our surprise, the intermediate only contains mono-tetrazolyl group while another cyano group cannot be transferred to tetrazolyl group in this reaction condition, but oxidized into car-

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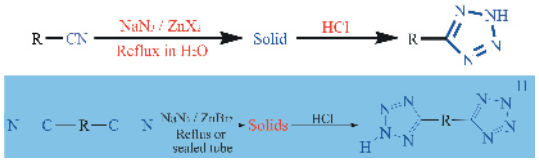
boxylate group. Herein we report the solid state structure and fluorescent property of an unexpected intermediate or precipitate formed in the preparation of 5-substituted 1H-bis-tetrazoles from di-nitrile in water used $CdCl_2$ as kewis acid.



Scheme 1

Scheme 2

1 Experimental

Chemicals and solvents in this work were purchased from Aldrich and used as received. Caution: Aza salts are explosive and should be handled with great care. The FTIR spectra were recorded as solid in KBr matrix in the range 4 000~400 cm^{-1} on Nicolet Inpact 170S FTIR spectrometer. Elemental analyses were performed on Perkin-Elmer 240C elemental analyzer.

1.1 Synthesis of monoaqua-4-tetrazolyl-benzenecarboxylate cadmium(Ⅱ) (Te-Ph-CA)Cd(H_2O) (1)

Hydrothermal treatment of $CdCl_2$ (1.0 mmol), 1,4-dicyanobenzene (1.0 mmol), NaN_3 (2.5 mmol) and water (2 mL) for 2 days at 160 ℃ yielded a pale-yellow block crystalline **1** with only one pure phase. The yield of **1** was about 55% based on 1,4-dicyanobenzene. Anal. calc. for $C_8H_6N_4O_3Cd$: C, 30.13; H, 1.88; N, 17.58. Found: C, 30.24; H, 1.75; N, 17.70. IR (KBr, cm^{-1}): 3 374 (br, m), 3 086 (w), 1 681(m), 1 588 (s), 1 527(s), 1 422 (s), 1 406 (w), 1 356 (m), 1 307(w), 1 291 (m), 1 253(m), 1 169 (w), 1 102(w), 1 014 (m), 865 (m), 791 (m), 774 (m), 731 (w), 704(w), 536 (w), 508 (w).

1.2 Single crystal structure determination

A single crystal of **1** was prepared as described above; a pale yellow block crystal with a dimension of 0.05 mm × 0.1 mm × 0.1 mm was employed for structural analysis. Suitable single crystals of **1** were selected under a polarizing microscope and fixed with epoxy cement on fine glass fibres which were then mounted on a Bruker P4 diffractomerter with graphite-monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm) for cell determination and the subsequent data collection. The crystal structures were solved using direct methods with the help of the SHELXS-97 program[3]. Subsequent difference Fourier syntheses enabled all heavier atoms to be located. After several cycles of refinement, all hydrogen atoms were located from the successive difference Fourier syntheses. All non-hydrogen atoms were finally refined with anisotropic displacement parameters by full-matrix least-squares techniques. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. Detailed information about the crystal data and structure determination are summarized in Table 1. Selected inter atomic distances and bond angles are given in Table 2.

CCDC: 215388.

Table 1 Crystal data and structure refinement for 1

Empirical formula	$C_8H_6CdN_4O_3$
Formula weight	318.57
T / K	293(2)
Wavelength / nm	0.071 073
Crystal system	Monoclinic
Space group	$P2_1/c$
a / nm	1.246 26(8)
b / nm	0.734 38(5)
c / nm	1.076 62(7)
β / (°)	107.0830(10)
V / nm^3	0.941 88(11)
Z	4
ρ(cald) / ($g\cdot cm^{-3}$)	2.247
μ(Mo $K\alpha$)/ mm^{-1}	2.315
F(000)	616
Crystal size / mm	0.05 × 0.1 × 0.1
θ range for data collection /(°)	2.60~33.37
Index ranges	$-17\leqslant h\leqslant 19$, $-10\leqslant k\leqslant 10$, $-16\leqslant l\leqslant 13$
Reflections collected	8 564
Independent reflections	3 398 [R(int)=0.036 5]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3 398 / 0 / 153
Final R indices [$I>2\sigma(I)$]	R_1=0.035 5, wR_2=0.029 3
R indices (all data)	R_1=0.093 3, wR_2=0.085 2

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

Cd1-O1A	0.221 9(2)	Cd1-O1W	0.232 2(2)	Cd1-N1B	0.232 45(18)
Cd1-N4	0.233 54(19)	Cd1-N3C	0.237 2(2)	Cd1-O2A	0.247 8(2)
N3-N2	0.133 6(3)	N2-N1	0.130 6(3)		
O1W-Cd1-N1B	82.15(8)	O1A-Cd1-N4	103.00(7)	N1B-Cd1-N3C	87.31(7)
N4-Cd1-N3	95.40(8)	N4-Cd1-O2A	158.42(6)	N3C-Cd1-O2A	89.82(7)
O1A-Cd1-O1W	89.63(8)	O1A-Cd1-N1B	151.46(7)	O1W-Cd1-N1	82.15(8)
O1W-Cd1-N4	84.41(8)	N1B-Cd1-N4	103.32(7)	O1A-Cd1-N3C	101.00(8)
O1W-Cd1-N3C	169.10(8)	O1A-Cd1-O2A	55.43(7)	O1W-Cd1-O2A	94.32(8)
N1B-Cd1-O2A	97.81(6)				

Symmetry transformation use to generate equivalent atoms: A: 2–*x*, 1/2+*y*, 3/2+*z*; B: 1–*x*, –*y*, 1–*z*; C: *x*, –1/2–*y*, 1/2+*z*.

2 Results and discussion

Pale yellow monoaqua-4-tetrazolyl-benzenecarboxylate cadmium(Ⅱ) (**1**) was obtained by the hydrothermal reaction of 1,4-dicyanobenzene and NaN_3 with $CdCl_2$. In its IR spectrum, a peak at 1 422 cm^{-1} suggests the formation of tetrazole group occurred, while two strong peak at 1 588 and 1 527cm^{-1} indicates the intermediate contains a carboxylate group in it. A broad peak at 3 374 cm^{-1} suggests water molecule may present in **1**. All of these are confirmed by solid state single crystal structure determination late. Additionally the IR spectrum indicates that no azide group is presented in **1**, quite different from that found in CdN_3 (3-ptz)(ptz=5-(3-pyridyl) tetrazolate)[2].

The Three-dimensional polymeric structure of **1** is revealed by X-ray single crystal diffraction study. The local coordination geometry around the Cd(Ⅱ) center in **1** can be best described as a slightly octahedron (Fig.1). The Cd(Ⅱ) center is bonded to three O atoms from a μ_2-carboxylate and water, and to three tetrazole nitrogen atoms from three different tetrazole moieties. Overall, 4-tetrazolyl-benzenecarboxylate ligand in **1** acts as pentadendate bridging linker to connect four Cd centers, result in the formation of a 3D network, as shown in Fig.2. Furthermore, the tetrazole moiety in the ligand is used as tridentate spacer to link three Cd(Ⅱ) centers resulting in the formation of a six-membered ring (Cd1-N4-N1-Cd1C-N4C-N1C) composed of two Cd atoms and four N atoms (Fig.1). The Cd-O distances (0.221 9~0.247 8 nm) are quite similar to normal Cd-OCO distance (0.230 7~0.244 8 nm) found in [(TPT) (py)Cd] (TPT =terephthalato)[4a] [Cd (2-PBEA)$_2$ (H_2O)] (PBEA=4-[2-(2-pyridyl)ethenyl]benzoate)[4b] and [Cd(μ_2-H_2O)(L_2)) (L=4-quinolinecarboxylato)[4c]. Apparently Cd-O_{water} bond length (0.232 2(2) nm) is slightly longer than one of Cd-$O_{carboxylate}$ in **1**, lead to the easy removal of water as supported by TGA [thermogravimetric analysis was performed on the polycrystalline sample, indicating that one strike clean weight loss step occurred at *ca.* 116 ℃ (5.45% loss), corresponding to the removal of one water molecule per formula unit (5.65% calc.) while no weight loss was recorded

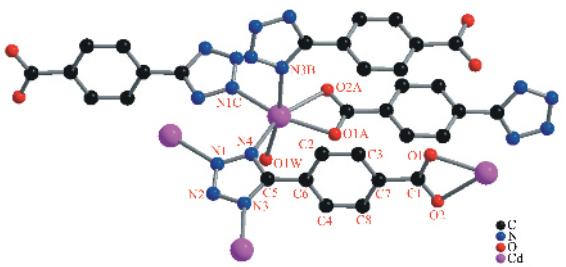


Fig.1 An asymmetric unit representation of **1** in which Cd center displays six-coordinated geometry

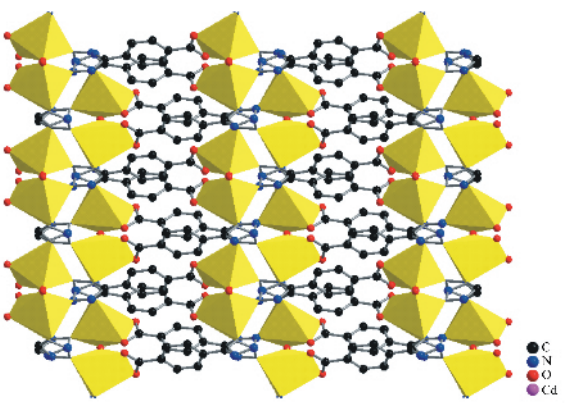


Fig.2 A three-dimensional view of **1** along with *c*-axis highlighting the Cd octahedron

between the temperature 116 and 460 ℃, probably suggesting the formation of a stable phase formulated as (Te-Ph-CA)Cd]. It is clear that the bond distances of Cd-Ntetrazole (0.232 4~0.237 2 nm) are comparable to those found in $Cd_3(OH)Cl_2$(4-PTZ) and Cd(4-PTZ)$_2$ $(H_2O)_2$ (4-PTZ=5-(4-pyridyl)tetrazole)[2].

From a topological perspective the underlying network is particularly interesting. The structure can be best described as related to PtS topology. If 4-tetrazolyl-benzenecarboxylate is treated as a baricenter of the tetrazole (baricenter 0.588-0.234-0.359) the ligand becomes 4-connected and the Cd 4-connected too (the water molecule contributes with some extra H-bonds that can be ignored in the topological analysis of the network). The μ_2 carboxylic group is assumed one-connected since is bounded only to one Cd atom. The distances baricenter-tetrazole: Cd are 3.450, 3.438, 3.495, 9.527 (Fig.3). The analysis of the simplified net with only baricenters and Cd atoms give a binodal net of PtS topology with the ligand equivalent-to the square planar Pt and the cadmium atoms to the tetrahedral sulphur atoms in PtS (Fig.4). The network

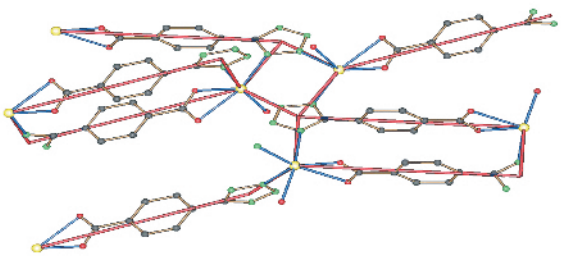


Fig.3　A simple picture of **1** in which Cd center has 4-connections

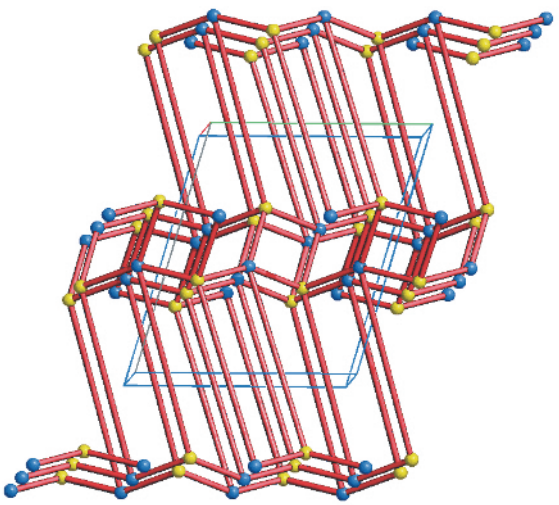


Fig.4　A PtS-like network representation of **1**

is single and not interpenetrated but quite distorted. Several examples of PtS networks are known[5]. However, to the best of our knowledge, **1** is the first example of tetrazole metal coordination polymer with such topology even through there is many tetrazole metal coordination compounds reported in the literature[6].

The most important feature of the structure of 1 is that its three-dimensionally condensed polymeric structure leads to the significant enhancement of fluorescent intensity, *ca.* 5~6 times larger than that of the free ligand, probably due to coordination of 4-tetrazolyl-benzenecarboxylate to Cd(Ⅱ) increasing the ligand conformation rigidity, thereby reducing the nonradiative decay of the intraligand excited state. Similar enhancement of the intraligand fluorescent has also been reported for $[Zn(Norf)_2 \cdot 4H_2O]_n$ (Norf =norfloxacin)[7a], $[Cd(TPT)(Py)]_n$[4a] and $[Zn(PEBA)_2]_n$ (PEBA=4-[2-(4-pyridyl)ethenyl]benzoato)[7b]. The emission of **1** λ_{max}= 465 nm (Fig.5) is neither MLCT (metal-to-ligand-charge-transfer) nor LMCT (ligand-to-metal-charge-transfer) in nature, and can tentatively be assigned to the intraligand fluorescent emission since a weakly similar emission (λ_{max}=472 nm) is recorded for the free H_2Te-Ph-CA.

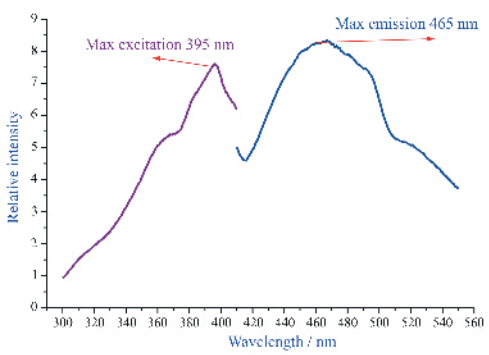


Fig.5　Solid state fluorescent emission of **1** at room temperature

In conclusion, althogh compound **1** contains one tetrazole gronp in ligand rather than the anticipated two tetrazole in ligand, the succesful generation of the tetrazole ring in copound **1** is consistent with Demko — Sharpless suggestion that the solid intermediates formed in their generation of substituted tetrazoles are tetrazolato complexes. The results also provide strong encoutagement that novel metal coordination polymers may be produced by the hydrothernal generation of bridging ligands in the presence of appropriate metal ions.

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