Hydrothermal Synthesis, Crystal Structure and Properties of a 1D Metal-organic Coordination Polymer $[Cd(pztmb)_2(H_2O)_2]_n$

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Hydrothermal reaction of $Cd(NO_3)_2 \cdot 4H_2O$ with a flexible asymmetrical bridging ligand, 4-(2-pyrazinylthiomethyl)benzoic acid (Hpztmb), at 120 °C yielded a novel one-dimensional Cd(II) coordination polymer $[Cd(pztmb)_2(H_2O)_2]_n$ (**1**), which has been characterized by IR spectroscopy, elemental analysis, thermogravimetry, and X-ray crystallography. The metal-organic chain of the complex is held together with its neighbors *via* O-H···O hydrogen bonds and face-to-face π-π interactions leading to a three-dimensional supramolecular network. Compound **1** exhibits a fluorescence emission around 396 nm.

Key words: 4-(2-Pyrazinylthiomethyl)benzoic Acid, Metal-organic Chain, Hydrogen Bond, π-π Interactions, Supramolecular Structure

Introduction

The design and synthesis of functional metal-organic frameworks are of great interest owing to their fascinating variety of architectures and topologies, as well as due to their potential applications as microporous, magnetic, nonlinear optical, and fluorescent materials [1 – 8]. In principle, some control over the topology of supramolecular architectures can be gained by a judicious selection of reaction-influencing factors, such as the structure of the organic ligand, the coordination geometry preference of the metal, the solvent system, the temperature, the inorganic counterions [9, 10], the action of a template, the metal-to-ligand ratio [11 – 13], and even the crystallization method [14 – 16]. Among them, a particularly challenging and critical issue in this field is the rational choice and assembly of metal ions and organic bridging ligands [17]. Much interest is focused at present on the construction of Cd(II)-containing coordination polymers in view of the ability of this cation to form bonds with different donors simultaneously, its large radius, and variable coordination modes [18, 19]. Some coordination polymers, in particular those containing long and flexible monoanionic ligands with hybrid pyridyl or pyrimidyl and benzoic carboxylate moieties have recently been reported [20, 21]. With the aim of a better understanding of the influence of N-heterocyclic rings on the resultant structure and preparing new materials with interesting structural topologies and optimized physical properties, we are currently engaged in the research of self-assembly reactions between metal ions and sulfur-containing asymmetrical linkers [22]. Sulfide moieties are well known as redox-active functional groups that could enhance electronic asymmetry in the products [23].

According to the situation above, for the work presented in this paper we selected the relatively flexible sulfur-containing asymmetrically linking ligand 4-(2-pyrazinylthiomethyl)benzoic acid (Hpztmb) for a self-assembly of a novel one-dimensional Cd(II) coordination polymer. $[Cd(pztmb)_2(H_2O)_2]_n$ (**1**) was thus obtained and structurally characterized, which represents a significant advancement in this field. The photoluminescence and thermal properties of **1** have also been investigated.

Experimental Section

Materials and measurements

All the reagents and solvents for syntheses were commercially available at analytical grade and were used without further purification or with purification by standard methods prior to use. Elemental analyses for C, H and N were carried out on a Perkin-Elmer 240 elemental analyzer. The Fourier transform infrared (FT-IR) spectra were obtained in the range of 4000 – 400 cm^{-1} from KBr pellets on a Bruker VECTOR 22 spectrometer. Luminescence spectra for the solid samples were recorded on a Hitachi 850 fluorescence spectropho-

Table 1. Crystal data and structure refinement parameters of the coordination polymer **1**.

Empirical formula	$C_{24}H_{22}CdN_4O_6S_2$
Formula weight	638.98
Crystal color and habit	colorless block
Crystal size, mm^3	$0.2 \times 0.18 \times 0.16$
Temperature, K	296(2)
Radiation; wavelength, Å	MoK_α; 0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	5.8204(8)
b, Å	15.169(2)
c, Å	14.6671(18)
β, deg	108.554(5)
V, Å^3	1227.6(3)
Z	2
D_{calcd}, g cm^{-3}	1.73
μ(MoK_α), mm^{-1}	1.1
F(000), e	644
Reflns. collected / independent / R_{int}	12178 / 2973 / 0.022
Index ranges h,k,l	±7, ±20, ±19
Data / ref. parameters	2973 / 169
$R1^a$ / $wR2^b$ [$I \geq 2\sigma(I)$]	0.0198 / 0.0791
$R1^a$ / $wR2^b$ (all data)	0.0230 / 0.0846
GOF^c on F^2	1.023
Largest diff. peak / hole, e Å^{-3}	+0.32 / −0.33

[a] $R1 = \Sigma\|F_o|-|F_c\|/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o{}^2-F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2)+(AP)^2+BP]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2,0)+2F_c{}^2)/3$ and A and B are constants adjusted by the program; [c] GoF $= S = [\Sigma w(F_o{}^2-F_c{}^2)^2/(n_{obs}-n_{param})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

tometer. Thermogravimetric measurements were carried out from r. t. to 700 °C on crystalline samples in a nitrogen stream using a SDT 2960 thermal analyzer at a heating rate of 20 °C min^{-1}.

*Preparation of $[Cd(pztmb)_2(H_2O)_2]_n$ (**1**)*

A mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (46.2 mg, 0.15 mmol), Hpztmb (12.4 mg, 0.05 mmol) and NaOH (2.0 mg, 0.05 mmol) in 10 mL of distilled water was sealed in a Teflon-lined stainless-steel autoclave and heated under autogeneous pressure to 120 °C for 3 d. After the mixture was slowly cooled to r. t., colorless block-shaped crystals of complex **1** were obtained. Yield: 70 % (based on cadmium). – $C_{24}H_{22}CdN_4O_6S_2$ (638.98): calcd. C 45.11, H 3.47, N 8.77; found C 45.03, H 3.41, N 8.72. – IR (KBr, cm^{-1}): ν = 3418 (s), 3237 (w), 3084 (w), 2923 (m), 1710 (w), 1592 (s), 1556 (s), 1498 (m), 1387 (s), 1343 (vs), 1131 (vs), 1057 (s), 837 (m), 798 (m), 767 (m), 731 (s), 643 (m), 454 (m) cm^{-1}.

X-Ray crystallographic study

A single crystal with appropriate dimensions was mounted on a Bruker SMART APEX CCD diffractometer [24] and investigated with graphite-monochromatized MoK_α radiation at r. t. using the ω-scan technique. The structure was solved by Direct Methods using the program SHELXS-97. All non-hydrogen atoms were refined anisotropically on F^2 with full-matrix least-squares techniques using SHELXL-97 [25, 26]. The hydrogen atoms were assigned common isotropic displacement factors and included in the final refinement by using geometrical constraints. Crystal structure data are summarized in Table 1. Relevant bond lengths and bond angles are given in Table 2.

Table 2. Selected bond lengths (Å) and bond angles (deg) for the coordination polymer **1**[a].

Cd(1)-O(1)$^{\#1}$	2.3073(11)	Cd(1)-O(1)$^{\#2}$	2.3073(11)
Cd(1)-O(1W)	2.3316(12)	Cd(1)-O(1W)$^{\#3}$	2.3316(12)
Cd(1)-N(1)$^{\#3}$	2.3707(13)	Cd(1)-N(1)	2.3707(13)
O(1)$^{\#1}$-Cd(1)-O(1)$^{\#2}$	180	O(1)$^{\#1}$-Cd(1)-O(1W)	92.45(4)
O(1)$^{\#2}$-Cd(1)-O(1W)	87.55(4)	O(1)$^{\#1}$-Cd(1)-O(1W)$^{\#3}$	87.55(4)
O(1)$^{\#2}$-Cd(1)-O(1W)$^{\#3}$	92.45(4)	O(1W)-Cd(1)-O(1W)$^{\#3}$	180
O(1)$^{\#1}$-Cd(1)-N(1)$^{\#3}$	92.40(4)	O(1)$^{\#2}$-Cd(1)-N(1)$^{\#3}$	87.60(4)
O(1W)-Cd(1)-N(1)$^{\#3}$	85.65(4)	O(1W)$^{\#3}$-Cd(1)-N(1)$^{\#3}$	94.35(4)
O(1)$^{\#1}$-Cd(1)-N(1)	87.60(4)	O(1)$^{\#2}$-Cd(1)-N(1)	92.40(4)
O(1W)-Cd(1)-N(1)	94.35(4)	O(1W)$^{\#3}$-Cd(1)-N(1)	85.65(4)
N(1)$^{\#3}$-Cd(1)-N(1)	180		

[a] Symmetry codes: $^{\#1}$ $-x+2, -y, -z+1$; $^{\#2}$ $x, y, z+1$; $^{\#3}$ $-x+2, -y, -z+2$.

CCDC 805669 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Description of the crystal structure

Complex **1** crystallizes in the monoclinic system in space group $P2_1/c$. The metal-ligand connectivity pattern is depicted in Fig. 1. The asymmetric unit consists of one Cd(II) ion, one pztmb$^-$ ligand and two coordinated water molecules. The Cd atom is six-coordinated with four O atoms and two N atoms to form a distorted octahedral coordination geometry, with two oxygen atoms from two coordinated water molecules and the other four atoms from four different pztmb anion ligands. Adjacent Cd atoms are linked by a pair of ligands to form an infinite polymeric chain containing 24-membered macrometalla-

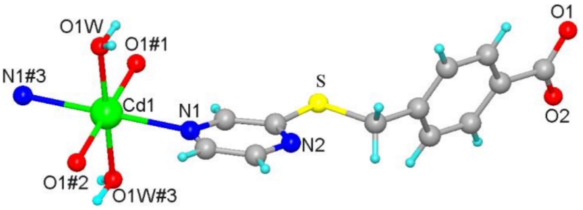

Fig. 1. The connectivity pattern in complex **1**.

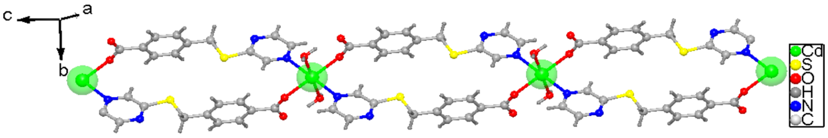

Fig. 2. A view of the chain structure of **1**.

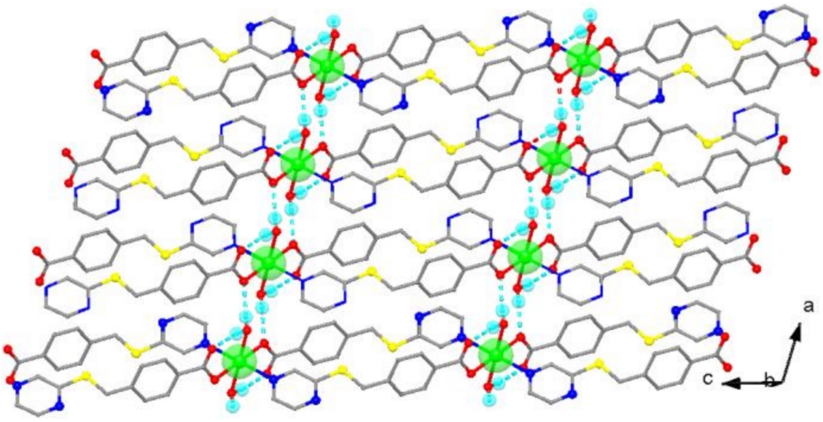

Fig. 3. A view of the layer structure of **1** generated through intra- and inter-chain hydrogen bonds.

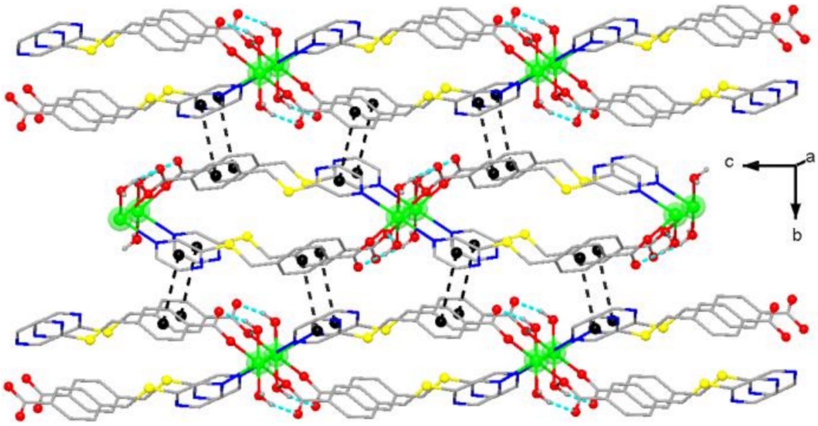

Fig. 4. The supramolecular structure of compound **1**. Dashed lines indicate hydrogen bonds and π-π interactions. All hydrogen atoms have been omitted for clarity.

cyclic rings with a Cd$\cdots$Cd distance of 14.67 Å and a Cd$\cdots$Cd$\cdots$Cd angle of 180°, as shown in Fig. 2. Hydrogen bonding interactions are generally very important for generating supramolecular architectures [27]. In the title complex there is one type of an intramolecular O-H$\cdots$O hydrogen bond between the carboxylate oxygen atom O(2) of the pztmb$^-$ ligand and the O(1W) atom of a coordinated water molecule in the same chain, which plays an important role in stabilizing the 1D structure. The O$\cdots$O distance and the O–H$\cdots$O angle are 2.6902(17) Å and 161° for O(1W)–H(1WB)$\cdots$O(2)$^{\#1}$ (#1: $-x$+2, $-y$, $-z$+1). The coordinated H_2O molecules also form inter-chain hydrogen bonds [O(1W)$\cdots$O(1)$^{\#5}$ 2.8073(17) Å] with the carboxylate oxygen atoms O(1) of the pztmb$^-$ ligands of adjacent chains with an O(1W)–H(1WA)$\cdots$O(1)$^{\#5}$ angle of 175.5° (#5: $-x$+1, $-y$, $-z$+1).

As shown in Fig. 3, with the help of these inter-chain hydrogen bonds, each infinite chain becomes part of a layer. Detailed structural analyses have revealed that the layers are further connected with neighboring ones thereby generating a remarkable three-dimensional supramolecular network through face-to-face π-π interactions, as depicted in Fig. 4. The centroid-centroid distance between phenylene rings is 3.785 Å, and the dihedral angle is 4.7°. This arrangment contributes to the stability of the supramolecular network [28].

Thermal analysis of the coordination polymer 1

Thermogravimetric analysis (TGA) was conducted to study the thermal stability of the title complex,

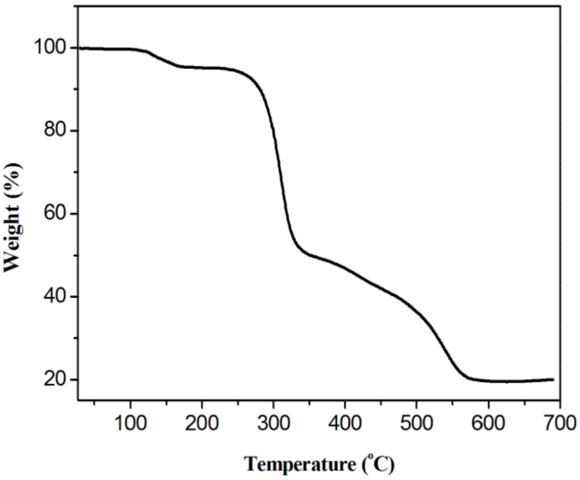

Fig. 5. Thermogravimetric analysis (TGA) curve for **1**.

which is an important aspect for metal-organic frameworks [29]. The TGA curve has three degradation steps in the range 29 – 694 °C. As depicted in Fig. 5, the first gradual weight loss of 5.4 % occurs between 29 and 192 °C (calcd: 5.6 %), corresponding to the loss of the two coordinated water molecules per formula unit Then, a plateau region is observed from 192 to 225 °C. On raising the temperature further, two consecutive decompositions take place in the temperature range of 225 – 617 °C The weight loss of 37.7 % occuring from 225 to 321 °C corresponds to the release of one pztmb$^-$ ligand (calcd: 38.4 %). Subsequently, at 322 – 617 °C the further weight loss is due to the decomposition of the other pztmb$^-$ ligand. The calculated and observed overall losses correlate quite well (found: 80.0 %, calcd: 79.1 %). Above 617 °C, no weight loss is observed, and the final residue obtained corresponds to the formation of cadmium(II) oxide (obsd: 19.9 %, calcd: 20.1 %).

*Luminescence properties of complex **1***

A number of complexes involving the Cd(II) ion have been investigated because of their potential application as luminescent materials [30, 31]. Thus, we studied the luminescence spectrum of the title complex and of the free ligand Hpztmb in the solid state at r. t. As shown in Fig. 6, upon excitation at 373 nm, complex **1** exhibits an intense emission maximum at 396 nm, while the emission maximum of the ligand Hpztmb is at 389 nm upon excitation at 368 nm. In comparison with the free ligand, for **1** there is a slight red-shift of about 7 nm. The spectrum can tentatively be assigned to the intraligand n-π^* or π-π^* fluorescence emission [32]. It is also noteworthy that the relative intensity of the fluorescence emission for **1** is much stronger than that for the free ligand which is probably due to the fact that the ligand chelates the metal center. Thereby it also effectively increases the conformational rigidity and reduces the loss of energy by radiationless decay [33 – 35].

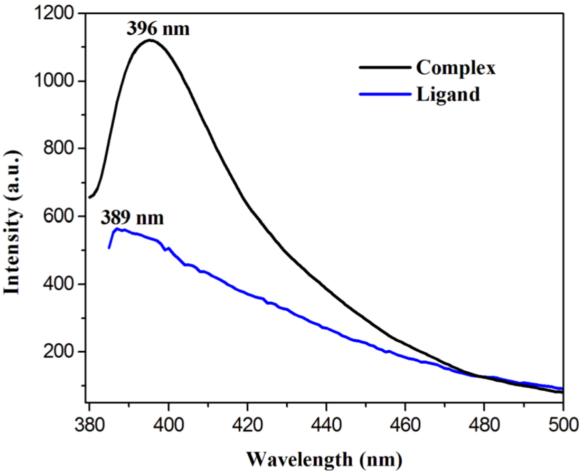

Fig. 6. The emission spectrum of **1** and the free ligand Hpztmb in the solid state at room temperature.

Conclusion

In summary, we present here a novel one-dimensional Cd(II) coordination polymer [Cd(pztmb)$_2$(H$_2$O)$_2$]$_n$ assembled from the relatively flexible sulfur-containing asymmetrical linker Hpztmb under hydrothermal conditions. Our results not only further confirm that the selected asymmetrically linking ligand is a favorable building block for complexes but also illustrate that hydrogen bonds and π-π interactions have great influence on the formation of the supramolecular architecture.

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