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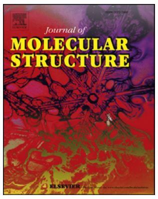

Three Cd(II) complexes based on pyridine containing mercapto-triazole and aromatic multi-carboxylates: Syntheses, structures and luminescent properties

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Three new Cd(II) complexes, $[Cd_2(2\text{-aptt})_2(L_1)(H_2O)]_n$ (**1**), $\{[Cd_3(2\text{-aptt})_2(L_2)_2]\cdot 4H_2O\}_n$ (**2**) and $\{[Cd_3(2\text{-aptt})_2(L_3)]\cdot 2H_2O\}_n$ (**3**) [2-apttH = 4-amino-3-(2-pyridyl)-1H-1,2,4-triazoleq-5-thione, H_2L_1 = terephthalic acid, H_2L_2 = isophthalic acid, H_4L_3 = pyromellitic acid], have been synthesized under the same reaction condition but tuned by different aromatic multi-carboxylates. The X-ray single crystal diffraction analysis reveals that complexes **1**–**3** all display 2D architectures with different features depending on the spatial arrangements of coordinated ligands as well as their unlike coordination modes. The 2D architecture of **1** constructs from Cd(II)–aptt$^-$ layer structure and "wave-like" Cd(II)–L_1^{2-} chains. Cd(II)–aptt$^-$ chains and Cd(II)–L_2^{2-} chains connect each other to generate the 2D grid structure of **2**. “Butterfly-like” Cd(II)–2-aptt$^-$ chains are distributed under or on the surface formed by Cd(II) and L_3^{4-} anions, giving rise to the 2D framework of **3**. Moreover, the thermal stabilities of complexes **1**–**3** were investigated. The luminescent properties of complexes **1**–**3** and the free ligand were also studied.

1. Introduction

Metal-organic frameworks (MOFs) constructed by metal ions and multifunctional organic ligands are currently one of the most intensive research topics, in view of their novel topological structures [1–3] and potential applications such as magnetism, fluorescence, bio-medicine, molecular recognition, gas adsorption and storage, catalysis, etc. [4–11]. To date, although great efforts have been taken by many researchers in this field [12–16], it is an urgent challenge to predict and control the synthesis of desired structures, partially as a result of selection of organic ligands possessing appropriate functional groups and predetermined coordination modes [17–19]. Recently, compounds with N/S-donor, especially mercapto-triazole and mercapto-thiadiazole derivatives, which possess a wide variety of biological activity, have been extensively researched in the fields of pesticides and medicines [20–22]. A few of findings have shown that these compounds can form MOFs through multiple bonding interactions, and can exhibit diverse coordination modes under different synthetic conditions [23–26]. Therefore, it deserves further attention for the sake of more versatile structures and properties in the future. On the other hand, aromatic carboxylates have been widely used as auxiliary ligands to construct MOFs due to their versatile coordination modes, strong coordination ability to metal centers, and provision of hydrogen bonding sites [27–29]. In addition, MOFs composed of metal ions and multi-carboxylic ligands can easily form porous structures, which widely are used in adsorption, gas storage, catalysis [30–32].

Taking above reasons into account, we hereby focus our attention on exploring systematically the MOFs based on 4-amino-3-(2-pyridyl)-1H-1,2,4-triazole-5-thione (2-apttH) and aromatic multi-carboxylates. In this paper, we have successfully synthesized three new Cd(II) complexes (Scheme 1), namely, $[Cd_2(2\text{-aptt})_2(L_1)(H_2O)]_n$ (**1**), $\{[Cd_3(2\text{-aptt})_2(L_2)_2]\cdot 4H_2O\}_n$ (**2**) and $\{[Cd_3(2\text{-aptt})_2(L_3)]\cdot 2H_2O\}_n$ (**3**). The structures of complexes **1**–**3** were determined by X-ray single crystal diffraction analysis and characterized by infrared spectra (IR), elemental analyses and thermogravimetric analyses (TGA). In addition, the solid-state luminescence properties of complexes **1**–**3** were also investigated.

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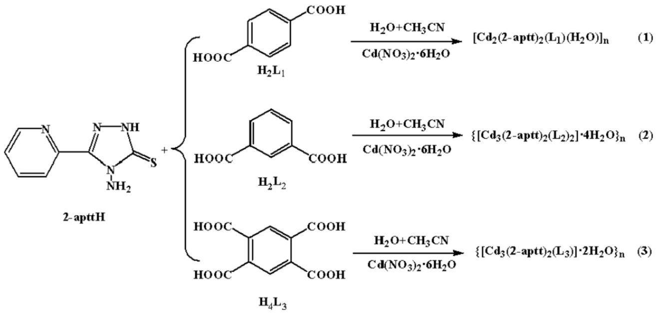

Scheme 1. Preparation routes for three mixed-ligand complexes.

2. Experimental

2.1. Materials and general methods

Ligand 2-apttH was synthesized according to the related published literature method [33]. Auxiliary ligands terephthalic acid (H_2L_1), isophthalic acid (H_2L_2) and pyromellitic acid (H_4L_3) were purchased from Aldrich. Co. $Cd(NO_3)_2·6H_2O$ and acetonitrile were supplied by Alfa Aesar. All chemicals were of reagent grade and used without further purification. The infrared spectra were determined in the region from 400 cm^{-1} to 4000 cm^{-1} with KBr pellets on a BRUKER TENSOR 27 spectrophotometer. Elemental analyses (C, H, and N) were carried out on a FLASH EA 1112 elemental analyzer. TGA measurements were performed by heating the crystalline sample from 30 to 850 °C at a rate of 10 °C/min in air with a Netzsch STA 409 PC differential thermal analyzer, whereas fluorescence spectra were characterized at room temperature with Hitachi F-7000 Fluorescence Spectrophotometer. The excitation and emission slit width were both 2.5 nm, and response time was 0.5 s.

2.2. Synthesis

2.2.1. $[Cd_2(2\text{-aptt})_2(L_1)(H_2O)]_n$ (**1**)

A mixture of $Cd(NO_3)_2·6H_2O$ (0.0058 g, 0.03 mmol), 2-apttH (0.0048 g, 0.03 mmol), H_2L_1 (0.0092 g, 0.03 mmol), water/acetonitrile (3:1, 4 mL) solution was sealed in a 10 mL teflon lined stainless steel autoclave and heated at 120 °C for 3 days, and then slowly cooled to room temperature. Well-formed yellow blocks of complex **1** were separated suitably for X-ray single crystal diffraction. Elemental analysis Calcd (%) for $C_{22}H_{14}Cd_2N_{10}O_5S_2$: C, 33.53; H, 1.78; N, 17.78. Found: C, 33.51; H, 1.98; N, 17.69. Selected IR (KBr, cm^{-1}): 3408.56 (w, ν_{N-H}), 1634.26 (w, $\nu_{C=O}$), 1597.62 (m, $\nu_{C=C}$), 1547.42 (s, $\gamma_{=C\text{-}N\text{-}H}$), 1451.47 (w, $\nu_{C=C}$), 1372.13 (s, $\nu_{=C\text{-}N}$), 1306.05 (m, $\nu_{=C\text{-}N}$), 1252.18 (w, $\nu_{C=S}$).

2.2.2. $\{[Cd_3(2\text{-aptt})_2(L_2)_2]·4H_2O\}_n$ (**2**)

Yellow block crystals of complex **2** were prepared in a similar method as for **1** but using H_2L_2 (0.0048 g, 0.03 mmol) in place of H_2L_1. Elemental analysis Calcd (%) for $C_{3.75}H_{2.25}Cd_{0.38}N_{1.25}O_{1.50}S_{0.25}$: C, 32.54; H, 1.64; N, 12.64. Found: C, 33.50; H, 1.59; N, 12.71. Selected IR (KBr, cm^{-1}): 3442.73 (s, ν_{N-H}), 1600.98 (s, $\nu_{C=C}$), 1539.95 (s, $\nu_{=C\text{-}N}$), 1453.45 (w, $\nu_{C=O}$), 1305.00 (w, $\nu_{C=S}$).

2.2.3. $\{[Cd_3(2\text{-aptt})_2(L_3)]·2H_2O\}_n$ (**3**)

The same synthetic method as that for **1** was used except that H_4L_3 (0.0076 g, 0.03 mmol) was replaced by H_2L_1. Yellow needle crystals of complex **3** were separated suitably for X-ray single crystal diffraction. Anal. Calc. for $C_{12}H_9Cd_{1.50}N_5O_{5.50}S$: C, 28.58; H, 1.79; N, 13.89. Found: C, 28.32; H, 1.30; N, 13.79. Selected IR (KBr, cm^{-1}): 3441.07 (s, ν_{N-H}), 1601.90 (w, $\nu_{C=O}$), 1557.13 (s, $\nu_{C=C}$), 1430.38 (w, $\nu_{C=S}$), 1376.49 (s, $\nu_{=C\text{-}N}$).

2.3. Crystal structure determination

The intensity data of complexes **1**–**3** was collected at $T = 293(2)$ K on a Rigaku Saturn 724 CCD diffractometer with graphite monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). A suitable single crystal for X-ray diffraction was mounted on a glass fiber. The structure was solved by direct methods and was refined on F^2 by full-matrix least-squares technique. All calculations were completed with the SHELXL-97 crystallographic software package [34]. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical restrains. Crystallographic crystal data and processing parameters for **1**–**3** are given and summarized in Table 1. Selected bond lengths (Å) and bond angles (°) of the complexes are listed in Table 2.

3. Results and discussion

3.1. Synthesis and IR spectra

As shown in Scheme 1, complexes **1**–**3** were prepared by the same procedure and condition except for auxiliary ligands. It is very interesting that these complexes exhibit various 2D structures, which are mainly ascribed to the spatial arrangements of coordinated ligands as well as their unlike coordination modes. The results of the work suggest that the method of getting diverse MOFs may be implemented by changing auxiliary multi-carboxylic ligands. The infrared spectra and elemental analyses of complexes **1**–**3** are fully consistent with their formations. The most important and characteristic stretching frequencies of the complexes appear in the range of 1252–1642 cm^{-1} for functional groups including —C=O, —C=C-, —C=N-, —C=S. No bands in the region 1690–1730 cm^{-1}, which demonstrates complete deprotonation of the carboxyl groups [35].

3.2. Description of crystal structures

3.2.1. Crystal structure of **1**

X-ray single crystal diffraction analysis indicates that complex **1** belongs to orthorhombic space group *Pbca* and displays a 2D structure. As illustrated in Fig. 1a, there are two crystallographically independent Cd(II) ions (Cd1, Cd2), both of them are six-coordinated. Cd1 ion adopts octahedral coordination environment, in which Cd1 ion coordinates three 2-aptt⁻ ligands merely. In addition, the equatorial plane is taken up by N2, N5, N6, and N7A, while axial positions are filled by N10 and S1B. Cd2 ion has the same octahedral arrangement with Cd1 ion, and is coordinated two sulfur atoms (S1, S2C) from two 2-aptt⁻ ligands and four oxygen atoms (O1, O2, O3C, O5) from two L_1^{2-} anions and one water molecule. All the bond lengths of **1** are in agreement with those reported Cd(II) coordination polymers [36,37]. In complex **1**, two Cd1 centers are bridged by four 2-aptt⁻ ligands to form binuclear structure units, with the Cd···Cd distance of 4.7045(10) Å (Fig. 1b). Furthermore, the binuclear structure units link each other, extending to a 2D Cd(II)—aptt⁻ layer structure. Meanwhile, L_1^{2-} anions bridge the Cd2 ions to generate "wave-like" 1D Cd(II)—L_1^{2-} chains, which link the 2D Cd(II)—aptt⁻ layer structure into the final 2D structure of 1 (Fig. 1c). In addition, the structure of complex **1** is further reinforced by the π···π stacking interactions (3.6883 (5) Å) between adjacent pyridine rings.