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Syntheses, crystal structures and properties of two new coordination complexes containing 1,2,4,5-benzenetetracarboxylate and imidazole: $[Ni_2(Him)_{12}\cdot(bta)\cdot 8H_2O]$ and $[Cd_2(Him)_4(\mu_4\text{-bta})]$

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Abstract

Two new coordination complexes, $[Ni_2(Him)_{12}\cdot(bta)\cdot 8H_2O]$ **1** and $[Cd_2(Him)_4(bta)]$ **2**, (H_4bta = 1,2,4,5-benzenetetracarboxylic acid, Him = imidazole) were prepared under hydrothermal conditions and their structures were determined by single-crystal X-ray diffraction. X-ray diffraction reveals that complex **1**, consisting of two crystallographically independent $[Ni(Him)_6]^{2+}$ fragments, an uncoordinated bta^{4-} anion and eight lattice water molecules, displays an interesting 3D supramolecular network constructed by cationic layers (layer A) and anionic layers (layer B) with ABAB sequence through hydrogen bonding interactions. In complex **2**, each bta ligand links four metal ions to form a one dimensional (1D) double chain. The 1D double metal chains are assembled into a 3D supramolecular network through $N-H\cdots O$ hydrogen bonding and $C-H\cdots\pi$ interactions. Complex **2** shows strong blue fluorescence at room temperature.

Keywords: Supramolecular structure; Anionic and cationic layers; Fluorescence; 1,2,4,5-Benzenetetracarboxylate; Imidazole

1. Introduction

The rational design and synthesis of new extended supramolecular networks are of great interest and have brought forth diversities of frameworks with fascinating structural motifs [1–9]. In general, extended networks possessing higher dimensionalities can be obtained by the assembly of coordination complexes (or polymers) with lower dimensionalities via hydrogen-bonding, $\pi-\pi$ interaction or other intermolecular contacts. An important synthetic method for design and tailor-making of such supramolecular materials utilizes suitable terminal ligands that can coordinate to metal ions through one primary coordination site, while at the same time participate in additional bonding interactions (hydrogen bonding or other molecular contacts) at peripheral sites. An advantage of the method is that it may combine the flexibility of the weaker interactions with the strength of coordination bonding. The choice of imidazole (Him) as a terminal ligand arises as it may provide supramolecular recognition sites for $N-H\cdots O$, $\pi-\pi$, $C-H\cdots\pi$ and $C-H\cdots O$ molecular contacts to form interesting supramolecular structures. Transition metal complexes containing imidazole groups have been widely reported [10–16], and in these systems, the use of imidazole, which fills up coordination spaces around the metal ions, as a terminal ligand promotes the molecular dimensionality of coordination complexes through hydrogen bonding and other intermolecular contacts. 1,2,4,5-Benzenetetracarboxylic acid (H_4bta) ligand has been widely employed in the construction of coordination complexes due to its diverse binding modes as a organic linker which allow it to form diversities of structures from discrete molecules [17] to one- (1D) [18–21], two- (2D) [21–23] or three-dimensional (3D) [24–26] networks, however, only 10 complexes based on bta and imidazole co-ligand are reported to date [13,15,27–33]. These complexes can be classified as discrete binuclear

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complex [27], 1D single chain [13,28–31], 1D double chain [15,32] and 2D sheet [33]. Here, we present structures and characterization of two new coordination complexes constructed by bta ligands and imidazole as terminal ligands, $[Ni_2(Him)_{12} \cdot (bta) \cdot 8H_2O]$ **1** and $[Cd_2(Him)_4(bta)]$ **2**. **1** is a new mononuclear complex, while the structure of complex **2** is 1D double chain being isomorphic with the reported complexes $[M_2(Him)_4(bta)]$ (M = Zn [32] and Co [15]). Complexes **1** and **2** both display interesting 3D supramolecular networks. In the formation of supramolecular network of complexes **1** and **2**, Him ligand behaves as a unique and efficient hydrogen bonding synthon.

2. Experimental section

2.1. Materials and methods

All chemicals purchased were of reagent grade and used without further purification. Elemental analysis (C, H, N) was performed on a Perkin–Elmer 240C elemental analyzer. IR spectrum was measured on a Perkin–Elmer Spectrum One FT-IR spectrometer using KBr pellets. Thermalgravimetric analysis (TGA) was performed on a Perkin–Elmer TGA-7000 thermogravimetric analyzer under the flowing air at a temperature ramp rate of 20 °C min^{-1}. Fluorescent spectrum was obtained on a LS 55 florescence/phosphorescence spectrophotometer at room temperature.

2.2. Syntheses of complexes

2.2.1. Synthesis of complex *1*

A mixture of $Ni(NO_3)_2 \cdot 6H_2O$ (0.30 g, 1 mmol), H_4bta (0.25 g, 1 mmol), imidazole (0.15 g, 2.2 mmol), KOH (0.05 g, 0.9 mmol) and water (12 ml) was stirred for 30 min at room temperature, then transferred to and sealed in a 25 ml Teflon-lined stainless steel reactor, and was heated 120 °C for 72 h. Upon cooling to room temperature, the blue crystals were filtered and washed with water. Yield: 55% based on Ni. Anal. Calcd for $C_{46}H_{66}Ni_2N_{24}O_{16}$ **1**: C, 41.54; H, 4.97; N, 25.29. Found: C, 41.62; H, 4.88; N, 25.35.

2.2.2. Synthesis of complex *2*

A mixture of $3CdSO_4 \cdot 8H_2O$ (0.41 g, 0.5 mmol), H_4bta (0.25 g, 1 mmol), imidazole (0.12 g, 1.8 mmol) KOH (0.07 g, 1.3 mmol) and water (15 ml) was stirred for 30 min at room temperature, then transferred to and sealed in a 25 ml Teflon-lined stainless steel reactor, and was heated at 170 °C for 72 h. Upon cooling to room temperature, the purple crystals were filtered and washed with water. Yield: 38% based on Cd. Anal. Calcd for $C_{22}H_{18}Cd_2N_8O_{82}$ **2**: C, 35.33; H, 2.35; N, 14.99. Found: C, 35.37; H, 2.29; N, 15.11. IR (KBr, cm^{-1}): 3148m, 2804w, 1574s, 1380s, 1069s, 745m, 655m.

2.3. Crystal structure determination

The crystal structures were determined by single-crystal X-ray diffraction experiment. The reflection data were collected on a Bruker SMART CCD area-detector diffractometer (MoKα radiation, graphite monochromator) at room temperature with ω-scan mode. Empirical adsorption correction was applied to all data using SADABS program. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL 97 software [34]. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference maps and refined with isotropic temperature factors in complexes **1** and **2**. All calculations were carried out using SHELXTL 97 [34] and PLATON 99 [35]. The crystallographic data and pertinent information are summarized in Table 1. The selected bond lengths and angles are listed in Table 2.

3. Results and discussion

3.1. Synthesis

Complexes **1** and **2** were synthesized from H_4bta, Him and $Ni(NO_3)_2 \cdot 6H_2O$ or $3CdSO_4 \cdot 8H_2O$ under hydrothermal conditions. As is well-known, a number of factors involved in the hydrothermal reactions can affect the final products, including the reaction temperature, molar ratio of the starting materials, the solvent system, and the pH value of the reaction mixture, etc. During the exploration of $H_4bta/Him/M^{2+}$ system, we noticed the reactions

Table 1
The crystallographic data for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{46}H_{66}N_{24}Ni_2O_{16}$	$C_{22}H_{18}Cd_2N_8O_8$
Formula weight	1328.65	747.26
Crystal system	Triclinic	Triclinic
Space group	$\bar{P}$	$\bar{P}$
a (Å)	9.8611(6)	8.219(5)
b (Å)	12.0589(7)	9.652(5)
c (Å)	13.4428(8)	9.682(5)
α (°)	92.8750(10)	94.729(7)
β (°)	92.7730(10)	101.248(4)
γ (°)	113.2970(10)	104.698(7)
Volume	1462.30(15)	649.9(6)
Z	1	1
ρ_{calc} (g cm^{-3})	1.509	1.909
Absorption coefficient (mm^{-1})	0.732	1.699
Crystal size (mm)	0.31 × 0.21 × 0.17	0.25 × 0.20 × 0.17
θ range (°)	1.52–26.03	2.40–25.99
Reflections collected	8888	3579
Unique reflections (R_{int})	5628 (0.0132)	2466 (0.0112)
Goodness-of-fit on F^2	1.035	1.082
R indexes $[I > 2\sigma(I)]$[a]	$R_1 = 0.0292$, $wR_2 = 0.0748$	$R_1 = 0.0266$, $wR_2 = 0.0639$
R (all data)[a]	$R_1 = 0.0334$, $wR_2 = 0.0778$	$R_1 = 0.0280$, $wR_2 = 0.0649$

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR = [\sum w(F_o^2 - F_c^2)_2/\sum w(F_o^2)^2]^{1/2}$.