

Note

# Novel Cu<sup>II</sup>, Co<sup>II</sup> and Pb<sup>II</sup> supramolecular networks of pyridine-2,6-dicarboxylate (pydc) in cooperation with a bent dipyridyl spacer via coordinative, hydrogen-bonding and aromatic stacking interactions

Miao Du <sup>\*</sup>, Hua Cai, Xiao-Jun Zhao

*College of Chemistry and Life Science, Tianjin Normal University, 241 Wei Jin Road, Tianjin 300074, PR China*

Received 17 April 2005; received in revised form 23 July 2005; accepted 3 August 2005

Available online 19 September 2005

## Abstract

Reaction of M(OAc)<sub>2</sub> (M<sup>II</sup> = Cu<sup>II</sup> for **1**, Co<sup>II</sup> for **2**, and Pb<sup>II</sup> for **3**) with pyridine-2,6-dicarboxylic acid (H<sub>2</sub>pydc) in presence of a dipyridyl spacer 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (bpo) affords three novel metal-organic supramolecular networks [Cu<sub>2</sub>(bpo)(pydc)<sub>2</sub>·(H<sub>2</sub>O)<sub>3</sub>]·2.75H<sub>2</sub>O (**1**), [Co(bpo)(pydc)(H<sub>2</sub>O)<sub>2</sub>]·(H<sub>2</sub>O) (**2**) and [Pb(pydc)]<sub>n</sub> (**3**), which have been structurally determined by single-crystal X-ray diffraction. The dimeric Cu-pydc coordination framework bridged by a bpo spacer in **1** is hydrogen-bonded to four others to result in a two-dimensional (2-D) sheet array. The neutral monomeric molecules in **2** have an ordered 3-D stacking stabilized via hydrogen bonds and significant π–π interactions in the lattice, possessing large porous channels with the inclusion of guest solvates. In coordination polymer **3**, the Pb<sup>II</sup> ion takes the unusual distorted capped trigonal prismatic geometry (PbNO<sub>6</sub>) and each pydc dianion binds to four Pb<sup>II</sup> centres to form a 2-D infinite network. The thermal stabilities of these complexes have also been investigated.

© 2005 Elsevier B.V. All rights reserved.

*Keywords:* Crystal structure; Pyridinecarboxylate; Supramolecular assembly; Coordination polymer; Porous network

## 1. Introduction

In the past decade, much effort has been devoted to the design and controlled crystallization of coordination supramolecules and polymers with potential application as catalytic, conductive, luminescent, magnetic, spin-transition, non-linear optical, and/or nanoporous materials, and it is well established that such metal-involved assembly processes can be influenced by many factors used for crystallization [1–6]. Aside from the fundamental and strong metal-ligand coordination driven force, other relatively weak intermolecular interactions such as hydrogen bonding and aromatic stacking are also useful tools in construction of the crystalline materials, and a variety of infinitely extended networks have been generated via interplay of these valid interactions [7,8].

An important aspect of this relatively fresh chemistry is the development of new synthetic strategies based on the well-designed organic ligands [5]. Besides the most common bridging ligands such as dipyridyl compounds and di-/poly-carboxylic acids, chelating ligands giving rise to particularly robust coordination complexes can also furnish effective building blocks for extended hydrogen-bonded networks [9]. Pyridine-2,6-dicarboxylic acids (H<sub>2</sub>pydc, see Chart 1) is a good chelating reagent with limited steric hindrance and can provide further possibility to form polymeric complexes through bridging coordination of carboxylates under approximate conditions [10]. Very recently, Bharadwaj et al. [11] reported the metal-organic frameworks of Cu<sup>II</sup> with pydc and different spacers such as 4,4'-bipyridine or pyrazine under hydrothermal conditions, displaying diverse supramolecular networks from 1-D to 3-D. On the other hand, oxadiazole-containing angular dipyridyl ligands, such as 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (bpo, see Chart 1), were successfully utilized

<sup>\*</sup> Corresponding author. Tel./fax: +86 22 23540315.

E-mail address: [dumiao@public.tpt.tj.cn](mailto:dumiao@public.tpt.tj.cn) (M. Du).

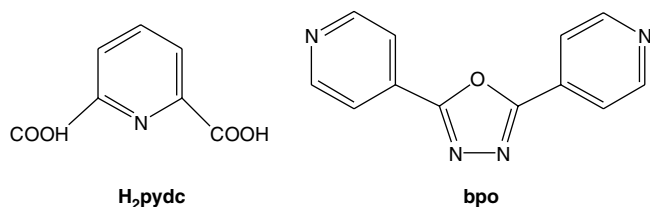


Chart 1.

to construct attractive metal-organic coordination solids [12,13] and organic cocrystalline materials [14,15] due to their advantage as building blocks with the potential ability to participate in the formation of coordination, hydrogen-bonding and aromatic stacking interactions. Thus, we anticipate that the incorporation of pydc chelating ligand and bpo spacer would produce novel coordination frameworks upon metal complexation. The present contribution will describe the hydrothermal synthesis, molecular/supramolecular structures and thermal properties of three such complexes, including  $[\text{Cu}_2(\text{bpo})(\text{pydc})_2(\text{H}_2\text{O})_3] \cdot 2.75\text{H}_2\text{O}$  (**1**),  $[\text{Co}(\text{bpo})(\text{pydc})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})$  (**2**) and  $[\text{Pb}(\text{pydc})_n]$  (**3**).

## 2. Experimental

### 2.1. Materials and general methods

With the exception of 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (bpo), which was synthesized as described in our previous work [12–15], all of the starting materials and reagents were obtained commercially and used as received. Fourier transform (FT)-IR spectra (KBr pellets) were taken on an AVATAR-370 (Nicolet) spectrometer. Elemental (carbon, hydrogen and nitrogen) analyses were performed on a CE-440 (Leemanlabs) analyzer. Thermogravimetric analysis (TGA) experiments were carried out on a Dupont thermal analyzer from room temperature to 800 °C under nitrogen atmosphere at a heating rate of 10 °C/min.

### 2.2. Syntheses of complexes 1–3

#### 2.2.1. $[\text{Cu}_2(\text{bpo})(\text{pydc})_2(\text{H}_2\text{O})_3] \cdot 2.75\text{H}_2\text{O}$ (**1**)

A methanol solution (10 mL) containing  $\text{H}_2\text{pydc}$  (30 mg, 0.18 mmol) was added to an aqueous solution (15 mL) of  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (44 mg, 0.22 mmol). After ca. 3 min of vigorous mixing, a methanol solution (8 mL) of bpo (22 mg, 0.10 mmol) was added and the pH value of the solution was adjusted to ca. 7 by triethylamine. The filtrate of the above mixture was allowed to evaporate slowly under ambient conditions. Rectangle cyan single crystals of **1** suitable for X-ray diffraction were obtained over a period of 1 week in 51% yield (based on  $\text{H}_2\text{pydc}$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3430b, 3081w, 2921w, 1628s, 1482w, 1429m, 1337m, 1215w, 1173w, 1082w, 776w, 738m, 684w. Elemental analysis suggests the escape of lattice water molecules of **1** after dry in vacuum, which is further identified by TGA result as described below. *Anal.* Calc. for  $\text{C}_{26}\text{H}_{20}\text{Cu}_2\text{N}_6\text{O}_{12}$ : C,

42.45; H, 2.74; N, 11.43. Found: C, 42.54; H, 2.57; N, 11.45%. It is worthy to note that complex **1** could also be prepared under the same hydrothermal conditions as described below.

#### 2.2.2. $[\text{Co}(\text{bpo})(\text{pydc})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})$ (**2**)

A mixture of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (59 mg, 0.24 mmol),  $\text{H}_2\text{pydc}$  (17 mg, 0.10 mmol), NaOH (40 mg, 0.10 mmol) and bpo (22 mg, 0.10 mmol) in water (10 mL) was heated at 140 °C for 3 days in a sealed Teflon-lined stainless steel vessel (20 mL) under autogenous pressure. After the reaction mixture was slowly cooled down to the room temperature at a rate of 5 °C/h, red lamellar single crystals were produced with a yield of 52% (based on  $\text{H}_2\text{pydc}$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3250b, 1622s, 1572w, 1540w, 1485m, 1427m, 1362m, 1279m, 1218w, 1185w, 1063w, 833m, 774m, 726m. *Anal.* Calc. for  $\text{C}_9\text{H}_{17}\text{CoN}_5\text{O}_8$ : C, 45.43; H, 3.41; N, 13.94. Found: C, 45.42; H, 3.25; N, 13.70%.

#### 2.2.3. $[\text{Pb}(\text{pydc})_n]$ (**3**)

The same synthetic procedure as for complex **2** was employed except that  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  was replaced by  $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ , resulting in prism pink single-crystals suitable for X-ray diffraction in 65% yield. FT-IR (KBr pellet,  $\text{cm}^{-1}$ ): 1609s, 1579s, 1459w, 1422m, 1380m, 1353m, 1271m, 1180w, 1141w, 1069m, 1017m, 913m, 824w, 768m, 728m, 693w, 663m. *Anal.* Calc. for  $\text{C}_7\text{H}_3\text{NO}_4\text{Pb}$ : C, 22.58; H, 0.81; N, 3.76. Found: C, 22.55; H, 0.64; N, 3.62%.

### 2.3. X-ray crystallographic data collection and structural determination

Single crystal X-ray diffraction data collections of **1–3** were performed on a Bruker Apex II CCD diffractometer at 293(2) K with Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Semi-empirical absorption corrections were applied using the SADABS program, and the program SAINT [16] was utilized for integration of the diffraction profiles. The ratios of minimum to maximum apparent transmission are 0.591 for **1**, 0.406 for **2** and 0.378 for **3**. All structures were solved by direct methods using SHELXS program of the SHELXL package and refined with SHELXL [17]. The heavy atoms were located from the *E*-maps and other non-H atoms in successive difference Fourier syntheses. The final refinements were performed by full-matrix least-squares methods with anisotropic thermal parameters for non-H atoms on  $F^2$ . The C-bound H atoms were generated with assigned isotropic thermal parameters, and those of water molecules were first found in difference electron density maps and then placed in the calculated sites with fixed thermal factors. The H atoms of the disordered lattice water in **1** and **2** were not located. The refinements converge to final  $(\Delta/\sigma)_{\text{max}} \leq 0.002$  for all the cases. Further crystallographic data and structural analyses of **1–3** are summarized in Table 1.

Download English Version:

<https://daneshyari.com/en/article/1311784>

Download Persian Version:

<https://daneshyari.com/article/1311784>

[Daneshyari.com](https://daneshyari.com)