Inorganica Chimica Acta 362 (2009) 1730–1738

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

A series of 1-D to 3-D metal–organic coordination architectures assembled with V-shaped bis(pyridyl)thiadiazole under co-ligand intervention

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ARTICLE INFO

Article history:
Received 16 June 2008
Received in revised form 2 August 2008
Accepted 22 August 2008
Available online 2 September 2008

Keywords:
2,5-Bis(4-pyridyl)-1,3,4-thiadiazole
Polycarboxylate
Coordination polymer
co-ligand intervention

ABSTRACT

Six new coordination polymers based on V-shaped linkage 2,5-bis(4-pyridyl)-1,3,4-thiadiazole (bpt) and transition metal ions, $[Co(bpt)(pm)_{0.5}(H_2O)]_n \cdot 3nH_2O$ (**1**), $[Cu_2(bpt)(pm)(H_2O)_4]_n$ (**2**), $[Co(bpt)(pydc)]_n \cdot 2nCHCl_3 \cdot nH_2O$ (**3**), $[Cu_2(bpt)(pydc)_2(H_2O)_2]_n$ (**4**), $[Cu_2(bpt)(pydco)_2(H_2O)_2]_n \cdot nH_2O$ (**5**) and $[Cd(bpt)(pydco)]_n$ (**6**) (H_4pm = pyromellitic acid, H_2pydc = pyridine-2,6-dicarboxylic acid, H_2pydco = pyridine-2,6-dicarboxylic acid *N*-oxide), have been synthesized under the intervention of various polycarboxylate ligands. Complex **1** exhibits a 3-D 4-connected structure with 1-D nanosized open channels encapsulated lots of water molecules. Complex **2** represents a 2-D grid containing two types of rectangular windows. When pydc and pydco instead of pm, complexes **3** and **6** were obtained with highly undulated 2-D layers. The interlayers of **3** are filled with two kinds of solvent molecules, whereas **6** is a double-layered framework without free molecules. Complexes **4** and **5** consist of two distinct 1-D infinite chains held together to form different 2-D supramolecular networks. Importantly, bpt spacer shows changeful conformational geometries and generates complicated crystalline architectures with the introduction of polycarboxylate ligands. Additionally, thermal stability of complexes **1**, **3** and **5**, fluorescent properties of 6 and X-ray powder diffraction of **1** have also been investigated.

1. Introduction

The design and construction of polymeric metal–organic frameworks (MOFs) with intriguing structural motifs, unique chemical and physical properties leading to potential applications in catalysis, luminescence, magnetism, sorption, ion exchange, nonlinear optics, electricity has been attracting enormous interest in supramolecular chemistry and material chemistry [1,2]. In this regard, much attention has been devoted to the deliberate control of self-assembly infinite coordination networks via selecting different ligands, metal ions, solvent system, synthetic methods and so on, especially many new organic ligands contributing to the occurrence of the varieties of novel polymers [3]. In the last decades, a lot of metal–organic frameworks have been obtained by using linear 4,4′-bipyridine, 1,2-bis(4-pyridyl)ethene and other bipyridine-like N,N′-donor ligands [4]. Our group has already constructed some fascinating architectures utilizing these common ligands [5]. However, the V-shaped N,N′-ligands, such as 2,5-bis(4-pyridyl)-1,3,4-oxadiazole, 4-amino-2,5-bis(4-pyridyl)-1,2,4-triazole, and 2,5-bis(4-pyridyl)-1,3,4-thiadiazole are still limited as building blocks [6–8]. As a matter of fact, there is a higher possibility of achieving the versatile, unpredictable and interesting structures depending on the biting angle of these bent N,N′-donor ligands. One of these bent organic compounds, 2,5-bis(4-pyridyl)-1,3,4-thiadiazole as a new member of crystal engineering family, has engaged the current concerns recently because of several interesting characteristics: (a) the bent ligand has flexible coordination modes than general 4,4′-bipyridine-like ligands due to two more potential N-donor atoms; (b) generally, longer ligand will lead to larger voids. The bpt ligand (ca. 10.8 Å) is longer than those (usually 4,4′-bipyridine, 7.1 Å) containing planar centers; (c) its changeful conformational geometries favor a synergistic effect with auxiliary ligand; (d) maybe it has potential biological activities attributing to the presence of thiadiazole ring [4,8,9]. Accordingly, we have chosen the V-shaped bridging N,N′-donor ligand 2,5-bis(4-pyridyl)-1,3,4-thiadiazole with the expectation of novel functional polymers.

On the other hand, because of the diversity of the coordination modes and high structural stability of the multidentate O-donor organic polycarboxylate ligands, the introduction of an O-containing auxiliary ligand may affect the self-assembly of polymer, lead to new structural evolution and allow fine-tuning of the structural motif to some extent [10]. So, it is undoubtedly a better choice to construct coordination polymers from bpt spacer under polycarboxylate intervention. Up to date, only three complexes based on bpt and polycarboxylate ligands have been synthesized by Zhang and Tong [9,11]. Du et al. took on some investigations of a similar bent 2,5-bis(4-pyridyl)-1,3,4-oxadiazole, however, the cases of

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doi:10.1016/j.ica.2008.08.028

mixed-ligands are very rare [12]. In this paper, we present two types of assistant polycarboxylate ligands to investigate the formation and control of structure. One is the classical pyromellitic acid which consists of a rigid planar C_{10} backbone and four freely rotating and flexible carboxylic groups [13]. The other is the remarkable dicarboxylate ligands of pyridine-2,6-dicarboxylic acid and its *N*-oxide with a rigid pyridyl ring and two carboxylic groups [10a,14,15]. Various functional crystalline architectures consisting of one-, two-, or three-dimensional structures could be afforded with the introduction of these distinct polycarboxylate co-ligands possessing different molecular backbone and coordinated sites. Herein, a series of new Co^{II}, Cu^{II} and Cd^{II} coordination polymers with bpt ligand and the polycarboxylate acids, including $[Co(bpt)(pm)_{0.5}(H_2O)]_n \cdot 3nH_2O$ (**1**), $[Cu_2(bpt)(pm)(H_2O)_4]_n$ (**2**), $[Co(bpt)(pydc)]_n \cdot 2nCHCl_3 \cdot nH_2O$ (**3**), $[Cu_2(bpt)(pydc)_2(H_2O)_2]_n$ (**4**), $[Cu_2(bpt)(pydco)_2(H_2O)_2]_n \cdot nH_2O$ (**5**) and $[Cd(bpt)(pydco)]_n$ (**6**), were synthesized and characterized. The systematic investigation of the effect of the conformation geometries of bpt spacer, organic counteranions, along with different metal ions on the ultimate frameworks, will be represented and discussed. In addition, thermal stability of **1**, **3** and **5**, fluorescent property of **6** and X-ray powder diffraction of **1** have also been explored.

2. Experimental

2.1. Reagents and physical measurement

All chemicals purchased were commercially available and used without further purification, except H_2pydco which was synthesized according to the literature [16]. Elemental analyses (C, H and N) were recorded on a Perkin–Elmer model 240C instrument. Infrared spectra were performed on KBr pellets with a Nicolet 170SX FT-IR spectrophotometer in the range 4000–400 cm^{-1}. Thermal analyses were determined with a Netzsch STA 449C microanalyzer under flowing N_2 atmosphere at a heating rate of 10 °C min^{-1}. Luminescence spectra for the solid samples were investigated with a Hitachi F-4500 fluorescence spectrophotometer. The X-ray powder diffraction pattern was recorded with a Pigaku D/Max 3III diffractometer.

2.2. Synthesis of $[Co(bpt)(pm)_{0.5}(H_2O)]_n \cdot 3nH_2O$ (**1**)

A mixture of $Co(OAc)_2 \cdot 4H_2O$ (0.2 mmol, 0.050 g), H_4pm (0.1 mmol, 0.022g), bpt (0.2 mmol, 0.048 g), H_2O (8 mL), C_2H_5OH (4 mL), and several dripping of DMF and triethylamine was heated at 140 °C for 3 days in a sealed Teflon-lined stainless steel vessel (25 mL) under autogenous pressure. Slow cooling of the reaction mixture to room temperature gave brown block crystals. Yield: 55%. *Anal.* Calc. for $C_{17}H_{17}CoN_4O_8S$: C, 41.14; H, 3.45; N, 11.29. Found: C, 41.16; H, 3.34; N, 11.28%. IR (KBr, cm^{-1}) for 1: 3500 (s), 1572 (s), 1492 (w), 1426 (m), 1380 (s), 1316 (w), 1223 (w), 1138 (w), 1113 (w), 1068 (m), 999 (m), 925 (w), 830 (s), 775 (w), 708 (m), 611 (s), 520 (m), 473 (m).

2.3. Synthesis of $[Cu_2(bpt)(pm)(H_2O)_4]_n$ (**2**)

A mixture of $Cu_2(OH)_2CO_3$ (0.8 mmol, 0.177 g), H_4pm (0.4 mmol, 0.087 g), bpt (0.4 mmol, 0.096 g), H_2O (8 mL), and C_2H_5OH (2 mL), was heated at 150 °C for 3 days in a sealed Teflon-lined stainless steel vessel (25 mL) under autogenous pressure. Slow cooling of the reaction mixture to room temperature gave blue block crystals. Yield: 61%. *Anal.* Calc. for $C_{22}H_{18}Cu_2N_4O_{12}S$: C, 38.32; H, 2.63; N, 8.12. Found: C, 38.37; H, 2.60; N, 8.10%. IR (KBr, cm^{-1}) for **2**: 3732 (w), 3410 (s), 3093 (w), 2923 (m), 2854 (w), 1611 (w), 1584 (s), 1553 (s), 1490 (m), 1423 (s), 1365 (s), 1329 (m), 1128 (m), 1055 (w), 998 (w), 865 (w), 817 (m), 757 (w), 709 (m), 668 (w), 597 (m), 516 (w), 476 (m), 425 (w).

2.4. Synthesis of $[Co(bpt)(pydc)]_n \cdot 2nCHCl_3 \cdot nH_2O$ (**3**)

Fifteen millilitres aqueous and CH_3OH (1:2) mixed solution of H_2pydc (0.2 mmol, 0.033 g), NaOH (0.4 mmol, 0.016 g), and $Co(OAc)_2 \cdot 4H_2O$ (0.2 mmol, 0.050 g) was carefully layered upon 15 mL CH_3OH and $CHCl_3$ mixed solution of bpt (0.2 mmol, 0.048 g). The resultant solution was allowed to stand undisturbed at room temperature for several months, yielding pink block crystals. Yield: 57%. *Anal.* Calc. for $C_{21}H_{15}Cl_6CoN_5O_5S$: C, 34.98; H, 2.10; N, 9.71. Found: C, 34.96; H, 2.06; N, 9.77%. IR (KBr, cm^{-1}) for 3: 3743 (w), 3414 (m), 3089 (w), 2968 (w), 1610 (s), 1577 (s), 1430 (s), 1391 (s), 1357 (s), 1279 (m), 1220 (w), 1182 (w), 1113 (w), 1067 (m), 1026 (w), 998 (w), 916 (w), 832 (s), 759 (s), 698 (s), 664 (m), 606 (m), 533 (w), 483 (w), 431 (w).

2.5. Synthesis of $[Cu_2(bpt)(pydc)_2(H_2O)_2]_n$ (**4**)

A mixture of $Cu(OAc)_2 \cdot H_2O$ (0.4 mmol, 0.080 g), H_2pydc (0.4 mmol, 0.066 g), bpt (0.2 mmol, 0.048 g), H_2O (10 mL), and CH_3OH (1 mL) was adjusted to pH 7 with 1 M NaOH solution and then heated at 125 °C for 3 days in a sealed Teflon-lined stainless steel vessel (25 mL) under autogenous pressure. Slow cooling of the reaction mixture to room temperature gave blue block crystals. Yield: 53%. *Anal.* Calc. for $C_{26}H_{18}Cu_2N_6O_{10}S$: C, 42.57; H, 2.47; N, 11.46. Found: C, 42.61; H, 2.45; N, 11.44%. IR (KBr, cm^{-1}) for 4: 3371 (m), 3084 (w), 1679 (m), 1614 (s), 1593 (s), 1551 (m), 1428 (s), 1412 (m), 1355 (s), 1332 (s), 1257 (w), 1217 (m), 1169 (m), 1143 (w), 1092 (w), 1080 (m), 1067 (w), 1040 (w), 998 (w), 909 (w), 884 (w), 846 (w), 826 (s), 779 (s), 736 (m), 719 (s), 692 (s), 662 (w), 609 (s), 550 (w), 488 (w), 437 (m).

2.6. Synthesis of $[Cu_2(bpt)(pydco)_2(H_2O)_2]_n \cdot nH_2O$ (**5**)

The same synthetic method as that for **4** was used except that H_2pydc was replaced by H_2pydco (0.4 mmol, 0.073 g) and pH value was adjusted to 6, affording dark blue block crystals. Yield: 61%. *Anal.* Calc. for $C_{26}H_{20}Cu_2N_6O_{13}S$: C, 39.85; H, 2.57; N, 10.72. Found: C, 39.84; H, 2.55; N, 10.75%. IR (KBr, cm^{-1}) for **5**: 3441 (m), 3084 (w), 1634 (s), 1477 (w), 1396 (s), 1352 (s), 1243 (w), 1221 (w), 1187 (m), 1064 (w), 1029 (w), 1000 (w), 917 (w), 853 (s), 772 (s), 713 (s), 614 (s), 476 (w).

2.7. Synthesis of $[Cd(bpt)(pydco)]_n$ (**6**)

The same synthetic route as that for **5** was used except that metal salt was replaced by $Cd(OAc)_2 \cdot 2H_2O$ (0.4 mmol, 0.105 g), forming pale-brown block crystals. Yield: 50%. *Anal.* Calc. for $C_{19}H_{11}Cd N_5O_5S$: C, 42.75; H, 2.08; N, 13.12. Found: C, 42.76; H, 2.02; N, 13.17%. IR (KBr, cm^{-1}) for **6**: 3742 (w), 3373 (w), 2922 (s), 2857 (m), 1643 (m), 1588 (s), 1550 (m), 1464 (w), 1426 (m), 1366 (m), 1329 (m), 1256 (w), 1214 (w), 1095 (w), 988 (w), 823 (s), 764 (w), 692 (s), 606 (m), 480 (w).

2.8. Crystallographic data collection and refinement

Single-crystal diffraction data **1**–**6** were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. The data integration and reduction were processed with SAINT software. The structures were solved by the direct method using SHELXTL and embarked on a full-matrix least-squares refinement on F^2 with