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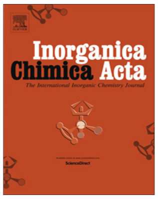

4,4′-(Pyridine-2,5-diyl)dibenzoic acid as a building block for Cd(II) and Mn(II) coordination compounds: Synthesis, structural features and properties

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ABSTRACT

Two new coordination compounds, namely a 3D metal–organic framework (MOF) $\{[Cd_2(L)_2(phen)_2]\cdot H_2O\}_n$ (**1**) and a discrete 0D dimer $[Mn(L)_{0.5}(HL)(phen)_2]_2\cdot 2H_2O$ (**2**), were generated by a hydrothermal method from the metal(II) chlorides, 4,4′-(pyridine-2,5-diyl)dibenzoic acid (H_2L) as a main building block, and an ancillary 1,10-phenanthroline (phen) ligand. The products **1** and **2** were characterized by IR spectroscopy, elemental, thermogravimetric, and single-crystal X-ray diffraction analyses. Compound **1** possesses an intricate 3D metal–organic framework based on tetracadmium(II) double-helicate units which, after simplification, resulted in a 4-fold interpenetrated underlying net with the **dia** topology. Compound **2** features a dimeric molecular structure, which is extended (0D → 1D) by hydrogen bonds into a 1D double chain network. It was topologically classified as a simple 3-connected ladder with the SP 1-periodic net (4,4)(0,2) topology. The luminescent (for **1**) and magnetic (for **2**) properties were also investigated and discussed.

1. Introduction

The design, synthesis and applications of coordination polymers have achieved a great progress over the past decade [1–4]. Various coordination polymers or metal–organic frameworks (MOFs) have shown a multitude of versatile architectures and topological motifs [5–8], accompanied with desirable properties and potential applications in various fields ranging from luminescence, molecular magnetism and catalysis to selective gas absorption and separation systems [2,9–12]. Many multi-carboxylate or heterocylic carboxylic acids have been designed and used as building blocks for the preparation of functional coordination polymers or MOFs [1,2,6,7,10,12–15]. In particular, we and others have reported a diversity of coordination compounds with intriguing architectures and interesting properties based on carboxylic acid building blocks [13–24]. As a continuation of our research in this field, we have tested the hydrothermal self-assembly reactions of Cd(II) and Mn(II) chlorides with 4,4′-(pyridine-2,5-diyl)dibenzoic acid (H_2L) as a novel main building block and 1,10-phenanthroline (phen) as an ancillary ligand (Scheme 1). The choice of H_2L has been governed by its virtually unexplored application in coordination chemistry, as attested by a search of the Cambridge Structural Database that revealed no examples of structurally characterized compounds derived from this dicarboxylic acid. Hence, in this paper, we open up the application of H_2L toward the design of metal–organic compounds and report the synthesis and characterization of the two novel coordination compounds, namely a 3D metal–organic framework $\{[Cd_2(L)_2(phen)_2]\cdot H_2O\}_n$ (**1**) and a discrete 0D dimer $[Mn(L)_{0.5}(HL)(phen)_2]_2\cdot 2H_2O$ (**2**).

2. Experimental

2.1. Materials and physical measurements

All chemicals and solvents were of A.R. grade and used without further purification. Carbon, hydrogen, and nitrogen content in **1** and **2** was determined using an Elementar Vario EL elemental

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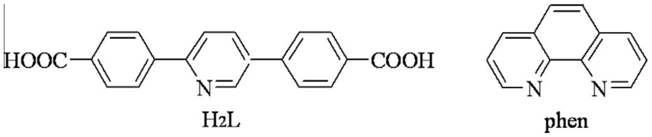

Scheme 1. Structural formulae of ligands used in this work.

analyzer. IR spectra were recorded in KBr pellets on a Bruker EQUINOX 55 spectrometer. Thermogravimetric analysis (TGA) was performed under N_2 atmosphere with a heating rate of 10 °C/min on a LINSEIS STA PT1600 thermal analyzer. Powder X-ray diffraction patterns (PXRD) were determined with a Rigaku-Dmax 2400 diffractometer using Cu-*Kα* radiation ($\lambda = 1.54060$ Å), in which the X-ray tube was operated at 40 kV and 40 mV. Magnetic susceptibility data were collected in the 2–300 K temperature range with a Quantum Design SQUID Magnetometer MPMS XL-7 with a field of 0.1 T. A correction was made for the diamagnetic contribution prior to data analysis. Excitation and emission spectra were recorded for the solid samples on an Edinburgh FLS920 fluorescence spectrometer at room temperature.

2.1.1. $\{[Cd_2(L)_2(phen)_2]\cdot H_2O\}_n$ (**1**)

A mixture of H_2L (0.1 mmol, 32.0 mg), phen (0.1 mmol, 19.8 mg), $CdCl_2\cdot H_2O$ (0.1 mmol, 22.8 mg), NaOH (0.2 mmol, 8.0 mg) and H_2O (8 mL) was placed in a Teflon-lined stainless steel vessel (20 mL), heated to 160 °C for 3 days, and then cooled to room temperature over 24 h. Colorless block single crystals of **1** were obtained in 60% yield (37.10 mg, based on Cd). Elemental analysis (%) for $C_{61}H_{39}N_7Cd_2O_9$: calcd, C, 59.14; H, 3.17; N, 7.91; found, C, 59.55; H, 3.27; N, 7.57. IR (cm^{-1}): 3064 w, 1608 m, 1583 s, 1541 s, 1513 w, 1470 w, 1389 s, 1220 w, 1181 w, 1140 w, 1015 m, 998 w, 842 s, 784 s, 755 w, 726 s, 637 w, 528 w.

2.1.2. $[Mn(L)_{0.5}(HL)(phen)_2]_2\cdot 2H_2O$ (**2**)

This product was synthesized in the similar way as that described for **1**, except that $CdCl_2\cdot H_2O$ was replaced by $MnCl_2\cdot 4H_2O$ (0.10 mmol, 19.8 mg). Yellow block single crystals of **2** were obtained in 65% yield (29.56 mg, based on Mn). Elemental analysis (%) for $C_{53}H_{36}N_5MnO_7$: calcd, C, 69.97; H, 3.99; N, 7.70; found, C, 70.24; H, 4. 06; N, 7.56. IR (cm^{-1}): 3056 w, 1686 m, 1608 w, 1590 s, 1553 m, 1515 s, 1472 w, 1426 s, 1365 s, 1248 m, 1143 m, 1102 w, 1048 w, 1013 w, 999 w, 864 w, 842 s, 809 w, 786 m, 755 w, 729 s, 708 m, 637 w, 520 w.

2.2. Crystallography

The crystallographic data for **1** and **2** were obtained on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature using the φ/ω scanning technique. The structures were solved using direct methods and successive Fourier difference synthesis (SHELXS-97) [25], and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [25]. All the hydrogen atoms (except those bound to water molecules) were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations at the final stage of full-matrix least-squares refinement. The hydrogen atoms of water molecules were located by difference maps and constrained to ride on their parent O atoms. The crystal data for **1** and **2** are summarized in Table 1 and selected bond lengths are listed in Table 2. Hydrogen bonds in the compound **2** are given in Table 3.

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

Compound	**1**	**2**
Formula	$C_{61}H_{39}Cd_2N_7O_9$	$C_{53}H_{36}MnN_5O_7$
Formula weight	1238.79	909.81
Space group	$P2/c$	$P\bar{1}$
a (Å)	16.1866(4)	10.5073(6)
b (Å)	10.4245(3)	14.9488(8)
c (Å)	30.8202(8)	15.2058(12)
α (°)	90	113.872(6)
β (°)	103.526(3)	100.432(6)
γ (°)	90	91.659(5)
V ($Å^3$)	5056.3(2)	2134.1(2)
Z	4	2
D_{calc} (g/cm^{-3})	1.627	1.416
μ (mm^{-1})	0.911	0.373
$F(000)$	2488	940
Reflections collected	20833	15776
Unique reflections	8982	8365
R_{int}	0.0455	0.0368
θ range (°)	3.18–25.05	3.00–26.00
Data/restraints/parameters	8982/48/769	8365/0/596
		$-15 \leqslant l \leqslant 15$
Final R indices [$I > 2\sigma(I)$]	0.0396, 0.0958	0.0620, 0.1652
R_1 and wR_2 [all data]	0.0502, 0.1038	0.1071, 0.2056
Goodness-of-fit	1.058	1.029

3. Results and discussion

3.1. Crystal structure of $\{[Cd_2(L)_2(phen)_2]\cdot H_2O\}_n$ (**1**)

Single crystal X-ray diffraction study reveals that **1** is composed of two crystallographically unique Cd(II) atoms, two distinct μ_2- and μ_4-L^{2-} blocks, two terminal phen ligands, and one lattice water molecule. Both the Cd1 and Cd2 centers are six-coordinated by four O and two N atoms, constructing a distorted octahedral $\{CdO_4N_2\}$ geometry (Fig. 1a). The Cd–O bonds range from 2.204(3) to 2.414(3) Å, whereas the Cd–N distances vary from 2.347(4) to 2.377(4) Å, which are comparable to those found in other reported Cd(II) compounds [15,21,22]. The carboxylate groups of L^{2-} bridge alternately four Cd(II) atoms in a *syn-anti* coordination mode to produce a tetracadmium(II) double-helicate unit (Fig. 1b). A double-helicate binuclear Cd(II) compound $[Cd_2(spy)_2][PF_6]_4\cdot MeCN$ (spy = 2,2′:6′,2″6″,2‴:6‴,2⁗:6⁗,2⁗′-sexipyridine) was reported, in which the two Cd atoms adopted six-coordinate N_6 environments and the intramolecular Cd···Cd distance was 4.173(4) Å [26a]. This is apparently the first example of a double-helical tetracadmium(II) unit in the coordination polymers. Within the Cd_4 unit of **1**, the distances of adjacent Cd(II) ions are in the 4.296(4)–4.302(4) Å range, being longer than those reported for other coordination polymers bearing carboxylate-bridged tetracadmium(II) blocks [26b,c]. In **1**, the Cd_4 units are multiply linked by the L^{2-} blocks to form an intricate 3D framework (Fig. 1c), in which the carboxylate groups of L^{2-} ligands adopt μ_2-η^1:η^1 bidentate modes.

To get further insight into this very complex 3D metal–organic framework of compound **1**, we have topologically analyzed the structure using the TOPOS program and following the concept of the simplified underlying net [27,28]. Such a net has been obtained by omitting the terminal phen ligands and reducing the bridging μ_2-L and μ_4-L moieties to their centroids (first simplification step [27]), giving rise to a tetranodal 3,4,4,4-connected 3D interpenetrated framework (Fig. 1d and e) with the point symbol of $(4.10^2)_2(4^3.6^2.8)_2(4^4.6^2)_3$. This net was simplified further (second simplification step [27]) by treating the Cd_4 units as cluster nodes, resulting in a uninodal 4-connected framework with the point symbol of (6^6) and common **dia** topology (Fig. 1f) [27–30]. This underlying framework is built from the 4-connected