Inorganic Chemistry Communications 14 (2011) 711–714

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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

A divalent cadmium coordination polymer featuring a complex tetranodal 3-D topology and hexadecameric water clusters

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ARTICLE INFO

Article history:
Received 18 March 2010
Accepted 21 February 2011
Available online 17 March 2011

Keywords:
Coordination polymer
Cadmium
Crystal structure
Water cluster
Hydrogen bonding
Luminescence

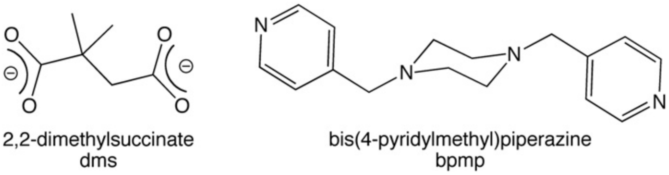
ABSTRACT

The luminescent coordination polymer $\{[Cd_2(dms)_2(bpmp)_{1.5}]{\bullet}8H_2O\}_n$ (1, dms = 2,2-dimethylsuccinate, bpmp = bis(4-pyridylmethyl)piperazine) exhibits $[Cd_2(dms)_2(bpmp)]_n$ layers partially pillared by other crystallographically distinct bpmp ligands into a complex 3-D 3,4,5-connected tetranodal network. Hydrogen-bonded hexadecameric water molecule clusters lie in incipient channels.

Divalent metal dicarboxylate coordination polymers have been widely studied in recent years, because of their potentially useful properties such as gas storage [1], gas separation [2], ion exchange [3], catalysis [4], non-linear optics [5], and luminescence [6]. Additionally, the aesthetics of their underlying network topologies provides a significant impetus for continued exploratory synthesis. Synergistic cooperation between metal coordination geometry, specific carboxylate binding and bridging modes, and the geometric disposition of carboxylate donor groups during self-assembly is reflected in the wide variety of coordination polymer topologies that have been observed to date [7]. Given the challenges inherent in *a priori* prediction and design of specific networks, exploratory synthesis continues to develop the scope of coordination polymer topologies. A recent successful approach towards the generation of new topologies has been the simultaneous employment of aliphatic α,ω-dicarboxylate dicarboxylate and dipyridyl tethering ligands. For example, $\{[Cd(succinate)(N,N'\text{-bispyridin-4-ylmethylsuccinamide})]{\bullet}H_2O\}_n$ possesses a very rare 6^6 self-penetrated layered topology [8], and $\{[Cd(succinate)(bpmp)(CH_3OH)]\ {\bullet}2H_2O\}_n$ (bpmp = bis(4-pyridylmethyl)piperazine) manifests a chiral layered network with a unique 6^58 topology [9]. In light of the unprecedented topologies of these two succinate/long-spanning dipyridine dual-ligand cadmium coordination polymers, we aimed to examine the effect of *gem*-dimethyl group substitution on the underlying topology. We present here a discussion of the synthesis, structural characterization, luminescence, and thermal properties of $\{[Cd_2(dms)_2(bpmp)_{1.5}]{\bullet}8H_2O\}_n$ (**1**, dms = 2,2-dimethylsuccinate, Scheme 1), which manifests a complex 3-D tetranodal network topology. The water molecules of crystallization in **1** also form an intriguing hydrogen-bonded cluster morphology.

Colorless blocks of compound **1** were prepared in moderate yield from the hydrothermal reaction of cadmium nitrate, H_2dms and bpmp in a 1:1:2 mol ratio [10]. It is plausible that some quantity of bpmp in the reaction mixture acts to deprotonate the H_2dms precursor, and is therefore unable to bind to cadmium. The infrared spectrum of polycrystalline **1** indicated the presence of antisymmetric and symmetric carboxylate stretching bands at 1599/1565 cm^{-1} and 1426/1412 cm^{-1}, respectively. A moderately intense, broad band centered on 3396 cm^{-1} marks the presence of the hydrogen-bonded water molecules of crystallization.

Single-crystal X-ray diffraction revealed that the asymmetric unit of **1** (Fig. S1) contains two divalent cadmium atoms, two dms ligands (*dms-A*, O1–O4; *dms-B*, O5–O8), halves of three crystallographically distinct bpmp ligands (*bpmp-A*, N1–N2; *bpmp-B*, N3–N4; *bpmp-C*, N5–N6), and



Scheme 1. Ligands used in this study.

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doi:10.1016/j.inoche.2011.02.013

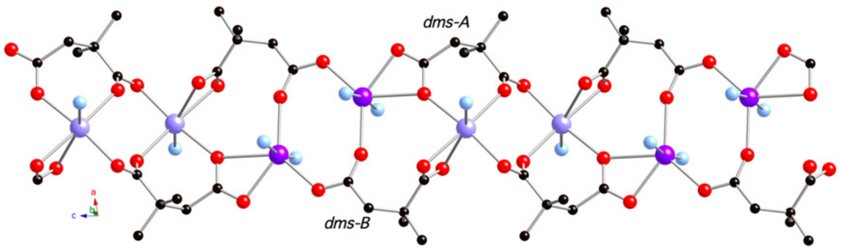

Fig. 1. A $[\mathrm{Cd_2(dms)_2}]_n$ chain motif in **1**. Cd1 and Cd2 atoms are shown in light and dark purple, respectively.

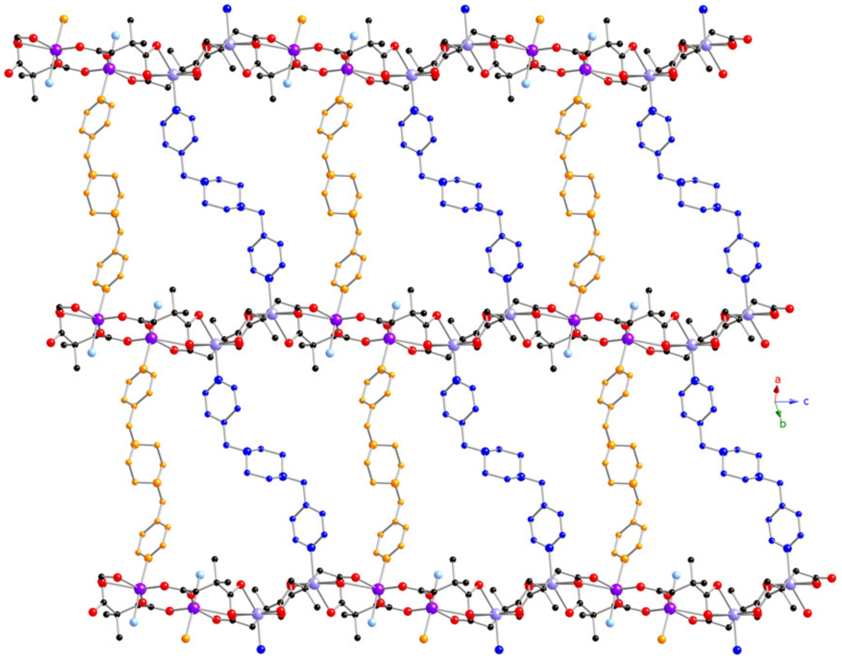

Fig. 2. A $[\mathrm{Cd_2(dms)_2(bpmp)}]_n$ layer in **1**, with $[\mathrm{Cd_2(dms)_2}]_n$ chains linked by *bpmp-A* and *bpmp-B* ligands, which are drawn in blue and orange, respectively, in the online version of this article.

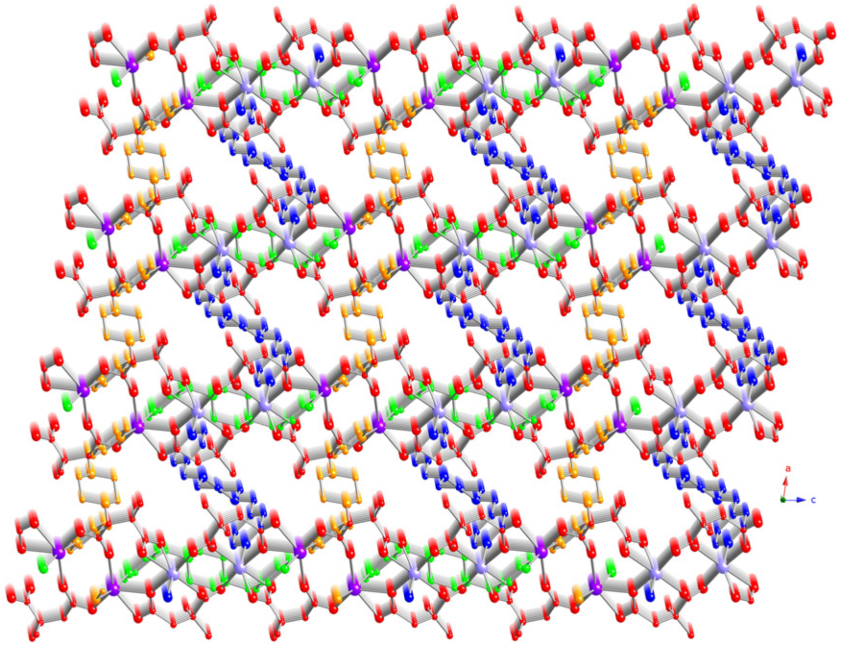

Fig. 3. Three-dimensional $[\mathrm{Cd_2(dms)_2(bpmp)_{1.5}}]_n$ coordination polymer network in **1**, viewed down the *b* crystal direction. The dms, *bpmp-A*, *bpmp-B*, and *bpmp-C* ligands are drawn in red, blue, orange, and green, in the online version of this article.