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Synthesis, crystal structures and photophysical properties of two supramolecular complexes of cadmium(II)

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Abstract

The reaction of $Cd(NO_3)_2$ with 5-sulfoisophthalic acid monosodium salt (NaH_2sip) in the presence of piperazine (pip) or ethylenediamine (en) produced three-dimensional supramolecular complexes $[Cd(sip)(Hpip)(H_2O)_2]$ (**1**) and $[Cd(sip)(H_2O)_3] \cdot 0.5(H_2en) \cdot H_2O$ (**2**). In both compounds, the Cd^{2+} atoms are linked by sip^{3-} into a one-dimensional zig zag chain. The resultant negative ribbons are charge balanced by the coordinated protonated pip (Hpip) in **1** but by free, half occupied H_2en in **2**. The zigzag chains are further linked together by hydrogen bonds and π–π stacking interactions to form supramolecular open frameworks. Both **1** and **2** show violet–blue photoluminescence at room temperature.

Keywords: Supramolecular complexes; Cadmium complexes; Crystal structures; Photoluminescence

Demand for new porous materials that function as molecular sieves and catalysts has fueled a burgeoning interest in crystal engineering [1]. This solution-based approach to solid synthesis involves the use of molecular components with well-defined directional bonding preferences as reactants for constructing extended crystalline structures. The key to successful construction of supramolecular architecture is the control and manipulation of coordination bonds and non-covalent interactions by carefully selecting the coordination geometry of the metal centers and the organic ligands containing appropriate functional groups (such as polycarboxylic acid and multipyridine) [2]. Up to now, a large number of supramolecular complexes with various dimensions and topologies have been achieved through judicious choice of organic linkers and metal ions [3].

The approach to supramolecular framework employed in this work is to use the trifunctional linker NaH_2sip that are selected under the following considerations: (1) It contains both the dicarboxylate groups of strong coordinating ability and sulfonate group as suitable hydrogen bond acceptor [4]; (2) π–π stacking interactions between the aromatic rings may facilitate ordered, non-interpenetrated open frameworks. In this contribution, the self-assembly of Cd(II) with sip^{3-} in the presence of templates such as piperazine or ethylenediamine has been investigated, which leads to the supramolecular open framework materials $[Cd(sip)(Hpip)(H_2O)_2]$ (**1**) and $[Cd(sip)(H_2O)_3] \cdot 0.5(H_2en) \cdot H_2O$ (**2**) [5]. Both compounds have been characterized by X-ray crystallography [6], fluorescence spectroscopy and IR spectra.

As shown in Fig. 1, the Cd(II) atoms are bridged by sip^{3-} to form an infinite zigzag chain. Each cadmium center has distorted octahedral coordination geometry.

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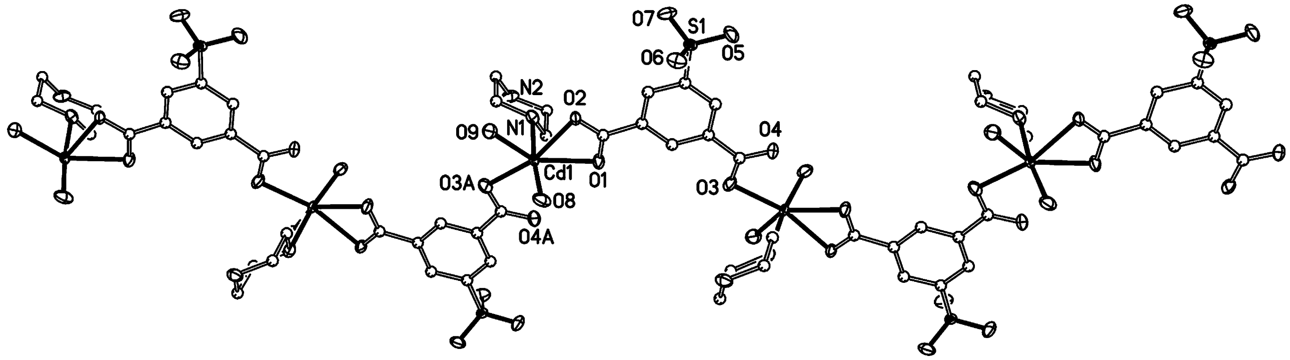

Fig. 1. ORTEP drawing of the infinite zigzag chain of **1** with 70% probability thermal ellipsoids. Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (°): Cd1–O1 2.356(1), Cd1–O2 2.380(1), Cd1–O8 2.324(1), Cd1–O9 2.328(1), Cd1–N1 2.381(2), Cd1–O3A 2.239(1) and O1–Cd1–O2 55.62(4), O2–Cd1–O9 82.27(5), O1–Cd1–O3A 137.39(5), O9–Cd1–O3A 85.41(5), O8–Cd1–N1 173.43(5), O8–Cd1–O1 86.50(5), O8–Cd1–O2 86.53(5), O8–Cd1–O9 83.28(6), O8–Cd1–O3A 100.63(5), N1–Cd1–O1 88.17(5), N1–Cd1–O2 87.29(5), N1–Cd1–O9 98.09(6), N1–Cd1–O3A 85.89(5). A: $-x + 3/2$, $-y$, $z + 1/2$.

The equatorial positions are taken up by two chelating carboxylate oxygen donors from one sip^{3-}, one monodentate carboxylate oxygen from another and one water molecule. The axial positions are occupied by protonated pip nitrogen atom and one water molecule. The angles formed by the equatorial atoms range from 55.62(4)° (the chelating angle O1–Cd–O2) to 137.39(5)° (O1–Cd–O3A, A: $-x + 3/2$, $-y$, $z + 1/2$), indicative of serious distortion of the $[CdO_5N]$ octahedron. The bond length between Cd and the monodentate oxygen atom (2.239(1) Å) is slightly shorter than the other Cd–O (2.324(1)–2.380(1) Å, av. 2.347 Å) and Cd–N bonds (2.381(2) Å). Note that one-dimensional coordination polymer $[Cu(H_2O)_2(Hsip)] \cdot 2H_2O \cdot 0.5$ (pip) was reported very recently, which contained free (non-coordinated) organic amine molecules [7].

Fig. 2 shows the supramolecular open framework structure built of the infinite zigzag chains through the interchain hydrogen bonds and π–π interactions. The following four types of hydrogen bonds link the chains into the three-dimensional architecture: (i) hydrogen bonds between the coordinated water molecules and the carboxylate oxygen atoms (O8···O2B = 2.691 Å, B: $x - 1/2$, y, $-z - 1/2$); (ii) hydrogen bonds between coordinated water molecules and sulfonate oxygen atoms (O8···O5C = 2.899 Å, C: $x - 1/2$, $-y - 1/2$, $-z - 1$, O9···O7B = 2.800 Å, O9···O6D = 2.861 Å, D: x, $-y - 1/2$, $z + 1/2$); (iii) hydrogen bonds between the

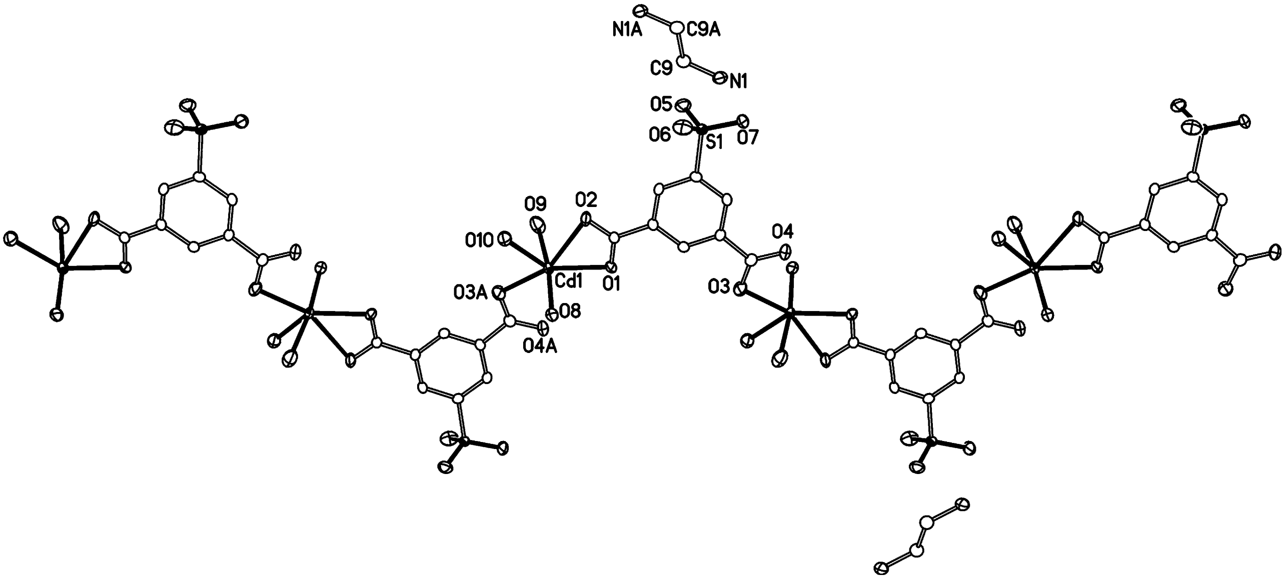

Fig. 2. ORTEP drawing of the infinite zigzag chain of **2** with the thermal ellipsoids are drawn at the 70% probability level. The hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (°): Cd1–O1 2.246(1), Cd1–O2 2.472(1), Cd1–O8 2.371(2), Cd1–O9 2.342(2), Cd1–O10 2.313(2), Cd1–O3A 2.184(1) and O1–Cd1–O2 55.48(5), O2–Cd1–O10 76.73(5), O1–Cd1–O3A 147.92(5), O10–Cd1–O3A 81.94(5), O8–Cd1–O9 173.15(5), O8–Cd1–O1 86.36(5), O8–Cd1–O2 97.86(5), O8–Cd1–O10 85.73(5), O8–Cd1–O3A 92.31(6), O9–Cd1–O1 100.49(5), O9–Cd1–O2 86.18(5), O9–Cd1–O10 89.84(6), O9–Cd1–O3A 81.88(6). A: $-x + 1$, $y - 1/2$, $-z + 1/2$.