

NOTE

Metal Ion-Driven Assembly of Cd(II) Coordination Polymer Constructed by Asymmetric Diphenic acid and Imidazole-Containing Ligand: Syntheses, Crystal Structures and Luminescent Properties

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A new metal coordination polymer, $[\text{Cd}(\text{bpdc})(\text{L})_{0.5}](\mathbf{1})$ [H_2bpdc = biphenyl-2,4'-dicarboxylic acid and L = 1,4-bis(2-methyl imidazol-3-ium-1-yl)biphenyl], has been synthesized and characterized by single-crystal X-ray diffraction, elemental analysis and IR spectra. Complex $[\text{Cd}(\text{bpdc})(\text{L})_{0.5}](\mathbf{1})$ is, triclinic space group $P-1$ with $a = 8.673(5) \text{ \AA}$, $b = 9.658(5) \text{ \AA}$, $c = 11.493(5) \text{ \AA}$, $\beta = 85.169(5)^\circ$, $V = 917.1(8) \text{ \AA}^3$, $Z = 1$, $M_r = 471.75$, $D_c = 1.708 \text{ g/cm}^3$, $F(000) = 470$ and $\mu = 1.221 \text{ mm}^{-1}$. Complex $\mathbf{1}$ features a 2D sql topological net.

Keywords: Crystal structure, Cadmium(II), Coordination polymer.

The design and synthesis of coordination polymers, have achieved considerable interest in the realm of crystal engineering, not only owing to their tremendous potential applications as functional materials, but also because of their intriguing variety of architectures and topologies¹⁻⁴. Consequently, a series of studies in this field have mainly focused on the design and preparation, as well as the structure-property relationships. At present, significant progress has been achieved. Nevertheless, it is still a great challenge to predict and control the synthesis of final products at this stage. The following factors, such as the coordination geometry of the nature of organic ligands, the coordination geometry of metal ions, metal-ligand ratio and the pH value of the solution, *etc.*, which may influence the self-assembly of coordination polymeric frameworks with unique structures and functions⁵⁻⁸.

All reagents and solvents employed were commercially available and used as received. C, H and N analyses were carried out with a Perkin-Elmer 240C elemental analyzer. FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer as a dry KBr pellet in the 4000-400 cm^{-1} range.

$[\text{Cd}(\text{bpdc})(\text{L})_{0.5}](\mathbf{1})$: The mixtures of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.5 mmol, 0.145 g), biphenyl-2,4'-dicarboxylic acid (H_2bpdc) (0.5 mmol, 0.121 g), 1,4-bis(2-methyl imidazol-3-ium-1-yl)biphenyl (L) (0.5 mmol, 0.119 g), NaOH (1 mmol, 0.04 g) 12 mL of water were placed in a 25 mL Teflon reactor which was heated to 120 $^\circ\text{C}$ for 3 days and then cooled to room temperature. Colourless block crystals of Cd(II) coordination polymer were collected in 48 % yield based on Cd after washing with

ethanol several times. Elemental Anal. Calcd (%) for $\text{C}_{21}\text{H}_{15}\text{N}_2\text{O}_4\text{Cd}$: C, 53.47; H, 3.21; N, 5.94. Found: C, 53.45; H, 3.22; N, 5.93. IR (KBr, ν_{max} , cm^{-1}): 1607 s, 1554 s, 1489 s, 1350 s, 1263 m, 1132 m, 1089 m, 942 m, 836 m, 741 m.

X-ray crystallography: Single crystal X-ray diffraction analyses of complexes $\mathbf{1}$ and $\mathbf{2}$ were carried out on a Bruker SMART APEXII CCD diffractometer equipped with a graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) by using a ω -scan mode. Empirical absorption correction was applied using the SADABS programs⁹. All the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program SHELXL 97¹⁰. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically calculations and their positions and thermal parameters were fixed during the structure refinement.

Description of the crystal structure $[\text{Cd}(\text{bpdc})(\text{L})_{0.5}](\mathbf{1})$: Complex $\mathbf{1}$ shows a two-dimensional layer structure with triclinic system space group $P-1$. As shown in Fig. 1, the Cd(II) ion is coordinated by five oxygen atoms for three carboxylate groups of two bpdc^{2-} ligands [Cd-O, ranging from 2.172 (3) \AA to 2.630 (3) \AA] and one nitrogen atom from L ligand [Cd(1)-N(1) = 2.212 (2) \AA]. In Cd(II) complex, the carboxylate groups adopt bis-chelating ($\mu_1\text{-}\eta^1$: η^1) and chelating/bridging ($\mu_2\text{-}\eta^1$: η^2) modes. The dihedral angle between two phenyl rings is 57.51 $^\circ$. The $\mu_2\text{-}\eta^1$: η^2 carboxylate groups connect Cd(II) ions to form a one-dimensional chain (Fig. 2). The 1D chains are further connected by L ligands to construct 2D structure (Fig. 3). If the dinuclear Cd(II) units and organic ligands can be viewed

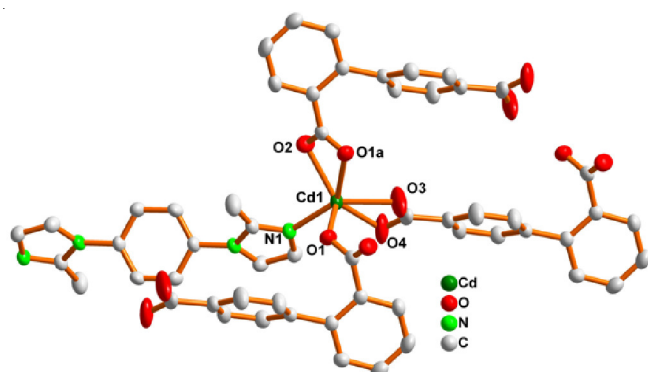


Fig. 1. Coordination environment of Cd(II) atom in complex 1

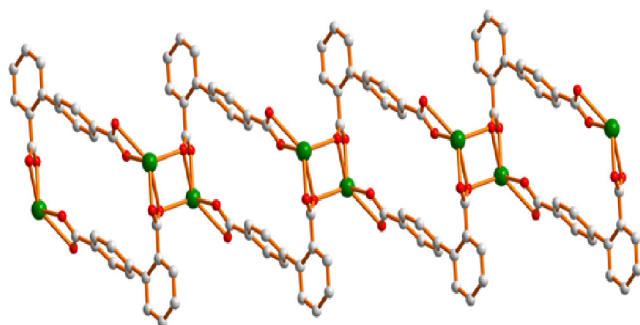


Fig. 2. 1D Chain constructed by carboxylate ligands and Cd(II) ions

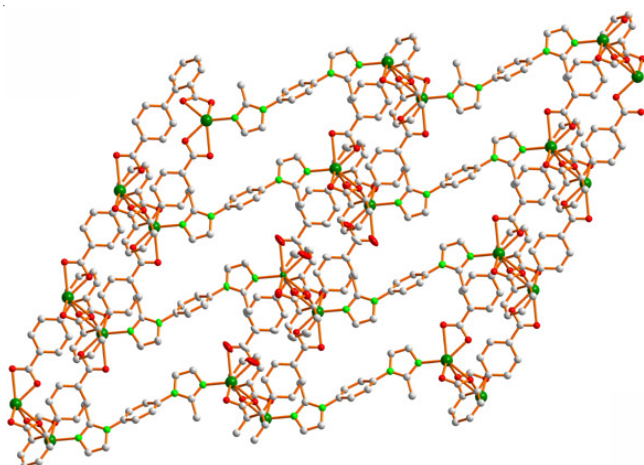


Fig. 3. 2D layer structure for complex 1

as nodes and linkers, the structure can be simplified as a 4-connected *sql* layer net. In 1, the 2D layers stack together with a -ABC- sequence parallel to the *bc* plane (Fig. 4).

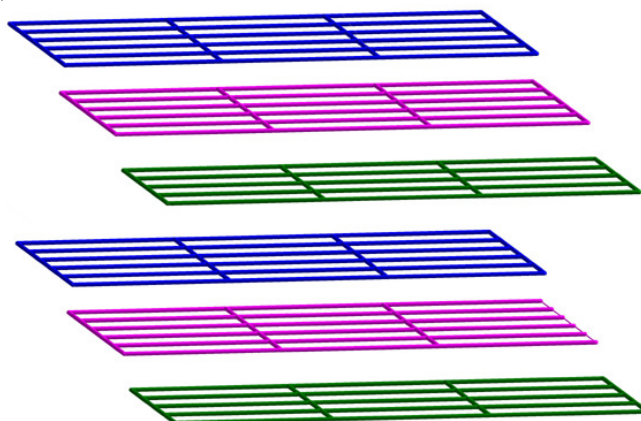


Fig. 4. Packing diagram depicting the ABC type stacks of 2D sheet in Cd(II) complex

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