Synthesis, characterization and crystal structure of a 2D Cd(II) complex with a 4,4'-diazenediylidphthalic acid ligand

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An exploration of the cadmium-L system under hydrothermal condition, has led to the isolation of a novel framework \([\text{Cd}(\text{L})_{0.5}(\text{H}_2\text{O})_3]_n(\text{I})\) (\(\text{H}_4\text{L} = 4,4'\text{-diazenediylidphthalic acid}\)). Single-crystal X-ray analysis reveals that it crystallizes in the triclinic space group P-1. \(a = 5.746(3)\) Å, \(b = 6.526(4)\) Å, \(c = 14.701(8)\) Å, \(\alpha = 92.348(8)^\circ\), \(\beta = 99.622(6)^\circ\), \(\gamma = 106.877(7)^\circ\). The Cd²⁺ ions are linked into an extended 2-D rectangle-like structure via L ligands, which exhibits an attractive three-connected honeycomb topological network.

1 Introduction

The rational design and syntheses of novel coordination polymers have achieved considerable progress in the field of supramolecular chemistry and crystal engineering, owing to their potential applications as gas storage [1], sensor technology [2], separation processes [3], ion exchange [4], luminescence [5], magnetism [6], and catalysis [7], as well as due to their intriguing variety of architectures and topologies. Crystal engineering of solid-state supramolecular entities such as coordination polymers has provided a nice bit of successful examples for the rational assembly of target materials, which are normally realized by deliberate design of the ligands with adjustable connectivity and/or judicious selection of metal ions with specific coordination tendency [8]. Lots of supramolecular frameworks have already been prepared in the past decade based on the principle of crystal engineering. In the construction of novel metal-organic frameworks (MOFs), polycarboxylate ligands, such as 1,2-benzenedicarboxylate, 1,3,5-benzenetricarboxylate and 1,2,4,5-benzenetetracarboxylate, have been extensively employed to synthesize such metal-organic complexes in possession of multidimensional networks and interesting properties [9-10]. 4,4'-Diazenediylidphthalic acid ligands [11], as a member of multidentate O-donor, is rarely used. We have reported its structure in absence of metal ion. However, its following structure features inspire our continue to researching interests: (a) it has four carboxylate groups that may be completely or partially deprotonated, depending on the pH; (b) the carboxylate groups may induce core aggregation, and it should be feasible to link discrete cluster into an extended network via versatile bridging abilities; (c) carboxylic acid is a good candidate for the construction of novel metal–organic compounds, because carboxyl groups can bind to central metal ions and form C–O–M–O four-membered rings, thereby improving the stability of transition metal–organic frameworks. Taking account of the above factors, we have previous studied the assembly of L ligand with transition metal ion under mild conditions. In this paper, we report a novel two-dimensional structure with three-connected honeycomb topological network, namely \([\text{Cd}(\text{L})_{0.5}(\text{H}_2\text{O})_3]_n(\text{I})\), which constructed from a rectangle-like grid net.

2 Experimental

Materials and physical measurements All reagents in the syntheses were analytical grade. Elemental analyses for carbon, hydrogen and nitrogen were performed on a Vario EL III elemental analyzer. The infrared

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spectra (4000 ~ 600 cm\(^{-1}\)) were recorded by using KBr pellet on an Avatar\textsuperscript{TM} 360 E. S. P. IR spectrometer. The crystal determination was performed on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromated Mo K\textsubscript{α} radiation (\(\lambda = 0.71073\) Å).

**Synthesis of the complex** A mixture of H\textsubscript{4}L (0.018 mmol, 25 mg), and Cd(OAc)\textsubscript{2}·4H\textsubscript{2}O (0.15 mmol, 28 mg) in distilled water (15 mL) (pH = 5) was placed in a Teflon-lined stainless steel vessel, heated to 150 °C for 9 days, and then cooled to room temperature over 12 h. Colorless block crystals of 1 were obtained. Anal. (%) calcd for C\textsubscript{8}H\textsubscript{9}CdNO\textsubscript{7}: C, 27.97; H, 2.64; N, 4.07; Found: C, 27.81; H, 2.55; N, 4.09. IR (KBr, cm\(^{-1}\)) 3421(Vs), 2929(W), 1651(Vs), 1504(Vs), 1438(S), 1216(S), 1029(M), 837(M), 628(W).

**Crystallographic data collection and structure determination** Single-crystal data were collected at 298(2) K on a Bruker Smart Apex II diffractometer equipped with graphite-monochromated Mo K\textsubscript{α} radiation. The structure was solved using direct methods and successive Fourier difference synthesis (SHELXS-97) [12], and refined using the full-matrix least-squares method on \(F^2\) with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [13]. The final agreement factor values are \(R_1 = 0.0503\), \(wR_2 = 0.1286\), \(w = 1/[\sigma^2(F_0^2)+(0.0665P)^2+2.3500P]\) where \(P = (F_0^2+2F_c^2)/3\). A summary of the crystallographic data is given in Table 1. Selected bond distances and angles, and parameters of hydrogen bonds are given in Table 2, Table 3, respectively.

### Table 1 Crystallographic data.

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>C\textsubscript{8}H\textsubscript{9}CdNO\textsubscript{7}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>4343.57</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>298(2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>(a = 5.746(3)Å, \ b = 6.526(4)Å, \ c = 14.701(8)Å, \ \alpha = 92.748(8), \ \beta = 99.622(6), \ \gamma = 106.877(7)°)</td>
</tr>
<tr>
<td>Volume, Z</td>
<td>517.8(5) Å(^3), 2</td>
</tr>
<tr>
<td>Calculated density (Kg/m(^3))</td>
<td>2.204</td>
</tr>
<tr>
<td>Crystal size (mm(^3))</td>
<td>0.28×0.21×0.17</td>
</tr>
<tr>
<td>(\theta) Range for data collection (º)</td>
<td>2.8-25.5</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>2741</td>
</tr>
<tr>
<td>Independent reflection</td>
<td>1871</td>
</tr>
<tr>
<td>Final R indices ([I&gt;2\sigma(I)])</td>
<td>(R_1 = 0.0768, \ wR_2 = 0.2448)</td>
</tr>
<tr>
<td>(R) indices (all data)</td>
<td>(R_1 = 0.0832, \ wR_2 = 0.2482)</td>
</tr>
</tbody>
</table>

Crystallographic Data Center as supplementary publication number CCDC-683994. Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK; E-mail: deposit@ccdc.cam.ac.uk.

### Table 2 Selected bond lengths (Å) and angles (º) for 1. (Symmetrical codes: #1: -1+x,-1+y,z; #2: x,-1+y,z).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (º)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(1)-O(1)</td>
<td>2.344(12)</td>
<td></td>
</tr>
<tr>
<td>Cd(1)-O(1W)</td>
<td>2.344(12)</td>
<td></td>
</tr>
<tr>
<td>Cd(1)-O(1W)</td>
<td>2.304(11)</td>
<td></td>
</tr>
<tr>
<td>Cd(1)-O(2)</td>
<td>2.333(12)</td>
<td></td>
</tr>
<tr>
<td>Cd(1)-O(2W)</td>
<td>2.333(12)</td>
<td></td>
</tr>
<tr>
<td>Cd(1)-O(2W)</td>
<td>2.248(17)</td>
<td></td>
</tr>
<tr>
<td>Cd(1)-O(3)</td>
<td>2.390(14)</td>
<td></td>
</tr>
<tr>
<td>Cd(1)-O(3W)</td>
<td>2.390(14)</td>
<td></td>
</tr>
<tr>
<td>Cd(1)-O(4)</td>
<td>2.255(12)</td>
<td></td>
</tr>
<tr>
<td>Cd(1)-O(4W)</td>
<td>2.255(12)</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3 Selected parameters of hydrogen bonds for 1 (Å, º).

<table>
<thead>
<tr>
<th>D-H···A</th>
<th>D-A</th>
<th>&lt;D-H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1W)-H(1A)--O(2)</td>
<td>2.746(16)</td>
<td>130</td>
</tr>
<tr>
<td>O(1W)-H(1B)--O(3)</td>
<td>2.866(17)</td>
<td>103</td>
</tr>
<tr>
<td>O(2W)-H(2B)--O(3)</td>
<td>2.738(17)</td>
<td>107</td>
</tr>
<tr>
<td>O(3W)-H(3A)--O(2)</td>
<td>3.368(18)</td>
<td>145</td>
</tr>
<tr>
<td>O(1W)-H(1A)--O(1)</td>
<td>3.272(16)</td>
<td>148</td>
</tr>
</tbody>
</table>

### 3 Results and discussion

As shown in figure 1, the asymmetric unit consists of one crystallographically Cd(II) ions, a half L tetraanion and three coordinated water molecules. Figure 1 shows the asymmetric unit as well as the centre of symmetry related unit. All carboxylic groups of H\textsubscript{4}L are deprotonated, in agreement with the IR data in which no characteristic absorption bands of the –COOH group at 1700-1750 cm\(^{-1}\) are observed. Each Cd(II) ion is six-coordinated by oxygen atoms from three different L ligands and another three oxygen atoms from three...
coordinated water molecules, forming a distorted octahedral geometry. The bond lengths of Cd–O range from 2.255(12) to 2.390(14) Å with an average value of 2.283(3) Å, which are similar to those found in other transition-metal complexes of carboxylates [14]. The O–Cd(1)–O angles range from 78.1(5) to 168.2(4)°, which indicates Cd center has a distorted octahedral environment. The L ligand in 1 acts as a hexadentate ligand: two 4,4′-carboxylate groups adopt a trans conformation and bis(bidentate) bridging modes, while the other two 4,4′-carboxylate groups exhibit a bis(monodentate) bridging fashions, the pair of phenyl rings of the ligand is nearly coplanar. On the basis of the connection mode, the Cd(II) atoms are bridged by the linear phthalic groups of L ligands to form zigzag chains. The adjacent chains are further connected by the oxygen atoms of the another carboxylate groups in two different L ligands to shape a 2-D layer. Interestingly, the 2-D layer is a rare bilayer framework with a distance of 5.47(7) Å (based on Cd1···Cd1) between the two single layers. When viewed down along the crystallographic a-axis, approximately rectangular channels with dimensional of 13.49×10.09 Å (base on N1···N1 and Cd1···Cd1) are formed in 1 (figure 2). As far as we known, such 2-D bilayer is still rare in the systems of metal-carboxylate complexes [15]. If, for reasons of classifying the net, we define chelate ring as a single point of connection to Cd (making each L ligand effectively single linker), then both Cd atoms are depicted as three-connected nodes, the framework can be represented simply by connecting the Cd nodes according to the connectivity defined by the L ligands. A better insight into the nature of this intricate framework can be achieved by the application of topological approach, i.e. reducing multidimensional structure to node– and –connection nets [16]. This type of network is referred to an attractive three-connected honeycomb topological network. As shown in figure 3.

Fig. 1 Coordination environment of Cd(II) ion. (Online color at www.crt-journal.org)

Fig. 2 A viewing of 2-D grid network in 1. (Online color at www.crt-journal.org)

Fig. 3 Perspective view of honeycomb topological net. (Online color at www.crt-journal.org)

Fig. 4 A view of the 3-D supramolecular structure. (Online color at www.crt-journal.org)
The neighboring 2-D bilayers are further connected to each other by O–H⋯O hydrogen bonds between oxygen atoms of uncoordinated carboxylate groups and coordinated water molecules to complete final 3-D supramolecular architecture (figure 4). Herein in this complex, hydrogen-bonded interactions play an important role in forming the supramolecular structure by self-assembly and stabilizing (Table 3).

4 Conclusion

In summary, we have prepared an attractive honeycomb topological net, containing uneven three-coordinate nodes. These result is interesting not only for topological structure type but also for understanding the relationship between the structure and property. We are presently exploring the other V-shaped polycarboxylate complexes and studying the relationship between their coordinate modes and structures.

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References