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Two-dimensional Cu^{II} and first Pb^{II} coordination polymers based on a flexible 1,4-cyclohexanedicarboxylate ligand displaying different conformations and coordination modes

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Abstract

Two novel metal–organic hybrid coordination polymers { $[Cu(bpo)(chdc)(H_2O)](H_2O)_{0.5}_n$ (1) and $[Pb(chdc)(H_2O)]_n$ (2) have been synthesized under different conditions and structurally characterized by single-crystal X-ray diffraction technique, where H₂chdc refers to a flexible 1,4-cyclohexanedicarboxylic acid ligand and bpo is 2,5-bis(4-pyridyl)-1,3,4-oxadiazole. Complex 1 has a two-dimensional (2-D) grid-like [11.28 × 13.63 Å²] framework in which the Cu^{II} centers are extended via bidentate bridging ligands bpo and *e,e-trans*-chdc along two directions, exhibiting large porous cavities. Coordination polymer **2** represents the first Pb^{II} complex of H₂chdc in which the larger Pb^{II} centers are connected by *e,a-cis*-chdc anions to afford a 2-D close-knit structure. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

The rapid development in metal-organic hybrid coordination polymers with fascinating structural topologies and functions has received considerable attention [1,2]. The rational design via self-assembly driven by coordination and/or hydrogen-bonded force has been proven to be an effective and facile synthetic strategy in this realm [3], which depends on a variety of parameters, basically including the suitable pre-designed organic ligands (building blocks) and metal centers with versatile coordination geometries (nodes). Recently, we have intensely devoted to the self-assemblies based on the unusual angular dipyridyl ligands containing oxadiazole spacer. typically, 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (bpo, Scheme 1), which could potentially provide both discrete and divergent (from one-dimensional, 1-D to

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three-dimensional, 3-D) coordination frameworks [4-9]. Of further interests, only a few coordination polymers based on flexible ligands have been documented so far probably due to their low symmetry and the flexibility of the backbones, which make them more difficult to forecast and control the final coordination networks [1-3]. 1,4-Cyclohexanedicarboxylic acid (H₂chdc) is a flexible diacid ligand that usually adopts chair-type backbone but with different cis- or trans-conformations (see Scheme 1) and varied coordination modes of carboxylate groups upon metal complexation under appropriate conditions [10-13]. Very recently, a well written work [14] on the successful separation of cis- and trans-conformations of H₂chdc within a Cd^{II}/H₂chdc/ 1,10-phenanthroline reaction system, predominantly relying on the temperature and pH value, has been reported. Thus, we anticipate that the incorporation of both distinctive dicarboxylic- and dipyridyl-type bridging ligands would lead to the formation of interesting coordination frameworks when binding to the metal

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Scheme 1.

ions. In this contribution, we will report our recent results on the preparation and structural analysis of two new two-dimensional (2-D) coordination polymers, $\{[Cu(bpo)(chdc)(H_2O)](H_2O)_{0.5}\}_n$ (1) possessing large porous cavities and $[Pb(chdc)(H_2O)]_n$ (2) representing the first Pb^{II} complex with H₂chdc.

2. Experimental

2.1. Materials and general methods

With the exception of the ligand 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (bpo), which was synthesized as described in our previous publications [4–9], all of the starting materials and solvents were obtained commercially and used as received without further purification. The raw flexible ligand H₂chdc is a mixture of *cis*- and *trans*-conformations in a ratio of 3:2. Fourier transform (FT)-IR spectra (KBr pellets) were taken on an AVA-TAR-370 (Nicolet) spectrometer. Elemental (carbon, hydrogen and nitrogen) analyses were performed on a CE-440 (Leemanlabs) analyzer.

2.2. Syntheses of the complexes

2.2.1. { $[Cu(bpo)(chdc)(H_2O)](H_2O)_{0.5}$ }_n (1)

A solution of H₂chdc (29 mg, 0.17 mmol) in methanol (15 mL) was added to an aqueous solution (10 mL) of Cu(OAc)₂ · H₂O (43 mg, 0.2 mmol). After ca. 5 min of vigorous mixing, a methanol solution (5 mL) of bpo (22 mg, 0.1 mmol) was added. The mixture was stirred thoroughly for 30 min and the resultant filtrate was allowed to evaporate slowly under ambient conditions. Lamellar blue single crystals of **1** suitable for X-ray analysis were obtained after 10 days in 50% yield (based on bpo). IR (KBr, cm⁻¹): 3444 b, 1697 s, 1650 s, 1620 m, 1560 vs, 1539 vs, 1512 s, 1420 m, 1336 w, 1223 w, 839 m, 716 m, 670 m. *Anal.* Calc. for C₂₀H₂₁CuN₄O_{6.5}: C,

49.53; H, 4.36; N, 11.55%. Found: C, 49.34; H, 4.78; N, 11.71%.

2.2.2. $[Pb(chdc)(H_2O)]_n$ (2)

A mixture of Pb(NO₃)₂ (33 mg, 0.1 mmol), H₂chdc (34 mg, 0.2 mmol) and bpo (22 mg, 0.1 mmol) in water (10 mL) was heated at 140 °C for three days in a sealed Teflon-lined stainless steel vessel (20 mL) under autogenous pressure. After the reaction system was slowly cooled down to the room temperature at a rate of 5 °C/h, colorless prism crystals of **2** were obtained in 75% yield (based on Pb(NO₃)₂ salt). IR (KBr, cm⁻¹): 3433 b, 2932 s, 2856 m, 1528 vs, 1415 vs, 1300 m, 1215 w, 1146 w, 1036 w, 929 m, 847 w, 774 m, 733 m, 652 m, 587 m, 531 m, 469 m. *Anal.* Calc. for C₈H₁₂PbO₅: C, 24.30; H, 3.06%. Found: C, 24.21; H, 2.89%.

2.3. X-ray crystallographic data collection and structural determination

Single crystal X-ray diffraction data collections of complexes 1 ($0.23 \times 0.12 \times 0.06$ mm) and 2 ($0.20 \times 0.16 \times$ 0.11 mm) were performed on a Bruker Apex II CCD diffractometer at 293(2) K with Mo Ka radiation $(\lambda = 0.71073 \text{ Å})$. A total of 17253 (for 1) and 2758 (for 2) reflections were collected, of which 5394 (for 1) and 953 (for 2) are independent. Both structures were solved by direct methods and refined by full-matrix leastsquares with SHELXTL package (semi-empirical absorption corrections were applied using SADABS program). Metal atoms in each structure were located from the E-maps and the other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for nonhydrogen atoms on F^2 . H atoms of organic ligands were generated with assigned isotropic thermal parameters, and those of coordinated water were first found in difference electron density maps, and then placed in

the calculated sites and included in the final refinement. H atoms of disordered guest water molecules in **1** were not located.

2.3.1. Crystallographic data for $C_{20}H_{21}CuN_4O_{6.5}$ (1)

 $M_{\rm r} = 484.95$, monoclinic, space group C2/c (No. 15), a = 22.670(8), b = 27.223(10), c = 10.787(4) Å, $\beta = 108.674(5)^{\circ}$, V = 6307(4) Å³, Z = 8, $D_{\rm c} = 1.021$ g cm⁻³, $\mu = 0.725$ mm⁻¹, $F(0\ 0\ 0) = 2000$, S = 0.991, R = 0.0688 and wR = 0.1464.

2.3.2. Crystallographic data for $C_8H_{12}PbO_5$ (2)

 $M_{\rm r} = 395.37$, monoclinic, $P2_1/m$ (No. 11), a = 7.971(2), b = 7.204(2), c = 8.664(3) Å, $\beta = 94.956(3)^{\circ}$, V = 495.6(2) Å³, Z = 2, $D_{\rm c} = 2.649$ g cm⁻³, $\mu = 17.013$ mm⁻¹, $F(0\ 0\ 0) = 364$, S = 0.990, R = 0.0366 and wR = 0.0981.

3. Results and discussion

Complex 1 was synthesized by the reaction of Cu^{II} salt and mixed chdc/bpo ligands at room temperature. Single crystal X-ray diffraction analysis shows that 1 has a 2-D neutral coordination network with large porous cavities. As shown in Fig. 1(a), each Cu^{II} center is coordinated to two N atoms from distinct bpo molecules, two O atoms awarded by the monodentate carboxylate groups of two anionic chdc ligands with the most stable *e,e-trans*-conformational isomer and one axial water ligand. Hence, the coordination polyhedron around the Cu^{II} center could be best described as a slightly distorted square-based pyramid (see archived CIF file for detailed bond geometries), with a τ parameter of 0.11 ($\tau = 0$ for an ideal square pyramidal geometry and $\tau = 1$ for an ideal trigonal bipyramidal) [15].

Fig. 1(b) shows the 2-D lamellar network of 1. Along the crystallographic *b*-axis, the adjacent Cu^{II} centers are linked via the bridging bpo ligands in trans arrangement to form 1-D chains. The chdc anions further extend these chains along the *a* direction via two unidentate carboxylate groups, resulting in the final 2-D grid-type layer, with the dimensions of 13.63×11.28 Å² for each repeating unit (see Fig. S1). Analysis of the crystal packing of 1 reveals that these 2-D layers adopt the closely stacking mode (see Fig. S2) with an A(-A)A(-A) sequence along the [0 0 1] direction, creating large quadrate cavities, as depicted in Fig. 1(c). Although this packing mode clearly reduces the size of the porous channels compared with the parallel overlap-fashion, a computation [16] of the voids of the host networks of 1 still shows a value of 2805 \AA^3 (44.5% of the unit cell). Allowing for the volume of the included water molecules, there still remains 2319 Å³ of void space, corresponding to 36.8% of the unit-cell volume. The porous







Fig. 1. (a) A portion view of **1** showing the coordination sphere of Cu^{II} and conformation of chdc with atom labeling of the asymmetric unit. (b) 2-D grid-like network structure of **1**. Hydrogen atoms are omitted for clarity. (c) Space-filling model of the 3-D packing diagram of **1** showing the large porous cavities.

nature of **1** can also be reflected from its rather low crystal density (1.021 g cm⁻³). Additionally, this structure is further stabilized by the interlayer O6–H6A···O4ⁱ and O6–H6B···O3ⁱ (i = x, -y, z - 1/2) hydrogen bonds (bond geometries: H···O, 1.870 and 1.927 Å; O···O, 2.699 and 2.761 Å; O–H···O, 163.8 and 168.5°), between each coordinated water molecule and two uncoordinated carboxylate oxygen atoms of chdc from the adjacent 2-D layer.

 Pb^{II} is a favorable component for the construction of unusual coordination polymers or polynuclear complexes due to its large ion radius, a variety of coordination geometries and the possible occurrence of a stereochemically active lone pair of electrons [17]. In



Fig. 2. (a) A portion view of **2** showing the coordination sphere of Pb^{II} and conformation/coordination modes of chdc with atom labeling of the asymmetric unit. (b) 2-D close-knit layered structure of **2**. Hydrogen atoms and water ligands are omitted for clarity. (c) 3-D parallel packing diagram of **2** viewing from the [0 0 1] direction.

order to further explore the potential coordination possibility of chdc, the first Pb^{II}-chdc complex [Pb(chdc)- $(H_2O)_n$ (2) was prepared under hydrothermal condition and structurally determined by X-ray diffraction technique. Although the starting ligand bpo is not involved in the final product, it is a necessary element to afford the coordination polymer 2. As shown in Fig. 2(a), the local crystallographic unit, with a mirror symmetry passing through C5-C1-C4-C6, comprises one Pb^{II} center, a doubly deprotonated chdc anionic ligand and a water ligand. The Pb^{II} ion is hepta-coordinated to six carboxylate O atoms of chdc with e.a-cis-conformation and one water molecule, adopting an unusual distorted capped trigonal prismatic geometry. The Pb-O bond distances are in the range of 2.463(7)-2.673(7) Å (see archived CIF file for detailed bond geometries). Each chdc synchronously binds to four Pb^{II} atoms, and two different coordination modes of the carboxylate groups, including symmetric bidentate chelate for O1-C5-O1ⁱ and µ-O,O-η-O,O'-µ-O',O for O2-C6- $O2^{i}$ (i = x, -y + 3/2, z), are observed. As a consequence, the Pb^{II} centers are connected by chdc ligands, leading to the formation of a 2-D close-knit network as illustrated in Fig. 2(b). Another alternative description, perhaps more revealing from the structural viewpoint of supramolecular network, is to consider as follows. The neighboring Pb^{II} centers (Pb...Pb separation of 8.664(3) Å) are linked by chdc with two carboxylate groups (symmetric bidentate chelate modes) along the [0 0 1] direction to form 1-D zigzag chains, which are connected to afford a 2-D net via further Pb-O coordination interactions along the [0 1 0] direction. In the resulting Pb_2O_2 dimeric subunit, the $Pb \cdots Pb$ distance is 4.152(2) Å and the Pb–O–Pb bridging angle is 107.8(3)°. Investigation of the crystal packing of 2 suggests that these 2-D layers are in parallel stacking fashion (see Fig. 2(c) and Fig. S3) and there are no solvent-accessible voids in the crystal lattice.

4. Conclusion and remarks

As illustrated in the previous study [13,14], the flexible backbone of chdc may favor *e,e-trans*-conformation at higher temperature and pH value. However, in this work, we can conclude that chdc takes the *e,e-trans*-conformation in the 2-D open porous network 1 and *e,a-cis*-conformation in the 2-D close-knit architecture 2, although the former was prepared at room temperature and the latter under hydrothermal condition at 140 °C. Furthermore, the rather diverse coordination modes of the carboxylate groups of chdc are observed in both cases. These differences may result from the nature of the Pb^{II} center, such as the larger radius and thus higher coordination numbers compared with that of Cu^{II}, which could affect the conformation and binding

modes of chdc in the resulting coordination polymers. This work may provide helpful information for constructing other relative metal–organic coordination frameworks and further investigations on such an interesting system are still in progress in our laboratory.

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Appendix A. Supplementary data

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center (CCDC Nos. 257634 and 257635). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

Three color figures including (Fig. S1) Space-filling model of the 2-D open network in 1, (Fig. S2) Space-filling model of 3-D packing diagram of 1 with an A(-A)A sequence, and (Fig. S3) 3-D parallel packing diagram of 2 viewing from the [0 1 0] direction. Supplementary data

associated with this article can be found, in the online version at doi:10.1016/j.ica.2005.07.006.

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