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Hydrothermal Syntheses and Crystal Structure of a Novel One-Dimensional Pb(II) Coordination Polymer with Chenodeoxycholic Acid Ligand[1]

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Abstract—A novel 1D chain-like coordination polymer, $\{[Pb(CDCA)_2(DMF)] \cdot DMF \cdot 2H_2O]\}_n$ (**I**) (HCDCA = chenodeoxycholic acid, DMF = dimethyl formamide), has been synthesized by hydrothermal method and characterized by single crystal X-ray diffraction, IR spectroscopy, and elemental analysis (CIF file CCDC no. 996098). X-ray diffraction analyses indicated that **I** displays distorted octahedral metal centers with secondary building units $[Pb(CDCA)_2(DMF)]$ bridged by a pair of μ_2-COO$^-$-bridges. In the crystal, interchain O–H···O hydrogen bonds are present and assemble the neighboring 1D chain into a (4,4) sql type three-dimensional (3D) supramolecular topological network.

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INTRODUCTION

Metal complexes of carboxylic acid and its derivatives, especially coordination polymers, have been greatly developed in the past decades, not only for their intriguing topological variety and the theoretical prediction of the assembling processes, but also for their fascinating potential applications in functional materials [1–8]. The structures of coordination polymers can be effectively influenced by multiple factors, such as the coordination trend of metal ions, ligands, solvent system, templates, counterions, noncovalent interactions, and so on [9–16]. Among those mentioned above, the most important ones are the geometrical and electronic properties of the ligands and metal ions.

Bile acids and their derivatives contain multiple rotatable hydroxyl and carboxylate groups and can form inclusion crystals with many organic compounds. While most previous structural research has focused on cholic acid and its many inclusion compounds [17–20], more recent research has examined the many possible solvated structures of chenodeoxycholic acid. In a search of the Cambridge Structural Database [21], we found only ten crystal structures containing chenodeoxycholic acid. Of these structures, only five were clathrate compounds, including chenodeoxycholic acid complexed with phenanthrene [22], 2-acetylnaphthalene [23], ethyl acetate [24], bromobenzene [25] and *p*-xylene [26]. Recently, the crystal structure of chenodeoxycholic acid without any guest molecules has also been obtained [27]. Chenodeoxycholic acid (HCDCA) with both a flexible and a rigid moieties has multifunctional coordination sites with chelating and bridging ability through O atom of the hydroxyl and carboxylate groups. In addition, the ligands may take part in the formation of intermolecular and intramolecularl attractions whilst the oxygen atoms may function as the acceptors or donors to form the potential hydrogen bonds. These weak intermolecular attractions have significantly influenced further assemblies of the polymers formation high-dimensional supramolecular architectures in solid structures [28]. Less attention, however, has been paid to chenodeoxycholic acid salt or metal complexes.

On the other hand, as a heavy *p*-block metal ion, lead(II), with its large radius and flexible coordination environment, exhibits variable coordination number and geometry with ligands [8, 29]. And the intrinsic features of lead(II) inspire chemists' extensive interests in its coordination chemistry, photophysics, and photochemistry [30]. Moreover, the impact of the toxic heavy metal lead on the natural environment is reflected in the wealth of recent literature concerning the health hazards posed by lead to humans [31]. In view of the steady increase in the amount of lead released into the environment by human activity, the removal of this toxic metal from the human body using chelating agents is a good method. Up to now, many metal complexes based on carboxylic acid and its derivatives have been studied. However, studies on the coordination behavior of bile acid ligands toward metal coordination compounds are comparatively

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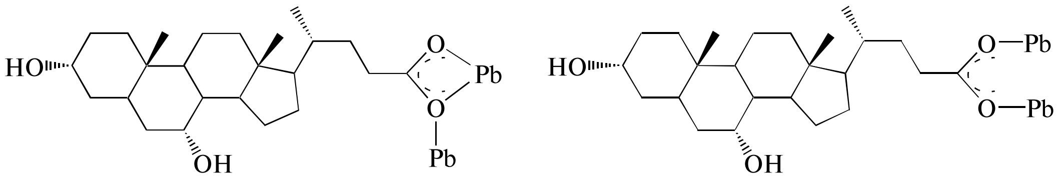
rare. Following the above consideration, we herein present the synthesis and structure of the complex $\{[Pb(CDCA)_2(DMF)] \cdot DMF \cdot 2H_2O]\}_n$ (**I**) (Scheme), which has been structurally characterized by single-crystal X-ray diffraction, IR spectroscopy and elemental analysis.

(a)

$$2HCDCA + Pb(Ac)_2 \cdot H_2O + 2NaOH \xrightarrow[160°C,\ 96\ h]{5\ mL\ DMF,\ 10\ mL\ H_2O} \{[Pd(CDCA)_2(DMF) \cdot DMF \cdot 2H_2O]\}_n$$

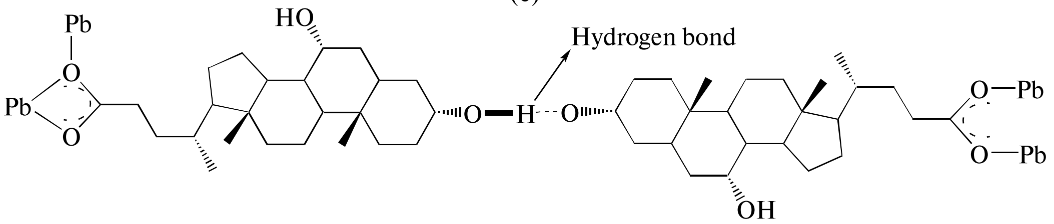
The synthesis for **I**.

(b)



The coordination modes of the CDCA⁻ in **I**.

(c)



View of the simplified interchain hydrogen bond mode of the CDCA⁻ ligand in **I**.

Scheme.

EXPERIMENTAL

Materials and methods. All starting chemicals were commercially available and used as received without further purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400II elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range of 4000–450 cm^{-1} on a Bio-Rad FTS-7 spectrometer.

Synthesis of I was carried out from a reaction mixture of $Pb(Ac)_2 \cdot H_2O$ (0.190 g, 0.5 mmol), HCDCA (0.392 g, 1 mmol), NaOH (0.040 g, 1 mmol), and distilled H_2O (10 mL), DMF (5 mL) in a 25 mL Teflon reactor, under autogenous pressure at 160°C for 4 days. Then it was cooled to room temperature at a rate of 5°C h^{-1}. Light-colorless block crystals of compound **I** suitable for X-rays diffraction analysis were obtained (0.24 g, the yield was 20% based on metal).

For $C_{54}H_{96}N_2O_{12}Pb$

anal. calcd., %:	C, 55.27;	H, 8.19;	N, 2.39.
Found, %:	C, 55.24;	H, 8.17;	N, 2.42.

IR (KBr; ν, cm^{-1}) 3328 s, 2908 m, 1719 s, 1616 s, 1459 s, 1328 m, 1240 m, 1118 m, 780 s.

X-ray crystallography. A prism-shaped single crystal of **I** with size of 0.20 × 0.18 × 0.12 mm was used for structure determination. Data were collected at 296(2) K on a Bruker SMART APEX CCD area-detector diffractometer equipped with a graphite-monochromatic MoK_α (λ = 0.71073 Å) radiation by using a multi-scan mode. The raw frame data were integrated with the SAINT program [32] and absorption corrections were applied by using the SADABS program [33]. The unit cell data were obtained with the least-squares refinements and the structure was solved by direct methods with SHELXTL-97 program [34]. The final refinement was performed by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms on F^2. All H atoms were placed geometrically and were subsequently refined in a riding-model approximation with distances of $d_{C–H}$ = 0.93–0.98 and $d_{O–H}$ = 0.82–0.85 Å, and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(O)$. The crystal data are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Hydrogen bonds are listed in Table 3. The atomic coordinates and other parameters of structure **I** have been deposited with the Cambridge Crystallographic Data Centre (no. 996098; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULT AND DISCUSSION

Single-crystal X-ray diffraction analysis reveals that complex **I** crystallizes with a one-dimensional coordination polymer which is connect with alternate [Pb(CDCA)$_2$(DMF)] block through a pair of μ_2-COO$^-$. As shown in figure, a, the asymmetric unit is comprised of one Pb^{2+} ion, two deprotonated HCDCA ligands, one coordinated DMF molecule, and one DMF solvate as well as two water solvate molecules. Each Pb^{2+} ion is six-coordinated by five carboxylate oxygen atoms from four CDCA$^-$ and one oxygen donor from one terminal DMF ligand, exhibiting a distorted octahedral geometry (Table 2). The Pb–O$_{\text{carboxylate}}$ and Pb–O$_{\text{DMF}}$ lengths are in the range of 2.415(10)–2.750(10) and 2.497(11) Å, respectively, which are in agreement with those reported for Pb(II) coordination polymers with carboxylic ligands [8–15]. Each Pb^{2+} ion sits at a symmetry center and was coordinated by two pairs of symmetry-related carboxylate groups. It is worth mentioning that the CDCA$^-$ ligands show two distinct types of coordination modes in **I** (Scheme b and figure, b). One is μ_2-bridging with each carboxylate in a μ_2-η^2:η^1-chelating/bridging mode and the other is μ_2-bridging with one carboxylate in a μ_2-η^1:η^1-*syn-syn*-bridging fashion. Due to such unique connectivity, the distorted Pb$_2$O$_{11}$ polyhedral units are interlinked to each other in an apex-sharing fashion to form an infinite 1D rod along the *x* axis (figure, c). These rods can be viewed as infinite rod-shaped secondary building units (SBUs), which are further extended into the final 3D open framework by interchain O–H···O hydrogen bonds (Scheme c). A better insight into the structure of **I** can be obtained by the standard procedure of reducing multidimensional structures to simple node-and-linker reference nets known as the topological approach. Further analysis of the crystal packing reveals a (4,4) sql type network topology considering each rod as a four-connected node. Herein, the rods are regarded as connected nodes and hydrogen bonds of O–H···O as linkers. From the topological point of view, this rod unit can be defined as a 4-connected node. Thus, the overall structure of **I** is a 3D layered structure with the short Schläfli symbol of 4^46^2 (TD10 = 221) [35]. In another way of topological analysis, the [Pb$_2$O$_{10}$] unit can be viewed as a six-connected node (Scheme c), keeping CDCA···CDCA ligands as a hydrogen bonding dimmer linker, respectively. So the 3D metal organic frameworks (MOFs) of **I** can be considered to be six-connected net, and it can be regarded as a (4^4, 5^{10}, 7) topology analyzed by the TOPOS program. In order to minimize the big void cavities and stabilize the frame-

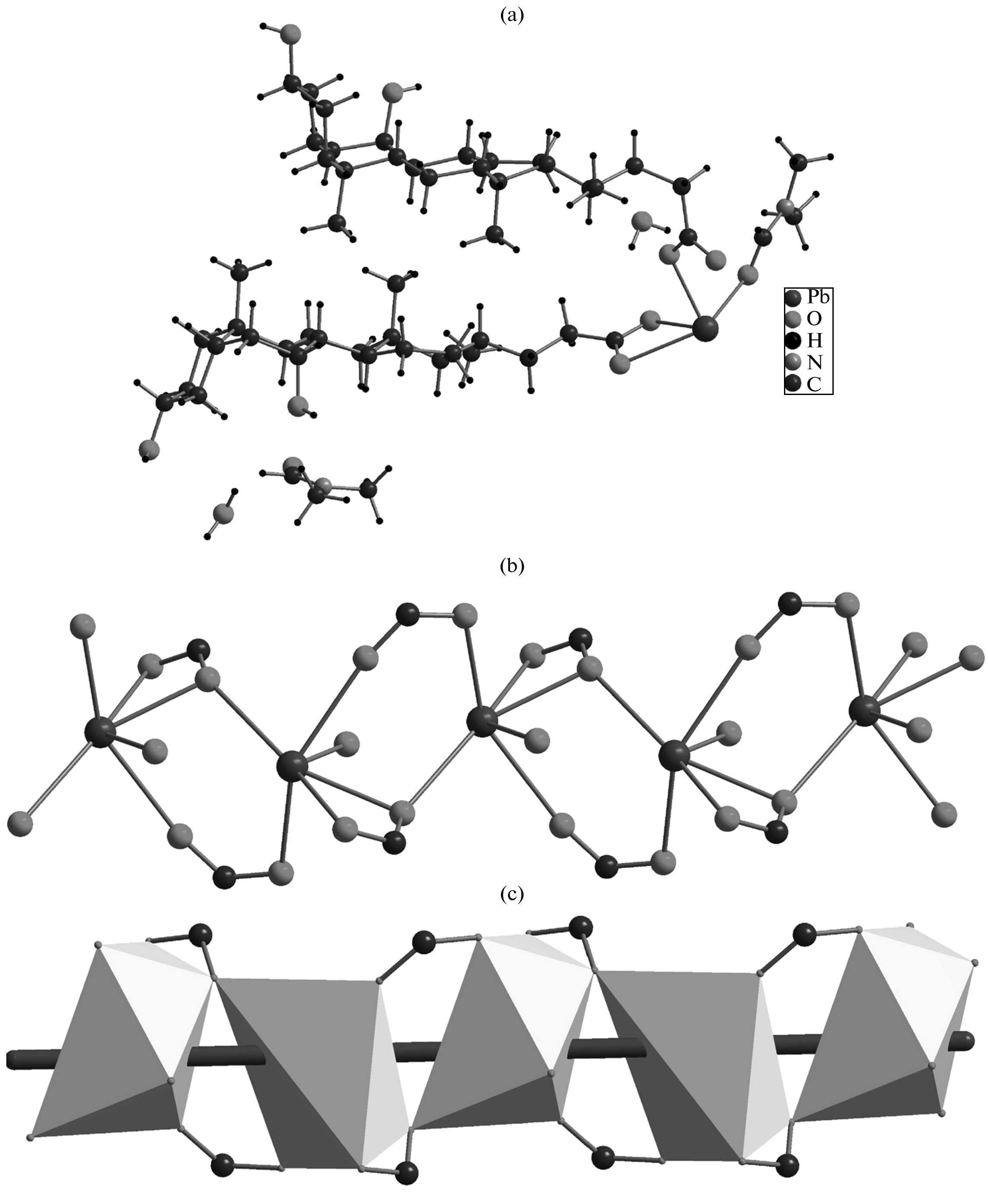
Table 1. Crystallographic data and refinement parameters for **I**

Parameter	Value
Formula weight	1172.52
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions:	
a, Å	7.651(3)
b, Å	19.565(8)
c, Å	36.408(15)
V, Å^3	5450(4)
Z	4
F(000)	2448
ρ_{calcd}, g/cm^3	1.429
Crystal size, mm	0.20 × 0.18 × 0.12
μ, mm^{-1}	3.157
Scan mode	ω–2θ
θ Range, deg	1.53–25.50
Limiting indices *h*, *k*, *l*	$-9 \le h \le 6$, $-23 \le k \le 23$, $-44 \le l \le 36$
Reflections collected	10149
Independent reflections, R_{int}	4931 (0.1839)
Max and min transmission	0.537 and 0.685
Parameters	628
Goodness-of-fit on F^2	0.998
R indices, $I > 2\sigma(I)$	$R_1 = 0.0723$, $wR_2 = 0.1231$
R indices, all data	$R_1 = 0.1766$, $wR_2 = 0.1590$
Largest diff. peak and hole, *e* Å^{-3}	1.050 and –1.144

Table 2. Selected bond lengths (Å) and angles (deg) for structure **I***

Bond	*d*, Å	Bond	*d*, Å
Pb(1)–O(1)	2.415(10)	Pb(1)–O(5)	2.420(9)
Pb(1)–O(9)	2.497(11)	Pb(1)–O(6)$^{\text{i}}$	2.657(12)
Pb(1)–O(2)	2.661(10)	Pb(1)–O(1)$^{\text{ii}}$	2.750(10)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(1)Pb(1)O(5)	78.4(3)	O(1)Pb(1)O(9)	77.8(4)
O(5)Pb(1)O(9)	78.3(4)	O(1)Pb(1)O(6)$^{\text{i}}$	78.2(3)
O(5)Pb(1)O(6)$^{\text{i}}$	147.6(4)	O(9)Pb(1)O(6)$^{\text{i}}$	75.2(3)
O(1)Pb(1)O(2)	49.3(3)	O(5)Pb(1)O(2)	88.4(4)
O(9)Pb(1)O(2)	127.0(3)	O(6)$^{\text{i}}$Pb(1)O(2)	93.0(3)
O(1)Pb(1)O(1)$^{\text{ii}}$	150.6(3)	O(5)Pb(1)O(1)$^{\text{ii}}$	107.1(3)
O(9)Pb(1)O(1)$^{\text{ii}}$	75.3(3)	O(6)$^{\text{i}}$Pb(1)O(1)$^{\text{ii}}$	83.7(3)
O(2)Pb(1)O(1)$^{\text{ii}}$	155.9(3)	C(1)O(1)Pb(1)	100.5(10)

* Symmetry codes: $^{\text{i}}x + 1/2, -y + 3/2, -z + 2$; $^{\text{ii}}x - 1/2, -y + 3/2, -z + 2$.



The asymmetric unit of **I** (a); the 1D plot structure for **I**, showing the Pb_2O_{11} units are linked to form the coordination polymer by bridging carboxylate oxygens (C, N, H atoms and water, DMF solvates have been omitted, except for bridging carboxylate carbons and coordinated DMF oxygen atoms) (b); polyhedral representation of the infinite 1D rod SBUs (c).

work, the potential void cavities are filled by water, DMF solvate molecules as well as another identical network, resulting in a 2-fold interpenetrating array.

The network is based on a $(PbCDCA)_4$ rhombus, a 66-membered metal-organic ring formed by four $CDCA^-$ ligands and four quadruply connected Pb^{2+} ions. The $(PbCDCA)_4$-grids are joined together by sharing the Pb apices to give the final 3D layer structure. The edge Pb···Pb distance of the rhombus grid is 20.76(7) Å, and the Pb···Pb separations through

Table 3. Geometric parameters of hydrogen bonds for **I***

Contact D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
O(3)–H(3)···O(12)$^{\text{iii}}$	0.82	2.13	2.86(2)	152
O(4)–H(4)···O(8)$^{\text{iv}}$	0.82	2.11	2.879(16)	155
O(8)–H(8)···O(10)$^{\text{iv}}$	0.82	1.91	2.680(14)	156
C(21)–H(21*B*)···O(3)	0.97	2.38	3.041(17)	125
C(45)–H(45*A*)···O(7)	0.97	2.45	3.084(18)	122

* Symmetry codes: $^{\text{iii}}\,x - 1, y, z$; $^{\text{iv}}\,-x, y - 1/2, -z + 3/2$.

the diagonal of the rhombus are 19.56(5) and 30.40(8) Å.

In the crystal structure, it is noteworthy that this 3D layer structure is further connect with pairs of intermolecular O–H···O and non-classical C–H···O hydrogen bonds involving the uncoordinated hydroxyl O, the uncoordinated DMF and water, and help to stabilize the coordination polymer (Table 3). These intermolecular contacts may be regarded as weak hydrogen bonds, but their contribution to the overall lattice energy cannot be ignored. Molecules from neighboring stacks interdigitate with each other in the x axis direction, thus leading to an interwoven three-dimensional network held together by O–H···O and C–H···O interactions.

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