

Organic-Acid Effect on the Structures of a Series of Lead(II) Complexes

Jin Yang,[†] Jian-Fang Ma,^{*†} Ying-Ying Liu,[†] Ji-Cheng Ma,[†] and Stuart R. Batten^{*‡}*Key Lab for Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China, and School of Chemistry, Monash University, Victoria 3800, Australia*

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An investigation into the dependence of coordination polymer architectures on organic-acid ligands is reported on the basis of the reaction of $\text{Pb}(\text{NO}_3)_2$ and eight structurally related organic-acid ligands in the presence or absence of N-donor chelating ligands. Eight novel lead(II)–organic architectures, $[\text{Pb}(\text{adip})(\text{dpdp})]_2$ **1**, $[\text{Pb}(\text{glu})(\text{dpdp})]$ **2**, $[\text{Pb}(\text{suc})(\text{dpdp})]$ **3**, $[\text{Pb}(\text{fum})(\text{dpdp})] \cdot \text{H}_2\text{O}$ **4**, $[\text{Pb}_2(\text{oba})(\text{dpdp})_2] \cdot 2(\text{dpdp}) \cdot 2(\text{NO}_3) \cdot 2\text{H}_2\text{O}$ **5**, $[\text{Pb}_2(1,4\text{-bdc})(\text{dpdp})_2] \cdot \text{H}_2\text{O}$ **6**, $[\text{Pb}(\text{dpdc})(\text{dpdp})]$ **7**, and $[\text{Pb}(1,3\text{-bdc})(\text{dpdp})] \cdot \text{H}_2\text{O}$ **8**, where dpdp = dipyrido[3,2-a:2',3'-c]-phenazine, H_2adip = adipic acid, H_2glu = glutaric acid, H_2suc = succinic acid, H_2fum = fumaric acid, H_2oba = 4,4'-oxybis(benzoic acid), 1,4- H_2bdc = benzene-1,4-dicarboxylic acid, H_2dpdc = 2,2'-diphenyldicarboxylic acid, and 1,3- H_2bdc = benzene-1,3-dicarboxylic acid, were successfully synthesized under hydrothermal conditions through varying the organic-acid linkers and structurally characterized by X-ray crystallography. Compounds **1–8** crystallize in the presence of organic-acid linkers as well as secondary N-donor chelating ligands. Diverse structures were observed for these complexes. **1** and **5** have dinuclear structures, which are further stacked via strong π – π interactions to form 2D layers. **2–3** and **6–8** feature chain structures, which are connected by strong π – π interactions to result in 2D and 3D supramolecular architectures. Compound **4** contains 2D layers, which are further extended to a 3D structure by π – π interactions. A systematic structural comparison of these 8 complexes indicates that the organic-acid structures have essential roles in the framework formation of the Pb(II) complexes.

Introduction

The rational design and synthesis of novel discrete and polymeric metal-organic complexes have attracted intense interest owing to the realization of their potential for use as functional materials in catalysis, molecular recognition, separation, and nonlinear optics.¹ In this aspect, considerable progress has been made on the theoretical prediction and network-based approaches for controlling the topology and geometries of the networks to produce useful functional materials.² However, it is still a great challenge to predict the exact structures through controlling the factors that affect the framework formation, and therefore, systematic research on this topic is still very necessary for understanding the roles of the factors in the formation of metal coordination frameworks. Several factors, including the coordination environment of metal nodes, structural characteristics of the

polydentate ligands, solvents, templates, counterions, non-covalent interactions such as aromatic–aromatic interactions that stabilize certain architectures, and so on, may all play a role in determining the network structure of a compound.³

Up to now, the design and control over coordination compounds is mainly focused on the incorporation of *s*-, *d*-, and even *f*-block metals as coordination centers, whereas less attention has been paid to the *p*-block metals despite their important applications in electroluminescent devices and fluorescent sensors.⁴ Lead(II), as a heavy *p*-block metal ion, possesses a large radius, a variable stereochemical activity, and a flexible coordination environment, which provides unique opportunities for the construction of novel network of topologies and interesting properties. So far, the effect of organic-acid ligands on the structure formation of *s*-, *d*-, and even *f*-block metal complexes has been investigated, however, systematic elucidation of the dependence of such factors on the formation of lead(II) framework complexes is still comparatively rare, especially in the presence of a secondary N-donor chelating ligand.⁵ So far, 1,10-phenanthroline (phen) has been widely used to build supramolecular architectures

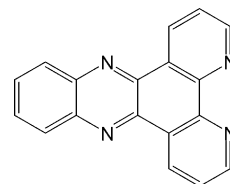
* To whom correspondence should be addressed. E-mail: jianfangma@yahoo.com.cn, Fax: +86-431-8509-8620 (J.-F.M.), E-mail: stuart.batten@sci.monash.edu.au, Fax: +61-3-9905-4597 (S.R.B.).

[†] Northeast Normal University.

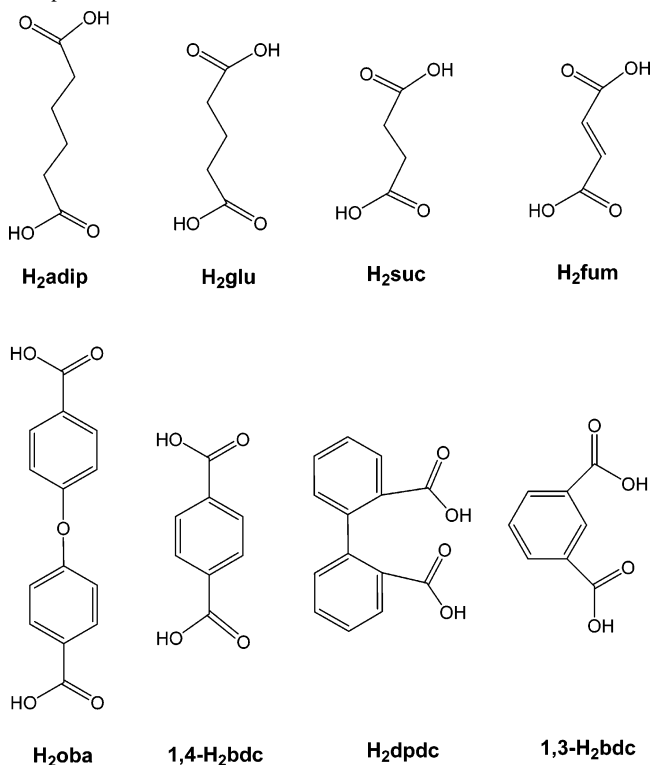
[‡] Monash University.

because of its excellent coordinating ability and large conjugated system that can easily form π - π interactions. However, far less attention has been given to their derivatives. Dipyrido[3,2-a:2',3'-c]-phenazine (dppd) as an important phen derivative possesses fruitful aromatic systems and is a good candidate for the construction of metal-organic supramolecular architectures (Scheme 1). In this work, through precise control of the organic-acid linker structural

Scheme 1. Structure of the dpdp Ligand



Scheme 2. Organic-Acid Ligands Used in the Construction of Pb(II) Compounds



features such as shape, size, and flexibility (Scheme 2), in the presence of secondary N-donor chelating ligands, a remarkable class of lead(II) complexes with rich architectures has been obtained: [Pb(adip)(dpdp)]₂ **1**, [Pb(glu)(dpdp)] **2**, [Pb(suc)(dpdp)] **3**, [Pb(fum)(dpdp)]·H₂O **4**, [Pb₂(oba)(dpdp)₂]·2(dpdp)·2(NO₃)·2H₂O **5**, [Pb₂(1,4-bdc)₂(dpdp)₂]·H₂O **6**, [Pb-(dpdc)(dpdp)] **7**, and [Pb(1,3-bdc)(dpdp)]·H₂O **8**, where H₂adip = adipic acid, H₂glu = glutaric acid, H₂suc = succinic acid, H₂fum = fumaric acid, H₂oba = 4,4'-oxybis-

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(benzoic acid), 1,4-H₂bdc = benzene-1,4-dicarboxylic acid, H₂dpdc = 2,2'-diphenyldicarboxylic acid, and 1,3-H₂bdc = benzene-1,3-dicarboxylic acid. On the basis of synthesis and structural characterization, the influence of organic-acid linkers on the control of the final complex structures is discussed in detail. Furthermore, the role of weak intermolecular forces such as aromatic π - π stacking interactions in the creation of molecular architectures has also been investigated for the obtained compounds.

Experimental Section

Materials and Methods. All of the reagents of analytical grade were purchased and used without further purification. The dpdp ligand was synthesized by following the procedures described previously.⁶ A Perkin-Elmer 240 elemental analyzer was used to collect microanalytical data. The inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV ICP spectrometer. The luminescent spectra were measured on a Perkin-Elmer LS55 spectrometer.

Synthesis of [Pb(adip)(dpdp)]₂ 1. The pH value of a mixture of Pb(NO₃)₂ (0.5 mmol), dpdp (0.5 mmol), and H₂adip (0.5 mmol) in 8 mL distilled water was adjusted to between 5 and 6 by the addition of triethylamine. The resultant solution was heated at 170 °C in a Teflon-lined stainless steel autoclave for 4 days. The reaction system was then slowly cooled to room temperature. Pale-yellow crystals of **1** suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water, and dried in air at ambient temperature. Yield: 36% based on Pb(II). Elemental analysis and ICP results for C₂₄H₁₈N₄O₄Pb: Calcd: C 45.50, H 2.86, N, 8.84, Pb 32.70; Found: C 45.77, H 2.69, N 8.90, Pb 32.51.

Synthesis of [Pb(glu)(dpdp)] 2. Complex **2** was synthesized by a method similar to that of complex **1**, using H₂glu (0.5 mmol) instead of H₂adip as the organic-acid ligand source. Pale-yellow block crystals were obtained in a 44% yield based on Pb(II). Elemental analysis and ICP results for C₂₃H₁₆N₄O₄Pb: Calcd: C 44.59, H 2.60, N, 9.04, Pb 33.44; Found: C 44.38, H 2.71, N 9.16, Pb 33.31.

Synthesis of [Pb(suc)(dpdp)] 3. Complex **3** was synthesized by a method similar to that of complex **1**, using H₂suc (0.5 mmol) instead of H₂adip as the organic-acid ligand source. Pale-yellow block crystals were obtained in a 42% yield based on Pb(II). Elemental analysis and ICP results for C₂₂H₁₄N₄O₄Pb: Calcd: C 43.64, H 2.33, N, 9.25, Pb 34.22; Found: C 43.53, H 2.19, N 9.34, Pb 34.36.

Synthesis of [Pb(fum)(dpdp)]·H₂O 4. Complex **4** was synthesized by a method similar to that of complex **1**, using H₂fum (0.5 mmol) instead of H₂adip as the organic-acid ligand source. Pale-yellow block crystals were obtained in a 37% yield based on Pb(II). Elemental analysis and ICP results for C₂₂H₁₄N₄O₅Pb: Calcd: C 42.51, H 2.27, N, 9.01, Pb 33.33; Found: C 42.40, H 2.35, N 9.21, Pb 33.14.

Synthesis of [Pb₂(oba)(dpdp)₂·2(dpdp)·2(NO₃)·2H₂O] 5. Complex **5** was synthesized by a method similar to that of complex **1**, using H₂oba (0.5 mmol) instead of H₂adip as the organic-acid ligand source. Pale-yellow block crystals were obtained in a 61% yield based on Pb(II). Elemental analysis and ICP results for C₈₆H₅₂N₁₈O₁₃Pb₂: Calcd: C 52.71, H 2.67, N, 12.86, Pb 21.15; Found: C 53.23, H 2.55, N 12.66, Pb 21.47.

Synthesis of [Pb₂(1,4-bdc)₂(dpdp)₂]·H₂O 6. Complex **6** was synthesized by a method similar to that of complex **1**, using 1,4-H₂bdc (0.5 mmol) instead of H₂adip as the organic-acid ligand source. Pale-yellow block crystals were obtained in a 39% yield based on Pb(II). Elemental analysis and ICP results for C₅₂H₃₀N₈O₉Pb₂: Calcd: C 47.13, H 2.28, N 8.46, Pb 31.27; Found: C 47.25, H 2.41, N 8.32, Pb 31.11.

Synthesis of [Pb(dpdc)(dpdp)] 7. Complex **7** was synthesized by a method similar to that of complex **1**, using H₂dpdc (0.5 mmol) instead of H₂adip as the organic-acid ligand source. Pale-yellow block crystals were obtained in a 47% yield based on Pb(II). Elemental analysis and ICP results for C₃₂H₁₈N₄O₄Pb: Calcd: C 52.67, H 2.49, N, 7.68, Pb 28.40; Found: C 52.44, H 2.66, N 7.39, Pb 28.51.

Synthesis of [Pb(1,3-bdc)(dpdp)]·H₂O 8. Complex **8** was synthesized by a method similar to that of complex **1**, using 1,3-H₂bdc (0.5 mmol) instead of H₂adip as the organic-acid ligand source. Pale-yellow block crystals were obtained in a 41% yield based on Pb(II). Elemental analysis and ICP results for C₂₆H₁₆N₄O₅Pb: Calcd: C 46.50, H 2.40, N, 8.34, Pb 30.85; Found: C 46.72, H 2.28, N 8.52, Pb 30.71.

Crystal Structure Determinations. Single-crystal X-ray diffraction data for complexes **5** and **6** were recorded on a Bruker-AXS Smart CCD diffractometer, using a ω scan technique with Mo K α radiation ($\lambda = 0.71073$ Å). Crystallographic data for compounds **1–4**, **7**, and **8** were collected on a Rigaku RAXIS-RAPID single-crystal diffractometer equipped with a narrow-focus, 5.4 kW sealed-tube X-ray source (graphite-monochromated Mo K α radiation, $\lambda = 0.71073$ Å) at a temperature of 20 ± 2 °C. Data processing was accomplished with the PROCESS-AUTO processing program. All of the structures were solved by the Direct Method of SHELXS-97⁷ and refined by full-matrix least-squares techniques using the SHELXL-97⁸ program. Non-hydrogen atoms were refined with anisotropic temperature parameters, and hydrogen atoms of the ligands were refined as rigid groups. Further details for structural analysis are summarized in Tables 1 and 2.

Results and Discussion

Syntheses and Single-Crystal X-ray Structures of 1–8. Hydrothermal syntheses favor crystallization of compounds **1–8**.^{9,10} In our first attempts, we only obtained a small quantity of microcrystals unsuitable for single-crystal X-ray diffraction under the hydrothermal conditions. Then, we sensed that changing the pH value of the reaction mixture may be helpful for crystal growth. In view of this, we adjusted the pH values of the reaction system. As expected, at pH 5–6 well-formed single crystals of **1–8** that are

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Table 1. Crystallographic Data for Compounds 1–4

compound	1	2	3	4
formula	C ₂₄ H ₁₈ N ₄ O ₄ Pb	C ₂₃ H ₁₆ N ₄ O ₄ Pb	C ₂₂ H ₁₄ N ₄ O ₄ Pb	C ₂₂ H ₁₄ N ₄ O ₅ Pb
fw	633.61	619.59	605.56	621.58
space group	<i>P</i> –1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> –1
<i>a</i> (Å)	8.770(5)	15.737(3)	15.106(5)	6.8124(14)
<i>b</i> (Å)	9.733(5)	7.8514(16)	7.885(5)	8.1738(16)
<i>c</i> (Å)	12.857(5)	16.347(3)	15.741(5)	18.070(4)
α (deg)	81.219(5)	90	90	90.88(3)
β (deg)	81.435(5)	99.06(3)	93.945(5)	93.82(3)
γ (deg)	74.993(5)	90	90	102.61(3)
<i>V</i> (Å ³)	1040.7(9)	1994.5(7)	1870.5(15)	979.3(3)
<i>Z</i>	2	4	4	2
ρ (g cm ^{–3})	2.022	2.063	2.1506	2.108
μ (mm ^{–1})	8.148	8.500	9.061	8.660
GOF on <i>F</i> ²	1.064	1.039	1.058	1.077
<i>R</i> [<i>I</i> > 2σ(<i>I</i>)] ^{a,b}	R1 = 0.0254, wR2 = 0.0454	R1 = 0.0395, wR2 = 0.0727	R1 = 0.0398, wR2 = 0.0903	R1 = 0.0371, wR2 = 0.0768

^a R1 = ||*F*_o| – |*F*_c||/|*F*_o|. ^b wR2 = {[w(*F*_o² – *F*_c²)] / [w(*F*_o²)]^{1/2}.

Table 2. Crystallographic Data for Compounds 5–8

compound	5	6	7	8
formula	C ₈₆ H ₅₂ N ₁₈ O ₁₃ Pb ₂	C ₅₂ H ₃₀ N ₈ O ₉ Pb ₂	C ₃₂ H ₁₈ N ₄ O ₄ Pb	C ₂₆ H ₁₆ N ₄ O ₅ Pb
fw	1959.84	1325.22	729.69	671.62
space group	<i>Pccn</i>	<i>P</i> –1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> –1
<i>a</i> (Å)	22.067(3)	9.677(3)	7.7814(16)	6.1464(12)
<i>b</i> (Å)	18.186(2)	11.884(4)	24.643(5)	9.902(2)
<i>c</i> (Å)	19.244(3)	11.988(4)	13.928(3)	19.151(4)
α (deg)	90	100.375(5)	90	104.74(3)
β (deg)	90	112.273(4)	103.83(3)	90.03(3)
γ (deg)	90	95.158(5)	90	104.59(3)
<i>V</i> (Å ³)	7722.6(18)	1235.8(7)	2593.2(9)	1088.3(4)
<i>Z</i>	4	1	4	2
ρ (g cm ^{–3})	1.686	1.781	1.869	2.049
μ (mm ^{–1})	4.434	6.867	6.554	7.801
GOF on <i>F</i> ²	1.177	1.012	1.063	1.072
<i>R</i> [<i>I</i> > 2σ(<i>I</i>)] ^{a,b}	R1 = 0.0725, wR2 = 0.1585	R1 = 0.0519, wR2 = 0.1254	R1 = 0.0397, wR2 = 0.0733	R1 = 0.0374, wR2 = 0.0702

^a R1 = ||*F*_o| – |*F*_c||/|*F*_o|. wR2 = {[w(*F*_o² – *F*_c²)]/[w(*F*_o²)]^{1/2}.

suitable for single-crystal X-ray diffraction were obtained in satisfying yields under hydrothermal conditions.

Selected bond distances and angles for compounds 1–8 are listed in Tables S1–S8 (Supporting Information). The crystal structure of **1** consists of a discrete dinuclear [Pb(adip)(dpdp)]₂. The [Pb(adip)(dpdp)]₂ dimer comprises two adip, two dpdp ligands, and two Pb(II) atoms and possesses a crystallographic center of symmetry located at the midpoint of two Pb(II) centers (Figure 1a). Each Pb(II) atom in **1** is primarily coordinated by four oxygen atoms from two bis-chelating adip ligands (Pb1–O1 = 2.556(3), Pb1–O2 = 2.455(3), Pb1–O3 = 2.350(3), Pb1–O4 = 2.607(3) Å) and two nitrogen atoms from a chelating dpdp ligand (Pb1–N1 = 2.800(3), Pb1–N2 = 2.730(3) Å) to furnish a distorted [PbN₂O₄] pentagonal bipyramidal geometry.^{5g} The O1, O2, O4, N1, and N2 atoms comprise the equatorial plane, whereas the O3 atom and the lone pair of electrons are located in the axial positions. The Pb(II) center deviates from the coordination plane by ca. 0.59 Å. The N2 atom from the chelating dpdp ligand has a weak bonding interaction with the Pb(II) atom (Pb1–N1 = 2.800(3) Å), which is longer than ones found in [Pb(endc)₂(phen)]_n and [Pb(endc)(phen)·3H₂O]₂ complexes (from 2.491(3) to 2.614(4) Å) (endc = endonorbornene-cis-5,6-dicarboxylate),^{4d} indicative of weak interactions between the nitrogen atom and the lead(II) center. The adjacent Pb(II) atoms are bridged by two adip ligands to form a dimer with a long Pb–Pb distance of 9.019 Å.

Notably, the dpdp ligands are arranged in a parallel fashion at both sides of a dimer (Figure 1b), leading to a structure suitable to form π–π interactions. Indeed, the lateral dpdp ligands from adjacent dimers are paired to furnish strong π–π interactions (ca. 3.54 and 3.49 Å) resulting in an interesting 2D supramolecular layer in the *bc* plane (Figure S1 in Supporting Information).

To investigate the influence of organic-acid spacer length on the complex framework, two short fatty acid ligands, glutaric acid (H₂glu) and succinic acid (H₂suc), were used to react with Pb(NO₃)₂ and dpdp under similar reaction conditions as those used for preparing **1**, and two new, complexes [Pb(glu)(dpdp)] **2** and [Pb(suc)(dpdp)] **3**, were formed. When H₂glu and H₂suc were utilized, respectively, two similar helical chain structures of **2** and **3** were obtained. In **2**, the Pb(II) center is located in a distorted pentagonal bipyramidal coordination sphere formed by four oxygen atoms from two distinct glu ligands, two nitrogen atoms from one chelating dpdp ligand, and a lone electron pair (Figure 2a). The carboxylate oxygen atoms (O1, O2, and O4A) from the glu ligands and two nitrogen atoms (N1 and N2) from the same dpdp ligand make up the basal plane, whereas the axial positions are occupied by one oxygen atom (O3A) and the lone pair of electrons. A notable feature for **2** is the presence of a helical chain (Figure 2b). The glu ligands bridge each pair of adjacent Pb(II) atoms into a single-stranded helical chain with a long pitch of 7.851 Å. The dpdp

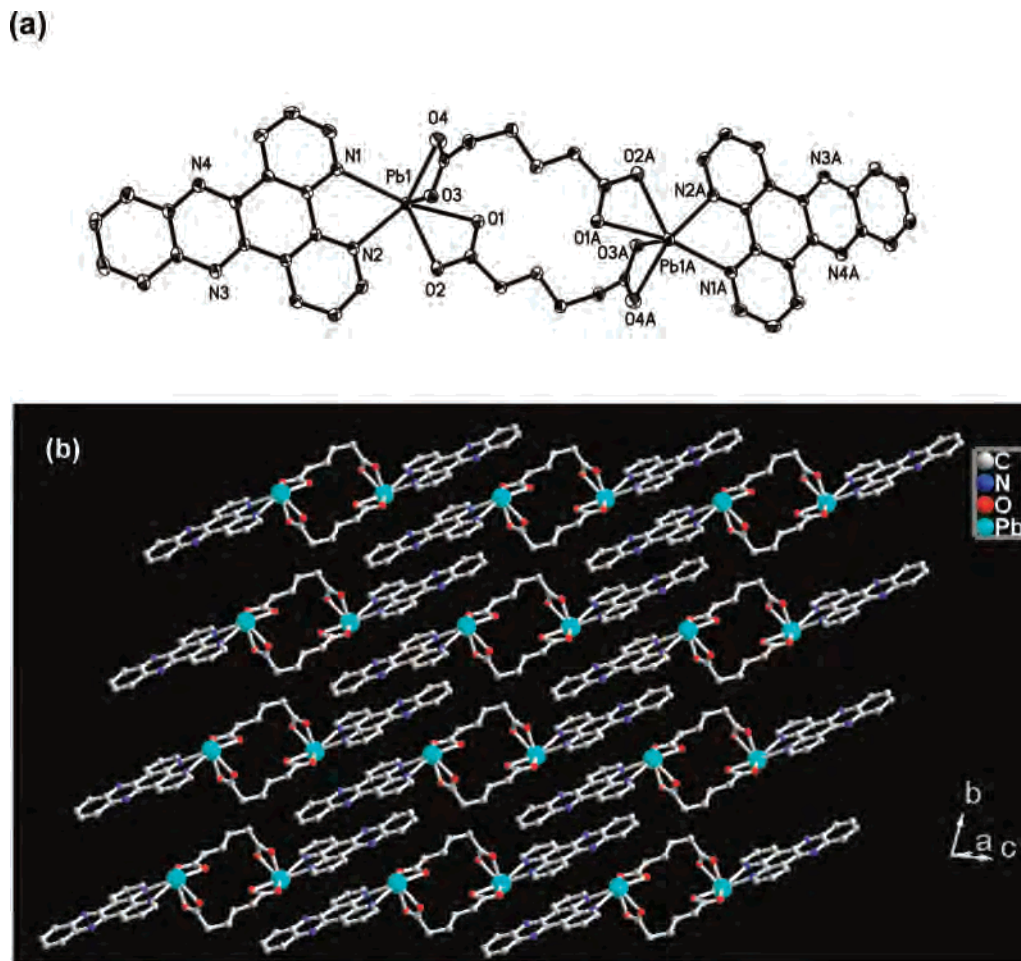


Figure 1. (a) View of the dinuclear compound **1** (all of the hydrogen atoms are omitted for clarity) and (b) the 2D supramolecular structure of **1** formed through π - π interactions.

ligands are alternately attached to both sides of the helical chain. Another interesting point is the presence of supramolecular interactions between such dpdp ligands (Figure S2 in Supporting Information). The approximately parallel orientation of the dpdp ligands allows pairing of neighboring related single-stranded helical chains to generate a supramolecular layer under the direction of aromatic π - π stacking interactions among the dpdp pairs (Figure 2c). Two adjacent helical chains of the same supramolecular layer show opposite chiralities. The face-to-face distance between the paired dpdp rings is about 3.40 Å, indicating a strong aromatic π - π stacking interaction. In fact, π - π stacking interactions play an important role in the formation and stabilization of the supramolecular structure.

It should be pointed out that in **2** and **3**, although H₂glu and H₂suc differ in the number of -CH₂- groups in their alkyl chains, they show quite similar helical chain structures (Figure 3). However, a small difference exists between these two compounds. As shown in Tables S2 and S3 (Supporting Information), the average Pb-O bond distance in **2** (2.488 Å) is slightly shorter than the corresponding one in **3** (2.514 Å), whereas the average Pb-N bond distance in **2** (2.734 Å) is longer than the corresponding one in **3** (2.682 Å). Additionally, the pitch of the helical chain in **2** is slightly shorter than that in **3** (7.885 Å), because of the influence of fatty acid spacer length.

To examine the influence of the flexibility of the fatty acid on the assembly of supramolecular entities, a rigid fatty acid, H₂fum, was used instead of flexible H₂glu or H₂suc. Consequently, compound [Pb(fum)(dpdp)]·H₂O **4**, which contains the H₂fum ligand and features a new layer structure, was obtained. An ORTEP view of **4** is shown in Figure 4a. Each asymmetric unit consists of one Pb(II) atom, one fum, one dpdp, and one lattice water molecule. The Pb(II) center is six-coordinated by four carboxylate oxygen atoms from four different fum anions and by two nitrogen atoms from the same chelating dpdp ligand in a severely distorted pentagonal bipyramidal geometry. The distances of the Pb-O bonds range from 2.582(5) to 2.619(5) Å, which are close to those of {[Pb(L_b)(H₂O)]·(H₂O)_{0.25}}_n (from 2.450(4) to 2.662(5) Å) (H₂L_b = 2,4-dinitro-5-hydroxybenzoic acid).^{4c} In the structure of **4**, each fum ligand bridges four Pb(II) centers in a tetradentate mode, generating a novel layer structure (Figure 4b). These layers are decorated with dpdp ligands alternately at two sides of each layer. It is worth noting that the 2D layers repeat in an -ABAB- stacking sequence instead of the stacking fashion observed in other layer compounds.¹¹ Additionally, the interplanar distance between two neighboring dpdp ligands of adjacent layers are ca. 3.54 and 3.50 Å (Figure S4 in Supporting Informa-

(11) Chen, C.-L.; Goforth, A. M.; Smith, M. D.; Su, C.-Y.; zur Loye, H.-C. *Inorg. Chem.* **2005**, *44*, 8762.

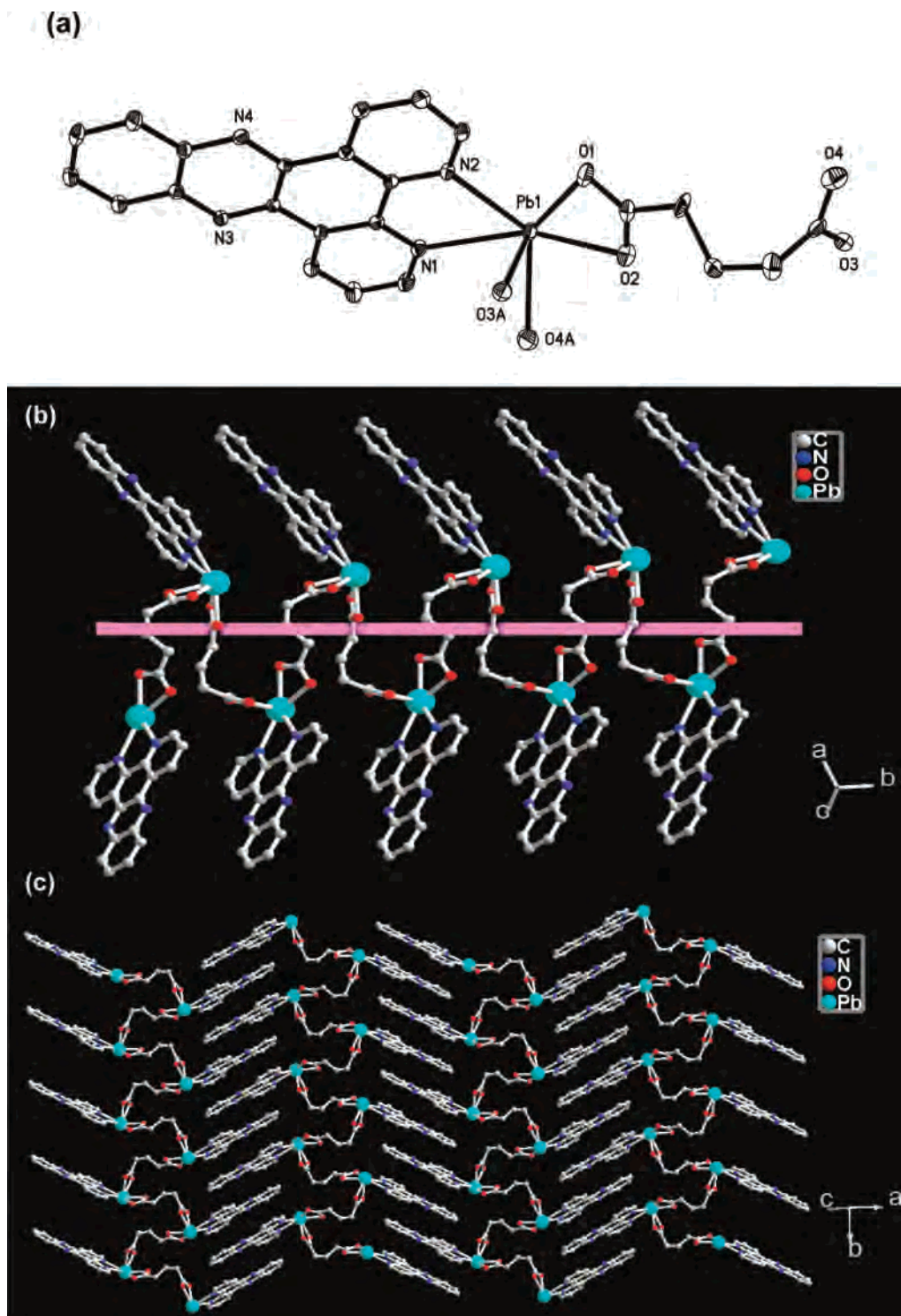


Figure 2. (a) Coordination environment of the Pb(II) center in compound **2** (all of the hydrogen atoms are omitted for clarity), (b) the 1D helical chain structure of **2**, and (c) the layer structure of **2** formed through π - π stacking interactions.

tion), respectively, indicating the presence of face-to-face π - π interactions that further stabilize the crystal structure and extend the layers to a unique 3D supramolecular structure (Figure 4c). Notably, significant O-H \cdots O hydrogen bonds involving the free water molecule (O1W) and weakly coordinated carboxylate oxygen atoms are also present within the supramolecular structure.

To evaluate the effects of bulky phenyl groups of the dicarboxylate ligands within the framework formation of their

complexes, four structurally related ligands, H₂oba, 1,4-H₂bdc, H₂dpdc, and 1,3-H₂bdc, were utilized to react with Pb(NO₃)₂ using a preparation procedure similar to that for **1–4**. Complexes **5–8** were obtained. In **5**, each Pb(II) center coordinates to two carboxylate oxygen atoms and two dpdp nitrogen atoms (Figure 5a). The overall geometry is best described as a distorted tetragonal pyramid. The O1, O2, N1, and N2 atoms lie in equatorial positions, and a lone electron pair lies in the apical position. It is noteworthy that

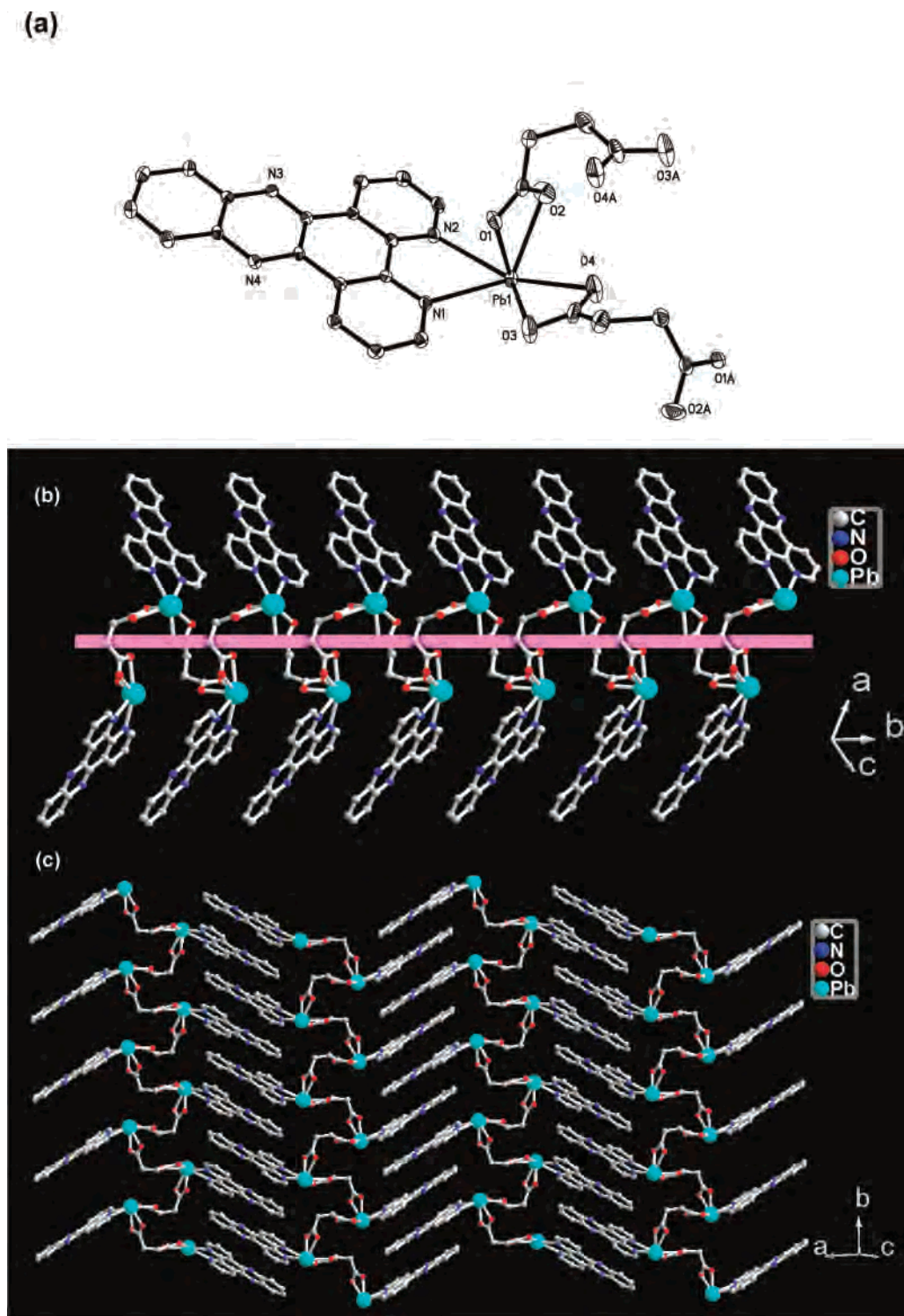


Figure 3. (a) Coordination environment of the Pb(II) center in compound **3** (all of the hydrogen atoms are omitted for clarity), (b) the 1D helical structure of **3**, and (c) the layer structure of **3** formed through π - π interactions.

the lower coordination numbers of the Pb(II) center are clearly different from those in **1–4**, probably as a result of steric hindrance from the aromatic dicarboxylate groups. It should be also noted that for the lattice nitrate group there is also a weak coordination interaction between the O4 atom and the center Pb(II) atom, with the Pb1–O4 distance being 2.799 Å. Thus, if the weak Pb1–O4 bond is considered, the coordination geometry of the central Pb(II) atom can also be described as a very distorted octahedron. The oba ligand

links two Pb(II) atoms to form a dinuclear structure. In the dimer, the Pb–O (carboxylate) bond distances are 2.495(9) and 2.574(8) Å, respectively, being comparable to those of other Pb(II) complexes in this report. A striking feature of compound **5** is the presence of free lattice dpdp ligands. To the best of our knowledge, such an aromatic system is the first example observed in Pb(II) complexes.⁵ In contrast with compounds **1–4**, compound **5** has a Pb(II)/dpdp ratio of 1:2. Although we changed the various molar ratios in the reaction

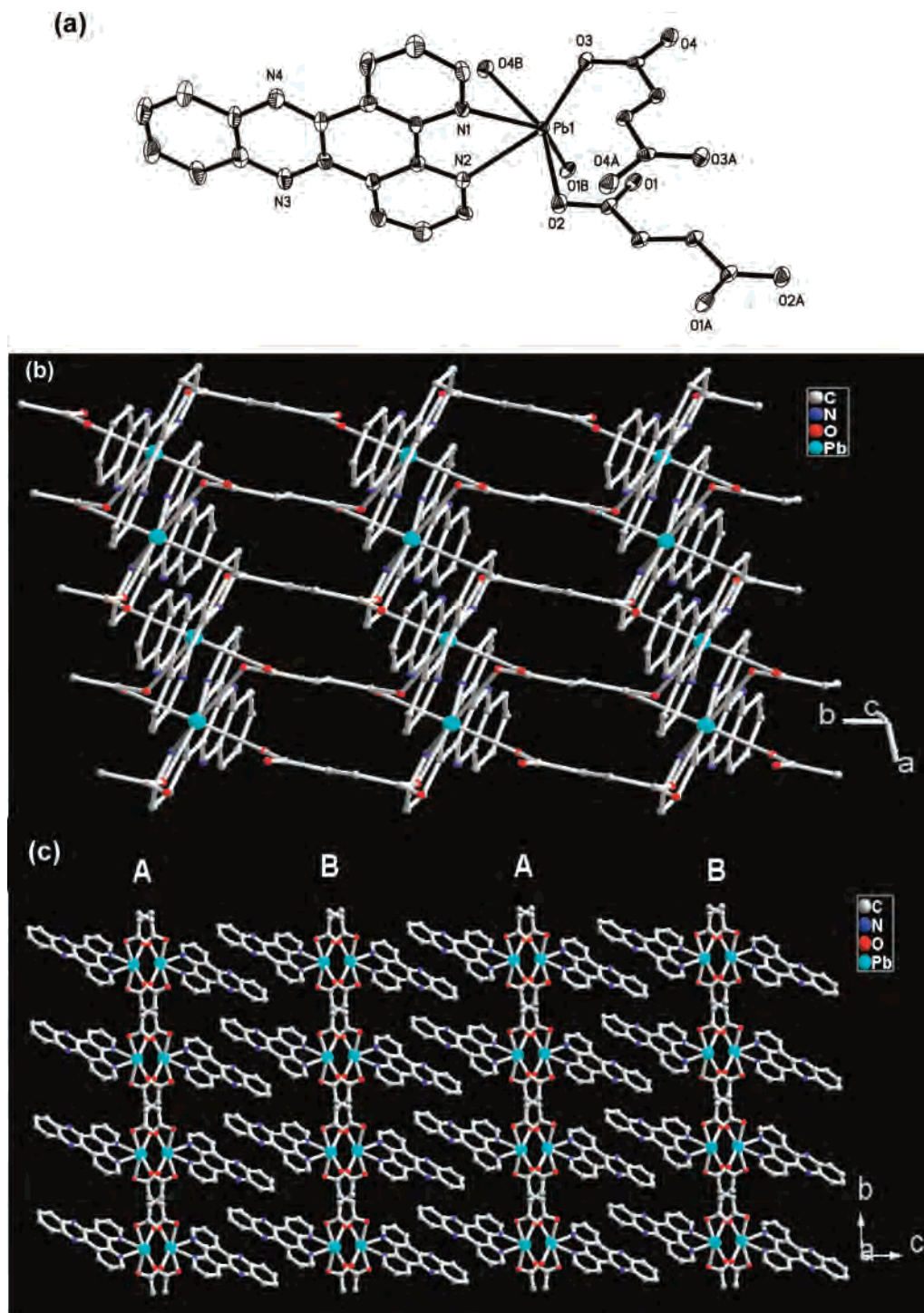


Figure 4. (a) Coordination environment of the Pb(II) center in compound **4** (all of the hydrogen atoms are omitted for clarity), (b) the layer structure of **4**, and (c) the 3D supramolecular structure of **4** formed through interlayer π - π interactions.

mixtures, the same compound **5** was always obtained. Furthermore, the free and coordinating dpdp ligands are held face-to-face through π - π interactions to generate an interesting two-stranded helical motif (Figure 5b). There are also strong π - π interactions, which are both intrachain (ca. 3.57 Å) and interchain (ca. 3.49 Å, Figure S5 in Supporting Information) in nature and form columnar aromatic stackings as shown in Figure 5c. The overall structure thus formed is a 2D polymeric framework via the columnar aromatic stacking involving two-stranded helical motifs (Figure 5c).

To investigate the influence of the length of a ligand spacer on the structure of a complex, a short 1,4-H₂bdc ligand instead of a H₂oba ligand was used, and a new complex [Pb₂(1,4-bdc)₂(dpdp)₂·H₂O **6** was obtained and structurally determined. In the asymmetric unit of **6**, there exists one Pb(II) atom, two 1,4-bdc ligands, one dpdp ligand, and half of a water molecule (Figure 6a). The Pb(II) atom is six-coordinated by two nitrogen atoms of one chelating dpdp ligand and four oxygen atoms of two 1,4-bdc ligands in a distorted [PbN_2O_4] pentagonal bipyramidal geometry. The

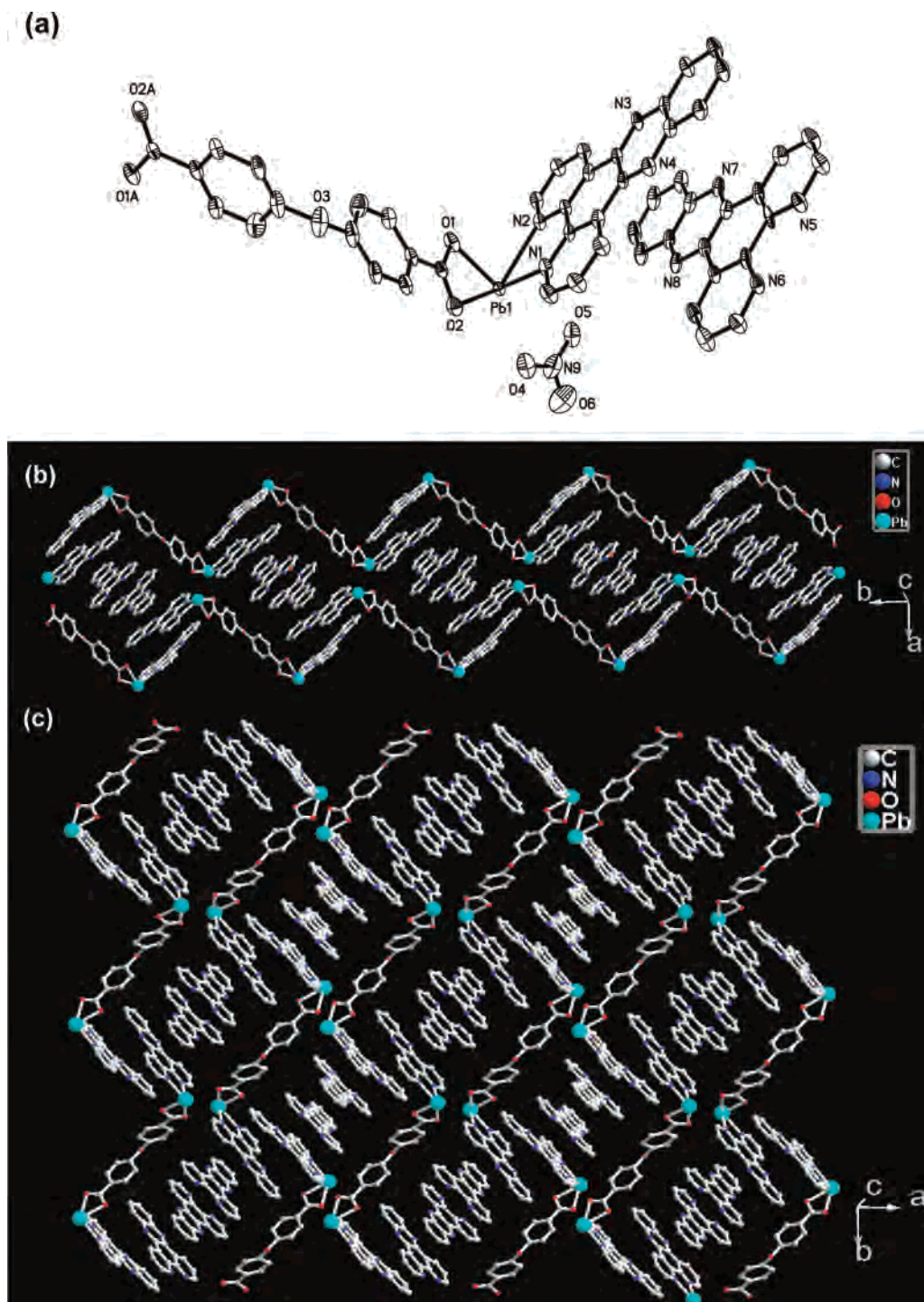


Figure 5. (a) Coordination environment of the Pb(II) center in compound **5** (all of the hydrogen atoms are omitted for clarity), (b) the two-stranded helical structure of **5**, and (c) the layer structure of **5** formed through π - π interactions.

O1, O3, O4, N1, and N2 atoms comprise the basal plane, whereas the O2 atom and the lone pair of electrons occupy the axial positions. The average Pb–O bond length is 2.550 Å, with the O–Pb–O bond angles varying from 49.73(18) to 119.8(2)°, which compares well with those in **5**. In **6**, each Pb(II) atom is linked to two other Pb(II) atoms through the bis-chelating 1,4-bdc ligands, forming a unique zigzag chain structure with a pitch of 15.29 Å, where the Pb–Pb–Pb angle, defined by the orientation of the 1,4-bdc ligands in the chain, is 83.2°. The ddpd ligands in **6** are extended on both sides of the chain in a parallel fashion (Figure 6b).

It is noteworthy that there are two types of π - π interactions in **6**. First, the neighboring zigzag chains interact through π - π stackings between the ddpd and 1,4-bdc ligands (ca. 3.39 Å, Figure S6 in Supporting Information), leading to interesting 2D supramolecular layers (Figure 6c). Second, the 2D layers repeat in an -ABAB- stacking sequence as observed in **4** through another type of π - π interactions between the ddpd ligands (ca. 3.55 Å, Figure S6 in Supporting Information), which extends the 2D supramolecular arrays into an interesting 3D supramolecular structure (Figure 6d).

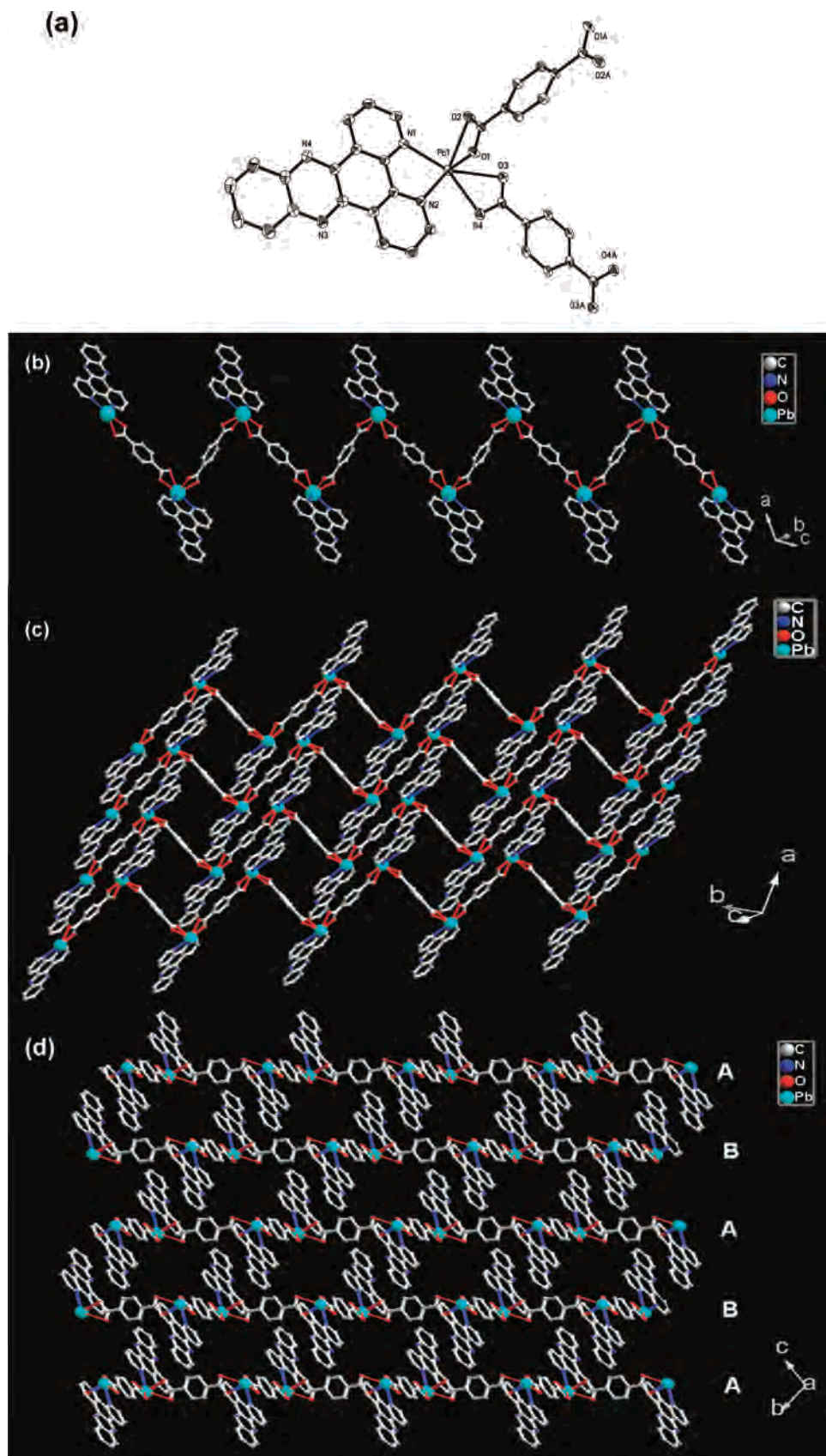


Figure 6. (a) Coordination environment of the Pb(II) center in compound **6** (all of the hydrogen atoms are omitted for clarity), (b) the zigzag chain structure of **6**, (c) the 2D supramolecular structure of **6** formed through interchain π - π interactions, and (d) the 3D structure of **6** formed through π - π interactions between different supramolecular layers.

To investigate the effects of carboxylate position on the structure of a compound, the two ligands H_2dpdc and 1,3-

H_2bdc were used. Single-crystal X-ray structural analysis revealed that the structure of **7** contained one crystallographi-

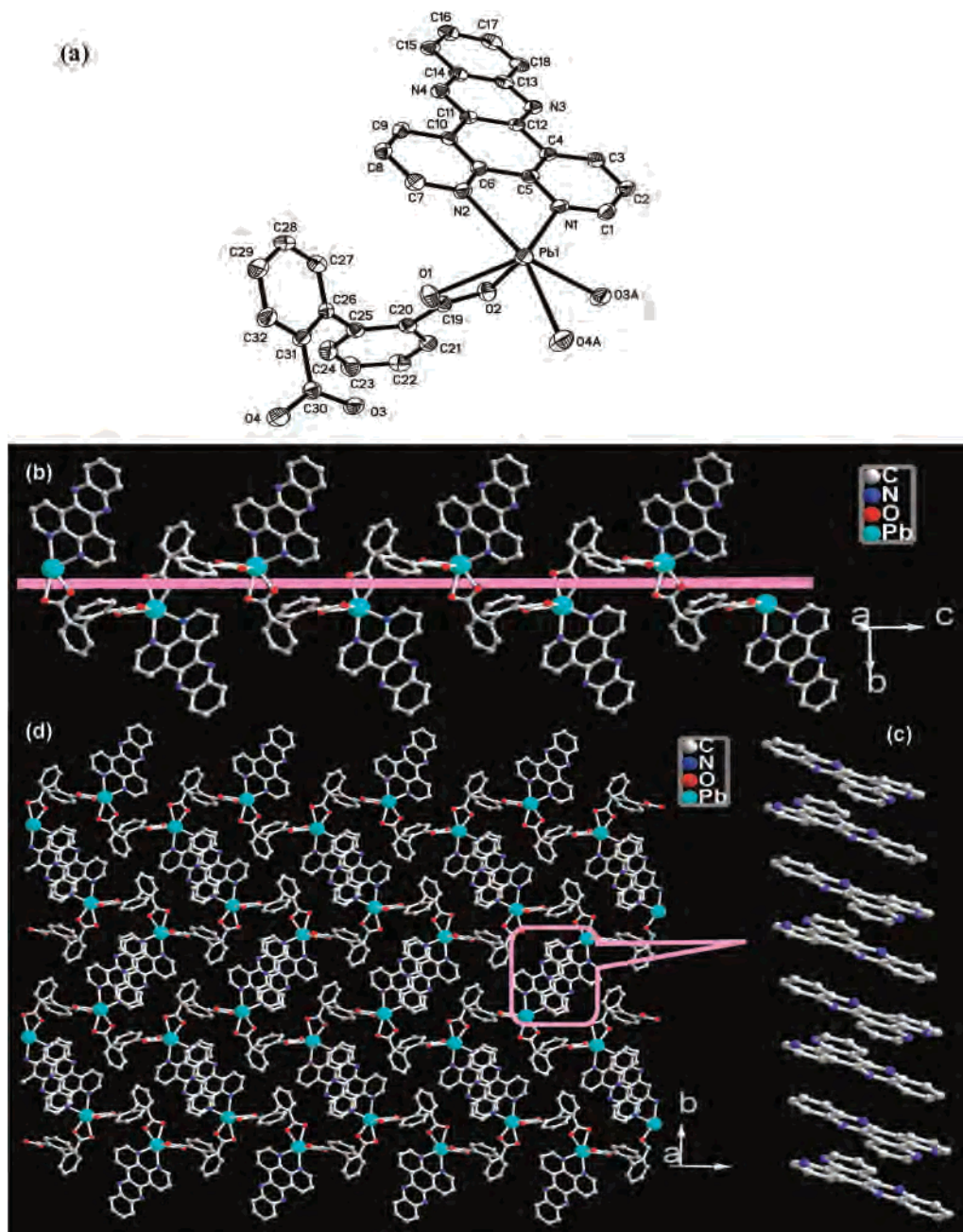


Figure 7. (a) Coordination environment of the Pb(II) center in compound **7** (all of the hydrogen atoms are omitted for clarity), (b) the helical chain structure of **7**, (c) the unusual 1D supramolecular dpdp arrays through two types of π - π interactions, and (d) the 3D supramolecular structure of **7** formed through the 1D supramolecular dpdp arrays.

cally unique Pb(II) atom, one dpdc ligand, and one dpdp ligand. An ORTEP view of the local coordination geometry around the Pb(II) atom is shown in Figure 7a. The Pb(II) atom is located in the center of a distorted pentagonal bipyramidal coordination geometry, which is defined by four oxygen atoms of two dpdc ligands, two nitrogen atoms from one chelating dpdp ligand, and the lone pair of electrons. The Pb–O bond lengths are in the range of 2.289(4)–2.643(4) Å, and the O–Pb–O angles vary from 51.12(13) to 120.63(14)°. The Pb–O bond lengths correspond to those observed in $[\text{Pb}_6(\text{dpdc})_4\text{O}_2]_n$ (from 2.248(7) to 2.741(9) Å).^{4f} Each pair of adjacent Pb(II) atoms are bridged by one dpdc ligand to form a helical chain with a pitch of 13.928 Å. The dpdp ligands are extended in a parallel fashion at both sides

of a single-stranded helical chain (Figure 7b). Interestingly, the aromatic stacking of dpdp ligands forms a 1D supramolecular dpdp array through two types of π - π interactions (Figure 7c). The neighboring helical chains interact through these π - π stackings (ca. 3.29 Å, Figure S7 in Supporting Information) to form 2D supramolecular layers. Furthermore, another type of π - π interaction between the dpdp ligands (ca. 3.28 Å, Figure S7 in Supporting Information) in neighboring layers extend the 2D supramolecular arrays into an interesting 3D supramolecular structure, which is the striking features of complex **7** (Figure 7d).

Unexpectedly, when 1,3-H₂bdc instead of H₂dpdc was used, structurally different chains are formed in **8** under a similar hydrothermal reaction for the preparation of **7**. As

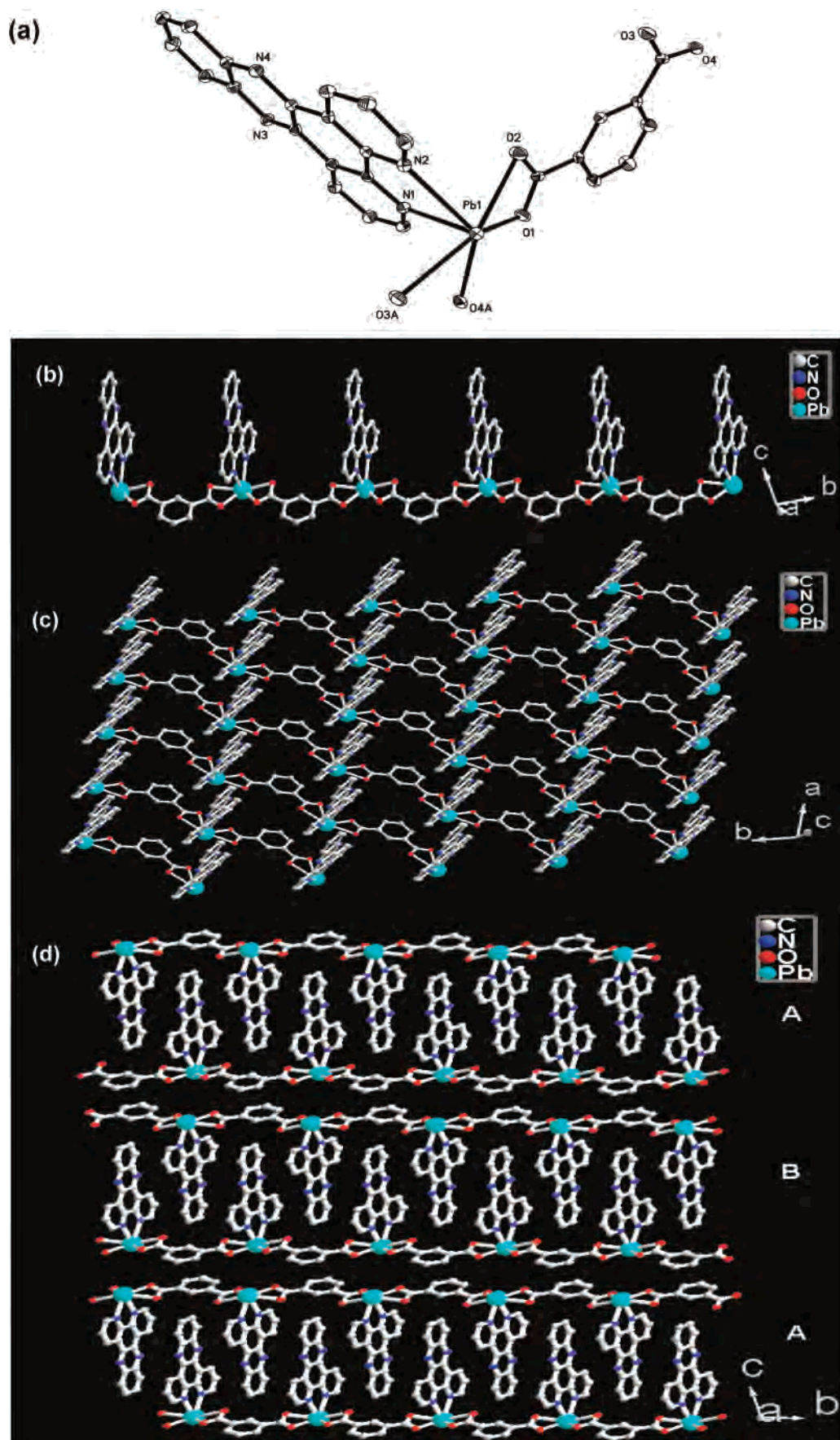


Figure 8. (a) Coordination environment of the Pb(II) center in compound **8** (all of the hydrogen atoms are omitted for clarity), (b) the chain structure of **8**, (c) the layer structure of **8** formed through interchain π - π interactions, and (d) the double-layer structure of **8** formed through π - π interactions from different supramolecular layers.

shown in Figure 8a, the Pb(II) atom in **8** is coordinated by four oxygen atoms from two bis-chelating 1,3-bdc ligands and two nitrogen atoms from a chelating dpdp ligand to furnish a highly distorted pentagonal bipyramidal coordination sphere. The Pb–O distances in **8** vary from 2.423(4) to 2.700(4) Å, which are close to those found in $\text{Pb}_2(\text{PMIDA}) \cdot 1.5\text{H}_2\text{O}$ (from 2.331(9) to 2.876(9) Å) ($\text{H}_4\text{PMIDA} = \text{H}_2\text{O}_3\text{-PCH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$).⁴⁸ Each pair of adjacent Pb(II) atoms is bridged by the 1,3-bdc bridges to give rise to a zigzag chain. Unlike the structures of **5–7**, the dpdp ligands in **8** are almost extended on one side of the zigzag chain in a slightly slanted fashion (Figure 8b). The chains are extended into 2D layers through π – π intercalations between the dpdp ligands from adjacent chains with a face-to-face distance of about 3.32 Å (Figure 8c and Figure S8 in Supporting Information). These 2D layers are further extended through off-set aromatic π – π stacking interactions of dpdp groups (ca. 3.41 Å, Figure S8 in Supporting Information) into the final unusual supramolecular double-layer structure (Figure 8d). It is worth noting that double-layer coordination polymers have been reported; however, lead(II) complexes with a supramolecular double-layer feature constructed by π – π interactions have rarely been documented.¹² From the results presented above, it is concluded that the variation of organic-acid ligands result in structural changes, and sometimes it is the dominant factor determining the supramolecular structural features of the coordination compounds.

Among compounds **1–8**, only compound **5** shows luminescent property, which is described in the Supporting Information.

In addition to compounds **1–8**, two related compounds, $[\text{Pb}_6(1,4\text{-bdc})_6(\text{DMF})_7]$ **9** and $[\text{Pb}_2(1,4\text{-bdc})_2(\text{DMF})_2(\text{H}_2\text{O})]$ **10**, have also been synthesized under solvothermal conditions in the absence of dpdp. The syntheses and structures of **9** and **10** are described in the Supporting Information.

Effect of Organic Acid. The effects of the organic-acid ligands on the supramolecular structures of compounds **1–8** have been clearly demonstrated. Through varying the organic-acid ligands under similar synthesis conditions, eight related Pb(II) compounds were successfully isolated and they exhibit significant differences in their supramolecular architecture due to the presence of the different organic-acid ligands. Generally, the role of organic-acid ligands can be explained in terms of their differences in shape, size, and flexibility. In this work, to investigate the influence of the spacer length ($-\text{CH}_2-$) and flexibility of fatty acid ligands on the complex structures, typical fatty acids such as H_2adip , H_2glu , H_2suc , and H_2fum were used under similar synthetic conditions. The H_2adip , H_2glu , and H_2suc ligands possess flexibility owing to the presence of $-\text{CH}_2-$ spacers between the two carboxylate groups. The only structural difference in the three flexible ligands is the length of their alkyl chains (ligand spacer). In contrast with H_2suc , the H_2fum ligand shows

relatively rigid coordination properties due to the presence of a $-\text{CH}=\text{CH}-$ spacer between the two carboxylate groups. These geometrical differences in the fatty acids result in the formation of **1–4** with quite distinct supramolecular architectures under similar synthetic conditions. In **1**, two twisted adip ligands bridge two Pb(II) centers to form a very stable dinuclear structure. Clearly, the longer adip ligand helps the formation of the discrete complex **1**. **2** and **3** exhibit similar helical structures, whereas compound **4** possesses a layer structure. The structural discrepancy between **1** relative to **2** and **3** highlights the effects of ligand spacers upon the supramolecular framework formation of the complexes. However, the differences between **3** and **4** show the importance of ligand flexibility on the complex constructions. Simultaneously, the influence of aromatic acid ligands such as H_2oba , 1,4- H_2bdc , H_2dpdc , and 1,3- H_2bdc on the complex structures is also revealed by the structural differences of **5–8**. The common feature of the four ligands is that each contains a large aromatic group. The long oba ligand is a benzoic acid-based ligand, where the two phenyl rings can freely twist around the $-\text{O}-$ group to meet the requirements of the coordination geometries of metal ions in the assembly process. H_2dpdc as a flexible ligand allows the two carboxylate groups to bridge the metals from different directions. In contrast, the short 1,4- H_2bdc and 1,3- H_2bdc ligands are very rigid and not twisted. Like the structure of **1**, compound **5** also adopts a dinuclear structure, where a 2D supramolecular structure constructed through π – π interactions is observed. Thus, it is clear that the long and flexible nature of the oba ligand is an important factor during the formation of **5**. Compounds **6** and **8** show similar zigzag chain structures, and the chains recognize each other under the direction of π – π interactions to give the 3D and 2D supramolecular structures, respectively. The structural differences among **5**, **6**, and **8** can be attributed to the differences in the length and flexibility in their organic-acid ligands. In comparison with **5**, **6**, and **8**, the striking feature of **7** is the presence of single-stranded helices. The key factor for the formation of helical chains is presumed to be the geometry and flexibility of the dpdc ligand. Obviously, as far as compounds **1–8** are concerned, the length and flexibility of the organic-acid ligands are the most critical factors in determining the final supramolecular structures of the coordination compounds.

Conclusions

A series of Pb(II) coordination complexes with various organic-acid ligands have been successfully prepared under hydro(solvo)thermal conditions and structurally characterized, giving lead(II)–organic architectures from dinuclear to 3D structures. The structural differences among **1–8** shows the important role played by organic acids. The crystal structures of compounds **1–4** indicate that the flexibility and spacer length of the fatty acid are essential in determining the final structures of their compounds. The structural discrimination among **5–8** indicates the influence of flexibility, length, and carboxylate position of aromatic acid ligands on structure formation of their complexes. This work

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Organic-Acid Effect

greatly enriches the chemistry of self-assembly of Pb(II)-based coordination compounds. The results also present a feasible strategy for controlling the synthesis of framework architectures by organic-acid ligand design. Further studies are now under way in our laboratory.

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east Normal University, and Science Foundation for Young Teachers of Northeast Normal University (grant 20060304).

Supporting Information Available: Ten X-ray crystallographic files (CIF), selected bond distances and angles, the syntheses and structures for compounds **9** and **10**, intermolecular π - π interactions for **1-8**, as well as the luminescent property for compound **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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