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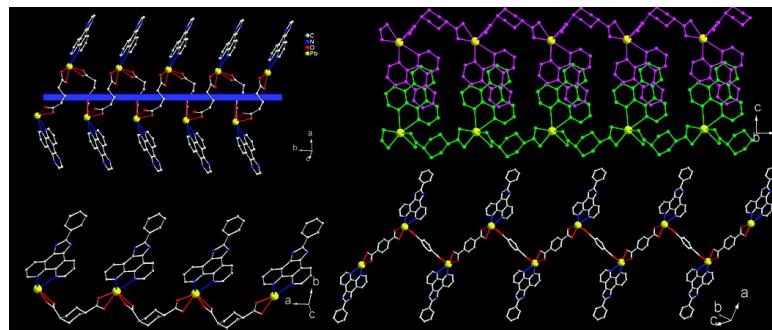
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# A Series of Lead(II) Complexes with $\pi$ – $\pi$ Stackings: Structural Diversities by Varying the Ligands

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**ABSTRACT:** Twelve structurally diverse complexes,  $[\text{Pb}_2(\text{pzp})_2(\text{adip})(\text{NO}_3)_2]$  **1**,  $[\text{Pb}(\text{pzp})(\text{glu})]$  **2**,  $[\text{Pb}(\text{pzp})(\text{chdc})] \cdot [\text{Pb}(\text{pzp})(\text{chdc})] \cdot \text{pzp} \cdot \text{H}_2\text{O}$  **3**,  $[\text{Pb}_2(\text{ndc})_2(\text{pzp})_2(\text{H}_2\text{O})] \cdot 0.5\text{H}_2\text{O}$  **4**,  $[\text{Pb}(\text{pzp})(1,3\text{-bdc})(\text{H}_2\text{O})_{0.5}] \cdot \text{H}_2\text{O}$  **5**,  $[\text{Pb}(\text{pzp})(1,2\text{-bdc})] \cdot \text{H}_2\text{O}$  **6**,  $[\text{Pb}_2(\text{ptc})_2(\text{adip})(\text{NO}_3)_2]$  **7**,  $[\text{Pb}(\text{ptc})(\text{glu})]$  **8**,  $[\text{Pb}(\text{ptc})(\text{chdc})]$  **9**,  $[\text{Pb}(\text{ptc})(\text{dpdc})]$  **10**,  $[\text{Pb}(\text{ptc})(1,3\text{-bdc})] \cdot 2.5\text{H}_2\text{O}$  **11**, and  $[\text{Pb}(\text{ptc})(1,4\text{-bdc})] \cdot 0.75\text{H}_2\text{O}$  **12**, where  $\text{H}_2\text{adip}$  = adipic acid,  $\text{H}_2\text{glu}$  = glutaric acid,  $\text{H}_2\text{chdc}$  = 1,4-cyclohexanedicarboxylic acid,  $\text{H}_2\text{ndc}$  = 1,4-naphthalenedicarboxylic acid, 1,4- $\text{H}_2\text{bdc}$  = benzene-1,4-dicarboxylic acid,  $\text{H}_2\text{dpdc}$  = 2,2'-diphenyldicarboxylic acid, 1,3- $\text{H}_2\text{bdc}$  = benzene-1,3-dicarboxylic acid, 1,2- $\text{H}_2\text{bdc}$  = benzene-1,2-dicarboxylic acid, pzp = pyrazino[2,3-f][1,10]phenanthroline, and ptc = 2-phenyl-1*H*-1,3,7,8,-tetraaza-cyclopenta[*I*]-phenanthrene, have been hydrothermally synthesized. Compounds **7** and **10** possess dinuclear structures, which are further extended by  $\pi$ – $\pi$  interactions to form supramolecular layers and chains, respectively. **1–6**, **8–9**, and **11–12** feature chain structures, which are then stacked by  $\pi$ – $\pi$  interactions to result in 2D or 3D supramolecular architectures. The structural differences among such complexes show that the organic acids and neutral chelating ligands have important influences on the structures.

## Introduction

The construction of discrete and polymeric metal-organic complexes is currently attracting considerable attention in view of their interesting structural topologies and properties.<sup>1</sup> In this regard, much progress has been made on the design and synthesis of novel coordination frameworks and the relationships between their structures and properties.<sup>2</sup> Generally, two different types of interactions (covalent bonds and noncovalent intermolecular forces) can be used to construct varied supramolecular architectures. To date, much research has focused on controlling motifs of metal-organic complexes through coordination bonds, whereas relatively less attention has been given to noncovalent  $\pi$ – $\pi$  interactions.<sup>3</sup> The  $\pi$ – $\pi$  interaction can be one of the most powerful noncovalent intermolecular interactions for directing the supramolecular architectures. Also, conjugated  $\pi$ -systems that strongly influence the physical properties of final products are of considerable interest in coordination compounds.<sup>4</sup> Therefore, the design of versatile functional ligands which are capable of coordinating to a metal ion while providing the  $\pi$ -conjugated system for organizing their complexes into extended networks through  $\pi$ – $\pi$  interactions is quite desirable. Up to now, the 1,10-phenanthroline ligand has been widely used to construct supramolecular architectures because of its excellent coordinating ability and large conjugated system that can easily form  $\pi$ – $\pi$  interactions. However, its derivatives such as pyrazino[2,3-f][1,10]phenanthroline (pzp) and 2-phenyl-1*H*-1,3,7,8,-tetraaza-cyclopenta[*I*]-phenanthrene (ptc), as good candidates for construction of metal-organic supramolecular architectures, have received far less attention.<sup>5</sup>

Lead(II), a heavy toxic metal, is commonly found in critical life cycles due to its widespread use in numerous industrial applications.<sup>6</sup> The possible molecular mechanisms of lead(II) toxicity may be involved in several different types of

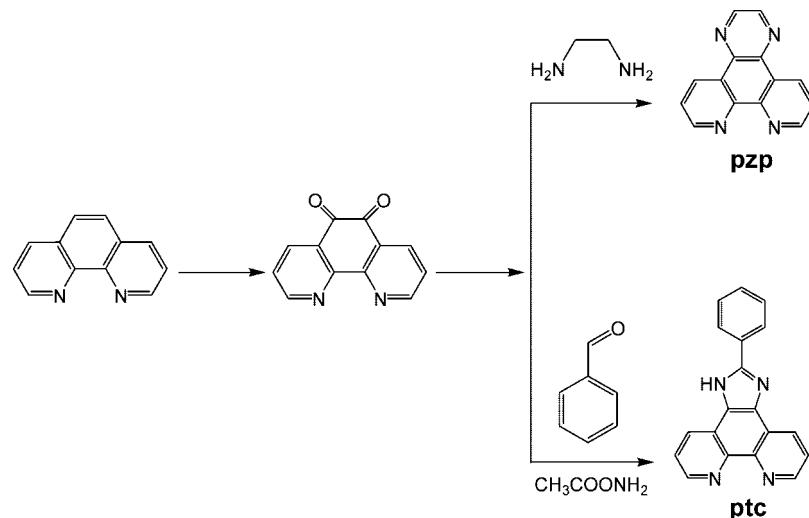
proteins.<sup>7</sup> Therefore, a good knowledge of the Pb(II) coordination properties, including aspects such as the lone pair of electrons, coordination number, and coordination geometry, is crucial for the understanding of the toxicological properties of lead(II).<sup>8</sup> In contrast to transition metals, the main group lead(II) possess unique coordination preferences and electronic properties observed rarely in the rest of the periodic table, presenting unique opportunities for the preparation of novel structures with new and interesting characteristics.<sup>9</sup> In this regard, several types of 1D → 2D or 3D supramolecular architectures assembled from Pb(II) centers with aromatic dicarboxylates and new derivatives of phen have been reported by our group and others.<sup>5c,10e</sup> In our attempt to investigate the design and control of the self-assembly of main group metal-organic architectures with flexible or rigid ligands, various supramolecular complexes with interesting structures were successfully isolated.<sup>10</sup> It is well-known that both organic acid and neutral chelating ligand have important effects on the structures of their complexes.<sup>11</sup> As a continuation of our work, in this contribution, we selected pzp and ptc as the neutral chelating ligands (Scheme 1), and 12 new Pb(II) complexes with different structures,  $[\text{Pb}_2(\text{pzp})_2(\text{adip})(\text{NO}_3)_2]$  **1**,  $[\text{Pb}(\text{pzp})(\text{glu})]$  **2**,  $[\text{Pb}(\text{pzp})(\text{chdc})] \cdot [\text{Pb}(\text{pzp})(\text{chdc})] \cdot \text{pzp} \cdot \text{H}_2\text{O}$  **3**,  $[\text{Pb}_2(\text{ndc})_2(\text{pzp})_2(\text{H}_2\text{O})] \cdot 0.5\text{H}_2\text{O}$  **4**,  $[\text{Pb}(\text{pzp})(1,3\text{-bdc})(\text{H}_2\text{O})_{0.5}] \cdot \text{H}_2\text{O}$  **5**,  $[\text{Pb}(\text{pzp})(1,2\text{-bdc})] \cdot \text{H}_2\text{O}$  **6**,  $[\text{Pb}_2(\text{ptc})_2(\text{adip})(\text{NO}_3)_2]$  **7**,  $[\text{Pb}(\text{ptc})(\text{glu})]$  **8**,  $[\text{Pb}(\text{ptc})(\text{chdc})]$  **9**,  $[\text{Pb}(\text{ptc})(\text{dpdc})]$  **10**,  $[\text{Pb}(\text{ptc})(1,3\text{-bdc})] \cdot 2.5\text{H}_2\text{O}$  **11**, and  $[\text{Pb}(\text{ptc})(1,4\text{-bdc})] \cdot 0.75\text{H}_2\text{O}$  **12**, where  $\text{H}_2\text{adip}$  = adipic acid,  $\text{H}_2\text{glu}$  = glutaric acid,  $\text{H}_2\text{chdc}$  = 1,4-cyclohexanedicarboxylic acid,  $\text{H}_2\text{ndc}$  = 1,4-naphthalenedicarboxylic acid, 1,4- $\text{H}_2\text{bdc}$  = benzene-1,4-dicarboxylic acid,  $\text{H}_2\text{dpdc}$  = 2,2'-diphenyldicarboxylic acid, 1,3- $\text{H}_2\text{bdc}$  = benzene-1,3-dicarboxylic acid, and 1,2- $\text{H}_2\text{bdc}$  = benzene-1,2-dicarboxylic acid, were obtained by varying the organic acids and neutral chelating ligands (Schemes 2 and 3). Because the organic acids show different structures, the

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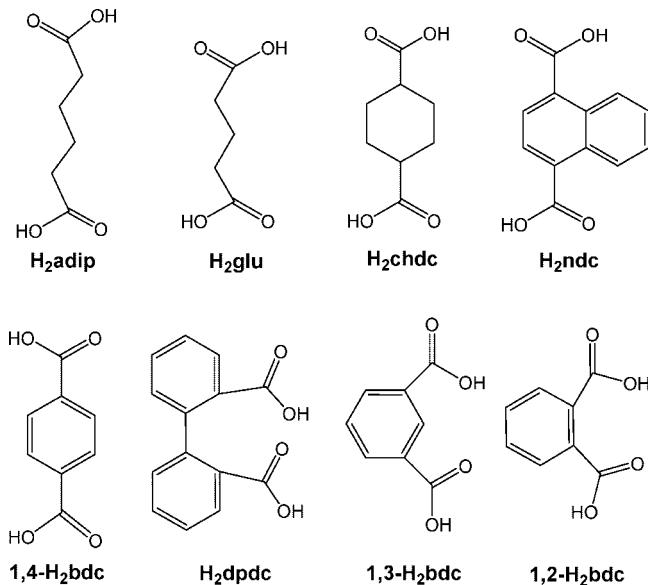
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Scheme 1. Structures of the pzp and ptc Ligands



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



assembly processes of complexes **1–6** and **7–12** are mainly determined by the nature of the organic acids.<sup>11</sup>

## Experimental Section

**Materials and Methods.** All reagents of analytical grade were purchased and used without further purification. The neutral chelating ligands pzp and ptc were synthesized according to the literature.<sup>12</sup> 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.

**Synthesis of [Pb<sub>2</sub>(pzp)<sub>2</sub>(adip)(NO<sub>3</sub>)<sub>2</sub>] 1.** Pb(NO<sub>3</sub>)<sub>2</sub> (0.166 g, 0.5 mmol), pzp (0.120 g, 0.5 mmol), and H<sub>2</sub>adip (0.073 g, 0.5 mmol) were dissolved in distilled water (12 mL), and triethylamine was added until the pH value of the system was adjusted to between 5 and 6. The resultant solution was heated at 160 °C in a Teflon-lined stainless steel autoclave for 3 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: 45% based on Pb(II). Elemental analysis and ICP results for C<sub>17</sub>H<sub>12</sub>N<sub>5</sub>O<sub>5</sub>Pb: Calcd (%): C, 35.60; H, 2.11; N, 12.21; Pb, 36.13. Found (%): C, 35.34; H, 2.05; N, 12.50; Pb, 36.33.

**Synthesis of [Pb(pzp)(glu)] 2.** The preparation of **2** was similar to that of **1** except that H<sub>2</sub>glu (0.066 g, 0.5 mmol) was used instead of H<sub>2</sub>adip as the organic acid ligand. Pale yellow block crystals were obtained in a 41% yield based on Pb(II). Elemental analysis and ICP results for C<sub>19</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub>Pb: Calcd (%): C, 40.07; H, 2.48; N, 9.84; Pb, 36.38. Found (%): C, 40.35; H, 2.77; N, 9.43; Pb, 36.50.

**Synthesis of [Pb(pzp)(chdc)]·[Pb(pzp)(chdc)]·pzp·H<sub>2</sub>O 3.** The preparation of **3** was similar to that of **1** except that H<sub>2</sub>chdc (0.085 g, 0.5 mmol) was used instead of H<sub>2</sub>adip as the organic acid ligand. Pale yellow block crystals were obtained in a 37% yield based on Pb(II). Elemental anal. and ICP results for C<sub>58</sub>H<sub>48</sub>N<sub>12</sub>O<sub>9</sub>Pb<sub>2</sub>. Calcd (%): C, 47.34; H, 3.29; N, 11.42; Pb, 28.16. Found (%): C, 47.61; H, 3.14; N, 11.31; Pb, 28.35.

**Synthesis of [Pb<sub>2</sub>(pzp)<sub>2</sub>(ndc)<sub>2</sub>(H<sub>2</sub>O)]·0.5H<sub>2</sub>O 4.** The preparation of **4** was similar to that of **1** except that H<sub>2</sub>ndc (0.108 g, 0.5 mmol) was used instead of H<sub>2</sub>adip as the organic acid ligand. Pale yellow block crystals were obtained in a 33% yield based on Pb(II). Elemental anal. and ICP results for C<sub>104</sub>H<sub>62</sub>N<sub>16</sub>O<sub>19</sub>Pb<sub>4</sub>. Calcd (%): C, 46.81; H, 2.34; N, 8.40; Pb, 31.06. Found (%): C, 46.66; H, 2.55; N, 8.51; Pb, 31.37.

**Synthesis of [Pb(pzp)(1,3-bdc)(H<sub>2</sub>O)<sub>0.5</sub>]·H<sub>2</sub>O 5.** The preparation of **5** was similar to that of **1** except that 1,3-H<sub>2</sub>bdc (0.083 g, 0.5 mmol) was used instead of H<sub>2</sub>adip as the organic acid ligand. Pale yellow block crystals were obtained in a 55% yield based on Pb(II). Elemental anal. and ICP results for C<sub>44</sub>H<sub>30</sub>N<sub>8</sub>O<sub>11</sub>Pb<sub>2</sub>. Calcd (%): C, 41.91; H, 2.40; N, 8.88; Pb, 32.86. Found (%): C, 41.83; H, 2.52; N, 8.49; Pb, 32.71.

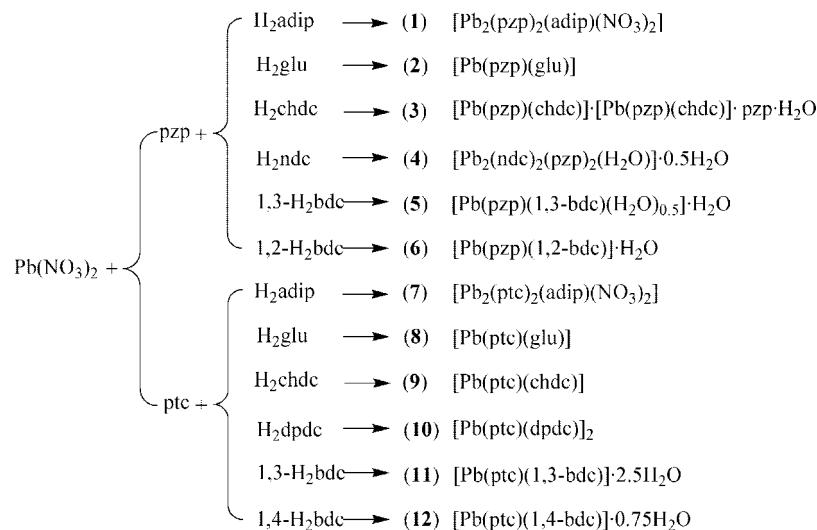
**Synthesis of [Pb(pzp)(1,2-bdc)]·H<sub>2</sub>O 6.** The preparation of **6** was similar to that of **1** except that 1,2-H<sub>2</sub>bdc (0.083 g, 0.5 mmol) was used instead of H<sub>2</sub>adip as the organic acid ligand. Pale yellow block crystals were obtained in a 36% yield based on Pb(II). Elemental anal. and ICP results for C<sub>22</sub>H<sub>14</sub>N<sub>4</sub>O<sub>5</sub>Pb. Calcd (%): C, 42.51; H, 2.27; N, 9.01; Pb, 33.34. Found (%): C, 42.67; H, 2.44; N, 8.77; Pb, 33.12.

**Synthesis of [Pb<sub>2</sub>(ptc)<sub>2</sub>(adip)(NO<sub>3</sub>)<sub>2</sub>] 7.** The preparation of **7** was similar to that of **1** except that ptc (0.148 g, 0.5 mmol) was used instead of pzp as the neutral ligand. Pale yellow block crystals were obtained in a 51% yield based on Pb(II). Elemental anal. and ICP results for C<sub>44</sub>H<sub>32</sub>N<sub>10</sub>O<sub>10</sub>Pb<sub>2</sub>. Calcd (%): C, 41.44; H, 2.53; N, 10.98; Pb, 32.50. Found (%): C, 41.27; H, 2.21; N, 10.64; Pb, 32.79.

**Synthesis of [Pb(ptc)(glu)] 8.** The preparation of **8** was similar to that of **7** except that H<sub>2</sub>glu (0.066 g, 0.5 mmol) was used instead of H<sub>2</sub>adip as the organic acid ligand. Pale yellow block crystals were obtained in a 43% yield based on Pb(II). Elemental anal. and ICP results for C<sub>24</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>Pb. Calcd (%): C, 45.50; H, 2.86; N, 8.84; Pb, 32.70. Found (%): C, 45.73; H, 2.65; N, 8.58; Pb, 32.91.

**Synthesis of [Pb(ptc)(chdc)] 9.** The preparation of **9** was similar to that of **7** except that H<sub>2</sub>chdc (0.085 g, 0.5 mmol) was used instead of H<sub>2</sub>adip as the organic acid ligand. Pale yellow block crystals were obtained in a 43% yield based on Pb(II). Elemental anal. and ICP results for C<sub>27</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub>Pb. Calcd (%): C, 48.14; H, 3.29; N, 8.32; Pb, 30.76. Found (%): C, 48.36; H, 3.58; N, 8.65; Pb, 30.39.

Scheme 3. Syntheses of Compounds 1–12



**Synthesis of [Pb(ptc)(dpdc)]<sub>2</sub> 10.** The preparation of **10** was similar to that of **7** except that H<sub>2</sub>dpdc (0.121 g, 0.5 mmol) was used instead of H<sub>2</sub>adip as the organic acid ligand. Pale yellow block crystals were obtained in a 52% yield based on Pb(II). Elemental anal. and ICP results for C<sub>66</sub>H<sub>40</sub>N<sub>8</sub>O<sub>8</sub>Pb<sub>2</sub>. Calcd (%): C, 53.29; H, 2.71; N, 7.53; Pb, 27.86. Found (%): C, 53.49; H, 2.63; N, 7.27; Pb, 27.48.

**Synthesis of [Pb(ptc)(1,3-bdc)]·2.5H<sub>2</sub>O 11.** The preparation of **11** was similar to that of **7** except that 1,3-H<sub>2</sub>bdc (0.083 g, 0.5 mmol) was used instead of H<sub>2</sub>adip as the organic acid ligand. Pale yellow block crystals were obtained in a 44% yield based on Pb(II). Elemental anal. and ICP results for C<sub>27</sub>H<sub>20</sub>N<sub>4</sub>O<sub>6</sub>Pb. Calcd (%): C, 46.09; H, 2.86; N, 7.96; Pb, 29.45. Found (%): C, 46.42; H, 2.65; N, 8.13; Pb, 29.29.

**Synthesis of [Pb(ptc)(1,4-bdc)]·0.75H<sub>2</sub>O 12.** The preparation of **12** was similar to that of **7** except that 1,4-H<sub>2</sub>bdc (0.083 g, 0.5 mmol) was used instead of H<sub>2</sub>adip as the organic acid ligand. Pale yellow block crystals were obtained in a 29% yield based on Pb(II). Elemental anal. and ICP results for C<sub>27</sub>H<sub>19</sub>N<sub>4</sub>O<sub>4.75</sub>Pb. Calcd (%): C, 47.51; H, 2.81; N, 8.21; Pb, 30.35. Found (%): C, 47.91; H, 2.53; N, 8.11; Pb, 30.16.

**Crystal Structure Determinations.** Diffraction data for complex **2** were recorded on a Bruker-AXS Smart CCD diffractometer, using a  $\omega$  scan technique with Mo K $\alpha$  radiation ( $\lambda = 0.71073\text{\AA}$ ). Diffraction data for complex **11** were recorded on an Oxford Diffraction Gemini R CCD diffractometer, using a  $\omega$  scan technique with Cu K $\alpha$  radiation ( $\lambda = 1.54184\text{\AA}$ ). Diffraction data for complexes **1**, **3–10**, and **12** were collected on a Rigaku RAXIS-RAPID single crystal diffractometer with MoK $\alpha$  radiation ( $\lambda = 0.71073\text{\AA}$ ). All the structures were solved by Direct Method of SHELXS-97<sup>13</sup> and refined by full-matrix least-squares techniques using the SHELXL-97<sup>14</sup> 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 Table 1.

## Results and Discussion

**Structures of 1–12.** Selected bond distances and angles for compounds **1–12** are shown in Tables S1–S12 (see the Supporting Information). To survey the influence of different organic acids on the structures of the complexes, we primarily selected pyrazino[2,3-f][1,10]phenanthroline (pzp) as neutral chelating ligand, and synthesized six lead(II) dicarboxylate complexes with pzp.

To examine the influence of organic acid spacer length on the complex framework, we used three organic acids H<sub>2</sub>adip, H<sub>2</sub>glu, and H<sub>2</sub>chdc, to react with Pb(NO<sub>3</sub>)<sub>2</sub> and pzp under similar reaction conditions, and three new complexes [Pb<sub>2</sub>(pzp)<sub>2</sub>(adip)(NO<sub>3</sub>)<sub>2</sub>] **1**, [Pb(pzp)(glu)] **2**, and [Pb(pzp)(chdc)]·[Pb(pzp)(chdc)]·pzp·H<sub>2</sub>O **3**, were obtained. As shown in Figure 1a, in compound **1**, the central Pb(II) atom is seven coordinate,

bonding to three carboxylate oxygen atoms from two different adip ligands (Pb1–O1 = 2.412(4), Pb1–O2 = 2.496(4), and Pb1–O2B = 2.830(4)  $\text{\AA}$ ), two nitrate oxygen atoms from one nitrate anion (Pb1–O3 = 2.681(4) and Pb1–O4 = 2.780(6)  $\text{\AA}$ ), and two nitrogen atoms from one pzp molecule (Pb1–N1 = 2.615(4) and Pb1–N2 = 2.557(4)  $\text{\AA}$ ). The Pb–O bond lengths vary greatly from 2.412(4) to 2.830(4)  $\text{\AA}$  in **1**. The adip ligand links four Pb(II) atoms with its two chelating/bridging carboxylate groups to form an infinite 1D chain structure (Figure 1b). It is interesting to note that the pzp ligands are attached to both sides of the chain. The centroid-to-centroid distance between two neighboring pzp ligands of adjacent chains is 3.56  $\text{\AA}$  (face-to-face distance of 3.38  $\text{\AA}$ , see Figure S1 in the Supporting Information), further extending the chains into an interesting 2D supramolecular assembly (Figure 1c).

As shown in Figure 2a, the Pb(II) atom of **2** is coordinated by two nitrogen atoms from one pzp ligand (Pb1–N1 = 2.747(4) and Pb1–N2 = 2.691(4)  $\text{\AA}$ ), and four carboxylate oxygen atoms from two different glu anions (Pb1–O1 = 2.592(4), Pb1–O2 = 2.499(4), Pb1–O3A = 2.355(4), and Pb1–O4A = 2.586(4)  $\text{\AA}$ ), showing a distorted pentagonal-bipyramidal coordination environment. The N1, N2, O1, O2, and O4A atoms comprise the basal plane, whereas the O3A atom and the lone pair of electrons occupy the axial positions. Each glu anion coordinates to two Pb(II) atoms with its chelating carboxylate oxygen atoms, and the Pb(II) atoms are bridged by glu anions to form a polymeric helical chain propagating along the crystallographic *b* axis with a pitch of 7.50  $\text{\AA}$  (Figure 2b). The pzp ligands are attached to the helical chain of glu anions and Pb(II) atoms, acting as a bidentate ligand. As shown in Figure 2c, the pzp ligands from neighboring helical chains are well-matched with each other, and adjacent chains are linked through  $\pi$ – $\pi$  stacking interactions between two pzp rings with the centroid–centroid distance being 3.55  $\text{\AA}$  (face-to-face distance of 3.43  $\text{\AA}$ , see Figure S2 in the Supporting Information), extending the chains into a 2D supramolecular assembly. It is believed that the very strong  $\pi$ – $\pi$  stacking interactions play an important role in stabilizing the helical structure and the supramolecular layer.<sup>15</sup>

As shown in Figure 3a, there are two kinds of crystallographically unique Pb(II) atoms in **3**. Each Pb(II) atom is six-coordinated by two nitrogen atoms from one pzp ligand (Pb1–N1 = 2.700(8), Pb1–N2 = 2.710(8), Pb2–N5 = 2.731(7), and Pb2–N6 = 2.718(8)  $\text{\AA}$ ), and four carboxylate oxygen atoms

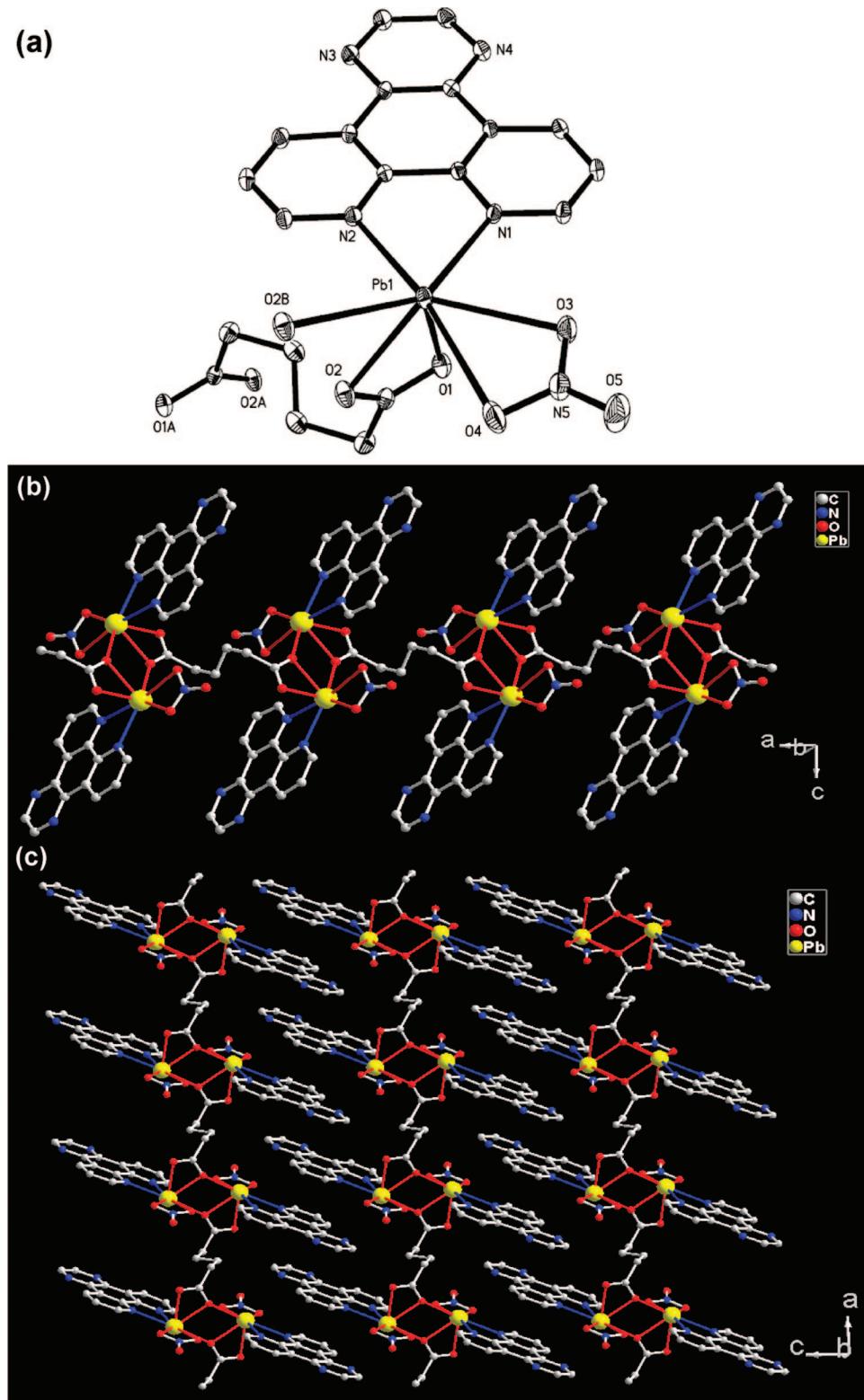
Table 1. Crystallographic Data for Compounds 1–12

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>
formula	$C_{17}H_{12}N_5O_5Pb$	$C_{19}H_{14}N_4O_4Pb$	$C_{38}H_{48}N_{12}O_9Pb_2$	$C_{10}H_{12}N_2O_9Pb_2$	$C_{44}H_{30}N_6O_5Pb$	$C_{22}H_{14}N_8O_{10}Pb_2$	$C_{44}H_{32}N_{10}O_{10}Pb_2$	$C_{24}H_{18}N_4O_4Pb$	$C_{27}H_{22}N_8O_4Pb$	$C_{66}H_{40}N_8O_8Pb_2$	$C_{51}H_{37}N_8O_3Pb_2$	$C_{27}H_{19}N_8O_4Pb_2$
formula mass	573.51	569.53	1471.50	2668.46	1261.14	621.56	1275.18	633.61	673.68	1487.44	1420.30	682..65
space group	$P\bar{1}$	$P\bar{1}/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$a$ (Å)	8.2899(17)	12.4199(11)	8.8647(18)	9.3240(19)	7.1636(14)	7.2740(15)	12.283(3)	9.1613(18)	9.3797(3)	9.4663(19)		
$b$ (Å)	8.6388(17)	7.5024(7)	10.648(2)	13.562(3)	9.2479(18)	12.231(2)	10.590(2)	9.984(2)	10.420(2)	11.932(2)	10.833(2)	
$c$ (Å)	12.100(2)	18.5981(16)	27.091(5)	18.148(4)	15.909(3)	12.714(3)	15.526(3)	13.171(3)	12.059(2)	15.6963(5)	13.159(3)	
$\alpha$ (deg)	83.76(3)	90	100.12(3)	95.33(3)	104.98(3)	90	90.86(3)	99.34(3)	93.42(3)	101.07(2)	94.19(3)	
$\beta$ (deg)	88.29(3)	98.68(12)	90.24(3)	90.47(3)	91.05(3)	96.48(3)	95.14(3)	98.33(3)	90.76(3)	91.98(3)	90.383(3)	106.42(3)
$\gamma$ (deg)	81.61(3)	90	91.79(3)	100.64(3)	103.37(3)	92.11(3)	90	111.80(3)	98.24(3)	112.88(3)	114.053(3)	105.72(3)
$V$ (Å <sup>3</sup> )	852.1(3)	1713.1(3)	2516.2(9)	2244.8(8)	987.1(3)	1029.1(4)	2011.6(7)	1034.9(4)	1208.7(4)	1328.7(5)	1237.17(7)	1229.5(4)
$Z$	2	4	2	1	2	2	2	2	2	1	1	2
$\rho$ (g cm <sup>-3</sup> )	2.235	2.208	1.942	1.974	2.121	2.006	2.105	2.033	1.851	1.906	1.844	
$\mu$ (mm <sup>-1</sup> )	9.944	9.885	6.758	7.563	8.595	8.240	8.436	8.193	7.021	6.397	13.726	6.906
GOF on $F^2$	1.056	0.962	1.164	1.037	1.116	1.046	1.025	1.139	1.133	1.157	1.073	1.073
$R$ [ $ I  > 2\sigma(I)$ ] <sup>a</sup>	$R_1 = 0.0314$	$R_1 = 0.0334$	$R_1 = 0.0407$	$R_1 = 0.0314$	$R_1 = 0.0323$	$R_1 = 0.0261$	$R_1 = 0.0374$	$R_1 = 0.0288$	$R_1 = 0.0236$	$R_1 = 0.0255$	$R_1 = 0.0353$	$R_1 = 0.0755$
	$wR_2 = 0.0657$	$R_2 = 0.0697$	$R_2 = 0.1545$	$wR_2 = 0.0688$	$wR_2 = 0.0717$	$R_2 = 0.0711$	$wR_2 = 0.0831$	$wR_2 = 0.0856$	$wR_2 = 0.0831$	$wR_2 = 0.0529$	$wR_2 = 0.0643$	$wR_2 = 0.0755$

<sup>a</sup>  $R_1 = \sum |F_0| - |F_0| / \sum |F_0| wR_2 = \{\sum [w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)]^2\}^{1/2}$ .

from two chdc anions ( $Pb1-O5 = 2.360(7)$ ,  $Pb1-O6 = 2.526(7)$ ,  $Pb1-O3A = 2.547(8)$ ,  $Pb1-O4A = 2.554(7)$ ,  $Pb2-O1 = 2.551(7)$ ,  $Pb2-O2 = 2.534(8)$ ,  $Pb2-O7A = 2.399(6)$ , and  $Pb2-O8A = 2.481(7)$  Å). Two kinds of crystallographically unique Pb(II) atoms (Pb1 and Pb2) are bridged by chdc molecules, respectively, forming two unique 1D helical chains, which is the most fascinating and peculiar structural feature of **3**. Although helical structures have been widely studied, to date only a few examples of two unique helical molecules coexisting in the same structure have been characterized.<sup>16,17</sup> Unlike the structures of **1** and **2**, the pzp ligands in **3** are extended on one side of the chain. The pzp ligands from two neighboring chains are paired to furnish strong  $\pi-\pi$  interactions (centroid-to-centroid distance of 3.48 Å and face-to-face distance of 3.41 Å, see Figure S3 in the Supporting Information), generating an interesting double chain structure (Figure 3b). The double chains are further extended into a final 2D supramolecular assembly (Figure 3c) through another type of  $\pi-\pi$  interactions between the coordinating and free pzp ligands with the centroid-to-centroid distance of 3.55 Å (face-to-face distance of 3.45 Å, see Figure S3 in the Supporting Information).

To study the influence of the carboxylate positions on their complex structures, three bulky ligands containing phenyl groups H<sub>2</sub>ndc, 1,3-H<sub>2</sub>bdc, and 1,2-H<sub>2</sub>bdc were selected to react with Pb(NO<sub>3</sub>)<sub>2</sub> under similar synthetic conditions, and three new complexes [Pb<sub>2</sub>(ndc)<sub>2</sub>(pzp)<sub>2</sub>(H<sub>2</sub>O)]·0.5H<sub>2</sub>O **4**, [Pb(pzp)(1,3-bdc)(H<sub>2</sub>O)<sub>0.5</sub>]·H<sub>2</sub>O **5**, and [Pb(pzp)(1,2-bdc)]·H<sub>2</sub>O **6** were obtained. As shown in Figure 4a, the asymmetric unit of **4** consists of two unique Pb(II) atoms, two unique ndc ligands, two unique pzp ligands, and one coordinating water molecule. The Pb1 atom is coordinated by five carboxylate oxygen atoms from three different ndc ligands (Pb1-O1 = 2.714(4), Pb1-O2 = 2.573(4), Pb1-O5 = 2.678(3), Pb1-O5A = 2.727(3), and Pb1-O6A = 2.729(4) Å), two nitrogen atoms from one pzp ligand (Pb1-N5 = 2.624(4) and Pb1-N6 = 2.644(4) Å), and one coordinating water molecule (Pb1-O1w = 2.611(4) Å). The Pb2 atom is surrounded by three carboxylate oxygen atoms from two different ndc ligands (Pb2-O8 = 2.282(4), Pb2-O3A = 2.487(4), and Pb2-O4A = 2.632(4) Å), and two nitrogen atoms from one pzp ligand (Pb2-N1 = 2.713(4) and Pb2-N2 = 2.555(4) Å). The Pb–O bond lengths vary greatly from 2.282(4) to 2.729(4) Å in **4**. The ndc ligands in **4** exhibit two different coordination modes. For convenience, the ndc anions containing the oxygen atoms labeled O1 and O5 are designated ndc1 and ndc2, respectively. For ndc1, each carboxylate moiety chelates one Pb(II) atom in a bidentate mode. For ndc2, one carboxylate moiety connects two Pb(II) atoms, whereas the other is coordinated to another Pb(II) center in a monodentate fashion. Thus two adjacent Pb1 atoms in **4** are bridged by two carboxylate oxygen atoms of ndc2 ligand to generate a dinuclear unit with Pb1–Pb1 distance of 4.333 Å (Figure 4b). The dinuclear units are interconnected to Pb2 atoms, furnishing 1D double chain ribbons along the *b* axis, which exhibit large rings comprising four bridging ndc ligands, two dinuclear units and two Pb2 atoms. The double chain ribbon is decorated with pzp ligands on two sides of the double chain. As illustrated in Figure 4c, the double chains are interconnected by the aromatic  $\pi-\pi$  interactions between two pzp ligands [N5–N8/C25–C38 at (*x*, *y*, *z*) and (-*x*, -*y*, -*z*)] to generate a 2D supramolecular assembly (centroid-to-centroid distance of 3.88 Å and face-to-face distance of 3.39 Å, see Figure S4 in the Supporting Information). In addition, these 2D supramolecular assemblies are further extended into a 3D supramolecular framework (Figure 4d) through another type of  $\pi-\pi$  interaction between

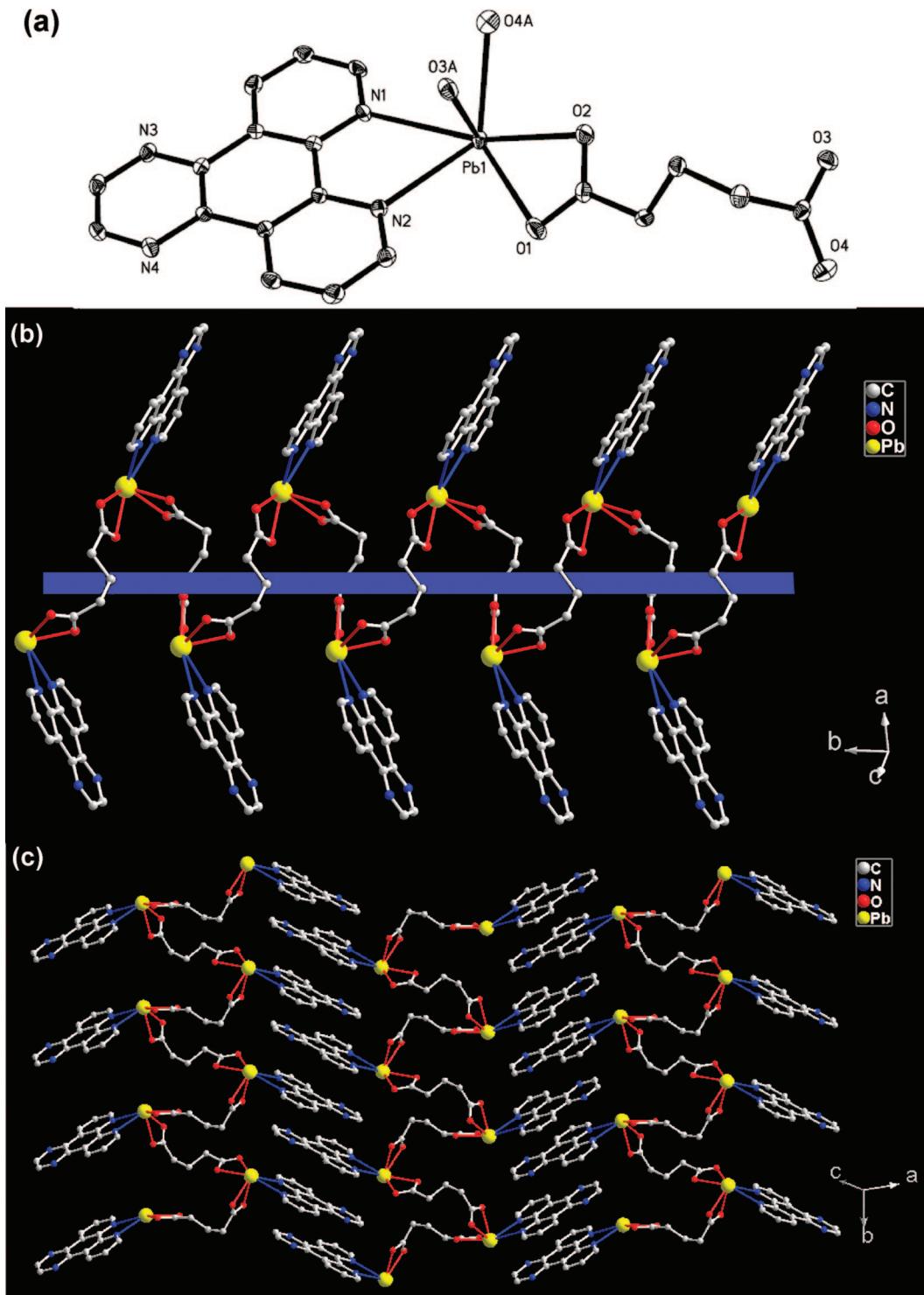


**Figure 1.** (a) Coordination environment of the Pb(II) center in compound **1** (thermal ellipsoids are at the 25% probability level), (b) the 1D chain structure, and (c) the 2D supramolecular assembly formed through  $\pi$ - $\pi$  stacking interactions.

two pzp ligands [N1–N4/C39–C52 at  $(x, y, z)$  and  $(-1 - x, 1 - y, 1 - z)$ ] (centroid-to-centroid distance of 3.50 Å and face-to-face distance 3.43 Å, see Figure S4 in the Supporting Information).

As shown in Figure 5a, the Pb(II) atom of **5** is seven-coordinated by two nitrogen atoms from one pzp ligand ( $\text{Pb}1-\text{N}1 = 2.504(5)$  and  $\text{Pb}1-\text{N}2 = 2.671(5)$  Å), one water molecule ( $\text{Pb}1-\text{O}2\text{w} = 2.721(14)$  Å), and four carboxylate

oxygen atoms from two 1,3-bdc ligands ( $\text{Pb}1-\text{O}1 = 2.382(4)$ ,  $\text{Pb}1-\text{O}2 = 2.724(4)$ ,  $\text{Pb}1-\text{O}3\text{A} = 2.621(4)$ , and  $\text{Pb}1-\text{O}4\text{A} = 2.482(4)$  Å). The Pb–O bond lengths vary greatly from 2.382(4) to 2.724(4) Å in **5**. The Pb(II) atoms are bridged by 1,3-bdc ligands to form a 1D infinite polymeric chain structure (Figure 5b). Like the structure of **3**, the pzp ligands in **5** are also attached on one side of the chain. Notably, there exist two types of  $\pi$ - $\pi$  interactions in **5**. The neighboring chains interact

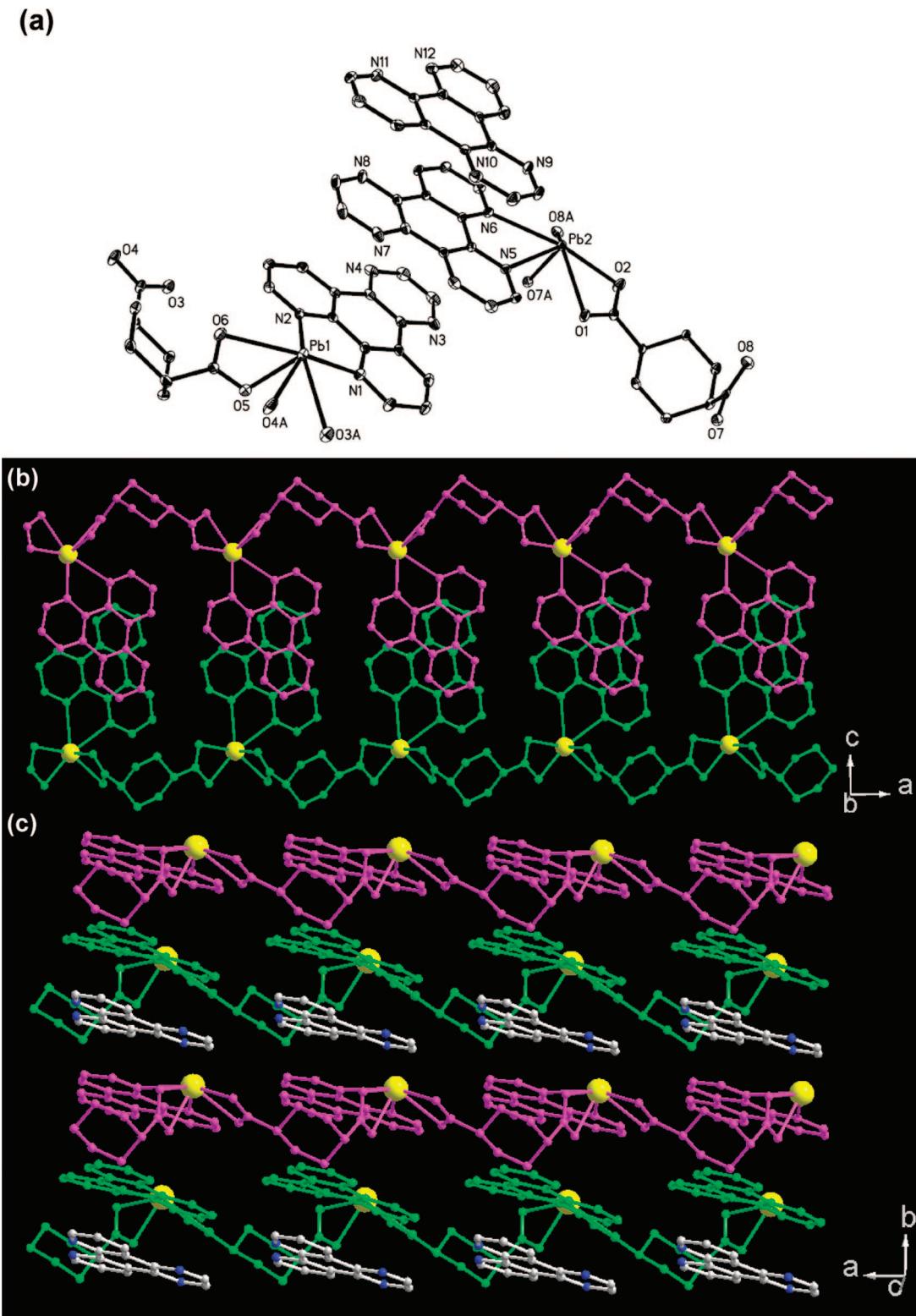


**Figure 2.** (a) Coordination environment of the Pb(II) center in compound **2** (thermal ellipsoids are at the 25% probability level), (b) the 1D helical chain structure, and (c) the 2D supramolecular assembly formed through  $\pi$ - $\pi$  stacking interactions.

through one type of  $\pi$ - $\pi$  stackings between two pzp ligands (centroid-to-centroid distance of 4.20 Å and face-to-face distance of 3.42 Å, see Figure S5 in the Supporting Information) to form an interesting 2D supramolecular assembly (Figure 5c). Two adjacent 2D supramolecular arrays are linked by another type of  $\pi$ - $\pi$  interactions between two pzp ligands (centroid-to-centroid distance of 3.85 Å and face-to-face distance of 3.49 Å, see Figure S5 in the Supporting Information), giving an interesting ladder (Figure 5d). Furthermore, the ladders are connected by third  $\pi$ - $\pi$  interaction between two 1,3-bdc ligands

(centroid-to-centroid distance of 3.91 Å and face-to-face distance of 3.45 Å, see Figure S5 in the Supporting Information). Obviously, the  $\pi$ - $\pi$  stacking interactions play an important role in the formation and stabilization of the 3D supramolecular structure of **5**.<sup>15</sup>

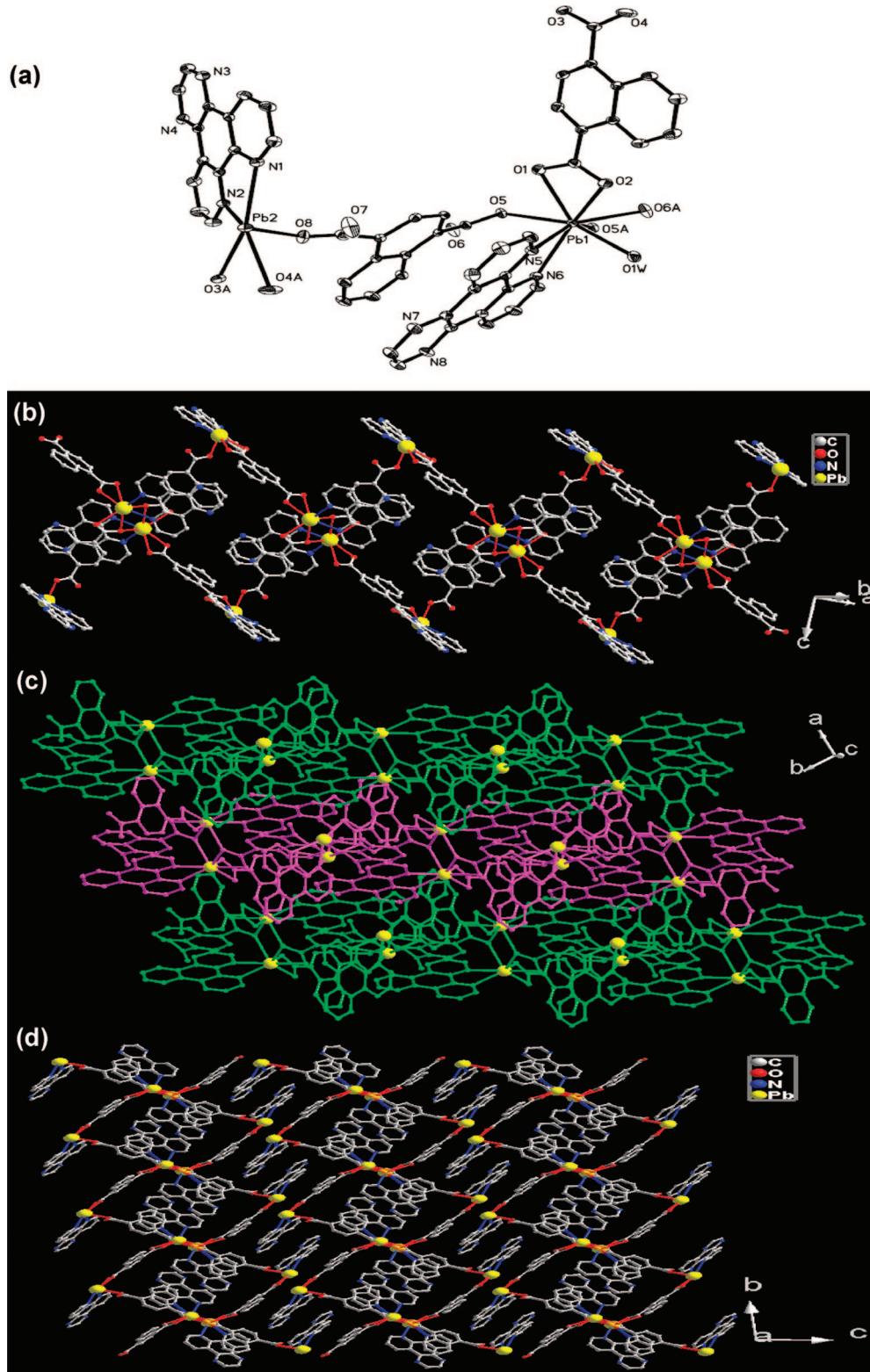
As shown in Figure 6a, the Pb(II) center of **6** shows a distorted pentagonal-bipyramidal coordination environment consisting of two nitrogen atoms from one pzp molecule ( $\text{Pb1-N1} = 2.643(4)$  and  $\text{Pb1-N2} = 2.788(4)$  Å) and four carboxylate oxygen atoms from three different 1,2-bdc ligands ( $\text{Pb1-O1}$



**Figure 3.** (a) Coordination environments of the Pb(II) centers in compound **3** (thermal ellipsoids are at the 20% probability level), (b) the two types of helical chain structure, and (c) the 2D supramolecular assembly formed through  $\pi-\pi$  stacking interactions.

$= 2.416(3)$ ,  $\text{Pb}1-\text{O}2 = 2.753(4)$ ,  $\text{Pb}1-\text{O}2\text{A} = 2.753(4)$ , and  $\text{Pb}1-\text{O}4\text{A} = 2.495(4)$  Å. It is noteworthy that the two carboxylate groups of 1,2-bdc ligand exhibit different coordination modes: one carboxylate group coordinates to one Pb(II) atom, whereas the other bridges two Pb(II) atoms. The 1,2-bdc ligands connect Pb(II) centers to form a double chain (Figure 6b). The pzp ligands of neighboring chains are involved in  $\pi-\pi$  interactions with a centroid-to-centroid distance of 3.67 Å (face-

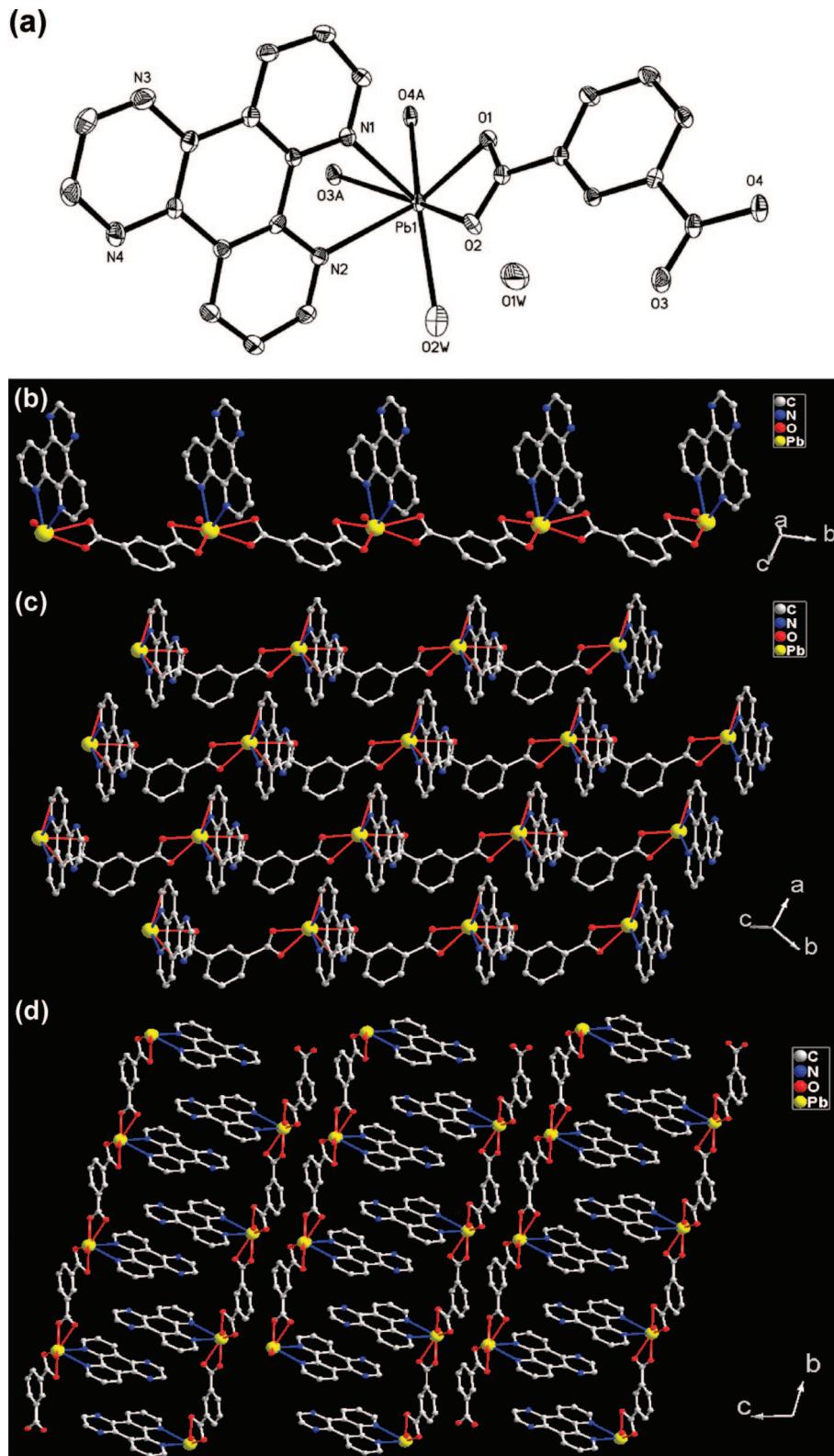
to-face distance of ca. 3.53 Å, see Figure S6 in the Supporting Information). As a result, the double chains of the compound **6** are linked by the  $\pi-\pi$  interactions to yield a 2D supramolecular assembly (Figure 6c). On the basis of the results presented above, it is suggested that the variation of organic acid ligands such as the spacer length and the orientation of the two carboxylate groups can result in structural changes as well as  $\pi-\pi$  interaction features of their coordination compounds.



**Figure 4.** (a) Coordination environment of the Pb(II) center in compound 4 (thermal ellipsoids are at the 20% probability level), (b) the 1D double chain structure, (c) the 2D supramolecular assembly formed through  $\pi-\pi$  stacking interactions, and (d) the 3D supramolecular structure of 4.

To further investigate the structural influence of the organic acid, we have synthesized compounds **7–12** containing ptc and determined their structures by X-ray diffraction. Furthermore, to further study the effect of organic acid spacer length on the complex structure, we reacted three organic acid ligands H<sub>2</sub>adip, H<sub>2</sub>glu, and H<sub>2</sub>chdc with Pb(NO<sub>3</sub>)<sub>2</sub> and the ptc ligand under similar reaction conditions, resulting in three new structures: [Pb<sub>2</sub>(ptc)<sub>2</sub>(adip)(NO<sub>3</sub>)<sub>2</sub>] **7**, [Pb(ptc)(glu)] **8**, and [Pb(ptc)(chdc)]

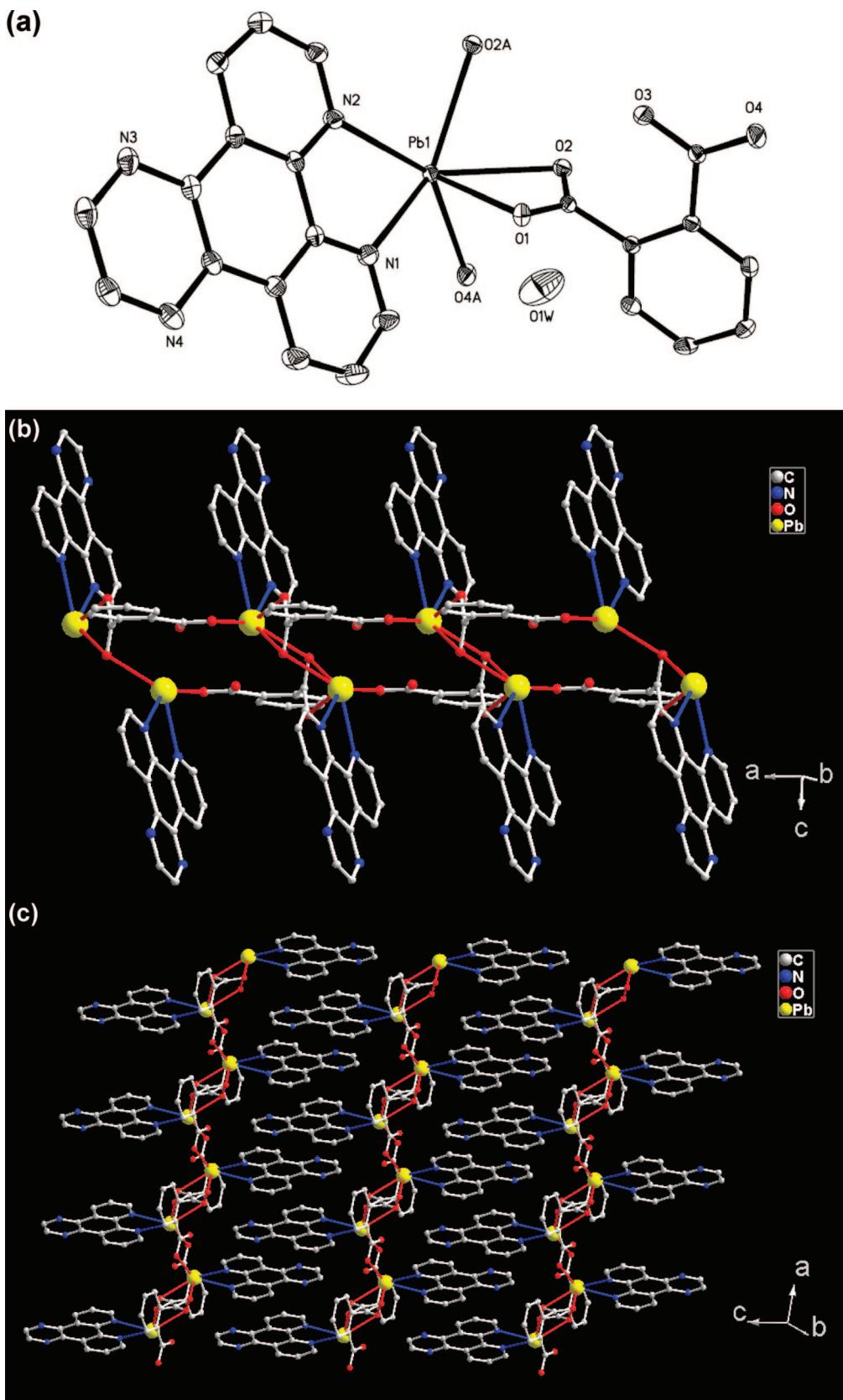
**9**. Compound **7** shows a discrete centrosymmetric dinuclear structure (Figure 7a). The Pb(II) center is six-coordinated by two nitrogen atoms from one ptc ligand (Pb–N1 = 2.550(3) Å) and Pb–N2 = 2.597(3) Å), and two carboxylate oxygen atoms from one adip ligand and two oxygen atoms from one nitrate anion in a distorted pentagonal-bipyramidal geometry (Pb1–O1 = 2.555(3), Pb1–O2 = 2.394(3), Pb1–O3 = 2.736(4), and Pb1–O4 = 2.747(4) Å). The O1, O3, O4, N1, and N2 atoms



**Figure 5.** (a) Coordination environment of the Pb(II) center in compound 5 (thermal ellipsoids are at the 25% probability level), (b) the 1D chain structure, (c) the 2D supramolecular assembly formed through  $\pi-\pi$  stacking interactions, and (d) the 3D supramolecular structure formed through  $\pi-\pi$  stacking interactions.

form the equatorial plane, while the O2 atom and the lone pair of electrons are located in the axial positions. The Pb–O bond lengths vary greatly from 2.394(3) to 2.747(4) Å in 7. Interestingly, like the structure of 6, there are also two kinds of  $\pi-\pi$  interactions in 7. First, the adjacent dimers interact through  $\pi-\pi$  stackings between two pzp ligands (centroid-to-centroid distance of 3.69 Å and face-to-face distance of 3.34 Å, see Figure S7 in the Supporting Information), generating supramolecular chains (Figure 7b). Second, supramolecular chains are further stacked through another type of  $\pi-\pi$  interactions between two pzp ligands (centroid-to-centroid distance of 3.89 Å and face-to-face distance of 3.47 Å, see Figure S7 in the Supporting

Information), generating supramolecular chains (Figure 7b). Second, supramolecular chains are further stacked through another type of  $\pi-\pi$  interactions between two pzp ligands (centroid-to-centroid distance of 3.89 Å and face-to-face distance of 3.47 Å, see Figure S7 in the Supporting

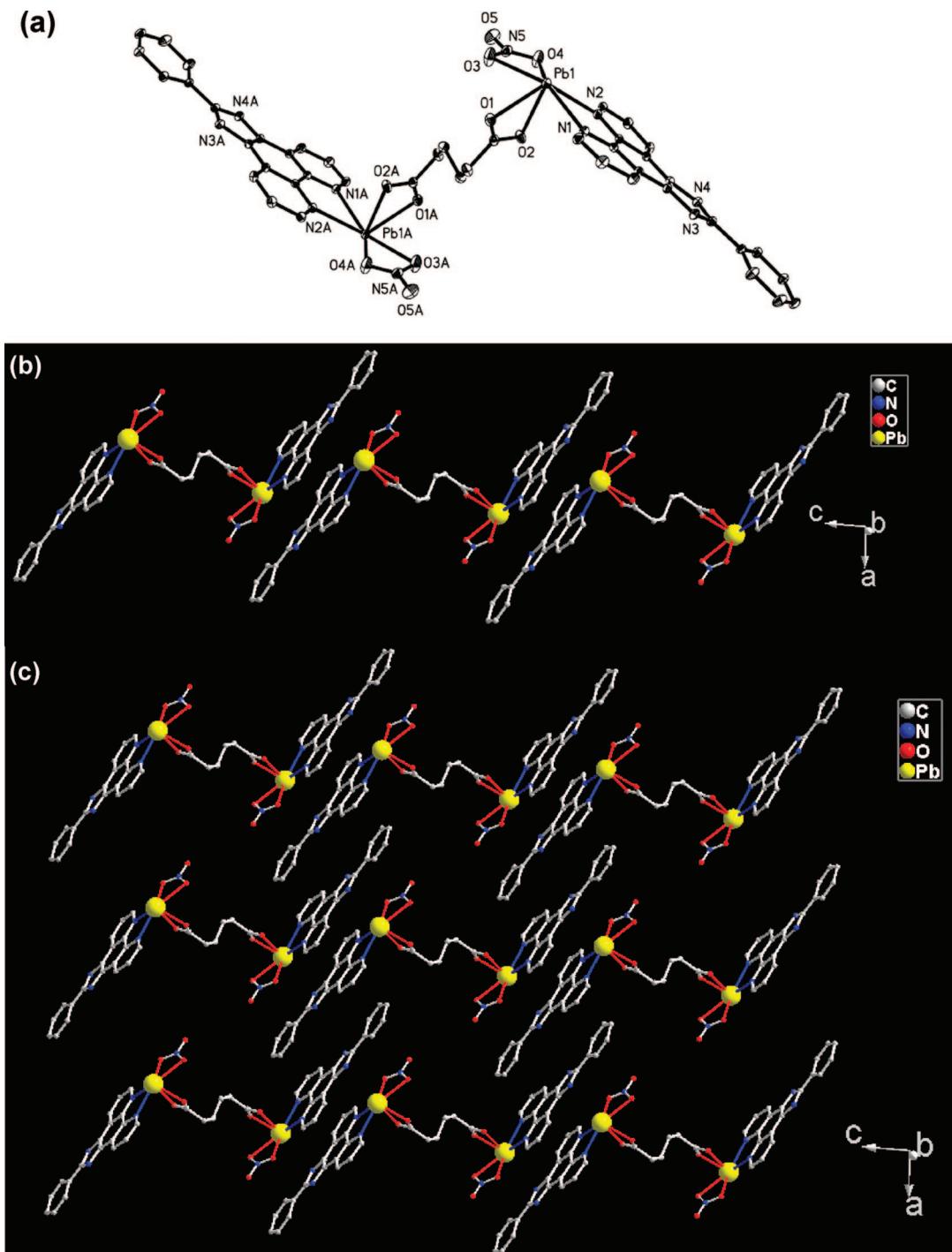


**Figure 6.** (a) Coordination environment of the Pb(II) center in compound **6** (thermal ellipsoids are at the 25% probability level), (b) the double chain structure, and (c) the 2D supramolecular assembly formed through  $\pi-\pi$  stacking interactions.

Information), extending the 1D supramolecular arrays into a 2D supramolecular assembly (Figure 7c).

As shown in Figure 8a, the Pb(II) center in **8** shows a distorted pentagonal-bipyramidal coordination sphere consisting of two

nitrogen donors from one ptc ligand ( $\text{Pb1-N1} = 2.598(5)$  and  $\text{Pb1-N2} = 2.609(5)$  Å), and four carboxylate oxygen atoms from two glu anions ( $\text{Pb1-O1} = 2.483(5)$ ,  $\text{Pb1-O2} = 2.656(6)$ ,  $\text{Pb1-O3} = 2.399(5)$ , and  $\text{Pb1-O4} = 2.600(6)$  Å). As shown



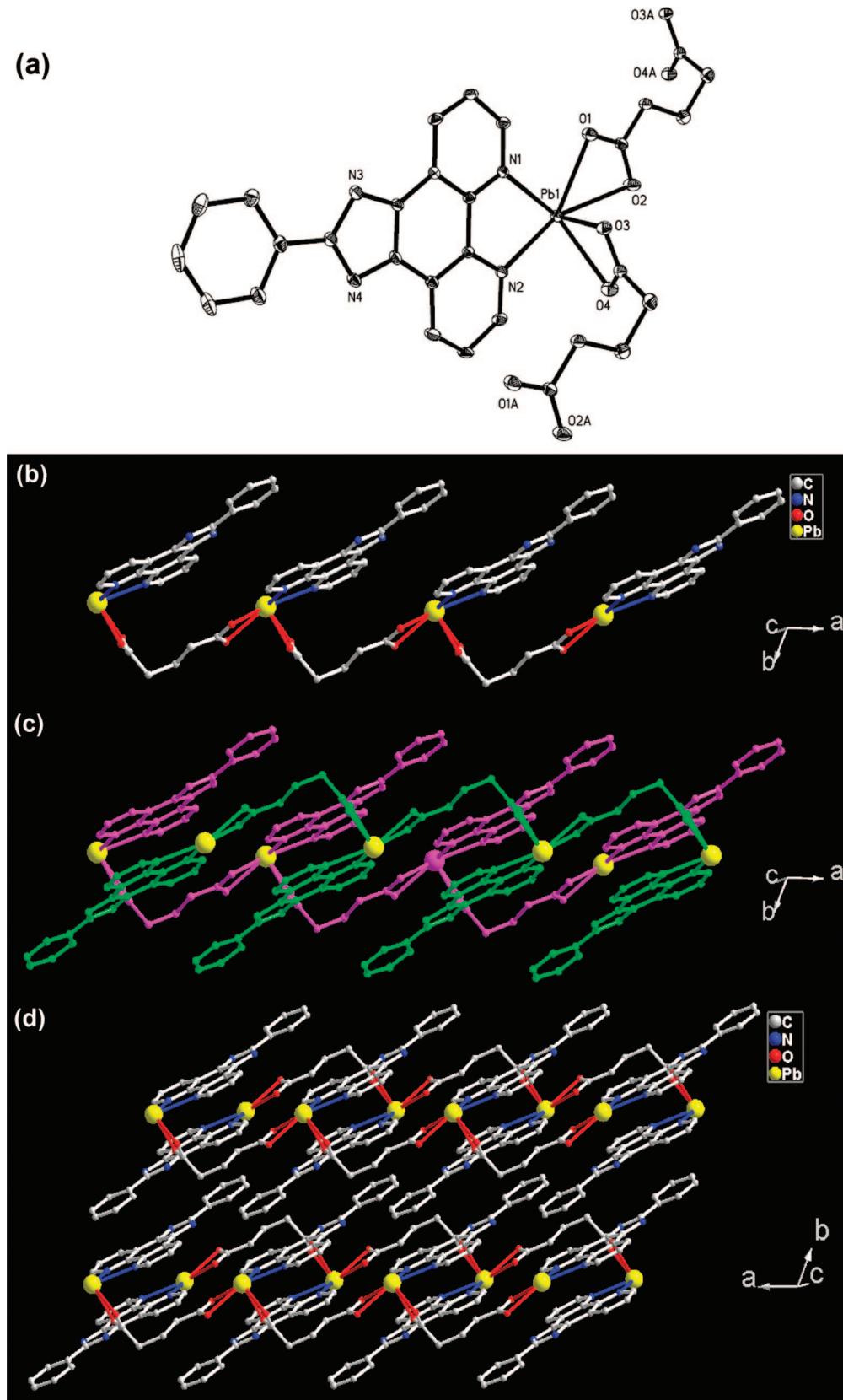
**Figure 7.** (a) View of the dinuclear compound **7** (thermal ellipsoids are at the 20% probability level), (b) the 1D supramolecular chain formed through  $\pi-\pi$  interactions, and (c) the 2D supramolecular assembly formed through  $\pi-\pi$  interactions.

in Figure 8b, the Pb(II) atoms are bridged by glu ligands to form a 1D chain structure. Like the structures of **3** and **5**, the ptc ligands in **8** are also attached on one side of the chain. Each ptc ring has two  $\pi-\pi$  interactions with the centroid–centroid distances being 3.67 and 3.69 Å (face-to-face distances of 3.41 and 3.48 Å, see Figure S8 in the Supporting Information), respectively. Two neighboring chains interact through one type of  $\pi-\pi$  interactions, resulting in a double chain structure (Figure 8c). There also exists another type of face-to-face  $\pi-\pi$  stacking interactions between the adjacent double chains, leading to a 2D supramolecular assembly (Figure 8d).

As shown in Figure 9, compound **9** shows a quite similar structure to that of **8**. However, small difference can be observed

for these two compounds. The Pb–Pb distance (8.59 Å) bridged by the dicarboxylate in **8** is shorter than that in **9** (9.16 Å), indicating the influence of dicarboxylate spacer lengths.

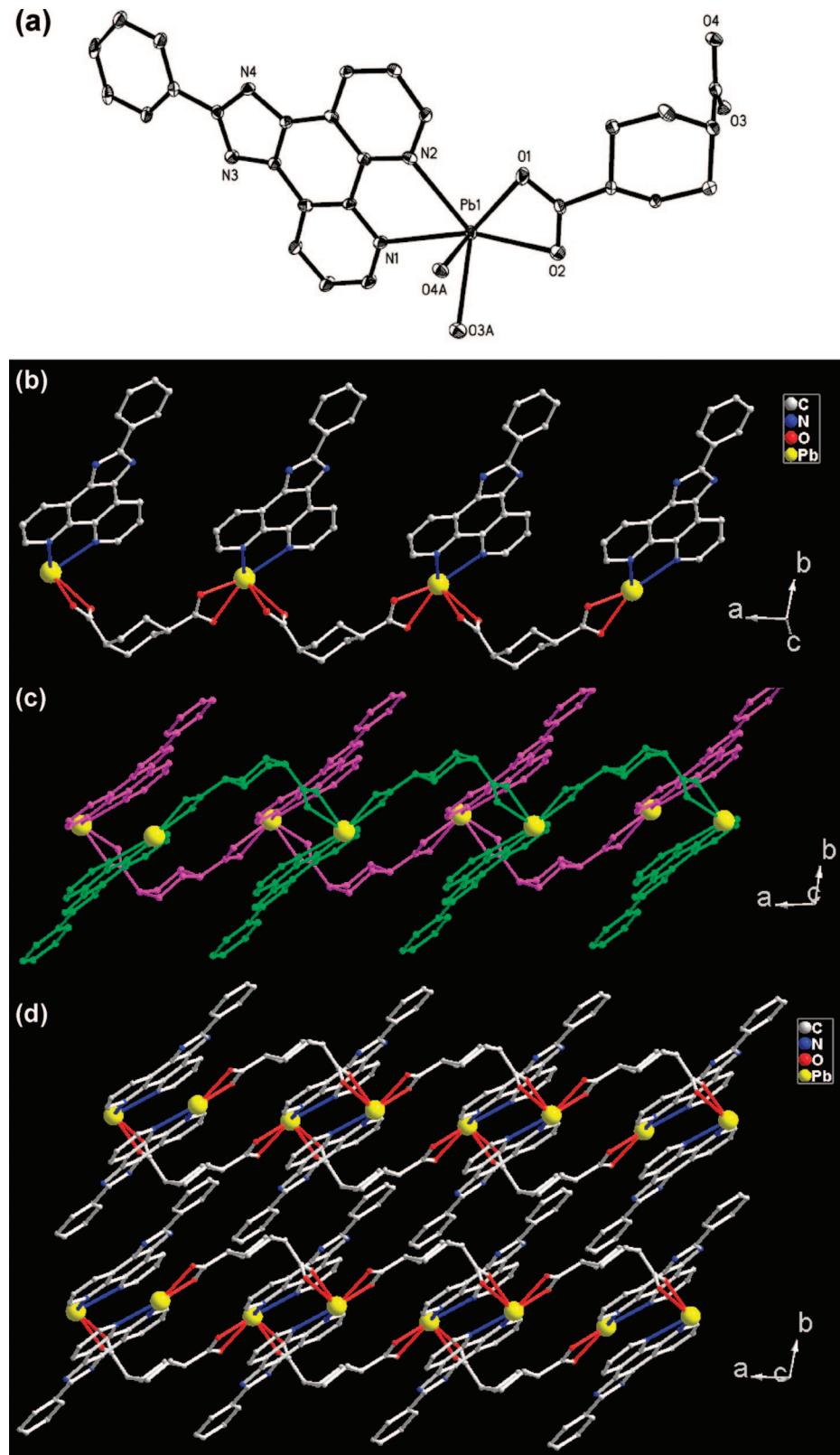
To explore the role of aromatic dicarboxylic acids with different geometries ( $H_2dpdc$ , 1,3- $H_2bdc$  and 1,4- $H_2bdc$ ), the reactions of dicarboxylic acid ligands with Pb(II) atoms were carried out in the presence of the ptc ligand, affording three new complexes:  $[Pb(ptc)(dpdc)]_2$  **10**,  $[Pb(ptc)(1,3-bdc)] \cdot 2.5H_2O$  **11**, and  $[Pb(ptc)(1,4-bdc)] \cdot 0.75H_2O$  **12**. As shown in Figure 10a, compound **10** has a dinuclear structure. The Pb(II) center is five-coordinated by two nitrogen atoms from one ptc ligand ( $Pb1-N1 = 2.648(4)$  and  $Pb1-N2 = 2.523(3)$  Å), and three carboxylate oxygen atoms from two dpdc ligands ( $Pb1-O1 =$



**Figure 8.** (a) Coordination environment of the Pb(II) center in **8** (thermal ellipsoids are at the 20% probability level), (b) the 1D supramolecular double chain constructed by  $\pi$ - $\pi$  interactions, and (c) the 2D supramolecular assembly constructed by  $\pi$ - $\pi$  interactions.

2.684(4), Pb1–O2 = 2.345(3), and Pb1–O4A = 2.289(3) Å. The Pb–O bond lengths are in the range of 2.289(4)–2.684(4) Å. Each pair of adjacent Pb(II) atoms are bridged by two dpdc ligands to form a dinuclear structure with the Pb–Pb distance

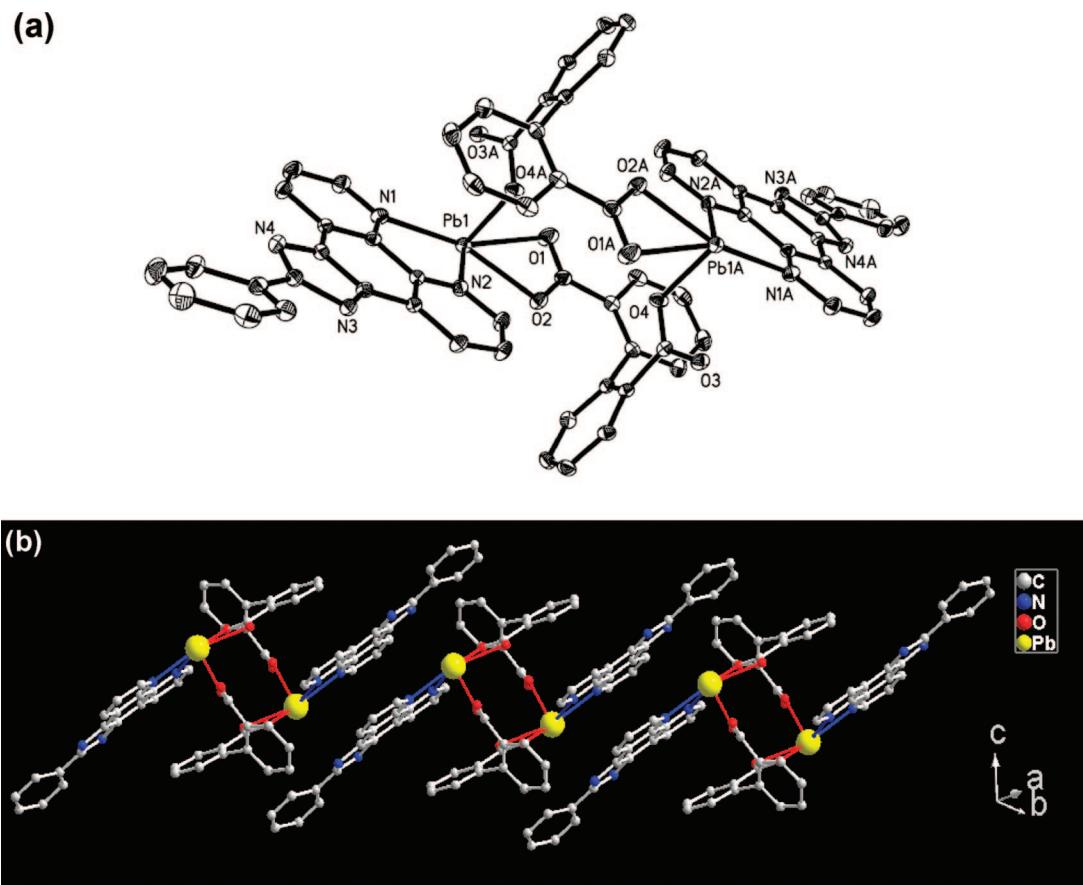
of 13.93 Å. It should be pointed out that the related compound  $[\text{Pb}_6(\text{dpdc})_4\text{O}_2]_n$  displayed a 1D chain structure, where neighboring Pb(II) centers were bridged by carboxylate oxygen atoms of dpdc ligands.<sup>18</sup> In **10**, adjacent dimers are linked together



**Figure 9.** (a) Coordination environment of the Pb(II) center in **9** (thermal ellipsoids are at the 20% probability level), (b) the 1D chain structure, (c) the 1D double chain constructed by  $\pi-\pi$  interactions, and (d) the 2D supramolecular assembly constructed by  $\pi-\pi$  interactions.

through  $\pi-\pi$  stackings (centroid-to-centroid distance of 3.49 Å and face-to-face distance of 3.30 Å, see Figure S10 in the Supporting Information) between two ptc ligands, generating 1D supramolecular chains (Figure 10b). Clearly, intermolecular  $\pi-\pi$  stacking interactions contribute to the stabilization of the structure of **10**.

Figure 11a shows the coordination environment of the Pb(II) atom in **11**: six-coordinate with a distorted pentagonal-bipyramidal environment. The equatorial plane is defined by four carboxylate oxygen donors (O1, O2, O3A, and O4A) and one nitrogen atom (N1) from a ptc ligand. One nitrogen atom (N2) and the lone pair of electrons occupy the axial positions. Pb(II) centers are

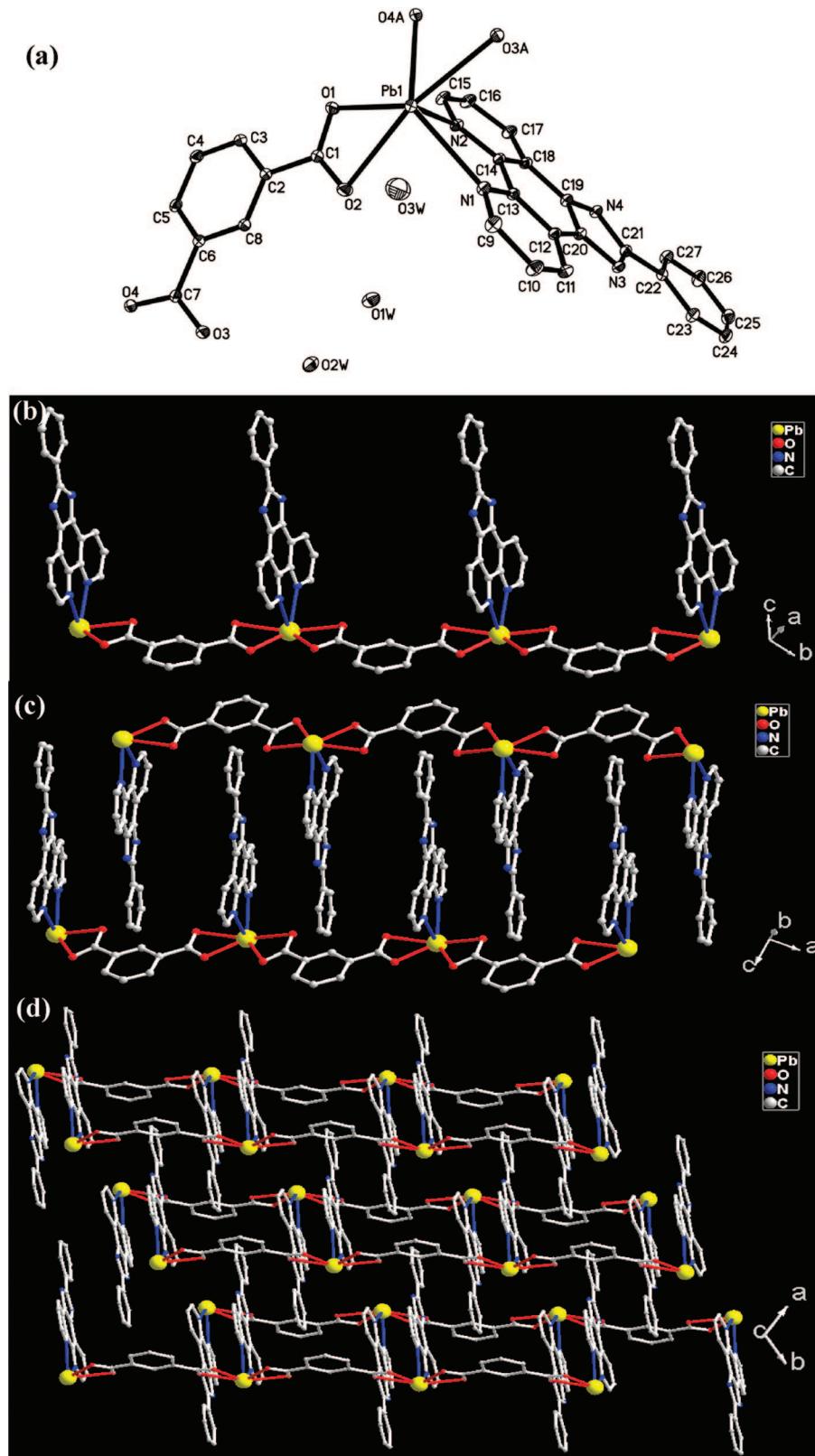


**Figure 10.** (a) View of the dinuclear **10** (thermal ellipsoids are at the 20% probability level), and (b) the 1D supramolecular chain constructed by  $\pi$ - $\pi$  interactions.

bridged by 1,3-bdc anions to generate a 1D chain structure (Figure 11b). The ptc ligands in **11** are attached on one side of the chain. Interesting double chain structures are formed through one type of  $\pi$ - $\pi$  stackings between two ptc ligands (centroid-to-centroid distance of 3.51 Å and face-to-face distance of 3.36 Å, see Figure 11c and Figure S11 in the Supporting Information). Another type of  $\pi$ - $\pi$  interaction between the two ptc ligands (centroid-to-centroid distance of 3.79 Å and face-to-face distance of 3.33 Å, see Figure S11 in the Supporting Information) extends the 1D supramolecular arrays into a 2D supramolecular assembly (Figure 11d).

As shown in Figure 12a, the Pb(II) atom of **12** is six-coordinated by four carboxylate oxygen atoms from two different 1,4-bdc ligands ( $\text{Pb1-O1} = 2.551(4)$ ,  $\text{Pb1-O2} = 2.625(4)$ ,  $\text{Pb1-O3} = 2.548(4)$ , and  $\text{Pb1-O4} = 2.510(4)$  Å) and two nitrogen atoms from one ptc molecule ( $\text{Pb1-N1} = 2.651(4)$  and  $\text{Pb1-N2} = 2.558(5)$  Å). Pb(II) atoms are bridged by 1,4-bdc ligand to form a 1D zigzag chain (Figure 12b). Unlike the structures of **8** and **11**, the ptc molecules are coordinated to the Pb(II) atoms from the two sides of the chain. There exist  $\pi$ - $\pi$  stacking interactions between the ptc and 1,4-bdc molecules (centroid-to-centroid distance of 3.47 Å and face-to-face distance of 3.33 Å, see Figure S12 in the Supporting Information), which extends the 1D chains into a 2D supramolecular assembly (Figure 12c). In addition, neighboring supramolecular layers are further linked by another type of  $\pi$ - $\pi$  interaction between two ptc ligands with a centroid-to-centroid of 3.88 Å (face-to-face distance of 3.52 Å, see Figure S12 in the Supporting Information), leading to a supramolecular assembly (Figure 12d).

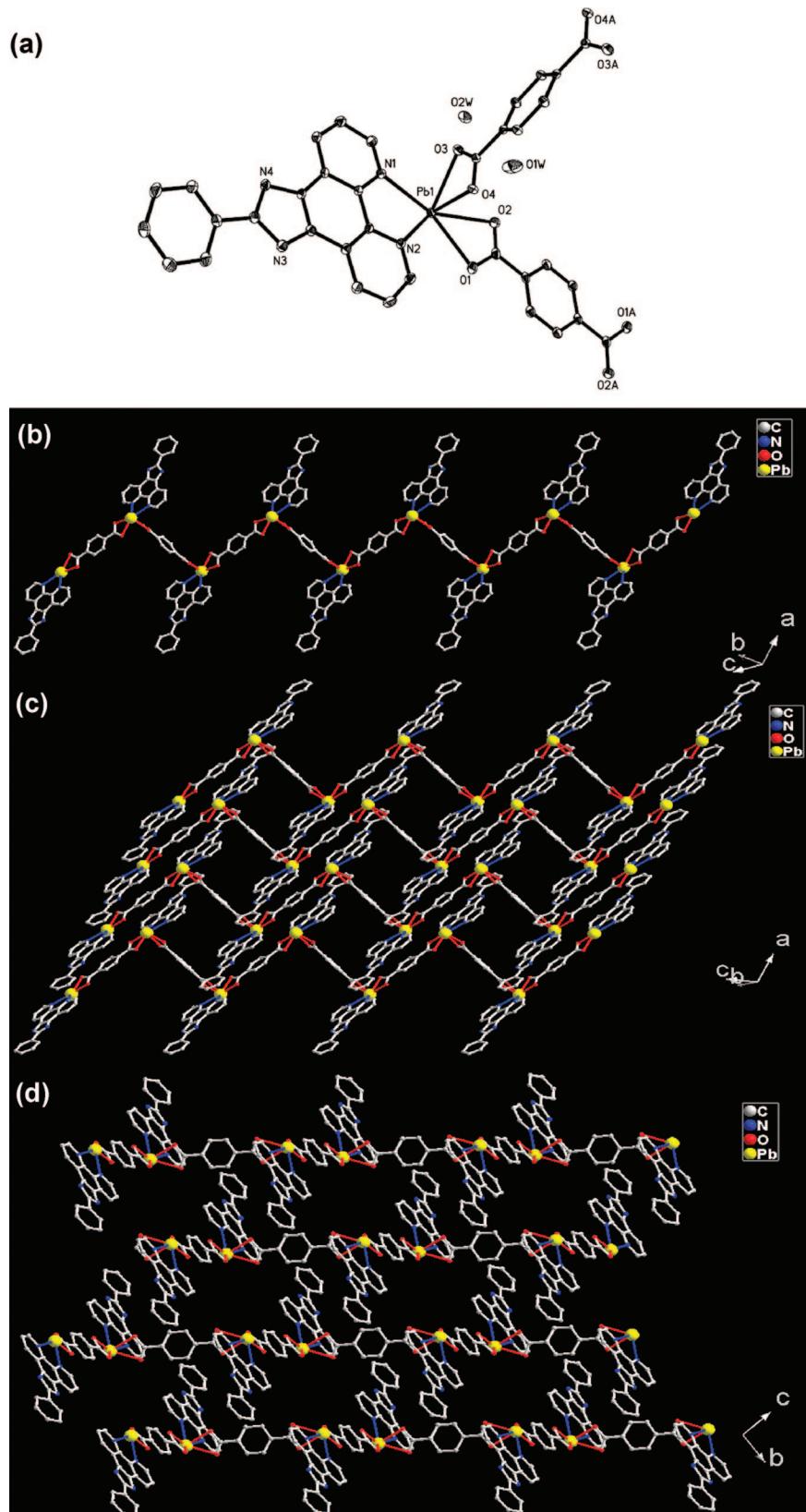
**Role of the Lone Pair of Lead(II) on Coordination Geometries of Compounds **1–12**.** The stereochemical activity of the lone pair of electrons is an interesting issue, which is always discussed. The geometries of Pb(II) complexes can be classified as holo- and hemidirected. Holodirected refers to Pb(II) complexes in which the bonds to ligand atoms are placed throughout the surface of the encompassing globe, whereas hemidirected refers to those cases in which the bonds to ligand atoms are directed throughout only part of an encompassing globe.<sup>19</sup> In compounds **1–3** and **6–12**, the coordination sphere of the central Pb(II) atom is hemidirected, leaving a void in ligand bond distribution. This open space may be assigned to the stereochemical activity of the lone pair of electrons. In **4**, the Pb1 atom is eight-coordinated by five carboxylate oxygen atoms, two nitrogen atoms, and one coordinating water molecule. The bonds to the ligand atoms are distributed throughout the surface of the encompassing Pb1 sphere. However, the Pb2 atom is surrounded by three carboxylate oxygen atoms and two nitrogen atoms, which supports the notion of a stereochemically inactive lone pair of electrons. Therefore, in **4**, the coordination sphere of Pb1 atom can be considered as holo-directed, whereas the one of the Pb2 atom can be regarded as somewhat hemidirected. The Pb(II) atom of **5** is seven-coordinated by two nitrogen atoms, one water molecule, and four carboxylate oxygen atoms. Like the coordination of the ligands around Pb1 atom in **4**, the coordination of the ligands at the opening does not leave room for a lone pair of electrons in **5**. Therefore, this coordination sphere also can be considered as somewhat holodirected.



**Figure 11.** (a) Coordination environment of the Pb(II) center in **11** (thermal ellipsoids are at the 20% probability level), (b) the 1D chain structure, (c) the 1D double chain constructed by  $\pi-\pi$  interactions, and (d) the 2D supramolecular assembly constructed by  $\pi-\pi$  interactions.

**Influence of the Organic Acid on the Assembly Process.** Compounds **1–6** were hydrothermally synthesized with the same Pb/organic acid/pzp ratio of 1:1:1. The structural differences of complexes **1–6** imply that the flexible  $-(CH_2)_n-$  backbone and the carboxylate position are the key factors behind the discrepancy in structure and type of  $\pi-\pi$  interaction of their

complexes. In **1–3**, three fatty acid ligands H<sub>2</sub>adip, H<sub>2</sub>glu, and H<sub>2</sub>chdc were utilized, respectively, in order to investigate the influence of spacer lengths on the complex structures. It can be seen that the H<sub>2</sub>adip, H<sub>2</sub>glu, and H<sub>2</sub>chdc ligands with different spacer lengths possess flexibility because of the presence of  $-CH_2-$  spacers between the two carboxylate groups. Compound



**Figure 12.** (a) Coordination environment of the Pb(II) center in **12** (thermal ellipsoids are at the 20% probability level), (b) the 1D zigzag chain structure, (c) the 2D supramolecular assembly constructed by  $\pi$ - $\pi$  interactions, and (d) the 3D supramolecular structure constructed by  $\pi$ - $\pi$  interactions.

1 shows a 1D linear chain structure, which is further stacked by  $\pi$ - $\pi$  stacking interactions to yield 2D supramolecular layers. Compound **2** has a 1D helical chain, which is further extended by  $\pi$ - $\pi$  interactions to form 2D supramolecular layers. Com-

ound **3** contains two types of 1D helical chain, which are further connected through two types of  $\pi$ - $\pi$  interactions to again generate 2D supramolecular architectures. Clearly, these spacer length differences in the fatty acids result in the formation

of **1–3** with quite distinct architectures under similar synthetic conditions. The structural differences in **4–6** mainly highlight the effect of carboxylate position upon the framework formation of the complexes. The H<sub>2</sub>ndc, 1,3-H<sub>2</sub>bdc and 1,2-H<sub>2</sub>bdc are all rigid ligands, with the two carboxylate groups of ndc, 1,3-bdc and 1,2-bdc possessing 180, 120, and 60° angles, respectively. Although compounds **4–6** were synthesized under similar conditions, their structures are very different. Thus, the structural differences in **4–6** show the influence of the carboxylate positions on the complex constructions. Simultaneously, the influence of flexible -(CH<sub>2</sub>)<sub>n</sub>- backbones and the carboxylate positions on the complex structures is also revealed by the structural difference in **7–12**. Compounds **7–12** were synthesized with the same Pb/organic acid/ptc ratio of 1:1:1. Compound **7** has a dinuclear structure, while compounds **8** and **9** feature chain structures. These results further confirm that the lengths of the flexible -(CH<sub>2</sub>)<sub>n</sub>- spacers have a great influence on the structures of their Pb(II) complexes. Like that of compounds **4–6**, the influence of carboxylate positions on the complex structures is also demonstrated by the structural differences of **10–12**. The H<sub>2</sub>dpdc is a relatively flexible ligand, where the two carboxylate groups can bridge the metals from different directions. In contrast, the 1,3-bdc and 1,4-bdc ligands are very rigid, and the two carboxylate groups have 120 and 180° angles, respectively. Compound **10** adopts a dinuclear structure, whereas compounds **11** and **12** show chain structures. When comparing compound **11** with **12**, we can observe that the ptc ligands in **11** are extended on one side of the chain, whereas in **12** they are attached on both sides of the chain. This result further demonstrates that the carboxylate positions play important roles in the assembly process.

**Influence of the Neutral Chelating Ligand on the Assembly Process.** It should be noted that the neutral chelating ligands (pzp and ptc) also have an important function in the formation of the final structures. Although both the pzp and ptc molecules are planar, there is an additional phenyl group present in the ptc ligand. These bulky phenyl groups in the backbone may significantly increase the steric hindrance of the ptc ligand, leading to structural differences in their complexes. The effects of these neutral chelating ligands on the complexes are discussed below.

(1) The neutral chelating ligands can influence the coordination modes of the organic acids. In **1**, the adip bridges four Pb(II) atoms in a chelating/bridging mode, generating a linear chain. However, in **7**, the adip acts as a bis-chelating ligand, forming a dinuclear Pb(II) complex under similar synthetic conditions.

(2) The neutral chelating ligands can influence the Pb–Pb distance bridged by the organic acids. In the helical chain of **2**, the Pb–Pb distance bridged by the glu ligand is 8.84 Å, whereas in **8**, the glu ligands connect neighboring Pb(II) atoms to form a linear chain with a Pb–Pb distance of 8.59 Å.

(3) The molar ratio of Pb to neutral ligand in the products can be adjusted by changing the neutral chelating ligands. Under similar synthetic conditions, **3** with a Pb:chdc:pzp ratio of 1:1:1.5 was isolated, whereas **9** with a Pb:chdc: ptc ratio of 1:1:1 was isolated upon change of chelate.

(4) The supramolecular structures constructed by π–π interactions can be modified by varying the neutral chelating ligands. Although compounds **5** and **11** show similar chain structures, the π–π interactions of the neutral ligands in them are slightly different. In **5**, the linear chains interact through one type of π–π interaction to form a supramolecular layer. Furthermore, another type of π–π interaction extends the structure into an interesting double layer structure. However,

in **11**, the linear chains connected each other through one type of π–π interaction to generate double chain structures, which are further linked by another type of π–π interaction to yield a supramolecular layer. It is noteworthy that the structure of **1** is entirely different from that of the related structure [Pb(adip)(dpdp)]<sub>2</sub> (dpdp is dipyrido[3,2-a:2',3'-c]phenazine), where the two Pb(II) atoms are bridged by two adip ligands to form a dimer.<sup>10e</sup> Neighboring dimers are further stacked via strong π–π interactions to form 2D layers. The structure of **4** is different from that of the related structure [Pb(ndc)(dpdp)], in which the neighboring 1D ladders interact by π–π stacking between the dpdp ligands to form an interesting 2D supramolecular assembly.<sup>5c</sup> The structure of **4** is also entirely different from that of the related polymer [Pb(ndc)(ptc)]·0.5H<sub>2</sub>O.<sup>5c</sup> In that structure, the ptc ligands of each chain are stacked with those of an adjacent chain through π–π interactions, generating a ladderlike structure. The ladders recognize each other through another type of aromatic π–π stacking interaction of the ptc ligands, which results in a wavy layer. However, the structure of **2** is similar to the reported structure [Pb(glu)(dpdp)].<sup>10e</sup> Although the structures of pzp and dpdp differ, the two compounds show quite similar helical chain structures.

## Conclusion

A series of Pb(II) dicarboxylate complexes with phen derivatives have been hydrothermally synthesized under similar synthetic conditions. The complexes form either molecular or 1D polymeric structures which associate in the crystal lattice through extensive π–π interactions. The influence of organic acids and neutral ligands on the structures of the complexes has been studied. The structural differences among **1–6** and **7–12** highlight the effects of organic acids on the framework formation of the complexes, whereas the differences between **1** and **7**, **2** and **8**, **3** and **9**, and **5** and **11** show the importance of the neutral ligands on the complex construction. The luminescence properties of the compounds demonstrate that they may be good candidates for luminescence materials. Further research on rational design and construction of lead(II) compounds with interesting supramolecular structures as well as physical properties is currently underway in our laboratory.

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**Supporting Information Available:** Twelve X-ray crystallographic files (CIF); selected bond distances and angles and intermolecular π–π interactions for **1–12**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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