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Structural Variation from 1D to 3D: Effects of Ligands and Solvents on the Construction of Lead(II)–Organic Coordination Polymers

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Abstract: A series of Pb^{II} coordination polymers [Pb(ndc)(dpp)] (**1**), [Pb(ndc)(ptcp)]$\cdot$0.5H_2O (**2**), [Pb(ndc)(dppz)] (**3**), [Pb(ndc)(tcpn)$_2$] (**4**), [Pb_2(ndc)$_2$(tcpp)] (**5**), [Pb(Hndc)$_2$]$\cdot H_2O$ (**6**), [Pb(ndc)(dma)] (**7**), [Pb(bdc)(dma)] (**8**), [Pb(*trans*-chdc)(H_2O)] (**9**), and [Pb_2(*cis*-chdc)$_2$]$\cdot NH(CH_3)_2$ (**10**), where ndc = 1,4-naphthalenedicarboxylate, dpp = 4,7-diphenyl-1,10-phenanthroline, ptcp = 2-phenyl-1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthrene, dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine, tcpn = 2-(1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthren-2-yl)naphthol, tcpp = 4-(1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthren-2-yl)phenol, dma = *N*,*N*-dimethylacetamide, bdc = 1,4-benzenedicarboxylate, and chdc = 1,4-cyclohexanedicarboxylate, have been synthesized from a hydrothermal or solvothermal reaction system by varying the ligands or the solvents. Compounds **1**–**5** crystallize with an N-donor chelating ligand and an aromatic dicarboxylate linker. Compounds **1**–**4** are 1D polymers with different π–π stacking interactions, whereas compound **5** consists of 2D layers. The structures of compounds **7**, **8**, and **10** are 3D frameworks formed by connection of the Pb^{II} centers by organic acid ligands. Compound **7** is chiral although the ndc ligand is achiral, while the framework of **8** is a typical 3D (3,4)-connected net. Compound **10** is the first example of Pb^{II} wheel cluster [Pb_8O_8] units bridged by carboxylate groups. Compound **6** contains 1D chains which are further extended to a 3D structure by π–π interactions. Compound **9** consists of a 2D network constructed by Pb^{II} centers and *trans*-chdc ligands. The structural differences between **7** and **8** and between **9** and **10** indicate the importance of solvents for framework formation of the coordination polymers. By varying the solvent the *cis* and *trans* conformations of H_2chdc in **9** and **10** were separated completely. The photoluminescence and nonlinear optical properties of the coordination polymers have also been investigated.

Keywords: carboxylate ligands · lead · luminescence · nonlinear optics · supramolecular chemistry

Introduction

The design and synthesis of coordination polymers with unusual structures and properties are attracting increasing attention, not only for their interesting molecular topologies, but also for their potential applications as functional materials.[1,2] Until recently, research on coordination polymers has focused on incorporation of s-, d-, and even f-block metal ions as coordination centers, while less consideration has been given to the metals of the p block, despite their importance in electroluminescence, photovoltaic conversion, fluorescent sensors, and organic light-emitting diodes.[3] As a heavy p-block metal ion, lead(II), with its large radius, flexible coordination environment, and variable stereochemical activity, provides unique opportunities for formation of unusual network topologies with interesting properties.[4]

Nevertheless, it is still a great challenge to predict the exact structures and compositions of polymeric compounds assembled by coordination bonds and/or π–π interactions.[5] The factors affecting packing of molecules and structure formation in crystallization are intricate and need to be further understood. The coordination environment of metal nodes, solvent, the nature of ligands used to connect the metal nodes, metal/ligand ratio, and noncovalent interactions such as aromatic–aromatic interactions that help stabilize certain architectures can all play a role in determining the network structure of a coordination polymer.[6] Systematic elucida-

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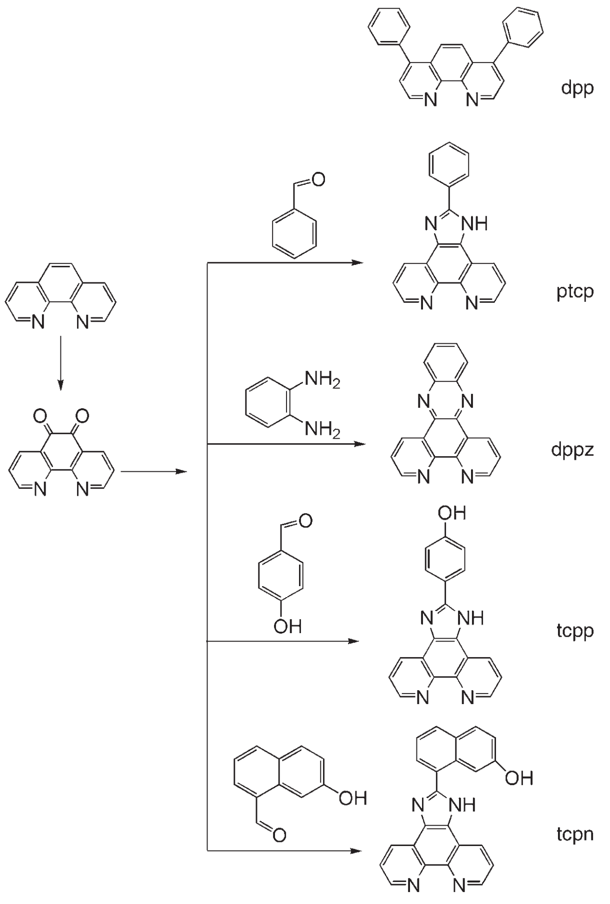
Supporting information for this article (selected bond lengths and angles, luminescence spectra, and intermolecular π–π interactions for **1**–**10**) is available on the WWW under http://www.chemeurj.org/ or from the author.

tion of the effects of solvent and organic ligands on formation of the final structure has not been thoroughly conducted, and particularly the influence of N-donor chelating ligands on network construction by π–π interactions has rarely been documented.[7] By using differently structured dicarboxylate linkers and precisely controlling NCL features such as shape, functionality, and length (Scheme 1), a remarkable class of lead(II) materials with rich architectures and functions have been obtained. Here we report representative lead(II) dicarboxylate coordination polymers with or without N-donor chelating ligand: [Pb(ndc)(dpp)] (**1**), [Pb(ndc)(ptcp)]$\cdot$0.5 H_2O (**2**), [Pb(ndc)(dppz)] (**3**), [Pb(ndc)(tcpn)$_2$] (**4**), [Pb_2(ndc)$_2$(tcpp)] (**5**), [Pb(Hndc)$_2$]$\cdot H_2O$ (**6**), [Pb(ndc)(dma)] (**7**), [Pb(bdc)(dma)] (**8**), [Pb(*trans*-chdc)(H_2O)] (**9**), and [Pb_2(*cis*-chdc)$_2$]$\cdot NH(CH_3)_2$ (**10**), where ndc = 1,4-naphthalenedicarboxylate, dpp = 4,7-diphenyl-1,10-phenanthroline, ptcp = 2-phenyl-1*H*-1,3,7,8-tetraazacyclopenta[*l*]-phenanthrene, dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine, tcpn = 2-(1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthren-2-yl)-naphthol, tcpp = 4-(1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthren-2-yl)phenol, dma = *N*,*N*-dimethylacetamide, bdc = 1,4-benzenedicarboxylate, and chdc = 1,4-cyclohexanedicarboxylate On the basis of synthesis and structural characterization, the effects of ligands and solvents on the construction of the coordination polymers are unraveled. In addition, the photoluminescence and nonlinear optical properties of the obtained compounds have also been investigated in detail.



Scheme 1. The N-donor chelating ligands (NCLs) used in the construction of coordination polymers.

Results and Discussion

Structures of 1–10: Compounds **1**–**3** have a Pb^{II}/ N-donor chelating ligand ratio of 1. Although we varied the Pb^{II}/N-donor chelating ligand ratio (1/1, 1/1.5, 1/2, 1.5/1 and 2/1) in the reaction mixtures, the same compounds **1**–**3** were obtained. Investigation of the structures of **1**–**6** reveals significant π–π interactions which guide the formation and stabilize the final structures. Selected bond lengths and angles for compounds **1**–**10** are listed in Tables S1–S10.

As shown in Figure 1 a,the asymmetric unit of **1** contains two ndc ligands, two dpp ligands, and two crystallographically independent Pb^{II} centers. Each Pb^{II} center adopts a distorted $\mathbf{:}PbN_2O_3$ tetragonal-bipyramid geometry by coordinating to two nitrogen atoms from a chelating dpp and three oxygen atoms from two distinct ndc ligands, and the sixth coordination site is occupied by the lone pair of electrons.[8]

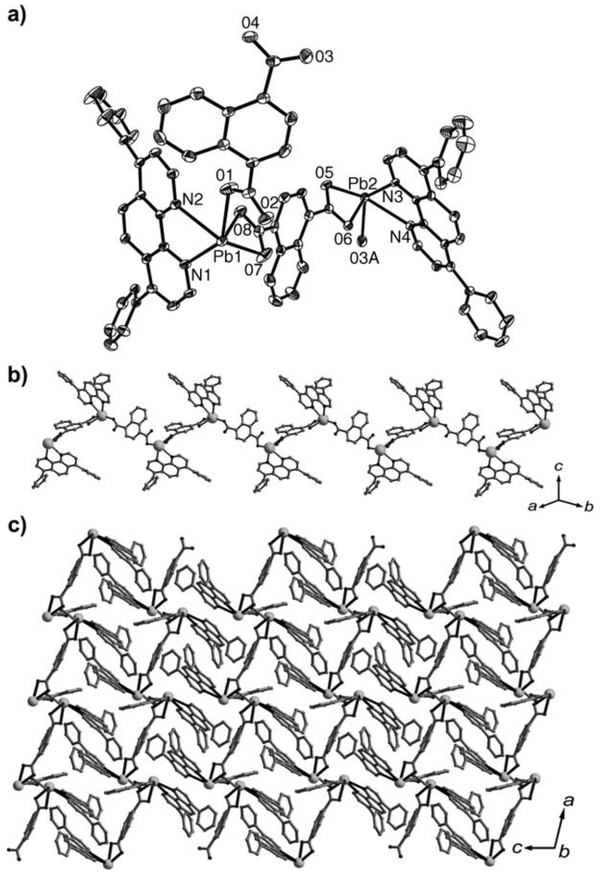
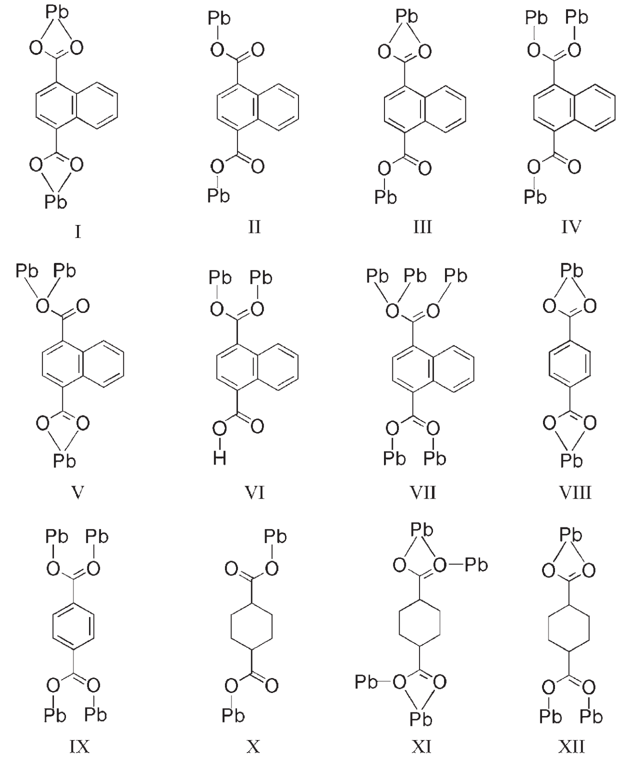


Figure 1. Coordination environment of Pb^{II} ions in **1** (a, all hydrogen atoms omitted for clarity), the 1D chain structure of **1** (b), and the 2D layer structure of **1** formed by interchain π–π interactions (c).

Atoms N1, N2, O1, and O7 constitute the base of the pyramid, whereas O8 and the lone pair of electrons occupy the axial positions with a Pb1–O8 distance of 2.408(5) Å. The Pb–O distances in **1** range from 2.391(6) to 2.519(5) Å, and the O-Pb-O angles from 51.53(17) to 116.43(19)°. The carboxyl groups of H_2ndc are all deprotonated in **1**, and they exhibit different coordination modes. In mode I, the two carboxylate moieties of ndc chelate two Pb^{II} ions, while in mode II, each carboxylate moiety of ndc is bonded to one Pb^{II} ion (Scheme 2).[9] As illustrated in Figure 1 b, each ndc ligand connects two Pb^{II} centers in mode I or mode II, leading to zigzag chains with pitches of 11.399 and 11.646 Å, respectively, where the Pb-Pb-Pb angle, defined by the orientation of the ndc ligands in the chain, is 98.5°. The dpp ligands are alternately attached to both sides of a single-stranded zigzag chain. More interestingly, the lateral dpp ligands from adjacent chains are paired to furnish moderately strong C–H–π interactions (ca. 3.646 and 3.657 Å; see Figure S1). When these interactions are taken into account, the 1D chain becomes a 2D network (Figure 1 c).



Scheme 2. Coordination modes of the ndc, bdc, and chdc ligands in **1**–**10**.

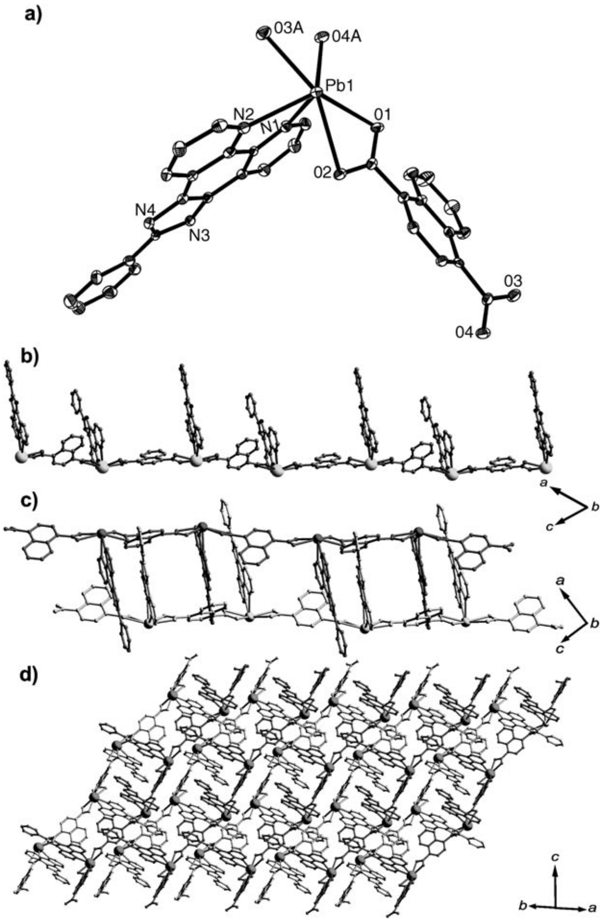


Figure 2. Coordination environment of Pb^{II} ions in **2** (a, all hydrogen atoms omitted for clarity), the 1D arm-shaped chain structure of **2** (b), the 1D ladder structure of **2** formed by π–π interaction between ptcp ligands (c), and the 2D layer structure of **2** formed by interchain π–π stacking interactions (d).

To investigate the influence of NCLs on the complex frameworks, two bulkier ligands ptcp and dppz were used under the same reaction conditions as for **1**, and two new coordination polymers [Pb(ndc)(ptcp)]·0.5 H_2O (**2**) and [Pb(ndc)(dppz)] (**3**) were obtained. When ptcp is used instead of dpp, structurally different chains are formed in **2**. The asymmetric unit of **2** contains one Pb^{II} ion, one ndc ligand, and one ptcp ligand (Figure 2 a). The Pb^{II} ion is coordinated by four oxygen atoms of two ndc ligands and two nitrogen atoms of one chelating ptcp ligand to furnish a distorted PbN_2O_4 pentagonal-bipyramidal geometry.[10] The O1, O2, O3A, O4A, and N2 atoms comprise the basal plane, while the N4 atom and the lone pair of electrons occupy the axial positions. The average Pb–O bond lengths are 2.568 Å, and the O-Pb-O bond angles, which vary from 50.50(14) to 151.90(16)°, are very close to those of **1**. The Pb–N bond lengths lie in the range of 2.462(5)–2.544(6) Å (Pb–N1 and Pb–N2), slightly shorter than the corresponding bond lengths in **1**. Each pair of adjacent Pb^{II} ions is bridged by one ndc ligand (mode I) to form an arm-shaped chain structure running along the *b* axis with a pitch of 11.571 Å, in which the Pb-Pb-Pb angle, defined by the orientation of the ndc ligands in the chain, is 138.5°. Differing from the dpp molecules in **1**, the ptcp ligands in **2** extend solely on one side of the chain in a slanted fashion (Figure 2 b). The ptcp ligands of each chain are stacked with those of an adjacent chain through π–π interactions (Figure S2), generating a ladderlike double-chain structure (Figure 2 c).[11] The effective length of each ptcp ligand of about 9.951 Å, thus provides the possibility for stacking. The double chains recognize each other through another type of aromatic π–π stacking interaction of the ptcp ligands (Figure S2), which results in a wavy layer (Figure 2d) different from that found in **1**, because in **2** all the ptcp ligands are arranged on one side of each single chain.

For compound **3**, the asymmetric unit is composed of two Pb^{II} ions, two ndc ions, and two dppz ligands. Figure 3a illustrates the coordination environments of the two crystallographically independent Pb^{II} ions, which have similar distorted tetragonal-bipyramidal geometries. The Pb2 atom is coordinated by three oxygen atoms (O2, O5, and O8A) of ndc ions and two nitrogen atoms (N3 and N4) from one chelating dppz ligand. The O2, O5, O8A, and N3 atoms comprise the basal plane, while the N4 atom and the lone pair of electrons occupy the axial positions. The Pb−N and Pb−O bond lengths in **3** are near to those in **1** and **2**. In contrast to those in **1** and **2**, the carboxylate groups of the two ndc ligands in **3** adopt different coordination modes (III and IV). In mode III, one carboxylate moiety of ndc chelates one Pb^{II} ion, while the other is coordinated to Pb^{II} in a monodentate fashion (Scheme 2). In mode IV, one carboxylate moiety of ndc bridges two Pb^{II} ions, while the other is connected to a Pb^{II} ion in a monodentate mode (Scheme 2). Compound **3** consists of interesting 1D ladder chains (Figure 3b), the repeating unit of which is formed by three ndc ligands and four Pb^{II} centers. Two crystallographically distinct dppz ligands (dihedral angle ca. 3.4°) are attached to both sides of the 1D ladder. In addition, the neighboring 1D ladders interact by π–π stacking between the dppz ligands, which leads to interesting 2D supramolecular layers in the *bc* plane (Figure 3c). There are two types of π–π interactions between the dppz ligands: parallel dppz interaction (ca. 3.592 Å) in the same ladder, and dppz interaction (ca. 3.601 Å) between two different ladders (see Figure S3).

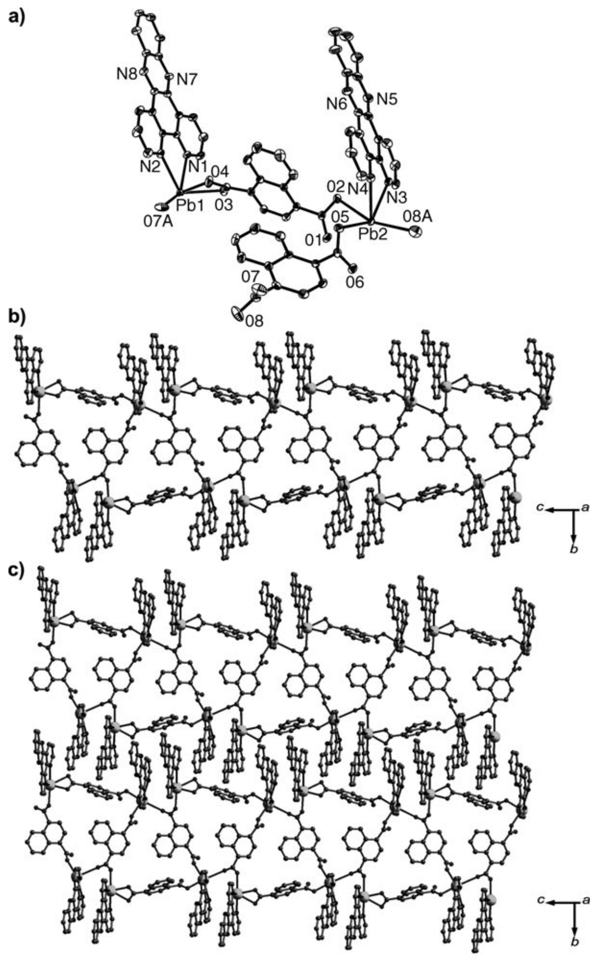


Figure 3. Coordination environment of Pb^{II} ions in **3** (a, all hydrogen atoms omitted for clarity), the 1D ladder structure of **3** (b), and the 2D layer structure of **3** formed by interladder π–π interactions (c).

In contrast to compounds **1**–**3**, compound **4** has a Pb^{II}/N-donor chelating ligand ratio of 1/2. Although we changed the Pb^{II}/N-donor chelating ligand molar ratio (1/1, 1/1.5, 1/2, 1.5/1, and 2/1) in the reaction mixtures, the same compound **4** was obtained. Compound **4** also features an arm-shaped chain structure constructed from one Pb^{II} ion, two tcpn ligands, and one ndc ligand. As depicted in Figure 4a, each Pb^{II} ion in **4** is surrounded by four oxygen atoms from three ndc ligands, and four nitrogen atoms from two tcpn ligands. To the best of our knowledge, a coordination number as high as 8 (excluding the lone pair of electrons) has rarely been observed in Pb^{II} complexes.[4] It is known that the two possible ground-state geometries for a nine-vertex polyhedron are the symmetrical tricapped trigonal prism with D_{3h} symmetry and the monocapped square antiprism with C_{4v} symmetry.[12] The polyhedron of the Pb^{II} coordination sphere for compound **4** is best described as a distorted tricapped trigonal prism with the ninth site occupied by its lone pair of electrons. The Pb−O distances ranging from 2.746(6) to 2.755(5) Å are comparable to those observed in related Pb^{II} compounds.[4] Each carboxylate group of the ndc ligand chelates one Pb^{II} ion in mode I (Scheme 2), leading to 1D arm-shaped chains (Figure 4b). The tcpn ligands extend on both sides of the chain, and the planes of adjacent tcpn ligands are nearly parallel. These parallel tcpn ligands are paired to furnish strong aromatic π–π stacking interactions with a face-to-face distance of about 3.455 Å (see Figure S4), which extend the arm-shaped chains into a wavy supramolecular layers in the *bc* plane (Figure 4c).

Compound **5** has a Pb^{II}/NCL ratio of 2/1. Although we changed the Pb^{II}/tcpp molar ratio (1/1, 1/1.5, 1/2, 1.5/1 and 2/1) in the reaction mixtures, the same compound **5** was obtained. Single-crystal structure analysis revealed that **5** has a layered network structure built from interlinking of ndc ligands with Pb^{II} ions. The asymmetric unit contains two crystallographically inequivalent Pb^{II} ions (Pb1 and Pb2), one tcpp ligand, and two ndc ligands (Figure 5a). The Pb1 center is located in a distorted tetragonal-bipyramidal coordination sphere, formed by three oxygen atoms from two different ndc ligands, two nitrogen atoms from one chelating tcpp ligand, and an electron lone pair. The carboxylate oxygen atoms (O1, O5, and O6) of the ndc ligands and one nitrogen atom (N2) from the tcpp ligand make up the basal

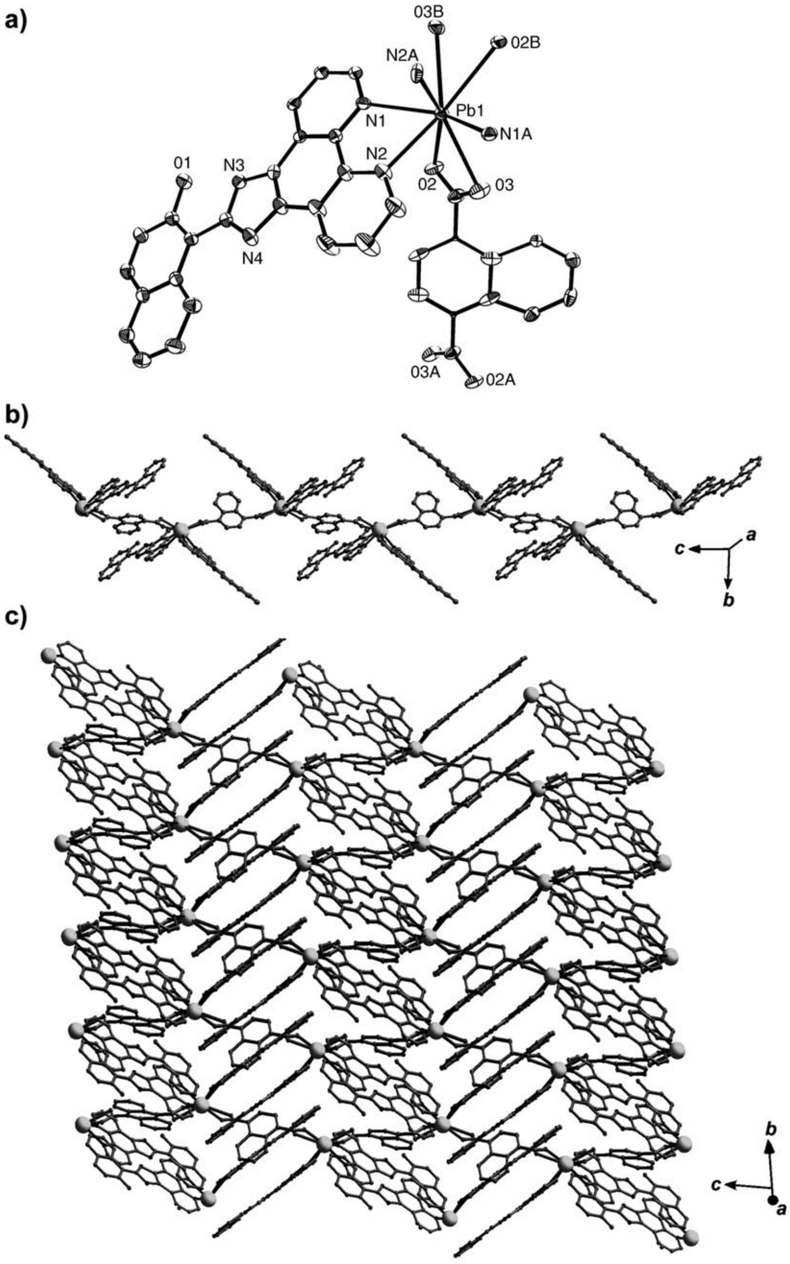


Figure 4. Coordination environment of Pb^{II} ions in compound **4** (a, all hydrogen atoms omitted for clarity), the 1D arm-shaped chain structure of **4** (b), and the 2D layer structure of **4** formed by interchain π–π interactions between tcpn ligands (c).

plane, while the axial positions are occupied by one nitrogen atom (N1) and the lone pair of electrons. In the structure of **5** one ndc ligand is coordinated to the Pb^{II} centers in coordination mode I, while the carboxylate moiety of the other bridges two Pb^{II} ions through one oxygen atom, while the other chelates one Pb^{II} ion (mode V in Scheme 2). The coordination modes in compound **5** generate a novel 2D layer structure with (4,4) grids (Figure 5b). Each corner of the (4,4) grids is occupied by a binuclear Pb^{II} subunit. In addition, the interplanar distance between two neighboring tcpp ligands of adjacent layers of about 3.566 Å (see Figure S5) indicates the presence of face-to-face π–π interactions that further stabilize the crystal structure and extend the layers into a unique double-layer structure (Figure 5c). Although double-layer coordination polymers have been reported,[13] s^2 metal complexes with a double layer formed by π–π interactions have not been documented. On the basis of the results presented above, we conclude that variation of the N-donor chelating ligand leads to structural changes, and sometimes is the dominant factor determining the supramolecular structural features of the coordination polymers.

To investigate effect of the solvent on structure formation, we synthesized single crystals of **6** in aqueous solution and of **7** in dma solution. The influence of solvent on the final network is demonstrated by the resulting structures of the compounds. The reaction of $Pb(NO_3)_2$ and H_2ndc under hydrothermal conditions at a temperature of 185 °C gave rise to the coordination polymer [Pb(Hndc)$_2$]·H_2O (**6**) as colorless prismatic crystals. As shown in Figure 6a, each Pb^{II} center in **6** is coordinated to six carboxylate oxygen atoms from four different Hndc ligands. The coordination geometry of the Pb^{II} ion can be described as a distorted pentagonal bipyramid with the seventh site occupied by the lone pair of electrons. The Pb^{II}–O distances of 2.456(13)–2.713(14) Å are similar to those around the Pb^{II} centers in compounds **1**–**5**. The Hndc ligands in the asymmetric unit of **6** adopt a new coordination mode (mode VI in Scheme 2): only one carboxyl group is deprotonated and coordinates to two adjacent Pb^{II} centers, whereas the other carboxyl group is free. Planar centrosymmetric Pb_2O_2 ring units are formed (Figure 6b) and these units are bridged with a Pb–Pb distance of 4.16 Å in the same ring to generate a 1D chain.[14] Careful inspection of the structure of **6** reveals that the ndc ligands are alternately attached to both sides of the chain, and are orientated either approximately parallel or perpendicular to the

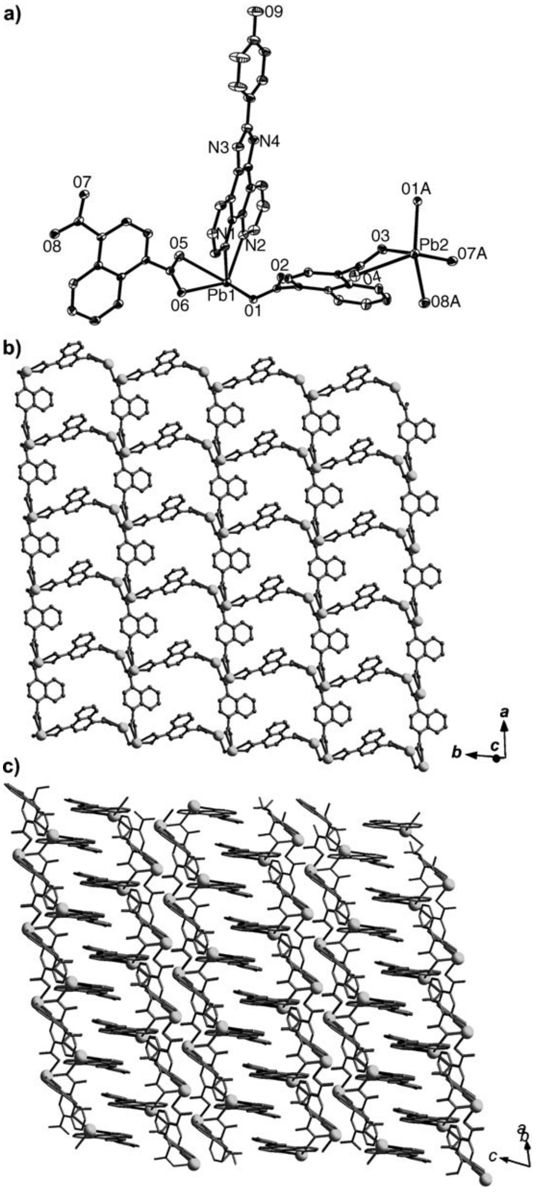


Figure 5. Coordination environment of Pb^{II} ions in **5** (a, all hydrogen atoms omitted for clarity), the 2D network structure of **5** (b), and the 2D double layer structure of **5** formed by interlayer π–π interactions (c).

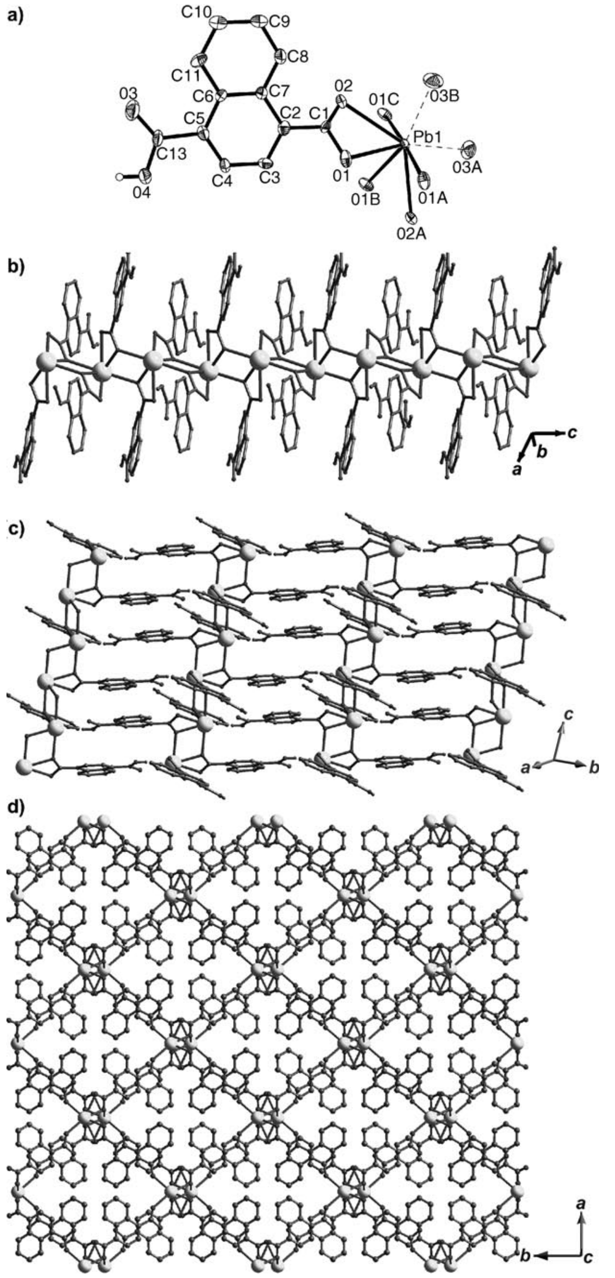


Figure 6. Coordination environment of Pb^{II} ions in **6** (a, all hydrogen atoms omitted for clarity), the 1D chain structure of **6** (b), the 2D layer structure of **6** formed by approximately parallel ndc π–π interactions of different chains (c), and the 3D structure of **6** formed by both approximately parallel and perpendicular ndc π–π interactions (d).

chain. The ndc ligands with the approximately parallel orientation pair with their centrosymmetrically related ndc ligands in the neighboring chains to generate a 2D supramolecular structure directed by aromatic π–π stacking between the parallel ndc pairs (Figure 6c). The face-to-face distance between the paired ndc ligands of about 3.559 Å indicating strong aromatic π–π stacking interaction (see Figure S6). Furthermore, the 2D supramolecular structures are held together through approximately perpendicular ndc π–π stacking interactions to form a 3D supramolecular structure (Figure 6d).

Unlike compound **6**, compound **7** was synthesized in dma solution. A single-crystal X-ray diffraction study revealed an extended 3D coordination framework that crystallizes in the chiral space group $P2_12_12_1$ (no. 19).[15] The asymmetric unit of **7** consists of one Pb^{II} center, one ndc ion, and one coordinating dma molecule. As shown in Figure 7a, each Pb^{II} ion is six-coordinate, surrounded by five oxygen atoms from four ndc ligands (O1, O2A, O3A, O4A, and O4B) and one terminal dma molecule (O5) in a distorted pentagonal-bipyramidal coordination sphere, in which four oxygen atoms (O1, O5, O2A and O4B) and the lone pair of electrons make up the basal plane, while the axial positions are occupied by two oxygen atoms (O3A and O4A) from ndc mole-

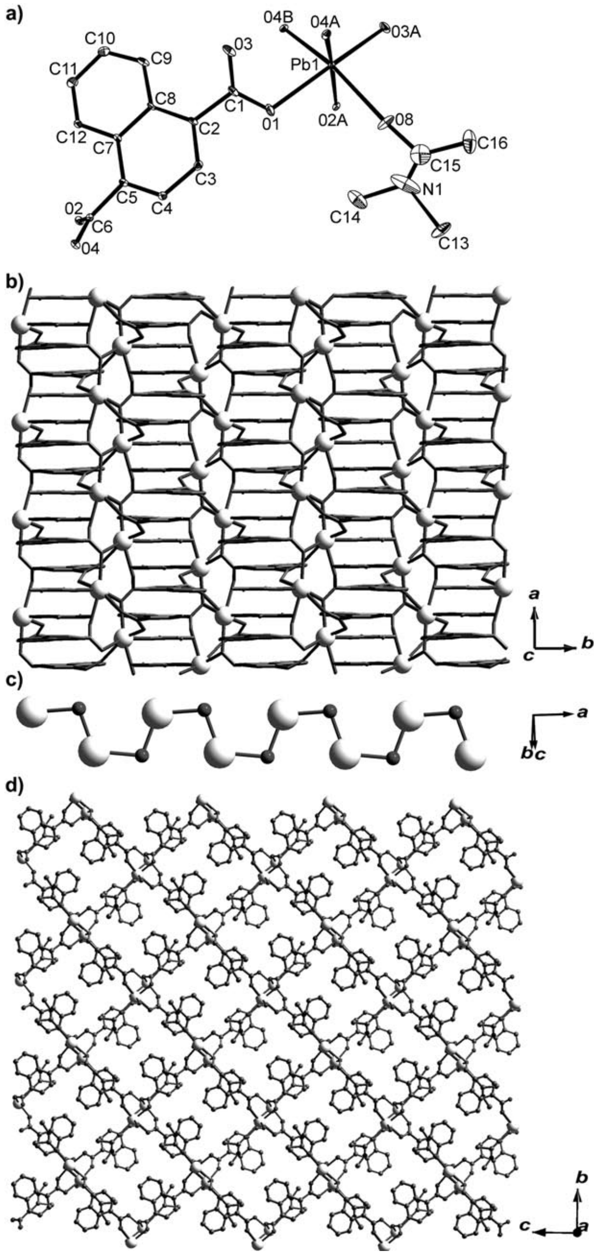


Figure 7. Coordination environment of Pb^{II} ions in **7** (a, all hydrogen atoms are omitted for clarity), the 3D chiral framework structure of **7** in the *ab* plane (b), the 1D inorganic O-Pb-O chain in **7** (c), and the 3D chiral framework structure of **7** in the *bc* plane (d).

cules. The Pb–O distances range from 2.379(5) to 2.702(4) Å, and the O-Pb-O angles from 69.42(15) to 168.24(13) Å. Furthermore, the $:PbO_6$ polyhedra are edge-shared through the O4 atom of ndc ligand to form a 1D inorganic PbO chain running along the [001] direction (Figure 7b and c). The ndc ligand adopts an unusual coordination mode in **7** (mode VII in Scheme 2): four carboxylate oxygen atoms coordinate to five metal ions, whereby one carboxylate is tridentate, and the other bidentate. In **7** neighboring O-Pb-O chains are bridged by the ndc ligands in all four directions to form a rare 3D chiral open framework (Figure 7d). Whereas chiral coordination compounds reported so far usually involved d-block transition metals and 4f lanthanide elements, p-block metal–organic compounds with a chiral structure are rare.[16] Compound **7** is an additional example of a chiral p-block metal–organic polymer obtained by use of achiral ligands.

To investigate the influence of the organic acid ligand (ndc and bdc) on the structure, an analogous rigid bdc ligand was used under the same reaction conditions as for **7**, and a completely different coordination polymer [Pb(bdc)(dma)] (**8**) was obtained. X-ray structure determination revealed that **8** has a unique 3D structure. As shown in Figure 8a, the central Pb^{II} ion is coordinated by five oxygen atoms of three bdc ligands and one dma molecule in a tetragonal-bipyramid coordination sphere, in which the three carboxylate oxygen atoms (O1, O2A, and O4) and one dma oxygen atom (O5) make up the basal plane, while the axial positions are occupied by one oxygen atom (O3) from a bdc ligand and the lone pair of electrons. The carboxylate Pb–O bond lengths and O-Pb-O bond angles are in the ranges 2.440(4)–2.699(4) Å and 53.02(11)–150.66(16)°, all of which are comparable to those found in **7**. Interestingly, in **8** one of the two bdc linkers coordinates to two Pb^{II} ions in a bis-chelating coordination mode, while the other bdc ligand connects four Pb^{II} centers in a bis-bidentate mode (modes VIII and IX in Scheme 2). The bdc linkers in the bis-bidentate mode bridge the Pb^{II} centers and generate a 2D extended layer network (Figure 8b). Furthermore, all of the bdc linkers in the bis-chelating coordination mode connect the Pb^{II} ions from adjacent layers to form an interesting 3D open framework structure (Figure 8c). Topological analysis of the framework was performed by considering each bis-bidentate bdc ligand as a 4-connected node (Figure 8c) and each Pb^{II} ion as a 3-connected node because each bis-bidentate bdc ligand bridges four equivalent Pb^{II} ions and each Pb^{II} ion is connected to three bdc ligands. In addition, the ratio of 3-connected to 4-connected nodes is 2/1. Thus, this structure is a typical 3D (3,4)-connected net with an unusual AB_2 (A = 4-connected vertices, B = 3-connected vertices) composition in contrast to the usual A_3B_4 nets constructed by the Catalan or Archimedean types (Figure 8d).[17]

Compounds **9** and **10** also exhibit solvent effects, as demonstrated by the corresponding structures. Compound **9** was synthesized by hydrothermal reaction of $Pb(NO_3)_2$ and 1,4-cyclohexanedicarboxylic acid (H_2chdc, mixture of *cis* and *trans* forms in a ratio of 3/2) in a molar ratio of 1/1. The H_2chdc ligand has three possible conformations: *a*,*a*-*trans*-, *e*,*e*-*trans*-, and *e*,*a*-*cis*-H_2chdc. The *e*,*e*-*trans* form is thermodynamically more stable than the *e*,*a*-*cis* form because of the presence of two equatorial substituents in the latter, and the *a*,*a*-*trans* form is the least stable due to 1,3-diaxial hindrance.[18] Single-crystal structure analysis shows that the central Pb^{II} ion of **9** is coordinated by five oxygen atoms from three different carboxylate groups and one water molecule in a distorted $:PbO_5$ tetragonal-bipyramidal coordination sphere (Figure 9a). The carboxylate Pb–O bond lengths and O-Pb-O bond angles are in the ranges 2.285(4)–

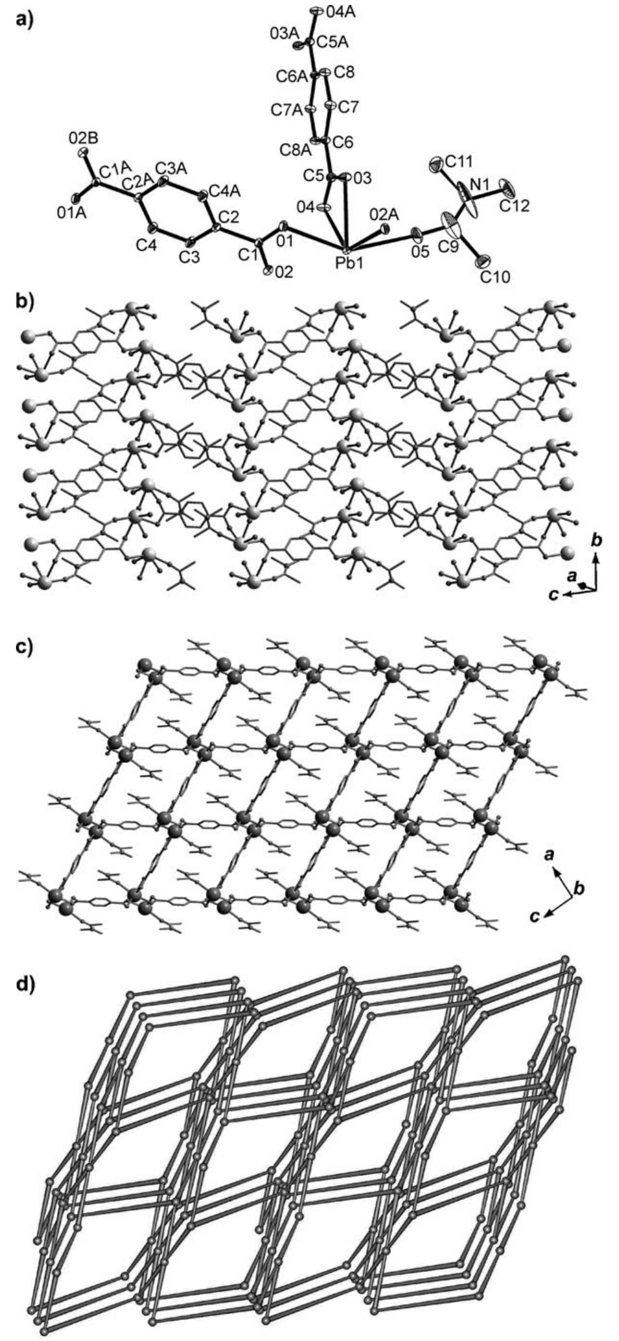


Figure 8. Coordination environment of Pb^{II} ions in compound **8** (a, all hydrogen atoms omitted for clarity), the 2D network structure in **8** constructed by tetradentate bdc ligands (b), the 3D framework structure of **8** (c), and schematic representation of the 3D (3,4)-connected net (d).

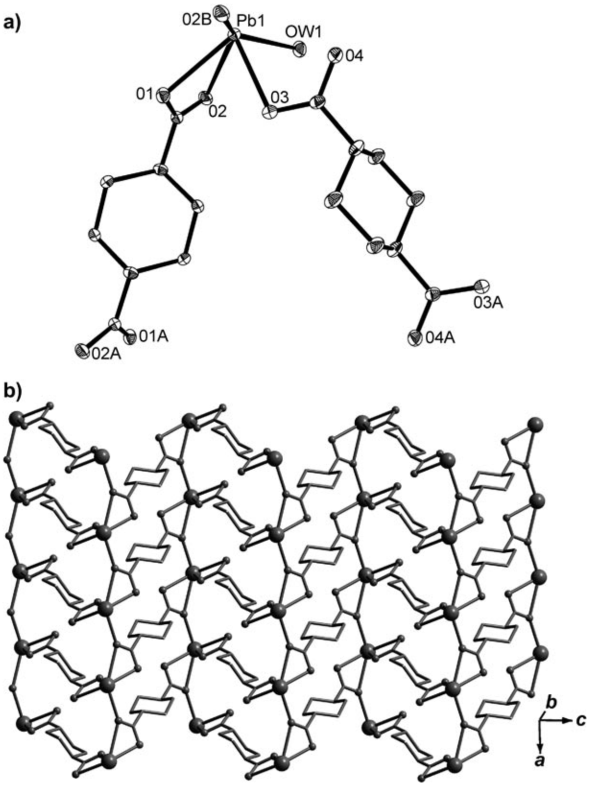


Figure 9. Coordination environment of Pb^{II} ions in **9** (a, all hydrogen atoms are omitted for clarity), and the 2D network structure in **9** constructed by chdc ligands (b).

2.736(4) Å and 50.24(12)–140.95(15)°. More interestingly, the H_2chdc ligands are deprotonated and only *e*,*e*-*trans* form of the chdc ligand is present in **9**. In addition, the *trans*-chdc ligands show two coordination modes (modes X and XI in Scheme 2): in mode X, one *e*,*e*-*trans*-chdc ligand links two Pb^{II} ions by its two monodentate carboxylate groups, while in mode XI *e*,*e*-*trans*-chdc links four Pb^{II} ions with its two chelating/bridging carboxylate groups to form an infinite ladder structure. Adjacent ladders are further connected together by the bridging oxygen atoms of the carboxylate groups (mode X) into a layer (Figure 9b).

Compound **10** was synthesized from the solvothermal reaction of $Pb(NO_3)_2$, H_2chdc, and dma. Single-crystal structure analysis revealed that **10** is a rare 3D body-centered cubic (bcc) framework with the formula $[Pb_2(\textit{cis}\text{-chdc})_2][NH(CH_3)_2]$.[19] Surprisingly, only *cis*-chdc ligands are present in **10**. The asymmetric unit of **10** consists of two Pb^{II} centers, two *cis*-chdc (modes XI and XII in Scheme 2), and one $NH(CH_3)_2$ guest molecule formed by decomposition of the dma molecule (Figure 10a).[20] The Pb1 atom is bound to six *cis*-chdc oxygen atoms, and Pb2 is bound to four *cis*-chdc oxygen atoms. The two nonequivalent Pb^{II} ions adopt distorted $\mathbf{:}PbO_6$ pentagonal-bipyramid and $\mathbf{:}PbO_4$ tetragonal-pyramidal coordination geometries, respectively. The Pb–O distances range from 2.372(10) to 2.737(8) Å, comparable to those observed in the related compounds **6**–**9**. A unique feature of **10** is the presence of eight-connected $[Pb_8(\textit{cis}\text{-chdc})_8]$ wheel clusters (Figure 10b and c). The Pb^{II} ions are linked by μ_2-O atoms of *cis*-chdc bridges to give an unprecedented nanosized $[Pb_8(\textit{cis}\text{-chdc})_8]$ neutral wheel cluster and, to the best of our knowledge, this is currently the largest Pb^{II} wheel with bridging oxygen atoms.[21] Wheel clusters have attracted intense interest, not only because of their fascinating physical properties, but also because of the architectural beauty of their structures. So far, most of the work in this

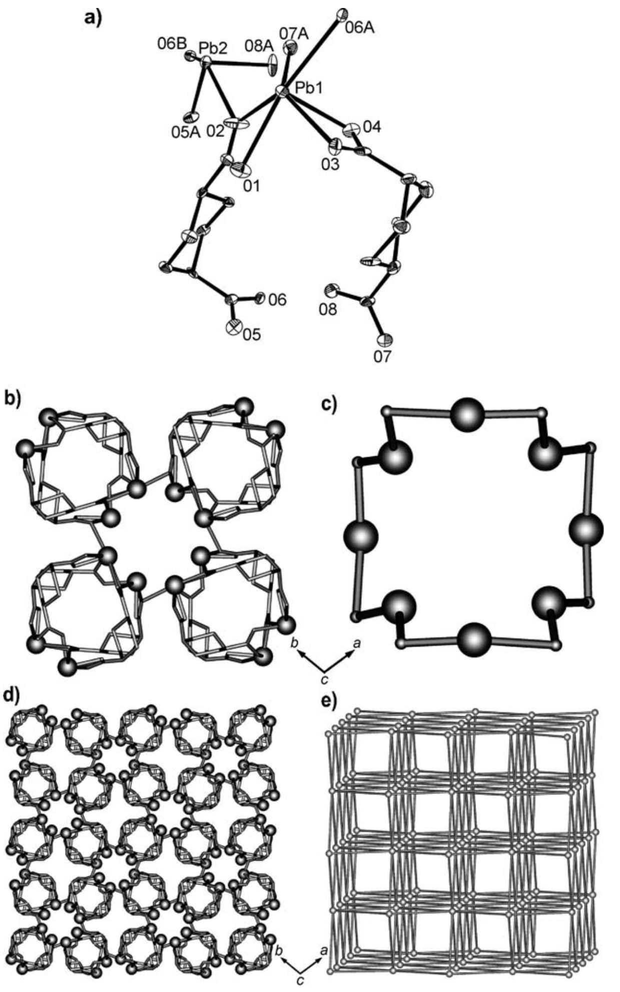


Figure 10. Coordination environment of Pb^{II} ions in **10** (a, all hydrogen atoms omitted for clarity), the nanosized $[Pb_8(\textit{cis}\text{-chdc})_8]$ wheel cluster constructed by eight Pb^{II} centers and eight *cis*-chdc ligands (b), view of the $[Pb_8O_8]$ cluster (c), the 3D framework structure of **10** (d), and schematic representation of the 3D bcc-type net based on $[Pb_8O_8]$ clusters as nodes (e). The Pb^{II} ion is indicated by solid ball in a)–d).

area has focused on the assembly of transition metal and lanthanide wheels, and the analogous chemistry of p-block elements such as Pb has hardly been investigated.[21] The metal wheels in **10** are further linked to each other to generate a rare 3D bcc-type net (also called CsCl net) based on $[Pb_8O_8]$ clusters as the eight-connected nodes (Figure 10d and e). Although the bcc-type net is commonly described in textbooks, such topologies with eight-connected nodes have only appeared in a few examples.[19]

Effects of ligand and solvent: The role of the N-donor chelating ligand in determining the supramolecular structures of coordination polymers **1**–**5** have been clearly demonstrated. By varying the N-donor chelating ligand under the same synthesis conditions, we obtained five related compounds with three different Pb^{II}/ N-donor chelating ligand ratios. The compounds show great discrepancy in supramolecular structure because of the presence of the different N-donor chelating ligands. The nature (size and shape) of the N-donor chelating ligand is the underlying factor behind the discrepancy in structure and type of π–π interaction.[7] The two phenyl rings of dpp deviate slightly from the phenanthroline plane, while the ptcp, dppz, tcpp, and tcpn molecules are planar. The bulky phenyl groups in the backbone significantly increase the steric hindrance of the dpp ligand. In contrast to ptcp, the additional hydroxyl group present in the tcpp ligand results in different Pb^{II}/ N-donor chelating ligand ratios in the formed coordination compounds. These geometrical differences in the NCLs lead to the formation of **1**–**5** with quite distinct supramolecular structures under similar synthetic conditions. Compounds **1**–**4** have a 1D chain structure with Pb^{II}/ N-donor chelating ligand ratios of 1/1 and 1/2, while **5** displays a 2D network structure with a Pb^{II}/NCL ratio of 2/1. However, although the Pb^{II} ions have different coordination spheres and various coordination numbers, the final products do not depend on the metal-to-neutral ligand ratio in the reaction mixtures. Various metal-to-neutral ligand ratios were used in the reactions, but only compounds **1**–**5** were isolated as products. Clearly, for **1**–**5**, the structure of the N-donor chelating ligand is the dominant factor determining the final supramolecular structure of the coordination polymer.

The effects of the organic acid ligand were demonstrated by the formation of compounds **7**, **8**,and **10** under the same synthesis conditions. The rodlike ndc, bdc, and the relatively flexible chdc molecules have interesting features that are conducive to formation of versatile coordination structures. Both bdc and ndc are rigid rodlike ligands, while the ndc has a larger conjugated π system owing to the additional phenyl ring.[9] In comparison with ndc and bdc, the nonaromatic chdc is a relatively flexible ligand having three possible conformations.[18] Although compounds **7**, **8**, and **10** were synthesized under the same conditions, the structures of the compounds are completely different from one another. Thus, it is clear that the role played by organic acids with different ring structures (ndc, bdc, and chdc) is crucial in determining the network topology of the resultant coordination polymers. Additionally, in contrast to the formation of **7** and **8**, during the formation of **10** the dma molecule decomposes to a neutral dimethylamine molecule, which acts as a template[20] in the crystallization of the compound. This may be another factor that leads to the structural differences among these compounds.

The solvent is also an important factor in determining the structures of **6** and **7**, and **9** and **10**. The solvothermal reaction of H_2ndc or H_2chdc and $Pb(NO_3)_2$ in dma solution produces blocklike crystals of **7** or **10**, whereas needlelike crystals of **6** or **9** are formed under hydrothermal conditions. In general, the effects of solvents can be explained in terms of their difference in size, shape, and coordination ability.[22] As dma and H_2O molecules have different steric structures the resultant networks of compounds **6** and **7** also differ. In compound **10** the dma molecule decomposes to a neutral dimethylamine molecule, whereas the water molecule coordinates to the Pb^{II} ion in **9**, and naturally these two compounds have different network structures as well. The solvent is also an important factor for formation of the final structures of **6** and **7**. Compound **6** with a 1D chain structure was synthesized by mixing $Pb(NO_3)_2$ and H_2ndc under a hydrothermal conditions, while **7** with a rare 3D chiral framework was obtained under solvothermal conditions. Notably, the solvents also play crucial roles in conformational separation of chdc ligands during the formation of **9** and **10**. Although the separation of *cis* and *tran*s conformations of H_2chdc was successfully realized by careful adjustment of pH value,[23] there is no report on complete separation of *cis* and *trans* conformations of H_2chdc by means of solvent effects, especially by complexation of p-block metals. Compound **10** is the first example of coordination polymers constructed with heavy metals such as Pb in which the *cis* and *trans* conformations of H_2chdc are separated by changing solvent. Thus, the structural differences among compounds **7** and **8**, and **9** and **10** show the importance of solvent in framework formation of the coordination polymers.

Photoluminescence properties: Luminescence is of great importance in photochemistry and photophysics.[24] With regard to coordination compounds, studies have been essentially restricted to d^{10} and 4f metals, and little attention has been paid to the luminescence of coordination polymers of main group metals such as Pb.[8] The Pb^{II} compounds are a potential class of functional materials and ideal systems for investigation of structure–property relationships. The photoluminescence spectra of **1**–**10** and the free ligands were examined in the solid state at room temperature (Table 1). The ligands exhibit emissions at 472 nm for H_2ndc (excitation at 392 nm),[9] at 390 nm for H_2bdc (excitation at 347 nm),[20] at 387 and 404 nm for dpp (excitation at 347 nm), at 475 nm for ptcp (excitation at 393 nm), at 444 nm for dppz (excitation at 328 nm), at 381 and 424 nm for tcpn (excitation at 255 nm), at 430 nm for tcpp (excitation at 267 nm), and at 325 nm for H_2chdc (excitation at 252 nm); see Figure S7. The emission bands for these free ligands are probably attributable to the $\pi^* \rightarrow n$ transitions.[9,20] On complexation of these ligands with Pb^{II} ions, the emissions arising from the free ligands were not observable. Compounds **1**–**10** each show an emission peak located in the red region (Table 1 and Figure S8). The emission peak varies slightly with ligand, as evidenced by a slight shift in emission from 605 to 621 nm (Table 1). Generally, the emission of s^2 compounds in the solid state originates from the $^3P_1$ level ($^3P_1 \rightarrow {}^1S_0$, $^3P_2 \rightarrow {}^1S_0$, and $^1P_1 \rightarrow {}^1S_0$).[25] The energy of these transitions depends on the metal and is slightly modified by the organic ligands, but the essential features of the spectra do not change.[26] The low-energy emissions of **1**–**10** have been commonly observed for other s^2 metal complexes, and these emissions can be assigned to a metal-centered transition involving the s and p metal orbitals, as proposed by Vogler et al.[27] These results imply that the coordination of the organic ligands to Pb^{II} ions, although it yields different topological structures, has no significant influence on the emission mechanism of the metal coordination polymers.

Table 1. Luminescence data for organic ligands and complexes **1**–**10** in the solid state.

Compound	λ_{ex} [nm]	λ_{em} [nm]	Ligand	λ_{ex} [nm]	λ_{em} [nm]
1	453	614	H_2ndc	392	472
2	480	620	H_2bdc	347	390
3	458	617	dpp	347	387 and 404
4	474	621	ptcp	393	475
5	450	620	dppz	328	444
6	466	613	tcpn	255	381 and 424
7	451	612	tcpp	267	430
8	443	605	H_2chdc	252	325
9	466	608			
10	465	607			

Nevertheless, the photoluminescent intensity of the coordination polymers is affected by the aromaticity of the ligand. On excitation, **9** and **10** emit red light significantly more weakly than **1**–**8**. Energy transfer may be involved in the luminescent process of the compounds. In **1**–**8**, it is possible for the delocalized π bonds of the dicarboxylate ligand to interact effectively with the p orbitals of the Pb^{II} center, and this results in easier energy transfer from the ligand, which absorbs the energy of the excitation light, to the metal center.[28] In other words, the metal center in **1**–**8** is more easily excited in the presence of the aromatic ligand, and the resulting luminescence is stronger for these compounds. In contrast, **9** and **10** contain a nonaromatic ligand, and the interaction between the π-orbitals of the carboxylate groups and the p orbitals of the lead(II) ion may be weaker in the absence of an aromatic ring in the ligand. As a result, energy transfer from the ligand to the metal center is less effective[20] for **9** and **10** during photoluminescence, and this leads to weaker emissions for these two compounds. The ligand in **6** and **7** has a naphthalene ring, whereas that in **8** contains a benzene ring. The photoluminescence of the first two compounds is more intense than that of the third. This further demonstrates that aromaticity plays a role in emission intensity of the coordination compounds. However, other factors, such as ligand rigidity, may also influence emission intensity, as the ligands in **6**–**8** are more rigid than that in **9** and **10**. Compounds **1**–**5** contain both ndc and NCL, but their luminescence intensities are comparable to those for **6** and **7**, that is, the N-donor chelating ligand plays a less important role in emission intensity of the compounds.

Nonlinear optical properties: Second-harmonic generation (SHG) is only found in noncentrosymmetric materials.[29] Due to the practical importance of second-order nonlinear optical (NLO) properties in many technological applications, there has been intense interest in employing crystal-engineering strategies to generate desirable materials.[30] A chiral framework is itself noncentrosymmetric, and therefore **7** is an acentric compound that has potential application as an NLO-active material. A powder sample of **7** was investigated by optical SHG at room temperature to confirm its acentricity and evaluate its second-order NLO properties. The intensity of the green light (frequency-doubled output: $\lambda = 532$ nm) produced by **7** is about 0.9 times that produced by potassium dihydrogenphosphate (KDP) powder, that is, the SHG effect is slightly weaker than that of KDP. The of SHG effect of **7** is consistent with its chiral space group. Solid **7** is totally transparent in the visible region and insoluble in common solvents because of its neutral 3D polymeric structure. To our knowledge, this is the first example of an NLO Pb^{II} coordination polymer constructed from achiral components.[31]

Conclusion

A variety of Pb^{II} coordination polymers with dicarboxylate ligands (ndc, bdc and chdc) have been prepared under hydro(solvo)thermal conditions. The N-donor chelating ligand, the organic acid, and the solvent all affect the network structure of the coordination polymer products. The crystal structures of **1**–**5** indicate that the geometry and size of the N-donor chelating ligand, which provides potential supramolecular recognition sites for π–π stacking interactions, are essential in determining the structure of the final assembly. The structural differences among **7**, **8** and **10** highlight the effects of organic acid ligands on framework formation of the complexes. The solvents used in the preparation of **6** and **7** and **9** and **10** also have significant effects on structure formation because of the difference in steric hindrance. By changing the solvent the *cis* and *trans* conformations of H_2chdc in **9** and **10** are separated completely, and large Pb^{II} wheels [Pb_8(*cis*-chdc)$_8$] with bridging carboxylate oxygen atoms were isolated. The photoluminescence and nonlinear optical properties of the compounds indicate that they may be good candidates for luminescent materials. This work greatly enriches the chemistry of self-assembly of Pb^{II}-based coordination polymers.

Experimental Section

Materials and physical measurements: The ligands dpp (Aldrich), H_2chdc (Aldrich), H_2ndc, H_2bdc and other reagents of analytical grade (Huifeng Chemical Factory, China) were purchased and used without further purification. The ligands ptcp, dppz, tcpn, and tcpp were synthesized by following the procedures described previously.[32] CHN elemental analysis was conducted on a Perkin-Elmer 240C element analyzer, and inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV ICP spectrometer. The photoluminescent properties of the compounds were measured on a Perkin-Elmer LS55 spectrometer. Second-harmonic generation was tested on a powder sample by the Kurtz and Perry method.[33] Second-harmonic intensity data were obtained by placing a powder sample in an intense fundamental beam from a Q-switched Nd:YAG laser of wavelength 1064 nm.

[Pb(ndc)(dpp)] (1): $Pb(NO_3)_2$ (0.5 mmol), H_2ndc (0.5 mmol), and dpp (0.5 mmol) were dissolved in distilled water (10 mL), and triethylamine was added until the pH value of the system was adjusted to about 5.5. The resulting solution was stirred for about 0.5 h at room temperature, sealed in a 23-mL Teflon-lined stainless steel autoclave and heated at 185 °C for 10 days under autogenous pressure. Then the reaction system was slowly cooled to room temperature. Colorless block 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: 44.7% based on Pb^{II}. Elemental and ICP analysis $C_{72}H_{44}N_4O_8Pb_2$ (%): calcd: C 57.37, H 2.94, N 3.72, Pb 27.49; found: C 57.81, H 2.66, N 3.91, Pb 27.24.

[Pb(ndc)(ptcp)]·0.5 H_2O (2): Compound **2** was prepared in the same way as **1**, using ptcp (0.5 mmol) instead of dpp as the neutral ligand source. Pale yellow block crystals were obtained in 55% yield based on Pb^{II}. Elemental and ICP analysis for $C_{31}H_{19}N_4O_5Pb$ (%): calcd: C 50.68, H 2.61, N, 7.63, Pb 28.20; found: C 50.37, H 2.79, N 7.23, Pb 28.51.

[Pb(ndc)(dppz)] (3): Compound **3** was prepared in the same way as **1**, using dppz (0.5 mmol) instead of dpp as the neutral ligand source. Pale yellow block crystals were obtained in 69% yield based on Pb^{II}. Elemental and ICP analysis for $C_{60}H_{32}N_8O_8Pb_2$ (%): calcd: C 51.21, H 2.29, N, 7.96, Pb 29.45; found: C 51.67, H 2.13, N 8.33, Pb 29.31.

[Pb(ndc)(tcpn)$_2$] (4): Compound **4** was prepared in the same way as for **1**, using tcpn (0.5 mmol) instead of dpp as the neutral ligand source. Pale yellow block crystals were obtained in 57% yield based on Pb^{II}. Elemental and ICP analysis for $C_{29}H_{16}N_4O_3Pb_{0.5}$ (%): calcd: C 60.89, H 2.82, N, 9.79, Pb 18.11; found: C 60.37, H 2.93, N 9.71, Pb 18.32.

[Pb$_2$(ndc)$_2$(tcpp)] (5): Compound **5** was prepared in the same way as **1**, using tcpp (0.5 mmol) instead of dpp as the neutral ligand source. Pale yellow block crystals were obtained in a 54% yield based on Pb^{II}. Elemental and ICP analysis for $C_{43}H_{24}N_4O_9Pb_2$ (%): calcd: C 44.71, H 2.09, N, 4.85, Pb 35.88; found: C 44.85, H 2.51, N 4.37, Pb 35.63.

[Pb(Hndc)$_2$]·H_2O (6): $Pb(NO_3)_2$ (0.5 mmol) and H_2ndc (0.5 mmol) were dissolved in distilled water (10 mL). The resulting mixture was stirred for about 0.5 h at room temperature, sealed in a 23-mL Teflon-lined stainless steel autoclave, and heated at 185 °C for 10 days under autogenous pressure. Then the reaction system was gradually cooled to room temperature at a rate of 10 °C h^{-1}. Colorless crystals of **6** 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: 67% based on Pb^{II}. Elemental and ICP analysis for $C_{12}H_8O_{4.5}Pb_{0.5}$ (%): calcd: C 43.97, H 2.46, Pb 31.61; found: C 43.66, H 2.61, Pb 31.38.

[Pb(ndc)(dma)] (7): $Pb(NO_3)_2$ (0.5 mmol) and H_2ndc (0.5 mmol) were dissolved in dma (10 mL). The resulting mixture was stirred for about 0.5 h at room temperature, sealed in a 23-mL Teflon-lined stainless steel autoclave, and heated at 185 °C for 10 days under autogenous pressure. Then the reaction system was gradually cooled to room temperature at a rate of 10 °C h^{-1}. Pale yellow crystals of **7** suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with dma, and dried in air at ambient temperature. Yield: 78% based on Pb^{II}. Elemental and ICP analysis for $C_{16}H_{15}NO_5Pb$ (%): calcd: C 37.79, H 2.97, N, 2.75, Pb 40.75; found: C 37.49, H 3.25, N 2.39, Pb 40.81.

[Pb(bdc)(dma)] (8): Compound **8** was prepared in the same way as **7**, using $Pb(NO_3)_2$ (0.5 mmol) and H_2bdc (0.5 mmol) as reactants. Pale yellow crystals were obtained in 65% yield based on Pb^{II}. Elemental and ICP analysis for $C_{12}H_{13}NO_5Pb$ (%): calcd: C 31.44, H 2.86, N, 3.06, Pb 45.20; found: C 31.75, H 3.16, N 3.18, Pb 45.33.

[Pb(*trans*-chdc)(H_2O)] (9): $Pb(NO_3)_2$ (0.5 mmol) and H_2chdc (0.5 mmol) were dissolved in distilled water (10 mL). The resulting mixture was stirred for about 0.5 h at room temperature, sealed in a 23-mL Teflon-lined stainless steel autoclave, and heated at 185 °C for 10 days under autogenous pressure. Then the reaction system was gradually cooled to room temperature at a rate of 10 °C h^{-1}. Colorless crystals of **9** suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with water, and dried in air at ambient temperature; 31% yield based on Pb^{II}. Elemental and ICP analysis for $C_8H_{12}O_5Pb$ (%): calcd: C 24.30, H 3.06, Pb 52.41; found: C 23.96, H 3.29, Pb 52.19.

[Pb$_2$(*cis*-chdc)$_2$]·NH(CH_3)$_2$ (10): Compound **10** was prepared in the same way as **7**, using $Pb(NO_3)_2$ (0.5 mmol) and H_2chdc (0.5 mmol) as reactants. Pale yellow crystals were obtained in a 61% yield based on Pb^{II}. Elemen-

Table 2. Crystallographic data for **1**–**5**.

Compound	**1**	**2**	**3**	**4**	**5**
formula	$C_{72}H_{44}N_4O_8Pb_2$	$C_{31}H_{19}N_4O_5Pb$	$C_{60}H_{32}N_8O_8Pb_2$	$C_{29}H_{16}N_4O_3Pb_{0.5}$	$C_{43}H_{24}N_4O_9Pb_2$
formula mass	1507.49	734.69	1407.32	572.05	1155.04
space group	$P\bar{1}$	$C2/c$	$P2_1/c$	$C2/c$	$P\bar{1}$
a [Å]	9.8841(14)	15.718(3)	16.355(3)	25.809(5)	9.769(2)
b [Å]	14.010(2)	19.876(4)	19.595(4)	8.6938(17)	12.256(3)
c [Å]	22.019(3)	16.084(3)	15.185(3)	23.260(5)	17.200(3)
α [°]	93.253(2)	90	90	90	69.43(3)
β [°]	100.084(2)	94.24(3)	99.29(3)	116.17(3)	74.62(3)
γ [°]	92.196(3)	90	90	90	82.63(3)
V [Å^3]	2993.5(7)	5011.2(17)	4802.6(17)	4684.0(16)	1857.5(7)
Z	2	8	4	8	2
ρ [gcm^{-3}]	1.672	1.948	1.946	1.622	2.065
μ [mm^{-1}]	5.679	6.786	7.073	3.667	9.118
GOF on F^2	0.953	1.030	1.040	1.065	0.964
R_1[a] [$I>2\sigma(I)$]	0.0431	0.0457	0.0306	0.0649	0.0333
wR_2[b] [$I>2\sigma(I)$]	0.0865	0.0638	0.0601	0.0942	0.0820

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 3. Crystallographic data for **6**–**10**.

Compound	**6**	**7**	**8**	**9**	**10**
formula	$C_{12}H_8O_{4.5}Pb_{0.5}$	$C_{16}H_{15}NO_5Pb$	$C_{12}H_{13}NO_5Pb$	$C_8H_{12}O_5Pb$	$C_{18}H_{27}NO_8Pb_2$
formula mass	327.78	508.48	458.42	395.37	799.79
space group	$C2/c$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$	$P\bar{4}2_1/c$
a [Å]	16.814(3)	7.0499(14)	11.553(2)	5.0630(10)	19.603(3)
b [Å]	17.895(4)	14.581(3)	6.7992(14)	8.1658(16)	19.603(3)
c [Å]	7.2417(14)	15.023(3)	17.058(3)	11.528(2)	12.331(3)
α [°]	90	90	90	91.29(3)	90
β [°]	114.10(3)	90	92.49(3)	90.09(3)	90
γ [°]	90	90	90	95.63(3)	90
V [Å^3]	1989.0(7)	1544.3(5)	1338.7(5)	474.19(16)	4738.5(14)
Z	8	4	4	2	8
ρ [gcm^{-3}]	2.189	2.187	2.275	2.769	2.242
μ [mm^{-1}]	8.543	10.950	12.618	17.783	14.233
GOF on F^2	1.041	1.020	1.061	1.039	1.013
R_1[a] [$I>2\sigma(I)$]	0.0928	0.0260	0.0266	0.0320	0.0473
wR_2[b] [$I>2\sigma(I)$]	0.2350	0.0573	0.0554	0.0676	0.0971

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

tal and ICP analysis results for $C_{18}H_{27}NO_8Pb_2$ (%): calcd: C 27.03, H 3.40, N, 1.75, Pb 51.81; found: C 26.87, H 3.85, N 1.49, Pb 51.34.

Crystal structure determination: Crystallographic data of compounds **1** and **5** were collected at room temperature on a Bruker-AXS Smart CCD diffractometer equipped with a normal-focus, 2.4 kW X-ray source (graphite-monochromated $Mo_{K\alpha}$ radiation with $\lambda=0.71073$ Å) operating at 50 kV and 40 mA with increasing ω (width of 0.3° and exposure time 30 s per frame). Crystallographic data of compounds **2**–**4** and **6**–**10** 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 $Mo_{K\alpha}$ radiation, $\lambda=0.71073$ Å) at a temperature of 20 ± 2 °C. Data were processed with the PROCESS-AUTO program. The structures of the compounds were solved by direct methods using the program SHELXS-97[34] and refined by full-matrix least-squares techniques against F^2 using the SHELXTL-97[35] crystallographic software package. All non-hydrogen atoms were easily found from the difference Fourier maps and refined anisotropically, whereas the hydrogen atoms of the organic molecules were placed by geometrical considerations and added to the structure-factor calculation. Crystallographic data and structure refinement parameters for **1**–**10** are summarized in Tables 2 and 3. CCDC-608791–CCDC-608800 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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