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Hybrid Structures Formed by Lead 1,3-Cyclohexanedicarboxylates

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By the employment of hydrothermal methods, four lead 1,3-cyclohexanedicarboxylates with the compositions $Pb(1,3\text{-CHDC})(H_2O)$, **I**, $[(OPb_4)_2(OH)_2(C_2O_4)(1,3\text{-CHDC})_4]\cdot H_2O$, **II**, $Pb_2(1,3\text{-CHDC})_2(H_2O)$, **III**, and $(OPb_3)(1,3\text{-CHDC})_2$, **IV**, have been prepared and characterized. Of these, **I** and **II** have layered structures while **III** and **IV** have three-dimensional structures. **I**–**III** are hybrid structures possessing extended inorganic connectivity in one or two-dimensions (I^n, $n = 1$ or 2) involving infinite Pb–O–Pb linkages along with zero or one-dimensional organic connectivity (O^m, $m = 0$ or 1). **I** contains two types of layers with different connectivities (I^1O^1 and I^2O^0). **III** is a truly 3-D hybrid compound with I^2O^1 type connectivity. **IV** has three-dimensional organic connectivity (O^3) but no inorganic connectivity (I^0). The conformation of the CHDC anion is *e*,*e* in **I**–**III** and *a*,*e* in **IV**. In all these compounds, the lead atom has hemi- or holodirected coordination geometry.

Introduction

Besides aluminosilicates and phosphates, metal carboxylates form a wide variety of open framework structures.[1−3] Metal carboxylates have also enabled the design and synthesis of novel architectures, some of which exhibit useful properties such as sorption, catalysis, luminescence, and magnetism. Thus, Yaghi and co-workers[4] have used the zinc dicarboxylates to synthesize a MOF-5-based *reticular* family of materials with low density and high capacity for hydrogen storage. Férey and co-workers[5] have reported trinuclear chromium cluster-based benzene di- and tricarboxyaltes with unit cell volumes going up to 700 000 Å^3. Of particular interest are the inorganic−organic hybrid compounds formed by metal carboxylates.[6−11] These hybrid compounds possess inorganic and organic connectivities of different dimensionalities. A classification has been provided recently on the basis of the dimensionality ($\boldsymbol{n}$,$\boldsymbol{m}$) of the inorganic ($\boldsymbol{I}$) and the organic ($\boldsymbol{O}$) connectivities ($\boldsymbol{I^nO^m}$).[11] According to this classification, simple molecular coordination compounds would be of the type $\boldsymbol{I^0O^0}$. Hybrid compounds with inorganic connectivity in one or more dimensions ($n > 0$) containing extended M−X−M (X = O, N, Cl, S) connectivity are known. The literature on metal benzenedicarboxylates shows that the 1,4-benzenedicarboxylates generally form three-dimensional hybrid structures while the 1,2-dicarboxylates favor two-dimensional hybrid structures, both with extended M−O−M linkages.[12−14] Recent studies of cyclohexanedicarboxylates (CHDCs) suggests that both 1,2- and 1,4-CHDCs form hybrid compounds with extended M−O−M connectivity, with the 1,2-CHDCs generally possessing layered structures.[15−23] To our knowledge there are not many

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Table 1. Synthetic Conditions for the 1,3-CHDCs, **I**−**IV**

compd no.	formula	composition (mol ratio)				temp, °C	yield based on Pb, %
		$Pb(NO_3)_2$	1,3-H_2CHDC	NaOH (5 M soln)	water		
I	$Pb(1,3\text{-}C_8H_{10}O_4)(H_2O)$	0.330 g, 1 mM (2)	0.088 g, 0.5 mM (1)	1 mM, 0.2 mL (2)	278 mM, 5 mL	150	38
II	$[(OPb_4)_2(1,3\text{-}C_8H_{10}O_4)_4(C_2O_4)(OH)_2]\cdot H_2O$	0.330 g, 1 mM (2)	0.088 g, 0.5 mM (1)	1.5 mM, 0.3 mL (3)	278 mM, 5 mL	200	31
III	$Pb_2(1,3\text{-}C_8H_{10}O_4)_2(H_2O)$	0.330 g, 1 mM (2)	0.088 g, 0.5 mM (1)	0.5 mM, 0.1 mL (1)	278 mM, 5 mL	200	36
IV	$OPb_3(1,3\text{-}C_8H_{10}O_4)_2$	0.330 g, 1 mM (2)	0.088 g, 0.5 mM (1)	1.5 mM, 0.3 mL (3)	278 mM, 5 mL	180	39

investigations of the 1,3-CHDC compounds.[22−24] We have, therefore, carried out an investigation on the synthesis and characterization of 1,3-CHDC compounds and indeed found that they form hybrid organic−inorganic compounds with extended inorganic connectivity of varied dimensions. We also find that the CHDC anion in these compounds can be in the equatorial−equatorial (*e*,*e*) as well as the axial−equatorial (*a*,*e*) conformations.[25] The lead atoms in the 1,3-CHDC compounds exhibit hemi- as well as holodirected coordination geometry.

Experimental Section

Materials. $Pb(NO_3)_2$ (Qualigens, Mumbai, India, 99%), 1,3-cyclohexanedicarboxylicacid, 1,3-H_2CHDC [Aldrich, 98%, mixture of cis and trans (anti) compounds], and NaOH (Merck, Mumbai, India, 99%) of high purity and double distilled water were used for the synthesis.

Synthesis and Characterization. The Pb 1,3-CHDCs were synthesized under hydrothermal conditions by heating homogenized reaction mixtures in a 23 mL PTFE-lined bomb in the temperature range 150−200 °C for 72 h under autogenous pressure. The pH of the starting reaction mixture was generally in the range 5−6. The pH after the reaction did not show appreciable change. The products of the hydrothermal reactions were vacuum-filtered and dried under ambient conditions. The starting compositions and synthetic conditions for the different compounds synthesized by us are given in Table 1. All the compounds were obtained as single phase, except **II**, whose crystals were obtained admixed with small quantities of polycrystalline **I** and **IV** powder. The crystals were separated under a polarizing microscope and used for all the characterization. The yield based on the lead was generally grater than 30%.

Elemental analyses of **I**−**IV** were satisfactory. Anal. Calcd for **I** ($C_{16}H_{24}Pb_2O_{10}$): C, 24.29; H, 3.04. Found: C, 24.22; H, 3.12. Calcd for **II** ($C_{34}H_{44}Pb_8O_{25}$): C, 16.26; H, 1.75. Found: C, 16.33; H, 1.69. Calcd for **III** ($C_{16}H_{22}Pb_2O_9$): C, 24.86; H, 2.85. Found: C, 24.80; H, 2.91. Calcd for **IV** ($C_{16}H_{20}Pb_3O_9$): C, 19.64; H, 2.05. Found: C, 19.71; H, 2.01.

Powder XRD patterns of the products were recorded using Cu Kα radiation (Rich-Seifert, 3000TT). The patterns agreed with those calculated for single-crystal structure determination. Thermogravimetric analysis (TGA) was carried out (Metler-Toledo) in an oxygen atmosphere (flow rate = 50 mL/min) in the temperature range 25−800 °C (heating rate = 5 °C/min).

Infrared (IR) spectra of KBr pellets of **I**−**IV** were recorded in the mid-IR region (Bruker IFS-66v). Compounds **I**−**IV** show characteristic bands for the functional groups.[26−28] The bands around 1550 and 1400 cm^{-1} are assigned to carboxylate $\nu_{asC=O}$ and $\nu_{sC=O}$ stretching, and the absence of a band at 1700 cm^{-1} confirms the binding of carboxylate group to the lead cation. The bands at 3558 (ν_{asO-H}), 3470 (ν_{sO-H}), 1245 $(\delta_{O-H})_{in-plane}$, and 616 cm^{-1} $(\delta_{O-H})_{out-of-plane}$ indicate the presence of hydroxyl groups and their ligation to the lead cation in **II**.

Thermogravimetric analyses for **I**−**IV** are as follows. For **I**, the first weight loss of 4.96% (calcd 4.55%) occurred around 180 °C and the second weight loss of 43.59% (calcd 43.02%) was in the 280−470 °C range. For **II**, the total weight loss of 33.2% (calcd 32.69%) occurred in the 130−450 °C range. For **III**, the first weight loss of 2.46% (calcd 2.33%) occurred around 150 °C and the second weight loss of 31.63% (calcd 31.07%) was in the 300−450 °C range. For **IV**, the total weight loss of 35.0% (calcd 34.78%) occurred in the 250−425 °C range. The total weight loss matches very well with the loss of CO_2, with (**I**−**III**) or without (**IV**) H_2O, and the formation of PbO (PDF No. 00-004-0561) in all the cases.

A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued to a thin glass fiber. Crystal structure determination by X-ray diffraction was performed on a Bruker-Nonius diffractometer with Kappa geometry attached with an APEX-II CCD detector and a graphite monochromator for the X-ray source (Mo Kα radiation, $\lambda = 0.710\,73$ Å) operating at 50 kV and 30 mA. An empirical absorption correction based on symmetry-equivalent reflections was applied using the SADABS program.[29] The structure was solved and refined using the SHELXTL-PLUS suite of programs.[30] For the final refinement the hydrogen atoms on the cyclohexane rings were placed geometrically and held in the riding mode. The hydrogen atoms on the water molecules were located in the difference Fourier map, and the O−H distance was constrained to 0.85 Å. Final refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for the hydrogen atoms. All the hydrogen atoms were included in the final refinement, except the hydrogen atoms on O(100) in **III**; the hydrogen atoms of this water molecule could not be located in the difference Fourier map. Some of the carbon atoms of the CHDC anion (C14−C17) were disordered, so the C−C distances involving

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Table 2. Crystal Data and Structure Refinement Parameters for the 1,3-CHDCs, **I**−**IV**

param	**I**	**II**	**III**	**IV**
empirical formula	$C_{16}H_{24}Pb_2O_{10}$	$C_{34}H_{44}Pb_8O_{25}$	$C_{16}H_{22}Pb_2O_9$	$C_{16}H_{20}Pb_3O_9$
fw	790.73	2510.20	772.74	977.89
cryst system	orthorhombic	monoclinic	triclinic	monoclinic
space group	*Pbca* (No. 61)	*C*2/*m* (No. 12)	$P\bar{1}$ (No. 2)	*C*2/*c* (No. 12)
a/Å	14.0078(3)	8.1086(2)	9.1442(5)	16.3279(6)
b/Å	8.8268(2)	29.9463(8)	9.7893(5)	13.6071(5)
c/Å	31.6165(7)	11.5853(3)	11.0738(6)	18.8434(6)
α/deg	90	90	92.922(3)	90
β/deg	90	103.0100(10)	97.147(2)	112.182(2)
γ/deg	90	90	107.695(2)	90
V/Å^3	3909.19(15)	2740.96(12)	932.89(9)	3876.7(2)
Z	8	2	2	8
D(calc)/g cm^{-3}	2.687	3.041	2.751	3.351
μ/mm^{-1}	17.257	24.548	18.071	26.041
tot. data collcd	50 632	19 662	17 716	31 818
unique data	3339	2407	3343	3347
obsd data [$I > 2\sigma(I)$]	3032	2201	3035	2752
R_{merg}	0.0201	0.0214	0.0303	0.0308
goodness of fit	1.308	1.218	1.149	1.071
R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0282^a$ $wR_2 = 0.0688^b$	$R_1 = 0.0344^a$ $wR_2 = 0.1042^b$	$R_1 = 0.0300^a$ $wR_2 = 0.0821^b$	$R_1 = 0.0341^a$ $wR_2 = 0.0683^b$
R indexes (all data)	$R_1 = 0.0321^a$ $wR_2 = 0.0701^b$	$R_1 = 0.0418^a$ $wR_2 = 0.1232^b$	$R_1 = 0.0344^a$ $wR_2 = 0.0930^b$	$R_1 = 0.0496^a$ $wR_2 = 0.0748^b$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, and $P = [\max(F_o^2,0) + 2(F_c)^2]/3$, where $a = 0.0182$, $b = 38.2775$ for **I**, $a = 0.0658$, $b = 72.9605$ for **II**, $a = 0.0467$, $b = 6.7206$ for **III**, and $a = 0.0658$, $b = 72.9605$ for **IV**.

these atoms were constrained to 1.550 Å. Details of the structure solution and final refinements for the compounds **I**−**IV** are given in Table 2.

Results and Discussion

Structures of Lead 1,3-Cyclohexanedicarboxylates. Four different lead 1,3-cyclohexanedicarboxylates, **I**−**IV**, have been synthesized and characterized. Of these, **I** and **II** possess layered structures while **III** and **IV** have three-dimensional structures. The 1,3-CHDC anions in these compounds exhibit seven different coordinational modes with different connectivities and conformations as shown in Figure 1. The lead cations are in either hemi- or holodirected geometry with the coordination numbers in the range 5−8 (Figure 2). We shall now discuss the structures of these different compounds.

Two-Dimensional Pb(1,3-CHDC)(H_2O). The 1,3-cyclohexanedicarboxylate Pb(1,3-CHDC)(H_2O), **I**, has a two-dimensional structure with an asymmetric unit of 28 non-hydrogen atoms (Figure 3a). There are two crystallographically distinct Pb^{2+} ions Pb(1) and Pb(2), two CHDC anions, and two terminal water molecules in the asymmetric unit. The anions exhibit two types of coordination modes with acid-1 having (1121) connectivity (Figure 1a) and acid-2 having (1212) connectivity[31] (Figure 1b). Both of them are in the anti, *e*,*e* conformation with torsional angles in the 172.33−172.66° range. Pb(1) is hemidirected and five-coordinated by oxygen atoms (PbO_5) from four different CHDC anions (acid-1) (Figure 2a). Two of the oxygens have μ_3 connections linking Pb(1) with two other Pb(1) atoms. Thus, Pb(1)O_5 polyhedra share corners with each other forming an infinite one-dimensional Pb−O−Pb chain. The chains are further connected by CHDC anions (acid-1), each anion binding to four different Pb^{2+} cations of adjacent Pb−O−Pb chains to form an infinite two-dimensional layer structure. This gives rise to a I^1O^1 type hybrid structure as per the recent classification[11] (Figure 3b). The active lone pair of the hemidirected Pb(1)O_5 polyhedra projects on both sides of the layer (layer-1) as in Figure 4. The Pb−O bond lengths are in the 2.388−2.805 Å range.

Pb(2) is eight-coordinated by oxygen atoms (PbO_8) and has a holodirected geometry (Figure 2a). Among the eight oxygens of (PbO_8), two are from two different terminal water molecules and the other six from four different CHDC anions (acid-2). Four among these six oxygens have μ_3 connections linking Pb(2) with three other Pb(2)'s. Thus, each Pb(2)O_8 polyhedron shares an edge with another Pb(2)O_8, forming a dimer of Pb_2O_{14}. The dimers are further connected to each other by sharing a corner each with four dimers, forming an infinite two-dimensional Pb−O−Pb layer with a (4,4) square lattice and a hybrid connectivity of the type I^2O^0 (Figure 3c). The CHDC anions (acid-4) decorate both sides of the layer (layer-2) as in Figure 4. The Pb−O bond lengths are in the 2.453−2.834 Å range. There is no apparent hydrogen bonding in **I**, and van der Waals interactions between layers appear to be the main stabilizing factor (Figure 4).

Two-Dimensional $[(OPb_4)_2(OH)_2(C_2O_4)(1,3\text{-CHDC})_4]\cdot H_2O$. We have been able to obtain a lead oxalate−cyclohexanedicarboxylate, $[(OPb_4)_2(OH)_2(C_2O_4)(1,3\text{-CHDC})_4]\cdot H_2O$, **II**, where the oxalate moiety was generated in situ from the 1,3-CHDC under the hydrothermal synthesis. Similar cases, where the ligands are formed in situ during the synthesis, have been reported in the literature.[32−34] The formation of the oxalate in the synthesis of **II** is rather

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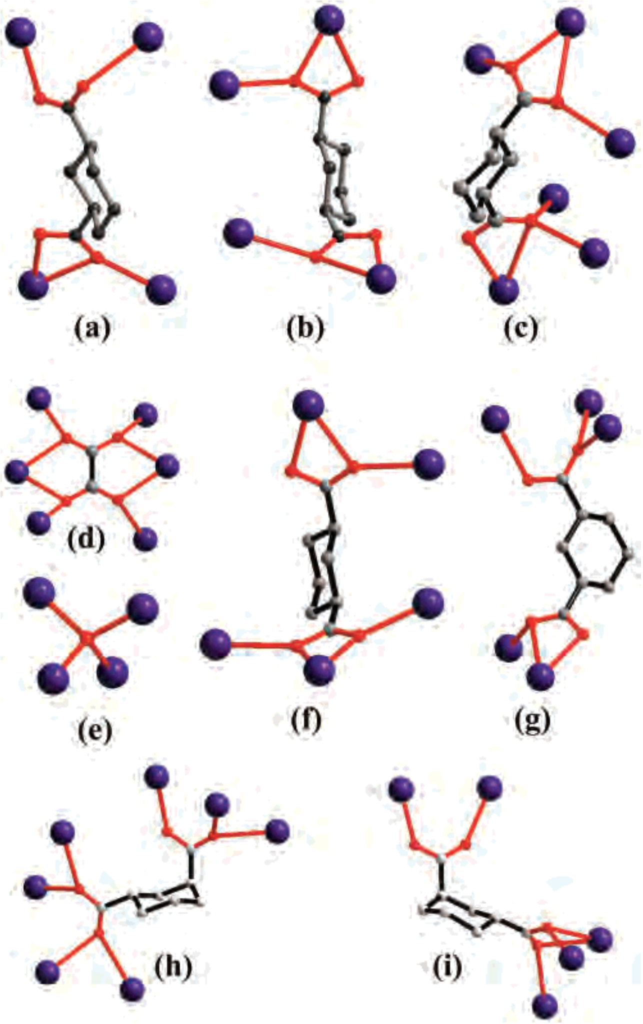

Figure 1. Coordination modes of the 1,3-CHeDC, oxalate, and oxo anions in **I**−**IV**.

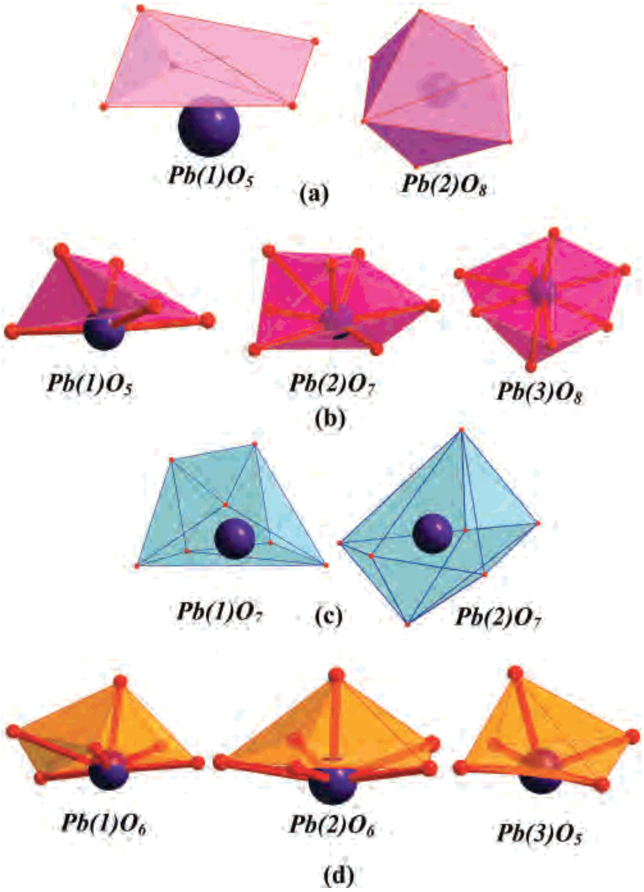

Figure 2. PbO_n ($n = 5-8$) polyhedra showing the coordination geometry of lead atoms.

unusual. This can happen if 1,3-H_2CHDC undergoes an oxidative decarboxylation to produce cyclohexene or cyclohexadiene. Cyclic olefins in the gas phase are known to produce oxalic acid on oxidation at high temperatures.[35−37]

II has a two-dimensional structure with an asymmetric unit of 16.75 non-hydrogen atoms (Figure 5a). The Pb^{2+} cations are in three crystallographically distinct positions with Pb(1) and Pb(3) landing with 0.5 occupancies in 4*f* and 4*h* special positions, respectively, and Pb(2) with a full occupancy. One CHDC anion, one-quarter of the oxalate anion (with C at 4*h*), one hydroxyl anion (with the O at 4*f*), one independent oxo dianion (at 4*f*), and one-quarter of a lattice water molecule (at 2*a*) are also in the asymmetric unit. Three of the four anions are shown in Figure 1c−e. The CHDC anion in the anti, *e*,*e* conformation with a torsional angle of 176.74(2)° has (2223) connectivity and binds to six Pb^{2+} cations [three Pb(2) and three Pb(3)]. The oxalate anion has (2222) connectivity and binds to six Pb^{2+} cations [two Pb(1) and four Pb(2)]. The independent oxo dianion binds to four Pb^{2+} cations [two Pb(1) and two Pb(2)] to form an OPb_4 tetrahedron. The hydroxyl anion binds to three Pb^{2+} cations [one Pb(1) and two Pb(2)].

Pb(1) is hemidirected and coordinated by five oxygen atoms (PbO_5) (Figure 2b). Among the five oxygens of Pb(1)O_5, two with μ_3 connectivity are from a single oxalate anion, another two with μ_4 connectivity are from two different oxo dianions, and the fifth one with a μ_4 connectivity is from the hydroxyl anion. Thus, the oxygens with μ_3 and μ_4 connections link Pb(1) with two other Pb(1) atoms by sharing edges and two different Pb(2) atoms by sharing edges. The Pb−O bond lengths are in the 2.314−2.635 Å range.

Pb(2) is slightly hemidirected and coordinated by seven oxygen atoms (PbO_7) (Figure 2b). Among the seven oxygens of Pb(2)O_7, the oxo and the hydroxyl anions have μ_4 connectivity; the other one with μ_3 connectivity is from the oxalate anion. The remaining four (one with monodentate, one with μ_3, and two with μ_4 connectivity) are from three different CHDC anions. These oxygens link Pb(2) with two Pb(2) and two Pb(1) atoms, by sharing edges. They also connect Pb(2) with two Pb(3) atoms, by sharing a face each. The Pb−O bond lengths are in the 2.459−2.919 Å range.

Pb(3) is holodirected and coordinated by eight oxygen atoms (PbO_8) (Figure 2b). All the eight oxygens are from

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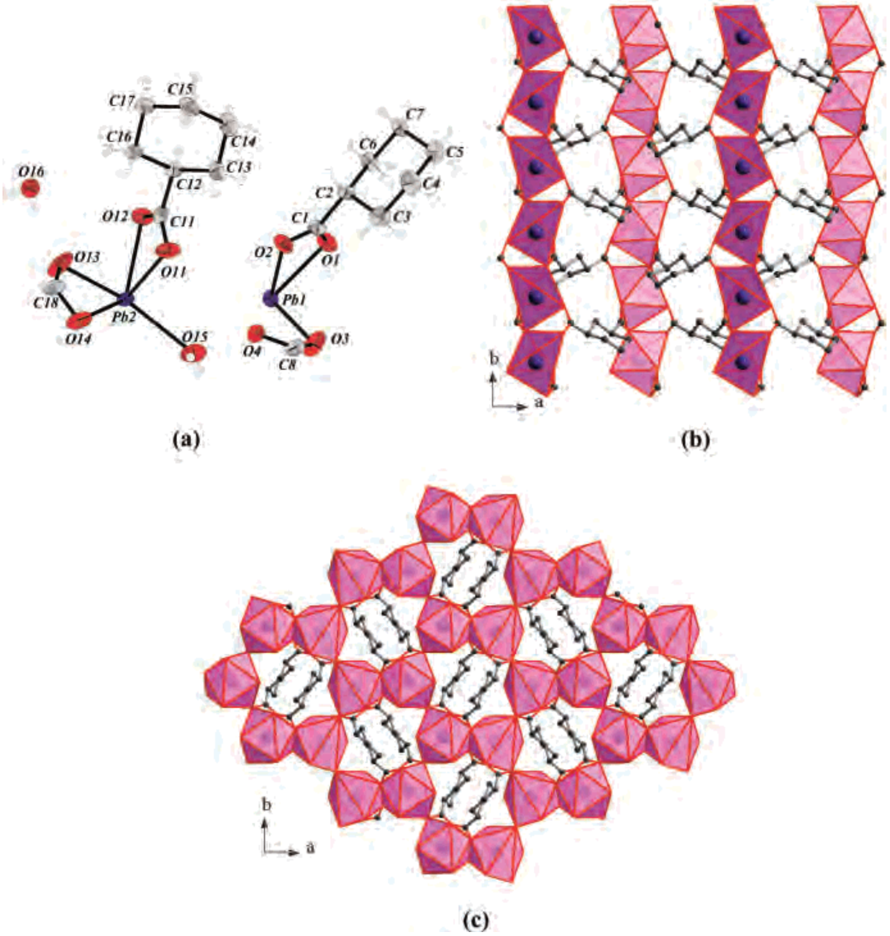

Figure 3. (a) ORTEP plot of **I**. Thermal ellipsoids are shown at 50% probability. Views are shown of the layers and the infinite Pb−O−Pb linkages in (b) layer-1 and (c) layer-2 of Pb(1,3-CHDC)(H_2O), **I**.

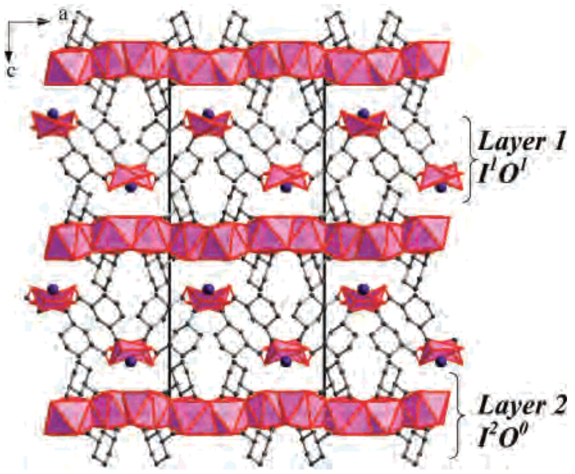

Figure 4. Packing arrangement in Pb(1,3-CHDC)(H_2O), **I** (viewed along the *b*-axis).

six different CHDC anions. Among the eight oxygens, two have μ_3 connectivity and the other two μ_4 connectivity. These oxygens link Pb(3) with two other Pb(3) atoms, by sharing edges, and with two different Pb(2) atoms, by sharing faces. The Pb−O bond lengths are in the 2.583−2.905 Å range. These connectivities lead to the formation of a secondary building unit (SBU) of the composition $Pb_8(OH)_2O_{26}$, which includes two edge-shared OPb_4 tetrahedra and two hydroxyl groups (Figure 5b). The SBU is made up of two $Pb(1)O_5$, four $Pb(2)O_7$, and two $Pb(3)O_8$ polyhedra. The oxalate anion connects the adjacent SBUs to form an infinite 1-D chain. Each SBU is connected to four other SBUs, leading to the formation of a (4,4) square lattice with infinite two-dimensional Pb−O−Pb connectivity (***I^2O^0***) (Figure 5c). The CHDC anions (acid-4) decorate both sides of the layer, and the lattice water molecule resides in the 1-D channel (7.1 Å × 3.0 Å) between the layers (Figure 6). The water molecules are H-bonded to the hydroxyl groups projecting in the channel. Platon-Solv analysis showed 17.2% of the unit cell volume to be solvent accessible.[38,39]

Three-Dimensional Pb_2(1,3-CHDC)$_2$(H_2O). The 1,3-cyclohexanedicarboxylate Pb_2(1,3-CHDC)$_2$(H_2O), **III**, has a three-dimensional structure with an asymmetric unit of 27 non-hydrogen atoms (Figure 7a). There are two crystallographically distinct Pb^{2+} ions, two CHDC anions, and one terminal water molecule in the asymmetric unit. On the basis of the coordination modes, the anions can be classified into two types: (a) acid-1 with (1222) connectivity (Figure 1f); (b) acid-2 with (1221) connectivity (Figure 1g). Both of them

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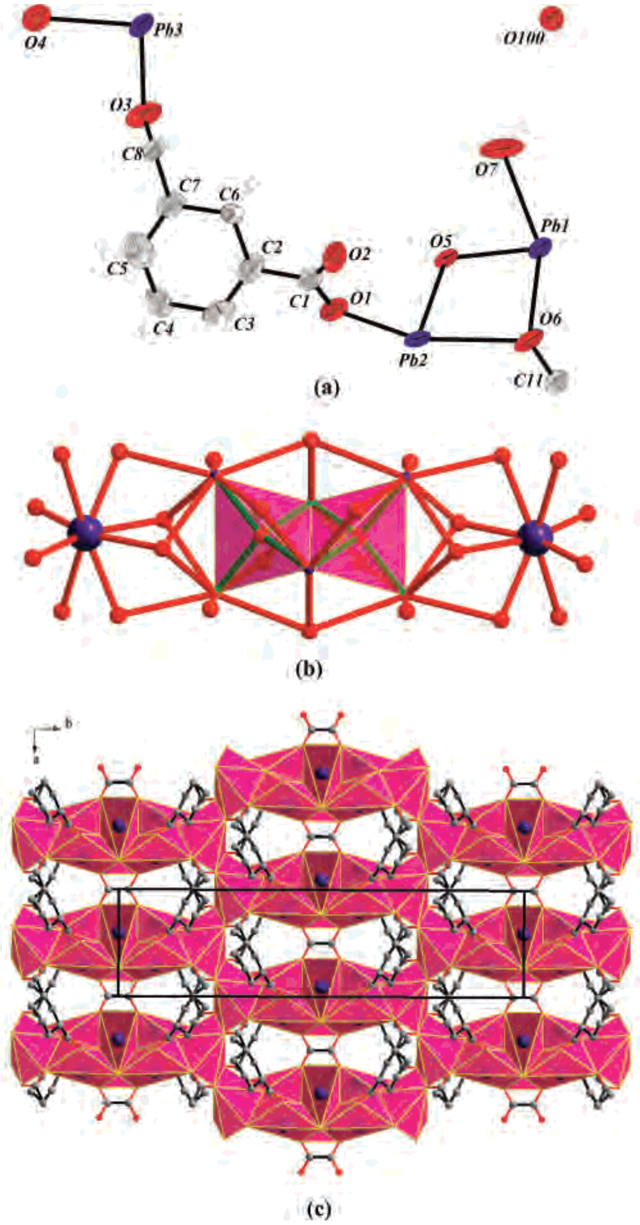


Figure 5. (a) ORTEP plot of **II**. Thermal ellipsoids are shown at 50% probability. Also shown are (b) $Pb_8(OH)_2O_{26}$ secondary building unit and (c) a view of the layer and the infinite Pb−O−Pb linkages in $[(OPb_4)_2(OH)_2(C_2O_4)(1,3\text{-CHDC})_4]\cdot H_2O$, **II**.

are in the anti (*e*,*e*) conformation with torsional angles in the 168.9−180° range. Pb(1) and Pb(2) are both seven-coordinated as PbO_7 units (Figure 2c). Among the seven oxygens of $Pb(1)O_7$, one is from the terminal water molecule and six are from four different CHDC anions (three acid-1 and one acid-2). Four of these oxygens have μ_3 connections linking one Pb(1) with another Pb(1) through two oxygen atoms and with two different Pb(2) atoms through two oxygens. Thus, the $Pb(1)O_7$ polyhedra share edges with each other forming a dimeric $Pb(1)_2O_{13}$ unit. The Pb−O bond lengths are in the 2.418−2.899 Å range.

The seven oxygens of $Pb(2)O_7$ come from six different CHDC anions (two acid-1 and four acid-2). Six of these oxygens have μ_3 connections linking Pb(2) with two different Pb(1) through two oxygen atoms and with two other Pb(2) through four oxygen atoms. Thus, each $Pb(2)O_7$ polyhedron shares an edge with another forming a dimeric $Pb(2)_2O_{13}$ unit. The dimers are connected to each other through two μ_3 oxygens, forming an infinite one-dimensional Pb−O−Pb chain. The chains are connected by the $Pb(1)_2O_{13}$ dimer into a two-dimensional Pb−O−Pb layer (Figure 7c). The layers can also be viewed as a (4,4) square lattice consisting of tetranuclear secondary building units (SBU) of Pb_4O_{18} with two Pb(1) and Pb(2) each (Figure 7b). Acid-1 which connects

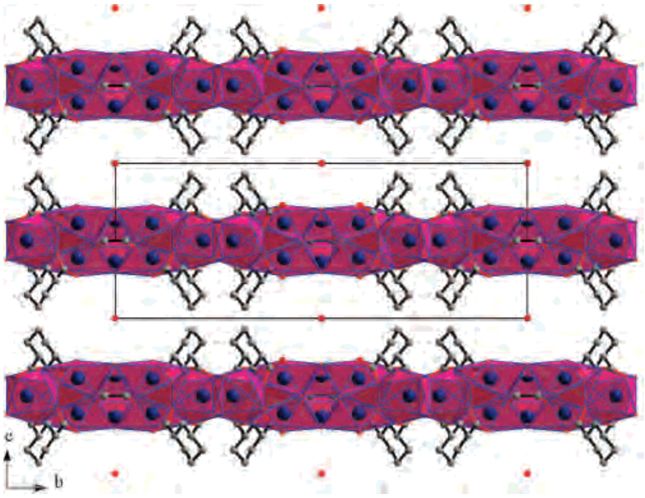


Figure 6. (a) Packing arrangement in $[(OPb_4)_2(OH)_2(C_2O_4)(1,3\text{-CHDC})_4]\cdot H_2O$, **II** (viewed along the *a*-axis), and (b) view of the pores (lattice water residing in the pore).

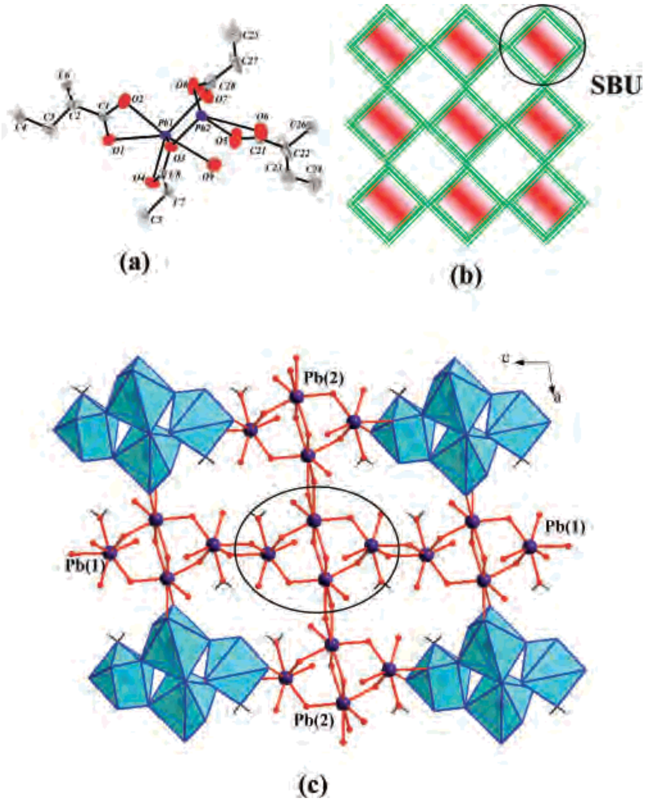


Figure 7. (a) ORTEP plot of **III**. Thermal ellipsoids are shown at 50% probability. Also shown are (b) a schematic of the (4,4) square lattice with the SBUs and (c) a view of the layer with infinite Pb−O−Pb linkages in $[(OPb_4)_2(OH)_2(C_2O_4)(1,3\text{-CHDC})_4]\cdot H_2O$, **II**.

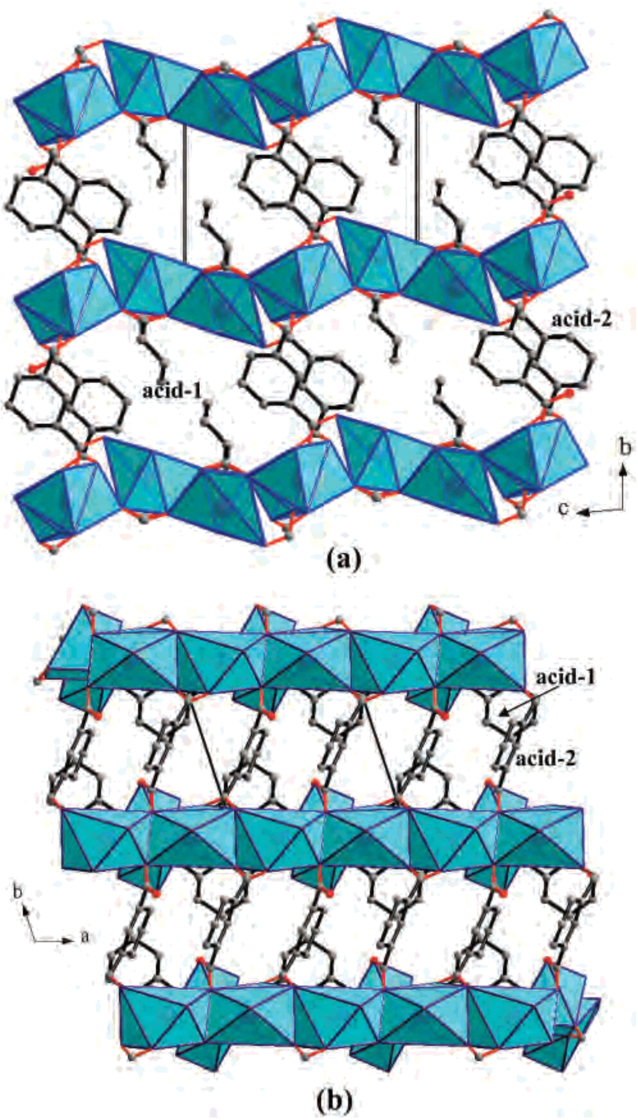


Figure 8. 3D-structure of Pb$_2$(1,3-CHDC)$_2$(H$_2$O), **III**, (a) viewed along the *a*-axis and (b) viewed along the *c*-axis.

the Pb cations within the layer (intralayer) decorates both sides of the layer. The layers are further connected by acid-2, forming a three-dimensional structure with the ***I*^{2}*O*^{1}** type (Figure 8). The Pb−O bond lengths are in the 2.450−2.685 Å range.

Three-Dimensional (OPb$_3$)(1,3-CHDC)$_2$. (OPb$_3$)(1,3-CHDC)$_2$, **IV**, has a three-dimensional structure without any inorganic connectivity (***I*^{0}*O*^{3}**). It has an asymmetric unit with 28 non-hydrogen atoms (Figure 9a). There are three Pb^{2+} cations in three crystallographically distinct positions, two CHDC anions, and one independent oxo dianion in the asymmetric unit. Both the CHDC anions (acid-1 and acid-2, Figure 1h,i) are in the cis (*a*,*e*) conformation with the torsional angle of 120.95(1) and 99.31(1)°. They have (1222) and (1122) connectivities, respectively. Acid-1 binds to seven Pb^{2+} cations [two Pb(1), three Pb(2), and two Pb(3)], and acid-2 binds to five Pb^{2+} cations [one Pb(1), two Pb(2), and two Pb(3)]. The independent oxo dianion binds to four Pb^{2+} cations [two Pb(1), one Pb(2), and one Pb(3)] to form a OPb$_4$ tetrahedron.

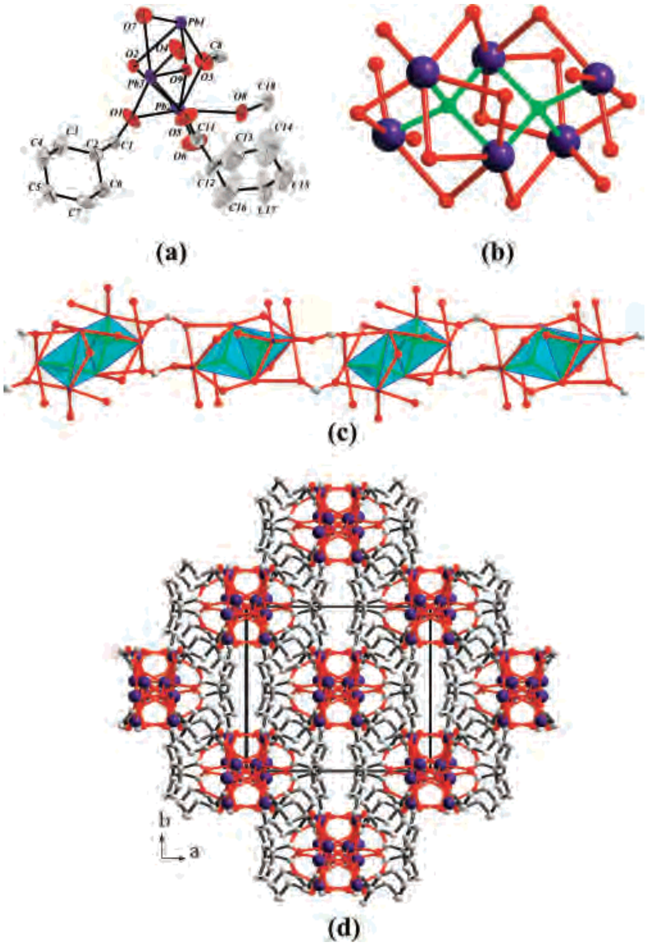


Figure 9. (a) ORTEP plot of **IV**. Thermal ellipsoids are shown at 50% probability. Also shown are (b) the Pb$_6$O$_{18}$ secondary building unit, (c) the chain formed by the connectivity of SBUs through the carboxylate, and (d) the 3D-structure of (OPb$_3$)(1,3-CHDC)$_2$, **IV**, viewed along the *c*-axis.

Pb(1) is hemidirected and coordinated by six oxygen atoms (PbO$_6$) (Figure 2d). Among the six oxygens of Pb(1)O$_6$, four with μ_3 connectivity are from three different CHDC anions and the remaining two with μ_4 connectivity are from two different oxo dianions. These oxygen atoms link Pb(1) with an another Pb(1) by sharing an edge, with two different Pb(2) atoms by sharing an edge with one and by sharing a face with another, and with two different Pb(3) by sharing a corner to one and by sharing an edge to another. The Pb−O bond lengths are in the 2.286−2.871 Å range.

Pb(2) is also hemidirected and coordinated by six oxygen atoms (PbO$_6$) (Figure 2d). Among the six oxygens of Pb(2)O$_6$, one oxo anion has μ_4 connectivity. The remaining oxygens are from five different CHDC anions with one oxygen having μ_2 connectivity and other four with μ_3 connectivity. These oxygens link Pb(2) with two Pb(1) and also connect Pb(2) with one Pb(3) by edge sharing. The Pb−O bond lengths are in the 2.245−2.764 Å range.

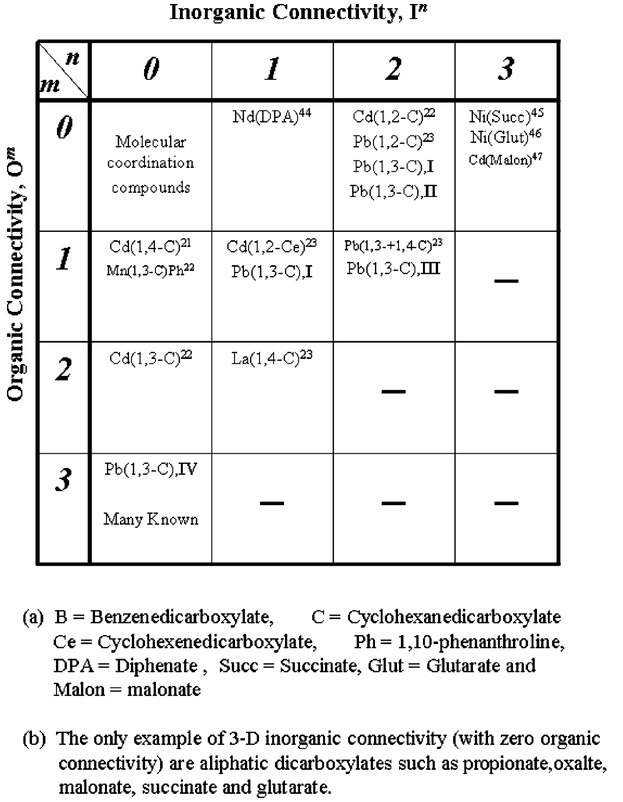
Pb(3) is also hemidirected but coordinated by five oxygen atoms (PbO$_5$) (Figure 2d). Among the six oxygens of Pb(2)O$_6$, one oxo anion is having μ_4 connectivity. The remaining four oxygens are from four different CHDC anions; two have μ_3 connectivity, and the other two have μ_2 connectivity. These oxygens link Pb(3) with two other Pb(1) and one Pb-

(2), by sharing an edge. The Pb−O bond lengths are in the 2.305−2.700 Å range. These connectivities lead to the formation of a secondary building unit (SBU) of Pb_6O_{18}, which includes two edge-shared OPb_4 tetrahedra (Figure 9b). The SBU is constructed by sharing $Pb(1)O_6$, $Pb(2)O_6$, and $Pb(3)O_5$ polyhedra. A carboxylate of acid-2 connects the adjacent SBUs to form an infinite 1-D chain (Figure 9c), and the chains get connected to four other adjacent chains by CHDC anions to form the infinite three-dimensional structure ($\boldsymbol{I^0O^3}$) (Figure 9d).

Coordination Geometry of Lead. The coordination geometry of the PbO_n polyhedra in Pb(II) compounds is hemidirected for low coordination numbers (2−5) and holodirected for high coordination numbers (9, 10). For intermediate coordination numbers (6−8), either type of stereochemistry is found.[40,41] Ab initio molecular orbital studies of gas-phase Pb(II) complexes show that a hemidirected geometry occurs if the ligand coordination number is low, the ligands are hard, and there are attractive interactions between the ligands.[42,43] In such cases, the lone pair orbital has p character and fewer electrons are transferred from the ligands to the bonding orbitals of Pb(II), giving rise to more ionic bonds. Holodirected geometry occurs when the coordination number is high and the ligands are soft and bulky or show strong interligand repulsion. The lone pair orbital has negligible p character when the geometry is holodirected, and the bonds are more covalent than in the hemidirected structures. The Pb(II) cations in **I** exhibit both hemi- and holodirected geometry with coordination numbers 5 and 8, respectively. The Pb(II) cations in **II** also exhibit both types of geometry. $Pb(1)O_5$ and $Pb(2)O_7$ are hemidirected with coordination numbers 5 and 7, respectively, whereas $Pb(3)O_8$ is holodirected with coordination number 8. In **III**, seven-coordinated Pb(1) and Pb(2) show hemi- and holodirected geometry. The hemidirectness of $Pb(1)O_7$, though not very prominent, nevertheless may be due to the presence of the terminal water molecule and six carboxylate oxygens. The holodirected $Pb(2)O_7$ has only carboxylate oxygens. All the Pb(II) cations in **IV** exhibit only hemidirected geometry with coordination numbers 6 and 5.

An examination of the inorganic and organic connectivities in these hybrid compounds would be in order. In Table 3, we have shown a matrix with organic and inorganic connectivities.[2,11] We show the range of possibilities in terms of the dimensionality of the organic and the inorganic connectivities. The overall dimensionality of the structure is then represented with the notation $\boldsymbol{I^nO^m}$, the sum of the exponents, $\boldsymbol{m + n}$, giving the overall dimensionality of the structure. The entire family of molecular coordination compounds are contained within a single box ($\boldsymbol{I^0O^0}$) in Table 3 {i.e., both M−L−M (m) and inorganic connectivity (n) = 0}. The remaining three boxes in the first column represent the coordination polymers with overall dimensionality 1−3. The three boxes in the second column represent hybrid compounds with one-dimensional inorganic connectivity ($\boldsymbol{I^1}$) and with an overall dimensionality between 1 and 3. The two boxes in the third column represent hybrid compounds with two-dimensional inorganic connectivity ($\boldsymbol{I^2}$) and with the overall dimensionality of 2 or 3. The first box in the fourth column represents a rare class of hybrid compound ($\boldsymbol{I^3O^0}$) with a three-dimensional inorganic connectivity ($\boldsymbol{I^3}$) and with the overall dimensionality of 3. There are examples of all of these classes of hybrid materials. Currently there are no examples for the empty boxes in the bottom right part of the Table 3. As seen from the table, there are many dicarboxylates with 1-, 2-, and 3-D organic connectivity and with zero and 1-D inorganic connectivity.[22,23] There are very few compounds with 2- or 3-D inorganic connectivity.[45−47] Another notable observation is that all the three isomers (1,2-, 1,3-, and 1,4-) of cyclohehanedicarboxylic acids favor the formation of hybrid compounds, but the presence of secondary ligands and chelating amines such as 1,10-phenanthroline and 2,2-bipyridine decreases the overall dimensionality of the hybrid compounds.[21−23] In 1,3- and 1,4-CHDC compounds,[21] the cis (a,e) conformation also does not favor extended inorganic connectivity.

Table 3. Description of Hybrid Carboxylate Inorganic Connectivity, $\boldsymbol{I^n}$



Inorganic Connectivity, I^n

Organic Connectivity, O^m

m \ n	0	1	2	3
0	Molecular coordination compounds	Nd(DPA)[44]	Cd(1,2-C)[22] Pb(1,2-C)[23] Pb(1,3-C),I Pb(1,3-C),II	Ni(Succ)[45] Ni(Glut)[46] Cd(Malon)[47]
1	Cd(1,4-C)[21] Mn(1,3-C)Ph[22]	Cd(1,2-Ce)[23] Pb(1,3-C),I	Pb(1,3-+1,4-C)[23] Pb(1,3-C),III	—
2	Cd(1,3-C)[22]	La(1,4-C)[23]	—	—
3	Pb(1,3-C),IV Many Known	—	—	—

(a) B = Benzenedicarboxylate, C = Cyclohexanedicarboxylate Ce = Cyclohexenedicarboxylate, Ph = 1,10-phenanthroline, DPA = Diphenate , Succ = Succinate, Glut = Glutarate and Malon = malonate

(b) The only example of 3-D inorganic connectivity (with zero organic connectivity) are aliphatic dicarboxylates such as propionate,oxalte, malonate, succinate and glutarate.

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Concluding Remarks. We have successfully synthesized and characterized four 1,3-CHDCs of lead with layered and 3-dimensional structures. Compounds **I**−**III** contain 1,3-CHDC anions in the anti (*e*,*e*) conformation, exhibiting infinite Pb−O−Pb linkages, but compound **IV** with 1,3-CHDC anions in the cis (*a*,*e*) conformation does not have infinite Pb−O−Pb linkages. The lead atom is in either hemi- or holodirected in **I**−**IV**. The hybrid 1,3-CHDC compounds **I**−**III** show 1- or 2-D inorganic connectivity along with zero or 1-D organic connectivity. Compound **IV**, however, shows 3-D organic connectivity with no inorganic connectivity.

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Supporting Information Available: A crystallographic information file (CIF) for compounds **I**−**IV**. This material is available free of charge via the Internet at http://pubs.acs.org.

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