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Lamellar and Three-Dimensional Hybrid Compounds Formed by Cyclohexene- and Cyclohexanedicarboxylates of Pb, La, and Cd

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Abstract: To establish factors that determine the formation of three-dimensional hybrid structures of metal dicarboxylates involving metal–oxygen–metal linkages, we have investigated metal dicarboxylates derived from 1,2-cyclohexene as well as 1,2-, 1,3-, and 1,4-cyclohexane dicarboxylic acids. Thus, we have synthesized a 1,2-cyclohexenedicarboxylate of Cd, [Cd(1,2-CHeDC)(H_2O)] (**I**), a 1,2-cyclohexanedicarboxylate of Pb, [Pb(1,2-CHDC)] (**II**), and three 1,4-cyclohexanedicarboxylates of La [La_2(1,4-CHDC)$_3$(H_2O)$_4$] (**III**), [La_3(1,4-HCHDC)$_2$(1,4-CHDC)$_5$(H_2O)$_2$]$\cdot H_2O$ (**IV**) and [La_2(1,4-CHDC)$_3$(H_2O)]$\cdot 2.5\,H_2O$ (**V**) under hydrothermal conditions and determined their structures. A mixed dicarboxylate involving both 1,3- and 1,4-cyclohexenedicarboxylates of Pb, [Pb_3O(1,3-CHDC)(1,4-CHDC)]$\cdot 0.5\,H_2O$ (**VI**) and a 1,4-cyclohexanedicarboxylate of Pb, [Pb_6O_2(1,4-CHDC)$_3$(1,4-HCHDC)$_2$], have also been synthesized and characterized. While the 1,2-dicarboxylates have layered structures, the 1,4-dicarboxylates and the mixed dicarboxylates possess three-dimensional structures. Interestingly, both the 1,2 and 1,4-dicarboxylates are true hybrid compounds composed of infinite M-O-M linkages. The equatorial–equatorial (e,e) conformation is adopted commonly in all these compounds, although less stable conformations are encountered occasionally. The formation of the layered and the three-dimensional structures can be understood based on the relative disposition of the two carboxylic groups, the 1,4-isomer favoring the three-dimensional structure. Based on the results of the present study along with the available literature, we conclude that in order to obtain three-dimensional hybrid structures with metal–oxygen–metal networks, it appears necessary to make use of the 1,4-cyclohexanedicarboxylic acid.

Keywords: cadmium · carboxylate ligands · organic–inorganic hybrid composites · lanthanum · lead · solid-state structures

Introduction

Metal carboxylates have emerged as a large family of open framework materials,[1] next only to aluminosilicates[2] and phosphates.[3] Interest in metal carboxylate chemistry has enhanced recently, because of the increasing importance of hybrid inorganic–organic compounds with potential applications in separation, catalysis, and gas storage.[4] A few novel metal–organic framework and open-framework compounds with varying pore volumes and sorption properties have been reported in the last few years.[4,5] An inherent feature of such hybrid materials is that they combine the rigidity of the inorganic framework with the flexibility of the organic part. In view of these features, several groups are exploring various aspects of hybrid materials that employ metal carboxylates.[6–8] Studies of metal benzenedicarboxylates seem to suggest that the 1,4-dicarboxylates generally form three-dimensional structures while the 1,2-dicarboxylates favor metal–oxygen–metal (M-O-M) linkages.[7] Layered 1,2-cyclohexenedicarboxylates (CHeDCs) of Mn also possesses infinite M-O-M linkages.[8] In a recent study of 1,2-, 1,3-and 1,4-cyclohexanedicarboxylates (CHDCs) of Cd and Mn, infinite M-O-M linkages have been found to occur in the 1,2-CHDCs and three-dimensional structures in the 1,4-CHDCs.[9] In view of these observations, we considered it important to explore whether infinite M-O-M linkages are only characteristic of 1,2-CHDCs and CHeDCs, while three-dimensional structures are solely formed by the 1,4-CHDCs. More importantly, it was also our purpose to examine whether three-dimensional hybrid structures of CHDCs containing M-O-M linkages can be prepared. Another aspect of interest was the conformation adopted by the cyclohexane

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dicarboxylates. It is to be noted that in the 1,2-CHDCs, the *cis*-isomer has the equatorial–equatorial (ee) or the axial–equatorial (ae) conformations and the *trans*-isomer has the axial–axial (aa) conformation. However, in the 1,4-CHDCs, the *trans*-isomers have the ee or the aa conformations, while the *cis*-isomer has the ae conformation. Amongst all these conformers, the ee conformation is generally most stable.[10]

In this article, we report the results of our investigations on 1,2-CHeDCs as well as 1,2-, and 1,4-CHDCs of Pb, La, and Cd. The study confirms that the 1,2-CHeDCs and CHDCs generally possess layered structures and that the 1,4-CHDCs form three-dimensional structures. More importantly, M-O-M linkages occur not only in the layered 1,2-derivatives, but also in the three-dimensional 1,4-CHDCs derivatives. We also find that a three-dimensional mixed dicarboxylate of Pb involving both 1,3- and 1,4-CHDCs is composed of infinite M-O-M linkages.

Results and Discussion

Our investigations of the metal dicarboxylates prepared under hydrothermal conditions have yielded [Cd(1,2-CHeDC)(H_2O)] (**I**) and [Pb(1,2-CHDC)] (**II**), both with layered structures containing infinite M-O-M linkages. We have obtained three 1,4-CHDCs, [La_2(1,4-CHDC)$_3$(H_2O)$_4$] (**III**), [La_3(1,4-HCHDC)$_2$(1,4-CHDC)$_5$(H_2O)$_2$]·H_2O (**IV**), and [La_2(1,4-CHDC)$_3$(H_2O)]·2.5H_2O (**V**) with three-dimensional structures, possessing infinite M-O-M linkages. Interestingly, a mixed dicarboxylate, [Pb_3O(1,3-CHDC)(1,4-CHDC)]·0.5H_2O (**VI**) also possesses a three-dimensional structure with infinite M-O-M linkages. These dicarboxylates exhibit a variety of binding modes with the metal ions. In what follows, we discuss the structures of these compounds along with the ring conformations prevalent in them.

1,2-Cyclohexene and cyclohexane dicarboxylates: Cadmium 4-cyclohexene-1,2-dicarboxylate, [Cd(1,2-CHeDC)(H_2O)] (**I**), was obtained in two different polymorpic forms, **A** and **B**. In both the polymorphs, **I** has a two-dimensional layered structure made up of infinite one-dimensional Cd-O-Cd chains connected by the CHeDC anions. Both were crystallized in orthorhombic system, albeit in different space groups [*Pnc*2 (no.30) for **A** and *Pbcn* (no.60) for **B**]. The layered structures in **A** and **B** are similar and only differ in their packing arrangement.

The asymmetric units of both **A** and **B** have 14 non-hydrogen atoms. The Cd^{2+} ion is in a distorted octahedral environment, coordinated by six oxygen atoms. Five of the oxygen atoms are from three different CHeDC anions and the sixth one is from a water molecule. Among the five oxygen atoms of the carboxylate anions, two have μ_3 connections (connecting two metal centers and a carbon atom). Thus, each CdO_6 octahedron shares its corner with two other CdO_6 octahedra, forming an infinite Cd-O-Cd chain. The Cd−O bond lengths are in the range 2.208–2.403 Å. The CHeDC anions are in the *cis* ae conformation with a connectivity[11] of (1211) as shown in Figure 1 (top). The torsional angles are 70.41° and 67.96° in the **A** and **B** polymorphs, respectively. The Cd-O-Cd chains in **I** are further connected by the CHeDC anions through the carboxylate groups with (12) and (11) connectivity. Thus, each CHeDC anion connects two different chains, forming an infinite two-dimensional layered network as shown in Figure 1 (middle).

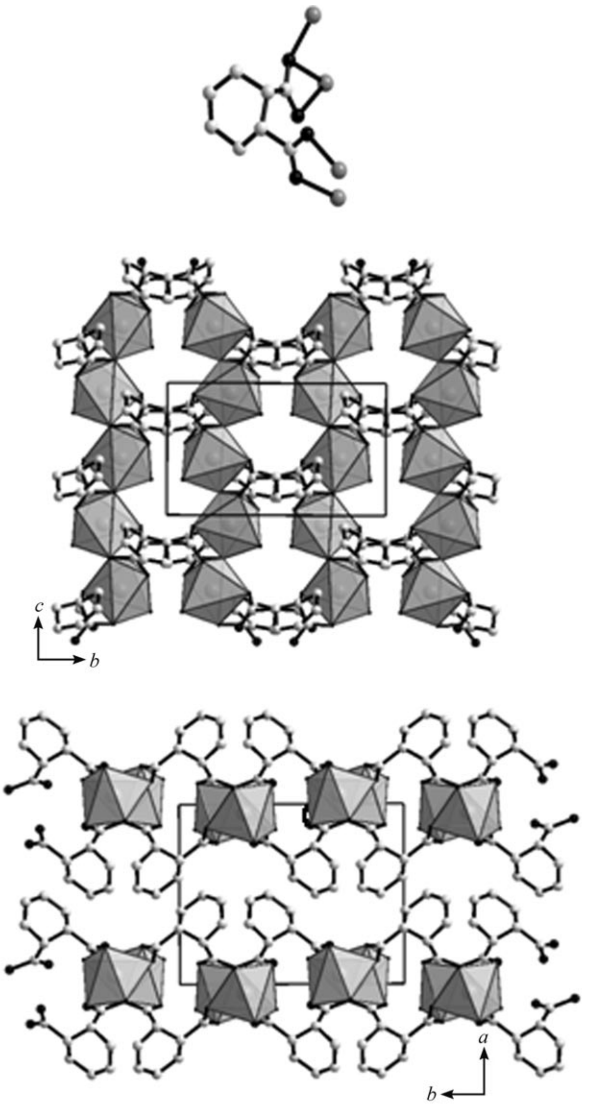

Figure 1. Coordination mode of the 1,2-CHeDC (top), layered structure viewed along the *a* axis (middle), and the packing arrangement viewed along the *c* axis (bottom) in compound **IA**.

Both the sides of the layer structure in **I** are decorated by the CHeDC rings (Figure 1, bottom). The rings on either side of a layer are oriented in the same direction. These layers are packed differently in the third dimension in the **A** and **B** polymorphs as shown in Figure 2. The orientation (along the *c* axis) of the projected rings of the two adjacent layers is the same in **A** (Figure 2, top), but is in opposite di-

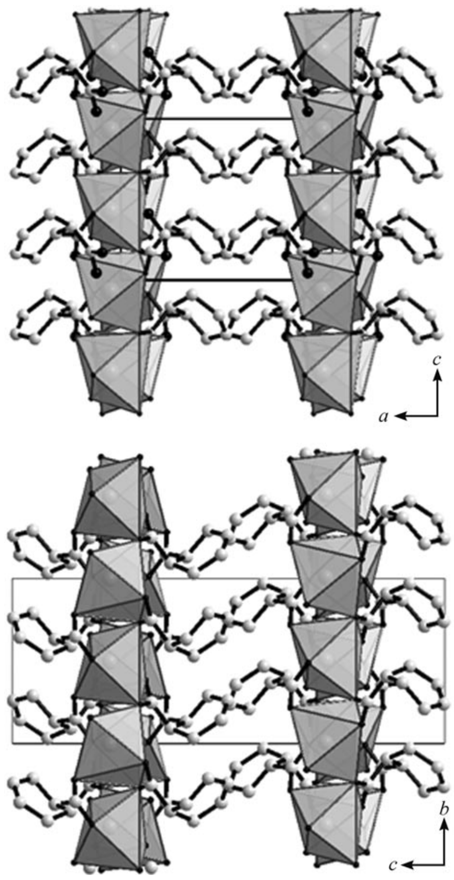

Figure 2. The packing arrangement in **IA** viewed along the *b* axis (top) and in **IB** viewed along the *a* axis (bottom).

rections (along the *b* axis) in **B** (Figure 2, bottom). This leads to different nearest ring–ring interactions in the two polymorphs. The nearest C···C distance between the adjacent layers is 1.683 Å in **A** and 3.7 Å for **B**. Thus, the heat of formation for **A** is more endothermic than that of **B** by 26 $kcal\,mol^{-1}$, as calculated by the AM1 level Gaussian 03 suite of programs.[12] The occurrence of polymorphism, involving different arrangements of packing, indicates that the layers are first formed through covalent connectivity, followed by packing through supramolecular interactions.

In the recent literature, two Mn 1,2-cyclohexenedicarboxylates, [Mn(1,2-CHeDC)(H_2O)] and [Mn_4(1,2-CHeDC)-(H_2O)]·0.3 H_2O have been reported.[8] Both these have layered structures and contain infinite M-O-M linkages. We find that the 1,2-CHeDc anions in these compounds are in the *trans* ee conformation unlike in **I**, which has the *cis* ae conformation.

Lead 1,2-cyclohexanedicarboxylate, [Pb(1,2-CHDC)] (**II**), is a layered compound with an asymmetric unit containing 26 non-hydrogen atoms. The two crystallographically distinct lead atoms sits at 4*e* position and coordinate to all the eight μ_3 oxygen atoms of the two crystallographically distinct CHDC anions with (2222) connectivity (Figure 3, top). The carboxylate groups are in the ee form, with torsion angles of 63.6 and 53.7°. Each PbO_8 polyhedron is connected to three polyhedra, by sharing an edge (through two μ_3-oxygen atoms) and two faces (through three μ_3-oxygen atoms), thus forming an infinite two-dimensional Pb-O-Pb (3,6-net) honeycomb layer (Figure 3, middle). Both sides of the honeycomb layers are decorated with the projection of CHDC rings. The projected CHDC rings on each side of the layer are of same crystallographic type. These layers are stacked, along the *a* axis, in such a way that the projected rings on the neighboring layers are of same type, but with opposite orientation (Figure 3, bottom) as in the case of **IB**. The nearest C···C distance between the two types of adjacent layers are 3.867 and 4.01 Å. The Pb−O bond lengths are in the range of 2.432–2.856 Å.

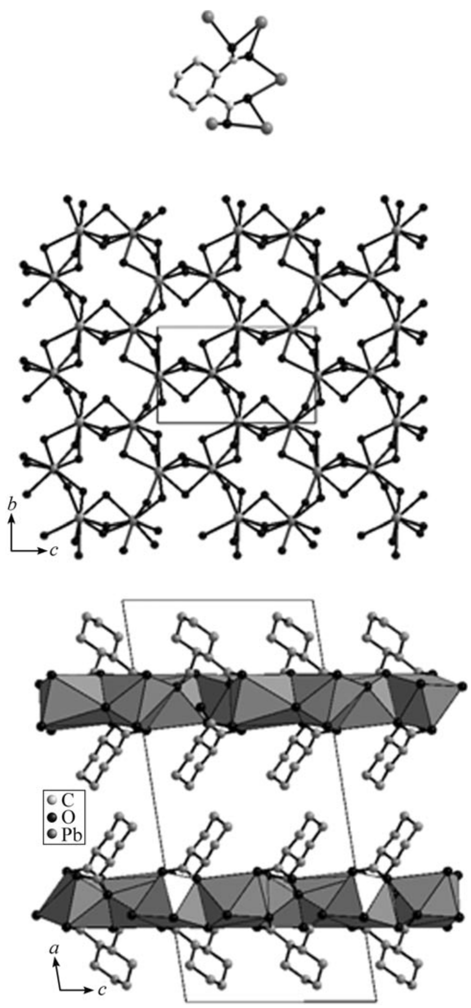

Figure 3. Coordination mode of the 1,2-CHDC (top), infinite Pb-O-Pb linkage (middle), and the packing arrangement (viewed along the *b* axis; bottom) in **II**.

Recently, a 1,2-cyclohexanedicarboxylate compound of Cd, [Cd(1,2-CHDC)] was synthesized and characterized.[9] This compound also has a layered structure, possessing infinite two-dimensional Cd-O-Cd linkages. The 1,2-CHDC anions in this compound are in the ee conformation just as in **II**.

1,4-Cyclohexanedicarboxylates: The lanthanum cyclohexanedicarboxylate, $[La_2(1,4\text{-}CHDC)_3(H_2O)_4]$ (**III**), has a three-dimensional structure with an asymmetric unit of 40 non-hydrogen atoms. There are two crystallographically distinct La^{3+} ions, three CHDC anions, and four terminal water molecules in the asymmetric unit. The anions can be categorized into four types, based on their coordination modes: 1) acid-1 (Figure 4a) 2) acid-2 (Figure 4b) 3) acid-3 (Figure 4c), and 4) acid-4 (Figure 4d). All of them are in the *trans* ee conformation with torsional angles in the 168.9–180° range. Both La(1) and La(2) are in a distorted tricapped trigonal-prism environments (LaO_9) with nine-coordinated oxygen atoms. Among the nine oxygen atoms, two are from two terminal water molecules and seven come from five different CHDC anions [three from acid-1, one from acid-2, and one from acid-4 for La(1); and one from acid-1, three from acid-2, and one from acid-3 for La(2)]. Thus, two LaO_9 polyhedra share an edge with each other forming the dimer La_2O_{17}. The dimers are connected to each other alternatively through a μ_3-oxygen atom, forming an infinite one-dimensional La-O-La chain. The chains are connected by acid-1 and acid-2 into a two-dimensional layer (Figure 4e). The layers are connected by acid-3 (which connects La(2) dimers between the layers), forming a three-dimensional structure (Figure 4f). The La-O-La chains between the layers are cross-linked by acid-4 (which connects La(1) dimers) forming a three-dimensional network (Figure 4f). The La–O bond lengths are in the range 2.501–2.755 Å. On heating at 200° C, **III** loses the coordinated water molecules and transforms to another crystalline compound. The dehydrated compound reverts back to the original structure of **III** upon exposure to water vapor as indicated by the powder diffraction patterns (Figure 5).

$[La_3(1,4\text{-}HCHDC)_2(1,4\text{-}CHDC)_5(H_2O)_2]\cdot H_2O$ (**IV**) also has a three-dimensional structure with an asymmetric unit of 73 non-hydrogen atoms. There are three crystallographically independent La^{3+} ions, 5.5 cyclohexanecarboxylate anions and one lattice water molecule in the asymmetric unit. The anions can be categorized into two classes based on the deprotonation level ($HCHDC^-$ and $CHDC^{2-}$) and the coordination modes (as in Figure 6a–e). La(1) is in a distorted tricapped square-antiprism environment (LaO_{11}) with eleven coordinated oxygen atoms that come from six different cyclohexanecarboxylate anions and one terminal water molecule. Among the ten oxygen atoms (of the anions), five have μ_3 connections linking La(1) with La(2) through three oxygen atoms and La(3) through two oxygen atoms. La(2) is in a distorted dodecahedral environment (LaO_8) and coordinated to eight oxygen atoms from eight different cyclohexanedicarboxylate anions. Among the eight oxygen atoms, four have μ_3 connections linking La(2) with La(1) through three oxygen atoms and La(3) through one oxygen. La(3) also has a distorted dodecahedral environment (LaO_8) with one oxygen atom from a terminal water molecule and seven from six different cyclohexanecarboxylate anions. Among the seven oxygen atoms, three have μ_3 connections linking La(3) with La(1) through two oxygen atoms and La(1) through one

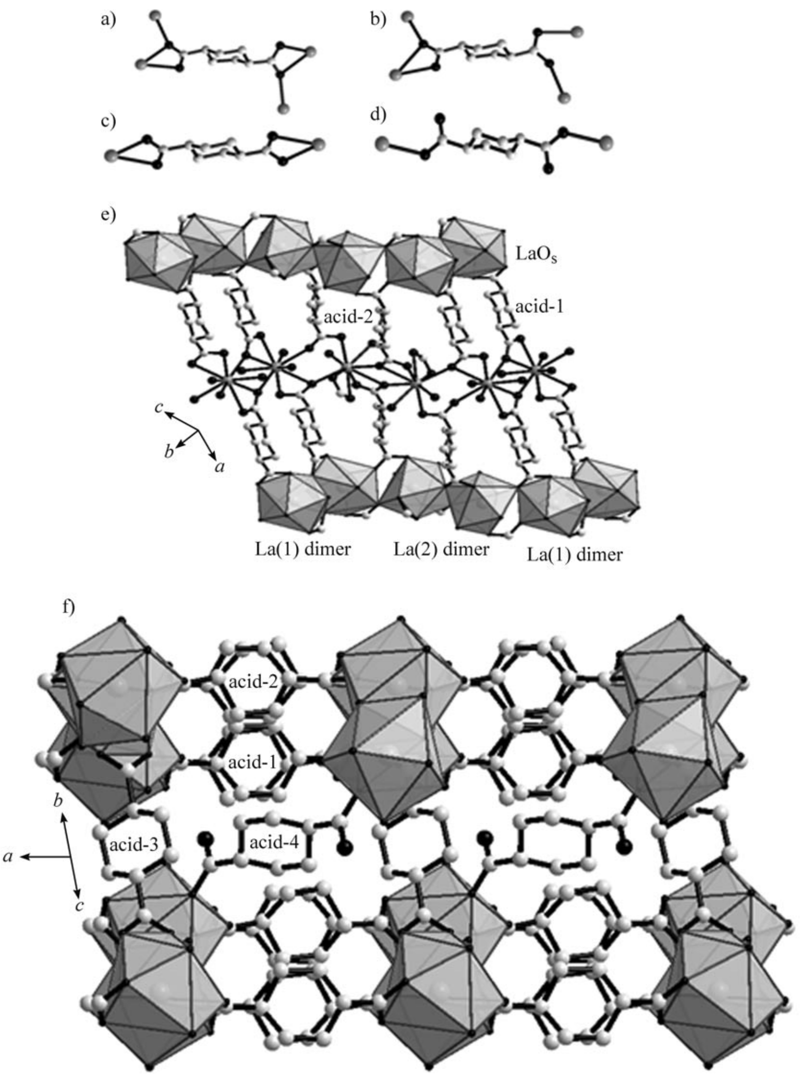

Figure 4. a)–d) Various coordination modes of the 1,4-CHDC (see text for details), e) view of the layer, and f) the three-dimensional structure in **III**.

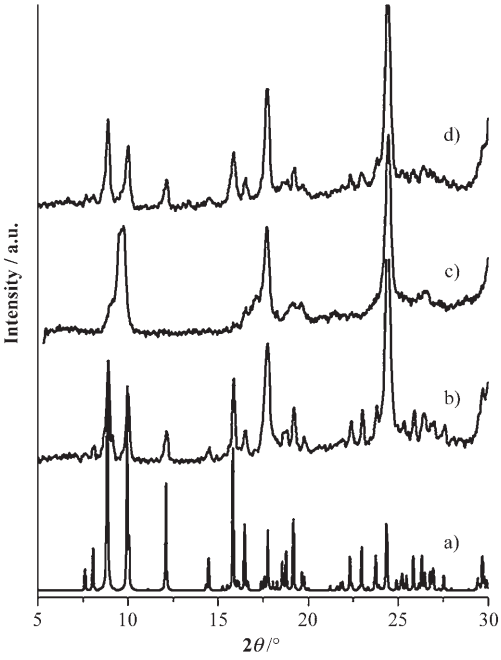

Figure 5. Powder XRD patterns of **III**: a) simulated, b) as-synthesized, c) after heating at 200°C, and d) after exposing the dehydrated sample to water vapor.

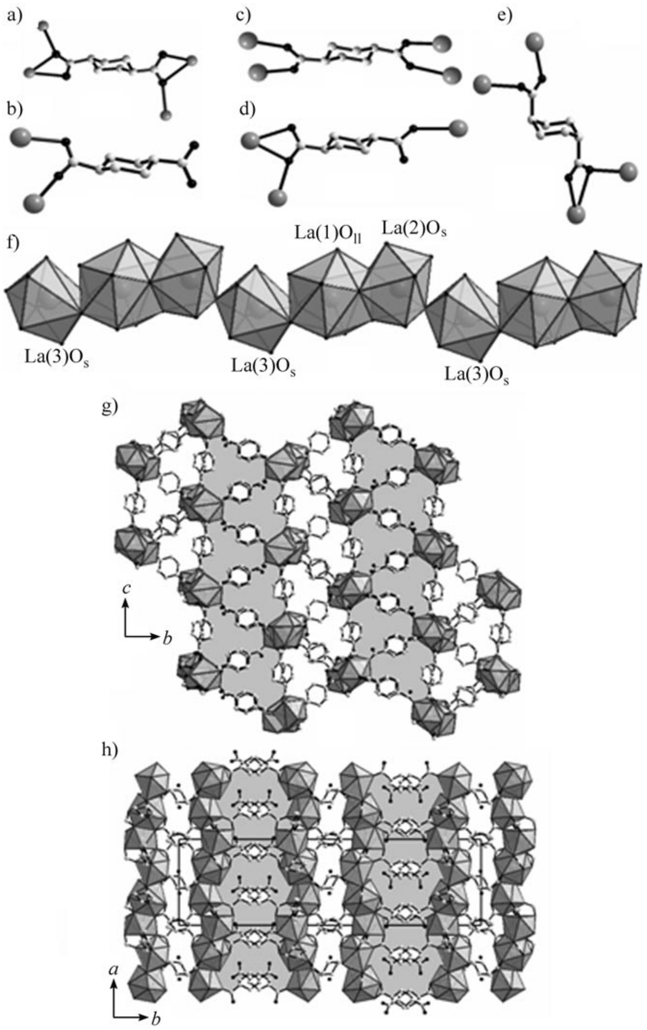

Figure 6. a)–e) Various coordination modes of the 1,4-CHDC (see text for details), f) infinite one-dimensional La-O-La chain, g) three-dimensional structure, showing two types of channels (viewed along *a* axis) and h) the three-dimensional structure (viewed along *c* axis) in **IV**.

oxygen atom. The La–O bond lengths are in the range 2.406–2.744 Å. The La(1)O$_{11}$ polyhedron shares its face with La(2)O$_8$ through three μ_3 oxygen atoms forming a dinuclear unit. These units are linked to each other through La(3)O$_8$ by sharing an edge with La(1)O$_{11}$ and a corner with La(2)O$_8$, forming an infinite one-dimensional La-O-La chain along the *a* axis (Figure 6f). All the cyclohexanecarboxylate anions that connect these one-dimensional chains are in the *trans* conformation (ten in the ee form and one in the aa form). The torsional angles are in the range 172–180°. Each La-O-La chain is connected to six similar chains to form a three-dimensional structure with two types of triangular channels along the *a* axis (Figure 6g). Free carboxylic acid groups (protonated) project from the walls in one type of channel (highlighted with gray in Figure 6h), whereas in the other type of channel, lattice water molecules are situated between the acid linkers.

[La$_2$(1,4-CHDC)$_3$(H$_2$O)]·2.5 H$_2$O (**V**) has a three-dimensional structure with an asymmetric unit of 39.5 non-hydrogen atoms. There are two crystallographically distinct La^{3+} ions, three CHDC anions, a terminal water molecule, and 2.5 lattice water molecules in the asymmetric unit. The three anions can be categorized into two types, based on their coordination modes: 1) acid-1 (Figure 7a) 2) acid-2 and acid-3 (Figure 7b). Acid-1 is in the *trans* ee conformation with torsional angles in the 2.1–4 ° range, whereas acid-2 and acid-3 are in the *cis* ae conformation with torsional angles in the 69.6–77.22 ° range for the axial carboxyl group and 174–179.9 ° range for the equatorial carboxyl group. La(1) is in a distorted dodecahedral environment (LaO$_8$), coordinated to eight oxygens from seven different cyclohexanedicarboxylate anions (three from acid-1, three from acid-2, and one from acid-3). Among the eight oxygen atoms, four have μ_3 connections linking La(1) with La(1) through two oxygen atoms and with La(2) through two oxygen atoms. La(2) is in a nine-coordinated environment (LaO$_9$), the nine oxygen atoms coming from a terminal water molecule and five different cyclohexanedicarboxylate anions (one from acid-1, one from acid-2, and three from acid-3). Among the nine oxygen atoms, four have μ_3 connections linking La(2) with La(2) through two oxygen atoms and with La(1) through two oxygen atoms. Thus, two LaO$_8$ polyhedra share an edge, forming the La$_2$O$_{15}$ dimer. Similarly, two LaO$_9$ polyhedra share an edge, forming the La$_2$O$_{17}$ dimer. The dimers are connected to each other alternatively through two μ_3-oxygen atoms, forming an infinite one-dimensional La-O-La chain. The chains are connected by acid-2 and acid-3 into a two-dimensional layer (Figure 7c). The layers are connected by acid-1, forming a three-dimensional structure with one-di-

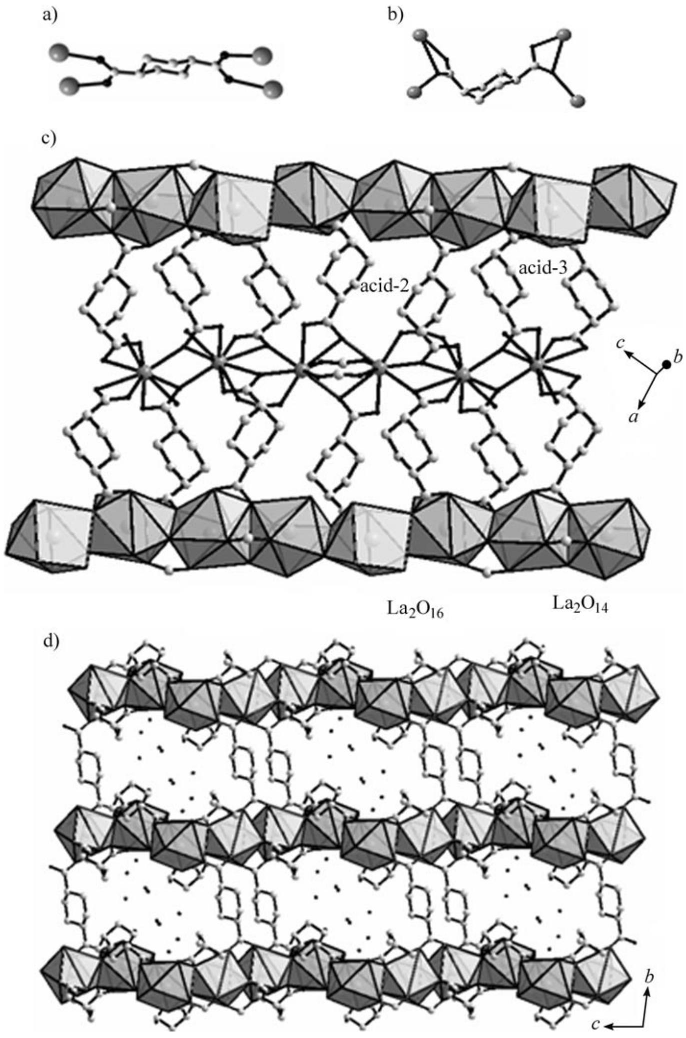

Figure 7. a) and b) coordination modes of the 1,4-CHDC, c) view of the layer and d) the three-dimensional structure in **V**.

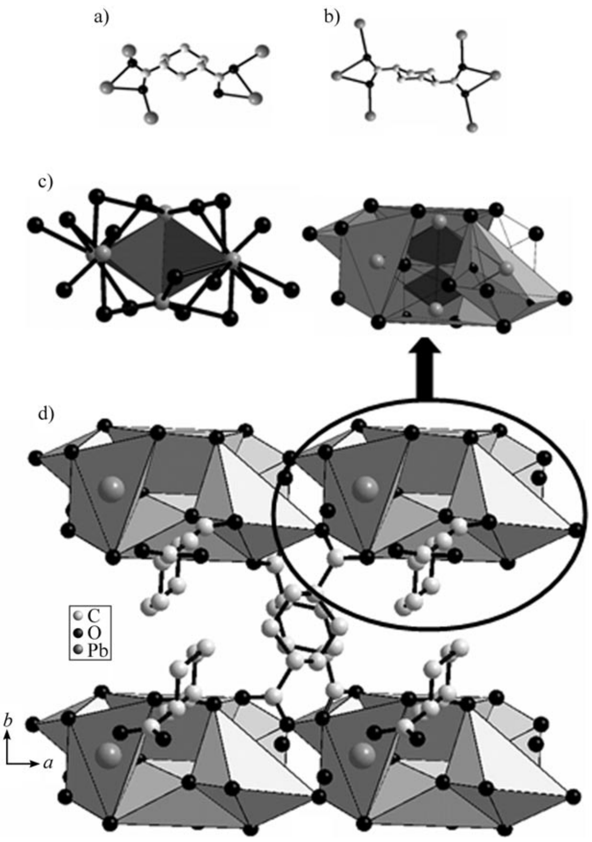

Figure 8. a) and b) coordination modes of the CHDC, c) the Pb_6O_{19} secondary building units, and d) three-dimensional structure (viewed along the *c* axis) in **VI**.

mensional channels running along the *a* axis (Figure 7d). The lattice water molecules are situated in these channels. The La−O bond lengths are in the range 2.412–2.756 Å.

Mixed cyclohexanedicarboxylate: We have been able to isolate a monobasic lead cyclohexanedicarboxylate, containing both the 1,3- and 1,4-carboxylates. The compound with the formula, $[Pb_3O(1,3\text{-CHDC})(1,4\text{-CHDC})]\cdot 0.5\,H_2O$ (**VI**) has a three-dimensional structure. There are three crystallographically distinct Pb^{2+} ions and two cyclohexanecarboxylate anions in the asymmetric unit (of three types, one from 1,3-CHDC and two from 1,4-CHDC). The 1,3-CHDC anion has (1222) connectivity (Figure 8a) and the two 1,4-CHDC anions have a two-fold axis of symmetry with (2222) connectivity (Figure 8b). The Pb(1) and Pb(2) atoms are seven-coordinate and Pb(3) is five-coordinate to oxygen atoms of the three CHDC anions and one independent oxygen atom, O(9). The independent oxygen atom O(9) is tetrahedrally coordinated to four lead atoms to form a OPb_4 tetrahedron. Each OPb_4 tetrahedron shares an edge, to form a O_2Pb_6 dimer. The O_2Pb_6 dimer is buried inside a cluster of six PbO_n ($n=7$ and 5) ployhedra, to form a Pb_6O_{19} unit (Figure 8c). The Pb_6O_{19} units are connected by sharing two corners to form a one-dimensional Pb-O-Pb chain along the *a* axis. The Pb−O bond lengths are in the range 2.272–3.051 Å. The Pb-O-Pb chains are connected by the 1,4-CHDC anions along the *b* axis and the 1,3-CHDC anion (1222) along the *a* axis leading to a three-dimensional open framework structure (Figure 8d). The water molecule is disordered over two positions with half occupancy, residing between two Pb-O-Pb chains and two 1,3-CHDC anions. The 1,3- and 1,4-CHDC anions are in the ee form, with torsion angles of 8.40 and 180°, respectively.

We have also been able to isolate a dibasic lead 1,4-cyclohexanedicarboxylate, $[Pb_6O_2(1,4\text{-CHDC})_3(1,4\text{-HCHDC})_2]$, with a three-dimensional structure (Figure 9). We have been able to solve the structure albeit with a large *R* value due to certain crystallographic artifacts. The three-dimensional structure of this compound is interesting, in that it contains six- and seven-coordinate Pb atoms. A Pb_3O_{15} unit acts as a building block to form the three-dimensional structure with layers comprising Pb-O-Pb linkages, along with an eight-membered aperture along the *b* axis.

Structures of several metal 1,4-CHDCs have been described in the recent literature.[9,10] These include 1,4-

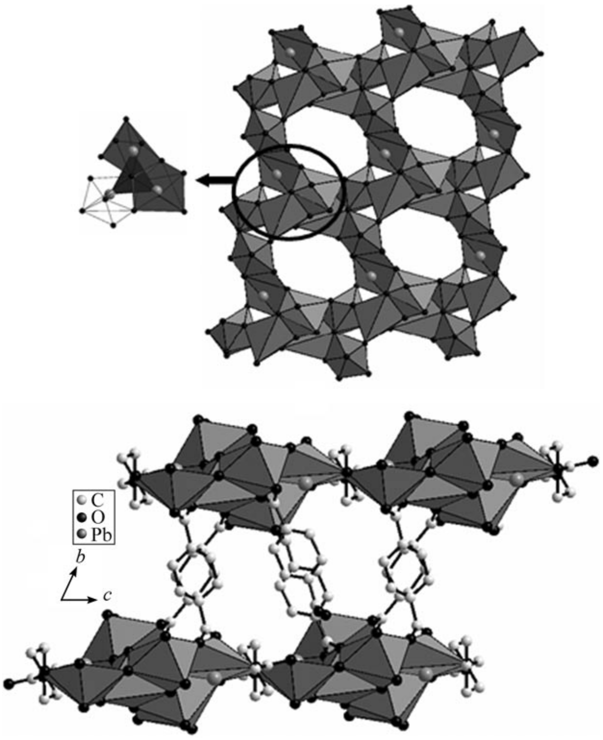

Figure 9. Pb_3O_{15} secondary building units and infinite Pb-O-Pb linkages (top) and the three-dimensional structure (viewed along the *a* axis; bottom) in $[Pb_6O_2(1,4\text{-CHDC})_3(1,4\text{-HCHDC})_2]$.

CHDCs of Cd, Mn, and La, $[Cd_2(1,4\text{-CHDC})_2(1,10\text{-phen})_2]\cdot 3.5\,H_2O$, $[Cd_4(1,4\text{-HCHDC})_2(1,4\text{-CHDC})_3(1,10\text{-phen})_4]\cdot 1,4\text{-}H_2CHDC\cdot 6\,H_2O$, $[Cd(1,4\text{-CHDC})(2,2'\text{-bipy})]\cdot H_2O$, $[Cd_3(1,4\text{-CHDC})_3(1,10\text{-phen})_2]\cdot 4\,H_2O$, $[Mn_3(1,4\text{-CHDC})_3(1,10\text{-phen})_2]\cdot 4\,H_2O$, and $[La(1,4\text{-CHDC})(1,4\text{-HCHDC})]$, all with layered structures. The only three-dimensional 1,4-CHDC structure reported is the $[La(1,4\text{-CHDC})_2(H_2O)_2]\cdot 2\,H_2O$ compound, which contains infinite one-dimensional La-O-La linkages. It appears, that while the 1,4-CHDCs of different dimensionalities can be formed, the three-dimensional structures are favored only by these isomers. Furthermore the three-dimensional structures possess infinite M-O-M linkages. We have generally found the CHDC anions to be in the stable ee conformation. However, the less common conformations such as ae and aa can also occur in certain CHDCs.

Conclusion

The present study shows that it is possible to form inorganic–organic hybrid structures of 1,2-CHeDCs and CHDCs as well as 1,4-CHDCs with infinite M-O-M linkages. The three-dimensional structures are, however, formed only with 1,4-CHDC due to the 180° disposition of the two carboxylic groups in the acid. Both 1,2-CHDCs and 1,2-CHeDCs occur as layered structures out of structural necessity. The equatorial–equatorial conformation occurs predominantly in these cyclohexane-based dicarboxylates although we have encountered one with the axial–axial conformation and another with the axial–equatorial conformation.

It is also interesting to note the variety of coordination modes adopted by the dicarboxylates. In the lead carboxylates, irrespective of their coordination number (5, 7, and 8), the lone pair of electrons on the Pb^{2+} ion causes the coordination geometry to be distorted and hemi-directed (Figure 10). The mixed dicarboxylate of Pb involving both 1,3- and 1,4-CHDCs belongs to a rather rare family of hybrid oxo-centered Pb compounds.[13]

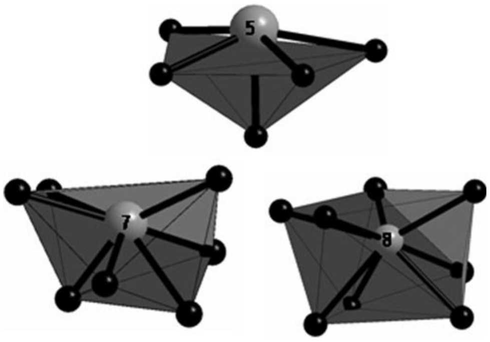

Figure 10. PbO_n ($n = 5$, 7, and 8) polyhedra, showing the hemidirected nature of lead atoms.

Experimental Section

All the La– and Pb–CHDC compounds as well as the Cd–CHeDC compounds were synthesized under hydrothermal conditions by heating the corresponding homogenized reaction mixture in a 23 mL PTFE-lined bomb at 180 or 200 °C for 72 h under autogeneous pressure. The pH of the starting reaction mixture was generally in the range 5–7. 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 for the different compounds synthesized by us are given in Table 1. Both polymorphs of **I** were obtained from the same reaction mixture.

Powder XRD patterns of the products were recorded by using $Cu_{K\alpha}$ radiation (Rich-Seifert, 3000TT). The patterns agreed with those calculated for single-crystal structure determination. Thermogravimetric analysis (TGA) was carried out (Metler-Toledo) in oxygen atmosphere (flow rate $= 50\,\text{mL}\,\text{min}^{-1}$) in the temperature range 25 to 900 °C (heating rate $= 5\,°\text{C}\,\text{min}^{-1}$). Infra-red (IR) spectroscopic studies were carried out in the mid-IR region as a KBr pellet (Bruker IFS-66v). The spectra showed characteristic bands of the carboxylate units. Room-temperature photoluminescence spectra of samples were recorded on powdered samples. A Perkin–Elmer spectrometer (LS-55) with a single-beam setup was employed by using a xenon lamp (50 W) as the source and a photomultiplier tube as the detector.

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 Siemen's Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) operating at 40 kV and 40 mA. Empirical absorption corrections based on symmetry equivalent reflections were applied by using the SADABS program.[14] The structures were solved and refined using SHELXTL-PLUS suite of program.[14] For the final refinement the hydrogen atoms on the carboxylic acid were placed geometrically and held in the riding mode. Final refinement included atomic positions for all the atoms, anisotropic thermal pa-

Table 1. Starting compositions for compounds **I–VI** synthesized.[a]

	Formula	Composition			
		Metal	Acid	Additive 1/Additive 2	Water
I[b]	[Cd(1,2-$C_8H_8O_4$)(H_2O)]	$Cd(OAc)_2 \cdot 2H_2O$ (0.272 g, 1 mM)	1,2-CHe(4)DC anhydride (0.08 g, 0.5 mM)	NaOH (0.2 mL of 5 M solution, 1 mM)/ –	278 H_2O (5 mL, 278 mM)
II	[Pb(1,2-$C_8H_{10}O_4$)]	$Pb(NO_3)_2$ (0.3302 g, 1 mM)	1,2-CHDC anhydride (0.1542 g, 1 mM)	ethylene diamine (0.07 mL, 1 mM)/ NaOH (0.2 mL of 5 M solution, 1 mM)	278 H_2O (5 mL, 278 mM)
III	[La_2(1,4-$C_8H_{10}O_4$)$_3$(H_2O)$_4$]	$La(NO_3)_3 \cdot 4H_2O$ (0.0978 g, 0.3 mM)	1,4-CHDC (0.1054 g, 0.6 mM)	NaOH (0.24 mL of 5 M solution, 1.2 mM)/ –	1853 H_2O (10 mL, 556 mM)
IV	[La_3(1,4-$C_8H_{11}O_4$)$_2$-(1,4-$C_8H_{10}O_4$)$_{3.5}$]·H_2O	$La(NO_3)_3 \cdot 4H_2O$ (0.0978 g, 0.3 mM)	1,4-CHDC (0.0527 g, 0.3 mM)	K_2CO_3 (0.0628 g, 0.3 mM)/ piperazine (0.0264 g, 0.3 mM)	370 H_2O (2 mL, 111 mM)
V	[La_2(1,4-$C_8H_{10}O_4$)$_3$(H_2O)]·2.5 H_2O	$La(NO_3)_3 \cdot 4H_2O$ (0.0978 g, 0.3 mM)	1,4-CHDC (0.0527 g, 0.3 mM)	2,3-dihydroxybenzoic acid (0.0264 g, 0.3 mM)/ NaOH (0.12 mL of 5 M solution, 0.6 mM)	370 H_2O (2 mL, 111 mM)
VI	[Pb_3O(1,3-$C_8H_{10}O_4$)-(1,4-$C_8H_{10}O_4$)]·0.5 H_2O	$Pb(NO_3)_2$ (0.0991 g, 0.3 mM)	1,3-CHDC (0.0172 g, 0.1 mM) 1,4-CHDC (0.0172 g, 0.1 mM)	ethylene diamine (0.7 mL, 1 mM) / NaOH (0.04 mL of 5 M solution, 0.2 mM)	278 H_2O (5 mL, 278 mM)

[a] Temperature used was 180 °C, except for **VI** for which 200 °C was used. [b] Polymorphs **A** and **B**.

Table 2. Crystal data and structure refinement parameters for **I** and **II**.

	IA	**IB**	**II**
formula	$C_8H_{10}CdO_5$	$C_8H_{10}CdO_5$	$PbO_4C_8H_{10}$
M_r	298.58	298.58	377.35
crystal system	orthorhombic	orthorhombic	monoclinic
space group	*Pnc*2 (no. 30)	*Pbcn* (no. 60)	$P2_1/c$ (no.14)
a [Å]	9.7988(13)	12.2003(1)	24.6142(4)
b [Å]	12.184(2)	7.3856(1)	6.9028(2)
c [Å]	7.3722(2)	19.6160(1)	11.5058(1)
α [°]	90	90	90
β [°]	90	90	98.931(1)
γ [°]	90	90	90
V [Å^3]	880.2(2)	1767.53(3)	1931.21(7)
Z	4	8	8
ρ_{calcd} [g cm^{-3}]	2.192	2.244	2.596
μ [mm^{-1}]	2.470	2.460	17.452
data collected	7367	6618	7509
unique data	2072	1272	2746
observed data [$I > 2\sigma(I)$]	1908	1124	1823
R_{merg}	0.0397	0.0350	0.0602
R indexes [$I > 2\sigma(I)$]	$R_1=0.0553$[a]; $wR_2=0.1610$[b]	$R_1=0.0246$[a]; $wR_2=0.0615$[b]	$R_1=0.0412$[a]; $wR_{2=}0.1020$[b]
R indexes (all data)	$R_1=0.0597$[a]; $wR_2=0.1680$[b]	$R_1=0.0277$[a]; $wR_2=0.0629$[b]	$R_1=0.0750$[a]; $wR_{2=}0.1096$[b]

	III	**IV**	**V**	**VI**
formula	$C_{24}H_{38}La_2O_{16}$	$C_{44}H_{63}La_3O_{25}$	$C_{24}H_{37}La_2O_{15.5}$	$Pb_3O_{9.5}C_{16}H_{21}$
M_r	860.36	1407.68	851.36	986.9
crystal system	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a [Å]	11.5096(1)	11.6959(2)	9.8785(3)	9.6476(9)
b [Å]	12.0694(3)	39.6296(7)	11.1986(4)	10.936(1)
c [Å]	12.4462(2)	11.5434(1)	14.7456(4)	11.090(1)
α [°]	94.8310(10)	90	93.919(2)	64.636(1)
β [°]	116.0460(10)	105.0000(10)	97.409(2)	77.988(1)
γ [°]	101.3690(10)	90	104.517(2)	84.311(1)
V [Å^3]	1493.98(5)	5168.10(14)	1557.34(8)	1034.0(2)
Z	2	4	1	2
ρ_{calcd} [g cm^{-3}]	1.913	1.809	1.816	3.170
μ [mm^{-1}]	2.894	2.520	2.774	24.411
data collected	6258	21 457	14 013	4331
unique data	4252	7438	5346	2939
observed data [$I > 2\sigma(I)$]	3838	6009	4556	2151
R_{merg}	0.0281	0.0478	0.0242	0.0722
R indexes [$I > 2\sigma(I)$]	$R_1=0.0296$[a]; $wR_2=0.0756$[b]	$R_1=0.0300$[a]; $wR_2=0.0596$[b]	$R_1=0.0367$[a]; $wR_2=0.0965$[b]	$R_1=0.0700$[a]; $wR_{2=}0.1603$[b]
R indexes (all data)	$R_1=0.0326$[a]; $wR_2=0.0769$[b]	$R_1=0.0451$[a]; $wR_2=0.0658$[b]	$R_1=0.0475$[a]; $wR_2=0.1157$[b]	$R_1=0.0802$[a] $wR_2=0.1632$[b]

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. $w=1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P=[\max.(F_o^2,0) + 2(F_c)^2]/3$, in which $a=0.0867$ and $b=6.3045$ for **IA**, $a=0.0380$ and $b=0$ for **IB** and $a=0.0275$ and $b=0.3070$ for **II**, $a=0.0420$ and $b=0$ for **III**, $a=0.0143$ and $b=0$ for **IV**, $a=0.0466$ and $b=9.7765$ for **V**, and $a=0.0174$ and $b=0$ for **VI**.

rameters for all the non-hydrogen atoms, and isotropic thermal parameters for the hydrogen atoms, except for **VI**. All the hydrogen atoms were included in the final refinement, except the hydrogen atoms on C(4) to C(6) in **I**. For **V** and **VI**, the hydrogen atoms of the water molecules could not be located in the difference Fourier map and not included in the final refinement. Details of the structure solution and final refinements for the compounds **I** to **VI** are given in Table 2.

CCDC-613532–613537 and -622800 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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