1,2-, 1,3- and 1,4-Benzenedicarboxylates of Cd and Zn of different dimensionalities: Process of formation of the three-dimensional structure†

A. Thirumurugan and C. N. R. Rao*

A systematic study of the benzenedicarboxylates (BDCs) formed by cadmium and zinc with the three isomeric dicarboxylic acids in the presence or absence of amines has been carried out. Several BDCs have been prepared under hydrothermal conditions and their structures established by X-ray crystallography. It is pointed out that the formation of the three-dimensional structures is most favored in the case of 1,4-benzenedicarboxylic acid. An example of a Zn 1,4-BDC where the three-dimensional structure is formed favorably with the increase in reaction temperature is discussed. A one-dimensional chain structure is shown to transform to a three-dimensional structure as a function of time at an appropriate temperature.

Introduction

Benzenedicarboxylic acids are ideal ligands to design novel coordination polymers and open framework structures.[1–5] In the last few years, several metal–organic frameworks (MOFs) have been reported in the literature, with interesting properties such as porosity, sorption, catalysis, non-linear optics, luminescence, and magnetism.[6–10] Thus, Yaghi and coworkers have reported interesting cubic zinc benzenedicarboxylates with porous structures having some hydrogen sorption properties.[11] An interesting aspect of benzenedicarboxylic acids is their ability to form MOFs in the presence or absence of chelating aromatic amines by utilizing weak supramolecular interactions along with solvent molecules, which may be coordinated or present as solvent of crystallization. The structures formed by benzenedicarboxylic acids vary from one-dimensional chains to three-dimensional architectures. There are, however, very few examples of systems wherein structures with all the three dimensionalities occur with the same metal or ligands.[12,13] Our particular interest is in the dimensionality of the benzenedicarboxylates (BDCs). We have carried out a systematic investigation of the compounds formed by cadmium and zinc with the three isomeric benzenedicarboxylic acids in order to examine the structural and dimensional variations caused by the different dispositions of the two carboxylic acid groups, the values of dispersion angles being $60°$, $120°$, $180°$ respectively in the 1,2-, 1,3- and 1,4-isomers. We have carried out the synthesis of these BDCs in the presence and absence of 2,2′-bipyridine (2,2′-bipy) or 1,10-phenanthroline (1,10-phen) and tried to examine the role of the amine and the water molecules on the dimensionality of the BDCs. While some of the Cd and Zn BDCs that we obtained during the course of our study have been reported by other

workers, we have found new compounds with interesting structures. The study has enabled us to arrive at some generalizations on the factors determining the dimensionality of the BDCs. More importantly, we have examined the mode of evolution of the three-dimensional structures of the BDCs and have been able to show how a one-dimensional chain may be a precursor of the three-dimensional structure.

Experimental

All the Cd and Zn BDCs were synthesized by hydrothermal methods by heating the corresponding homogenized reaction mixture in a 23 ml PTFE-lined bomb at 180 °C for 72 h. The pH of all the starting reaction mixture are in the range 5 to 6. The pH after the reaction did not show appreciable change. The products of the hydrothermal reactions were vacuum filtered and dried at ambient conditions. The starting compositions for the different new BDCs synthesized by us are as follows: **Ia** (monoclinic), $[Cd(H_2O)(C_8H_4O_4)(C_{10}H_8N_2)]$: $Cd(OAc)_2·2H_2O$ (0.272 g, 1 mM), (1,2-BDC) (0.169 g, 1 mM), (2.2′-bipy) (0.158 g, 1 mM), piperidine (0.1 ml, 1 mM), H_2O (5 ml, 278 mM); **Ib** (orthorhombic), $[Cd(H_2O)(C_8H_4O_4)-(C_{10}H_8N_2)]$: $Cd(OAc)_2·2H_2O$ (0.272 g, 1 mM), (1,2-BDC) (0.339 g, 1 mM), (2.2′-bipy) (0.316 g, 1 mM), piperidine (0.2 ml, 2 mM), H_2O (5 ml, 278 mM); **II** $[Cd(H_2O)(C_8H_4O_4)-(C_{12}H_8N_2)]$: $Cd(OAc)_2·2H_2O$ (0.272 g, 1 mM), (1,2-BDC) (0.169 g, 1 mM), (1,10-phen) (0.199 g, 1 mM), NaOH (0.4 ml of 5 M solution, 2 mM), H_2O (5 ml, 278 mM); **III** $[Zn(H_2O)-(C_8H_4O_4)(C_{12}H_8N_2)]·H_2O$: $Zn(OAc)_2·2H_2O$ (0.223 g, 1 mM), (1,2-BDC) (0.169 g, 1 mM), (1,10-phen) (0.199 g, 1 mM), NaOH (0.4 ml of 5 M solution, 2 mM), H_2O (5 ml, 278 mM); **IV** $[Cd(H_2O)(C_8H_4O_4)]$: $Cd(OAc)_2·2H_2O$ (0.272 g, 1 mM), (1,3-BDC) (0.169 g, 1 mM), (1,2-diaminopropane) (0.172 ml, 2 mM), H_2O (5 ml, 278 mM); **V** $[Cd(C_8H_4O_4)(C_{12}H_8N_2)]·H_2O$: $Cd(OAc)_2·2H_2O$ (0.272 g, 1 mM), (1,4-BDC) (0.169 g, 1 mM),(1,10-phen) (0.199 g, 1 mM), H_2O (5 ml, 278 mM). Powder XRD patterns of the products were recorded using Cu Kα radiation (Rich-Seifert, 3000TT). The pattern agreed with those calculated for single crystal structure determination.

Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560064, India. E-mail: cnrrao@jncasr.ac.in; Fax: +91 80 8462766

† Electronic supplementary information (ESI) available: Selected bond distances and angles and CIFs. See http://www.rsc.org/suppdata/jm/b5/b504666a/

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

Table 1 Crystal data and structure refinement parameters for **I** and **II**

Structure parameter	Ia	Ib	II
Empirical formula	$C_{18}H_{14}CdN_2O_5$	$C_{18}H_{14}CdN_2O_5$	$C_{40}H_{26}Cd_2N_4O_9$
Formula weight	450.71	450.71	929.47
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$, (no. 14)	$Pna2_1$, (no. 33)	$C2/c$, (no. 15)
$a/Å$	9.8105(2)	10.4092(2)	22.1574(4)
$b/Å$	9.9054(2)	19.7245(5)	10.1982(2)
$c/Å$	17.7854(2)	8.4632(2)	30.7709(2)
$\beta/°$	101.7710(10)	90	102.3600(10)
$V/Å^3$	1691.99(5)	1737.63(7)	6792.00(19)
Z	4	4	8
$D_{(calc)}/g\ cm^{-3}$	1.769	1.723	1.822
μ/mm^{-1}	1.323	1.289	1.320
Total data collected	6704	6895	13674
Unique data	2435	2406	4864
Observed data [$I > 2\sigma(I)$]	2008	2318	4077
R_{merg}	0.0321	0.0242	0.0295
R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0257^a$; $wR_2 = 0.0651^b$	$R_1 = 0.0160^a$; $wR_2 = 0.0369^b$	$R_1 = 0.0268^a$; $wR_2 = 0.0614^b$
R indexes [all data]	$R_1 = 0.0356^a$; $wR_2 = 0.0690^b$	$R_1 = 0.0169^a$; $wR_2 = 0.0372^b$	$R_1 = 0.0372^a$; $wR_2 = 0.0659^b$

$^a R_1 = \Sigma \|F_0| - |F_c\|/\Sigma |F_0|$; $^b wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_0)^2 + (aP)^2 + bP]$, $P = [\max.(F_0^2,0) + 2(F_c)^2]/3$, where $a = 0.0368$ and $b = 0.1976$ for **Ia**, $a = 0.0171$ and $b = 0.0$ for **Ib**, and $a = 0.0247$ and $b = 10.2529$ for **II**.

Table 2 Crystal data and structure refinement parameters for **III, IV** and **V**

Structure parameter	III	IV	V
Empirical formula	$C_{20}H_{16}ZnN_2O_6$	$C_8H_6CdO_5$	$C_{40}H_{26}CdN_4O_9$
Formula weight	445.75	294.53	931.47
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$, (no. 14)	$Pbcm$, (no. 57)	$P2_1/n$, (no. 14)
$a/Å$	9.6430 (0)	6.5021(1)	10.4883(2)
$b/Å$	8.9796(1)	6.9509(2)	13.1483(1)
$c/Å$	21.4183(3)	18.3199(1)	13.1207(2)
$\beta/°$	90.7590(10)	90.0	106.6530(10)
$V/Å^3$	1854.45(3)	829.15(11)	1733.50(5)
Z	4	4	2
$D_{(calc)}/g\ cm^{-3}$	1.596	2.335	1.784
μ/mm^{-1}	1.366	2.627	1.293
Total data collected	7392	3106	7056
Unique data	2648	621	2485
Observed data [$I > 2\sigma(I)$]	2364	541	2058
R_{merg}	0.0191	0.0374	0.0317
R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0261^a$; $wR_2 = 0.0701^b$	$R_1 = 0.0221^a$; $wR_2 = 0.0610^b$	$R_1 = 0.0277^a$; $wR_2 = 0.0622^b$
R indexes [all data]	$R_1 = 0.0306^a$; $wR_2 = 0.0723^b$	$R_1 = 0.0253^a$; $wR_2 = 0.0626^b$	$R_1 = 0.0392^a$; $wR_2 = 0.0668^b$

$^a R_1 = \Sigma \|F_0| - |F_c\|/\Sigma |F_0|$; $^b wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_0)^2 + (aP)^2 + bP]$, $P = [\max.(F_0^2,0) + 2(F_c)^2]/3$, where $a = 0.0383$ and $b = 1.2413$ for **III**, $a = 0.0353$ and $b = 0.2568$ for **IV**, and $a = 0.0253$ and $b = 1.6834$ for **V**.

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 Kα radiation, $\lambda = 0.71073$ Å) operating at 40 kV and 40 mA.‡ An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS program.[14] The structure was solved and refined using the SHELXTL-PLUS suite of program.[15] All the hydrogen atoms of the carboxylic acids were located in the difference Fourier maps. 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 parameters for all the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. All the hydrogen atoms are included in the final refinement for **Ib** and **III**. The hydrogen atoms associated with the water molecules (coordinated or lattice water) of **Ia**, **II**, **IV** and **V** are located in the difference Fourier map, but not stable during refinement, hence these hydrogen atoms are excluded from the "final refinement". Full-matrix least-squares refinement against |F^2| was carried out using the SHELXTL-PLUS[15] suite of programs. Details of the structure solution and final refinements for the compounds **I** to **V** are given in Tables 1 and 2. We obtained **VI**, [Zn(H$_2$O)$_2$(C$_8$H$_4$O$_4$)] and **VII**, [Zn(H$_2$O)(C$_8$H$_4$O$_4$)], starting with a mixture of ZnSO$_4$·4H$_2$O (0.29 g, 1 mM), (1,4-BDC) (0.169 g, 1 mM), NaOH (0.4 ml of 5 m solution, 2 mM) and H$_2$O (5 ml, 278 mM) under hydrothermal conditions. The powder XRD patterns of **VI** and **VII** recorded were consistent with the structures determined by single crystal structure determination.
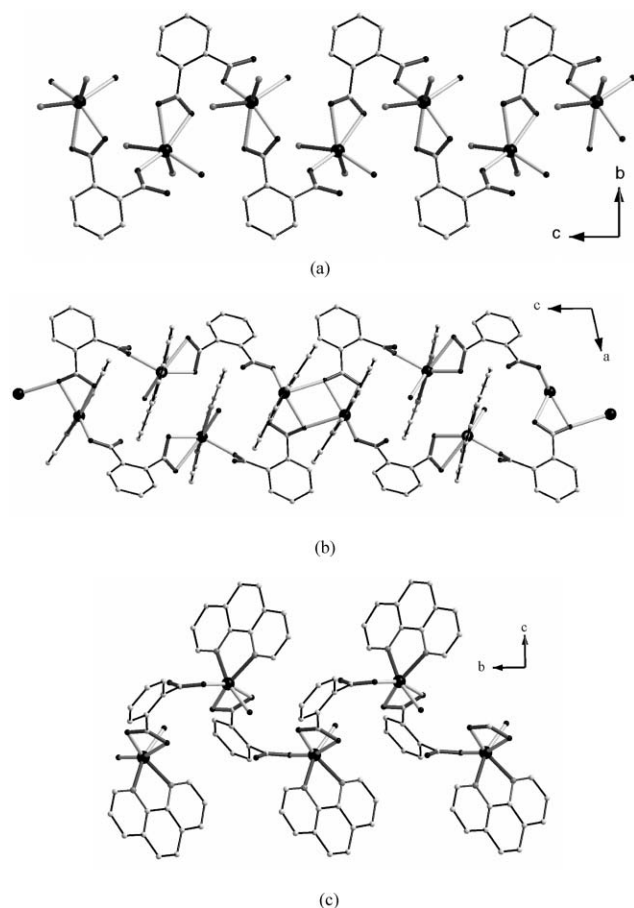
‡ CCDC reference numbers 267489, 267490, 267491, 267492, 267493 and 267494. See http://www.rsc.org/suppdata/jm/b5/b504666a/ for crystallographic data in CIF or other electronic format.

Besides examining the effect of the reaction temperature on the product obtained from the reaction mixture, we have studied the effect of temperature and time on the one-dimensional compound **VI** to see whether it transforms to the three-dimensional **VII** or to any other structure, by subjecting the solid products obtained to powder X-ray diffraction.

Results and discussion

1,2-Benzenedicarboxylates

We have been able isolate a 1,2-BDC of Cd with 2,2′-bipyridine [Cd(H$_2$O)(C$_8$H$_4$O$_4$)(C$_{10}$H$_8$N$_2$)], **I** in two polymorphic forms, monoclinic (**Ia**) and orthorhombic (**Ib**). Both the polymorphs consist of one-dimensional helical chains formed by distorted CdN$_2$O$_4$ octahedra linked by the dicarboxylic acid (Fig. 1a). The polymorphs exist as racemic mixtures of right- and left-handed infinite helical one-dimensional chains. The Cd–O bond distance ranges from 2.226 to 2.445 Å in **Ia** and from 2.213 to 2.429 Å in **Ib**. The CdN$_2$O$_4$ octahedron coordinates to a terminal 2,2′-bipy and to a water molecule. The remaining three oxygen atoms come from

two different carboxylic acid molecules, one with the monodentate and the other with the bidentate carboxylate group. Thus each tridentate carboxylic acid molecule with (1110) connectivity[16] links two cadmium atoms, giving rise to a half turn unit of the helical one-dimensional chain. The neighboring Cd–Cd distances are 5.974 Å and 5.597 Å respectively in **Ia** and **Ib** and the pitches of the helical chains are 9.905 Å and 8.463 Å. These differences arise because of the difference in the dihedral angles between the carboxylate groups in the two polymorphs. The helical structure of **I** is stabilized in the crystal by interchain CH–π and CH···O interactions. The interchain CH–π interactions between the 2,2-bipy and the carboxylic acid rings are 2.983 Å, 139.1° and 2.998 Å, 146.7° respectively in **Ia** and **Ib**, while the interchain CH···O interactions are 2.211 Å, 161.8° and 2.446 Å, 166.4°. These interactions seem to be stronger in the monoclinic form than in the orthorhombic form. We have been able to obtain a one-dimensional helical chain with zinc analogous to **I**, [Zn(H$_2$O)(C$_8$H$_4$O$_4$)(C$_{10}$H$_8$N$_2$)] in the orthorhombic form, but the same compound has been prepared under different preparative conditions by Yao et al.[17]

Cadmium also forms a 1,2-BDC with 1,10-phen, with a one-dimensional chain structure, the composition being, [Cd(H$_2$O)(C$_8$H$_4$O$_4$)(C$_{12}$H$_8$N$_2$)], **II**. The structure shown in Fig. 1b contains Cd in two crystallographically independent distorted octahedral environments. In the CdN$_2$O$_4$ octahedra, the Cd–O bond distance ranges from 2.177 to 2.538 Å and the Cd–N bond distance from 2.343 to 2.391 Å. Sharing of the edges of two similar octahedra gives rise to a dinuclear unit, and two such dinuclear units get connected by four carboxylic acid molecules with two different type of coordination [(1110) and (2110) connectivity], giving rise to a four membered ring. Connectivity of these rings yields a helical ribbon like structure, stabilized by inter- and intra-chain π–π stacking interactions (3.476 to 3.651 Å) in the crystal.

Zinc forms a 1,2-BDC of the formula, [Zn(H$_2$O)(C$_8$H$_4$O$_4$)(C$_{12}$H$_8$N$_2$)]·H$_2$O, **III** with 1,10-phen which has a helical one-dimensional chain structure as shown in Fig. 1c. The helical structure and the connectivity are similar to those in **I**. The Zn–O bond distance in **III** ranges from 2.177 to 2.538 Å and the Zn–N bond distances are 2.143 and 2.155 Å. The distorted ZnN$_2$O$_4$ octahedra (with one coordinated water and a terminal chelating 1,10-phen) are connected by the two different tridentate carboxylic acid molecules with (1110) connectivity. This connectivity results in a helical chain with a pitch of 8.980 Å, where the neighboring Zn–Zn distance is 5.986 Å. The helical structure is stabilized in the crystal by weak interchain CH–π interaction between the 1,10-phen and 1,2-BDC (3.010 Å, 137.9°), the interchain π–π interactions between the 1,10-phen molecules (3.687 to 3.789 Å) and the CH···O hydrogen bonds between the coordinated water and 1,10-phen (2.424 Å, 170.3°) or 1,2-BDC (2.574 Å, 136.5°).

In the absence of chelating amines, we obtained a Cd BDC with a two-dimensional layer structure with the formula [Cd(H$_2$O)(C$_8$H$_4$O$_4$)], consisting of a honeycomb (6,3-net) structure where Cd is in a distorted pentagonal bipyramid environment. However, this compound has been reported in the literature.[18] We have not been able to isolate a two-dimensional Zn-1,2-BDC.

Fig. 1 (a) Structure of [Cd(H$_2$O)(C$_8$H$_4$O$_4$)(C$_{10}$H$_8$N$_2$)], **I**, viewed along the *a*-axis. The carbon atoms in 2,2′-bipy are not shown, (b) Structure of [Cd$_2$(H$_2$O)(C$_8$H$_4$O$_4$)$_2$(C$_{12}$H$_8$N$_2$)$_2$], **II**, viewed along the *b*-axis, (c) Structure of [Zn(H$_2$O)(C$_8$H$_4$O$_4$)(C$_{12}$H$_8$N$_2$)]·H$_2$O, **III**, viewed along the *a*-axis.

1,3-Benzenedicarboxylates

Cadmium and zinc form 1,3-BDCs of the general composition $[M(C_8H_4O_4)(A)]$, M = Cd or Zn and A = 2,2'-bipy or 1,10-phen with slightly different one-dimensional ribbon-like chains depending on the amine. The 1,3-BDCs of Cd and Zn with 1,10-phen are isomorphic, with the metal in the distorted octahedral and trigonal environment respectively. The metal atoms are connected by the chelating and bridging carboxylate groups to form helical ribbon like chains with dinuclear units. These chain structures have been described recently by Zhang et al.[19]

We have obtained a new two-dimensional layer compound, $[Cd(H_2O)(C_8H_4O_4)]$, **IV**, devoid of any amine, where Cd is in a distorted pentagonal bipyramidal environment (CdO_7) with Cd–O bond distances in the 2.238–2.680 Å range. (Fig. 2). The CdO_7 polyhedron is formed by a coordinated water molecule and six oxygens from tridentate carboxylic acid groups of the four different molecules with (2121) connectivity. The edge-sharing polyhedra are connected by the carboxylic acid molecules to form one-dimensional chains. The chains get interconnected by the carboxylic acids to form an extended two-dimensional layer structure. The structure is stabilized by interlayer CH–π interaction (2.823 Å, 119.0°) between the 1,3-BDC rings. A Zn 1,3-BDC of the formula $[Zn(H_2O)(C_8H_4O_4)]$, with a two-dimensional layer (4,4-net), where Zn is in a distorted tetrahedral environment has been reported.[20] The layer consists of chains of ZnO_4 units connected by the bridging carboxylate groups.

1,4-Benzenedicarboxylates

A cadmium 1,4-BDC of the formula $[Cd(H_2O)(C_8H_4O_4)(C_{10}H_8N_2)]$ consisting of a one-dimensional zig-zag chain, where 2,2'-bipy is the terminal ligand and the carboxylic acid acts as the linker has been reported recently by Xu et al.[21] Here, Cd adopts a distorted octahedral geometry (CdN_2O_4), the octahedra being connected by a monodentate and a chelating bidentate carboxylate group from two different carboxylic acid molecules to form the chain. Zinc forms a one-dimensional 1,4-BDC with a zig-zag chain structure with 1,10-phen.[22] The compound with the formula $[Zn(H_2O)(C_8H_4O_4)(C_{12}H_8N_2)]$ has (ZnN_2O_3) distorted trigonal
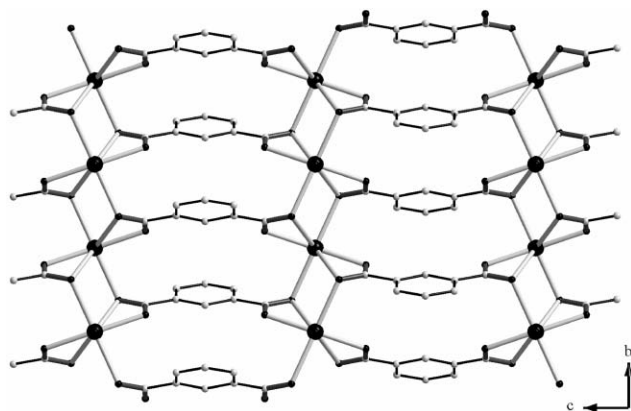
bipyramid units. With 2,2'-bipy, Zn forms a compound, $[Zn(C_8H_4O_4)(C_{10}H_8N_2)]\cdot(C_{10}H_8N_2)$, with a one-dimensional zig-zag chain structure, where free 2,2-bipy molecules are present in the structure.[23] Here, distorted ZnN_2O_4 octahedra units are connected by the two chelating bidentate carboxylates to form a one-dimensional chain.

We have obtained a new two-dimensional layer compound, $[Cd(C_8H_4O_4)(C_{12}H_8N_2)]\cdot H_2O$, **V**, with Cd in a distorted pentagonal bipyramidal environment (Fig. 3). The CdN_2O_5 polyhedron has Cd–O bond distances in the 2.341–2.590 Å range and the Cd–N bond distances are 2.340 and 2.408 Å. Each Cd atom is coordinated to the two nitrogen atoms of a terminal 1,10-phen molecule, two oxygens from a chelating carboxylate group (11) of a carboxylic acid molecule with (1111) connectivity and three oxygens from a tridentate carboxylate (21) of another carboxylic acid molecule with (2121) connectivity. Two such polyhedra form an edge-sharing dimer by sharing the μ_2 oxygen atom from a tridentate carboxylate (21). This carboxylic acid unit links the dimer units into a one-dimensional chain. Two chelating bidentate

(a)

(b)
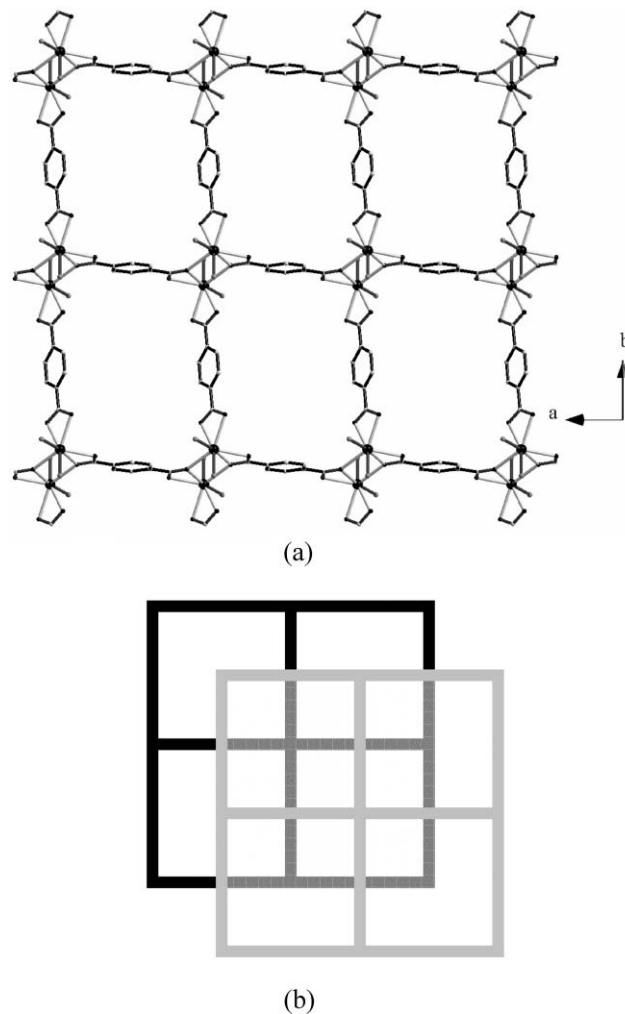
Fig. 3 (a) Structure of $[Cd(C_8H_4O_4)(C_{12}H_8N_2)]\cdot H_2O$, **V**, viewed along the c-axis. The carbon atoms in 1,10-phen are not shown, (b). Schematic illustration of the adjacent layer stacking in $[Cd(C_8H_4O_4)(C_{12}H_8N_2)]\cdot H_2O$, **V**

Fig. 2 Structure of $[Cd(H_2O)(C_8H_4O_4)]$, **IV**, viewed along the a-axis.

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carboxylates of another carboxylic acid unit (1111) connect the one-dimensional chains into an extended two-dimensional square network (4,4-net). The two chelating 1,10-phen molecules in each dimeric unit project into opposite sides of the layer, thereby preventing the formation of a three-dimensional interpenetrating network of the 1,4-BDC. The structure is stabilized by interlayer CH–π interaction (2.604 Å, 141.3°) between the 1,10-phen and 1,4-BDC along with the C–H···O interaction (2.349 Å, 175.2°) between the 1,10-phen and free water molecule.

In the absence of any chelating amine, we find that Zn forms 1,4-BDCs with a one-dimensional chain structure, $[Zn(H_2O)_2(C_8H_4O_4)]$, **VI**, and a three-dimensional structure $[Zn(H_2O)(C_8H_4O_4)]$, **VII**. We show the structures of **VI** and **VII** in Fig. 4, both of which have been reported earlier.[24,25] We will come back to these structures later, when we discuss the transformation of the chain structure to the three-dimensional structure. In **VI**, Zn is in a distorted tetrahedral environment with two coordinating water molecules and two oxygens from the monodentate carboxylate, the polyhedra being connected by the carboxylate units to form the one-dimensional chains. In **VII**, Zn is in a trigonal bipyramidal environment with a coordinated water and four oxygens from the carboxylate. The zig-zag chains of ZnO_5 and 1,4-BDC units are connected to form the three-dimensional structure with a one-dimensional channel along the *b*-axis.

Property of three-dimensional structures

Results of our extended investigations of the cadmium and zinc benzenedicarboxylates formed by the three isomeric
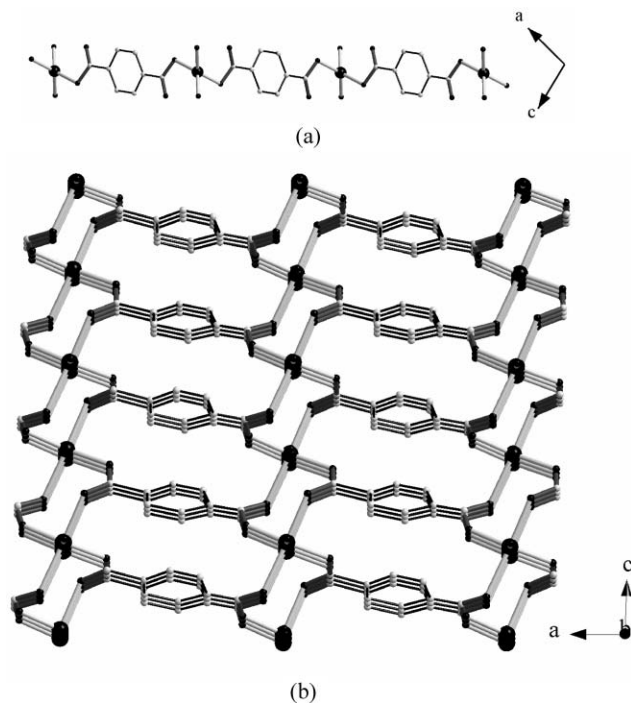
Fig. 4 (a) Structure of $[Zn(H_2O)_2(C_8H_4O_4)]$, **VI**, viewed along the *b*-axis, (b) Structure of $[Zn(H_2O)(C_8H_4O_4)]$, **VII**, viewed along the *b*-axis.

dicarboxylic acids in the presence or absence of the amines have been instructive. With 1,2-bezenedicarboxylic acid, we could only obtain one- and two-dimensional compounds. A survey of the literature shows that no three-dimensional 1,2-BDC is reported so far with any metal. This is clearly because of the unfavorable 60° dispersion angle between the two carboxylic acid groups. With the 1,3-benzenedicarboxylic acid, with a dispersion angle of 120°, we could obtain only one- and two-dimensional compounds. The three-dimensional 1,3-BDCs reported in the literature are based on the paddle wheel secondary-building units (SBUs) and contain coordinating amines.[4b,5b] 1,4-Benzenedicarboxylic acid, however, forms several three-dimensional structures, with or without interpenetration based on mono and dinuclear units or the paddle-wheel unit.[3b–e,4c,4d,26] Thus, Férey and coworkers have recently synthesized a Zn 1,4-BDC with diethylformamide.[27] We surmise that the formation of the three-dimensional structures is facilitated in 1,4-BDCs because of the favorable dispersion angle of 180° between the two carboxylate groups.

Process of formation of a three-dimensional Zn 1,4-BDC

Since we could readily form both one- and three-dimensional zinc 1,4-BDCs in the absence of a chelating amine, we considered it of significance to examine the relation between the two 1,4-BDCs of different dimensionalities. For this purpose, we have studied the time and temperature dependence of the products obtained from a starting reaction mixture containing $ZnSO_4 \cdot 4H_2O$, 1,4-BDC and NaOH in H_2O with the molar ratio (1 : 1 : 2 : 278) maintained at a fixed temperature. On keeping the reaction mixture at 75 °C for 72 h, we obtained the one-dimensional compound $[Zn(H_2O)_2(C_8H_4O_4)]$, **VI**, in pure form. On keeping the reaction mixture at 180 °C for 72 h, the three-dimensional compound $[Zn(H_2O)(C_8H_4O_4)]$, **VII** was obtained. The powder XRD patterns of **VI** and **VII** obtained at 75 °C and 180 °C are shown in Fig. 5(a) and (c) respectively. On keeping the reaction mixture at 125 °C for 72 h, we obtained a new compound designated as **N**. We show the powder XRD pattern of **N** in Fig. 5(b). It is possible that **N** has a two-dimensional layer structure, but we have not been able to establish the structure based on a single-crystal study. The water content decreases on going from the one-dimensional **VI** to three-dimensional **VII** and the coordination mode of the carboxylate also changes. Thus, the carboxylate changes from a bidentate (1010) to a tetradentate (1111) ligand with the coordination number of zinc increasing from four to five. These results are similar to those reported by Foster, Cheetham *et al.*, who find an increase in dimensionality and a decrease in water content in cobalt succinate with the increase in the reaction temperature.[12]

In order to establish the relation between one-dimensional **VI** and three-dimensional **VII**, we have studied the effect of time and temperature on **VI** under hydrothermal conditions. At 150 °C, **VI** transforms to a mixture of **VI** and the new phase **N** after 3 h as shown in Fig. 6(b). After 72 h, we obtain a mixture of **VI** and **VII** as shown in Fig. 6(c). However, at 180 °C **VI** transforms into **VII** in 3 h (Fig. 6(d)). These studies show that it is likely that the three-dimensional structure is formed by the transformation of one-dimensional structure.
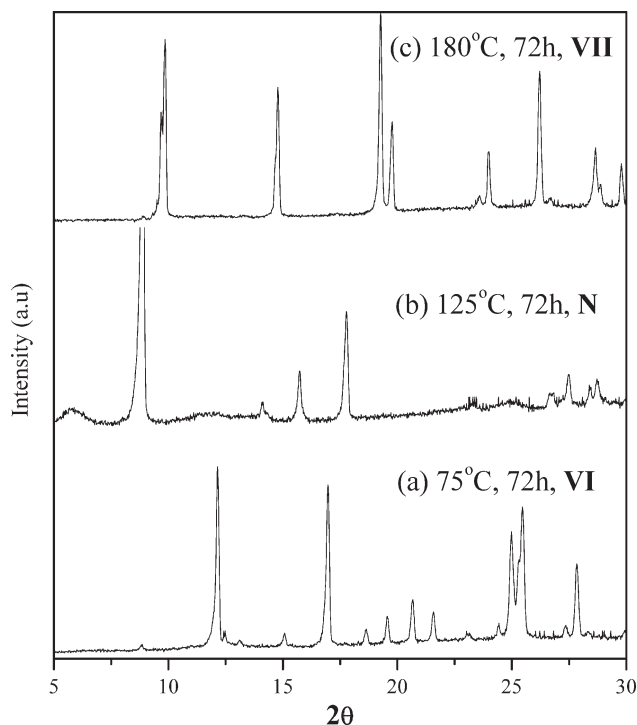
Fig. 5 Powder XRD patterns of a reaction product obtained on heating a reaction mixture of for 72 h at different temperature.
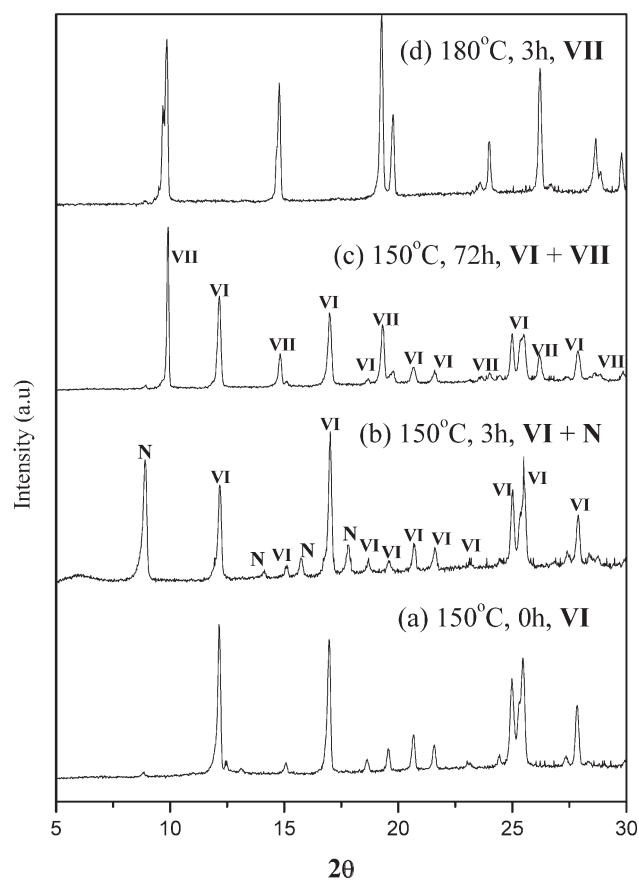

Fig. 6 Powder XRD patterns of products obtained on heating the one-dimensional compound **VI**.

We are not certain that the transformation proceeds through a two-dimensional structure. In this context, the observation of an intermediate phase **N** is significant. The transformation of a one-dimensional BDC structure to a three-dimensional structure and the possible presence of a dimensional hierarchy in the BDCs find a counterpart in open-framework metal phosphates.[28] It has been found that there is a progressive building-up of dimensionality in the open-framework metal phosphates and that the zero- and one-dimensional structures transform to higher dimensional structures on heating for a period of time at an appropriate temperature.

Conclusions

Benzenedicarboxylates of Cd and Zn of different dimensionalities are formed with or without the presence of amine and/or water molecules. The three-dimensional structures are however, favored most in the case of 1,4-benzenedicarboxylic acid because of the right disposition of the two carboxylic groups. Preliminary results indicate that the three-dimensional structure of a Zn 1,4-BDC is formed by the transformation of the one-dimensional structure. The occurrence of a dimensional hierarchy and the progressive building-up of dimensionality found in the benzenedicarboxylates becomes significant considering that a similar situation occurs in open-framework metal phosphates.[28]

Acknowledgements

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