Syntheses, structures and properties of cadmium benzenedicarboxylate metal–organic frameworks[†]

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The products isolated from the reaction between Cd(NO₃)₂·4H₂O and 1,4-benzenedicarboxylic acid $(H_2 bdc)$ in DMF are very dependent on the conditions. At 115 °C, the reaction gives $[Cd(bdc)(DMF)]_{\infty}$ 1, which has a three-dimensional network structure, whereas at 95 °C, 1 is formed alongside $[Cd_3(bdc)_3(DMF)_4]_{\infty}$ 2, which has a two-dimensional network structure. When the reaction is carried out under pressure, it yields $[Cd_3(bdc)_3(DMF)_4]_{\infty}$ 3, which is a supramolecular isomer of 2. The structure of 3 differs from that of 2 regarding the way the $Cd_3(O_2CR)_6$ units are interlinked to form layers. When the reaction was carried out in DMF that had undergone partial hydrolysis, the only isolated product was $\{(NMe_2H_2)_2[Cd(bdc)_2] \cdot 2DMF\}_{\infty}$ 4. Compound 4 has a three-dimensional triply-interpenetrated diamondoid structure, with dimethylammonium cations and DMF molecules included within the pores. The reaction between $Cd(NO_3)$, $4H_2O$ and H_2bdc in DEF gave $[Cd(bdc)(DEF)]_{\infty}$ 5, regardless of the solvent quality. Compound 5 has a three-dimensional network structure. The reaction of Cd(NO₃)₂·4H₂O and 1,3-benzenedicarboxylic acid (H₂mbdc) in DMF gave $[Cd(mbdc)(DMF)]_{\infty}$ 6 which has a bilayer structure. The thermal properties of the new materials have been investigated, and the coordinated DEF molecules from 5 can be removed on heating to 400 °C without any change in the powder X-ray diffraction pattern. The H₂ sorption isotherm for the desolvated material shows marked hysteresis between adsorption and desorption, and less adsorption than predicted by simulations. Kinetic data indicate that the hysteresis is not due to mass transfer limitations, and the most likely explanation for this behaviour lies in partial collapse of the framework to an amorphous phase under the conditions of activation.

Introduction

Coordination networks—otherwise known as metal–organic frameworks (MOFs)—have attracted considerable interest over the past few years.^{1,2} This is largely a result of their potential for porosity, and the implications of this in applications such as gas storage³ and catalysis.⁴ Perhaps the most successful class of ligands for developing coordination networks is that based on diand tri-carboxylates. These linkers connect together small metal-carboxylate aggregates, which are often referred to as secondary building units (SBUs).¹ The structures adopted by the resulting coordination networks are determined largely by the geometry of the SBUs and the distribution of carboxylate groups in the ligands, although reports have shown that the synthetic conditions can be crucial in determining the nature of the isolated product.^{5,6}

Carboxylates have attracted attention in the synthesis of MOFs for several reasons—(i) the M–O bonds are relatively labile, so

that 'mistakes' made in assembling the network can be readily corrected, allowing crystalline compounds to be formed; (*ii*) the ligands are anionic, so combination with metal centres can give neutral networks, meaning that counter-ions do not occupy the pores; (*iii*) the presence of the SBUs as opposed to single metal centres means the network nodes are larger, so interpenetration is less common; and (*iv*) the bridging coordination modes adopted within the SBUs appears to lead to robust networks that are able to withstand removal of solvent from the pores.

Although the reactions of many transition metals with dicarboxylates have been studied, those of zinc(II) have been particularly noteworthy.7,8 Yaghi and co-workers have reported a number of interesting structures, and impressive methane and hydrogen adsorption properties for compounds such as [Zn₄O(bdc)₃] (MOF-5, bdc = 1,4-benzenedicarboxylate, terephthalate) which has a simple cubic structure, based on $Zn_4O(O_2CR)_6$ SBUs that are interconnected by the benzene groups of the benzenedicarboxylate ligands.9 Given the interest in zinc(II) dicarboxylates, it is surprising that the related chemistry of the heavier Group 12 analogue, cadmium, has received rather less attention. Although there are a number of reports on cadmium(II) mixed ligand systems containing both dicarboxylates and N-donor ligands, which can be terminal, such as phenanthroline¹⁰ and ammonia,¹¹ or bridging, such as 4,4'-bipy,12 simple reactions with dicarboxylic acids which are analogous to the synthesis of MOF-5 have not been reported. In this paper we report the synthesis of six new

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cadmium(II) networks containing either 1,4-benzenedicarboxylate or 1,3-benzenedicarboxylate (*m*bdc) that were all prepared under relatively mild (*i.e.* non-solvothermal) conditions. In addition, we report the thermal properties of the new three-dimensional network materials, and gas adsorption studies on the one that retains its framework structure following solvent removal.

Results and discussion

Synthesis

The product from the reaction between $Cd(NO_3)_2 \cdot 4H_2O$ and 1,4-benzenedicarboxylic acid in DMF is acutely dependent on the conditions employed. When the reagents were heated to 115 °C for 5 h in DMF, the reaction produced $[Cd(bdc)(DMF)]_{\infty}$ 1 as the sole product. Carrying out the reaction at a lower temperature (95 °C) led to a mixture of 1 and $[Cd_3(bdc)_3(DMF)_4]_{\infty}$ 2, where 2 is the minor product. When the reaction was carried out in a sealed system at 115 °C under a pressure of 1.5–5 atmospheres of dinitrogen or compressed air, the isolated product was $[Cd_3(bdc)_3(DMF)_4]_{\infty}$ 3, which is a supramolecular isomer of 2.

The reaction is also sensitive to the quality of the solvent. Use of DMF in which partial hydrolysis has occurred led to the formation of $\{(NMe_2H_2)_2[Cd(bdc)_2]\cdot 2DMF\}_{\infty} 4$, with no evidence for the formation of either 1 or 2. The formation of 4 can also be templated by addition of $[NMe_2H_2]Cl$ to the reaction mixture or by addition of a few drops of acid to reduce the pH to 4.

The reaction between $Cd(NO_3)_2 \cdot 4H_2O$ and 1,4benzenedicarboxylic acid in DEF is less dependent on the synthetic conditions and the solvent quality, affording $[Cd_3(bdc)_3(DEF)_2]_{\infty}$ **5**, regardless of the latter. Furthermore, addition of $[NEt_2H_2]Cl$ did not lead to a change of product, in contrast to the observations in DMF or for the related zinc(II) system in either DMF or DEF. The reaction of $Zn(NO_3)_2 \cdot 6H_2O$ with H_2bdc in DEF gives $[Zn_4O(bdc)_3]$ (MOF-5), though on addition of $[NEt_2H_2]Cl$ the compound $\{(NEt_2H_2)_2[Zn_3(bdc)_4]\cdot 2.5DEF\}_{\infty}$ is formed instead.⁶

In order to investigate the effect of the relative orientation of the carboxylate groups on the network structure, the reaction of $Cd(NO_3)_2$ ·4H₂O with 1,3-benzenedicarboxylic acid (H₂*mbdc*) was also investigated. When the reaction was carried out at 90 °C, the compound $[Cd(mbdc)(DMF)]_{\infty}$ 6 was formed as the sole product.

The syntheses of compounds **1–6** are summarised in Scheme 1. No evidence was observed for any interconversions involving **1–5**.



Table 1	Selected bond lengths (Å) and bond angles (°) for 14
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Cd(1)–O(1)	2.494(2)	Cd(1)–O(5)	2.274(2)
Cd(1) - O(2)	2.2788(19)	Cd(1)–O(2)"	2.3947(19)
Cd(1) - O(3)	2.517(2)	Cd(1) - O(3)'	2.349(2)
Cd(1) - O(4)	2.256(2)		
O(2)-Cd(1)-O(1)	54.87(7)	O(4)-Cd(1)-O(5)	125.22(8)
O(4)-Cd(1)-O(3)	54.70(7)	O(5)-Cd(1)-O(2)"	79.34(7)
O(5)-Cd(1)-O(1)	144.16(8)	O(5)-Cd(1)-O(3)'	81.20(7)
O(5)–Cd(1)–O(2)	96.71(7)	O(4)-Cd(1)-O(1)	90.53(8)
O(5)–Cd(1)–O(3)	86.36(7)		

^{*a*} Primed atoms generated by the symmetry operation -x + 1, -y, -z + 1. Double primed atoms generated by the symmetry operation -x, -y, -z + 1.

Structures

 $[Cd(bdc)(DMF)]_{\infty}$ 1. The asymmetric unit of 1 consists of one cadmium centre, which is coordinated to two halves of bdc anions and one DMF molecule. The remaining portion of each of bdc anion is generated by inversion symmetry. The carboxylate groups bridge between two cadmium centres, coordinating κ^1 - to one and κ^2 - to the other. Each cadmium centre is 7-coordinate and bonded to two κ^1 -carboxylates, two κ^2 -carboxylates and a DMF ligand. Selected bond lengths and angles are given in Table 1. The bridging carboxylate groups link the cadmium centres into infinite chains, as shown in Fig. 1, which contain non-bonded Cd \cdots Cd contacts of 3.65 and 3.86 Å. These chains can be regarded as infinite $\{Cd(O_2CR)_2\}_{\infty}$ SBUs, which are cross-linked by the benzene rings of the bdc ligands into the three-dimensional network shown in Fig. 2. The network contains rhomboidal pores, which are partly filled by the coordinated DMF molecules.



Fig. 1 The cadmium carboxylate chains present in the structure of $[Cd(bdc)(DMF)]_{\infty}$ 1.



Fig. 2 Part of the three-dimensional network present in the structure of $[Cd(bdc)(DMF)]_{\infty}$ 1. Hydrogen atoms have been omitted for clarity.



Fig. 3 The $Cd_3(\mu-O_2CR)_6$ SBU present in the structure of $[Cd_3(bdc)_3(DMF)_4]_{\infty}$ 2. Part (a) shows a side-on view and part (b) shows the directions in which the bdc ligands radiate out from the Cd_3 unit.

The structure of **1** is related to that previously reported for $[Cd(bdc)(py)]_{\infty}$.¹¹ This compound has similar $\{Cd(O_2CR)_2\}_{\infty}$ SBUs, with pyridine ligands taking the place of the DMF ligands in **1**. $[Cd(bdc)(py)]_{\infty}$ crystallises in a different space group to **1** (C2/c), however, and only contains one independent carboxylate.

Supramolecular isomers of $[Cd_3(bdc)_3(DMF)_4]_{\infty}$, 2 and 3. The asymmetric unit of 2 consists of one and a half cadmium centres, one and a half bdc anions and two DMF molecules. Cd(2) lies on a twofold axis, and the half bdc ion lies proximate to an inversion centre. Two-fold rotational symmetry intrinsic to the space group serves to generate Cd₃(O₂CR)₆ SBUs. Selected bond lengths and angles are given in Table 2. The DMF molecules are coordinated to the two outer cadmium centres, as shown in Fig. 3a, and this prevents further propagation of the Cd₃ unit into a chain similar to that observed for 1.

Within each Cd₃ unit, the central Cd(2) atom has a distorted octahedral geometry. It is κ^1 -coordinated to six carboxylate groups, and the *cis* angles range from 76.59(4)–100.97(5)°. The two symmetry related Cd(1) atoms are 7-coordinate, and are κ^1 -coordinated to one carboxylate and κ^2 -coordinated to two carboxylates in addition to the two DMF molecules.

The $Cd_3(O_2CR)_6$ SBUs are linked together by the benzene rings of the bdc anions to form a sheet structure (Fig. 4) containing rhombohedral pores that are capped by the coordinated DMF molecules.

The asymmetric unit of **3** consists of two full cadmium atoms [Cd(1) and Cd(3)], two half-occupancy cadmium atoms [Cd(2) and Cd(4)], two full and two halves of bdc anions, the halves lying proximate to inversion centres, and four DMF molecules. Selected bond lengths and angles are given in Table 3. In the structure, the bdc anions bridge between linear $Cd_3(O_2CR)_6$ SBUs similar to those observed in **2** to generate a layer structure. The four independent cadmium atoms in the asymmetric unit are connected

Table 2 Selected bond lengths (Å) and bond angles (°) for 2^a

Cd(1)–O(1)	2.3030(13)	Cd(1)–O(6)	2.2611(13)
Cd(1) - O(2)	2.4661(13)	Cd(1) - O(7)'	2.2970(13)
Cd(1) - O(3)	2.2801(14)	Cd(2) - O(8)'	2.2175(13)
Cd(1) - O(4)	2.6035(14)	Cd(2)-O(2)	2.4620(13)
Cd(1)–O(5)	2.2886(14)	Cd(2)-O(4)	2.2863(13)
O(1)-Cd(1)-O(2)	55.17(5)	O(6) - Cd(1) - O(5)	95.96(5)
O(3)-Cd(1)-O(1)	171.85(5)	O(2)-Cd(2)-O(2)*	165.66(6)
O(5)-Cd(1)-O(7)	175.82(5)	O(8)"-Cd(2)-O(4)	164.81(5)

^{*a*} Primed atoms generated by the symmetry operation x, -y, z - 1/2. Double primed atoms generated by the symmetry operation -x, -y, -z + 1. Asterisked atoms generated by the symmetry operation -x, y, -z + 1/2.



Fig. 4 The two-dimensional layer structure present in the structure of $[Cd_3(bdc)_3(DMF)_4]_{\infty}$ **2**. Hydrogen atoms have been omitted for clarity.

to two independent $Cd_3(O_2CR)_6$ SBUs, one containing Cd(1) and Cd(2), and the other containing Cd(3) and Cd(4). The two independent SBUs have very similar structures, with the central metal in each case located at an inversion centre, and one of these is shown in Fig. 5a.

The central Cd(2) and Cd(4) atoms are κ^1 -coordinated to six carboxylate oxygen atoms. These cadmium centres display distorted octahedral geometry, with *cis* angles ranging between 87.00(5) and 93.00(5)° for Cd(2) and between 85.42(5) and 94.58(5)° for Cd(4). The terminal Cd(1) and Cd(3) atoms are coordinated to two κ^1 -carboxylates, one κ^2 -carboxylate and two DMF molecules. The geometries around these atoms are distorted octahedral, with the presence of the κ^2 -carboxylate ensuring the distortions are far greater than those for the central cadmium atoms. *cis* angles range from 55.50(4) to 109.89(6)° for Cd(1) and from 55.60(4) to 110.10(5)° for Cd(3).

Table 3 Selected bond lengths (Å) and bond angles (°) for 3^a

Cd(1)–O(2)	2.2021(13)	Cd(3)–O(3)	2.2158(13)
Cd(1)–O(5)	2.2296(13)	Cd(3) - O(7)'	2.2078(13)
Cd(1)–O(9)	2.3641(13)	Cd(3)–O(13)	2.3827(13)
Cd(1)–O(10)	2.3707(13)	Cd(3)–O(14)	2.3565(13)
Cd(1)–O(11)	2.2490(14)	Cd(3)–O(15)	2.3564(13)
Cd(1)–O(12)	2.3977(14)	Cd(3)–O(16)	2.2733(14)
Cd(2)–O(1)	2.2336(13)	Cd(4)–O(4)	2.2161(14)
Cd(2)–O(6)	2.2449(13)	Cd(4)–O(8)'	2.2651(12)
Cd(2)–O(10)	2.3145(12)	Cd(4)–O(14)	2.3244(12)
O(2)–Cd(1)–O(9)	150.36(5)	O(3)-Cd(3)-O(15)	167.89(5)
O(5)–Cd(1)–O(12)	173.35(5)	O(7)"-Cd(3)-O(13)	145.91(5)
O(11)-Cd(1)-O(10)	150.97(5)	O(16)–Cd(3)–O(14)	165.69(5)
O(9)–Cd(1)–O(10)	55.50(4)	O(14)-Cd(3)-O(13)	55.60(4)

^{*a*} Primed atoms generated by the symmetry operation x, y-1, z+1. Double primed atoms generated by the symmetry operation x, y-1, z+1.



Fig. 5 One of the two independent $Cd_3(\mu-O_2CR)_6$ SBUs present in the structure of $[Cd_3(bdc)_3(DMF)_4]_{\infty}$ 3. Part (a) shows a side-on view and part (b) shows the directions in which the bdc ligands radiate out from the Cd_3 unit.

The dicarboxylate ligands link the $Cd_3(O_2CR)_6$ SBUs into layers containing triangular pores (Fig. 6). Each layer includes both independent SBUs. Coordination of the DMF molecules to the terminal Cd(1) and Cd(3) atoms ensures there are only weak interactions between the layers.



Fig. 6 The two-dimensional layer structure present in the structure of $[Cd_3(bdc)_3(DMF)_4]_{\infty}$ 3. Hydrogen atoms have been omitted for clarity. Only the oxygen atoms of the coordinated DMF molecules are shown.

Compounds 2 and 3 have identical formulae and both contain $Cd_3(O_2CR)_6$ SBUs. In both cases these units are interlinked to form sheet structures, but there are significant differences between the two networks. 2 and 3 can therefore be regarded as supramolecular isomers.

The differences in the sheets are related to differences in the $Cd_3(O_2CR)_6$ SBUs. In **3** there are two independent SBUs, but both are linear, with $Cd \cdots Cd \cdots Cd$ angles of 180° . Furthermore, each of the terminal Cd atoms is connected to the central Cd atom by two μ - $\kappa^1 O, \kappa^1 O'$ carboxylates and one μ - $\kappa^1 O, \kappa^2 O, O'$ carboxylate. Together these factors result in the carboxylate groups radiating from the central Cd₃ spine at approximately 60° angles from each other (Fig. 5b).

For **2**, the Cd···Cd ···Cd angle is reduced to 157°, and this distortion from linearity occurs in tandem with there being two μ - $\kappa^1 O$, $\kappa^2 O$, O' carboxylates and only one μ - $\kappa^1 O$, $\kappa^1 O'$ carboxylate.

This leads to greater distortions from regular octahedral geometry around the central atom and, as a result, the carboxylate groups radiate from the central Cd_3 spine in a less regular manner than in **3** (Fig. 3b).

Side views of the sheets in 2 and 3 are shown in Fig. 7, with the linkers depicted in a simplified form. In both cases, six dicarboxylates radiate from each $Cd_3(O_2CR)_6$ SBU, and two of these connect an 'upper' part of the SBU with a 'lower' part of a neighbouring SBU. Looking along an axis generated by the SBUs, this gives a 'criss-cross' of dicarboxylates for 3 but a parallel arrangement for 2. This difference is related to the symmetry present in the SBUs, with the central atom of the $Cd_3(O_2CR)_6$ unit sitting on an inversion centre in 3 but a 2-fold rotation axis in 2.



Fig. 7 Side on view of the sheets in (a) compound **2** and (b) compound **3**. The bdc ligands are shown as simple lines between the carboxylate groups for clarity. DMF ligands have also been omitted.

The $Cd_3(O_2CR)_6$ SBUs observed in **2** and **3** are similar to those seen previously in the compound $(BMIM)_2[Cd_3(bdc)_3Br_2]$ (BMIM = 1-butyl-3-methylimidazolium).¹³ In this case, the bromide ligands terminate the Cd₃ units, and the sheets formed through the bridging bdc ligands have the same triangular pores as those in **3**.

There are also several examples of zinc-based networks containing analogous SBUs. The compounds $\{[Zn_3 (bdc)_3(OH_2)_2] \cdot 4DMF\}_{\infty}^7$ and $\{[NEt_2H_2][Zn_3(bdc)_4] \cdot 2.5DEF\}_{\infty}^6$ both contain $Zn_3(O_2CR)_6$ SBUs, though in these cases the terminal zinc centres are 4-coordinate. In both of these compounds, the SBUs are connected into layers by the bdc ligands in a similar manner to those in **3**, and for $\{[NEt_2H_2][Zn_3(bdc)_4] \cdot 2.5DEF\}_{\infty}$ these layers are cross-linked by an additional bdc to form

Table 4Selected bond lengths (Å) and bond angles (°) for 4^a

Cd(1)–O(1)	2.4530(18)	Cd(1)–O(3)'	2.3143(15)
Cd(1)–O(2)	2.391(2)		
O(2)-Cd(1)-O(1)	53.66(6)	O(3)'-Cd(1)-O(3)"	117.74(8)

^{*a*} Primed atoms generated by the symmetry operation -x + 1/4, y - 1/4, z - 1/4. Double primed atoms generated by the symmetry operation x + 3/4, -y + 3/4, z - 1/4.

a three-dimensional coordination network. The compound $\{[Zn_3(bdc)_3(MeOH)_4]\cdot 2MeOH\}_\infty$ also contains $Zn_3(O_2CR)_6$ SBUs, but in this instance they are directly linked by the bdc ligands into a three-dimensional network.¹⁴

 $\{[NMe_2H_2]_2[Cd(bdc)_2]\cdot 2DMF\}_{\infty}$ 4. The asymmetric unit of 4 consists of half of a cadmium atom, located on a two-fold rotational axis, one bdc anion, one $NMe_2H_2^+$ cation, in which one of the carbons is equally disordered over two positions, and one DMF molecule disordered over two positions. Selected bond lengths and angles are given in Table 4.

The bdc anions bridge between the cadmium centres to generate a three-dimensional network structure. Each cadmium centre in **4** is 6-coordinate, and bonded to two κ^1 -carboxylates and two κ^2 -carboxylates (Fig. 8). There is some asymmetry in the κ^2 -coordination, with Cd(1)–O(1) 2.4530(18) Å and Cd(1)–O(2) 2.391(2) Å. For the κ^1 -coordination, Cd(1)–O(3) is 2.3143(15) Å, whereas the non-coordinated distance Cd(1)…Cd(4) is 2.705(2) Å.

Coordination to four carboxylate groups means that each cadmium centre can be regarded as a flattened tetrahedral node. The benzene rings of the bdc ligands link these nodes into a diamondoid network which is triply interpenetrated, as shown in Fig. 9. The network contains cadmium(II) centres and bdc anions in the ratio 1:2, so consequently the network is anionic. This charge is balanced by the presence of dimethylammonium cations, which interact through hydrogen bonds with the carboxylate oxygen atoms [N(3) \cdots O(4) 2.941 Å, H(3A) \cdots O(4) 2.21 Å, N(3)–H(3A) \cdots O(4) 139°; N(3) \cdots O(3) 2.909 Å, H(3A) \cdots O(3) 2.30 Å, N(3)–H(3A) \cdots O(3) 125°]. The DMF molecules are not coordinated and are included as guests within the pores, where they act as hydrogen bond acceptors to the dimethylammonium cations [N(3) \cdots O(5) 2.646 Å, H(3B) \cdots O(5) 1.80 Å, N(3)–H(3B) \cdots O(5) 158°].



Fig. 8 The cadmium environment in the structure of $\{[NMe_2H_2]_2[Cd(bdc)_2]\cdot 2DMF\}_{\infty} 4$.



Fig. 9 The triply interpenetrated network structure of $\{[NMe_2H_2]_2[Cd(bdc)_2] \cdot 2DMF\}_{\infty}$ 4. Hydrogen atoms, dimethylammonium cations and included DMF molecules have been omitted for clarity.

The formation of 4 rather than 1 with poorer quality solvent arises because of hydrolysis within the DMF.15 This hydrolysis generates $NMe_2H_2^+$ cations, which template the formation of the network observed in 4. In order to verify that a templating effect was indeed occurring, [NMe₂H₂]Cl was added to the reaction mixture. In these cases, compound 4 was observed as the only product regardless of the quality of the DMF used. While the hydrolysis of DMF is well established, an alternative way of generating NMe₂H₂⁺ is via decarbonylation, and this can occur when DMF is heated with base.¹⁶ Although the absence of added base implies decarbonylation is not the only process at work, it is possible that NMe₂H formed through hydrolysis is able to facilitate decarbonylation, and thus amplify the concentrations of NMe₂H₂⁺. This may explain why mixtures of 1 and 4 have not been observed. We have previously shown that the purity of DMF is important in determining the isolated product from the reaction of Zn(NO₃)₂·6H₂O with H₂bdc. These observations with $Cd(NO_3)_2 \cdot 4H_2O$ reveal that the effect is more general.

 $[Cd_3(bdc)_3(DEF)_2]$ 5. The asymmetric unit of 5 consists of one and a half cadmium centres, one and a half bdc anions and one DEF molecule, which is disordered over two sites in a 70: 30 ratio. Selected bond lengths and angles are given in Table 5.

In a similar manner to the structures of **2** and **3**, the structure of **5** consists of a $Cd_3(O_2CR)_6$ trimer with three bridging carboxylate groups between the central Cd(1) atom and each of the terminal Cd(2) atoms. The central Cd(1) atom adopts a distorted octahedral

Table 5Selected bond lengths (Å) and bond angles (°) for 5^a

Cd(1)–O(1)	2.1971(15)	Cd(2)–O(4)'''	2.3043(13)
Cd(1)–O(3)"	2.3876(13)	Cd(2) - O(5)	2.5560(15)
Cd(1)–O(5)	2.3005(15)	Cd(2)–O(6)	2.2741(16)
Cd(2)–O(2)	2.2209(18)	Cd(2)–O(7)	2.279(5)
Cd(2)-O(3)"	2.4453(13)	Cd(2)-O(7A)	2.203(16)
Cd(2)-O(4)"	2.3649(14)		
O(1)-Cd(1)-O(5)'	168.17(7)	O(2)-Cd(2)-O(7)	174.33(16)
O(3)"-Cd(1)-O(3)*	170.63(8)	O(6)-Cd(2)-O(4)"	176.21(7)
O(4)"-Cd(2)-O(3)"	53.92(4)		

^{*a*} Primed atoms generated by the symmetry operation -x, y, -z + 1/2. Double primed atoms generated by the symmetry operation x, -y + 1, z + 1/2. Asterisked atoms generated by the symmetry operation -x, -y + 1, -z. Triple primed atoms generated by the symmetry operation -x + 1/2, y + 1/2, -z + 1/2. geometry, with *cis* angles in the range $81.36(5)-101.11(10)^{\circ}$. Cd(1) lies on a 2-fold axis and the half bdc ions lie proximate to inversion centres.

Each Cd(2) atom is 7-coordinate, and bonded to two κ^2 carboxylates, two κ^1 -carboxylates and a DEF ligand. One of the κ^1 -carboxylates derives from a neighbouring trimer, and this interaction links the trimers into infinite chains, as shown in Fig. 10. The three structurally independent carboxylate groups each adopt a different binding mode: that containing O(1) and O(2) exhibits the $\kappa^1 O, \kappa^1 O$ -coordination mode, that containing O(5) and O(6) adopts the $\kappa^1 O, \kappa^2 O, O'$ -coordination mode, and that containing O(3) and O(4) has the $\kappa^1 O, \kappa^2 O, O', \kappa^1 O'$ coordination mode.



Fig. 10 The cadmium carboxylate chains present in the structure of $[Cd_3(bdc)_3(DEF)_2]_{\infty}$ 5. Hydrogen atoms and minor components of the disordered solvent molecules have been omitted for clarity.

The infinite chains are connected into a three-dimensional network through the bdc ligands, and the gross structure contains rhombohedral pores, as shown in Fig. 11, into which the coordinated DEF ligands project. A coordination number of 7 for Cd(2) occurs together with a distortion from linearity of the Cd₃ unit, as witnessed by a Cd···Cd···Cd angle of 144°. It is notable that a similar distortion was observed in **2**, which also contained rhombohedral pores. In both **2** and **5**, the central cadmium in each Cd₃ unit is located on a two-fold axis.



Fig. 11 Part of the three-dimensional network present in the structure of $[Cd_3(bdc)_3(DEF)_2]_{\infty}$ 5. Hydrogen atoms and minor components of the disordered solvent molecules have been omitted for clarity.

Compound **5** is formed in DEF regardless of the quality of solvent used or the presence of added [NEt₂H₂]Cl. The insensitivity of the reaction in DEF to the presence of NEt₂H₂⁺ may be a consequence of the larger size of this cation with respect to NMe₂H₂⁺, rendering it incapable of being accommodated within the pores of the interpenetrated anionic ${Cd(bdc)_2}_n$ network observed in **4**.

 $[Cd(mbdc)(DMF)]_{\infty}$ 6. Though the gross structure is unambiguous, there were problems in refinement of the model in the crystal structure of 6, as noted in the Experimental section, which prevents meaningful discussion of the bond length and bond angle data. The asymmetric unit of 6 contains four cadmium centres, four *m*bdc ligands and four molecules of DMF. Although there are four independent cadmium centres, the differences between them are minor. Each is bonded to four carboxylates and a DMF ligand. The cadmium centres are connected into pairs by two μ - $\kappa^1 O$, $\kappa^2 O$,O-carboxylate groups, and these pairs are linked into chains by two further bridging carboxylate groups. Two orientations of these chains are shown in Fig. 12.



Fig. 12 Two views of the cadmium carboxylate chains present in the structure of $[Cd(mbdc)(DMF)]_{\infty}$ 6. The DMF ligands have been omitted for clarity.

The *m*bdc ligands connect the chains into bilayers, as shown in Fig. 13. The two sheets that comprise each bilayer are separated by approximately 3.3 Å, whilst the distance between bilayers is greater (approximately 8.0 Å) in order to accommodate the DMF molecules.

Two cadmium–*m*bdc structures that do not contain *N*-donor ligands have been previously reported. $[Cd(mbdc)(H_2O)]_{\infty}$ forms a two-dimensional structure in which *m*bdc ligands interlink zigzag cadmium–carboxylate chains into layers.¹⁷ The compound $\{(NH_2Me_2)_2[Cd_3(mbdc)_4]\}_{\infty}$ also contains cadmium–carboxylate chains, but in this case they are formed from the linking together of $Cd_3(\mu$ -O₂CR)₆ units in a similar manner to that observed in **5**.¹⁸ The chains are interconnected into a three-dimensional network by the *m*bdc ligands. As with **4**, the dimethylammonium cations are derived from decomposition of the DMF solvent.

Thermal properties

Of 1. Analysis of **1** by TGA revealed that **1** remains unchanged until 180 °C, then loses 11% of its mass by 220 °C, and a further 10% by 350 °C. These two mass losses together account for the coordinated DMF (calc. 20.3%). The desolvated material starts to lose mass more rapidly as the temperature approaches 450 °C, and



Fig. 13 Top and side views of one of the bilayers present in the structure of $[Cd(mbdc)(DMF)]_{\infty}$ 6.

by 550 °C it is converted into CdO (experimental mass remaining 36%, calc. 36.7%).

Separate samples of 1 were heated at 250 °C and 400 °C, to generate 1a and 1b respectively. Microanalyses on 1a and 1b confirmed their identities as $[Cd(bdc)(DMF)_{0.5}]$ (1a) and [Cd(bdc)] (1b). Powder X-ray diffraction patterns revealed many of the peaks for 1a and 1b were identical to those for 1, though additional peaks of low intensity were present in both cases. This suggests a new phase is formed as a minor product on heating, though the majority of 1 loses coordinated DMF without destruction of the network.

Of 4. Analysis of 4 by TGA revealed that on heating it remains unchanged until 120 °C. A 22% mass loss between 120 °C and 200 °C corresponds to removal of the included DMF molecules (calc. loss 21.5%). The desolvated network remains stable until 250 °C, then steadily loses mass until 500 °C, after which the mass loss is accelerated, finally yielding CdO at 550 °C (experimental mass loss 20%, calc. 18.9%).

Powder X-ray diffraction patterns recorded after heating samples of **4** to 210 °C were very different to those of **4**, suggesting that a substantial rearrangement of the network structure occurs in conjunction with loss of the included solvent. Attempts to exchange the included DMF molecules for more volatile guests proved unsuccessful. Immersion of samples of **4** in chloroform or acetone led to no changes in the TGA or powder X-ray diffraction patterns after 3 d, suggesting no guest exchange had occurred. In contrast, immersion of samples of **4** in methanol led to significant changes in the powder X-ray diffraction patterns after only 10 min. The peaks associated with **4** had diminished in intensity, whereas a new set of peaks had appeared. After further immersion, these new peaks increased in relative intensity. These observations suggest that methanol converts **4** into another, as yet uncharacterised, compound. A number of MOFs are known to dissolve and reprecipitate in new structural forms,¹⁹ so it is possible that a similar process is also occurring here.

Of 5. On heating, **5** remains unchanged until 200 °C, then loses 10% of its mass between 200 °C and 300 °C. This material is then stable until 370 °C, when it loses a further 10% of its mass before 400 °C. Both of these steps correspond to the loss of one of the coordinated DEF molecules (calc. 9.8% for each). The desolvated material undergoes a further mass loss between 450 °C and 550 °C, yielding CdO (experimental mass remaining 36%, calc. 37.3%).

Samples of 5 were heated to 300 °C and 400 °C, to generate **5a** and **5b** respectively. Microanalyses confirmed the identities of these materials as $Cd_3(bdc)_3(DEF)$ (**5a**) and Cd(bdc) (**5b**), and the reduction of the observed percentage of nitrogen from 2.98% in 5 (calc. 2.71%) to 1.73% in **5a** (calc. 1.51%) and 0% in **5b** is particularly striking. Powder X-ray diffraction experiments confirmed that the network structure of **5** was retained in **5a** and **5b**, though broadening of the peaks may indicate some loss of crystallinity.

Of 6. Analysis of 6 by TGA revealed that it lost 20% of its mass between 80 °C and 230 °C, then remained unaltered until 500 °C. The 20% mass loss corresponds to the coordinated DMF molecules (calc. 20.3%). Between 530 °C and 570 °C, 6 underwent a further mass loss to form CdO (experimental mass remaining 37%, calc. 36.7%). In contrast to the isomeric network 1, 6 loses DMF in a single step.

Gas adsorption properties of 5b

The powder X-ray diffraction experiments revealed that **5b** retained the three-dimensional network structure of **5** after loss of the coordinated DEF molecules. Therefore, **5b** should contain rhombohedral pores, so was deemed a good candidate for gas adsorption studies.

Experimental single-component adsorption isotherms on **5b** were obtained for nitrogen, krypton and hydrogen at 77 K. Examples of these data are shown in Fig. 14 and 15. From Fig. 14 it can be seen that the adsorption isotherm for nitrogen is of Type I form. Although it was not developed for microporous materials, the BET model performs surprisingly well if the two consistency criteria are taken into account.²⁰ firstly, the pressure range is selected so that the values $v(P_0 - P)$ are increasing with increasing P/P_0 , and



Fig. 14 Adsorption isotherms for nitrogen (\blacksquare) and krypton (\blacklozenge) on 5b obtained at 77 K.

secondly, the intercept of the BET plot must be positive. The BET surface area calculated in this way is $13 \text{ m}^2 \text{ g}^{-1}$.

A single component Langmuir isotherm can be fitted to the adsorption isotherm for krypton ($r^2 = 0.9820$). The monolayer capacity and interaction energy parameters obtained from the fit were not significantly affected by the choice of reference state (liquid/solid) for krypton at 77 K. The apparent surface area of **5b** calculated, using the customary value for the cross-sectional area of krypton mentioned in the literature (0.202 nm²),²¹ from the Langmuir monolayer capacity was 15 m² g⁻¹. Considering the simplicity of the models used and uncertainties in the customary molecular areas, this value is in good agreement with that obtained for nitrogen.

The accessible surface area calculated in a geometric manner from the crystallographic data of the perfect crystal provides a useful tool to assess the quality of a synthesised sample.²² Calculation of the accessible surface area in the structure of **5b**, determined with a N₂ sized probe molecule, suggests a much higher theoretical value—735 m² g⁻¹—than that observed in the nitrogen and krypton adsorption measurements. One possible explanation for this is that partial structural collapse has occurred on removal of the DEF ligands. Though there is no evidence for another structure in the powder X-ray diffraction experiments, these cannot rule out partial formation of an amorphous phase, which is either non-porous or significantly less porous than **5b** is expected to be from the crystal structure of **5**.

From Fig. 15 it can be seen that the hydrogen isotherm for **5b** has a Type I form expected for adsorption in a microporous solid and/or supercritical adsorption. There is marked hysteresis between adsorption and desorption isotherms. This hysteresis has been previously observed²³ for MOF equilibrium isotherms, and in the absence of kinetic data, was attributed to mass transfer limitations. However, in our studies, data on the kinetics of adsorption and desorption were obtained simultaneously with the isotherms. These data demonstrated that each point in the hydrogen adsorption and desorption isotherms in Fig. 15 reached equilibrium rapidly, and were not associated with significant temperature excursions. Hence, the observed hysteresis is not due to mass transfer effects in this case.

Simulation of hydrogen adsorption/desorption in **5b** does not replicate the hysteresis observed in the experiments, and reveals the saturation loading is anticipated at approximately 10 bar (Fig. 16), compared with 0.5 bar as observed. In addition, the



Fig. 15 Adsorption (\blacksquare) and desorption (\blacklozenge) isotherms for hydrogen on 5b obtained at 77 K.



Fig. 16 Simulation of hydrogen adsorption (\blacksquare) and desorption (\blacktriangle) in 5b.

maximum amount of hydrogen adsorbed in the simulation is 24 mg g⁻¹, compared to 4 mg g⁻¹ experimentally. As with the nitrogen adsorption data, the differences between the experimental data and that predicted for **5b** are consistent with partial collapse of the porous **5b** framework under the high temperature activation conditions. As the simulations show that hydrogen saturation loading, even in the perfect crystal (2.4 wt% and 36 g dm⁻³), is far from the DOE 2010 targets for hydrogen storage (6 wt% and 45 g dm⁻³) **5b** is not a promising material for hydrogen storage. Consequently, we did not invest further time in trying to improve the activation procedure of **5**.

Conclusions

We have demonstrated that the outcome of the reaction between Cd(NO₃)₂·4H₂O and H₂bdc in DMF is very dependent on the synthetic conditions, with temperature, pressure and solvent quality all factors that affect the nature of the observed product(s). Four new coordination networks have been structurally characterised from this reaction, with [Cd(bdc)(DMF)]_∞ 1 and {(NMe₂H₂)₂[Cd(bdc)₂]·2DMF}_∞ 4 adopting three-dimensional networks while the two supramolecular isomers of [Cd₃(bdc)₃(DMF)₄]_∞ (2 and 3) adopt twodimensional arrays.

The effect of temperature on MOF synthesis is well documented,⁵ and solvothermal conditions are widely used to prepare MOFs. In this work, the increase in pressure that led to formation of **3** was not undertaken to access a higher temperature. Why the change in pressure should lead to a change in product is not yet well understood, but it is noteworthy that the calculated density of **3** (1.809 g cm⁻³) is marginally greater than that of its supramolecular isomer **2** (1.781 g cm⁻³).

While it is well known in organometallic chemistry that solvent quality is important in determining the outcome of a reaction, this principle is less established in MOF chemistry. A degree of hydrolysis in the DMF solvent can lead to NMe₂H₂⁺ cations, which template the formation of the anionic network observed in **4**. We have previously noted this effect in the analogous zinc chemistry.⁶

The reaction between Cd(NO₃)₂·4H₂O and H₂bdc in DEF is much more robust than that in DMF, yielding [Cd(bdc)(DEF)]_∞ **5** as the only product, regardless of the temperature, pressure or solvent quality. This is in contrast to the analogous zinc chemistry, in which NEt₂H₂⁺ plays a similar role to NMe₂H₂⁺. Compound **5** loses the coordinated DEF without change in the powder Xray diffraction pattern on heating to 400 $^{\circ}$ C, and the desolvated network reversibly adsorbs hydrogen with rapid adsorption and desorption kinetics. However, the amount of hydrogen uptake is lower than anticipated on the basis of simulations, suggesting that partial framework collapse to an amorphous phase has occurred.

Experimental

Microanalysis (C, H and N) were carried out by Mr Alan Carver (University of Bath Microanalytical Service). IR spectra were recorded as KBr discs on a Nicolet Nexus FTIR spectrometer. Powder diffraction data were recorded on a Bruker D8 diffractometer fitted with Goebal mirrors and a 0.2 mm beam slit, and in each case, unless noted in the text, the experimental pattern showed a good match with that simulated from the single crystal analysis. Thermogravimetric analyses were performed on a Perkin Elmer TGA 7 instrument from 30 °C to 600 °C at a heating rate of 10 °C min⁻¹ under a flow of N₂. Nitrogen adsorption measurements were carried out using a Micromeritics ASAP 2400 instrument, while hydrogen and krypton adsorption measurements were conducted using a Hiden intelligent gravimetric analyser (IGA).

Synthesis of $[Cd(bdc)(DMF)]_{\infty}$ (1)

Cd(NO₃)₂·4H₂O (0.520 g, 1.69 mmol) and H₂bdc (0.501 g, 3.02 mmol) were added to DMF (60 cm³) and the mixture was stirred at 115 °C until a colourless solution was obtained. Stirring was then stopped, and the mixture maintained at 115 °C for a further 5 h. Colourless crystals of **1** were separated by filtration. Yield 0.240 g (41%). ν (CO₂)/cm⁻¹ 1653s. Found C, 37.8; H, 3.15; N, 4.05%. Calc. for C₁₁H₁₁CdNO₅ (349.6): C, 37.8; H, 3.17; N, 4.01%.

Synthesis of $[Cd(bdc)(DMF)]_{\infty}$ (1) and $[Cd_3(bdc)_3(DMF)_4]_{\infty}$ (2)

The procedure described above to prepare 1 was repeated with the temperature maintained at 95 °C for 5 h, rather than 115 °C. Colourless crystals of 1 and 2 were separated from the solvent by filtration, but could not be separated from each other. Combined yield 0.415 g. X-Ray powder diffraction data revealed 1 to be the major product.

Synthesis of $[Cd_3(bdc)_3(DMF)_4]_{\infty}$ (3)

Cd(NO₃)₂·4H₂O (0.520 g, 1.69 mmol) and H₂bdc (0.501 g, 3.02 mmol) were dissolved in DMF (60 cm³) at 115 °C in a Büchi miniclave reactor, which was then sealed and pressurised with 3 bar of nitrogen. The solution was heated for 5 h, then colourless crystals of **3** were separated by filtration. Yield 0.515 g (82%). ν (CO₂)/cm⁻¹ 1653s, 1539s. Found C, 38.5; H, 3.34; N, 4.39%. Calc. for C₃₆H₄₀Cd₃N₄O₁₆ (1122.0): C, 38.5; H, 3.59; N, 4.99%.

Synthesis of $\{(NMe_2H_2)_2[Cd(bdc)_2]{\cdot}2DMF\}_\infty$ (4)

1,4-Benzenedicarboxylic acid (H₂bdc) (0.501 g, 3.02 mmol) was dissolved in DMF (50 cm³) at 115 °C, and a solution containing Cd(NO₃)₂·4H₂O (0.520 g, 1.69 mmol) and dimethylammonium chloride (0.080 g, 0.98 mmol) in DMF (10 cm³) was added. The reaction mixture was stirred for 5 min, then stirring was stopped

and the mixture maintained at 115 °C for a further 5 h. Colourless crystals of **4** were separated by filtration. Yield 0.27 g (24%). ν (CO₂)/cm⁻¹ 1675s, 1558s. Found C, 45.1; H, 5.40; N, 6.52%. Calc. for C₂₃H₃₁CdN₃O₉ (**4** – DMF, 605.9): C, 45.6; H, 5.16; N, 6.93%.

Synthesis of $[Cd_3(bdc)_3(DEF)_2]_{\infty}$ (5)

Cd(NO₃)₂·4H₂O (0.086 g, 0.279 mmol) and H₂bdc (0.045 g, 0.271 mmol) were dissolved in DEF (10 cm³), and the solution was heated at 115 °C for 5 h. After this time, yellow crystals were separated by filtration. Yield 0.039 g (41%). Found C, 39.2; H, 3.52; N, 2.98%. Calc. for $C_{34}H_{34}Cd_3N_2O_{14}$ (1031.9): C, 39.6; H, 3.32; N, 2.71%.

Synthesis of $[Cd(mbdc)(DMF)]_{\infty}$ (6)

Cd(NO₃)₂.4H₂O (0.500 g, 1.62 mmol) and 1,3benzenedicarboxylic acid (H₂*m*bdc) (0.539 g, 3.24 mmol) were dissolved in DMF (60 cm³), and the solution heated at 90 °C for 5 h. Colourless crystals formed on cooling to room temperature, and these were separated by filtration. Yield 0.255 g (45%). Found C, 37.8; H, 3.26; N, 4.02%. Calc. for C₁₁H₁₁CdNO₅ (349.6): C, 37.8; H, 3.17; N, 4.01%.

Crystallography

Single crystals of compounds **2**, **3**, **4** and **6** were analysed using a Nonius Kappa CCD diffractometer and Mo-K_a radiation ($\lambda =$ 0.71073 Å). Data for **1** and **5** were collected at Daresbury Station 9.8 ($\lambda = 0.68970$ Å and 0.68680 Å, respectively). Details of the data collections, solutions and refinements for **1–5** are given in Table 6. The structures were universally solved using SHELXS-97 and refined using full-matrix least squares in SHELXL-97.²⁴ Multiscan absorption corrections were applied throughout and convergence was uneventful, with the following exceptions and points of note.

The asymmetric unit of **4** consists of half of a cadmium atom (located on a special position), one bdc anion, one dimethylammonium cation, in which one of the carbons is equally disordered over two positions, and one DMF molecule disordered over two positions.

The asymmetric unit of **5** consists of one whole cadmium, half of a cadmium located on a special position, one whole bdc, half of a bdc (with the remainder generated *via* a space group symmetry operation) and one whole DEF molecule. The solvent molecule is disordered over two sites in a 70:30 ratio.

Several datasets were collected for **6**, of which the optimum was at 250 K. Although the sample appeared single under a polarising microscope, a data collection at 150 K failed to solve/refine properly using any intelligent model. Initially it was assumed that the crystal was extremely twinned, until it was noted that the diffraction pattern intensities altered perceptibly at the higher temperature. Borderline absence conditions resulted in attempts to solve and refine in many space groups, although no one space group could satisfy all absence conditions. Notwithstanding this, the refinement was adequate to provide unambiguous determine metric parameters. Selected crystallographic data for **6**: $C_{11}H_{11}CdNO_5$, M = 349.61, monoclinic, $P112_1/b$, a = 13.1670(4), b = 17.5870(5), c = 22.0960(7) Å, a = 90, $\beta = 90$, $\gamma = 90.000(1)^\circ$.

Table 6 Crystallographic data for compounds 1–5

	1	2	3	4	5
Formula	$C_{11}H_{11}CdNO_5$	$C_{36}H_{40}Cd_3N_4O_{16}$	$C_{36}H_{40}Cd_3N_4O_{16}$	$C_{26}H_{38}CdN_4O_{10}$	$C_{34}H_{34}Cd_3N_2O_{14}$
М	349.61	1121.92	1121.92	679.00	510.91
T/K	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P\overline{1}$	C2/c	$P\overline{1}$	Fdd2	C2/c
a/Å	7.4523(9)	28.1090(4)	10.1270(1)	9.7830(2)	25.0960(11)
b/Å	9.7764(12)	9.1930(1)	12.6120(1)	21.2010(4)	10.7885(5)
c/Å	9.8469(12)	17.8780(2)	16.6790(2)	27.8110(5)	17.5107(8)
$a/^{\circ}$	118.255(2)	90	75.459(1)	90	90
β/°	102.118(2)	115.112(1)	88.924(1)	90	128.996(3)
y/°	91.358(2)	90	87.271(1)	90	90
$U/Å^3$	611.51(13)	4183.12(9)	2059.65(4)	5768.26(19)	3684.6(3)
Ζ	2	4	2	8	4
μ (Mo-K _a)/mm ⁻¹	1.797	1.585	1.610	0.819	1.785
Reflections collected	8031	29343	46686	15349	18981
Independent reflections	4205	4776	12980	4207	5385
R(int)	0.0428	0.0393	0.0433	0.0393	0.0376
$R1, wR2 [I > 2\sigma(I)]$	0.0372, 0.0965	0.0208, 0.0450	0.0265, 0.0605	0.0225, 0.0494	0.0255, 0.0673
R indices (all data)	0.0391, 0.0972	0.0244, 0.0463	0.0332, 0.0635	0.0268, 0.0509	0.0282, 0.0691
Largest diff. peak, hole/e $Å^{-3}$	0.893, -0.757	0.679, -0.538	1.424, -1.301	0.222, -0.762	0.659, -0.576

Simulations

The multi-purpose simulation code music²⁵ was used to calculate the hydrogen adsorption isotherms with grand canonical Monte Carlo (GCMC) simulations. All interatomic interactions were modelled with a standard Lennard-Jones potential. Hydrogen was represented by a two-centred model.²⁶ The parameters for the framework were taken from the UFF force field²⁷ with the positions of the framework atoms fixed at their crystallographic positions. Lorentz–Bertholot mixing rules were used to calculate hydrogen/framework parameters. Interactions beyond 12.8 Å were neglected. For each point of the isotherm, two million GCMC steps were performed with 800 000 taken for equilibration and 1 200 000 to sample the data. The excess amount adsorbed was calculated as outlined previously.²⁸

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