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Open-Framework Cadmium Succinates of Different Dimensionalities

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Open-framework cadmium succinates, $[CN_3H_6]_2[Cd_2(C_4H_4O_4)(Cl)_2]$, **I**; $[CN_3H_6]_2[Cd(C_4H_4O_4)_2]$, **II**; $Cd_2(C_4H_4O_4)_2(C_4N_2H_8)(H_2O)_3$, **III**; $[C_4N_2H_{12}][Cd_2(C_4H_4O_4)_3]\cdot 4H_2O$, **IV**; $Cd(C_4H_4O_4)(H_2O)_2$, **V**; and $Cd_3(C_4H_4O_4)_2(OH)_2]$, **VI**, of different dimensionalities have been synthesized by hydrothermal procedure by employing two different strategies, one involving the reaction of Cd salts with organic-amine succinates and the other involving the hydrothermal reaction of Cd salts with a mixture of succinic acid and the organic amine. While the latter procedure yields structures without any amine in them, the former gives rise to amine templated cadmium succinates with open architectures. By employing guanidinium succinate we have obtained **I** and **II**, and with piperazinium succinate we obtained **III** and **IV**. Of these **I** has a one-dimensional chain structure, **IV** has a layered structure, and **II** and **III** have three-dimensional architectures. The two cadmium succinates without incorporation of amine, **V** and **VI**, possess layered and three-dimensional structures, respectively. The three-dimensional structures **II** and **III** exhibit interpenetration similar to that in diamondoid and α-polonium type structures, respectively.

Introduction

Besides the large families of open-framework aluminosilicates and phosphates,[1] several other types of open architectures have been synthesized and characterized in the past few years. Of the latter families, the metal carboxylates form an important class of materials.[2−7] Recently a large variety of open-framework metal oxalates have been described in the literature;[8,9] however, very few open-framework metal succinates are known to date. To our knowledge the only reports of open-framework metal succinates are those of cobalt,[10] nickel,[11] iron,[12] and manganese.[13] No open-framework metal succinate appears to have been synthesized in the presence of organic amines. We have attempted to prepare cadmium succinates with open architectures by employing different synthetic routes, one of them employing organic-amine succinates as a starting material. This method was chosen in the light of the successful synthesis of open-framework zinc oxalates of different dimensionalities by the reaction organic-amine oxalates with Zn salts.[14] We have reacted organic-amine succinates with

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Table 1. Synthesis Conditions and Analyses for Compound **I**−**VI**

reactant mole ratios	temp (°C)	time (h)	CHN ratios[c] (%)	product
$CdCl_2$:3.0$[CN_3H_6][C_4H_5O_4]$1.45$C_5H_{10}NH$: 31.0*n*-C_4H_9OH:213.0H_2O	100	48		$[CN_3H_6]_2[Cd_2(C_4H_4O_4)(Cl)_2]$ (**I**) + $[CN_3H_6]_2[Cd(C_4H_4O_4)_2]$ (**II**)
$CdCl_2$:3.0$[CN_3H_6][C_4H_5O_4]$:1.45$C_5H_{10}NH$: 31.0*n*-C_4H_9OH: 213.0H_2O	100	72	26.1:4.3:18.6 (25.8:4.3:18.1)	$[CN_3H_6]_2[Cd(C_4H_4O_4)_2]$ (**II**)
$CdCl_2$:1.7$[C_4N_2H_{12}][C_4H_4O_4]$: 1.6$C_5H_{10}NH$: 1.34.2$H_2O$: 35.2*n*-$C_4H_9OH$	150	80	25.9:3.5:3.4 (26.2:3.7:4.7)	$Cd_2(C_4H_4O_4)_2(C_4N_2H_8)(H_2O)_3$ (**III**)
$CdCl_2$:2.0$[C_4N_2H_{12}][C_4H_4O_4]$:2.0$C_5H_{10}NH$: 1.67.9$H_2O$: 22.0*n*-$C_4H_9OH$	150 80 (wb)[d]	48 14	26.2:4.3:0 (26.2:4.4:0)	$[C_4N_2H_{12}][Cd_2(C_4H_4O_4)_3]\cdot 4H_2O$ (**IV**)
$CdCl_2$:2.0TMEN[b]:3.0$C_4H_6O_4$: 2.0$C_5H_{10}NH$: 168.0H_2O:22.0*n*-C_4H_9OH	150	54	18.6:2.1:0 (18.2:3.0:0)	$Cd(C_4H_4O_4)(H_2O)_2$ (**V**)
$CdCl_2$:2.1DABCO[a]:2.0$C_4H_6O_4$:2.0$C_5H_{10}NH$: 447.0H_2O:44.0*n*-C_4H_9OH	150	78	16.2:1.7:0 (15.9:1.6:0)	$Cd_3(C_4H_4O_4)_2(OH)_2$ (**VI**)

[a] Diazabicyclo[2,2,2]octane [b] Tetramethylethylenediamine [c] Calculated CHN ratios within parentheses. [d] wb = water bath.

cadmium salts to obtain cadmium succinates of the compositions $[CN_3H_6]_2[Cd_2(C_4H_4O_4)(Cl)_2]$, **I**; $[CN_3H_6]_2[Cd(C_4H_4O_4)_2]$, **II**; $Cd_2(C_4H_4O_4)_2(C_4N_2H_8)(H_2O)_3$, **III**; and $[C_4N_2H_{12}][Cd_2(C_4H_4O_4)_3]\cdot 4H_2O$, **IV**. In addition, we have obtained $Cd(C_4H_4O_4)(H_2O)_2$, **V**, and $Cd_3(C_4H_4O_4)_2(OH)_2]$, **VI**, by the hydrothermal reaction of a cadmium salt and succinic acid in the presence of an amine. While **I** is a one-dimensional chain, **IV** and **V** have layered structures. **II**, **III**, and **VI** are three-dimensional architectures, with **II** having an interpenetrated diamondoid structure and **III** the interpenetrated α-polonium type structure;[15] **VI** has an non-interpenetrated structure.

Experimental Section

We have employed two methods for the synthesis of the open-framework cadmium succinates, one where the succinates of organic amines were reacted with a Cd salt and another where the Cd salt was reacted with a mixture of succinic acid and the amine. Both types of reactions were carried out under hydrothermal conditions. The succinates of guanidine (GUS) and piperazine (PIPS) were prepared by slow evaporation from a solution of the corresponding organic amine and succinic acid (1:2 or 1:1 ratio) in a water−*n*-butanol mixture on a water bath.

Compounds **I**−**IV** were prepared by the reaction of Cd^{2+} ions with the organoamine-succinates under hydrothermal conditions. Typically, for the preparation of **II**, 0.552 g of guanidinium succinate (GUS) was dissolved in a *n*-butanol + water (3 mL + 4 mL) mixture. Then, 0.21 g of cadmium chloride and 0.15 mL of piperidine were added to the above, and the contents stirred to homogeneity. The final mixture of composition $CdCl_2$:3$[CN_3H_6][C_4H_5O_4]$:1.45$C_5H_{11}N$:31*n*-C_4H_9OH:213H_2O was sealed in a PTFE lined stainless steel autoclave and heated at 100 °C for 72 h. Attempts to avoid interpenetration in **II**, by introducing suitable guest species, were so far unsuccessful. A similar procedure was employed for the synthesis of **I**−**IV**. In the case of **V** and **VI** the organic amine and the succinic acid were taken in the desired proportions in the starting reaction mixture. Piperidine was employed as the secondary base to deprotonate the succinic acid completely. The synthetic conditions employed for the synthesis of **I**−**VI** are presented in Table 1.

Initial characterization of the products was carried out using powder X-ray diffraction (XRD), chemical analysis, thermogravimetric analysis (TGA), and IR spectroscopy. The powder XRD patterns indicated that the products were new materials and were entirely consistent with the structures determined using single-crystal X-ray diffraction. As a representative example, a comparison of the simulated and the experimental powder XRD patterns of compound **III** is presented in Figure 1. The least-squares fit (Cu Kα) using the powder XRD pattern generated from the single-crystal structure solution yielded the following lattice parameters: a = 9.020(6) Å; b =13.844(11) Å; c = 15.625(9) Å; β = 106.02(7)°.

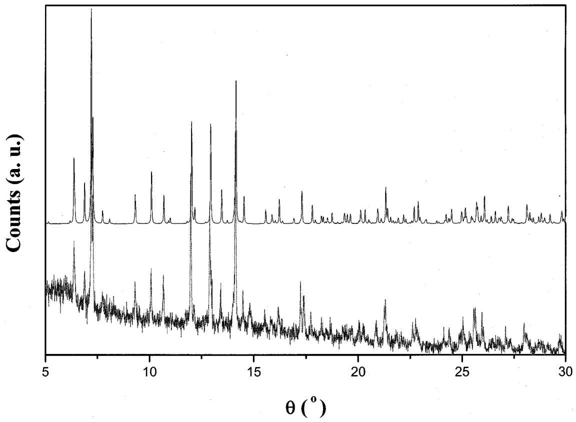

Figure 1. Simulated and the experimental powder XRD patterns of $Cd_2(C_4H_4O_4)_2(C_4N_2H_8)(H_2O)_3$, **III**.

Thermogravimetric analysis was carried out under N_2 atmosphere (50 mL min^{-1}) in the range 25−700 °C. **II** showed a sharp mass loss, followed by a long tail, with total mass loss of 83.16% in the range 300−750 °C, which is in agreement with the mass loss calculated for the loss of the organic moieties in the structure (calc 81.33%). Both **III** and **IV** showed two distinct mass losses. For **III** a gradual mass loss of 7.9% in the range 140−200 °C corresponds to the loss of bound water molecules (calc 9.1%), and the second of 47.4% in the range 300−480 °C corresponds to the loss of the amine and the succinate units (calc 47.8%). For **IV**, a gradual mass loss of 8.3% in the range 100−160 °C corresponds to the loss of water molecules (calc 9.8%). The second mass loss of 52.2% corresponds to the loss of the organic species (calc 55.2%). For **V**, a mass loss of 50.0% in the range 150−750 °C due to the loss of the bound water and the succinate units (calc 51.0%) was observed. A small mass loss was observed above 500 °C in **II**, **III**, **IV**, and **V** due to the slow evaporation of CdO. In all the cases the powder XRD pattern of the product of decomposition showed good crystalline peaks corresponding to the mineral Monteporite, CdO (JCPDS: 05-0640).

Infrared spectroscopic studies of KBr pellets showed characteristic features of the dicarboxylate.[16] The various observed bands

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Table 2. Crystal Data and Structure Refinement Parameters for Compounds **I**−**VI**

crystal parameter	**I**	**II**	**III**	**IV**	**V**	**VI**
empirical formula	$C_6H_{16}N_6O_4Cl_2Cd$	$C_{10}H_{20}N_6O_8Cd$	$C_{12}H_{22}N_2O_{11}Cd_2$	$C_8H_{12}NO_8Cd$	$C_4H_8O_6Cd$	$C_8H_{10}O_{10}Cd_3$
formula mass	419.55	464.6	595.12	362.59	264.50	603.36
cryst syst	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$Fddd$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$Pbca$
a (Å)	8.3714 (2)	7.4194 (6)	9.0509 (2)	8.6967 (10)	7.1277 (7)	10.7106 (4)
b (Å)	15.0361 (3)	17.963 (2)	13.8641 (1)	8.9678 (10)	15.144 (2)	6.8922 (3)
c (Å)	12.5310 (1)	24.574 (2)	15.7025 (3)	9.2970 (10)	7.1918 (7)	17.0335 (5)
α (deg)	90	90	90	64.820 (2)	90	90
β (deg)	106.33 (1)	90	106.015 (1)	84.253 (2)	111.335 (2)	90
γ (deg)	90	90	90	74.222 (2)	90	90
volume (Å^3)	1514.17 (5)	3275.1 (5)	1894.05 (6)	631.35 (12)	723.12 (12)	1257.41 (8)
Z	4	8	4	2	4	4
μ (mm^{-1})	1.813	1.389	2.304	1.761	3.001	5.078
θ range (deg)	2.17−23.15	2.81−23.31	1.99−23.27	2.42−23.28	2.69−23.29	2.39−23.37
total no. of data collected	6130	597	7844	2656	2925	4688
no. of obsd data ($\sigma > 2\sigma(I)$)	658	589	970	1101	686	1214
R_1, wR_2 [$I > 2\sigma(I)$]	0.0408, 0.0984	0.0152, 0.369	0.0304, 0.0742	0.0334, 0.0813	0.0211, 0.0497	0.0207, 0.0501
wR_2 (all data)	0.1034	0.0369	0.0781	0.0870	0.0509	0.0522
goodness of fit (S)	1.023	1.134	1.022	1.177	1.003	1.026
no. of variables	180	79	280	188	133	118
largest diff map peak and hole (e Å^{-3})	1.140 & −1.145	0.228 & −0.360	0.930 & −1.026	0.618 & −0.622	0.853 & −0.460	0.628 & −0.464

were as follows: ν_{as}(C=O) at 1551(s) cm^{-1} and ν_s(C=O) at 1404(s) cm^{-1} (**II**); 1547(s) cm^{-1} and 1404(s) cm^{-1} (**III**); 1568(s) and 1420(s) cm^{-1} (**IV**); 1546(s) and 1427(s) cm^{-1} (**V**); 1553(s) and 1418(s) cm^{-1} (**VI**); ν_s(O−C−O) at 1241(s) cm^{-1} (**II**); 1222(s) cm^{-1} (**III**); 1223(s) cm^{-1} (**IV**); 1266(s) cm^{-1} (**V**); 1219(s) cm^{-1} (**VI**); δ(O−C−O) at 818(m) cm^{-1} (**II**); 806(m) cm^{-1} (**III**); 804(m) cm^{-1} (**IV**); 829(m) cm^{-1} (**V**); and 812(m) cm^{-1} (**VI**). The presence of bound water molecules in **III** gives rise to ρ_w(H_2O) at 556(m) and ρ_r(H_2O) at 858(m) cm^{-1} bands. Multiple bands due to the ρ_w(N−H), ρ_r(N−H), and ρ_t(N−H) are observed in **II**, **III**, and **IV** in the 1050−650 cm^{-1} region. In all compounds multiple bands in the region 3000−2400 cm^{-1} appear due to the ν_s(CH_2) and ν_a(CH_2) vibrations; meanwhile, ρ_w(CH_2) and ρ_r(CH_2) bands occur in the 1200−950 cm^{-1} region. In **II**, **III**, and **IV**, ν_s(N−H) and ν_a(N−H) bands appear in the 3400−3000(w) cm^{-1} region. In **VI**, a broad band appears at 3551 cm^{-1} due to the presence of bridging −OH group.

Single-Crystal Structure Determination. A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued at the tip of a thin glass fiber with cyanoacrylate (super glue) adhesive. Single-crystal structure determination by X-ray diffraction was performed on a Siemens 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 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1321 frames with ω scans (width of 0.30° and exposure time of 20 s per frame) in the θ range 1.99−23.37°. Pertinent experimental details for the structure determinations are presented in Table 2.

The structure was solved and refined by using the SHELXTL-PLUS[17] suite of programs. An absorption correction based on symmetry equivalent reflections was applied using the SADABS program, wherever required.[18] The hydrogen positions for all the compounds were initially located in the difference Fourier maps, and for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all hydrogen atoms. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS package of programs. Details of the crystal data and final refinements are given in Table 2. Selected structural parameters of **I**−**VI** are presented as Supporting Information.

Results

[CN_3H_6]$_2$[$Cd_2(C_4H_4O_4)(Cl)_2$], I. The asymmetric unit of **I** contains 19 non-hydrogen atoms, of which 11 belong to the cadmium chlorosuccinate chains and the rest to the amine molecule. The Cd atom is coordinated to four succinate oxygens and two chlorine atoms, forming a distorted octahedron with an average Cd−O/Cl distance of 2.458 Å. The average O/Cl−Cd−O/Cl angle is 100.8°. The succinate units and the amine molecules have the usual bond distances and angles. Selected bond distances and angles in **I** are presented as Supporting Information. The Cd atoms are connected to two succinate units, forming a one-dimensional chain with two pendant chlorine atoms (Figure 2). The protonated guanidinium cations occupy the interchain spaces and interact with the succinate oxygens and the pendant Cl atoms via hydrogen bonds. A noteworthy feature in **I** is the presence of M−Cl···H interactions, which have been shown to play an important role in crystal engineering,[19,20] being prominent in organic/organometallic compounds.[21] Such interactions are, however, not known in extended solids. It appears that the M−Cl···H interactions in **I** (Figure 2), with

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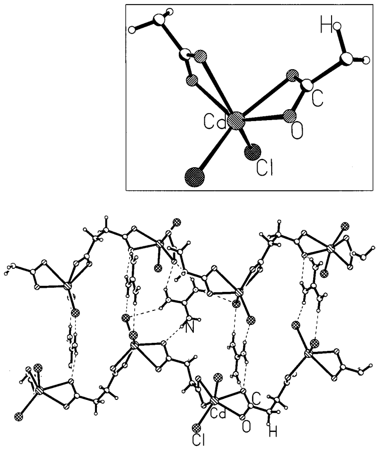

Figure 2. One-dimensional chain formed by the connectivity between the Cd atoms and the succinate moieties present in $[CN_3H_6]_2[Cd_2(C_4H_4O_4)(Cl)_2]$, **I**. Hydrogen bonds and the weak electrostatic interactions between the amine and the succinate O atoms and the Cl atoms, respectively, are shown by dotted lines. Inset shows the effective tetrahedral coordination around the Cd center, provided by the succinate and the two Cl atoms.

Cd−Cl(1)···H = 2.874 and Cd−Cl(2)···H = 2.734 Å distances (classified as intermediate distances),[19] make a significant contribution in stabilizing the lower dimensional structure of **I**.

$[CN_3H_6]_2[Cd(C_4H_4O_4)_2]$, II. The asymmetric unit of $[CN_3H_6]_2[Cd(C_4H_4O_4)_2]$, **II**, contains eight non-hydrogen atoms. The cadmium atom sits in a special position and is coordinated with eight nearest oxygen neighbors, forming a square anti-prismatic arrangement, with Cd−O distances in the range 2.350(1)−2.506(1) Å (av 2.428 Å) and an average O−Cd−O angle of 90.7°. The various distances and angles associated with the succinate and amine molecules are as expected. Selected bond distances and angles in **II** are listed as Supporting Information.

The structure of **II** consists of tetrahedral units formed by the connectivity between four succinate units and a Cd atom with an average angle of 110.6°. Four such tetrahedra surround a central one, forming a supertetrahedron. The supertetrahedra are connected to give rise to the adamantane unit (Figure 3). The adamantane units are linked to form the diamondoid network. One diamondoid lattice is interpenetrated by another (Figure 4), as in diamondoid networks.[15,22−24]

The structure of **II** can also be viewed as honeycomb-like layers possessing large 12-membered apertures (six Cd and six succinate units, 16.306 × 12.741 Å), formed by the in-plane connectivity between the Cd and three succinate units, cross-linked by one out-of-plane succinate unit (Figure 5a). This is somewhat similar to the connectivities observed in the three-dimensional zinc oxalate $2[C_3H_7NH_3]^+$-$[Zn_2(C_2O_4)_3]^{2+}\cdot 3H_2O$.[25] The succinate units are connected to create catenation and interpenetration, contributing negatively to the total porosity of the solid. Such a behavior is known in interpenetrating structures.[15,22−24,26] Interpenetration in **II** reduces the 12-membered channels to smaller eight-membered channels (∼5.4 × 8.8 Å, shortest O−O contact not including the van der Waals radii) along the *a*-axis (Figure 5b). The protonated guanidinium cations occupy the center of the channels.

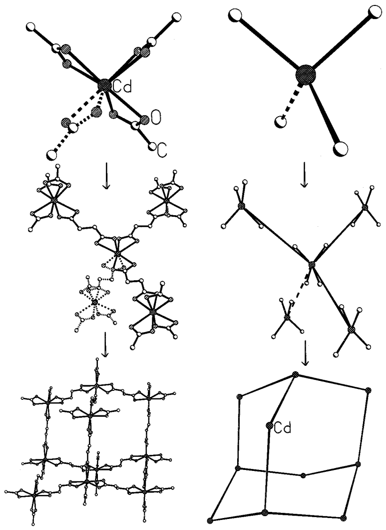

Figure 3. Structure of $[CN_3H_6]_2[Cd(C_4H_4O_4)_2]$, **II**, showing the basic cadmium succinate tetrahedron, the supertetrahedron, and the adamantane unit, demonstrating scale-up chemistry.

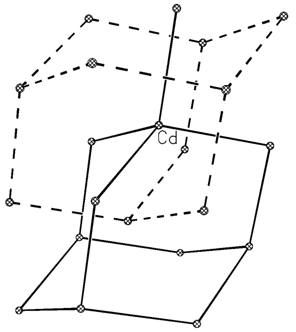

Figure 4. Structure of **II**, showing the "normal interpenetration" present in it.

$Cd_2(C_4H_4O_4)_2(C_4N_2H_8)(H_2O)_3$, III. The asymmetric unit of $Cd_2(C_4H_4O_4)_2(C_4N_2H_8)(H_2O)_3$ consists of 27 non-hydrogen atoms. Of which, two are the crystallographically independent Cd atoms. Cd(1) is octahedrally coordinated, being connected to three succinate oxygens, two bound water molecules, and one nitrogen atom from the amine, at an average Cd−O/N distance of 2.362 Å. Cd(2) is coordinated to four succinate oxygens, one water molecule, and a nitrogen atom with an average Cd−O/N distance of 2.332 Å. The O/N−Cd−O/N angles are in the range 53.1(1)−168.0(1)°

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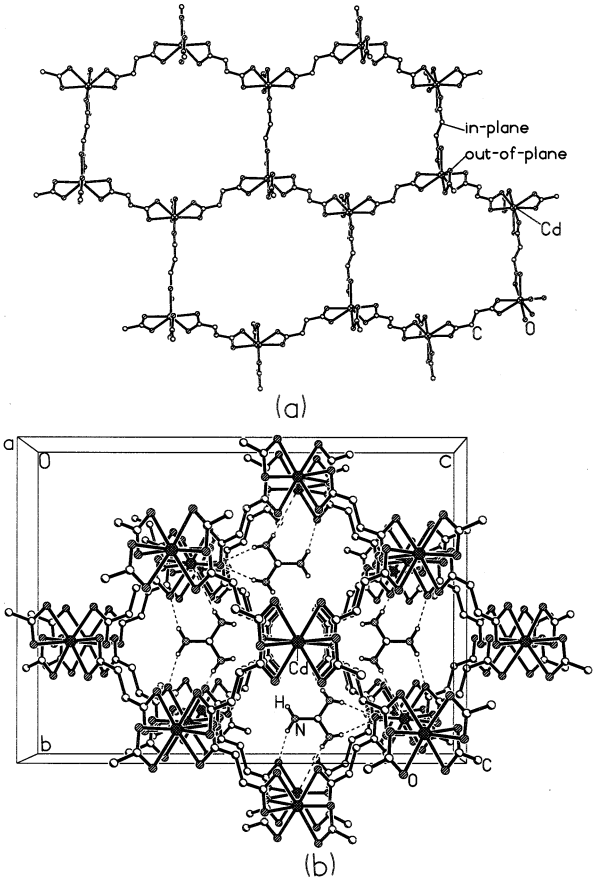

Figure 5. (a) Honeycomb-like apertures in **II** formed by the cadmium and the in-plane succinate units and their cross-linking by the out-of-plane succinate moieties. (b) Eight-membered channels present along the *a*-axis in **II**. Note the presence of the protonated guanidinium molecules in the channels.

(av O/N−Cd(1)−O/N = 99.9°; av O/N−Cd(2)−O/N = 103.5°).

The three-dimensional framework structure of **III** consists of a hybrid layer formed by the connectivity between the Cd, two in-plane succinates, and one piperazine molecule, giving rise to a 12-membered rectangular aperture (11.472 × 8.220 Å (Figure 6a). The hybrid layers are cross-linked by an out-of-plane succinate unit in a monodendate fashion to form the three-dimensional structure. The structure of **III** can also be viewed alternatively as consisting of a cadmium succinate layer with small 10-membered apertures (11.680 × 7.027 Å) pillared by a piperazine molecule as shown in Figure 6b. This is indeed an unusual structure wherein piperazine bonds to the Cd atom, giving rise to channels along all the crystallographic axes. The channel dimensions are 11.5 × 8.2 Å along the *a*-axis (Figure 7a) and 8.72 × 8.38 along the *b*-axis (Figure 7b) (shortest O−O contact distance not including the van der Waals radii). Since the amine molecule is directly bound to the Cd center, only the water molecules coordinated to the Cd protrude into the channels. On linking the cadmium centers, we realize a rectangular box (see the inset of Figure 7a), with the corners of the box occupied by the Cd_2O_2 dimers, (Cd(1)Cd(2)-O(5)O(1)), O(1) and O(5) being the succinate oxygens bonded to C(4). The dimer acts as a four-connecting center and is connected by four succinate and two piperazine arms to adjacent dimers, forming a rectangular box. The rectangular box shares its faces with the neighboring ones, forming the three-dimensional structure. Another independent network with identical connectivity interpenetrates this structure as shown in Figure 8, the interpenetration being similar to that in the α-polonium related structure. Such a structure has been observed in metal nitriles[27,28] and halides[29,30] and seldom in other metal-organic frameworks.[15,31,32]

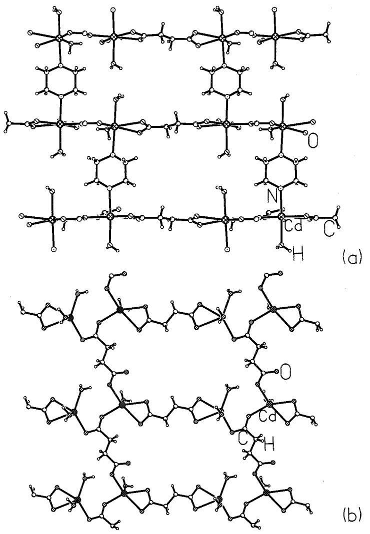

Figure 6. (a) Structure of $Cd_2(C_4H_4O_4)_2(C_4N_2H_8)(H_2O)_3$, **III**, showing the hybrid metal-organic layer formed by the connectivity between the Cd centers via the in-plane succinates and piperazine units, in the *bc*-plane. Note the presence of 12-membered apertures within the layers. (b) Perspective view of the cadmium succinate layer topology present in **III**.

$[C_4N_2H_{12}][Cd_2(C_4H_4O_4)_3]\cdot 4H_2O$, IV. The asymmetric unit of **IV** contains 18 non-hydrogen atoms, of which 13 atoms belong to the framework and five to the amine and the water molecules. The Cd−O distances are in the range 2.239(4)−2.401(4) Å (av 2.331 Å), and the O−Cd−O bond angles are in the range 55.0(1)−146.9(2)° (av 101.6°). Selected bond distances and angles in **IV** are listed as Supporting Information.

The two-dimensional structure of **IV** consists of macroanionic cadmium succinate sheets separated by piperazinium cations and water molecules. The individual layers are built-up from the connectivity between Cd and the succinate units. Of the three succinate units connected to the Cd atoms, two have a regular bidendate connection and the remaining one has a monodendate connection (Figure 9). The monodendate succinate oxygen gets triply coordinated and connects two Cd atoms to form Cd_2O_2 dimers. Such Cd_2O_2 dimers are

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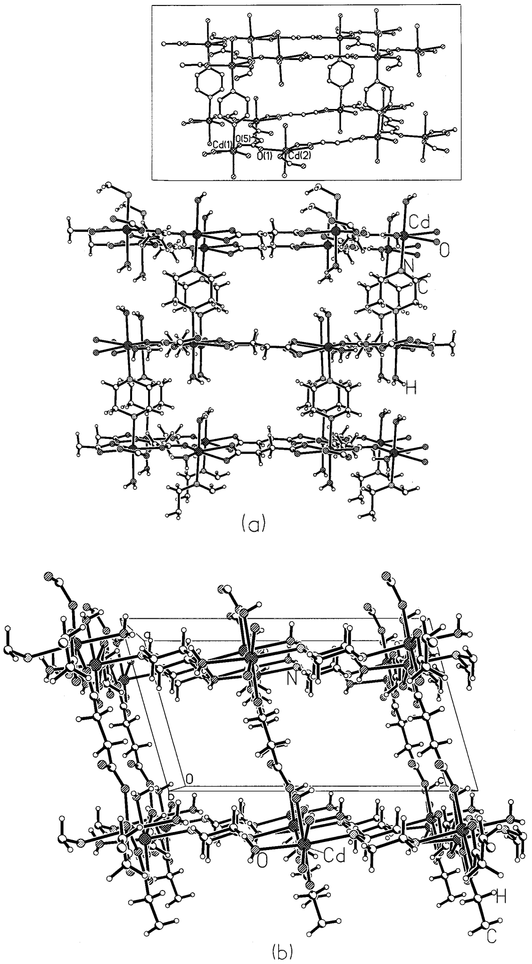

Figure 7. (a) Perspective view of **III**, along the *a*-axis, showing 12-membered rectangular channels. Inset shows the rectangular box, which may be considered to be the basic building unit formed by the connectivity between the Cd centers via succinate units and piperazine pillars. (b) Perspective view of **III**, along the *b*-axis, showing the eight-membered rhombic channels.

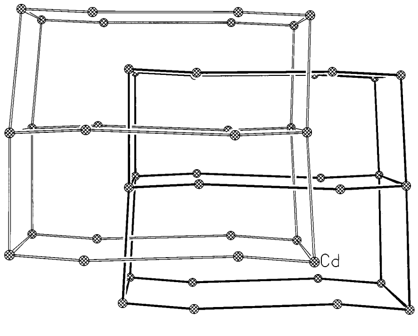

Figure 8. Interpenetration present in **III**, akin to that in the in α-polonium-related network.

connected by succinate units, giving rise to perforated layers with an eight-membered aperture (6.281 × 8.429 Å) in the *ac*-plane (Figure 9). The doubly protonated amine molecules occupy the center of the apertures. Additionally, there are small four-membered apertures (4.012 × 5.220 Å) formed by the connectivity between the Cd and the bischelating succinates, which are aligned along the *a*-axis, forming one-dimensional tunnels within each layer (Figure 10). Interestingly, the amine molecules in **IV** lie in the plane of the layer and form strong N−H···O interactions with the succinate O atoms (Figure 9), in contrast to the layered metal oxalates,[33] where the charge-balancing organic-amine cations reside in the interlamellar region. The water molecules in **IV** reside in the interlamellar region (Figure 10), which is relatively less hydrophobic than the apertures within the layers.

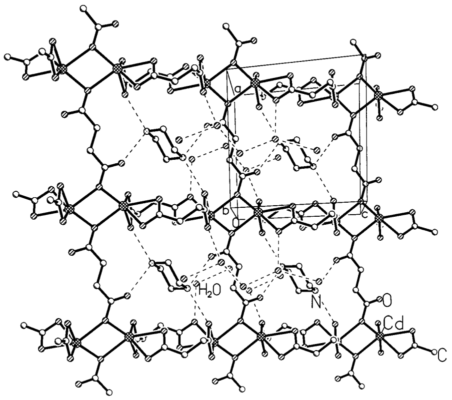

Figure 9. Structure of $[C_4N_2H_{12}][Cd_2(C_4H_4O_4)_3]\cdot 4H_2O$, **IV**, showing the layers formed by the connectivity between the Cd_2O_{10} dimers and the succinate units. Note the presence of extraframework protonated piperazine and the guest water molecules in the eight-membered apertures present within the layer and also the monodendate binding mode exhibited by the succinates.

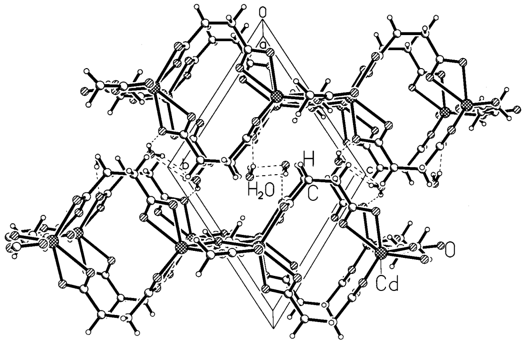

Figure 10. Perspective view of **IV** along the *a*-axis showing one-dimensional tunnels formed by the small four-membered apertures present within the layer and also the stacking of the layers along the [011] direction. Note the presence of guest water molecules in the interlamellar region. Hydrogen bonding with the framework is shown as dotted lines (amine molecules are not shown for clarity).

$Cd(C_4H_4O_4)(H_2O)_2$, V. The asymmetric unit of $Cd(C_4H_4O_4)(H_2O)_2$, **V**, consists of 11 non-hydrogen atoms (Cd, succinate, and two bonded water molecules). The cadmium atom is seven-coordinated with respect to the oxygen atoms, of which five are from the succinates and the other two are from the water molecules. Thus, the coordination geometry of the Cd atoms is a pentagonal bipyramid (see the inset in Figure 11). Five succinate oxygens occupy the equatorial positions with an average Cd−O distance and O−Cd−O angle of 2.393 Å and 107.6°, respectively, while the bonded water molecules occupy the apical positions with an average Cd−O(w) distance of 2.296 Å and making an average O−Cd−O angle of 89.8° with the equatorial oxygens (see Supporting Information). The connectivity between the Cd

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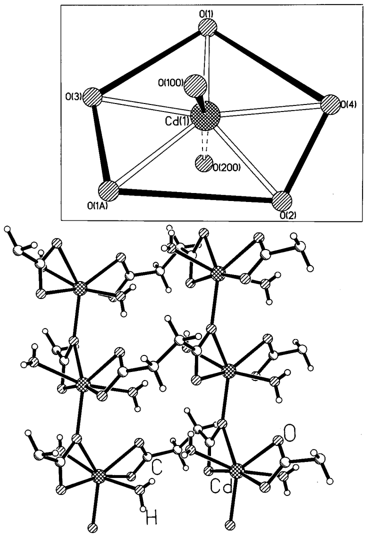

Figure 11. Perspective view of the layer in the *ac*-plane present in $Cd(C_4H_4O_4)(H_2O)_2$, **V**, formed by the connectivity between the Cd atoms and the succinate units. Inset shows the pentagonal bipyramidal coordination around the Cd atom.

centers and the succinate units, in **V**, results in perforated two-dimensional layers with eight-membered apertures in the *ac*-plane (Figure 11). Such layers are stacked along the *b*-axis and are stabilized by weak interactions. The two coordinated water molecules participate in the cohesion of the structure with hydrogen bonds between the layers as observed earlier in $Co_4(OH)_2(H_2O)_2(C_4H_4O_4)_3 \cdot 2H_2O$[10] and $Mn(H_2O)_4(C_4H_4O_4)$.[13]

$Cd_3(C_4H_4O_4)_2(OH)_2$], VI. The asymmetric unit of **VI** contains 11 non-hydrogen atoms. There are two crystallographically independent Cd atoms, both of which are octahedrally coordinated with respect to the oxygens. The Cd−O distances are in the range 2.257(3)−2.393(3) Å (av 2.316 Å), and the average O−Cd−O angle is 109.4°. Selected bond distances and angles are presented in the Supporting Information. The three-dimensional structure of **VI** is made up of two-dimensional Cd−O layers cross-linked by the succinate units. The Cd−O layers are formed by simpler building units. Thus, two Cd−O octahedra are joined through their edges and by two more Cd−O octahedra above and below through their corners, forming a Cd_4O_{18} tetrameric clusters. The tetrameric clusters have the appearance of SBU-4 units (see the inset in Figure 12) proposed for Ga and Fe phosphates. (Typically, SBU-4 is formed by two edge/corner-sharing octahedra capped by two tetrahedra on top and bottom through corner-sharing.)[34] The Cd_4O_{18} tetramers are joined together forming infinite Cd−O sheets (Figure 12), which are cross-linked by succinates to give rise to the three-dimensional structure (Figure 13). Similar structures have been found earlier in Co-succinates.[10]

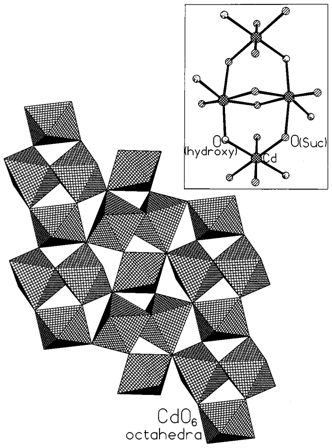

Figure 12. Polyhedral view of the cadmium-oxide layers present in $Cd_3(C_4H_4O_4)_2(OH)_2$, **VI**, formed by the corner-sharing SBU-4 type units, lying in the *ab*-plane. Inset shows the SBU-4 basic building unit.

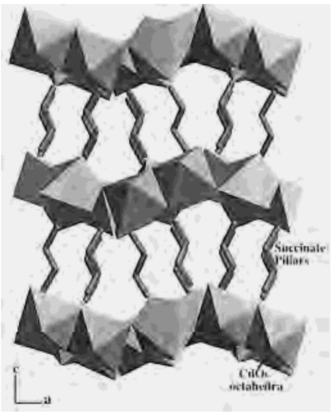

Figure 13. Structure of **VI** showing the connectivity between the cadmium-oxide layers through the succinate linkers, forming small eight-membered empty channels along the *b*-axis.

Discussion

Six cadmium succinates, **I**−**VI**, have been synthesized hydrothermally, of which **I**−**IV** were obtained starting with the organic-amine succinate precursors. While the amines are incorporated in **I**−**IV**, they are absent in **V** and **VI**, which were prepared by the reaction of Cd salts with a mixture of succinic acid and the amine. Thus, it is only in the Cd succinates obtained from amine succinates that the amines are present in the open-framework structure. The use of organic-amine succinates also appears to facilitate the reaction to occur at lower temperatures.

I has a chain structure with the Cd atoms linked to two succinate units; it possesses two terminal Cl atoms (Figure 2). The coordination environment around Cd is tetrahedral if we consider the two succinates as two nodes and the two chlorines as the other two nodes (see the inset in Figure 2). Compound **II** also has a four-connecting tetrahedron, but connected only by succinate units (Figure 3). It appears that **I** is the precursor of **II**, wherein the chlorine atoms in **I** are replaced by the succinates, thereby forming the three-dimensional structure. This observation also gains support from the fact that **II** can be prepared in pure form, while **I** always occurs as a coproduct with **II**.

The structure of **II** is built up from the four-connecting Cd nodes, through the succinate linkers. This type of four-connecting nodes results in the adamantane units and thereby in diamondoid frameworks.[15,22−24,35−38] The building-up process is an example of scale-up chemistry,[39] reminiscent

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[34] (a) Ferey, G. *J. Fluorine Chem.* **1995**, *72*, 187, and references therein. (b) Ferey, G. *C. R. Acad. Sci. Paris* **1998**, 1−13.

of self-similar structures, as shown in Figure 3. The diamondoid lattice in **II** can be considered as being derived from $Cd(CN)_2$ (Cd−Cd = ∼4.46 Å) by the replacement of the nitrile unit by the succinate unit, thereby causing a larger aperture (Cd−Cd = 9.43 Å). The interpenetration in **II** (Figure 4) is similar to that in $Cd(CN)_2$, which is classified as normal interpenetration.[15]

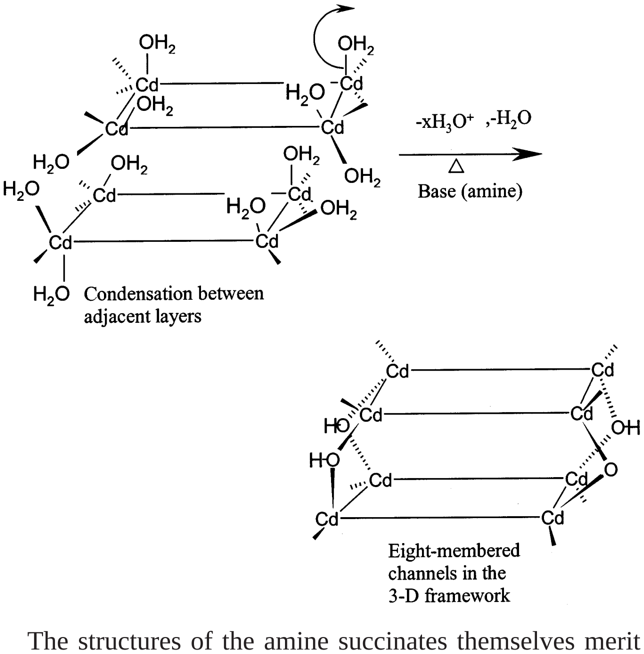
Compound **III** also has an interpenetrated structure, but unlike in **II**, the three-dimensional connectivity in **III** arises not entirely from the linking of the Cd centers by the succinate units. Instead, the connectivities in **III** involve the piperazine moieties, giving rise to a α-polonium type interpenetrated structure (Figure 8) rather than a diamondoid network. The structure of **III** is comparable to that of the other hybrid metal-organics with the α-polonium related structure, such as cadmium(hexakis(imidazol-1-ylmethyl)-benzene)$F_2 \cdot 14H_2O$.[40] If interpenetration can be avoided in **II** and **III** by the introduction of suitable guest species into the appropriate sites,[2d,15,22−24,26] they can be rendered porous.

Ligation by polyfunctional amines such as 4,4′-bipyridine forming rigid networks is known to occur in oxalates and related systems.[41,42] Ancillary ligation by water molecules has been observed in two-dimensional metal succinate architectures.[10,13] The ligation in **III** by piperazine is unusual, as the amine connects Cd atoms in two different Cd succinate layers, acting as a pillar, thereby giving rise to the three-dimensional character of the structure (Figure 7a).

The cadmium succinate layers in **II**, **III**, **IV**, and **V** present an interesting comparison. In **II**, the two in-plane succinate units are connected to the Cd centers in a bidendate fashion, forming honeycomb-like layers (Figure 4a). On the other hand, the cadmium succinate layers in **III** have two different types of in-plane succinate units, one showing a monodendate bonding and the other a bidendate bonding (Figure 6b). One can also view the structure of **III** in terms of the hybrid metal-organic layers, formed by the linking of the Cd atoms by the in-plane succinate and piperazine units (Figure 6a). Similar hybrid metal-organic networks have been found in systems involving rigid bipyridyl ligands.[41,42] The macroanionic layer in **IV** with the formula $[Cd_2(C_4H_4O_4)]^{2-}$ has Cd_2O_2 dimers connected by the succinate units (Figure 9). In addition, **IV** possesses unique four-membered apertures, so aligned as to form one-dimensional tunnels along the *a*-axis (Figure 10), wherein the amine is located. The two-dimensional architecture in **IV** is distinctly different from the honeycomb architectures of many of the metal oxalates.[14,25,33] Although both **IV** and **V** contain layers involving three-coordinated succinate oxygens, the difference in the succinate connectivity (monodendate in **IV** and bidendate in **V**) results in apertures of much smaller size (6.129 × 4.737 Å) in **V** (Figure 11). Two-dimensional architectures containing three-coordinated oxygens are often observed in metal dicarboxylates.[10,43−45] Monodendate binding by the succinate units in framework metal-succinate compounds[10,45] appears to be more frequent than in oxalate-based compounds.[46]

The three-dimensional architecture in **VI** is distinctly different from that in **II** or **III**. In **VI**, the structure consists of two-dimensional sheets with Cd−O−Cd linkages connected by succinate pillars with no guest species. This is reflected in the reduced dimensions of the channels. The structure of **VI** is comparable to that of the cobalt succinate, $Co_5(OH)(C_4H_4O_4)_4$, described by Ferey and co-workers.[10] **VI** comprises a SBU-4 like unit (see inset in Figure 12), observed in the fluorinated metal phosphate frameworks.[34] The connectivity of the cadmium-oxide layer by the succinate linkers is similar to that observed in other metal dicarboxylates.[10]

It has been suggested recently that the complex three-dimensional architectures in open-framework metal phosphates may result from the transformation of lower dimensional structures into the higher dimensional ones, involving progressive building up.[47] A hierarchy of zinc oxalates of different dimensionalities has also been reported.[14] In this context, it is worth noting that the structure of **V** could be related to that of **VI**. Thus, the 2D layer of **V** can be condensed to yield to **VI**. The water molecules bound to the Cd centers in **V** can condense on heating, resulting in a −OH group, bridging the Cd centers of the adjacent layers (-μ_2-type bridge), forming the eight-membered channels in **VI**. A schematic representation of the possible mechanism of transformation is as follows.



$\xrightarrow[\Delta \text{ Base (amine)}]{-xH_3O^+ \text{ ,}-H_2O}$

Condensation between adjacent layers

Eight-membered channels in the 3-D framework

The structures of the amine succinates themselves merit some discussion. In GUS, the anion is the monohydrogen

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(35) (a) MacGillivray, L. R.; Subramaniam, S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1325. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. J. *J. Chem. Soc., Chem. Commun.* **1994**, 2755.

(36) (a) Yaghi, O. M.; Li, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 207. (b) Yaghi, O. M.; Li, H.; Groy, T. L. *Inorg. Chem.* **1997**, *36*, 4292.

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succinate, $C_4H_5O_4^-$, while in PIPS it is the fully deprotonated $C_4H_4O_4^{2-}$, despite guanidine (p$K_a \approx 12.7$) being a stronger base than piperazine (p$K_a \approx 4.2$). It is possible that the extent of deprotonation of succinic acid depends on the different mole ratios of the amine and the acid employed in the synthesis (GUS, CN_3H_5:$2C_4H_6O_4$; PIPS, $C_4N_2H_{10}$:$C_4H_6O_4$). It would be interesting to perform a systematic study of the variation in the structure of the amine-succinate with the change in the amine:acid ratio and its effect on the structure of the open-framework material obtained. Succinic acid, with a small difference between the pK_{a1} and pK_{a2} values (p$K_{a1} \approx 4.61$ and p$K_{a2} \approx 5.61$), seems to respond more sensitively to such compositional variations than oxalic acid, with a large difference (p$K_{a1} \approx 1.23$ and p$K_{a2} \approx 4.19$).

Supporting Information Available: Tables listing various bond distances and angles for all the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(43) Vaidhyanathan, R.; Neeraj, S.; Prasad, P. A.; Natarajan, S.; Rao, C. N. R. *Angew. Chem., Int. Ed.* **2000**, *39*, 3470.

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