Solvothermal Synthesis of a Layered Open-Framework Chlorocadmium Oxalate, $Cd_2(C_2O_4)_{0.5}Cl_3NaCl{\cdot}4H_2O$

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The metathesis reaction between $CdCl_2{\cdot}2H_2O$ and sodium oxalate in *n*-hexanol under solvothermal conditions yields a hybrid compound of formula $Cd_2(C_2O_4)_{0.5}Cl_3NaCl{\cdot}4H_2O$. It consists of one-dimensional chains formed by Cd and Cl atoms, containing μ_2(Cl) and μ_3(Cl) bridges, and cross-linked by oxalate units to give a layered structure. The Na^+ ions and water molecules occupy the interlamellar spaces.

Introduction

A variety of inorganic open-framework compounds containing extra-framework alkali metal ions and other cations have been synthesized in recent years.[1−3] Intercalation of cations and anions in cages and cavities (cryptands, spherands, siderands, coronates) is also well documented in host-guest chemistry.[4] Thus Na^+, K^+, Cl^- and $NO_3{}^-$ have been incorporated into inorganic host compounds. Interestingly, extended structures of alkali halides such as KCl, RbCl, and CsBr, of varying dimensionalities, have been recently incorporated in host lattices of cadmium oxalate.[5−8] The $NH_4{}^+Cl^-$ ion-pair has been introduced in the cage formed by the anionic cluster of isopolyvanadate and phenylphosphonate units.[9] The use of solvothermal techniques to prepare hybrid organic-inorganic solids has resulted in materials inaccessible by other means.[10−13] In our efforts to synthesize hybrid open architectures incorporating alkali halides and other inorganic guests by means of solvothermal routes, we have obtained a two-dimensional cadmium oxalate of the composition $Cd_2(C_2O_4)_{0.5}Cl_3NaCl{\cdot}4H_2O$ (**I**), wherein the NaCl unit is accommodated in the cadmium oxalate structure. The synthesis of **I** seems to have become possible because of the solvothermal conditions employed by us with *n*-hexanol as the solvent; **I** is not obtained under hydrothermal conditions.

Results and Discussion

The asymmetric unit of **I** consists of 14 non-hydrogen atoms with two crystallographically distinct, octahedrally coordinated Cd atoms. Whilst Cd(1) is linked by three chlorine atoms, two oxalate oxygens and one bonded water molecule, Cd(2) is connected by six chlorine atoms. The average Cd(1)−O/Cl and Cd(2)−Cl distances are 2.459 Å and 2.631 Å, respectively (Table 1). The framework structure of **I** is formed by linkages involving $Cd(1)O_3Cl_3$, $Cd(2)Cl_6$ and oxalate units. The Cd(2) atoms are connected to each other through chloride bridges, giving rise to infinite one-dimensional chains, and the Cd(1) atoms are connected to these chains by μ_2(Cl)- and μ_3(Cl)-type chloride bridges (Figure 1). These one-dimensional building units are cross-linked by oxalate units giving rise to a layered architecture (Figure 2). Adjacent layers are shifted by 1/2 the unit cell length along the [1 0 1] direction, giving rise to ABAB-type layer stacking. Extra-framework Na^+ ions occupy spaces in the interlamellar regions along with water molecules (Figure 3). The environment around the Na^+ ion in **I** can be considered to be octahedral with five water molecules (av. Na−O = 2.411 Å) and a chloride, which is also attached to two Cd atoms. The Na−Cl distance is 2.999 Å, slightly longer than the distance in bulk NaCl (2.814 Å). Selected bond lengths and angles in **I** are presented in Table 1.

The one-dimensional $CdCl_2$ chain in **I** is similar to the double chain in ABX_3.[14] The structure of **I** can therefore be considered as originating from $CdCl_2$, which under the non-aqueous conditions employed for the synthesis can give rise to $NaCdCl_3$ chains. Cross-linking of the chlorocadmium chains by the oxalate units would then yield the layer present in **I**, the process being somewhat similar to the assembly of molecular metal clusters by organic linkers described by Yaghi and co-workers.[15] The cadmium chloride chains in **I** are also related to the infinite one-dimensional chains formed by the pyramidal β-$[AsS_4]^{3-}$ units observed in the potassium tin thioarsenide compound $KSnAsS_5$.[16] One can visualize the structure of **I** to be arising from the replacement of the $[AsS_4]^{3-}$ units by $[Cd(C_2O_4)Cl_2(H_2O)]^{2-}$ units and simultaneously replacing the Sn^{4+} by Cd^{2+} units, as represented schematically on the next page.

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Table 1. Selected bond lengths and bond angles for $Cd_2(C_2O_4)_{0.5}Cl_3NaCl\cdot4H_2O$ (**I**)[a]

Moiety	Distance (Å)	Moiety	Distance (Å)
Cd(1)−O(1)#1	2.292(3)	Cd(2)−Cl(3)#3	2.6756(11)
Cd(1)−O(2)	2.304(3)	Na(1)−O(300)	2.322(5)
Cd(1)−O(10)	2.357(4)	Na(1)−O(100)	2.358(4)
Cd(1)−Cl(1)	2.5303(11)	Na(1)−O(200)	2.382(4)
Cd(1)−Cl(2)	2.5404(11)	Na(1)−O(200)#2	2.421(4)
Cd(1)−Cl(3)	2.7284(10)	Na(1)−O(10)	2.571(4)
Cd(2)−Cl(4)	2.5839(11)	Na(1)−Cl(2)	2.999(2)
Cd(2)−Cl(4)#2	2.5908(11)	C(1)−O(2)	1.249(5)
Cd(2)−Cl(1)#3	2.6199(11)	C(1)−O(1)	1.253(5)
Cd(2)−Cl(2)	2.6479(11)	C(1)−C(1)#1	1.569(8)
Cd(2)−Cl(3)	2.6690(11)		

Moiety	Angle (°)	Moiety	Angle (°)
O(1)#1−Cd(1)−O(2)	72.41(10)	Cl(4)−Cd(2)−Cl(2)	91.02(4)
O(1)#1−Cd(1)−O(10)	88.43(14)	Cl(4)#2−Cd(2)−Cl(2)	92.43(3)
O(2)−Cd(1)−O(10)	93.11(12)	Cl(1)#3−Cd(2)−Cl(2)	176.38(4)
O(1)#1−Cd(1)−Cl(1)	165.68(8)	Cl(4)−Cd(2)−Cl(3)	94.38(3)
O(2)−Cd(1)−Cl(1)	93.93(8)	Cl(4)#2−Cd(2)−Cl(3)	174.67(3)
O(10)−Cd(1)−Cl(1)	96.80(12)	Cl(1)#3−Cd(2)−Cl(3)	90.51(3)
O(1)#1−Cd(1)−Cl(2)	95.39(8)	Cl(2)−Cd(2)−Cl(3)	86.33(3)
O(2)−Cd(1)−Cl(2)	167.08(8)	Cl(4)−Cd(2)−Cl(3)#3	177.46(3)
O(10)−Cd(1)−Cl(2)	90.73(10)	Cl(4)#2−Cd(2)−Cl(3)#3	91.27(3)
Cl(1)−Cd(1)−Cl(2)	97.86(4)	Cl(1)#3−Cd(2)−Cl(3)#3	87.55(3)
O(1)#1−Cd(1)−Cl(3)	86.99(8)	Cl(2)−Cd(2)−Cl(3)#3	90.35(3)
O(2)−Cd(1)−Cl(3)	87.86(8)	Cl(3)−Cd(2)−Cl(3)#3	83.57(3)
O(10)−Cd(1)−Cl(3)	174.79(11)	C(1)−O(1)−Cd(1)#1	116.8(3)
Cl(1)−Cd(1)−Cl(3)	88.24(3)	C(1)−O(2)−Cd(1)	116.3(3)
Cl(2)−Cd(1)−Cl(3)	87.24(3)	O(2)−C(1)−O(1)	125.5(4)
Cl(4)−Cd(2)−Cl(4)#2	90.82(3)	O(2)−C(1)−C(1)#1	117.5(4)
Cl(4)−Cd(2)−Cl(1)#3	90.98(3)	O(1)−C(1)−C(1)#1	117.0(4)
Cl(4)#2−Cd(2)−Cl(1)#3	90.56(4)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, y, -z + 1/2$; #2 $-x + 1, -y + 1, -z$; #3 $x, -y + 1, z + 1/2$; #4 $-x + 1/2, -y + 1/2, -z$

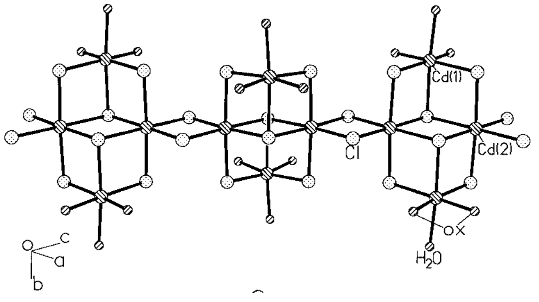


Figure 1. Structure of $Cd_2(C_2O_4)_{0.5}Cl_3NaCl\cdot4H_2O$ (**I**) showing the one-dimensional chlorocadmium double chain [note the presence of infinite -(μ_2Cl)- and -(μ_3Cl)- bridges]

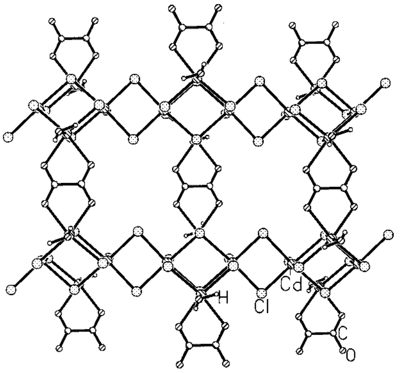
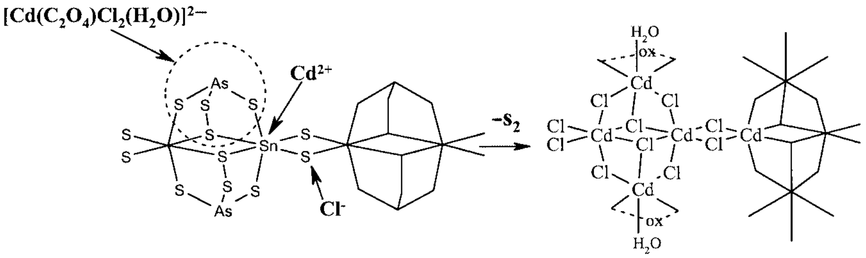


Figure 2. Structure of **I**, showing the two-dimensional chlorocadmium oxalate layer lying in the *ac* plane



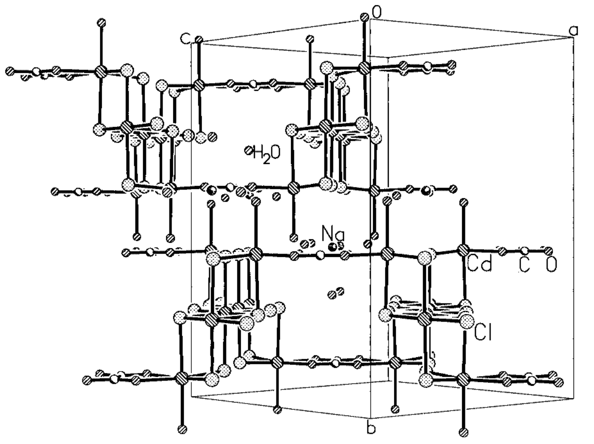
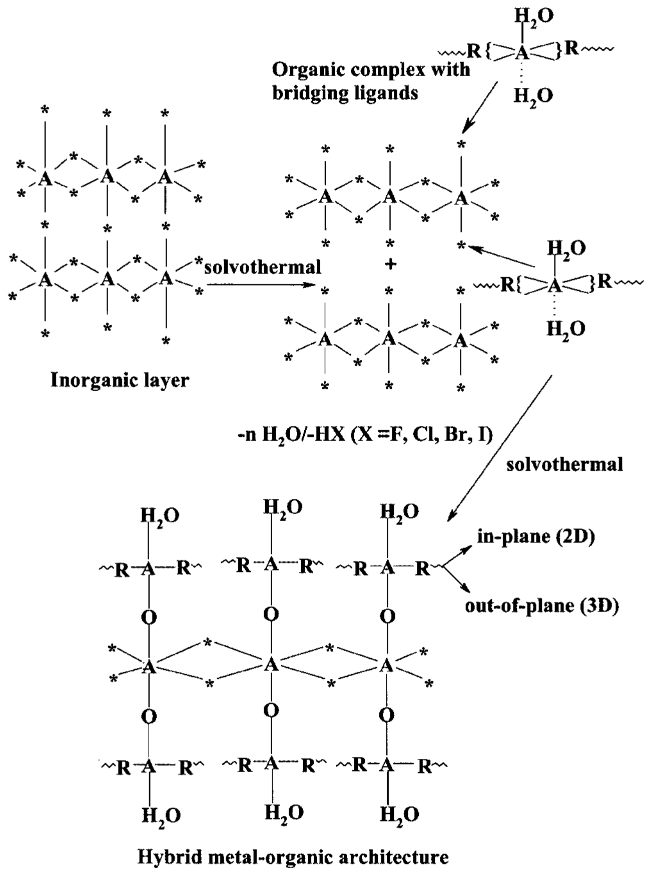


Figure 3. The stacking of the chlorocadmium oxalate layers in **I**; the adjacent layers are shifted by half of the unit cell along the [1 0 1] direction. Note the presence of extra-framework Na^+ ions and water molecules in the interlamellar spaces

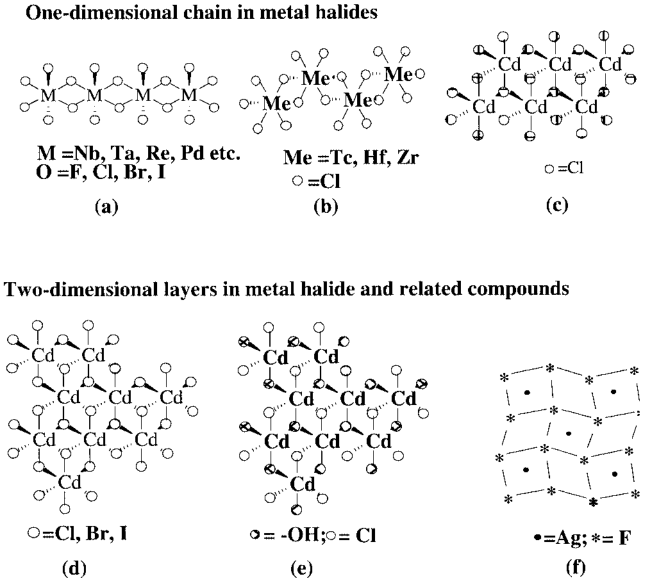
The above schematic suggests a new strategy for designing hybrid metal-organic frameworks, wherein one inorganic anion is replaced by another anion possessing an organic ligand, which in turn facilitates the extension of the structure into higher dimensions. A more general schematic representing this notion to illustrate the building up of three-dimensional hybrid metal-organic frameworks by aligning the lower-dimensional structures of metal halides and metal hydroxides by the introduction of metal complexes with organic ligands (dicarboxylate, bipyridyl, nicotinate etc.) capable of bridging the lower dimensional inorganic structures is presented in Scheme 1. Depending on the mode of linking of the organic linkers, the hybrid metal-organic structures can either be two- or three-dimensional. The possibility that the lower-dimensional structures can be generated by the partial disintegration of the higher dimensional parent structure under suitable reaction conditions is also indicated in Scheme 1. This possibility can be realized by observing the close structural relationships among some of the well-known lower-dimensional inorganic structures shown in Scheme 2. A similar notion has been proposed by Wood and co-workers[17−19] to describe the possible building of the cobalt squarate framework from the parent cobalt hydroxide with a brucite structure. Notably, the structural relationship between the Cd(OH)Cl and Cu(OH)Cl to brucite has been noted recently.[20]

It is likely that many such hybrid metal-organic structures with open-architectures can be made by employing other different organic linkers. In this context, we should draw attention to a new three-dimensional, open-framework, neutral and anhydrous chlorocadmium compound $[CdCl_2(C_4H_8N_2)]$ (**II**),[21] synthesized using solvothermal route by us, wherein the amine performs the role of linking the one-dimensional chlorocadmium chains into three-dimensions (Figure 4). Interestingly, in **II**, the channels are hydrophobic and empty. Assembling such predetermined polymeric units via organic pillars or linkers provides an interesting methodology for combining the dimensionality of the electronic exchange pathways and the open frameworks.[22]



Scheme 1. A general scheme illustrating the building up of complex hybrid metal-organic architectures by aligning the lower-dimensional structures of metal halides/hydroxides by replacing the Cl^- or OH^- ions with metal complexes possessing organic ligands capable of bridging these lower dimensional inorganic structures. Depending on the mode of linking that the organic linkers provide the hybrid metal-organic structures can either be two- or three-dimensional. The probable generation of the low-dimensional structures by the partial disintegration of the higher dimensional parent structure under suitable reaction conditions has also been indicated. A = any metal; * = F, Cl, Br, I, -OH, H_2O; R = dicarboxylate, bipyridyl, nicotinate etc. Note that the one-dimensional inorganic chains can be introduced directly into the reaction medium

The framework structure of **I** has certain unusual features which merit discussion. The position of the chloride, Cl(2), in **I** provides an interesting comparison with the layered chlorocadmium oxalate, $[Rb_2Cd(NO_3)(Cl)(C_2O_4)(H_2O)]$,[6] chlorozinc phosphate, $[C_6NH_{14}][ZnCl(HPO_4)]$[23] and the tin(II) phosphate, $[C_3H_{12}N_2]2[SnPO_4]$.[24] Although the Cl(2) atom in **I** is a bridging chloride its position is similar to that of the pendant Cl atoms in the chlorocadmium oxalate, chlorozinc phosphate and the lone pairs in the Sn^{II} phosphate (Figure 5a−d). The lone-pair of electrons in $[C_3H_{12}N_2]2[SnPO_4]$ and the chlorine atoms in $[C_6NH_{14}][ZnCl(HPO_4)]$ and $[Rb_2Cd(NO_3)(Cl)(C_2O_4)(H_2O)]$ point in a direction perpendicular to the plane of the layer, with the charge-compensating organic amine mol-



Scheme 2. Some of the low-dimensional structures of metal halogen and related inorganic solids; (a) the *cis*-oriented 1-D chains in NbI_4, $TaCl_4$, WCl_4; (b) the *trans*-oriented 1-D chains in $TcCl_4$, $ZrCl_4$, $PtCl_4$; (c) the $CdCl_3$ double chain present in NH_4CdCl_3; (d) the structure of CdX_2 (X = Cl, Br, I); (e) a layer in Cd(OH)Cl; (f) the layer in AgF. Note the similarity in the structure of the double chain in (c) and the cadmium chloride chain in **I** and also the structural relationship existing among the structures shown here

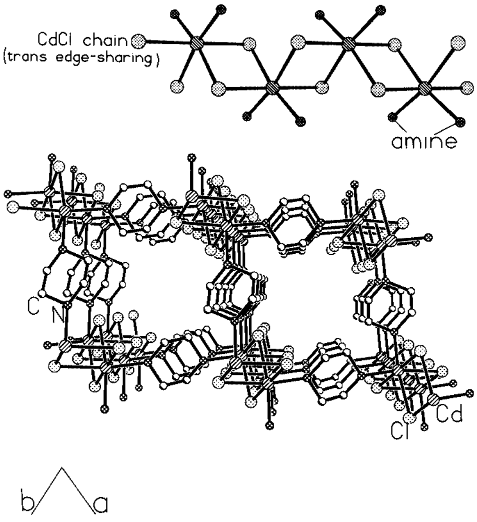


Figure 4. Structure of $[CdCl_2(C_4N_2H_8)]$ (**II**) showing the square hydrophobic channels present along the *a* axis formed by alignment of the Cd-chloro chains by the piperazine units; the inset shows the one-dimensional Cd-chloro chains formed by trans-edge sharing between the $CdCl_4N_2$ octahedra

ecule or the cation situated in the inter-lamellar space. In **I**, Cl(2) points into the inter-lamellar region occupied by the sodium (Figure 5a). Both the Cl atoms and the lone pairs orient themselves perpendicular to the plane of the metal oxalate layer and, satisfying their steric requirements, protrude into the interlayer spaces, making them available for chemical exploitation. Incorporation of halide ions, hydroxy groups or lone pairs in designed compounds, wherein they are made to occupy specific positions with predetermined orientations (based on stereochemical requirements) may enable the formation of materials possessing high chemospecificity.

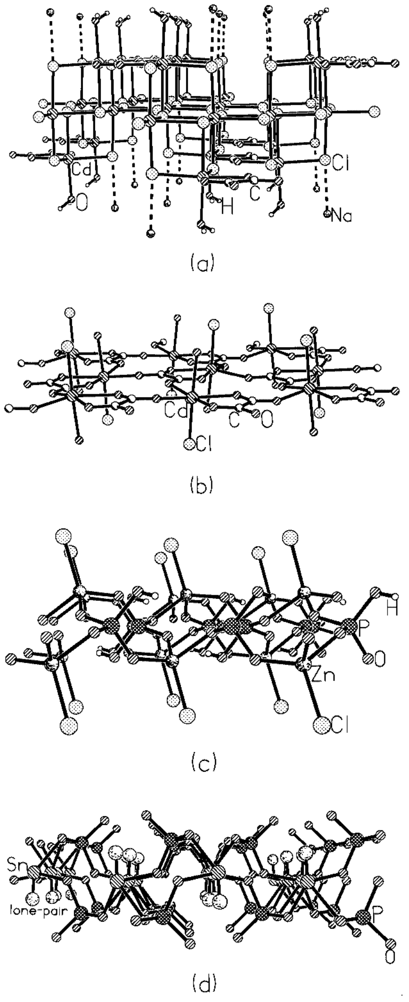


Figure 5. (a) Structure of **I**, showing the Cl(2) atoms pointing to the interlamellar region and the Na···Cl interaction (shown in dotted bonds) between the framework Cl(2) and the guest Na atoms; (b) structure of $[Rb_2Cd(NO_3)(Cl)(C_2O_4)(H_2O)]$, showing the pendant Cl atoms pointing into the interlayer regions; (c) structure of $[C_6NH_{14}][ZnCl(HPO_4)]$, showing the pendant Cl atoms protruding into the interlayer space; (d) structure of $[N_2C_3H_{12}]2[SnPO_4]$, with the pendant Cl atoms protruding into the interlamellar space

The arrangement of the extra-framework Na^+ cations gives rise to certain noteworthy features. The octahedrally coordinated sodium shares an edge with neighboring NaO_5Cl octahedra via bridging water molecules, forming an $Na_2O_8Cl_2$ dimer. These dimers are oriented in such a manner as to form strong O(w)−H···O(w) hydrogen bonds [O(w) = water oxygen] with the adjacent dimer, giving rise to a hydrogen-bond-stabilized one-dimensional ladder (Figure 6). Such low-dimensional structures formed by the guest species, involving weak interactions, contribute to the overall stability of these structures.[25]

In summary, the synthesis and structure of a new open-framework two-dimensional chlorocadmium oxalate compound (**I**) has been achieved. The formation of **I** could be

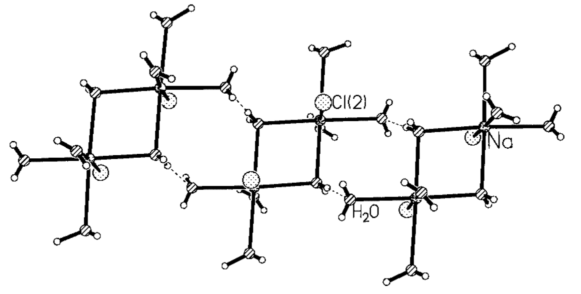


Figure 6. Figure shows the one-dimensional ladder-like structure formed by the $Na_2O_8Cl_2$ dimers *via* O(w)−H···O(w) hydrogen-bond interactions

the result of incomplete dissociation of the starting $CdCl_2$ under solvothermal conditions, facilitating the facile cross-linking by the oxalate units. It is likely that other such unusual structures can be formed under solvothermal conditions by employing other linkers.

Experimental Section

$Cd_2(C_2O_4)_{0.5}Cl_3NaCl\cdot 4H_2O$ (**I**) was synthesized by the metathesis reaction between $CdCl_2\cdot 2H_2O$ and sodium oxalate under solvothermal conditions. Typically, sodium carbonate (0.026 g) and oxalic acid (0.1879 g) were dissolved in 3 mL of dry *n*-hexanol. The mixture was stirred for two hours at room temperature. $CdCl_2\cdot 2H_2O$ (0.20 g) and 0.07 mL of glacial acetic acid were added to the mixture and the contents were stirred to homogeneity (45 mins). The final mixture of the composition $CdCl_2\cdot 2H_2O$:Na_2CO_3:$H_2C_2O_4\cdot 2H_2O$:CH_3COOH:*n*-$C_6H_{13}OH$ (1:0.25:1.5:1.2:24) was sealed in a 23 mL PTFE-lined stainless steel autoclave and heated to 150 °C for 60 h. The product — colorless hexagonal plate-like and/or rod-like crystals — was filtered, washed with deionized water and dried under ambient conditions. Both type of crystals with different morphologies were identified to be compound **I**. The role of acetic acid is not clear to us. The water molecules present in **I** could have come from the use of $CdCl_2\cdot 2H_2O$ and $H_2C_2O_4\cdot 2H_2O$. The same reaction when carried out in the presence of water (hydrothermally) did not yield **I**. The EDAX studies resulted in an Na:Cd:Cl ratio of 1.0:1.9:4.1, which is in agreement with the calculate values (1.0:2.0:4.0); the elemental microanalysis showed: $Cd_2(C_2O_4)_{0.5}Cl_3NaCl\cdot 4H_2O$ (**I**): calcd. C 2.4, H 1.6; found C 2.7, H 1.5.

Initial characterization of **I** was carried out by powder X-ray diffraction, thermogravimetric analysis (TGA), IR spectroscopy, elemental microanalysis and EDAX studies. The powder XRD patterns indicated that the products were new materials and were entirely consistent with the structures determined using the single-crystal X-ray diffraction (see Supporting Information). A least-squares fit (Cu-K_α) of the XRD patterns, using the *hkl* indices generated from the single-crystal structure gave the following lattice parameters: a = 12.216(8), b = 17.2104(10), c = 11.834(8) Å, β = 101.507(9) for **I**. IR spectra (KBr pellet) showed characteristic features of the dicarboxylate units.[26] The various bands are: ν_{as}(C=O) at 1646(s) cm^{-1} and ν_s(C=O) at 1417(w) cm^{-1}; ν_s(C-O) + δ(O-C=O) at 1312(s) cm^{-1}; δ(O-C=O)+ ν(MO) at 790(m) cm^{-1}; ν(MO) + ν(C-C) at 516(m) cm^{-1}; ν(MO) + ring def. at 438(w) cm^{-1}. A broad band appears in the 3550−3300 cm^{-1} region due to the presence of water molecules in the structure.

TGA studies of **I** indicate two distinct mass losses. A gradual mass loss in the range 100−300 °C (obsd. 14.3%) due to the loss of four water molecules (14.2%). The second mass loss of 15.7% in the range of 350−450 °C is due to the loss of the oxalate moiety (calcd. 17.4%). Above 500 °C, a gradual loss was observed due to the slow evaporation of the Cd compound.

Single-Crystal Structure Determination: A suitable single crystal of **I** was selected under a polarizing microscope and glued at the tip of a thin glass fiber with cyanoacrylate (superglue) adhesive. 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-K_α radiation, λ = 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 2.07 to 23.30°. Pertinent experimental details for the structure determinations are presented in Table 2.

The structure was solved and refined by using SHELXTL-PLUS[27] suite of programs. An absorption correction based on symmetry equivalent reflections was applied using the SADABS program.[28] The last cycles of refinement included atomic positions for all the atoms and anisotropic thermal parameters for all the 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 bond lengths and angles for compound **I** are presented in Table 1. CCDC-203041 (**I**) and CCDC-203042 (**II**) contain the supplementary crystallographic data for this paper. These data can be ob-

Table 2. Crystal data and structure refinement parameters for $Cd_2(C_2O_4)_{0.5}Cl_3NaCl\cdot 4H_2O$, **I**

Empirical formula	$Cd_2(C_2O_4)_{0.5}Cl_3NaCl\cdot 4H_2O$
Crystal system	Monoclinic
Space group	*C*2/*c* (No. 15)
Crystal size (mm)	0.10 × 0.0.08 × 0.06
a (Å)	12.2177 (12)
b (Å)	17.2361 (12)
c (Å)	11.8314 (9)
α (°)	90.0
β (°)	101.41 (1)
γ (°)	90.0
Volume (Å^3)	2442.3 (3)
Z	8
Formula mass	505.69
ρ_{calc} (gcm^{-3})	2.750
λ (Mo-K_α) Å	0.71073
μ (mm^{-1})	4.389
θ range (°)	2.07− 23.30
Total data collected	5012
Index ranges	$-13 \le h \le 13$, $-19 \le k \le 19$, $-11 \le l \le 13$
Unique data	1769
Observed data [$I > 2\sigma(I)$]	1477
Refinement method	Full-matrix least-squares on $|F^2|$
R_{merg}	0.0411
R indexes [$I > 2\sigma(I)$]	R_1 = 0.0239,[a] wR_2 = 0.0496[b]
R (all data)	R_1 = 0.0304, wR_2 = 0.0515
Goodness of fit ($S_{obs.}$)	1.027
No. of variables	160
Largest difference map peak and hole e·Å^{-3}	0.674 and −0.452

[a] $R_1 = ||F_0| - |F_c||/|F_0|$. [b] $wR_2 = \{[w(F_0^2 - F_c^2)^2]/[w(F_0^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_0)^2 + (aP)^2 + bP]$, $P = [\max.(F_0^2,0) + 2(F_c)^2]/3$, where a = 0.0103 and b = 0.0000.

tained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information Available (see footnote on the first page of this article): A figure showing a comparison of the simulated and the experimental powder XRD patterns of **I**.

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[21] $[CdCl_2(C_4N_2H_8)]$, **II**, M_r = 267.42, monoclinic, space group *C2/c* (no.15), a = 9.5500(11), b = 13.601(2), c = 6.6499(8) Å, β = 90.868(2)°; V = 863.6(2) Å^3, Z = 8, μ = 3.069mm^{-1}, D_c = 2.057 g·cm^{-3}. A total of 1770 reflections were collected in the θ range 2.61 to 23.29° of which 585 with $I > 2\sigma(I)$ were considered to be observed. Final R = 0.0513, S_{obs} = 1.014 were obtained for 59 parameters. The average Cd−Cl distance and Cd−N distances are 2.682 and 2.345(4) Å, respectively.

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