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Articles

Hybrid Inorganic−Organic Host−Guest Compounds: Open-Framework Cadmium Oxalates Incorporating Novel Extended Structures of Alkali Halides

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Four unusual inorganic−organic nanocomposites containing extended alkali halide structures, present as layers or as three-dimensional units, have been synthesized by a metathetic reaction carried out under hydrothermal conditions. These compounds, with cadmium oxalate host lattices and the alkali halide structures as guests, have the compositions $[RbCl][Cd_6(C_2O_4)_6]\cdot 2H_2O$, **I;** $2[CsBr][Cd(C_2O_4)]\cdot H_2O$, **II;** $2[CsBr][Cd_2(C_2O_4)(Br)_2]\cdot 2H_2O$, **III;** and $3[RbCl][Cd_2(C_2O_4)(Cl_2)]\cdot H_2O$, **IV**. Crystal data for **I**, rhombohedral, space group = R-3 (no. 148), $a = 9.3859(3)$, $c = 23.9086(8)$ Å; $V = 1824.05(1)$ Å^3, $Z = 18$, $M = 1359.51$, $\rho_{calcd} = 3.702$ g cm^{-3}, μ(Mo Kα) = 7.375 mm^{-1}, $R_1 = 0.04$, $wR_2 = 0.0904$ [537 observed reflections with $I > 2\sigma(I)$]; for **II**, orthorhombic, space group = $Pbcm$ (no. 57), $a = 6.0854(6)$, $b = 11.0793(11)$, $c = 16.889(2)$ Å; $V = 1138.7(2)$ Å^3, $Z = 8$, $M = 644.06$, $\rho_{calcd} = 3.745$ g cm^{-3}, μ(Mo Kα) = 15.219 mm^{-1}, $R_1 = 0.04$, $wR_2 = 0.08$ [408 observed reflections with $I > 2\sigma(I)$]; for **III**, orthorhombic, space group = $Cmcm$ (no.63), $a = 23.6151(14)$, $b = 10.2528(6)$, $c = 7.8199(6)$ Å; $V = 1894.2(2)$ Å^3, $Z = 16$, $M = 970.33$, $\rho_{calcd} = 3.374$ g cm^{-3}, μ(Mo Kα) = 14.487 mm^{-1}, $R_1 = 0.03$, $wR_2 = 0.0744$ [651 observed reflections with $I > 2\sigma(I)$]; for **IV**, monoclinic, space group = $P2_1/c$ (no. 14), $a = 8.0648(2)(3)$, $b = 22.9026(4)$, $c = 9.3967(3)$ Å; $V = 1681.10(7)$ Å^3, $Z = 4$, $M = 782.53$, $\rho_{calcd} = 3.076$ g cm^{-3}, μ(Mo Kα) = 11.961 mm^{-1}, $R_1 = 0.04$, $wR_2 = 0.093$ [2071 observed reflections with $I > 2\sigma(I)$]. Compounds **I**−**IV** possess many unusual structural features. While **I** has interpenetrating lattices of the three-dimensional cadmium oxalate and RbCl with an expanded lattice, giving rise to a super rock-salt cell, **II** possesses alternating cadmium oxalate and CsBr layers, the latter comprising six-membered CsBr rings. Compounds **III** and **IV** have isolated cadmium oxalate units (zero-dimensional) linked and stabilized by the alkali halides.

Introduction

A large variety of supramolecular organic and inorganic structures have been described in the recent literature.[1−4] These include several types of host−guest compounds,[2] as well as metal−organic and −inorganic open-framework structures.[4−7] In many of the host−guest compounds, ions, ion pairs, or molecules have been accommodated in the cages or cavities.[3,8] A novel departure from the traditional host−guest chemistry is the recent discovery of cadmium oxalates incorporating extended alkali halide structures of different dimensionalities.[9] These materials can be considered to be

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Table 1. Synthesis Conditions and Analysis for Compounds I−IV

reactant mole ratios	temp, °C	time, h	EDAX ratios	product
$CdCl_2$:$0.5Rb_2CO_3$:$5H_2C_2O_4$: $1.5CH_3COOH$:$88n$-C_4H_9OH: $220H_2O$	150	78	Cd:Rb:Cl 6.5:1.0:1.1	[RbCl][$Cd_6(C_2O_4)_6$]·$2H_2O$ (**I**)
$CdBr_2$:Cs_2CO_3:$1.47H_6C_4O_4$:$70n$-C_4H_9OH:$150H_2O$	150	108	Cd:Cs:Br 1.1:1.5:1.5	2[CsBr][$Cd(C_2O_4)$] ·H_2O (**II**)
$CdBr_2$:$(COOCs)_2$:$1.95CH_3COO$:$40n$-C_4H_9OH:$62H_2O$	150	80	Cd:Cs:Br 1.1:1.1:1.8	2[CsBr][$Cd_2(C_2O_4)(Br)_2$]·$4H_2O$ (**III**)
$CdCl_2$:Rb_2CO_3:$H_2C_2O_4$:$2CH_3COOH$:$33n$-C_4H_9OH:$33H_2O$	150	80	Cd:Rb:Cl 1.0:1.5:2.5	3[RbCl][$Cd_2(H_2O)C_2O_4)(Cl)_2$]·H_2O (**IV**)

organic−inorganic nanocomposites or hetero superlattices wherein the oxalate and alkali halide units are either intricately connected in three-dimensions or occur discretely in alternate layers. In view of the novelty of these hybrid structures, we considered it highly desirable to explore newer systems incorporating such alkali halide structures. In the present study, we describe a three-dimensional cadmium oxalate structure, [RbCl][$Cd_6(C_2O_4)_6$]·$2H_2O$, **I**, incorporating RbCl in the rock-salt (*Fm*3*m*) structure, with a unit-cell parameter double that of the normal RbCl. The structure of **I** is even more fascinating in that the oppositely charged cluster ions form a rock-salt supercell, by using the RbCl lattice as a template. We then have a layered cadmium oxalate, 2[CsBr][$Cd(C_2O_4)$]·H_2O, **II**, having CsBr in a graphitic layered architecture formed by six-membered rings, and two other cadmium oxalates, 2[CsBr][$Cd_2(C_2O_4)(Br)_2$]·$2H_2O$, **III**, and 3[RbCl][$Cd_2(C_2O_4)(Cl_2)$]·H_2O, **IV**, where the alkali halide layers comprising different types of rings act as bridges between the oxalate units. The alkali halide units in **III** form a layered structure with eight-ring apertures. Compounds **I**−**IV** constitute members of a new class of hybrid host−guest materials and are likely to possess novel dielectric, optical, and other properties in view of the periodic arrangement of the organic and inorganic components.

Experimental Section

Compounds **I**−**IV** were prepared by metathetic reaction under hydrothermal conditions. Typically for the synthesis of **I**, 0.057 g of Rb_2CO_3 was dissolved in 4 mL of *n*-butanol and 2 mL of water mixture. Oxalic acid, 0.313 g, and $CdCl_2$, 0.1 g, were added, and the contents were stirred for 20 min. Finally 0.04 mL of glacial acetic acid was added and the mixture was stirred to homogeneity. The final mixture with the composition $CdCl_2$:$0.5Rb_2CO_3$:$5H_2C_2O_4$:$1.5CH_3COOH$:$90C_4H_9OH$:$220H_2O$ was sealed in a PTFE-lined stainless steel autoclave and heated at 150 °C for 72 h. The resulting product, a crop of truncated cubelike crystals suitable for single-crystal X-ray study, was filtered, washed, and dried at room temperature. A similar synthesis procedure was employed for the preparation of compounds **II**−**IV** and is presented in Table 1.

The initial characterization was carried out using powder X-ray diffraction (XRD), EDAX, and chemical analysis. The powder XRD patterns indicated that the products were new materials; the patterns were entirely consistent with the structures determined by using single-crystal X-ray diffraction. As a representative example, powder data for compound **I** is presented in Table 2.

Thermogravimetric analysis of compounds **I** and **II** were carried out in O_2 atmosphere (50 mL min^{-1}) in the range room temperature to 700 °C. While **I** showed two distinct mass losses, **II** had three distinct mass losses. For **I**, a gradual mass loss around 100 °C followed by a sharp mass loss in the range 350−400 °C (42.0%) was found due to the loss of the extra framework water and oxalate (calcd 41.5%). A mass loss above 500 °C was found due to the slow evaporation of CdO. For compound **II**, a sharp mass loss of 2.3% around 150 °C corresponds to the loss of extra framework water (calcd 2.8) and the second mass loss of 16% around 350 °C corresponds to the loss of oxalate units. Above 600 °C there was loss due to the evaporation of CdO. In both **I** and **II**, the powder XRD pattern of the product of decomposition was characteristic of CdO, mineral monteporite (JCPDS: 05-0640).

Table 2. X-ray Powder Data for I, [RbCl][$Cd_6(C_2O_4)_6$]·$2H_2O$

H	*K*	*L*	$2\theta_{obsd}$	$\Delta(2\theta)^a$	d_{calcd}	$\Delta(d)^b$	$I_{rel}{}^c$
0	0	3	11.102	0.000	7.970	0.000	11
1	0	1	11.498	0.000	7.696	0.000	9
1	0	2	13.163	0.008	6.722	0.004	52
1	0	4	18.485	0.060	4.815	0.015	8
1	1	0	19.007	0.097	4.693	0.024	20
1	1	3	21.996	0.017	4.044	0.003	14
0	0	6	22.369	0.059	3.985	0.010	11
2	0	2	23.179	0.065	3.848	0.011	8
2	0	4	26.560	0.040	3.361	0.005	100
1	0	7	28.480	0.137	3.149	0.015	11
2	1	1	29.384	0.075	3.047	0.008	17
1	1	6	29.444	0.040	3.038	0.004	13
2	1	2	30.135	0.105	2.976	0.010	9
2	1	4	32.804	0.030	2.732	0.002	7
0	0	9	33.739	0.000	2.657	0.000	15
2	0	7	34.395	0.101	2.615	0.007	6
2	1	5	34.751	0.046	2.585	0.003	18
3	0	3	35.045	0.068	2.565	0.005	7
2	0	8	37.439	0.091	2.408	0.006	11
1	1	9	39.086	0.128	2.312	0.007	6
3	1	1	40.211	0.034	2.244	0.002	48
3	0	6	40.248	0.001	2.241	0.000	27
3	1	2	40.703	0.024	2.215	0.001	11
3	1	5	44.424	0.002	2.039	0.000	4

[a] $2\theta_{obsd} - 2\theta_{calcd}$. [b] $d_{obsd} - d_{calcd}$. [c] $100I/I_{max}$. LSQ fitted lattice parameter (Cu Kα): $a = 9.3773(5)$, $b = 9.3773(5)$, $c = 23.8786(9)$ Å, $V = 1818.4(3)$ Å^3.

Infrared spectroscopic studies as a KBr pellet showed characteristic features of the bischelating oxalate.[10] The various bands for compounds **I**−**IV** are as follows: ν_{as}(C═O) 1612−1672 cm^{-1}; ν_s(O−C−O) 1372 and 1311 (s) cm^{-1} (**I**), 1374 and 1310 (s) cm^{-1} (**II**), 1372 (m) and 1310 (s) cm^{-1} (**III**), 1373 and 1312 (s) cm^{-1} (**IV**); δ(O−C═O) 803 (m), 790 (w), and 774 (w) cm^{-1} (**I**), 800 (w) and 773 (s) cm^{-1} (**II**), 773 (s) and 731 (w) cm^{-1} (**III**), 802 and 776 (m) cm^{-1} (**IV**). The extraframework water molecules showed characteristic bands around 3550 (s) cm^{-1} in all the cases. The M−O (M = Cd) stretching vibrations ν_s(M−O) and ν_s(C−C) are also observed at 512 and 441 (s) cm^{-1} (**I**), 513 (m) cm^{-1} (**II**), 514 (w) cm^{-1} (**III**), 512 and 441 (s) cm^{-1} (**IV**). The various infrared bands are consistent with the structure determined by single-crystal studies.

Single-Crystal Structure Determination. A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued to a thin glass fiber with cyano-acrylate (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, $\lambda = 0.710\ 73$ 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 20s per frame) in the 2θ range 3−46.5°. Pertinent experimental details for the structure determinations are presented in Table 3.

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Table 3. Crystal Data and Structure Refinement Parameters for $[RbCl][Cd_6(C_2O_4)_6]\cdot 2H_2O$, I; $2[CsBr][Cd(C_2O_4)]\cdot H_2O$, II; $2[CsBr][Cd_2(C_2O_4)(Br)_2]\cdot 4H_2O$, III; and $3[RbCl][Cd_2(H_2O)(C_2O_4)(Cl)_2]\cdot H_2O$, IV

parameters	**I**	**II**	**III**	**IV**
empirical formula	$H_4C_{12}Cd_6C_{l1}O_{26}Rb_1$	$H_2C_2Cd_1Br_2O_5Cs_2$	$H_8C_2Cd_1Br_4O_5Cs_2$	$H_4C_2Cd_2Cl_5O_6Rb_3$
crystal system	rhombohedral	orthorhombic	orthorhombic	monoclinic
space group	*R*-3 (no. 148)	*Pbcm* (no. 57)	*Cmcm* (no. 63)	$P2_1/c$ (no. 14)
crystal size, mm	0.09, 0.09, 0.09	0.08, 0.06, 0.07	0.08, 0.10, 0.12	0.08, 0.06, 0.09
a, Å	9.3859(3)	6.0854(6)	23.6251(14)	8.0648(2)
b, Å	9.3859(3)	11.0793(11)	10.2528(6)	22.9026(4)
c, Å	23.9086(8)	16.889(2)	7.8199 (58)	9.3967(3)
α	90°	90°	90°	90°
β	90°	90°	90°	104.399**(10)**°
γ	120°	90°	90°	90°
vol, $Å^3$	1824.05(10)	1138.7(2)	1894.2(2)	1681.10(7)
Z	18	8	16	4
formula mass	1359.51	644.06	970.33	782.53
r_{calcd}, g cm^{-3}	3.702	3.745	3.374	3.076
λ (Mo Kα), Å	0.71073	0.71073	0.71073	0.71073
μ, mm^{-1}	7.375	15.219	14.487	11.961
θ range	2.56−23.26°	2.41−23.27°	1.72−23.24°	1.78−23.25°
total data collected	2598	4407	3894	6939
index ranges	$-10 \le h \le 6, -7 \le k \le 10, -26 \le l \le 24$	$-6 \le h \le 6, -12 \le k \le 11, -18 \le l \le 14$	$-21 \le h \le 26, -11 \le k\ 11, -8 \le l \le 8$	$-7 \le h \le 8, -21 \le k \le 25, -10 \le l \le 8$
unique data	589	855	770	2405
obsd data ($I > 2\sigma(I)$)	537	408	651	2071
refinement method	full-matrix least-squares on $\|F^2\|$	full-matrix least-squares on $\|F^2\|$	full-matrix least-squares on $\|F^2\|$	full-matrix least-squares on $\|F^2\|$
R_{int}	0.0887	0.0647	0.0535	0.0950
R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0355,^a\ wR_2 = 0.0904^b$	$R_1 = 0.0377,^a\ wR_2 = 0.0827^b$	$R_1 = 0.0334,^a\ wR_2 = 0.0744^b$	$R_1 = 0.0409,^a\ wR_2 = 0.0931^b$
R (all data)	$R_1 = 0.0414$, $wR_2 = 0.0980$	$R_1 = 0.0485$, $wR_2 = 0.0879$	$R_1 = 0.0428$, $wR_2 = 0.0784$	$R_1 = 0.0516$, $wR_2 = 0.1008$
goodness of fit	1.155	1.005	1.073	1.133
no. of variables	71	66	55	163
largest difference map peak and hole e$Å^{-3}$	0.806 and 1.595	1.129 and 1.625	1.338 and 0.618	0.775 and 1.652

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] /\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max.\ (F_o^2, 0) + 2(F_c)^2]/3$; where $a = 0.0565$, $b = 9.1718$ for I; $a = 0.0493$, b = 0.0000 for **II**; $a = 0.0431$, $b = 14.3797$ for **III;** and $a = 0.0352$, $b = 10.3425$ for **IV** .

The structure was solved by direct methods using SHELXS-86[11] and difference Fourier syntheses. An absorption correction based on symmetry equivalent reflections was applied using SADABS program.[12]The hydrogen positions associated with the water molecules in the case of compounds **I**−**IV** could not be located from the difference Fourier map. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using SHELXTL-PLUS[13] package of programs. Details of the final refinements are given in Table 3. The final atomic coordinates, selected bond distances, and angles for compounds **I** are presented in Tables 4 and 5, for **II** in Tables 6 and 7, for **III** in Tables 8 and 9, and for **IV** in Tables 10 and 11.

Table 4. Final Atomic Coordinates [x10^4] and Equivalent Isotropic Displacement Parameters [$Å^2$ x 10^3] for I, $[RbCl][Cd_6(C_2O_4)_6]\cdot 2H_2O$

atom	*x*	*y*	*z*	*U*(eq)[a]
Cd(1)	2567(1)	3862(1)	96(1)	15(1)
Rb(1)	0	0	0	18(1)
Cl(1)	3333	6667	1667	15(1)
O(1)	1121(7)	5001(7)	587(2)	19(1)
O(2)	3151(8)	3164(8)	96(2)	24(2)
O(3)	2194(8)	1212(8)	1048(2)	25(2)
O(4)	4191(8)	3795(7)	1697(2)	19(1)
C(1)	342(11)	4467(11)	136(4)	19(2)
C(2)	2770(11)	934(10)	1481(4)	15(2)
O(100)	6667	3333	767(20)	232(18)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results

$[RbCl][Cd_6(C_2O_4)_6]\cdot 2H_2O$, I. The asymmetric unit of **I** contains 10 non-hydrogen atoms, of which seven atoms make up cadmium oxalate host framework, and the remaining three are the guest molecules (Rb, Cl, and water). The Cd is six coordinated with respect to the oxygen atoms forming a triangular prism with Cd−O distances in the range 2.292(5)−2.384(6) Å (av 2.339 Å). The oxygens are linked to the carbon atoms forming the oxalate unit, with average C−O distances of 1.248 Å (Table 5). The O−Cd−O bond angles are in the range 69.8(2)−148.5(2)° (av 102.9°) (Table 5). The Rb ions are coordinated by 12 oxygen atoms at a distance of ~3 Å and the Cl^- ions are surrounded by six cadmium atoms at ~2.9 Å (Table 5). These geometrical parameters are in good agreement with those reported for similar compounds.

The framework structure of **I** consists of a network of cadmium and oxalate units. The connectivity between these units is such that they form an unusual cadmium oxide cluster of the composition $[Cd_6O_{24}]$. The clusters are connected into three-dimensions by the oxalate units. The Cl^- ions are located inside these clusters (Figure 1) with the charge compensating Rb^+ ions located in the cavities formed between these clusters (Figure 2). The Rb^+ and Cl^- ions are perfectly ordered in three dimensions forming an independent rock-salt (*Fm*3*m*) structure with interpenetrating *fcc* lattices (Figure 3). The cubic unit cell parameter of RbCl is 13.452 Å, which is roughly double that in ordinary RbCl

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[11] Sheldrick, G. M. *SHELXS-86 Program for Crystal Structure Determination*; University of Gottingen: Gottingen, Germany 1986; *Acta Crystallogr.* **1990**, *A35*, 467.

[12] Sheldrick, G. M. *SADABS Siemens Area Detector Absorption Correction Program*; University of Gottingen: Gottingen, Germany, 1994.

[13] Sheldrick, G. M. *SHELXS-93 Program for Crystal Structure Solution and Refinement*; University of Gottingen: Gottingen, Germany, 1993.

Table 5. Selected Bond Distances and Bond Angles for I, $[RbCl][Cd_6(C_2O_4)_6]\cdot 2H_2O$

moiety^a	distance, Å	moiety^a	distance, Å
Cd(1)O(1)	2.292(5)	Rb(1)O(3)#5	3.078(6)
Cd(1)O(2)	2.327(6)	Rb(1)O(3)	3.078(6)
Cd(1)O(3)	2.341(6)	Cl(1)Cd(1)#7	2.8919(6)
Cd(1)O(4)	2.342(6)	Cl(1)Cd(1)#1	2.8918(6)
Cd(1)O(4)#1	2.348(6)	Cl(1)Cd(1)#8	2.8918(6)
Cd(1)O(1)#2	2.384(6)	Cl(1)Cd(1)#7	2.8918(6)
Cd(1)Cl(1)	2.8917(6)	Cl(1)Cd(1)#2	2.8918(6)
Rb(1)O(2)	2.973(6)	O(1)C(1)	1.259(11)
Rb(1)O(2)#3	2.973(6)	O(1)Cd(1)#7	2.384(6)
Rb(1)O(2)#4	2.973(6)	O(2)C(1)#6	1.237(11)
Rb(1)O(2)#5	2.973(6)	O(3)C(2)	1.252(10)
Rb(1)O(2)#6	2.973(6)	O(4)C(2)#9	1.253(10)
Rb(1)O(2)#4	2.973(6)	O(4)Cd(1)#8	2.348(5)
Rb(1)O(3)#3	3.078(6)	C(1)O(2)#4	1.237(11)
Rb(1)O(3)#6	3.078(6)	C(1)C(1)#10	1.57(2)
Rb(1)O(3)#4	3.078(6)	C(2)O(4)#9	1.253(10)
Rb(1)O(3)#4	3.078(6)	C(2)C(2)#9	1.53(2)

moiety^a	angle, deg	moiety^a	angle, deg
O(1)Cd(1)−O(2)	93.2(2)	O(2)Cd(1)−O(1)#2	69.8(2)
O(1)Cd(1)−O(3)	136.1(2)	O(3)Cd(1)−O(1)#2	123.0(2)
O(2)Cd(1)−O(3)	73.0(2)	O(4)Cd(1)−O(1)#2	87.7(2)
O(1)Cd(1)−O(4)	148.5(2)	O(4)#1−Cd(1)O(1)#2	147.4(2)
O(2)Cd(1)−O(4)	114.3(2)	O(2)#4−C(1)O(1)	126.4(8)
O(3)Cd(1)−O(4)	70.2(2)	O(2)#4−C(1)C(1)#10	117.3(10)
O(1)Cd(1)−O(4)#1	81.8(2)	O(1)C(1)−C(1)#10	116.2(10)
O(2)Cd(1)−O(4)#1	141.2(2)	O(3)C(2)−O(4)#9	124.8(8)
O(3)Cd(1)−O(4)#1	84.2(2)	O(3)C(2)−C(2)#9	118.0(9)
O(4)Cd(1)−O(4)#1	85.35(7)	O(4)#9−C(2)C(2)#9	117.3(9)
O(1)Cd(1)−O(1)#2	87.9(3)		

[a] Symmetry transformations used to generate equivalent atoms: #1, $y - {}^{1}/_{3}, -x + y + {}^{1}/_{3}, -z + {}^{1}/_{3}$; #2, $-y + 1, x - y + 1, z$; #3, $-x, -y, -z$; #4, $x - y, x, -z$; #5, $-x + y, -x, z$; #6, $y, -x + y, -z$; #7, $-x + {}^{2}/_{3}, -y + {}^{4}/_{3}, -z + {}^{1}/_{3}$; #8, $x - y + {}^{2}/_{3}, x + {}^{1}/_{3}, -z + {}^{1}/_{3}$; #9, $-x + {}^{2}/_{3}, -y + {}^{1}/_{3}, -z + {}^{1}/_{3}$; #10, $-x, -y + 1, -z$.

Table 6. Final Atomic Coordinates [$x10^4$] and Equivalent Isotropic Displacement Parameters [$Å^2$ x 10^3] for II, $2[CsBr][Cd(C_2O_4)]\cdot H_2O$

atom	x	y	z	U(eq)^a
Cd(1)	8496(2)	871(1)	2500	21(1)
Cs(1)	6536(1)	3910(1)	3847(1)	32(1)
Br(1)	8483(2)	809(1)	896(1)	40(1)
C(1)	8168(20)	1994(10)	2500	15(3)
C(2)	3271(21)	1789(12)	2500	23(3)
O(1)	7119(15)	1053(8)	2500	28(2)
O(2)	5319(13)	1983(8)	2500	30(2)
O(3)	2291(15)	816(7)	2500	29(2)
O(4)	9807(13)	2882(8)	2500	29(2)
O(100)	2733(18)	2500	5000	93(5)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(6.570 Å) as shown in Figure 4. The [100] RbCl planes run along the [111] direction of I (Figure 3). An alternate way to describe the structure of **I** would be to consider the Cl^- ion as being at the center of a cluster of six Cd atoms arranged in such a manner that they form the six vertexes of an octahedron, with the next nearest oxygen neighbors forming the trigonal prisms with Cd atoms. Accordingly, **I** could be considered as a super rock-salt arrangement of two types of clusters, $[ClCd_6(C_2O_4)_3]^{5+}$ and $[Rb(H_2O)_2(C_2O_4)_3]^{5-}$. This type of arrangement is reminiscent of Chevrel phases.[14]

Table 7. Selected Bond Distances and Bond Angles for II, $2[CsBr][Cd(C_2O_4)]\cdot H_2O$

moiety^a	distance, Å	moiety^a	distance, Å
Cd(1)O(1)	2.290(8)	Br(1)Cs(1)#10	3.6706(13)
Cd(1)O(2)	2.293(8)	Br(1)Cs(1)#3	3.7153(12)
Cd(1)O(3)#1	2.310(9)	Br(1)Cs(1)#5	3.7336(13)
Cd(1)O(4)	2.367(9)	C(1)O(1)	1.223(13)
O(3)Cd(1)#11	2.310(9)	C(1)O(4)#3	1.240(13)
Cd(1)Br(1)	2.7099(11)	C(1)C(2)#5	1.61(2)
Cd(1)Br(1)#2	2.7100(11)	C(2)O(3)	1.233(14)
Cs(1)Br(1)#2	3.6603(13)	C(2)O(2)	1.264(14)
Cs(1)Br(1)#8	3.6706(13)	C(2)C(1)#7	1.61(2)
Cs(1)Br(1)#9	3.7153(12)	O(3)Cs(1)#5	3.185(6)
Cs(1)Br(1)#7	3.7336(13)	O(3)Cs(1)#6	3.185(6)
Br(1)Cs(1)#2	3.6602(13)	O(4)C(1)#9	1.240(13)

moiety^a	angle, deg	moiety^a	angle, deg
O(1)Cd(1)−O(2)	101.0(3)	O(3)#1−Cd(1)Br(1)	90.14(3)
O(1)Cd(1)−O(3)#1	110.0(3)	O(4)Cd(1)−Br(1)	91.43(3)
O(2)Cd(1)−O(3)#1	149.0(3)	O(1)C(1)−O(4)#3	127.8(11)
O(1)Cd(1)−O(4)	178.2(3)	O(1)C(1)−C(2)#5	115.5(11)
O(2)Cd(1)−O(4)	77.2(3)	O(4)#3−C(1)C(2)#5	116.7(10)
O(3)#1−Cd(1)O(4)	71.8(3)	O(3)C(2)−O(2)	128.7(12)
O(1)Cd(1)−Br(1)	88.58(3)	O(3)C(2)−C(1)#7	118.0(11)
O(2)Cd(1)−Br(1)	90.63(3)	O(2)C(2)−C(1)#7	113.3(11)

[a] Symmetry transformations used to generate equivalent atoms: #1, $x + 1, y, z$; #2, $x, y, -z + {}^{1}/_{2}$; #3, $-x + 2, y - {}^{1}/_{2}, -z + {}^{1}/_{2}$; #4, $-x + 2, y - {}^{1}/_{2}, z$; #5, $-x + 1, y - {}^{1}/_{2}, -z + {}^{1}/_{2}$; #6, $-x + 1, y - {}^{1}/_{2}, z$; #7, $-x + 1, y + {}^{1}/_{2}, -z + {}^{1}/_{2}$; #8, $x, -y + {}^{1}/_{2}, z + {}^{1}/_{2}$; #9, $-x + 2, y + {}^{1}/_{2}, -z + {}^{1}/_{2}$; #10, $x, -y + {}^{1}/_{2}, z - {}^{1}/_{2}$; #11, $x - 1, y, z$; #12, $x, -y + {}^{1}/_{2}, -z + 1$.

Table 8. Final Atomic Coordinates [$x10^4$] and Equivalent Isotropic Displacement Parameters [$Å^2$ x 10^3] for III, $2[CsBr][Cd_2(C_2O_4)(Br)_2]\cdot 2H_2O$

atom	x	y	z	U(eq)^a
Cd(1)	1243(1)	4005(1)	2500	28(1)
Cs(1)	3116(1)	3170(1)	2500	47(1)
Br(1)	1692(1)	1663(1)	2500	52(1)
Br(2)	3074(1)	0	0	33(1)
C(1)	0	3522(9)	1499(13)	22(2)
O(1)	468(2)	3522(5)	772(6)	32(1)
O(200)	4173(3)	1145(7)	2500	33(2)
O(100)	101(69)	118(72)	6151(186)	739(227)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 9. Selected Bond Distances and Bond Angles for III, $2[CsBr][Cd_2(C_2O_4)(Br)_2]\cdot 2H_2O$

moiety^a	distance, Å	moiety^a	distance, Å
Cd(1)O(1)#1	2.329(5)	Cs(1)Br(1)	3.703(2)
Cd(1)O(1)	2.329(5)	Br(1)Cs(1)#6	3.610(2)
Cd(1)O(200)#2	2.405(7)	Br(2)Cd(1)#6	2.7332(8)
Cd(1)Br(1)	2.6248(14)	Br(2)Cd(1)#4	2.7332(8)
Cd(1)Br(2)#3	2.7332(8)	C(1)O(1)	1.243(7)
Cd(1)Br(2)#4	2.7332(8)	C(1)O(1)#8	1.243(7)
Cs(1)Br(1)#2	3.610(2)	C(1)C(1)#1	1.57(2)

moiety^a	angle, deg	moiety^a	angle, deg
O(1)#1−Cd(1)O(1)	70.9(2)	O(1)C(1)−C(1)#1	117.2(5)
O(1)#1−Cd(1)O(200)#2	82.7(2)	O(1)#8−C(1)C(1)#1	117.2(5)
O(1)Cd(1)−O(200)#2	82.7(2)	C(1)O(1)−Cd(1)	115.7(5)
O(1)C(1)−O(1)#8	125.6(9)	Cd(1)#6−O(200)Cs(1)	105.6(2)

[a] Symmetry transformations used to generate equivalent atoms: #1, $x, y, -z + {}^{1}/_{2}$; #2, $-x + {}^{1}/_{2}, y + {}^{1}/_{2}, -z + {}^{1}/_{2}$; #3, $-x + {}^{1}/_{2}, -y + {}^{1}/_{2}, z + {}^{1}/_{2}$; #4, $-x + {}^{1}/_{2}, -y + {}^{1}/_{2}, -z$; #5, $-x + {}^{1}/_{2}, -y + {}^{1}/_{2}, -z + 1$; #6, $-x + {}^{1}/_{2}, y - 1/_{2}, -z + {}^{1}/_{2}$; #7, $x, -y, z - {}^{1}/_{2}$; #8, $-x, y, z$; #9, $x, -y, -z + 1$.

$2[CsBr][Cd(C_2O_4)]\cdot H_2O$, II. The asymmetric unit of **II** contains 10 non-hydrogen atoms, of which eight atoms make up cadmium bromo-oxalate host framework and the remaining two are the guest molecules (Rb and water). The Cd atom is in an octahedral coordination with four oxygen and two bromine atoms. The Cd−O distances are in the range 2.290(8)−2.367(9) Å (av 2.315 Å), and the Cd−Br distances have an average value of 2.710 Å. The oxygens, in turn, are linked with carbon

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(14) (a) Subba Rao, G. V.; Balakrishnan, G. *Bull. Mater. Sci. (India)* **1984**, *6*, 283 and the references therein. (b) Subba Rao, G. V. *Proc. Ind. Natl. Sci. Acad.* **1986**, *52A*, 292.

Table 10. Final Atomic Coordinates [x10^4] and Equivalent Isotropic Displacement Parameters [Å^2 x 10^3] for IV, 3[RbCl][$Cd_2(C_2O_4)(Cl_2)$]·H_2O

atom	*x*	*y*	*z*	*U*(eq)[a]
Cd(1)	3176(1)	4425(1)	4647(1)	24(1)
Cd(2)	62(1)	3703(1)	9969(1)	22(1)
Rb(1)	393(1)	3103(1)	5741(1)	33(1)
Rb(2)	4892(1)	2793(1)	2861(1)	36(1)
Rb(3)	4799(1)	4150(1)	9398(1)	36(1)
Cl(1)	4605(3)	3526(1)	6111(3)	30(1)
Cl(2)	1497(3)	3657(1)	2765(3)	35(1)
Cl(3)	4832(3)	5177(1)	6845(3)	33(1)
Cl(4)	2435(3)	3006(1)	10294(3)	32(1)
Cl(5)	2212(3)	3009(1)	9392(3)	28(1)
C(1)	902(11)	5002(4)	10186(10)	22(2)
C(2)	47(12)	5220(4)	4394(10)	23(2)
O(1)	1282(8)	5181(3)	3804(7)	30(2)
O(2)	1511(8)	4507(3)	9666(7)	28(2)
O(3)	1605(8)	4528(3)	10268(7)	29(2)
O(4)	1083(8)	5612(3)	4100(7)	29(2)
O(10)	1496(8)	3782(3)	7500(7)	28(2)
O(100)	7572(10)	3677(4)	3508(9)	51(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 11. Selected Bond Distances and Bond Angles for IV, 3[RbCl][$Cd_2(C_2O_4)(Cl_2)$]·H_2O

moiety[a]	distance, Å	moiety[a]	distance, Å
Cd(1)O(4)#1	2.286(6)	Rb(2)Cl(4)#9	3.646(3)
Cd(1)O(1)	2.315(6)	Rb(3)Cl(5)	3.343(3)
Cd(1)Cl(3)#2	2.549(2)	Rb(3)Cl(3)	3.365(3)
Cd(1)Cl(1)	2.583(2)	Rb(3)Cl(1)	3.371(3)
Cd(1)Cl(2)	2.620(3)	Rb(3)Cl(4)#10	3.408(3)
Cd(1)Cl(3)	2.765(3)	Rb(3)Cl(3)#11	3.796(3)
Cd(2)O(2)	2.293(6)	Cl(1)Rb(2)#5	3.418(3)
Cd(2)O(3)	2.316(6)	Cl(2)Cd(2)#8	2.618(2)
Cd(2)O(10)	2.327(6)	Cl(3)Cd(1)#2	2.549(2)
Cd(2)Cl(4)	2.569(2)	Cl(3)Rb(3)#11	3.796(3)
Cd(2)Cl(5)	2.585(2)	Cl(4)Rb(2)#12	3.281(3)
Cd(2)Cl(2)#3	2.618(2)	Cl(4)Rb(1)#5	3.369(3)
Rb(1)Cl(5)#6	3.342(3)	Cl(4)Rb(3)#4	3.408(3)
Rb(1)Cl(4)#6	3.369(3)	Cl(4)Rb(2)#13	3.646(3)
Rb(1)Cl(2)	3.386(3)	Cl(5)Rb(1)#5	3.342(3)
Rb(1)Cl(5)	3.386(3)	Cl(5)Rb(2)#5	3.414(2)
Rb(1)Cl(1)	3.465(3)	Cl(5)Rb(2)#3	3.470(3)
Rb(2)Cl(4)#7	3.281(3)	C(1)O(3)	1.237(11)
Rb(2)Cl(2)	3.362(3)	C(1)O(2)#14	1.249(11)
Rb(2)Cl(5)#6	3.414(2)	C(1)C(1)#14	1.58(2)
Rb(2)Cl(1)#6	3.418(3)	C(2)O(1)	1.258(11)
Rb(2)Cl(5)#8	3.470(3)	C(2)O(4)	1.259(11)
Rb(2)Cl(1)	3.543(3)	C(2)C(2)#1	1.54(2)

moiety[a]	angle, deg	moiety[a]	angle, deg
O(4)#1−Cd(1)O(1)	72.3(2)	O(3)C(1)−C(1)#14	118.1(9)
O(2)Cd(2)−O(3)	72.0(2)	O(2)#14−C(1)C(1)#14	116.1(10)
O(2)Cd(2)−O(10)	88.2(2)	O(1)C(2)−O(4)	124.3(8)
O(3)Cd(2)−O(10)	84.8(2)	O(1)C(2)−C(2)#1	118.0(10)
O(3)C(1)−O(2)#14	125.8(8)	O(4)C(2)−C(2)#1	117.7(10)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x, -y + 1, -z + 1$; #2, $-x + 1, -y + 1, -z + 1$; #3, $x, y, z + 1$; #4, $x - 1, y, z$; #5, $x, -y + {}^1/_2, z + {}^1/_2$; #6, $x, -y + {}^1/_2, z - {}^1/_2$; #7, $x + 1, -y + {}^1/_2, z - {}^1/_2$; #8, $x, y, z - 1$; #9, $x + 1, y, z - 1$; #10, $x + 1, y, z$; #11, $-x + 1, -y + 1, -z + 2$; #12, $x - 1, -y + {}^1/_2, z + {}^1/_2$; #13, $x - 1, y, z + 1$; #14, $-x, -y + 1, -z + 2$.

forming the oxalate unit, with average C−O distances of 1.240 Å (Table 7). The various bond angles, viz., O−Cd−O, O−Cd−Br, and Br−Cd−Br have values in the range 71.8(3)−178.2(3)° (av 114.5°), 88.58(3)−91.43(3)° (av 90.2°), and 177.06(6)° (Table 7). The Cs^+ ions are eight-coordinated by four oxygen and bromine atoms at average distances of ~3.2 and 3.7 Å (Table 7). The various geometrical parameters found in **II** are in good agreement with those reported for similar compounds.

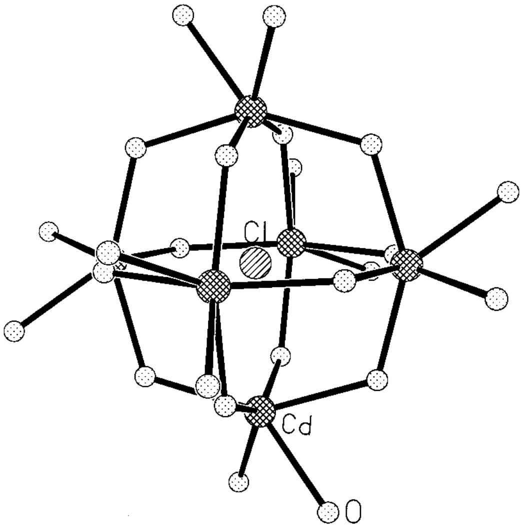

Figure 1. Figure showing a single [Cd_6O_{24}] cluster with the Cl^- ions at the center.

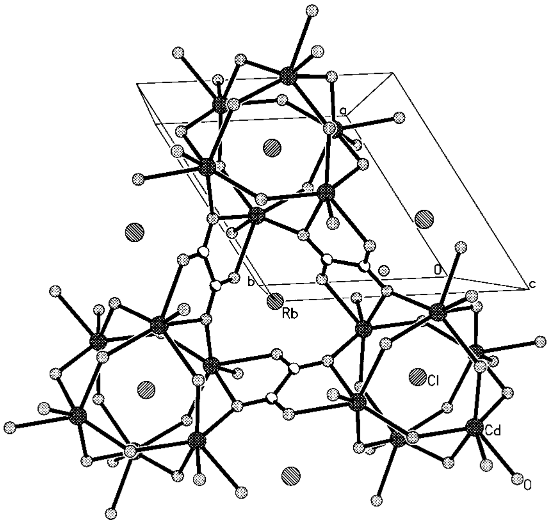

Figure 2. Structure of **I** in the *ab* plane. Note that the Rb^+ ions are positioned outside the cluster unit.

The framework structure of **II** consists of a network of cadmium and oxalate units forming layers (Figure 5). The Br^- ions connected to the cadmium protrude into the interlamellar space. The Cs^+ ions along with a water molecule occupy the interlamellar space (Figure 5). The relative positions between the Cs^+ and Br^- ions are such that they form a graphite-like layer (Figure 6). Such an arrangement creates two closely spaced hexagonal CsBr layers separated by 3.67 Å. The CsBr layers are made of neutral hexagonal units of Cs_3Br_3, with chair conformation as in cyclohexane. The unusual layered alkali halide structures in **II** are stabilized by the cadmium oxalate layers, present after every two CsBr layers, by providing additional coordination for the Cs^+ ions through the oxalate oxygens.

2[CsBr][$Cd_2(C_2O_4)(Br)_2$]·2H_2O, III, and 3[RbCl][$Cd_2(C_2O_4)(Cl_2)$]·H_2O, IV. The structures of **III** and **IV** have some common features and can be described together. The asymmetric units of **III** and **IV** contain 8 and 18 non-hydrogen atoms, respectively. The crystallographically distinct cadmium atom in **III** is octahedrally coordinated to oxygen and bromine atoms. There

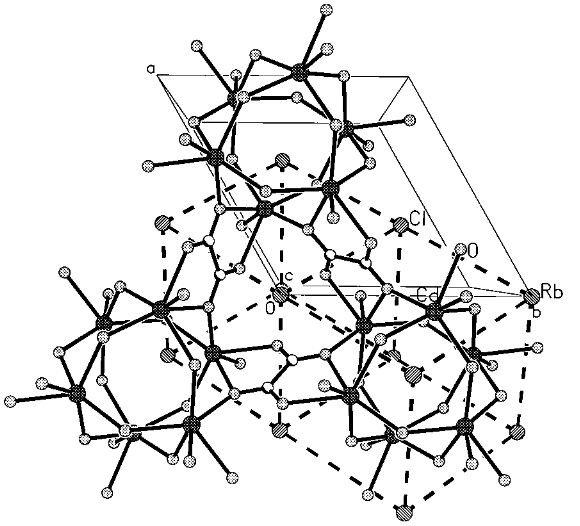

Figure 3. Structure showing the *Fm*3*m* lattice of RbCl within the parent cadmium oxalate structure.

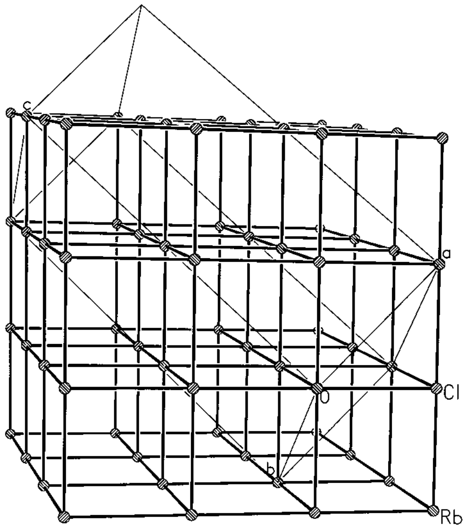

Figure 4. Structure of RbCl in **I**. Note that RbCl is along the [*111*] lattice.

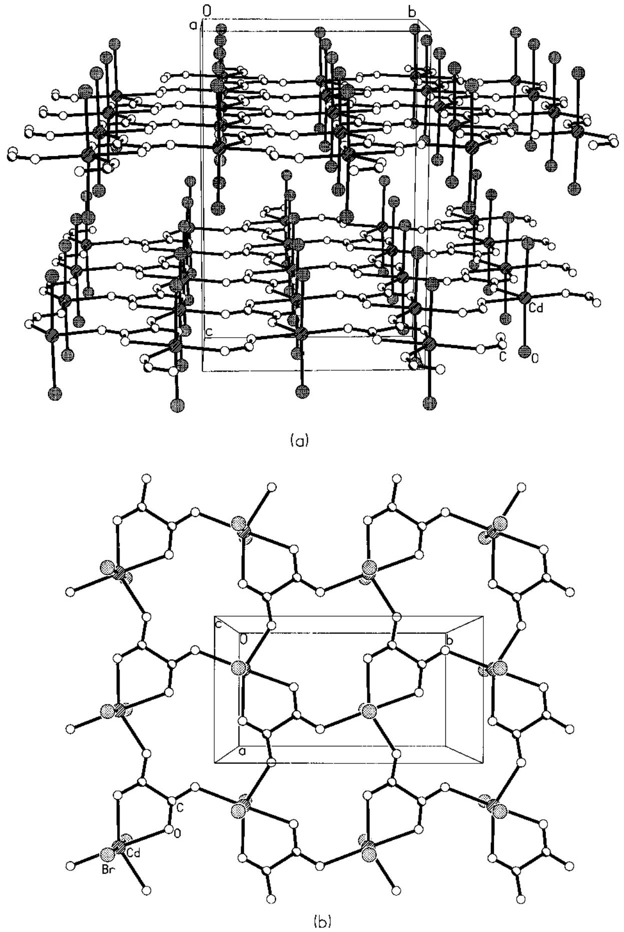

Figure 5. (a) Structure of **II** in the *bc* plane showing the layer arrangement. Note that the Br atoms point into the interlamellar space. Cs and water molecules are not shown for purposes of clarity. (b) Structure of **II** showing a single layer of the cadmium oxalate.

are three Cd−O and three Cd−Br linkages with average distances of 2.354 and 2.697 Å. The longer Cd−O linkage with a distance of 2.405(7) Å belongs to the terminal water molecule. The oxygen atoms are connected to a carbon atom forming the oxalate unit, with average C−O distances of 1.243 Å (Table 9). The Cs^+ ions are eight coordinated by bromine atoms and possess an additional coordination through the terminal water molecule. The average Cs−Br distance is 3.824 Å, while the O−Cd−O, O−Cd−Br, and Br−Cd−Br bond angles have values in the ranges 70.9(2)−82.7(2)° (av 78.8°), 84.30(12)−179.7(2) (av 118.3°), and 91.33(4)−95.91(3)° (av 94.4°) (Table 9). The O−C−O bond angles and the other observed geometrical parameters are in satisfactory agreement with those reported for similar compounds (Table 9).

There are two crystallographically independent cadmium atoms in **IV**, both of which are octahedrally coordinated by oxygen and chlorine atoms. While Cd(1) possesses two Cd−O (av 2.3005 Å) and four Cd−Cl linkages (av 2.629 Å), Cd(2) has three Cd−O (av 2.312 Å) and Cd−Cl (av 2.591 Å) connections. The oxygen atoms are connected to carbon atoms and form the oxalate unit with average C−O distances of 1.251 Å (Table 11). There are three unique Rb atoms with Rb(1) and Rb(8), being eight coordinated, and Rb(3) is seven coordinated with chlorine and oxygen atoms. Thus, Rb(1) has five Rb−Cl (av 3.390 Å) and three Rb−O (av 2.978 Å) linkages, Rb(2) has seven Rb−Cl (av 3.448 Å) and one Rb−O (2.914(9) Å) bondings, and Rb(3) has five Rb−Cl (av 3.457 Å) and two Rb−O (av 2.893 Å) connectivities (Table 11). The average O−Cd−O, O−Cd−Cl, and Cl−Cd−Cl bond angles have values of 72.3, 107.24, and 107.5° for Cd(1) and 81.7, 117.1, and 95.18° for Cd(2). These are typical values and are in agreement with those observed earlier for similar compounds.

The framework structures of **III** and **IV** consist of linkages involving cadmium and oxalate units. Connectivity between the two moieties gives rise to interesting structural features. Thus, both **III** and **IV** possess isolated monomeric cadmium oxalate units connected together by the alkali halides, viz., CsBr and RbCl. In **III**, the isolated cadmium oxalate units are connected with the alkali halide in such a manner as to form a three-dimensionally extended channel structure containing water molecules (Figure 7). The alkali halide units are present as eight-membered rings with the chair conformation as in cyclooctane (Figure 8). The

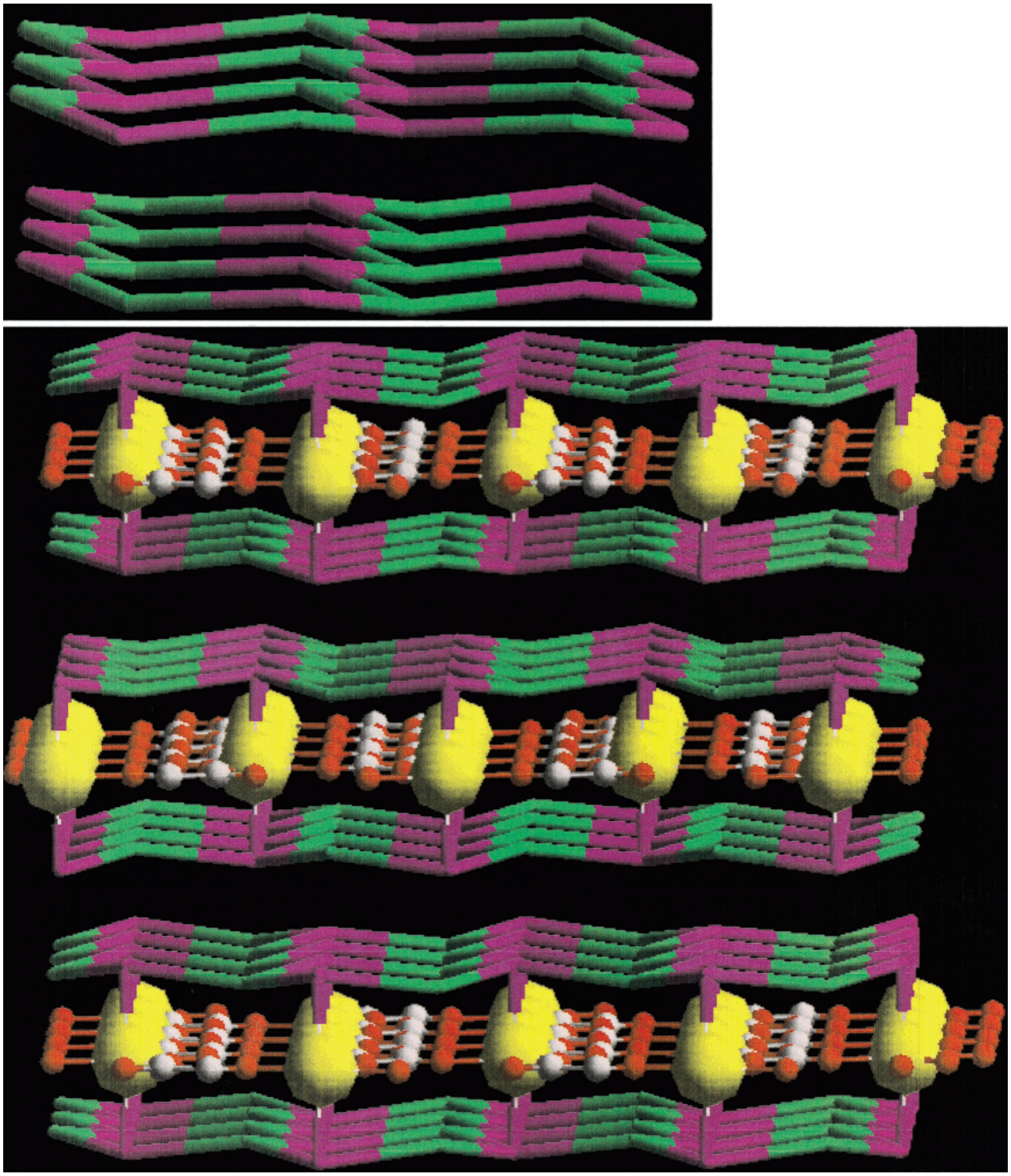

Figure 6. Structure of **II** showing the CsBr lattice within the layers. Inset shows the CsBr lattice alone. Note that alternate CsBr layers have larger separation. (Color scheme: yellow, Cd; white, C; red, O; purple, Br; green, Cs.)

connectivity between the isolated oxalate units along with the chloride ions in **IV** results in an interpenetrating layerlike arrangement (Figure 9). The layers are so positioned in a helical fashion, with the immediate next layer arranged in the opposite direction, thus canceling total helicity of the structure (Figure 10). Accordingly, the Rb^+ ions also reflect the helical nature of the layers and form a helical strand between the cadmium chloro-oxalate layers (Figure 10). The alkali halide, however, does not form an independent lattice in **IV**.

Discussion

Four novel cadmium oxalates incorporating extended alkali halide structures, $[RbCl][Cd_6(C_2O_4)_6]\cdot 2H_2O$, **I**, $2[CsBr][Cd(C_2O_4)]\cdot H_2O$, **II**, $2[CsBr][Cd_2(C_2O_4)(Br)_2]\cdot 2H_2O$, **III**, and $3[RbCl][Cd_2(C_2O_4)(Cl_2)]\cdot H_2O$, **IV**, have been prepared hydrothermally as good quality single crystals. The reaction itself involves simple metathetic exchange between a cadmium halide and an alkali oxalate. The cadmium oxalates **I** and **IV** are formed with RbCl; **II** and **III** are formed with CsBr. Though RbCl is part of the structure in both **I** and **IV**, the way the alkali halide units are arranged within the host cadmium oxalate is very different. In **II** and **III**, the CsBr has a layered structure with different apertures, but the host lattice possesses completely different structures. These fine differences in the structures are likely to result from the differences in experimental conditions such as the composition, time, and temperature (Table 1), but we are not yet in a position to relate the two.

The host oxalate structures have different architectures in **I**−**IV**, ranging from isolated cadmium oxalate

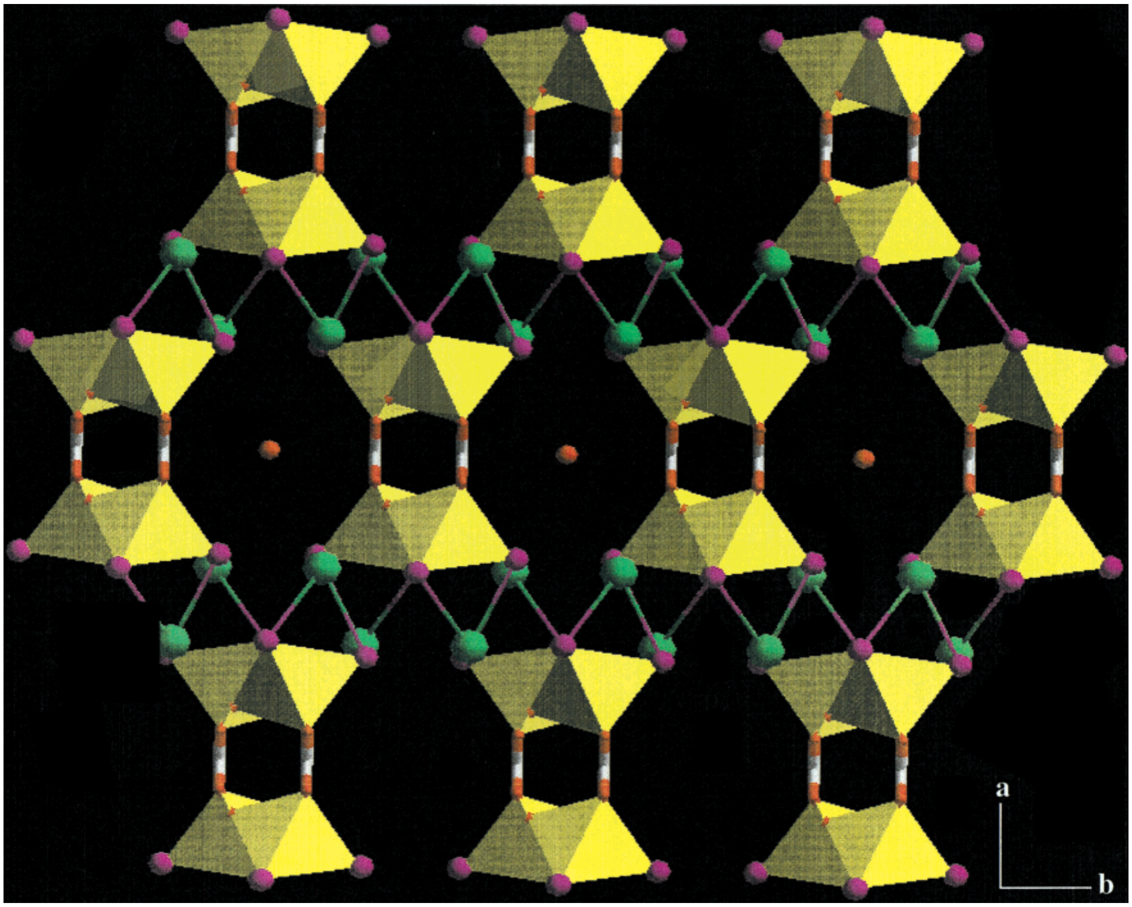

Figure 7. Structure of **III** showing the channels formed by the connectivity between the isolated cadmium oxalate and CsBr. Note that the water molecules occupy these channels. (Color scheme: yellow, Cd; white, C; red, O; purple, Br; green, Cs.)

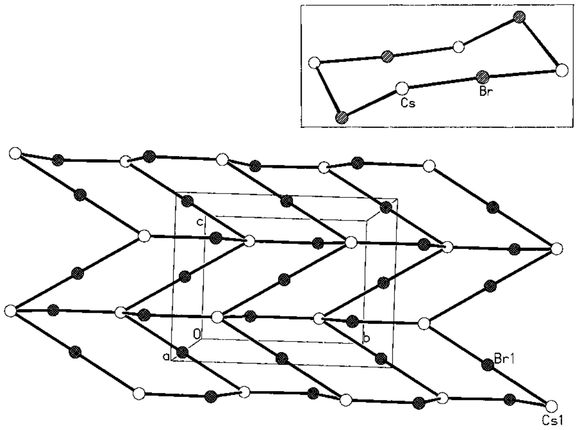

Figure 8. Layered structure of CsBr in **III**. Inset shows the CsBr in chair conformation.

units to three-dimensionally extended architectures. While **I** possesses two interpenetrating lattices of three-dimensional cadmium oxalate and a *Fm*3*m* RbCl lattice, **II** has a layered cadmium oxalate architecture (two-dimensional) with a layered CsBr structure. Compounds **III** and **IV** have isolated cadmium oxalate units (zero-dimensional) linked and stabilized by the alkali halides. The isolated cadmium oxalate units in **IV** are linked via a chlorine atom to form a sheet of cadmium chlorooxalate that is arranged in a helical fashion. These are indeed unique architectures. In addition to the uniqueness of the host structures, the alkali halide guest species also possesses remarkable architectures.

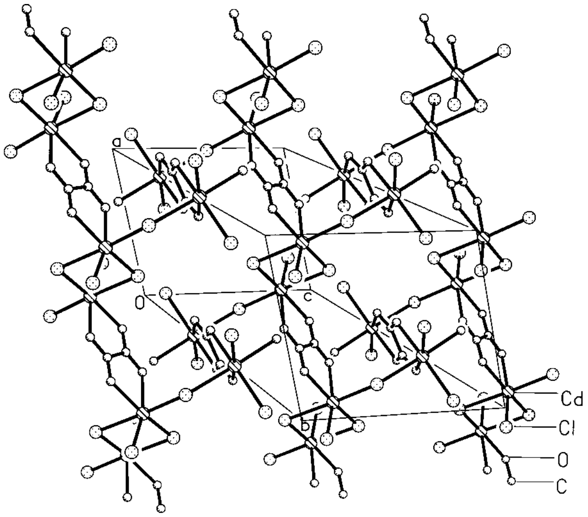

Figure 9. Structure of **IV** showing a single layer resulting from the connectivity between the isolated cadmium oxalate and chlorine atoms.

In **I**, RbCl forms a face-centered lattice with unit-cell parameters which are approximately double that of the normal RbCl. In **II**, CsBr forms a layered architecture with the layers closely resembling that of graphite. The six-membered Cs_3Br_3 ring, in **II**, is in a chair conformation of the cyclohexane. The two closely spaced CsBr layers have a thickness of 3.67 Å. The thickness of the oxalate layers is 10.62 Å. Accordingly, **II** can be considered to be a genuine hetero-lattice or nanocomposite

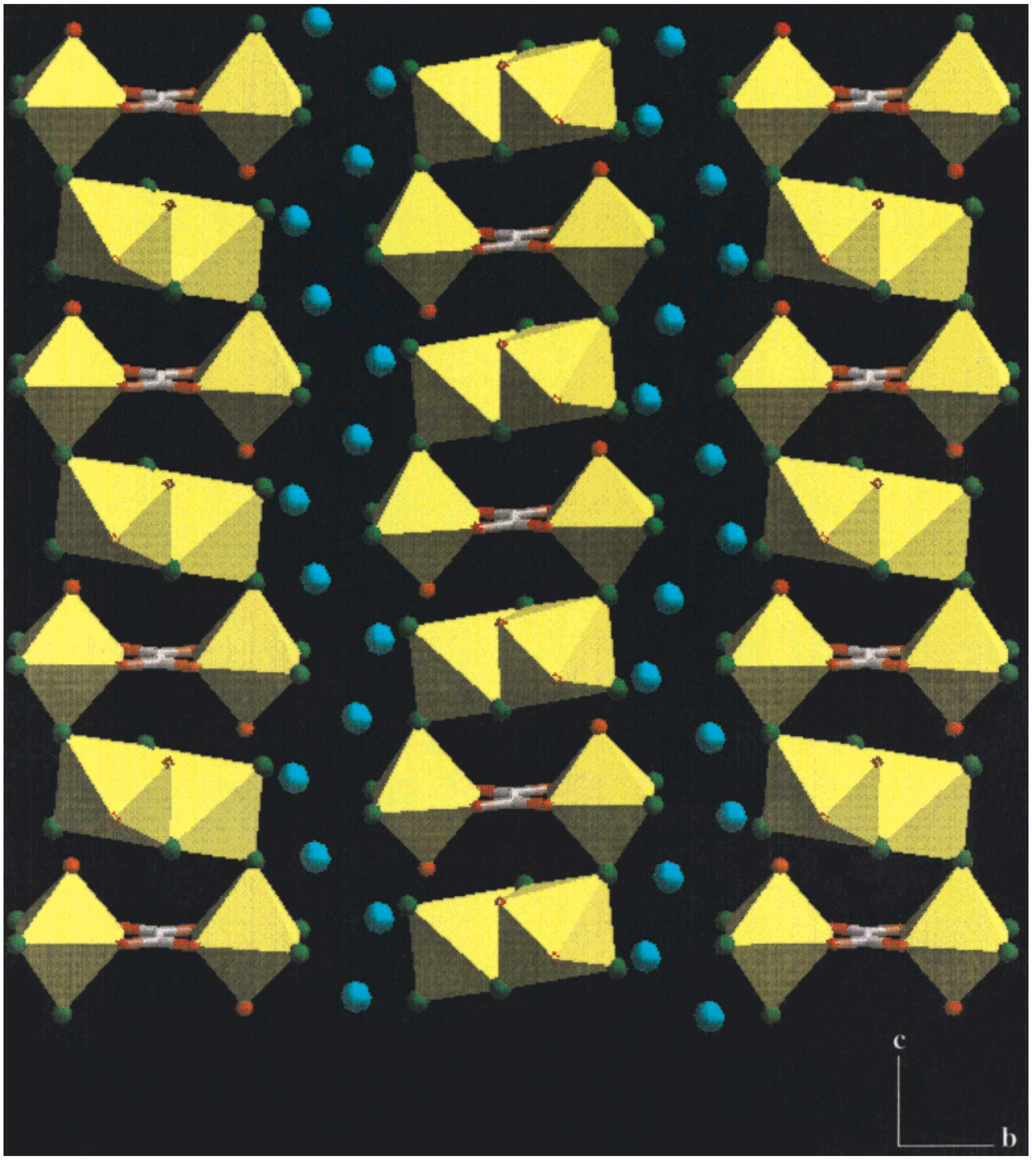

Figure 10. Structure of **IV** along the *a* axis showing the cadmium chloro-oxalate layers and the Rb atoms. Note that both the cadmium chloro-oxalate and the Rb atoms form a helical structure. (Color scheme: yellow, Cd; white, C; red, O; purple, Cl; green, Rb)

with alternating organic and inorganic layers (Figure 6). In **III**, CsBr again forms a layered structure but is unusual in that it consists exclusively of eight-membered rings that resemble the chair conformation of cyclooctane (Figure 8). What is interesting in **III** is that the isolated cadmium oxalate units are situated between these CsBr layers and act as a pillar through Cd−Br connectivity. The thickness of the CsBr layers in **III** is ~3.7 Å, which is similar to the closely spaced CsBr layers in **II** (Figure 7). The oxalate layer has a thickness of 5.87 Å, which is roughly half that observed in **II**. In **IV**, the chlorine atoms connect the Cd ions of the isolated cadmium oxalate unit and form a two-dimensional layer with a right-handed helical strand with the immediate next layer having the opposite handedness, canceling the total helicity of the structure. The Rb atoms situated between these sheets reflect the helical nature of the cadmium chloro-oxalate layer (host), with the Rb atoms from the neighboring strand so positioned as to cancel the helicity of the structure. Thus, there is no independent alkali halide lattice in **IV** (Figure 10).

The distances between the alkali metal and the halogen ions in compounds **I**−**III** provide an interesting comparison. In **I**, the Rb−Cl distance is 6.726 Å, while in RbCl with rock-salt structure, it is 3.285 Å (Figure 4). In the case of compounds **II** and **III**, the average Cs−Br distance is ~3.7 Å, which is comparable to the Cs−Br distance (3.72 Å) in body-centered CsBr. It may be noted that in **I**, the RbCl forms a lattice identical to that of normal RbCl, but with double the unit-cell dimensions, whereas in **II** and **III** the CSBr forms unusual layered architectures despite having nearly similar distances between Cs and Br as in normal CsBr. These observations demonstrate the role of host−guest interactions in these structures.

Host−guest structures of the type observed in **I**−**IV** possessing expanded RbCl and layered CsBr are indeed most unusual. These structures are formed because the host structures provide the additional coordination necessary for the alkali halide ions. Thus, the expanded rock-salt structure of RbCl is made possible by the stability provided by the extra coordination due to the

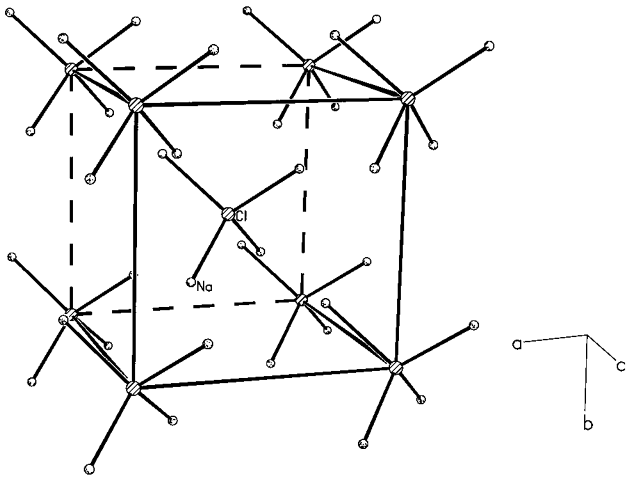

Figure 11. Structure of **V**, showing the body-centered cubic arrangement of the [ClNa$_4$] units.

oxalate units. What is truly interesting, however, is that such beautiful structures are formed by a simple metathetic reaction carried out under hydrothermal conditions. Such a reaction under ambient conditions would clearly give a mixture of the Cd oxalate and the alkali halide. In this connection, it may be noted that the structures reported herein are different from those resulting from ion-exchange in layered solids, such as metal−anion arrays within the oxide hosts.[15] Thus, in the layered $RbLaNb_2O_7$, the Rb^+ ions, situated in the interlamellar region, are exchanged topotactically by copper halide, CuX_2 (X = Cl and Br), in evacuated and sealed quartz tubes at 325 °C.[15] This gives rise to a unique situation wherein the ability to prepare hosts at high temperatures, with varying interatomic spacings and topologies, is combined with the low-temperature ion-exchange methods to construct metal−anion arrays. The host−guest structures of **I**−**IV** are somewhat comparable to the KCl/CsCl structures reported in a phosphate framework.[16] Accordingly, in $A_2[M_3(X_2O_7)_2]$-[salt] (A = Rb, Cs; M = Mn, Cu; X = P, As), synthesized under molten salt conditions (>600 °C), the phosphate network is formed around the alkali metal chloride salts, the salt probably acting as a structure-directing template. The super rock-salt structure formed by the clusters in **I** can be considered to be a result of templating by the underlying RbCl lattice. This is reminiscent of organic molecules employed in conventional low-temperature hydrothermal methods for the synthesis of extended framework architectures.

It is likely that many more materials containing alkali and alkaline earth halides in unusual coordinations and structures may be formed by a suitable choice of the framework. In this direction, we have just isolated a new cadmium succinate, $[NaCl][Cd_5(H_4C_4O_4)_2Na_6]$, **V**, incorporating NaCl. In **V**, however, we have extra Na^+ ions in addition to the alkali halide, similar to the metal−anion arrays within the oxide hosts established in Dion-Jacobson structures.[15] The alkali halide does not form any independent lattice in **V**. The relative positions of Na^+ and Cl^- ions in **V** are such that four Na^+ ions coordinate one Cl^- ion in a tetrahedral fashion. The tetrahedral [ClNa$_4$] units form a body-centered cube within the cadmium succinate structure (Figure 11).

The new types of hybrid host−guest compounds incorporating novel alkali halide structures are likely to possess novel properties. In particular, they would be expected to exhibit interesting optical and dielectric properties. The three-dimensional organic−inorganic periodic superlattice would also bestow certain unusual properties. It would be of interest to analyze the Infrarad and Raman spectra of the alkali halide guests in these compounds. Such studies will be pursued, although at this stage we primarily report the structures, which are unique in their own merit.

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