

Open-Framework Cadmium Oxalates with Channels Stabilized by Alkali Metal Ions

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IN HONOR OF PROFESSOR PAUL HAGENMULLER ON THE OCCASION OF HIS 80TH BIRTHDAY

Two new cadmium oxalates, $M_4Cd_2(C_2O_4)_4 \cdot 4H_2O$, $M = Na$ (I) and K (II) with open architectures have been synthesized hydrothermally. The Cd atoms have the unusual eight-coordination with respect to the oxalate oxygens. The connectivity between the Cd and oxalate units forms layers with 12-membered apertures (six Cd and six oxalate units), with the layers interpenetrating to give rise to three-dimensional structures possessing 8-membered channels (four Cd and four oxalate units), wherein the Na^+ and K^+ ions are nestled. The Na^+ ion conductivity in I is rather low, but the activation energy for conduction is comparable to those in glasses. Crystal data for I: monoclinic, space group $P2_1/n$ (No. 14), $a = 12.8779(8)$, $b = 11.444(7)$, $c = 14.1301(8)$ Å, $\beta = 113.01(10)^\circ$, $V = 1916.7(2)$ Å³, $Z = 4$, $M = 732.84$, $R_1 = 0.032$; for II, orthorhombic, space group $Fdd2$ (No. 43), $a = 14.686(2)$, $b = 18.080(2)$, $c = 7.8162(8)$ Å, $V = 2075.4(4)$ Å³, $Z = 8$, $M = 398.64$, $R_1 = 0.021$.

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INTRODUCTION

Open-framework inorganic structures have assumed great importance in recent years not only because of their potential applications, but also due to the fascinating structural features exhibited by them (1). Of these, the metal phosphates constitute one of the largest families (2). A large number of new open-framework materials with aliphatic and aromatic dicarboxylic acids have also been synthesized and characterized (3,4), with many of the transition metal dicarboxylates exhibiting interesting magnetic properties (4). Of particular interest are the extended network structures formed by the oxalates. The oxalates, especially those of transition metals, with layered and other architectures containing organic amines have been studied during the

past decade or so (5–9). The synthesis, structure, and properties of the oxalates of tin(II) and zinc were reported recently (10–12). These oxalates possess zero-, one-, two-, and three-dimensional structures and were synthesized by hydrothermal methods in the presence of organic amines. The three-dimensional zinc oxalate structure possesses two types of oxalate units, one forming the layer and the other acting as a bridge between the layers. Similar functionality of the oxalate units has also been observed in the recently discovered metal phosphate-oxalates, in which the oxalate units generally connect the metal phosphate layers through an *out-of-plane* linkage (13,14). A cadmium oxalate with a layer structure has also been reported recently (15). *Out-of-plane* connectivity of the oxalate units has been observed in a cadmium oxalate with three-dimensional architecture, in which cadmium oxalate layers are pillared by oxalate units (15). Our continued investigations of the cadmium oxalates have resulted in the discovery of two new open-framework oxalates, with the general formula, $M_4Cd_2(C_2O_4)_4 \cdot 4H_2O$, $M = Na$ (I) and K (II). In this paper, we describe the structure and properties of these three-dimensional cadmium oxalates, which appear to be the first examples of the open-framework oxalates stabilized by alkali metal ions.

EXPERIMENTAL

Synthesis and Initial Characterization

The compounds I and II have been synthesized under hydrothermal conditions. In a typical synthesis, 0.26 g of sodium carbonate was dispersed in a mixture of *n*-butanol and water (4.5 ml + 1.1 ml). Oxalic acid (0.31 g) and 0.51 g of cadmium chloride were added to the above under continuous stirring. Finally, 0.28 ml of glacial acetic acid was added and the contents stirred to homogeneity. The resultant gel with the composition, $CdCl_2 : H_2C_2O_4 : Na_2CO_3 : 2CH_3COOH : 20C_4H_9OH : 25H_2O$, was transferred, sealed in a 23-ml PTFE-lined stainless

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steel autoclave (Parr, Moline, USA) and heated at 150°C for 80 h under autogeneous pressure. The resultant product containing a crop of needle-shaped crystals was filtered under vacuum and dried at ambient conditions. For the synthesis of **II**, 0.27 g of potassium oxalate was dispersed in mixture of *n*-butanol and water (4.5 ml + 1.5 ml). Cadmium chloride (0.22 g) and 0.11 ml of glacial acetic acid were added to the above under continuous stirring. Finally, 0.1 ml of 1,3-diaminopentane (DAP, DYTEK) was added and the contents were homogenized. The final mixture had the composition, CdCl₂:1.5K₂C₂O₄:0.84DAP:1.93CH₃COOH:44C₄H₉OH:84H₂O. The mixture was sealed in an autoclave and heated at 150°C for 80 h to result in fine needle-like crystals. The crystals were filtered and dried under ambient conditions. Initial characterization was carried out using powder X-ray diffraction (XRD), Thermogravimetric analysis (TGA), and EDAX. The EDAX analysis indicated a *M*:Cd ratio of 2:1 (*M* = Na, K).

Ionic conductivity measurements have been carried out to evaluate the mobility of the alkali ions in these

solids. Since the K⁺ is much bigger than the Na⁺ ions, the studies have been carried out only on compound **I**. Typically, cylindrical pellets of the samples (0.5 mm in thickness and 0.8 cm in diameter) were coated with silver paint on either side and preannealed at 90°C for 2 h before the experiment. Ionic conductivity measurements were carried out using a standard setup coupled with an impedance analyzer (Model HP-4192A) in the frequency range from 10 Hz to 10 MHz. A two-terminal capacitor configuration with silver electrode was employed in the range 298–493 K, and the temperature was measured using Pt–Rh thermocouple positioned close to the sample.

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 cyanoacrylate (superglue) adhesive. Single-crystal structure determination by X-ray diffraction was

TABLE 1
Crystal Data and Structure Refinement Parameters for **I**, Na₄Cd₂(C₂O₄)₄·4H₂O, and **II** K₂Cd(C₂O₄)₂·2H₂O

Parameters	I	II
Empirical formula	C ₈ O ₂₀ H ₈ Cd ₂ Na ₄	C ₄ O ₁₀ H ₄ CdK ₂
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>F</i> dd2 (No. 43)
Crystal size (mm)	0.08 × 0.08 × 0.12	0.18 × 0.18 × 0.16
<i>a</i> (Å)	12.8779(8)	14.686(2)
<i>b</i> (Å)	11.4440(7)	18.080(2)
<i>c</i> (Å)	14.1301(8)	7.8162(8)
α (°)	90	90.0
β (°)	113.01(10)	90.0
γ (°)	90	90.0
Volume (Å ³)	1916.7(2)	2075.4(4)
<i>Z</i>	4	8
Formula mass	732.84	398.64
ρ_{calc} (g cm ⁻³)	2.54	2.552
λ (MoK α) Å	0.71073	0.71073
μ (mm ⁻¹)	2.414	2.949
θ Range (°)	1.82–23.31	3.16–23.28
Total data collected	7810	2079
Index ranges	– 14 ≤ <i>h</i> ≤ 14, – 11 ≤ <i>k</i> ≤ 12, – 15 ≤ <i>l</i> ≤ 12	– 9 ≤ <i>h</i> ≤ 16, – 20 ≤ <i>k</i> ≤ 19, – 8 ≤ <i>l</i> ≤ 8
Unique data	2762	750
Observed data (<i>I</i> > 2 σ (<i>I</i>))	2157	732
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
<i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.032, w <i>R</i> ₂ = 0.066	<i>R</i> ₁ = 0.021, w <i>R</i> ₂ = 0.054
<i>R</i> (all data)	<i>R</i> ₁ = 0.053, w <i>R</i> ₂ = 0.073	<i>R</i> ₁ = 0.022, w <i>R</i> ₂ = 0.054
Goodness of fit	1.067	1.127
No. of variables	311	105
Largest difference map peak and hole eÅ ⁻³	0.821 and – 0.585	0.443 and – 0.808

$${}^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|$$

$${}^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)] \}^{1/2}, w = 1 / [\sigma^2(F_o)^2 + (aP)^2 + bP], P = [\max(F_o^2, 0) + 2(F_c)^2] / 3, \text{ where } a = 0.0197 \text{ and } b = 2.3004 \text{ for } \mathbf{I} \text{ and } a = 0.0321 \text{ and } b = 0.0 \text{ for } \mathbf{II}.$$

performed on a Siemens Smart-CCD diffractometer equipped with a normal-focus, 2.4-kW sealed tube X-ray source (MoK α 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 30 s per frame) in the 2θ range 3° to 46.5°. Pertinent experimental details for the structure determinations are presented in Table 1.

The structure was solved by direct methods using SHELXS-86 (17) and difference Fourier syntheses. An empirical absorption correction based on the SADABS (18) program was applied for both the compounds. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all non hydrogen atoms. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS (19) package of programs. Details of the final refinements

TABLE 2
Atomic Coordinates [$\times 10^4$] and Equivalent Isotropic Displacement Parameters [$\text{Å}^2 \times 10^3$] for **I**, $\text{Na}_4\text{Cd}_2(\text{C}_2\text{O}_4)_4 \cdot 4\text{H}_2\text{O}$

Atom	x	y	z	$U(\text{eq})^a$
Cd(1)	2130(1)	3631(1)	6803(1)	16(1)
Cd(2)	3225(1)	2638(1)	3058(1)	16(1)
O(1)	3531(3)	3462(4)	6182(4)	24(1)
O(2)	1512(4)	1728(4)	6399(4)	27(1)
O(3)	3340(4)	4936(4)	7956(4)	29(1)
O(4)	6537(4)	1523(4)	3182(4)	32(1)
O(5)	1589(4)	5602(4)	6279(4)	32(1)
O(6)	1325(3)	3591(4)	4920(3)	20(1)
O(7)	3510(3)	2290(4)	8000(4)	22(1)
O(8)	38(4)	3637(4)	6211(3)	23(1)
O(9)	3651(4)	1808(4)	1718(4)	31(1)
O(10)	3983(3)	3129(4)	4838(3)	19(1)
O(11)	1788(3)	3325(4)	3576(4)	23(1)
O(12)	5155(4)	2028(4)	3668(4)	26(1)
O(13)	2271(4)	3884(4)	1606(4)	25(1)
O(14)	3272(4)	728(4)	3821(4)	29(1)
O(15)	983(4)	-390(4)	1734(4)	27(1)
O(16)	1561(3)	1475(4)	2071(4)	22(1)
C(1)	3287(5)	3320(5)	5240(5)	16(2)
C(2)	3012(5)	5976(6)	7954(5)	17(2)
C(3)	5529(5)	1746(5)	3010(5)	17(2)
C(4)	1931(5)	6329(6)	6998(5)	18(2)
C(5)	2013(5)	3419(5)	4513(5)	16(2)
C(6)	-333(6)	3361(6)	6886(5)	22(2)
C(7)	2640(5)	-28(6)	3246(5)	20(2)
C(8)	1631(5)	381(6)	2258(5)	20(2)
Na(1)	0	5000	5000	20(1)
Na(2)	830(2)	2694(2)	468(2)	26(1)
Na(3)	-125(2)	2167(2)	4867(2)	29(1)
Na(4)	0	0	0	30(1)
Na(5)	99(2)	2416(2)	2489(2)	31(1)
O(100)	-1641(4)	1216(4)	5071(4)	32(1)
O(200)	459(4)	876(4)	3874(4)	30(1)
O(300)	1766(4)	1005(4)	43(4)	33(1)
O(400)	-268(4)	4075(4)	1077(5)	46(2)

^a U_{eq} is defined as one-third of the orthogonalized tensor U_{ij} .

TABLE 3
Selected Bond Distances for **I**, $\text{Na}_4\text{Cd}_2(\text{C}_2\text{O}_4)_4 \cdot 4\text{H}_2\text{O}$

Moiety	Distance (Å)	Moiety	Distance (Å)
Cd(1)-O(1)	2.302(4)	C(6)-C(3) # 1	1.547(9)
Cd(1)-O(3)	2.308(4)	C(7)-O(13) # 6	1.260(8)
Cd(1)-O(2)	2.312(4)	C(7)-C(8)	1.562(9)
Cd(1)-O(4) # 1	2.361(5)	Na(1)-O(5)	2.244(4)
Cd(1)-O(5)	2.390(5)	Na(1)-O(6)	2.383(4)
Cd(1)-O(6)	2.449(4)	Na(1)-O(8)	2.302(4)
Cd(1)-O(7)	2.454(4)	Na(1)-O(5) # 8	2.244(5)
Cd(1)-O(8)	2.489(4)	Na(1)-O(8) # 8	2.302(4)
Cd(2)-O(9)	2.366(5)	Na(1)-O(6) # 8	2.383(4)
Cd(2)-O(11)	2.375(4)	Na(2)-O(13)	2.356(5)
Cd(2)-O(10)	2.383(4)	Na(2) # 2-O(12)	2.366(5)
Cd(2)-O(12)	2.393(4)	Na(2) # 2-O(10)	2.383(5)
Cd(2)-O(13)	2.405(5)	Na(2)-O(16)	2.509(5)
Cd(2)-O(14)	2.427(4)	Na(2)-O(12) # 9	2.366(5)
Cd(2)-O(16)	2.444(4)	Na(2)-O(10) # 9	2.383(5)
Cd(2)-O(15) # 3	2.446(4)	Na(2)-O(300)	2.473(5)
O(4)-Cd(1) # 5	2.361(5)	Na(2)-O(400)	2.487(6)
O(15)-Cd(2) # 6	2.446(4)	Na(3)-O(2)	2.412(5)
O(1)-C(1)	1.252(8)	Na(3)-O(6)	2.457(5)
O(2)-C(2) # 4	1.231(8)	Na(3)-O(8)	2.484(5)
O(3)-C(2)	1.263(8)	Na(3) # 2-O(7)	2.609(5)
O(4)-C(3)	1.251(7)	Na(3)-O(100)	2.349(5)
O(5)-C(4)	1.252(8)	Na(3)-O(200)	2.354(5)
O(6)-C(5)	1.245(7)	Na(3)-O(7) # 9	2.609(5)
O(7)-C(4) # 4	1.239(7)	Na(4)-O(15)	2.320(5)
O(8)-C(6)	1.262(8)	Na(4) # 3-O(10)	2.473(4)
O(9)-C(6) # 5	1.251(7)	Na(4)-O(15) # 10	2.320(5)
O(10)-C(1)	1.253(7)	Na(4)-O(10) # 9	2.473(4)
O(11)-C(5)	1.244(8)	Na(4)-O(10) # 6	2.473(4)
O(12)-C(3)	1.245(8)	Na(4)-O(300)	2.528(4)
O(13)-C(7) # 3	1.260(8)	Na(4)-O(300) # 10	2.528(4)
O(14)-C(7)	1.247(7)	Na(5)-O(16)	2.434(5)
O(15)-C(8)	1.241(8)	Na(5)-O(11)	2.358(5)
O(16)-C(8)	1.275(8)	Na(5) # 2-O(1)	2.363(5)
C(1)-C(5)	1.563(9)	Na(5)-O(1) # 9	2.363(5)
C(2)-O(2) # 7	1.231(8)	Na(5)-O(7) # 9	2.445(5)
C(2)-C(4)	1.567(9)	Na(5)-O(200)	2.538(6)
C(3)-C(6) # 5	1.547(9)	Na(5)-O(400)	2.659(6)
C(4)-O(7) # 7	1.239(7)	Na(5) # 2-O(7)	2.445(5)
C(6)-O(9) # 1	1.251(7)		

Note. Symmetry transformations used to generate equivalent atoms: # 1 $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; # 2 $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; # 3 $-x - \frac{3}{2}, y + \frac{1}{2}, -z - \frac{7}{2}$; # 4 $-x - \frac{3}{2}, y - \frac{1}{2}, -z - \frac{5}{2}$; # 5 $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; # 6 $-x - \frac{3}{2}, y - \frac{1}{2}, -z - \frac{7}{2}$; # 7 $-x - \frac{3}{2}, y + \frac{1}{2}, -z - \frac{5}{2}$; # 8 $-x - 2, -y + 1, -z - 3$; # 9 $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; # 10 $-x - 2, -y, -z - 4$.

are given in Table 1. The final atomic coordinates and selected bond distances and angles for **I** are presented in Tables 2, 3, and 4, and for **II** in Tables 5, 6, and 7.

RESULTS

$\text{Na}_4\text{Cd}_2(\text{C}_2\text{O}_4)_4 \cdot 4\text{H}_2\text{O}$, **I**

The asymmetric unit of **I** contains 35 nonhydrogen atoms (Fig. 1), of which 26 belong to the framework. There are two

TABLE 4
Selected Bond Angles for I, $\text{Na}_4\text{Cd}_2(\text{C}_2\text{O}_4)_4 \cdot 4\text{H}_2\text{O}$

Moiety	Angle (°)	Moiety	Angle (°)
O(1)–Cd(1)–O(3)	84.9(2)	O(14)–Cd(2)–O(16)	68.10(14)
O(1)–Cd(1)–O(2)	94.1(2)	O(9)–Cd(2)–O(15) # 2	104.5(2)
O(3)–Cd(1)–O(2)	148.8(2)	O(11)–Cd(2)–O(15) # 2	89.7(2)
O(1)–Cd(1)–O(4) # 1	149.6(2)	O(10)–Cd(2)–O(15) # 2	71.1(2)
O(3)–Cd(1)–O(4) # 1	79.2(2)	O(12)–Cd(2)–O(15) # 2	84.3(2)
O(2)–Cd(1)–O(4) # 1	86.7(2)	O(13)–Cd(2)–O(15) # 2	66.8(2)
O(1)–Cd(1)–O(5)	98.0(2)	O(14)–Cd(2)–O(15) # 2	147.2(2)
O(3)–Cd(1)–O(5)	69.1(2)	O(16)–Cd(2)–O(15) # 2	143.3(2)
O(2)–Cd(1)–O(5)	141.4(2)	C(1)–O(1)–Cd(1)	120.5(4)
O(4) # 1–Cd(1)–O(5)	100.2(2)	C(2) # 3–O(2)–Cd(1)	116.8(4)
O(1)–Cd(1)–O(6)	69.3(2)	C(2)–O(3)–Cd(1)	118.4(4)
O(3)–Cd(1)–O(6)	131.4(2)	C(3)–O(4)–Cd(1) # 4	120.1(4)
O(2)–Cd(1)–O(6)	75.8(2)	C(4)–O(5)–Cd(1)	114.1(4)
O(4) # 1–Cd(1)–O(6)	139.4(2)	C(5)–O(6)–Cd(1)	115.4(4)
O(5)–Cd(1)–O(6)	74.5(2)	C(4) # 3–O(7)–Cd(1)	110.4(4)
O(1)–Cd(1)–O(7)	75.3(2)	C(6)–O(8)–Cd(1)	115.2(4)
O(3)–Cd(1)–O(7)	79.1(2)	C(6) # 4–O(9)–Cd(2)	117.5(4)
O(2)–Cd(1)–O(7)	70.6(2)	C(1)–O(10)–Cd(2)	116.7(4)
O(4) # 1–Cd(1)–O(7)	76.4(2)	C(5)–O(11)–Cd(2)	118.1(4)
O(5)–Cd(1)–O(7)	148.0(2)	C(3)–O(12)–Cd(2)	117.2(4)
O(6)–Cd(1)–O(7)	128.5(2)	C(7) # 2–O(13)–Cd(2)	117.5(4)
O(1)–Cd(1)–O(8)	141.2(2)	C(7)–O(14)–Cd(2)	116.1(4)
O(3)–Cd(1)–O(8)	125.3(2)	C(8)–O(15)–Cd(2) # 5	115.7(4)
O(2)–Cd(1)–O(8)	72.3(2)	C(8)–O(16)–Cd(2)	116.2(4)
O(4) # 1–Cd(1)–O(8)	67.7(2)	O(1)–C(1)–O(10)	125.3(6)
O(5)–Cd(1)–O(8)	75.3(2)	O(1)–C(1)–C(5)	116.8(6)
O(6)–Cd(1)–O(8)	72.09(14)	O(10)–C(1)–C(5)	117.9(6)
O(7)–Cd(1)–O(8)	129.04(14)	O(2) # 6–C(2)–O(3)	126.0(6)
O(9)–Cd(2)–O(11)	146.3(2)	O(2) # 6–C(2)–C(4)	118.5(6)
O(9)–Cd(2)–O(10)	144.3(2)	O(3)–C(2)–C(4)	115.4(6)
O(11)–Cd(2)–O(10)	69.10(14)	O(12)–C(3)–O(4)	125.7(6)
O(9)–Cd(2)–O(12)	68.8(2)	O(12)–C(3)–C(6) # 4	117.1(6)
O(11)–Cd(2)–O(12)	144.1(2)	O(4)–C(3)–C(6) # 4	117.1(6)
O(10)–Cd(2)–O(12)	75.5(2)	O(7) # 6–C(4)–O(5)	125.2(6)
O(9)–Cd(2)–O(13)	75.9(2)	O(7) # 6–C(4)–C(2)	118.7(6)
O(11)–Cd(2)–O(13)	82.3(2)	O(5)–C(4)–C(2)	116.1(6)
O(10)–Cd(2)–O(13)	128.5(2)	O(11)–C(5)–O(6)	126.3(6)
O(12)–Cd(2)–O(13)	126.4(2)	O(11)–C(5)–C(1)	116.2(6)
O(9)–Cd(2)–O(14)	91.2(2)	O(6)–C(5)–C(1)	117.5(6)
O(11)–Cd(2)–O(14)	92.8(2)	O(9) # 1–C(6)–O(8)	124.9(6)
O(10)–Cd(2)–O(14)	79.3(2)	O(9) # 1–C(6)–C(3) # 1	117.4(6)
O(12)–Cd(2)–O(14)	74.6(2)	O(8)–C(6)–C(3) # 1	117.7(6)
O(13)–Cd(2)–O(14)	146.0(2)	O(14)–C(7)–O(13) # 5	125.7(6)
O(9)–Cd(2)–O(16)	75.6(2)	O(14)–C(7)–C(8)	118.5(6)
O(11)–Cd(2)–O(16)	75.0(2)	O(13) # 5–C(7)–C(8)	115.8(6)
O(10)–Cd(2)–O(16)	129.6(2)	O(15)–C(8)–O(16)	126.7(6)
O(12)–Cd(2)–O(16)	127.0(2)	O(15)–C(8)–C(7)	116.7(6)
O(13)–Cd(2)–O(16)	78.1(2)	O(16)–C(8)–C(7)	116.5(6)

Note. Symmetry transformations used to generate equivalent atoms: # 1 $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; # 2 $-x - \frac{3}{2}, y + \frac{1}{2}, -z - \frac{7}{2}$; # 3 $-x - \frac{3}{2}, y - \frac{1}{2}, -z - \frac{5}{2}$; # 4 $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; # 5 $-x - \frac{3}{2}, y - \frac{1}{2}, -z - \frac{7}{2}$; # 6 $-x - \frac{3}{2}, y + \frac{1}{2}, -z - \frac{5}{2}$.

crystallographically independent Cd atoms and five Na atoms. Of the five Na atoms, two [Na(1) and Na(4)] occupy special positions with a site occupancy of 0.5. All the Cd atoms occupy general positions. The framework structure of

TABLE 5
Atomic Coordinates [$\times 10^4$] and Equivalent Isotropic Displacement Parameters [$\text{\AA}^2 \times 10^3$] for II, $\text{K}_2\text{Cd}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$

Atom	x	y	z	$U(\text{eq})^a$
Cd(1)	0	0	300(1)	12(1)
K(1)	1091(1)	703(1)	− 3978(2)	32(1)
C(1)	1356(3)	1366(3)	523(7)	15(1)
C(2)	− 1595(3)	1183(3)	− 178(6)	14(1)
O(1)	1144(3)	860(2)	− 527(5)	21(1)
O(2)	− 2143(3)	1685(2)	103(6)	23(1)
O(3)	− 1358(3)	698(2)	886(5)	25(1)
O(4)	1891(2)	1887(2)	239(6)	23(1)
O(100)	2123(4)	− 96(3)	− 6180(7)	53(1)

^a U_{eq} is defined as one-third trace of the orthogonalized tensor U_{ij} .

I is built up by the linkages between the Cd and the oxalate units with each Cd bound to eight oxygens. The oxygens are bound to the carbon atoms forming the network structure. Conversely, the oxalate ions are connected to Cd atoms forming the architecture. The coordination environment around the cadmium is a dodecahedral arrangement with respect to the oxygen atoms. The Cd–O distances in the range 2.302(4)–2.489(4) Å (average Cd(1)–O = 2.383 and Cd(2)–O = 2.405 Å). Of the eight oxygen atoms bound to each of the Cd atoms, four are associated with Cd–O distances in the range 2.302(4)–2.361(4) Å for Cd(1) and 2.366(5)–2.393(4) Å for Cd(2) and the other four with distances in the 2.390(4)–2.489(4) Å for Cd(1) and 2.405(5)–2.446(4) Å for Cd(2) range. These are, in most cases, formally the single- and double-bonded oxygens bound to

TABLE 6
Selected Bond Distances in II, $\text{K}_2\text{Cd}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$

Moiety	Distance (Å)	Moiety	Distance (Å)
Cd(1)–O(1) # 1	2.379(4)	K(1)–O(100)	2.710(5)
Cd(1)–O(1)	2.379(4)	K(1)–O(1)	2.713(4)
Cd(1)–O(2) # 2	2.384(4)	K(1)–O(4) # 4	2.822(4)
Cd(1)–O(2) # 3	2.384(4)	K(1)–O(4) # 5	2.838(4)
Cd(1)–O(3)	2.404(4)	K(1)–O(3) # 6	2.863(4)
Cd(1)–O(3) # 1	2.404(4)	K(1)–O(2) # 6	2.889(4)
Cd(1)–O(4) # 4	2.457(4)	K(1)–O(2) # 7	3.225(4)
Cd(1)–O(4) # 5	2.457(4)	K(1)–O(100) # 8	3.258(5)
C(1)–O(4)	1.246(6)	K(1) # 9–O(2)	2.889(4)
C(1)–O(1)	1.268(6)	K(1) # 10–O(2)	3.225(4)
C(1)–C(2) # 3	1.557(7)	K(1) # 9–O(3)	2.863(4)
C(2)–O(2)	1.233(6)	K(1) # 8–O(4)	2.822(4)
C(2)–O(3)	1.257(6)	K(1) # 3–O(4)	2.838(4)
C(2)–C(1) # 5	1.557(7)	K(1) # 4–O(100)	3.258(5)

Note. Symmetry transformations used to generate equivalent atoms: # 1 $-x, -y, z$; # 2 $-x - \frac{1}{4}, y - \frac{1}{4}, z + \frac{1}{4}$; # 3 $x + \frac{1}{4}, -y + \frac{1}{4}, z + \frac{1}{4}$; # 4 $-x + \frac{1}{4}, y - \frac{1}{4}, z - \frac{1}{4}$; # 5 $x - \frac{1}{4}, -y + \frac{1}{4}, z - \frac{1}{4}$; # 6 $x + \frac{1}{4}, -y + \frac{1}{4}, z - \frac{3}{4}$; # 7 $x + \frac{1}{2}, y, z - \frac{1}{2}$; # 8 $-x + \frac{1}{4}, y + \frac{1}{4}, z + \frac{1}{4}$; # 9 $x - \frac{1}{4}, -y + \frac{1}{4}, z + \frac{3}{4}$; # 10 $x - \frac{1}{2}, y, z + \frac{1}{2}$.

TABLE 7
Selected Bond Angles in **I**, $\text{K}_2\text{Cd}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$

Moiety	Angle (°)	Moiety	Angle (°)
O(1)#1–Cd(1)–O(1)	148.4(2)	O(3)–Cd(1)–O(4)#4	133.93(12)
O(1)#1–Cd(1)–O(2)#2	69.27(13)	O(3)#1–Cd(1)–O(4)#4	67.44(13)
O(1)–Cd(1)–O(2)#2	139.88(13)	O(1)#1–Cd(1)–O(4)#5	79.42(13)
O(1)#1–Cd(1)–O(2)#3	139.87(13)	O(1)–Cd(1)–O(4)#5	74.94(12)
O(1)–Cd(1)–O(2)#3	69.27(13)	O(2)#2–Cd(1)–O(4)#5	144.48(12)
O(2)#2–Cd(1)–O(2)#3	82.0(2)	O(2)#3–Cd(1)–O(4)#5	114.59(12)
O(1)#1–Cd(1)–O(3)	79.00(13)	O(3)–Cd(1)–O(4)#5	67.44(13)
O(1)–Cd(1)–O(3)	107.12(12)	O(3)#1–Cd(1)–O(4)#5	133.93(12)
O(2)#2–Cd(1)–O(3)	89.91(13)	O(4)#4–Cd(1)–O(4)#5	70.8(2)
O(2)#3–Cd(1)–O(3)	73.40(13)	O(4)–C(1)–O(1)	125.8(5)
O(1)#1–Cd(1)–O(3)#1	107.12(12)	O(4)–C(1)–C(2)#3	118.2(4)
O(1)–Cd(1)–O(3)#1	79.00(13)	O(1)–C(1)–C(2)#3	116.0(4)
O(2)#2–Cd(1)–O(3)#1	73.40(13)	O(2)–C(2)–O(3)	125.2(5)
O(2)#3–Cd(1)–O(3)#1	89.91(13)	O(2)–C(2)–C(1)#5	118.7(4)
O(3)–Cd(1)–O(3)#1	158.1(2)	O(3)–C(2)–C(1)#5	116.1(4)
O(1)#1–Cd(1)–O(4)#4	74.94(12)	C(1)–O(1)–Cd(1)	118.0(3)
O(1)–Cd(1)–O(4)#4	79.42(13)	C(2)–O(2)–Cd(1)#5	117.7(4)
O(2)#2–Cd(1)–O(4)#4	114.59(12)	C(2)–O(3)–Cd(1)	118.0(3)
O(2)#3–Cd(1)–O(4)#4	144.48(12)	C(1)–O(4)–Cd(1)#3	115.2(4)

Note. Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, z$; #2 $-x - \frac{1}{4}, y - \frac{1}{4}, z + \frac{1}{4}$; #3 $x + \frac{1}{4}, -y + \frac{1}{4}, z + \frac{1}{4}$; #4 $-x + \frac{1}{4}, y - \frac{1}{4}, z - \frac{1}{4}$; #5 $x - \frac{1}{4}, -y + \frac{1}{4}, z - \frac{1}{4}$.

the carbon atoms, respectively. The variations in the distances are also reflected in the C–O bonding as well (Table 3). The O–Cd–O angles in the range $66.8(2)^\circ$ – $149.6(2)^\circ$ (average O–Cd(1)–O = 100.1° and O–Cd(2)–O = 100.2°) and the O–C–O bond angles are in the range $124.9(6)^\circ$ – $126.7(6)^\circ$ (average 125.7°) (Table 4). These geometrical parameters are in the range expected for this type of bonding and agree well with previously determined structures of the cadmium oxalates (15, 16). Bond valence sum calculations (20) indicated that the valence states of the various species forming the framework are Cd^{2+} , C^{4+} , O^{2-} , as expected.

The framework structure of **I** is built up of linkages involving the Cd and the oxalate units. The structure can be

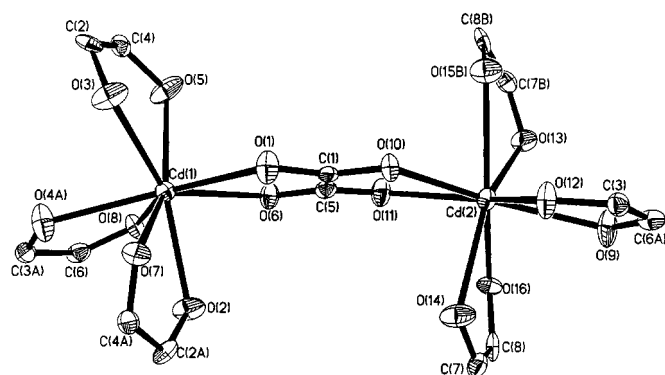


FIG. 1. ORTEP plot of the framework of **I**, $\text{Na}_4\text{Cd}_2(\text{C}_2\text{O}_4)_4 \cdot 4\text{H}_2\text{O}$. Thermal ellipsoids are given at 50% probability.

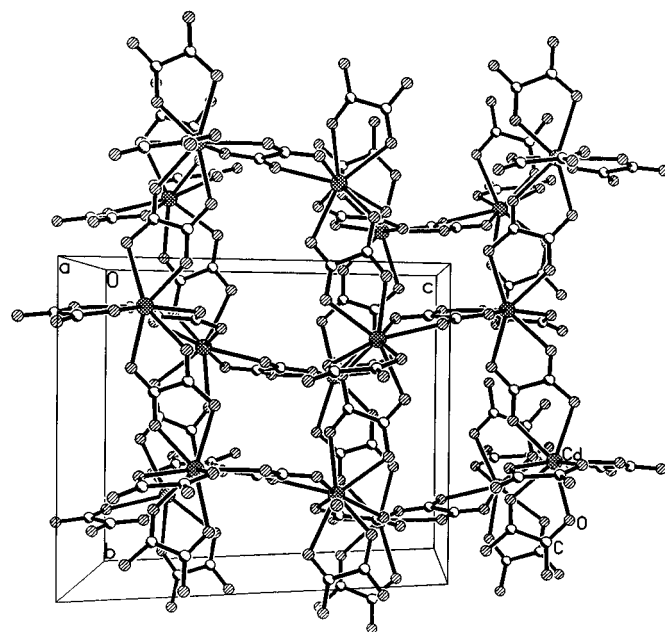


FIG. 2. Structure of **I** along the *b* axis showing the eight-membered channels. Na^+ ions and water molecules are omitted for clarity.

understood in terms of simpler building units involving two-dimensional layers. Thus, of the four oxalate groups that connect one Cd atom, two have *in-plane* connectivity and the other two have *out-of-plane* connectivity. The *in-plane* connectivity between the oxalates and Cd atoms form a layer-like arrangement with 12-membered apertures (made of six cadmium and six oxalate units) of width $11.6 \times 5.4 \text{ \AA}$ (longest O–O contact distances not including van der Waals radii). It is to be noted that each adjacent layer is translated by half a unit-cell, and the *out-of-plane* oxalate group connects to the neighboring layer above and below. This type linkage creates interpenetration between the layers and forms a three-dimensional structure with 8-membered channels (made of four cadmium and four oxalate units) of differing width along the *b* axis (Fig. 2). The width of these channels is 4.6×7.0 and $5.1 \times 7.6 \text{ \AA}$ (shortest oxygen–oxygen contact distance not including the van der Waals radii). The Na atoms along with water molecules occupy these channels. The linkages between the oxalates and the cadmium are reminiscent of the connectivity observed in the phosphate-oxalates described recently (13), where the *out-of-plane* connectivity of the oxalates leads to the three-dimensional structure.

Impedance measurements off a sample of **I** gave typical complex plane plots with a rather broad arc at high frequencies at 298 K. Lower frequency effects can be seen in the form of an inclined spike at higher temperatures (say 398 K). Plots of the imaginary part of the impedance, Z'' , and the electric modulus, M'' , against log frequency, showed single peaks with associated capacitance values of ~ 12.4 and

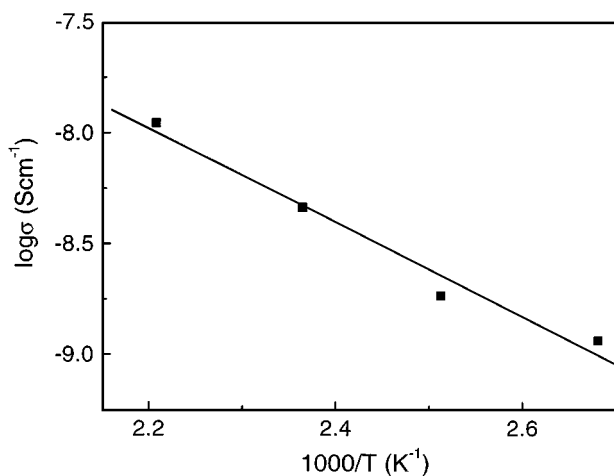


FIG. 3. Arrhenius plot of the overall pellet conductivity for I.

20 pF, respectively, for M'' and Z'' . An Arrhenius plot of the conductivity of the pellet gave a low value of the energy of activation, although the conductivities are small, in the 10^{-8} – 10^{-9} S cm $^{-1}$ range (Fig. 3).

$K_2Cd(C_2O_4)_2 \cdot 2H_2O$, II

The asymmetric unit of **II** contains nine nonhydrogen atoms (Fig. 4a), of which seven belong to the framework. The framework structure of **II** is built up by the linkages between the Cd atoms and the oxalate ions. There are eight oxygen atoms that surround the cadmium and have a dodecahedron-type arrangement as shown in Fig. 4b. There is only one independent Cd atoms in the asymmetric unit with Cd–O distances in the range 2.379(4)–2.457(4) Å (average Cd–O = 2.406 Å). Of the eight oxygen atoms bound to each of the Cd atoms, four are associated with Cd–O distances in the range 2.379(4)–2.384(4) Å and the other four with distances in the range 2.404(4)–2.457(4) Å. These distances arise from the single- and double-bonded oxygens connected to the carbon atoms, respectively. The variations in the distances are also reflected in the C–O bonding as well (Table 3). The O–Cd–O angles are in the range 67.4(4)°–158.1(2)° (average O–Cd(1)–O = 100.2°) and the average O–C–O bond angle is 125.5° (Table 4). These geometrical parameters are in the range expected for this type of bonding and agree well with previously determined structures of the cadmium oxalates (15,16). Bond valence sum calculations (20) indicated that the valence states of the various species forming the framework are Cd $^{2+}$, C $^{4+}$, O $^{2-}$, as expected.

The framework structure of **II** is built up from linkages involving the oxalates and the Cd atoms. As in **I**, two oxalates link up with the Cd atoms in an *in-plane* manner to give rise to a layer with 12-membered aperture and the remaining two oxalates connects these layers in an *out-of-*

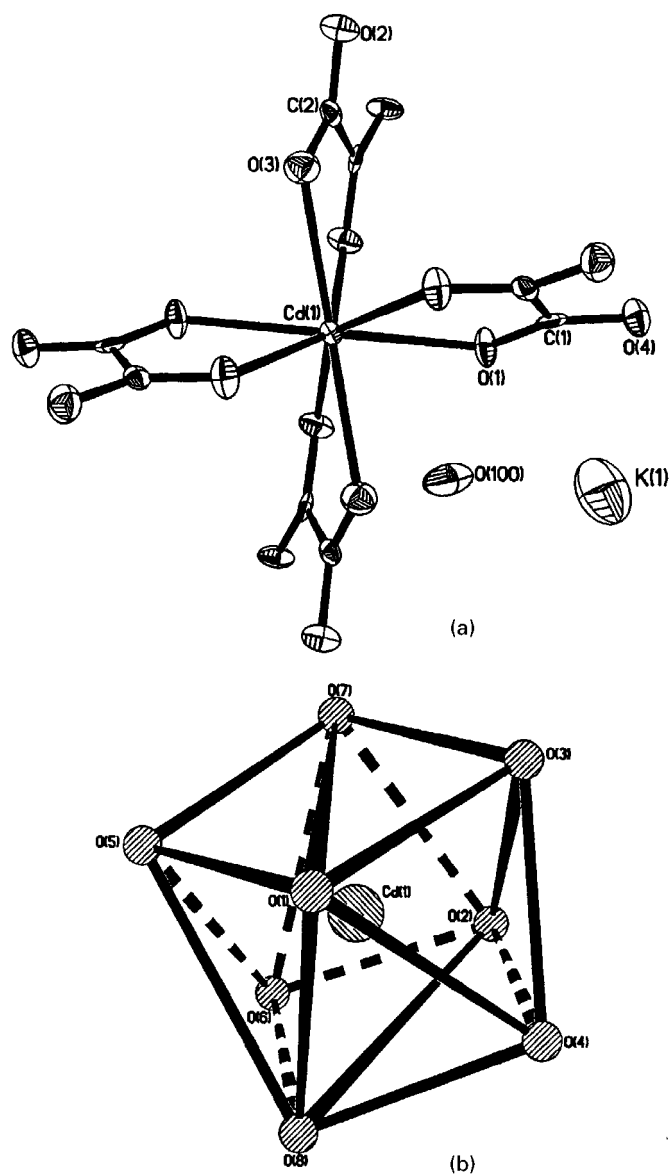


FIG. 4. (a) ORTEP plot of **II**, $K_2Cd(C_2O_4)_2 \cdot 2H_2O$. Thermal ellipsoids are given at 50% probability. (b) The coordination environment around Cd atoms. Note the oxygens form a dodecahedral arrangement.

plane fashion forming 8-membered channels as shown in Fig. 5. The channels in **II** are uniform and have width of 5.6×5.8 Å. The K $^+$ and water molecules occupy these channels.

DISCUSSION

Two new cadmium oxalates, $Na_4Cd_2(C_2O_4)_4 \cdot 4H_2O$, **I**, and $K_2Cd(C_2O_4)_2 \cdot 2H_2O$, **II**, have been synthesized hydrothermally and their structures determined by single-crystal methods. Since the synthesis involves kinetically controlled solvent-mediated reactions, there is no apparent

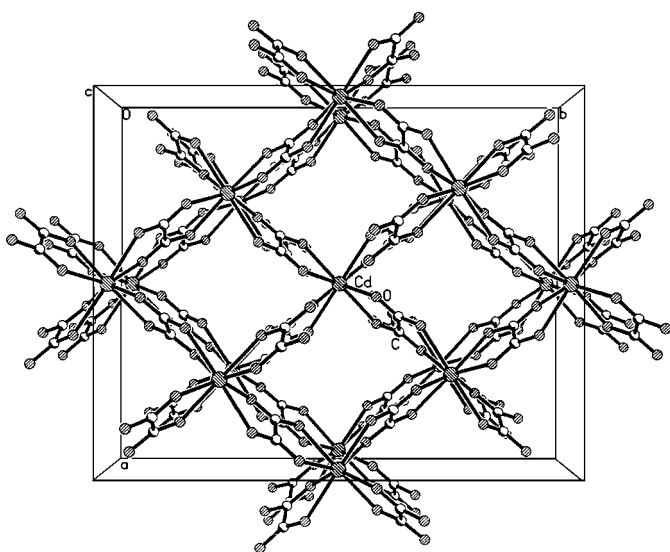


FIG. 5. Structure of **II** along the *c* axis showing the uniform eight-membered channels.

correlation between the starting composition and the stoichiometry of the solid product. **I** and **II**, along with the recently described cadmium oxalate, $K[C_3N_2H_5][Cd(C_2O_4)_2]$ (16), form a series of compounds in a family of three-dimensional oxalates possessing channels. Though **I** and **II** have been prepared under similar conditions, subtle differences exist between the two. Thus, **II** has been synthesized in the presence of additional amine, while **I** was prepared devoid of any added amine in the synthesis mixture. The exact role of the amine molecule during the synthesis of **II** is not yet clear, the absence of which forms a condensed phase. Glacial acetic acid in the reaction mixture probably controls the pH during the reaction. Such pH control by the acetate anions has been effected in many metal substituted aluminum phosphates (*MeAlPOs*) (21). It is to be noted that both **I** and **II** have similar linkages involving Cd and oxalate units, but the connectivity between Cd and oxalate units create distinct differences between the two structures. While **I** is formed with channels of differing dimensionalities, **II** has uniform channels (Figs. 2 and 5). In both the cases, the charge-compensating alkali ions along with water molecules occupy these channels.

The structures of **I** and **II** along with the coordination environment of cadmium merits some discussion. In **I** and **II**, the Cd atoms are eight-coordinated with respect to the oxygen atoms, resulting in a dodecahedral arrangement (see Figs. 1 and 4b), unlike in the layered cadmium oxalate reported earlier, $CdC_2O_4 \cdot 3H_2O$ (15), where the Cd was only seven-coordinated. Among the layered oxalates, the honeycomb architecture appears to be more common, especially among the transition metal oxalates (6, 7). The central metal atom in these compounds is predominantly six-coor-

ordinated with respect to the nearest neighbors (oxygen atoms). In the three-dimensional oxalates of yttrium described recently (22), the yttrium atoms are eight- and nine-coordinated with respect to the oxygens, and possess three-dimensional architectures with channels. The higher coordination of the metal atom appears to favor the formation and stabilization of the three-dimensional structures, especially in the case of the cadmium oxalates. While the seven-coordination of the cadmium gives rise to the layered structure (15), the eight-coordinated cadmium gives rise to the three-dimensional architecture (16). In **I** and **II**, Cd is eight-coordinated, forming three-dimensional structures with channels. It is noteworthy that the oxalate units perform the dual role—that of linking the cadmium within the layer and with the neighboring ones by *in-plane* and *out-of-plane* connections. Such a connectivity also gives rise to the three-dimensional architecture in the zinc oxalate, $2[C_3H_7NH_3][Zn_2(C_2O_4)_3]$ (11) and is reminiscent of the phosphate oxalate structures reported recently (13,14).

Though recent studies have shown that a large number of oxalates of Zn of varying dimensions can be synthesized under appropriate conditions (11,12), those of cadmium are much less studied. The present results indicate that it is possible to prepare three-dimensional cadmium oxalates by employing hydrothermal methods, with a careful choice of the reactants. Further studies are presently underway.

REFERENCES

- (a) J. M. Thomas, *Angew. Chem. Int. Ed.* **38**, 3588 (1999); (b) J. M. Thomas, *Chem. Eur. J.*, **3**, 1557 (1997).
- A. K. Cheetham, G. Ferey, and T. Loiseau, *Angew. Chem. Int. Ed.* **38**, 3268 (1999).
- (a) F. Serpaggi and G. Ferey, *J. Mater. Chem.* **8**, 2737 (1998); (b) D. Riou and G. Ferey, *J. Mater. Chem.* **8**, 2733 (1998); (c) F. Serpaggi, T. Luxbacher, A. K. Cheetham, and G. Ferey, *J. Solid State Chem.* **145**, 580 (1999).
- (a) S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, and I. D. Williams, *Science* **283**, 1148 (1999); (b) T. M. Reineke, M. Eddaoudi, M. Fehr, D. Kelly, and O. M. Yaghi, *J. Am. Chem. Soc.* **121**, 1651 (1999); (c) T. M. Reineke, M. Eddaoudi, M. O'Keeffe, and O. M. Yaghi, *Angew. Chem. Int. Ed.* **38**, 2590 (1999).
- (a) C. Livage, C. Egger, M. Nogues, and G. Ferey, *J. Mater. Chem.* **8**, 2743 (1998); (b) C. Livage, C. Egger, and G. Ferey, *Chem. Mater.* **11**, 1546 (1999); (c) R. Kuhlman, G. L. Schemek, and J. W. Kolis, *Inorg. Chem.* **38**, 194 (1999).
- (a) R. Sieber, S. Decurtins, H. Stoeckli-Evans, C. Wilson, D. Yufit, J. A. K. Howard, S. C. Capelli, and A. Hauser, *Chem. Eur. J.* **6**, 361 (2000); (b) S. Decurtins, H. W. Schmalle, R. Pellaux, P. Schneuwly, and A. Hauser, *Inorg. Chem.* **35**, 1451 (1996); (c) S. Decurtins, H. W. Schmalle, P. Schneuwly, J. Enslin, and P. Gütllich, *J. Am. Chem. Soc.* **116**, 9521 (1994).
- (a) H. Tamaki, Z. J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto, and H. Okawa, *J. Am. Chem. Soc.* **114**, 6974 (1994); (b) C. Mathoniere, S. G. Carling, and P. Day, *J. Chem. Soc. Chem. Commun.* 1551 (1994); (c) M. Clemente-Leon, E. Coronado, J.-R. Galán-Mascarós, and C.J. Gómez-García, *Chem. Commun.* 1727 (1997).

8. (a) J. Glerup, P. A. Goodson, D. J. Hodson, and K. Michelson, *Inorg. Chem.* **34**, 6255 (1995); (b) M. Hernández-Molina, F. Lloret, C. Ruiz-Pérez, and M. Julve, *Inorg. Chem.* **37**, 4131 (1998); (c) R. P. Farrel, T. W. Hambley, and P. A. Lay, *Inorg. Chem.* **34**, 757 (1995).
9. (a) R. Pellaux, H. W. Schmalle, S. Decurtins, P. Fischer, F. Fauth, B. Ouladdiaf, and T. Hauss, *Physica B* **234–236**, 783 (1997); (b) S. Decurtins, H. W. Schmalle, R. Pellaux, A. Hauser, M. E. von Arx, and P. Fischer, *Syn. Metals* **85**, 1689 (1997); (c) S. Decurtins, H. W. Schmalle, P. Schneyuwly, R. Pellaux, and J. Enslin, *Mol. Cryst. Liq. Crystallogr.* **273**, 167 (1995); (d) R. Pellaux, H. W. Schmalle, R. Huber, P. Fischer, T. Hauss, B. Ouladdiaf, and S. Decurtins, *Inorg. Chem.* **36**, 2301 (1997).
10. (a) S. Ayyappan, A. K. Cheetham, S. Natarajan, and C. N. R. Rao, *Chem. Mater.* **10**, 3746 (1998); (b) S. Natarajan, R. Vaidyanathan, C. N. R. Rao, S. Ayyappan, and A. K. Cheetham, *Chem. Mater.* **11**, 1633 (1999).
11. R. Vaidyanathan, S. Natarajan, A. K. Cheetham, and C. N. R. Rao, *Chem. Mater.* **11**, 3636 (1999).
12. R. Vaidyanathan, S. Natarajan, and C. N. R. Rao, *J. Chem. Soc. Dalton Trans.* 699, (2001).
13. (a) A. Choudhury, S. Natarajan, and C. N. R. Rao, *Chem. Mater.* **11**, 2316 (1999); (b) A. Choudhury, S. Natarajan, and C. N. R. Rao, *Chem. Eur. J.* **6**, 1168 (2000), and the references therein.
14. (a) P. Lightfoot, Z. A. D. Lethbridge, R. E. Morris, D. S. Wragg, P. A. Wright, Å. Kvik, and G. B. M. Vaughan, *J. Solid State Chem.* **143**, 74 (1999); (b) Y.-F. Huang and K.-H. Lii, *J. Chem. Soc. Dalton Trans.* 4085 (1998); (c) H.-M. Lin, K.-H. Lii, Y.-C. Jiang, and S.-L. Wang, *Chem. Mater.* **11**, 519 (1999).
15. S.-H. Huang, R.-J. Wang, and T. C. W. Mak, *J. Crystallogr. Spectroscopy. Res.* **20**, 99 (1990).
16. P. A. Prasad, S. Neeraj, S. Natarajan, and C. N. R. Rao, *Chem. Commun.* 1251 (2000).
17. G. M. Sheldrick, "SHELXL-86 A Program for the Solution of Crystal Structures." University of Göttingen, Germany, 1993.
18. G. M. Sheldrick, "SADABS User Guide," University of Göttingen, Germany (1993).
19. G. M. Sheldrick, "SHELXTL-PLUS Program for Crystal Structure Solution and Refinement." University of Göttingen, Germany, 1993.
20. I. D. Brown and D. Aldermatt, *Acta Crystallogr. B* **41**, 244 (1984).
21. P. A. Wright, S. Natarajan, J. M. Thomas, R. G. Bell, P. L. Gai-Boyes, R. H. Jones, and J. Chen, *Angew. Chem. Int. Ed. Engl.* **31**, 1472 (1992), and references therein.
22. R. Vaidyanathan, S. Natarajan, and C. N. R. Rao, *Chem. Mater.* **13**, 185 (2001).