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Three-Dimensional Yttrium Oxalates Possessing Large Channels

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Two new open-framework yttrium oxalates have been prepared, for the first time, employing hydrothermal methods in the presence of organic amines. The crystal data for these oxalates are as follows: **I**, $[C_6N_2H_{16}]_{0.5}[Y(H_2O)(C_2O_4)_2]\cdot 2H_2O$, triclinic, space group $P(-1)$ (no. 2), $a = 8.229(3)$, $b = 9.739(1)$, $c = 9.754(3)$ Å, $\alpha = 60.74(1)$, $\beta = 72.36(1)$, $\gamma = 84.67(1)°$, $V = 648.5(1)$ Å^3, $Z = 2$, $M = 377.1$, $D_{calc} = 1.931$ g cm^{-3}, $\mu = 4.554$ mm^{-1}, Mo Kα, $R_1 = 0.054$, $wR_2 = 0.13$; **II**, $[C_5N_2H_{12}][Y(C_2O_4)_2]$, monoclinic, space group Cc (no. 9), $a = 11.552(1)$, $b = 17.168(1)$, $c = 8.719(1)$ Å, $\beta = 130.64(1)°$, $V = 1312.1(1)$ Å^3, $Z = 2$, $M = 365.1$, $D_{calc} = 1.848$ g cm^{-3}, $\mu = 4.48$ mm^{-1}, Mo Kα, $R_1 = 0.023$, $wR_2 = 0.057$. The Y atom is 9-coordinated in **I**, forming a D_{3h} triply capped trigonal prism, and 8-coordinated in **II**, forming a square antiprism. The three-dimensional framework structures of **I** and **II** are built up by *in-plane* linkages between the Y and the oxalate moieties, forming layers with 12-membered honeycomb-like apertures, pillared by another oxalate in an *out-of-plane* manner. While **I** possesses channels along all the crystallographic directions, **II** has channels only in one direction. Adsorption studies indicate that water and methanol can be reversibly adsorbed in **I**.

Introduction

A vast variety of three-dimensional open-framework aluminosilicates and metal phosphates have been synthesized and characterized in recent years.[1] However, there are only a few open-framework metal carboxylates reported hitherto. The members of this family are by and large metal dicarboxylates,[2−4] other than oxalates. The only three-dimensional open-framework oxalates reported to date are those of tin(II) and zinc synthesized in the presence of organic amines.[5,6] The structures of these oxalates exhibit some interesting features. While, the layered oxalates possess honeycomb networks, the three-dimensional structures are formed by the oxalate units acting as a bridge linking the layers. In view of the limited number of open-framework oxalates known, we have been exploring the possibility of synthesizing new open-framework metal oxalate structures. Considering the propensity of rare earths to form interesting dicarboxylates,[2,3] we attempted the synthesis of rare-earth oxalates in the presence of organic amines under hydrothermal conditions and have succeeded in isolating two new open-framework three-dimensional yttrium oxalates for the first time. Yttrium oxalate with a layered structure has been discussed recently.[7] The yttrium oxalates, $[C_6N_2H_{16}]_{0.5}[Y(H_2O)(C_2O_4)_2]\cdot 2H_2O$, **I**, and $[C_5N_2H_{12}][Y(C_2O_4)_2]$, **II**, constitute a new family of open-framework materials, with three-dimensional architectures possessing channels, and show adsorptive properties.

Experimental Section

Synthesis and Initial Characterization. The yttrium oxalates, **I** and **II**, were synthesized hydrothermally in the presence of 1,2-diaminopropane (1,2-DAP) and 1,3-diaminopropane (1,3-DAP), respectively. For the synthesis of **I**, 0.365 g of yttrium nitrate was dissolved in 1 mL of deionized water and 0.29 mL of acetic acid was added to the same under constant stirring. Oxalic acid (0.63 g) and 1,2-diaminopropane (1,2-DAP) (0.43 mL) are added to the above and the mixture was homogenized for 30 min. The final mixture had the composition, 1:5:5:5:55 $Y(NO_3)_3$:$H_2C_2O_4$:CH_3COOH:1,2-DAP:H_2O. The starting mixture was stirred to attain homogeneity, transferred into a 23-mL (fill factor = 40%) PTFE bottle, sealed in a stainless steel autoclave (Parr, USA) and heated at 180 °C for 6 days. The resulting product, a crop of rodlike crystals, was filtered, washed with deionized water, and dried at ambient conditions. **I** was one of the main products of the reaction along with the condensed yttrium oxalate, $Y_2(C_2O_4)_3\cdot$

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Table 1. Crystal Data and Structure Refinement Parameters for I, $[C_6N_2H_{16}]_{0.5}[Y(H_2O)(C_2O_4)_2]\cdot 2H_2O$ and II $[C_5N_2H_{12}][Y(C_2O_4)_2]$

	I	**II**
empirical formula	$YO_{11}C_7N_1H_{14}$	$YO_8C_9N_2H_{12}$
crystal system	triclinic	monoclinic
space group	$P(-1)$ (no. 2)	Cc (no. 9)
crystal size (mm)	0.08 × 0.08 × 0.16	0.12 × 0.12 × 0.12
a (Å)	8.229(3)	11.552(1)
b (Å)	9.739(1)	17.168(1)
c (Å)	9.754(3)	8.719(1)
α (deg)	60.74(1)	90.0
β (deg)	72.36(1)	130.64(1)
γ (deg)	84.67(1)	90.0
volume (Å^3)	648.5(1)	1312.1(1)
Z	2	2
formula mass	377.1	365.1
ρ_{calc} (g cm^{-3})	1.931	1.848
λ (Mo Kα) Å	0.71073	0.71073
μ (mm^{-1})	4.554	4.48
θ range (deg)	2.40−23.21	2.37−23.26
total data collected	2760	2689
index ranges	$-4 \leq h \leq 9$, $-10 \leq k \leq 10$, $-9 \leq l \leq 10$	$-9 \leq h \leq 12$, $-19 \leq k \leq 18$, $-9 \leq l \leq 8$
unique data	1834	1402
observed data ($I > 2\sigma(I)$)	1569	1285
refinement method	full-matrix least-squares on $\lvert F^2 \rvert$	full-matrix least-squares on $\lvert F^2 \rvert$
R_{merg}	0.0454	0.0252
R indexes [$I > 2\sigma(I)$]	$R_1 = 0.054^a$, $wR_2 = 0.13^b$	$R_1 = 0.023$, $wR_2 = 0.057$
R (all data)	$R_1 = 0.062$, $wR_2 = 0.13$	$R_1 = 0.027$, $wR_2 = 0.060$
goodness of fit	1.01	1.1
no. of variables	205	226
largest difference map peak and hole (eÅ^{-3})	1.022 and −1.437	0.803 and −0.306

[a] $R_1 = \sum \lvert \lvert F_o \rvert - \lvert F_c \rvert \rvert / \sum \lvert F_o \rvert$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2(F_c)^2]/3$, where $a = 0.0774$ and $b = 0.0$ for **I** and $a = 0.1000$ and $b = 0.0$ for **II**.

Table 2. Atomic Coordinates [×10^4] and Equivalent Isotropic Displacement Parameters [Å^2 × 10^3] for I, $[C_6N_2H_{16}]_{0.5}[Y(H_2O)(C_2O_4)_2]\cdot 2H_2O$

atom	x	y	z	U_{eq}[a]
Y(1)	6704(1)	8413(1)	7868(1)	20(1)
O(1)	6902(6)	9068(6)	9881(6)	29(1)
O(2)	5300(7)	3395(5)	9631(6)	33(1)
O(3)	8817(6)	8284(5)	5614(5)	28(1)
O(4)	5602(6)	10082(6)	11532(6)	31(1)
O(5)	4632(6)	8120(5)	6732(6)	29(1)
O(6)	9131(6)	10280(5)	6711(5)	25(1)
O(7)	6702(6)	5777(5)	8189(5)	28(1)
O(8)	8874(8)	6948(7)	9171(9)	34(1)
O(9)	6596(6)	10783(6)	5298(6)	32(1)
C(1)	4430(8)	9235(8)	5411(8)	22(2)
C(2)	5729(9)	9760(7)	10392(8)	21(2)
C(3)	10071(8)	10565(8)	5326(8)	21(2)
C(4)	5581(9)	4760(8)	9365(8)	24(2)
O(100)	10826(13)	8857(14)	9462(12)	77(3)
O(200)	8149(10)	4174(8)	12251(10)	49(2)
N(1)	9878(14)	3655(10)	6533(11)	81(3)
C(11)	8338(12)	4221(11)	5892(11)	54(2)
C(12)	8496(10)	5914(9)	4816(9)	32(2)
C(13)	7001(17)	6500(16)	4186(18)	96(5)

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

Table 3. Selected Bond Distances for I, $[C_6N_2H_{16}]_{0.5}[Y(H_2O)(C_2O_4)_2]\cdot 2H_2O$[a]

moiety	distance (Å)	moiety	distance (Å)
Y(1)−O(1)	2.393(4)	O(1)−C(2)	1.245(8)
Y(1)−O(2)$^{\#1}$	2.382(5)	O(2)−C(4)	1.254(8)
Y(1)−O(3)	2.405(4)	O(3)−C(3)$^{\#3}$	1.269(8)
Y(1)−O(4)$^{\#2}$	2.395(5)	O(4)−C(2)	1.269(8)
Y(1)−O(5)	2.400(5)	O(5)−C(1)	1.263(8)
Y(1)−O(6)	2.424(4)	O(6)−C(3)	1.241(8)
Y(1)−O(7)	2.430(4)	O(7)−C(4)	1.251(8)
Y(1)−O(8)	2.444(6)	O(9)−C(1)$^{\#4}$	1.250(8)
Y(1)−O(9)	2.462(5)	C(3)−O(3)$^{\#3}$	1.269(8)
C(1)−C(1)$^{\#4}$	1.543(13)	C(3)−C(3)$^{\#3}$	1.545(13)
C(2)−C(2)$^{\#2}$	1.532(13)	C(4)−C(4)$^{\#1}$	1.559(14)
		Organic Moiety	
N(1)−C(11)	1.522(14)	C(12)−C(13)	1.484(13)
C(11)−C(12)	1.450(11)	N(1)−C(12)$^{\#5}$	1.481(12)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1, -y + 1, -z + 2$; (#2) $-x + 1, -y + 2, -z + 2$; (#3) $-x + 2, -y + 2, -z + 1$; (#4) $-x + 1, -y + 2, -z + 1$; (#5) $-x + 2, -y + 1, -z + 1$.

$2H_2O$ (JCPDS: 40-1461). For the synthesis of **II**, a mixture of the composition, 1:5:5:5:55 $Y(NO_3)_3$:$H_2C_2O_4$:CH_3COOH:1,3-DAP:H_2O was heated at 180 °C for 5 days in the autoclave to obtain rodlike crystals. A critical examination under an optical microscope revealed that **II** was formed as a single phase. The yields of the products were 40 and 50% for **I** and **II**, respectively. X-ray diffraction (XRD) patterns on the powdered crystals indicated that the products were new, the pattern being consistent with the structures determined by single-crystal X-ray diffraction. Thermogravimetric analysis (TGA) was carried out in a nitrogen atmosphere in the range between 25 and 700 °C.

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 (superglue) adhesive. Single-crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4-kW sealed tube X-ray source (Mo Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1321 frames with ω scans (width of 0.30° and exposure time of 30 s per frame) in the 2θ range 3°−46.5°. Pertinent experimental details for the structure determinations are presented in Table 1.

The structures were solved by direct methods using SHELXS-86[8] and difference Fourier syntheses. In **I**, the amine molecule is present equally in two symmetry-related positions and the 1,2-DAP molecule is near the inversion center. This gives rise to two positions of the amine with equal populations related by inversion symmetry. In **II**, the amine, 1,3-DAP, that we started with reacted with acetic acid present in the reaction mixture as described later. All the hydrogen positions for both compounds were initially located in the difference Fourier maps and were refined isotropically. An empirical absorption correction based on the SADABS[9] 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, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against $\lvert F^2 \rvert$ was carried out using the SHELXTL-PLUS[10] package of programs. Details of the final refinements are given in Table 1. The final atomic coordinates and selected bond distances and angles for **I** are presented in Tables 2−4 and for **II** in Tables 5−7.

Results

$[C_6N_2H_{16}]_{0.5}[Y(H_2O)(C_2O_4)_2]\cdot 2H_2O$, I. The asymmetric unit of **I** contains 20 non-hydrogen atoms (Figure 1a), of which 14 atoms belong to the framework. The framework structure of **I** is built up by the linkages

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Table 4. Selected Bond Angles for I, $[C_6N_2H_{16}]_{0.5}[Y(H_2O)(C_2O_4)_2]\cdot 2H_2O^a$

moiety	angle (deg)	moiety	angle (deg)
O(2)$^{\#1}$−Y(1)−O(1)	74.9(2)	O(5)−Y(1)−O(7)	70.2(2)
O(2)$^{\#1}$−Y(1)−O(4)$^{\#2}$	73.6(2)	O(3)−Y(1)−O(7)	68.7(2)
O(1)−Y(1)−O(4)$^{\#2}$	67.7(2)	O(6)−Y(1)−O(7)	127.9(2)
O(2)$^{\#1}$−Y(1)−O(5)	81.5(2)	O(2)$^{\#1}$−Y(1)−O(8)	85.2(2)
O(1)−Y(1)−O(5)	140.5(2)	O(1)−Y(1)−O(8)	68.8(2)
O(4)$^{\#2}$−Y(1)−O(5)	75.4(2)	O(4)$^{\#2}$−Y(1)−O(8)	135.2(2)
O(2)$^{\#1}$−Y(1)−O(3)	136.4(2)	O(5)−Y(1)−O(8)	140.6(2)
O(1)−Y(1)−O(3)	132.5(2)	O(3)−Y(1)−O(8)	78.5(2)
O(4)$^{\#2}$−Y(1)−O(3)	142.1(2)	O(6)−Y(1)−O(8)	73.8(2)
O(5)−Y(1)−O(3)	86.0(2)	O(7)−Y(1)−O(8)	70.4(2)
O(2)$^{\#1}$−Y(1)−O(6)	144.1(2)	O(2)$^{\#1}$−Y(1)−O(9)	136.8(2)
O(1)−Y(1)−O(6)	70.4(2)	O(1)−Y(1)−O(9)	111.7(2)
O(4)$^{\#2}$−Y(1)−O(6)	101.1(2)	O(4)$^{\#2}$−Y(1)−O(9)	70.6(2)
O(5)−Y(1)−O(6)	132.5(2)	O(5)−Y(1)−O(9)	66.8(2)
O(3)−Y(1)−O(6)	68.0(2)	O(3)−Y(1)−O(9)	71.8(2)
O(2)$^{\#1}$−Y(1)−O(7)	67.7(2)	O(6)−Y(1)−O(9)	67.6(2)
O(1)−Y(1)−O(7)	126.0(2)	O(7)−Y(1)−O(9)	122.3(2)
O(4)$^{\#2}$−Y(1)−O(7)	130.9(2)	O(8)−Y(1)−O(9)	137.7(2)
C(2)−O(1)−Y(1)	119.3(4)	O(5)−C(1)−C(1)$^{\#4}$	116.8(7)
C(4)−O(2)−Y(1)$^{\#1}$	119.9(4)	O(1)−C(2)−O(4)	126.2(6)
C(3)$^{\#3}$−O(3)−Y(1)	117.2(4)	O(1)−C(2)−C(2)$^{\#2}$	117.5(7)
C(2)−O(4)−Y(1)$^{\#2}$	118.9(4)	O(4)−C(2)−C(2)$^{\#2}$	116.3(7)
C(1)−O(5)−Y(1)	120.7(4)	O(6)−C(3)−O(3)$^{\#3}$	125.2(6)
C(3)−O(6)−Y(1)	116.0(4)	O(6)−C(3)−C(3)$^{\#3}$	118.7(7)
C(4)−O(7)−Y(1)	118.3(4)	O(3)$^{\#3}$−C(3)−C(3)$^{\#3}$	116.1(7)
C(1)$^{\#4}$−O(9)−Y(1)	118.9(4)	O(7)−C(4)−O(2)	126.7(6)
O(9)$^{\#4}$−C(1)−O(5)	126.4(6)	O(7)−C(4)−C(4)$^{\#1}$	116.6(7)
O(9)$^{\#4}$−C(1)−C(1)$^{\#4}$	116.8(7)	O(2)−C(4)−C(4)$^{\#1}$	116.7(7)
Organic Moiety			
C(12)$^{\#5}$−N(1)−C(11)	112.3(7)	C(11)−C(12)−C(13)	112.5(9)
C(12)−C(11)−N(1)	111.4(7)	N(1)$^{\#5}$−C(12)−C(13)	112.1(8)
C(11)−C(12)−N(1)$^{\#5}$	109.1(7)		

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1, -y + 1, -z + 2$; (#2) $-x + 1, -y + 2, -z + 2$; (#3) $-x + 2, -y + 2, -z + 1$; (#4) $-x + 1, -y + 2, -z + 1$; (#5) $-x + 2, -y + 1, -z + 1$.

Table 5. Atomic Coordinates [$\times 10^4$] and Equivalent Isotropic Displacement Parameters [$Å^2 \times 10^3$] for II, $[C_5N_2H_{11}][Y(C_2O_4)_2]$

atom	x	y	z	$U_{eq}{}^a$
Y(1)	4410(4)	1280(1)	2605(5)	24(1)
O(1)	6706(11)	1705(6)	3615(15)	33(3)
O(2)	5685(11)	759(7)	5843(14)	40(3)
O(3)	5238(11)	2365(7)	4722(15)	40(3)
O(4)	2081(11)	1750(6)	1524(14)	29(2)
O(5)	3523(11)	2369(5)	384(14)	28(2)
O(6)	5722(11)	166(4)	2700(13)	37(3)
O(7)	3185(11)	784(6)	−670(12)	27(2)
O(8)	3093(10)	176(5)	2530(12)	32(2)
C(1)	7371(16)	2343(7)	4842(18)	26(3)
C(2)	1529(13)	2283(8)	495(18)	23(3)
C(3)	5190(14)	−194(7)	1056(17)	22(3)
C(4)	3714(17)	−156(7)	4130(20)	28(3)
N(1)	8332(16)	−724(9)	5908(20)	56(4)
C(10)	8142(33)	−1629(14)	6103(33)	117(9)
C(11)	9639(23)	−1954(4)	7806(29)	51(4)
C(12)	10483(27)	−1605(15)	9582(41)	176(18)
N(2)	10570(15)	−742(9)	9154(22)	52(4)
C(13)	9446(22)	−371(3)	7728(28)	41(2)
C(14)	9390(31)	491(4)	7523(41)	72(3)

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

Table 6. Selected Bond Distances in II, $[C_5N_2H_{11}][Y(C_2O_4)_2]^a$

moiety	distance (Å)	moiety	distance (Å)
Y(1)−O(1)	2.303(11)	O(1)−C(1)	1.36(2)
Y(1)−O(2)	2.351(10)	O(2)−C(3)$^{\#1}$	1.20(2)
Y(1)−O(3)	2.343(10)	O(3)−C(2)$^{\#2}$	1.32(2)
Y(1)−O(4)	2.340(10)	O(4)−C(2)	1.14(2)
Y(1)−O(5)	2.388(10)	O(5)−C(1)$^{\#3}$	1.19(2)
Y(1)−O(6)	2.407(9)	O(6)−C(3)	1.29(2)
Y(1)−O(7)	2.370(9)	O(7)−C(4)$^{\#4}$	1.30(2)
Y(1)−O(8)	2.405(9)	O(8)−C(4)	1.22(2)
C(1)−C(2)$^{\#2}$	1.551(7)	C(3)−C(4)$^{\#4}$	1.536(7)
Organic Moiety			
N(1)−C(10)	1.59(3)	N(2)−C(13)	1.24(2)
C(10)−C(11)	1.47(3)	N(1)−C(13)	1.37(2)
C(11)−C(12)	1.32(3)	C(13)−C(14)	1.486(10)
C(12)−N(2)	1.55(3)		

[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) $x, -y, -z + {}^1/_2$.

Table 7. Selected Bond Angles in II, $[C_5N_2H_{11}][Y(C_2O_4)_2]^a$

moiety	angle (deg)	moiety	angle (deg)
O(1)−Y(1)−O(4)	141.34(11)	O(7)−Y(1)−O(5)	72.6(3)
O(1)−Y(1)−O(3)	70.7(4)	O(1)−Y(1)−O(8)	144.2(3)
O(4)−Y(1)−O(3)	79.4(4)	O(4)−Y(1)−O(8)	73.7(3)
O(1)−Y(1)−O(2)	89.8(4)	O(3)−Y(1)−O(8)	125.0(4)
O(4)−Y(1)−O(2)	105.8(4)	O(2)−Y(1)−O(8)	67.8(3)
O(3)−Y(1)−O(2)	75.0(4)	O(7)−Y(1)−O(8)	79.2(4)
O(1)−Y(1)−O(7)	102.1(4)	O(5)−Y(1)−O(8)	131.7(3)
O(4)−Y(1)−O(7)	90.6(3)	O(1)−Y(1)−O(6)	72.3(4)
O(3)−Y(1)−O(7)	148.4(4)	O(4)−Y(1)−O(6)	145.1(4)
O(2)−Y(1)−O(7)	136.50(11)	O(3)−Y(1)−O(6)	132.8(4)
O(1)−Y(1)−O(5)	80.9(4)	O(2)−Y(1)−O(6)	76.6(4)
O(4)−Y(1)−O(5)	68.3(3)	O(7)−Y(1)−O(6)	67.9(3)
O(3)−Y(1)−O(5)	75.91(12)	O(5)−Y(1)−O(6)	125.3(4)
O(2)−Y(1)−O(5)	150.9(4)	O(8)−Y(1)−O(6)	75.39(10)
C(1)−O(1)−Y(1)	118.3(9)	O(1)−C(1)−C(2)$^{\#2}$	116.9(10)
C(3)$^{\#1}$−O(2)−Y(1)	120.3(8)	O(4)−C(2)−O(3)$^{\#3}$	129.6(12)
C(2)$^{\#2}$−O(3)−Y(1)	120.9(8)	O(4)−C(2)−C(1)$^{\#3}$	117.2(8)
C(2)−O(4)−Y(1)	120.0(9)	O(3)$^{\#3}$−C(2)−C(1)$^{\#3}$	113.2(8)
C(1)$^{\#3}$−O(5)−Y(1)	115.2(9)	O(2)$^{\#4}$−C(3)−O(6)	129.0(12)
C(3)−O(6)−Y(1)	120.6(7)	O(2)$^{\#4}$−C(3)−C(4)$^{\#4}$	116.7(8)
C(4)$^{\#4}$−O(7)−Y(1)	119.6(8)	O(6)−C(3)−C(4)$^{\#4}$	114.3(8)
C(4)−O(8)−Y(1)	116.6(9)	O(8)−C(4)−O(7)$^{\#1}$	124.2(13)
O(5)$^{\#2}$−C(1)−O(1)	123.9(13)	O(8)−C(4)−C(3)$^{\#1}$	118.4(9)
O(5)$^{\#2}$−C(1)−C(2)$^{\#2}$	119.2(8)	O(7)$^{\#1}$−C(4)−C(3)$^{\#1}$	117.4(8)
Organic Moiety			
C(13)−N(1)−C(10)	113.5(12)	C(13)−N(2)−C(12)	123.0(13)
C(11)−C(10)−N(1)	109(2)	N(2)−C(13)−N(1)	120.9(8)
C(12)−C(11)−C(10)	120(2)	N(2)−C(13)−C(14)	125(2)
C(11)−C(12)−N(2)	105(2)	N(1)−C(13)−C(14)	112(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) $x, -y, -z + {}^1/_2$.

between the Y and the oxalate units with each Y atom bound to nine oxygens, which are, in turn, bound to carbon atoms, forming a network structure. Conversely, the oxalate ions are connected to the yttrium atoms forming the architecture. The coordination environment of Y atoms is an idealized D_{3h} triply capped trigonal prism as shown in Figure 1b with Y−O distances in the range 2.382(5)−2.462(5) Å (average 2.415 Å). Of the eight oxalate oxygens bound to yttrium, four are associated with Y−O distances in the range 2.382(5)−2.400(5) Å and the other four with distances in the 2.405(4)−2.462(5) Å range. The variations in the distances are also reflected in the C−O bonding as well (Table 3). The O−Y−O angles are in the range 66.8(2)°−144.1(2)° (average 124.1°) and the O−C−O bond angles are in the range 125.2(6)°−126.7(6)° (average 126.1°) (Table 4). These structural parameters are in the range expected for this type of bonding. The Y(1)−O(8) linkage with a distance of 2.444(6) Å is formally a water molecule. Two types of water molecules are present in **I**; one bound to Y and the other free water molecule present in the channels. Bond valence sum calculations[11] indicated

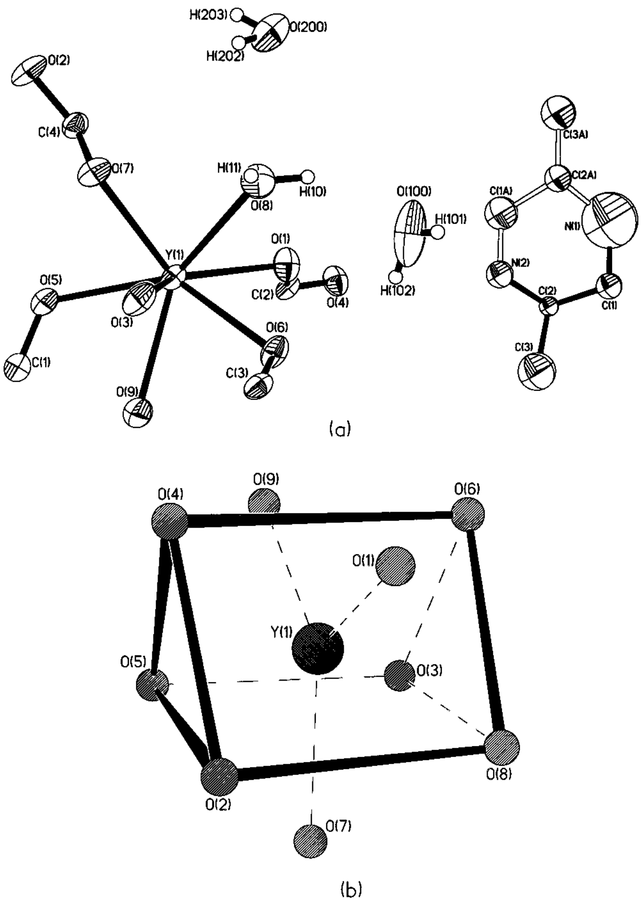

Figure 1. (a) ORTEP plot of **I**, $[C_6N_2H_{16}]_{0.5}[Y(H2O)(C_2O_4)_2]\cdot 2H_2O$. Thermal ellipsoids are given at 50% probability. Note the symmetry relation in the amine molecule. (b) The coordination environment around yttrium showing the D_{3h} triply capped trigonal prism.

that the valence states of the various species forming the framework are Y^{3+}, C^{4+}, and O^{2-}, as expected.

The structure of **I** can be understood in terms of simpler building units formed by the linkages between the Y atom and the oxalate units. The connectivity between these units form layers that are linked then to one another, giving rise to a three-dimensional architecture. Thus, three oxalate units ($C(1)C(1)O_4$, $C(3)C(3)O_4$, and $C(4)C(4)O_4$) connect the Y atom in an in-plane manner, forming a honeycomb-like layer with 12-membered apertures, along the *a* axis (Figure 2a), and the fourth oxalate ($C(2)C(2)O_4$) bridges the layers in an out-of-plane fashion, forming the one-dimensional channels (width, 7.9 × 8.6 Å, longest atom−atom contact distance not including the van der Waals radii). Along the *c* axis, the connectivity between the $C(2)C(2)O_4$, $C(3)C(3)O_4$, and $C(4)C(4)O_4$ oxalates and the Y atom gives rise to an elliptical 12-membered channel through an in-plane connectivity (Figure 2b), which is bridged by the $C(1)C(1)O_4$ oxalate, forming other one-dimensional channels of width 7.5 × 9.1 Å. Similar connectivity, along the *b* axis, gives rise to rectangular 12-membered channels of width 9.1 × 4.9 Å into which the bonded water molecule protrudes (Figure 3). Thus, the two types of water molecules, present in **I**, are in the same channels. The amine molecules along with the water molecules occupy the channels. Thus, **I** is a truly three-dimensional structure possessing channels, along all the crystallographic directions.

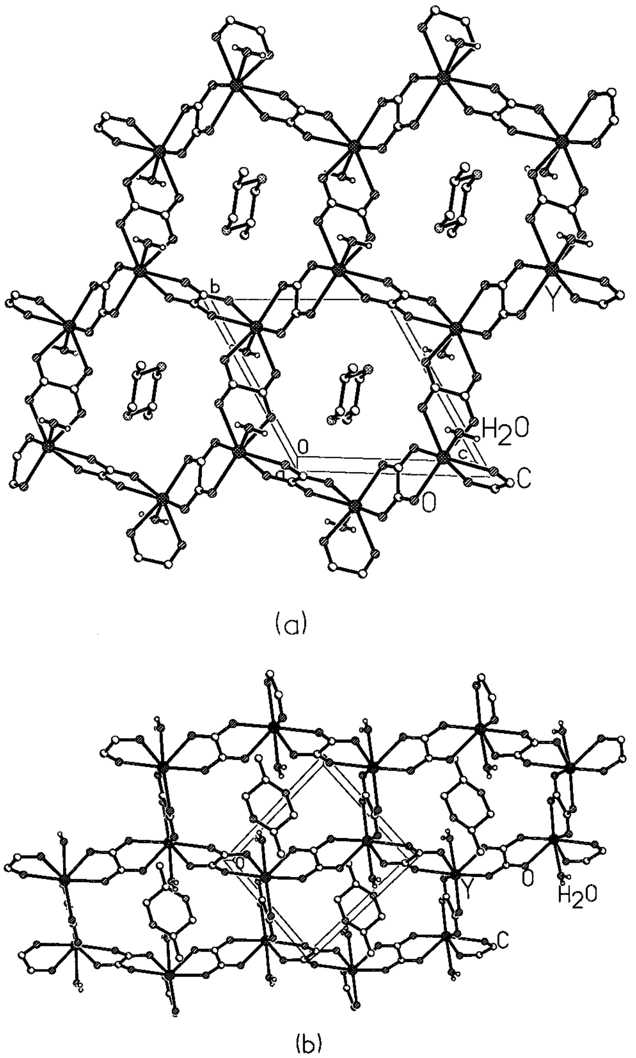

Figure 2. (a) Structure of **I** showing the honeycomb-like layers along the *a* axis. The layers are bridged by an oxalate unit, forming the channels. Hydrogens on the amine and the free water molecules are not shown. (b) Structure of **I** along the *c* axis showing the layer arrangement. The bound water molecules point into the 12-membered aperture. Hydrogens on the amine and the free water molecule are not shown.

$[C_5N_2H_{12}][Y(C_2O_4)_2]$, II. The asymmetric unit of **II** contains 20 non-hydrogen atoms (Figure 4a), of which 13 belong to the framework. The structure of **II** also consists of a network of Y and oxalate units. The Y atoms in **II** are coordinated to eight oxalate oxygens or four oxalate units. The coordination environment around yttrium is a distorted square-antiprismatic arrangement with respect to the oxygen atoms as depicted in Figure 4b. The framework structure of **II** can be understood in terms of simpler building units involving two-dimensional layers. Thus, three oxalate units link up with the Y atom in an in-plane manner, forming honeycomb-like layers with 12-membered apertures as shown in Figure 5. The fourth oxalate unit connects these layers in an out-of-plane manner, resulting in a 12-membered one-dimensional channel of width 7.1 × 8.2 Å along the *c* axis as shown in Figure 6. The channels in **II** occur only along one direction. The amine molecule present in the

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(11) Brown, I. D.; Aldermatt, D. *Acta Crystallogr., Sect. B* **1984**, *41*, 244.

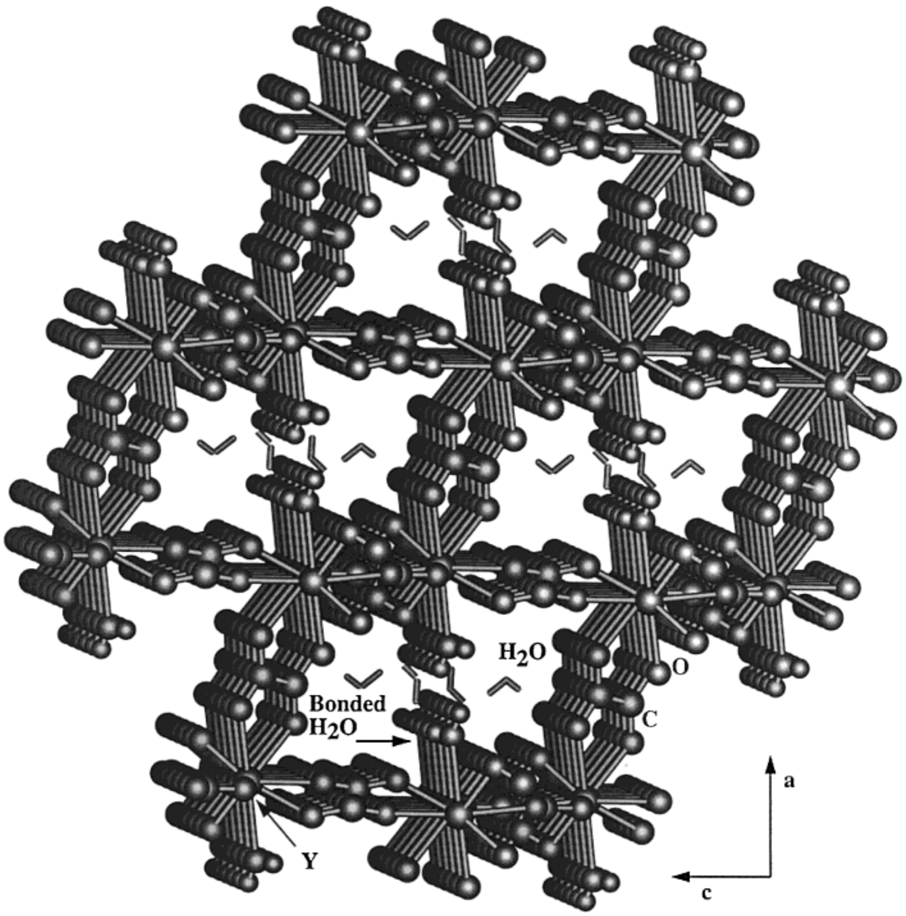

Figure 3. Structure of **I** along the *b* axis showing rectangular channels. The amine molecules are not shown. Note the close proximity between the bound water molecules.

channels is 2-methyl-3-4-5-6-tetrahydropyrimid-1-ene, resulting from the in situ reaction of 1,3-DAP with acetic acid.

The Y−O distances in **II** are in the range 2.303(11)−2.407(9) Å (average 2.363 Å) (Table 6). The O−Y−O and O−C−O bond angles are in the range 67.8(3)°−150.9(4)° (average 100.2°) and 123.9(13)°−129.6(12)° (average 126.7°), respectively (Table 7).

TGA studies of **I** and **II** were carried out in a nitrogen atmosphere from room temperature to 700 °C using a heating rate of 10°/C. The results are presented in Figure 7. In the case of **I** the mass loss occurs in three steps, whereas in **II** a single sharp mass loss is seen. In **I**, the mass loss in the range 100−200 °C of 9.8% corresponds to the loss of free water molecules (9.6%) and a continuous two-step mass loss of 54% in the 300−450 °C region corresponds to the loss of the bound water and carbon dioxide and amine molecules (calculated 58.4%). For **II**, a single sharp mass loss of 60% in the 425−550 °C range corresponds to the loss of carbon dioxide and the amine molecules (calculated 66%). The powder XRD patterns of the decomposed products indicated a poorly crystalline product with very weak reflections, which corresponds to yttrium oxide, Y_2O_3 (JCPDS: 25-1200).

Adsorption studies, carried out gravimetrically using a Cahn electric balance, show that a dehydrated sample of **I** adsorbs water and methanol reversibly. While the water adsorption exhibits a Langmuir type I adsorption isotherm, the methanol is of type VI (Figure 8). The observed weight changes at 25 °C correspond to 2 and 1 molecules of water and methanol per unit cell, respectively. The weight change observed with water is in agreement with the framework formula derived from the crystallographic study, indicating the structural integrity of the sample for reversible adsorption.

Discussion

Two new open-framework yttrium oxalates, $[C_6N_2H_{16}]_{0.5}[Y(H_2O)(C_2O_4)_2]\cdot 2H_2O$ (**I**) and $[C_5N_2H_{12}][Y(C_2O_4)_2]$ (**II**), which have been obtained as good quality single crystals by hydrothermal methods, are both members of a new family of framework solids with similar framework connectivities. Although both the materials involve bonding between the oxalate units and yttrium atoms, they exhibit distinct differences. In **I**, the connectivity leads to a three-dimensional architecture with channels along all the crystallographic axes; in **II** the channels are present in only one direction. In both cases, the amine molecules occupy the channels. Additionally, free and bound water molecules are also present in the channels of **I**.

The yttrium oxalates, **I** and **II**, are distinctly different from the open-framework Sn(II) and Zn oxalates reported in the last 2 years.[5,6] In the Sn(II) and Zn oxalates, the Sn and Zn atoms are 6-coordinated with respect to the oxalate oxygens, while in **I** and **II**, the Y atoms are 8-coordinated. The framework of the Sn(II) oxalates are layered and the Zn oxalates occur both as honeycomb layers and three-dimensional architectures.

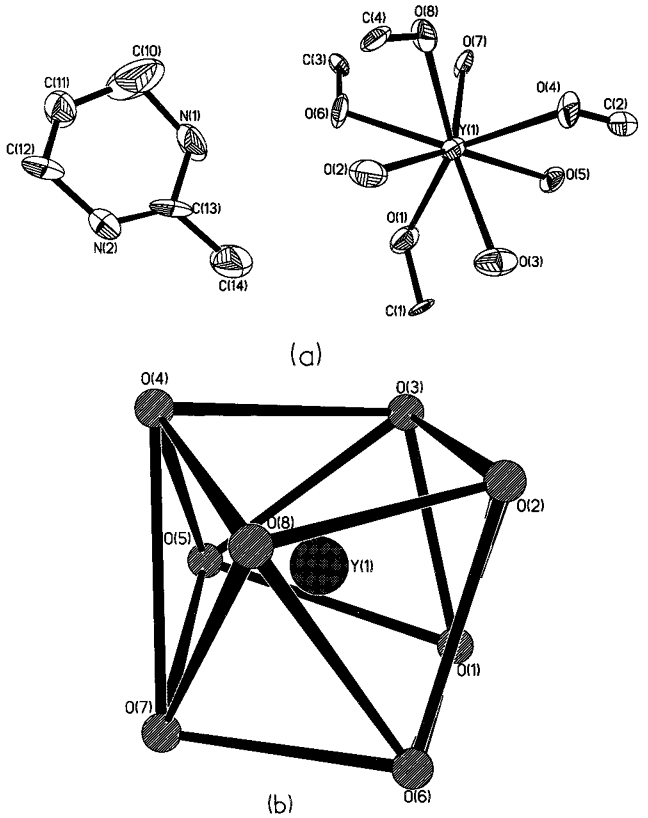

Figure 4. (a) ORTEP plot of **II**, $[C_5N_2H_{11}][Y(C_2O_4)_2]$. Thermal ellipsoids are given at 50% probability. (b) The coordination around the yttrium atom. Note that the oxygens form a square antiprismatic arrangement.

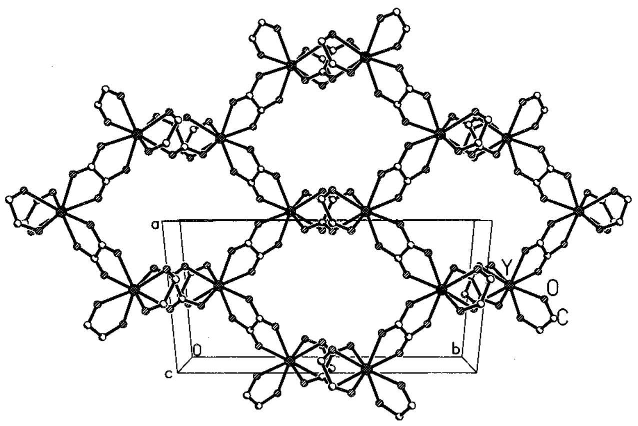

Figure 5. Structure of **II** along the *c* axis showing the layer arrangement. The amine molecules are not shown.

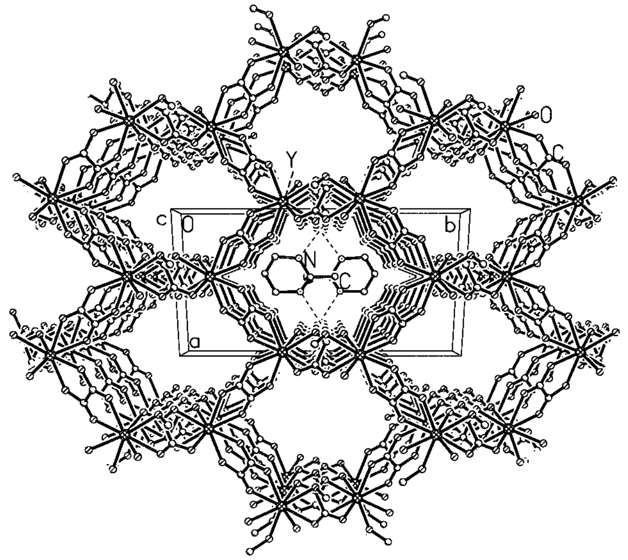

Figure 6. Structure of **II** along the *c* axis showing the 12-membered channels. The amine molecules are shown in only one channel. Hydrogens on the amines are not shown.

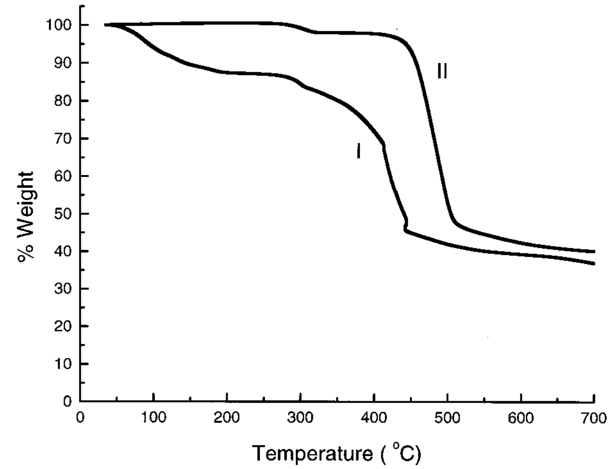

Figure 7. TGA curves of **I** and **II**.

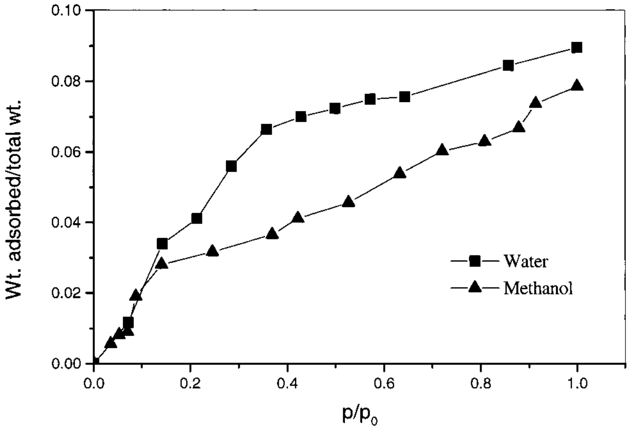

Figure 8. Room-temperature adsorption isotherms for H_2O and CH_3OH in a dehydrated sample of **I**.

The three-dimensional Zn oxalate structure results from the out-of-plane connectivity of one of the oxalate units.[6] In addition, the layered Sn(II) and Zn oxalates have 12-membered apertures within the layers, resulting from the linkage between M (M = Sn and Zn) and three oxalate units. In the present structures, however, the higher coordination of the Y atoms facilitates the formation of 12-membered apertures through the linkage of one Y atom with three oxalate units. These layers with apertures are then bridged by one additional oxalate moiety, giving rise to the observed three-dimensional structure with 12-membered channels. Such a connectivity is also reminiscent of the linkages observed in the recently discovered family of iron oxalate phosphates, which possess iron phosphate sheets cross-linked (out-of-plane) by oxalate units.[12]

It is noteworthy that the structures of **I** and **II** are somewhat related. There is also a superficial similarity

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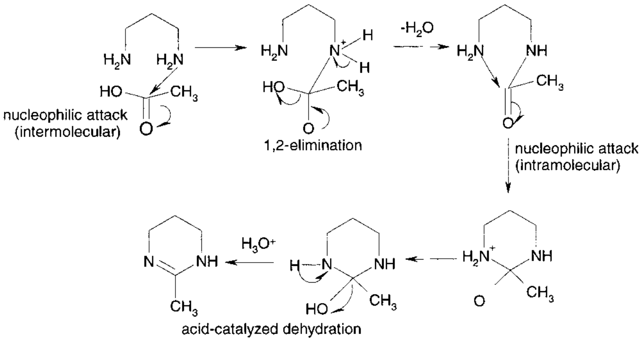
[12] (a) Choudhury, A.; Natarajan, S.; Rao, C. N. R. *Chem. Mater.* **1999**, *11*, 3216. (b) Choudhury, A.; Natarajan, S.; Rao, C. N. R. *Chem. Eur. J.* **2000**, *6*, 1168.

of the amines in **I** and **II** caused by the dynamic disorder of the amine in **I**. In **II**, the amine molecule, 2-methyl-3-4-5-6-tetrahydropyrimid-1-ene, is formed in situ by the reaction between 1,3-DAP and acetic acid. The formation of new types of amines under hydrothermal conditions has been observed before.[13] The formation of 2-methyl-3-4-5-6-tetrahydropyrimid-1-ene can be explained on the basis of nucleophilic attack followed by β-elimination as shown in the scheme shown here.



Conclusions

The present study shows that open-framework yttrium oxalates can be prepared hydrothermally in the presence of organic amines. This is the first time, to our knowledge, that yttrium oxalates with open architectures have been synthesized and characterized. Of the two oxalates described here, one has channels along all the crystallographic directions while the other has channels in only one direction. The three-dimensional nature of the channels in **I** is also reflected in its reversible adsorptive nature. The isolation and characterization of novel yttrium oxalates in the presence of amines suggests that it would be profitable to pursue this approach for the synthesis of other related oxalates.

Supporting Information Available: Tables of crystallographic data for **I** and **II** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] Chippindale, A. M.; Natarajan, S.; Thomas, J. M.; Jones, R. H. *J. Solid State Chem.* **1994**, *111*, 18.