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Polyhedron 22 (2003) 3037–3042

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Synthesis and X-ray structures of 2D coordination networks based on dinuclear and trinuclear vanadium oxo clusters

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Received 1 May 2002; accepted 17 July 2002

Abstract

Two new 2D coordination polymers $[V_2O_3(\text{nicotinate})_3]\cdot EtOH$ (**1**) and $[V_3O_5(\text{nicotinate})_4(H_2O)_2]\cdot 3H_2O$ (**2**) have been synthesized by treating V_2O_5 and nicotinic acid under hydro(solvo)thermal conditions. Compounds **1** and **2** adopt 2D framework structures built from dinuclear and trinuclear vanadium oxo clusters, respectively. Each $V_2O_3(\text{nicotinate})_3$ building unit in **1** is linked to four adjacent units to form a puckered 2D network, and the 2D sheets stack in an *ABAB* pattern to result in rectangular-shaped interlayer open channels that are occupied by included ethanol molecules. The $[V_3O_5(\text{nicotinate})_4(H_2O)_2]$ building unit in **2** is also linked to four adjacent trivanadium clusters to form a 2D rhombic coordination network. The 2D sheets in **2** adopt an *AA* stacking pattern, presumably steered by the $V2=O$ moieties, to afford interlayer open channels that are occupied by included water molecules.

Keywords: Solid-state; X-ray structures; 2D coordination networks; Vanadium oxo clusters

1. Introduction

The field of solid-state supramolecular chemistry has undergone revolutionary growth over the past decade [1]. The combination of organic bridging ligands and metallic nodes has allowed the synthesis of numerous polymeric coordination networks with diverse topologies and many potential exploitable functions such as second harmonic generation [2], magnetism [3], heterogeneous catalysis [4], and gas sorption and storage [5]. More recently, metal clusters have been shown to be excellent building blocks for the construction of many interesting coordination networks that exhibit unprecedented porosity and interesting magnetic properties [6,7]. In particular, Zubieta and co-workers [6] have extensively investigated the combination of vanadate and molybdate clusters and various organic spacers and have obtained a variety of interesting organic–inorganic hybrid materials. The incorporation of organic spacers into inorganic oxide phases has indeed provided a powerful method for structural as well as functional modification of these novel solid-state materials.

Our group has recently explored the synthesis of second-order nonlinear optical materials via the use of unsymmetrical pyridinecarboxylate bridging ligands [2,8]. As an extension of this work, we have examined the reactions of nicotinic acid and V_2O_5 with the hope of generating interesting organic–inorganic hybrid materials containing vanadate cluster building units and rigid nicotinate spacers. We wish to report here the synthesis and structural characterization of two novel 2D coordination polymers $[V_2O_3(\text{nicotinate})_3]\cdot EtOH$ (**1**) and $[V_3O_5(\text{nicotinate})_4(H_2O)_2]\cdot 3H_2O$ (**2**). Compounds **1** and **2** adopt 2D framework structures built from dinuclear and trinuclear vanadium oxo clusters, and possess open channels that are occupied by ethanol and water guest molecules, respectively.

2. Experimental

2.1. Materials and methods

All of the chemicals were purchased from Aldrich and used without further purification. The IR spectra were recorded from KBr pellets on a Perkin–Elmer Paragon 1000 FT-IR spectrometer.

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doi:10.1016/S0277-5387(03)00429-7

*2.2. Synthesis of [V_2O_3 (nicotinate)$_3$]· EtOH (**1**) and [V_3O_5 (nicotinate)$_4$ (H_2O)$_2$]·$3H_2O$ (**2**)*

A mixture of V_2O_5 (0.0450 g, 0.25 mmol), nicotinic acid (0.123 g, 1.0 mmol) was thoroughly mixed with ethanol (0.4 ml) and water (0.6 ml) in a heavy-walled Pyrex tube. The tube was frozen under liquid nitrogen, sealed, and placed inside an oven at 130 °C. After a week of heating, blue platy crystals were obtained along with unknown brown powder. After washing with copious amounts of water, blue crystals were obtained. Yield: 0.016 g (12.0%). IR (KBr, cm^{-1}): 3511 (w), 3129 (w), 2967 (w), 1625 (s), 1566 (s), 1401 (s), 1360 (s), 1317 (ms), 1194 (s), 1163 (ms), 1120 (w), 1049 (s), 1035 (ms), 983 (s), 954 (s), 851 (w), 841 (w), 765 (s), 707 (ms), 691 (s), 653 (ms), 613 (ms), 591 (ms), 491 (ms).

Compound **2** was obtained in trace amounts in the form of light-brown rod-shape single crystals from the above reaction.

2.3. X-ray collections and structure determination

X-ray single crystal data collections for compounds **1** and **2** were carried out on an Enraf-Nonius CAD4-Turbo diffractometer equipped with Cu Kα radiation and a Siemens SMART system equipped with a CCD detector and Mo Kα radiation. Both structures were solved by direct methods using SHELX-TL [9]. Of the 4070 (3730) unique reflections measured for **1** (**2**), 2241 (1733) reflections with $I > 2\sigma(I)$ were used in structure solution and refinements. All the non-hydrogen atoms of the framework structures in **1** were refined by full-matrix least squares using anisotropic displacement parameters, while the ethanol molecules were refined using isotropic displacement parameters. All the hydrogen atoms in **1** were located by idealized geometric placing. The V2 center, O8 and O10 atoms in **2** are disordered around a crystallographic inversion center with an occupancy factor of 0.5. All the non-hydrogen atoms in **2** were refined by full-matrix least squares using anisotropic displacement parameters, while all the hydrogen atoms were located in Fourier maps and refined using isotropic displacement parameters. Final refinement gave $R1 = 0.058$ (0.048), $wR2 = 0.138$ (0.073), and goodness-of-fit = 0.985 (0.842) for **1** (**2**). Experimental details for X-ray data collection of **1** and **2** are presented in Table 1, while selected bond distances and angles for **1** and **2** are listed in Table 2.

3. Results and discussion

3.1. Synthesis

Compound **1** was obtained as light blue platy crystals by a hydro(solvo)thermal reaction between V_2O_5 and nicotinic acid in a mixture of ethanol and water at 130 °C. Compound **2** was obtained as light-brown needle-like crystals as a very minor phase in the above reaction. The IR spectra of **1** and **2** show clearly the presence of carboxylate peaks as 1550 and 1400 cm^{-1} [10].

3.2. X-ray single crystal structure of **1**

A single crystal X-ray diffraction study revealed that **1** is a complex 2D rhombohedral network and crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit consists of two vanadium centers, three nicotinate ligands, two terminal and one bridging oxygen atoms, and one ethanol guest molecule (Fig. 1). There are two coordination modes for the three bridging nicotinate groups: two of them adopt an *exo*-tridentate

Table 1
Crystallographic data for compounds **1** and **2**

Compound	**1**	**2**
Empirical formula	$V_2C_{20}H_{19}N_3O_{10}$	$V_3C_{24}H_{26}N_4O_{18}$
Formula weight	563.26	811.31
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	11.121(3)	11.037(1)
b (Å)	10.747(3)	10.632(1)
c (Å)	19.787(4)	14.252(2)
β (°)	104.86(3)	111.998(2)
V (Å^3)	2285.6(8)	1550.7(2)
Z	4	2
T (°C)	25	−75
λ	1.54178 (Cu Kα)	0.71073 (Mo Kα)
ρ_{calc} (g/cm^3)	1.64	1.74
μ (cm^{-1})	74.2	9.74
$R1$	0.058	0.048
$wR2$	0.138	0.073
Goodness-of-fit	0.985	0.842
Min. and max. residual densities (e/Å^3)	−0.52, 0.90	−0.35, 0.49

Table 2
Selected bond distances (Å) and angles (°) for compounds **1** and **2**

1[a]		**2**[b]	
Bond distances			
V1–O7	1.614(4)	V1–O1	1.592(3)
V1–O9	1.957(4)	V1–O5	1.965(2)
V1–O2	2.040(4)	V1–O3	1.996(2)
V1–N3B	2.157(5)	V1–N2A	2.154(2)
V1–O4	2.160(4)	V1–O6	2.028(2)
V1–N1A	2.176(5)	V1– O2	2.231(3)
V2–O8	1.585(4)	V2–O8	1.56(2)
V2–O9	1.975(4)	V2–O5	1.932(3)
V2–O5	2.008(4)	V2–O7	2.073(3)
V2–O1	2.033(4)	V2–O5B	2.020(2)
V2–N2C	2.159(5)	V2–O7B	2.025(3)
V2–O3	2.249(4)		
Bond angles			
O7–V1–O9	102.3(2)	O1–V1–O5	102.8(2)
O7–V1–O2	95.7(2)	O1–V1–O3	99.3(2)
O9–V1–O2	92.8(2)	O5–V1–O3	90.98(9)
O7–V1–N3B	92.1(2)	O1–V1–O6	96.1(2)
O9–V1–N3B	89.2(2)	O5–V1–O6	91.27(9)
O2–V1–N3B	171.5(2)	O3–V1–O6	163.6(1)
O7–V1–O4	170.9(2)	O1–V1–N2A	93.8(2)
O9–V1–O4	86.0(2)	O5–V1–N2A	163.5(2)
O2–V1–O4	87.5(2)	O3–V1–N2A	87.0(1)
N3B–V1–O4	84.4(2)	O6–V1–N2A	86.2(1)
O7–V1–N1A	90.7(2)	O1–V1–O2	174.0(2)
O9–V1–N1A	166.9(2)	O5–V1–O2	83.1(2)
O2–V1–N1A	87.3(2)	O3–V1–O2	81.8(2)
N3B–V1–N1A	88.9(2)	O6–V1–O2	82.3(2)
O4–V1–N1A	80.9(2)	O2–V1–N2A	80.3(2)
O8–V2–O9	101.6(2)	O8–V2–O5	107.3(8)
O8–V2–O5	102.1(2)	O8–V2–O5B	105.6(8)
O9–V2–O5	89.8(2)	O5–V2–O5B	147.05(8)
O8–V2–O1	96.1(2)	O8–V2–O7B	107.3(5)
O9–V2–O1	90.3(2)	O5B–V2–O7	83.0(1)
O5–V2–O1	161.3(2)	O5B–V2–O7B	89.2(1)
O8–V2–N2C	93.0(2)	O8–V2–O7	104.4(5)
O9–V2–N2C	165.5(2)	O5–V2–O7	90.3(1)
O5–V2–N2C	86.9(2)	O5–V2–O7B	79.7(1)
O1–V2–N2C	88.3(2)	O7–V2–O7B	148.2(1)
O8–V2–O3	171.9(2)		
O9–V2–O3	85.9(2)		
O5–V2–O3	80.8(2)		
O1–V2–O3	80.5(2)		
N2C–V2–O3	79.6(2)		

[a] Symmetry transformations: $A = 1 - x, -y, -z$; $B = 2.5 - x, 1.5 + y, 0.5 - z$; $C = 2.5 - x, 2.5 + y, 0.5 - z$.
[b] Symmetry transformations: $A = 1.5 - x, -0.5 + y, 1.5 - z$; $B = 1 - x, 3 - y, 2 - z$.

linkage with a coordinating pyridyl group and μ_2, η^2-carboxylate bridge, while the other one adopts an *exo*-bidentate linkage with a coordinating pyridyl group and monodentate carboxylate group. The V1 center coordinates to a terminal oxygen atom with a V1–O7 distance of 1.614(4) Å, to one bridging oxygen atom with a V1–O9 distance of 1.957(4) Å, to two oxygen atoms of two different μ_2, η^2-carboxylate groups (O2 and O4), and to two pyridyl nitrogen atoms of the nicotinate groups. The V1 center adopts a distorted octahedral geometry with the *cis* angles ranging from 80.9(2)° to 102.3 (2)°. The V2 center coordinates to a terminal oxygen atom with a V2–O8 distance of 1.585(4) Å, to one bridging oxygen atom with a V2–O9 distance of 1.975(4) Å, to an oxygen atom of the monodentate carboxylate group (O5), to two oxygen atoms of two different μ_2, η^2-carboxylate groups (O1 and O3), and to one pyridyl nitrogen atom of a nicotinate group. The V2 center also adopts a distorted octahedral geometry with the *cis* angles ranging from 79.6(2)° to 102.1 (2)°. The separation between the two vanadium centers is 3.54 Å, while the V1–O9–V2 angle is 128°.

Each V_2O_3(nicotinate)$_3$ building unit in **1** is linked to four adjacent units to form a 2D puckered sheet (Fig. 2).

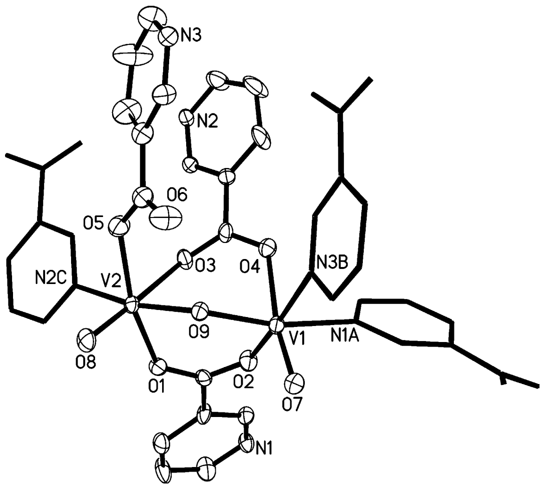

Fig. 1. Coordination environment of **1**. The asymmetric unit (excluding ethanol) is shown with ellipsoids at 50% probability.

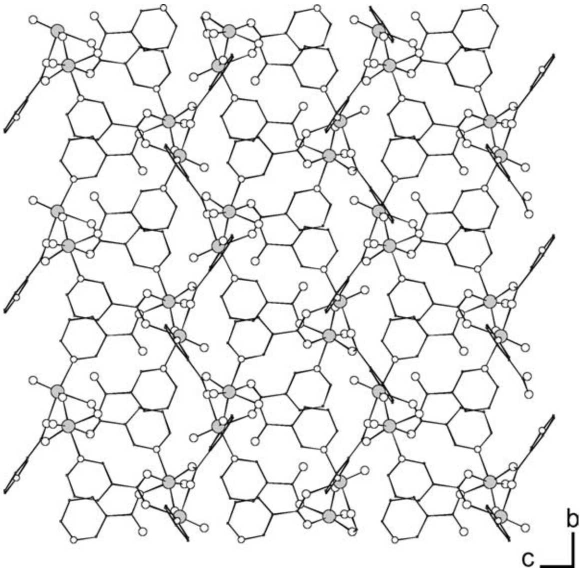

Fig. 2. A view of 2D sheet of V_2O_3(nicotinate)$_3$ in **1** down the *a* axis. The circles with decreasing sizes represent V, O, N, and C, respectively.

There exist three different kinds of bridges for the linking of V_2O_3(nicotinate)$_3$ building units: two single bridges formed by *exo*-tridentate nicotinate groups, one double bridge formed by *exo*-tridentate nicotinate groups, and one double bridge formed by *exo*-bidentate nicotinate groups. The puckered nature of the 2D sheets of **1** can be clearly shown with a view of **1** down the *b* axis (Fig. 3(a)). Interestingly, the V_2O_3(nicotinate)$_3$ layers in **1** adopt a *ABAB* stacking pattern in the *ac* plane, and adjacent layers have been shifted by 6.35 Å to result in rectangular-shaped open channels which are occupied by the ethanol molecule (Fig. 3(b)). The vanadium centers in **1** are on average in a +4.5 oxidation state.

3.3. X-ray single crystal structure of 2

A single crystal X-ray diffraction study reveals that **2** also adopts a 2D framework structure and crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit

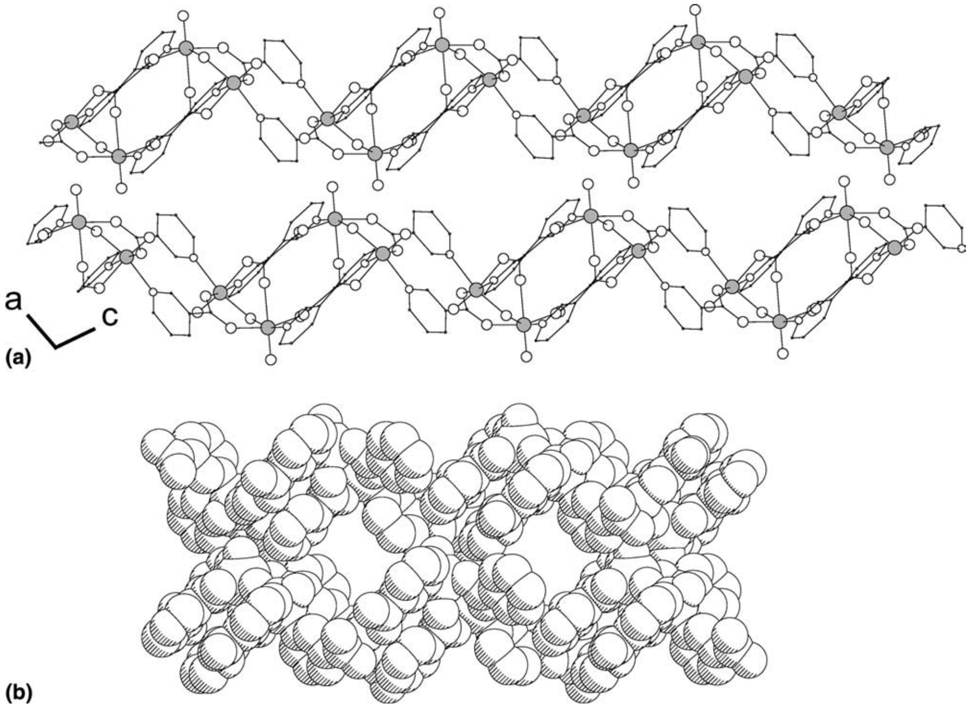

Fig. 3. (a) A view of 2D puckered sheet of **1** down the *b* axis. (b) A space-filling model showing the open channels formed between the 2D layers in **1**. These open channels are occupied by ethanol molecules which have been removed for clarity.

consists of one and a half vanadium atoms, one and a half terminal oxygen atoms, one bridging oxygen atom, two nicotinate groups, one coordinating water molecule, and one and a half included water guest molecules (Fig. 4). One of the nicotinate groups adopts an *exo*-tridentate linkage with a coordinating pyridyl group and μ_2, η^2-carboxylate bridge, whereas the other nicotinate group only coordinates to a vanadium center (V1) through its monodentate carboxylate group. The V1 center is coordinated to an oxygen atom of the monodentate carboxylate group, an oxygen atom of the *exo*-tridentate μ_2, η^2-carboxylate group, one pyridyl nitrogen atom, a bridging oxygen atom (V1–O5 distance of 1.96 Å), a terminal oxygen atom (V1–O1 distance of 1.59 Å), and a water molecule (V1–O2 distance of 2.23 Å). The V1 center adopts a distorted octahedral geometry with the *cis* angles ranging from 80.3(2)° to 102.8(2)°. The V2 center coordinates to two oxygen atoms of two different μ_2, η^2-carboxylate group, two bridging oxygen atoms, and one terminal oxygen atom with a V2–O8 distance of 1.56(2) Å. The V2 center adopts a distorted square pyramidal coordination geometry with the terminal oxygen atom at the apical position. The V centers in **2** are on average in a +4.667 oxidation state.

Each V2 center in **2** is connected to two neighboring V1 centers via two bridging oxo groups and two μ_2, η^2-carboxylate groups to form the [V_3O_5(nicotinate)$_4$(H_2O)$_2$] building unit (Fig. 4). Each [V_3O_5(nicotinate)$_4$(H_2O)$_2$] building unit is then linked to four adjacent trivanadium units through four *exo*-tridentate nicotinate groups to form a 2D rhombic coordination network (Fig. 5). It is interesting to note that the

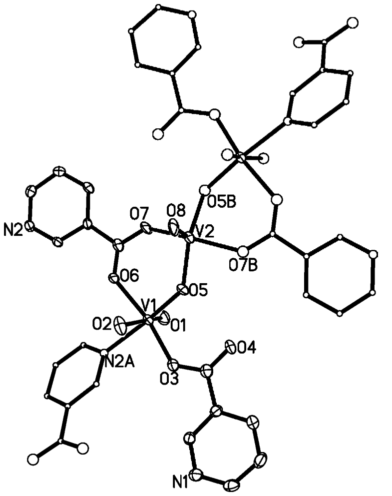

Fig. 4. Coordination environment of **2**. The asymmetric unit (excluding water guest molecules) is shown with ellipsoids at 50% probability.

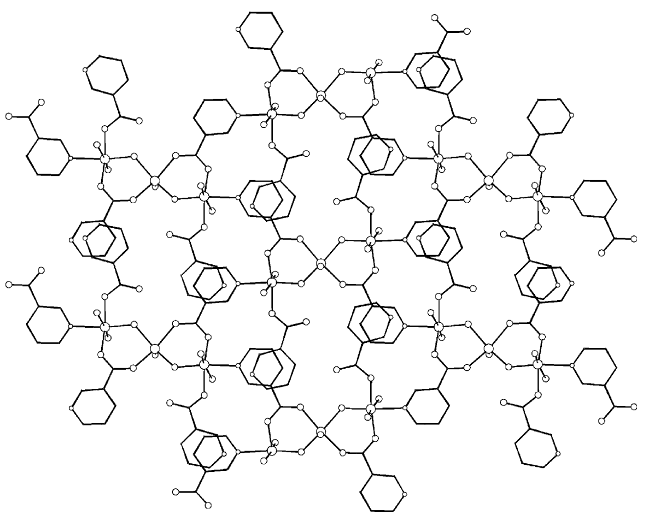

Fig. 5. A view of 2D framework of **2** built from the [V_3O_5(nicotinate)$_4$(H_2O)$_2$] building units. The π–π stacking interactions between the *exo*-tridendate and monodentate nicotinate groups are clearly evident.

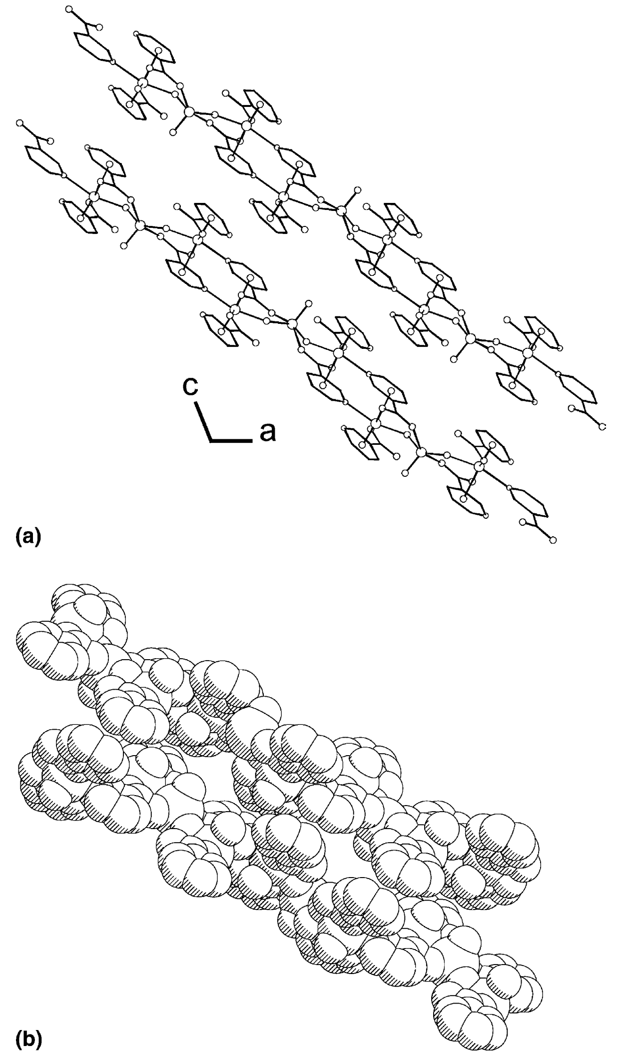

Fig. 6. (a) Stacking of 2D sheets of [V_3O_5(nicotinate)$_4$(H_2O)$_2$] of **2** as viewed down the *b* axis. (b) A space-filling model of **2** as viewed down the *b* axis. Open channels formed between 2D layers are occupied by water guest molecules.

dangling (non-coordinating) pyridyl rings of the nicotinate groups form strong π–π stacking interactions with the pyridyl rings of the *exo*-tridentate nicotinate groups with a centriod-to-centroid distance of 3.576(5) Å. The 2D sheets of **2** adopt an *AA* stacking pattern, presumably steered by the V2 = O moieties which adopt an alternate up-down orientation among adjacent rows in the same layer but are pointing at the same direction among different layers (Fig. 6(a)). A space-filling model indicates that open channels also form between adjacent layers in **2**; these open channels are occupied by water guest molecules. There exist extensive hydrogen bonding interactions in **2**. The water guest molecule O9 forms a strong hydrogen bond with the V2 = O moiety with an O8–O9 distance of 2.84(1) Å and an O9–H9B–O8 angle of 164.7(1)°. The water molecule O9 also forms a hydrogen bond with non-coordinating carboxylate oxygen atom O4 with an O4–O9 distance of 2.84(1) Å and an O9–H9A–O4 angle of 171.4(1)°. The coordinating water molecule O2 forms a hydrogen bond with non-coordinating pyridyl nitrogen atom N1 with an O2–N1 distance of 2.79(1) Å and an O2–H2B–N1 angle of 167.3(1)°.

In summary, we have synthesized and structurally characterized two new 2D coordination polymers based on dinuclear and trinuclear vanadium oxo clusters as secondary building units and nicotinate groups as the bridging ligands. Both **1** and **2** adopt open framework structures with their open channels occupied by ethanol and water guest molecules, respectively. This work thus supports previous observations that porous coordination networks can be constructed using metal-containing secondary building units and rigid bridging ligands [6,7].

Acknowledgements

We acknowledge NSF (CHE-9875544) for financial support. We also thank Dr. Scott R. Wilson at University of Illinois at Urbana-Champaign and Professor Bruce M. Foxman at Brandeis University for X-ray data collections. We thank Dr. R. Xiong for help with initial experiments. W.L. is an Alfred P. Sloan Fellow, an Arnold and Mabel Beckman Young Investigator, a Cottrell Scholar of Research Corporation, and a Camille Dreyfus Teacher-Scholar.

References

[1] (a) M. Munakata, L.P. Wu, T. Kuroda-Sowa, Adv. Inorg. Chem. 46 (1999) 173;
(b) M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 34 (2001) 319;
(c) M.J. Zaworotko, B. Moulton, Chem. Rev. 101 (2001) 1629;
(d) S.R. Batten, R. Robson, Angew. Chem., Int. Ed. Engl. 37 (1998) 1461.

[2] O.R. Evans, W. Lin, Acc. Chem. Res. 35 (2002) 511.

[3] (a) J.R. Galan-Mascaros, K.R. Dunbar, Chem. Commun. (2001) 217;
(b) J.S. Miller, Inorg. Chem. 39 (2000) 4392.

[4] (a) J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim, Nature 404 (2000) 982;
(b) O.R. Evans, H.L. Ngo, W. Lin, J. Am. Chem. Soc. 123 (2001) 10395.

[5] M. Kondo, M. Shimamura, S.-i. Noro, S. Minakoshi, A. Asami, K. Seki, S. Kitagawa, Chem. Mater. 12 (2000) 1288.

[6] (a) J. Kim, B. Chen, T.M. Reineke, H. Li, M. Eddaoudi, D.B. Moler, M. O'Keeffe, O.M. Yaghi, J. Am. Chem. Soc. 123 (2001) 8239;
(b) P.J. Hagrman, D. Hagrman, J. Zubieta, Angew. Chem., Int. Ed. Engl. 38 (1999) 2638.

[7] (a) M.P. Shores, L.G. Beauvais, J.R. Long, J. Am. Chem. Soc. 121 (1999) 775;
(b) M.V. Bennett, M.P. Shores, L.G. Beauvais, J.R. Long, J. Am. Chem. Soc. 122 (2000) 6664.

[8] (a) W. Lin, O.R. Evans, R.-G. Xiong, Z. Wang, J. Am. Chem. Soc. 120 (1998) 13272;
(b) W. Lin, Z. Wang, L. Ma, J. Am. Chem. Soc. 121 (1999) 11249;
(c) O.R. Evans, R.-G. Xiong, Z. Wang, G.K. Wong, W. Lin, Angew. Chem., Int. Ed. Engl. 38 (1999) 536;
(d) W. Lin, L. Ma, O.R. Evans, Chem. Commun. (2000) 2263.

[9] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Refinement, Universität Göttingen, Germany, 1997.

[10] R.C. Mehrotra, R. Bohra, Metal Carboxylates, Academic Press, New York, 1983.