Mesoporous Vanadoborates

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Construction of Mesoporous Frameworks with Vanadoborate Clusters**

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Dedicated to Professor Xiaodong Zou on the occasion of her 50th birthday

Abstract: *A new porous vanadoborate was synthesized by employing the scale chemistry theory with the vanadoborate cluster $V_{10}B_{28}$. The twofold interpenetrated **lvt** network was assembled with zinc-containing elliptical vanadoborate clusters and Zn polyhedra. The single **lvt** framework contains a three-dimensional $38\times38\times20$ ring channel system with the pore size (24.7×12.7 Å) reaching the mesoscale, thus indicating the possibility of constructing 3D ordered mesopores with vanadoborate clusters. The porosity of the SUT-7 structure was confirmed by CO_2 adsorption of the as-synthesized materials.*

Crystalline inorganic materials including micro- or/and mesopores are of great importance because of their diverse channel systems and wide applications in adsorption, catalysis, and separation.[1–4] Mesoporous crystalline materials with a channel size above 2 nm are of special interest as the enlargement of the pores can enhance the diffusion of large organic molecules into the pores when the materials are used as catalysts or supports. However, there are only a few inorganic examples reported with such mesopores, such as ITQ-43[5] (a 28-ring germanium silicate), SU-M,[6] JLG-12[7] (a 30-ring germanate), ITQ-37[8] (a 30-ring germanium silicate), and NTHU-13,[9] a series of gallium zincophosphites with ring sizes from 24-ring to 72-ring. Compared to the metal–organic frameworks (MOFs), where the pore size can be expanded and designed in a more rational way through reticular chemistry[4,10] or modular chemistry,[11,12] the expansion of the pore size in the inorganic crystalline materials is much slower. Several strategies[9,13] have been proposed to circumvent this challenge. Müller et al.[14] and Khan[15] introduced linkages between isolated cluster compounds to create porosity, while Férey[16,17] proposed the scale chemistry method and predicted that the larger the structure building unit (SBU), the larger the pores. Very recently, Wang and coworkers[9] demonstrated that the channels in the phosphate framework can be successfully expanded by using templates with longer carbon chains. Of these three strategies, the first two are very successful with cluster-based building units, such as the germanates.[7,18]

Vanadoborates are interesting compounds assembled from vanadoborate clusters. Four types of vanadoborate clusters and their derivatives with different connections of VO_5 and BO_3/BO_4 polyhedra are mainly reported: V_6B_{20},[19,20] $V_{10}B_{28}$,[21,22] $V_{12}B_{18}$,[23–25] and $V_{12}B_{16}$[23,26,27] (Figure 1). Although these clusters were discovered decades ago, few 3D framework structures have been reported in which they were used as building units.[27,28] In our previous study, we succeeded in linking $V_{12}B_{18}$ to form the 3D framework SUT-6.[29] The $V_{12}B_{18}$ cluster in SUT-6 has D_{3d} point-group symmetry and prefers a six-coordinated net (**hxg** in SUT-6). This high coordination number of $V_{12}B_{18}$ makes its surround-

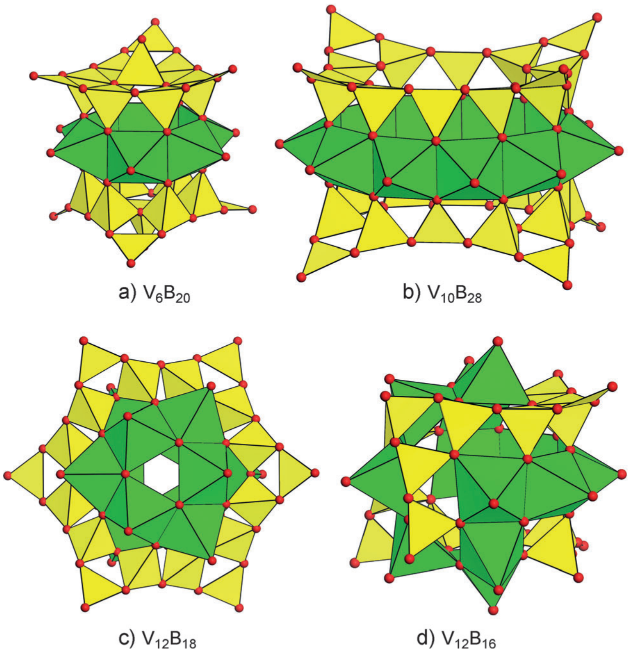
a) V_6B_{20} b) $V_{10}B_{28}$ c) $V_{12}B_{18}$ d) $V_{12}B_{16}$

Figure 1. Four typical vanadoborate clusters: a) V_6B_{20}, b) $V_{10}B_{28}$, c) $V_{12}B_{18}$, and d) $V_{12}B_{16}$. All clusters consist of edge-shared VO_5 square pyramids, BO_3 triangles, and BO_4 tetrahedra. Color scheme: red, oxygen; yellow, boron; green, vanadium.

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ings very crowded and results in small pores in SUT-6. Inspired by this observation and the scale chemistry strategy, we chose the largest vanadoborate cluster $V_{10}B_{28}$ as the structure building unit to build 3D frameworks. $V_{10}B_{28}$ has D_{2h} point-group symmetry and acts as a four-coordinated node, which could facilitate the formation of mesopores in the SUT-7 framework.

SUT-7 was synthesized hydrothermally from a mixture of $NH_4B_5O_{10}\cdot4H_2O$ (4.6 mmol), NH_4VO_3 (1.8 mmol), H_3BO_3 (9.2 mmol), $Zn(NO_3)_2\cdot6H_2O$ (2 mmol), $NH(CH_2CH_2CH_2NH_2)_2$ (14 mmol), and H_2O (110 mmol) in a molar ratio of about 1:0.4:2:0.43:3:110. The mixture was sealed in a 23 mL stainless-steel autoclave with a teflon tube, heated at 180 °C for 7 days, and then cooled to room temperature in air. Green block crystals (see Figure S1a in the Supporting Information) of SUT-7 were recovered by filtration (yield: 82 %, based on NH_4VO_3). Similar to the synthesis of SUT-6, the amount of amine plays an important role in the formation of SUT-7. Keeping all other parameters fixed under the optimized conditions, a high yield of pure SUT-7 was only obtained when the amount of amine was between 12 mmol and 16 mmol. In addition, the Zn/V ratio was found to be even more crucial for the synthesis of SUT-7. We studied its influence over the range of 1:18 to 3:1, with the total amount of zinc and vanadium fixed at about 3.8 mmol. These experiments resulted in the formation of two more phases. When the Zn/V ratio was 1:18, a zero-dimensional structure, **VB-5**, with $V_{12}B_{18}$ clusters (see Figure S2a in the Supporting Information) was obtained. Increasing the Zn/V ratio to 4:15 resulted in the formation of another zero-dimensional structure, **VB-6**, with both $[Zn(H_2O)_2]_2V_{12}B_{18}$ (see Figure S2b in the Supporting Information) and $V_{12}B_{18}$ clusters. Further increasing the Zn/V ratio from 7:12 to 3:2 resulted in the formation of SUT-7 with $V_{10}B_{28}$ clusters, thus indicating that a sufficient amount of Zn was required for the formation of SUT-7. Note that the Zn atoms not only worked as the bridging polyhedral, but also facilitated the formation of the $V_{10}B_{28}$ clusters; no $V_{10}B_{28}$ cluster was formed with lower amounts of Zn.

Single-crystal X-ray diffraction studies on SUT-7 shows it crystallizes in the $P4_2/nnm$ space group with $a = 26.7659(1)$ Å and $c = 14.7911(2)$ Å. The SUT-7 framework is mainly constructed from $(V_{10}B_{28}O_{74}H_8)^{8-}$ clusters (Figure 1 b), which are frequently found in the reported vanadoborates. The $V_{10}B_{28}$ cluster consists of an edge-shared V_{10} ring sandwiched by two B_{14} rings. Inside the ellipsoidal cavity of the $V_{10}B_{28}$ cluster, there is a $Zn_4(BO_3H_2)$ unit (Figure 2 a), and these tetrahedrally coordinated Zn atoms assisted the formation of the $V_{10}B_{28}$ cluster.[22] Outside the $V_{10}B_{28}$ cluster, there are an additional four five-coordinated Zn atoms, which further link the clusters into a 3D framework, as discussed below.

The 3D framework of SUT-7 can be clearly shown by using rectangles to represent the $V_{10}B_{28}$ clusters, where the corners of the rectangle are located at the ZnO_5 polyhedra and the long/short edges represent five/four polyhedra (Figure 2 a). Although there are thousands of networks with four-coordinated nodes, only a very few of them, such as **nbo**, **rhr**, and **lvt**, are regular or semiregular nets with planar four-coordinated nodes. Both **rhr** and **lvt** fit the rectangular shape of $V_{10}B_{28}$ clusters, and our structure turns out to have an interpenetrated **lvt** net (i.e. the **lvt-c** net in Figure 2 b,c) with the optimum symmetry. **lvt** is actually a relatively common semiregular net for metal–organic frameworks[30,31] and pure organic compounds,[32] but SUT-7 is the first example of an inorganic microporous material, as far as we know.

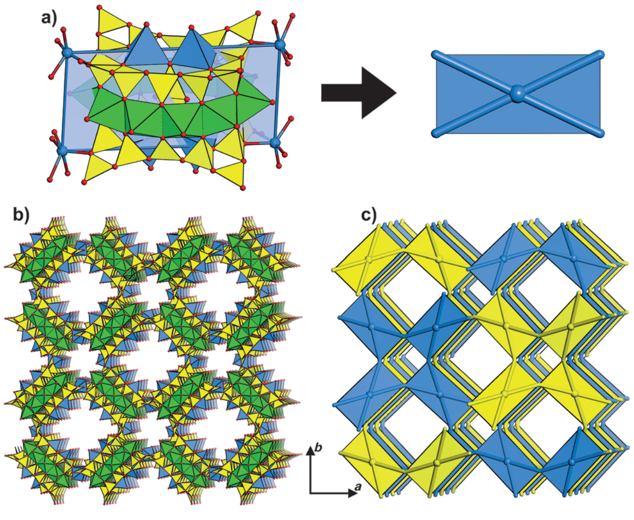

Figure 2. Cluster and 3D structure of SUT-7. a) The $V_{10}B_{28}$ cluster with a $Zn_4(BO_3H_2)$ unit inside and four ZnO_5 polyhedra outside can be abstracted into a rectangle; b) the 3D framework structure of SUT-7; c) the structure of SUT-7 is represented by two interpenetrated **lvt** nets with nodes shown as rectangles (in blue and yellow), that is, the **lvt-c** net.

A single **lvt** net contains mainly two types of rings: 4-rings and 8-rings. After being decorated by $V_{10}B_{28}$ in SUT-7, they become 16-rings and 38-rings (see Figure S3 in the Supporting Information). Considering that an oxygen atom has a diameter of 2.7 Å, the 16-ring has a size of 3.3 × 3.3 Å, which is almost blocked because of the oxygen atoms pointing into the pores. This 16-ring can only be observed along the [001] direction (Figure 3 a,b). The 38-ring has a mesoscale pore opening, that is, 24.7 × 12.7 Å, which is the largest so far for vanadoborates. The single **lvt** net of SUT-7 based on the 38-rings contains a 3D channel system, which was viewed along different directions (Figure 3). When two **lvt** nets were interpenetrated by shifting half of the *c*-axis, the channel system formed by the 38-rings along the [110] and [101] directions were almost blocked (see Figure S4 in the Supporting Information), while the large channels along the [001] direction were maintained with a pore opening of 6.0 × 9.5 Å.

The porosity of the as-synthesised SUT-7 was tested by the adsorption of N_2 and CO_2. No N_2 uptake was observed at 77 K; however, it shows CO_2 uptake at 273 K. The surface area of the as-synthesised SUT-7 was $143\,m^2g^{-1}$ ($230.5\,m^2cm^{-3}$), as calculated from the CO_2 isotherm by the Dubinin–Radushkevich method (see Figure S5 in the Supporting Information). There are two main possible reasons for the difference in the N_2 and CO_2 adsorption. One possible explanation is that CO_2 has a smaller kinetic diameter than N_2 (3.3 versus 3.6 Å), and if the organic templates are not thoroughly removed, the pores are so narrow that only CO_2 can diffuse into them. The difference in the temperature of

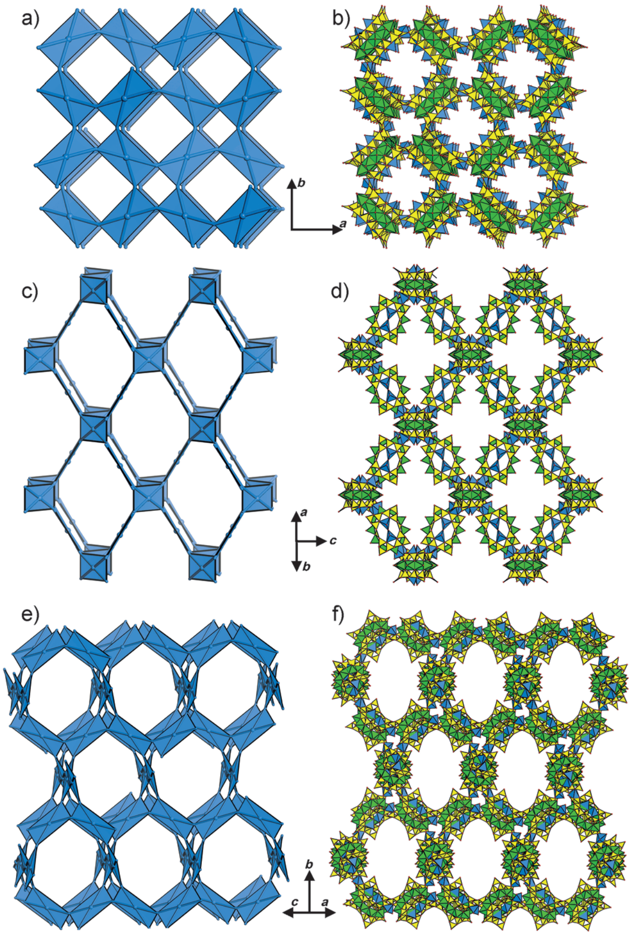

Figure 3. Channel system of the single **lvt** net in SUT-7. a,b) Views along the [100] direction; c,d) views along the [110] direction; e,f) views along the [101] direction. Each $V_{10}B_{28}$ cluster in (a), (c), and (e) is presented as a rectangle for a clear view of the channel system.

the measurements must also be considered. The N_2 adsorption was carried out at 77 K, while CO_2 uptake was measured at 273 K. The diffusion of a gas is also better at a higher temperature. When the pores are densely filled with organic compounds, an inverse (unusual) temperature dependency might also be observed.[33] The in situ IR spectroscopic measurements also confirmed that there are both physisorbed and chemisorbed CO_2 molecules in the as-synthesised SUT-7 (see Figure S6 in the Supporting Information). Note that the broad IR band observed is not similar to the bands for carbamate formation on materials modified with propylamine groups.[34] The formation of the unknown chemical bonds indicated by this broad band is partially responsible for the irreversible CO_2 adsorption of SUT-7 (see Figure S7 in the Supporting Information).

In conclusion, a three-dimensional open framework vanadoborate SUT-7 was successfully synthesized by using the scale chemistry strategy. SUT-7 shows a rare twofold interpenetrated **lvt** net. The 3D 38 × 38 × 20 ring channel system of the single **lvt** net represents the largest ring size in vanadoborates materials. The key factors for the synthesis of SUT-7 were studied carefully by systematic experiments, which indicate that the amount of template and Zn/V ratio are very important. The structure of SUT-7 indicates that the use of bigger building blocks with a smaller number of neighboring clusters could be a good strategy to build crystalline ordered mesoporous frameworks. The CO_2 adsorption experiment confirmed the porosity of as-synthesized SUT-7.

Experimental Section

Materials: Ammonium metavanadate (99 %, Sigma–Aldrich), boric acid (99.5 %, Sigma–Aldrich), ammonium pentaborate octahydrate (99 %, Sigma–Aldrich), bis(3-aminopropyl)amine (98 %, Sigma–Aldrich), and $Zn(NO_3)_2\cdot 6H_2O$ (98 %, Sigma–Aldrich) were used without further purification; the bis(3-aminopropyl)amine (BAPA) was melted to enable measurement by volume.

Synthesis: Optimized synthesis condition for the synthesis of SUT-7: A mixture of $NH_4B_5O_{10}\cdot 4H_2O$ (1.2650 g, 4.6 mmol), NH_4VO_3 (0.2106 g, 1.8 mmol), H_3BO_3 (0.5686 g, 9.2 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (0.5950 g, 2 mmol), $NH(CH_2CH_2CH_2NH_2)_2$ (1.96 mL, 14.0 mmol), and H_2O (9.2 mL) in a molar ratio of about 1:0.4:2:0.43:3:110 was sealed in a 23 mL stainless-steel autoclave with a teflon tube, heated at 180 °C for 7 days, and then cooled to room temperature in air. Green block crystals (see Figure S1a in the Supporting Information) of SUT-7 were recovered by filtration, washed with distilled water, and dried in air (yield: 82 %, based on NH_4VO_3). After further investigation of the experimental conditions, it was found that SUT-7 can also be obtained in low yield without boric acid, while only lower dimensional compounds were formed without $NH_4B_5O_8\cdot 4H_2O$. The amount of BAPA was not only used to control the pH value in the H_3BO_3/BAPA buffer but also used as a template during the formation of the framework.

Single-crystal X-ray diffraction: Single-crystal X-ray diffraction data were collected at 100 K on an Oxford Diffraction Xcalibur 3 diffractometer, with $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data reduction was performed using the CrysAlisPro program,[35] and Gaussian adsorption correction was applied. The structure was solved by direct methods. Non-hydrogen atoms were located directly from difference Fourier maps. Final structure refinements were performed with the SHELX program[36,37] by minimizing the sum of the squared deviation of F^2 using a full-matrix technique. The high symmetry and large pore sizes of SUT-7 as well as disorders of the templates and water molecules in the pores precluded the location of these guest molecules in the channel. The PLATON/SQUEESE program[38] was used to remove scattering contributions from disordered guest molecules and to produce solvent-free diffraction intensities, which were used in the final structure refinement. CCDC 985772, 985773, and 985774 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

CO_2 adsorption**:** Adsorption and desorption isotherms of N_2 and CO_2 were measured using a Micromeritics ASAP2020 device. N_2 adsorption was measured at 77 K. Volumetric uptake of CO_2 under equilibrium conditions was measured at 273.15 K from 0.1 Torr to atmospheric pressure. Prior to the adsorption measurements, the sample was treated under dynamic vacuum conditions at 353 K for 10 h.

In situ IR spectroscopy: A Varian 670-IR spectrometer equipped with a home-made transmission cell and vacuum system and a mercury cadmium telluride (MCT) detector was used. A few micrograms of SUT-7 were dispersed in ethanol and the suspension was spread on a ZnSe window. A very thin layer of SUT-7 formed on the ZnSe window after evaporation of the ethanol. The window with the layer was placed into the cell for transmission IR measurement. It was treated under dynamic vacuum conditions ($< 10^{-6}$ Torr) at 353 K for 10 h in the cell. IR background spectra were measured on the samples under near vacuum conditions after degassing as described above. In situ transmission IR spectra of SUT-7 were recorded after being equilibrated with CO$_2$. The contributions of gaseous CO$_2$ to the IR spectra were compensated by subtracting the corresponding CO$_2$ absorbance spectra recorded in the same cell at different pressures. Pure carbon dioxide ($>$ 99.9992 %) was supplied as a gas by Linde and used as received.

Other characterization: Organic element analysis of the as-made materials was determined by elemental analysis performed on an ElementarVario MICRO CUBE elemental analyzer. Results for SUT-7: Calcd (%): C 3.17, H 3.41, N 5.22; found (%): C 3.16, H 3.41, N 5.58. Inductively coupled plasma (ICP) analysis shows that V/Zn = 1.57:1.00, close to the theoretical ratio of 1.66:1. The chemical formula can be written as $Zn_6V_{10}B_{29}O_{85}H_{18}\cdot 1.5\,NH(CH_2CH_2CH_2NH_3)_2\cdot 9\,NH_4\cdot 36\,H_2O$. Thermogravimetric (TG) analysis of SUT-7 was conducted in a platinum crucible under nitrogen by using a PerkinElmer TGA7 instrument and heating between 20 and 800 °C at a rate of 10 °C min^{-1}. X-ray photoelectron spectroscopy (XPS, AXIS Ultra, Kratos Analytical Ltd.) of the SUT-7 crystals was performed using a monochromatic Al$_{K\alpha}$ X-ray source ($h\nu = 1486.7$ eV). In situ PXRD experiments were performed on a X′Pert PANalytical PRO MRD using Cu$_{K\alpha}$ radiation ($\lambda = 1.5418$ Å) and variable slits. The sample was heated in an Anton–Parr XRK900 reaction chamber. The chamber was equilibrated for 2 min prior to data collection. The samples were heated in air from 30 °C to 150 °C at a heating rate of 7 °C min^{-1}. PXRD patterns were first recorded at room temperature and 50 °C, then up to 150 °C at increments of 50 °C.

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[1] A. Corma, *Chem. Rev.* **1997**, *97*, 2373 – 2420.

[2] M. E. Davis, *Nature* **2002**, *417*, 813 – 821.

[3] A. K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem.* **1999**, *111*, 3466 – 3492; *Angew. Chem. Int. Ed.* **1999**, *38*, 3268 – 3292.

[4] M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke, O. M. Yaghi, *J. Solid State Chem.* **2000**, *152*, 3 – 20.

[5] J. Jiang, J. L. Jorda, J. Yu, L. Baumes, E. Mugnaioli, M. J. Diaz-Cabanas, U. Kolb, A. Corma, *Science* **2011**, *333*, 1131 – 1134.

[6] X. Zou, T. Conradsson, M. Klingstedt, M. S. Dadachov, M. O'Keeffe, *Nature* **2005**, *437*, 716 – 719.

[7] X. Ren, Y. Li, Q. Pan, J. Yu, R. Xu, Y. Xu, V. Uni, *J. Am. Chem. Soc.* **2009**, *131*, 14128 – 14129.

[8] J. Sun, C. Bonneau, A. Cantín, A. Corma, M. J. Díaz-Cabañas, M. Moliner, D. Zhang, M. Li, X. Zou, *Nature* **2009**, *458*, 1154 – 1157.

[9] H.-Y. Lin, C.-Y. Chin, H.-L. Huang, W.-Y. Huang, M.-J. Sie, L.-H. Huang, Y.-H. Lee, C.-H. Lin, K.-H. Lii, X. Bu, et al., *Science* **2013**, *339*, 811 – 813.

[10] D. J. Tranchemontagne, Z. Ni, M. O'Keeffe, O. M. Yaghi, *Angew. Chem.* **2008**, *120*, 5214 – 5225; *Angew. Chem. Int. Ed.* **2008**, *47*, 5136 – 5147.

[11] M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319 – 330.

[12] H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A. C. Whalley, Z. Liu, S. Asahina, et al., *Science* **2012**, *336*, 1018 – 1023.

[13] G. Férey, *Science* **2001**, *291*, 994 – 995.

[14] A. Müller, E. Krickemeyer, S. K. Das, P. Kögerler, S. Sarkar, H. Bögge, M. Schmidtmann, S. Sarkar, *Angew. Chem.* **2000**, *112*, 1674 – 1676; *Angew. Chem. Int. Ed.* **2000**, *39*, 1612 – 1614.

[15] M. I. Khan, *J. Solid State Chem.* **2000**, *152*, 105 – 112.

[16] G. Férey, *Science* **1999**, *283*, 1125 – 1126.

[17] G. Férey, *J. Solid State Chem.* **2000**, *152*, 37 – 48.

[18] S. Huang, K. Christensen, M. V. Peskov, S. Yang, K. Li, X. Zou, J. Sun, *Inorg. Chem.* **2011**, *50*, 9921 – 9923.

[19] I. D. Williams, M. Wu, H. H. Sung, X. X. Zhang, J. Yu, *Chem. Commun.* **1998**, 2463 – 2464.

[20] X. Liu, J. Zhou, L. An, R. Chen, F. Hu, Q. Tang, *J. Solid State Chem.* **2013**, *201*, 79 – 84.

[21] T. Yamase, M. Suzuki, K. Ohtaka, *Dalton Trans.* **1997**, *44*, 2463 – 2472.

[22] M. Wu, T. S.-C. Law, H. H.-Y. Sung, J. Cai, I. D. Williams, *Chem. Commun.* **2005**, 1827 – 1829.

[23] J. T. Rijssenbeek, D. J. Rose, R. C. Haushalter, J. Zubieta, *Angew. Chem.* **1997**, *109*, 1049 – 1052; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1008 – 1010.

[24] P. Hermosilla-Ibáñez, P. E. Car, A. Vega, J. Costamagna, F. Caruso, J.-Y. Pivan, E. Le Fur, E. Spodine, D. Venegas-Yazigi, *CrystEngComm* **2012**, *14*, 5604 – 5612.

[25] J. Zhou, X. Liu, F. Hu, H. Zou, R. Li, X. Li, *RSC Adv.* **2012**, *2*, 10937 – 10940.

[26] Y.-Q. Sun, G.-M. Li, Y.-P. Chen, *Dalton Trans.* **2012**, *41*, 5774 – 5777.

[27] X. Liu, J. Zhou, H.-P. Xiao, C. Kong, H. Zou, Q. Tang, J. Li, *New J. Chem.* **2013**, *37*, 4077 – 4082.

[28] J. Zhou, X. Liu, R. Chen, X.-P. Xiao, F. Hu, H. Zou, Y. Zhou, C. Liu, L. Zhu, *CrystEngComm.* **2013**, *15*, 5057.

[29] H. Chen, Y. Deng, Z. Yu, H. Zhao, Q. Yao, X. Zou, J. Sun, *Chem. Mater.* **2013**, *25*, 5031 – 5036.

[30] V. A. Blatov, L. Carlucci, G. Ciani, D. M. Proserpio, *CrystEngComm* **2004**, *6*, 378 – 395.

[31] P. Yang, J. Wu, H. Zhou, B. Ye, *Cryst. Growth Des.* **2012**, *12*, 99 – 108.

[32] I. A. Baburin, V. A. Blatov, L. Carlucci, G. Ciani, D. M. Proserpio, *Cryst. Growth Des.* **2008**, *8*, 519 – 539.

[33] Z. Bacsik, R. Atluri, A. E. Garcia-Bennett, N. Hedin, *Langmuir* **2010**, *26*, 10013 – 10024.

[34] Z. Bacsik, N. Ahlsten, A. Ziadi, G. Zhao, A. E. Garcia-Bennett, B. Martín-Matute, N. Hedin, *Langmuir* **2011**, *27*, 11118 – 111128.

[35] Crysalis Sofware Syst. Version 171.35.19, Xcalibur CCD Syst. Oxford Diffr. Ltd., **2001**.

[36] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112 – 122.

[37] G. M. Sheldrick, Program for solution of crystal structures, University of Göttingen, **1997**.

[38] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7 – 13.