

Hydrothermal synthesis and characterization of a new 3D vanadium(III) phosphite (C₄H₈N₂H₄)_{0.5}(C₄H₈N₂H₃)[V₄(HPO₃)₇(H₂O)₃]1.5H₂O

Suhua Shi, Li Wang, Hongming Yuan, Guanghua Li, Jianing Xu, Guangshan Zhu,
Tianyou Song, Shilun Qiu*

*Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Department of Chemistry, Jilin University, Changchun City,
Jilin Province 130023, China*

Received 4 March 2004; received in revised form 11 June 2004; accepted 16 June 2004

Abstract

A new vanadium(III) phosphite, (C₄H₈N₂H₄)_{0.5}(C₄H₈N₂H₃)[V₄(HPO₃)₇(H₂O)₃]1.5H₂O, has been synthesized hydrothermally by using V₂O₅, H₃PO₃ as reactants, piperazine as the structure-directing agent. The as-synthesized product was characterized by powder X-ray diffraction, IR spectroscopy, inductively coupled plasma analysis, thermogravimetric analysis, and SQUID magnetometer. Single-crystal X-ray diffraction analysis shows that the title compound crystallized in the trigonal space group $P\bar{3}c1$ (No. 165) with the parameters: $a = 13.4678(4)$ Å, $c = 18.3171(8)$ Å, $V = 2877.27(17)$ Å³ and $Z = 4$. Its structure is built up by alternation of octahedral VO₆ or VO₅(H₂O) and pseudo-pyramidal HPO₃ units to form infinite 2D layers, and these layers are interconnected by sharing vertex-oxygen with octahedral VO₆ units to generate a 3D open-framework structure with 12-membered ring channels in a and b directions, respectively, where there exist entrapped diprotonated and mono-protonated piperazine cations, and water molecules. Magnetic measurement indicates that paramagnetic behavior is observed down to 4 K.

© 2004 Published by Elsevier Inc.

Keywords: Hydrothermal synthesis; Vanadium phosphite; 3D open-framework

1. Introduction

After the discovery of microporous aluminophosphates, considerable efforts have been directed toward the synthesis of new open-framework transition-metal phosphates, due to their potential applications in catalysis, adsorption, ionic conduction, ion exchange, separation and electronics. Vanadium phosphates not only exhibit a rich structural and compositional diversity, but also display interesting magnetic properties. Hydrothermal synthesis has been successful for the preparation of microporous materials and other important solids. A variety of 1D chain [1–4], 2D layer

[1,5–9], and 3D open-framework structure [10–23] vanadium phosphates were prepared in the presence of organic amine, and alkali metal cation or metal complex as structure-directing agents. It is interesting that [HN(CH₂CH₂)₃NH]K_{1.35}[V₅O₉(PO₄)₂]H₂O [23] contains largest voids and lowest framework atom densities, and [(CH₃)₂NH₂]K₄[(VO)₁₀(H₂O)₂(OH)₄(PO₄)₇]H₂O [10] shows chiral intertwined double helices structure. More recently, a few organo-templated vanadium phosphites such as 1D (C₂H₁₀N₂)[V(HPO₃)F₃] [24], 2D [HN(Me)(C₂H₄)₂N(Me)H][(VO)₄(OH)₂(HPO₃)₄] and 3D [H₂N(CH₂CH₂)₂NH₂][(VO)₃(HPO₃)₄(H₂O)₂] [25] and (CN₃H₆)₂(VO)₃(HPO₃)₄H₂O [26] have been synthesized and characterized. Vanadium phosphites containing organic templates mentioned above are of special interests, because the pseudo-pyramidal geometry of the

*Corresponding author. Fax: +86-431-892-5459.

E-mail address: lh1222@mail.jlu.edu.cn (S. Qiu).

phosphite $[\text{HPO}_3]^{2-}$ unit may lead to novel connectivity patterns compared to those observed in vanadium phosphates containing tetrahedral PO_4 units. Most vanadium phosphates and phosphites involve mixed oxidation states of vanadium. Only a few 1D chain and 2D layer phosphates containing pure V(III) were reported up to date, and a 3D phosphite containing pure V(III) is reported in the literature [27]. In this paper, we report the synthesis, X-ray crystal structure, and magnetic property of a novel 3D vanadium(III) phosphite containing 2D intersecting 12-membered ring channels.

2. Experimental

2.1. Synthesis and characterization

To a solution of 0.070 g V_2O_5 in 8 mL H_2O , was added 1.000 g H_3PO_3 with stirring, followed by the addition of 0.777 g piperazine. The molar composition of the initial mixture was $\text{V}_2\text{O}_5\text{:H}_3\text{PO}_3\text{:piperazine:H}_2\text{O} = 1\text{:}30\text{:}10\text{:}1110$. The mixture was further stirred for 30 min and heated at 170 °C for 4 d in a Teflon-lined stainless steel autoclave (filled up to ~75% volume capacity) under autogenous pressure, followed by slow cooling down to the ambient temperature. Light-green crystals of the title compound were collected by filtration, washed with distilled water, and air-dried. The yield of product was 40% in weight based on vanadium.

Powder X-ray diffraction (XRD) data were obtained using SHIMADAZU XRD-6000 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), with the step size and the count time of 0.02° and 4 s, respectively. The elemental analysis was conducted on a Perkin–Elmer 2400 elemental analyzer. Inductively coupled plasma (ICP) analysis was performed on a Perkin–Elmer Optima 3300DV ICP instrument. FT-IR spectrum was recorded on a Nicolet Impact 410 spectrometer between 400 and 4000 cm^{-1} using the KBr pellet method. Thermogravimetric analysis (TGA) were conducted on a Perkin–Elmer TGA 7 thermogravimetric analyzer with a heating rate of 10 °C min^{-1} under flowing nitrogen gas up to 800 °C.

Magnetic measurement was carried out with a superconducting quantum interference device magnetometer in a field of 5000 Oe. Magnetic susceptibility dependence of temperature range of 4–300 K.

2.2. Crystal structure determination

A single crystal of the title compound (size: $0.25 \times 0.25 \times 0.19 \text{ mm}^3$) was mounted on a thin glass fiber with cyanoacrylate adhesive. The intensity data were collected on a Siemens Smart CCD diffractometer

equipped with a normal-focus, 2.4 kW sealed-tube X-ray source (graphite-monochromatic $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$)) operating at 50 kV and 40 mA. No significant decay was observed during the data collection. Data were processed on a Pentium PC using Bruker AXS Windows NT SHELXTL software package (version 5.10) [28,29]. Neutral atom scattering factors were taken from Cromer and Waber [30]. Empirical absorption correction was applied. The structure was solved by direct method. All the nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and located in the difference Fourier map.

3. Results and discussion

3.1. Characterization

ICP analysis for the product gave the vanadium:phosphorus ratio of the title compound was ca. 0.6, which is in good agreement with the value of 4:7 obtained from the single-crystal X-ray diffraction analysis. Elemental analysis showed that C, H, and N are 7.47%, 3.97%, and 4.51%, respectively, in agreement with the expected values of 7.38, 3.38, and 4.30 wt% of C, H and N on the basis of the empirical formula given by the single-crystal structure analysis. Thermogravimetric analysis show one major weight loss followed by a tail. The weight loss (exp. 9.3%) was observed in the temperature range of 100–420 °C and could be attributed to the loss of extra-framework water molecule (calc. 2.8%) and the partial mono-protonated piperazine, and the weight loss (exp. 5.8%) in the 420–800 °C range corresponds to the loss of partial mono-protonate and diprotonated aminium (calc. 4.5%). It is difficult to assign the weight loss of the mono-protonated piperazine cations (calc. 8.9%) to individual reaction steps unambiguously. A power XRD study shows that the compound became noncrystalline after the decomposition of the occluded template. IR spectrum of the sample showed that the large band at 3430 cm^{-1} arises from O–H and N–H stretching vibrations, and the intense bands at 1115 and 996 cm^{-1} were associated with the stretching vibrations of V–O and P–O bonds, respectively. There appeared the absorptions at 2388 cm^{-1} as well due to the stretching vibrations of the P–H groups in phosphite anions.

3.2. Description of structure

As shown in Fig. 1, there are three crystallographically distinct V and P atoms, respectively, in the asymmetric unit of the title compound. All of vanadium atoms are in octahedral environment formed by six O

atoms with an average V–O bond length of 2.008 Å, typical for vanadium(III) [31], which is consistent with the bond valence sum calculation (BVS) [BVS(V1)=3.4, BVS(V2)=3.2, BVS(V3)=3.3] [32]. V(1) bonds to five bridging oxygen atoms [$d(\text{V–O})=1.962\text{--}2.004$ Å] and one terminal oxygen atom of a water molecule. Each of V(2) and V(3) shares six oxygen atoms with adjacent P atoms and is octahedrally coordinated (V(2)–O bond length: 2.012 Å, and V(3)–O: 2.008 Å). The value of the O–V–O bond angle lies within a narrow range, indicating that V(2) and V(3) atoms lie at the center of relatively regular octahedron formed by six oxygen atoms. The P atoms are all pseudo-pyramidally coordinated by oxygen atoms with average bond lengths of 1.527 Å for P1–O, 1.525(4) Å for P2–O and 1.518(3) Å for P3–O, respectively. The terminal P–H bond lengths are 1.41, 1.45, and 1.32 Å, respectively, which are similar to the P–H bond lengths reported in H_3PO_3 previously

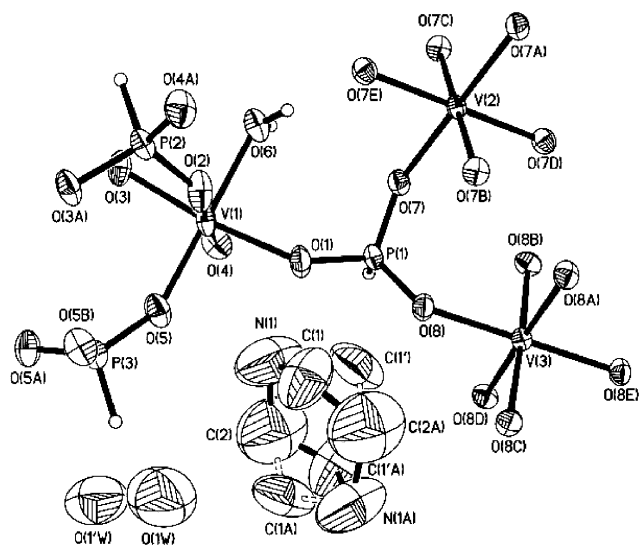


Fig. 1. Asymmetric unit of $(\text{C}_4\text{N}_2\text{H}_{12})_{0.5}(\text{C}_4\text{N}_2\text{H}_{11})[\text{V}_4(\text{HPO}_3)_7(\text{H}_2\text{O})_3]1.5(\text{H}_2\text{O})$ (50% thermal ellipsoids; H atoms represented by spheres of arbitrary radius).

[33]. The existence of P–H bonds is also proved by IR spectrum, which exhibits strong absorption at 2388 cm^{-1} [34]. There are one crystallographically distinct piperazine molecule and two water molecules in asymmetric unit. The piperazine molecules exist in either mono-protonated or diprotonated form in the structure.

The structure of the title compound consists of 3D open-framework with intersecting 12-member ring channels and protonated piperazine cations and water molecules residing in the channels. The 2D sheets with 4,6-member rings of V centered VO_6 , $\text{VO}_5(\text{H}_2\text{O})$ and P-centered HPO_3 units are first formed (shown in Fig. 2), and then linked together by sharing vertex-oxygen atoms of VO_6 units to generate a 3D open-framework structure with 12-membered ring channels along a and b directions, respectively (shown in Fig. 3). Its inorganic framework is similar to those of $[\text{C}_3\text{N}_2\text{H}_5]_3[\text{In}_8(\text{HPO}_4)_{14}(\text{H}_2\text{O})_6](\text{H}_3\text{O})(\text{H}_2\text{O})_5$ [35] and $[\text{HN}(\text{CH}_2\text{CH}_2)_3\text{NH}]_3[\text{Fe}_8(\text{HPO}_4)_{14}(\text{PO}_4)_2(\text{H}_2\text{O})_6]$ [36]. One of the differences between them is terminal P–H group in the title compound versus P–OH group in both compounds mentioned above. The piperazine has been used as the organic template in the synthesis of vanadium phosphates [6–7,9,19], most of which have 2D layered structures. To our best knowledge, only two examples of 3D piperazine templated vanadium phosphates have been described previously [17,37]. The negative charge of network is compensated by protonated piperazines in the crystal lattice. A few examples of zeolites, microporous aluminophosphates, and transition metal phosphate and phosphite with multidimensional 12-ring channels have been reported previously. The title compound demonstrates the first example of 3D open-framework possessing 2D intersecting 12-ring channels in the V/P/O system.

In addition, the mixed-valence vanadium seems to be a common feature in 3D open-framework vanadium phosphates. Up to date only Al, In, Ga, and Fe are known to exhibit pure +3 oxidation state in 3D

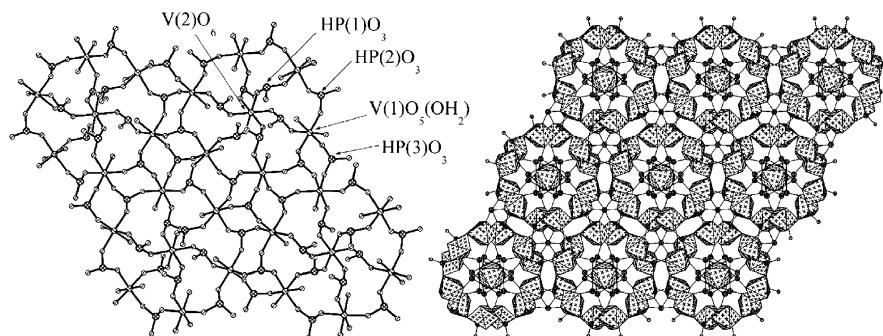


Fig. 2. (Left) Polyhedral view down [001] of $[\text{V}_4(\text{HPO}_3)_7(\text{H}_2\text{O})_3]^{2-}$ structure showing the connectivity of $\text{V}(2)\text{O}_6$ octahedra, $\text{V}(1)\text{O}_5(\text{H}_2\text{O})$ octahedra and HPO_3 tetrahedra (hydrogen atoms are not shown for clarity). (Right) View of unit cell along the c axis showing stacking of layers. The V sites are represented by the octahedra and the P sites are solid black spheres. Oxygen sites are gray spheres.

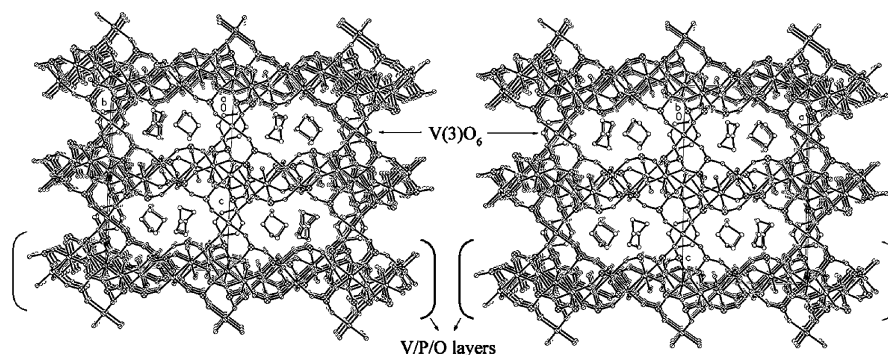


Fig. 3. Perspective view of the structure of $(\text{C}_4\text{N}_2\text{H}_{12})_{0.5}(\text{C}_4\text{N}_2\text{H}_{11})[\text{V}_4(\text{HPO}_3)_7(\text{H}_2\text{O})_3]1.5(\text{H}_2\text{O})$ showing 2D- channels in which the piperazinium dications reside respectively along [100] (left) and [010] (right). Nonframework water molecules have been omitted for clarity.

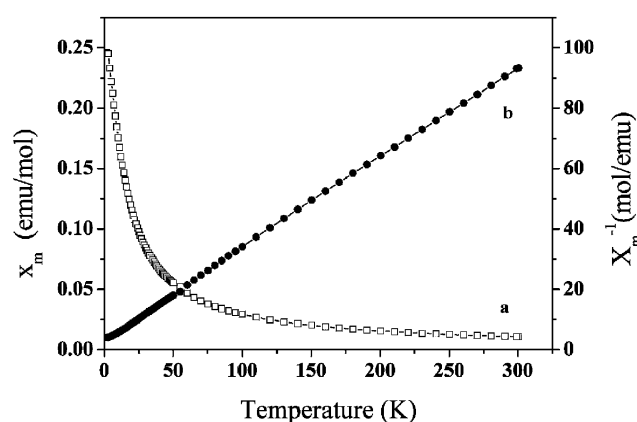


Fig. 4. Magnetic susceptibility and reciprocal susceptibility as a function of temperature for the vanadium phosphite.

open-frameworks. The compounds containing pure V(III) are scarce for both vanadium phosphate and vanadium phosphite, and were only observed in 1D $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)[\text{V}(\text{OH})(\text{HPO}_4)_2] \cdot \text{H}_2\text{O}$ [4] and 2D $[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3][\text{V}(\text{H}_2\text{PO}_4)(\text{P}_2\text{O}_7)]$ [38]. It is noteworthy that the title compound is a new example of a 3D open-framework vanadium phosphite, in which the vanadium atoms are at the +3 oxidation state exclusively.

3.3. Physical data

The magnetic measurements of the title compound were performed on powdered samples ranging from 300 to 4 K. The plots of χ_m and χ_m^{-1} vs. T curves for present compound are shown in Fig. 4. The results indicate that the compound obeys the Curie–Weiss law: $\chi_m = C_m/(T - \theta)$, where χ_m is the measured magnetic susceptibility, T the temperature (K), C_m the Curie constant and θ the Weiss constant, with $C_m = 2.598 \text{ emu K mol}^{-1}$, $\theta = -15.7 \text{ K}$. They show the existence of antiferromagnetic interactions in the title compound. The effective magnetic moment at 300 K is

$2.65 \mu_B$ per V atom, in good agreement with the theoretical spin-only value for trivalent vanadium.

4. Conclusions

In summary, the title compound represents a new member of trivalent-metal phosphite 3D open-frameworks, and this study has demonstrated that the use of piperazine molecules as the template under mild hydrothermal conditions can result in the formation of a novel vanadium(III) phosphite with new structural and oxidation state features. The title compound containing 2D intersecting 12-membered ring channels can be regarded as being constructed from the inorganic V/P/O layers pillared by VO_6 octahedral. The compound behaved antiferromagnetic over the temperature range of 4–300 K. Our investigation shows that it is possible to form novel trivalent vanadium phosphites 3D open-framework materials containing removable organic templates which might have many potential applications. And because the μ_3 -coordination for the phosphites is different from the μ_4 -coordination for the phosphates, so it presents further challenges in the hydrothermal synthesis of organically templated open-framework phosphites.

Acknowledgments

This work was supported by the State Basic Research Project (G2000077507), and the National Science Foundation of China (Nos. 29873017 and 20101004).

References

- [1] R. Finn, J. Zubieta, Chem. Commun. 14 (2000) 1321.
- [2] Z. Bircsak, A.K. Hall, W.T.A. Harrison, J. Solid State Chem. 142 (1999) 168.

- [3] Y.M. Tsai, S.L. Wang, C.H. Huang, K.H. Lii, *Inorg. Chem.* 38 (1999) 4183.
- [4] Y.P. Zhang, C.J. Warren, A. Clearfield, R.C. Haushalter, *Polyhedron* 16 (1998) 2575.
- [5] X.M. Zhang, M.L. Tong, S. Feng, X.M. Chen, *J. Chem. Soc. Dalton Trans.* 14 (2001) 2069.
- [6] J. Do, R.P. Bontchev, A.J. Jacobson, *J. Solid State Chem.* 154 (2000) 514.
- [7] V. Soghomonian, Q. Chen, Y.P. Zhang, R.C. Haushalter, C.J. O'Connor, C. Tao, J. Zubieta, *Inorg. Chem.* 34 (1995) 3509.
- [8] D. Riou, G. Férey, *J. Solid State Chem.* 111 (1994) 422.
- [9] V. Soghomonian, R.C. Haushalter, Q. Chen, J. Zubieta, *Inorg. Chem.* 34 (1994) 1700.
- [10] C.H. Huang, L.H. Huang, K.H. Lii, *Inorg. Chem.* 40 (2001) 2625.
- [11] V. Soghomonian, Q. Chen, R.C. Haushalter, J. Zubieta, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 610.
- [12] V. Soghomonian, Q. Chen, R.C. Haushalter, J. Zubieta, *Chem. Mater.* 5 (1993) 1595.
- [13] V. Soghomonian, Q. Chen, R.C. Haushalter, J. Zubieta, C.J. O'Connor, Y.S. Lee, *Chem. Mater.* 5 (1993) 1690.
- [14] T. Loiseau, G. Férey, *J. Solid State Chem.* 111 (1994) 416.
- [15] Y.P. Zhang, A. Clearfield, R.C. Haushalter, *Chem. Mater.* 7 (1995) 1221.
- [16] W.T.A. Harrison, K. Hsu, A.J. Jacobson, *Chem. Mater.* 7 (1995) 2004.
- [17] X.H. Bu, P.Y. Feng, G.D. Stucky, *Chem. Commun.* 13 (1995) 1337.
- [18] G. Bonavia, R.C. Haushalter, J. Zubieta, *J. Solid State Chem.* 126 (1996) 292.
- [19] V. Soghomonian, R.C. Haushalter, J. Zubieta, C.J. O'Connor, *Inorg. Chem.* 35 (1996) 2826.
- [20] M. Roca, M.D. Marcos, P. Amorós, A.B. Beltrán-Porter, A.J. Edwards, D.B. Beltrán-Porter, *Inorg. Chem.* 35 (1996) 5613.
- [21] Y. Lu, R.C. Haushalter, J. Zubieta, *Inorg. Chim. Acta* 268 (1998) 257.
- [22] H.B. Du, L.B. Liao, Z.Z. Yang, Z.S. Ma, M. Xiong, *Acta Chim. Sinica* 59 (2001) 274.
- [23] M.I. Khan, L.M. Meyer, R.C. Haushalter, A.L. Schweitzer, J. Zubieta, J.L. Dye, *Chem. Mater.* 8 (1996) 43.
- [24] S. Fernandez, J.L. Mesa, J.L. Pizarro, L. Lezama, M.L. Arriortua, T. Rojo, *Chem. Mater.* 15 (2003) 1204.
- [25] G. Bonavia, J. DeBord, R.C. Haushalter, D. Rose, J. Zubieta, *Chem. Mater.* 7 (1995) 1995.
- [26] W.T.A. Harrison, *Solid State Sci.* 5 (2003) 297.
- [27] S. Fernandez, J.L. Mesa, J.L. Pizarro, L. Lezama, M. Arriortua, T. Rojo, *Chem. Mater.* 14 (2002) 2300.
- [28] Software packages SMART and SAINT, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1996.
- [29] G.M. Sheldrick, SHELXTL-NT, Version 5.1, Bruker AXS Inc., Madison, WI, 1997.
- [30] D.T. Cromer, J.T. Waber, *International Tables for X-ray Crystallography*, Vol. 4, Kynoch Press, Birmingham, AL, 1974 Table 2.2A.
- [31] M. Schindler, F.C. Hawthorne, W.H. Baur, *Chem. Mater.* 12 (2000) 1248.
- [32] I.D. Brown, *J. Appl. Crystallogr.* 29 (1996) 479.
- [33] Z. Shi, G.H. Li, D. Zhang, J. Hua, S.H. Feng, *Inorg. Chem.* 42 (2003) 2357 and references therein.
- [34] D.J. Williams, J.S. Kruger, A.F. Mcleroy, A.P. Wilkinson, J.C. Hanson, *Chem. Mater.* 11 (1999) 2241.
- [35] A.M. Chippindale, S.J. Brech, A.R. Coeley, W.M. Simpson, *Chem. Mater.* 8 (1996) 2259.
- [36] K.H. Lii, Y.F. Huang, *J. Chem. Soc., Dalton Trans.* 13 (1997) 2221.
- [37] G. Bonavia, R.C. Haushalter, J. Zubieta, *J. Solid State Chem.* 126 (1996) 292.
- [38] A.M. Chippindale, *Chem. Mater.* 12 (2000) 818.