

Organo-Directed Synthesis of Manganese Vanadates with Variable Stoichiometry and Dimensionality: 1-D [(Hen)₂Mn(VO₃)₄], 2-D [H₂en]₂[Mn(VO₃)₆], and 3-D [H₂en][MnF(VO₃)₃]

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The use of organic reagents for the structure direction of inorganic solids has been of great value in the field of microporous materials such as zeolites and metal phosphates.¹ The extension of this approach to transition metal oxides is particularly attractive for their catalytic² or magnetic properties and the development of new cathode materials for Li batteries.³ In the past few years a number of molybdenum⁴ and vanadium oxides⁵ with organic counterions, as well as hybrid organic–inorganic solids of bimetallic oxides⁶ have been prepared.

In hydrothermal syntheses, both pH⁷ and temperature⁸ play crucial roles in determining the isolated solid phases. In attempting to synthesize mixed-metal vanadium borate phases,⁹ we recently prepared the first examples of organically templated manganese divanadates [H₂en][Mn₃(V₂O₇)₂(H₂O)₂] **MnVO-1** and [(Hpn)₂Mn₃(V₂O₇)₂] **MnVO-2**, which were of magnetic interest, since their Mn^{II} centers associate as trimers or ladder-

like chains.¹⁰ These were formed hydrothermally at 140 °C with pH 6–8, while pure V^{IV} borate phases were formed at 160–180 °C and pH 8–10. We have now continued a fuller exploration of the en system, using a pH range of 6–8 and even lower temperatures (80 or 110 °C) and report three new compounds **MnVO-3**, **MnVO-4**, and **MnVO-5**, which considerably extend the range of structures and stoichiometries seen for these organic–inorganic hybrid solids.

First the reaction of V₂O₅:Mn(OAc)₂:en:AcOH:H₂O in 1:2:9:5:100 ratio for 4 days at 80 °C gives 60% yield of **MnVO-3**, [(Hen)₂Mn(VO₃)₄]. This forms red-brown blocks up to 0.5 mm dimension and is phase pure by microscopic examination, X-ray powder diffraction, and combustion analysis.¹¹ A single-crystal structure determination¹² shows **MnVO-3** to be a 1-D inorganic chain polymer, with pendant coordinated organic groups (Figure 1). The Mn centers occur as isolated octahedra with [MnN₂O₄] coordination spheres consisting of two *trans*-amino groups and four oxygens from two separate (VO₃)_n chains. Monoprotonation of the pendant ethylenediamines results in overall charge neutrality, since the oxidation states found by valence sum calculations,¹³ as in all compounds **MnVO-n**, are Mn^{II} and V^V.

If reaction temperatures are raised from 80 to 140 °C, or with longer reaction times, the yield of the 1-D compound **MnVO-3** decreases and the product becomes mostly **MnVO-1**, which is a 3-D network polymer. In certain syntheses a minor component **MnVO-4** is also formed as clear orange plates. This comprises ~10% of the isolated product at 110 °C (pH 8, 4 days).¹⁴ Single-crystal structure determination¹⁵ reveals **MnVO-4** to be the salt [H₂en]₂[Mn(VO₃)₆] which has an interesting 2-D “double layer” sheet structure for the metal oxide component. The sheet has an open-framework and features [MnV₂], [Mn₂V₆], and [Mn₂V₇] rings. The cavity formed by the eight- and nine-membered rings interacts with the ethylene diammonium counterions through several N–H···O–V hydrogen bonds (Figure 2). Overall the topology is quite different and more complex than in **MnVO-3**. Some structural components such as the pyrovanadate chains and the isolated Mn octahedra are

(1) Davis, M. E. *Acc. Chem. Res.* **1993**, *26*, 111. Oliver, S.; Kuperman, A.; Ozin, G. A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 47.

(2) Sheldon, R. A. *Stud. Surf. Sci. Catal.* **1997**, *110*, 351. Arends, I. W. C. E.; Sheldon, R. A.; Wallau, M.; Schuchardt, U. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1144. Hartman, M.; Kevan, L. *Chem. Rev.* **1999**, *99*, 635.

(3) Li, W.; Dahn, J. R.; Wainwright, D. S. *Science* **1994**, *264*, 1115. Thackeray, M. M.; Thomas, J. O.; Whittingham, M. S. *M.R.S. Bull.* **2000**, *25*, 39–46.

(4) Kahn, M. I.; Chen, Q.; Zubieta, J. *Inorg. Chim. Acta* **1993**, *213*, 328. Guo, J.; Whittingham, M. S.; Zavalij, P. Y. *Chem. Mater.* **1994**, *6*, 357. Xu, Y.; An, L.-H.; Koh, L.-L. *Chem. Mater.* **1996**, *8*, 814. Harrison, W. T. A.; Dussack, L. L.; Jacobson, A. J. *Acta Crystallogr.* **1996**, *C52*, 1075. Zapf, P. J.; Haushalter, R. C.; Zubieta, J. *Chem. Commun.* **1997**, 321. Guillou, N.; Ferey, G. *J. Solid State Chem.* **1997**, *132*, 224. Zapf, P. J.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1997**, *9*, 2019.

(5) Riou, D.; Ferey, G. *Inorg. Chim. Acta* **1995**, *34*, 6520. Nazar, L. F.; Koene, B. E.; Britten, J. F. *Chem. Mater.* **1996**, *8*, 327. Zhang, Y.; O'Connor, C. J.; Clearfield, A.; Haushalter, R. C. *Chem. Mater.* **1996**, *8*, 595. Zhang, Y.; Haushalter, R. C.; Clearfield, A. *Chem. Commun.* **1996**, 1055. Chirayil, T.; Zavalij, P. Y.; Whittingham, M. S. *J. Mater. Chem.* **1997**, *7*, 2193. Zavalij, P. Y.; Whittingham, M. S. *Acta Crystallogr.* **1997**, *C53*, 1374.

(6) Hagrman, D.; Hagrman, P. J.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3165. Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2639.

(7) The critical effect of pH on hydrothermal synthesis of vanadium oxides is discussed in: Chirayil, T.; Boylan, E. A.; Mamak, M.; Zavalij, P. Y.; Whittingham, M. S. *Chem. Commun.* **1997**, 33.

(8) The use of low temperatures in assisting formation of metastable oxide phases has been reviewed. Gopalakrishnan, J. *Chem. Mater.* **1995**, *7*, 1265.

(9) Williams, I. D.; Chui, S. S.-Y.; Lo, S. M.-F.; Wu, M.; Cha, J. A.; Law, T. S.-C.; Sung, H. H.-Y.; Shek, F. L.-Y.; Gao, J. L.; Fasina, T. M. *Stud. Surf. Sci. Catal.* **2000**, *129*, 459–466.

(10) Williams, I. D.; Law, T. S.-C.; Sung, H. H.-Y.; Wen, G.; Zhang, X. X. *Solid State Sci.* **2000**, *2*, 47.

(11) Synthesis of **MnVO-3**: V₂O₅ (90 mg, 0.5 mmol), Mn(OAc)₂·4H₂O (250 mg, 1 mmol), en (0.2 mL, 4.5 mmol), AcOH (2.5 mmol) in 1.8 mL of H₂O (50 mmol) were reacted for 4 days at 80 °C in a Teflon-lined Parr vessel (23 mL). Yield: 80 mg of **MnVO-3**. (~60% yield based on V). Thermal gravimetric analysis (4 °C min⁻¹ in air) –Δw (200–450 °C) = 20.4%. EDAX gave a Mn:V ratio of 1:3.8. Elemental combustion analysis: found (calc); C 8.48 (8.38); H 3.19 (3.14); N 9.65 (9.77)%.

(12) Crystal data for **MnVO-3**: C₄H₁₈MnN₄O₁₂V₄, Fw = 572, monoclinic, *P*2₁/*n*, *a* = 5.811(1), *b* = 17.884(4), *c* = 8.417(2) Å, β = 101.04(1)°, *V* = 858.5(3) Å³, *D*_c = 2.22 g cm⁻³ for *Z* = 2. 1942 unique data to 2θ_{max} = 55° and 115 least squares parameters gave *R* = 0.025, *wR*2 = 0.059 (all data) and final Δe.d. ±0.35 e Å⁻³.

(13) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

(14) Synthesis of **MnVO-4**: As for **MnVO-3** above, but at 110 °C. Isolated ~10 mg of **MnVO-4** as a minor component with **MnVO-1** and **MnVO-3**. EDAX gave Mn:V ratio 1:5.7.

(15) Crystal data for **MnVO-4**: [C₄H₂₀N₄][MnO₁₈V₆], Fw = 772.8, triclinic, *P*–1, *a* = 8.074(1), *b* = 8.522(1), *c* = 8.794(1) Å, α = 77.83(1), β = 63.44(1), γ = 83.60(2)°, *V* = 529.0(1) Å³, *D*_c = 2.43 g cm⁻³ for *Z* = 1. A total of 1990 unique data to 2θ_{max} = 52.0° and 151 parameters gave *R* = 0.046, *wR*2 = 0.115 (all data) and final Δe.d. +0.98/–0.64 e Å⁻³.

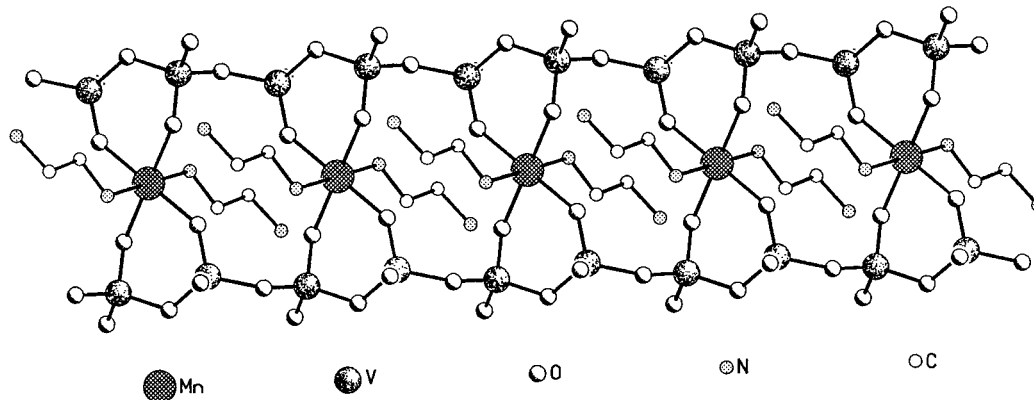


Figure 1. Chain structure of $[(\text{Hen})_2\text{Mn}(\text{VO}_3)_4]$, **MnVO-3**.

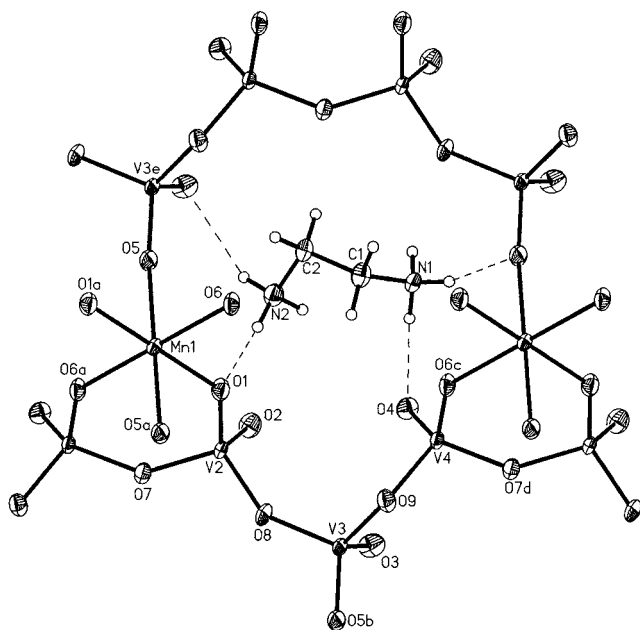


Figure 2. Thermal ellipsoid plot of $[\text{H}_2\text{en}]_2[\text{Mn}(\text{VO}_3)_6]$ **MnVO-4** (40%), showing interaction of the organic counterion with a nine-membered $[\text{Mn}_2\text{V}_7]$ ring.

retained. In **MnVO-4** the coordination sphere is $[\text{MnO}_6]$ with the six oxygens from four separate $(\text{VO}_3)_n$ chains.¹⁶

As is reasonable from consideration of their dimensionalities, the above findings suggest that **MnVO-3** is a kinetic product of the system and that **MnVO-1** is a more thermodynamically stable solid, with the 2-D sheet compound **MnVO-4** intermediate between the two. Hence short times and low temperatures favor the 1-D polymer and longer times or higher temperatures the 3-D material and explain why only low yields of **MnVO-4** can ever be isolated. With addition of mineralizers, use of higher temperatures or different pH the solution speciation is modified and other solids form.

One example is **MnVO-5**, $[\text{H}_2\text{en}][\text{MnF}(\text{VO}_3)_3]$ from $\text{V}_2\text{O}_5:\text{Mn}(\text{OAc})_2:\text{en}:\text{AcOH}:\text{NaBF}_4:\text{H}_2\text{O}$ in 1:2:6:5:1:100 ratio (110 °C, 4days).¹⁷ The reduction of en (or an addition of HF as an alternate source of F^-) causes a

decrease in pH to 6. Fluoride may act as a mineralizer to assist crystallization but can also play a noninnocent role. Recently we have reported its incorporation into the frameworks of a variety of main group and transition-metal phosphates.¹⁸ In this system fluoride appears to be incorporated in a highly facile manner. Control of its availability by use of the complex tetrafluoroborate anion in NaBF_4 is optimal, yielding 70% **MnVO-5**. The structure of **MnVO-5** has quite different topological characteristics from the other two phases, although again Mn^{II} octahedra and V^{V} tetrahedral building blocks are involved. A single-crystal structure analysis¹⁹ shows it is an open 3-D solid, with an anionic metal oxy-fluoride framework. The fluoride ions are incorporated in bent $(\text{Mn}-\mu-\text{F})$ chains, $[\text{Mn}-\text{F} = 2.074(4), 2.087(4)$ Å, $\text{F}-\text{Mn}-\text{F} = 175.3(2)$, $\text{Mn}-\text{F}-\text{Mn} = 128.2(2)^\circ]$.

The anionic framework in **MnVO-5** is charge balanced by organic counterions which reside in six-membered ring tunnels which run along the crystallographic c axis (Figure 3). Whereas the (VO_3) units in **MnVO-3** and **MnVO-4** were arranged in infinite chains of corner shared $[\text{VO}_4]$ tetrahedra, in **MnVO-5** they form rectangular cyclo-hexavanadate $[\text{V}_6\text{O}_{18}]$ rings, shown in Figure 4. The four vanadate units at the ring corners are each connected to two Mn of the $[\text{Mn}(\text{F})_n]$ chains which run along the a axis, which is perpendicular to the $[\text{V}_6\text{O}_{18}]$ plane. The other two vanadates of the ring form the long edges of the rectangle. They are unconnected to Mn centers and each have two terminal oxygens which hydrogen bond to the NH_3R groups of the organic (H_2en) cations. While hexacyclic rings are a common feature of silicate chemistry, as in the beryl family, this is a rare example of a hexavanadate analogue. Not only is the observation of $[\text{V}_6\text{O}_{18}]$ rings in **MnVO-5** unique, the entire family of organic manganese vanadates **MnVO- n** have no obvious direct structural analogues among purely inorganic transition-metal vanadate phases, although certain components and features may be found in common. This is well-

(16) $[\text{VO}_3]_n$ chains are also found in a butyl-1,4-diammonium salt $[\text{H}_2\text{bn}][\text{VO}_3]_2$; Riou, D.; Férey, G. *J. Solid State Chem.* **1996**, *124*, 151.

(17) Synthesis of **MnVO-5**: As for **MnVO-4**, except en (0.13 mL, 3 mmol), NaBF_4 (110 mg, 1.0 mmol). Reaction pH: 6. Yield: 105 mg of **MnVO-5**, (~70% yield based on V). TGA: $-\Delta w(250-450^\circ\text{C}) = 14.6\%$, XPS gave a Mn:V:F ratio of 1.1:2.8:1.0. Elemental combustion analysis: found (calc); C 5.88 (5.54); H 2.42 (2.31); N 6.34 (6.47)%.

(18) (a) Du, H.; Pang, W.; Chen, J.; Yu, J.; Williams, I. D. *Chem. Commun.* **1997**, 823. (b) Sung, H. H.-Y.; Yu, J.; Williams, I. D. *J. Solid State Chem.* **1998**, *140*, 46. (c) Williams, I. D.; Yu, J.; Du, H.; Chen, J.; Pang, W. *Chem Mater.* **1998**, *10*, 773. (d) Yu, J.; Sung, H. H.-Y.; Williams, I. D. *J. Solid State Chem.* **1999**, *142*, 241.

(19) Crystal data for **MnVO-5**: $\text{C}_2\text{H}_{10}\text{FMnN}_2\text{O}_9\text{V}_3$, $F_w = 432.9$, orthorhombic, $Pbcn$, $a = 14.805(3)$, $b = 7.485(1)$, $c = 21.038(4)$ Å, $V = 2331.3(7)$ Å³, $D_c = 2.47\text{ g cm}^{-3}$ for $Z = 8$. 2026 data to $2\theta_{\text{max}} = 50^\circ$ and 163 parameters gave $R1 = 0.044$, $wR2 = 0.100$ [for data $I > 2\sigma(I)$] and final $\Delta e.d. = +0.60/-0.58 \text{ e } \text{Å}^{-3}$.

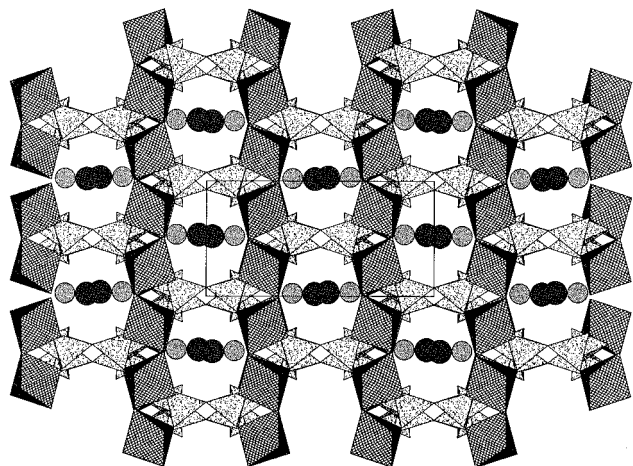


Figure 3. Polyhedral representation of **MnVO-5** along the *c* axis, showing the $\text{Mn}(\mu\text{-F})$ chains and $[\text{H}_2\text{en}]$ inside the microchannels.

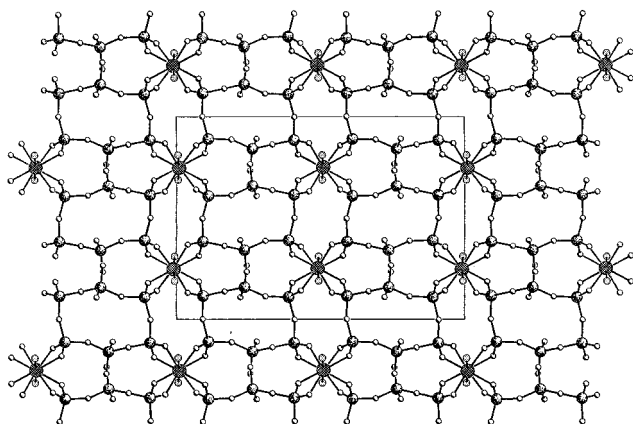


Figure 4. View along the *a* axis of $[\text{H}_2\text{en}][\text{MnF}(\text{VO}_3)_3]$ **MnVO-5**, showing the $[\text{V}_6\text{O}_{18}]$ rings.

illustrated by the case of $[\text{K}_2\text{Mn}(\text{VO}_3)_4]$ ²⁰ which is stoichiometrically related to **MnVO-3** but has Mn centers connected to four $[\text{VO}_3]$ chains as found in **MnVO-4**. Overall though this is quite different from either of these two “organic” phases and has a 3-D oxide network surrounding potassium-filled cavities.

Two key factors which may play a role in the novel structural arrangements of the metal oxide moieties in **MnVO-*n*** are the relatively low temperatures employed in synthesis (80–140 °C) which allow metastable arrangements to form, as well as the spatial and interfacial structure-directing forces of the organic moieties, including the formation of hydrogen bonds. Variable

(20) Liao, J.-H.; Sigala, C.; Guyomard, D.; Piffard, Y. *Acta Crystallogr.* **1996**, *C52*, 283.

oxidation state also played a major role in the wide composition and structural diversity of the previously reported “organic” molybdates⁴ and vanadates.⁵ In contrast only Mn^{II} and V^{V} oxidation states have been found in the **MnVO-*n*** compounds we have described. This probably reflects the relatively narrow range of reaction conditions used, rather than the propensity of the system to yield other REDOX combinations. Survey of the inorganic manganese vanadates shows that $\text{Mn}^{\text{II}}/\text{V}^{\text{V}}$ is also the most frequently observed valence combination in both natural minerals²¹ and synthetic phases.²² Whittingham et al. have recently reported two mixed-valence manganese vanadates.²³ In addition the reduced oxide $[\text{Mn}_2^{\text{IIIV}}\text{VO}_4]$ is known,²⁴ as well as the more oxidized species $\text{Cs}_3[\text{Mn}_3^{\text{IIIIV}}\text{V}_4\text{VO}_{16}]$,²⁵ and compounds incorporating polyoxo-metalate cluster anions with Mn^{IV} and V^{V} .²⁶ Manganese vanadates with open frameworks, such as **MnVO-1** and **MnVO-5**, thus offer the prospect of yielding redox-active microporous solids if the organic templates can be removed from their channels by ion exchange.

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Supporting Information Available: Structure determination summaries and tables for **MnVO-3**, **MnVO-4**, and **MnVO-5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(21) Mn^{II} and V^{V} are also found in the minerals Brakebuschite, $[\text{Pb}_2\text{Mn}(\text{VO}_4)_2\text{H}_2\text{O}]$: Donaldson, M. D.; Barnes, W. H. *Am. Miner.* **1955**, *40*, 597. Pyrobelonite, $[\text{PbMn}(\text{OH})(\text{VO}_4)]$: Donaldson, M. D.; Barnes, W. H. *Am. Miner.* **1955**, *40*, 580. Thortveitite $[\text{Mn}_2\text{V}_2\text{O}_7]$: Dorm, E.; Marinder, B. O. *Acta Chem. Scand.* **1967**, *21*, 590. Nord, A. G. *Neues Jahrb. Miner.* **1984**, 283. And Reppiaite $[\text{Mn}_5(\text{OH})_4(\text{VO}_4)_2]$: Basso, R.; Lucchetti, G.; Zefiro, L.; Palenzona, A. *Z. Krist.* **1992**, *201*, 223.

(22) For example $[\text{BaMn}_2(\text{VO}_4)_2]$: von Postel, M.; Müller-Buschbaum, H. *Z. Anorg. Allg. Chem.* **1992**, *615*, 97. $[\text{LiMnVO}_4]$: Sato, M.; Kano, S. *Chem. Lett.* **1994**, 427. Padhi, A. K.; Archibald, W. B.; Nanjundaswamy, K. S.; Goodenough, J. B. *J. Solid State Chem.* **1997**, *128*, 267. $[\text{Mn}(\text{VO}_3)_2](\text{H}_2\text{O})_n$, *n* = 1, 2, 4: Liao, J.-H.; Drezen, T.; Leroux, F.; Guyomard, D.; Piffard, Y. *Eur. J. Solid State Chem.* **1996**, *33*, 411. $[\text{K}_2\text{Mn}_3(\text{OH})_2(\text{VO}_4)_2]$: Liao, J.-H.; Guyomard, D.; Piffard, Y.; Tournoux, M. *Acta Crystallogr.* **1996**, *C52*, 284.

(23) Zhang, F.; Whittingham, M. S. *Electrochem. Comm.* **2000**, *2*, 69–71. Zhang, F.; Zavalij, P. Y.; Whittingham, M. S. *J. Mater. Chem.* **1999**, *9*, 3137–3140.

(24) Bernier, J. C.; Poix, P.; Michel, A. *Bull. Chim. Soc. Fr.* **1963**, 1724.

(25) This has a 2-D sheet structure which is unrelated to **MnVO-1** or **MnVO-2**. Le Page, Y.; Strobel, P. *Inorg. Chem.* **1982**, *21*, 620.

(26) Ichida, H.; Nagai, K.; Sasaki, Y.; Pope, M. T. *J. Am. Chem. Soc.* **1989**, *111*, 586.