

**Luís Cunha-Silva,<sup>a</sup> Fa-Nian Shi,<sup>a</sup>  
 Jacek Klinowski,<sup>b</sup> Tito Trindade,<sup>a</sup>  
 João Rocha<sup>a</sup> and Filipe A.  
 Almeida Paz<sup>a\*</sup>**

<sup>a</sup>Department of Chemistry, University of Aveiro, CICECO, 3810-193 Aveiro, Portugal, and  
<sup>b</sup>Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England

Correspondence e-mail: fpaz@dq.ua.pt

**Key indicators**

Single-crystal X-ray study  
 T = 180 K  
 Mean  $\sigma(C-C) = 0.004 \text{ \AA}$   
 H-atom completeness 89%  
 R factor = 0.040  
 wR factor = 0.110  
 Data-to-parameter ratio = 15.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

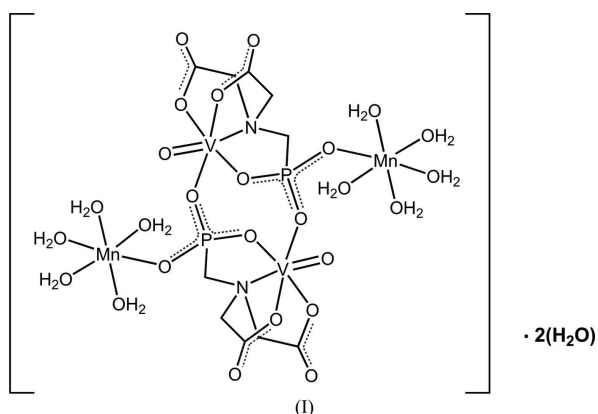
**Decaquadioxobis[ $\mu_3$ -N-(phosphonomethyl)-iminodiacetato]dimanganesedivanadium dihydrate**

The crystal structure of the title compound,  $[Mn_2V_2(C_5H_6NO_7P)_2O_2(H_2O)_{10}] \cdot 2H_2O$ , contains a centrosymmetric dimeric  $[V_2O_2(pmida)_2]^{4-}$  unit [where  $H_4pmida$  is N-(phosphonomethyl)iminodiacetic acid] connecting two neighbouring  $Mn^{2+}$  cations through the phosphonate groups. The crystal structure is characterized by the presence of an extensive network of strong and highly directional O—H...O hydrogen bonds, involving the water molecules (coordinated and uncoordinated) and the functional groups of  $pmida^{4-}$ .

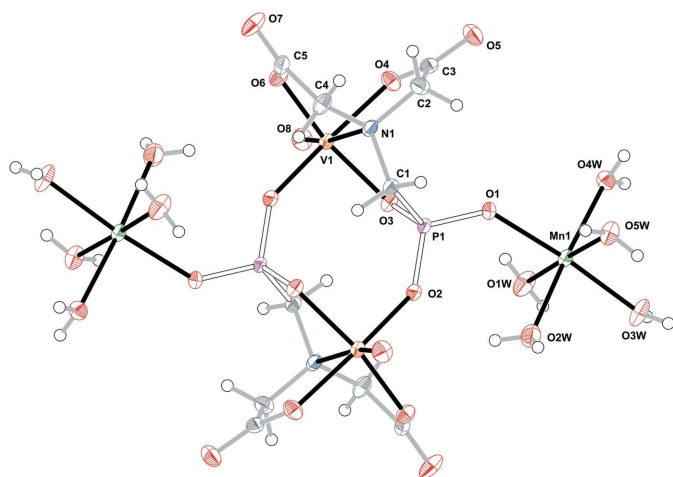
Received 13 December 2006  
 Accepted 15 December 2006

**Comment**

Since the report by Hoskins & Robson (1990), research focused on the structural design and synthesis of novel coordination-based materials, in which the topology is extended from discrete complexes to one, two or three dimensions, has seen a great and exponential growth (for recent reviews see Cheetham *et al.*, 2006; Kitagawa & Uemura, 2005). During the course of our ongoing research on novel multi-dimensional hybrid crystalline materials incorporating N-(phosphonomethyl)iminodiacetic acid ( $H_4pmida$ ) residues (Mafra *et al.*, 2006; Almeida Paz *et al.*, 2004; Almeida Paz, Shi, Trindade *et al.*, 2005; Almeida Paz, Shi, Mafra *et al.*, 2005; Almeida Paz, Rocha, Klinowski *et al.*, 2005; Shi *et al.*, 2005; Shi, Almeida Paz, Trindade & Rocha, 2006; Shi, Almeida Paz, Girginova, Amaral *et al.*, 2006; Shi, Almeida Paz, Girginova, Rocha *et al.*, 2006), we have isolated the crystalline material  $[Mn_2V_2O_2(pmida)_2(H_2O)_{10}] \cdot 2H_2O$  [where  $pmida^{4-}$  is  $(C_5H_6NO_7P)^{4-}$ ], (I), whose crystal structure at the temperature of 180 (2) K we report here.



The title compound, (I), contains two crystallographically unique metal centres, Mn1 and V1, both exhibiting octahedral coordination geometries,  $\{MnO_6\}$  and  $\{VO_5N\}$  (Fig. 1; Table 1). Mn1 is coordinated by five water molecules plus one O atom



**Figure 1**

The structure of the tetranuclear centrosymmetric  $[\text{Mn}_2\text{V}_2\text{O}_2(\text{pmida})_2(\text{H}_2\text{O})_{10}]$  complex, showing the labelling scheme for all non-H atoms belonging to the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres. The water molecule of crystallization, O6W, was omitted for clarity. Symmetry transformation used to generate non-labelled atoms:  $2 - x, -y, -z$ .

from the  $\mu_3$ -bridging phosphonate group of pmida<sup>4-</sup> (Fig. 1), with a coordination geometry resembling a quasi-regular octahedron [Mn–O bond lengths ranging from 2.092 (2) to 2.236 (2) Å; *cis* and *trans* O–Mn–O angles found in the 86.85 (10)–93.21 (11)° and 175.14 (10)–178.21 (9)° ranges, respectively; see Table 1]. The intermetallic Mn1...Mn1<sup>i</sup> distance between *exo*-coordinated manganese(II) centres (and across the unit depicted in Fig. 1) is of 10.175 (3) Å, while the shortest Mn1...V1<sup>i</sup> distance within the tetranuclear unit is 5.368 (1) Å [symmetry code: (i)  $2 - x, -y, -z$ ].

The core of the neutral tetranuclear  $[\text{Mn}_2\text{V}_2\text{O}_2(\text{pmida})_2(\text{H}_2\text{O})_{10}]$  molecule is composed of the anionic centrosym-

metric  $[\text{V}_2\text{O}_2(\text{pmida})_2]^{4-}$  dimeric unit, first described by Crans *et al.* (1998). The geometrical aspects of this unit, in particular the highly distorted octahedral coordination mode of V1 (Table 1) plus the coordination fashion of the pmida<sup>4-</sup> ligand (which forms with V1 three five-membered chelate rings; see Fig. 1), are typical and in good agreement with those described in detail in our previous reports (Almeida Paz *et al.*, 2004; Almeida Paz, Shi, Trindade *et al.*, 2005; Almeida Paz, Shi, Mafra *et al.*, 2005; Almeida Paz, Rocha, Klinowski *et al.*, 2005; Shi *et al.*, 2005; Shi, Almeida Paz, Trindade & Rocha, 2006; Shi, Almeida Paz, Girginova, Amaral *et al.*, 2006; Shi, Almeida Paz, Girginova, Rocha *et al.*, 2006).

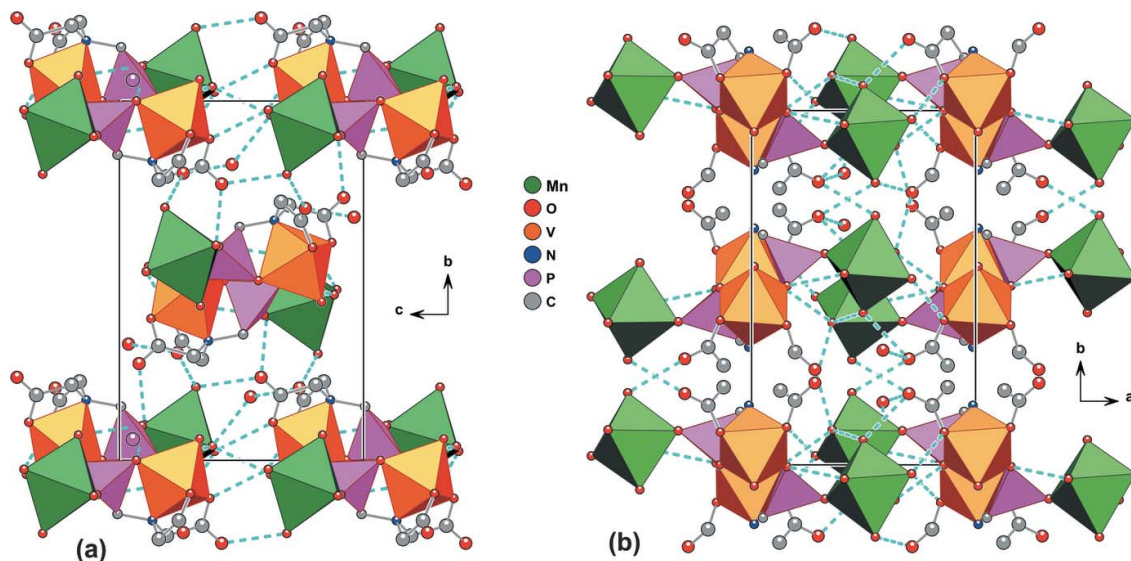
In the extended solid-state  $[\text{Mn}_2\text{V}_2\text{O}_2(\text{pmida})_2(\text{H}_2\text{O})_{10}]$  molecular units pack closely in a typical brick-wall-like fashion along the crystallographic [010] direction (Fig. 2*a*), mediated by an extensive network of strong and highly directional O–H...O hydrogen-bonding interactions, which also involve the water molecule of crystallization (Fig. 2 and Table 3).

## Experimental

Chemicals were readily available from commercial sources and were used as received without further purification: *N*-(phosphonomethyl)iminodiacetic acid hydrate ( $\text{H}_4\text{pmida}$ ,  $\text{C}_5\text{H}_{10}\text{NO}_7\text{P}$ , 97% Fluka), vanadium(IV) oxide sulfate pentahydrate ( $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ , 99% Sigma–Aldrich), manganese(II) acetate tetrahydrate ( $\text{MnC}_4\text{H}_6\text{O}_4 \cdot 4\text{H}_2\text{O}$ , 99.0% Fluka), 4,4'-trimethylenedipyridine (TMD,  $\text{C}_{13}\text{H}_{14}\text{N}_2$ , 98%, Aldrich).

Synthesis was typically carried out in a PTFE-lined stainless steel reaction vessel (*ca* 40 ml), under autogeneous pressure and static conditions in a preheated oven at 393 K. The reaction took place over a period of 3 d, after which the vessel was removed from the oven and left to cool to ambient temperature before opening. The title compound proved to be air- and light-stable.

The title compound was synthesized from a mixture containing 0.40 g of  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ , 0.61 g of  $\text{MnC}_4\text{H}_6\text{O}_4 \cdot 4\text{H}_2\text{O}$ , and 0.40 g of



**Figure 2**

Perspective views of the crystal packing of the title compound, viewed along the (a) [100] and (b) [001] directions of the unit cell. Hydrogen bonds are represented as light-blue dashed lines. H atoms have been omitted for clarity. For details on the hydrogen-bonding geometry see Table 2.

H<sub>4</sub>pmida, and 0.24 g of TMD in ca 15 g of distilled water. The mixture was stirred thoroughly at ambient temperature for 30 minutes, yielding a suspension with a molar composition of 1.4:1.4:1.0:0.7:473, which was transferred to the reaction vessel. After reacting, a small quantity of green/blue single crystals of the title compound were isolated as a pure phase by vacuum filtering, washed with copious amounts of distilled water (ca 3 × 50 ml), and then air-dried at ambient temperature. The same material can also be isolated as large single crystals by slow evaporation (in the open air) of the autoclave mother liquor over a period of one month. It is of considerable interest to note that similar reactions where TMD was not included in the starting reactive mixture failed to lead to the isolation of the title material.

Crystal data

[Mn<sub>2</sub>V<sub>2</sub>(C<sub>5</sub>H<sub>6</sub>NO<sub>7</sub>P)<sub>2</sub>O<sub>2</sub>·(H<sub>2</sub>O)<sub>10</sub>·2H<sub>2</sub>O]  
*M<sub>r</sub>* = 906.11  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 10.096 (2) Å  
*b* = 14.934 (3) Å  
*c* = 10.848 (2) Å  
 β = 110.52 (3)°  
*V* = 1531.8 (6) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.965 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 μ = 1.61 mm<sup>-1</sup>  
*T* = 180 (2) K  
 Prism, brown  
 0.15 × 0.10 × 0.09 mm

Data collection

Nonius KappaCCD diffractometer  
 Thin-slice ω and φ scans  
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)  
*T<sub>min</sub>* = 0.794, *T<sub>max</sub>* = 0.869  
 17432 measured reflections  
 3502 independent reflections  
 2880 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.059  
*θ<sub>max</sub>* = 27.5°

Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.040  
*wR*(*F*<sup>2</sup>) = 0.110  
*S* = 1.05  
 3502 reflections  
 233 parameters  
 H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 3.2528P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 (Δ/σ)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 1.05 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.95 e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

Mn1—O1	2.092 (2)	V1—O2 <sup>i</sup>	1.991 (2)
Mn1—O1W	2.164 (2)	V1—O3	1.988 (2)
Mn1—O2W	2.212 (2)	V1—O4	2.030 (2)
Mn1—O3W	2.152 (2)	V1—O6	2.028 (2)
Mn1—O4W	2.236 (2)	V1—O8	1.598 (2)
Mn1—O5W	2.187 (2)	V1—N1	2.370 (3)
O1—Mn1—O1W	88.63 (9)	O2 <sup>i</sup> —V1—O4	163.79 (9)
O1—Mn1—O2W	90.18 (9)	O2 <sup>i</sup> —V1—O6	86.89 (9)
O1—Mn1—O3W	175.14 (10)	O2 <sup>i</sup> —V1—N1	88.32 (9)
O1—Mn1—O4W	92.29 (8)	O3—V1—O2 <sup>i</sup>	90.96 (9)
O1—Mn1—O5W	93.12 (9)	O3—V1—O4	87.04 (9)
O1W—Mn1—O2W	93.21 (11)	O3—V1—O6	154.03 (9)
O1W—Mn1—O4W	89.40 (9)	O3—V1—N1	79.41 (9)
O1W—Mn1—O5W	178.21 (9)	O4—V1—N1	75.50 (9)
O2W—Mn1—O4W	176.45 (9)	O6—V1—O4	87.90 (9)
O3W—Mn1—O1W	87.68 (10)	O6—V1—N1	74.66 (9)
O3W—Mn1—O2W	86.85 (10)	O8—V1—O2 <sup>i</sup>	101.24 (11)
O3W—Mn1—O4W	90.85 (9)	O8—V1—O3	103.95 (11)
O3W—Mn1—O5W	90.58 (9)	O8—V1—O4	94.85 (11)
O5W—Mn1—O2W	87.12 (10)	O8—V1—O6	101.86 (11)
O5W—Mn1—O4W	90.21 (9)	O8—V1—N1	169.72 (10)

Symmetry code: (i) -x + 2, -y, -z.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1W—H1C...O4W <sup>ii</sup>	0.845 (10)	1.982 (12)	2.813 (3)	167 (4)
O1W—H1D...O5 <sup>ii</sup>	0.84 (3)	1.92 (3)	2.759 (3)	171 (3)
O2W—H2C...O2	0.83 (4)	2.15 (3)	2.847 (3)	142 (4)
O2W—H2D...O6W <sup>iii</sup>	0.84 (4)	1.880 (17)	2.675 (6)	160 (4)
O3W—H3A...O4 <sup>ii</sup>	0.84 (3)	1.920 (16)	2.735 (3)	163 (4)
O3W—H3B...O6 <sup>iv</sup>	0.84 (3)	1.93 (3)	2.745 (3)	166 (4)
O4W—H4C...O7 <sup>v</sup>	0.844 (10)	1.856 (11)	2.698 (3)	175 (3)
O4W—H4D...O3 <sup>ii</sup>	0.85 (3)	1.94 (3)	2.778 (3)	173 (4)
O5W—H5A...O5 <sup>vi</sup>	0.84 (3)	1.996 (15)	2.803 (3)	161 (4)
O5W—H5B...O7 <sup>iv</sup>	0.841 (10)	1.989 (12)	2.823 (3)	171 (3)

Symmetry codes: (ii) -x + 1, -y, -z; (iii) x, y, z - 1; (iv) x - 1, y, z - 1; (v) x - 1, -y + ½, z - ½; (vi) x, -y + ½, z - ½.

H atoms bound to carbon were placed in idealized positions and allowed to ride on their parent atoms with *U<sub>iso</sub>* fixed at 1.2 times *U<sub>eq</sub>*(C) (C—H = 0.99 Å). H atoms associated with the five crystallographically unique coordinated water molecules were markedly visible in difference Fourier maps, and were included in subsequent least-squares refinement cycles with the O—H and H...H distances restrained to 0.84 (1) and 1.37 (1) Å, respectively, to ensure a chemically reasonable geometry of water molecules. These H atoms were also allowed to ride on their parent atoms with *U<sub>iso</sub>* fixed at 1.5 times *U<sub>eq</sub>*(O).

The crystallographically unique water molecule of crystallization was found to be severely affected by disorder, which prevented a sensible refinement using anisotropic displacement parameters. In fact, both the highest peak and deepest hole from the final difference Fourier synthesis were found close to this (0.01 and 0.64 Å, respectively). Therefore, the O atom from this molecule was refined assuming an isotropic displacement parameter. H atoms associated with this water molecule could not be located in difference Fourier maps, and attempts to place them in calculated positions did not lead to a reasonable model for the geometrical aspects of the resulting hydrogen-bonding interactions. Therefore, these H atoms were omitted from the present structural model but were included in the chemical formula of the compound.

Data collection: COLLECT (Nonius 1998); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: SCALEPACK and DENZO (Otwinowski & Minor, 1997); program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXTL (Bruker 2001); molecular graphics: DIAMOND (Brandenburg, 2006); software used to prepare material for publication: SHELXTL.

We are grateful to *Fundação para a Ciência e Tecnologia* (FCT, Portugal) for their general financial support (POCI/QUI/58377/2004 supported by FEDER), and also for the postdoctoral research grants Nos. SFRH/BPD/9309/2002 (to FNS) and SFRH/BPD/14410/2003 (to LCS).

References

Almeida Paz, F. A., Rocha, J., Klinowski, J., Trindade, T., Shi, F.-N. & Mafra, L. (2005). *Prog. Solid State Chem.* **33**, 113–125.  
 Almeida Paz, F. A., Shi, F.-N., Klinowski, J., Rocha, J. & Trindade, T. (2004). *Eur. J. Inorg. Chem.* pp. 2759–2768.  
 Almeida Paz, F. A., Shi, F.-N., Mafra, L., Makal, A., Wozniak, K., Trindade, T., Klinowski, J. & Rocha, J. (2005). *Acta Cryst.* **E61**, m1628–m1632.

- Almeida Paz, F. A., Shi, F.-N., Trindade, T., Klinowski, J. & Rocha, J. (2005). *Acta Cryst.* **E61**, m2247–m2250.
- Altomare, A., Casciaro, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Brandenburg, K. (2006). *DIAMOND*. Version 3.1d. Crystal Impact GbR, Bonn, Germany.
- Bruker (2001). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cheetham, A. K., Rao, C. N. R. & Feller, R. K. (2006). *Chem. Commun.* pp. 4780–4795.
- Crans, D. C., Jiang, F. L., Anderson, O. P. & Miller, S. M. (1998). *Inorg. Chem.* **37**, 6645–6655.
- Hoskins, B. F. & Robson, R. (1990). *J. Am. Chem. Soc.* **112**, 1546–1554.
- Kitagawa, S. & Uemura, K. (2005). *Chem. Soc. Rev.* **34**, 109–119.
- Mafra, L., Almeida Paz, F. A., Shi, F.-N., Rocha, J., Trindade, T., Fernandez, C., Makal, A., Wozniak, K. & Klinowski, J. (2006). *Chem. Eur. J.* **12**, 363–375.
- Nonius (1998). *COLLECT*. Nonius BV Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography, Part A*, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Shi, F.-N., Almeida Paz, F. A., Girginova, P. I., Amaral, V. S., Rocha, J., Klinowski, J. & Trindade, T. (2006). *Inorg. Chim. Acta*, **359**, 1147–1158.
- Shi, F.-N., Almeida Paz, F. A., Girginova, P. I., Mafra, L., Amaral, V. S., Rocha, J., Makal, A., Wozniak, K., Klinowski, J. & Trindade, T. (2005). *J. Mol. Struct.* **754**, 51–60.
- Shi, F.-N., Almeida Paz, F. A., Girginova, P. I., Rocha, J., Amaral, V. S., Klinowski, J. & Trindade, T. (2006). *J. Mol. Struct.* **789**, 200–208.
- Shi, F.-N., Almeida Paz, F. A., Trindade, T. & Rocha, J. (2006). *Acta Cryst.* **E62**, m335–m338.