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Hybrid open frameworks (MIL-*n*). Part 3[†] Crystal structures of the HT and LT forms of MIL-7: a new vanadium propylenediphosphonate with an open-framework. Influence of the synthesis temperature on the oxidation state of vanadium within the same structural type

D. Riou* and G. Férey

Institut Lavoisier UMR CNRS C173, Université de Versailles S^t-Quentin-en-Yvelines, 45 Avenue des Etats-Unis, 78035 Versailles cedex, France

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The hydrothermal synthesis and structure determinations of two vanadium propylenediphosphonate compounds are presented. MIL-7, formulated as $[(VO)_2(OH)(H_2O)\{O_3P(CH_2)_3PO_3\}](H_2O)_2(NH_4)$, is synthesized at 200 °C. Its structure is monoclinic [space group *C*2/*c* (no. 15)] with lattice parameters $a=14.2928(2)$ Å, $b=10.2440(2)$ Å, $c=18.9901(1)$ Å, $\beta=96.658(1)°$, $V=2761.69(7)$ Å^3, $Z=8$. The three-dimensional framework is built up from inorganic V^{IV}–P–O layers strongly related by the alkyl chains. Upon heating hydrothermally the same initial mixture but at 170 °C one obtains a different phase, formulated as $[V_2O_3(H_2O)\{O_3P(CH_2)_3PO_3\}](H_2O)_2(NH_4)$, the structure of which is closely related to MIL-7. Its symmetry is monoclinic [space group *C*2/*c* (no. 15)] with lattice parameters $a=14.8998(8)$ Å, $b=10.2903(6)$ Å, $c=18.515(1)$ Å, $\beta=101.079(1)°$, $V=2785.9(3)$ Å^3, $Z=8$. The topology of the inorganic layers is almost identical, but presents a mixed valence V^{IV}–V^{V} state in a 1 : 1 ratio.

Introduction

Numerous organically templated metallophosphates with open-framework structures have been evidenced since the work of Flanigen and coworkers[1] devoted to the AlPO family. This large class of materials has been extended (i) to mixed Co-GaPO by Chippindale *et al.*,[2] (ii) to 3d transition metal phosphates, principally vanadium and cobalt by the groups of Haushalter[3] and Stucky[4] respectively and (iii) to oxyfluorinated phosphates by Kessler with Cloverite[5] and our team with the ULM-*n* compounds.[6] In this last series ($n \leqslant 19$),[7] we have shown that it is possible to obtain some magnetic compounds, synthesizing for the first time some oxyfluorinated iron phosphates with open frameworks.[8]

One common feature to all these phases is the difficulty of removing the organic template; only a small number retain a good crystallinity after the thermal degradation of the template. To avoid this problem, we have recently initiated a new approach for hybrid open-framework compounds using alkyldiphosphonic acids. Indeed, we have published MIL-2, MIL-3[9] and MIL-5[10] (for Materials of Institut Lavoisier), some vanadodiphosphonates with three-dimensional open-frameworks. In these phases, the alkyl chains participate in building the three-dimensional structure by strong covalent P–C and C–C linkages. The cavities of the frameworks contain some ammonium cations and water molecules. In the case of MIL-5, the framework is neutral and inserts solely some water molecules.

This paper deals with the synthesis and the structure determination of $[(V^{IV}O)_2(OH)(H_2O)\{O_3P(CH_2)_3PO_3\}](H_2O)_2(NH_4)$, denoted MIL-7, a new vanadodiphosphonate with a 3D-structure synthesized with propylenediphosphonic acid. The structure of the compound obtained at lower temperatures is also determined and discussed.

Experimental

Chemical investigations

MIL-7 was synthesized hydrothermally from NH_4VO_3 (99%, Prolabo), propylenediphosphonic acid (Alfa) and desionized water in the molar ratio 1 : 0.6 : 500. The mixture was heated at 473 K during four days. The initial pH was approximatively 3 and increased up to 6 at the end of the reaction. After filtering, MIL-7 is obtained as isolated parallelepipedic blue crystals. The IR spectrum, recorded on a Nicolet Magna-IR 550 in the range 2000–300 cm^{-1}, presents a strong band around 1410 cm^{-1} corresponding to the NH_4^+ cationic vibrations. The bands located around 1190, 1035 and 770 cm^{-1} are attributable to PO_3, $\nu(V{=}O_{terminal})$ and $\nu(V{-}O_{bridging})$ respectively. TG analysis performed with a TA Instruments TGA 2050 apparatus under nitrogen flow shows (i) up to 150 °C a first weight loss (≈11.5%) corresponding to the dehydration and the partial departure of the ammonium cations, this transformation does not affect the crystallinity of the product, (ii) up to 600 °C a continuous weight loss (≈9.4%) corresponding both to the departure of the remaining NH_4^+ and the beginning of the degradation of the propyl chains. The resulting product is rather amorphous but shows the strongest peaks of α-$VOPO_4$.

By heating the mixture previously described at 170 rather than 200 °C, a sheath of dark green crystals is obtained. Their XRD pattern and IR spectra are very similar to those of MIL-7. Note that the crystal used for the crystallographic study presented here, was obtained in a more concentrated mixture (molar ratio 1 : 0.6 : 150).

Structure determinations

Single crystals of both phases were optically selected and their quality tested by Laue photography. The data were collected up to $2\theta=60°$ on a three-circle Siemens SMART diffractometer equipped with a CCD bidimensional detector. The monochromatized wavelength was $\lambda(\text{Mo-K}\alpha)=0.71073$ Å. Both phases show monoclinic symmetry [space group *C*2/*c* (no. 15)] with lattice parameters $a=14.2928(2)$, $b=10.2440(2)$, $c=18.9901(1)$ Å, $\beta=96.658(1)°$, $V=2761.69(7)$ Å^3 and $a=14.8998(8)$, $b=10.2903(6)$, $c=18.515(1)$ Å, $\beta=101.079(1)°$, $V=2785.9(3)$ Å^3 for MIL-7 and its low-temperature (LT) form, respectively. The data were corrected for absorption effects with the SADABS[11] program, and the structures were solved using the SHELX-TL structure

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[†] Part 2: see ref. 10 of this paper.

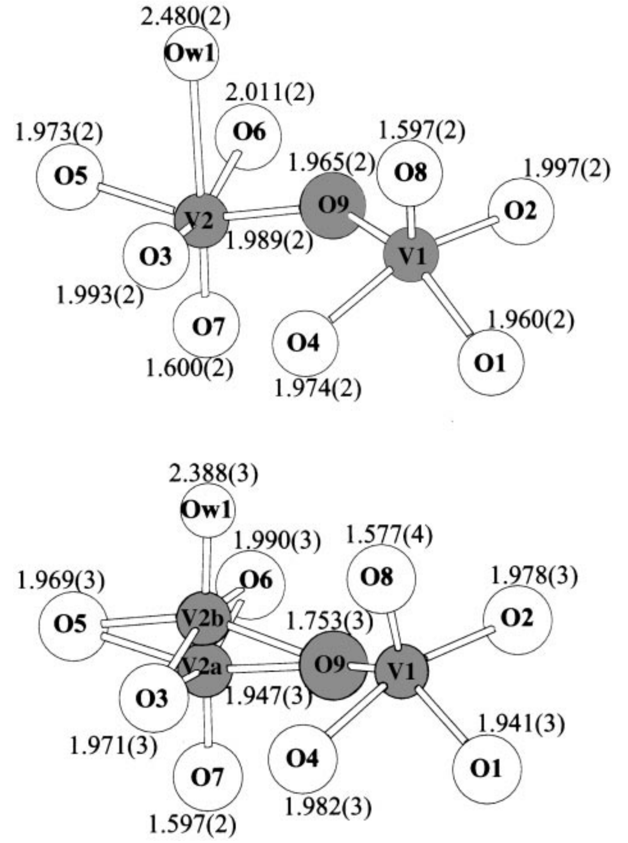

Fig. 1 Vicinities of the vanadium atoms in MIL-7 (top) and its low-temperature form (bottom). In MIL-7LT, the V–O distances (Å) are given for V(2a).

Table 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (10^3 Å^2) for $[(VO)_2(OH)(H_2O)\{O_3P(CH_2)_3PO_3\}]$-$(H_2O)_2(NH_4)$, MIL-7

Atom	x	y	z	U_{eq}[a]
V(1)	1554(1)	6147(1)	894(1)	16(1)
V(2)	2276(1)	4439(1)	−2192(1)	19(1)
P(1)	2149(1)	6251(1)	−749(1)	15(1)
P(2)	3338(1)	1675(1)	−1694(1)	15(1)
O(1)	2036(1)	5746(2)	−6(1)	24(1)
O(2)	3078(1)	6997(2)	−759(1)	22(1)
O(3)	3445(1)	973(2)	−2388(1)	22(1)
O(4)	3171(1)	712(2)	−1098(1)	22(1)
O(5)	2111(1)	5064(2)	−1232(1)	23(1)
O(6)	2529(1)	2665(2)	−1759(1)	22(1)
O(7)	3324(2)	4909(2)	−2280(1)	40(1)
O(8)	433(1)	6243(2)	755(1)	32(1)
O(9)	1909(2)	3487(2)	−3095(1)	31(1)
C(1)	1194(2)	7339(2)	−1046(1)	21(1)
C(2)	4421(2)	2535(2)	−1433(1)	23(1)
C(3)	255(2)	6628(2)	−1209(2)	26(1)
Ow1	700(2)	3625(2)	−1977(1)	42(1)
Ow2	3372(2)	2095(3)	345(2)	63(1)
Ow3	9(2)	9037(3)	492(2)	81(1)
N	4473(5)	5943(4)	−3176(3)	118(2)
H(1a)	1136(2)	7991(2)	−683(1)	26
H(1b)	1339(2)	7789(2)	−1470(1)	26
H(2a)	4570(2)	3071(2)	−1826(1)	27
H(2b)	4332(2)	3112(2)	−1041(1)	27
H(3a)	127(2)	6146(2)	−791(2)	32
H(3b)	309(2)	6001(2)	−1585(2)	32

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

determination package. Geometrical constraints were applied to locate the hydrogen atoms of the alkyl chains. The refinement converged to $R_1(F_o)=0.0335$, $wR_2(F_o^2)=0.0966$ and $R_1(F_o)=0.0483$, $wR_2(F_o^2)=0.1315$ with 3886 and 4137 unique reflections $[I \geq 2\sigma(I)]$ for MIL-7 and MIL-7(LT) respectively.

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (10^3 Å^2) for $[V_2O_3(H_2O)\{O_3P(CH_2)_3PO_3\}]$-$(H_2O)_2(NH_4)$, MIL-7(LT)

Atom	x	y	z	U_{eq}[a]
V(1)	1674(1)	6176(1)	929(1)	29(1)
V(2a)[b]	2423(1)	4462(1)	−2167(1)	26(1)
V(2b)[c]	1923(8)	4181(6)	−2195(3)	22(2)
P(1)	2158(1)	6208(1)	−747(1)	22(1)
P(2)	3377(1)	1659(1)	−1667(1)	22(1)
O(1)	2096(2)	5751(3)	29(1)	32(1)
O(2)	3029(2)	7000(2)	−734(2)	29(1)
O(3)	3338(2)	928(3)	−2386(1)	31(1)
O(4)	3285(2)	742(3)	−1029(1)	31(1)
O(5)	2148(2)	4989(2)	−1211(1)	30(1)
O(6)	2651(2)	2710(3)	−1715(2)	32(1)
O(7)	3432(2)	5022(4)	−2120(2)	58(1)
O(8)	612(3)	6379(3)	864(3)	70(1)
O(9)	2223(4)	3700(4)	−3147(2)	79(2)
C(1)	1188(3)	7208(3)	−1103(2)	27(1)
C(2)	4478(3)	2422(4)	−1444(2)	29(1)
C(3)	283(2)	6482(2)	−1242(2)	33(1)
Ow1	937(2)	3530(2)	−2264(2)	99(2)
Ow2	3450(2)	2066(2)	376(2)	119(2)
Ow3	107(2)	9123(2)	566(2)	132(3)
N	4249(2)	5877(2)	−3274(2)	199(7)
H(1a)	1156(3)	7907(3)	−757(2)	33
H(1b)	1278(3)	7598(3)	−1561(2)	33
H(2a)	4569(3)	2938(4)	−1863(2)	35
H(2b)	4480(3)	3010(4)	−1035(2)	35
H(3a)	222(2)	6000(2)	−804(2)	39
H(3b)	274(2)	5865(2)	−1639(2)	39

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] Occupancy = 88%. [c] Occupancy = 12%.

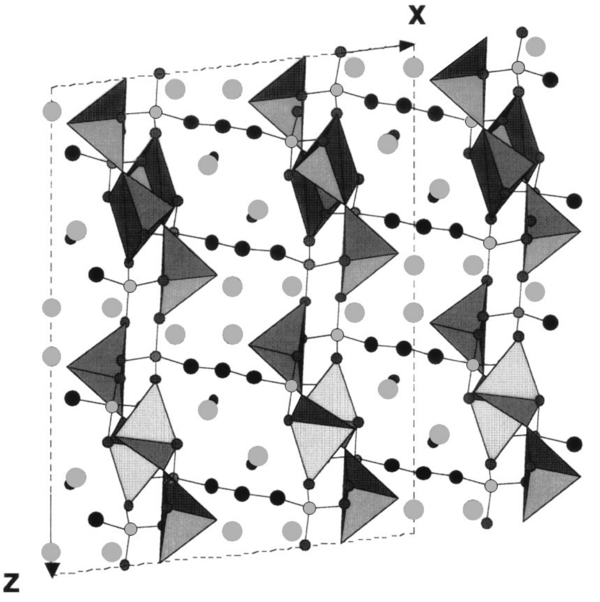

Fig. 2 Projection along [010] of MIL-7. A ball-and-stick model was choosen for the diphosphonic groups. Large circles: black = C, gray = water; small circles: black = P, gray = NH_4^+.

For the latter structure, a strong peak of electronic residual density (>8 e Å^{-3}) was observed in the vicinity of V(2) and the reliability factor remained around 9%. The reliability was improved by splitting this crystallographic site into two different positions whose the occupancy factors were refined to 0.88 and 0.12. That leads to the situation drawn in Fig. 1. In MIL-7, Ow1 corresponds to a water molecule whereas in MIL-7(LT) O1 corresponds to a terminal oxygen atom for 88% and a water molecule for 12% (and *vice versa* for O7).

Atomic coordinates are given in Tables 1 and 2 for MIL-7 and MIL-7(LT) respectively. Principal bond distances appear in Fig. 1. Full crystallographic details, excluding structure

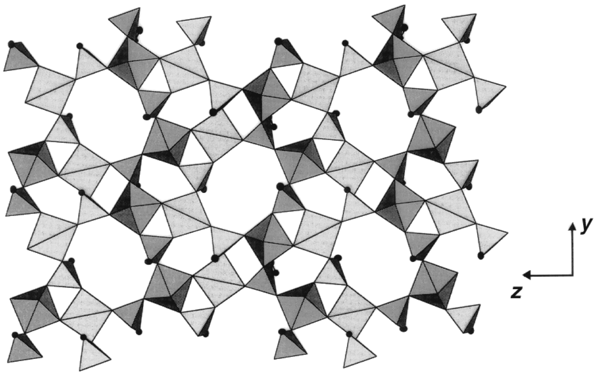

Fig. 3 Projection along [100] of MIL-7 showing the V–P–O inorganic layers.

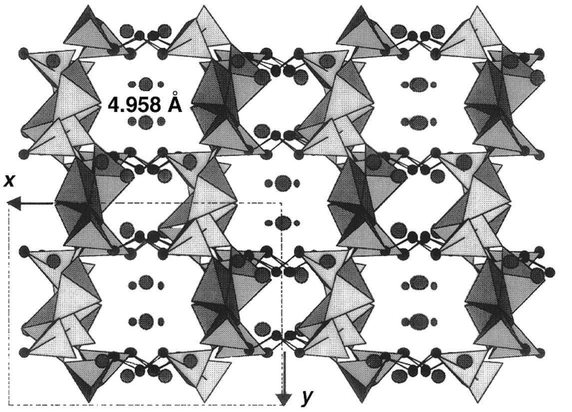

Fig. 4 Projection of MIL-7 along [001] showing the tunnels occupied by the water molecules (large circles) and ammonium cations (small circles).

factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/119.

Description

[(VO)$_2$(OH)(H$_2$O){O$_3$P(CH$_2$)$_3$PO$_3$}](H$_2$O)$_2$(NH$_4$) (MIL-7) presents a pillared structure (Fig. 2) constituted by the stacking along [100] of inorganic layers connected by the organic propyl chains. Water molecules and ammonium ions are inserted between the V–P–O layers. In the inorganic layers, the two vanadium sites adopt square pyramidal coordination with four V–O distances in the basal plane in the range 1.960(2)–2.011(2) Å and a fifth shorter bond corresponding to a vanadyl V=O linkage [1.597(2) and 1.600(2) Å]. Furthermore, *trans* to the vanadyl bond, V(2) presents a very long distance to a water molecule (Fig. 1). The inorganic layers (Fig. 3) are built up from dimers of V(1)O$_5$ and V(2)O$_5$ square pyramids bridged by the O(9) oxygen atom, these dimers being related by the PO$_3$C phosphonate groups. According to the data of Brese and O'Keeffe,[12] both V(1) and V(2) are in oxidation state V^{4+}, and the valency of O(9) is 1.2 showing unambiguously that O(9) corresponds to a hydroxyl group. In the phosphonates, as is usually observed, the P–O distances are in the range 1.520(2)–1.541(2) Å, shorter than the P–C distances [1.802(2) and 1.799(2) Å]. The connections between the dimers of square pyramids and the tetrahedral phosphonate units lead to the formation of layers characterized by the simultaneous presence of five- and eight-membered rings. Such V–P–O layers have already been described by Zubieta and coworkers in the organically templated monophosphonate [(C$_2$H$_5$)$_2$NH$_2$][(CH$_3$)$_2$NH$_2$][V$_4$O$_4$(OH)$_2$(C$_6$H$_5$PO$_3$)$_4$].[13] It is of note that the same layers have been observed by Beltran-Porter in [H$_3$N(CH$_2$)$_2$NH$_3$]$_2$[H$_3$N(CH$_2$)$_2$NH$_2$][Fe^{III}(H$_2$O)$_2$(V^{IV}O)$_8$(OH)$_4$(HPO$_4$)$_4$(PO$_4$)$_4$]·4H$_2$O,[14] where the connections between the V–P–O layers are ensured *via* Fe^{III}O$_4$(H$_2$O)$_2$ octahedra. To our knowledge, this is the first time that such an analogy between the pillared role of an organic chain and an inorganic fragment is observed in a structure. This example confirms the possibility of obtaining three-dimensional frameworks free of template since the ethylenediamine molecules are substituted by water molecules and ammonium cations (Fig. 4).

The low-temperature form of MIL-7 presents a structure that is almost identical. The more important differences are (i) the disorder around the V(2) site already described, (ii) the mixed valency V^{IV}–V^{V} observed in the inorganic layers and explaining the change of color: blue for MIL-7 and dark green for MIL-7(LT). The change of oxidation state concerns solely the V(1) site (Fig. 1). An increase of the V(1)–O(9) distance is observed [from 1.753(3) to 1.965(2) Å]; consequently, the bridging atom of the vanadium dimers is transformed from a hydroxyl group in MIL-7 to an oxygen atom in its low-temperature form.

This structure provides a nice example of a structural type which can accept different oxidation states of vanadium, whilst retaining the initial topology. In MIL-7, all the vanadium are +IV whereas MIL-7LT is a mixed valence compound V^{IV}–V^{V}. The change of valence state is a consequence of the oxygen atom bridging the two polyhedra of the dimer being O^{2-} (at 170 °C) or OH^{-} (at 200 °C). As yet, we have no explanation for this phenomenon. Perhaps the reducing character of the phosphonate increases with temperature and leads to the formation of one V^{4+} which leads to protonation of O(9) with H^{+} coming from the solution, to preserve electroneutrality.

References

1 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146.
2 A. M. Chippindale and R. I. Walton, *J. Chem. Soc., Chem. Commun.*, 1994, 2453; A. M. Chippindale and A. R. Cowley, *Chem. Commun.*, 1996, 673; A. M. Chippindale and A. R. Cowley, *Zeolites*, 1997, **18**, 176.
3 M. I. Khan, L. M. Meyer, R. C. Haushalter, A. L. Schweitzer, J. Zubieta and J. L. Dye, *Chem. Mater.*, 1996, **8**, 43.
4 P. Feng, X. Bu and G. D. Stucky, *Nature*, 1997, **388**, 735.
5 M. Estermann, L. B. McCusker, C. Baerlocher, A. Merrouche and H. Kessler, *Nature*, 1991, **352**, 320.
6 Th. Loiseau and G. Férey, *J. Solid State Chem.*, 1994, **111,** 403; *J. Mater. Chem.*, 1996, **6**, 1073.
7 G. Férey, *J. Fluorine Chem.*, 1995, **72**, 187; *C. R. Acad. Sci. Paris, Ser. II*, 1998, **1**, 1.
8 M. Cavellec, D. Riou, C. Ninclaus, J. M. Grenèche and G. Férey, *Zeolites*, 1996, **17**, 250; M. Cavellec, J. M. Grenèche, D. Riou and G. Férey, *Microporous Mater.*, 1997, **8**, 103; M. Cavellec, D. Riou, J. M. Grenèche and G. Férey, *J. Magn. Magn. Mater.*, 1996, **163**, 173; M. Cavellec, C. Egger, J. Linares, M. Nogues, F. Varret and G. Férey, *J. Solid State Chem.*, 1997, **134**, 349.
9 D. Riou, O. Roubeau and G. Férey, *Microporous and Mesoporous Materials*, 1998, **23**, 23.
10 D. Riou, C. Serre and G. Férey, *J. Solid State Chem.*, in press.
11 G. M. Sheldrick, SADABS program: Siemens area detector absorption corrections, G. Sheldrick, unpublished work.
12 N. E. Brese and M. O'Keeffe, *Acta Crystallogr., Sect. B*, 1991, **47**, 192.
13 M. I. Khan, Y. S. Lee, C. J. O'Connor, R. C. Haushalter and J. Zubieta, *J. Am. Chem. Soc.*, 1994, **116**, 4525.
14 M. Roca, M. D. Marcos, P. Amoros, A. Beltran-Porter, A. J. Edwards and D. Beltran-Porter, *Inorg. Chem.*, 1996, **35**, 5613.

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