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Hybrid open frameworks: synthesis, structure and thermal behaviour of MIL-26, a new three-dimensional vanadium(IV) ethylcarboxyphosphonate $Na[V^{IV}O(O_3P(CH_2)_2CO_2)]\cdot 2H_2O$

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$Na[V^{IV}O(O_3P(CH_2)_2CO_2)]\cdot 2H_2O$, MIL-26, was synthesized hydrothermally at 453 K for 24 h under autogenous pressure. Its three-dimensional open structure was determined by single crystal X-ray diffraction. MIL-26 is monoclinic (space group $P2_1$, no. 4) with cell parameters at 293 K: $a = 6.4041(3)$, $b = 17.6252(8)$, $c = 7.7271(3)$ Å, $\beta = 95.586(2)°$, $Z = 4$, $V = 868.04(7)$ Å^3. Its framework is constituted of double chains based on isolated $V^{IV}O_6$ octahedra linked by PO_3C tetrahedral groups of the $[O_3PCH_2CH_2CO_2]^{3-}$ organic cations. At the other end of each organic chain, CO_2^- chelates a VO_6 octahedron of a neighbouring chain. Each double chain is connected to four others by these organic chains thus defining elliptical channels along [100] in which water molecules and Na^+ cations are located.

Introduction

For some years the synthesis of transition metal based microporous solids such as phosphates has been an active area in regard to their potential applications in catalysis or magnetic properties combined with molecular sieving.[1–10] Extensive use of organic amines as structure directing agents during the hydrothermal synthesis promotes open-framework solid formation, but with organic agents often filling the channels or the cages of the open structures. Moreover, the removal of this organic part of the compound by thermal treatment, in order to obtain real open-framework materials, often leads to the collapse of the crystalline structure. So, a way for avoiding the awkward space filling of organic amines was to develop a new route of synthesis: the use of organo phosphonic or diphosphonic acids instead of amines in the synthesis of open-framework materials.[11–18] Following the same idea, the use of chelating dicarboxylic acids led to new open-framework materials.[19–22]

In this paper we report the hydrothermal synthesis, structure determination and thermal behaviour of a new three-dimensional open-framework compound formulated $Na[V^{IV}O(O_3P(CH_2)_2CO_2)]\cdot 2H_2O$ or MIL-26.

Experimental

Synthesis

MIL-26 or $Na[V^{IV}O(O_3P(CH_2)_2CO_2)]\cdot 2H_2O$ was synthesized hydrothermally at 453 K for 24 h from a mixture of VCl_3 (Alfa, 99%), 2-carboxyethylphosphonic acid (Aldrich, 94%), H_2O and NaOH. The initial molar ratio was 1 VCl_3 : 4 2-carboxyethylphosphonic acid : 500 H_2O. The reagents (0.0873 g of VCl_3, 0.3424 g of 2-carboxyethylphosphonic acid and 5 ml of H_2O) were introduced in the 23 ml Teflon container of a Parr acid digestion autoclave. The initial pH of the solution was adjusted to *ca.* 6 by using 0.5 ml of a solution of NaOH (10 M). After heating at 453 K the final pH remained unchanged. The resulting product was filtered off, washed with distilled water and dried at room temperature. It consisted of very thin needle shaped blue crystals as shown in Fig. 1. The X-ray diffractogram (Fig. 2) obtained on a Siemens D5000 diffractometer ($\lambda_{Cu} = 1.5406$ Å) characteristic of MIL-26 is in excellent agreement with that calculated from the structure determination.

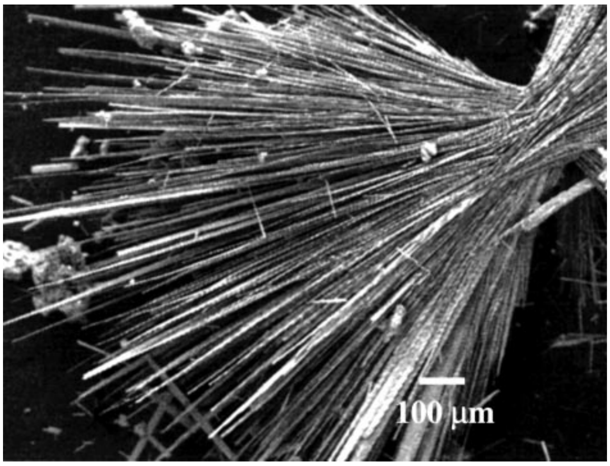

Fig. 1 SEM photograph of thin needle shaped crystals of MIL-26.

Analyses

Chemical elemental analyses of the sample indicated the following results (weight %): Na, 8.1 (calc.: 8.3); V, 18.6 (calc.: 18.4); P, 11.6 (calc.: 11.2). This gives a 1 Na : 1 V : 1 P atomic ratio in agreement with the structural formula.

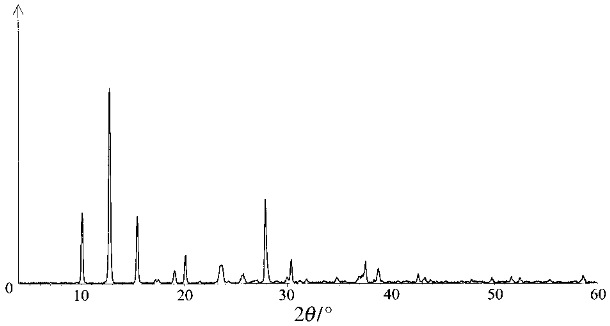

Fig. 2 Experimental X-ray diffractogram of MIL-26 ($\lambda_{Cu} = 1.5406$ Å).

TGA measurements were performed on *ca.* 10 mg of the compound under O_2 gas flow, using a TA-Instrument type 2050 analyser. The heating rate was 5 °C min^{-1} from 30 to 600 °C. The TGA curve (Fig. 3) indicates two distinct weight losses, the first (11.4%) occurring in the range 30–150 °C, the second (18.4%) in the range 350–550 °C. The first step can be attributed to dehydration of the compound (calc. = 13.0%). This dehydration is reversible. The second global loss which probably includes the calcination of the organic part of $(O_3P(CH_2)_2CO_2)$ is more complex as shown by the following thermodiffractometric study.

A thermodiffractogram (Fig. 4, 30–600 °C range) was obtained on a Siemens D5000 diffractometer equipped with a furnace, at the same heating rate of 5 °C min^{-1} (λ_{Co} = 1.7890 Å) from 30 to 800 °C. It confirmed the TGA curve appearance: the dehydration of MIL-26 occurs at 120 °C. The anhydrous phase is stable up to 350–360 °C. At this temperature a phase transition occurs leading to an unknown phase stable in the range 360–460 °C; at 460 °C a second transition leads to another unidentified phase stable in the range 460–540 °C. Above 540 °C the compound becomes amorphous.

Structural determination

A suitable thin needle shaped single crystal of MIL-26 was isolated for data collection at 293 K on a Siemens-type SMART three-circle diffractometer equipped with a CCD detector. An absorption correction specifically for the CCD detector was applied to all data using the SADABS program.[23]

The structure was first solved in the centrosymmetric space group $P2_1/n$ (no. 14), by direct methods using the TREF option of the SHELXTL crystallographic software package.[24] Heaviest atoms (V, P) were first located. The remaining atoms were deduced from Fourier-difference map calculations. Hydrogen atoms of CH_2 groups were localized applying geometrical constraints (HFIX 23). All the atoms were refined with an anisotropic thermal motion except H atoms for which a common isotropic factor was applied. Refinement with 2292 unique reflections ($I > 2\sigma(I)$) gave $R1(F_o) = 0.0717$ and $wR2(F_o^2) = 0.1959$; these high R values are possibly explained by the unfavourable crystal shape and the medium crystalline quality. At the end of this refinement all the cationic (V, P) environments were well defined as well as the organic part of the structure, but we observed a distorted octahedral Na^+ environment constituted of six Na–O bond lengths in the 2.45–3.31 Å range and an unacceptable very short Na···Na distance of 2.41 Å. Moreover, the presence of the (−4 0 1) reflection (I/I_{max} = 4%) suggested in the non-centrosymmetric space group $P2_1$ (no. 4). Subsequent refinement gave the R values in Table 1. All the cationic environments as well as the organic part were well defined and the bond distances of the two Na^+ cations varying in the range 2.40–3.03 Å for Na1 and 2.44–3.17 Å for Na2 are more satisfactory. The Na···Na distance equal to 3.34 Å is more reasonable. The resolution of the structure in the non-centrosymmetric space group led to important changes in the channels whereas the framework remained unchanged overall.

Similar cases have been observed in the organic–inorganic ULM-3[25] and ULM-4[26] aluminophosphates whose structures were solved in non-centrosymmetric space groups: the non-centrosymmetry of the global structure is induced by the non-centric subnetwork of the organic diamines in the channels of the structure, whereas the inorganic skeleton can be considered as centrosymmetric.

Crystal data measurements in the non-centrosymmetric space group $P2_1$ are summarized in Table 1. Atomic coordinates and principal bond lengths are given in Tables 2 and 3.

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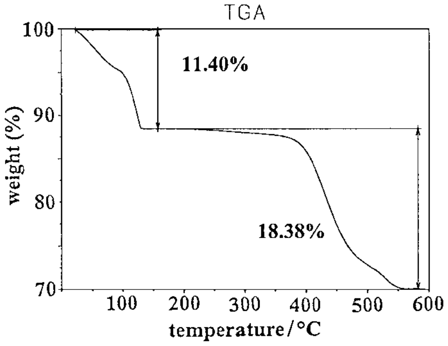

Fig. 3 TGA curve of MIL-26 under O_2 gas flow. The first weight loss corresponds to the dehydration of the compound which is reversible.

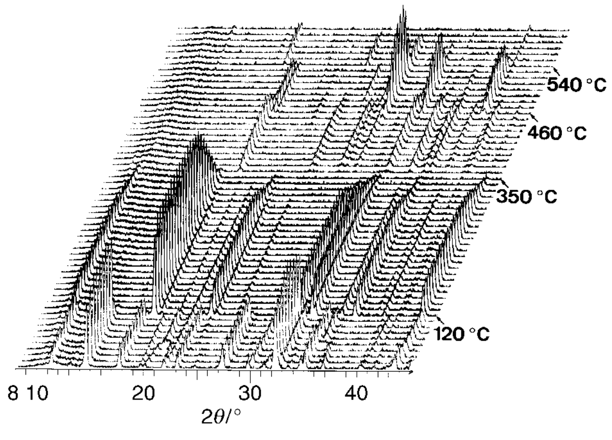

Fig. 4 Thermodiffractogram of MIL-26 in the 30–600 °C range (λ_{Co} = 1.7890 Å). Measurements were made every 10 °C.

Description of the structure

The three-dimensional open structure of MIL-26 (Fig. 5) can be described as the connection by organic chains of 'inorganic' double chains. The latter, displayed in Fig. 6, are constituted of isolated distorted $V^{IV}O_6$ octahedra sharing three oxygen vertices with the PO_3C tetrahedral groups of the organic $[O_3P(CH_2)_2CO_2]^{3-}$ anions (Table 3). This type of double inorganic chain where octahedra and tetrahedra strictly alternate is also encountered in $VO(HPO_4)\cdot 4H_2O$.[27] In the latter, double chains are isolated one from the other owing to the presence of a terminal hydroxyl vertex in the HPO_4 tetrahedra. In MIL-26 this terminal (OH) group is replaced by a C atom (PO_3C tetrahedra), the starting point of the $[O_3PCH_2CH_2CO_2]^{3-}$ organic chains. This is responsible for the three-dimensional character of the structure. Indeed, at the other end of the organic chains, CO_2^- carboxylate groups ($C(3A)O_2^-$ and $C(3B)O_2^-$) chelate vanadium octahedra of a neighbouring double chain *via* O(7)/O(8) apices for the V(2)

Table 1 Crystal data and structure refinement for MIL-26

Formula	$Na[VO(O_3P(CH_2)_2CO_2)]\cdot 2H_2O$
Formula weight	277 g
Crystal system	Monoclinic
Space group	$P2_1$ (no. 4)
a/Å	6.4041(3)
b/Å	17.6252(8)
c/Å	7.7271(3)
β/°	95.586(2)
V/Å^3, Z	868.04(7), 4
μ/cm^{-1}	13.94
Reflections collected	6153
Independent reflections	3357 [R(int) = 0.0563]
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0628$, $wR2 = 0.1605$

Table 2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for MIL-26. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*x*	*y*	*z*	*U*(eq)
V(1)	4884(4)	4333(1)	6821(4)	17(1)
V(2)	161(4)	2511(1)	8187(3)	12(1)
P(1A)	61(5)	4299(3)	7553(6)	15(1)
P(2B)	5030(5)	2551(2)	7435(5)	13(1)
O(1)	475(17)	3604(7)	8740(17)	21(3)
O(2)	4638(17)	3244(7)	6237(17)	17(3)
O(3)	−2049(12)	4264(6)	6488(14)	16(3)
O(4)	7122(17)	2580(7)	8536(14)	29(3)
O(5)	1711(17)	4426(7)	6313(14)	22(3)
O(6)	3262(13)	2470(7)	8635(14)	16(2)
O(7)	241(20)	2175(8)	1213(20)	32(3)
O(8)	34(20)	1409(7)	8983(17)	23(3)
O(9)	5090(19)	4464(8)	8853(16)	29(3)
O(10)	4681(21)	4644(7)	3823(17)	27(3)
O(11)	4964(19)	5442(8)	5955(19)	28(4)
O(12)	−11(17)	2429(9)	6109(16)	31(3)
C(1A)	85(24)	5088(9)	9018(23)	20(4)
C(1B)	4981(30)	1744(10)	5995(24)	32(5)
C(2B)	5139(26)	953(10)	6875(19)	26(5)
C(2A)	−89(24)	5841(9)	8095(24)	29(5)
C(3B)	4871(23)	5317(10)	4352(26)	21(4)
C(3A)	186(26)	1510(11)	0641(28)	29(5)
OW1	3338(18)	3726(10)	1245(19)	54(5)
OW2	−1656(20)	3986(9)	3495(15)	40(3)
OW3	−325(25)	5266(13)	3372(26)	92(7)
OW4	4765(27)	6691(11)	8351(20)	86(7)
Na(1)	1505(15)	3210(8)	3540(16)	102(5)
Na(2)	−3407(18)	2986(9)	1706(17)	116(5)
H(1A1)	−1074(24)	5037(9)	9730(23)	55(11)
H(1A2)	1377(24)	5078(9)	9786(23)	55(11)
H(1B1)	3689(30)	1762(10)	5229(24)	55(11)
H(2B1)	6421(26)	932(10)	7653(19)	55(11)
H(2B2)	3971(26)	893(10)	7573(19)	55(11)
H(2A1)	−1342(24)	5842(9)	7282(24)	55(11)
H(2A2)	1111(24)	5906(9)	7434(24)	55(11)

octahedron and O(10)/O(11) apices for the V(1) octahedron respectively (Table 3, Fig. 6). Each double chain is linked to four neighbouring ones (Fig. 5) thus defining a three-dimensional open framework with *ca.* 11.2 × 6.1 Å elliptical channels in the [100] direction in which water molecules and Na^+ ions are located. In the [010] direction small six-membered apertures on these elliptical channels are also observed. According to Table 3, a vanadyl group is present in each vanadium octahedron with a shorter bond length. In this compound the vanadium oxidation state was confirmed by bond-valence analysis.

Table 3 Principal bond lengths (Å) in MIL-26

V(1)–O(9)	1.579(13)	V(2)–O(12)	1.605(13)
V(1)–O(2)	1.976(12)	V(2)–O(1)	1.980(13)
V(1)–O(3)	2.009(8)	V(2)–O(6)	1.984(9)
V(1)–O(5)	2.038(11)	V(2)–O(4)	1.995(12)
V(1)–O(11)	2.068(14)	V(2)–O(8)	2.041(13)
V(1)–O(10)	2.372(14)	V(2)–O(7)	2.408(15)
P(1A)–O(5)	1.510(12)	P(2B)–O(4)	1.516(11)
P(1A)–O(3)	1.514(10)	P(2B)–O(6)	1.538(9)
P(1A)–O(1)	1.537(13)	P(2B)–O(2)	1.539(14)
P(1A)–C(1A)	1.793(19)	P(2B)–C(1B)	1.804(16)
C(1A)–C(2A)	1.505(24)	C(1B)–C(2B)	1.550(26)
C(2A)–C(3A)	1.536(26)	C(2B)–C(3B)	1.468(25)
C(3A)–O(7)	1.252(23)	C(3B)–O(10)	1.256(23)
C(3A)–O(8)	1.288(24)	C(3B)–O(11)	1.254(23)
Na(1)–OW1	2.399(10)	Na(2)–OW4	2.442(23)
Na(1)–OW2	2.441(18)	Na(2)–OW2	2.444(12)
Na(1)–O(7)	2.633(19)	Na(2)–OW1	2.455(21)
Na(1)–O(12)	2.675(19)	Na(2)–O(4)	2.605(18)
Na(1)–O(2)	2.749(18)	Na(2)–O(7)	2.797(20)
Na(1)–O(5)	3.026(19)	Na(2)–O(6)	3.172(19)
Na(1)··· Na(2)	3.346(15)		

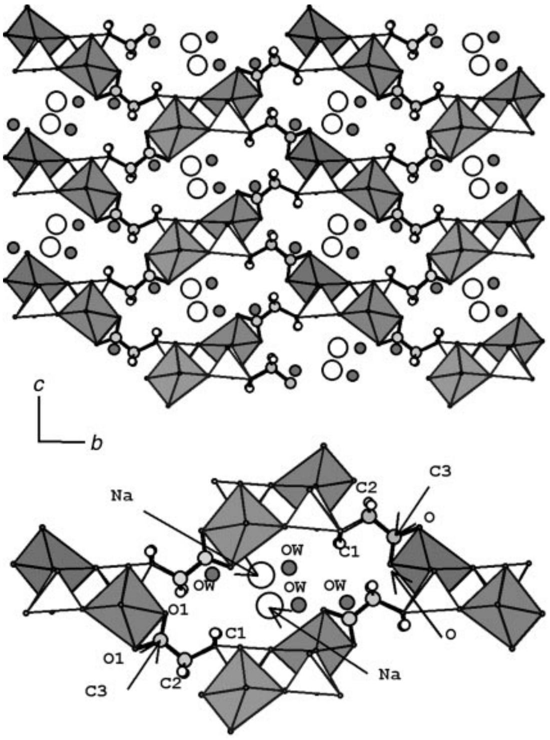

Fig. 5 Projection of the MIL-26 structure along [100] showing elliptical channels in which water molecules (black circles) and Na^+ ions (white large circles) are located. A channel is delimited by four double chains connected by organic chains. PO_3C tetrahedra are white and VO_6 octahedra are grey.

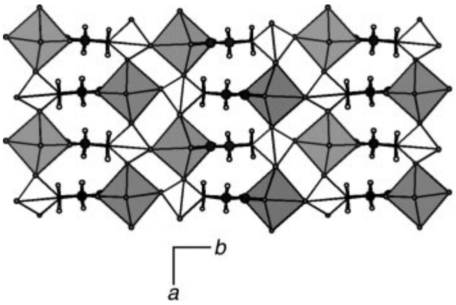

Fig. 6 Projection of the structure along [001] showing the formation of double chains through the connection of isolated octahedra by organic anions.

Conclusion

The use of 2-carboxyethylphosphonic acid with vanadium in order to synthesize a hybrid organic–inorganic material with an open framework was successful. The next step will probably be to synthesize a hybrid compound starting from vanadium and dicarboxylic acids. Furthermore, transposition can be made to iron systems; substitution of iron for vanadium could result in an interesting magnetic ordering temperature associated with new open-framework materials. Such experiments are currently in progress.

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