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Hydrothermal synthesis, structure determination from powder data of a three-dimensional zirconium diphosphonate with an exceptionally high thermal stability: $Zr(O_3P\text{-}(CH_2)\text{-}PO_3)$ or MIL-57

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$Zr(O_3P\text{-}(CH_2)\text{-}PO_3)$ or MIL-57 was prepared in a pure form under hydrothermal conditions (3 days, 493 K, autogenous pressure). Its structure was solved *ab initio* from laboratory powder X-ray diffraction data. This compound is monoclinic (space group $P2_1$ (no. 14)) with $a = 7.589(1)$, $b = 8.110(1)$, $c = 5.056(1)$ Å, $\beta = 103.934(1)°$, $V = 302.14(1)$ Å^3 and $Z = 2$. Its three-dimensional structure is built up from zirconium(IV) octahedra linked together *via* diphosphonate groups. This delimits a three-dimensional network with three and seven-member-ring tunnels along the c axis. The thermal behaviour, deduced from TGA and X-ray thermodiffractometry has been investigated and reveals that MIL-57 is stable under air atmosphere up to 1023 K, which is the highest temperature reported to date for a hybrid inorganic–organic solid. A brief comparison between structures of MIL-57 and ZrP_2O_7 is also reported.

Introduction

The synthesis of hybrid inorganic–organic porous solids is actually a hot topic.[1–5] By associating different organic linkers and the multiple properties of transition or rare-earth metals, this allows the creation of a large number of porous solids with original pore shape and dimensions and sometimes unique physical properties. In such structures, organic species can act either as pillars, linkers and associates with inorganic layers, chains or clusters of transition or rare-earth metals.

In the field of tetravalent metal-based hybrid inorganic–organic porous solids, results are still scarce, mostly because of the relative chemical inertness of these cations. Clearfield and co-workers reported series of pillared zirconium phosphonates,[6] some of them exhibiting a porosity.[7] Recently, a porous titanium polymer coordination was also reported using dihydroxybiphenyl linkers under solvothermal conditions.[8]

We also initiated a systematic study of the titanium(IV) diphosphonate system and recently reported a monodimensional, MIL-10 or $TiO(O_3P\text{-}(CH_2)\text{-}PO_3)(NH_4)_2$, and the three-dimensional titanium(IV) diphosphonates MIL-22 or $Ti_3O_2(H_2O)_2(O_3P\text{-}(CH_2)\text{-}PO_3)_2{\cdot}2H_2O$ and MIL-25$_n$ (n = 2, 3) or $Ti(O_3P\text{-}(CH_2)_n\text{-}PO_3)$.[9–11]

This paper deals with the synthesis, the crystal structure and the thermal behaviour of a new three-dimensional zirconium diphosphonate with an open structure: $Zr(O_3P\text{-}(CH_2)\text{-}PO_3)$ or MIL-57.

Experimental

Synthesis and chemical analysis

The title compound was hydrothermally synthesised (T = 493 K, autogenous pressure for 3 days) from a mixture of hydrous $ZrOCl_2$ (Aldrich, 97%), $H_2O_3P\text{-}(CH_2)\text{-}PO_3H_2$ (Alfa 97%), HF (Prolabo Normapur 40%), and H_2O in the molar ratio 1.0 : 1.0 : 1.0 : 500 introduced in this order without stirring in a Teflon-lined steel autoclave. At 493 K, a white crystalline powder of MIL-57 is obtained. The pH remains strongly acidic (<1) during the reaction.

Quantitative elemental analyses indicated P/Zr, P/C ratios respectively equal to 2.2, 1.81 which is in good agreement with the theoretical values: 2 and 2. A TGA experiment performed on a TA-Instrument type 2050 analyser apparatus, under oxygen atmosphere, indicated almost no weight loss in the 273–1273 K range; the departure of the organic moieties and their replacement by oxygen atoms at temperatures above 1073 K explained the absence of any observed loss (theoretical loss: 0.7%). The infrared spectrum of the title compound clearly showed the presence of the vibrational bands characteristic of the –(P–O–Zr)– groups around 1100 cm^{-1}; the bands at 2980 and 2915 cm^{-1} also indicated the presence of CH_2 groups characteristic of the organic part of the diphosphonate agents.

The X-ray thermodiffractometry, performed in the furnace of a Siemens D-5000 diffractometer in the θ–θ mode showed several steps in the decomposition. This point will be discussed further in this paper.

Structure determination

Single crystals could not be obtained even with an increase in synthesis time, in synthesis temperature, or by varying the stoichiometry. The powder diffraction pattern of MIL-57 was collected on a D5000 (θ–2θ mode) Siemens diffractometer with $\lambda_{Cu}(K\alpha1, K\alpha2) = 1.54059, 1.54439$ Å. Its pattern was indexed with the Dicvolgv program.[12] A monoclinic solution with adequate figures of merit was found (M/F(20) = 54/87 (0.0079, 29)). Systematic absences were consistent with the space group $P2_1$ or $P2_1/m$ (no.11).

To minimise the preferred orientation effect on the XRD pattern of MIL-57, the powder was pulverised with a Mac Crone grinder in ethanol (Prolabo, 95%) and dried at 373 K. The fine powder was then mounted in a top-loaded Mac Murdie type sample-holder which led to a reduction of the preferred orientation effect.

The pattern matching was performed with Fullprof2k using the Winplotr package.[13,14] The direct method used Expo.[15] The structure of MIL-57 was then refined, also using Fullprof. A six parameter polynomial function was used to adjust the

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Table 1 Crystal data and structure refinement parameters for MIL-57

Formula	Zr(O_3P-(CH_2)-PO_3)
M/g mol^{-1}	263.18
Calculated density/g cm^{-3}	2.89
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	7.589(1)
b/Å	8.110(1)
c/Å	5.056(1)
β/°	103.934(1)
V/Å^3	302.14(1)
Z	2
Figures of Merit	M_{20} = 54; F_{20} = 87
Radiation (λCu/Å: $K_{\alpha1}$, $K_{\alpha2}$)	1.54059, 1.54439
2θ range/°	10–80
No. reflections	207
No. atoms	10
No. intensity-dependent parameters	32
No. profile parameters	18
R_p	0.075
R_{wp}	0.107
R_B	0.029
R_F	0.023

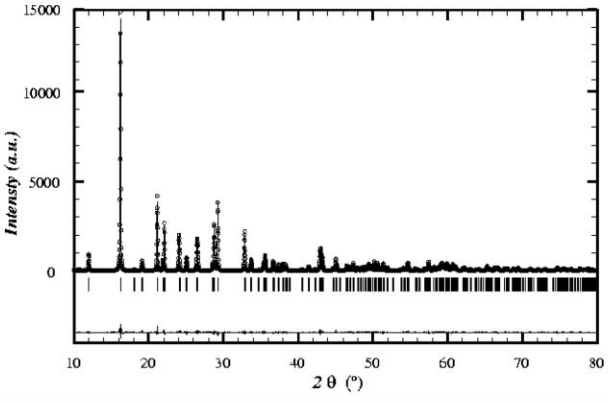

Fig. 1 Final Rietveld plot of MIL-57.

Table 2 Atomic coordinates for MIL-57

Atom	x	y	z
Zr	0.7697(3)	0.295(1)	0.2961(4)
P(1)	0.609(10)	0.541(2)	0.754(1)
P(2)	−0.0138(8)	0.623(2)	0.100(1)
O(1)	0.113(2)	0.626(2)	−0.100(2)
O(2)	0.959(2)	0.454(2)	0.217(2)
O(3)	0.058(1)	0.746(2)	0.336(2)
O(4)	0.605(2)	0.389(2)	0.941(3)
O(5)	0.665(2)	0.482(2)	0.490(3)
O(6)	0.420(2)	0.624(2)	0.666(2)
C	−0.239(2)	0.706(2)	0.931(3)

Table 3 Principal bond lengths (in Angströms) for MIL-57

Zr–O(1)	2.02(2)	Zr–O(2)	2.04(2)
Zr–O(3)	2.04(1)	Zr–O(4)	2.07(1)
Zr–O(5)	2.07(2)	Zr–O(6)	2.04(2)
P(1)–O(4)	1.56(2)	P(1)–O(5)	1.57(2)
P(1)–(O6)	1.55(2)	P(1)–C	1.86(2)
P(2)–O(1)	1.56(1)	P(2)–O(2)	1.53(2)
P(2)–(O3)	1.55(2)	P(2)–C	1.84(2)

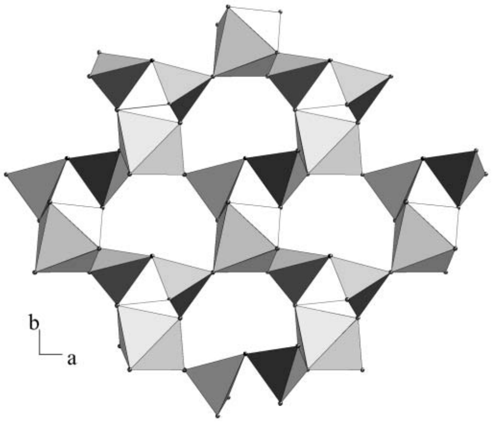

Fig. 2 Polyhedral representation of the structure of MIL-57 along the *c* axis.

background with a pseudo-Voigt function to determine the peak profile. Two asymmetry parameters, an overall thermal parameter and a preferred orientation correction parameter were also applied during refinements. Due to the high quality of the X-ray data, no distance and angle constraints were applied during the refinement. The preferred orientation vector was chosen as the direction parallel to the channels. Details of the structure determination are summarised in Table 1.

The final agreement factors are satisfying: R_p = 7.5%, R_{wp} = 10.7% and R_{Bragg} = 2.9%. The final Rietveld plot is reported in Fig. 1. Atomic coordinates are given in Table 2 while bond distances are reported in Table 3.

Results and discussion

MIL-57 is three-dimensional (Fig. 2). Its structure is built up from the corner-sharing of ZrO_6 octahedra and (PO_3-CH_2-PO_3) groups, with two types of linkage: Zr–O–P and P–C–P. The ZrO_6 octahedra are almost regular (Zr–O = 2.05 Å). The diphosphonate units share all their oxygen atoms with the zirconium ones. This creates seven- and three-member-ring channels along the *c* axis.

The interatomic distances are very well defined for a structure based on laboratory powder diffraction data: Zr–O and P–O distances are within the 2.02–2.07 Å and 1.53–1.57 Å ranges, respectively, while the P–C distances are usual (1.84 and 1.86 Å).

MIL-57 is topologically equivalent with an iron(III) lithodiphosphate, $LiFeP_2O_7$, synthesised at high temperatures.[16] In the latter solid, the seven member-ring channels are filled with lithium cations. In our case, however, the small cavities exhibit a low porosity since the –CH_2 groups are pointing towards the channels.

The thermal stability of MIL-57 is exceptional regarding to other metallophosphonates and hybrid inorganic–organic solids. The TGA measurement, performed between 293 and 1273 K under oxygen atmosphere, shows no significant weight loss in the whole temperature range. The X-ray thermodiffractogram under air atmosphere of MIL-57 (Fig. 3), indicates no structural change below 1023 K.

At higher temperatures, MIL-57 decomposes and the dense zirconium phosphate ZrP_2O_7 crystallises with no evidence of ZrO_2, as expected from the formula. The existence of diphosphate groups reveals a kind of structural memory. The departure of the carbon between the two P atoms probably

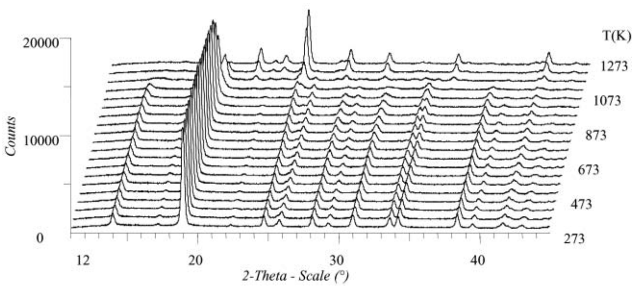

Fig. 3 X-Ray thermodiffractogram of MIL-57 under air atmosphere.

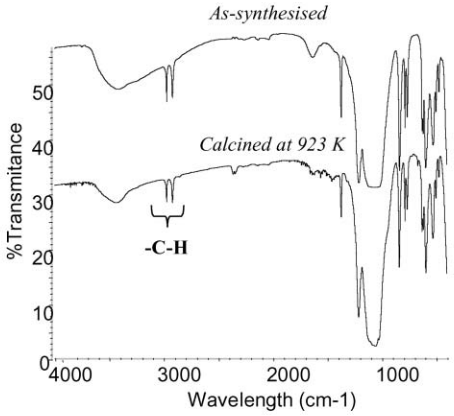

Fig. 4 Infrared spectra of MIL-57 as-synthesised and MIL-57 calcined overnight at 973 K.

occurs at temperatures between 1023 and 1173 K, collapsing the structure, but the short range topology is kept and the further heating under air atmosphere leads to the diphosphate form ZrP_2O_7.[17] At this stage, this structural change from MIL-57 to ZrP_2O_7 could be simply a structural change between two forms of the diphosphate, if the methylene group was replaced upon heating by an oxygen atom with retention of the structure of MIL-57. Infrared spectroscopy however rules out this hypothesis since experiments performed on MIL-57 and its calcined form, obtained by heating MIL-57 at 973 K under air overnight, indicates both that the structure is kept and that the organic group is still present within the framework at 973 K (see Fig. 4).

Despite similar composition, albeit carbon in MIL-57 is replaced by oxygen atoms in ZrP_2O_7, these two solids exhibit different structures (Fig. 2, 5).

ZrP_2O_7 is a dense phase exhibiting five member-rings and no porosity at all while MIL-57 possesses seven member-rings and a small porosity. This can be explained through the mode of connection of the diphosphonate or diphosphate units (Fig. 6).

In MIL-57, each unit acts as a tridendate group grafted directly on a zirconium atom, sharing vertices with the zirconium octahedra and connecting five different octahedra; in ZrP_2O_7, the diphosphate exhibits a different binding mode, connecting six different zirconium atoms. In addition, in both cases, tetrahedra of each unit are in the first case pointing in the same direction while in ZrP_2O_7, they are oriented in the opposite direction. Finally, the topology of MIL-57 can be obtained starting from ZrP_2O_7, removing one octahedra from the super-unit (see Fig. 6), rotating the diphosphate until each tetrahedron points in the same direction and by connecting the last free oxygen to one of the zirconium octahedra. In MIL-57, the super-unit points towards five directions of the space, instead of six as in the case of ZrP_2O_7. This creates additional space and explains the lower density of MIL-57 compared to ZrP_2O_7 (*i.e.* 2.89 instead of 3.33 g cm^{-3}). Unlike the super-units of ZrP_2O_7, super-units of MIL-57 exhibit no centre of symmetry (Fig. 6). This explains why ZrP_2O_7 and MIL-57 are centro- and noncentro-symmetric, respectively.

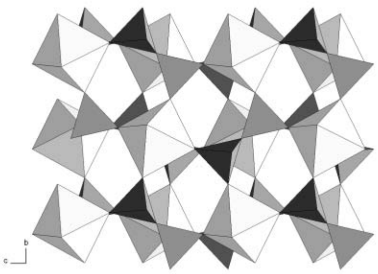

Fig. 5 Polyhedral representation of the structure of ZrP_2O_7 along the *a* axis.

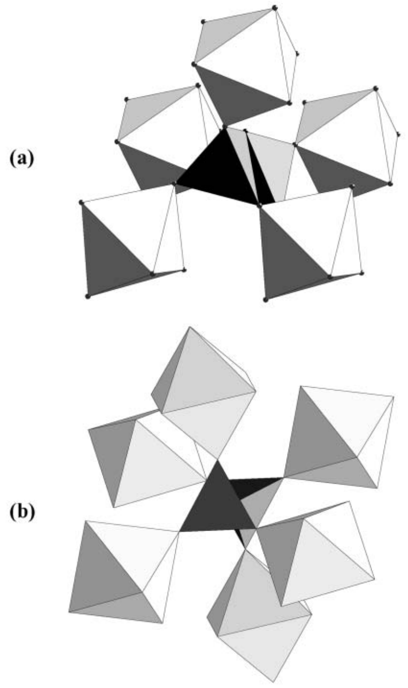

Fig. 6 Comparison of the connecting mode of the diphosphonate or diphosphate units in MIL-57 (a) and ZrP_2O_7 (b).

In conclusion, MIL-57 is one of the rare examples of three-dimensional zirconium diphosphonate with an open structure characterised up to now, and the first whose structure does not exhibit a pillared structure. This result enlightens once again the original behaviour of the methylenediphosphonic acid under hydrothermal conditions. It acts as a variant of a pyrophosphate while diphosphonic acids with longer chains usually lead to pillared structures. MIL-57 exhibits also an exceptional thermal resistance, the highest reported so far for a hybrid inorganic–organic solid. Other similar compounds are currently under study to enlarge the field of microporous hybrid phases based on tetravalent metals.

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