Inorg. Chem. **2001,** *40,* 723−725

Hydrothermal Synthesis and ab Initio Structural Resolution from X-ray Powder Diffraction of a New Open Framework Cu(II) Carboxyethylphosphonate: $Na[Cu(O_3P-(CH_2)_2-CO_2)]$

Myriam Riou-Cavellec,* Morgane Sanselme, Nathalie Guillou, and Gérard Férey

Institut Lavoisier, UMR CNRS 8637, Université de Versailles, 45 Avenue des Etats-Unis,
78035 Versailles Cedex, France

Received July 11, 2000

$Na[Cu(O_3P-(CH_2)_2-CO_2)]$, or MIL-39 (for Material of Institut Lavoisier), was synthesized hydrothermally at 443 K for 72 h under autogenous pressure. Its three-dimensional open structure was determined from X-ray powder diffraction. MIL-39 is monoclinic, it crystallizes in the space group $P2_1/m$, (No. 11) with the following cell parameters at 293 K: $a = 8.808(1)$ Å, $b = 6.4149(8)$ Å, $c = 5.3418(8)$ Å, $\beta = 105.75(1)°$, $Z = 2$. Its framework contains double rows built from isolated distorted CuO_5 square pyramids linked by PO_3C tetrahedral groups from $(O_3P-(CH_2)_2-CO_2)^{3-}$ organic moieties. At the other end of these latter moieties, the carboxylate group links two different Cu polyhedra of two neighboring chains. These connections define two types of channels along [010].

Introduction

Recently, new, original open-framework materials have been synthesized hydrothermally using organic species such as diphosphonic[1−6]or di/tricarboxylic[7−10] acids. The syntheses of hybrid organic−inorganic compounds using both functional carboxylic and phosphonic groups have also been reported in the literature.[11−16] Layered compounds[11,12] and also pillared/three-dimensional[13−16] open-framework compounds in which both different functional groups participate in the formation of the three-dimensional framework have been discovered.

In this paper, we report the hydrothermal synthesis, the ab initio structural determination from X-ray powder diffraction of a new three-dimensional, open-framework copper carboxyethylphosphonate compound formulated as $Na[Cu(O_3P-(CH_2)_2-CO_2)]$, or MIL-39 (for Material of Institut Lavoisier). Structural comparison with the three-dimensional compound MIL-26,[16] or $Na[V^{IV}O(O_3P-(CH_2)_2-CO_2)](H_2O)_2$, will be presented.

Table 1. Crystallographic Data for MIL-39

formula	$Na[Cu(O_3P-(CH_2)_2-CO_2)]$
fw (g mol^{-1})	237.51
cryst syst	monoclinic
space group	$P2_1/m$
a (Å)	8.808(1)
b (Å)	6.4149(8)
c (Å)	5.3418(8)
β (deg)	105.75(1)
V (Å^{-3})	290.48(5)
Z	2
figures of merit	$M_{20} = 79$; $F_{30} = 80$ (0.0075, 50)
radiation (Å)	1.5418
2θ range (deg)	8−108
no. reflns	785
no. atoms	10
no. structural params	21
R_P	0.034
R_{WP}	0.045
R_B	0.059
R_F	0.058

Experimental Section

Synthesis. MIL-39 was synthesized hydrothermally from $CuCl_2$, $2H_2O$ (Prolabo), carboxyethylphosphonic acid (Aldrich, 94%), and water. The molar ratios in the initial mixture were 1:1:100 $CuCl_2{\cdot}2H_2O/H_2O/H_2O_3P-(CH_2)_2-CO_2H/H_2O$. The pH of the above solution was controlled and raised to ca. 6−7 using a NaOH solution (10 mol L^{-1}) in order to deprotonate the acidic groups. Reactants were introduced in a Teflon lined vessel, then sealed in a Parr acid digestion bomb. The latter was heated at 170 °C for 72 h under autogenous pressure. At the end of the reaction, the pH of the solution was ca. 6, and the resulting product was filtered, washed with water, and dried at room temperature. It consisted of a well-crystallized blue powder.

Analysis. Semiquantitative energy dispersive X-ray (EDX) analysis of the obtained powder (performed on a JEOL 5800 LV scanning microscope equipped with Oxford Linkisis analyzer) gave us the following ratio: 1:1:1 Cu/P/Na.

Elemental analysis results indicated the following (wt %): Cu, 26.66 (calcd, 26.75); P, 12.56 (calcd, 13.04); C, 14.53 (calcd, 15.15); Na, 9.36 (calcd, 9.68). This confirmed the ratio 1:1:3:1 Cu/P/C/Na.

---

* To whom correspondence should be addressed. E-mail: cavellec@chimie.uvsq.fr. Fax: (33) (0) 1 39 25 43 58.

(1) Le Bideau, J.; Payen, C.; Palvadeau, P.; Bujoli, B. *Inorg. Chem*. **1994**, *33*, 4885.

(2) Thompson, M. E. *Chem. Mater*. **1994**, *6*, 1168.

(3) Maeda, K.; Akimoto, J.; Kiyozumi, Y.; Mizukami, F. *Angew. Chem., Int. Ed. Engl*. **1995**, *34* (11), 1199.

(4) Bonavia, G.; Haushalter, R. C.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem*. **1996**, *35*, 5603.

(5) (a) Clearfield, A. *Curr. Opin. Solid State Mater. Sci*. **1996**, *1*, 268. (b) *Chem. Mater*. **1998**, *10*, 2801 and references therein.

(6) Riou, D.; Roubeau, O.; Férey, G. *Microporous Mesoporous Mater*. **1998**, *23*, 23.

(7) Yaghi, O. M.; Davis, C. E.; Li, G.; Li, H. *J. Am. Chem. Soc*. **1997**, *119*, 2861.

(8) Serpaggi, F.; Férey, G. *J. Mater. Chem*. **1998**, *8*, 2737.

(9) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Guy Orpen, A.; Williams, I. D. *Science* **1999**, *283*, 1148.

(10) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 277.

(11) Burwell, D. A.; Thompson, M. E. *Chem. Mater*. **1991**, *3*, 14 and references therein.

(12) Bortun, A. I.; Bortun, L.; Clearfield, A.; Jaimez, E.; Villa-Garcia, M. A.; Garcia, J. R.; Rodriguez, J. *J. Mater. Res*. **1997**, *12* (4), 1122.

(13) Drumel, S.; Janvier, P.; Barboux, P.; Bujoli-Doeuff, M.; Bujoli, B. *Inorg. Chem*. **1995**, *34*, 148 and references therein.

(14) Distler, A.; Sevov, S. C. *Chem. Commun*. **1998**, 959.

(15) Ayyapan, S.; Diaz de Delgado, G.; Cheetham, A. K.; Férey, G.; Rao, C. N. R. *J. Chem. Soc*., *Dalton Trans*. **1999**, 2905.

(16) Riou-Cavellec, M.; Sanselme, M.; Férey, G. *J. Mater. Chem*. **2000**, *10*, 745.

10.1021/ic000758j CCC: $20.00

Table 2. X-ray Powder Diffraction Pattern of MIL-39

hkl	$2\theta_{obsd}$ (deg)	$2\theta_{calcd}$ (deg)	d_{obsd} (Å)	I_{obsd}	*hkl*	$2\theta_{obsd}$ (deg)	$2\theta_{calcd}$ (deg)	d_{obsd} (Å)	I_{obsd}
100	10.431	10.426	8.48	100	$\bar{3}12$	42.978	42.972	2.1027	1
001	17.229	17.233	5.14	21	130	43.612	43.616	2.0735	4
$\bar{1}10$	17.319	17.321	5.11	14	$\bar{1}22$	44.086	44.098	2.0523	<1
$\bar{1}01$	17.570	17.564	5.04	19	410	45.002	45.011	2.0127	2
200	20.934	20.940	4.240	15	022	45.203	45.163	2.0042	<1
011	22.135	22.139	4.012	14	$\bar{2}22$	45.712	45.719	1.9831	1
$\bar{1}11$	22.404	22.400	3.965	2	031	45.937	45.925	1.9739	4
101	22.511	22.510	3.946	2	202		45.952		
$\bar{2}01$	23.272	23.274	3.819	26	131	46.064	46.063	1.9687	2
111	26.473	26.494	3.364	1	212	48.194	48.208	1.8866	3
$\bar{2}11$	27.142	27.153	3.282	2	$\bar{2}31$	48.751	48.768	1.8663	1
020	27.780	27.790	3.208	34	122		48.775		
201	30.742	30.740	2.906	4	321	49.697	49.698	1.8330	2
300	31.636	31.637	2.826	19	$\bar{3}22$	49.829	49.821	1.8284	4
$\bar{3}01$	31.709	31.696	2.819	9	401	50.806	50.818	1.7955	2
021	32.887	32.884	2.721	5	411	52.946	52.918	1.7279	1
$\bar{1}21$	33.069	33.066	2.706	18	231	53.136	53.131	1.7222	1
$\bar{1}02$	33.527	33.541	2.670	2	$\bar{5}11$	54.035	54.028	1.6956	3
$\bar{1}12$	36.425	36.423	2.464	5	500		54.041		
102	39.251	39.253	2.2933	5	302	54.341	54.329	1.6868	1
301	40.337	40.346	2.2340	17	$\bar{3}03$	54.550	54.521	1.6808	5
$\bar{3}20$	42.600	42.604	2.1204	4	222		54.555		
400		42.624			$\bar{1}32$	54.973	54.972	1.6689	3
311	42.827	42.835	2.1097	1					

The experimental density $d_{exp} = 2.60(2)$ g cm^{-3} measured using a Micromeritics 1330 Accupyc pycnometer is close to the theoretical one of $d_{calc} = 2.71$ g cm^{-3}.

TGA measurements of the title compound were performed under an O_2 gas flow using a TA-Instrument type 2050 analyzer. The heating rate was 5 °C min^{-1} from 30 to 600 °C. On the TGA curve, we observed a unique weight loss at 350 °C, which probably included the calcination of the organic part of the structure ($\%_{theo} = 23.6$; $\%_{exp} \approx 27.8$). The resulting product at 600 °C was identified and mainly corresponded to the copper diphosphate $Na_2Cu(P_2O_7)$[17]and also to copper oxide, CuO.

Structure Determination from X-ray Powder Diffraction. 1. X-ray Data Analysis and Indexing. The X-ray powder diffraction data of MIL-39 was collected on a Siemens D5000 diffractometer using Cu Kα radiation (α = 1.5418 Å). To avoid preferred orientation effects, hand-ground powder was side-loaded in the sample holder. The powder diffraction pattern was scanned over an angular range of 6−116° (2*θ*). The counting times were 20 s step^{-1} to 59.98° (2*θ*) and 40 s step^{-1} from 60.00° (2*θ*) to the end of the scan to improve the counting statistics of the high-angle region. The full pattern was then scaled to the lower counting time. The contribution of Cu $K\alpha_2$ radiation was removed from the pattern by means of the software package DIFFRACT-AT, and an accurate determination of the peak positions and relative intensities for Cu $K\alpha_1$ radiation contribution was carried out. The pattern indexing was performed by means of the computer program DICVOL91[18] from the 21st lines, with an absolute error on peak positions of 0.03° (2*θ*). A monoclinic solution was then found with satisfactory figures of merit [$M_{20} = 39$, $F_{20} = 68$ (0.0102, 29)].

From the complete data set, reviewed by means of the program NBS*AIDS83,[19] the refined cell parameters given in Table 1 were obtained with new figures of merit. The powder diffraction data are reported in Table 2 for Cu $K\alpha_1$ radiation (α = 1.5406 Å). Systematic absences ($0k0$, $k = 2n + 1$) were consistent with the two space groups $P2_1$ and $P2_1/m$.

Table 3: Positional Parameters and Their Standard Deviations for MIL-39 [Overall Isotropic Temperature Factor $B_{ov} = 1.23(7)$ Å^2]

atom	*x*	*y*	*z*
Cu	0.8267(3)	$^1/_4$	0.5240(4)
P	0.1855(6)	$^1/_4$	0.5945(8)
Na	0	0	0
O1	0.636(1)	$^1/_4$	0.225(2)
O2	0.7993(9)	$^1/_4$	0.979(2)
O3	0.1777(6)	0.0613(7)	0.421(1)
O4	0.0546(8)	$^1/_4$	0.731(1)
C1	0.3584(9)	$^1/_4$	0.875(2)
C2	0.511(1)	$^1/_4$	0.766(2)
C3	0.666(2)	$^1/_4$	0.001(3)

2. Structure Solution and Refinement. Calculations were performed with the EXPO package, integrating EXTRA,[20] a full pattern decomposition program, and the new version of SIRPOW (SIR97).[21] The centrosymmetric space group $P2_1/m$ was chosen to solve the structure. Direct methods and Fourier calculations allowed locating all non-hydrogen atoms excepted the carbon of the carboxylic function (C3 in Table 3). The corresponding atomic coordinates were used as a starting model in the Rietveld refinement using FULLPROF program[22] in winPLOTR software.[23] A pseudo-Voigt function was selected to describe individual line profiles. To describe the angular dependence of the peak fullwidth at half-maximum, the usual quadratic function in tan(*θ*) was used and unit cell and instrumental parameters were allowed to vary. At this stage of the refinement, the structure model indicators converged to $R_B = 0.185$ and $R_F = 0.158$ and a last Fourier-difference calculation was undertaken using SHELXL.[24] It revealed unambiguously the missing carbon atom. The next Rietveld refinement including this carbon atom converged to $R_B = 0.152$ and $R_F = 0.138$, confirming atomic coordinates of C3 atom. The final Rietveld refinement carried out in the angular ranges 8−108° (2*θ*) involved the following parameters: 19 atomic coordinates, 1 overall temperature factor, 1 scale factor, 1 zero point, 4 cell parameters, 3 half-width parameters, and 2 line asymmetry parameters, 2 variables for the angular variation of *η*, and 6 polynomial background coefficients. One region of the powder

---

(17) Leonowicz, M. E.; Johnson, J. W.; Brody, J. F.; Shannon, H. F.; Newsam, J. M. *J. Solid State Chem.* **1985**, *56*, 370.

(18) Boultif, A.; Louër, D. *J. Appl. Crystallogr*. **1991**, *24*, 987.

(19) Mighell, A. D.; Hubbard, C. R.; Stalik, J. K. *NBS*AIDS80: A Fortran Program for Crystallographic Data Evaluation*; Technical Note No. 1141; National Bureau of Standards: Gaithersburg, MD, 1981. NBS*AIDS83 is an expanded version of NBS*AIDS80].

(20) Altomare, A.; Burla, M. C.; Giacovazzo, G.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G. EXTRA: A Program for Extracting Structure-Factor Amplitudes from Powder Diffraction Data. *J. Appl. Crystallogr.* **1995**, *28*, 842.

(21) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A; Moliterni, A. G. G.; Polidori, G.; Spagna, R. SIR97: A New Tool for Crystal Structure Determination and Refinement. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(22) Rodriguez-Carvajal, J. FULLPROF program in collected abstracts of Powder Diffraction Meeting, Toulouse, France, 1990; p 127.

(23) Roisnel, T.; Rodriguez-Carvajal, J. WinPLOTR program in abstract of 7th European Powder Diffraction Conference, Barcelona, Spain, 2000; p 71.

(24) Sheldrick, G. M. *SHELXL-93, a program for crystal structure determination*; University of Göttingen: Göttingen, Germany, 1993.

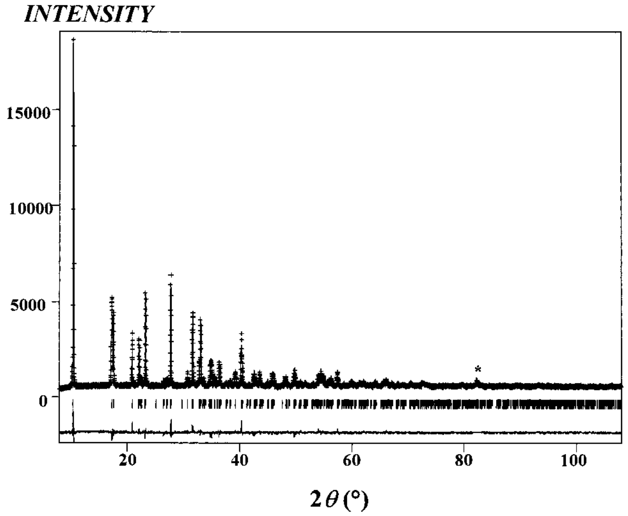

Figure 1. Final Rietveld plot showing the agreement between calculated and observed patterns of MIL-39. The asterisk corresponds to a peak due to the sample holder.

Table 4: Selected Bond Distances (Å) and Angles (deg) for MIL-39

Within the Distorted CuO_5 Square Pyramid					
Cu−O1	1.98(1)	O1−Cu−O2	120.0(6)	O2−Cu−O3^{b}	81.3(3)
Cu−O2	2.512(8)	O1−Cu−O3^{a}	94.1(5)	O2−Cu−O4^{c}	79.1(5)
Cu−O3^{a}	2.020(5)	O1−Cu−O3^{b}	94.1(5)	O3^{a}−Cu−O3^{b}	162.5(4)
Cu−O3^{b}	2.020(5)	O1−Cu−O4^{c}	161.0(8)	O3^{a}−Cu−O4^{c}	88.6(4)
Cu−O4^{c}	2.012(8)	O2−Cu−O3^{a}	81.3(3)	O3^{b}−Cu−O4^{c}	88.6(4)
Within the Organic Part $(O_3P-(CH_2)_2-CO_2)^{3-}$					
P−O3	1.514(5)	O3−P−O3^{d}	106.1(5)	O3^{d}−P−C1	113.0(8)
P−O3^{d}	1.514(5)	O3−P−O4	112.3(7)	O4−P−C1	100.3(8)
P−O4	1.521(9)	O3−P −C1	113.0(8)		
P−C1	1.82(1)	O3^{d}−P−O4	112.3(7)		
C1−C2	1.60(2)	C2−C1−P	107(1)	O1^{e}−C3−O2	122(2)
C2−C3	1.59(2)	C1−C2−C3	110(1)		
C3−O1^{e}	1.30(2)	C2−C3−O1^{e}	113(1)		
C3−O2	1.21(2)	C2−C3−O2	125(2)		
Within the Sodium Octahedron					
Na−O2^{f}	2.368(6)	O2^{f}−Na−O2^{g}	180	O2^{g}−Na−O4^{j}	77.2(4)
Na−O2^{g}	2.368(6)	O2^{f}−Na−O3	102.7(4)	O3−Na−O3^{h}	180
Na−O3	2.399(5)	O2^{f}−Na−O3^{h}	77.3(3)	O3−Na−O4^{i}	106.2(4)
Na−O3^{h}	2.399(5)	O2^{f}−Na−O4^{i}	77.2(4)	O3−Na−O4^{j}	73.8(3)
Na−O4^{i}	2.290(5)	O2^{f}−Na−O4^{j}	102.8(3)	O3^{h}−Na−O4^{i}	73.8(3)
Na−O4^{j}	2.290(5)	O2^{g}−Na−O3	77.3(3)	O3^{h}−Na−O4^{j}	106.2(4)
		O2^{g}−Na−O3^{h}	102.7(4)	O4^{i}−Na−O4^{j}	180
		O2^{g}−Na−O4^{i}	102.8(3)		

[a] Symmetry code: $1 - x, {}^{1}/_{2} + y, 1 - z$. [b] Symmetry code: $1 - x, -y, 1 - z$. [c] Symmetry code: $1 + x, y, z$. [d] Symmetry code: $x, {}^{1}/_{2} - y, -z$. [e] Symmetry code: $x, y, z + 1$. [f] Symmetry code: $x - 1, y, z - 1$. [g] Symmetry code: $1 - x, y - {}^{1}/_{2}, 1 - z$. [h] Symmetry code: $-x, -y, -z$. [i] Symmetry code: $x, y, z - 1$. [j] Symmetry code: $-x, y - {}^{1}/_{2}, 1 - z$.

pattern was excluded (2θ from 81.7° to 83°) because of the presence of a spurious diffraction line of the dural sample holder. Figure 1 shows the final fit obtained between calculated and observed patterns. It corresponds to satisfactory crystal structure model indicators and profile factors ($R_F = 0.058$, $R_P = 0.034$). Details of refinements are summarized in Table 1. Final atomic parameters are given in Table 3. Selected bond distances and angles are listed in Table 4.

Results and Discussion

MIL-39 or $Na[Cu(O_3P-(CH_2)_2-CO_2)]$ is a three-dimensional open structure (Figure 2). Its structure can be described as a connection of “inorganic” double rows through the carboxyl end of organic $(O_3P(CH_2)_2CO_2)^{3-}$ moieties. In fact, these double chains are built from isolated CuO_5 square pyramids bonded by PO_3C tetrahedral units. The copper displays a distorted coordination polyhedron (distortion[25] $\Delta \times 10^3 = 9.2$); Cu−O bond lengths vary in the 1.98−2.512 Å range (see Table 4) with four distances around 2 Å and a longer one at 2.512 Å. The five oxygen vertexes of the Cu polyhedra are shared with three different PO_3C tetrahedra and with two different bridging carboxylate groups of two organic $(O_3P-(CH_2)_2-\mathit{CO_2})^{3-}$ units (Figure 3, Table 4). In MIL-39, a carboxylate group is bridging between two Cu polyhedra belonging to distinct double chains (Figure 2). This is the main structural difference when MIL-39 is compared with the vanadium-based carboxyethylphosphonate MIL-26[16] or $Na[V^{IV}O(O_3P-(CH_2)_2-CO_2)](H_2O)_2$. Indeed, similar inorganic double rows are also observed in MIL-26 in which the $V^{(IV)}$ cations adopt a distorted VO_6 octahedral coordination. Three oxygen vertexes of a VO_6 octahedron are shared with three different PO_3C tetrahedra as in MIL-39, but a free oxygen apex is also observed corresponding to a shorter vanadyl bond. On the other hand, in MIL-26, the two remaining oxygen ligands of vanadium come from a single chelating carboxylate group.

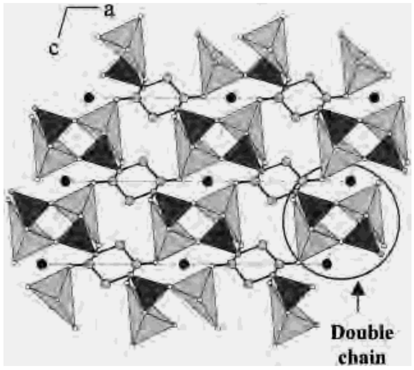

Figure 2. Projection along [010] of the three-dimensional structure of MIL-39. CuO_5 polyhedra are light-gray. PO_3C tetrahedra are dark-gray. Na^+ cations located in the channels are represented in black.

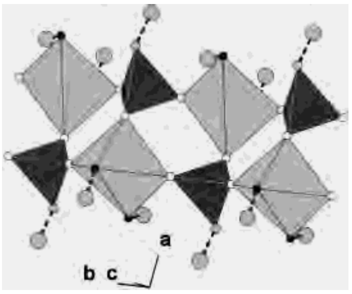

Figure 3. Representation of an “inorganic” double chain showing the arrangement between Cu polyhedra (light) and PO_3C tetrahedra (dark). Oxygen vertexes that are shared with the CO_2^- carboxylate groups are displayed in black in the pairs of circles separated by dashes.

Both MIL-26 and MIL-39 have open structures. Indeed, in MIL-26, a double chain is connected to four neighboring rows through aliphatic chains, thus allowing the formation of quite large elliptical channels, whereas in MIL-39, a double chain is linked to six other chains, inducing two types of smaller channels along [010]. Sodium countercations adopt quite a regular octahedral coordination: Na−O bond lengths varying from 2.290(5) to 2.399(5) Å (Table 4). They are located in the smallest oval channels displayed by this new hybrid compound.

IC000758J

---

[25] Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.