

# Hydrothermal Synthesis, Structure Determination, and Magnetic Properties of Three New Copper(II) Methyleneidiphosphonates with Hybrid Frameworks (MIL-54, 55, 56), and of the Cu Homologue of $\text{Na}_2\text{Co}(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3)\cdot(\text{H}_2\text{O})$

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The hydrothermal investigation of the quaternary system  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ /methylenediphosphonic acid/NaOH/ $\text{H}_2\text{O}$  leads to four compounds. Three of them present a new structural type; the fourth is isostructural with a cobalt compound and is already published. Varying experimental parameters such as the initial pH or the temperature allows isolation of each compound as a pure phase. The exception is  $\text{Cu}_2(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3)$  (labeled MIL-54) which presents a dense three-dimensional framework; the three other compounds are built up from layers between which water molecules and/or  $\text{Na}^+$  cations are intercalated. Both MIL-54 and  $\text{Na}_2\text{Cu}(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3)\cdot(\text{H}_2\text{O})$  are orthorhombic in the space group *Pnma* (no. 62) with lattice parameters  $a = 13.7056(1)$  Å,  $b = 7.9953(2)$  Å,  $c = 4.9209(1)$  Å, and  $V = 539.23(2)$  Å<sup>3</sup> for MIL-54; in the space group *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>* (no. 19),  $a = 9.0155(2)$  Å,  $b = 10.1795(2)$  Å,  $c = 16.2084(3)$  Å, and  $V = 1487.50(5)$  Å<sup>3</sup> for  $\text{Na}_2\text{Cu}(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3)\cdot(\text{H}_2\text{O})$ . The two other phases are monoclinic (SG: *C2/c* (no. 15)) with lattice parameters  $a = 19.193(1)$  Å,  $b = 8.6892(5)$  Å,  $c = 9.1904(5)$  Å,  $\beta = 105.858(2)$ °, and  $V = 1474.4(1)$  Å<sup>3</sup>, and  $a = 17.750(4)$  Å,  $b = 6.210(1)$  Å,  $c = 23.200(5)$  Å,  $\beta = 94.12(3)$ °, and  $V = 2550.7(9)$  Å<sup>3</sup> for  $\text{Cu}_3(\text{H}_2\text{O})_2(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3\text{H})_2\cdot(\text{H}_2\text{O})$  (noted MIL-55) and  $\text{Na}_3\text{Cu}_5(\text{O}_3\text{P}-\text{CH}_2\text{PO}_3\text{H}_x)\cdot(\text{H}_2\text{O})_2$  ( $x = 0.75$ ) (noted MIL-56), respectively. The magnetic behavior of these solids was studied and explained from structural considerations: the three-dimensional MIL-54 and  $\text{Na}_2\text{Cu}(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3)\cdot(\text{H}_2\text{O})$  exhibit an antiferromagnetic behavior below  $T_N \approx 45(2)$  and 50(2) K, respectively, and the other compounds are paramagnetic. Finally, the structural evolution of the title solids depending on the pH is discussed via the connections of trimeric building units.

## 1. Introduction

Hybrid organic–inorganic solids provide numerous compounds whose framework is built up from the ionic-covalent connection of inorganic moieties via organic molecules functionnalized by complexing groups such as carboxylates or phosphonates,<sup>1–4</sup> with the dimensionality of the final solid being largely influenced by the number of complexing groups. For example, the association of one monophosphonic acid with a metallic cation leads, most of the time, to layered structures useful in the field of intercalation chemistry.<sup>5,6</sup> In contrast, diphosphonic acids are expected to give rise to three-dimensional structures with open frameworks.

Compared to the family of organically templated metallocphosphates, these structures do not contain any organic template whose degradation often leads to the collapse of the inorganic framework: their cavities are just filled by inorganic cations and/or water molecules which are easily removable. So, these solids with an accessible porosity can be directly used in various applications such as ions exchange, catalysis, or gas separation.

Among the numerous studies devoted to the metal alkylidiphosphonate compounds,<sup>7–15</sup> a lot of them are

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(1) Férey, G. *Chem. Mater.* **2001**, *13*, 3084.

(2) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O’Keeffe, M.; Yaghi, O. *Science* **2002**, *295*, 469.

(3) Barthelet, K.; Marrot, J.; Riou, D.; Férey, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 281.

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

(5) Clearfield, A. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 268.

(6) Zhang, Y.; Scott, K. J.; Clearfield, A. *Chem. Mater.* **1993**, *5*, 495.

(7) Poojary, D. M.; Zhang B.; Clearfield A. *J. Am. Chem. Soc.* **1997**, *119*, 12550.

(8) Riou, D.; Belier, F.; Serre, C.; Nogues, M.; Vichard, D.; Férey, G. *Int. J. Inorg. Mat.* **2000**, *2*, 29.

(9) Riou, D.; Férey, G. *J. Mater. Chem.* **1998**, *8*, 2733–2735.

(10) Riou, D.; Serre, C.; Provost, J.; Férey, G. *J. Solid State Chem.* **2000**, *155*, 238.

(11) Riou, D.; Baltazar, P.; Férey, G. *Solid State Sci.* **2000**, *2*, 127.

(12) Ninclaus, C.; Serre, C.; Riou, D.; Férey, G. *C. R. Acad. Sci. 1998*, *t. 1*, Série II c, 551.

(13) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubietta, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 223.

(14) Soghomonian, V.; Haushalter, R. C.; Zubietta, J. *Chem. Mater.* **1995**, *7*, 1648.

(15) Soghomonian, V.; Diaz, R.; Haushalter, R. C.; O’Connor, C. J.; Zubietta, J. *Inorg. Chem.* **1995**, *34*, 4460.

**Table 1. Conditions for Hydrothermal Synthesis of  $\text{Cu}_2(\text{O}_3\text{P-CH}_2\text{-PO}_3)$  (MIL-54),  $\text{Cu}_3(\text{H}_2\text{O})_2(\text{O}_3\text{P-CH}_2\text{-PO}_3\text{H})_2\cdot(\text{H}_2\text{O})$  (MIL-55),  $\text{Na}_3\text{Cu}_5(\text{O}_3\text{P-CH}_2\text{PO}_3\text{H}_x)_4\cdot(\text{H}_2\text{O})_2$  ( $x = 0.75$ ) (MIL-56), and  $\text{Na}_2\text{Cu}(\text{O}_3\text{P-CH}_2\text{-PO}_3)\cdot(\text{H}_2\text{O})$  (Compound 4)**

	$\text{CuCl}_2\cdot 2\text{H}_2\text{O}/\text{H}_2\text{O}_3\text{P-CH}_2\text{-PO}_3\text{H}_2\cdot\text{H}_2\text{O}$	$\text{pH}/\text{pH}_f$	$T\text{ (K)}/t\text{ (days)}$	yield	chemical analysis	crystals
MIL-54 $\text{Cu}_2(\text{O}_3\text{P-CH}_2\text{-PO}_3)$	1:1:500	1.5/1.5	473/3	50%	%Cu = 41.4 (theor 42.5%) %P = 20.2 (theor 20.7%) %C = 4.5 (theor 4.0%)	brownish parallel-epipeds
MIL-55 $\text{Cu}_3(\text{H}_2\text{O})_2(\text{O}_3\text{P-CH}_2\text{-PO}_3\text{H})_2\cdot(\text{H}_2\text{O})$	1:1:100	1/1	393–443/2	50%	%Cu = 31.5 (theor 32.3%) %P = 21.6 (theor 21.0%) %C = 4.6 (theor 4.1%)	blue platelets
MIL-56 $\text{Na}_3\text{Cu}_5(\text{O}_3\text{P-CH}_2\text{PO}_3\text{H}_x)_4\cdot(\text{H}_2\text{O})_2$ ( $x = 0.75$ )	1:1:250 + NaOH (10 M)	2–6/2–6 * <sup>a</sup>	443/2	90%	%Na = 5.9 (theor 6.2%) %Cu = 27.7 (theor 28.6%) %P = 21.7 (theor 22.4%) %C = 4.4 (theor 4.3%)	blue needles
Compound 4 $\text{Na}_2\text{Cu}(\text{O}_3\text{P-CH}_2\text{-PO}_3)\cdot(\text{H}_2\text{O})$	1:1:250 + NaOH (10 M)	7–10/7–10 * <sup>a</sup>	443/2	60%	%Na = 13.9 (theor 15.4%) %Cu = 20.4 (theor 21.2%) %P = 19.2 (theor 20.7%) %C = 4.1 (theor 4.0%)	green needles

<sup>a</sup> \* Indicates the initial pH is a function of NaOH amount.

**Table 2. Experimental Data Collection for  $\text{Cu}_2(\text{O}_3\text{P-CH}_2\text{-PO}_3)$  (MIL-54),  $\text{Cu}_3(\text{H}_2\text{O})_2(\text{O}_3\text{P-CH}_2\text{-PO}_3\text{H})_2\cdot(\text{H}_2\text{O})$  (MIL-55),  $\text{Na}_3\text{Cu}_5(\text{O}_3\text{P-CH}_2\text{PO}_3\text{H}_x)_4\cdot(\text{H}_2\text{O})_2$  ( $x = 0.75$ ) (MIL-56), and  $\text{Na}_2\text{Cu}(\text{O}_3\text{P-CH}_2\text{-PO}_3)\cdot(\text{H}_2\text{O})$  (Compound 4)**

	MIL-54	MIL-55	MIL-56	compound 4
chemical formula	$\text{Cu}_2(\text{O}_3\text{P-CH}_2\text{-PO}_3)$	$\text{Cu}_3(\text{H}_2\text{O})_2(\text{O}_3\text{P-CH}_2\text{-PO}_3\text{H})_2\cdot(\text{H}_2\text{O})$	$\text{Na}_3\text{Cu}_5(\text{O}_3\text{P-CH}_2\text{PO}_3\text{H}_x)_4\cdot(\text{H}_2\text{O})_2$ ( $x = 0.75$ )	$\text{Na}_2\text{Cu}(\text{O}_3\text{P-CH}_2\text{-PO}_3)\cdot(\text{H}_2\text{O})$
formula weight (g·mol <sup>-1</sup> )	300	592.5	1113.5	297.5
crystal size	$0.100 \times 0.06 \times 0.02$	$0.300 \times 0.04 \times 0.005$	$0.200 \times 0.04 \times 0.01$	$0.32 \times 0.04 \times 0.02$
symmetry	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	$Pnma$ (no. 62) $a = 13.7056(1)$ Å $b = 7.9953(2)$ Å $c = 4.9209(1)$ Å	$C 2/c$ (no. 15) $a = 19.193(1)$ Å $b = 8.6892(5)$ Å $c = 9.1904(5)$ Å $\beta = 105.858(2)$ °	$C 2/c$ (no. 15) $a = 17.750(4)$ Å $b = 6.210(1)$ Å $c = 23.200(5)$ Å $\beta = 94.12(3)$ °	$P 2_12_12_1$ (no. 19) $a = 9.0155(2)$ Å $b = 10.1795(2)$ Å $c = 16.2084(3)$ Å
volume (Å <sup>3</sup> ), $Z$	539.23(2), 4	1474.4(1), 4	2550.7(9), 4	1487.50(5), 8
$\rho_{\text{calc}}, \rho_{\text{meas}}$ (g·cm <sup>-3</sup> )	3.684, 3.566(8)	2.679, 2.75(2)	2.901, 2.822(3)	2.658, 2.677(9)
collected intensities	3415	5035	5585	10680
unique $I \geq 2\sigma(I)$ , $R_{\text{int}}$	771, 0.0222	1917, 0.0323	1832, 0.0870	3960, 0.0290
$R1(F_0)$ , $wR2(F_0^2)$	0.0339, 0.0907	0.0330, 0.0829	0.0665, 0.1466	0.0293, 0.0654

carried out from the diphosphonic acid with the shortest alkyl chain: the methylenediphosphonic acid.<sup>11,16–25</sup> It is also the most stable at high temperature and its geometrical characteristics are closely related to those of the diphosphate groups which are particularly adapted for connection with octahedral networks.<sup>26, 27</sup>

This paper deals with the study of the reactivity of copper(II) toward methylenediphosphonic acid. By varying several experimental parameters such as temperature or pH of the initial mixture, we have prepared four copper diphosphonates with different structural types, dimensionality and copper coordination.  $\text{Cu}_2(\text{O}_3\text{P-CH}_2\text{-PO}_3)$  (labeled MIL-54) presents a three-dimensional dense structure, whereas  $\text{Cu}_3(\text{H}_2\text{O})_2(\text{O}_3\text{P-CH}_2\text{-PO}_3\text{H})_2\cdot(\text{H}_2\text{O})$  (noted MIL-55) and  $\text{Na}_3\text{Cu}_5(\text{O}_3\text{P-CH}_2\text{PO}_3\text{H}_x)_4\cdot(\text{H}_2\text{O})_2$  ( $x = 0.75$ ) (noted MIL-56) exhibit layered structures. Finally,  $\text{Na}_2\text{Cu}(\text{O}_3\text{P-CH}_2\text{-PO}_3)\cdot(\text{H}_2\text{O})$  (noted compound 4) is a two-dimensional solid isostructural with a cobalt compound already described by Sevov et al.<sup>25</sup>

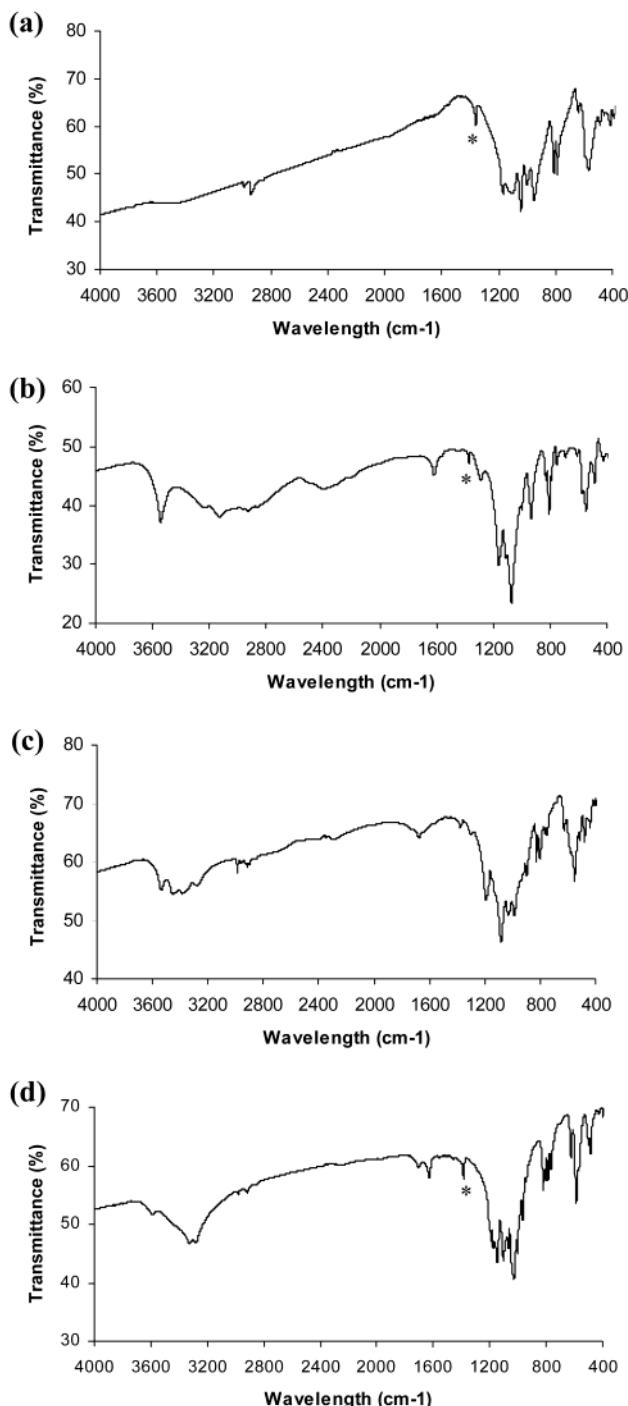
The magnetic behaviors of all these compounds are described, and the structural evolution of these phases vs pH is explained in terms of connection of trimeric building units.

## 2. Experimental Section

**Hydrothermal Synthesis.** The four title compounds were synthesized from a mixture of  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ , methylenediphosphonic acid, and distilled water. For compounds MIL-56 and compound 4, a 10 M solution of NaOH was added dropwise to adjust the initial pH: from 2 to 6, MIL-56 is synthesized as a single phase with various yields, and for higher pH (in the range 7–10) solid 4 crystallizes. The mixtures were hydrothermally heated in a Parr Teflon-lined steel autoclave under autogenous pressure, the filling rate being approximately 25%. After the mixtures were allowed to cool, the solids were filtered, washed with deionized water, and finally dried in air at room temperature. Details on the conditions for the syntheses are given in Table 1.

**Chemical Analysis.** The IR spectra, carried out on a Nicolet Magna IR 550 spectrometer, present, for all the solids, the bands characteristics of the phosphonate functions and methyl groups in the ranges 850–1500 cm<sup>-1</sup> and 2950–3030

- (16) Bonavia, G.; Haushalter, R. C.; O'Connor, C. J.; Zubietta, J. *Inorg. Chem.* **1996**, *35*, 5603.
- (17) Huan G.; Johnson, J. W.; Jacobson, A. J.; Rerola, J. S. *J. Solid State Chem.* **1990**, *89*, 220.
- (18) Riou, D.; Serre, C.; Férey, G. *Int. J. Inorg. Mater.* **1998**, *2*, 551.
- (19) Lohse, D. L.; Sevov, S. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 1619.
- (20) Gao, Q.; Guillou, N.; Nogues, M.; Cheetham, A. K.; Férey, G. *Chem. Mater.* **1999**, *11*, 2937.
- (21) Barthelet, K.; Merlier, C.; Serre, C.; Riou-Cavellec, M.; Riou, D.; Férey, G. *J. Mater. Chem.* **2002**, *12*, 1132.
- (22) Paulet, C.; Serre, C.; Loiseau, T.; Riou, D.; Férey, G. *C. R. Acad. Sci.* **1998**, *t. 2*, Série II c, 631.
- (23) Barthelet, K.; Jouve, C.; Riou, D.; Férey, G. *Solid State Sci.* **2000**, *2*, 871.
- (24) Barthelet, K.; Riou, D.; Férey, G. *Solid State Sci.* **2001**, *1*–2, 203.
- (25) Distler, A.; Lohse, D. L.; Sevov, S. C. *J. Chem. Soc., Dalton Trans.* **1999**, 1805.
- (26) Raveau, B. *Proceed. Indian Acad. Sci.* **1986**, *96*, 416.
- (27) Costentin, G.; Raveau, B. *Rev. Inorg. Chem.* **1993**, *13*, 77.



**Figure 1.** IR spectra of  $\text{Cu}_2(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3)$  (a),  $\text{Cu}_3(\text{H}_2\text{O})_2(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3\text{H})_2\cdot(\text{H}_2\text{O})$  (b),  $\text{Na}_3\text{Cu}_5(\text{O}_3\text{P}-\text{CH}_2\text{PO}_3\text{H})_4\cdot(\text{H}_2\text{O})_2$  ( $x = 0.75$ ) (c), and  $\text{Na}_2\text{Cu}(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3)\cdot(\text{H}_2\text{O})$  (d); (\*) = impurity.

$\text{cm}^{-1}$ , respectively. These spectra confirm the presence or absence of water molecules or of hydroxyl groups and allow the different kinds of water molecules (coordinated or not) to be distinguished (Figure 1). Indeed, no bands are observed above  $3030\text{ cm}^{-1}$  for MIL-54 which does not contain any kind of water molecule or hydroxyl group. The spectrum of MIL-55, containing both linked and free water molecules, presents a large band in the range  $2590\text{--}3740\text{ cm}^{-1}$  and a narrow band at  $3550\text{ cm}^{-1}$ . The formula of MIL-56 indicates the presence of hydroxyl groups, confirmed by a narrow band at  $3550\text{ cm}^{-1}$  and of water molecules of crystallization, responsible for the presence of a broad band between  $3100$  and  $3520\text{ cm}^{-1}$ . Finally, the quite large band in the range  $3080\text{--}3730\text{ cm}^{-1}$  in the spectrum of **4** is characteristic of free water molecules.

**Table 3. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Cu}_2(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3)$  (MIL-54)**

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Cu(1)	3931(1)	5611(1)	1111(1)	22(1)
P(1)	4869(1)	2500	3996(2)	8(1)
P(2)	2748(1)	2500	2878(2)	9(1)
O(1)	2843(1)	4084(3)	1212(5)	14(1)
O(2)	4962(2)	4075(3)	2227(5)	12(1)
O(3)	4380(2)	7500	3711(6)	11(1)
O(4)	3235(2)	7500	-551(7)	12(1)
C	3678(3)	2500	5432(9)	12(1)
H(1)	3601	3481	6572	15

**Table 4. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Cu}_3(\text{H}_2\text{O})_2(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3\text{H})_2\cdot(\text{H}_2\text{O})$  (MIL-55).**

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Cu(1)	2500	2500	5000	11(1)
Cu(2)	1910(1)	-1158(1)	4325(1)	13(1)
P(1)	2953(1)	193(1)	2394(1)	10(1)
P(2)	1056(1)	-2179(1)	1072(1)	11(1)
O(1)	1078(1)	-1328(3)	2539(3)	14(1)
O(2)	2271(1)	-3638(3)	3891(3)	13(1)
O(3)	2453(1)	271(3)	3426(3)	15(1)
O(4)	1581(1)	1627(3)	5238(3)	15(1)
O(5)	3056(1)	1421(3)	6842(3)	14(1)
O(6)	252(1)	-2023(3)	31(3)	17(1)
O(7)	1276(2)	-1951(4)	5565(3)	24(1)
C	1159(2)	-4196(4)	1476(4)	15(1)
H(1A)	1046(2)	-4748(4)	522(4)	18
H(1B)	802(2)	-4493(4)	1998(4)	18
Ow	0	584(4)	2500	16(1)

Thermogravimetric measurements, performed on a TGA 2050 instrument under  $\text{O}_2$  flow with a heating rate of  $5\text{ }^{\circ}\text{C}/\text{min}$  between  $20$  and  $600\text{ }^{\circ}\text{C}$ , also confirm the presence or absence of water molecules: no weight loss for MIL-54, a weight loss of  $10.5\%$  between  $100$  and  $400\text{ }^{\circ}\text{C}$  for MIL-55 (theor = 9.1%), a weight loss of 3.5% between  $150$  and  $300\text{ }^{\circ}\text{C}$  for MIL-56 (theor = 3.2%), and a weight loss of 6.0% between  $25$  and  $350\text{ }^{\circ}\text{C}$  for compound **4** (theor = 6.1%). After  $400\text{--}500\text{ }^{\circ}\text{C}$ , depending on the compound, phosphonate groups decompose. This degradation is coupled with a phenomenon of oxidation of the methylenediphosphonate into a residue corresponding to a mixture of diphosphate and monophosphate.

The density was measured with a Micromeritics multi-pycnometer operating under He flow.

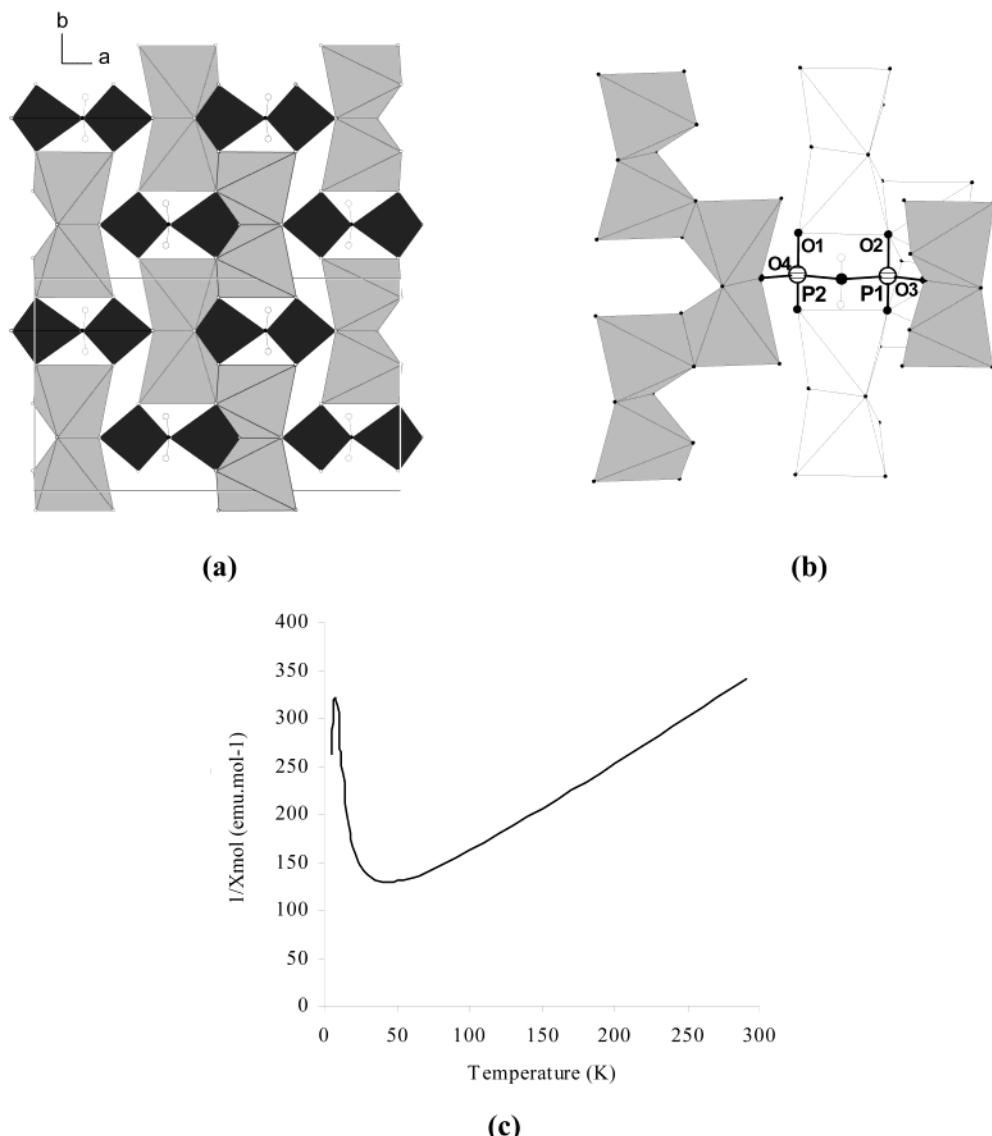
**Structure Determination.** The four structures were solved by single-crystal X-ray diffraction. The crystals were optically selected, glued onto a thin glass fiber mounted on a goniometer head, then introduced in a three-circle Siemens SMART diffractometer equipped with a bidimensional CCD detector using a  $\text{Mo}(\text{K}\alpha)$  monochromatized wavelength ( $\lambda = 0.71073\text{ \AA}$ ). The collected data were reduced and corrected from Lorentz polarization effects using the program SAINT.<sup>28</sup> A semi-empirical absorption correction was then applied (program SAD-ABS, G. Sheldrick, unpublished). The structure determination was achieved using the SHELX-TL program.<sup>29</sup> By direct methods, the heaviest atoms (copper, sodium, and phosphorus) were located. All remaining atoms could be located from Fourier difference syntheses. Finally, geometrical constraints were applied to locate the hydrogen atoms of the  $-\text{CH}_2-$  groups even if they have not been refined. The hydrogen atoms from water molecules have not been located.

Crystallographic and chemical data for the four compounds are summarized in Table 2, and the atomic coordinates are presented in Tables 3–6.

**Magnetic Measurements.** The magnetization (*M*) was measured as a function of the temperature for the four compounds in the range  $2\text{--}300\text{ K}$  using a Squid quantum

(28) Blesing, R. *Acta Crystallogr.* **1995**, *A51*, 33.

(29) Sheldrick, G. M. SHELX-TL, version 5.03, Siemens Analytical X-ray Instrument: Madison, WI, 1994.



**Figure 2.**  $\text{Cu}_2(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3)$  (MIL-54): projection along [001] (a), connection between chains via diphosphonate group (b), and  $\chi^{-1} = f(T)$  curve.

design device. The resulting magnetic susceptibilities  $\chi = \text{M}/\text{H}$  were then deduced.

### 3. Phenomenological Description of Structures and Magnetism

$\text{Cu}_2(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3)$  (MIL-54) is a dense three-dimensional compound (Figure 2a) in which  $\text{Cu}^{2+}$  are in a distorted trigonal bipyramidal environment (four distances between 1.928(2) and 2.073(2) Å and one longer at 2.250(2) Å). The  $\text{CuO}_5$  polyhedra are connected together via their edges to form infinite zigzag chains along [010]. The connections between these chains are ensured by the methylenediphosphonate groups. Such a group chelates edges of two polyhedra  $\text{CuO}_5$  from the same chain via oxygen O(1) and O(2), and join this chain with two adjacent ones via oxygen O(3) and O(4) (Figure 2b). Figure 2c shows that MIL-54 exhibits an antiferromagnetic behavior below  $T_N = 45(2)$  K. The fitting of the linear part of the  $\chi$  curve in the temperature range 150–300 K allows calculation of a  $\theta_p$  value close to –60 K, revealing strong antiferromagnetic interactions between the magnetic cations. The calculated Curie

constant is approximately 0.5 per  $\text{Cu}^{2+}$  cation in correct agreement with the spin only value of 0.375 expected for a  $3d^9$  cation.

$\text{Cu}_3(\text{H}_2\text{O})_2(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3\text{H})_2(\text{H}_2\text{O})$  (MIL-55) corresponds to a stacking along [100] of neutral layers between which water molecules are intercalated (Figure 3a). Within the layers, the copper atoms are distributed on two crystallographic sites: Cu(1) in an octahedron (hatched in Figure 3) elongated by a Jahn–Teller effect well-known for  $\text{Cu}^{2+}$  (four equatorial distances shorter than the two axial ones: 1.972(2) and 1.981(3) Å vs 2.406(2) Å, and Cu(2) in a trigonal bipyramidal (TBP) with four equivalent distances between 1.940(2) and 1.999(3) Å and one longer distance of 2.334(2) Å). Each trigonal bipyramidal is chelated by one diphosphonate group and shares one edge with another  $\text{CuO}_5$  TBP to form hexameric building units (Figure 3b). The mixed layers are built up from the connection of these hexamers with  $\text{CuO}_6$  octahedra in such a way that each octahedron is chelated by two diphosphonates of two different hexamers and shares its two remaining apexes with two other hexamers. Each diphosphonate group

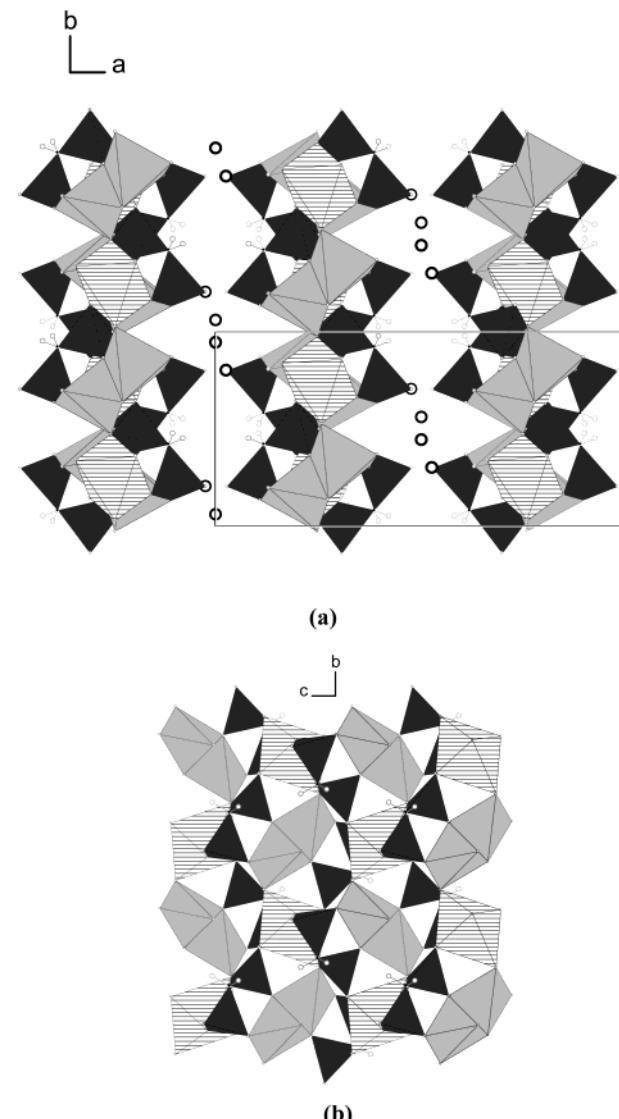
**Table 5. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Na}_3\text{Cu}_5(\text{O}_3\text{P}-\text{CH}_2\text{PO}_3\text{H}_x)_4\cdot(\text{H}_2\text{O})_2$  ( $x = 0.75$ ) (MIL-56)**

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Cu(1)	9681(1)	1529(3)	5410(1)	15(1)
Cu(2)	12500	2500	5000	13(1)
Cu(3)	11137(1)	4933(3)	5802(1)	13(1)
P(1)	10719(2)	3638(6)	4551(2)	11(1)
P(2)	8436(2)	-378(6)	6103(2)	12(1)
P(3)	11567(2)	-65(6)	5913(2)	10(1)
P(4)	11168(2)	7517(6)	6980(2)	15(1)
Na(1)	12500	-2500	5000	38(3)
Na(2)	10228(4)	2493(10)	6769(3)	34(2)
O(1)	10996(5)	1777(15)	5946(4)	12(2)
O(2)	11212(5)	7983(15)	5605(4)	17(2)
O(3)	11351(5)	4289(14)	4987(4)	11(2)
O(4)	12269(5)	558(15)	5624(4)	14(2)
O(5)	8116(5)	-93(16)	6690(4)	19(2)
O(6)	10317(5)	1594(15)	4759(4)	11(2)
O(7)	10437(5)	8809(16)	7042(4)	21(3)
O(8)	11527(5)	6938(15)	7587(4)	18(2)
O(9)	9048(5)	1332(16)	6039(4)	17(2)
O(10)	9862(5)	4579(14)	5584(4)	10(2)
O(11)	12169(5)	251(15)	4382(4)	16(2)
O(12)	11020(5)	5507(15)	6621(4)	17(2)
C(1)	11837(8)	9165(22)	6638(6)	12(3)
H(1A)	11925(8)	10460(22)	6867(6)	14
H(1B)	12312(8)	8392(22)	6642(6)	14
C(2)	11112(8)	2969(22)	3889(6)	13(3)
H(2A)	11479(8)	4061(22)	3804(6)	15
H(2B)	10714(8)	2992(22)	3580(6)	15
Ow	10885(6)	2938(18)	7736(5)	31(3)

**Table 6. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Na}_2\text{Cu}_3(\text{O}_3\text{P}-\text{CH}_2\text{PO}_3)\cdot(\text{H}_2\text{O})$  (Compound 4)**

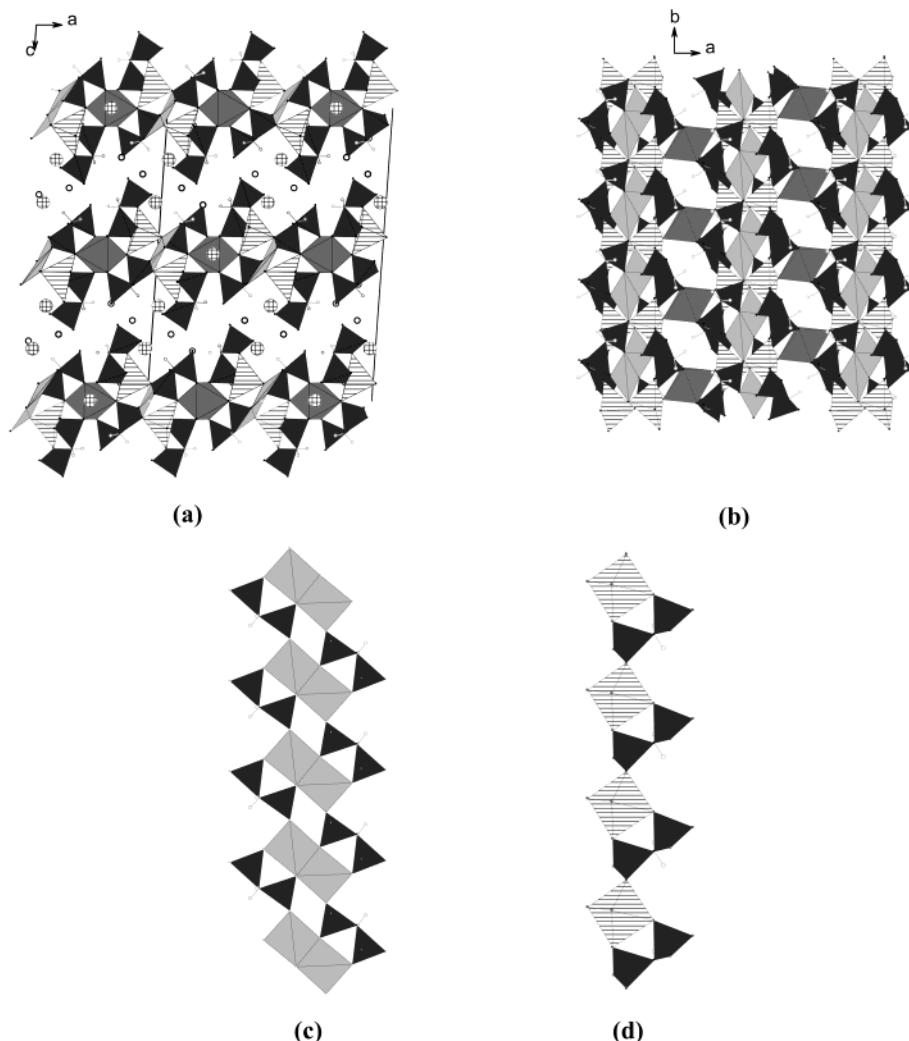
atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Cu(1)	2190(1)	1203(1)	9386(1)	12(1)
Cu(2)	2423(1)	6154(1)	9102(1)	14(1)
P(1)	-743(1)	6220(1)	10429(1)	11(1)
P(2)	4370(1)	3596(1)	9373(1)	11(1)
P(3)	2002(1)	-113(1)	8222(1)	12(1)
P(4)	2014(1)	3511(1)	8091(1)	11(1)
Na(1)	13(2)	6168(2)	7484(1)	31(1)
Na(2)	-3930(2)	6280(2)	9720(1)	21(1)
Na(3)	-956(2)	3703(2)	8976(1)	26(1)
Na(4)	3206(2)	5747(2)	10938(1)	31(1)
O(1)	889(2)	6239(3)	10243(2)	20(1)
O(2)	1281(3)	2403(2)	8581(2)	17(1)
O(3)	1131(3)	-294(2)	8851(2)	15(1)
O(4)	3743(3)	4903(2)	9651(2)	21(1)
O(5)	-1453(3)	7553(2)	10240(2)	17(1)
O(6)	1760(3)	-640(2)	7351(2)	20(1)
O(7)	-1595(3)	5141(2)	9988(2)	17(1)
O(8)	3612(4)	2464(3)	9803(2)	25(1)
O(9)	1452(3)	4835(2)	8402(2)	19(1)
O(10)	6026(3)	3575(3)	9477(2)	24(1)
O(11)	1641(3)	7423(2)	8317(2)	20(1)
O(12)	1773(3)	3307(3)	7182(2)	22(1)
C(1)	3968(4)	3466(4)	8301(2)	15(1)
H(1A)	4375(4)	2649(4)	8092(2)	18
H(1B)	4448(4)	4183(4)	8010(2)	18
C(2)	-1061(3)	5946(3)	11514(2)	14(1)
H(2A)	-486(3)	6573(3)	11831(2)	16
H(2B)	-726(3)	5071(3)	11660(2)	16
Ow(1)	6338(3)	6276(3)	8298(2)	30(1)
Ow(2)	2541(4)	3540(3)	11473(2)	44(1)

presents a terminal oxygen (O(6) on P(2)) whose bond valence calculation<sup>30</sup> unambiguously shows that it corresponds to a hydroxyl function. This structure presents strong structural relationships with the three isostructural compounds  $\text{M}_2(\text{H}_2\text{O})(\text{O}_3\text{P}-\text{CH}_2\text{PO}_3)$  ( $\text{M} = \text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ). These latter exhibit similar layers except

**Figure 3.** Projections of  $\text{Cu}_3(\text{H}_2\text{O})_2(\text{O}_3\text{P}-\text{CH}_2\text{PO}_3\text{H}_x)_4\cdot(\text{H}_2\text{O})_2$  (MIL-55) along [001] (a) and of one layer along [100] (b); (hollow and small circles for water molecules and hydrogen atoms, respectively).

that the metal polyhedra are all regular octahedra but, unlike MIL-55, they are three-dimensional. Indeed, the connection between the layers is assumed by an extra metal in a tetrahedral environment leading to a metal/P equal to 1 instead of the  $\text{Cu}/\text{P} = 3/4$  observed in MIL-55. From the magnetic point of view, MIL-55 is paramagnetic whatever the temperature. The magnetic susceptibility curve is fitted by a Curie–Weiss law with a Curie constant per  $\text{Cu}^{2+}$  cation and a  $\theta_P$  temperature approximatively equal to 0.42 and 19 K, respectively.

$\text{Na}_3\text{Cu}_5(\text{O}_3\text{P}-\text{CH}_2\text{PO}_3\text{H}_x)_4\cdot(\text{H}_2\text{O})_2$  ( $x = 0.75$ ) (MIL-56) is a layered structure containing water molecules and sodium cations between the layers (Figure 4a). Each layer is built up from the connection of complex tripled chains oriented along [010] by isolated  $\text{CuO}_6$  octahedra (Figure 4b). These octahedra are distorted according to the Jahn–Teller effect (two axial distances longer than the four equatorial distances: 2.321(9) Å vs 1.951(9) and 2.057(9) Å. The chains are constituted by one chain containing copper (chain A) in square planar coordination with four equivalent distances in the range 1.908(9)–1.979(9) Å surrounded by two chains contain-

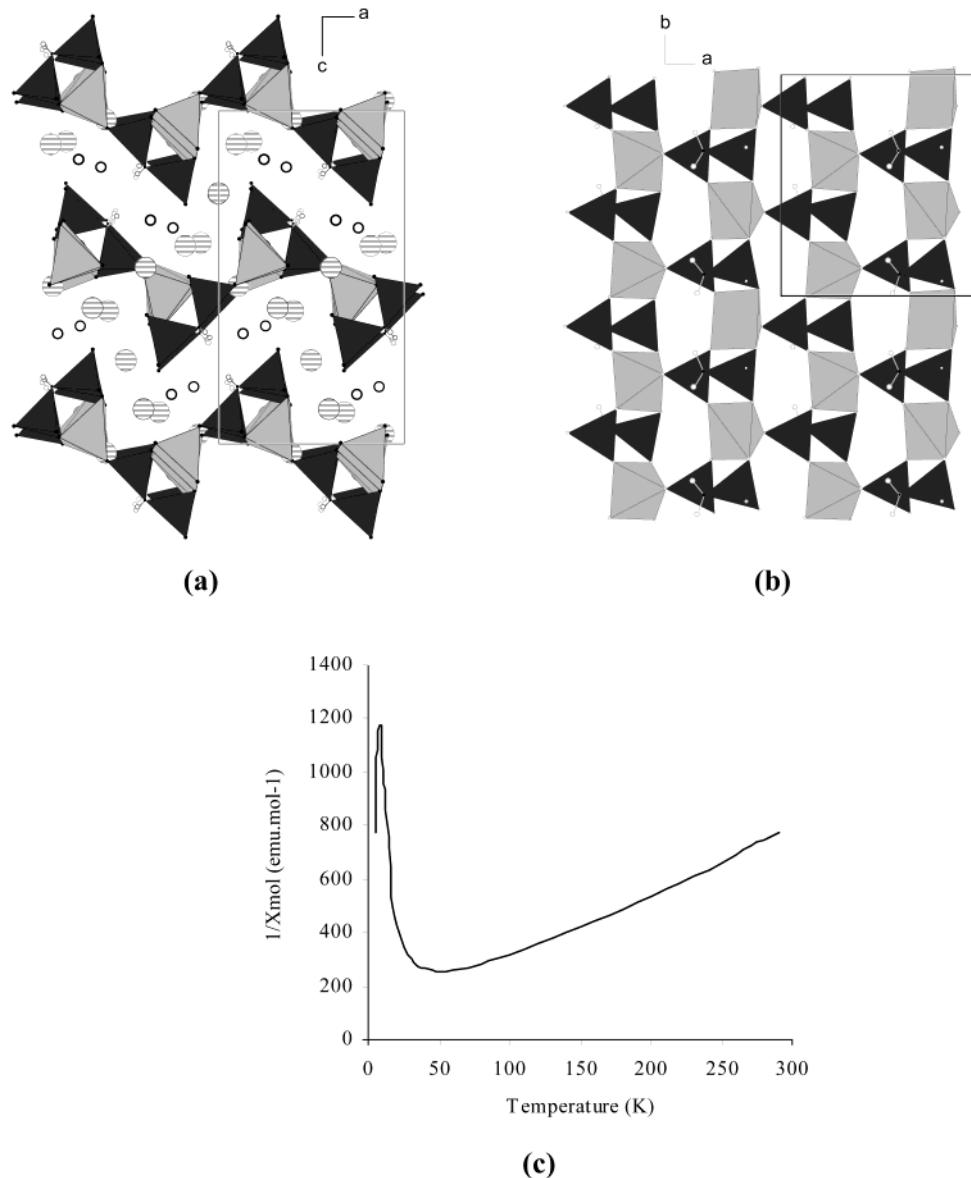


**Figure 4.**  $\text{Na}_3\text{Cu}_5(\text{O}_3\text{P}-\text{CH}_2\text{PO}_3\text{H}_x)_4\cdot(\text{H}_2\text{O})_2$  ( $x = 0.75$ ) (MIL-56): projection of the structure along [010] (a), of one layer along [001] (b), of one chain A (c), and of one chain B (d); (large hatched circles = sodium, small black circles = water molecules).

ing copper in a bipyramid trigonal environment (chain B) (two distances at 1.96(6) Å, two others close to 2 Å, and one longer, 2.295(9) Å). The chains noted A are built up from dimers of square planar copper  $\text{Cu}(1)\text{O}_4$  which share one edge, connected together via chelating diphosphonate groups (Figure 4c). The chains noted B result from the connection of trimers composed by one  $\text{Cu}(3)\text{O}_5$  chelated by one diphosphonate group (Figure 4d). Each  $\text{Cu}(3)\text{O}_5$  shares also one oxygen with  $\text{Cu}(2)\text{O}_4$  ( $\text{O}(10)$ ) and one with a phosphorus of diphosphonate unit of chain A ( $\text{O}(3)$ ) leading to the connection between the two kinds of chains. The tripled chains are constituted from one chain A sandwiched between two chains B. Finally, the bidimensionality of the structure is achieved via the  $\text{Cu}(1)\text{O}_6$  octahedron which is chelated by a diphosphonate group of chain A via oxygen  $\text{O}(3)$  and  $\text{O}(11)$  and share the oxygen  $\text{O}(4)$  which is the connecting point between two trimers in chain B. The result in this structure is that all the diphosphonate groups contain terminal oxygen atoms. For electroneutrality reasons, some of these atoms had to be protonated. However, both bond valence calculations and structure determination do not allow location of the hydroxyl functions. It was assumed that the protons are randomly distributed on the different terminal atoms

with a filling rate leading to the chemical formula  $\text{Na}_3\text{Cu}_5(\text{O}_3\text{P}-\text{CH}_2\text{PO}_3\text{H}_x)_4\cdot(\text{H}_2\text{O})_2$  ( $x = 0.75$ ). MIL-56 is paramagnetic in the temperature range 5–300 K, and the fitting of the  $\chi^{-1}$  curve allows calculation of a Curie constant of 0.376 per  $\text{Cu}^{2+}$  cation in perfect agreement with the theoretical spin only value and a Curie–Weiss temperature close to 10 K.

$\text{Na}_2\text{Cu}(\text{O}_3\text{P}-\text{CH}_2\text{PO}_3)\cdot(\text{H}_2\text{O})$  **4** is a layered compound isostructural with a cobalt analog synthesized by Sevov et al.<sup>25</sup> where the interlamellar space is filled both by water molecules and sodium cations (Figure 5a). The corrugated layers are constituted from chains running along [010] of  $\text{CuO}_5$  square pyramids and diphosphonate groups in strict alternance. The apical oxygen of the square pyramid is shared with a phosphonate function of an adjacent chain leading to a bidimensional structure (Figure 5b). Each diphosphonate unit keeps a nonshared oxygen identified by valence bond calculation as a hydroxyl group. **4** exhibits an antiferromagnetic behavior below  $T_N = 50$  K (Figure 5c). The linear part of the  $\chi^{-1}$  graph provides a Curie constant of 0.39 per  $\text{Cu}^{2+}$  and a  $\theta_P$  temperature slightly negative ( $\approx -11$  K) revealing antiferromagnetic coupling between the magnetic cations.



**Figure 5.**  $\text{Na}_2\text{Cu}(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3)\cdot(\text{H}_2\text{O})$ : projection along [010] (a) and along [001] showing one layer (b) and  $\chi^{-1} = f(T)$  curve; (large hatched circle = sodium, small black circle = water molecules).

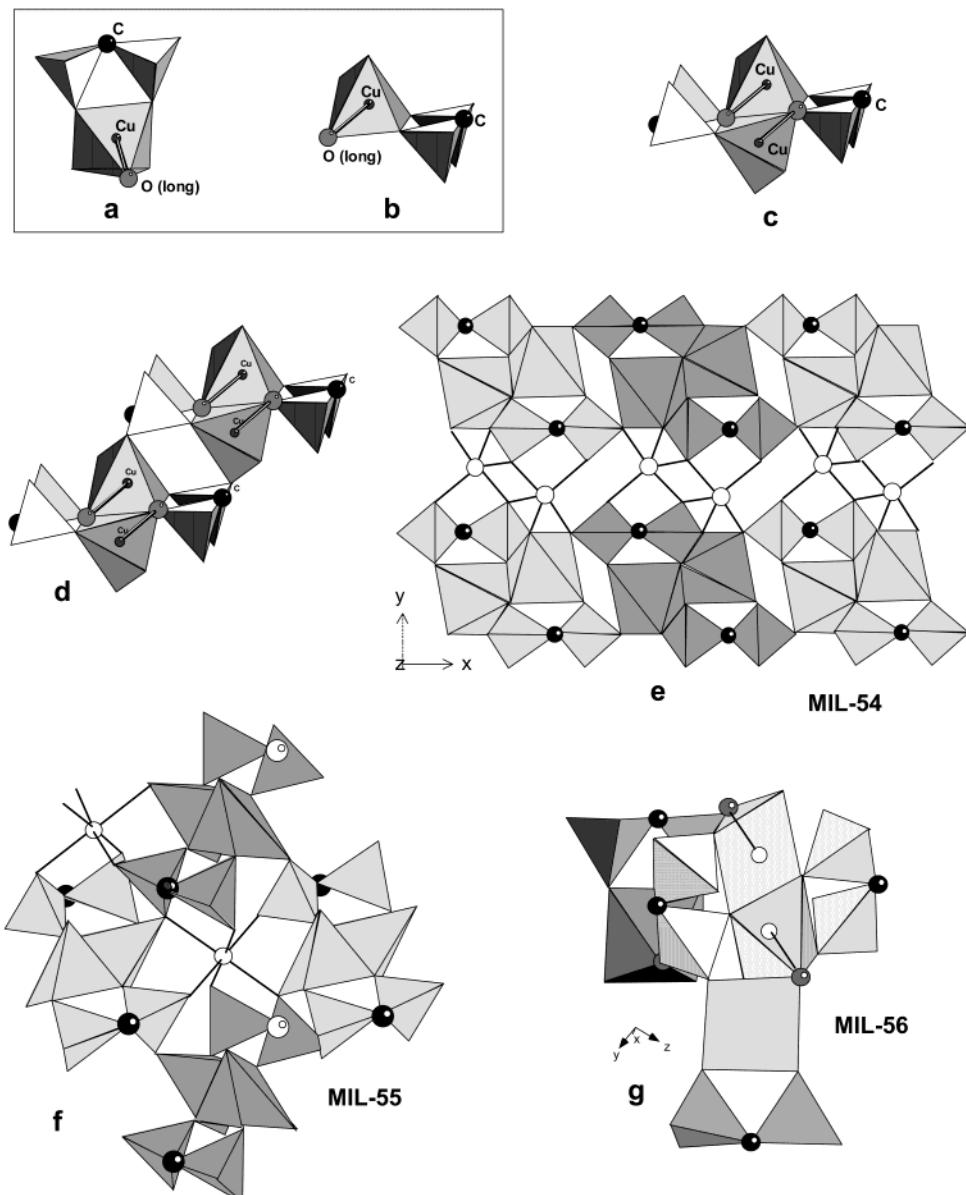
#### 4. Correlations Between Chemistry, Structure and Magnetism of the Phases

The four solids described above appear at different pHs. Whereas MIL-54 and -55 are formed at very low pH, the introduction of NaOH for increasing the latter leads to incorporation of sodium ions in the structures in MIL-56 and **4**. Despite this introduction, the four phases have common structural features which can suggest some explanations of the structural evolution with pH.

Indeed, all the structures are built from the same building unit. It is formed by one methylenediphosphonate (PCP) group and a 5-fold coordinated copper intermediate between square pyramid (SQ) and trigonal bipyramidal (TBP) (Figure 6a,b). In the copper polyhedron, the Jahn-Teller effect exists, characterized by an elongation of one Cu–O bond. The formula of the building unit can be written  $[\text{Cu}_{\text{aq}}(\text{PCP})]$  (*aq* when a water molecule belongs to the Cu polyhedron). When the shape of the Cu polyhedron is close to SQ (Figure 6a), both the free apexes of PCP and the axial Cu–O

bond are in *cis*-position relative to the equatorial plane of the SQ. Moreover, the long Cu–O bond, due to the Jahn-Teller effect, is the axial one. On the contrary, in a TBP coordination, that we shall consider topologically as a distortion of the equatorial plane of the SQ, the free apexes of PCP and the “axial” Cu–O bond are in *trans*-position relative to the “equatorial” plane of the SQ, and the long bond is this time in the “equatorial” plane (Figure 6b). In the following, we shall label these building units as *UU* (for *up-up*, SQ-PCP) and *UD* (*up-down*, TBP-PCP).

At very low pH, the structures are exclusively built from *UD* units, and these units are dimerized (Figure 6c), two TBP sharing one edge, with the free apexes of PCP and the long Cu–O bonds in opposite directions for the two members of the dimer. The formula of these dimers is therefore  $[\text{Cu}_{\text{aq}}(\text{PCP})_2]^{UDUD}$ . The corner sharing of these dimers (Figure 6d) build up the skeleton of the structures of MIL-54 and -55 (Figure 6e,f). In both cases, the corresponding framework does not include the total amount of copper, but it can be considered, for sake



**Figure 6.** Square-pyramidal SQ (a) and trigonal bipyramidal TBP (b) building units with diphosphonate groups; dimerization of TBP and orientation of the long Cu–O bonds within the dimer (c) and corner-sharing connection of dimers (d); MIL-54 (e), MIL-55 (f), and MIL-56 (g) structures described in terms of dimers and monomers.

of homogeneous description of the family, that it traps the remaining Cu as occluded species with 5-fold and octahedral coordination, respectively. In these conditions, the structural formulas of MIL-54 and -55 can be written  $\text{Cu}_2[\text{Cu}_2(\text{PCP})_2]^{UDUD}$  and  $\text{Cu}_2[\text{Cu}_{2aq}(\text{PCP})_2]_2^{UDUD}$ ,  $(\text{H}_2\text{O})_2$ .

When the pH increases, Na ions are introduced in the structure, but the  $[\text{Cu}_{aq}(\text{PCP})]$  units are always present. In MIL-56 or  $\text{Na}_3\text{Cu}_5(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3\text{H})_4 \cdot (\text{H}_2\text{O})_2$  (Figure 6g) both dimers  $[\text{Cu}_2(\text{PCP})_2]^{UDUD}$  and  $UU$  monomers participate in the skeleton (one dimer for two monomers) and the structural formula is  $\text{Na}_3\text{Cu}[\text{Cu}_2(\text{PCP})_2]^{UDUD}[\text{Cu}(\text{PCP})]_2^{UU}, (\text{H}_2\text{O})_2$ . The 'occluded' Cu corresponds to Cu(2) in octahedral coordination, which links the two triple chains described in Section 3. Finally, in **4** isotopic with the Co compound described by Sevov, only  $[\text{Cu}(\text{PCP})]^{UU}$  are present, linked by corners to ensure the layers of the structure, leading to the structural formula  $\text{Na}_2[\text{Cu}(\text{PCP})]^{UU}, (\text{H}_2\text{O})$ , and this time, to no occluded Cu ions.

The recapitulation of chemical, structural, and magnetic features classified at increasing pH, as shown in Table 7, suggests some relationships between pH and the structural evolution of the copper diphosphonates described here. The following seems clear: (i) low pH favors the existence of  $[\text{Cu}_{aq}(\text{PCP})]^{UD}$  building units and their dimerization into  $[\text{Cu}_{aq2}(\text{PCP})_2]^{UDUD}$  species; (ii) the lower the pH, the larger the condensation of these dimers; and (iii) increasing pH affects the dimerization; as at pH 6, both dimers and monomers coexist, and it seems that high pH favors the existence of  $[\text{Cu}(\text{PCP})]^{UU}$  monomers, which are the only observed species at basic pH.

From the magnetic point of view, the existence of Jahn–Teller effects obviously plays a role but, at first glance, less important than the dimensionality of the magnetic interactions. Indeed, MIL-55 and -56, which are two-dimensional, are paramagnets with weak antiferromagnetic interactions, explained both by the 2D character and the  $90^\circ$  superexchange interactions as

**Table 7. Recapitulation of Chemical, Structural, and Magnetic Features Classified at Increasing pH Values**

dim. solid	pH	structural formula	magnetic behavior	$T_N$	$\theta_p$
2D MIL-55	1	$\text{Cu}_2[\text{Cu}_{2a}(\text{PCP})_2]_2^{UDUD}, 2\text{H}_2\text{O}$	P		-19K
3D MIL-54	1.5	$\text{Cu}_2[\text{Cu}_2(\text{PCP})_2]^{UDUD}$	AF	45K	-60K
2D MIL-56	2-6	$\text{Na}_3\text{Cu}[\text{Cu}_2(\text{PCP})_2]^{UDUD}$ $[\text{Cu}(\text{PCP})_2]_2^{UU}, (\text{H}_2\text{O})_2$	P		-10K
2D <b>4</b>	7-10	$\text{Na}_2[\text{Cu}(\text{PCP})_2]_2^{UU}, (\text{H}_2\text{O})$	AF	50K	-11K

sociated with the existence of edge-sharing within the dimers. The existence of antiferromagnetism in MIL-54 ( $T_N = 45$  K,  $\theta_p = -60$  K) is due to its 3D character and also to the particular disposition of the long Cu–O bonds within the dimers (Figure 6c) which involve the  $d_{z2}$  orbitals of each monomer and therefore a strong AF character between the Cu carriers. This explains the high value of  $\theta_p$  compared to that of the other phases.

Despite its 2D character, the AF characteristics of **4** ( $T_N = 50$  K,  $\theta_p = -11$  K) merit a comment. In this solid, the monomers are square pyramids, and therefore, the  $d_{x^2-y^2}$  orbitals bear the single electron. Moreover, the monomers are isolated from each other, and the magnetic interactions correspond to double superexchange Cu–O–O–Cu ones via two oxygens of the phosphonate group. In the structure, the  $[\text{Cu}_{\text{S}Q}(\text{PCP})]$  form corner-linked chains along  $y$  with Cu–Cu distances of 5.06 Å and Cu–O–O angle close to 140°, whereas two consecutive chains in the (001) plane are linked by corners, with Cu–Cu distances of 5.6 Å and a 107° Cu–O–O angle. From these geometrical characteristics, ferromagnetic interaction can be expected within the chains, and an antiferromagnetic interaction can be expected from chain to chain, thus explaining the observed AF. The propagation of the magnetic interaction from one plane to the other can also be explained by double exchange,

via the oxygens which belong to low-coordinated sodium ions ( $\text{Na}(1)\text{O}_5$ ) which link two planes. This suggestion could explain also both the high  $T_N$  (50 K) and the low value of  $\theta_p$  (-11 K) which includes the sum of both F and AF couplings.

## 5. Conclusions

This study showed the existence and the structure of four phases in the system  $\text{NaOH}$ –Cu-phosphonate. All of them are built up from the same building unit  $[\text{Cu}(\text{P–C–P})]$  with copper in either square-pyramidal or trigonal bipyramidal coordination. In the latter case, dimerization of these units is observed at low pH. As soon as pH increases, the dimerization becomes less and less important, and leads to structures containing either both dimers and monomers (MIL-56 at pH 6) or only square-pyramidal monomers at higher pH. The magnetism of these phases has been discussed as a function of the structures.

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