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Synthesis and Crystal Structure of Two Members of a New Type of Layered Compound: Copper(II) Hydroxyphosphonates

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Two original layered copper(II) hydroxyphosphonates $Cu_{2.5}(O_3P(CH_2)_2NH_3)(OH)_2(SO_4)$ (monoclinic $P2_1/n$ (No. 14), $a = 5.442(1)$ Å, $b = 20.570(4)$ Å, $c = 8.529(2)$ Å, $\beta = 93.18(3)°$, $Z = 4$) and $Cu_2(O_3P(CH_2)_2NH_2)(OH)(NO_3)\cdot H_2O$ (monoclinic $P2_1$ (No. 4), $a = 8.392(2)$ Å, $b = 6.132(1)$ Å, $c = 9.097(2)$ Å, $\beta = 104.11(3)°$, $Z = 2$) were prepared from copper sulfate or nitrate, (2-aminoethyl)phosphonic acid, and sodium hydroxide in water. In both cases, the anion of the starting copper salt was retained in the structure. For the first compound, the sulfate groups were part of the layer, while, for the second, the nitrate groups were present in the interlayer space, in a manner similar to that observed in layered double hydroxides.

Introduction

The preparation of new three-dimensional open frameworks based on phosphonates has received considerable attention in the past three years, with examples of 3-D copper(II) and aluminum(III) methylphosphonates[1,2] as well as pillared layered structures (PLS) prepared from bis(phosphonic acids).[3−9] Parallel to that, we have demonstrated in recent papers[10,11] that functionalized phosphonic acids $H_2O_3P{-}R{-}Z$ can also act as efficient building blocks for the self-assembly of PLS. Thus, simply by varying the number of potential binding sites of the Z functional end that can participate in the cohesion of the network (three oxygen atoms for PO_3H_2, two oxygen atoms for CO_2H, and one nitrogen atom for NH_2), it is possible to modulate the structural arrangement of the phosphonate framework. One of those PLS, $Zn(O_3P(CH_2)_2NH_2)$,[11] exhibits unidimensional channels in which the nitrogen atoms are present as two face-to-face columns, parallel to the axis of these tunnels. Attempts to complex copper cations by the nitrogen atoms present in these cavities resulted in the destruction of the structure and led to two members of a new type of layered compound: the copper(II) hydroxyphosphonates $Cu_{2.5}(O_3P(CH_2)_2NH_3)(OH)_2(SO_4)$ and $Cu_2(O_3P(CH_2)_2NH_2)(OH)(NO_3)\cdot H_2O$.

Experimental Section

Materials and Methods. All starting materials were purchased from Aldrich Chemical Co. and were used as received. The chemical analyses were performed by the CNRS Analysis Laboratory (Vernaison). FTIR spectra were obtained on a Nicolet 20SX FT-IR spectrometer with the usual KBr pellet technique. A Perkin-Elmer TGS2 thermogravimetric analyzer was used to obtain thermogravimetric analysis (TGA) thermograms that were run in an air atmosphere from room temperature to 250 °C at a scan rate of 5 °C/min.

Synthesis of $Cu_{2.5}(O_3P(CH_2)_2NH_3)(OH)_2(SO_4)$, 1. A mixture of copper sulfate (2 mmol), (2-aminoethyl)phosphonic acid (1 mmol), and 2 mL of a 1 M sodium hydroxide solution with water (15 mL) was placed in the polytetrafluoroethylene (PTFE) cell (23 mL capacity) of an autoclave, which was sealed and placed in a drying oven at 110 °C for 4 days. Product **1** was obtained as blue crystals that were collected by filtration, washed with water and acetone, dried at room temperature, and used for the structure determination (yield: 82%). This compound was also prepared from a mixture of $Zn(O_3P(CH_2)_2NH_2)$[11] (0.2 mmol) with an excess of copper sulfate (2 mmol) in 17 mL of water, placed in an autoclave at 110 °C for 5 days (yield: 40%). Anal. Found: N, 3.38; C, 5.79; H, 2.20. Calcd: N, 3.39; C, 5.82; H, 2.19. IR (KBr): 3445 (s), 3290−2860 (m, v br), 1169 (s), 1146 (vs), 1095 (vs), 1063 (vs), 1036 (vs), 1003 (s), 944 (s), 591 (m) cm^{-1}. TGA (room temperature to 250 °C): 0% (consistent with the absence of water in this material). The Cu/P ratio measured by energy-dispersive X-ray spectroscopy (EDX) was in good agreement with the expected value, and no zinc was detected in our phase when prepared from $Zn(O_3PC_2H_4NH_2)$.

Synthesis of $Cu_2(O_3P(CH_2)_2NH_2)(OH)(NO_3)\cdot H_2O$, 2. The crystals used for the structural determination were prepared by mixing $Zn(O_3P(CH_2)_2NH_2)$ [11] (0.1 mmol) and copper nitrate (1 mmol) in 17 mL of water, in the PTFE cell of an autoclave. After the cell was sealed and the mixture reacted at 110 °C in a drying oven for 4 days, **2** was obtained in 38% yield. This compound was also prepared from a mixture of copper nitrate (2 mmol), (2-aminoethyl)phosphonic acid (1 mmol), and 2 mL of a 1 M sodium hydroxide solution with water (15 mL) in an autoclave, which was sealed and placed in a drying oven at 110°C for 4 days (yield: 66%). Anal. Found: N, 7.88; C, 6.93; H, 2.61. Calcd: N, 8.07; C, 6.92; H, 2.61. IR (KBr): 3500−3200 (m, v br), 3317 (s), 3267 (m), 1384 (vs), 1370 (vs), 1150 (s), 1127 (s), 1113 (s), 1029 (vs), 986 (vs), 524 (m) cm^{-1}. TGA (room temperature to 280 °C): 5.3% (consistent with the expected value for the loss of the water molecule occurring at 130 °C). The Cu/P and Cu/S ratios

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Table 1. Crystallographic Data for the Copper Hydroxyphosphonates

	1	2
chem formula	$Cu_{2.5}PO_9C_2SNH_9$	$Cu_2PO_8C_2N_2H_9$
fw	413.00	347.17
space group	$P2_1/_n$ (No. 14)	$P2_1$ (No. 4)
a, Å	5.442(1)	8.392(2)
b, Å	20.570(4)	6.132(1)
c, Å	8.529(2)	9.097(2)
β, deg	93.18(3)	104.11(3)
V, Å^3	953.3(5)	454.0(2)
Z	4	2
ρ_{calcd}, g cm^{-3}	2.87	2.54
ρ_{obsd}, g cm^{-3}	2.97	2.62
T, °C	25 ± 1	25 ± 1
λ , Å	0.7107 (Mo Kα)	0.5609 (Ag Kα)
μ, cm^{-1}	45.40	13.10
R	0.022	0.062
R_w	0.024	0.071

[a] $R(F_o) = \sum||F_o - |F_c||/\sum|F_o|$. [b] $R_w(F_o) = [\sum w(|F_o - |F_c|)^2/\sum w(F_o{}^2)]^{1/2}$; $w = 4F_o{}^2/(\sigma(F_o{}^2))^2$.

Table 2. Positional Parameters and Thermal Parameters for the Atoms of $Cu_{2.5}(O_3PC_2H_4NH_3)(OH)_2(SO_4)$

atom	x	y	z	U_{eq},[a] Å^2
Cu(1)	0	0.5	0.5	0.0109(6)
Cu(2)	−0.00896(9)	−0.01576(5)	0.82714(6)	0.0089(4)
Cu(3)	0.13994(9)	0.06308(5)	0.50965(6)	0.0112(4)
P	0.5672(2)	0.0971(1)	0.2901(1)	0.0108(9)
S	0.2059(2)	0.1399(1)	−0.2069(1)	0.0146(9)
O(1)	−0.1775(6)	0.0399(3)	−0.0240(4)	0.0101(7)
O(2)	−0.5850(5)	0.0571(3)	0.1705(3)	0.0113(7)
O(3)	0.1296(5)	−0.0179(3)	0.3837(4)	0.0107(7)
O(4)	0.4649(5)	0.0909(3)	0.4523(3)	0.0122(7)
O(5)	0.4085(7)	0.1865(3)	0.8168(4)	0.028(1)
O(6)	−0.1574(5)	0.0802(3)	0.2967(3)	0.0106(7)
O(7)	0.0109(6)	0.1570(3)	0.8988(4)	0.0230(9)
O(8)	0.0986(6)	0.1457(3)	0.6252(4)	0.0167(8)
O(9)	−0.7105(6)	0.0725(3)	−0.1867(4)	0.0180(8)
N	0.2214(9)	0.2584(4)	−0.8798(6)	0.023(1)
C(1)	0.5400(9)	0.1794(5)	−0.7774(6)	0.019(1)
C(2)	0.280(1)	0.2061(5)	−0.7627(6)	0.024(1)
H(1)	0.17(1)	−0.070(4)	0.035(9)	0.05
H(2)	−0.22(1)	0.033(5)	−0.395(8)	0.05
H(3)	0.18(1)	0.240(4)	−0.972(8)	0.05
H(4)	0.09(1)	0.278(4)	−0.847(8)	0.05
H(5)	0.34(1)	0.283(4)	−0.890(8)	0.05
H(6)	0.64(1)	0.201(4)	−0.722(8)	0.05
H(7)	0.58(1)	0.174(4)	−0.881(8)	0.05
H(8)	0.26(1)	0.219(4)	−0.664(8)	0.05
H(9)	0.16(1)	0.170(4)	−0.790(8)	0.05

[a] The copper, phosphorus, and sulfur atoms were refined anisotropically and are given in the form of the equivalent displacement parameter defined as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*A_{ij}$.

measured by EDX were in good agreement with the expected values, and no zinc was detected in our phase when prepared from $Zn(O_3PC_2H_4NH_2)$.

X-ray Structure Analysis. $Cu_{2.5}(O_3P(CH_2)_2NH_3)(OH)_2(SO_4)$, 1. A blue needle having approximate dimensions 0.02 × 0.06 × 0.15 mm was mounted on a glass fiber. All measurements were made on a Siemens P-4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Cell constants and an orientation matrix for data collection were obtained from least-squares refinement of the setting angles of 25 randomly oriented reflections in the range $10° \leq 2\theta \leq 35°$, corresponding to a monoclinic cell. As a check on crystal and instrument stability, three representative reflections were measured every 60 min, and no decay was observed. An empirical absorption correction based on ψ-scan measurements was applied, which resulted in transmission factors ranging from 0.38 to 0.95, and the data were corrected for Lorentz and polarization effects. The data were collected out to 60° in 2θ using the $\omega-2\theta$ scan technique ($h = 0, +6$; $k = -9, +9$; $l = -20, +20$). On the basis of the systematic absences and the successful refinement of the structure, the space group was found to be $P2_1/n$. The atomic scattering factors were taken from Cromer and Waber,[12] and anomalous dispersion corrections were taken from Cromer and Ibers.[13] For the data reduction, structure solution and refinement, programs in the SHELXTL PLUS package,[14] were used on a microVAX 3900 computer. A total of 3034 reflections were measured, of which 963 were unique ($R_{int} = 0.018$) with the condition $I \geq 2\sigma(I)$.

The structure was solved by a combination of direct methods and Fourier syntheses. The positions of the H atoms were located from a last difference Fourier map and refined with fixed thermal parameters. The copper, phosphorus, and sulfur atoms were refined anisotropically, while the oxygen, nitrogen, and carbon atoms were refined isotropically, in order to keep a reasonable data to parameter ratio. The final cycle of full matrix least-squares refinement for 118 variables converged (largest parameter shift was 0.03 times its estimated standard deviation (esd)) with unweighted and weighted agreement factors of $R = 0.022$ and $R_w = 0.024$. Crystallographic data and refinement conditions are listed in Table 1. Positional and thermal parameters are given in Table 2, and selected bond distances and angles are listed in Table 3.

$Cu_2(O_3P(CH_2)_2NH_2)(OH)(NO_3)\cdot H_2O$, 2. The single crystal study was undertaken using a blue needle of approximate dimensions 0.03 × 0.045 × 0.22 mm, rotating along the b axis. A Weissenberg study revealed monoclinic symmetry, and the lattice parameters obtained were $a \approx 8.39$ Å, $b \approx 6.13$ Å, $c \approx 9.10$ Å, and $\beta \approx 104°$, but very faint and diffuse lattice rows appeared on the first level Weissenberg photograph. These diffuse rows, parallel to a^*, were located halfway between "normal" rows, thus implying a doubling of the c parameter. Furthermore, taking into account the periodic reinforcement of the intensity along a^*, the a parameter should be multiplied by 8. The zero level Weissenberg photograph showed normal diffraction spots only. Consequently, defects are present via stacking disorder in the b direction. They could be accounted for by considering a ($8a$, b, $2c$) supercell; however, due to the faint and diffuse character of the reflections, the corresponding measurements were not possible. We have checked that this feature was invariably present, by studying several single crystals taken from different preparations. Thus, the small unit cell parameters mentioned above were refined from 15 automatically centered reflections on a Siemens P-4 diffractometer with graphite-monochromated Ag Kα radiation ($\lambda = 0.560\,87$ Å). The data were collected out to 60° (in 2θ) using the $\omega-2\theta$ scan technique, as described for the previous structure ($h = 0, +6$; $k = -9, +9$; $l = -20, +20$). An empirical absorption correction based on ψ-scan measurements was applied, which resulted in transmission factors ranging from 0.47 to 0.98. For the data reduction, structure solution and refinement, programs in the SHELXTL PLUS package,[14] were used on a microVAX 3900 computer. On the basis of the systematic absences ($0k0$, $k = 2n + 1$), the space group was found to be $P2_1/m$ or $P2_1$. Of the 2356 reflections which were collected, 1092 were unique ($R_{int} = 0.058$) and observed with $I \geq 2\sigma(I)$. Attempts to refine the structure in the centrosymmetric group $P2_1/m$ were then carried out, and most of the atoms were forced to lie in special positions. The description of the structure involved strong disorder for the aminoethyl chains as well as for the nitrate groups and did not provide adequate agreement between observed and calculated intensities. Consequently, the noncentrosymmetric alternative $P2_1$ was tested, and an average structure was solved by a combination of direct methods and Fourier syntheses. The nonhydrogen atoms were refined anisotropically, except for the atoms of the nitrate groups that were refined isotropically. The final cycle of full matrix least-squares refinement for 113 variables converged (largest parameter shift was 0.03 times its esd) with unweighted and weighted agreement factors of $R = 0.062$ and $R_w = 0.071$. Positional and thermal parameters are given in Table 4, and selected bond distances and angles are listed in Table 5. While the appearance of the the extra diffuse and faint diffraction spots indicates the presence of a supercell (probably

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Table 3. Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of $Cu_{2.5}(O_3PC_2H_4NH_3)(OH)_2(SO_4)$[a]

Cu(1)−O(1)^{a}	1.959(4)	Cu(3)−O(3)^{d}	1.997(4)
Cu(1)−O(1)^{b}	1.959(4)	Cu(3)−O(4)	1.947(3)
Cu(1)−O(2)^{a}	1.945(4)	Cu(3)−O(6)	2.391(3)
Cu(1)−O(2)^{b}	1.945(4)	Cu(3)−O(8)	1.984(5)
Cu(1)−O(9)^{a}	2.422(5)	P−O(2)^{g}	1.520(4)
Cu(1)−O(9)^{b}	2.422(5)	P−O(4)	1.525(3)
Cu(2)−O(1)^{c}	1.974(4)	P−O(6)^{g}	1.536(3)
Cu(2)−O(1)^{d}	1.977(3)	P−C(1)^{c}	1.79(1)
Cu(2)−O(2)^{e}	2.369(3)	S−O(5)^{h}	1.466(5)
Cu(2)−O(3)^{d}	2.003(4)	S−O(7)^{h}	1.472(4)
Cu(2)−O(6)^{d}	1.950(4)	S−O(8)^{h}	1.521(3)
Cu(2)−O(9)^{f}	2.442(4)	S−O(9)^{g}	1.468(7)
Cu(3)−O(3)	1.982(6)	C(1)−C(2)	1.528(9)
		C(2)−N	1.49(1)

O(1)^{a}−Cu(1)−O(1)^{b}	180	O(3)^{d}−Cu(2)−O(6)^{d}	83.6(2)
O(1)^{a}−Cu(1)−O(2)^{a}	94.4(2)	O(3)^{d}−Cu(2)−O(9)^{f}	83.5(2)
O(1)^{a}−Cu(1)−O(2)^{b}	85.6(2)	O(6)^{d}−Cu(2)−O(9)^{f}	98.6(2)
O(1)^{a}−Cu(1)−O(9)^{a}	93.8(2)	O(3)−Cu(3)−O(3)^{d}	81.7(2)
O(1)^{a}−Cu(1)−O(9)^{b}	86.2(2)	O(3)−Cu(3)−O(4)	96.3(2)
O(1)^{b}−Cu(1)−O(2)^{a}	85.6(2)	O(3)−Cu(3)−O(6)	73.4(2)
O(1)^{b}−Cu(1)−O(2)^{b}	94.4(2)	O(3)−Cu(3)−O(8)	171.5(1)
O(1)^{b}−Cu(1)−O(9)^{a}	86.2(2)	O(3)^{d}−Cu(3)−O(4)	162.0(2)
O(1)^{b}−Cu(1)−O(9)^{b}	93.8(2)	O(3)^{d}−Cu(3)−O(6)	86.1(1)
O(2)^{a}−Cu(1)−O(2)^{b}	180	O(3)^{d}−Cu(3)−O(8)	93.8(2)
O(2)^{a}−Cu(1)−O(9)^{a}	89.8(2)	O(4)−Cu(3)−O(6)	110.6(1)
O(2)^{a}−Cu(1)−O(9)^{b}	90.2(2)	O(4)−Cu(3)−O(8)	90.1(2)
O(2)^{b}−Cu(1)−O(9)^{a}	90.2(2)	O(6)−Cu(3)−O(8)	99.2(2)
O(2)^{b}−Cu(1)−O(9)^{b}	89.8(2)	O(2)^{g}−P−O(4)	110.5(2)
O(9)^{a}−Cu(1)−O(9)^{b}	180	O(2)^{g}−P−O(6)^{g}	113.3(2)
O(1)^{c}−Cu(2)−O(1)^{d}	80.5(2)	O(2)^{g}−P−C(1)^{c}	105.3(3)
O(1)^{c}−Cu(2)−O(2)^{e}	74.7(2)	O(4)−P−O(6)^{g}	110.6(2)
O(1)^{c}−Cu(2)−O(3)^{d}	103.6(2)	O(4)−P−C(1)^{c}	110.1(3)
O(1)^{c}−Cu(2)−O(6)^{d}	171.8(2)	O(6)^{g}−P−C(1)^{c}	106.8(3)
O(1)^{c}−Cu(2)−O(9)^{f}	86.2(2)	O(5)^{h}−S−O(7)^{h}	108.8(3)
O(1)^{d}−Cu(2)−O(2)^{e}	109.7(1)	O(5)^{h}−S−O(8)^{h}	109.0(3)
O(1)^{d}−Cu(2)−O(3)^{d}	167.6(2)	O(5)^{h}−S−O(9)^{g}	112.1(3)
O(1)^{d}−Cu(2)−O(6)^{d}	93.3(2)	O(7)^{h}−S−O(8)^{h}	107.8(2)
O(1)^{d}−Cu(2)−O(9)^{f}	85.2(2)	O(7)^{h}−S−O(9)^{g}	112.5(3)
O(2)^{e}−Cu(2)−O(3)^{d}	82.7(1)	O(8)^{h}−S−O(9)^{g}	106.5(3)
O(2)^{e}−Cu(2)−O(6)^{d}	102.8(2)	P^{h}−C(1)−C(2)	111.9(5)
O(2)^{e}−Cu(2)−O(9)^{f}	152.9(2)	C(1)−C(2)−N	111.7(5)

[a] Atom related by the following, indicated with superscript letter: ^{a} $-{}^{1}/_{2} - x$, ${}^{1}/_{2} + y$, ${}^{1}/_{2} - z$; ^{b} ${}^{1}/_{2} + x$, ${}^{1}/_{2} - y$, ${}^{1}/_{2} + z$; ^{c} x, y, $1 + z$; ^{d} $-x$, $-y$, $1 - z$; ^{e} $-1 - x$, $-y$, $1 - z$.; ^{f} $1 + x$, y, $1 + z$; ^{g} $1 + x$, y, z; ^{h} x, y, $-1 + z$.

Table 4. Positional Parameters and Thermal Parameters for the Non-Hydrogen Atoms of $Cu_2(O_3P(CH_2)_2NH_2)(OH)(NO_3)\cdot H_2O$

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Cu(1)	0.0014(2)	0	0.0017(3)	0.0171(5)
Cu(2)	0.2877(2)	0.250(1)	−0.0838(2)	0.0180(5)
P	0.6549(4)	0.255(2)	0.9244(4)	0.017(1)
O(1)	0.042(1)	0.275(3)	0.880(1)	0.018(1)
O(2)	0.046(1)	0.240(5)	1.210(1)	0.033(2)
O(3)	−0.236(2)	0.041(3)	0.946(2)	0.024(1)
O(4)	0.239(2)	−0.042(3)	1.023(2)	0.022(1)
O(5)	0.519(1)	0.277(3)	1.006(1)	0.024(1)
O(6)	0.083(1)	0.756(7)	1.443(1)	0.037(3)
O(7)	0.238(2)	0.451(3)	1.458(2)	0.036(4)
O(8)	0.200(2)	0.624(4)	1.664(2)	0.039(4)
N(1)	0.286(2)	0.114(3)	−0.278(2)	0.021(2)
N(2)	0.171(2)	0.615(4)	1.521(2)	0.024(3)
C(1)	0.564(1)	0.284(4)	−0.275(1)	0.023(3)
C(2)	0.448(3)	0.087(5)	−0.323(2)	0.027(3)

[a] All of the non-hydrogen atoms were refined anisotropically (except the atoms of the NO_3 groups) and are given in the form of the equivalent displacement parameter defined in Table 2.

due to a slight disorder of the nitrate groups in the interlayer space), the important features of the structure are well-refined in the small unit cell, but this does not imply that the true symmetry in the supercell is itself acentric.

Table 5. Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of $Cu_2(O_3PC_2H_4NH_2)(OH)(NO_3)\cdot H_2O$[a]

Cu(1)−O(1)^{a}	2.09(2)	Cu(2)−N(1)	1.95(2)
Cu(1)−O(1)^{b}	1.84(2)	P−O(3)^{d}	1.59(2)
Cu(1)−O(2)^{a}	2.36(2)	P−O(4)^{e}	1.53(2)
Cu(1)−O(2)^{b}	2.46(2)	P−O(5)	1.51(1)
Cu(1)−O(3)^{a}	1.94(2)	P−C(1)^{f}	1.79(1)
Cu(1)−O(4)^{a}	1.97(2)	N(2)−O(6)	1.24(3)
Cu(2)−O(1)^{a}	2.009(9)	N(2)−O(7)	1.34(3)
Cu(2)−O(3)^{c}	2.28(2)	N(2)−O(8)	1.27(2)
Cu(2)−O(4)^{a}	2.12(2)	C(1)−C(2)	1.54(3)
Cu(2)−O(5)^{a}	1.922(8)	C(2)−N(1)	1.51(3)

O(1)^{a}−Cu(1)−O(1)^{b}	174.7(8)	O(1)^{a}−Cu(2)−N(1)	95.9(6)
O(1)^{a}−Cu(1)−O(2)^{a}	84.8(8)	O(3)^{c}−Cu(2)−O(4)^{a}	108.9(7)
O(1)^{a}−Cu(1)−O(2)^{b}	97.0(7)	O(3)^{c}−Cu(2)−O(5)^{a}	90.4(7)
O(1)^{a}−Cu(1)−O(3)^{a}	92.8(7)	O(3)^{c}−Cu(2)−N(1)	150.5(8)
O(1)^{a}−Cu(1)−O(4)^{a}	82.3(6)	O(4)^{a}−Cu(2)−O(5)^{a}	99.5(6)
O(1)^{b}−Cu(1)−O(2)^{a}	90.7(7)	O(4)^{a}−Cu(2)−N(1)	95.6(8)
O(1)^{b}−Cu(1)−O(2)^{b}	87.6(7)	O(5)^{a}−Cu(2)−N(1)	101.9(6)
O(1)^{b}−Cu(1)−O(3)^{a}	84.9(7)	O(3)^{d}−P−O(4)^{e}	111(1)
O(1)^{b}−Cu(1)−O(4)^{a}	100.6(6)	O(3)^{d}−P−O(5)	120(1)
O(2)^{a}−Cu(1)−O(2)^{b}	178.2(6)	O(3)^{d}−P−C(1)^{f}	107(1)
O(2)^{a}−Cu(1)−O(3)^{a}	94.5(6)	O(4)^{e}−P−O(5)	103(1)
O(2)^{a}−Cu(1)−O(4)^{a}	92.6(6)	O(4)^{e}−P−C(1)^{f}	108(1)
O(2)^{b}−Cu(1)−O(3)^{a}	85.5(7)	O(5)−P−C(1)^{f}	107.8(6)
O(2)^{b}−Cu(1)−O(4)^{a}	87.6(7)	O(6)−N(2)−O(7)	122(1)
O(3)^{a}−Cu(1)−O(4)^{a}	171.0(7)	O(6)−N(2)−O(8)	119(1)
O(1)^{a}−Cu(2)−O(3)^{c}	72.9(8)	O(7)−N(2)−O(8)	118(1)
O(1)^{a}−Cu(2)−O(4)^{a}	80.5(7)	P^{a}−C(1)−C(2)	107(1)
O(1)^{a}−Cu(2)−O(5)^{a}	162.1(4)	C(1)−C(2)−N(1)	113(2)

[a] Atoms related by the following, indicated with superscript letter: ^{a} x, y, $-1 + z$; ^{b} $-x$, $-{}^{1}/_{2} + y$, $1 - z$; ^{c} $-x$, ${}^{1}/_{2} + y$, $1 - z$; ^{d} $1 + x$, y, z; ^{e} $1 - x$, ${}^{1}/_{2} + y$, $2 - z$; ^{f} x, y, $1 + z$.

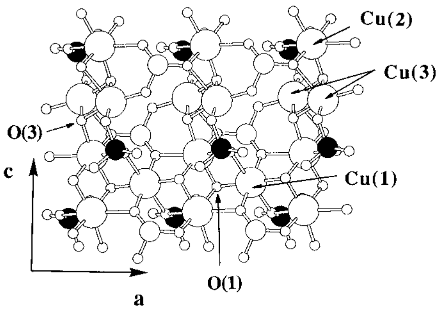

Figure 1. Schematic representation of a $Cu_{2.5}(O_3P(CH_2)_2NH_3)(OH)_2(SO_4)$ layer as seen perpendicular to the *b*-axis. The organic chains bound to phosphorus have been omitted for clarity.

Results

Structure of $Cu_{2.5}(O_3P(CH_2)_2NH_3)(OH)_2(SO_4)$, 1. The structure consists of layers (*a*,*c* plane, Figure 1), in which the copper atoms are present in three different environments, made of oxygen atoms from phosphonate, sulfate, and hydroxide groups. Two of them, Cu(1) and Cu(2), have a distorted 4 + 1 + 1 elongated tetragonal octahedral geometry, with two long apical bonds (2 × 2.422(5) Å for Cu(1) and 2.369(3)−2.442(4) Å for Cu(2)), and four shorter equatorial links (Figure 2). A distorted square pyramidal site is occupied by the third type of copper atoms, Cu(3). The structure is built up from a complex network of edge-sharing copper−oxygen polyhedra propagating in the *a*- and *c*-directions. Each of the two hydroxide oxygen atoms (O(1) and O(3)) is linked to three distinct copper atoms, as well as to a proton. A similar feature is observed in some metal hydroxynitrates (*i.e.* $Cu_4(NO_3)_2(OH)_6$[15] and $Zn_5(OH)_8(NO_3)_2\cdot 2H_2O$[16]) along with some metal hydroxyphosphates,such

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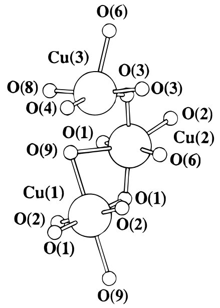

Figure 2. Schematic representation of the coordination about the copper atoms in $Cu_{2.5}(O_3P(CH_2)_2NH_3)(OH)_2(SO_4)$ and the numbering scheme used in the tables.

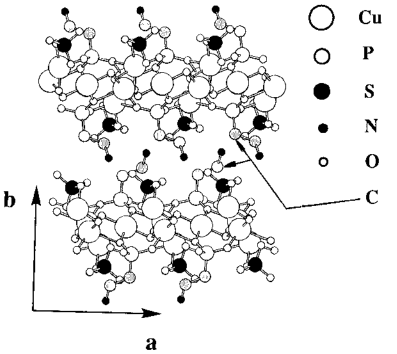

Figure 3. Schematic representation of $Cu_{2.5}(O_3P(CH_2)_2NH_3)(OH)_2(SO_4)$ as seen perpendicular to the *c*-axis.

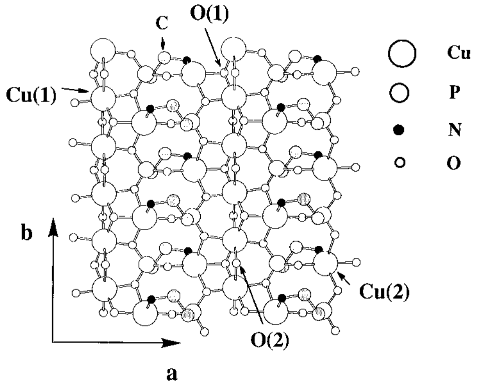

Figure 4. Schematic representation of a $Cu_2(O_3P(CH_2)_2NH_2)(OH)(NO_3)\cdot H_2O$ layer as seen perpendicular to the *c*-axis. The nitrate groups have been omitted for clarity.

as $M^{II}_2(OH)(PO_4)$, where M = Cu,[17] Zn, Co.[18] The layers of compound **1** are held together in the *b*-direction by van der Waals forces and hydrogen bonds between the NH_3^+ ends of the phosphonate alkyl chains and the two oxygen atoms of the sulfate groups that do not coordinate the copper atoms (Figure 3; *d*[N−O(5)] = 2.70(1) Å and *d*[N−O(7)] = 3.28(1) Å).

Structure of $Cu_2(O_3P(CH_2)_2NH_2)(OH)(NO_3)\cdot H_2O$, 2. This structure is also layered (*a*,*b* plane; Figure 4), with two environments for the copper atoms. The first one, Cu(1), is 6-fold coordinated by oxygen atoms (from phosphonate groups O(3) and O(4), hydroxide groups O(1), and the water molecule O(2)) in a distorted 4 + 1 + 1 elongated tetragonal geometry with two long apical bonds (2.35(2) and 2.44(2) Å), while the second one, Cu(2), has a distorted square pyramidal geometry made of four oxygen atoms and one nitrogen atom, N(1), present on the alkyl chain bound to phosphorus (Figure 5). The CuO_6 and CuO_4N polyhedra are sharing edges, forming zigzag chains running parallel to the *b*-direction. These chains are connected together in the *a*-direction by O−P−O bridges as well as O−P−C−C−N links. In this structure the hydroxide group is assumed to occupy the O(1) position which is bridging three distinct copper atoms, by analogy with compound **1**. This is also confirmed by calculating a bond-valence sum (close to 1) for O(1). The water molecule would therefore be located in the O(2) position, which is only connected to two metal atoms. The stacking of the layers along the *c*-direction is presented in Figure 6, with nitrate groups present between the sheets, and probably hydrogen bonds between two oxygen atoms of the NO_3 moieties on the one hand and the water molecule and the NH_2 group on the other hand (*d*[O(2)−O(6)] = 3.59(3) Å and d[O(8)−N(1)] = 3.18(3) Å).

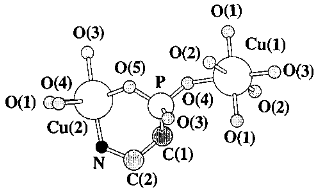

Figure 5. Schematic representation of the coordination about the copper atoms in $Cu_2(O_3P(CH_2)_2NH_2)(OH)(NO_3)\cdot H_2O$ and the numbering scheme used in the tables.

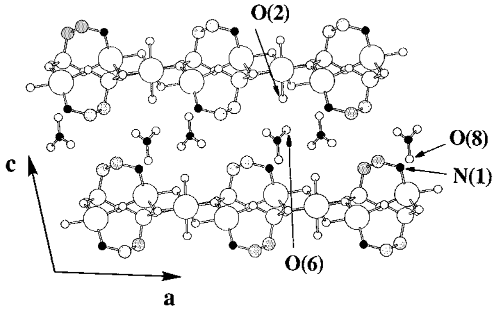

Figure 6. Schematic representation of $Cu_2(O_3P(CH_2)_2NH_2)(OH)(NO_3)\cdot H_2O$ as seen perpendicular to the *b*-axis.

Discussion

Parallel to the case of layered vanadium(IV) organophosphonates such as $[(C_2H_5)_4N][(VO)_3(OH)(H_2O)(C_2H_5PO_3)_3]\cdot H_2O$ and $[(C_2H_5)_2NH_2][(CH_3)_2NH_2][V_4O_4\ (OH)_2(C_6H_5PO_3)_4]$,[19] in which organic cationic templates are present to compensate the negative charge of the layers, the two copper hydroxyphosphonates **1** and **2** are two members of a new family of layered compound, in which the counteranion of the starting copper salt is retained in the structure. It is interesting to note that the formulation of $Cu_2(O_3P(CH_2)_2NH_2)(OH)(NO_3)\cdot H_2O$ is very similar to that of hydroxyphosphates $M^{II}_2(OH)(PO_4)$,[17,18] but the charge balance requires the presence of an anionic unit (NO_3^- ; IR, $\nu(NO_2)$ = 1384 cm^{-1}) when the phosphate group is replaced by a phosphonate group. These nitrate groups are located between the positively charged hydroxyphosphonate layers, in a manner comparable to that observed in layered double hydroxides (LDH's),[20] hydroxy double salts (HDS's; *i.e.*, $(M^{II}(M')^{II})_2(OH)_3(NO_3)$),[21] and hydroxynitrates.[15,16] In this case, the nitrate groups do not directly coordinate the metal atoms,

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while the sulfate groups in compound **1** are bound to copper atoms of the layer, as observed in hydroxy double nitrates exchanged by alkanesulfonate anions.[21] Another main difference between our two compounds is the role of the amino end of the phosphonate moieties. In compound **1**, these groups are protonated (IR, ν(NH) = 2860−3290 cm^{-1}) and point toward the interlayer space, as it is generally observed for metal (aminoalkyl)phosphonates[10a,22,23] or phosphate.[24] For compound **2**, the amino groups are directly coordinated to the metal atoms, as was already the case in $Zn(O_3PC_2H_4NH_2)$;[11] in the former compound, the two ends (NH_2 and PO_3) of the (2-aminoethyl)phosphonic acid groups are present in the same layer, participating in the cohesion of the bidimensional network, while in the latter, they act as “pillars”, leading to a three-dimensional pillared layered structure. It is noteworthy that if compounds **1** and **2** can be synthesized by reaction of (2-aminoethyl)phosphonic acid with the corresponding copper salt, as mentioned above, they can also be prepared by reaction of these copper salts with 3-D $Zn(O_3PC_2H_4NH_2)$. This clearly demonstrates the affinity of copper for amino ligands, to the extent that it is able to destroy this structure to yield copper hydroxyphosphonates, in which no zinc is present. When treated with other metal salts (*i.e.*, manganese, nickel), $Zn(O_3PC_2H_4NH_2)$ remained intact.

We are interested now to know if the preparation of copper hydroxyphosphonates can be extended to other anionic species, either by direct synthesis or by an intercalation/exchange process from compound **1** or **2**. A first result is the preparation of $Cu_2(O_3P(CH_2)_2NH_2)(OH)(Cl)$ in which the infrared NH absorption (three sharp bands in the 3100−3300 cm^{-1} region (NH stretching motion) and one sharp band at 1605 cm^{-1} (NH bending vibration)) are characteristic of the amine coordinated to the metal atom, as previously reported for $Zn(O_3PC_2H_4NH_2)$, compound **2**, or amine intercalates of copper or zinc phosphonates.[25] Complementary studies about the anionic exchange properties and magnetic properties of this new class of materials are currently in progress.

Acknowledgment. We acknowledge with grateful thanks Dr. Yves Piffard (UMR CNRS 110) for fruitful discussions concerning the X-ray structure refinements

Supporting Information Available: Tables giving a full presentation of the crystal data and anisotropic thermal parameters for nonhydrogen atoms (3 pages). Ordering information is given on any current masthead page.

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