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Preparation and Structure of $\mathrm{Cu^{II}(C_2H_5PO_3)}$. Structural Transition between Its Hydrated and Dehydrated Forms

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The crystal structure of $\mathrm{Cu^{II}(C_2H_5PO_3)}$ has been solved ab initio using direct methods and refined from X-ray powder diffraction data. This compound is monoclinic, space group $P2_1/c$, with $a = 10.7773(3)$ Å, $b = 5.6960(2)$ Å, $c = 7.6273(2)$ Å, $\beta = 94.47(1)°$, $Z = 4$, and $V = 466.8(2)$ Å^3. The Rietveld refinement gave $R_I = 0.047$, $R_p = 0.107$, $R_{wp} = 0.116$, and $R_{exp} = 0.104$. The layers rearrangement between its hydrated and dehydrated form is presented.

Introduction

In a previous study devoted to the preparation and characterization of iron phosphonates, we have reported the synthesis of the original $\mathrm{Fe^{II}(C_2H_5PO_3){\cdot}H_2O}$,[1,2] isostructural with the $\mathrm{M^{II}(RPO_3){\cdot}H_2O}$ series (M = Mn, Co, Ni, Zn) described at the same time by Mallouk et al.[3] and Clearfield et al.[4] At first we have focused a great deal of magnetic studies on $\mathrm{Fe^{II}(C_2H_5PO_3){\cdot}H_2O}$ for which a spin canting phenomenon has been established.[5] Therefore, the field of our magnetic measurements has been then extended to the $\mathrm{M^{II}(C_2H_5PO_3){\cdot}H_2O}$ series and the corresponding $\mathrm{M^{II}(C_2H_5PO_3)}$ dehydrated phases, including the copper(II) phosphonate homologues. However the $\mathrm{Cu^{II}(RPO_3){\cdot}H_2O}$ structure differs from the other members of the $\mathrm{M^{II}(RPO_3){\cdot}H_2O}$ family (M = Mg, Mn, Co, Ni, Zn), as nicely demonstrated by Clearfield et al.[6] (R = $\mathrm{CH_3}$, $\mathrm{C_6H_5}$). In the present paper, the original synthesis and the crystal structure of $\mathrm{Cu^{II}(C_2H_5PO_3)}$ are reported. This structure has been solved ab initio from X-ray powder diffraction data. Then we illustrate the structural transition between the hydrated and dehydrated material during the dehydration process.

Experimental Section

Materials and Methods. Chemicals used were of reagent grade quality and were obtained from Aldrich without further purification. Other methods and instruments used in the characterization of the copper phosphonates are described in a previous publication.[1]

Preparation of $\mathrm{Cu^{II}(C_2H_5PO_3)}$. A mixture of 1.763 g of $\mathrm{Cu(NO_3)_2{\cdot}3H_2O}$ (7.3 mmol) and 0.8 g of ethylphosphonic acid (7.3 mmol) was placed in the Teflon cell (20-mL capacity) of an autoclave. Then 19.5 mL of 0.75 M NaOH was added, and the autoclave was sealed and placed in a drying oven at 180 °C for 4 days. The amount of NaOH used corresponds to the neutralization of the diprotic phosphonic acid. The white crystalline product obtained was filtered off with suction, washed with water, and dried under vacuum. Yield: 93% (1.165 g). No reversibility of the dehydration was observed. This compound could also be prepared by thermal treatment of $\mathrm{Cu^{II}(C_2H_5PO_3){\cdot}H_2O}$ in air at 180 °C, but the crystallinity of the resulting material was too poor to allow any structure determination from its powder pattern.

Preparation of $\mathrm{Cu^{II}(C_2H_5PO_3){\cdot}H_2O}$. A mixture of 0.438 g of $\mathrm{Cu(NO_3)_2{\cdot}3H_2O}$ (1.8 mmol) and 0.2 g of ethylphosphonic acid (1.8 mmol) in 12 mL of distilled water was placed in a round-bottom flask. Then 36.2 mL of 0.1 M NaOH (3.6 mequiv $\mathrm{OH^-}$) was added and the reaction medium was refluxed for 3 days, giving $\mathrm{Cu^{II}(C_2H_5PO_3){\cdot}H_2O}$ as a pale blue solid in 86% (0.293 g). The already described $\mathrm{Cu^{II}(CH_3PO_3){\cdot}H_2O}$ and $\mathrm{Cu^{II}(C_6H_5PO_3){\cdot}H_2O}$ phases were synthesized by following the same procedure as above.

Crystallographic Study. The X-ray powder diffraction pattern of $\mathrm{Cu^{II}(C_2H_5PO_3)}$ was collected at room temperature in the Debye–Scherrer geometry for 3 h using an INEL CPS120 detector, whose potential in conventional structure characterizations, including ab-initio structure determinations, has been recently demonstrated.[7] Monochromatized Cu Kα_1 radiation was used, and the generator power was set to 40 kV × 30 mA. To obtain a better signal/background ratio, a homogeneous thin layer of powder was put on the external side of a 0.1 mm diameter capillary with modeling clay as a sticking agent. The experimental pattern (Figure 1) is typical of $\mathrm{M^{II}(RPO_3){\cdot}H_2O}$ compounds, with a very intense first reflection as compared with the other peaks which however are very well defined (see inset in Figure 1). The 20 first reflection positions were determined with the program PROLIX, specially designed to deal with INEL data,[8] and subsequently processed by the auto-indexing program DICVOL91.[9] All the peaks in the pattern could be indexed by the primitive monoclinic cell produced by DICVOL91 (Table I) with the conventional figures of merit $M_{20} = 45$ and $F_{20} = 87$ (0.0067, 34).[10,11] From the systematic absences, the space group $P2_1/c$ appeared likely.

In order to extract from the pattern the intensities of the individual reflections, the unit cell constrained refinement procedure described by Le Bail[12] was applied using the program MPROF.[13] The final refinement without structural information involved the cell constants, the zero-point, three half-width parameters, and the peak-shape parameters of the Pearson VII fraction. In addition, 10 parameters were used to refine the background as a double polynomial function. The final R factors calculated with background corrected counts[14] were $R_p = 0.076$, $R_{wp} = 0.088$, and $R_{exp} = 0.069$ for 557 reflections in the angular range 5.0–107.7° 2θ. This set of integrated intensities was then input to the direct-methods package SHELXS-86.[15] Atomic scattering factors and anom-

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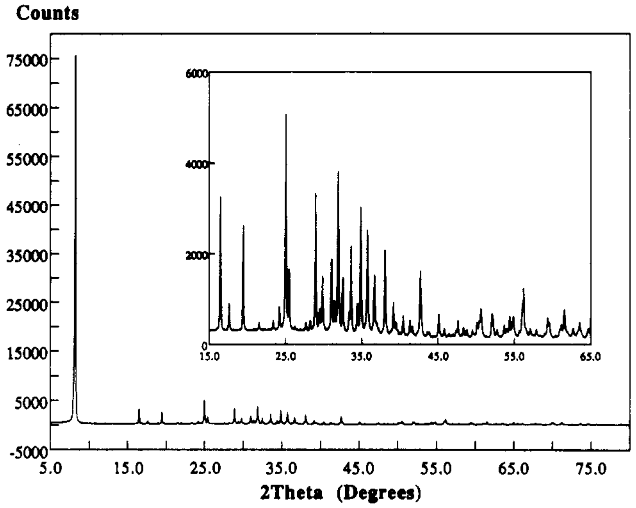

Figure 1. Experimental Inel X-ray powder diffraction pattern of $Cu^{II}(C_2H_5PO_3)$.

Table I. Crystallographic Data for $Cu(C_2H_5PO_3)$

$CuPO_3C_2H_5$	$\lambda(Cu\ K\alpha_1) = 1.540\,598$ Å
fw = 171.57	$D_c = 2.468$ g/cm^3
$a = 10.7773(3)$ Å	$\mu = 49.60$ cm^{-1}
$b = 5.6960(2)$ Å	no. of Rietveld refined params = 51 (30 structural params)
$c = 7.6273(2)$ Å	
$\beta = 94.47(1)°$	no. of reflcns = 556
$V = 466.8(2)$ Å^3	$R_I = 0.047$
$Z = 4$	$R_p = 0.107$
space group = $P2_1/c$ (No. 14)	$R_{wp} = 0.116$
$T = 21(1)$ °C	$R_{exp} = 0.104$

alous dispersion terms were taken from ref 16. The solution produced the starting positions of Cu, P, and two oxygen atoms. A Rietveld[17] refinement using this set of atomic coordinates as a structural model, followed by Fourier difference syntheses, allowed location of all the remaining oxygen and carbon atoms. The final Rietveld refinement of the positions along with the scale factor, the profile and background parameters previously mentioned, and the isotropic temperatures factors for each atom type led to good *R*-factor values $R_I = 0.035$, $R_p = 0.090$, $R_{wp} = 0.101$, and $R_{exp} = 0.068$. However, if the distances and angles are satisfactory, slightly negative values are obtained for the oxygen and carbon atom temperature factors. This may not be attributed to sample absorption effect, which is avoided by the capillary preparation used.[7] Hence we have supposed that the refinement procedure could be slightly biased owing to the drastic difference in intensity (*i.e.* in weight) between the (100) reflection and all other peaks in the pattern. Therefore the (100) reflection was excluded in a further Rietveld refinement, which rapidly converged to the *R*-factors gathered in Table I. Anisotropic temperature factors were refined for copper. The observed, calculated, and difference profiles are illustrated in Figure 2. We can notice the significant increase of $R_{exp} = 0.104$, which confirms the extreme weight assigned in the first Rietveld refinement to the data points involved in the first reflection, with respect to those of the rest of the pattern.

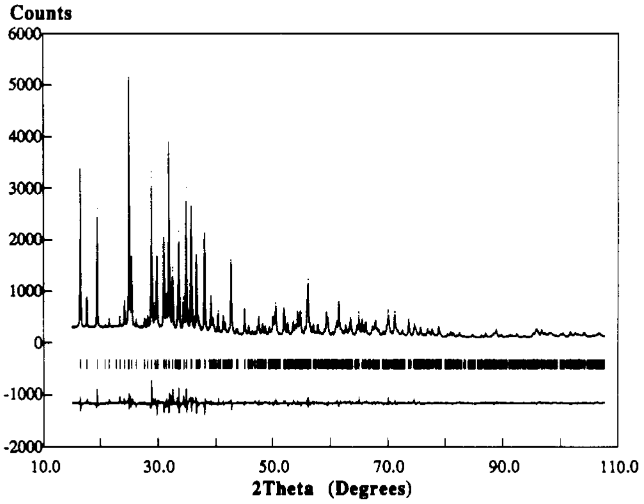

Figure 2. Observed (points), calculated (line), Bragg reflection (ticks), and difference profiles for $Cu^{II}(C_2H_5PO_3)$.

Table II. Positional Parameters and Thermal Parameters for the Non-Hydrogen Atoms of $Cu(C_2H_5PO_3)$

atom	site	*x*	*y*	*z*	*B*,[a] Å^2
Cu	4*e*	0.5429(2)	0.1143(3)	0.1801(3)	1.08(5)
P	4*e*	0.3439(3)	0.0940(6)	0.4628(4)	0.95(9)*
O(1)	4*e*	0.4182(6)	0.175(1)	0.9885(8)	0.6(1)*
O(2)	4*e*	0.6712(6)	0.032(1)	0.369(1)	0.6(1)*
O(3)	4*e*	0.5974(6)	0.052(1)	0.6738(8)	0.6(1)*
C(1)	4*e*	0.1844(8)	0.164(2)	0.382(1)	0.5(1)*
C(2)	4*e*	0.8881(9)	0.055(2)	0.674(1)	0.5(1)*

[a] Starred values denote *B* values of atoms refined isotropically. The copper atom was refined anisotropically and is given in the form of the equivalent displacement parameter defined as $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}A_iA_j$.

Table III. Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of $Cu(C_2H_5PO_3)$

1	2	3	1–2	1–2–3
O(1)A[a]	Cu	O(1)B[a]	1.937(6)	80.9(3)
O(1)A	Cu	O(2)		176.3(3)
O(1)A	Cu	O(3)B		89.7(2)
O(1)A	Cu	O(3)C[a]		90.0(3)
O(1)B	Cu	O(2)	2.151(7)	96.6(2)
O(1)B	Cu	O(3)B		98.6(2)
O(1)B	Cu	O(3)C		130.1(3)
O(2)	Cu	O(3)B	1.972(7)	89.9(2)
O(3)C	Cu	O(2)	1.991(6)	93.0(2)
O(3)B	Cu	O(3)C	2.166(6)	130.5(3)
O(1)C	P	O(2)B	1.546(7)	113.1(4)
O(1)C	P	O(3)B		108.4(4)
O(1)C	P	C(1)		108.7(4)
O(3)	P	O(2)B	1.509(7)	114.0(4)
O(2)B	P	C(1)	1.493(8)	103.4(4)
C(1)	P	O(3)B	1.824(9)	108.9(4)
C(2)B	C(1)	P	1.52(1)	111.5(6)

[a] Atom related by the following: A $(x, y, z-1)$; B $(1-x, -y, 1-z)$; C $(x, {}^1/_2 - y, z - {}^1/_2)$.

Results

Structure of $Cu^{II}(C_2H_5PO_3)$. Positional and thermal parameters of the atoms in the structure are given in Table II, and selected bond distances and angles are listed in Table III. Figure 3 shows the coordination environment of the Cu atom and the numbering scheme used in the tables. Each Cu atom has a distorted trigonal bipyramid coordination. The three coplanar oxygen atoms (O(1)B, O(3)B, O(3)C) have bond distances of 2.151(7), 2.166(6), and 1.991(6) Å, respectively. The two other oxygen atoms O(1)A and O(2) are nearly perpendicular to the plane and have bond lengths of 1.937(6) and 1.972(7) Å, respectively. The three oxygens of the phosphonate group are all bonded to Cu atoms. One of them, O(1), bridges two copper atoms, which are 3.115(3) Å apart, with a short and a long bond (Figure 4). These same two atoms are bridged by a second O(1) atom from another phosphonate group, forming a four-membered parallelogram-shaped ring. On the other hand, the O(3) oxygens also bridge two Cu atoms ($d_{Cu-Cu} = 3.203(3)$ Å), providing a zigzag Cu–O–Cu linking along the *b*-axis, with again a short and a long bond to the adjacent copper atoms. The layer can then be described as infinite rows consisting of four-membered rectangular rings connected together by two Cu–O(2)–P–O(3)–Cu bridges, running parallel to the *c*-axis. These chains are linked together in the *b*-axis direction by alternating Cu–O(3) and

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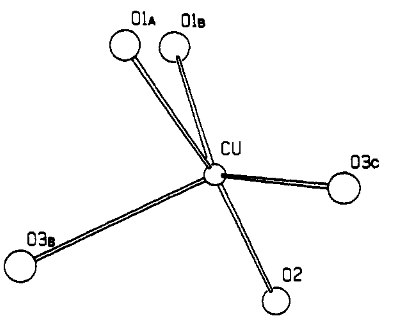

Figure 3. Schematic representation of the $Cu^{II}(C_2H_5PO_3)$ molecule showing the coordination about the copper atom and the numbering scheme used in the tables.

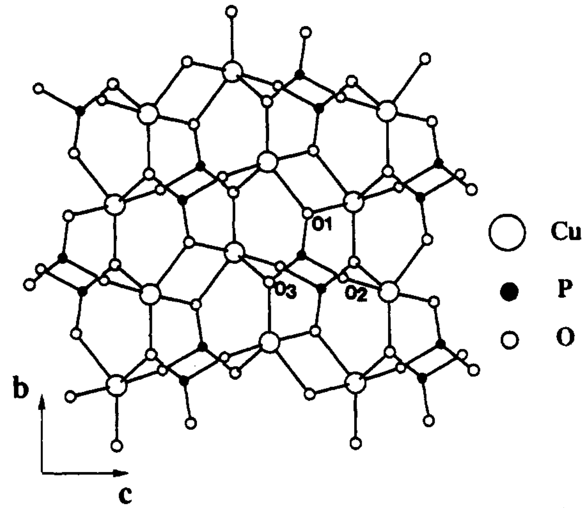

Figure 4. Schematic representation of a $Cu^{II}(C_2H_5PO_3)$ layer as seen perpendicular to the *a*-axis. Ethyl groups have been omitted for clarity.

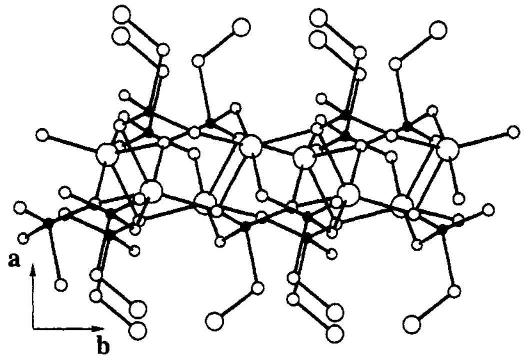

Figure 5. Layer arrangement of $Cu^{II}(C_2H_5PO_3)$ as viewed down the *c*-axis.

P–O(1) bonds. The layers are situated perpendicular to the *a*-axis with an interlayer spacing equal to *a* as shown in Figure 5, with ethyl groups pointing toward the interlamellar space above and below the CuO_3P inorganic layers, making van der Waals contacts between these layers.

Finally, we have checked that the structure of the dehydrated material obtained by thermal treatment of $Cu^{II}(C_2H_5PO_3)\cdot H_2O$ in air at 180 °C was the same as described above, since the IR spectra of $Cu^{II}(C_2H_5PO_3)$ prepared by both methods were the same. In addition, the X-ray powder diagrams are similar with a poorer crystallinity for the compound stemming from the thermal path.

Dehydration Process for $Cu^{II}(C_2H_5PO_3)\cdot H_2O$. Before illustrating the transition from the hydrated to the dehydrated form of $Cu^{II}(C_2H_5PO_3)\cdot H_2O$, we had to verify that the structure of this compound was the same as the one described by Clearfield et al.[6] for $Cu^{II}(CH_3PO_3)\cdot H_2O$ and $Cu^{II}(C_6H_5PO_3)\cdot H_2O$. This

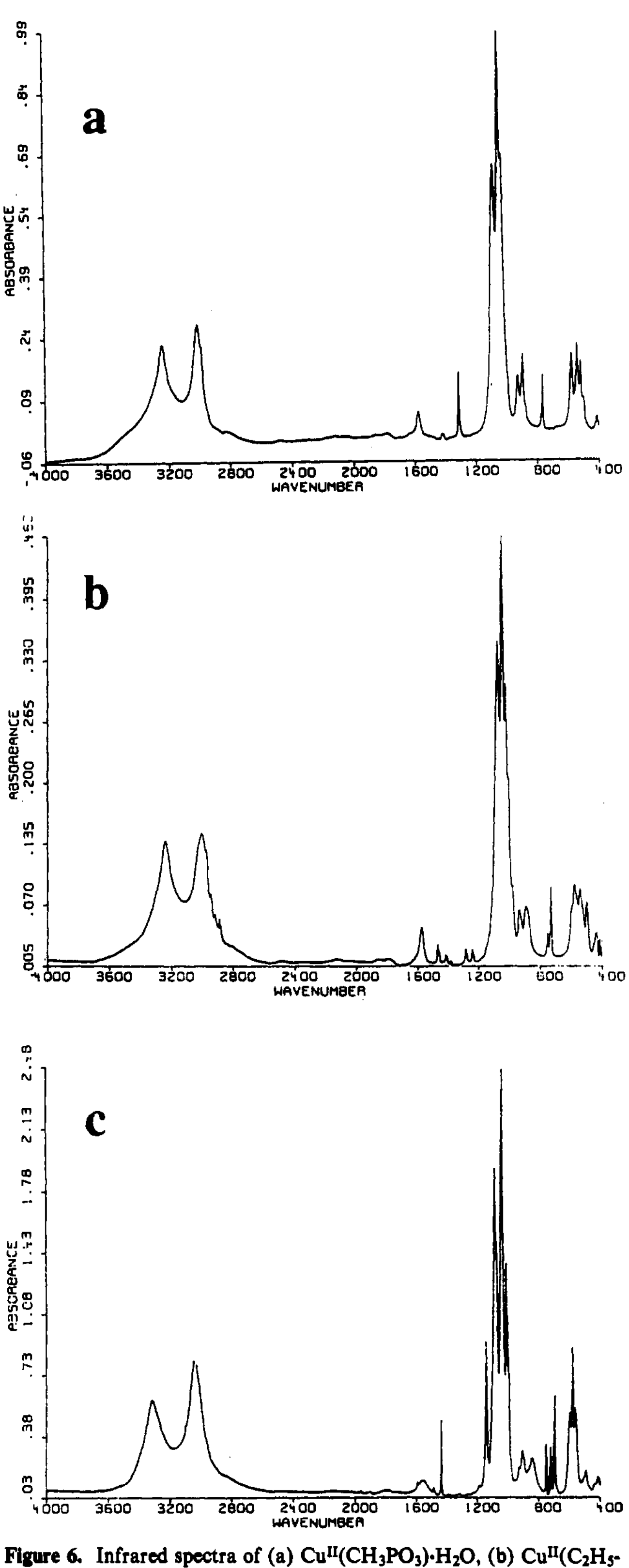

Figure 6. Infrared spectra of (a) $Cu^{II}(CH_3PO_3)\cdot H_2O$, (b) $Cu^{II}(C_2H_5PO_3)\cdot H_2O$, and (c) $Cu^{II}(C_6H_5PO_3)\cdot H_2O$.

was done by comparing TGA and IR data for the three materials. On thermogravimetric curves, the first weight loss is due to the coordinated water molecule and approximately occurs at the same temperature for the three compounds: 190 °C (R = CH_3), 175 °C (R = C_2H_5), and 155 °C (R = C_6H_5). The IR spectra are also very similar, particularly for the OH bending mode at 1578 (R = CH_3), 1575 (R = C_2H_5), and 1553 cm^{-1} (R = C_6H_5) and the two well-separated bands of the OH streching mode at 3247, 2994 cm^{-1}, 3240, 3000 cm^{-1}, and 3317, 3040 cm^{-1}, respectively. Moreover $Cu^{II}(CH_3PO_3)\cdot H_2O$ and $Cu^{II}(C_2H_5PO_3)\cdot H_2O$ are also

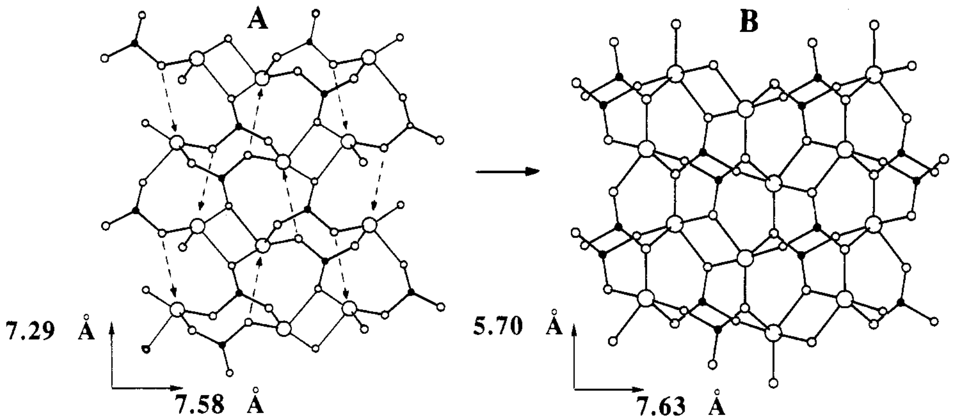

Figure 7. Schematic illustration of the structure transition during the dehydration of $Cu^{II}(C_2H_5PO_3)\cdot H_2O$ as seen perpendicular to the *a*-axis. Ethyl groups have been omitted for clarity. Data for structure A are from ref 6.

quite identical in the ν_a and ν_s PO_2 region with three strong bands at 1077, 1042, 1026 cm^{-1} ($R = CH_3$) and 1074, 1041, 1021 cm^{-1} ($R = C_2H_5$) (Figure 6). Therefore it is possible to infer from these results that the structures of $Cu^{II}(C_2H_5PO_3)\cdot H_2O$ and $Cu^{II}(RPO_3)\cdot H_2O$ ($R = CH_3$ and $R = C_6H_5$) are of the same type.

Consequently, a schematic illustration of the rearrangement within the layers during the dehydration process is presented in Figure 7. In the left part of the figure the structure (A) of $Cu^{II}(CH_3PO_3)\cdot H_2O$ according to Clearfield et al.[6] has been depicted and the water molecule has been artificially removed for clarity. The transition to the dehydrated form on the right part of the scheme (B) is then readily apparent. A shift of one of the phosphonate oxygens, materialized by a dashed arrow, occurs to occupy the vacant coordination site after the water removal. In other words, while in the hydrated phase only one of the phosphonate oxygen (corresponding to O(1) in Figure 4) is connected to two copper atoms; a supplementary one (corresponding to O(3) in Figure 4) shares this situation after dehydration. This reorganization of the layer induces a decrease of the parameter in this direction from 7.3 to 5.7 Å. In the other direction of this plane, the parameter is retained, as no modification of the linking is observed. Finally, the resulting distortion of the structure leads to an interlayer spacing increase from 9.92 Å (indexed on the basis of *h*00 lines only) to 10.78 Å. It would have been of course more convenient to solve the structure of $Cu^{II}(CH_3PO_3)$ or $Cu^{II}(C_6H_5PO_3)$ for the illustration of the dehydration process, but unfortunately these two compounds could not be prepared, except by thermal treatment of the corresponding hydrates. When the same conditions as described for the preparation of $Cu^{II}(C_2H_5PO_3)$ were used starting with phenylphosphonic acid, $Cu^{II}(C_6H_5PO_3)\cdot H_2O$ was produced. In the case of methylphosphonic acid, a new $Cu^{II}(CH_3PO_3)$ phase was obtained, whose characterization is under way, with IR and X-ray data different from the $Cu^{II}(CH_3PO_3)$ phase issued from thermal treatment.

Discussion

It is worth noting that in the $M^{II}(RPO_3)\cdot H_2O$ series (M = Mg, Co, Zn) both the monohydrate and the anhydrous phases have similar unit cell dimensions and space groups.[18,19] In the monohydrate phase, the metal ions are octahedrally coordinated by oxygen, with a water molecule occupying one of the coordination sites, while the coordination number is thought to be 5 for the metal ions in the anhydrous phase. One exception is reported in the case of nickel methylphosphonate,[18] where a structural change to an unindexed crystalline phase is observed after dehydration, in which the coordination around Ni^{2+} is supposed to remain octahedral. By comparison with our observations, it is reasonable to think that a structure transition likely occurs during the dehydration process, when the metal environment of the topochemically dehydrated phase is highly unstable. In the case of copper(II) phosphonates hydrates, a (4 + 1) tetragonal pyramidal geometry (4 Cu–O between 1.92 and 2.00 Å and 1 Cu–O around 2.35 Å)[6] is reported, different from the other members of the series for which the structure is probably unable to accommodate to a Jahn–Teller distorsion of the MO_6 octahedron to get a (4 + 2) coordination. If the dehydration of $Cu(RPO_3)\cdot H_2O$ was topotactic, a highly unfavorable coordination (highly distorted tetrahedral or trigonal pyramidal) would result upon water loss. That is probably the reason why a rearrangement takes place in the layer in order to keep the copper atom in a five-coordination site. The observed trigonal bipyramidal arrangement is relatively rare, but the bond lengths and angles of $Cu(C_2H_5PO_3)$ are consistent with previous examples given in the literature such as $Cu_2(AsO_4)OH$.[20]

The study of the magnetic properties of hydrated and dehydrated copper phosphonates is actually in progress and will be presented in a subsequent paper. In order to have an accurate understanding of the change in the magnetic behavior of these compounds during dehydration, bond lengths and angles of both hydrated and dehydrated materials (for a given substituent bound at phosphorus) must be known. Therefore a systematic study of the influence of the different experimental parameters (temperature, pressure, concentration, pH, ...) involved in the preparation of these materials has been started in order to find out the best conditions to obtain single crystals of the compounds for which the structure determinations are missing.

Supplementary Material Available: For $Cu(C_2H_5PO_3)$, Table S-I, giving the Inel X-ray powder diffraction data, and Table S-II, listing anisotropic thermal parameters for the Cu atom (1 page). Ordering information is given on any current masthead page.

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