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Hydrothermal Synthesis and Crystal Structures of Two Copper Vanadium Phosphates: $Cu_{0.5}[VOPO_4] \cdot 2H_2O$ and $Cu_{0.5}(OH)_{0.5}[VOPO_4] \cdot 2H_2O$

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Two layered copper vanadium phosphates, $Cu_{0.5}[OPO_4] \cdot 2H_2O$ (1) and $Cu_{0.5}(OH)_{0.5}[VOPO_4] \cdot 2H_2O$ (2), have been synthesized hydrothermally and their structures determined by single-crystal X ray crystallography. Phosphate 1 is monoclinic, space group $P2_1/m$, $a = 6.614$ (2) Å, $b = 8.930$ (2) Å, $c = 9.071$ (2) Å, $\beta = 103.79$ (2)°, $Z = 4$, $V = 520.3$ (3) Å^3. Refinement with 750 observed reflections for which $I \geq 3\sigma(I)$ gave R (R_w) = 0.051 (0.058). The structure has hydrated Cu^{2+} ions bonded to layers composed of distorted VO_6 octahedra and PO_4 tetrahedra. Each Cu^{2+} ion is bonded to only one layer and possesses a nearly square planar geometry but with two very long axial bonds. This results in a very distorted octahedral configuration composed of two phosphate oxygens, three water molecules, and one vanadyl oxygen. Phosphate 2 is triclinic, space group $P\bar{1}$, $a = 7.0124$ (8) Å, $b = 12.6474$ (9) Å, $c = 6.3022$ (6) Å, $\alpha = 90.079$ (8)°, $\beta = 96.076$ (9)°, $\gamma = 74.002$ (7)°, $Z = 2$, $V = 534.05$ (9) Å^3. Refinement using 2311 observed reflections with $I \geq 3\sigma(I)$ gave R (R_w) = 0.035 (0.043). The structure consists of $VOPO_4$ layers somewhat similar to those of 1, but with the layers bridged together through Cu dimers of $Cu_2(OH)_2(H_2O)_4$. Each Cu^{2+} ion is in a distorted square planar configuration.

INTRODUCTION

The V–P–O system has received considerable attention not only because of its relevance to catalysts (1), but also because of its rich and complex structural chemistry resulting from the variation in vanadium oxidation state and as well as in the ratio of vanadium to phosphorus. A family of compounds with the general composition of $M_xVOPO_4 \cdot nH_2O$, where M is an alkaline, alkaline earth, or a transition metal cation, and $x \leq 1$, was prepared by the redox intercalation reactions of $VOPO_4 \cdot 2H_2O$ with metal iodides in aqueous solution at room temperature (2). On the basis of powder X ray analysis, it was found that the layered tetragonal structure was retained with the hydrated metal cations in between the layers. However, detailed structural information was lacking because no single crystals were obtained from the redox intercalation reactions. Recently, hydrothermal methods has proved to be well suited for the synthesis and growth of single crystals of the compounds of $M_x[VOPO_4] \cdot nH_2O$. Crystals of $M_{0.5}[VOPO_4] \cdot nH_2O$ (M = Na, K, Ca, Sr, Pb, Co, Ni; n = 2, 1.5) have been prepared (3–6) by hydrothermal methods. Characterization of these compounds by single-crystal X ray analysis revealed interesting and complex structural diversity. By introducing other inorganic and organic cations into this system, rather complicated structures have been recently prepared (7, 8). In this paper we report the hydrothermal synthesis and structural characterization of two copper vanadium phosphates, $Cu_{0.5}[VOPO_4] \cdot 2H_2O$ (**1**) and $Cu_{0.5}(OH)_{0.5}[VOPO_4] \cdot 2H_2O$ (**2**). The former has a layered structure consisting of layers of $VOPO_4$ with Cu^{2+} ions in between the layers, while the structure of the latter has similar $VOPO_4$ layers that are linked together by unusual μ^3–OH bridged Cu dimers of composition $Cu_2(OH)_2(H_2O)_4$.

EXPERIMENTAL

Synthesis. Green plate-like crystals of compound **1** were obtained as a minor product (~10% yield) from hydrothermal reaction of $NaVO_3 : Mo : CuCl_2 \cdot 2H_2O : H_2O_3PC_6H_5 : (n\text{-}C_4H_9)_4NBr : H_3PO_4 : H_2O$ in a mole ratio of 3.4 : 2.3 : 0.83 : 2.0 : 3.7 : 556 at 160°C for 80 hr. The major product of this reaction was an unidentified dark brown powder. The optimum conditions for the preparation of **1** have not been discovered yet, although many reactions under different conditions have been carried out. The hydrothermal reaction of $VO_2 : CuO : H_3PO_4 : H_2O$ in a mole ratio of 3.3 : 1.3 : 10.1 : 389 gives approximately 20% of compound **2** as dark green platelets with the major product a green powder which contains Cu, V, and P. Characterization of the green powder is in progress.

X-ray crystallographic study. A greenish platelet of **1** having approximate dimensions of 0.3 × 0.3 × 0.06 mm

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TABLE 1
Crystallographic Data fo $Cu_{0.5}[VOPO_4] \cdot 2H_2O$ and $Cu_{0.5}(OH)_{0.5}[VOPO_4] \cdot 2H_2O$

	$Cu_{0.5}[VOPO_4] \cdot 2H_2O$	$Cu_{0.5}(OH)_{0.5}[VOPO_4] \cdot 2H_2O$
a (Å)	6.614(2)	7.0124(8)
b (Å)	8.930(2)	12.6474(9)
c (Å)	9.071(2)	6.3022(6)
α (deg)	90	90.079(8)
β (deg)	103.79(2)	96.076(9)
γ (deg)	90	74.002(7)
V (Å^3)	520.3(3)	534.05(9)
Z	4	4
Space group	$P2_1/m$	$P\bar{1}$
D_c (g/cm^3)	2.89	2.97
T (°C)	20 ± 1	20 ± 1
$\lambda(MoK_\alpha)$ (Å)	0.7107	0.7107
μ (cm^{-1})	37.8	40.3
Trans coeff	0.96–1.04	0.49–1.0
R	0.051	0.035
R_w	0.058	0.043
Goodness of fit	1.49	1.85

was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated MoK_α radiation and an 18-kW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 24 carefully centered reflections in the range $20.34° \leq 2\theta \leq 29.73°$, corresponded to a monoclinic cell. Based on the systematic absences ($0k0: k \neq 2n$) and the successful solution and refinement of the structure, the space group was determined to be $P2_1/m$. The data were collected out to 60° in 2θ using the ω–2θ scan technique at a speed of 8°/min in ω. A total of 1627 reflections were measured of which 1506 were unique (R_{int} for averaging equivalent reflections was 0.10). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection. An empirical absorption correction using the program DIFABS was applied (9). The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (10). The nonhydrogen atoms were refined anisotropically. All the hydrogen atoms were located from difference Fourier maps and included in the refinement with fixed positional and thermal parameters. The final cycle of full-matrix least-squares refinement was based on 750 observed reflections ($I \geq 3\sigma(I)$) and 97 variable parameters and converged with unweighted and weighted agreement factors of $R = S||F_o| - |F_c||/S|F_o| = 0.051$ and $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)]^{1/2} = 0.058$.

Crystallographic data for **1** and **2** are listed in Table 1.

$Cu_{0.5}(OH)_{0.5}[VOPO_4] \cdot 2H_2O$. The data were collected on a dark green platelet with approximate dimensions of 0.4 × 0.4 × 0.03 mm. Triclinic cell parameters and an orientaton matrix for data collection were obtained from a least-squares refinement using 23 reflections in the range $20.21° \leq 2\theta \leq 29.15°$. Based on a statistical analysis of intensity distribution and successful refinement of the structure, the space group was determined to be $P\bar{1}$. The data were collected out to 60° in 2θ by using the ω–2θ scan technique with a scan width of $(1.37 + 0.35 \tan \theta)°$ at a speed 16°/min in ω. A total of 2850 reflections were collected of which 2616 were unique (R_{int} for a averaging equivalent reflections is 0.038). Three representative reflections were measured every 150 reflections to monitor instrument and crystal stability. An empirical absorption correction basd on the ψ scans of several reflections was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were located from the ΔF maps but not refined. The final cycle of full-matrix least-squares refinement was based on 2311 observed reflections ($I \geq 3\sigma(I)$) and 181 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.035$ and $R_w = 0.043$. Neutral atom scattering factors were taken from Cromer and Waber (11) and anomalous dispersion correction was taken from those of Creagh and McAuley (12). All calculations were performed using the teXsan (10) crystallographic software package.

RESULTS

Structure of $Cu_{0.5}[VOPO_4] \cdot 2H_2O$. Positional and thermal parameters of the atoms in this structure are given in Table 2, and selected bond distances and angles are listed in Table 3. Figure 1 shows the coordination environment around the V and Cu atoms and the numbering

TABLE 2
Positional Parameters and B(eq) for the Nonhydrogen Atoms of $Cu_{0.5}[VOPO_4] \cdot 2H_2O$

Atom	x	y	z	$B(eq)^a$
Cu(1)	0.3356(3)	0.25	0.7902(2)	1.38(7)
V(1)	0.1039(4)	−0.25	0.5152(3)	0.81(9)
V(2)	0.0663(4)	0.25	1.0117(3)	0.95(9)
P(1)	0.0057(4)	−0.0019(3)	0.7476(3)	0.86(8)
O(1)	0.153(1)	0.1056(8)	0.8614(7)	1.1(3)
O(2)	0.152(1)	−0.0941(8)	0.6764(8)	1.2(3)
O(3)	−0.122(1)	−0.0958(8)	0.8312(7)	1.1(2)
O(4)	−0.150(1)	0.0922(8)	0.6306(7)	1.2(3)
O(5)	−0.143(2)	−0.25	0.468(1)	2.0(4)
O(6)	−0.179(2)	0.25	0.954(1)	2.3(5)
O(7)	0.465(2)	−0.25	0.581(1)	2.2(5)
O(8)	0.462(2)	0.25	1.077(1)	3.6(6)
O(9)	0.489(1)	0.411(1)	0.7262(9)	2.0(3)

$^a B(\text{eq}) = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}A_i \cdot A_j$.

TABLE 3
Selected Bond Distances (Å) and Angles (°) for $Cu_{0.5}[VOPO_4] \cdot 2H_2O$

Cu(1)	O(1)	1.979(7)	Cu(1)	O(1)[a]	1.979(7)
Cu(1)	O(9)	1.927(8)	Cu(1)	O(9)[a]	1.927(8)
V(1)	O(2)	1.989(7)	V(1)	O(2)[b]	1.989(7)
V(1)	O(4)[c]	2.005(7)	V(1)	O(4)[d]	2.005(7)
V(1)	O(5)	1.59(1)	V(1)	O(7)	2.32(1)
V(2)	O(1)	2.054(7)	V(2)	O(1)	2.054(7)
V(2)	O(3)[e]	1.953(7)	V(2)	O(3)[f]	1.953(7)
V(2)	O(6)	1.58(1)			
P(1)	O(1)	1.568(7)	P(1)	O(2)	1.526(7)
P(1)	O(3)	1.515(7)	P(1)	O(4)	1.540(7)
O(1)–Cu(1)–O(1)[a]		81.3(4)	O(1)–Cu(1)–O(9)		172.5(3)
O(1)–Cu(1)–O(9)[a]		91.2(3)	O(1)–Cu(1)–O(9)		91.2(3)
O(1)[a]–Cu(1)–O(9)[a]		172.5(3)			
O(2)–V(1)–O(2)[b]		88.9(4)	O(2)–V(1)–O(4)[c]		162.6(3)
O(2)–V(1)–O(4)[d]		88.3(3)	O(2)–V(1)–O(5)		99.9(4)
O(2)–V(1)–O(7)		80.6(3)	O(2)[b]–V(1)–O(4)[c]		88.3(3)
O(2)–V(1)–O(4)[d]		162.6(3)	O(2)[b]–V(1)–O(7)		80.6(3)
O(4)[c]–V(1)–O(5)		97.5(4)	O(4)[d]–V(1)–O(5)		97.5(4)
O(5)–V(1)–O(7)		179.2(5)	O(2)[b]–V(1)–O(5)		99.9(4)
O(4)[c]–V(1)–O(4)[d]		89.3(4)	O(4)[c]–V(1)–O(7)		82.0(3)
O(4)[d]–V(1)–O(7)		82.0(3)	O(1)–V(2)–O(1)[a]		77.8(4)
O(1)–V(2)–O(3)[e]		153.3(3)	O(1)[a]–V(2)–O(3)[f]		90.4(3)
O(1)–V(2)–O(6)		101.8(4)	O(1)–V(2)–O(3)[f]		90.4(3)
O(1)–V(2)–O(3)[e]		153.3(3)	O(1)–V(2)–O(6)		101.8(4)
O(3)[e]–V(2)–O(3)[f]		89.7(4)	O(3)[e]–V(2)–O(6)		104.1(4)
O(3)[f]–V(2)–O(6)		104.1(4)	O(1)–P(1)–O(2)		104.6(4)
O(1)–P(1)–O(3)		110.0(4)	O(1)–P(1)–O(4)		109.1(4)
O(2)–P(1)–O(3)		113.5(4)	O(2)–P(1)–O(4)		112.9(4)
O(3)–P(1)–O(4)		106.7(4)			

[a] Atom related by x, 0.5 − y, z.
[b] Atom related by x, − 0.5 − y, z.
[c] Atom related by − x, y − 0.5, 1 − z.
[d] Atom related by − x, − y, 1 − z.
[e] Atom related by − x, 0.5 + y, 2 − z.
[f] Atom related by − x, − y, 2 − z.
[g] Atom related by − x, 0.5 + y, 1 − z.

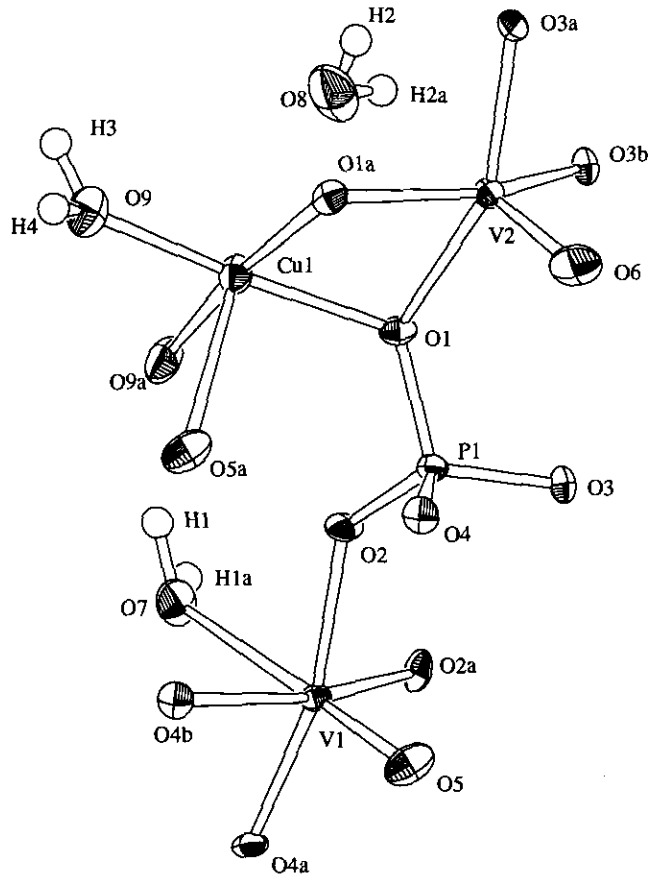

FIG. 1. An ORTEP drawing of $Cu_{0.5}[VOPO_4] \cdot 2H_2O$ molecule showing the coordination of the metal atoms and the numbering scheme used in the tables. Thermal ellipsoids are at the 50% probability level.

scheme used in the tables. The V(1) atom has a very distorted octahedral coordination formed by four phosphate oxygen atoms with V–O bond distances in the range of 1.989 (7)–2.005 (7) Å, one vanadyl oxygen atom (O5) with a bond length of 1.59 (1) Å, and one water molecule (O7) at a distance of 2.32 (1) Å. The V(2) atom has a similar coordination environment except that it has a water molecule (O8) at a greater distance of 2.54 (1) Å. Both of the V atoms have an oxidation state of +4 as indicated by the valence sum calculation (13) and their adoption of a typical coordination configuration of V(IV). The Cu^{2+} ion also has a very distorted octahedral coordination. The four equatorial Cu–O bonds are formed by two phosphate oxygens and two water molecules with bond distances in the range of 1.927 (8)–1.979 (7) Å. The two elongated Cu–O bonds are formed with the vanadyl oxygen O5a (symmetry related by $-x$, 0.5 + y, 1 − z) with a bond distance of 2.38 (1) Å, and one water molecule O(8) at a distance of 2.54 (1) Å. The phosphate group is connected to four vanadium atoms through its four oxygen atoms. One of the four phosphate oxygen atoms forms an additional bond with the Cu^{2+} ion, resulting in a short Cu–V contact of 3.0 Å. This structure is virtually layered (Fig. 2) with an interlayer distance of 6.6 Å which is the length of the a axis. The layer is constructed by the alternation of phosphate tetrahedra and vanadium octahedra (Fig. 3) as in the $MoOPO_4$ structure type. The interlayer regions are occupied by the Cu^{2+} ions and water molecules.

Structure of $Cu_{0.5}(OH)_{0.5}[VOPO_4] \cdot 2H_2O$. Positional and thermal parameters of the nonhydrogen atoms in this structure are given in Table 4, and selected bond distances and angles are listed in Table 5. Figure 4 shows the coordination environment around the V and Cu atoms and the numbering scheme used in the tables. The vanadium atom V(2) has a distorted octahedral coordination environment similar to those in compound **1**. The short V–O bond formed with the oxo-group has a bond length of 1.583 (4) Å. The *trans* position is occupied by a water molecule at a distance of 2.333 (4) Å. The rest of the V–O bonds are

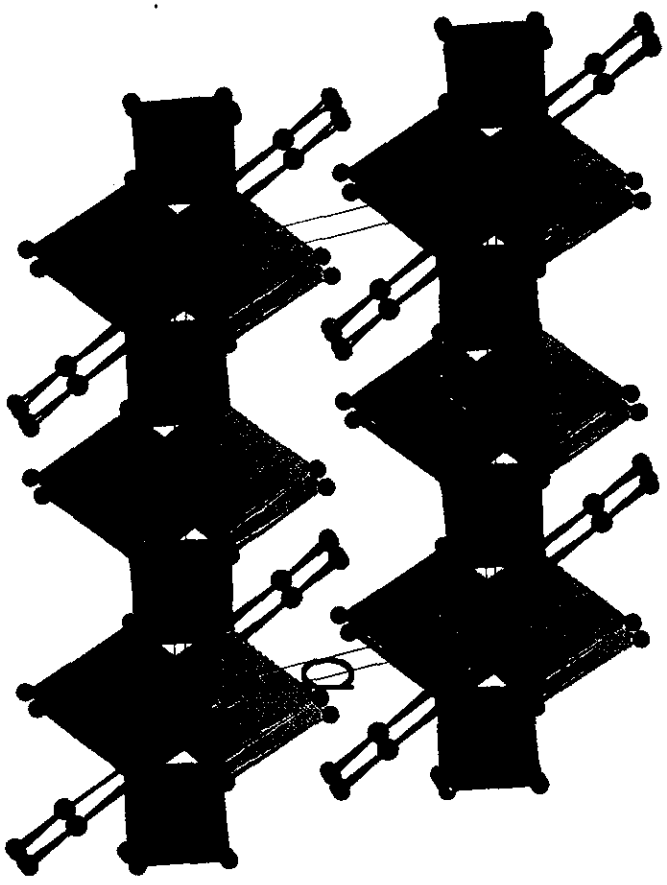

FIG. 2. A view down the c axis showing the layered nature of $Cu_{0.5}[VOPO_4] \cdot 2H_2O$. The VO_6 octahedra and PO_4 tetrahedra are represented as polyhedra. The H atoms and the two elongated bonds about the Cu are omitted for clarity.

formed with the phosphate oxygens with bond distances in the range of 1.955 (3)–1.964 (3) Å. The V(1) atom has a similar environment to that of the V(2) atom, except that the sixth bond is formed with an OH group at a distance of 2.304 (3) Å. At the same time, this OH is bonded to two Cu^{2+} ions making the OH group three coordinate. The two Cu^{2+} ions in the dimer are doubly bridged by two OH groups, and each of the two Cu^{2+} ions is bonded to two additional terminal water molecules, thus forming Cu dimers of composition $Cu_2(OH)_2(H_2O)_4$ with a Cu–Cu separation of 2.912 (3) Å (Fig. 5). Each of the two Cu^{2+} ions is in a distorted square planar configuration with all Cu–O bonds in the range of 1.941 (4)–1.992 (4) Å, and both are related to each other by an inversion center. The overall structure of this compound can be viewed as layers of VO_6 octahedra and PO_4 tetrahedra connected by the Cu dimers to form a three-dimensional network (Fig. 6). These Cu dimers are separated by 12.6 Å in the b direction, and 6.3 Å in the c direction, thus creating small voids filled with water molcules. Valence sum calculation (12) of the oxidation state for the V atoms

TABLE 4
Positional Parameters and B(eq) for the Nonhydrogen Atoms of $Cu_{0.5}(OH)_{0.5}[VOPO_4] \cdot 2H_2O$

Atom	x	y	z	B(eq)[a]
Cu(1)	−0.0070(1)	0.39998(5)	0.8889(1)	1.39(3)
V(1)	0.4147(1)	0.38736(5)	1.2361(1)	0.47(3)
V(2)	0.5918(1)	0.11028(6)	0.7635(1)	0.53(3)
P(1)	0.5022(2)	0.37369(8)	0.7508(2)	0.47(4)
P(2)	0.5056(2)	0.12311(8)	1.2521(2)	0.53(4)
O(1)	0.9399(6)	0.0610(3)	0.8013(6)	1.7(2)
O(2)	0.3555(5)	0.1472(3)	0.7385(6)	1.3(2)
O(3)	0.6453(5)	0.1039(3)	1.0747(5)	1.0(1)
O(4)	0.6424(5)	0.0993(3)	0.4627(5)	0.9(1)
O(5)	0.6516(5)	0.3535(3)	1.2565(6)	1.3(2)
O(6)	0.3692(5)	0.3992(3)	1.5368(5)	0.9(1)
O(7)	0.6401(5)	0.2558(2)	0.7611(5)	0.9(1)
O(8)	0.0053(6)	0.3574(3)	0.5851(6)	1.9(2)
O(9)	0.0077(6)	0.2534(3)	0.9938(7)	1.7(2)
O(10)	0.0712(5)	0.4439(2)	1.1795(5)	0.9(1)
O(11)	0.3618(5)	0.5496(2)	1.2170(5)	0.8(1)
O(12)	0.3576(5)	0.3898(3)	0.9232(5)	0.8(1)
O(13)	0.3692(5)	0.2415(2)	1.2409(5)	1.0(1)
O(14)	0.6375(5)	−0.0498(3)	0.7703(5)	1.0(1)
O(15)	1.0057(7)	0.1593(4)	0.4231(8)	2.6(2)

[a] $B(\text{eq}) = \frac{4}{3} \sum_i \sum_j \beta_{ij} A_i \cdot A_j$.

gives values of 4.39 for V(1) and 4.44 for V(2), which is in good agreement with the oxidation state of +4.5 for the V atoms based on stoichiometry.

DISCUSSION

Compound **1** belongs to the family of $A_{0.5}[VO(PO_4)] \cdot nH_2O$ (A = Na, K, Ca, Sr, Pb, Co, Ni, n = 2, 1.5). Most of their structures can be derived from the parent layered compound $VOPO_4 \cdot 2H_2O$ (14–16). The layer is constructed via the alternation of vanadium octahedra and phosphate tetrahedra. The introduction of a monovalent or a divalent metal not only leads to the partial or full reduction of V^{5+} to V^{4+}, but also affects the way the layers are stacked relative to one another as well as the arrangement of water molecules between the layers so as to accommodate the second metal ions. Although most of the compounds have similar compositions, their structures differ in detail, mostly in the coordination environment of the second metal due to the coordination requirements of the metals and the fact that phosphate oxygens may or may not form bonds with the second metal. It is not surprising therefore that the structure of compound **1** is different from the other members of the family, considering that Cu^{2+} is unlikely to adopt a regular octahedral configuration due to the Jahn-Teller distortion. While most of the compounds of the family are layered, $Ni_{0.5}[VOPO_4] \cdot 1.5\ H_2O$ (4) and $Pb_{0.5}[VOPO_4] \cdot 1.5\ H_2O$ (16) are three-dimensional network structures constructed

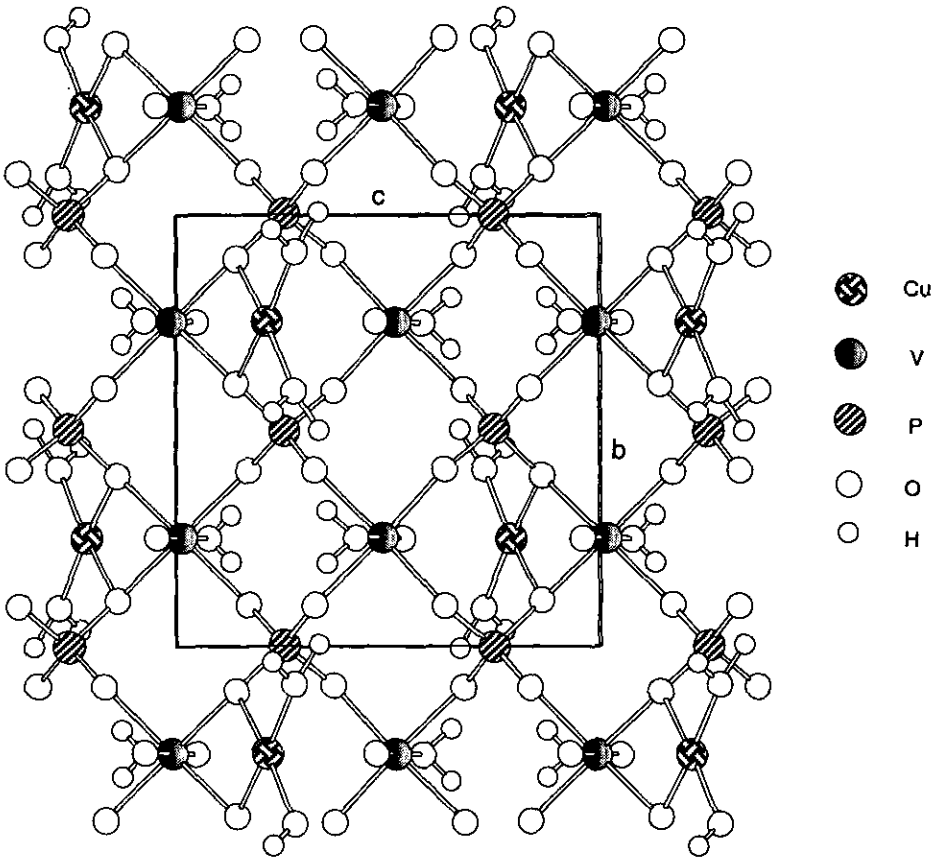

FIG. 3. Schematic representation of one layer of $Cu_{0.5}[VOPO_4] \cdot 2H_2O$.

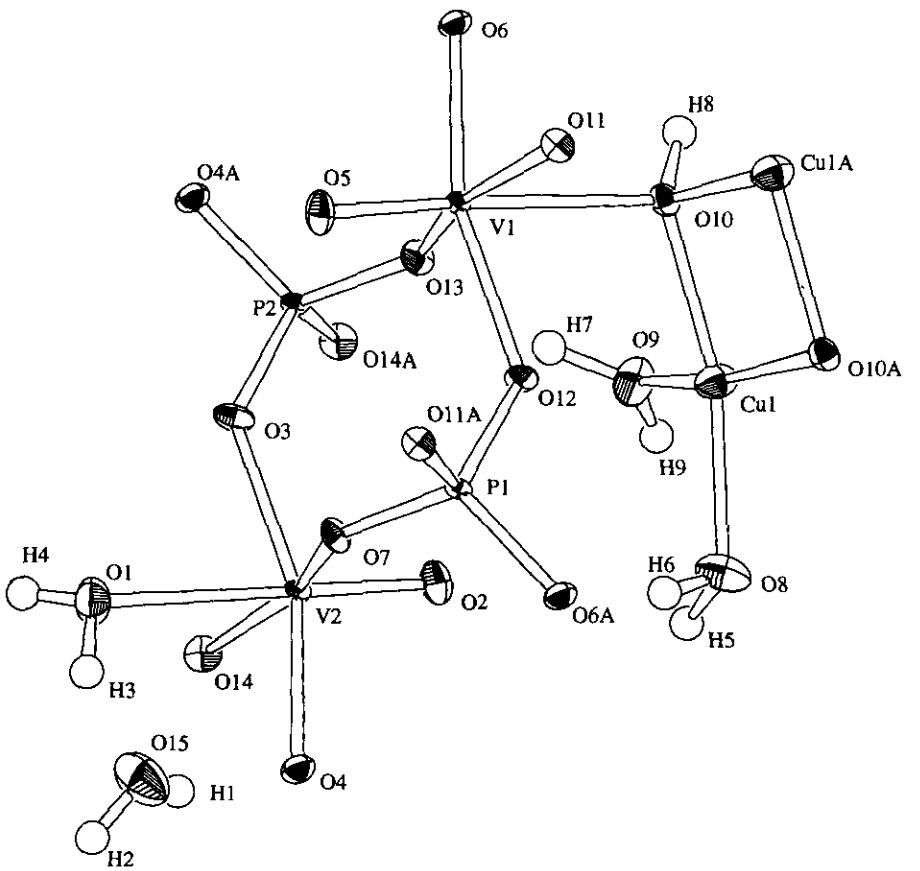

FIG. 4. An ORTEP drawing of $Cu_{0.5}(OH)_{0.5}[VOPO_4] \cdot 2H_2O$ molecule showing the coordination of the metal atoms and the numbering scheme used in the tables. Thermal ellipsoids are at the 50% probability level.

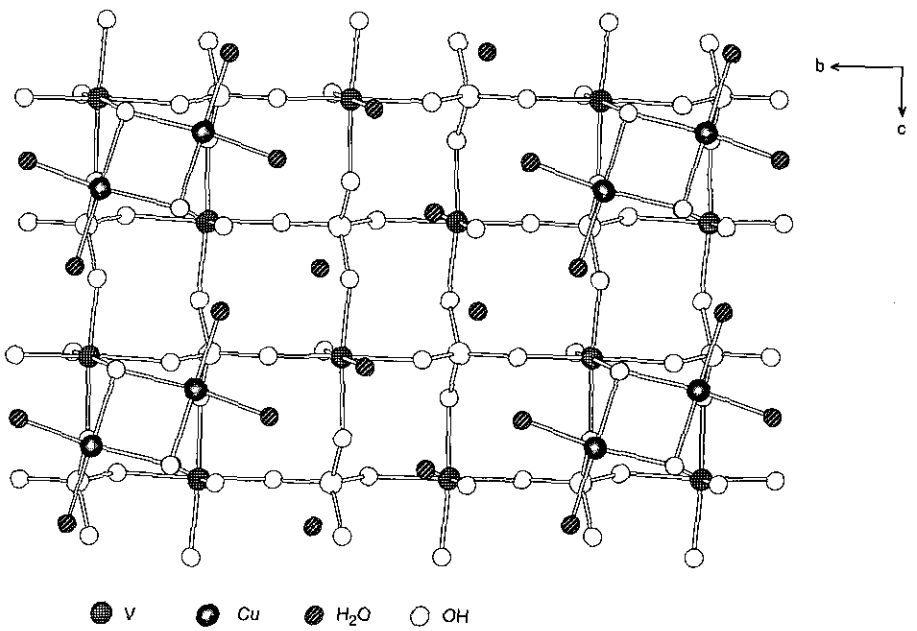

FIG. 5. A schematic representation of one layer of $Cu_{0.5}(OH)_{0.5}[VOPO_4] \cdot 2H_2O$.

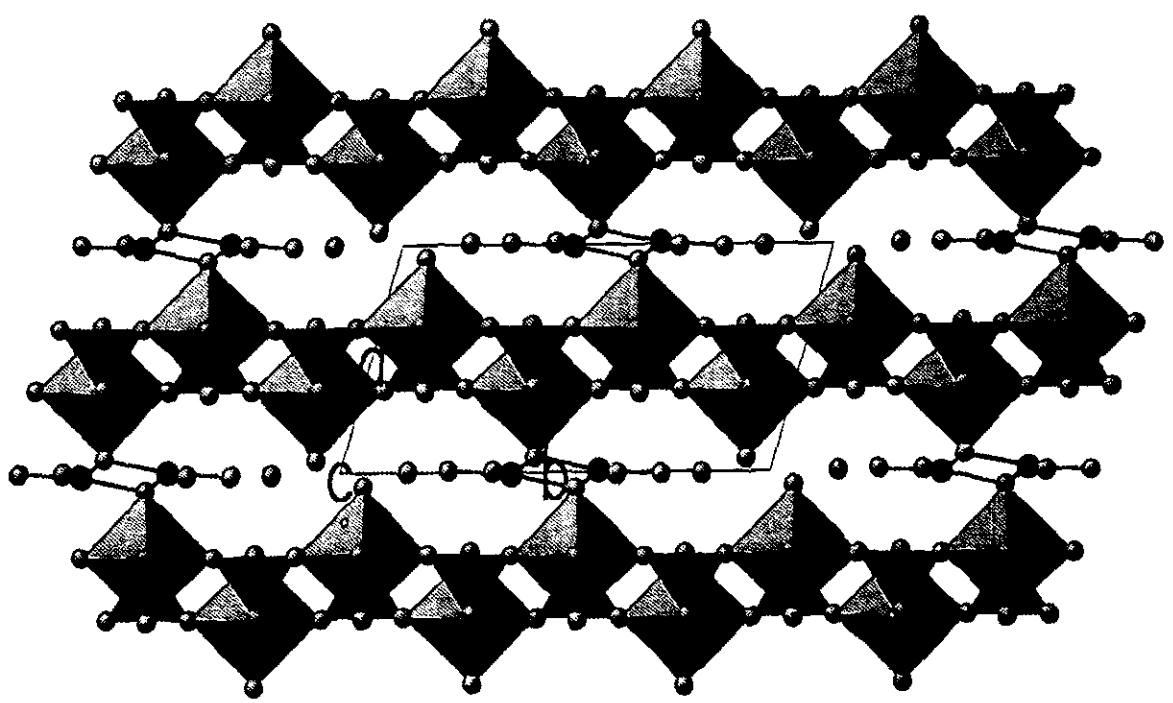

FIG. 6. A view down the c axis of $Cu_{0.5}(OH)_{0.5}[VOPO_4] \cdot 2H_2O$. The VO_6 octahedra and PO_4 tetrahedra are represented as polyhedra. The H atoms are omitted for clarity.

TABLE 5
Selectd Bond Distances (Å) and Angles (°) for $Cu_{0.5}(OH)_{0.5}[VOPO_4] \cdot 2H_2O$

Cu(1)	O(8)	1.992(4)	Cu(1)	O(9)	1.941(4)
Cu(1)	O(10)	1.979(3)	Cu(1)	O(10)[a]	1.939(3)
V(1)	O(5)	1.588(4)	V(1)	O(6)	1.954(3)
V(1)	O(10)	2.304(3)	V(1)	O(11)	1.984(3)
V(1)	O(12)	1.968(3)	V(1)	O(13)	1.958(3)
V(2)	O(1)	2.333(4)	V(2)	O(2)	1.583(4)
V(2)	O(3)	1.955(3)	V(2)	O(4)	1.964(3)
V(2)	O(7)	1.961(3)	V(2)	O(14)	1.961(3)
P(1)	O(6)[b]	1.537(3)	P(1)	O(7)	1.535(3)
P(1)	O(11)[c]	1.536(3)	P(1)	O(12)	1.539(3)
P(2)	O(3)	1.539(3)	P(2)	O(4)[d]	1.531(3)
P(2)	O(13)	1.536(3)	P(2)	O(14)[e]	1.539(3)
O(8)–Cu(1)–O(9)		94.6(2)	O(8)–Cu(1)–O(1)		161.(2)
O(8)–Cu(1)–O(10)[a]		93.6(1)	O(9)–Cu(1)–O(10)[a]		91.2(1)
O(9)–Cu(1)–O(10)		167.4(2)	O(10)–Cu(1)–O(10)[a]		84.1(1)
O(5)–V(1)–O(6)		100.6(2)	O(5)–V(1)–O(10)		175.2(2)
O(5)–V(1)–O(11)		99.2(2)	O(5)–V(1)–O(12)		99.6(2)
O(5)–V(1)–O(13)		100.1(2)	O(6)–V(1)–O(10)		83.5(1)
O(6)–V(1)–O(11)		89.0(1)	O(6)–V(1)–O(12)		159.8(1)
O(6)–V(1)–O(13)		88.5(1)	O(10)–V(1)–O(11)		78.3(1)
O(10)–V(1)–O(12)		7.3(1)	O(10)–V(1)–O(13)		82.4(1)
O(11)–V(1)–O(12)		87.9(1)	O(11)–V(1)–O(13)		160.7(1)
O(12)–V(1)–O(13)		87.9(1)	O(1)–V(2)–O(2)		178.4(2)
O(1)–V(2)–O(3)		79.9(1)	O(1)–V(2)–O(4)		79.6(1)
O(1)–V(2)–O(7)		79.3(1)	O(1)–V(2)–O(14)		82.2(1)
O(2)–V(2)–O(3)		99.9(2)	O(2)–V(2)–O(4)		100.6(2)
O(2)–V(2)–O(7)		99.2(2)	O(2)–V(2)–O(14)		99.4(2)
O(3)–V(2)–O(4)		159.5(1)	O(3)–V(2)–O(7)		89.2(1)
O(3)–V(2)–O(14)		88.7(1)	O(4)–V(2)–O(7)		88.0(1)
O(4)–V(2)–O(14)		87.6(1)	O(7)–V(2)–O(14)		161.5(1)
O(6)–P(1)–O(7)		111.4(2)	O(6)–P(1)–O(11)		111.3(2)
O(6)–P(1)–O(12)		105.6(2)	O(7)–P(1)–O(11)		106.5(2)
O(7)–P(1)–O(12)		111.0(2)	O(11)–O(1)–O(12)		111.2(2)
O(3)–P(2)–O(13)		111.3(2)	O(3)–P(2)–O(14)		112.0(2)
O(3)–P(2)–O(4)		105.8(2)	O(4)–P(2)–O(13)		111.2(2)
O(4)–P(2)–O(14)		111.8(2)	O(13)–P(2)–O(14)		105.0(2)

[a] Atom related by $-x, 1-y, 2-z$.
[b] Atom related by $x, y, z-1$.
[c] Atom related by $1-x, 1-y, 2-z$.
[d] Atom related by $x, y, 1+z$.
[e] Atom related by $1-x, -y, 2-z$.

from VO_6 octahedra and PO_4 tetrahedra in such a way that hydrophilic cavities are created in which the metal cation and H_2O molecules reside. This indicates that the water content in these compounds can have a profound influence on the way in which VO_6 and PO_4 are connected together. Further dehydration of these compounds leads to a new family of compounds with the composition $M_n[VOPO_4]$ (M = Li, Na, K, n = 1; Ca, Ba, n = 0.5) (18–23) whose structures cannot be derived directly from the parent compound $VOPO_4 \cdot 2H_2O$.

Compound **2** represents an unique example of the A–V–PO_4 (A = metal) system in which the second metal forms dimers between the $VOPO_4$ layers. A schematic representation of the Cu dimers and the water molecules in between the layers is provided in Fig. 7. The water molecules (including those bonded to V atoms) and the OH groups form a two-dimensional sheet between adjacent $VOPO_4$ layers. Each of the water molecules has four near neighbors at distances of less than 3 Å, indicating that these water molecules are extensively hydrogen-bonded to one another. This kind of arrangement also creates squares of water molecules suitable for additional Cu^{2+} ions to fit in the centers of these squares. If additional Cu^{2+} ions could be inserted between the Cu dimers along the **b** and **c** axes, it would force some of the water molecules to bridge two Cu atoms at an angle of 180°, which is an unlikely event. However, it would form reasonable infinite chains of Cu dimers if three additional Cu atoms are added to the centers of the three squares (marked by dashed lines in Fig. 7) between two Cu dimers along the diagonal of the b and c axes. The formation of this kind of chain is possible provided the extra positive charge is balanced by the replacement of water molecules by O^{2-}. The possibility of forming copper oxide chains and even a copper oxide layer between $VOPO_4$ layers is under exploration. The formation of the Cu dimers between the $VOPO_4$ layers may be unique to copper and this compound may exhibit interesting magnetic properties which are under investigation.

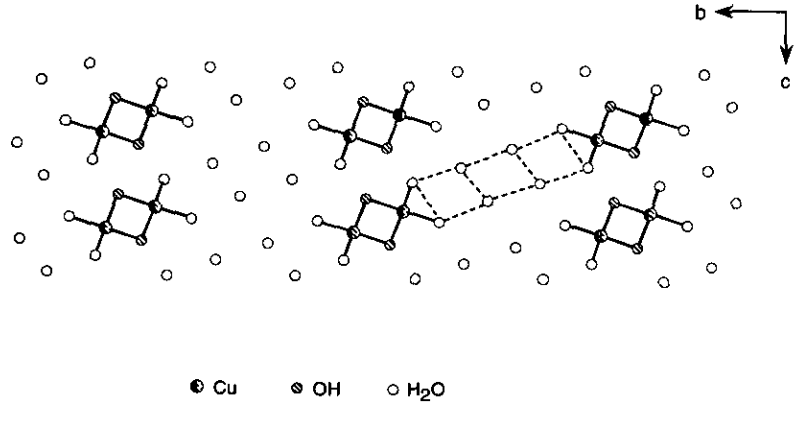

FIG. 7. Schematic representation of the Cu dimers and the interlamellar water molecules.

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