metal-organic compounds

Comparative study of two chemically isostructural polymers: [Cu$_2$(VO$_2$)-(HPO$_4$)$_2$(NO$_3$)(bpy)$_2$]·2H$_2$O/H$_3$PO$_4$ (bpy is 2,2′-bipyridine)

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The title compounds, poly[bis(2,2′-bipyridine)bis(μ_3-hydrogen phosphato)nitratodi-μ_2-oxo-dicopper(II)vanadium dihydrate], [Cu$_2$(VO$_2$)(HPO$_4$)$_2$(NO$_3$)(C$_{10}$H$_8$N$_2$)$_2$]·2H$_2$O, (I), and poly[bis(2,2′-bipyridine)bis(μ_3-hydrogen phosphato)nitrato-di-μ_2-oxo-dicopper(II)vanadium phosphoric acid solvate], [Cu$_2$(VO$_2$)(HPO$_4$)$_2$(NO$_3$)(C$_{10}$H$_8$N$_2$)$_2$]·H$_3$PO$_4$, (II), were obtained by similar hydrothermal methods but under different crystallization conditions. The trinuclear entity which serves as the basic unit in both structures presents two independent Cu^{II} ions immersed in similar square-pyramidal N$_2$O$_3$ environments plus an octahedral VO$_6$ core and is organized into a one-dimensional polymer, which is essentially identical in the two structures. The compounds are stabilized by different solvates, *viz.* two crystallization water molecules in (I) and a phosphoric acid molecule in (II), which provide the main structural differences through the diversity of interchain interactions in which they serve as bridges.

Comment

Vanadium phosphates have been extensively investigated in recent years due to their catalytic activity (Cheetham *et al.*, 1999), physical properties (mainly magnetic; Moreno *et al.*, 2003), ability as ionic interchangers, *etc.* Of particular interest is VO$_2$PO$_4$, a layered compound that can undergo intercalation reactions (Shi *et al.*, 2000). A variety of guest species, including pyridine, aniline, amides, amines, carboxylic acids, alcohols and diols (Yang & Lu, 2002), have been inserted between the layers by displacement of a coordinated water molecule. Other guest species, such as alkylammonium ions and ferrocene, have been intercalated through partial or complete reduction of V^V to V^{IV} (or an even lower oxidation

state) in the host structure (Shpeizer *et al.*, 2001; Huang *et al.*, 2001).

Our interest in vanadyl phosphates stems from the possibility of linking their polyhedra to create one-, two- or three-dimensional host structures with an organic or organometallic guest compound inside, to which the host can be bound either through strong covalent links or weaker hydrogen-bonded interactions.

Hydrothermal methods offer a feasible synthetic route to this type of compound through the chemical reaction of appropriate reagents in a sealed heated solution kept above ambient temperature and pressure (Feng & Xu, 2001). Under these conditions, the phosphate and vanadate polyhedra are prone to sharing vertices or edges, giving rise to chains, planes or three-dimensional structures (Pivan *et al.*, 2001).

In addition, this framework can bind to other systems, such as metal complexes, and thus give rise to compounds with a variety of interesting physical properties. In particular, magnetic coupling of metal centres can be achieved through this kind of architecture (Kahn, 1993; Kahn *et al.*, 1982). For this to happen, it is necessary that the metal centres be coordinated in proximity to one another, and this implies that the ligands involved should have coordinating centres relatively close to one another so as to render this feasible. We present here structural results arising from these ideas for two compounds, [Cu$_2$(VO$_2$)(HPO$_4$)$_2$(NO$_3$)(bpy)$_2$]·X, where bpy is 2,2′-bipyridine and X represents 2H$_2$O in (I) and H$_3$PO$_4$ in (II). These are two chemically isostructural systems obtained by hydrothermal methods, which only differ in the solvate molecules stabilizing the structures.
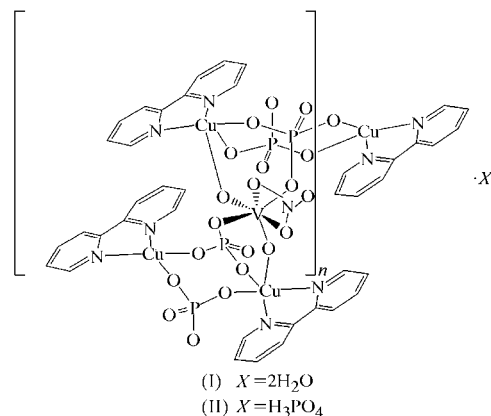

(I) X = 2H$_2$O
(II) X = H$_3$PO$_4$

Fig. 1 presents views of both structures, showing the common numbering scheme. The elemental unit is a trinuclear entity centred on two Cu^{II} ions and one vanadyl group, coordinated by two bpy, two phosphate and one nitrate ligand. The two structures are stabilized by different solvate units [water in (I) and phosphoric acid in (II)]. Each independent Cu atom (Cu1A and Cu1B) is surrounded by a five-coordinate environment provided by two N atoms from the chelating bpy unit and three O atoms from two symmetry-related phosphate units and the vanadyl group.

The Cu coordination polyhedron has the shape of a square pyramid, where the Cu—O$_{vanadyl}$ bond occupies the apical
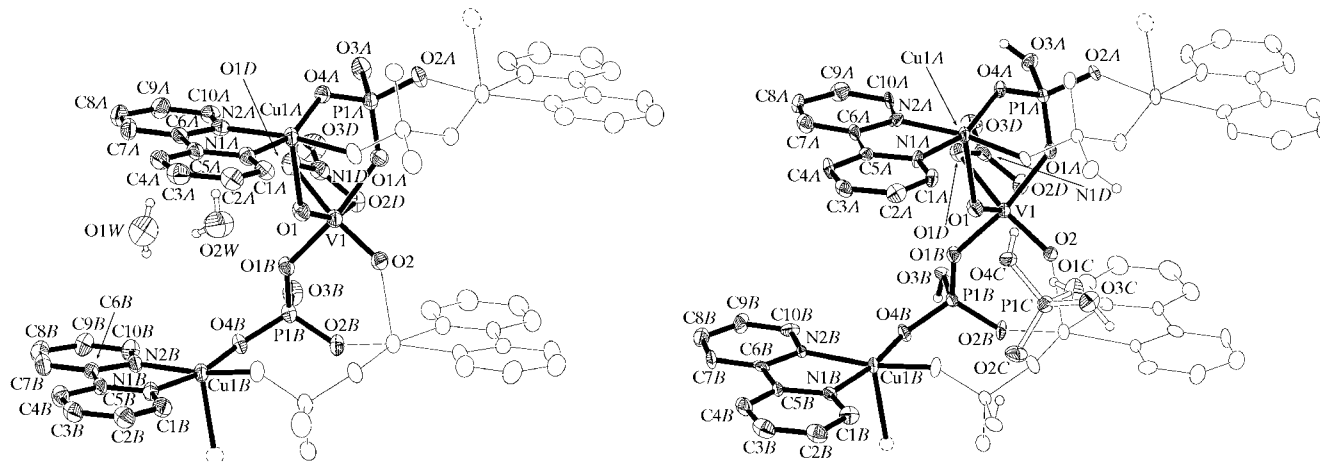
Figure 1
Molecular diagrams showing the numbering scheme used, as well as the way in which chains are formed, for compounds (I) (left) and (II) (right). Full ellipsoids denote the independent unit, with full bonds corresponding to the backbone and empty bonds to the solvent molecules. Empty ellipsoids represent the symmetry-generated part of the structure. Displacement ellipsoids are drawn at the 40% probability level. H atoms attached to C atoms have been omitted for clarity.
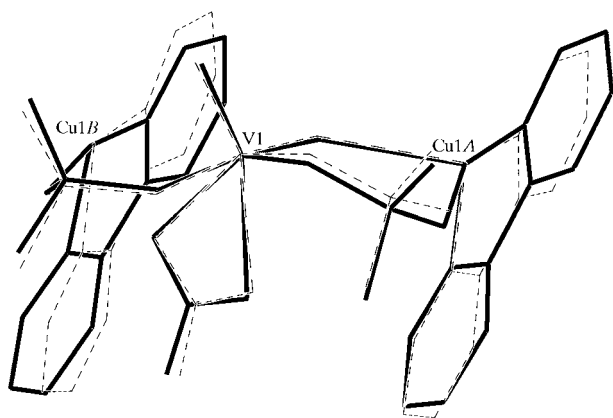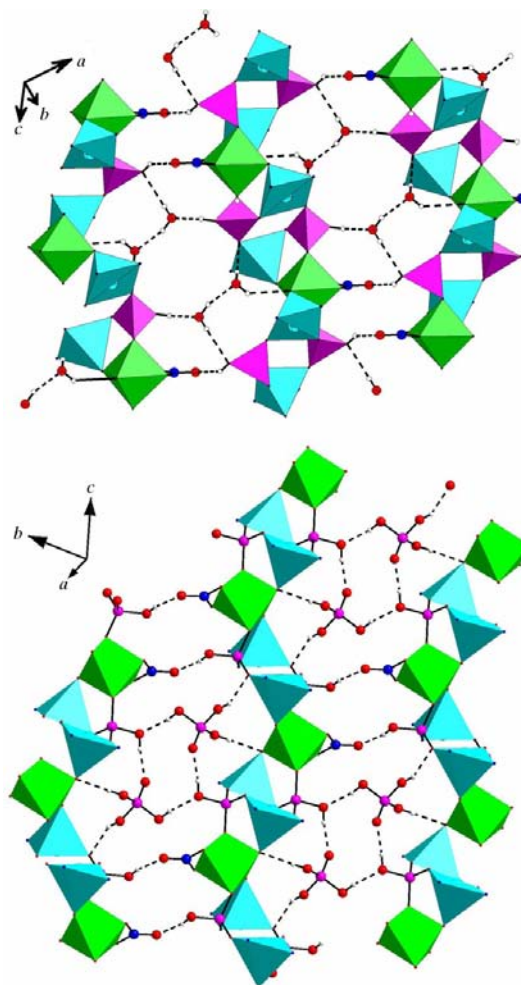

Figure 2
Superimposed drawings of the backbones of (I) and (II), showing their isostructural character.

position and the remaining Cu—N/O bonds establish the distorted square base.

The vanadyl group is immersed in an irregular octahedral environment, where the original geometry of the VO$_2$ entity is preserved, as shown by the extremely short V—O distances and the almost tetrahedral O1—V1—O2 angle. This is somewhat compensated by the chelating nitrate, with a small angle and two rather long V—O distances *trans* to atoms O1 and O2, in what could be considered the equatorial plane of the octahedron. Two phosphate atoms, O1*A* and O1*B*, complete the coordination, filling the apical positions at an intermediate distance from the cation. Besides the usual selected distances and angles provided by Tables 1 and 3, Table 5 gives additional information regarding the coordination polyhedra.

All the phosphate groups, together with the phosphoric acid molecule in (II), have regular geometries. The former present

Figure 3
Polyhedral diagram showing a lateral view of the chains and the manner in which they attach to each other through a diversity of hydrogen-bonding interactions mediated by the different solvents for compounds (I) (top) and (II) (bottom).

a very clear distinction between $P-O_{coord}$ and $P-OH$ bond lengths, the non-coordinated distance being longer by a percentage ranging from 5% to 9%. A similar situation arises with the solvate unit, in which the $P=O$ bond is shorter than the mean of the $P-OH$ bonds by a similar amount (ca 5%), as well as with the nitrate ($N=O < N-O_{coord}$ by ca 2.5–3%) (see Tables 1 and 3 for details).
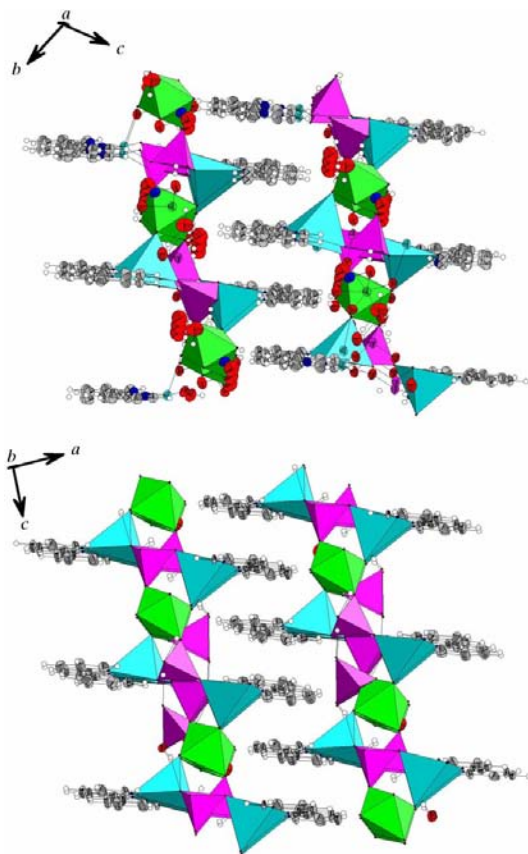
The HPO_4 units act as active coordination agents, giving rise to strongly coupled chains of polyhedra. Their elemental constituents are the dimeric units (A and B) which build up around two independent symmetry centres in $P\bar{1}$ [A at $(\frac{1}{2}, \frac{1}{2}, 0)$ and B at $(\frac{1}{2}, -1, \frac{1}{2})$ for (I), and A at $(1, 1, 0)$ and B at $(1, 1, \frac{1}{2})$ for (II)] and which result in very similar $Cu-O-P-O-(Cu'-O'-P'-O')$ loops (primes denote the inversion around the symmetry centres noted above). The V atom, in turn, has a twofold binding to each of the independent Cu^{II} ions, through one of the vanadyl O atoms on one side and through a longer $O-P-O$ bridge on the other. The intercationic distances arising from this arrangement are rather large: $Cu1A\cdots Cu1A^i = 5.077$ (1), $Cu1B\cdots Cu1B^{ii} = 5.013$ (1), $V1\cdots Cu1A = 3.634$ (1) and $V1\cdots Cu1B^{ii} = 3.578$ (1) Å for (I), and $Cu1A\cdots Cu1A^{iii} = 5.073$ (1), $Cu1B\cdots Cu1B^{iv} = 5.061$ (1), $V1\cdots Cu1A = 3.688$ (1) and $V1\cdots Cu1B^{iv} = 3.618$ (1) Å for

(II) [symmetry codes: (i) $-1 - x$, $-1 - y$, $-z$; (ii) $-1 - x$, $-3 - y$, $-1 - z$; (iii) $2 - x$, $2 - y$, $-z$; (iv) $2 - x$, $2 - y$, $1 - z$].

The resulting chains, flattened into the shape of strips with the aromatic groups protruding outward on the 'wide' side, are fairly isostructural, as can be assessed by inspection of Fig. 2, where both structures have been superimposed; the mean deviation is 0.32 (1) Å for all common atoms, reducing to 0.05 (1) Å when only the cations are considered.

The main differences between the two structures are due to the interchain interactions, which arise from two well differentiated effects. On one hand, the stronger hydrogen-bonding interactions mediated by the active donor solvates [H_2O in (I) and H_3PO_4 in (II)] link the chains through their 'narrow' dimension into hydrogen-bonded planes parallel to (011) in (I) and to (100) in (II) (see Tables 2 and 4, and Fig. 3). These hydrogen-bonded planes, in turn, interact with each other through weaker π–π contacts between interleaving bpy groups of neighbouring planes, at a graphitic distance (ca 3.4 Å) from each other (Table 6 and Fig. 4). In spite of the relative strengths of the forces involved, the second type of interaction leads to shorter intercationic distances (out-of-plane $Cu\cdots Cu$ < 5.7 Å $versus$ in-plane $Cu\cdots Cu$ > 9.5 Å).

In summary, we have generated two different, though basically isostructural, compounds from the same solution subjected to hydrothermal treatment. The compounds present the same polymeric one-dimensional motif and their structures differ only in the way in which the chains interact with each other through the different hydrogen-bonding schemes mediated by the different solvent molecules present.

Experimental

Both title compounds were obtained via hydrothermal synthesis. A mixture of V_2O_5 (0.84 mmol), 2,2'-bipyridine (0.85 mmol), Cu-$(NO_3)_2\cdot 3H_2O$ (1.68 mmol), zinc powder (1.62 mmol) and H_3PO_4 (5 ml, 1.48 M) was sealed in a Teflon-lined acid digestion bomb and heated at 390 K for 3 d under autogenous pressure, followed by slow cooling at a rate of 20 K h^{-1} to room temperature. The immediate product of the reaction consisted of green prismatic crystals of (II). Left unattended for several weeks, the remaining mother liquor yielded a crop of similarly shaped and coloured crystals, corresponding to compound (I).

Compound (I)

Crystal data

Figure 4
Polyhedral diagrams showing the linking of the hydrogen-bonded planes through weak π–π interactions between interleaved bpy groups of neighbouring planes in compounds (I) (top) and (II) (bottom).

$[Cu_2V(HPO_4)_2(NO_3)O_2-(C_{10}H_8N_2)_2]\cdot 2H_2O$	Mo $K\alpha$ radiation
$M_r = 812.39$	Cell parameters from 2933 reflections
Triclinic, $P\bar{1}$	$\theta = 5.0$–54.2°
$a = 10.5927$ (13) Å	$\mu = 2.08$ mm^{-1}
$b = 12.0359$ (15) Å	$T = 293$ (2) K
$c = 12.1655$ (15) Å	Prism, green
$\alpha = 107.090$ (2)°	$0.28 \times 0.24 \times 0.16$ mm
$\beta = 110.399$ (2)°	
$\gamma = 93.876$ (2)°	
$V = 1364.3$ (3) Å^3	
$Z = 2$	
$D_x = 1.978$ Mg m^{-3}	

Data collection

Bruker SMART CCD area-detector
  diffractometer
φ and ω scans
Absorption correction: multi-scan
  (SADABS; Sheldrick, 1996)
  $T_{min} = 0.57$, $T_{max} = 0.72$
5669 measured reflections
4697 independent reflections

3098 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 25.0°$
$h = -9 \rightarrow 12$
$k = -14 \rightarrow 12$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.085$
$S = 0.83$
4697 reflections
424 parameters
H atoms treated by a mixture of
  independent and constrained
  refinement

$w = 1/[\sigma^2(F_o^2) + (0.0234P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.012$
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1A—O2A^i	1.909 (3)	V1—O1D	2.281 (3)
Cu1A—O4A	1.922 (3)	V1—O2D	2.351 (4)
Cu1A—N2A	1.999 (4)	P1A—O4A	1.500 (3)
Cu1A—N1A	2.021 (4)	P1A—O2A	1.501 (3)
Cu1A—O1	2.360 (3)	P1A—O1A	1.528 (3)
Cu1B—O2B^{ii}	1.908 (3)	P1A—O3A	1.599 (4)
Cu1B—O4B	1.926 (3)	P1B—O2B	1.503 (3)
Cu1B—N1B	2.001 (4)	P1B—O4B	1.515 (3)
Cu1B—N2B	2.004 (4)	P1B—O1B	1.523 (3)
Cu1B—O2^{ii}	2.267 (3)	P1B—O3B	1.577 (4)
V1—O2	1.620 (3)	O1D—N1D	1.253 (5)
V1—O1	1.640 (3)	O2D—N1D	1.259 (5)
V1—O1B	1.952 (3)	O3D—N1D	1.221 (5)
V1—O1A	1.959 (3)		
O2A^i—Cu1A—O4A	96.83 (13)	N1B—Cu1B—O2^{ii}	95.49 (14)
O2A^i—Cu1A—N2A	170.68 (14)	N2B—Cu1B—O2^{ii}	95.69 (14)
O4A—Cu1A—N2A	92.42 (14)	O2—V1—O1	106.87 (17)
O2A^i—Cu1A—N1A	91.52 (15)	O2—V1—O1B	97.03 (15)
O4A—Cu1A—N1A	158.98 (16)	O1—V1—O1B	97.37 (14)
N2A—Cu1A—N1A	80.14 (16)	O2—V1—O1A	95.48 (15)
O2A^i—Cu1A—O1	90.03 (13)	O1—V1—O1A	97.87 (15)
O4A—Cu1A—O1	90.76 (12)	O1B—V1—O1A	156.54 (13)
N2A—Cu1A—O1	88.72 (14)	O2—V1—O1D	152.42 (15)
N1A—Cu1A—O1	108.56 (14)	O1—V1—O1D	100.71 (15)
O2B^{ii}—Cu1B—O4B	95.86 (13)	O1B—V1—O1D	78.85 (13)
O2B^{ii}—Cu1B—N1B	91.26 (15)	O1A—V1—O1D	80.87 (13)
O4B—Cu1B—N1B	168.04 (15)	O2—V1—O2D	97.45 (15)
O2B^{ii}—Cu1B—N2B	166.80 (16)	O1—V1—O2D	155.61 (15)
O4B—Cu1B—N2B	90.38 (14)	O1B—V1—O2D	81.07 (12)
N1B—Cu1B—N2B	80.78 (16)	O1A—V1—O2D	77.68 (13)
O2B^{ii}—Cu1B—O2^{ii}	95.54 (13)	O1D—V1—O2D	55.00 (12)
O4B—Cu1B—O2^{ii}	93.38 (13)		

Symmetry codes: (i) $-1-x, -1-y, -z$; (ii) $-1-x, -2-y, -1-z$.

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O3A—H3A···O3D^i	0.82 (4)	2.14 (5)	2.871 (5)	150 (5)
O3B—H3B···O2W	0.81 (4)	1.91 (5)	2.718 (5)	175 (6)
O1W—H1WA···O1^{ii}	0.83 (4)	2.35 (5)	2.973 (6)	132 (6)
O1W—H1WB···O4B^{iii}	0.83 (4)	2.18 (5)	3.006 (6)	179 (7)
O2W—H2WA···O1W	0.83 (4)	1.91 (5)	2.708 (7)	162 (5)
O2W—H2WB···O3A^i	0.82 (4)	2.37 (5)	3.186 (6)	177 (7)

Symmetry codes: (i) $-x, -1-y, -z$; (ii) $1+x, y, z$; (iii) $-x, -2-y, -1-z$.

Table 3
Selected geometric parameters (Å, °) for (II).

Cu1A—O4A	1.911 (5)	P1A—O4A	1.509 (6)
Cu1A—O2A^i	1.925 (6)	P1A—O1A	1.507 (6)
Cu1A—N2A	1.965 (7)	P1A—O2A	1.524 (6)
Cu1A—N1A	2.016 (7)	P1A—O3A	1.575 (6)
Cu1A—O1	2.432 (6)	P1B—O2B	1.501 (6)
Cu1B—O4B	1.920 (6)	P1B—O1B	1.512 (6)
Cu1B—O2B^{ii}	1.921 (6)	P1B—O4B	1.524 (6)
Cu1B—N1B	2.013 (7)	P1B—O3B	1.609 (6)
Cu1B—N2B	2.036 (7)	P1C—O2C	1.473 (6)
Cu1B—O2^{ii}	2.307 (6)	P1C—O3C	1.531 (6)
V1—O1	1.622 (6)	P1C—O1C	1.539 (7)
V1—O2	1.645 (6)	P1C—O4C	1.543 (6)
V1—O1B	1.958 (6)	O1D—N1D	1.269 (9)
V1—O1A	1.983 (6)	O2D—N1D	1.260 (9)
V1—O1D	2.213 (6)	O3D—N1D	1.234 (9)
V1—O2D	2.395 (7)		
O4A—Cu1A—O2A^i	96.7 (2)	N1B—Cu1B—O2^{ii}	96.8 (2)
O4A—Cu1A—N2A	93.2 (3)	N2B—Cu1B—O2^{ii}	96.9 (2)
O2A^i—Cu1A—N2A	170.0 (3)	O1—V1—O2	107.4 (3)
O4A—Cu1A—N1A	159.9 (3)	O1—V1—O1B	98.9 (3)
O2A^i—Cu1A—N1A	91.2 (3)	O2—V1—O1B	97.3 (3)
N2A—Cu1A—N1A	79.9 (3)	O1—V1—O1A	96.5 (3)
O4A—Cu1A—O1	91.8 (2)	O2—V1—O1A	94.1 (3)
O2A^i—Cu1A—O1	88.2 (3)	O1B—V1—O1A	157.0 (3)
N2A—Cu1A—O1	90.1 (2)	O1—V1—O1D	100.1 (3)
N1A—Cu1A—O1	107.0 (2)	O2—V1—O1D	152.5 (3)
O4B—Cu1B—O2B^{ii}	95.4 (2)	O1B—V1—O1D	78.5 (2)
O4B—Cu1B—N1B	170.7 (3)	O1A—V1—O1D	82.2 (2)
O2B^{ii}—Cu1B—N1B	92.5 (3)	O1—V1—O2D	155.1 (3)
O4B—Cu1B—N2B	90.3 (3)	O2—V1—O2D	97.3 (3)
O2B^{ii}—Cu1B—N2B	166.1 (3)	O1B—V1—O2D	80.2 (2)
N1B—Cu1B—N2B	81.0 (3)	O1A—V1—O2D	78.7 (2)
O4B—Cu1B—O2^{ii}	87.3 (2)	O1D—V1—O2D	55.2 (2)
O2B^{ii}—Cu1B—O2^{ii}	96.1 (2)		

Symmetry codes: (i) $2-x, 2-y, -z$; (ii) $2-x, 2-y, 1-z$.

Compound (II)

Crystal data

[Cu$_2$V(HPO$_4$)$_2$(NO$_3$)O$_2$-
  (C$_{10}$H$_8$N$_2$)$_2$]·H$_3$PO$_4$
$M_r = 874.35$
Triclinic, $P\bar{1}$
$a = 9.8343$ (13) Å
$b = 10.4632$ (14) Å
$c = 14.3210$ (19) Å
$\alpha = 72.070$ (2)°
$\beta = 89.900$ (2)°
$\gamma = 80.651$ (2)°
$V = 1381.6$ (3) Å^3

$Z = 2$
$D_x = 2.102$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2467
  reflections
$\theta = 5.8–51.3°$
$\mu = 2.13$ mm^{-1}
$T = 299$ (2) K
Prism, green
$0.32 \times 0.24 \times 0.18$ mm

Data collection

Bruker SMART CCD area-detector
  diffractometer
φ and ω scans
Absorption correction: multi-scan
  (SADABS; Sheldrick, 1996)
  $T_{min} = 0.55$, $T_{max} = 0.68$
8625 measured reflections

4812 independent reflections
2471 reflections with $I > 2\sigma(I)$
$R_{int} = 0.076$
$\theta_{max} = 25.0°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 11$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.161$
$S = 0.85$
4812 reflections
448 parameters

H atoms treated by a mixture of
  independent and constrained
  refinement
$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.016$
$\Delta\rho_{max} = 0.76$ e Å^{-3}
$\Delta\rho_{min} = -0.83$ e Å^{-3}

metal-organic compounds

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3A—H3$A\cdots$O3D[i]	0.84 (4)	2.02 (4)	2.848 (8)	169 (6)
O3B—H3$B\cdots$O2C[ii]	0.82 (4)	1.76 (4)	2.573 (8)	174 (5)
O1C—H1$C\cdots$O2	0.81 (4)	2.08 (4)	2.777 (9)	144 (2)
O3C—H3$C\cdots$O3B[iii]	0.82 (4)	1.83 (4)	2.647 (9)	169 (7)
O4C—H4$C\cdots$O2A[iv]	0.82 (4)	1.91 (4)	2.640 (8)	149 (7)

Symmetry codes: (i) $2-x, 3-y, -z$; (ii) $2-x, 2-y, 1-z$; (iii) $x, y-1, z$; (iv) $2-x, 2-y, -z$.

Table 5
Selected parameters for the coordination polyhedra in (I) and (II).

Cation	Polyhedral type	Basal plane	d_1 (Å)†	Apical atom	d_2 (°)‡
Compound (I)					
Cu1A	Square pyramid	O2A/O4A/N1A/N2A	0.19 (1)	O1	8.9 (1)
Cu1B	Square pyramid	O2B/O4B/N1B/N2B	0.02 (1)	O2	18.2 (1)
V1	Octahedron	O1D/O2D/O1/O2	0.02 (1)	O1	12.0 (1)
				O2	11.6 (1)
Compound (II)					
Cu1A	Square pyramid	O2A/O4A/N1A/N2A	0.18 (1)	O1	7.6 (1)
Cu1B	Square pyramid	O2B/O4B/N1B/N2B	0.07 (1)	O2	4.9 (1)
V1	Octahedron	O1D/O2D/O1/O2	0.03 (1)	O1	10.5 (1)
				O2	1.6 (1)

† d_1 is the mean linear deviation from the least-squares plane. ‡ d_2 is the angular deviation from the least-squares plane normal.

Table 6
Selected parameters (Å, °) for π–π interactions in (I) and (II).

Group 1, Group 2	IPD†	CCD‡	SA§
Compound (I)			
N1A/C1A–C5A, N2A[i]/C6A[i]–C10A[i]	3.44 (1)	3.64 (1)	19.2 (1)
N1B/C1B–C5B, N2B[ii]/C6B[ii]–C10B[ii]	3.41 (1)	3.64 (1)	20.1 (1)
N1A[i]/C1A[i]–C5A[i], N2B/C6B–C10B	3.35 (1)	3.74 (1)	26.2 (1)
N2A[i]/C6A[i]–C10A[i], N1B/C1B–C5B	3.39 (1)	3.64 (1)	22.3 (1)
Compound (II)			
N1A/C1A–C5A, N2A[iii]/C6A[iii]–C10A[iii]	3.35 (1)	3.67 (1)	24.1 (1)
N1B/C1B–C5B, N2B[iv]/C6B[iv]–C10B[iv]	3.37 (1)	3.67 (1)	23.2 (1)
N1A[iii]/C1A[iii]–C5A[iii], N2B/C6B–C10B	3.46 (1)	3.59 (1)	15.7 (1)
N2A[iii]/C6A[iii]–C10A[iii], N1B/C1B–C5B	3.37 (1)	3.61 (1)	21.1 (1)

† IPD is the interplanar distance. ‡ CCD is the centre-to-centre distance. § SA is the slippage angle (for nomenclature, see Janiak, 2000). Symmetry codes: (i) $-1-x$, $-1-y, -z$; (ii) $-1-x, -2-y, -1-z$; (iii) $2-x, 2-y, -z$; (iv) $2-x, 2-y, 1-z$.

H atoms attached to C atoms and unambiguously defined by stereochemistry were placed in calculated positions (C—H = 0.93 Å)

and allowed to ride, with U_{iso}(H) = $1.2U_{eq}$(C). Those attached to O atoms were located in late-stage difference maps and refined with restrained distances of O—H = 0.82 (1) Å and H$\cdots$H = 1.36 (2) Å. Full use of the CCDC package was made for searching in the Cambridge Structural Database (Allen, 2002).

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXTL/PC*.

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