

Solid state coordination chemistry of oxovanadium phosphates: hydrothermal syntheses and structures of the network and chain phosphate phases

$[\{\text{Cu}(\text{bpy})\}_2(\text{VO})_3(\text{PO}_4)_2(\text{HPO}_4)_2] \cdot 2\text{H}_2\text{O}$ and $[\{\text{Cu}(\text{terpy})\}_2(\text{VO}_2)_3(\text{PO}_4)(\text{HPO}_4)_2]$

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The hydrothermal reactions of Cu_2O , the appropriate polypyridine ligand, Na_3VO_4 , H_3PO_4 and H_2O at 200°C yield the two-dimensional material $[\{\text{Cu}(\text{bpy})\}_2(\text{VO})_3(\text{PO}_4)_2(\text{HPO}_4)_2] \cdot 2\text{H}_2\text{O}$ and the one-dimensional phosphate $[\{\text{Cu}(\text{terpy})\}_2(\text{VO}_2)_3(\text{PO}_4)(\text{HPO}_4)_2]$, examples of the structure-directing role of secondary metal–ligand subunits on the architectures of vanadium phosphates.

One approach to the design of novel materials exploits the often dramatic influence of organic molecules on inorganic microstructures.^{1,2} Zeolites,^{3,4} mesoporous materials of the MCM-41 class,⁵ and open framework metal phosphates^{6,7} are examples of families of materials which incorporate organic cations as structure-directing agents. An alternative approach introduces the organic component as a ligand, linking metal sites into complex metal–organic scaffoldings.^{8,9} A variant of this strategy as applied to molybdenum oxides employs secondary metal–ligand complex subunits, not only as charge-compensating and space-filling components, but also as intimate structural components of bimetallic oxide composite materials, exemplified by copper–molybdenum oxides such as $[\text{Cu}(4,4'\text{-bipyridylamine})\text{MoO}_4]$, $[\text{Cu}(o\text{-phen})\text{MoO}_4]$ and $[\text{Cu}(\text{tetraphenylporphyrin})\text{Cu}_2\text{Mo}_3\text{O}_{11}]$.^{10–12} Since both the ligand geometry and spatial extension, as well as the coordination preferences of the secondary metal site can be manipulated, considerable flexibility may be achieved in the spatial transmission of the structural information inherent at the ligated metal site. The success of this approach in the evolution of a wealth of new materials in the molybdenum oxide family encouraged us to explore the structure-directing role of copper–organonitrogen subunits in the industrially significant oxovanadium phosphate family of materials. The coordination preferences of the copper and the consequences of increased ligand bulk and denticity are evident in the structure of two novel bimetallic oxide phosphate materials, two dimensional $[\{\text{Cu}(2,2'\text{-bipyridyl})\}_2(\text{VO})_3(\text{PO}_4)_2(\text{HPO}_4)_2] \cdot 2\text{H}_2\text{O}$ (**1**) and one-dimensional $[\{\text{Cu}(\text{terpyridyl})\}_2(\text{VO}_2)_3(\text{PO}_4)(\text{HPO}_4)_2]$ (**2**).

Compound **1** was prepared as dark green rhombi in 40% yield from the hydrothermal reaction of Cu_2O , 2,2'-bipyridine, Na_3VO_4 , H_3PO_4 and H_2O at 200°C for 95 h.[†] Substitution of terpyridine for bipyridine in the reaction mixture and heating at 200°C for 50 h yielded **2** as emerald green rhombi in 50% yield. The infrared spectra of **1** and **2** exhibit strong bands in the $920\text{--}970\text{ cm}^{-1}$ range attributed to $\nu(\text{V}=\text{O})$ and a series of bands characteristic of the phosphate group in the $1100\text{--}1600\text{ cm}^{-1}$ range.

As shown in Fig. 1, the structure of **1**[‡] consists of copper–vanadium oxide–phosphate layers, decorated with 2,2'-bipyridyl groups projecting above and below into the interlamellar region. The network is constructed from the corner- and edge-sharing polyhedral connectivity of copper(II) square pyramids, vanadium(IV) octahedra and square pyramids and phosphate tetrahedra. The Cu(II) coordination geometry is defined by the nitrogen donors of the bpy ligand and three oxygen donors from each of two $\{\text{PO}_4\}^{3-}$ groups and the $-\text{OH}$ group of the $\{\text{HPO}_4\}^{2-}$ unit. The Cu–O and P–O bond lengths of 2.35 and 1.61 Å, respectively, and valence sum calculations¹³ establish

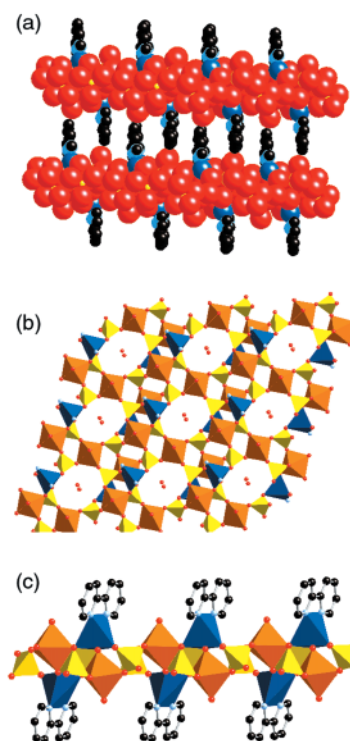


Fig. 1 (a) A space-filling view of the structure of **1**, parallel to the oxide layer. Red spheres, oxygen; dark blue spheres, copper; black spheres, carbon; light blue spheres, nitrogen. Hydrogen atoms have been omitted for clarity. (b) A view of the structure of **1**, normal to the plane of the bimetallic phosphate layer. The square pyramidal vanadium sites are represented as yellow polyhedra linking the $\{\text{Cu}_2(\text{bpy})_2(\text{VO})_2(\text{PO}_4)_2(\text{HPO}_4)_2\}$ chains with the vanadium octahedra in yellow, the copper sites in blue and the phosphate groups in violet. (c) A polyhedral representation of the $\{\text{Cu}_2(\text{bpy})_2(\text{VO})_2(\text{PO}_4)_2(\text{HPO}_4)_2\}$ chain. Selected bond lengths (Å): V1–O₁, 1.586(4); V1–O_{phosphate}, 1.964(3), av. of 4; V2–O₁, 1.607(2); V2–O_{phosphate}, 2.071(4), av. of 5; P–O, 1.531(4), av.; P–O(H), 1.605(2); Cu–O, 1.975(4), av.; Cu–O(H), 2.349(2).

this as the protonation site. The square pyramidal V(IV) site consists of a terminal apical oxo-group and four phosphate oxygen donors from each of four $\{\text{PO}_4\}^{3-}$ or $\{\text{HPO}_4\}^{2-}$ groups, while the octahedral V(IV) site features a terminal oxo-group and five oxygen donors from four $\{\text{PO}_4\}^{3-}$ groups. One phosphate group bridges three vanadium centers and a copper site, while the second bridges three vanadium and two copper sites, sharing two vertices with both vanadium and copper centers.

The structure of **1** may be best described as $\{\text{Cu}_2(\text{bpy})_2(\text{VO})_2(\text{PO}_4)_2(\text{HPO}_4)_2\}$ chains linked through square pyramidal $\{\text{VO}_3\}$ units into a 2-D network. Embedded within the chain are $\{\text{Cu}_2(\text{bpy})_2(\text{VO})_2(\text{PO}_4)_2\}$ clusters, constructed of a central ring of edge- and corner-sharing $\{\text{VO}_6\}$ octahedra and $\{\text{PO}_4\}$ tetrahedra capped by two $\{\text{CuO}_3\text{N}_2\}$ square pyramids. The phosphate groups of this cluster motif each link two copper and two vanadium sites, participating in edge-sharing with a

vanadium polyhedron and contributing two triply-bridging oxygen donors. The fourth vertex of each of these phosphate groups serves to bridge to the square pyramidal vanadium site. The individual clusters are linked into the chain motif through four corner-sharing $\{\text{PO}_4\}$ tetrahedra. The fourth vertex of each of these phosphate sites again bridges to the square pyramidal vanadium center. One consequence of this unprecedented polyhedral connectivity is to generate eight polyhedral connect rings $[\text{V}_4\text{P}_4\text{O}_8]$ which create network cavities. The water molecules of crystallization are situated within these cavities and strongly hydrogen-bonded to the phosphate oxygens and the protonated phosphate oxygen. Since these intralamellar cavities are contained within hydrophobic regions defined by the bipyridyl groups, there is no facile pathway for removal of H_2O from the crystal. This observation is confirmed by the thermal gravimetric analysis of **1** which exhibits no weight loss below 250°C , whereupon water is lost in two steps ($250\text{--}275^\circ\text{C}$ and $310\text{--}375^\circ\text{C}$). Ligand loss occurs above 400°C to give an amorphous gray powder at 650°C .

The structural consequences of increasing ligand bulk and denticity are apparent in the one-dimensional structure of **2**, shown in Fig. 2. The chain consists of exclusively corner-sharing vanadium(v) tetrahedra, square pyramids and trigonal bipyramids, copper square pyramids and $\{\text{PO}_4\}^{3-}$ and $\{\text{HPO}_4\}^{2-}$ tetrahedra. There are three distinct vanadium centers: an 'isolated' $\{\text{VO}_4\}$ tetrahedra site (*i.e.* no V–O–V linkages) and a binuclear site consisting of an oxo-bridged $\{\text{VO}_5\}$ trigonal bipyramid and $\{\text{VO}_5\}$ square pyramid. The $\{\text{PO}_4\}^{3-}$ group participates in corner-sharing to bridge the vanadium sites of the binuclear unit, the tetrahedral vanadium site and the copper. The remaining phosphate sites each bridge three metal centers and exhibit a pendant and protonated oxygen site. The terpy ligand occupies three coordination sites on the copper and introduces significant steric constraints, leaving two coordination sites available for linking to the oxovanadium phosphate chain. One copper site coordinates to two oxygen donors from two phosphorus tetrahedra, while the second bonds to a phosphorus oxygen and a bridging oxo-group of the trigonal bipyramidal vanadium site. The presence of three distinct vanadium polyhedra in **2** is a structurally unique feature for the oxovanadium phosphate family of materials.

Oxovanadium phosphates have received considerable attention as a result of their catalytic properties in organic

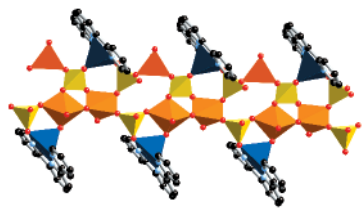


Fig. 2 A polyhedral representation of the structure of **2** using the same color scheme as for Fig. 1. Selected bond lengths (\AA): tetrahedral vanadium: V1–O_a, 1.614(4) and 1.633(3); V1–O_b, 1.838(3) and 1.861(3); trigonal bipyramidal vanadium: V2–O_a, 1.594(4); V2–O_b(–Ve), 1.703(3); V2–O_{phosphate}, 1.956(5), *av.*; square pyramidal vanadium: V3–O_a, 1.620(3); V3–O_b(–Cu), 1.647(3); V3–O_b(–V2), 1.987(3); V3–O_{phosphate}, 1.985(4), *av.*; Cu1–O_{phosphate}, 1.923(3) and 2.099(3); Cu1–N, 2.052(6), *av.*; Cu2–O_b(–V3), 2.241(3); Cu2–O_{phosphate}, 1.921(4); Cu2–N, 1.993(6), *av.*

oxidations^{14,15} and their intercalation properties.¹⁶ Significant activity has focused on structural modification and design of vanadyl phosphates through the introduction of organic substructures as templates and charge-compensating cations.^{6,17} The approach to hybrid oxometal–phosphate/organic solids illustrated by the isolation of **1** and **2** employs secondary metal–organic ligand subunits as covalent linkers to the oxometal phosphate substructure. This strategy not only yields novel structural types, but appears to afford primitive control over the dimensionality of the solid through manipulation of the steric requirements and denticity of the ligand. The evolution of synthetic design in such solids appears inherent in the systematic variation of the secondary metal and its coordination preferences, the organic ligand, and the hydrothermal reaction conditions.

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Notes and references

† Reactions were carried out in Teflon-lined Parr acid-digestion bombs at 30% fill volume. Reaction conditions summary: **1**, mole ratio for Cu_2O : 2,2'-bipy: terpy: Na_3VO_4 : H_3PO_4 : H_2O of 1.4: 1.1: 1.0: 1.3: 15.3: 1750; 200°C , 95 h, **2**, Cu_2O : terpy: Na_3VO_4 : H_3PO_4 : H_2O of 1.9: 1.0: 2.2: 19.6: 2060; 200°C , 50 h.

‡ Crystal data for: $\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_{10.5}\text{P}_2\text{CuV}_{1.5}$ **1**: triclinic $P\bar{1}$, $a = 8.1496(5)$, $b = 9.7211(6)$, $c = 11.9472(7)$ \AA , $\alpha = 106.811(1)$, $\beta = 98.943(1)$, $\gamma = 110.429(1)^\circ$, $V = 813.64(9)$ \AA^3 , $R1 = 0.040$ for 3665 reflections. For $\text{C}_{30}\text{H}_{24}\text{N}_6\text{O}_{18}\text{P}_3\text{Cu}_2\text{V}_3$ **2**: triclinic $P\bar{1}$, $a = 8.9915(5)$, $b = 11.3011(6)$, $c = 19.4556(11)$ \AA , $\alpha = 106.762(1)$, $\beta = 91.208(1)$, $\gamma = 103.984(1)^\circ$, $V = 1828.0(2)$ \AA^3 , $R1 = 0.0519$ for 8486 reflections. CCDC 182/1679.

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