

## A new hybrid organic–inorganic chain: [(phen)Cu– $\mu$ –( $\kappa^2O:O'$ -VP<sub>2</sub>O<sub>10</sub>H<sub>3</sub>)<sub>2</sub>– Cu(phen)]<sub>n</sub>

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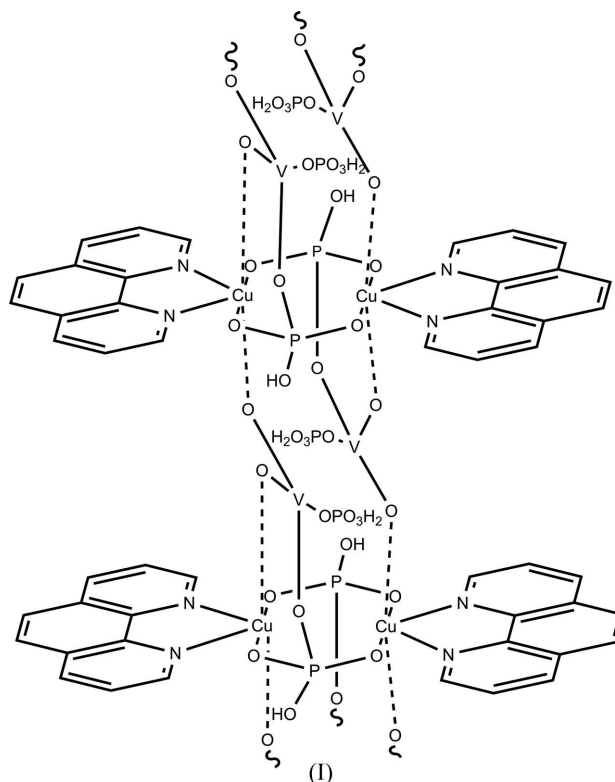
The structure of the title compound, poly[(dihydrogenphosphato- $\kappa O$ )( $\mu_3$ -hydrogenphosphato)di- $\mu$ -oxido-(1,10-phenanthroline)copper(II)vanadium(V)], [CuV(HPO<sub>4</sub>)(H<sub>2</sub>PO<sub>4</sub>)O<sub>2</sub>–(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>n</sub>], is defined by [(phen)Cu– $\mu$ –( $\kappa^2O:O'$ -VP<sub>2</sub>O<sub>10</sub>-H<sub>3</sub>)<sub>2</sub>–Cu(phen)] units (phen is 1,10-phenanthroline), which are connected to neighbouring units through vanadyl bridges. Neighbouring chains have no covalent bonds between them, although they interdigitate through the phen groups *via*  $\pi$ – $\pi$  interactions.

### Comment

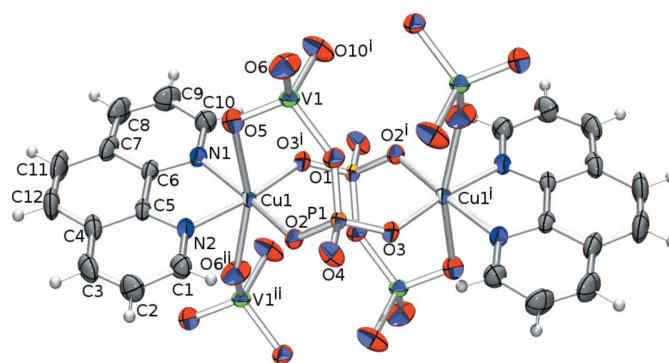
New materials based on hybrid organic–inorganic compounds are of interest due to their low density compared with pure inorganic materials (Yucesan *et al.*, 2005; Feng & Xu, 2001). Functionalized phosphovanadates have been studied extensively due to their catalytic and magnetic properties. From a catalytic point of view, they are interesting due to the interplay of the different possible oxidation states, and to their low solubility, which together make them good candidates for heterogeneous catalysis reactions. From a magnetic point of view, they are interesting due to the possibility of being functionalized by secondary paramagnetic complexes.

Vanadium oxides can possess several coordination geometries and therefore present a rich variety of structures by condensation through phosphates (Yang *et al.*, 2010; De Burgomaster *et al.*, 2010). The presence of organic ligands can drastically modify these structures. The use of copper(II) as a secondary metal also increases the range of possible structures, due to the structural plasticity of this metal ion (Ushak *et al.*, 2006; Venegas-Yazigi *et al.*, 2011). Using this structural plasticity, we have been using copper(II)–diimine complexes

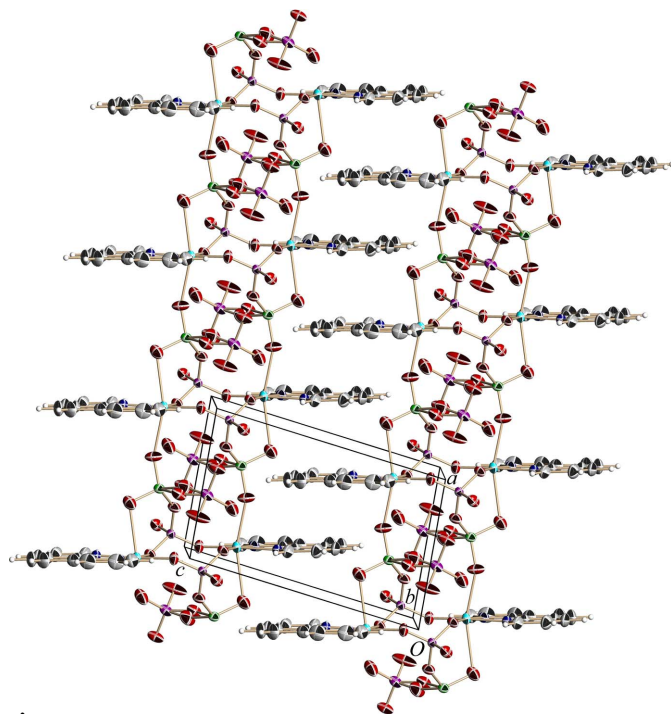
to functionalize vanadium–phosphate–oxide (VPO) frameworks, obtaining different organic–inorganic materials. In this paper, we present a new one-dimensional structure based on the VPO inorganic lattice.



The structure of the title compound, (I), is constructed from centrosymmetric (crystallographic) bimetallic [(phen)Cu– $\mu$ –( $\kappa^2O:O'$ -VP<sub>2</sub>O<sub>10</sub>H<sub>3</sub>)<sub>2</sub>–Cu(phen)] units (phen is 1,10-phenanthroline), shown in Fig. 1. Within this unit, the Cu<sup>II</sup> environment is defined by two N atoms of the phenanthroline ligand, two O atoms from two different phosphate groups and two O atoms from two different vanadyl groups. Therefore, the coordination geometry can be described as a slightly distorted and axially elongated octahedron, where the vanadyl O atoms are in the axial positions (Table 1).



**Figure 1**  
The centrosymmetric bimetallic [(phen)Cu– $\mu$ –( $\kappa^2O:O'$ -VP<sub>2</sub>O<sub>10</sub>H<sub>3</sub>)<sub>2</sub>–Cu(phen)] unit of (I). Displacement ellipsoids are drawn at the 50% probability level. The minor disorder component of atom O10 has been omitted for clarity. [Symmetry codes: (i)  $-x + 2, -y + 1, -z + 2$ ; (ii)  $x + 1, y, z$ .]



**Figure 2**  
Chains of  $[(\text{phen})\text{Cu}-\mu-(\kappa^2\text{O}:\text{O}'\text{-VP}_2\text{O}_{10}\text{H}_3)_2\text{-Cu}(\text{phen})]_n$  running along  $[100]$ . The zipped pattern between neighbouring chains is shown. The minor disorder component of atom O10 has been omitted for clarity.

The bond-valence sum for the V atom is 5.3, assuming tetrahedral geometry (Brown & Altermatt, 1985). This agrees well with the oxidation state of  $\text{V}^{\text{V}}$  computed from the observed crystal structure. This fact, combined with charge-balance analysis, leads us to establish the phosphovanadate fragments as  $[\text{VP}_2\text{O}_{10}\text{H}_3]^{2-}$ . Both the  $\text{V}^{\text{V}}$  and  $\text{P}^{\text{V}}$  atoms within this anion have tetrahedral environments.

The bimetallic unit contains two  $[\text{Cu}(\text{phen})]^{2+}$  fragments which are bonded through two O–P–O bridges from  $[\text{VP}_2\text{O}_{10}\text{H}_3]^{2-}$  groups. Consequently, the intermetallic distance within the unit is  $\text{Cu}^{\text{I}} \cdots \text{Cu}^{\text{I}}$  of 5.1420 (11) Å.

As described above, the coordination environment of each  $\text{Cu}^{\text{II}}$  centre of the bimetallic  $[(\text{phen})\text{Cu}-\mu-(\kappa^2\text{O}:O'\text{-VP}_2\text{O}_{10}\text{H}_3)_2\text{-Cu}(\text{phen})]$  unit is completed with vanadyl O atoms from neighbouring units. This leads to the formation of a covalent one-dimensional structure growing along the  $[100]$  direction. In this way, the chain is formed from two vertex-sharing  $\text{VO}_4$  tetrahedra from  $[\text{VP}_2\text{O}_{10}\text{H}_3]^{2-}$  anions connecting consecutive  $[(\text{phen})\text{Cu}-\mu-(\kappa^2\text{O}:O'\text{-VP}_2\text{O}_{10}\text{H}_3)_2\text{-Cu}(\text{phen})]$  units. The phen molecules are oriented perpendicular to the chain direction. The minimum distance between two phen molecules of neighbouring units is the same as the intermetallic  $\text{Cu}^{\text{I}} \cdots \text{Cu}^{\text{I}}$  distance of 7.2350 (14) Å.

No covalent bonds exist between neighbouring chains of (I). However, the crystal structure is stabilized by  $\pi$ – $\pi$  interactions between two adjacent phen molecules of two neighbouring chains, with a centroid–centroid ( $Cg1$ – $Cg2^{\text{iii}}$ ) distance of 3.852 (1) Å [ $Cg1$  and  $Cg2$  are the centroids of the N1/C6–C10 and C4–C7/C11/C12 rings, respectively; symmetry code: (iii)  $-x + 2, -y + 2, -z + 2$ ] (Fig. 2).

## Experimental

Cupric oxide ( $\text{CuO}$ ; 0.1934 g, 2.43 mmol), 1,10-phenanthroline (phen; 0.0849 g, 0.47 mmol), orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ; 0.41 g, 4.2 mmol), sodium vanadate ( $\text{NaVO}_3$ ; 0.0881 g, 1 mmol) and water ( $\text{H}_2\text{O}$ ; 10 ml, 555.56 mmol) in a 5.2:1:8.9:1.5:1182 molar ratio were mixed in a Teflon Parr reactor and then heated at 473 K for 4 d. The pH of the reaction mixture was 1.1. After the reaction solution had been allowed to cool to room temperature, the products were filtered off and dried at 313 K. Green rhombohedral crystals of (I) were separated manually under a microscope. These proved to be of good enough quality for single-crystal X-ray diffraction (yield 23.6%, based on V). IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): bands 1076 (*s*) and 1000 (*m*) are assigned to the P–O stretch, the band at 889 (*s*) is due to the stretching vibrations of the terminal  $\text{V}=\text{O}$  group, 773 (*s*) is assigned to the V–O–V stretching vibrations, 731 (*w*), 511 (*w*) and 413 (*w*) correspond to the stretching vibrations of the V–O or V–O–P bonds, and 1610 (*m*), 1601 (*m*) and 1473 (*s*) correspond to 1,10-phenanthroline. Analysis calculated for  $\text{C}_{12}\text{H}_{11}\text{CuN}_2\text{O}_{10}\text{P}_2\text{V}$ : C 27.74, H 2.13, N 5.39%; found: C 26.5, H 2.2, N 5.9%.

## Crystal data

$[\text{CuV}(\text{HPO}_4)(\text{H}_2\text{PO}_4)\text{O}_2(\text{C}_{12}\text{H}_8\text{N}_2)]$	$\gamma = 84.91 (3)^\circ$
$M_r = 519.66$	$V = 861.9 (3) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.2350 (14) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.705 (2) \text{ \AA}$	$\mu = 2.02 \text{ mm}^{-1}$
$c = 11.624 (2) \text{ \AA}$	$T = 293 \text{ K}$
$\alpha = 75.25 (3)^\circ$	$0.21 \times 0.11 \times 0.09 \text{ mm}$
$\beta = 82.58 (3)^\circ$	

## Data collection

Siemens SMART CCD area-detector diffractometer	16352 measured reflections
Absorption correction: multi-scan ( <i>SADABS</i> ; Bruker, 2001)	3031 independent reflections
$T_{\text{min}} = 0.56, T_{\text{max}} = 0.80$	2737 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.022$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	262 parameters
$wR(F^2) = 0.076$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.76 \text{ e \AA}^{-3}$
3031 reflections	$\Delta\rho_{\text{min}} = -0.49 \text{ e \AA}^{-3}$

The H-atom positions were calculated after each cycle of refinement using a riding model, with  $\text{C}-\text{H} = 0.93 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent})$ . Efforts to locate the phosphovanadate H atoms in the final Fourier difference map were unsuccessful; those reported for the formula are based on charge-balance analysis. During the final stages of refinement, some disorder was evident on the position of atom

**Table 1**

Selected geometric parameters (Å, °).

Cu1–N1	2.009 (2)	Cu1–O3 <sup>i</sup>	1.9122 (19)
Cu1–N2	2.003 (2)	Cu1–O5	2.632 (2)
Cu1–O2	1.9603 (19)	Cu1–O6 <sup>ii</sup>	2.399 (2)
O3 <sup>i</sup> –Cu1–O2	94.30 (9)	N2–Cu1–N1	82.42 (10)
O3 <sup>i</sup> –Cu1–N2	172.94 (9)	O3 <sup>i</sup> –Cu1–O6 <sup>ii</sup>	102.09 (10)
O2–Cu1–N2	92.16 (9)	O2–Cu1–O6 <sup>ii</sup>	92.22 (9)
O3 <sup>i</sup> –Cu1–N1	91.00 (9)	N2–Cu1–O6 <sup>ii</sup>	80.48 (10)
O2–Cu1–N1	173.99 (9)	N1–Cu1–O6 <sup>ii</sup>	89.43 (9)

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

O10, which bonds a vanadyl and a phosphate group. This is reasonable, since the terminal PO<sub>4</sub> group has no other covalent bond. The disorder was modelled by introducing two positions for O10, *A* and *B*, and their occupancies were subsequently refined subject to the condition that they summed to 1. When it was clear that the occupancies had reached constant values, *viz.* 0.60 and 0.40 for *A* and *B*, respectively, the values were set constant for the final refinement stages.

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 1999); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXTL-NT* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *SHELXTL-NT* and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL-NT*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: YP3013). Services for accessing these data are described at the back of the journal.

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