

Phosphonate based hybrid organic/inorganic open network compounds $[\text{Cu}(\text{bipy})(\text{VO}_2)_2(\text{O}_3\text{PCH}_2\text{PO}_3)\text{H}_2\text{O}]$ and $[\text{Cu}(\text{bipy})(\text{VO}_2)(\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_2\text{OH})] \cdot 1.5\text{H}_2\text{O}$

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Abstract

The hybrid organic/inorganic copper oxovanadium diphosphonates of formula $[\text{Cu}(\text{bipy})(\text{VO}_2)_2(\text{O}_3\text{PCH}_2\text{PO}_3)\text{H}_2\text{O}]$ **1**, which crystallizes in the orthorhombic symmetry, and $[\text{Cu}(\text{bipy})(\text{VO}_2)(\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_2\text{OH})] \cdot 1.5\text{H}_2\text{O}$ **2**, which crystallizes in the monoclinic symmetry, were obtained by the soft hydrothermal route. The layered VPOC structure of **1** may be described as a undulating $(\text{VO}_2)_2(\text{O}_3\text{PCH}_2\text{PO}_3)(\text{H}_2\text{O})^{2-}$ network formed by the link between the $\text{V}_2\text{PCO}_{10}$ rings via the diphosphonate fragments, creating 18-membered $\{\text{V}_4\text{P}_5\text{C}_2\text{O}_7\}$ cavities. The corrugated lamellar structure of **2** is obtained by the interconnection of four oxovanadium phosphorus $\text{V}_4\text{P}_8\text{C}_8\text{O}_8$ anionic rings with diphosphonate fragments, forming 28-atom cavities. In both compounds the copper diimine cation groups are coordinated to the chelating oxygen atoms of the PO_3 and oxovanadium groups, and do not participate in building the 2D-structure.

Keywords: Hydrothermal; Diphosphonate; VPO; Porous materials; Copper

1. Introduction

The oxovanadium phosphate compounds present a great diversity of structures, which is in part related to the oxidation state of vanadium, and to the way in which the different polyhedra of vanadium and phosphorus are condensed, sharing corners, edges and/or faces [1]. Many efforts have been made to synthesize this kind of new open frameworks based on the VPO sub-structure due to their potential applications as sorbents and catalysts [2–4].

The source of phosphorus can be simple tetrahedral phosphate anions or organic derivatized moieties of the tetrahedral phosphate subunits, in the form of diphosphonates, among others [5–10]. The latter present variations in the tether length in the diphosphonate compounds, from methylene to octylene, which may be used in generating new structural modifications in the VPO phases. In this way organic hydrophobic fragments may be introduced into the oxide substructure, the size variation of the organic part providing a method for the design of new porous materials.

In this context, we herein report on the structure of the two-dimensional compounds $[\text{Cu}(\text{bipy})(\text{VO}_2)_2(\text{O}_3\text{PCH}_2\text{PO}_3)\text{H}_2\text{O}]$ **1** with 18-membered $\{\text{V}_4\text{P}_5\text{C}_2\text{O}_7\}$ windows, and $[\text{Cu}(\text{bipy})(\text{VO}_2)(\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_2\text{OH})] \cdot 1.5\text{H}_2\text{O}$ **2** with 28-membered $\{\text{V}_4\text{P}_8\text{C}_8\text{O}_8\}$ windows (where bipy stands for 2,2'-bipyridine).

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2. Experimental

2.1. Syntheses

For the syntheses of the reported compounds the following reagents were used: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, V_2O_5 , 2,2'-bipyridine, methylenediphosphonic acid (as trisodium salt tetrahydrate), ethylene- and propylenediphosphonic acids. Reagents were purchased from Aldrich Chemicals, and Merck (copper nitrate). The hydrothermal reactions were carried out under autogenous pressure at 120 °C for 72 h, in 23 ml polytetrafluoroethylene-lined stainless steel bombs. After the reaction vessels were slowly cooled down to room temperature, the resulting products were filtrated off, washed with distilled water and dried under vacuum in a desiccator. Single crystals, suitable for X-ray diffraction studies and thermal analysis, were collected by visual examination under a microscope.

The hydrothermal reaction of V_2O_5 (0.0765 g), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.203 g), bipy (0.066 g), methylenediphosphonic acid (trisodium salt tetrahydrate) (0.132 g) and H_2O (5 ml) in a molar ratio of 1:2:1:1:662 gave dark-green prismatic crystals of **1**. The analogous reaction with ethylenediphosphonic acid yields blue crystals of **2**, and with propylenediphosphonic acid noncrystalline products are obtained.

2.2. Phase identification and thermal treatment

Phase identification was carried out with X-ray powder diffraction technique on a D5000 Siemens diffractometer using $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$).

Thermogravimetric measurements were performed with a TGA50 analyzer Shimadzu. The products were heated up to 1173 K under flowing N_2 (50 ml/min) and a heating rate of 2 K/min. for both compounds. The resulting products were analyzed by X-ray powder diffraction and showed unknown diffraction patterns.

2.3. Structure determination

Single crystal diffraction experiments were conducted at room temperature using an Enraf–Nonius diffractometer with graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and equipped with a CCD detector. The intensity data collection was performed in the ω - ϕ scanning mode with the goniometer and detector angular settings optimized using the program COLLECT [11]. The crystal-to-detector distance was 25 mm. The unit cell and the orientation matrix were refined using the entire data set of reflections. The diffraction spots were measured in full with a high accuracy, scaled with SCALEPACK, corrected for Lorentz-polarization correction and integrated using DENZO [11]. Data integration was made using SAINT [12]. Absorption corrections have been made using SADABS [13]. The structures were solved by means of direct methods (SHELXS-97) [14], and completed by Fourier

Table 1

Crystal data and summary of data collection, structure solution and refinement for $[\text{Cu}(\text{bipy})(\text{VO}_2)_2(\text{O}_3\text{PCH}_2\text{PO}_3)\text{H}_2\text{O}]$ **1** and $[\text{Cu}(\text{bipy})(\text{VO}_2)(\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_2\text{OH})] \cdot 1.5\text{H}_2\text{O}$ **2**

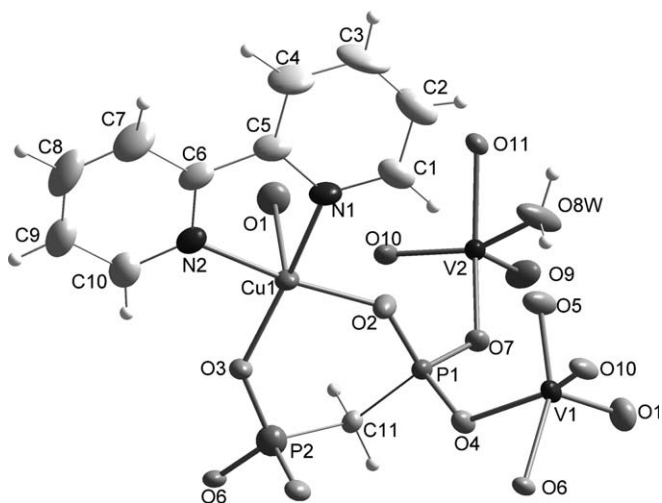
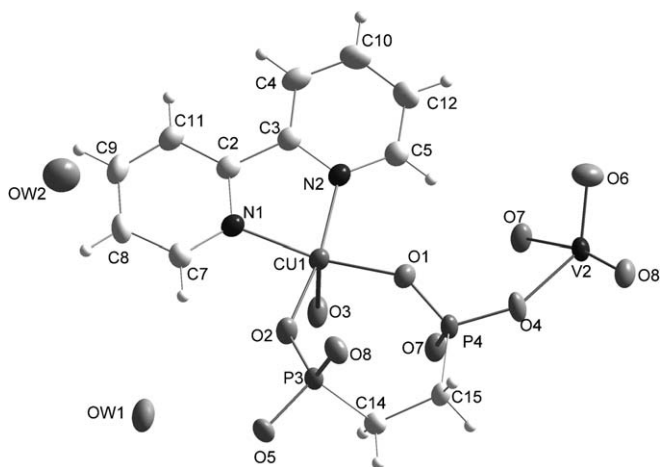
Empirical formula	$\text{C}_{11}\text{H}_{12}\text{CuN}_2\text{O}_{11}\text{P}_2\text{V}_2$ 1	$\text{C}_{12}\text{H}_{16}\text{CuN}_2\text{O}_{9.5}\text{P}_2\text{V}_2$ 2
Color; habit	Blue; needle	Blue; block
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbca</i>	<i>C2/c</i> ($n^\circ 15$)
Unit cell dimensions	$a = 13.582(1)$ $b = 13.301(1)$ $c = 20.126(2)$	$a = 18.062(2) \text{ \AA}$ $b = 13.182(1) \text{ \AA}$ $c = 15.349(2) \text{ \AA}$ $\beta = 107.21(2)^\circ$
Volume	$V = 3635.9(6) \text{ \AA}^3$	$V = 3490.8(6) \text{ \AA}^3$
Z	8	8
Formula weight	$575.59 \text{ g mol}^{-1}$	$516.69 \text{ g mol}^{-1}$
Density (calc.)	2.103 g cm^{-3}	1.968 g cm^{-3}
Absorption coefficient	24.05 cm^{-1}	19.9 cm^{-1}
Maximum 2θ	$2\theta \leq 46^\circ$	$2\theta \leq 50^\circ$
Data collected	$h : -15, +15$ $k : -15, +15$ $l : -23, +23$	$h : -21, +21$ $k : -15, +15$ $l : -18, +17$
Unique data after merging	2857	3073
Observed data ($>2.0\sigma(F^2)$)	2517	2550
Free parameters	270	255
R_{int}	0.0581	0.0597
Residuals R_1 ($F^2 > 2.0\sigma(F^2)$)	0.0410	0.0351
w R_2	0.0919	0.0841
Min., max. ($e/\text{\AA}^3$)	-0.33, +0.55	-0.52, +0.48
Goof	1.16	1.089

difference syntheses and then refined using SHELXL-97 [15]. The R values for the final cycle of the refinements based on F_0^2 are listed in Table 1, together with additional data collection and refinement details.

3. Results and discussion

3.1. Syntheses

To investigate the influence of the variation of the length of the diphosphonate space group on the formation of organo-inorganic hybrid compounds with an open network, we selected diphosphonate ligands with three organic tether lengths such as $-\text{CH}_2-$, $-\text{C}_2\text{H}_4-$ and $-\text{C}_3\text{H}_6-$. Other reactants and experimental conditions were kept the same for all the syntheses. In such a specific hydrothermal process, many factors may affect the formation and the crystal growth of products, such as the type of initial reactants, pH value, reaction time and temperature. When the sodium salt of methylenediphosphonic acid is used, the initial pH value is 5 and the final value is 2; when the ethylene and propylenediphosphonic acids are used the values were 1 and 2, respectively, while for both the final pH value was 1. In spite of having the same pH value when finalizing the reaction, it was not possible to obtain a crystalline product for the propylenediphosphonic ligand. In this

Fig. 1A. Asymmetric unit of $[\text{Cu}(\text{bipy})(\text{VO}_2)_2(\text{O}_3\text{PCH}_2\text{PO}_3)\text{H}_2\text{O}]$ **1**,Fig. 1B. Asymmetric unit of $[\text{Cu}(\text{bipy})(\text{VO}_2)(\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_2\text{OH})] \cdot 1.5\text{H}_2\text{O}$ **2**.

way, maintaining the experimental conditions and only varying the diphosphonate ligands, two different compounds were obtained: $[\text{Cu}(\text{bipy})(\text{VO}_2)_2(\text{O}_3\text{PCH}_2\text{PO}_3)\text{H}_2\text{O}]$ **1** and $[\text{Cu}(\text{bipy})(\text{VO}_2)(\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_2\text{OH})] \cdot 1.5\text{H}_2\text{O}$ **2**. Surprisingly **2** resulted to be the compound previously reported by Yucesan et al. [8]. The same compound has been obtained under different conditions: a different source of vanadium (V) (V_2O_5 instead of Na_3VO_4), a different stoichiometry of the starting reagents, and an heating time of 72 h, instead of 48 h as informed by Yucesan et al. This fact confirms that hydrothermal reactions are not stoichiometric, and the mechanisms involved during hydrothermal syntheses remain obscure [16].

3.2. Description of crystal structures

3.2.1. $[\text{Cu}(\text{bipy})(\text{VO}_2)_2(\text{O}_3\text{PCH}_2\text{PO}_3)\text{H}_2\text{O}]$ (**1**)

The asymmetric unit of compound **1** is represented in Fig. 1A, selected bond lengths and bond angles for **1** are given in Table 2. The copper atoms are in a square pyramidal environment: two nitrogen atoms from the bipy ligand ($d_{\text{Cu-N}}$: 1.983(4) Å and 1.986(4) Å), and two oxygen atoms from the chelating diphosphonate ligand ($d_{\text{Cu-O}}$: 1.906(3) Å and 1.907(3) Å) form the basal plane of the pyramid while the apical position is occupied by an oxygen atom from an oxo-vanadium group ($d_{\text{Cu-O}}$: 2.438(3) Å). Vanadium (V) atoms have square pyramidal geometries. The basal planes of the square pyramids are defined by: an unshared oxygen atom, from a vanadyl group for V1 ($d_{\text{V1-O}}$: 1.632(3) Å), and an oxygen atom from a water molecule for V2 ($d_{\text{V2-O}}$: 2.021(4) Å); two oxygen atoms from two different diphosphonate ligands ($d_{\text{V1-O}}$: 1.964(3) Å and 2.037(3) Å; $d_{\text{V2-O}}$: 1.921(3) Å and 1.932(3) Å), and an oxygen atom shared between the two vanadium atoms forming the $\text{V}_2\text{O}_9^{8-}$ entities ($d_{\text{V1-O}}$: 1.973(3) Å and $d_{\text{V2-O}}$: 1.673(3) Å). The apical position is occupied, for V1, by an oxygen atom shared with a copper(II) centre ($d_{\text{V1-O}}$: 1.606(3) Å), and for V2

Table 2
Selected bond lengths (Å) and bond angles (°), with their standard deviation in brackets, for $[\text{Cu}(\text{bipy})(\text{VO}_2)_2(\text{O}_3\text{PCH}_2\text{PO}_3)\text{H}_2\text{O}]$ **1**

<i>Cu1</i>					<i>P1</i>				
O2	1.906(3)				O2	1.505(3)			
O3	1.907(3)	96.2(1)			O7	1.530(3)	110.9(2)		
N1	1.983(4)	90.8(1)	166.8(1)		O4	1.531(3)	113.4(2)	107.9(2)	
N2	1.986(4)	172.2(1)	91.6(1)	81.4(2)	C11	1.791(4)	108.0(2)	108.6(2)	107.9(2)
O1	2.438(3)	91.5(1)	103.4(1)	87.5(1)					87.7(1)
<i>V1</i>					<i>P2</i>				
O1	1.606(3)				O3	1.505(3)			
O5	1.632(3)	106.0(2)			O6	1.516(3)	110.2(2)		
O4	1.964(3)	107.9(1)	95.5(1)		O11	1.530(3)	111.2(2)	111.8(2)	
O10	1.973(3)	107.8(1)	88.6(1)	141.3(1)	C11	1.801(4)	109.0(2)	108.5(2)	105.9(2)
O6	2.037(3)	103.2(1)	150.5(1)	79.1(1)					78.7(1)
<i>V2</i>									
O9	1.585(3)								
O10	1.673(3)	107.4(2)							
O7	1.921(3)	99.1(2)	96.8(2)						
O11	1.932(3)	100.1(2)	92.1(1)	155.3(1)					
O8W	2.021(4)	111.9(2)	140.5(2)	80.7(1)					
				77.9(1)					

by an unshared oxygen strongly bonded to the vanadium (d_{V2-O} : 1.585(3) Å). The methylenediphosphonic ligand shares all its oxygen atoms: two of them with one copper(II) centre (d_{P-O} : 1.505(3) Å and 1.505(3) Å), and the others with four vanadium atoms (1.516(3) Å $< d_{P-O} <$ 1.531(3) Å). Bond valence sums [17] were performed for the copper and vanadium atoms. The sums are consistent with the assumed divalent and pentavalent oxidation states for copper and vanadium, respectively 1.98 for Cu, 5.19 for V1 and 5.09 for V2, (see Table 2).

As frequently observed for oxovanadium phosphate compounds, a cyclic motif VOPOV is observed built up by the sharing of two oxygen atoms from a phosphorus tetrahedra (P1) of the methylenediphosphonate with two square pyramid VO₅ linked by vertex sharing. These groups are linked to each other by two oxygen atoms from the other phosphorus tetrahedra (P2). This generates infinite chains connected by the organic part of the diphosphonate group to form layers parallel to the [001] plane in which 18-membered {V₄P₅C₂O₇} cavities with an approximate free aperture of 3 × 5 Å² are observed (Fig. 2A).

The Cu(bipy)²⁺ least squares planes define a dihedral angle of 57.0° with the vanadium–phosphonate layer plane. The distance between two nearest neighbors at one side of each layer is 9.5120(10) Å, while the value for two nearest neighbors at opposite sides of the layer is 8.4276(9) Å. The shortest metal to metal distance in the solid corresponds to two cupric centers belonging to two consecutive layers and located between them: 5.1393(12) Å. The Cu(bipy)²⁺ fragments corresponding to these two neighbor atoms show their respective aromatic rings parallel one to

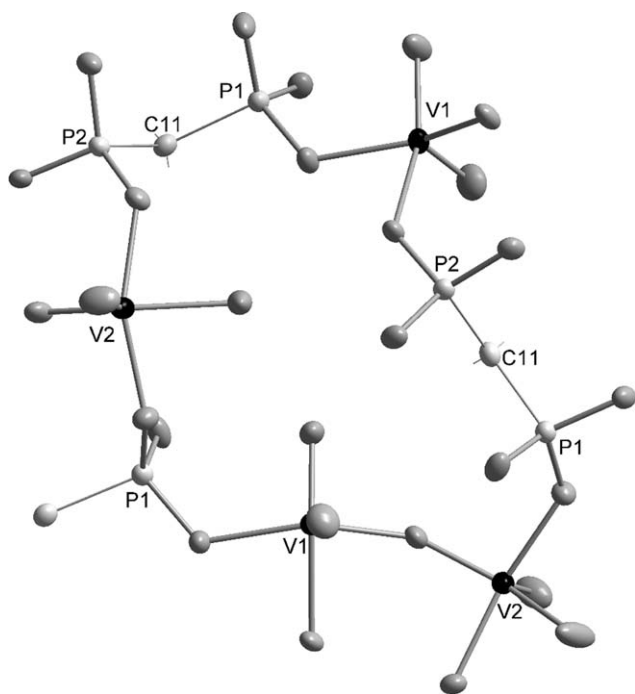


Fig. 2A. 18-Membered ring {V₄P₅C₂O₇} formed in the crystalline structure of 1.

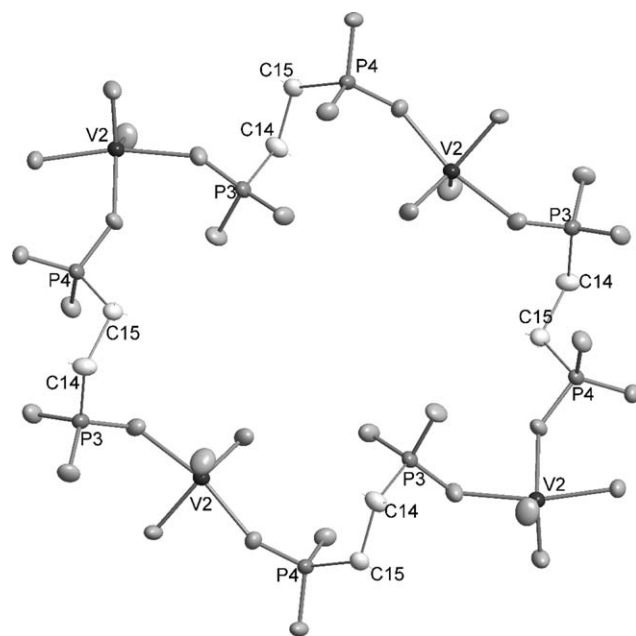


Fig. 2B. 28-Membered ring {V₄P₈C₈O₈} formed in the crystalline structure of 2.

the other, separated by 3.5 Å, defining a stacking pattern between two consecutive sheets separated by a distance of approximately 10.06 Å. The crystal packing of 1 is shown in Fig. 3A.

3.2.2. [Cu(bipy)(VO₂)(O₃P(CH₂)₂PO₂OH)] · 1.5H₂O (2)

The asymmetric unit of compound 2 is shown in Fig. 1B, selected bond lengths and bond angles for 2 are given in Table 3. The coordination sphere around the copper atoms is also square pyramidal as in compound 1: the basal plane is defined by the nitrogen atoms of the bipy ligand (Cu–N: 1.983(3) Å and 2.009(3) Å), and the oxygen atoms of each of the PO₃ groups from the chelating diphosphonate ligand (d_{Cu-O} : 1.913(2) Å and 1.932(2) Å), with an oxygen atom

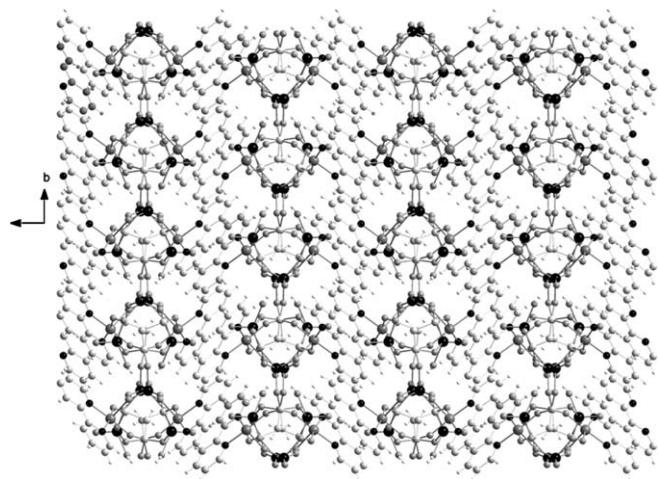


Fig. 3A. Crystalline packing for 1 along *a*.

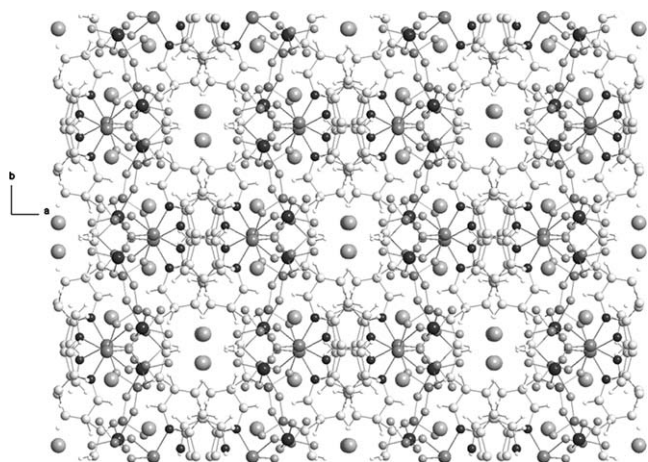


Fig. 3B. Crystalline packing for **2** along *c*, showing solvate water molecules.

from an oxovanadium group in the apical position ($d_{\text{Cu-O}}$: 2.264(2) Å). The vanadium (V) atom has a bipyramidal geometry with a terminal oxygen atom ($d_{\text{V-O}}$: 1.610(3) Å), three oxygen atoms from diphosphonate ligands (1.961(2) Å $< d_{\text{V-O}} <$ 2.018(2) Å), and the oxygen bonded to the copper atom ($d_{\text{V-O}}$: 1.632(2) Å). Thus, the diphosphonate ligands simultaneously chelate the copper centres and link to an oxovanadium group in a monodentate fashion. Each PO_3 group exhibits one pendant (P–O) group which is protonated. Bond valence calculations [17], performed for the copper and vanadium atoms, sum to 2.06 (Cu) and 5.02 (V), and are consistent with the divalent and pentavalent oxidation states of copper and vanadium, respectively.

The oxovanadium organic diphosphonate compound $\text{Cu}(\text{bipy})(\text{VO}_2)(\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_2\text{OH}) \cdot 1.5\text{H}_2\text{O}$ **2** presents a puckered bidimensional structure with layers parallel to the [100] plane. Each layer is formed by the square pyramidal copper(II) polyhedra, the vanadium(V) trigonal bipyramids, and phosphorus tetrahedra which are linked by the hydrophobic $\text{CH}_2\text{--CH}_2$ chain of the diphosphonate moiety. The layer structure can be described as formed of 18-membered $\{\text{V}_2\text{P}_2\text{O}_{14}\}$ rings in which the phosphorus atom is part of the diphosphonate ligand. The other phosphorus

from the diphosphonate spacer ensures the connectivity to a vanadium atom of the next nearest ring to generate large 28-membered cavities $\{\text{V}_4\text{P}_8\text{C}_8\text{O}_8\}$ with an approximate free aperture of $8 \times 8 \text{ \AA}^2$ (Fig. 2B). The packing of the layers is ensured by the bipy molecules which interdigitate with intermolecular distances of 3.4 Å. The bipy ligands extend from the layers in opposite directions, roughly along [101] with their mean plane parallel to the $[\bar{1}01]$ plane. In this way, the complex cations $\text{Cu}(\text{bipy})^{2+}$ stabilize the void regions within the anion structure by adopting charge compensating and space filling roles [9]. At last, tunnels with approximate cross-section of $3 \times 4 \text{ \AA}^2$ propagate along the *c*-direction in which part of the crystallization water molecules are located (Fig. 3B).

Similar layers consisting of $\text{V}_2\text{P}_2\text{O}_{14}$ rings with 16-membered voids $\{\text{V}_4\text{P}_4\text{C}_4\text{O}_4\}$ have been described by Soghomonian et al. [18] in which the compensating cations correspond to interlamellar ammonium species. In such reported open network, two diphosphonate fragments and two $\text{V}_2\text{P}_2\text{O}_{14}$ rings are responsible of the generation of the void spaces, while the 4-membered rings are fused through the vanadium atoms. In compound **2**, however, the same rings are isolated.

As already mentioned by Finn et al. [9], it is worth noting that the VPO sub-structure does not require copper to establish the network connectivity. In both compounds **1** and **2**, the copper atoms are slightly displaced off the mean plane of the cavities in opposite directions. In this way, the complex cations $\text{Cu}(\text{bipy})^{2+}$ stabilize the void regions within the anionic structure by adopting charge compensating and space filling roles [9].

While the interlayer distance is lower for compound **2** than for **1** ($d_{\text{inter}} = 8.75 \text{ \AA}$, $d_{\text{inter}} = 10.08 \text{ \AA}$, respectively) the crystal density is weaker for **2** than for **1** ($d = 1.981 \text{ g cm}^{-3}$ and $d = 2.103 \text{ g cm}^{-3}$, respectively). The existence of an extra methylene group in the phosphonate ligand for **2** may explain this result as significant differences in the inorganic VPOC structure are observed: the inorganic skeleton of **1** presents 18-membered $\{\text{V}_4\text{P}_5\text{C}_2\text{O}_7\}$ rings with an approximate free aperture of 15 \AA^2 while the network of **2** presents 28-membered cavities $\{\text{V}_4\text{P}_8\text{C}_8\text{O}_8\}$ with an approximate free aperture of 64 \AA^2 .

Table 3

Selected bond lengths (Å) and bond angles (°), with their standard deviation in brackets, for $\text{Cu}(\text{bipy})(\text{VO}_2)(\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_2\text{OH}) \cdot 1.5 \text{ H}_2\text{O}$ **2**

<i>Cu1</i>					<i>P1</i>				
O2	1.913(2)				O2	1.503(2)			
O1	1.932(2)	93.6(1)			O8	1.511(2)	112.3(2)		
N1	1.983(3)	89.9(1)	166.1(1)		O5	1.564(2)	108.8(1)	111.0(1)	
N2	2.009(3)	169.0(1)	93.9(1)	80.9(1)	C14	1.792(3)	112.7(2)	110.2(2)	101.2(2)
O3	2.264(2)	91.3(1)	98.9(1)	94.4(1)					
				95.4(1)					
<i>V2</i>					<i>P2</i>				
O6	1.610(3)				O7	1.521(2)			
O3	1.632(2)	109.4(1)			O4	1.523(2)	112.4(1)		
O4	1.961(2)	128.3(1)	122.2(1)		O1	1.525(3)	112.9(1)	111.3(1)	
O7	1.963(2)	93.8(1)	96.5(1)	84.6(1)	C15	1.793(3)	106.9(2)	104.3(2)	108.5(2)
O8	2.018(2)	93.7(1)	91.8(1)	81.8(1)					
				166.4(1)					

The large cavity in **2** allows the presence of two free water molecules but only one, linked to the vanadium atom, can be inserted in the layer cavity of compound **1**.

While the structure of **1** contains binuclear corner-sharing units of vanadium square pyramid, the structure of **2** exhibits trigonal bipyramid mononuclear vanadium centres. Moreover, the peculiar arrangement of the bipy ligands in compound **2** generate tunnels with an approximate cross-section of $3 \times 4 \text{ \AA}^2$, propagated along the *c*-direction (Fig. 3B) in which crystallization water molecules are located.

3.3. Thermal analysis

Thermal analysis for **1** shows a two steps loss of weight. The first one takes place in the range of 450–490 K and corresponds to the loss of the coordination water molecules ($\sim 3.8\%$ of weight loss). The intermediate product is thermally stable up to 550 K. The second one takes place in the range of 550–1173 K showing a gradual loss of weight of 25.6%, and it is attributed to the loss of the organic fragments (2,2'-bipyridine and the organic fragment of the diphosphonate group). The thermogravimetric analysis done under air atmosphere shows a similar behaviour.

Compound **2** shows in the range of 298–530 K a two step loss of weight due to the solvate water molecules ($\sim 6\%$ of total weight loss). This is due to the fact that two different crystallographic sites for the water molecules are present in the crystalline structure. The thermogravimetric analysis of the anhydrous form exhibits a gradual weight loss of 35.4% in the range of 550–1100 K, corresponding also to the loss of the organic species.

4. Conclusion

The two hybrid organic/inorganic compounds $[\text{Cu}(\text{bipy})(\text{VO}_2)_2(\text{O}_3\text{PCH}_2\text{PO}_3)\text{H}_2\text{O}]$ **1** and $\text{Cu}(\text{bipy})(\text{VO}_2)(\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_2\text{OH}) \cdot 1.5\text{H}_2\text{O}$ **2** have been synthesized using the soft hydrothermal route. The structures solved by single crystal X-ray diffraction present 18-membered $\{\text{V}_4\text{P}_5\text{C}_2\text{O}_7\}$ rings with an approximate free aperture of $3 \times 5 \text{ \AA}^2$ for compound **1**, and 28-membered cavities $\{\text{V}_4\text{P}_8\text{C}_8\text{O}_8\}$ with an approximate free aperture of

$8 \times 8 \text{ \AA}^2$ for compound **2**. For both compounds the complex cations $\text{Cu}(\text{bipy})^{2+}$ stabilize the void regions within the anionic structure by adopting charge compensating and space filling roles.

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