

Novel examples of hybrid organic–inorganic solids based on $V_4O_{12}^{4-}$ building blocks

E. Le Fur ^{a,*}, J.Y. Pivan ^a, S. Ushak ^b, D. Venegas-Yazigi ^b, E. Spodine ^{b,*}

^a *Sciences Chimiques de Rennes UMR 6226, CNRS-Université de Rennes 1-ENSCR, 35042 Rennes Cedex, France*

^b *Centro Para la Investigacion Interdisciplinaria Avanzada en Ciencia de los Materiales (CIMAT), Facultad de Ciencias Químicas y Farmaceuticas, Universidad de Chile, Casilla 233, Santiago, Chile*

Abstract

New hybrid organic/inorganic copper oxovanadium compounds of composition $[Cu(dpa)_2]_4V_4O_{12}$ (**1**), $Cu_2(bipy)_2V_4O_{12}$ (**2**), and $Cu_2(bipy)_2V_6O_{17}$ (**3**), which crystallize in the monoclinic **1**, **2** and triclinic **3** symmetry, respectively, were obtained by soft hydrothermal routes. The first two structures present isolated $[V_4O_{12}]^{4-}$ anionic units, the structure of **3** exhibits the same $[V_4O_{12}]^{4-}$ cycles coupled by V_2O_5 dimeric bridges propagated as an infinite chain along the *c*-direction **3**. For compound **1**, the copper(I) centers are bonded to four nitrogen atoms with a distorted tetrahedral geometry. For compounds **2** and **3**, the copper(II) centers are square pyramidal with two nitrogen atoms from the neutral diimine ligand and three oxygen atoms from the oxovanadium sub-unit. In all the compounds described herein, the vanadium ions are as V(V), occupying solely tetrahedral sites.

Keywords: Synthesis; X-ray crystal structures; Vanadates

1. Introduction

A powerful synthetic approach for the preparation of porous metal–organic frameworks is given by the combination of metal oxides with secondary metal centers in the form of complex ions, which can be regarded as the organizing entities of the oxide structure. The VO_4 unit can be considered as a building block for the preparation of oxovanadium based zeolitic materials, since the tetrahedral VO_4 unit present in many oxovanadium compounds has a topology similar to SiO_4 and AlO_4 moieties found in aluminosilicates. The term zeolitic materials in connection with organo–inorganic frameworks is not meant to imply that the full functionality of zeolites is expected to be reproduced. Thus, the oxovanadium metal–organic frameworks are extensively studied since conceptually they are expected

to exhibit catalytic and sorptive properties unobserved or similar to those observed in conventional zeolites.

The tetravanadate $[V_4O_{12}]^{4-}$ is actually being used as a building block for the preparation of novel organo–inorganic hybrid materials. This moiety has been reported in 0D compounds such as $[Fe(bipy)_3]_2[V_4O_{12}] \cdot 10H_2O$ [**1**], $[Zn(bipy)_2]_2[V_4O_{12}]$ [**2**], $[Mn(bipy)_2]_2[V_4O_{12}]$ [**3**]; in 1D compounds as reported for $[Co(phen)_2]_2[V_6O_{17}]$ [**4**], $[Ni(phen)_2]_2[V_6O_{17}]$ [**5**]. Also some 2D and 3D structures can be found in the literature, $[Cu_2(bipy)_2][V_6O_{17}]$ among others [**6–10**].

2. Experimental

2.1. Synthesis

The raw products were purchased from Aldrich and used without any further purification. The reaction mixture for the syntheses consists of $Cu(NO_3)_2 \cdot 3H_2O$, V_2O_5 , Zn and 2,2'-bipyridine (bipy) or 2,2'-dipyridylamine (dpa)

* Corresponding authors. Fax: +33 2 23 23 81 99 (E. Le Fur).

E-mail addresses: eric.le-fur@ensc-rennes.fr (E. Le Fur), espodine@ciq.uchile.cl (E. Spodine).

and Na₃(PO₄) (basic conditions) or ethylenediphosphonic acid (acid conditions). In each case, the mixture is loaded in a Teflon-lined stainless steel autoclave (23 mL) and heated at 120 °C for 72 h, and then the temperature is slowly lowered to 80 °C (10 °C/h). After the reaction, the vessel is cooled down to room temperature, the solid phase is filtered off, rinsed with water and dried under vacuum in a desiccator.

The hydrothermal reaction, in basic conditions, of V₂O₅ (0.0765 g), Cu(NO₃)₂ · 3H₂O (0.203 g), Na₃PO₄ (0.344 g), Zn (0.053 g), dipyrindylamine (0.072 g) and H₂O (5 mL) in a molar ratio of 1:2:5:1:662 gave orange crystals of **1**. The hydrothermal reaction in acid conditions of V₂O₅ (0.0765 g), Cu(NO₃)₂ · 3H₂O (0.203 g), Zn (0.053 g), bipy (0.066 g), ethylenediphosphonic acid (0.080 g) and H₂O (5 mL) in a molar ratio of 1:2:1:1:662 gave light-green plate crystals of **3**. When the amounts of the preceding reagents were reduced to half of the initial concentrations, light-green plate crystals corresponding to compound **2** were obtained. For the studied systems, the solid phase consists of crystals, together with unidentified by-products. Subsequent attempts involving different reaction temperatures, reaction time and concentration did not improve the yields of the reaction; thus optimal conditions to obtain compounds **1–3** as pure crystalline phases have been unsuccessful so far. Single crystals suitable for X-ray diffraction studies were collected by visual separation under a microscope.

2.2. Structure determination

The crystal structures of **1–3** were determined by single crystal X-ray diffraction methods. The experiments were conducted at room temperature using a Bruker SMART APEX diffractometer or a four-circle Nonius KappaCCD diffractometer, with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The intensity data collection was

performed in the ω - ϕ scanning mode, through the program COLLECT [11] for the KappaCCD. Data integration was made using SAINT [12] for the SMART APEX diffractometer while Lorentz-polarization correction, peak integration, and background determination were carried out with the program DENZO [13], frame scaling and unit-cell parameter refinement were performed with the program SCALEPACK [13] for the KappaCCD. The structures were solved using XS in SHELXTL by means of direct methods completed by Fourier difference syntheses and then refined using XL in SHELXTL [14] or SIR-97 [15] with SHELXL-97 [16] for structure refinement using WINGX software [17]. The R values for the final cycle of the refinements based on F_o^2 are listed in Table 1, together with additional data collection and refinement details. Bond distances and angles are listed in Table 2.

3. Results and discussion

3.1. Synthesis

A great variety of organic/inorganic hybrid 1D, 2D, even 3D, solids had been synthesized by using hydrothermal procedures in the last years [18–24]. Such factors as temperature, reaction time, pH, concentrations of the reactants and the nature of the starting reagents have been explored, among others, by different teams in order to find the best conditions to obtain pure phases and to optimize the experimental procedures. In the present work, we have used V₂O₅ as the unique source of vanadium, and have varied the molar ratios of the reactants, and the initial pH value, by using ethylenediphosphonic acid and Na₃PO₄ as sources of phosphorus. From our results, some parameters seem to be relevant to the nature of the obtained products. Increasing the pH value by the use of Na₃PO₄ instead of the diphosphonic acid and maintaining vanadium(V) as initial vanadium source leads to the reduction of copper(II)

Table 1
Crystal data and refinement details for [Cu(dpa)₂]₄V₄O₁₂ (**1**), Cu₂(bipy)₂V₄O₁₂ (**2**), Cu₂(bipy)₂V₆O₁₇ (**3**)

	1	2	3
Chemical formula	C ₁₆₀ H ₁₄₄ N ₄₈ Cu ₈ O ₂₄ V ₈	C ₄₀ H ₃₂ N ₈ Cu ₄ O ₂₄ V ₈	H ₁₆ C ₂₀ N ₄ Cu ₂ O ₁₇ V ₆
Formula weight	4039.10	1670.45	1017.08
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	13.063(1)	8.098(1)	7.949(1)
<i>b</i> (Å)	23.549(2)	17.367(2)	9.863(1)
<i>c</i> (Å)	14.136(1)	9.640(1)	10.521(1)
α (°)	90.	90.	98.61(0)
β (°)	107.39(0)	106.08(0)	102.9(1)
γ (°)	90.	90.	106.9(1)
<i>V</i> (Å ³)	4149.8(14)	1302.7(8)	748.8(8)
<i>T</i> (K)	293	293	293
λ (Mo K α) (Å)	0.71073	0.71073	0.71073
$\rho_{\text{calc.}}$ (g cm ⁻³)	1.616	2.129	2.255
μ (Mo K α) (mm ⁻¹)	1.511	3.050	3.260
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0757	0.0512	0.0312
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.1356	0.0664	0.0798
Goodness-of-fit	1.255	1.690	1.029

Table 2

Selected bond lengths (Å) and bond angles (°), with their standard deviation in brackets, for [Cu(dpa)₂]₄V₄O₁₂ (**1**), Cu₂(bipy)₂V₄O₁₂ (**2**) and Cu₂(bipy)₂V₆O₁₇ (**3**)

Complex (1)					
<i>Cu1</i>			<i>V2</i>		
N6	2.001 (9)		O2	1.620 (6)	
N1	2.000 (9)	120.8 (4)	O3	1.640 (7)	109.3 (4)
N2	2.015 (9)	119.5 (4)	O4	1.776 (7)	108.1 (3)
N4	2.025 (9)	93.1 (4)	O1	1.796 (6)	111.1 (3)
		121.8 (4)			110.5 (3)
		108.8 (4)			108.8 (3)
<i>Cu2</i>			<i>V1</i>		
N7	1.990 (9)		O5	1.612 (7)	
N11	1.995 (9)	131.45 (4)	O6	1.629 (6)	109.9 (4)
N10	2.004 (9)	113.6 (4)	O1	1.782 (7)	111.0 (3)
N9	2.040 (9)	91.8 (4)	O4	1.785 (7)	111.7 (4)
		108.0 (4)			109.7 (3)
		123.8 (4)			107.8 (3)
Complex (2)					
<i>Cu1</i>			<i>V2</i>		
O1	1.947 (3)		O5	1.616 (3)	
O6	1.959 (3)	92.5 (2)	O6	1.662 (3)	110.7 (2)
N1	1.976 (4)	92.3 (2)	O4	1.768 (4)	109.7 (2)
N2	1.977 (4)	173.8 (2)	O3	1.794 (3)	110.0 (2)
O5	2.201 (3)	92.3 (2)			104.8 (2)
		98.6 (1)			111.3 (2)
		100.8 (2)			110.4 (2)
		88.6(2)			
<i>V1</i>			<i>V2</i>		
O2	1.594 (4)		O5	1.616 (3)	
O1	1.670 (4)	108.9 (2)	O6	1.662 (3)	110.7 (2)
O3	1.795 (4)	108.7 (2)	O4	1.768 (4)	109.7 (2)
O4	1.797 (4)	109.6 (2)	O3	1.794 (3)	110.0 (2)
		111.1 (2)			111.3 (2)
		110.1 (2)			104.8 (2)
		108.5 (2)			110.4 (2)
Complex (3)					
<i>Cu1</i>			<i>V2</i>		
O3	1.919 (3)		O6	1.577 (3)	
O1	1.928 (3)	90.6 (1)	O5	1.728 (3)	108.6 (2)
N2	1.987 (3)	90.8 (1)	O7	1.743 (3)	110.8 (2)
N1	1.990 (3)	165.3(1)	O4	1.744 (3)	110.2 (2)
O2	2.255 (3)	97.7 (1)			109.9 (2)
		96.7 (1)			109.0 (2)
		95.1 (1)			108.3 (1)
		95.5(1)			
<i>V1</i>			<i>V3</i>		
O2	1.616 (3)		O9	1.583 (3)	
O3	1.643 (3)	111.0 (1)	O1	1.644 (3)	111.0 (2)
O8	1.761 (1)	110.2 (1)	O7	1.796 (3)	108.3 (2)
O4	1.796 (3)	107.7 (1)	O5	1.799 (3)	109.4 (2)
		112.6 (1)			111.8 (2)
		106.5 (1)			106.6 (2)

to copper(I), generating the molecular compound **1**. The reduction of copper(II) to copper(I) under hydrothermal conditions in the presence of oxidizable nitrogenous ligands is not unusual [25]. Besides, under the used synthetic conditions, whatever was the source of phosphorus, the isolated crystals corresponded to pure vanadate phases. While phosphorus is not incorporated into the product, the different sources of phosphorus play an important role in the hydrothermal synthesis, as attempts to prepare the isolated compounds in the absence of the mentioned reagents proved unsuccessful. The influence of reactants not present in the products had been previously noted [26,27].

Very recently, Xie and Mao reported the preparation of [Cu₂(bipy)₂][V₆O₁₇] directly from Cu(CH₃COOH)₂ and NH₄VO₃ without using a phosphorus reagent [10]. Higher temperature (170 °C) and longer period of heating (5 days) were used. Since the structure of the reported compound is the same as that of **3**, it becomes evident that a different nature of the initial source of vanadium or copper together with other variables of the hydrothermal route (temperature, internal pressure, etc.) can lead to the same product.

3.2. Structural description

3.2.1. [Cu(dpa)₂]₄V₄O₁₂ (**1**)

The structure of (**1**) consists of copper(I) complex cations with distorted tetrahedral geometry ($92.8^\circ < \alpha_{\text{N-Cu-N}} < 121.6^\circ$), the charge of which is compensated by V₄O₁₂⁴⁻ anions. The first coordination sphere of the copper(I) ion is defined by four nitrogen atoms from two dpa ligands ($1.99 \text{ \AA} < d_{\text{Cu-N}} < 2.02 \text{ \AA}$). The V₄O₁₂⁴⁻ anion exhibits a centrosymmetric eight membered ring structure, constructed from VO₄ tetrahedra, sharing vertices with two terminal oxo groups and two bridging oxo groups. The interatomic bond distances and angles compare well with the known values for such a coordination geometry ($1.612 \text{ \AA} \leq d_{\text{V-O}_{\text{term}}} \leq 1.637 \text{ \AA}$; $1.780 \text{ \AA} \leq d_{\text{V-O}_{\text{bond}}} \leq 1.793 \text{ \AA}$ and $106.7^\circ \leq \alpha_{\text{ovo}} \leq 111.7^\circ$). The V₄O₁₂⁴⁻ anions are organized in arrays of pseudo planes translated from each other by $T = 1/2(a + b)$ and rotated in 90° (Fig. 1a).

In addition, each V(V) site contributes two oxo groups to form hydrogen bonds with the NH group of different dipyridylamine ligands. Thus, the crystalline structure is

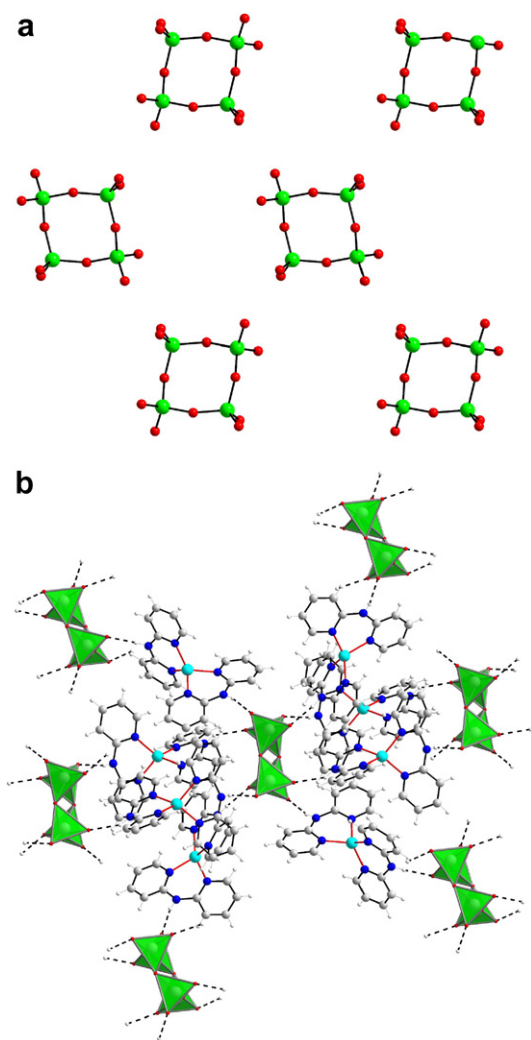


Fig. 1. (a) Arrays of the $[\text{V}_4\text{O}_{12}]^{4-}$ anions viewing along c -direction for $[\text{Cu}(\text{dpa})_2]_4\text{V}_4\text{O}_{12}$ (**1**). (b) View of the structure showing the formation of a *quasi* tridimensional network for $[\text{Cu}(\text{dpa})_2]_4\text{V}_4\text{O}_{12}$ (**1**) (the hydrogen bonding is emphasized by black dashed lines). Red circles: oxygen, green circles: vanadium, cyan circles: copper, grey circles: carbon, dark blue circles: nitrogen, green polyhedra: VO_4^{3-} tetrahedra. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

stabilized by the formation of strong hydrogen bonds between the NH groups of the ligands of the surrounding complex cations and the eight terminal oxygen atoms of the cyclic $[\text{V}_4\text{O}_{12}]^{4-}$, generating a *quasi* tridimensional network (Fig. 1b).

An example of a copper (I) complex with $[\text{V}_4\text{O}_{12}]^{4-}$ sub-units is $[\text{Cu}_2(\text{tpyprz})]_2\text{V}_4\text{O}_{12}$ [28]. In contrast to the reported molecular compound **1**, in which the vanadate sub-unit is a counteranion, this material based on vanadium oxide is two dimensional. It is built up of cationic $\text{Cu}_2(\text{tpyprz})^{2+}$ species forming chains, which are interconnected in the second dimension by the $[\text{V}_4\text{O}_{12}]^{4-}$ clusters. The vanadate sub-unit acts as a bidentate chelator to two copper sites from each of the two adjacent copper(I) ribbons.

3.2.2. $\text{Cu}_2(\text{bipy})_2\text{V}_4\text{O}_{12}$ (**2**)

Compound **2** is an oxide with a one-dimensional structure, generated by the interconnection of $\text{V}_4\text{O}_{12}^{4-}$ sub-units and copper square pyramids. The structure of **2** is clearly different to that of the isoformular compound $(\text{Cu}(\text{bipy})\text{V}_2\text{O}_6)$ previously described by De Bord et al. [29] in which infinite $[\text{VO}_3]_n^{n-}$ chains decorated by $\text{Cu}(\text{bipy})^{2+}$ are observed. In **2** the cyclic anion exhibits a centrosymmetric eight membered ring structure, constructed from VO_4 tetrahedra, sharing vertices with two terminal oxo groups and two bridging oxo groups. The interatomic bond distances and angles compare well with the known values for such a coordination geometry ($1.594 \text{ \AA} \leq d_{\text{V-Oterm}} \leq 1.670 \text{ \AA}$, and $1.768 \text{ \AA} \leq d_{\text{V-Obond}} \leq 1.797 \text{ \AA}$, and $108.70 \leq \alpha_{\text{ovo}} \leq 111.28^\circ$). These rings are linked through the copper(II) complex ions to form a chain which propagates along the [100] direction (Fig. 2a). The copper(II) atom has a square pyramidal environment, defined by two nitrogen atoms from the bipy ligand ($d_{\text{Cu-N}} = 1.977 \text{ \AA}$) and two oxygen atoms from one $[\text{V}_4\text{O}_{12}]^{4-}$ group ($d_{\text{Cu-O}} = 1.948 \text{ \AA}$), which form the basal plane, while the apical oxygen atom ($d_{\text{Cu-O}} = 2.202 \text{ \AA}$) comes from another $[\text{V}_4\text{O}_{12}]^{4-}$ anion. The angles in the square pyramid range from 81.5° to 100.76° . As can be seen in Fig. 2b, the infinite chains interpenetrate each other by the organic ligand to form planes parallel to (101).

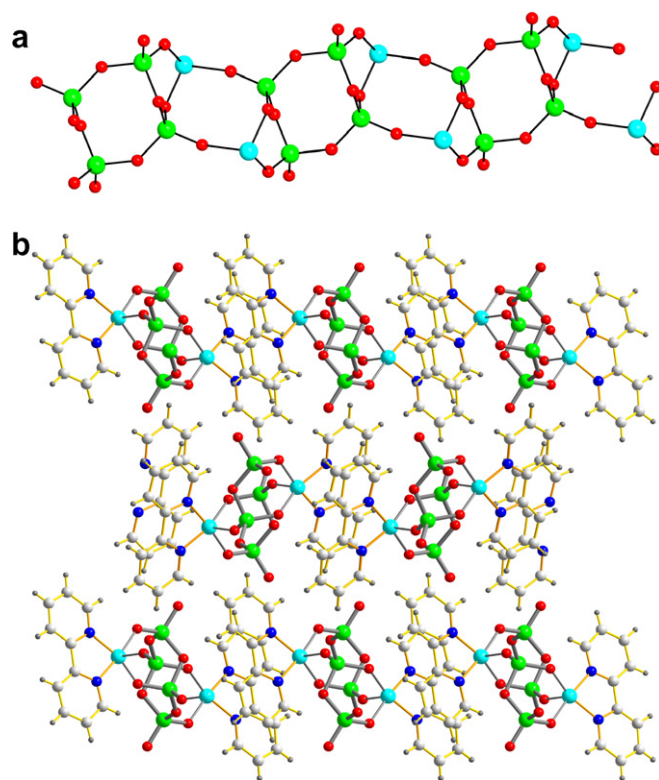


Fig. 2. (a) Infinite $\text{Cu}[\text{V}_4\text{O}_{12}]^{2-}$ chain from the condensation of the cyclic anion and square pyramidal copper(II) complex for $\text{Cu}_2(\text{bipy})_2\text{V}_4\text{O}_{12}$ (**2**). (b) View of the structure of **2** along the [100] direction showing the stacking of the diimine molecules from two adjacent chains. The $[\text{V}_4\text{O}_{12}]^{4-}$ anions are emphasized.

3.2.3. $\text{Cu}_2(\text{bipy})_2\text{V}_6\text{O}_{17}$ (**3**)

The structure of compound **3** is two-dimensional constructed from oxovanadium chains, connected by copper (II) square pyramids (Fig. 3a). Each chain is formed by the condensation of $[\text{V}_4\text{O}_{12}]^{4-}$ cycles and V_2O_5 dimers; this generates the V_6O_{17} species. The vanadium(V) ions are all in tetrahedral coordination with different types of oxygen atoms: terminal oxygens ($1.577 \text{ \AA} \leq d_{\text{V-O}_{\text{term}}} \leq 1.616 \text{ \AA}$), oxygen atoms shared with another vanadium ($1.730 \text{ \AA} \leq d_{\text{V-O}_{\text{bond}}} \leq 1.796 \text{ \AA}$), and oxygen atoms shared with coppers ($1.618 \text{ \AA} \leq d_{\text{V-O}_{\text{bond}}} \leq 1.649 \text{ \AA}$). The copper atoms occupy the center of the basal plane of a square pyramid, defined by two oxygen atoms from oxovanadium groups of one chain, ($1.914 \leq d_{\text{Cu-O}} \leq 1.924 \text{ \AA}$), and two nitrogen atoms from the organic ligand ($1.982 \leq d_{\text{Cu-N}} \leq 1.986 \text{ \AA}$). The apical position is occupied by an oxygen atom coming from the neighbouring oxovanadium chain ($d_{\text{Cu-O}} = 2.250 \text{ \AA}$). The inorganic planes are separated from each other by approximately 9 \AA , with the bipyridine ligands protruding from the inorganic planes and presenting π - π

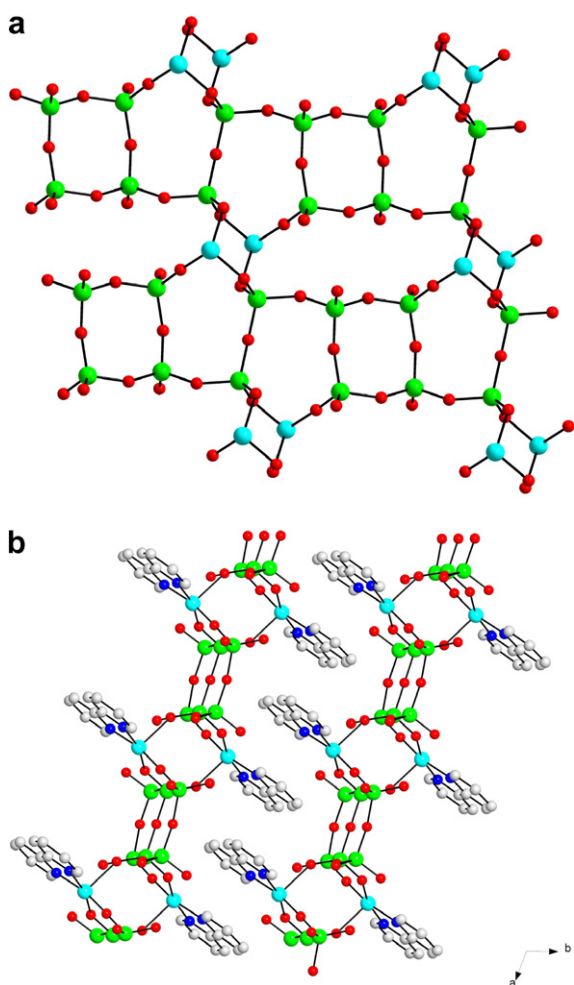


Fig. 3. (a) View of a layer $\text{Cu}_2\text{V}_6\text{O}_{17}$ of **3** with the infinite V_6O_{17} chains built up from the condensation of $[\text{V}_4\text{O}_{12}]^{4-}$ and $[\text{V}_2\text{O}_5]$ groups connected by copper atoms. (b) Packing of the structure with bipyridine protruding from the layers and interacting through π - π stacking.

stacking ($d \sim 3.5 \text{ \AA}$) between adjacent layers (Fig. 3b). Our structural results are in good agreement with those previously reported by Xie and Mao [10].

3.3. Structure discussion

In the three structures the $[\text{V}_4\text{O}_{12}]^{4-}$ anion presents the same internal symmetry (-1) while many other can be observed for the isoformular $[\text{P}_4\text{O}_{12}]^{4-}$ anion [30] (no symmetry, $2, 2/m, m, mm, \bar{4}, -\bar{4}_2/m$). The vanadium tetrahedra are very regular with vanadium-oxygen distances ranging from 1.578 to 1.800 \AA and O-V-O angles ranging from 104.77° to 112.08° and a mean value (109.46°) very close to the ideal value (109.28°). It can be noted that the anion is more or less distorted regarding the different structures (Fig. 4). This can be linked to the V-V-V angle: in **3** the V-V-V angles are, respectively, 89° and 91° and the cyclic anion is very regular, in **1** the V-V-V angles are, respectively, 86° and 93° with a slight distortion while in **2** a severe distortion is evidenced and consequently an important deviation from the ideal value of 90° is observed (V-V-V angles from 80.2° to 99.8°). These observations rule out the possibility of high internal symmetry.

The three structures present the same $[\text{V}_4\text{O}_{12}]^{4-}$ building unit. In **1**, the anion is isolated with only hydrogen bonding between the terminal oxygen atom and the hydrogen of NH group of the 2,2'-dipyridylamine group. In **2** the $(\text{V}_4\text{O}_{12})^{4-}$ anions are connected to each other through the copper atoms to generate infinite $\text{Cu}_2(\text{V}_4\text{O}_{12})^{4-}$ chains. In **3** the $[\text{V}_4\text{O}_{12}]^{4-}$ anions are connected to one another by V_2O_5 dimers; this generates oxovanadium infinite chains linked by copper atoms to form $\text{Cu}_2\text{V}_6\text{O}_{17}$ layer.

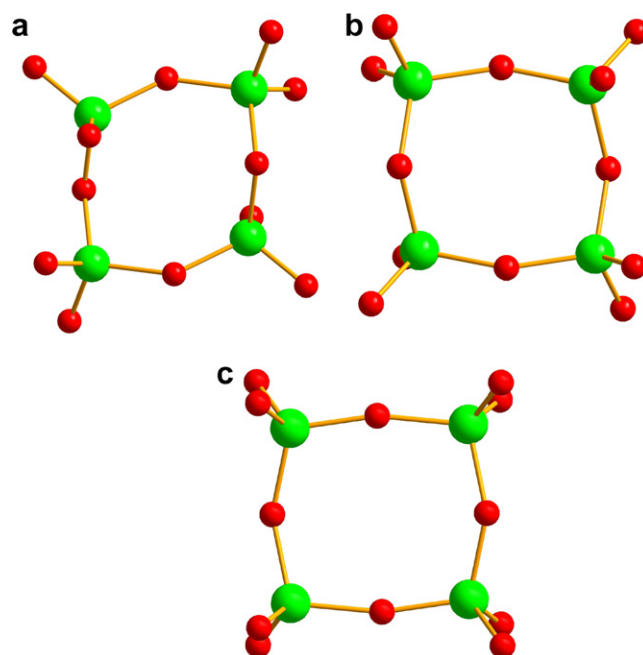


Fig. 4. Representation of the $[\text{V}_4\text{O}_{12}]^{4-}$ anion in the three structures: (a) in **3**, (b) in **1**, (c) in **2** showing the growing distortion of the geometry.

In all cases the building unit is the $[\text{V}_4\text{O}_{12}]^{4-}$ ring but the dimensionality of the framework is increased from 0D to 1D and 2D by adding copper centers and additional oxovanadium groups.

4. Conclusion

The reactions carried out in the presence of ethylenediphosphonic acid permitted the isolation of vanadium oxide–copper(II) crystalline products **2** and **3**, in modest yields. No crystals of vanadophosphonate nor vanadophosphate were obtained, but unidentified powders were also present. Basic medium favours the reduction of copper(II) to copper(I) under the used synthetic conditions, so when the diphosphonic acid was replaced by sodium phosphate, crystals of **1** were isolated. The copper(I) compound **1** is a molecular species, while the remaining compounds **2** and **3** are extended solids: 1D for **2** and 2D for **3**.

When the reagents are reduced to half the initial concentration, maintaining the other reaction conditions unaltered, the isolated crystalline products present different vanadium oxide species. The dilute reaction conditions generate **2** with the cyclic $[\text{V}_4\text{O}_{12}]^{4-}$ anion, while the concentrated reaction conditions produce the same cyclic anion connected by V_2O_5 units in **3**.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2007.10.008](https://doi.org/10.1016/j.ica.2007.10.008).

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