A Robust Open Framework Formed by Decavanadate Clusters and Copper(II) Complexes of Macrocyclic Polyamines: Permanent Microporosity and Catalytic Oxidation of Cycloalkanes

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ABSTRACT: The first decavanadate-based microporous hybrid, namely, $[\text{Cu}(\text{cyclam})][\{\text{Cu}(\text{cyclam})\}_2(\text{V}_{10}\text{O}_{28})]\cdot 10\text{H}_2\text{O}$ (**1**, cyclam = 1,4,8,11-tetraazacyclotetradecane) has been prepared by reaction of $(\text{VO}_3)^-$ anions and $\{\text{Cu}(\text{cyclam})\}^{2+}$ complexes in NaCl (aq) at pH 4.6–4.7, and characterized by elemental analyses, thermogravimetry, and X-ray diffraction techniques (powder, single-crystal). Compound **1** exhibits a POMOF-like supramolecular open-framework built up of covalent decavanadate/metalorganic layers with square-like voids, the stacking of which is aided by interlamellar cementing complexes and generates water-filled channels with approximate cross-sections of $10.4 \times 8.8 \text{ \AA}^2$. The framework is robust enough to remain virtually unaltered upon thermal evacuation of all water molecules of hydration, as demonstrated through single-crystal X-ray diffraction studies on the anhydrous phase **1a**. This permanent microporosity renders interesting functionality to **1**, such as selective adsorption of CO_2 over N_2 and remarkable activity as heterogeneous catalyst toward the H_2O_2 -based oxidation of the highly-stable, tricyclic alkane adamantane.

INTRODUCTION

Porous crystalline materials such as metal organic frameworks (MOFs) have attracted great attention due to their wide range of relevant applications.¹ These materials are constructed by coordination of metal ions or metal-containing units (nodes) to organic bridging ligands (linkers) to form open crystalline frameworks with permanent porosity. This feature qualifies them as suitable candidates for gas storage and separation, ion exchange, host-guest chemistry, magnetism, biomedicine and catalysis.² However, the synthesis of MOFs usually requires harsh conditions (e.g. high temperature or pressure, prolonged reaction times, harmful solvents, etc.), and removal of guest molecules from their cavities often leads to the collapse of the porous structure when flexible linkers are used. In this context, the incorporation of rigid and voluminous species such as metal clusters could increase the overall robustness

of the framework. Among metal clusters, polyoxometalates (POMs) have been identified as excellent building blocks for the construction of such robust, high-dimensional open structures.³

Polyoxometalates (POMs) are a family of anionic metal oxo clusters with large topological diversity and intrinsic multifunctional nature.⁴ Nowadays, POM-based crystalline solids with permanent porosity are of great interest because inherent features of POMs such as reversible redox properties or high catalytic site density can be combined with the characteristics derived from open-framework structures.^{3,5} Several examples have been reported in recent years and they include both supramolecular ionic compounds and covalent extended lattices (POMOFs). The former can be exemplified by Mizuno's series of hybrid salts in which $[\text{M}_3\text{O}\{\text{RCO}_2\}_6\text{L}_3]^+$ macrocations ($\text{M}^{\text{III}} = \text{Cr}, \text{Fe}$; L = terminal ligand) are combined with Keggin-type

[X_{M12}O₄₀]ⁿ⁻ (X = B, Si, P; M = W) heteropolyanions in microporous structures with tunable shape-selective sorption ability.⁵ Among POMOFs, four different approaches for assembling clusters into extended lattices can be identified according to Wang et al.:⁶ a) organically derivatized POM units linked by metal ions;⁷ b) POM clusters directly connected by metal ion linkers in fully inorganic open-frameworks;⁸ c) metal-substituted POMs connected through organic bridging ligands;⁹ d) POMs connected through metal-organic ligand-metal linking fragments.¹⁰ Compared to MOFs, the synthetic requirements for the assembly of POMOFs usually involve milder conditions, aqueous reaction media and easier counterion exchange. Moreover, configurable and more diverse architectures can be achieved in the resulting compounds because POM building blocks possess specific topological and chemical information that can be transferred to the final product.

A fifth subclass closely related to type b) above could also be proposed: that in which the metal ion linkers belong to discrete coordination complexes with peripheral organic ligands.^{3,11} Even though a considerable number of covalent extended networks based on POM clusters connected through metalorganic moieties have been prepared so far, to the best of our knowledge none of such hybrid compounds have exhibited genuine functions associated with porosity (e.g. adsorption, separation). This fact might be mainly due to the presence of pores with small sizes and/or inaccessible voids. Thus, the preparation of such type of functional porous open-frameworks is still a challenging issue in current synthetic POM chemistry.

Polyoxovanadates constitute an important POM subfamily, in which [H_nV₁₀O₂₈]⁽⁶⁻ⁿ⁾⁻ decavanadates are considered amongst the most relevant members as they are the predominant species in acidic aqueous solution.¹² While the coordinative role of small polyoxovanadate clusters (e.g. [V₄O₁₂]⁴⁻) toward transition-metal complexes has been long documented,¹³ most of the decavanadate-metalorganic hybrids known at present consists in ionic compounds,¹⁴ in which the structural stability simply relies on electrostatic forces and weak intermolecular interactions between the different components. Indeed, the first crystal structure involving metalorganic complex moieties covalently grafted at the surface of decavanadate anions was not reported until 2007,¹⁵ and almost all compounds with such characteristics that have been prepared later on consist in either discrete decorated clusters¹⁶ or mono-dimensional arrangements.¹⁷ To our knowledge, only two decavanadate/metalorganic hybrid lattices with covalent bi-dimensional nature can be found in the literature,¹⁸ namely (Hpz)₂[[Cu(pz)₄]₂(V₁₀O₂₈)·2H₂O (pz = pyrazole) and [[Ag₃(dmsO)₆]]₂[(Ag(dmsO)₂)(H₂V₁₀O₂₈)·2dmsO. It must be noted that none of these two compounds show porosity because of an alternate stacking of sheets that renders the cation/solvent-filled voids inaccessible.

Herein, we report the first supramolecular POMOF-like compound assembled from the stacking of covalent layers formed by decavanadate anions and metalorganic linkers, namely [Cu(cyclam)][{Cu(cyclam)}₂(V₁₀O₂₈)]·10H₂O (**1**)

(cyclam = 1,4,8,11-tetraazacyclotetradecane). The robustness of the open-framework and associated permanent microporosity of **1** has been confirmed by single-crystal X-ray diffraction studies on the thermally generated anhydrous phase **1a**, as well as by gas sorption measurements that reveal selective adsorption of CO₂ over N₂. The catalytic activity toward the C–H bond activation of highly-stable tricyclic alkanes, such as adamantane, has been assessed in heterogeneous phase.

EXPERIMENTAL SECTION

The *tert*-butylammonium metavanadate [(CH₃)₃CNH₃][VO₃] and dihydrogendecavanadate [(CH₃)₃CNH₃]₄[H₂V₁₀O₂₈]·8H₂O precursors were synthesized according to literature methods and identified by infrared (FT-IR) spectroscopy.¹⁹ All other chemicals were obtained from commercial sources and used without further purification. Carbon, hydrogen and nitrogen were determined on a Perkin-Elmer 2400 CHN analyzer. FT-IR spectra were obtained as KBr pellets on a SHIMADZU FTIR-8400S spectrometer. The thermogravimetric (TGA) analysis was carried out from room temperature to 800 °C at a rate of 5 °C min⁻¹ on a Mettler Toledo TGA/SDTA 851^e thermobalance under a 50 cm³ min⁻¹ flow of synthetic air. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Advance diffractometer operating at 30 kV/20 mA and equipped with Cu K_α radiation (λ = 1.5418 Å), a Vantec-1 PSD detector, an Anton Parr HTK2000 high-temperature furnace, and Pt sample holder. The powder patterns were recorded in 2θ steps of 0.033° in the 5 ≤ 2θ ≤ 35 range with an exposure time of 0.3 s per step. Data sets were acquired from 30 to 490 °C every 20 °C, with a heating rate of a 0.16 °C s⁻¹ between temperatures.

Synthetic Procedure

[Cu(cyclam)][{Cu(cyclam)}₂(V₁₀O₂₈)]·10H₂O (**1**). [(CH₃)₃CNH₃][VO₃] (0.170 g, 1.00 mmol) was dissolved in aqueous 1M NaCl (20 mL) and the pH was adjusted to 4.6–4.7 with aqueous 0.5M HCl. Then, a solution of CuSO₄·5H₂O (0.075 g, 0.30 mmol) and cyclam (0.040 g, 0.20 mmol) in aqueous 1M NaCl (15 mL) was added dropwise. The mixture was stirred for 2 hours and then filtered to remove a brown solid off. The resulting dark brown solution was left to slowly evaporate in an open container at room temperature and orange block-like crystals suitable for X-ray diffraction were obtained after 6 days. Yield: 44 mg (23% based on V (atomic). Anal. Calcd (found) for C₃₀H₉₂Cu₃N₁₂O₃₈V₁₀: C, 18.68 (18.51); H, 4.80 (4.69); N, 8.71 (8.60). IR (cm⁻¹): 3186(vs), 3165(vs), 2934(s), 2878(s), 1627(s), 1473(m), 1454(m), 1427(m), 1389(w), 1358(w), 1300(w), 1253(w), 1236(w), 1138(m), 1105(m), 1062(m), 1009(m), 960(vs), 883(m), 835(s), 748(s), 594(s), 532(s), 559(s), 440(s).

[Cu(cyclam)][{Cu(cyclam)}₂(V₁₀O₂₈)]·(**1a**). The anhydrous derivative **1a** can be obtained by heating single-crystals of **1** at 130 °C in an oven for 1h. A color change from orange to amber was produced upon dehydration.

X-ray Crystallography

Crystallographic data for compounds **1** and **1a** are given in Table 1. Intensity data were collected on an Agilent Technologies Super-Nova diffractometer. The diffractometer was equipped with monochromated Cu K α radiation ($\lambda = 1.54184$ Å) and Atlas CCD detector in the case of **1**, whereas the selected radiation and detector for **1a** were monochromated Mo K α ($\lambda = 0.71073$ Å) and Eos CCD. The data collection of **1** was carried out at 100 K. In the case of **1a**, a single crystal of **1** was heated in an oven to 303 K at a rate of 1 K min $^{-1}$ to achieve full dehydration, and immediately afterwards covered with Paratone[®] oil and placed under the N $_2$ stream of the diffractometer, which was ready to perform a full data collection at 100 K. Data frames were processed (unit cell determination, analytical absorption correction with face indexing, intensity data integration and correction for Lorentz and polarization effects) using the CrysAlis Pro software package.²⁰ The structures were solved using OLEX2²¹ and refined by full-matrix least-squares with SHELXL-2014/6.²² Final geometrical calculations were carried out with PLATON²³ as integrated in WinGX.²⁴ Thermal vibrations were treated anisotropically for all non-H atoms in both compounds. Hydrogen atoms of the organic ligands were placed in calculated positions and refined using a riding model with standard SHELXL parameters. Ten positions suitable for water molecules of hydration were located in the Fourier map of **1** and their occupancy was initially refined without restrictions. The resulting total number of 5.5 water molecules per half of decavanadate cluster was fixed to 5 during the final refinement as indicated by the TGA experiments. The space within the channels occupied by the water molecules of hydration was visualized by PyMol.²⁵

Sorption Measurements

The porous texture of **1** was characterized through the physical adsorption of the following gases: N $_2$ at -196 °C and CO $_2$ at 0 °C. The volumetric equipments Autosorb-6B and Autosorb-6 were used respectively. The measurements were performed on crystalline samples that were previously outgassed at 150 °C under vacuum for 4 hours. The Dubinin-Radushkevich (DR) equation^{26a} was used to calculate the micropore volume. The calculation of pore volumes has been done as follows: a) the volume of the narrow micropores or ultramicropores (V_{CO_2} , pore size < 0.8 nm) was estimated from the CO $_2$ DR plots at relative P/P_0 pressures lower than 0.015; b) the total volume of micropores (V_{N_2} , pore size < 2 nm) was calculated from N $_2$ DRs plots at relative P/P_0 pressures lower than 0.14.^{26b}

Catalytic tests

The oxidation of adamantane was conducted in a glass reactor (27 cm 3 of inner volume) located inside a stainless steel vessel (45 cm 3 of inner volume) coupled to a manometer to monitor the system pressure. The following reactants and solvent were used for the catalytic test: 25 mg of adamantane, 3 cm 3 of hydrogen peroxide (30%), 10 cm 3 of acetonitrile, two drops of concentrated HCl and 100 mg of the catalyst **1** ($5 \cdot 10^{-5}$ moles). For comparative purposes,

V $_2$ O $_5$ (Aldrich), and two Keggin-type heteropolyacids supported on ZrO $_2$ (H $_3$ [PMo $_{12}$ O $_{40}$] and H $_4$ [PVMo $_{11}$ O $_{40}$], 30 wt.% of POM) were also tested. A small Teflon-coated magnet was added to the mixture and the whole system was immersed in a thermostatic bath of polyethylene glycol at 75 °C while stirring at 800 rpm. A reaction time of 6 hours was selected as the optimum value to allow for complete conversion but minimizing hydrogen peroxide decomposition. Both shorter (3 hours) and longer (up to 12 hours) reaction times were also tested for comparative purposes. The reaction products of the oxidation of adamantane were identified by analyzing an aliquot of the solution (20 μ L) taken at the end of the reaction time with an Agilent 6890 gas chromatograph equipped with an HP-1 column of size 30 m $\times$ 250 μ m $\times$ 0.25 μ m and coupled to an Agilent 5975 mass spectrometer. Upon identification of all reaction products, the conversion and their evolution were quantitatively estimated using a flame ionization detector coupled to a properly calibrated Agilent 6890 gas chromatograph.

Table 1. Crystallographic data for **1** and **1a**

	1	1a
Empirical formula	C $_{30}$ H $_{92}$ Cu $_3$ N $_{12}$ O $_{38}$ V $_{10}$	C $_{30}$ H $_{72}$ Cu $_3$ N $_{12}$ O $_{28}$ V $_{10}$
FW(g mol $^{-1}$)	1929.2	1749.0
Crystal system	triclinic	triclinic
Space group	P-1	P-1
Temperature (K)	100(2)	100(2)
<i>a</i> (Å)	10.6665(8)	10.6838(3)
<i>b</i> (Å)	11.9325(9)	11.9275(6)
<i>c</i> (Å)	13.7832(8)	13.7285(7)
α (°)	95.752(5)	94.433(4)
β (°)	105.003(6)	104.596(3)
γ (°)	90.677(6)	92.604(3)
<i>V</i> (Å 3)	1684.7(2)	1684.08(13)
ρ_{calc} (g cm $^{-3}$)	1.902	1.725
μ (mm $^{-1}$)	12.928	2.320
λ (Å)	1.54184 (Cu K α)	0.71073 (Mo K α)
collected reflns	11577	10744
unique reflns (R_{int})	5977 (0.046)	5939 (0.027)
obsd reflns [$I > 2\sigma(I)$]	4821	4595
parameters	469	379
$R(F)^a$ [$I > 2\sigma(I)$]	0.057	0.040
$wR(F^2)^b$ [all data]	0.166	0.102
GoF	1.038	1.044

$$^a R(F) = \sum \|F_o - F_c\| / \sum \|F_o\|;$$

$$^b wR(F^2) = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

RESULTS AND DISCUSSION

Synthesis

Recently, we reported a new porous metavanadate- $\{\text{Cu}(\text{cyclam})\}$ hybrid able to undergo as much as three sequential and reversible SCSC transformations promoted by gradual dehydration upon heating from room temperature to 120 °C.²⁷ This compound was prepared from the self-assembly of $\{\text{VO}_3\}^-$ anions and $\{\text{Cu}(\text{cyclam})\}^{2+}$ complexes in basic aqueous medium under reflux conditions with the optimum pH value set at 9. Our systematic investigation of the influence of pH on the VO_3^- : Cu^{2+} : cyclam synthetic system allowed us to determine that such metavanadate hybrid could only be obtained at pH values above 6. We also found that a second decavanadate-containing hybrid derivative crystallized in the pH range 4–6, but unfortunately, this compound could only be isolated as traces in a mixture with an unidentified powder. Given the interesting thermal-dependent crystallochemistry observed in our previous work, we decided to optimize the synthetic procedure for this decavanadate-containing hybrid (**1**) and to investigate whether this compound could exhibit similar temperature-dependent crystal transitions as well.

We limited our synthetic studies to the pH range 4–6 and conducted several experiments in aqueous media to check the influence of the following parameters on the reaction outcome: pH, temperature, type of precursor (metavanadate vs. decavanadate), and solvent. Neither the temperature nor the precursors appear to have any apparent effect on the final product, as reactions carried out at different temperatures up to reflux conditions or using the preformed $[(\text{CH}_3)_3\text{CNH}_3]_4[\text{H}_2\text{V}_{10}\text{O}_{28}] \cdot 8\text{H}_2\text{O}$ resulted in similar mixtures of crystals of **1** with the powder as the major component. In contrast, the pH plays a key role for the isolation of the hybrid decavanadate in a pure manner. We managed to prepare **1** as a single, homogeneous crystalline phase at a controlled pH value of 4.6–4.7 as evidenced by the FT-IR spectra and the PXRD patterns (Figures S1–S3 in the Supporting Information), although the yield obtained was still certainly poor (around 1% with cyclam as the limitant). This is due to the formation of large amounts of a brown precipitate as the reaction proceeds, which contains the title compound but in impure bulk form as evidenced by FT-IR and PXRD analyses (Figures S4 in the Supporting Information).

Fortunately, a change in the solvent favored the formation of our hybrid decavanadate by increasing the yield of the crystalline phase and reducing the time for crystallization. When water was replaced with aqueous 1M NaCl and the optimized conditions determined above were applied (metavanadate precursor, room temperature, pH 4.6–4.7), formation of the impure bulk form was minimized and crystallization of **1** took place in a few days instead of the several weeks needed in the original attempts. The resulting yield was drastically improved to above 20%, proving that the ionic strength has a key influence in this particular synthetic system. It is worth mentioning that we also tried to prepare analogues of **1** but using other divalent transition metals (Mn^{II} , Co^{II} , Ni^{II} , and Zn^{II}) instead of Cu^{II} ,

but unfortunately, we could not obtain any crystalline material from these experiments. This fact confirms that the plasticity of the coordination sphere of the Cu^{II} centers and the Jahn–Teller elongation they undergo when involved in octahedral environments play a key role in the formation of **1**, as it will be shown in the structural description below.

Thermo-structural behavior

The thermal stability of **1** was investigated by TGA experiments, which show that the title compound decomposes through three mass loss stages (Figure 1). The first stage is observed from room temperature to ca. 95 °C and originates from the release of all water molecules of hydration. The experimental mass loss corresponds to 10 water molecules per decavanadate anion (calcd. 9.33%, found 8.94%). Completion of this stage leads to the anhydrous phase **1a**, which shows a significant range of thermal stability extending up to ca. 160 °C. Above this temperature, the anhydrous phase undergoes further decomposition via two overlapping mass loss stages associated with the combustion of the organic ligands and the breakdown of the POM framework. The overall mass loss for these two stages is in good agreement with three cyclam ligands per decavanadate anion (calcd. for $3\text{C}_{10}\text{H}_{24}\text{N}_4$ 31.10%; found 32.11%). The final residue is obtained at temperatures above ca. 550 °C (calcd. for $\text{Cu}_3\text{O}_{28}\text{V}_{10}$ 59.50%, found 58.95%).

Figure 1. TGA curve of **1** and photographs of crystals for **1** and its anhydrous derivative **1a**.

Variable-temperature powder X-ray diffraction measurements (TPXRD) between 30 and 490 °C show that compound **1** is able to maintain its crystallinity upon dehydration up to temperatures in the 150 to 170 °C range (Figure 2). No substantial modifications in neither the positions nor the intensities of the diffraction maxima are observed upon heating, although subtle variations can be noticed above 90 °C upon close inspection of the group of maxima in the 2θ range 25–27°. This temperature corresponds to the removal of all water molecules of hydration according

to the TGA curve, and hence to the formation of the anhydrous **1a** phase, which must display virtually identical crystal packing based on the observations above. The crystalline **1a** phase becomes amorphous at temperatures above 150 °C which nearly corresponds to the beginning of

the ligand combustion stage in the TGA curve. Signs of new high-temperature phases start appearing at *ca.* 310 °C. At temperatures above 490 °C, these phases forming the final residue of the thermal decomposition are defined enough for being identified as a mixture of orthorhombic Pmn_{21} V_2O_5 (PDF: 01-076-1803),²⁸ monoclinic $C_{2/c}$ $Cu_2V_2O_7$ (PDF: 01-073-1032),²⁹ and the orthorhombic Pmn_{21} phase of CuV_2O_6 (PDF: 00-016-0127)³⁰ in an approximate ratio 3 : 1 : 1 (Figure S5 in the Supporting Information).

Figure 2. Variable-temperature powder X-ray diffraction studies for **1**.

Crystal structures of **1** and **1a**

Compound **1** crystallizes in the triclinic $P\bar{1}$ space group and its asymmetric units contains one half of a decavanadate ($V_{10}O_{28}$)⁶⁻ anion and three crystallographically independent, centrosymmetric {Cu(cyclam)} moieties (Figure 2). Five water molecules of hydration disordered over ten positions complete the asymmetric unit. The structure of the decavanadate anion is well established and consists in an arrangement of 10 edge-shared {VO₆} octahedra with ideal D_{3h} symmetry. This arrangement can be described as a central {V₆O₁₂} core built of six VO₆ octahedra arranged in a 2 × 3 rectangular array and capped with two additional {VO₆} units on both sides (Figure 3 and S6 in the Supporting Information). The V–O bond lengths (Table S1 in the Supporting Information) are consistent with other decavanadate clusters reported in the literature.^{19b,31}

Figure 3. ORTEP view of **1** depicted at the 50% probability level, together with atom labelling (water molecules are omitted for clarity). Symmetry codes: i) 1-*x*, 1-*y*, -*z*; ii) 2-*x*, 1-*y*, 1-*z*; iii) 2-*x*, -*y*, -*z*; iv) 2-*x*, 1-*y*, -*z*.

Table 2. Bond lengths (Å) of the Copper(II) Centers in **1** and **1a**

	1		1a
Cu1A–N1A	1.995(5)	Cu1A–N1A	1.999(4)
Cu1A–N1A ⁱ	1.995(5)	Cu1A–N1A ⁱ	1.999(4)
Cu1A–N4A	1.992(7)	Cu1A–N4A	1.997(4)
Cu1A–N4A ⁱ	1.992(7)	Cu1A–N4A ⁱ	1.997(4)
Cu1B–N1B	2.001(5)	Cu1B–N1B	2.003(4)
Cu1B–N1B ⁱⁱ	2.001(5)	Cu1B–N1B ⁱⁱ	2.003(4)
Cu1B–N4B	2.021(5)	Cu1B–N4B	2.002(4)
Cu1B–N4B ⁱⁱ	2.021(5)	Cu1B–N4B ⁱⁱ	2.002(4)
Cu1B–O5	2.526(3)	Cu1B–O5	2.533(3)
Cu1B–O5 ⁱⁱ	2.525(3)	Cu1B–O5 ⁱⁱ	2.533(3)
Cu1C–N1C	2.020(5)	Cu1C–N1C	2.003(4)
Cu1C–N1C ⁱⁱⁱ	2.020(5)	Cu1C–N1C ⁱⁱⁱ	2.003(4)
Cu1C–N4C	1.997(5)	Cu1C–N4C	2.005(4)
Cu1C–N4C ⁱⁱⁱ	1.997(5)	Cu1C–N4C ⁱⁱⁱ	2.005(4)
Cu1C–O1	2.604(3)	Cu1C–O1	2.571(3)
Cu1C–O1 ⁱⁱⁱ	2.604(3)	Cu1C–O1 ⁱⁱⁱ	2.571(3)

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

There are two types of {Cu(cyclam)} units: the complexes Cu1B and Cu1C both play the role of linking moieties, whereas Cu1A is a charge balancing subunit. Selected bond lengths are given in Table 2. The coordination spheres of the Cu1B and Cu1C centers show elongated octahedral CuN₄O₂ geometries with the four N atoms of the cyclam ligand forming the equatorial plane and the axial positions occupied by terminal O atoms from (V₁₀O₂₈)⁶⁻ clusters. In contrast, the Cu1A moiety constitutes a square-planar

complex (Figure S7 in Supporting Information). According to the literature, transition metal complexes of the cyclam ligand can adopt up to 5 different geometrical isomers depending on the ligand conformation, and more specifically, on whether the N–H bonds are located above or below the MN_4 plane.³² Both Cu1B and Cu1C display the so-called *trans-III* configuration in which two N–H bonds point to one side of the CuN_4 equatorial plane and the other two N–H bonds point to the opposite side. This is in good agreement with the results reported previously, which have shown that the most favorable configuration of a $\{Cu(cyclam)\}$ complex with octahedral geometry is indeed the *trans-III*.³³ In regard to square planar complexes, these studies have also demonstrated that the *trans-I* configuration gains stability over the *trans-III* when the coordination number of the metal center is reduced. In our case, however, the configuration of the Cu1A moiety remains the same as that of Cu1B and Cu1C in spite of showing square-planar geometry.

The crystal packing of **1** consists in a supramolecular assembly of covalent hybrid layers in which the decavanadate anions are linked by the Cu1B and Cu1C bridging moieties along the [001] and [010] directions, respectively (Figure 4). Thus, each decavanadate anion results connected to four neighboring clusters through four complexes whose grafting sites are VO_6 octahedra belonging to either the central $\{V_6\}$ rectangular core (Cu1B) or to the dimeric caps (Cu1C). This arrangement leads to the formation of hybrid grids with water-accessible square-like voids in the yz plane. A closely related bi-dimensional lattice with similar connectivity between building blocks has been reported for the $(Hpz)_2[\{Cu(pz)_4\}_2(V_{10}O_{28})] \cdot 2H_2O$ (pz = pyrazole),^{18a} although with the voids filled with Hpz cations in contrast to **1** (Figure S8 in the Supporting Information). For the second bi-dimensional hybrid decavanadate known, namely $[\{Ag_3(dmsO)_6\}(\{Ag(dmsO)_2\}(H_2V_{10}O_{28}))] \cdot 2dmsO$,^{18b} the grafting sites for the metalorganic linkers are bridging O atoms of the $\{V_6\}$ core and the presence of linear trimeric $[Ag_3(dmsO)_6]^{3+}$ moieties renders a rectangular hybrid grid. In both cases, the voids are inaccessible because they are blocked on both sides by clusters from adjacent layers.

In our case, the stacking of hybrid grids along the [100] direction is such that the square-like voids result superimposed on each other and this type of supramolecular assembly generates channels parallel to the crystallographic x axis in which all of the water molecules are hosted (Figure 4a). Thus, the walls of these channels are delimited by rings of four $(V_{10}O_{28})^{6-}$ anions and four $\{Cu(cyclam)\}^{2+}$ complexes in alternate fashion with approximate cross-section of $10.4 \times 8.8 \text{ \AA}^2$ (distances $N4C \cdots N4C$ and $N1B \cdots N1B$, Figure 4b). The total solvent accessible volume is $428 \text{ \AA}^3$, which corresponds to approximately 25% of the unit cell volume as calculated using PLATON.²³ The surface representation of the

channel volume and that of the porous hybrid framework is given in Figure 4c.

Figure 4. a) Crystal packing of **1** viewed along the crystallographic y axis; b) Crystal packing of **1** viewed along the crystallographic x axis, with details of the hosted water molecules and the estimated dimensions of the channels; c) Surface representations of the channels running along the crystallographic x axis (left) and the surface of the porous network; color code: $\{VO_6\}$ (orange octahedra), Cu (blue polyhedra), N (green), O (red); hydrogen atoms are omitted for clarity.

Figure 5. Comparison of the extensive network of C–H...O (red) and N–H...O (green) interactions in **1** (top) and **1a** (bottom) with details of the H-bond network along the x axis. Color code: {VO₆} (orange), Cu (blue), N (green), O (red), H (pink).

The square-planar Cu₁A complex cation occupies interlamellar spaces and is sandwiched in between ditriangular faces of two (V₁₀O₂₈)⁶⁻ clusters belonging to different layers (Figure 4a). Indeed, the Cu₁A atom is located at a distance of 3.0730(2) Å from the plane formed by the bridging O atoms of these faces (O₁₂, O₁₅, O₂₄ and O₃₄). Despite the absence of any coordination bond connecting the layers, an extensive network of C–H...O and N–H...O interactions is established between the cyclam ligand of the Cu₁A complex and the surfaces of the sandwiching clusters. It should be noted that these interactions are more numerous and more favorable than those established by Cu₁B and Cu₁C complexes within layers (Tables S2 in the Supporting Information). As a result, the Cu₁A cation acts as an effective cementing agent to reinforce the stacking of the covalent layered lattices into a supramolecular open-framework material. In comparison, the water molecules of hydration do not appear to have any relevant structural role because they are weakly bound and do not interact with neither the cyclam ligands nor the terminal oxygen atoms of the clusters. In fact, only O₇W and O₉W appear to slightly contribute to the massive H-bond network amongst hybrid layers and Cu₁A cementing complexes (Figure 5). It is worth mentioning that another decavanadate-containing hybrid compound sharing similar metalorganic building blocks can be found in the literature, namely

[(CuL)_{0.5}(H₂L)_{1.5}][H₂V₁₀O₂₈]·6H₂O.^{17a} In this case, the macrocyclic polyamine ligand (L) is the hexamethyl derivative of cyclam (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and the inorganic cluster is diprotonated. The structure contains hybrid chains of alternating clusters and complexes, which arrange in supramolecular sheets via hydrogen bonding as opposed to the covalent bi-dimensional lattice of compound **1**.

Guest solvent molecules located in cavities or channels can often be removed from a given host material without causing the crystalline collapse of the porous framework. This should be the case for **1** according to the variable-temperature PXRD results. To determine whether the supramolecular three-dimensional assembly of **1** is robust enough to effectively maintain its open framework nature upon dehydration and to identify any structural change triggered by the release of the guest solvent, we attempted to perform single-crystal XRD experiments on crystals of **1** heated to 130 °C to evacuate all hydration water in the channels. Fortunately, the crystals maintained their integrity upon thermal treatment, and hence, full data collection on the **1a** anhydrous form could be carried out. As expected from the PXRD analyses, the structure of the anhydrous phase proved to be virtually identical to that of the hydrated **1**. Both the cell parameters and the relative arrangement of building blocks in the asymmetric unit, as

well as the bond lengths within and among the blocks, remained almost invariable as shown in Tables 1 and 2, as well as in Figures S9–S11 in the Supporting Information. Moreover, the dimensions of the channels did neither undergo significant variations when **1** was dehydrated into **1a** (Figure S12 in the Supporting Information), but for a subtle decrease of *ca.* 30 Å³ in the total solvent accessible void according to PLATON calculations (397 Å³, 24% of the unit cell)

This absence of significant modifications in the metal atom positions of the constituent building blocks upon evacuation of guest solvent molecules confirms the robustness of the open hybrid framework, as well as the fact that the water molecules (including O7W and O9W) do not fulfill any key structural role. This fact is consistent with the few intermolecular interactions observed between lattice water molecules and the decavanadate clusters or the cyclam ligands for the hydrated compound **1**. Nevertheless, some subtle changes in the extensive hydrogen-bonding network can be observed when transforming **1** into **1a**. The thermally triggered dehydration produces a rotation of the metal-organic complexes around their axial axes that slightly modifies some of the intermolecular C–H⋯O and N–H⋯O interactions between the cyclam ligands and the cluster surfaces (Figure 5 and Table S2 in the Supporting Information). This relative rotation is notably more accused for the Cu1B moiety (approximately 20°) than for the Cu1A and Cu1C complexes (less than 10°), but the overall number of favorable interactions is maintained nearly constant. Moreover, the interlamellar distance correlated with that of the Cu1A center to the plane formed by the O12, O15, O24 and O34 atoms remains virtually identical (3.0889(1) Å, Figure S9 in the Supporting Information), showing that our hybrid open-framework does not undergo any compression upon dehydration, and hence proving its robustness and permanent microporous nature.

Sorption Properties

The separation of small gases such N₂ and CO₂ is an important topic from industrial and environmental viewpoints. Since the channel dimensions found in the open-framework of **1** are larger than those of N₂ and CO₂, we decided to explore whether **1** could exhibit gas sorption properties. Our studies revealed that **1** does not exhibit the capability to adsorb N₂ while CO₂ adsorption does take place (Figure 6). This fact can be explained taking into account the presence of narrow microporosity in **1**. Although the kinetic diameter of the CO₂ and N₂ molecules (3.3 Å vs. 3.6 Å) are similar, the higher adsorption temperature for CO₂ confers the gas molecules a larger kinetic energy that favors their access into the narrow porosity, whereas N₂ molecules are kinetically restricted due to the low temperatures at which the adsorption of this gas is performed.^{26,34}

Compound **1** displays a type I isotherm for CO₂ adsorption, which is indeed characteristic of a microporous material (Figure 6). In regard to the characterization of its porous texture, it is first worth noticing that while the total micropore volume obtained from the N₂ adsorption corresponds to the whole range of microporosity (pore size up

to 2 nm), the CO₂ adsorption (V_{CO₂}) only provides specific information about narrow microporosity only (pore size < 0.8 nm). The volume of the micropores in **1** is 0.11 cm³ g^{−1}, while the BET (Brunauer–Emmett–Teller) surface area is 205 m² g^{−1}, as calculated from the CO₂ sorption isotherm at 273 K. These experimental data confirm that the micropores with approximate cross-sections of 10.4 × 8.8 Å² observed from single-crystal XRD studies (Figure 4b) are accessible and fully operative, which endows the hybrid open-framework of **1** with functionality in CO₂ capturing.

Figure 6. Type I isotherm of CO₂ adsorption at 0 °C for **1**.

Reports on BET data for POM-based crystalline open-framework materials are scarce.^{3b} A limited number of microporous hybrid compounds with CO₂ adsorption capability can be found in the literature. Mizuno's K₂[Cr₃O(OOCH)₆(4-ethylpyridine)₃]₂[α-SiW₁₂O₄₀] is a representative example as it shows a high CO₂/C₂H₂ sorption selectivity.^{5c} The closely related [Cr₃O(OOCCH=CH₂)₆(H₂O)₃]₃[α-PW₁₂O₄₀] ionic crystal displays shape-selective adsorption of CO₂ and C₂H₂ over the larger N₂ and methane molecules, due to the kinetic diameters of the former being comparable to the minimum pore aperture.^{5d} Compared to our compound, both examples show lower BET surface areas (75 and 50 m² g^{−1}, respectively) and this can be explained attending to their smaller channel apertures (3.5 Å and 3.3 Å, respectively). Some fully inorganic POM-based microporous materials have also displayed CO₂ sorption properties. For example, Ueda et al reported two inorganic microporous materials based on ε-Keggin-type clusters,^{8b,d} but both the BET surface areas and micropore volumes are approximately three to four times lower than those estimated for our compound. Wang et al. recently prepared the (TBA)₂[Cu^{II}(BBTZ)₂(α-Mo₈O₂₆)] POMOF (BBTZ = 1,4-bis(1,2,4-triazol-1-ylmethyl)-benzene), which exhibits the highest adsorption capacity reported for a POM-based hybrid.^{10a} The CO₂ uptake capacity at saturation of 165 cm³ g^{−1} at 195 K and 87.7 cm³ g^{−1} at 273 K is comparable to the best performing zeolite-like MOFs.^{2a} These results together with a remarkable BET surface area of 773 m² g^{−1} derive from the presence of a three-directional system of intersecting channels, as opposed to the system of parallel channels found in **1**. In fact,

the total solvent accessible volume is approximately 50% of the unit cell volume which is roughly twice the empty volume observed for our compound **1** upon thermal activation. To our knowledge, compound **1** is the first decavanadate-based crystalline material that exhibits CO₂ sorption capability as a straightforward consequence of i) the robust nature of its supramolecular open-framework structure and ii) the appropriate dimensions and accessibility of the channels.

Catalytic activity tests

The POM-catalyzed oxidation of hydrocarbons has been thoroughly studied over the past decades owing to its importance from industrial and synthetic viewpoints.³⁵ In this context, much attention has been paid to the oxidation of the tricyclic saturated hydrocarbon adamantane because this particular reaction is used as a probe to measure the C–H bond activation ability of a given catalyst. Thus, several compounds have been tested in both homogeneous and heterogeneous phase with different oxidizing agents (e.g. PhI, NaOCl, H₂O₂, O₂, alkyl hydroperoxides, percarboxylic acids), affording a great variety of results in terms of conversion and selectivity.³⁶

Table 3. Conversion of Adamantane and Selectivity after 6 Hours of Reaction in Different Cycles

Catalyst	Time (h)	Conv. (% mol)	^a Selectivity (%)			
			^b P ₁	P ₂	P ₃	P
None	24	0	—	—	—	—
H ₃ [PMo ₁₂ O ₄₀]	6	0	—	—	—	—
H ₄ [PVMo ₁₁ O ₄₀]	6	90	45	30	11	13
Compound 1	3	38	45	26	28	1
	6	99	36	20	31	13
V ₂ O ₅	6	50	22	23	8	47

^a based on the initial moles of adamantane; ^b P₁: 1-Adamantanol (1-AdOH), P₂: 2-Adamantanone (2-AdO), P₃: 2-Adamantanol (2-AdOH), P: Other products (1,3-Adamantanediol, 5-hydroxy-2-adamantanone, 1,3,5-Adamantanetriol). Experimental conditions: 75 °C, 4·10⁻⁵ moles of catalyst; 25 mg adamantane; 3 cm³ of hydrogen peroxide (30%); 10 cm³ of solvent (acetonitrile).

Scheme 1. H₂O₂-based Oxidation of Adamantane Using Compound **1** as Heterogeneous Catalyst

The catalytic activity of **1** toward the oxidation of adamantane has been explored in heterogeneous phase using hot acetonitrile as solvent and an environmentally friendly oxidant such as H₂O₂. Some other archetypal POM catalysts (H₃[PMo₁₂O₄₀] and H₄[PVMo₁₁O₄₀]), as well as V₂O₅, have also been tested in the same experimental conditions

for comparative purposes (Table 3). As expected, the reaction does not take place in the absence of any catalyst under the selected experimental conditions due to the high stability of the tricyclic alkane. It is also remarkable that the H₃[PMo₁₂O₄₀] heteropolyacid, which is a well-established oxidation catalyst for a range of organic substrates,³⁵ is in fact inactive in our conditions. The replacement of molybdenum centers with vanadium atoms in the framework of Keggin-type anions has proven to be beneficial for redox catalysis as it enhances the redox character of the cluster.³⁷ The higher catalytic activity observed for the mono-substituted H₄[PVMo₁₁O₄₀] species in this reaction (90% conversion after 6 h) is in good agreement with the comment above. In comparison, the catalytic activity of V₂O₅ is lower than that of the vanadium-containing Keggin type heteropolyacid (50% conversion after 6 h) despite the higher content of V atoms. These results are consistent with those reported by other authors, which suggests that vanadium constitutes the catalytic center for this reaction while the Keggin-type framework serves as scaffold to enhance its activity.³⁸

Compound **1** displays the highest activity among all catalysts tested in this study, reaching a conversion of 99% after just 6 hours of reaction. The distribution of the reaction products shows low-to-moderate selectivity toward 1-Adamantanol (1-AdOH) over other products from oxidation at secondary C–H bonds (2-AdOH, 2-Adamantanone). Selectivity toward 1-AdOH reaches a maximum of 45% after 3 h of reaction and decreases to 36% after 6 h due to the formation of other overoxidized side-products (Table 3 and Scheme 1). To our knowledge, no reports on the catalytic activity of decavanadate-containing compounds toward the H₂O₂-based oxidation of cycloalkanes can be found in the literature.

The fact that compound **1** affords the highest conversion in the shorter reaction time among all selected catalysts is worth remarking because vanadium substituted Keggin-type species like the H₄[PVMo₁₁O₄₀] comparative model have been identified as catalysts with the highest activity among POMs and certainly higher than those of transition-metal complexes such as VO(acac)₂.³⁵ As an illustrative comparison of the higher activity of **1**, 12 hours of reaction were needed to reach conversions in the 49–65% range when vanadium-substituted phosphomolybdate acids heterogenized in SBA15 mesoporous silica were used with butyronitrile as solvent.^{38a} When turning to homogeneous phase, several other POMs have been found to catalyze the oxidation of adamantane with H₂O₂ in acetonitrile, such as the divanadium-substituted phosphotungstate [γ-PW₁₀O₃₈V₂(μ-OH)(μ-O)]⁴⁻, hybrid species consisting of a metallosalen moiety covalently linked to a Keggin-type silicotungstate [SiW₁₁O₃₉]⁸⁻, or the [γ-SiW₁₀[Fe(OH)₂]₂O₃₈]⁶⁻ cluster.³⁹ These species yield conversions from 42 up to 98%, but the selectivity is much improved to values in the 74–94% range toward 1-AdOH except for the iron-containing catalyst, which affords a selectivity of 71% toward the 2-AdOH derivative.^{39d}

The high catalytic activity displayed by **1** could originate from its larger atomic proportion of vanadium per mole of

catalyst. However, the tested V_2O_5 does show a significantly lower conversion, and hence other effects must also be influencing the catalytic performance of **1**. The {Cu(cyclam)} metalorganic moieties coordinated to the {V₁₀O₂₈} clusters could very well be responsible for enhancing the catalytic activity of the V centers, in close analogy with the role of the Keggin scaffold in the vanadium-substituted phosphomolybdates. Moreover, the permanent porosity of the hybrid open-framework, as well as the dimensions of the channels in **1**, may also have a key enhancing effect.

CONCLUSIONS

The first POMOF-like hybrid compound with supramolecular microporous open-framework based on decavanadate clusters, namely [Cu(cyclam)][{Cu(cyclam)}₂(V₁₀O₂₈)·10H₂O (**1**), has been synthesized and fully characterized. The supramolecular architecture contains covalent decavanadate/{Cu(cyclam)} grids with square-like voids the stacking of which is driven by a massive network of intermolecular N–H...O and C–H...O interactions established with interlamellar cementing complexes. The structure is able to remain virtually unaltered upon thermal evacuation of guest solvent molecules located in the system of parallel channels generated by the stacking of the hybrid layers, as evidenced by a single crystal X-ray diffraction studies on the anhydrous **1a** derivative. The permanent microporous nature of **1** results in functional properties such as selective adsorption of CO₂ gas over N₂ and remarkable catalytic activity toward the oxidation of the highly-stable organic substrate adamantane in heterogeneous phase. To our knowledge, this is the first decavanadate-based hybrid compound that shows both CO₂ sorption capability and catalytic activity in the oxidation of cycloalkanes owing to its microporous nature, accessibility of channels and robustness of the framework.

ASSOCIATED CONTENT

Supporting Information

FT-IR spectra, PXRD patterns, structural figures and tables, and X-ray crystallographic data for **1** and **1a** in CIF format (CCDC 1426650, 1426651). The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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SYNOPSIS TOC

The supramolecular POMOF-like hybrid $[\text{Cu}(\text{cyclam})][\{\text{Cu}(\text{cyclam})\}_2(\text{V}_{10}\text{O}_{28})]\cdot 10\text{H}_2\text{O}$ (**1**) is constructed from the stacking of covalent decavanadate/ $\{\text{Cu}(\text{cyclam})\}$ layers and robust enough to retain its open-framework nature upon thermal removal of all solvent molecules hosted in the channels. The permanent microporous nature of **1** provides interesting functionality such as selective adsorption of CO_2 over N_2 molecules and catalytic activity toward the H_2O_2 -based oxidation of the highly-stable hydrocarbon adamantane.