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# Novel Vanadium(V) Compounds with a Layer Structure: Synthesis, Crystal Structures, and Solid State NMR Spectroscopy of $[(VO_2)_2(4,4'\text{-bpy})_{0.5}(4,4'\text{-Hbpy})(XO_4)]\cdot H_2O$ (X = P and As)

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A novel vanadium(V) phosphate and the arsenate analogue, $[(VO_2)_2(4,4'\text{-bpy})_{0.5}(4,4'\text{-Hbpy})(XO_4)]\cdot H_2O$ (X = P, As; bpy = bipyridine), have been synthesized under hydrothermal conditions and structurally characterized by single-crystal X-ray diffraction. They are the first structurally characterized compounds in the vanadium(V)/4,4′-bpy/phosphate (or arsenate) systems. The two compounds are isostructural and crystallize in the triclinic space group $P\bar{1}$ (No. 2) with $a = 7.9063(3)$ Å, $b = 10.2201(4)$ Å, $c = 12.1336(5)$ Å, $\alpha = 113.4652(7)°$, $\beta = 95.7231(7)°$, $\gamma = 94.4447(7)°$, and $Z = 2$ for the phosphate, and $a = 7.8843(6)$ Å, $b = 10.3686(7)$ Å, $c = 12.2606(9)$ Å, $\alpha = 113.464(1)°$, $\beta = 95.560(1)°$, $\gamma = 94.585(1)°$, and Z = 2 for the arsenate. The structure consists of phosphate-bridged vanadium(V) double chains linked through 4,4′-bpy ligands to form a sheet with the monoprotonated 4,4′-$\text{Hbpy}^+$ ligand being coordinated to the metal atom as a pendent group. The $^1$H MAS NMR spectrum exhibits four resonances at 14.2, 9.5, 7.2, and 3.7 ppm with an intensity ratio close to 1:6:6:2, corresponding to three different types of protons in 4,4′-bpy and 4,4′-$\text{Hbpy}^+$ and one type of protons in $H_2O$. The peak at 14.2 ppm can be assigned to the proton bonded to the pyridine nitrogen atom, which confirms the presence of 4,4′-$\text{Hbpy}^+$.

## Introduction

Recently, many researchers have used a hybrid approach to the synthesis of open-framework metal phosphates, in which an organic ligand is combined with an inorganic one.[1,2] As compared with inorganic ligands, the organic ligands have large sizes and a wide variety of means of connection. An interesting variant of the metal phosphate is obtained by incorporating the oxalate unit in the structure. A large number of oxalatophosphates of transition metals and group 13 elements have been prepared during the past few years.[3−9] A study of the literature about transition metal supramolecular architectures shows that the most extensively studied bridging organic ligand is 4,4′-bipyridine (4,4′-bpy).[1] We therefore extended our search for open frameworks into the 4,4′-bpy−phosphate system, and we have synthesized several interesting compounds.[10−13] As part of continuing work in this system, we synthesized a vanadium(V) compound with a layer structure which consists of neutral sheets of V/4,4′-bpy/$PO_4$.

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Metal phosphates with neutral layers are of interest with respect to intercalation reaction. These compounds are characterized by weak interlayer interactions such that they may accommodate large guest molecules by free adjustment of interlayer separation. The vanadyl phosphate dihydrate $VOPO_4\cdot 2H_2O$ is a well-known example that is capable of intercalating a wide variety of guest species, and as such it has been extensively studied. It readily undergoes redox intercalation reactions with alkali-metal and alkaline-earth-metal cations in the presence of a proper reducing agent.[14,15] It also forms a large number of intercalation compounds with a variety of molecular guests having Lewis base character. Intercalations of amines, heterocycles, carboxylic acids, amino acids, metallocenes, alcohols, aldehydes, and poly(oxyethylene) compounds have been studied.[16−18] These intercalation reactions permit controlled systematic changes in the electronic properties of the host lattice, and they are of practical use as sensors. To promote specific chemical reactions or to enhance particular physical properties, new types of host materials are often required. The synthesis of layered materials in which an organic group is attached to a layer through a covalent bond (derivatized layers) may offer the prospect of some interesting new systems. The organophosphonates of zirconium and vanadium have both been synthesized with a wide range of organic groups and shown to have interesting interlamellar reactivity.[19,20] Another type of layer derivatization is to modify the layer by coordination of organic group to the metal center. For example, reaction of $VOPO_4\cdot 2H_2O$ with pyridine leads to the formation of $VOPO_4\cdot$pyridine, which has all of the vanadium sites in the layer coordinated by pyridine.[16] Similar results were obtained with 4,4′-bipyridine, but the stoichiometry is $VOPO_4\cdot(4,4'\text{-bpy})_{0.5}$ and comparison of its interlayer spacing with those of other pyridine derivatives based on powder X-ray diffraction indicates that adjacent layers are cross-linked or pillared by the bifunctional ligand.[16] To our knowledge $VOPO_4\cdot(4,4'\text{-bpy})_{0.5}$ is the only known compound in the vanadium(V)/4,4′-bpy/phosphate system. However, its detailed structure is unknown due to the lack of a suitable crystal for X-ray structure analysis.

In this paper, we describe a novel layered vanadyl phosphate which consists of phosphate-bridged vanadium(V) double chains linked through 4,4′-bpy ligands to form a sheet with the monoprotonated 4,4′-$Hbpy^+$ ligand being coordinated to the metal atom as a pendent group. It is the first structurally characterized compound in the vanadium(V)/4,4′-bpy/phosphate system. The synthesis, crystal structure, and solid state NMR spectroscopy are reported. The arsenate analogue has also been synthesized and structurally characterized.

## Experimental Section

**Synthesis and Initial Characterization.** The hydrothermal reactions were carried out in Teflon-lined stainless steel Parr acid digestion bombs. All chemicals were purchased from Aldrich Chemicals. Arsenic acid was prepared from a reaction of $As_2O_3$ and $H_2O_2$. Reaction of $V_2O_5$ (0.5 mmol), 4,4′-bipyridine (10 mmol), $H_3PO_4$ (5 mmol), tetraethylammonium bromide (2 mmol), and $H_2O$ (10 mL) in a Teflon-lined acid digestion bomb at 160 °C for 3 days produced yellow crystalline product of [$(VO_2)_2(4,4'\text{-bpy})_{0.5}(4,4'\text{-Hbpy})(PO_4)$]$\cdot H_2O$, **1**, in 97% yield based on vanadium. The pH of the reaction mixture before hydrothermal reaction was 4.1. Powder X-ray diffraction pattern of the bulk product is in good agreement with the calculated pattern based on the results from single-crystal X-ray diffraction. Energy-dispersive X-ray fluorescence spectroscopy of several yellow crystals confirms the presence of V and P. Elemental analysis results of the bulk product are consistent with the stoichiometry of **1**. Anal. Found: C, 34.97; H, 2.92; N, 7.98%. Calcd: C, 35.04; H, 2.94; N, 8.17%. We have also carried out a retro synthesis without tetraethylammonium bromide in the reaction mixture; the product is a mixture of **1** and a considerable amount of orange needle crystals, which are soluble in ethanol and presumably a molecular compound. It appears that the use of tetraethylammonium bromide in the synthesis improves the yield. Yellow crystals of the arsenate analogue [$(VO_2)_2(4,4'\text{-bpy})_{0.5}(4,4'\text{-Hbpy})(AsO_4)$]$\cdot H_2O$, **2**, and a large amount of unidentified side product were obtained by heating a mixture of $V_2O_5$ (0.5 mmol), 4,4′-bipyridine (10 mmol), $H_3AsO_4$ (5 mmol), tetraethylammonium bromide (2 mmol), and $H_2O$ (10 mL) under the same reaction conditions. An optimum set of reaction conditions to prepare a single-phase product of **2** was not found.

**Single-Crystal X-ray Diffraction.** A suitable crystal of each compound was selected for indexing and intensity data collection on a Siemens SMART CCD diffractometer equipped with a normal focus, 3-kW sealed tube X-ray source. Intensity data were collected at room temperature in 1271 frames with $\omega$ scans (width 0.30° per frame). Empirical absorption corrections based on symmetry equivalents were applied.[21] The structures were solved by direct methods and difference Fourier syntheses. Bond-valence calculation results indicate that the vanadium atoms are pentavalent and O(9) is a water oxygen atom.[22] All 15 hydrogen atoms could be located. The final cycles of least-squares refinement included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The atomic coordinates and isotropic thermal parameters for all hydrogen atoms were fixed. All calculations were performed using the SHELXTL Version 5.1 software package.[23] The crystal data and structure refinement parameters are given in Table 1, and selected bond distances are given in Table 2.

**Solid State NMR Measurements.** All NMR spectra were acquired on a Bruker AVANCE-400 spectrometer, operating at 400.1 and 161.9 MHz for $^1H$ and $^{31}P$ nuclei, respectively. A Bruker probe equipped with 2.5 mm rotors was used. $^1H$ MAS NMR spectra were recorded at a spinning speed of 30 kHz to achieve good spectral resolution. The 90° pulse lengths of $^1H$ and $^{31}P$ were 4.0 and 5.5 $\mu$s, respectively. Recycle delays of 4 s were used for

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**Table 1.** Crystallographic Data for $[(VO_2)_2(4,4'\text{-bpy})_{0.5}(4,4'\text{-Hbpy})(PO_4)]\cdot H_2O$ (**1**) and $[(VO_2)_2(4,4'\text{-bpy})_{0.5}(4,4'\text{-Hbpy})(AsO_4)]\cdot H_2O$ (**2**)

| | **1** | **2** |
|---|---|---|
| chemical formula | $C_{15}H_{15}N_3O_9PV_2$ | $AsC_{15}H_{15}N_3O_9V_2$ |
| fw | 514.15 | 558.1 |
| space group | $P\bar{1}$ (No. 2) | $P\bar{1}$ (No. 2) |
| $a$, Å | 7.9063(3) | 7.8843(6) |
| $b$, Å | 10.2201(4) | 10.3686(7) |
| $c$, Å | 12.1336(5) | 12.2606(9) |
| α, deg | 113.4652(7) | 113.464(1) |
| $\beta$, deg | 95.7231(7) | 95.560(1) |
| $\gamma$, deg | 94.4447(7) | 94.585(1) |
| $V$, Å$^3$ | 887.5(1) | 907.4(2) |
| $Z$ | 2 | 2 |
| $T$, K | 296 | 296 |
| $\lambda$(Mo Kα), Å | 0.710 73 | 0.710 73 |
| $\rho_{calc}$, g·cm$^{-3}$ | 1.924 | 2.043 |
| $\mu$(Mo Kα), cm$^{-1}$ | 12.0 | 29.0 |
| $R_1$[a] | 0.0353 | 0.0245 |
| wR$_2$[b] | 0.0879 | 0.0691 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \Sigma\{[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o,0) + 2(F_c)^2]/3$, where $a = 0.0352$ and $b = 0.90$ for **1** and $a = 0.0368$ and $b = 0.60$ for **2**.

**Table 2.** Bond Lengths (Å) for $[(VO_2)_2(4,4'\text{-bpy})_{0.5}(4,4'\text{-Hbpy})(PO_4)]\cdot H_2O$ (**1**) and $[(VO_2)_2(4,4'\text{-bpy})_{0.5}(4,4'\text{-Hbpy})(AsO_4)]\cdot H_2O$ (**2**)[a]

| | | | |
|---|---|---|---|
| Compound **1** | | | |
| V(1)−O(1) | 1.950(2) | V(1)−O(4) | 1.940(2) |
| V(1)−O(5) | 1.622(2) | V(1)−O(6) | 1.625(2) |
| V(1)−N(1) | 2.229(2) | V(2)−O(2) | 1.948(2) |
| V(2)−O(3) | 1.942(2) | V(2)−O(7) | 1.616(2) |
| V(2)−O(8) | 1.619(2) | V(2)−N(3) | 2.210(2) |
| P(1)−O(1) | 1.541(2) | P(1)−O(2) | 1.528(2) |
| P(1)−O(3) | 1.528(2) | P(1)−O(4) | 1.530(2) |
| C(1)−C(3) | 1.393(3) | C(1)−N(1) | 1.338(3) |
| C(2)−N(1) | 1.345(3) | C(2)−C(5) | 1.375(3) |
| C(3)−C(4) | 1.392(3) | C(4)−C(5) | 1.391(3) |
| C(4)−C(6) | 1.485(3) | C(6)−C(7) | 1.390(4) |
| C(6)−C(10) | 1.392(4) | C(7)−C(8) | 1.377(4) |
| C(8)−N(2) | 1.331(4) | C(9)−C(10) | 1.377(4) |
| C(9)−N(2) | 1.328(4) | C(11)−C(13) | 1.386(3) |
| C(11)−N(3) | 1.336(3) | C(12)−C(14) | 1.378(3) |
| C(12)−N(3) | 1.343(3) | C(13)−C(15) | 1.399(3) |
| C(14)−C(15) | 1.391(3) | C(15)−C(15) | 1.483(4) |
| N(2)−H(13) | 1.073 | O(9)−H(14) | 0.812 |
| O(9)−H(15) | 0.798 | | |
| Compound **2** | | | |
| V(1)−O(1) | 1.960(2) | V(1)−O(4) | 1.940(2) |
| V(1)−O(5) | 1.624(2) | V(1)−O(6) | 1.624(2) |
| V(1)−N(1) | 2.226(2) | V(2)−O(2) | 1.949(2) |
| V(2)−O(3) | 1.942(2) | V(2)−O(7) | 1.622(2) |
| V(2)−O(8) | 1.619(2) | V(2)−N(3) | 2.202(2) |
| As(1)−O(1) | 1.688(2) | As(1)−O(2) | 1.677(2) |
| As(1)−O(3) | 1.670(2) | As(1)−O(4) | 1.676(2) |
| C(1)−C(3) | 1.389(3) | C(1)−N(1) | 1.340(3) |
| C(2)−N(1) | 1.345(3) | C(2)−C(5) | 1.370(3) |
| C(3)−C(4) | 1.396(3) | C(4)−C(5) | 1.395(3) |
| C(4)−C(6) | 1.484(3) | C(6)−C(7) | 1.396(4) |
| C(6)−C(10) | 1.388(4) | C(7)−C(8) | 1.376(4) |
| C(8)−N(2) | 1.330(4) | C(9)−C(10) | 1.380(4) |
| C(9)−N(2) | 1.330(4) | C(11)−C(13) | 1.380(3) |
| C(11)−N(3) | 1.344(3) | C(12)−C(14) | 1.376(3) |
| C(12)−N(3) | 1.340(3) | C(13)−C(15) | 1.394(3) |
| C(14)−C(15) | 1.397(3) | C(15)−C(15) | 1.480(4) |
| N(2)−H(13) | 1.061 | O(9)−H(14) | 0.748 |
| O(9)−H(15) | 0.803 | | |

[a] The C−H bond lengths are given in the Supporting Information.

$^1$H NMR. The chemical shifts were externally referenced to tetramethylsilane (TMS) for $^1$H NMR and 85% $H_3PO_{4(aq)}$ for $^{31}$P NMR.

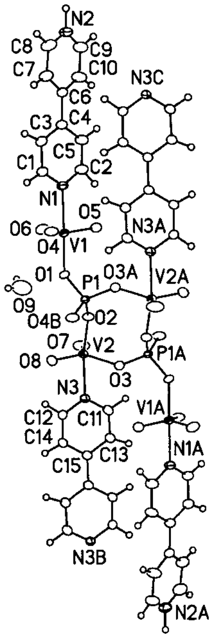

**Figure 1.** Local coordination of the vanadium atoms in $[(VO_2)_2(4,4'\text{-bpy})_{0.5}(4,4'\text{-Hbpy})(PO_4)]\cdot H_2O$ showing the atom-labeling scheme and eliipsoids at 50% probability. Small open circles represent hydrogen atoms.

## Results and Discussion

**Description of the Structure.** The two compounds are isostructural; therefore, only the structure of the phosphate is discussed. All atoms are at general positions. The asymmetric unit contains two $V^{5+}$ ions, two distinct 4,4′-bipyridine ligands, a $PO_4^{3-}$ anion, and a lattice water molecule. The 4,4′-bipyridine molecules are present in two distinct forms: one is neutral and the other one is monoprotonated. The neutral ligand is planar and sits on an inversion center. The other one is not planar; rather the rings are twisted at an angle of 13.7°. Figure 1 shows the coordination of the vanadium atoms in the structure. Each $V^{5+}$ cation has a distorted trigonal bipyramidal coordination in which two equatorial positions are occupied by terminal oxygen atoms, one axial position is occupied by the N atom of a bipyridine ligand, and the remaining positions are occupied by two $PO_4^{3-}$ anions. The *cis*-$VO_2$ arrangement with two very short V═O bonds is a feature characteristic of vanadium(V). Each phosphate ligand coordinates to four different vanadium atoms.

The structure consists of two-dimensional neutral sheets of V/4,4′-bpy/$PO_4$ in the *ac*-plane with the water molecules between the sheets (Figure 2). Each sheet is constructed from phosphate-bridged vanadium double chains along the *a*-axis, which are joined by neutral 4,4′-bpy ligands (Figure 3). The monoprotonated 4,4′-Hbpy$^+$ ligand coordinates to V(1) and extends away from the layer as a pendent group, which accounts for the comparatively larger thermal parameters of the atoms in 4,4′-Hbpy$^+$ than those in 4,4′-bpy. The 4,4′-Hbpy$^+$ ligand is oriented in a direction parallel to the neighboring 4,4′-bpy ligand in adjacent layer in an offset fashion; hence, the $\pi-\pi$ interaction is weak. The guest water molecules are located in a channel surrounded by two 4,4′-Hbpy$^+$ ligands and two phosphate-bridged vanadium double

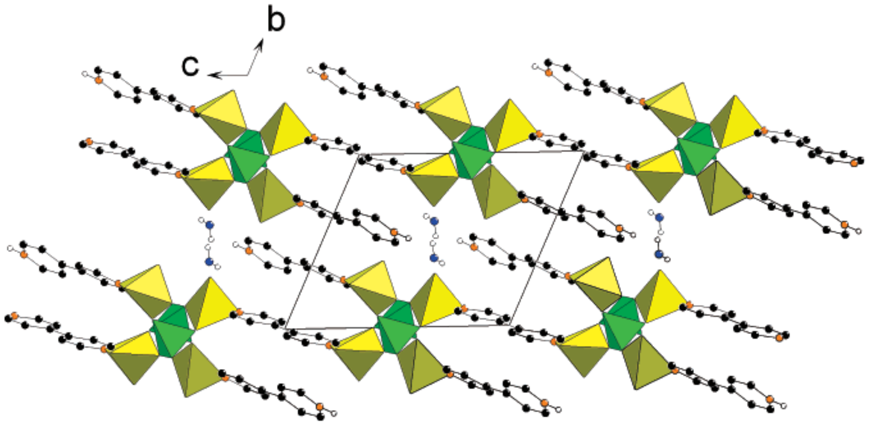

**Figure 2.** Structure of $[(VO_2)_2(4,4'\text{-bpy})_{0.5}(4,4'\text{-Hbpy})(PO_4)]\cdot H_2O$ viewed along the [100] direction. The $VO_4N$ trigonal bipyramids are shown in yellow, and $PO_4$ tetrahedra in green. Black circles, C atoms; orange circles, N atoms; blue circles, water O atoms; small open circles, H atoms.

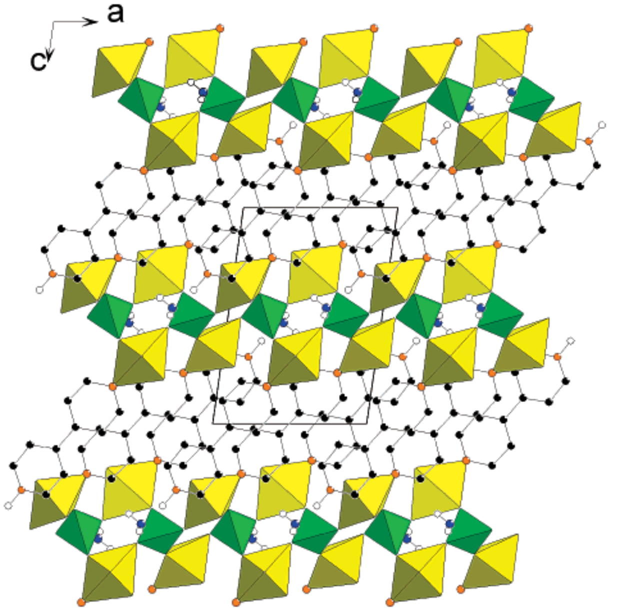

**Figure 3.** Section of a layer in $[(VO_2)_2(4,4'\text{-bpy})_{0.5}(4,4'\text{-Hbpy})(PO_4)]\cdot H_2O$ viewed along the [010] direction.

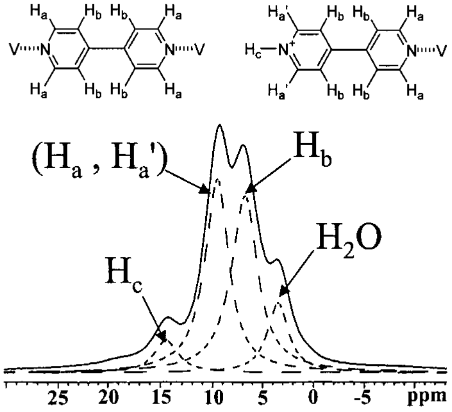

**Figure 4.** $^1H$ MAS NMR spectrum of $[(VO_2)_2(4,4'\text{-bpy})_{0.5}(4,4'\text{-Hbpy})(PO_4)]\cdot H_2O$ acquired at a spinning speed of 30 kHz. The spectrum was deconvoluted using four peaks in an intensity ratio close to 1:6:6:2 for three different types of protons in 4,4′-bpy and 4,4′-Hbpy and one type of proton in $H_2O$, respectively, as shown by dashed lines.

chains, and are held in the crystal lattice by hydrogen bonding ($H_2O\cdots H-N$, $d(O\cdots H) = 1.949$ Å, $d(O\cdots N) = 2.789$ Å, $\angle O-H-N = 132°$). The water molecule is not hydrogen bonded to any oxygen atoms in the host layers, as indicated from interatomic distances.

**$^1$H MAS NMR.** To address the issue of protonation of 4,4′-bipyridine, $^1H$ MAS NMR experiments were performed at a high spinning speed (30 kHz) to largely reduce strong $^1H-^1H$ dipolar interactions, and thus to achieve good spectral resolution. Figure 4 shows the $^1H$ MAS NMR spectrum of **1**, along with the assignments to specified protons as indicated in the inset of the figure. Four major resonances are observed at 3.7, 7.2, 9.5, and 14.2 ppm. The resonances at 7.2 and 9.5 ppm are indicated from a comparison with the $^1H$ solution NMR spectrum of 4,4′-bipyridine molecule to be assigned to the $H_b$ and ($H_a$, $H_a'$) protons in the aromatic ring, respectively. However, the spectral resolution is not high enough to distinguish resonances from closely similar $H_a$ and $H_a'$ protons. The peak at 14.2 ppm can be assigned to the proton bonded to the pyridine nitrogen atom based on its downfield character, which confirms the presence of monoprotonated 4,4′-$Hbpy^+$. The resonance at 3.7 ppm is ascribed to the protons of the guest water molecule. The $^1H$ NMR spectrum was deconvoluted using four peaks as shown in dashed lines in Figure 4. The intensity ratio of the four resonances at 14.2, 9.5, 7.2, and 3.7 ppm is equal to 1.0: 6.3:6.4:2.0, which is in good agreement with the stoichiometry of **1** (1:6:6:2) as determined from X-ray diffraction. The $^{31}P$ MAS NMR spectrum exhibits a single resonance at −0.7 ppm, which corresponds to only one type of phosphate in the structure.

In summary, the hydrothermal synthesis of the layered vanadyl phosphate $[(VO_2)_2(4,4'\text{-bpy})_{0.5}(4,4'\text{-Hbpy})(PO_4)]\cdot H_2O$ and its crystal structure have been described. The presence of 4,4′-$Hbpy^+$ is confirmed by $^1H$ MAS NMR spectroscopy. It is a new member of a growing class of layered compounds in which organic fragment is attached to a layer through a covalent bond, and it is also the first fully characterized compound in the vanadium(V)/4,4′-bpy/phosphate system. The other member of the system, $VOPO_4\cdot(4,4'\text{-bpy})_{0.5}$, was inferred from powder X-ray diffraction to consist of alternating organic and inorganic layers, where adjacent inorganic layers are pillared by 4,4′-bpy.[16] In contrast, the structure of $[(VO_2)_2(4,4'\text{-bpy})_{0.5}(4,4'\text{-Hbpy})$-

$(PO_4)]\cdot H_2O$ consists of phosphate-bridged vanadium(V) double chains linked through 4,4′-bpy ligands to form a sheet with the monoprotonated 4,4′-$Hbpy^+$ ligand being coordinated to the metal atom as a pendent group. The resulting layer structure is new and should show different kinds of interlamellar reactivity as compared with $VOPO_4\cdot 2H_2O$ and its pyridine or bipyridine derivatives. The new host structure may offer some possibilities for new chemical properties. Further research on the intercalation chemistry of the title compound is in progress.

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**Supporting Information Available:** Two X-ray crystallographic files, in CIF format, are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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