Inorg. Chem. **2001,** *40,* 2625−2627

Notes

Synthesis and Structure of $(4,4'\text{-}H_2bpy)[V_2(HPO_4)_4(4,4'\text{-}bpy)_2]$, a Novel Two-Dimensional Network Compound

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Received October 23, 2000

Introduction

The synthesis of open-framework metal phosphates has been a subject of intense research owing to their interesting structural chemistry and potential applications as ion-exchangers, catalysts, and adsorbents.[1] A large number of these materials are synthesized in the presence of organic amines as structure-directing agents. Recently, many research activities have focused on the synthesis of inorganic−organic hybrid frameworks.[2] As compared with inorganic ligands, the advantage of using organic multidentate ligands is the efficacy of rational design of crystalline solids through their coordinating propensities and geometries. We and others have synthesized a number of inorganic−organic hybrid frameworks, namely phosphato-oxalates of transition metals and Group 13 elements.[3−8] A study of the literature about transition metal supramolecular architectures shows that the most extensively studied bridging organic ligand is 4,4′-bipyridine, and a large number of 4,4′-bipyridine-bridged compounds with one-, two-, and three-dimensional structures have been reported.[2] Thus, a strategy for new inorganic−organic hybrid frameworks was conceived leading to the preparation of metal−phosphate-4,4′-bpy extended structures. The results presented here concern the novel compound $(4,4'\text{-}H_2bpy)[V_2(HPO_4)_4(4,4'\text{-}bpy)_2]$, **1**, which consists of octahedral vanadium(III) sites linked through both 4,4′-bpy and phosphate ligands into a 2-D layer structure with the uncoordinated 4,4′-bipyridinium cations between the layers.

Experimental Section

Synthesis and Initial Characterization. Via hydrothermal synthesis, a mixture of VCl_3 (1 mmol), 4,4′-bipyridine (10 mmol), H_3PO_4 (5 mmol), tetraethylammonium bromide (2 mmol), and H_2O (10 mL) was sealed in a Teflon-lined acid digestion bomb and heated at 165 °C for 3 days under autogenous pressure followed by slow cooling at 10 °C h^{-1} to room temperature. The resulting product consisted of green plate-shaped crystals of **1** as the only product in a yield of 77% based on vanadium. Powder X-ray diffraction pattern of the bulk product was in good agreement with the calculated pattern based on the results from single-crystal X-ray diffraction. A suitable green plate crystal was selected for structure determination by single-crystal X-ray diffraction. Elemental analysis confirmed the stoichiometry of **1**. Anal. Found: C, 37.66; H, 3.25; N, 8.71%. Calcd: C, 37.68; H 3.16; N, 8.79%.

TGA in air (ramp at 10 °C min^{-1} to 800 °C) revealed the onset of weight loss at ca. 200 °C in several overlapping steps, which was complete by ca. 750 °C. The final decomposition product was indicated from powder X-ray diffraction to be $VO(PO_3)_2$.[9] The observed total weight loss of 56.5% is somewhat larger than the calculated value 52.9% according to the equation $(H_2bpy)[V_2(HPO_4)_4(bpy_2) + {}^1/_2O_2 \rightarrow 2VO(PO_3)_2 + 3bpy + 3H_2O$. To determine the thermal stability of **1**, a sample was heated in air to 200, 250, 300, and 325 °C and kept there for 2 h for each temperature, followed by powder X-ray diffraction and elemental analysis. An ion-exchange experiment was performed by stirring **1** with 4 M $NH_4Cl_{(aq)}$ at room temperature and 50 °C overnight. Elemental analysis of the ion-exchanged products showed that ion-exchange did not occur at room temperature and about 60% of the H_2bpy^{2+} cations were replaced by NH_4^+ at 50 °C.

Single-Crystal X-ray Diffraction. X-ray intensity data were collected on a Siemens SMART CCD diffractometer in 1271 frames with ω scans (width 0.30° and exposure time of 20 s per frame). Of the 3986 unique reflections collected ($2\theta_{max} = 56.6°$, $R_{int} = 0.0331$), 3354 reflections were considered obverved [$F_o > 4\sigma(F_o)$] after empirical absorption correction ($T_{min/max} = 0.938/0.979$). Bond-valence calculation results indicate that O(4) and O(8) are hydroxo oxygen atoms, and both phosphate ligands are HPO_4^{2-}. All the H atoms except those bonded to the N atoms of the uncoordinated 4,4′-bipyridinium cation were found in difference Fourier maps. Both hydroxo groups receive hydrogen bonds from phosphate groups in adjacent V-phosphate-4,4′-bpy sheets as indicated by short O···O and O···H distances (O(4)···O(6) = 2.680 Å, O(6)···H(4O) = 1.741 Å, O(8)···O(1) = 2.688 Å, O(1)···H(8O) = 1.750 Å. Least-squares refinement (267 parameters) was performed with anisotropic thermal parameters for all non-hydrogen atoms and fixed isotropic thermal parameters for all H atoms. $(\Delta\rho)_{max,min} = 0.47, -0.44$ e $Å^{-3}$. The reliability factors converged to $R1 = 0.0449$, $wR2 = 0.1096$ and $S = 1.075$. The crystallographic data and bond lengths ar given in Tables 1 and 2, respectively.

Results and Discussion

The two-dimensional layer structure of **1** consists of anionic $\{[V_2(HPO_4)_4(4,4'\text{-}bpy)_2]^{2-}\}_\infty$ sheets in the *bc*-plane as shown in Figure 1. The local coordination of vanadium atoms is shown in Figure 2 with labeling of atoms. Adjacent sheets are connected by O−H···O hydrogen bonds to generate rectangular channels along the [001] direction in which the charge-compensating uncoordinated $(4,4'\text{-}H_2bpy)^{2+}$ cations are located (Figure 3). Each sheet contains phosphate-bridged vanadium(III) chains linked through 4,4′-bpy ligands. The three bpy molecules in the asymmetric unit are present in two distinct forms; one in the free state and the other two as ligands to vanadium. The $(4,4'\text{-}H_2bipy)^{2+}$ cation alternates with a bpy ligand along the *a*-axis. The vanadium ions, which sit on

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10.1021/ic001169g CCC: $20.00

Table 1. Crystallographic Data for $(4,4'\text{-}H_2bpy)[V_2(HPO_4)_4(4,4'\text{-}bpy)_2]$

chemical formula	$C_{30}H_{30}N_6O_{16}P_4V_2$
fw	956.36
space group	*P2* (No. 3)
a/Å	8.1434(9)
b/Å	11.434(1)
c/Å	10.090(1)
β/deg	107.060(2)
V/Å^3	898.2(3)
Z	1
T, °C	23
λ(Mo Kα), Å	0.71073
ρ_{calcd}, g·cm^{-3}	1.768
μ(Mo Kα), cm^{-1}	7.8
$R1^a$	0.0449
w$R2^b$	0.1096

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0530*P)^2 + 0.30*P]$ with P $= (\text{Max}F_o^2 + 2*F_c^2)/3$.

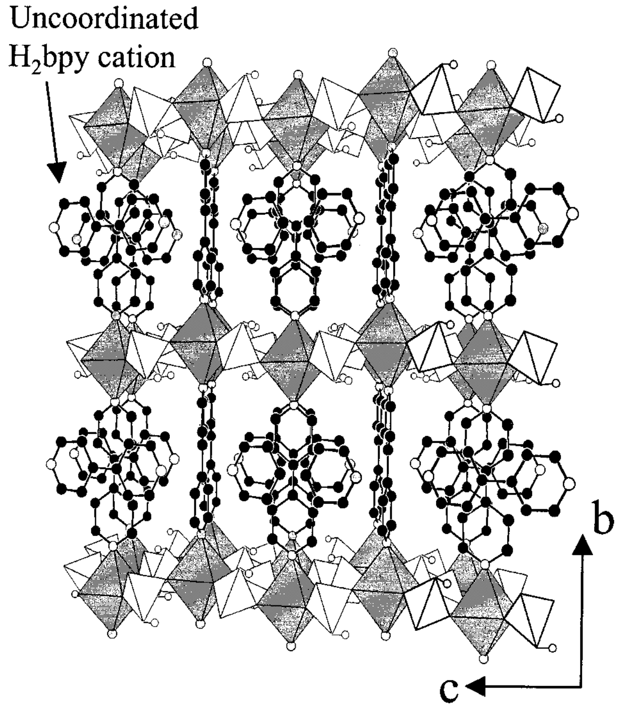

Figure 1. Structure of $(4,4'\text{-}H_2bpy)[V_2(HPO_4)_4(4,4'\text{-}bpy)_2]$ viewed along the [100] direction. Polyhedra with darker and lighter gray patterns are VO_4N_2 octahedra and PO_4 tetrahedra, respectively. Large solid circles, C atoms; stippled circles, N atoms; small open circles, H atoms.

crystallographic *2*-fold axes, display elongated octahedral coordination with four phosphate ligands (V−O = 1.947−1.950 Å for V(1) and 1.945−1.973 Å for V(2)) at the equatorial positions and two bpy ligands (V−N = 2.143, 2.164 Å for V(1) and 2.159, 2.181 Å for V(2)) at the axial positions. In this way, the double phosphate bridges give rise to the extension of the structure along the [001] direction while the bpy bridges extend along [010]. The V···V distances through the phosphate and bpy bridges are 5.11 and 11.43 Å, respectively, and the interplanar distances is 8.14 Å. Each $(4,4'\text{-}H_2bpy)^{2+}$ cation is clathrated in a rectangular channel between adjacent layers and is orientated in a direction orthogonal to the neighboring bpy ligands in an offset fashion; hence, the $\pi-\pi$ interaction is weak. The cation is not stabilized by any hydrogen bonds, as is indicated from the very long N···O and N···N distances. This accounts for the larger thermal apramenters of all atoms in the H_2bpy^{2+} cation and that the cations are readily exchanged with NH_4^+ at 50 °C. The two pyridyl rings of the bpy molecules within the sheets are rotated by 8.5° and 15.7° with respect to one another, while the pyridyl groups in the uncoordinated bpy molecules are nearly coplanar (2.2°). Powder X-ray diffraction and elemental analysis of the samples that have been heated in air reveal that compound **1** retains its layer structure intact at 300 °C with all the H_2bpy^{2+} cations being removed and decomposes at 325 °C with the loss of 4,4′-bpy ligand.

We have previously reported several compounds in the metal−phosphate-4,4′-bpy system. The structures of $[Ga_5(OH)_2(C_{10}H_9N_2)(C_2O_4)(HPO_4)_4]\cdot 2H_2O$ and $[Ga_4(C_{10}H_9N_2)_2(PO_4)(H_{0.5}PO_4)_2(HPO_4)_2(H_2PO_4)_2(H_2O)_2]\cdot H_2O$ contain a monodentate 4,4′-bpy ligand to a gallium atom with the other nitrogen of the ligand being protonated.[4,10] $[In_4(4,4'\text{-}bpy)_3(HPO_4)_4(H_2PO_4)_4]\cdot 4H_2O$ consists of neutral sheets of indium phosphate which are pillared through bidentate bridging 4,4′-bpy ligands.[11] The

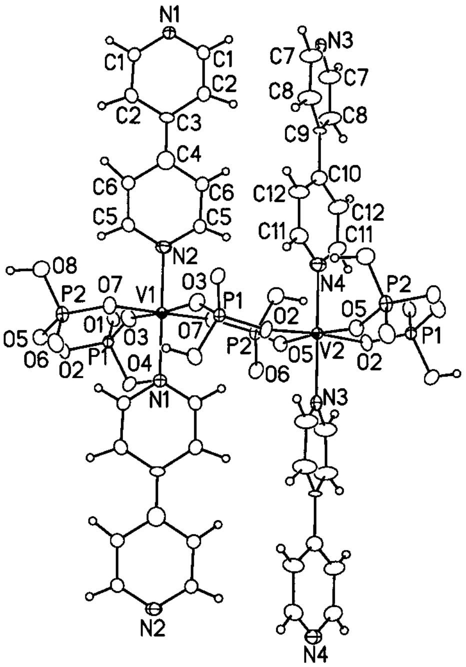

Figure 2. Local coordination of the vanadium atoms in an anionic $\{[V_2(HPO_4)_4(4,4'\text{-}bpy)_2]^{2-}\}_\infty$ sheet showing the atom-labeling scheme and ellipsoids at 50% probability. Small open circles represent hydrogen atoms.

Table 2. Bond Lengths (Å) for $(4,4'\text{-}H_2bpy)[V_2(HPO_4)_4(4,4'\text{-}bpy)_2]$

V(1)−O(3)	1.947(3) (2×)	V(1)−O(7)	1.950(3) (2×)
V(1)−N(1)	2.164(7)	V(1)−N(2)	2.143(7)
V(2)−O(2)	1.973(3) (2×)	V(2)−O(5)	1.945(3) (2×)
V(2)−N(3)	2.159(7)	V(2)−N(4)	2.181(7)
P(1)−O(1)	1.537(4)	P(1)−O(2)	1.498(3)
P(1)−O(3)	1.498(4)	P(1)−O(4)	1.577(4)
P(2)−O(5)	1.518(3)	P(2)−O(6)	1.561(4)
P(2)−O(7)	1.508(3)	P(2)−O(8)	1.560(4)
N(1)−C(1)	1.340(5)	N(2)−C(5)	1.343(6)
N(3)−C(7)	1.339(6)	N(4)−C(11)	1.346(6)
N(5)−C(13)	1.338(8)	N(5)−C(17)	1.317(8)
C(1)−C(2)	1.388(6)	C(2)−C(3)	1.410(6)
C(3)−C(4)	1.42(1)	C(4)−C(6)	1.409(7)
C(5)−C(6)	1.385(6)	C(7)−C(8)	1.368(6)
C(8)−C(9)	1.390(6)	C(9)−C(10)	1.53(1)
C(10)−C(12)	1.375(6)	C(11)−C(12)	1.378(6)
C(13)−C(14)	1.385(9)	C(14)−C(15)	1.399(8)
C(15)−C(15)	1.49(1)	C(15)−C(16)	1.396(8)
C(16)−C(17)	1.391(9)	O(4)−H(4O)	0.940
O(8)−H(8O)	0.953	C(1)−H(1C)	0.934
C(2)−H(2C)	1.010	C(5)−H(5C)	0.927
C(6)−H(6C)	1.087	C(7)−H(7C)	0.993
C(11)−H(11C)	0.982		

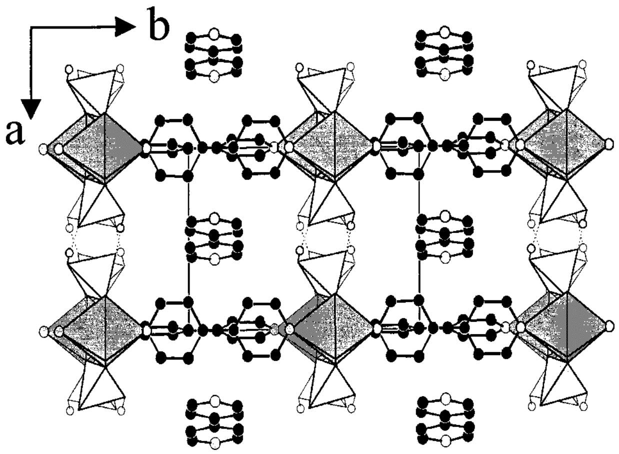

Figure 3. Structure of (4,4′-H_2bpy)[$V_2(HPO_4)_4$(4,4′-bpy)$_2$] viewed along the [001] direction. Dotted lines denote hydrogen bonds.

compound described here, with its unique layer structure, is the first metal phosphate to incorporate 4,4′-bipyridine in two distinct forms, one in the free state and the other one as a bridging ligand to two vanadium atoms. Although the dual role of 4,4′-bpy has been reported in the coordination polymer [Cu(4,4′-bpy)$_2$(H_2O)$_2$](ClO_4)$_4$·(4,4′-H_2bpy),[12] such a structure has not been encountered in any phosphate materials reported hitherto. This interesting compound provides potential for further exploration. For example, it may be possible to increase the size of the channels to generate novel structure types by replacing 4,4′-bpy with extended analogues such as 1,2-bis(4-pyridyl)ethene and bipyridylamine. Other trivalent metal cations such as Fe^{3+}, Ga^{3+}, and In^{3+} may also be employed. Further work on this theme is in progress.

Acknowledgment. We thank the National Science Council and Chinese Petroleum Corp. for support, and Ms. F.-L. Liao and Prof. S.-L. Wang at the National Tsing Hua University for X-ray data collection.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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