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Hydrothermal synthesis and crystal structure of a layered vanadium phosphate with a directly coordinated organonitrogen ligand: $[V_4O_7(HPO_4)_2(2,2'\text{-bipy})_2]$

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A layered vanadium phosphate $[V_4O_7(HPO_4)_2(2,2'\text{-bipy})_2]$ was synthesized and characterized (elemental analysis, IR and thermal analysis) by the hydrothermal reaction of $NaVO_3\cdot2H_2O$, ZnO, H_3PO_4, 2,2′-bipy and water. The compound $[V_4O_7(HPO_4)_2(2,2'\text{-bipy})_2]$ exhibits a unique 4,6,8-net structure with organonitrogen donors of 2,2′-bipy ligands coordinated directly to the vanadium phosphate framework.

Introduction

Contemporary interest in vanadium phosphate solid materials stems from their structural diversity[1–7] and potential applications in catalysis and materials science.[8,9] In studies of these materials, an astonishing variety of novel phases arise from the combination of vanadium phosphate progenitors and organic molecules. Such structural variety arises due to the versatility of vanadium in terms of its variable oxidation state (III, IV, and V) and coordination geometry (tetrahedral, square pyramidal, and octahedral), combined with the structure directing effect of the organic component. In the V–P–O system, an organic component may be introduced as a charge compensating and space-filling constituent,[10–12] it may also function as a ligand, coordinated directly to the vanadium phosphate scaffold or to a secondary metal center.[13–15] Although a large number of vanadium phosphates have been reported, the organic components in most of these complexes occur as charge compensating and space-filling constituents. To the best of our knowledge, vanadium phosphate complexes containing organic components functioning as ligands coordinated directly to the vanadium phosphate scaffold or to secondary metal centers are rare. As the connecting patterns of vanadium and phosphorus polyhedra can be greatly affected by coordinated organic components, a number of novel V–P–O frameworks could be discovered if organic moieties were made to function as a ligand coordinated to the vanadium phosphate scaffold or to a secondary metal center through modified synthetic conditions.

In this work we report on the hydrothermal synthesis and crystal structure of a novel layered vanadium phosphate with a directly coordinated organonitrogen ligand $[V_4O_7(HPO_4)_2(2,2'\text{-bipy})_2]$ **1** (2,2′-bipy = 2,2′-bipyridine). This compound possesses a unique 4,6,8-net structure.

Experimental

Materials and methods

Reagents were purchased commercially and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. V and P were determined by a Leeman inductively coupled plasma (ICP) spectrometer. The infrared spectrum was obtained on an Alpha Centaurt FT/IR spectrometer with a pressed KBr pellet in the 4000–400 cm^{-1} region. A Perkin-Elmer TGA7 thermogravimetric analyzer was used to obtain the TGA curve in N_2 with a temperature ramp rate of 10 °C min^{-1}.

Synthesis

A mixture of $NaVO_3\cdot2H_2O$ (0.088 g), ZnO (0.135 g), H_3PO_4 (0.327 g), 2,2′-bipy (0.087 g) and H_2O (10 ml) was stirred for 20 min in air. The mixture was then transferred to a Teflon-lined autoclave (20 ml) and kept at 160 °C for 96 h. After slow cooling to room temperature, black crystals were filtered off, washed with distilled water and dried in a desiccator at room temperature to give a yield of 50% based on V. ZnO is necessary for this reaction though zinc is not incorporated into the structure of compound **1**. The black crystals were manually selected for structural determination and further characterization. The ICP analysis showed that compound **1** contained 24.5% V and 7.4% P (Calcd: V, 24.8; P, 7.6%). The elemental analysis found: C, 29.0; H, 2.4; N, 6.7 (Calcd: C, 29.3; H, 2.2; N, 6.8%).

X-Ray crystallography

A black single crystal of **1** was mounted inside a glass fiber capillary. Data were collected on a R-axis RAPID IP diffractometer. Empirical absorption correction was applied. The structure was solved by the direct method and refined by full-matrix least squares on F^2 using the SHELXL-97 software.[16] All of the non-hydrogen atoms were refined anisotropically. H1 was located in its calculated position and H2 to H9 were located from difference Fourier maps. Further details of the X-ray structural analysis are given in Table 1. Selected bond lengths and angles are listed in Table 2.

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See http://www.rsc.org/suppdata/dt/b2/b203324k/ for crystallographic data in CIF or other electronic format.

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Table 1 Crystal data and structure refinement for **1**

Empirical formula	$C_{20}H_{18}N_4O_{15}P_2V_4$
Formula weight	820.08
T/K	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	8.3682(17)
b/Å	9.2153(18)
c/Å	9.5991(19)
α/°	97.04(3)
β/°	109.91(3)
γ/°	99.01(3)
V/Å^3	675.0(2)
Z	1
μ/mm^{-1}	1.545
Reflections collected	5006
Independent reflections	2863 [R(int) = 0.0469]
Final $R1$, $wR2$ induces [$I > 2\sigma(I)$]	0.0422, 0.1164
(all data)	0.0534, 0.1225

Table 2 Selected bond lengths (Å) and angles (°) for **1**

V(1)–O(6)	1.614(2)	V(1)–O(5)	1.654(2)
V(1)–O(7)	1.7773(6)	V(1)–O(3)	1.830(2)
V(2)–O(8)	1.596(2)	V(2)–O(1)	1.982(2)
V(2)–O(2)	1.983(2)	V(2)–O(5)	2.066(2)
V(2)–N(1)	2.138(3)	V(2)–N(2)	2.264(3)
P(1)–O(1)	1.509(2)	P(1)–O(2^1)	1.520(2)
P(1)–O(3^2)	1.557(2)	P(1)–O(4)	1.569(2)
O(6)–V(1)–O(5)	108.44(12)	O(6)–V(1)–O(7)	109.82(9)
O(5)–V(1)–O(7)	110.21(9)	O(6)–V(1)–O(3)	108.33(12)
O(5)–V(1)–O(3)	109.22(12)	O(7)–V(1)–O(3)	110.76(9)
O(8)–V(2)–O(1)	99.84(12)	O(8)–V(2)–O(2)	105.33(12)
O(1)–V(2)–O(2)	88.87(10)	O(8)–V(2)–O(5)	94.73(12)
O(1)–V(2)–O(5)	165.38(10)	O(2)–V(2)–O(5)	88.42(10)
O(8)–V(2)–N(1)	93.92(12)	O(1)–V(2)–N(1)	85.83(10)
O(2)–V(2)–N(1)	160.64(10)	O(5)–V(2)–N(1)	92.04(10)
O(8)–V(2)–N(2)	165.31(11)	O(1)–V(2)–N(2)	85.47(10)
O(2)–V(2)–N(2)	88.36(10)	O(5)–V(2)–N(2)	80.10(10)
N(1)–V(2)–N(2)	72.68(10)	O(1)–P(1)–O(2^1)	116.86(13)
O(1)–P(1)–O(3^2)	109.73(13)	O(2^1)–P(1)–O(3^2)	109.24(13)
O(1)–P(1)–O(4)	104.69(14)	O(2^1)–P(1)–O(4)	109.34(13)
O(3^2)–P(1)–O(4)	106.43(15)	P(1)–O(1)–V(2)	139.83(14)
P(1^1)–O(2)–V(2)	133.74(14)	P(1^3)–O(3)–V(1)	143.89(15)
V(1)–O(5)–V(2)	144.40(13)	V(1)–O(7)–V(1^4)	180.000(1)

Symmetry transformations used to generate equivalent atoms: ^{1} $-x, -y+2, -z+2$; ^{2} $x-1, y, z$; ^{3} $x+1, y, z$; ^{4} $-x+1, -y+1, -z+2$.

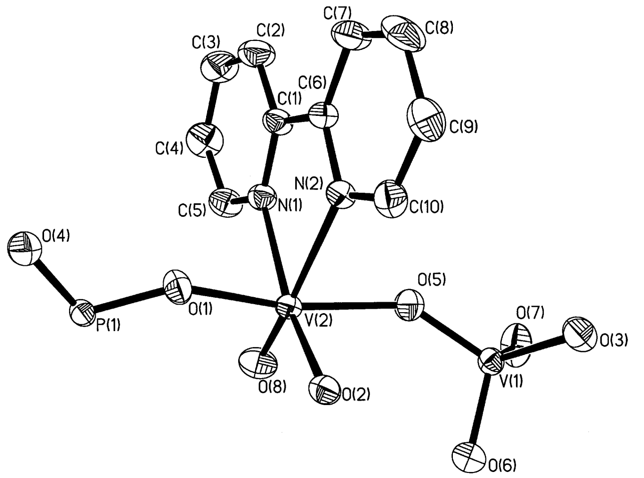

Fig. 1 Thermal ellipsoid plot of **1** showing the coordination environment around V and P and their connectivity.

Results and discussion

Vanadium may exist in oxidation states iii, iv, and v in the V–P–O system, and may adopt square pyramidal, octahedral or tetrahedral coordination, leading to a great variety of potential polyhedral connectivities. Fig. 1 shows the thermal ellipsoid plot of compound **1** and the coordination environment around the vanadium and phosphorus atoms. The V atoms have two different coordination environments with oxygen in this structure. The tetrahedral coordination about V(1) atom is defined by two vanadyl oxygen atoms with one from V(1) and the other from V(2), a phosphate oxygen and a terminal oxygen. The V(2) atom is octahedrally coordinated to two nitrogens of the 2,2′-bipy ligand, a terminal oxygen and three bridging oxygens, two of which are linked with V(1) and another linked with P. The PO_4 tetrahedron has three oxygens bridging to one V(1) atom and two V(2) atoms, the fourth oxygen atom is protonated with a P–O(4) distance of 1.569(2) Å (Table 2). Bond valence analysis shows that the tetrahedra are occupied by V^{5+} ions, and the octahedra by V^{4+} ions. This oxidation state is consistent with the overall charge balance of the compound, and confirmed by empirical bond length/valence sum calculations.[17,18] Though a number of mixed-valence vanadium phosphates have been described,[19,20] as far as we know, it is the first time tetrahedral V(v) and octahedral V(iv) have been reported to occur concurrently in one vanadium phosphate compound.

The structure of **1** may be best described as two adjacent spiral-shaped chains linked into a double-chain ribbon and the double-chain ribbons are further linked into a 2D network (Fig. 2). Two adjacent $\{V_4O_7(HPO_4)_2(2,2'\text{-bipy})_2\}_\infty$ chains are held together by the V2–O–P bond through the bridged oxygen atoms O2, to form a double-chain ribbon along the a axis. The double-chain ribbon is composed of alternating

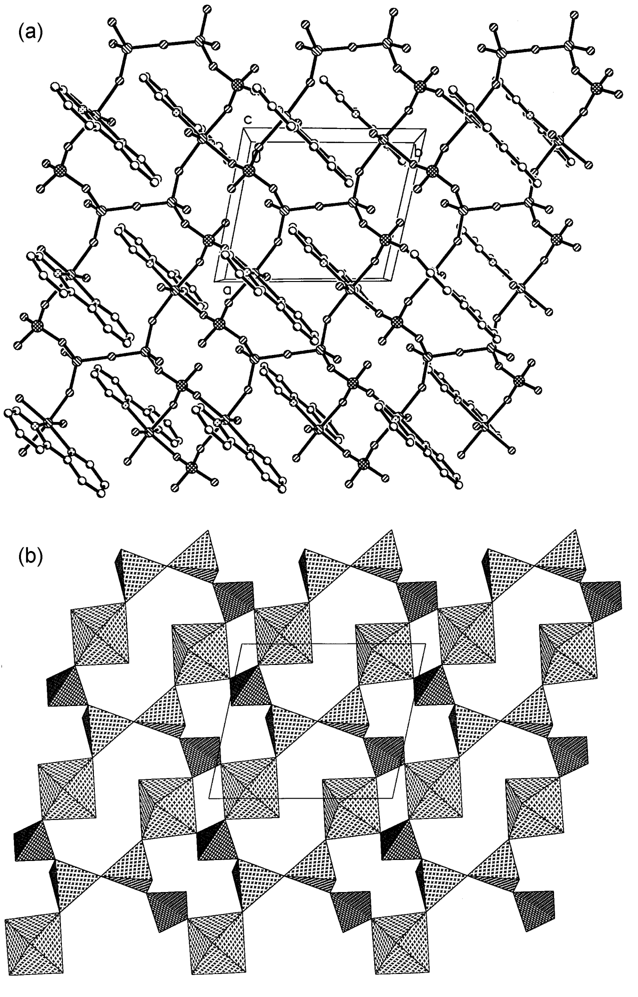

Fig. 2 (a) The 2D layer in **1**, viewed along the c axis direction. All H atoms are omitted for clarity. (b) Polyhedral representation of **1** packed along the c axis. All C and H atoms are omitted for clarity.

four-membered $\{V_2P_2O_4\}$ and six-membered $\{V_4P_2O_6\}$ rings. Moreover, protonated oxygen site O(4) exhibits a contact of 2.714 Å with O(6), indicating a significant H-bonding interaction between the two adjacent chains. All the ribbons are parallel to each other along the *a* axis, adjacent ribbons being held together by the V1–O7–V1 bond through the two corner-sharing VO_4 tetrahedra to produce a layer motif $\{V_4O_7(HPO_4)_2(2,2'\text{-bipy})_2\}_\infty$ in the {001} plane. Eight-membered rings $\{V_6P_2O_8\}$ are formed between adjacent double-chain ribbons. Alternatively, the $\{V_4O_7(HPO_4)_2(2,2'\text{-bipy})_2\}_\infty$ layer may be viewed as an extended 2D network structure with a unique 4,6,8-net. It is noteworthy that **1** is the first 2D layered vanadium phosphate constructed of 4,6,8-net sheets.

The formation of the unique 4,6,8-net structure may be attributed to two features in this compound. One is that the organonitrogen ligand was directly coordinated to the vanadium phosphate scaffolding. The other is that tetrahedral V(V) and octahedral V(IV) concurrently occurred in the vanadium phosphate framework. Though the latter feature first occurs in vanadium phosphates, it is often encountered in vanadium oxides, thus leading to some similarity between this layered structure and some vanadium oxides such as V_3O_7(phen)[21] and [(2,2′-biphen)Co]$V_3O_{8.5}$.[22]

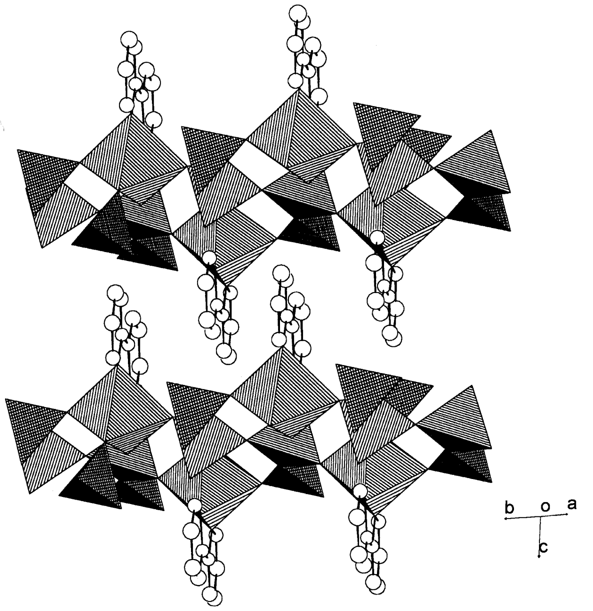

Fig. 3 View of the packing of **1**, parallel to the vanadium phosphate layer.

As shown in Fig. 3, the undulating vanadium phosphate layer of **1** is decorated with 2,2′-bipy groups projecting above and below into the interlamellar region. The adjacent layers are stably packed together and exhibit interesting 3D supramolecular arrays *via* π–π stacking interactions of the 2,2′-bipy groups between adjacent layers, which are parallel with each other and have an average distance of 3.25 Å.

In the IR spectrum of compound **1**, the bands at 964.8, 939.8, 889.2, 805.6, 658.3 and 598.4 cm^{-1} are due to the terminal V=O stretch or a V–O–V stretch. Bands at 1075.8 and 1007.0 cm^{-1} are assigned to the P–O stretch, and those in the 1201.8–1602.1 cm^{-1} region are characteristic of 2,2′-bipy. A broad band around 3436.6 cm^{-1} can be attributed to O–H stretching.

The TG curve of compound **1** can be divided into two weight loss steps. The first, which occurs in the range of 380–440 °C, is attributed to the removal of H_2O from HPO_4. The observed weight loss (2.32%) is in agreement with the calculated value (2.20%). The second, which occurs in the range 480–600 °C, corresponds to the loss of 2,2′-bipy. The observed weight loss in this step (36.78%) compares well with the calculated value (38.05%).

In summary, we have prepared a unique 4,6,8-net structure vanadium phosphate with organonitrogen donors of 2,2′-bipy ligands coordinated directly to the vanadium phosphate framework. This work further confirms the observation that the organic component may profoundly influence the structure of the vanadium phosphate framework. This work also shows that the hydrothermal technique is a powerful method for the synthesis of novel structural vanadium phosphate complexes.

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