

New Vanadium Phosphate $\{[(\text{phen})\text{V}^{\text{IV}}\text{O}]_2(\text{V}_2\text{O}_5)(\text{HPO}_4)\}_n$ with Chiral Layer ArchitectureChao Qin,[†] Lin Xu,^{*,†} Yongge Wei,[‡] Xinlong Wang,[†] and Fengyan Li[†]

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Received December 11, 2002

A new layered vanadium phosphate $\{[(\text{phen})\text{V}^{\text{IV}}\text{O}]_2(\text{V}_2\text{O}_5)(\text{HPO}_4)\}_n$ has been hydrothermally synthesized and structurally characterized by elemental analysis, IR, and single-crystal X-ray diffraction. This compound crystallized in the monoclinic space group $P2_1/c$ with $a = 9.979(2)$ Å, $b = 9.886(2)$ Å, $c = 15.298(3)$ Å, $\beta = 102.86(3)^\circ$, $V = 1471.3(5)$ Å³, and $Z = 4$. In the structure of this compound, two nitrogen atoms of 1,10-phen are directly coordinated to the vanadium skeleton. Interestingly, the crystal structure consists of two types of chiral layers, one left-handed and the other right-handed, which lead to a racemic solid-state compound. In each layer, there coexist three distinct rings, described as a 8-membered ring $\{\text{V}_2^{\text{oct}}\text{P}_2\text{O}_4\}$, 12-membered ring $\{\text{V}_2^{\text{oct}}\text{V}_2^{\text{tet}}\text{P}_2\text{O}_6\}$, and 16-membered ring $\{\text{V}_2^{\text{oct}}\text{V}_4^{\text{tet}}\text{P}_2\text{O}_8\}$.

It is well-known that vanadium may exhibit three kinds of oxidation states V(III), V(IV), and V(V), each adopting different coordination geometry such as square pyramidal, octahedral, tetrahedral, and trigonal bipyramidal forms.¹ This nature makes it possible to isolate vanadium complexes possessing various novel structures. The vanadium phosphate system, as an important family of vanadium oxides, has been receiving extensive attention not only because of structural diversity,^{2–10} but also potential applications in catalysis and material science.^{11,12} In the past decades, the preparation of

vanadium phosphates mainly focuses on the following aspects: (i) an organic component is introduced as a charge compensation and space-filling constituent, e.g., $\text{H}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{NH}_2[(\text{VO}_4)(\text{H}_2\text{O})_4(\text{HPO}_4)_2(\text{PO}_4)_2]$,¹³ $[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3][(\text{VO}_3)(\text{H}_2\text{O})_2(\text{PO}_4)_2(\text{HPO}_4)]$,¹⁴ and $[(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)_2[(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)][\text{V}(\text{H}_2\text{O})_2(\text{VO})_8(\text{OH})_4](\text{HPO}_4)] \cdot 2\text{H}_2\text{O}$;¹⁵ and (ii) an organic component as a ligand coordinates to a secondary metal site, e.g., $[\{\text{Cu}(\text{bpy})\}_2(\text{VO})_3(\text{PO}_4)(\text{HPO}_4)_2] \cdot 2\text{H}_2\text{O}$,¹⁶ $\text{Cu}(1,10\text{-phen})(\text{VO}_2)(\text{PO}_4)$,¹⁷ and $[\text{Zn}(2,2'\text{-bpy})(\text{VO}_2)(\text{PO}_4)]$.¹⁸ In comparison with the these complexes, vanadium phosphate complexes in which the organic ligand is directly coordinated to the vanadium phosphate skeleton are relatively unexplored.¹⁹

In particular, solid materials with either helical or chiral structure are of intense interest in chemistry and material science.²⁰ The fact that the Nobel prize in chemistry for 2001 went to three pre-eminent scientists working on chiral

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catalysis exhibits the ultimate importance of the chiral catalysts in applications. While solid materials having unusual structures are expected to increase in number, the exploration to prepare framework solids with chiral structures still remains a challenge.²¹ Fortunately, many results of investigation indicated that organic templates can dramatically influence the microstructures of framework solids under hydrothermal synthesis. As a result, it is possible to obtain vanadium phosphate complexes with chirality by the structure-directing effect of organic ligands. In view of this point, we made an effort and successfully isolated a layered compound $\{[(\text{phen})\text{V}^{\text{IV}}\text{O}]_2(\text{V}^{\text{V}}_2\text{O}_5)(\text{HPO}_4)_n\}$ (**1**). This compound not only contains unique 8-, 12-, and 16-membered rings but also consists of two kinds of chiral layers, one left-handed and the other right-handed, which lead to a racemic solid-state compound. Herein, we describe the hydrothermal synthesis and crystal structure of **1**. The results of elemental analysis and IR spectra are also presented to support the structural determination.

Experimental Section

Reagents were purchased commercially and used without further purification. The infrared spectrum was obtained on an Alpha Centaur FT/IR spectrometer with a pressed KBr pellet in the 4000–400 cm^{-1} region. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The content of V was determined by ICP-AES analysis.

Synthesis of $\{[(\text{phen})\text{V}^{\text{IV}}\text{O}]_2(\text{V}^{\text{V}}_2\text{O}_5)(\text{HPO}_4)_n\}$ (1**).** The hydrothermal reaction was carried out in a 20 mL Teflon-lined stainless steel autoclave under autogenous pressure with a filling capacity of 40%. A mixture of $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ (0.0632 g), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.0796 g), 1,10-phen (0.08 g), H_3PO_4 (0.2751 g), and H_2O (8 mL) in molar ratio 1:1:1:7:1111 was stirred briefly in air. This mixture was then transferred to a 20 mL Teflon-lined autoclave and heated to 180 °C for 4 days. After cooling to room temperature, dark block crystals of **1** were isolated mechanically, washed with water, and dried at ambient temperature (yield 50% based on V). Attempts to synthesize compound **1** without $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ proved to be unsuccessful, although the effect of FeCl_2 is not understood. The elemental analysis found C 32.09%, H 1.86%, N 5.32% (calcd C 33.18%, H 2.07%, N 5.45%). The ICP analysis found that compound **1** contained 22.45% V (calcd V 23.47%).

X-ray Crystallography. A block single crystal with dimensions of $0.291 \times 0.194 \times 0.1 \text{ mm}^3$ was carefully selected under a microscope and was mounted inside a glass fiber capillary. X-ray data were collected on a Rigaku R-AXIS RAPID IP diffractometer with the multiscan mode in the range $2.47^\circ < \theta < 27.48^\circ$. A total of 5529 (3298 unique, $R_{\text{int}} = 0.0660$) reflections were measured. The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXT-97

Table 1. Crystal Data and Structure Refinement for **1**

chemical formula	$\text{C}_{12}\text{H}_9\text{N}_2\text{O}_{7.5}\text{PV}_2$
fw	434.06
space group	$P2/c$
a , Å	9.979(2)
b , Å	9.886(2)
c , Å	15.298(3)
β , (deg)	102.86 (3)
V , Å ³	1471.3 (5)
Z	4
D_{calcd} , g cm^{-3}	1.960
temp, K	293(2)
λ , Å	0.71073
μ , cm^{-1}	14.24
$F(000)$	864
GOF	1.012
$R1^a$	0.0611
$wR2^b$	0.1332

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = \sum [(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}.$$

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

V(1)–O(1)	1.594(4)	V(2)–O(2)	1.653(4)
V(1)–O(3)	1.982(4)	V(2)–O(7)	1.7792(12)
V(1)–O(5)	1.988(4)	V(2)–O(6)	1.848(4)
V(1)–O(2)	1.998(4)	P–O(5)	1.511(4)
V(1)–N(1)	2.137(5)	P–O(3)	1.537(4)
V(1)–N(2)	2.308(4)	P–O(4)	1.567(4)
V(2)–O(8)	1.602(4)	P–O(6)	1.567(4)
O(1)–V(1)–O(3)	105.05(19)	O(8)–V(2)–O(7)	110.5(2)
O(1)–V(1)–O(5)	97.78(18)	O(2)–V(2)–O(7)	109.94(16)
O(1)–V(1)–O(2)	95.61(17)	O(2)–V(2)–O(6)	108.84(19)
O(3)–V(1)–O(5)	92.74(16)	O(8)–V(2)–O(6)	107.3(2)
O(3)–V(1)–O(2)	85.30(16)	O(7)–V(2)–O(6)	112.33(17)
O(3)–V(1)–N(1)	162.29(17)	O(3)–P–O(4)	107.4(2)
O(5)–V(1)–N(1)	86.29(16)	O(5)–P–O(6)	111.8(2)
O(2)–V(1)–N(1)	91.53(16)	O(3)–P–O(6)	108.6(2)
O(1)–V(1)–N(2)	166.27(19)	O(4)–P–O(6)	107.1(3)
O(3)–V(1)–N(2)	88.67(17)	V(2)–O(2)–V(1)	158.2(2)
O(5)–V(1)–N(2)	81.89(15)	P–O(3)–V(1)	139.2(2)
O(2)–V(1)–N(2)	84.72(16)	P–O(5)–V(1)	138.1(2)
N(1)–V(1)–N(2)	73.68(17)	P–O(6)–V(2)	144.8(3)

software. A semiempirical absorption correction (ψ -scan) was applied. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps. Structure solution and refinement based on 3298 independent reflections with $I > 2\sigma(I)$ and 222 parameters gave $R1 = 0.0611$, $wR2 = 0.1332$ $\{R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = \sum [(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}\}$.

Crystallographic data for **1** are summarized in Table 1. Atomic positional parameters, full tables of bond lengths and angles, and anisotropic temperature factors are available in the tables of Supporting Information. Selected bond lengths and angles are listed in Table 2.

Results and Discussion

Compound $\{[(\text{phen})\text{V}^{\text{IV}}\text{O}]_2(\text{V}^{\text{V}}_2\text{O}_5)(\text{HPO}_4)_n\}$ was synthesized by the hydrothermal method. The crystallization of **1** was found to be highly sensitive to the pH value of the starting mixture. The starting material of H_3PO_4 not only plays a bridging role but also adjusts the pH value of the reaction mixture. When the amount of H_3PO_4 is less than 0.275 g, the isolation of **1** has been unsuccessful, giving only a brown powder.

As shown in Figure 1, the thermal ellipsoid plot of compound **1** shows that vanadium atoms have two different coordination environments. From the charge balance and the

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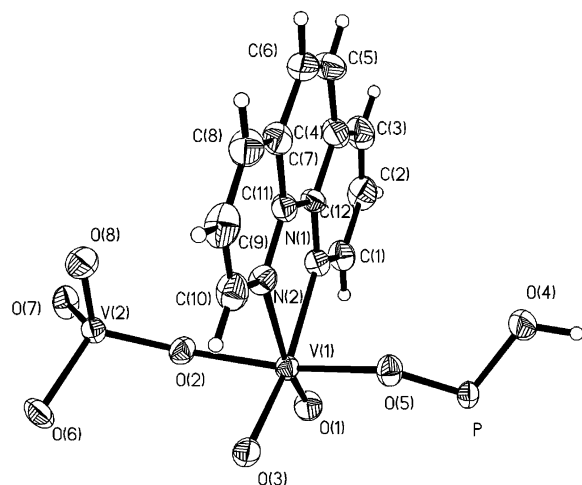


Figure 1. Atom labeling schemes and thermal ellipsoid plot of **1**.

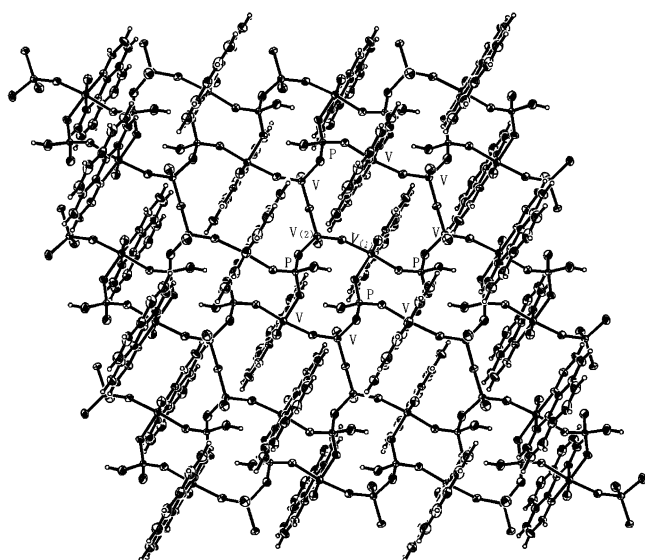


Figure 2. View of the 2D layer in **1** along the *b* axis direction highlights the coordination environment of V and P atoms and the connectivity of different rings.

intense color of **1**, we consider that there exists mixed-valence vanadium in the structure of **1**. Valence sum calculations,²² based on the observed V–O and V–N bond lengths, give the average values of 4.2 and 5.1 for calculated oxidation states of V(1) and V(2), respectively; this confirms that the six-coordinate V(1) site is present in the +4 oxidation state, while four-coordinate V(2) is in the +5 oxidation state. The partial conversion from the +5 to +4 oxidation state may result from either the appropriate pH value of the reaction mixture or the 1,10-phen ligand as a reductant. The distorted octahedral coordination around the tetravalent V(1) site is completed by two N atoms from the phen ligand with an average V–N bond distance of 2.223 Å, a terminal oxygen with V–O_t bond distance of 1.594 Å, and three bridging oxygen atoms with an average V–O_b bond distance of 1.989 Å (see Figure 2). In addition, two bridging oxygen atoms of the V(1) octahedron are further linked with P and V(V), respectively. The pentavalent V(2) site adopts tetra-

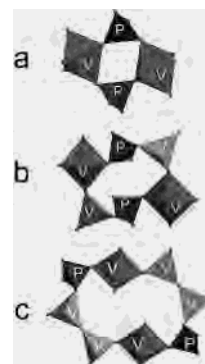


Figure 3. Polyhedral representation of the three types of rings found in **1**: (a) a four-ring containing two V(VI) and two phosphorus polyhedra, (b) a six-ring containing two V(VI), two V(V), and two phosphorus polyhedra, (c) an eight-ring containing two V(VI), four V(V), and two phosphorus polyhedra.

hedral geometry, defined by a terminal oxygen atom with V–O_t of 1.602 Å and three bridging oxygen atoms with average V–O_b bond distance of 1.760 Å, two of which are linked with one V(IV) atom and one V(V) atom and the third one is linked with a P atom. The tetrahedral coordination around the P atom is completed by three bridging oxygen atoms among which two are linked with a V(IV) atom and the third one with a V(V) atom, and a terminal oxygen atom which is protonated with a P–O(4) distance of 1.567 Å. Furthermore, the protonation of O(4) can be confirmed by valence sum calculations. The value of bond valence sums (BVS) for O(4) is 1.145, suggesting that it is a hydroxyl oxygen atom in view of the bond valence contribution of ~0.80 for an O–H bond.

Virtually, the structure of **1** is a two-dimensional mixed-valence vanadium phosphate layer with 1,10-phen groups coordinated to the vanadium(IV) sites (see Figure 2). It should be noted that there are three types of vanadium phosphate rings, that is, {V₂^{oct}P₂O₄}, {V₂^{oct}V₂^{tet}P₂O₆}, and {V₂^{oct}V₄^{tet}P₂O₈}, as illustrated in Figure 3. All the rings in the layer are connected together in a corner-sharing pattern. The connectivity of compound **1** can be best described as follows: first, 8-membered rings {V₂^{oct}P₂O₄} and 12-membered rings {V₂^{oct}V₂^{tet}P₂O₆} are alternatively connected together to form a double-chain ribbon along the *b* axis, and then, the adjacent ribbons are further linked by V(V) atoms of the 12-membered rings in a V(V)–O–V(V) mode to form a two-dimensional layer. By this step, the 16-membered rings {V₂^{oct}V₄^{tet}P₂O₈} are formed between the neighboring ribbons. These structural features are similar to those of the reported compound [V₄O₇(HPO₄)₂(2,2'-bipy)₂].¹⁹

The most interesting aspect of the structure of **1** is that it has a chiral layer architecture. Because these layers, being parallel to the *ac* plane, possess C₂ axis symmetry, each layer thus becomes a chiral component. As shown in Figure 4, the two types of chiral layers, one left-handed and the other right-handed, pairwise crystallize in a space group *P2/c* with an inversion center, leading to a racemic solid-state compound (see Figure 4b). While more studies are needed to clearly elucidate the causes of the chirality and the racemization, our results did provide some evidence for a tentative

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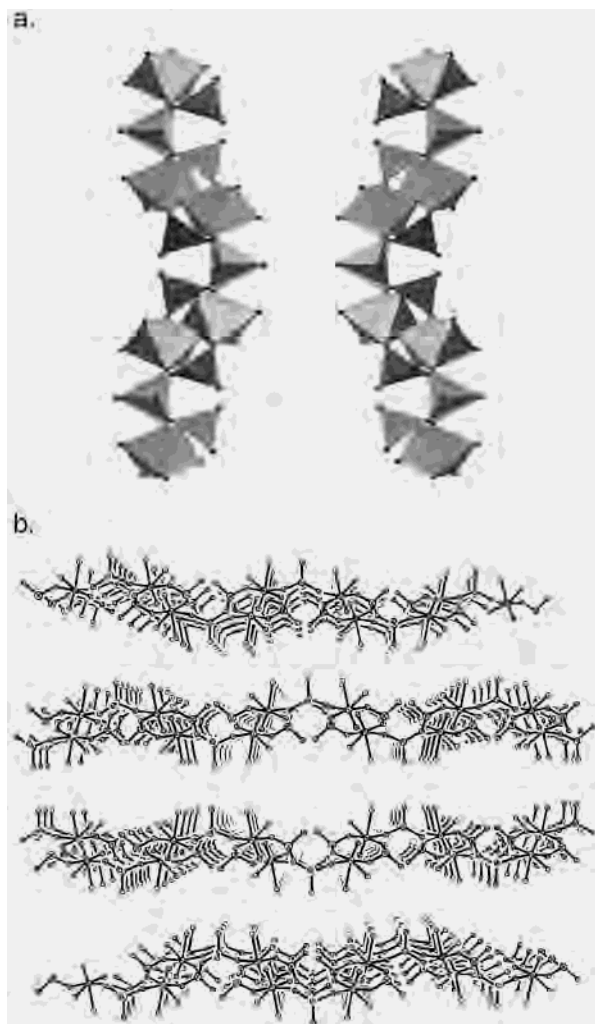


Figure 4. (a) Polyhedral representation of the two types of chiral layers in **1**, one left-handed and another right-handed, respectively, the phen groups are omitted for clarity. (b) View of the packing of **1** along the *a* axis direction.

explanation. A comparison of **1** with a similar compound of $[\text{V}_4\text{O}_7(\text{HPO}_4)_2(2,2'\text{-bipy})_2]$ suggests that the phenanthroline ligand may be responsible for the formation of the chiral framework. Although the two compounds have similar composition and structural moiety, with the only difference in employing two different organic ligands (*o*-phen and 2,2'-bipy) respectively, compound **1** has an enantiomorphous chiral crystal structure whereas $[\text{V}_4\text{O}_7(\text{HPO}_4)_2(2,2'\text{-bipy})_2]$ does not. Compared with 2,2'-bipy, the larger aromatic phen ligand could further enhance the π - π aromatic stacking interactions, which are a possible driving force to induce the formation of the chirality. A recent publication also demonstrated that phen and 2,2'-bipy play different roles in the formation of helical chains, in which $[\text{Cu}(\text{oba})(\text{phen})]_n$ (oba = 4,4-oxybis(benzoate)) appears to be double-stranded helices whereas $[\text{Cu}(\text{oba})(2,2'\text{-bipy})]_n$ appears to be single-stranded helical chains.²³ Analogously, several researches

also showed that the length of organic ligand plays an important role in the formation of noncentrosymmetric solids and helical chains.²⁴

In addition, the stacking of sheets manifests considerable overlap of the *o*-phenanthroline between the adjacent layers with an average interplanar separation of ca. 3.454 Å. Obviously, the π - π stacking interactions between the phen groups make the neighboring layers stably packed together.²⁵ However, there exists no hydrogen bonding between the chiral layers in compound **1**, so that the chiral layers are obviously separated (see Figure 4b). As a result, compound **1** crystallizes with an inversion center to form centrosymmetric solids, leading to the occurrence of the racemization. The weak intralayer hydrogen bonding interactions also perform a certain function on stabilizing the chiral layer structure of **1** and the representative hydrogen bond is O(4)-H(40)···O(3), whose length is 3.060 Å.

In the IR spectrum of **1**, vibration bands at 985, 917, 854, 799, 724, 690, and 647 cm^{-1} are due to the terminal V=O stretch or a V-O-V stretch. Bands at 1105, 1072, 1026, and 1008 cm^{-1} are assigned to $\nu(\text{P-O})$, and 1606, 1581, 1518, 1496, 1456, and 1425 cm^{-1} are characteristic of 1,10-phen. The vibration at 3137 cm^{-1} is associated with $\nu(\text{O-H})$.

Conclusions

A new layered vanadium phosphate $\{[(\text{phen})\text{V}^{\text{VI}}\text{O}]_2(\text{V}_2\text{O}_5)(\text{HPO}_4)\}_n$ has been synthesized by a hydrothermal method. Unlike those in previously reported vanadium phosphate complexes, the organic component in **1** is directly coordinated to the vanadium framework, and its crystal structure consists of two kinds of chiral layers, one left-handed and the other right-handed, which lead to a racemic solid-state compound. The structure-directing effect of the organic ligand is certainly responsibility for the formation of such a chiral framework. The presence of novel 8-, 12-, and 16-membered rings in this compound manifests that the hydrothermal method provides an effective route for synthesizing complexes possessing novel structure and potential applications.

Acknowledgment. This work is financially supported by the National Natural Science Foundation of China (Grant 29971006).

Supporting Information Available: Tables of bond distances, bond angles, anisotropic temperature factor parameters, and atomic coordinates for **1** and crystallographic information in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC026256I

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