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RAPID COMMUNICATION

Hydrothermal Synthesis and Crystal Structure of a One-Dimensional Ladder-like Chain Complex [$V^{V}_{4}O_{10}$(phen)$_2$]

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An organic–inorganic hybrid vanadium oxide [$V^{V}_{4}O_{10}$(phen)$_2$] has been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction. Red-brown crystals crystallize in the triclinic system, space group $P\bar{1}$, $a = 9.782(2)$, $b = 6.5124(14)$, $c = 19.765(4)$ Å, $\alpha = 89.94(2)^\circ$, $\beta = 100.66(2)^\circ$, $\gamma = 89.86(2)^\circ$, $V = 1237.4(4)$ Å^3, $Z = 2$, $\lambda(\mathrm{Mo}K\alpha) = 0.71073$ Å ($R(F) = 0.0302$ for 4342 reflections). Data were collected on a Siemens P4 four-circle diffractometer at 293 K in the range of $2.10 < \theta < 25.02^\circ$ using the ω-scan technique. The title compound, a non-mixed-valence hybrid tetravanadate, exhibits an infinite one-dimensional ladder-like chain with organonitrogen donors of phen ligands coordinated directly to the vanadium oxide framework, where the octahedral $\{VO_4N_2\}$ and tetrahedral $\{VO_4\}$ building blocks are linked by corner-sharing oxygen atoms. © 2002 Elsevier Science

Key Words: **organic–inorganic hybrid; tetravanadate; non-mixed-valence materials; hydrothermal synthesis; crystal structure.**

INTRODUCTION

A current focus on the chemistry of polyoxovanadates is the rational design and synthesis of organic–inorganic hybrid vanadium oxide clusters to explore their potential applications in catalysis, medicine, biology, electron conductivity, magnetism, and photochemistry (1–3). Recently, the introduction of the hydrothermal technique and the use of organic structure-directing agents have led to the production of various organic–inorganic vanadium oxide clusters with discrete clusters, one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) structures (4–21). In this field, the organic–inorganic hybrid tetravanadate clusters have been widely studied (6–14). The 2D layered tetravanadates are one of the common structural types, such as $[H_2N(CH_2)_4NH_2]V_4O_9$ (6), $[NH_3(CH_2)_3NH_3]V_4O_{10}$ (7), α-, β-$[H_3N(C_2H_4)_2NH_3]_2V_4O_{10}$ (8), α-, β-$[H_3NCH_2CH_2NH_3]V_4O_{10}$ (8), and $[VO_2(\mathrm{terpy})]V_4O_{10}$ (9). Another typical structure is discrete cyclo-tetravanadate clusters, such as $[Zn(\mathrm{bipy})_3]_2V_4O_{12}\cdot 11H_2O$ (10), $[Zn(\mathrm{bipy})_2]_2V_4O_{12}$ (10), $[Zn(\mathrm{phen})_2]_2V_4O_{12}\cdot H_2O$ (10), $[Ni(\mathrm{bipy})_3V_4O_{12}]\cdot 11H_2O$ (11), and $[H_2\mathrm{pn}][Mn_2(C_2O_4)(V_4O_{12})]$ (12). However, the 1D chainlike structure is rare (13,14). More recently, an important advance in the hybrid organic–vanadium oxide systems has been the study of organonitrogen ligands coordinated directly to the vanadium sites of the vanadium oxide scaffoldings (9, 15, 16). A number of such hybrids have hitherfore been synthesized by the hydrothermal method, e.g., 1D $[V_9O_{21}(\mathrm{bpy})_3]$ (15), 2D $[V_3O_7(\mathrm{phen})]$ (16), and $[V_9O_{22}(\mathrm{terpy})_3]$ (9). It is noteworthy that all three compounds are mixed-valence hybrid materials (9), while no example of a non-mixed-valence hybrid complex of this subgroup has been observed.

Here, we report a novel non-mixed-valence organic–inorganic hybrid vanadium oxide–1,10-phenanthroline (phen) complex, [$V^{V}_{4}O_{10}$(phen)$_2$] **1**, which exhibits an unusual one-dimensional ladder-like tetravanadate skeleton with the nitrogen donors of phen groups directly coordinated to the vanadium oxide backbones. To our knowledge, the 1D

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ladder-like chain of compound **1** has not been observed in the previously reported tetranuclear vanadates (6–14), although such ladder-like structure are well characterized in other systems (17–21), for example, the $[MoO_4\{Fe^{III}Cl(2,2'\text{-bpy})\}]$ (17).

EXPERIMENTAL

General Procedures

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. V was determined by a Leaman inductively coupled plasma (ICP) spectrometer. An IR spectrum was recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer using a KBr pellet. An ESR spectrum was recorded on a Japanese JES-FE3AX spectrometer at 293 K. XPS analysis was performed on a VG ESCALAB MK II spectrometer with a Mg $K\alpha$ (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during the analysis.

Hydrothermal Synthesis

A mixture of V_2O_5 (0.182 g, 1 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (0.242 g, 1 mmol), phen (0.396 g, 2 mmol), and H_2O (16 ml, 889 mmol) in the mole ratio 1:1:2:889 was sealed in a 47-mL Teflon-lined autoclave and heated to 170°C for 7 days. After cooling of the mixture to room temperature, red-brown block crystals of compound **1** were isolated in 20% yield by mechanical separation from a green amorphous solid. The compound was washed several times with distilled water and dried in air. The product cannot be obtained without $Cu(NO_3)_2 \cdot 3H_2O$ in the reaction system, although Cu is absent in **1**. The elemental analyses found C 39.52%, H 2.31%, N 7.91%, V 27.95%; calc for $C_{29}H_{16}N_4V_4O_{10}$, C 39.78%, H 2.21%, N 7.73%, V, 28.18%.

X-Ray Crystallography

The structure of compound **1** was determined by single-crystal X-ray diffraction. Crystallographic data are as follows: $C_{24}H_{16}N_4O_{10}V_4$, triclinic, $P\bar{1}$, $a = 9.782(2)$ Å, $b = 6.5124(14)$ Å, $c = 19.765(4)$ Å, $\alpha = 89.94(2)°$, $\beta = 100.66(2)°$, $\gamma = 89.86(2)°$, $V = 1237.4(4)$ Å^3, $Z = 2$, $D_{calc} = 1.944$ g/cm^3, λ (Mo$K\alpha$) = 0.71073 Å. A red-brown single crystal was mounted inside a glass fiber capillary. Data were collected on a Siemens P4 four-circle diffractometer at 293 K in the range of $2.10 < \theta < 25.02°$ using the ω-scan technique. Empirical absorption correction (ψ scan) was applied. The structure was solved by the direct method and refined by full-matrix least-squares on F^2 using the SHELXL-93 software. All of the nonhydrogen atoms were refined anisotropically. All the hydrogen atoms were located from difference Fourier maps. A total of 5772 (4342 unique, $R_{int} = 0.0207$) reflections were measured. Structure solution and refinement based on 4342 independent reflections with $I > 2\sigma(I)$ and 379 parameters gave $R1(wR2) = 0.0302$ (0.0685) $\{R1 = \sum \| F_o| - |F_c \| / \sum |F_o|;\ wR2 = \sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}\}$. The selected bond lengths are listed in Table 1. Crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters are given in Tables 2–6.

TABLE 1
Selected Bond Lengths (Å) for $[V_4O_{10}(phen)_2]$

V(1)–O(5)	1.589(2)	V(1)–O(2)	1.795(2)
V(1)–O(7A)	1.886(2)	V(1)–O(1)	1.887(2)
V(1)–N(11)	2.188(2)	V(1)–N(12)	2.297(2)
V(2)–O(9)	1.589(2)	V(2)–O(3)	1.795(2)
V(2)–O(4)	1.885(2)	V(2)–O(10)	1.886(2)
V(2)–N(22)	2.177(2)	V(2)–N(21)	2.298(2)
V(3)–O(6)	1.605(2)	V(3)–O(7)	1.731(2)
V(3)–O(1)	1.734(2)	V(3)–O(3)	1.769(2)
V(4)–O(8)	1.608(2)	V(4)–O(4)	1.731(2)
V(4)–O(10A)	1.732(2)	V(4)–O(2)	1.784(2)

RESULTS AND DISCUSSION

As shown in Fig. 1, the crystal structure of **1** consists of a 1D tetravanadate chain. The phen groups are directly coordinated to the vanadium oxide skeleton through the nitrogen ligands and project up and down to the chain. The planes of these phen groups are generally parallel with each other and the average distance is 6.50 Å. The tetravanadate backbone is constructed of tetrahedral $\{VO_4\}$ and octahedral $\{VO_4N_2\}$ building units connected by exclusively corner-sharing oxygen atoms as shown in Fig. 2. There are four crystallographically unique vanadium centers. The V(1) and V(2) sites both possess a distorted octahedral geometry and are coordinated by two N atoms of phen, three bridging oxo groups, and a terminal oxo ligand, while the V(3) and V(4) sites both exhibit a distorted tetrahedral geometry and are coordinated by three corner-sharing oxygen atoms and an unshared oxygen group. The distorted octahedral $\{VO_4N_2\}$ and tetrahedral $\{VO_4\}$ units are connected in an alternatively corner-sharing mode to form a $\{V_4O_4\}$ eight-membered ring. Through the μ_2-O(7) and μ_2-O(10) bridging oxygens, $\{V_4O_4\}$ rings are connected into an infinite 1D ribbon along the *b* axis. As a consequence, the structure can also be described as a ladder-like chain with the side rails provided by {–V(1)–O(2)–V(4)–} and {–V(2)–O(3)–V(3)–} linkages and rungs by the {–V(1)–O(2)–V(4)–} and {–V(2)–O(3)–V(3)–} linkages.

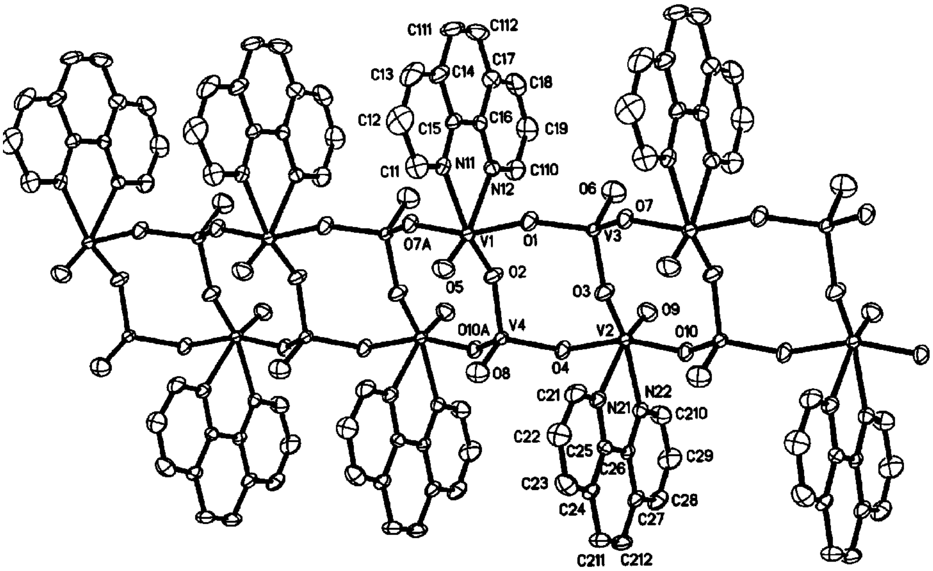

FIG. 1. View of the structure of the $[\mathrm{V}^{\mathrm{V}}_4\mathrm{O}_{10}(\mathrm{phen})_2]$ chain. The hydrogen atoms of the phen group are omitted for clarity.

The adjacent chains of $[\mathrm{V}^{\mathrm{V}}_4\mathrm{O}_{10}(\mathrm{phen})_2]$ are stably packed together and exhibit an interesting 3D structural supermolecular arrays via two types of interactions. One is the so-called π–π interactions of the phen groups between the neighboring chains, which are parallel with each other and have an average distance of 3.25 Å. The other is the significant hydrogen-bonding interactions between the unshared oxygen atoms of vanadium oxides and the hydrogen atoms of phen groups from adjacent chains. The representative hydrogen bonds are O(5) … H(18), O(8) … H(19), O(6) … H(22), and O(9) … H(23), whose lengths are 2.298, 2.484, 2.451, and 2.571 Å, respectively. Figure 3 shows the packing arrangement of the 1D chains along the *b* axis.

Charge balance considerations and red-brown coloration of the crystal **1** indicate that all vanadium sites exhibit V(V) oxidation state. The valence sum calculations (22) show that the sum of the formal oxidation states for the four vanadium

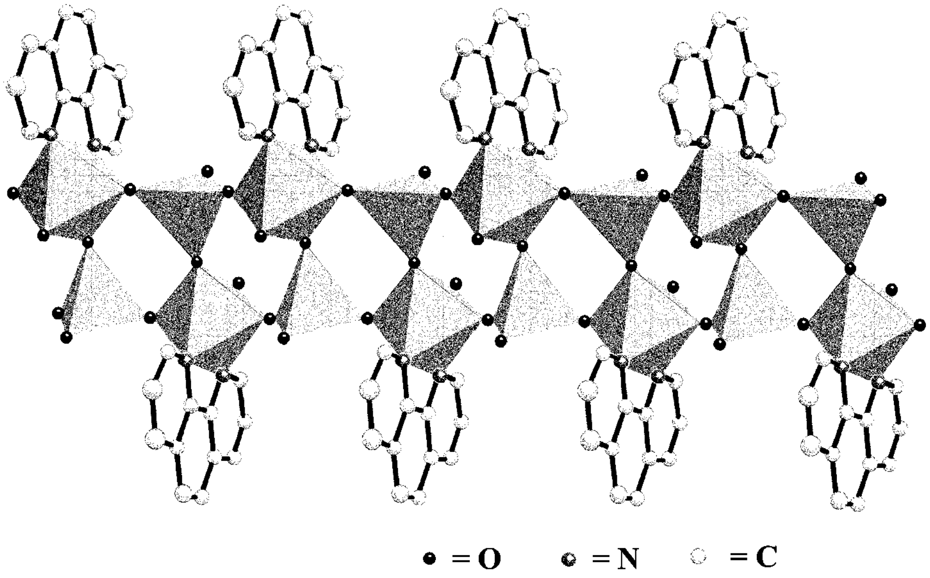

FIG. 2. A polyhedral representation of the structure of **1**.

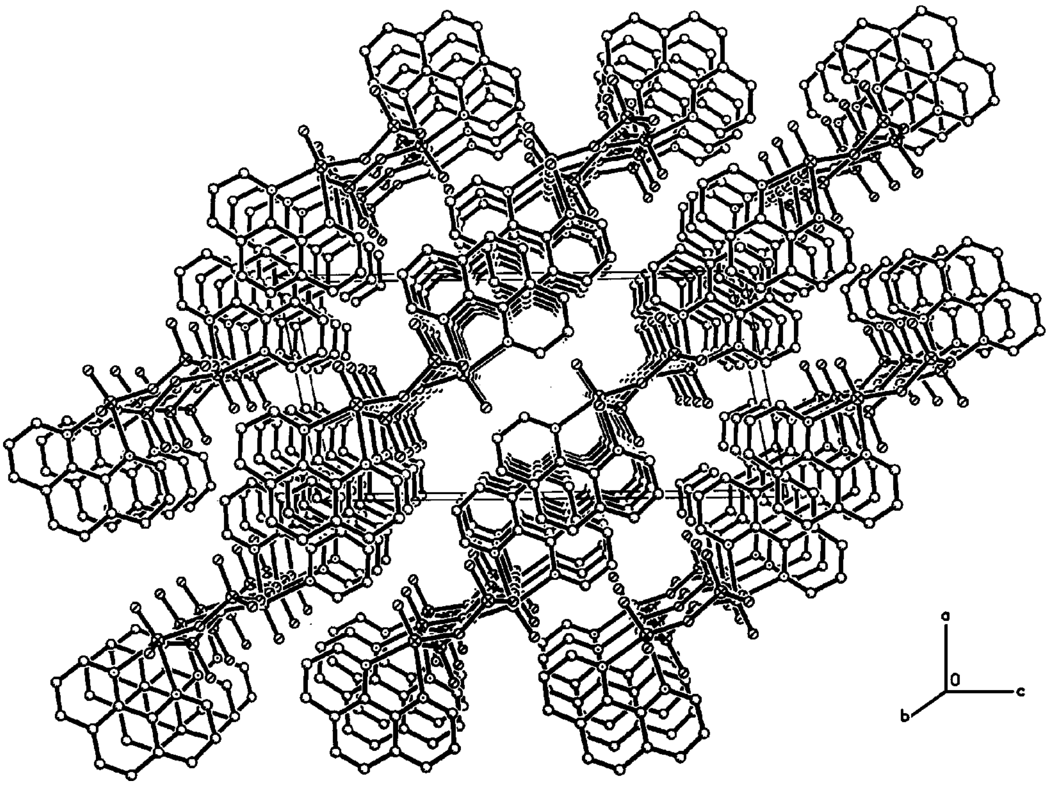

FIG. 3. View of the packing arrangement of **1** along the *b* axis.

atoms in one structural unit is 20.21 and the average value is 5.05. No signal in the ESR spectrum confirms that all the vanadium atoms are V^{5+}. This is also proved by XPS measurement of the compound in the energy region of V_{2p}.

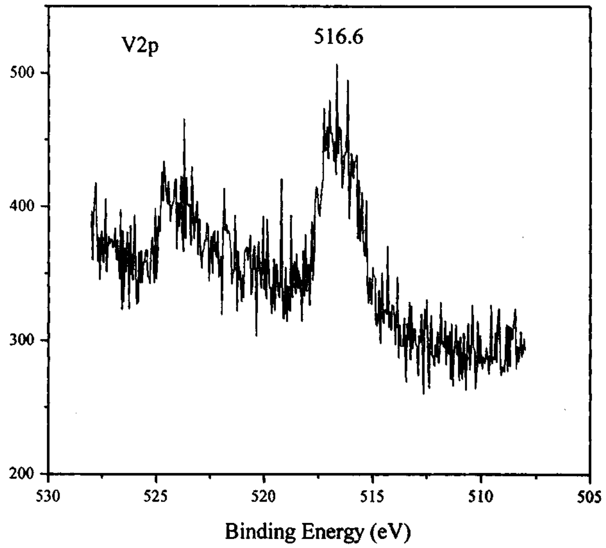

FIG. 4. The X-ray photoelectron spectra (XPS) of the $[V^{V}_{4}O_{10}(phen)_2]$.

The XPS spectrum gives one peak at 516.6 eV as shown in Fig. 4, attributable to V^{5+} (23). In contrast to $[V_9O_{21}(bipy)_4]$, $[V_3O_7(phen)]$, and $[V_9O_{22}(terpy)_3]$, which have a common feature in that all of them are mixed-valence materials and the vanadium sites coordinated to the organonitrogen ligands are reduced to V(IV) oxidation state (9), the V(1) and V(2) coordinated to the nitrogen ligands of phen in this case are still in V(V) oxidation state.

The IR spectrum of **1** exhibits the strong bands at 969, 851, 773, and 705 cm^{-1} attributed to v (V=O) or v[(V–O–V) and a series of characteristic peaks of phen in the 1140–1520 cm^{-1} range.

Hagrman and Zubieta recently predicted that organic amine ligand incorporation into the non-mixed-valence vanadium oxide substructure will emerge (9). The successful isolation of $[V^{V}_{4}O_{10}(phen)_2]$ in the present work not only provides a piece of evidence for his prediction, but also further confirms the power of the hydrothermal reactions for isolation of new metal oxide hybrids and the function of organic structure-directing agents for "tailoring" the microstructure of inorganic oxide (2,9,18). Owing to the "passivation" of the organonitrogen ligand to the surface of the vanadium oxide and the steric effect of the ligand (2,3,9), the 1D vanadium oxide chain in this communication is inhibited from forming the 2D layers.

TABLE 2
Crystal Data and Structure Refinement for 1

Identification code	1016a
Empirical formula	$C_{24}H_{16}N_4O_{10}V_4$
Formula weight	724.17
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$p\bar{1}$
Unit cell dimensions	$a = 9.782(2)$ Å alpha = 89.94(2)° $b = 65124(14)$ Å beta = 100.66(2)° $c = 19.765(4)$ Å gamma = 89.86(2)°
Volume, Z	1237.4(4) Å^3, 2
Density (calculated)	1.944 Mg/m^3
Absorption coefficient	1.534 mm^{-1}
F (000)	720
Crystal size	0.50 × 0.30 × 0.28 mm
θ range for data collection	2.10 to 25.02°
Limiting indices	$-11 \leq h \leq 11$, $-7 \leq k \leq 1$, $-23 \leq 1 \leq 23$
Reflections collected	5772
Independent reflections	4342 ($R_{\text{int}} = 0.0207$)
Absorption correction	Psi-scan
Max. and min. transmission	0.5476 and 0.4465
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4342/0/379
Goodness-of-fit on F^2	0.916
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0302$, $wR2 = 0.0685$
R indices (all data)	$R1 = 0.0463$, $wR2 = 0.0724$
Largest diff. peak and hole	0.341 and -0.435 eÅ^{-3}

TABLE 3
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for 1: U(eq) is Defined as One Third of the Trace of the Orthogonalized U_{ij} Tensor

	x	y	z	U (eq)
V(1)	4342(1)	7501(1)	1582(1)	16(1)
V(2)	5487(1)	2501(1)	3681(1)	16(1)
V(3)	3729(1)	2499(1)	1974(1)	15(1)
V(4)	6000(1)	7499(1)	3242(1)	16(1)
O(1)	4013(2)	4650(3)	1502(1)	23(1)
O(2)	4633(2)	7498(3)	2506(1)	24(1)
O(3)	4926(2)	2496(3)	2764(1)	26(1)
O(4)	5825(2)	5349(3)	3734(1)	22(1)
O(5)	5835(2)	7507(4)	1374(1)	32(1)
O(6)	2167(2)	2495(4)	2118(1)	37(1)
O(7)	4014(2)	354(3)	1502(1)	23(1)
O(8)	7482(2)	7503(4)	3001(1)	33(1)
O(9)	4117(2)	2499(3)	4006(1)	30(1)
O(10)	5826(2)	− 352(3)	3735(1)	23(1)
N(11)	3368(2)	7498(4)	493(1)	18(1)
N(12)	1976(2)	7502(4)	1530(1)	19(1)
C(11)	4087(4)	7499(5)	− 17(2)	33(1)
C(12)	3449(4)	7504(6)	− 707(2)	45(1)
C(13)	2031(4)	7503(6)	− 872(2)	42(1)
C(14)	1250(3)	7506(5)	− 356(2)	30(1)
C(15)	1963(3)	7499(5)	329(1)	19(1)
C(16)	1218(3)	7499(4)	887(1)	18(1)
C(17)	− 246(3)	7498(5)	748(2)	28(1)
C(18)	− 910(3)	7495(6)	1314(2)	39(1)
C(19)	− 146(4)	7492(6)	1965(2)	37(1)
C(110)	1306(3)	7501(5)	2051(2)	33(1)
C(111)	− 242(4)	7491(6)	− 476(2)	38(1)
C(112)	− 947(3)	7492(6)	45(2)	38(1)
N(11)	7752(2)	2500(4)	3516(1)	19(1)
N(22)	6806(2)	2504(4)	4697(1)	18(1)
C(21)	8198(3)	2495(5)	2925(2)	28(1)
C(22)	9609(3)	2497(5)	2882(2)	32(1)
C(23)	10585(3)	2495(5)	3468(2)	30(1)
C(24)	10154(3)	2503(5)	4111(2)	23(1)
C(25)	8716(3)	2496(4)	4100(1)	17(1)
C(26)	8210(3)	2507(4)	4736(1)	17(1)
C(27)	9154(3)	2499(5)	5360(1)	24(1)
C(28)	8591(3)	2501(5)	5965(2)	30(1)
C(29)	7198(4)	2511(6)	5923(2)	36(1)
C(210)	6318(3)	2506(5)	5284(2)	28(1)
C(211)	11091(3)	2489(5)	4758(2)	29(1)
C(212)	10607(3)	2503(5)	5356(2)	29(1)

TABLE 4
Bond Lengths (Å) and Angles (°) for 1

V(1)–O(5)	1.589(2)	V(1)–O(2)	1.795(2)
V(1)–O(7) #1	1.886(2)	V(1)–O(1)	1.887(2)
V(1)–N(11)	2.188(2)	V(1)–N(12)	2.297(2)
V(2)–O(9)	1.589(2)	V(2)–O(3)	1.795(2)
V(2)–O(4)	1.885(2)	V(2)–O(10)	1.886(2)
V(2)–N(22)	2.177(2)	V(2)–N(21)	2.298(2)
V(3)–O(6)	1.605(2)	V(3)–O(7)	1.731(2)
V(3)–O(1)	1.734(2)	V(3)–O(3)	1.769(2)
V(4)–O(8)	1.608(2)	V(4)–O(4)	1.731(2)
V(4)–O(10) #1	1.732(2)	V(4)–O(2)	1.784(2)
V(7)–V(1) #2	1.886(2)	O(10)–V(4) #2	1.732(2)
N(11)–C(11)	1.331(4)	N(11)–C(15)	1.352(4)
N(12)–C(110)	1.320(4)	N(12)–C(16)	1.348(4)
C(11)–C(12)	1.391(5)	C(11)–H(11)	0.93
C(12)–C(13)	1.365(5)	C(12)–H(12)	0.93
C(13)–C(14)	1.384(5)	C(13)–H(13)	0.93
C(14)–C(15)	1.403(4)	C(14)–C(111)	1.434(5)
C(15)–C(16)	1.432(4)	C(16)–C(17)	1.407(4)
C(17)–C(18)	1.393(5)	C(17)–C(112)	1.432(4)
C(18)–C(19)	1.363(5)	C(18)–H(18)	0.93
C(19)–C(110)	1.399(5)	C(19)–H(19)	0.93
C(110)–H(110)	0.93	C(111)–C(112)	1.341(5)
C(111)–H(111)	0.93	C(112)–H(112)	0.93
N(21)–C(21)	1.321(4)	N(21)–C(25)	1.348(3)
N(22)–C(210)	1.334(4)	N(22)–C(26)	1.362(4)
C(21)–C(22)	1.399(4)	C(21)–H(21)	0.93
C(22)–C(23)	1.358(4)	C(22)–H(22)	0.93
C(23)–C(24)	1.412(4)	C(23)–H(23)	0.93
C(24)–C(25)	1.403(4)	C(24)–C(211)	1.429(4)
C(25)–C(26)	1.434(4)	C(26)–C(27)	1.397(4)
C(27)–C(28)	1.407(4)	C(27)–C(212)	1.422(4)
C(28)–C(29)	1.349(5)	C(28)–H(28)	0.93

TABLE 4—*Continued*

C(29)–C(210)	1.390(4)	C(29)–H(29)	0.93
C(210)–H(210)	0.93	C(211)–C(212)	1.353 (4)
C(211)–H(211)	0.93	C(212)–H(212)	0.93
O(5)–V(1)–O(2)	106.42(11)	O(5)–V(1)–O(7) # 1	97.15(11)
O(2)–V(1)–O(7) #1	94.46(9)	O(5)–V(1)–O(1)	97.62(11)
O(2)–V(1)–O(1)	94.51(9)	O(7) #1–V(1)–O(1)	159.79(9)
O(5)–V(1)–N(11)	89.94(10)	O(2)–V(1)–N(11)	163.64(9)
O(7) #1–V(1)–N(11)	83.34(9)	O(1)–V(1)–N(11)	82.95(9)
O(5)–V(1)–N(12)	162.73(10)	O(2)–V(1)–N(12)	90.85(9)
O(7) #1–V(1)–N(12)	81.04(9)	O(1)–V(1)–N(12)	80.76(9)
N(11)–V(1)–N(12)	72.79(8)	O(9)–V(2)–O(3)	106.54(11)
O(9)–V(2)–O(4)	97.59(11)	O(3)–V(2)–O(4)	94.46(9)
O(9)–V(2)–O(10)	97.32(11)	O(3)–V(2)–O(10)	94.08(9)
O(4)–V(2)–O(10)	159.94(9)	O(9)–V(2)–N(22)	91.58(10)
O(3)–V(2)–N(22)	161.87(9)	O(4)–V(2)–N(22)	82.95(9)
O(10)–V(2)–N(22)	83.29(9)	O(9)–V(2)–N(21)	164.62(10)
O(3)–V(2)–N(21)	88.84(9)	O(4)–V(2)–N(21)	80.92(9)
O(10)–V(2)–N(21)	81.14(9)	N(22)–V(2)–N(21)	73.04(8)
O(6)–V(3)–O(7)	110.22(11)	O(6)–V(3)–O(1)	110.56(11)
O(7)–V(3)–O(1)	107.65(9)	O(6)–V(3)–O(3)	109.92(11)
O(7)–V(3)–O(3)	109.27(10)	O(1)–V(3)–O(3)	109.17(10)
O(8)–V(4)–O(4)	110.94(11)	O(8)–V(4)–O(10) #1	110.62(11)
O(4)–V(4)–O(10) #1	107.87(9)	O(8)–V(4)–O(2)	109.83(10)
O(4)–V(4)–O(2)	108.59(10)	O(10) #1–V(4)–O(2)	108.93(10)
V(3)–O(1)–V(1)	142.30(11)	V(4)–O(2)–V(1)	141.55(12)
V(3)–O(3)–V(2)	156.89(14)	V(4)–O(4)–V(2)	143.07(11)
V(3)–O(7)–V(1) #2	142.28(11)	V(4) #2–O(10)–V(2)	142.99(11)
C(11)–N(11)–C(15)	118.3(3)	C(11)–N(11)–V(1)	123.3(2)
C(15)–N(11)–V(1)	118.3(2)	C(110)–N(12)–C(16)	118.0(2)
C(110)–N(12)–V(1)	127.4(2)	C(16)–N(12)–V(1)	114.6(2)
N(11)–C(11)–C(12)	122.5(3)	N(11)–C(11)–H(11)	118.7(2)
C(12)–C(11)–H(11)	118.7(2)	C(13)–C(12)–C(11)	119.1(3)
C(13)–C(12)–H(12)	120.5(2)	C(11)–C(12)–H(12)	120.5(2)
C(12)–C(13)–C(14)	119.9(3)	C(12)–C(13)–H(13)	120.0(2)
C(14)–C(13)–H(13)	120.0(2)	C(13)–C(14)–C(15)	117.8(3)
C(13)–C(14)–C(111)	124.2(3)	C(15)–C(14)–H(111)	118.0(3)
N(11)–C(15)–C(14)	122.3(3)	N(11)–C(15)–C(16)	117.1(2)
C(14)–C(15)–C(16)	120.7(3)	N(12)–C(16)–C(17)	123.2(3)
N(12)–C(16)–C(15)	117.2(2)	C(17)–C(16)–C(15)	119.6(3)
C(18)–C(17)–C(16)	116.9(3)	C(18)–C(17)–H(112)	124.7(3)
C(16)–C(17)–C(112)	118.5(3)	C(19)–C(18)–C(17)	120.1(3)
C(19)–C(18)–H(18)	119.9(2)	C(17)–C(18)–H(18)	119.9(2)
C(18)–C(19)–C(110)	118.9(3)	C(18)–C(19)–H(19)	120.6(2)
C(110)–C(19)–H(19)	120.6(2)	N(12)–C(110)–C(19)	123.0(3)
N(12)–C(110)–H(110)	118.5(2)	C(19)–C(110)–H(110)	118.5(2)
C(112)–C(111)–C(14)	121.6(3)	C(112)–C(111)–H(111)	119.2(2)
C(14)–C(111)–H(111)	119.2(2)	C(111)–C(112)–C(17)	121.6(3)
C(111)–C(112)–H(112)	119.2(2)	C(17)–C(112)–H(112)	119.2(2)
C(21)–N(21)–C(25)	117.6(3)	C(21)–N(21)–V(2)	127.6(2)
C(25)–N(21)–V(2)	114.8(2)	C(210)–N(22)–C(26)	118.0(2)
C(210)–N(22)–V(2)	123.8(2)	C(26)–N(22)–V(2)	118.2(2)
N(21)–C(21)–C(22)	123.1(3)	N(21)–C(21)–H(21)	118.5(2)
C(22)–C(21)–H(21)	118.5(2)	C(23)–C(22)–C(21)	119.6(3)
C(23)–C(22)–H(22)	120.2(2)	C(21)–C(22)–H(22)	120.2(2)
C(22)–C(23)–C(24)	119.2(3)	C(22)–C(23)–H(23)	120.4(2)
C(24)–C(23)–H(23)	120.4(2)	C(25)–C(24)–H(23)	116.9(3)
C(25)–C(24)–C(211)	119.3(3)	C(23)–C(24)–C(211)	123.8(3)
N(21)–C(25)–C(24)	123.7(3)	N(21)–C(25)–C(26)	116.7(2)
C(24)–C(25)–C(26)	119.6(2)	N(22)–C(26)–C(27)	123.1(3)
N(22)–C(26)–C(25)	117.3(2)	C(27)–C(26)–C(25)	119.6(3)
C(26)–C(27)–C(28)	116.8(3)	C(26)–C(27)–C(212)	119.6(3)
C(28)–C(27)–C(212)	123.6(3)	C(29)–C(28)–C(27)	119.8(3)
C(29)–C(28)–H(28)	120.1(2)	C(27)–C(28)–H(28)	120.1(2)
C(28)–C(29)–C(210)	120.3(3)	C(28)–C(29)3–H(29)	119.8(2)
C(210)–C(29)–H(29)	119.8(2)	N(22)–C(210)–C(29)	121.9(3)
N(22)–C(210)–H(210)	119.0(2)	C(29)–C(210)–H(210)	119.0(2)
C(212)–C(211)–C(24)	120.8(3)	C(212)–C(211)–H(211)	119.6(2)
C(24)–C(211)–H(2111)	119.6(2)	C(211)–C(212)–C(27)	121.1(3)
C(211)–C(212)–H(212)	119.5(2)	C(27)–C(212)–H(212)	119.5(2)

Note. Symmetry transformations used to generate equivalent atoms: #1 x, $y+1$, z, #1 x, $y-1$, z.

TABLE 5

Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 1. The Anisotropic Displacement Factor Exponent Takes the Form $-2\pi^2$ [$(ha^*)^2U_{11} + \ldots + 2hka^*b^*U_{12}$]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V(1)	15(1)	15(1)	18(1)	0(1)	− 1(1)	− 1(1)
V(2)	16(1)	13(1)	16(1)	0(1)	− 2(1)	− 1(1)
V(3)	16(1)	14(1)	14(1)	0(1)	− 2(1)	− 1(1)
V(4)	18(1)	12(1)	16(1)	0(1)	− 2(1)	0(1)
O(1)	33(1)	14(1)	22(1)	2(1)	2(1)	2(1)
O(2)	29(1)	22(1)	18(1)	0(1)	− 6(1)	− 1(1)
O(3)	36(1)	18(1)	20(1)	− 1(1)	− 7(1)	0(1)
O(4)	33(1)	10(1)	21(1)	0(1)	− 2(1)	− 1(1)
O(5)	17(1)	38(2)	42(1)	− 1(1)	5(1)	0(1)
O(6)	25(1)	48(2)	39(1)	0(1)	11(1)	− 1(1)
O(7)	33(1)	13(1)	22(1)	− 2(1)	2(1)	− 2(1)
O(8)	25(1)	43(2)	32(1)	1(1)	7(1)	1(1)
O(9)	19(1)	30(1)	40(1)	− 1(1)	5(1)	− 2(1)
O(10)	33(1)	14(1)	21(1)	0(1)	− 1(1)	− 2(1)
N(11)	23(1)	14(1)	18(1)	1(1)	7(1)	− 1(1)
N(12)	19(1)	19(1)	17(1)	− 1(1)	3(1)	1(1)
C(11)	36(2)	32(2)	33(2)	0(2)	13(2)	0(2)
C(12)	58(3)	61(3)	21(2)	2(2)	19(2)	0(2)
C(13)	64(3)	47(2)	12(2)	− 3(2)	1(2)	− 4(2)
C(14)	39(2)	23(2)	22(2)	0(1)	− 7(1)	1(2)
C(15)	23(2)	14(2)	19(1)	3(1)	− 2(1)	− 1(1)
C(16)	16(1)	14(2)	23(2)	− 1(1)	3(1)	1(1)
C(17)	17(2)	25(2)	39(2)	1(2)	− 1(1)	0(1)
C(18)	20(2)	39(2)	61(2)	2(2)	14(2)	1(2)
C(19)	31(2)	43(2)	42(2)	− 2(2)	20(2)	− 2(2)
C(110)	35(2)	34(2)	25(2)	0(2)	10(1)	0(2)
C(111)	40(2)	35(2)	30(2)	0(2)	− 18(2)	− 4(2)
C(112)	23(2)	32(2)	50(2)	0(2)	− 14(2)	− 2(2)
N(21)	22(1)	16(1)	16(1)	0(1)	0(1)	0(1)
N(22)	19(1)	16(1)	17(1)	0(1)	2(1)	− 2(1)
C(21)	29(2)	34(2)	18(2)	0(1)	1(1)	1(2)
C(22)	33(2)	39(2)	24(2)	1(2)	11(1)	0(2)
C(23)	20(2)	32(2)	41(2)	− 2(2)	8(1)	− 3(2)
C(24)	19(2)	20(2)	30(2)	1(1)	3(1)	− 1(1)
C(25)	17(2)	13(2)	20(1)	− 3(1)	0(1)	0(1)
C(26)	19(2)	12(2)	18(1)	0(1)	0(1)	− 1(1)
C(27)	28(2)	18(2)	21(2)	− 1(1)	− 6(1)	0(1)
C(28)	39(2)	35(2)	15(2)	− 1(1)	− 3(1)	1(2)
C(29)	40(2)	51(2)	17(2)	− 1(2)	9(1)	3(2)
C(210)	26(2)	35(2)	23(2)	− 2(1)	6(1)	0(2)
C(211)	17(2)	33(2)	34(2)	0(2)	− 5(1)	− 1(2)
C(212)	23(2)	29(2)	29(2)	1(1)	− 11(1)	0(2)

TABLE 6
Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for 1

	x	y	z	U(eq)
H(11)	5053(4)	7497(5)	93(2)	33
H(12)	3982(4)	7509(6)	− 1051(2)	45
H(13)	1591(4)	7500(6)	− 1332(2)	42
H(18)	− 1876(3)	7495(6)	1247(2)	39
H(19)	− 583(4)	7483(6)	2344(2)	37
H(110)	1822(3)	7506(5)	2497(2)	31
H(111)	− 732(4)	7480(6)	− 927(2)	38
H(112)	− 1914(3)	7489(6)	− 53(2)	38
H(21)	7543(3)	2489(5)	2519(2)	28
H(22)	9877(4)	2499(5)	2454(2)	32
H(23)	11527(3)	2489(6)	3445(2)	30
H(28)	9177(3)	2495(5)	6393(2)	30
H(29)	6825(4)	2521(6)	6323(2)	36
H(210)	5361(4)	2504(5)	5266(2)	28
H(211)	12045(3)	2470(5)	4767(2)	29
H(212)	11234(3)	2516(5)	5771(2)	29

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