

Inorganic/Organic Hybrid Materials: Layered Vanadium Oxides with Interlayer Metal Coordination Complexes

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The hydrothermal reactions of V_2O_5 , $H_2C_2O_4$, $Ni(NO_3)_2$, ethylenediamine(en) or 1,2-diaminopropane(enMe) and water yield layered vanadium oxides with interlayer metal coordination complexes $[Ni(en)_2]_{0.5}[V_3O_7]$ (**1**) and $[Ni(enMe)_2]_{0.5}[H_2enMe]_{0.5}[V_6O_{14}]$ (**2**). **1** crystallizes in an orthorhombic system with space group *Pbcn* and cell parameters $a = 16.617(3)$ Å, $b = 6.6329(9)$ Å, and $c = 17.138(4)$ Å. **2** crystallizes in a triclinic system with space group $P\bar{1}$ and cell parameters $a = 6.6698(7)$ Å, $b = 10.8679(11)$ Å, and $c = 13.6097(13)$ Å. Both compounds are inorganic/organic compositions and consist of layered mixed-valence vanadium oxides with interlayers $\{Ni(en)_2\}^{2+}$ or $\{Ni(enMe)_2\}^{2+}$ and H_2enMe^{2+} . In the structure of **1**, a novel arrangement of vanadium and oxygen atoms of $\{V_3O_7\}^-$ was found different from that in its isomer $[Zn(en)_2][V_6O_{14}]$. In **2**, both $\{Ni(enMe)_2\}^{2+}$ and H_2enMe^{2+} serving as unusual pillars between $\{V_6O_{14}\}^{2-}$ layers were observed. Their infrared characters and thermal stabilities were also given.

Introduction

Crystal engineering of inorganic/organic hybrid materials has provoked significant interest in their new structural architectures and potential applications to the fields of photochemistry, electromagnetism, catalysis, and sorption.^{1–9} Studies on the syntheses of inorganic/organic hybrid materials built by polyoxometal building blocks and metal coordination complexes are recently well developed. A variety of novel oxides or metal–oxygen clusters such as hexanuclear clusters¹⁰ and one-,^{11–16} two-,^{13–18} and three-dimensional (3D)^{16,19}

framework structures were formed as “host” materials in which different coordination compounds and even organic amines were accommodated. Among a number of layered vanadium oxides, those intercalated with organic ammonium cations show promise for their variable framework compositions and mixed valence characteristics. These interesting compounds include $[H_3N(CH_2)_3NH_3]_{0.5}[V_2O_5]$,²⁰ $[enH_2]_{0.5}[V_2O_5]$,²¹ $[pipH_2]_{0.5}[V_2O_5]$,²¹ $[NH_3(CH_2)_4NH_3][VO_3]_2$,²² $[NiMe_4][V_3O_7]$,²³ $[H_3N(CH_2)_4NH_3][V_4O_9]$,²⁴ $[H_3N(CH_2)_3NH_3][V_4O_{10}]$,²⁵ $[HN(C_2H_4)_3NH][V_6O_{14}] \cdot H_2O$,^{26,27} $[Zn(en)_2][V_6O_{14}]$, $[Cu(en)_2][V_6O_{14}]$, and $[Cu(en)_2]_2[V_{10}O_{25}]$.²⁸ With an aim to develop crystal engineering of functional materials, we have used mild hydrothermal techniques to prepare microporous crystals,^{29–31} complex oxide electrolytes,^{32–34} and com-

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plex fluorides.^{35–37} Recently, we extended our interests to the hydrothermal assembly of inorganic/organic hybrid materials. In this article, we report the hydrothermal synthesis and X-ray single-crystal structures of $[\text{Ni}(\text{en})_2]_{0.5}[\text{V}_3\text{O}_7]$ (**1**) and $[\text{Ni}(\text{enMe})_2]_{0.5}[\text{H}_2\text{enMe}]_{0.5}[\text{V}_6\text{O}_{14}]$ (**2**).

Experimental Section

Synthesis and Characterization. Raw materials used in the synthesis are V_2O_5 , $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2$, ethylenediamine (en), 1,2-diaminopropane (enMe), and distilled water. In a typical synthesis of **1**, 0.054 g of V_2O_5 and 0.076 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was first added to 10 mL of distilled water, to which 0.087 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.14 g of en were mixed on stirring. The reaction mixture was sealed in a 20 mL Teflon-lined autoclave and heated under autogenous pressure at 160 °C for 5 days. Crystalline product was filtered, washed with distilled water, and dried at ambient temperature. Products were initially characterized by IR through the KBr pellet technique on a Nicolet 5DX FT-IR instrument. The IR data for **1** (in inverse centimeters) were as follows: 3438(m), 2919(w), 2850(w), 1643(w), 1513(w), 1454(w), 1392(w), 1326(w), 1025(w), 966(s), 940(s), 856(s), 817(s), 774(s), 654(s), 579(s), 558(s), 495(m), 462(s).

The synthesis of **2** involved mixing 0.054 g of V_2O_5 and 0.076 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ into 10 mL H_2O to form a solution, to which 0.087 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.090 g of enMe were added on stirring. The reaction condition was the same as those used in the synthesis of **1**. The IR data (in inverse centimeters) for **2** were as follows: 3436(m), 3328(m), 3249(m), 2921(m), 1585(m), 1494(m), 1454(m), 1384(m), 1199(m), 1025(s), 970(s), 871(s), 828(s), 781(s), 707(s), 642(s), 466(s).

Elemental analysis was performed on a Perkin-Elmer 240C elemental analyzer. Inductively coupled plasma (ICP) analysis was conducted on a Jarrzall-ash 800 Mark-II ICP instrument. A Perkin-Elmer DTA 1700 differential thermal analysis (DTA) and a Perkin-Elmer TGA 7 thermogravimetric analyzer (TGA) were used to obtain DTA and TGA curves in air with a rate of temperature increase of 10 °C min^{-1} .

Determination of Crystal Structure. Crystals of **1** and **2** suitable for single-crystal X-ray diffraction with size 0.160 mm \times 0.040 mm \times 0.020 mm and 0.280 mm \times 0.060 mm \times 0.020 mm were selected, respectively. Structural analyses for **1** and **2** were performed on a Siemens SMART CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ (Mo $K\alpha$) = 0.710 73 Å). The data were collected at temperature of 20 \pm 2 °C. Data processing was accomplished with the SAINT processing program.³⁸ Direct methods were used to solve structures using the SHELXTL crystallographic software package.³⁹ The two C of en in **1** occupy two split positions: C1–C1' and C2–C2'. Each C has occupancy of 0.5. C5, and the C5As (methyl of the H_2enMe) of **2** have occupancies of 0.5. Hydrogen atoms were located by a combination of difference Fourier map and the HYDROGEN program and were added to the structure factor calculation. All non-hydrogen atoms except C1, C1', C2, and C2' (structure **1**) and C4, C5, and N3 (structure **2**) were refined anisotropically.

Experimental X-ray data for **1** and **2** are listed in Table 1, atomic coordinate with isotropic temperature factors are listed in Tables 2 and 3, and selected bond lengths and angles are listed in Tables 4 and 5.

Table 1. Summary of Crystal Data for **1** and **2**

	1	2
emp. formula	$\text{C}_2\text{H}_8\text{N}_2\text{Ni}_{0.50}\text{V}_3\text{O}_7$	$\text{C}_{4.50}\text{H}_{16}\text{N}_3\text{NiV}_6\text{O}_{14}$
formula wt	354.28	700.55
crystal system	orthorhombic	triclinic
space group	Pbcn	P1
<i>a</i> (Å)	16.617(3)	6.6698(7)
<i>b</i> (Å)	6.6329(9)	10.8679(11)
<i>c</i> (Å)	17.138(4)	13.6097(13)
α (deg)	90	78.387(2)
β (deg)	90	80.097(2)
γ (deg)	90	77.684(2)
<i>V</i> (Å ³)	1888.9(7)	935.47(16)
<i>Z</i>	8	2
λ (Å)	0.71073	0.71073
<i>D</i> _{calc} (g cm ⁻³)	2.492	2.487
crystal size (mm)	0.160 \times 0.040 \times 0.020	0.280 \times 0.060 \times 0.020
μ (mm ⁻¹)	3.888	3.922
data/restraints/parameters	1331/0/131	2677/2/244
final R indices	0.0520, 0.1439	0.0454, 0.1346
[<i>I</i> > 2 σ (<i>I</i>)] <i>R</i> ₁ ^a , <i>wR</i> ₂ ^b		

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|. \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

Table 2. Atomic Positional Parameters ($\times 10^4$) and Isotropic Temperature Factors ($\text{Å}^2 \times 10^3$) for **1**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (equiv)
Ni	5000	0	5000	17(1)
V(1)	1617(1)	806(3)	2879(1)	18(1)
V(2)	3619(1)	826(3)	2129(1)	19(1)
V(3)	5008(1)	-1407(2)	2901(1)	13(1)
O(7)	4817(4)	778(10)	2200(4)	28(2)
O(6)	4975(3)	-691(9)	3804(3)	22(2)
O(5)	3422(4)	554(11)	1223(4)	27(2)
O(4)	1518(4)	514(11)	3805(4)	27(2)
O(3)	1167(4)	-1334(10)	2357(4)	26(2)
O(2)	2611(4)	952(10)	2678(4)	30(2)
O(1)	1151(4)	3193(9)	2610(3)	19(2)
N(2)	4069(8)	-2050(18)	5215(6)	72(4)
N(1)	4045(8)	1999(18)	4818(6)	69(4)
C(2)	3279(16)	-380(50)	5235(19)	44(7)
C(2')	3480(15)	-1490(40)	5478(15)	36(7)
C(1)	3429(14)	1370(40)	4570(13)	28(6)
C(1')	3265(13)	230(40)	4862(14)	28(6)

Results and Discussion

Synthesis. To obtain a desired polymeric state of V–O cluster, it is necessary to control a specific pH value of a solution containing vanadium. For example, new phases such as $\text{NMe}_4\text{V}_4\text{O}_{10}$, Li_xVO_2 , $\text{NMe}_4\text{V}_3\text{O}_7$, and Li_3VO_4 in V_2O_5 – NMe_4OH – LiOH – H_2O systems formed as pH value increased.²³ In our synthesis for coordination-pillared vanadium oxides, we hope to control polymeric states of vanadium by pH, although we emphasize layered and framework solids. Another consideration was the number of negative charges on V–O layers or frameworks so as to keep a relatively low negative charge on the layers for possibly linking pillared metal ions. In our cases, different pH values of solutions indeed gave some products with different ratios of V/O on layers. Oxalic acid served as a mediate reductant for ensuring the formation of tetravalent vanadium ions.

Structural Description. There are three vanadium atoms in the asymmetric unit of **1** (Figure 1a), showing two coordination states, tetrahedral $\text{VO}_4(\text{V}(1))$ and square-pyramidal $\text{VO}_5(\text{V}(2)$ and $\text{V}(3))$. $\text{V}(2)\text{O}_5$ and $\text{V}(3)\text{O}_5$ have apical oxygen atoms at distances of 1.598(7) and 1.620(6) Å and four basal oxygen atoms at distances in the range of 1.923(6)–1.995(7) Å and 1.897(7)–2.008-

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Table 3. Atomic Positional Parameters ($\times 10^4$) and Isotropic Temperature Factors ($\text{\AA}^2 \times 10^3$) for 2

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (equiv)
Ni	0	5000	5000	25(1)
V(1)	-5290(2)	7452(1)	7821(1)	19(1)
V(2)	-2689(2)	9200(1)	6578(1)	20(1)
V(3)	175(2)	6730(1)	7072(1)	17(1)
V(4)	3051(2)	4987(1)	8335(1)	17(1)
V(5)	-2231(2)	4994(1)	9133(1)	19(1)
V(6)	2840(2)	8768(1)	5686(1)	19(1)
O(1)	-6523(8)	8210(5)	8712(4)	33(1)
O(2)	-7073(7)	6560(4)	7354(3)	24(1)
O(3)	-4475(7)	5637(4)	8501(3)	22(1)
O(4)	-2445(7)	7630(4)	7581(3)	21(1)
O(5)	-5396(7)	8752(4)	6564(3)	22(1)
O(6)	-3058(8)	10375(5)	7165(4)	36(1)
O(7)	-2549(7)	9829(4)	5118(4)	25(1)
O(8)	340(7)	8503(4)	6357(3)	22(1)
O(9)	-13(8)	6034(5)	6158(3)	30(1)
O(10)	46(6)	5411(4)	8311(3)	22(1)
O(11)	2558(7)	4410(5)	9776(3)	28(1)
O(12)	3908(8)	3735(5)	7827(4)	34(1)
O(13)	-2001(8)	3468(5)	9393(4)	36(1)
O(14)	3819(8)	7632(5)	5052(4)	34(1)
N(1)	1784(9)	3445(6)	5820(5)	32(2)
N(2)	-2449(9)	4218(6)	5885(5)	29(1)
N(3)	4420(20)	8652(12)	630(10)	111(4)
C(1)	453(12)	2522(8)	6333(7)	39(2)
C(2)	-1656(12)	3257(8)	6715(6)	38(2)
C(3)	1398(14)	1567(8)	7180(7)	48(2)
C(4)	6090(30)	9375(19)	219(17)	162(8)
C(5)	8270(30)	8690(20)	-426(19)	78(7)

Table 4. Selected Bond Lengths (\AA) and Angles (deg) for 1

bond	length	bond	length
Ni-N(1) ^a	2.091(9)	V(2)-O(7)	1.995(7)
Ni-N(1)	2.091(9)	V(2)-O(5)	1.598(7)
Ni-N(2) ^a	2.093(10)	V(2)-O(3) ^b	1.957(7)
Ni-N(2)	2.093(10)	V(2)-O(2)	1.923(6)
Ni-O(6) ^a	2.101(6)	V(2)-O(1) ^c	1.968(6)
Ni-O(6)	2.101(6)	V(3)-O(7)	1.908(7)
V(1)-O(4)	1.607(7)	V(3)-O(7) ^d	1.897(7)
V(1)-O(3)	1.836(7)	V(3)-O(6)	1.620(6)
V(1)-O(2)	1.691(7)	V(3)-O(3) ^e	1.977(6)
V(1)-O(1)	1.821(6)	V(3)-O(1) ^c	2.008(7)
V(2)-V(3)	3.045(2)	V(2)-V(3) ^f	2.928(2)
bond	angle	bond	angle
N(1) ^a -Ni-N(1)	180.0(6)	O(4)-V(1)-O(2)	108.0(3)
N(1) ^a -Ni-N(2) ^a	82.9(6)	O(4)-V(1)-O(1)	108.2(3)
N(1)-Ni-N(2) ^a	97.1(6)	O(2)-V(1)-O(1)	108.3(3)
N(1) ^a -Ni-N(2)	97.1(6)	O(4)-V(1)-O(3)	110.3(3)
N(1)-Ni-N(2)	82.9(6)	O(2)-V(1)-O(3)	110.0(3)
N(2) ^a -Ni-N(2)	180.0(5)	O(1)-V(1)-O(3)	112.1(3)
N(1)-Ni-O(6)	88.7(3)	O(6)-V(3)-O(7) ^d	112.4(3)
N(2)-Ni-O(6)	90.9(3)	O(6)-V(3)-O(7)	111.9(3)
O(6) ^a -Ni-O(6)	180.000(1)	O(7) ^d -V(3)-O(7)	135.66(14)
O(5)-V(2)-O(2)	107.6(3)	O(6)-V(3)-O(3) ^e	103.8(3)
O(5)-V(2)-O(3) ^b	109.9(3)	O(7) ^d -V(3)-O(3) ^e	81.7(3)
O(2)-V(2)-O(3) ^b	91.1(3)	O(7)-V(3)-O(3) ^e	90.1(3)
O(5)-V(2)-O(1) ^c	110.3(3)	O(6)-V(3)-O(1) ^c	104.1(3)
O(2)-V(2)-O(1) ^c	90.2(3)	O(7) ^e -V(3)-O(1) ^c	89.6(3)
O(3) ^b -V(2)-O(1) ^c	137.4(3)	O(7)-V(3)-O(1) ^c	77.6(3)
O(5)-V(2)-O(7)	105.2(3)	O(3) ^f -V(3)-O(1) ^c	152.0(3)
O(2)-V(2)-O(7)	147.2(3)		
O(3) ^b -V(2)-O(7)	79.8(3)		
O(1) ^c -V(2)-O(7)	76.5(3)		

^{a-f}The following symmetry transformations were used to generate equivalent atoms: ^a-*x*+1, -*y*, -*z*+1. ^b-*x*+1/2, *y*+1/2, *z*. ^c-*x*+1/2, *y*-1/2, *z*. ^d-*x*+1, *y*-1/2, -*z*+1/2. ^e*x*+1/2, *y*, -*z*+1/2. ^f-*x*+1, *y*+1/2, -*z*+1/2.

(7) \AA , respectively. The shortest bond length of the V(1)-O₄ tetrahedral is 1.607 \AA , corresponding to the axial V=O; the remaining bonds have lengths from 1.691 to 1.836

Table 5. Selected Bond Lengths (\AA) and Angles (deg) for 2

bond	length	bond	length
Ni-N(2)	2.085(6)	V(4)-O(12)	1.602(5)
Ni-N(2) ^a	2.085(6)	V(3)-O(10)	1.984(4)
Ni-N(1)	2.087(6)	V(3)-O(9)	1.615(5)
Ni-N(1) ^a	2.087(6)	V(3)-O(8)	1.993(4)
Ni-O(9)	2.110(5)	V(3)-O(4)	1.902(4)
Ni-O(9) ^a	2.110(5)	V(3)-O(2) ^c	1.903(4)
V(1)-O(5)	1.988(4)	V(4)-O(11)	1.928(5)
V(1)-O(4)	1.914(4)	V(4)-O(10)	1.963(4)
V(1)-O(3)	2.005(4)	V(4)-O(3) ^c	1.991(4)
V(1)-O(2)	1.938(4)	V(4)-O(2) ^c	1.942(4)
V(1)-O(1)	1.611(5)	V(5)-O(13)	1.605(5)
V(2)-O(8)	1.994(4)	V(5)-O(11) ^d	1.699(5)
V(2)-O(7)	1.959(5)	V(5)-O(10)	1.808(4)
V(2)-O(6)	1.593(5)	V(5)-O(3)	1.795(4)
V(2)-O(5)	1.972(4)	V(6)-O(14)	1.608(5)
V(2)-O(4)	1.956(4)	V(6)-O(8)	1.809(4)
V(1)-V(2)	2.9298(15)	V(6)-O(7) ^e	1.685(4)
V(1)-V(4) ^b	3.0222(15)	V(6)-O(5) ^c	1.811(4)
V(2)-V(3)	2.9727(16)	V(3)-V(4)	2.9144(15)
N(3)⋯(1) ^f	2.941		
bonds	angle	bonds	angle
N(2)-Ni-N(2) ^a	180.0(3)	O(9)-V(3)-O(4)	111.3(2)
N(2)-Ni-N(1)	82.8(2)	O(9)-V(3)-O(2) ^c	114.5(2)
N(2) ^a -Ni-N(1)	97.2(2)	O(4)-V(3)-O(2) ^c	134.1(2)
N(2)-Ni-N(1) ^a	97.2(2)	O(9)-V(3)-O(10)	105.7(2)
N(2) ^a -Ni-N(1) ^a	82.8(2)	O(4)-V(3)-O(10)	89.27(18)
N(1)-Ni-N(1) ^a	180.000(1)	O(2) ^c -V(3)-O(10)	81.63(18)
N(2)-Ni-O(9)	88.4(2)	O(9)-V(3)-O(8)	101.9(2)
N(1)-Ni-O(9)	87.7(2)	O(4)-V(3)-O(8)	79.28(18)
O(9)-Ni-O(9) ^a	180.000(1)	O(2) ^c -V(3)-O(8)	88.37(19)
O(1)-V(1)-O(4)	110.1(2)	O(10)-V(3)-O(8)	152.33(19)
O(1)-V(1)-O(2)	111.2(2)	O(12)-V(4)-O(11)	106.7(2)
O(4)-V(1)-O(2)	138.6(2)	O(12)-V(4)-O(2) ^c	112.9(2)
O(1)-V(1)-O(5)	104.9(2)	O(11)-V(4)-O(2) ^c	140.3(2)
O(4)-V(1)-O(5)	81.66(18)	O(12)-V(4)-O(10)	107.2(2)
O(2)-V(1)-O(5)	90.50(18)	O(11)-V(4)-O(10)	89.18(19)
O(1)-V(1)-O(3)	105.3(2)	O(2) ^c -V(4)-O(10)	81.20(18)
O(4)-V(1)-O(3)	89.85(19)	O(12)-V(4)-O(3) ^c	106.4(2)
O(2)-V(1)-O(3)	76.80(18)	O(11)-V(4)-O(3) ^c	90.29(19)
O(5)-V(1)-O(3)	149.7(2)	O(2) ^c -V(4)-O(3) ^c	77.04(18)
O(6)-V(2)-O(4)	107.8(2)	O(10)-V(4)-O(3) ^c	145.0(2)
O(6)-V(2)-O(7)	109.7(2)	O(13)-V(5)-O(11) ^d	109.5(3)
O(4)-V(2)-O(7)	142.4(2)	O(13)-V(5)-O(3)	108.6(2)
O(6)-V(2)-O(5)	108.4(2)	O(11) ^d -V(5)-O(3)	108.9(2)
O(4)-V(2)-O(5)	81.04(18)	O(13)-V(5)-O(10)	109.5(2)
O(7)-V(2)-O(5)	88.94(18)	O(11) ^d -V(5)-O(10)	110.8(2)
O(6)-V(2)-O(8)	108.8(2)	O(3)-V(5)-O(10)	109.5(2)
O(4)-V(2)-O(8)	77.99(18)	O(14)-V(6)-O(7) ^e	109.2(3)
O(7)-V(2)-O(8)	88.33(19)	O(14)-V(6)-O(8)	109.0(2)
O(5)-V(2)-O(8)	141.4(2)	O(7) ^e -V(6)-O(8)	109.5(2)
		O(14)-V(6)-O(5) ^c	107.7(2)
		O(7) ^e -V(6)-O(5) ^c	110.5(2)
		O(8)-V(6)-O(5) ^c	110.8(2)

^{a-f}The following symmetry transformations were used to generate equivalent atoms. ^a-*x*, -*y*+1, -*z*+1. ^b*x*-1, *y*, *z*. ^c*x*+1, *y*, *z*. ^d-*x*, -*y*+1, -*z*+2. ^e-*x*, -*y*+2, -*z*+1. ^f1+*x*, *y*, 1-*z*.

\AA . Bond-length and bond-strength calculations were based on the method by Brown and Shannon⁴⁰ and the data from Brown and Altermatt.⁴¹ The bond valence sums for V(1), V(2), and V(3) are 4.92, 4.14, and 4.15, respectively, indicating that V(1) is pentavalent, whereas V(2) and V(3) are tetravalent. This was confirmed by their coordination states. The layer composition for **1** was $\{\text{V}^{5+}(\text{V}^{4+})_2\text{O}_7\}^-$.

The structure of **1** was constructed from $\{\text{Ni}(\text{en})\}^{2+}$ cations bridged through $\{\text{V}_3\text{O}_7\}^-$ layer sheets into a 3D framework. The Ni atom was in a NiO₂N₄ octahedral environment that lies approximately in a plane parallel

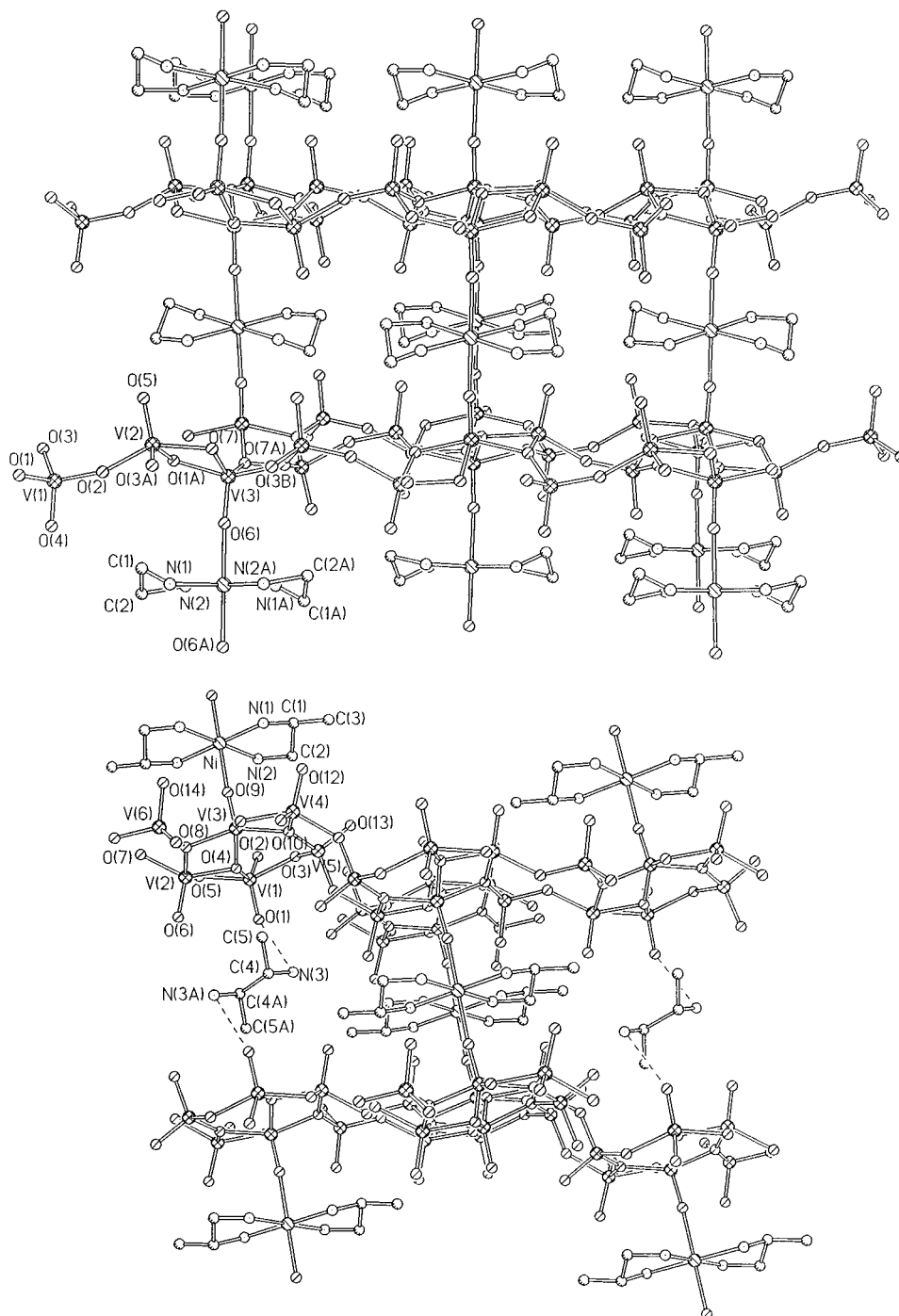


Figure 1. (a) View of the structure of **1** down the *b* axis showing the layers of vanadium oxide with interlayer $\{\text{Ni}(\text{en})_2\}^{2+}$. (b) View of the structure of **2** down the *a* axis showing the layers of vanadium oxide with interlayer $\{\text{Ni}(\text{enMe})_2\}^{2+}$ and $\{\text{H}_2\text{enMe}\}^{2+}$. Dashed lines indicate hydrogen bonds.

to $\{\text{V}_3\text{O}_7\}^-$ layers (Figure 1a), and bond to two trans apical O(6) atom of square-pyramidal V(3)O₅ from two adjacent layers. The bond angle of O–Ni–O is 180.00(1)°. The two Ni–O distances and four Ni–N distances are nearly equal (the average Ni–N distances are 2.09 Å and the Ni–O distances are 2.10 Å, in agreement with $r[\text{Ni}^{2+}(\text{C.N.VI})] + r(\text{O}^{2-}) = 2.04 \text{ \AA}$ ⁴²).

The asymmetric unit of **2** is shown in Figure 1b. The $\{\text{V}_6\text{O}_{14}\}^{2-}$ contains two VO₄ and four VO₅. The assignment of an oxidation state of +4 in the five-coordination configuration and +5 in the four-coordination configuration

was confirmed by valence sum calculations. The NiO₂N₄ octahedral environment for Ni atoms is the same as that in **1** (Ni–N distances, ca. 2.09 Å; Ni–O distances, ca. 2.11 Å; O–Ni–O bond angles, 180.00(1)°). Ni atoms were linked with O(9) atoms of square-pyramidal V(3)O₅. $\{\text{H}_2\text{enMe}\}^{2+}$ cations between the layers are oriented with their N atoms pointing toward oxide layers, forming hydrogen bonds with the adjacent oxide layers. Above and below, the N atoms are in close contact with the free apical oxygen atom O(1) of V(1)O₅ square pyramids at an N···O distance of 2.941 Å. The $\{\text{H}_2\text{enMe}\}^{2+}$ dications fill the empty space among four $\{\text{Ni}(\text{enMe})_2\}^{2+}$. It amounts to a shift of a half of a metal

(42) Shannon, R. D. *Acta Crystallogr.* **1976**, A32, 751.

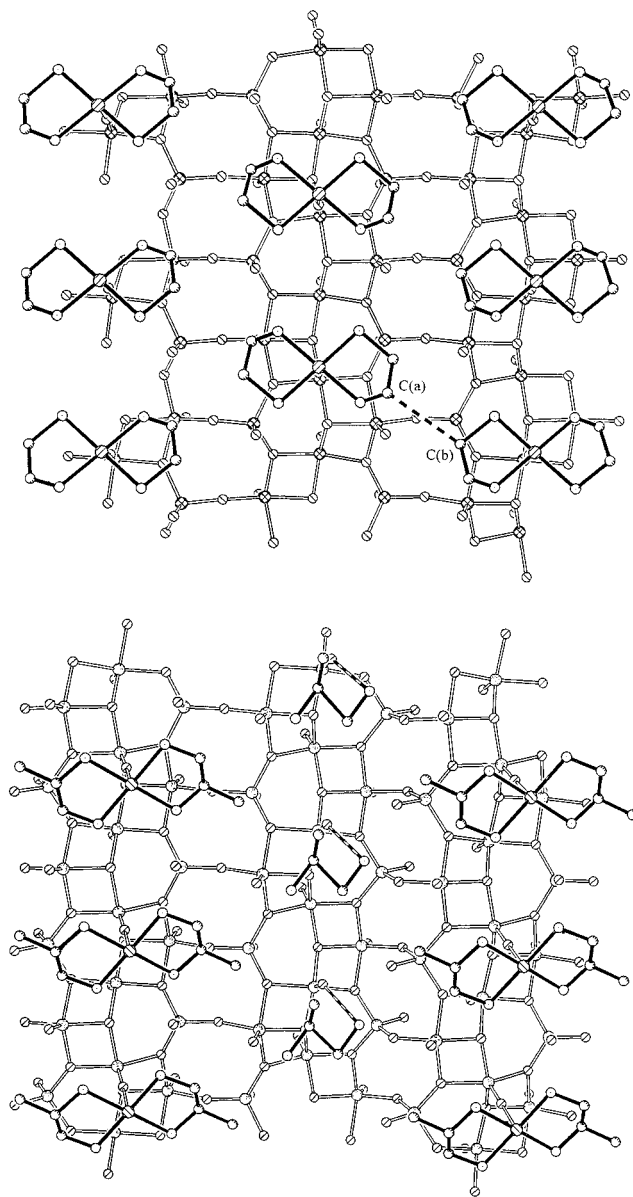


Figure 2. View of the connecting sites of metal coordination complex or organic amine with the vanadium oxide layers in (a) **1** and (b) **2**.

coordination complex in **1** (Figure 2). If the O(1) of V(1)-O₅ is linked with {Ni(enMe)}²⁺, the distance between neighboring methyls of two enMe is too short, having the steric hindrance of C(a) being 3.74 Å from C(b), Figure 2 (a). The structure of **2** is constructed from {Ni(enMe)₂}²⁺ and {H₂enMe}²⁺ through a {V₆O₁₄}²⁻ layer into a 3D framework.

The V–O layers of {V₃O₇}⁻ or {V₆O₁₄}²⁻ in **1** and **2** are all composed of edge-sharing VO₅ square pyramids, which form pairs of alternating “up” and “down” orientations as zigzag chains. Two chains were connected together by the VO₄ tetrahedron. The same type of {V₃O₇}⁻ or {V₆O₁₄}²⁻ layer is already encountered in the compounds [NMe₄][V₃O₇], [HN(C₂H₄)₃NH][V₆O₁₄]·H₂O, and [Zn(en)₂][V₆O₁₄] (and the same with [Cu(en)₂][V₆O₁₄]), and the topologies four kinds layers are schematically illustrated in Figure 3. The four frameworks differ each other from the direction of the apical oxygen in VO₅ or VO₄.

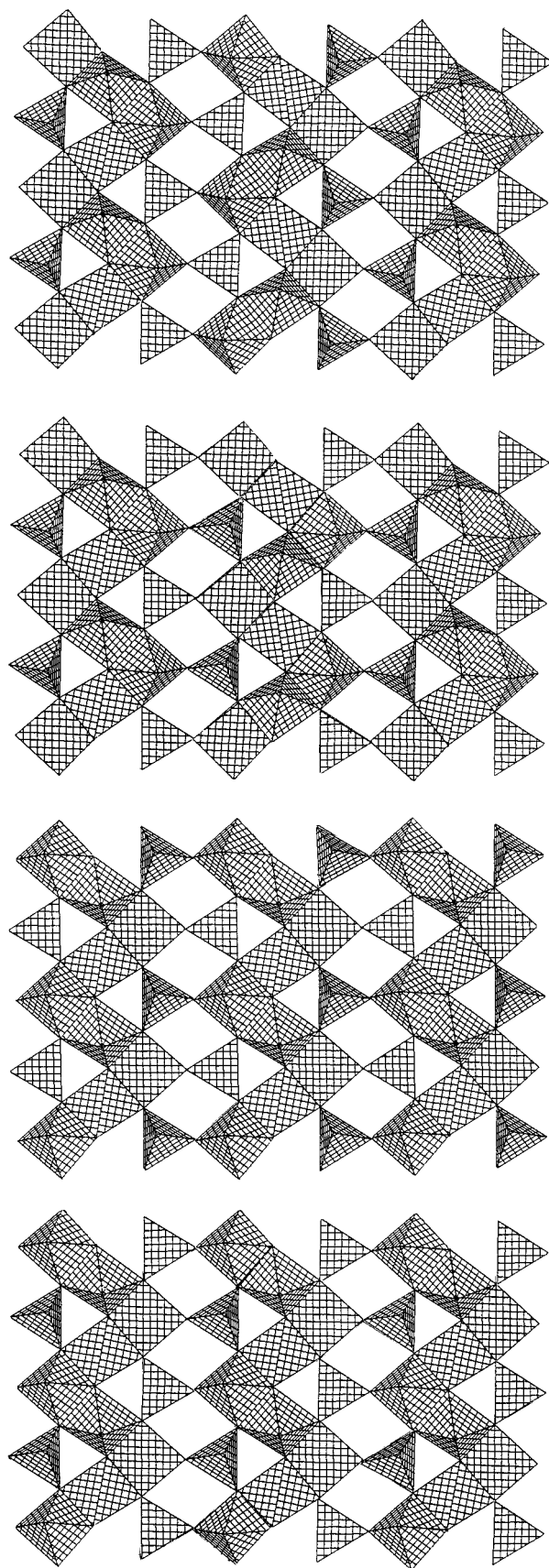


Figure 3. View of the vanadium oxide layers of (a) **1**, (b) **2** and [Zn(en)₂][V₆O₁₄], (c) [NMe₄][V₃O₇], and (d) [HN(C₂H₄)₃NH][V₆O₁₄]·H₂O.

As shown in Figure 3a,b, the structures are built up by the linkage of zigzag chains arranging in a manner of A–B–A–B through tetrahedral VO₄. In the zigzag

chains of **1**, the direction of apical oxygen of the neighboring square pyramids is exactly opposite, whereas only the apical oxygen of the middle pyramid are reverse in the case of **2**.

In Figure 3c,d, zigzag chains arrange in an A–A–A–A manner. The structures consist of similar chains to each other, but the different between them is that the directions of apical oxygen in the tetrahedral VO₄ are entirely opposite.

Thermal Analysis. The TGA–DTA of **1** showed that the en molecule is combusted from the crystal in the range of 270–390 °C with weight losses of 15.8% (calculated value of 16.7%) and weight losses of 2.2% in the range 520–600 °C consistent with oxidation of the {V₃O₇}⁻ from V^{4.33+} to V⁵⁺. The TGA–DTA of **2** indicated that the enMe is lost in two stages as heating with weight losses of 6.1% at 195–340 °C and 10.2% at 340–400 °C, respectively. The enMe of structure **2** is split between two crystallographic distinct sites in the ratio 1:2. {H₂enMe}²⁺ departed first, followed by the coordinated enMe with Ni. In addition, **2** had a weight gain of 2% at 520–600 °C, consistent with the oxidation of {V₆O₁₄}²⁻ from V^{4.33+} to V⁵⁺.

Conclusions

The successful hydrothermal isolation of inorganic/organic **1** and **2** provided novel examples of layered vanadium oxides linked through the metal coordination complex. It is evident that the hydrothermal technique affords a powerful method for the modified metal oxide structures and for the isolation of new inorganic/organic hybrid materials. It is noteworthy that the introduction of organic group can result in structure changes such as in the case of **2**.

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Supporting Information Available: Tables of experimental conditions and crystal data, atomic positional parameters, bond lengths and angles, anisotropic temperature factors, and structure factors for **1** and **2**. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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