

Ni(phen)(H₂O)(V₂O₆)的水热合成和晶体结构

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关键词: 有机-无机杂合物; 钒氧化物; 水热合成; 晶体结构

中图分类号: O614.51¹; O614.81³

文献标识码: A

文章编号: 1001-4861(2005)02-0217-04

Hydrothermal Synthesis and Crystal Structure of Ni(phen)(H₂O)(V₂O₆)

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Abstract: A novel compound Ni (phen)(H₂O)(V₂O₆) has been hydrothermally synthesized and structurally determined to be a two-dimensional compound, which contains {V₂O₆}_n²ⁿ⁻ chains interconnected by nickel(II) complexes via oxygen atoms. The crystallographic data measured by single-crystal X-ray diffraction analysis are as follows: C₁₂H₁₀N₂NiO₇V₂, *M_r*=454.81, monoclinic, space group *P*2₁/*c*, *a*=0.784 6(3), *b*=2.103 6(8), *c*=0.942 3(4) nm, β=112.872(5)°, *V*=1.433 0(10) nm³, *Z*=4, *D_c*=2.104 Mg·m⁻³, μ(Mo *K*α)=2.615 mm⁻¹, *F*(000)=904, *T*=298(2) K, 4 480 reflections collected, 2 470 independent (*R_{int}*=0.032 2), the final *R*=0.058 4 and *wR*₂=0.145 7 for 2 303 observed reflections with *I*>2σ(*I*). CCDC: 192520.

Key words: organic-inorganic hybrid; vanadium oxides; hydrothermal synthesis; crystal structure

0 Introduction

There has been extensive interest in organic-inorganic hybrid vanadium oxides and polyvanadate clusters owing to their structural diversity and potential application in catalysis and material science^[1~5]. Structural characteristics of these compounds have been summarized and divided into several classes by Hargman^[6] according to the role of the organic components. The organic components act as cation in compounds of class A, which including two types-one has V_xO_yⁿ⁻ layer, and the other has M'V_xO_yⁿ⁻ layer. They act as ligands to V_xO_y subunit and to M' in discrete cation in compounds of class B and C, respectively.

And in compounds of class D, they act as ligand to M' in M'V_xO_y structure, while the compound maybe one-, two- or three-dimensional. Owing to the ability of vanadium to adopt a variety of co-ordination geometries in various oxidation states, novel structural types could be discovered by modifying the transition metal ions, the organic groups and the synthetic conditions, etc. In this paper we report the hydrothermal synthesis and crystal structure of a layer compound Ni(phen)(H₂O)(V₂O₆), which contains {V₂O₆}_n²ⁿ⁻ chains interconnected by nickel(II) complexes via oxygen atoms. It falls into class D with two-dimensions. Its structure is different from those of any other reported compounds.

收稿日期:2004-04-06。收修改稿日期:2004-11-18。

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1 Experimental

1.1 Synthesis of the compound

The title compound was hydrothermal synthesized under autogenous pressure. The starting materials, NH_4VO_3 (0.468 g), $\text{Ni}(\text{OAc})_2$ (0.498 g), 1,10-phenanthroline (phen, 0.396 g) and water (10 mL), were mixed in a molar ratio of 2:1:1:278 under stirring for 0.5 h at room temperature. Then the mixture was sealed in a 23 mL Teflon lined stainless steel autoclave and heated at 160 °C for 3 d. The green crystalline products were washed with distilled water and dried at room temperature. The elemental analysis was performed on a Perkin-Elmer 2400 element analyzer.

1.2 X-ray crystallography

A green parallelepiped single crystal with dimensions of 0.35 mm × 0.35 mm × 0.20 mm was chosen for the measurement. Diffraction data were collected on a BRUCKER SMART CCD area detector with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm) at 298±2 K using the φ - ω scan technique. The intensity data were collected in the range of $1.94^\circ < \theta < 25.02^\circ$. A total of 4 480 reflections were collected, of which 2 470 ($R_{\text{int}}=0.032\ 2$) were unique and 2 303 were observed ($I > 2\sigma(I)$). The crystal structure was solved by direct methods and difference Fourier map with SHELXS-97 and refined by full-matrix least-squares techniques on F^2 with SHELXL-97. All of the hydrogen atoms were located based on geometrical analysis. The final refinement converged at $R=0.058\ 4$ and $wR_2=0.145\ 7$ ($w=1/[\sigma^2(F_o^2)+(0.055\ 6P)^2+1.000\ 0P]$, where $P=$

$(F_o^2+2F_c^2)/3$. $(\Delta\rho)_{\text{max}}=1\ 637$ and $(\Delta\rho)_{\text{min}}=-633\ \text{e}\cdot\text{nm}^{-3}$.
CCDC: 192520.

2 Results and discussion

The elemental analyses showed that the compound contained 31.30% C, 1.92% H and 6.53% N, which was consistent with the calculated values (31.69% C, 2.22% H, 6.16% N), according to the empirical formula of the compound- $\text{C}_{12}\text{H}_{10}\text{N}_2\text{NiO}_7\text{V}_2$.

The crystallographic data measured by single-crystal X-ray diffraction analysis show that the empirical formula of the compound was $\text{C}_{12}\text{H}_{10}\text{N}_2\text{NiO}_7\text{V}_2$, and the formula weight was 454.81. It belonged to monoclinic crystal system, $P2_1/c$ space group. The unit cell dimensions were $a=0.784\ 6(3)$, $b=2.103\ 6(8)$, $c=0.942\ 3(4)$ nm, and $\beta=112.872(5)^\circ$.

The selected bond lengths, bond angles and hydrogen bonds are listed in Tables 1, 2 and 3, respectively.

Fig.1 shows the thermal ellipsoid plots of the coordinations around the Ni and V atoms. Each of the two vanadium atoms V(1) and V(2) is co-ordinated by four oxygen atoms to make a distorted tetrahedral geometry. $\{\text{V}(1)\text{O}_4\}$ tetrahedra and $\{\text{V}(2)\text{O}_4\}$ tetrahedra are corner-shared by O(2) and O(3) atoms, and arranged alternately to form one-dimension $\{\text{V}_2\text{O}_6\}_n^{2n-}$ chains. The bond distances of the bridging oxygen and the vanadium atoms are close to each other (0.176 4(5)~0.179 7(4) nm). However, the two vanadium atoms, V(1) and V(2), are crystallographically distinct. $\{\text{V}(1)\text{O}_4\}$ tetrahedron has the only terminal oxygen atom, O(4),

Table 1 Selected bond lengths (nm)

Bond	Dist.	Bond	Dist.	Bond	Dist.
Ni(1)-O(6)#1	0.204 5(5)	V(1)-O(3)	0.179 7(4)	C(4)-C(5)	0.142 4(9)
Ni(1)-N(1)	0.206 4(5)	V(2)-O(6)	0.163 6(4)	C(7)-C(11)	0.140 8(9)
Ni(1)-N(2)	0.208 3(5)	V(2)-O(3)	0.176 9(4)	C(11)-C(12)	0.143 4(8)
V(1)-O(4)	0.160 7(5)	O(5)-Ni(1)#5	0.204 6(4)	C(6)-C(7)	0.142 6(9)
V(1)-O(2)	0.178 3(5)	N(1)-C(1)	0.131 9(8)	C(7)-C(8)	0.138 1(10)
V(2)-O(5)	0.163 8(4)	N(2)-C(10)	0.131 0(8)	C(8)-C(9)	0.139 6(11)
V(2)-O(2)#3	0.176 4(5)	C(1)-C(2)	0.139 3(9)	C(9)-C(10)	0.140 3(10)
O(2)-V(2)#4	0.176 4(5)	C(2)-C(3)	0.137 0(10)	Ni(1)-O(5)#2	0.204 6(4)
O(6)-Ni(1)#6	0.204 4(5)	C(3)-C(4)	0.140 8(9)	Ni(1)-O(1)	0.207 2(4)
N(1)-C(12)	0.136 8(7)	C(4)-C(12)	0.139 6(9)	Ni(1)-O(7)	0.212 0(5)
N(2)-C(11)	0.134 4(8)	C(5)-C(6)	0.135 4(11)	V(1)-O(1)	0.166 1(9)

Symmetry transformations used to generate equivalent atoms: #1: $x-1, -y+1/2, z-1/2$; #2: $x-1, y, z-1$; #3: $x, -y+1/2, z+1/2$; #4: $x, -y+1/2, z-1/2$; #5: $x+1, y, z+1$; #6: $x+1, -y+1/2, z+1/2$.

Table 2 Selected bond angles (°)

Angle		Angle		Angle	
O(6)#1-Ni(1)-O(5)#2	90.46(19)	O(1)-Ni(1)-N(2)	90.68(19)	V(2)-O(5)-Ni(1)#5	144.5(3)
O(5)#2-Ni(1)-N(1)	90.59(17)	O(5)#2-Ni(1)-O(7)	91.57(18)	C(1)-N(1)-C(12)	118.9(5)
O(5)#2-Ni(1)-O(1)	177.17(17)	O(1)-Ni(1)-O(7)	85.97(18)	C(12)-N(1)-Ni(1)	111.8(4)
O(6)#1-Ni(1)-N(2)	175.08(19)	N(2)-Ni(1)-O(7)	94.0(2)	C(10)-N(2)-Ni(1)	129.6(5)
N(1)-Ni(1)-N(2)	80.97(19)	O(4)-V(1)-O(2)	109.5(3)	N(1)-C(1)-C(2)	122.0(6)
O(6)#1-Ni(1)-O(7)	90.7(2)	O(4)-V(1)-O(3)	109.2(2)	C(2)-C(3)-C(4)	119.3(6)
N(1)-Ni(1)-O(7)	174.5(2)	O(2)-V(1)-O(3)	113.0(2)	C(3)-C(4)-C(5)	122.8(6)
O(6)#1-Ni(1)-N(1)	94.28(19)	O(5)-V(2)-O(2)#3	108.6(2)	C(6)-C(5)-C(4)	120.1(6)
O(6)#1-Ni(1)-O(1)	88.19(19)	O(5)-V(2)-O(3)	109.3(2)	C(8)-C(7)-C(11)	116.8(6)
N(1)-Ni(1)-O(1)	91.99(18)	O(2)#3-V(2)-O(3)	105.5(3)	C(11)-C(7)-C(6)	119.5(6)
O(5)#2-Ni(1)-N(2)	90.87(19)	V(2)#4-O(2)-V(1)	157.5(3)	C(10)-C(9)-C(8)	117.2(6)
N(2)-C(11)-C(7)	123.3(6)	O(5)#2-Ni(1)-O(7)	91.6(2)	O(6)-V(2)-O(2)#3	111.1(3)
C(7)-C(11)-C(12)	118.8(6)	O(1)-Ni(1)-O(7)	86.0(2)	O(6)-V(2)-O(3)	112.5(2)
N(1)-C(12)-C(11)	117.3(5)	O(4)-V(1)-O(1)	109.3(2)	V(1)-O(1)-Ni(1)	133.7(2)
N(1)-Ni(1)-O(1)	92.01(19)	O(1)-V(1)-O(2)	106.2(3)	V(2)-O(3)-V(1)	148.8(3)
O(5)#2-Ni(1)-N(2)	90.9(2)	O(1)-V(1)-O(3)	109.7(2)	V(2)-O(6)-Ni(1)#6	167.8(3)
O(1)-Ni(1)-N(2)	90.7(2)	O(5)-V(2)-O(6)	109.6(2)	C(1)-N(1)-Ni(1)	129.3(4)
C(10)-N(2)-C(11)	118.6(5)	C(3)-C(4)-C(12)	117.3(6)	C(5)-C(6)-C(7)	121.5(6)
C(11)-N(2)-Ni(1)	111.7(4)	C(12)-C(4)-C(5)	119.8(6)	C(7)-C(8)-C(9)	120.6(6)
C(3)-C(2)-C(1)	120.0(7)	N(2)-C(10)-C(9)	123.4(7)	C(8)-C(7)-C(6)	123.7(6)
N(2)-C(11)-C(12)	118.0(5)	N(1)-C(12)-C(4)	122.5(6)	C(4)-C(12)-C(11)	120.3(5)

Symmetry transformations used to generate equivalent atoms: #1: $x-1, -y+1/2, z-1/2$; #2: $x-1, y, z-1$; #3: $x, -y+1/2, z+1/2$; #4: $x, -y+1/2, z-1/2$; #5: $x+1, y, z+1$; #6: $x+1, -y+1/2, z+1/2$.

Table 3 Hydrogen bonds

D-H	$d(\text{D-H}) / \text{nm}$	$d(\text{H} \cdots \text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$	$d(\text{D} \cdots \text{A}) / \text{nm}$	A
O(7)-H(7A)	0.095 7	0.271 0	121.44	0.331 2	O(2)
O(7)-H(7B)	0.096 0	0.207 7	152.80	0.296 3	O(6) [$x-1, -y+1/2, z-1/2$]

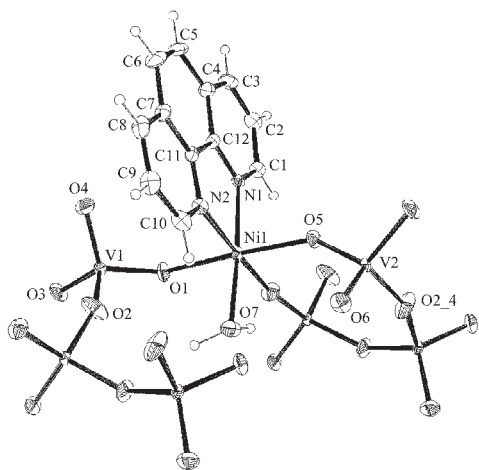


Fig.1 Thermal ellipsoid plot of the co-ordinations around the Ni and V atoms

with the shortest V-O distance (0.160 7(5) nm). So the {V(1)O₄} tetrahedron has only one oxygen atom, O(1),

left to co-ordinate to Ni, whereas {V(2)O₄} tetrahedron has both of the other two oxygen atoms, O(5) and O(6), to co-ordinate to Ni. The V-O bond lengths and O-V-O bond angles are in the ranges of 0.160 7(5) nm to 0.179 7(4) nm, and 106.2(3)° to 113.0(2)°, respectively, for V(1). And they are in the ranges of 0.163 8(4) nm to 0.176 9(4) nm, and 105.5(3)° to 112.5(2)°, respectively, for V(2). The Ni atom has a distorted octahedral environment. It coordinates to two N atoms from phen ligand and four O atoms, three of which (O(1), O(5) and O(6)) are from vanadium oxides and one (O(7)) from H₂O. The bond lengths of Ni-N [0.206 4(5)~0.208 3(5) nm] and Ni-O [0.204 5(5)~0.212 0(5) nm] are normal. Each [Ni(phen)(H₂O)]²⁺ fragment is connected to one {V₂O₆}_n²ⁿ⁻ chain through O(1), and to another through O(5) and O(6). Thus the {V₂O₆}_n²ⁿ⁻ chains of corner-sharing tetrahedra are interconnected

to construct the two-dimensional networks in the ac planes (Fig.2), which are then stacked to form channels along the [010] direction.

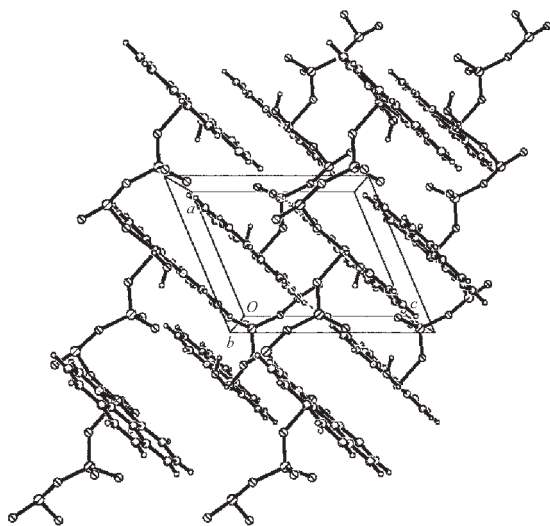


Fig.2 Crystal packing of the title compound

It is notable that the structure of $\text{Ni(phen)(H}_2\text{O)V}_2\text{O}_6$ is different from those of other 2-D compounds of class D that containing $\{\text{V}_2\text{O}_6\}_n^{2n-}$ chains of corner-sharing tetrahedra. For example: β - $[\text{Cu(terpy)V}_2\text{O}_6]^{[7]}$ consists of chains of corner-sharing $\{\text{VO}_4\}$ tetrahedra linked by binuclear Cu sites; $[\text{Cu(dpa)VO}_3]^{[8]}$ contains of chains of corner-sharing $\{\text{VO}_4\}$ tetrahedra linked to $\{\text{Cu(dpa)}\}_n^{n+}$ chains, in a parallel double-chain arrangement.

And it is instructive to compare the structure of the title compound with those of $[\text{Cu(en)V}_2\text{O}_6]^{[9]}$ and $[\text{M(Hdpa)}_2\text{V}_4\text{O}_{12}]^{[10]}$ ($\text{M}=\text{Co}, \text{Ni}$). $[\text{Cu(en)V}_2\text{O}_6]$ possesses 1-D chains, with one oxygen atom from each tetrahedron in the vanadium oxide chain involved in bonding with the copper coordination complex. Because of the interaction of each Cu with two oxygen atoms from two adjacent chains, the Cu can also be viewed as a distorted octahedral linked between the 1-D $\{\text{VO}_4\}$ tetrahedra chains. In the case of $[\text{M(Hdpa)}_2\text{V}_4\text{O}_{12}]^{[10]}$ ($\text{M}=\text{Co}, \text{Ni}$), there are folded $\{\text{VO}_3\}_n^{n-}$ chains of corner-sharing tetrahedra. Each $\{\text{VO}_4\}$ tetrahedron has one terminal

oxo group and one oxo group used to bridge the octahedral $\{\text{CoO}_4\text{N}_2\}^{2+}$ sites. Each Co(II) center is coordinated to four oxo groups, from two adjacent vanadate chains. The bimetallic oxide network displays two distinct cyclic submotifs, a ten-membered $\{\text{CoV}_4\text{O}_5\}$ ring and a 12-membered $\{\text{Co}_2\text{V}_4\text{O}_6\}$ ring. While in the title compound, each $\{\text{V(1)O}_4\}$ tetrahedron has one oxo group, and each $\{\text{V(2)O}_4\}$ tetrahedron has two oxo group used to bridge the octahedral $\{\text{NiO}_4\text{N}_2\}^{2+}$ sites. The two distinct cyclic submotifs are a 8-membered $\{\text{NiV}_3\text{O}_4\}$ ring and a 12-membered $\{\text{Ni}_2\text{V}_4\text{O}_6\}$ ring.

It is also of note that phen groups in adjacent layers are generally parallel and separated by 0.366 59 (0.001 53) nm, which indicate strong π - π stacking interactions^[11]. These interactions and the hydrogen bonds existing within the layer (Table 3, $\text{O(7)-H(7A)}\cdots\text{O(2)}$, 0.331 2 nm, $\text{O(7)-H(7B)}\cdots\text{O(6)}$ (symmetry codes: $x-1, -y+1/2, z-1/2$), 0.296 3 nm) stabilize the structure of the compound.

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