Inorg. Chem. **2002**, *41*, 140–143

Inorganic Chemistry
Note

Hydrothermal Synthesis and Crystal Structure of a Novel Two-Dimensional Vanadium Oxide Complex with a 6,14-Net Sinusoidal Ruffling Anionic Layer: [Ni(phen)$_2$V$_4$O$_{11}$] (phen = 1,10-Phenanthroline)

Cai-Ming Liu,[†] **Yang-Long Hou, Jing Zhang, and Song Gao***

State Key Laboratory of Rare Earth Materials Chemistry and Applications and PKU-HKU Joint Laboratory on Rare Earth Materials and Bioinorganic Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

Received July 10, 2001

Introduction

Recently, the design of vanadium oxides templated or coordinated by transition-metal complexes or fragments has been an important advance in the field of organic–inorganic hybrid vanadium oxide materials.[1] One remarkable feature of such vanadium oxides is that the organic component does not act as a charge-compensating constituent again; it functions as a ligand, coordinated directly to the oxide scaffolding or to a secondary metal center.[2] Many examples including discrete clusters, one-dimensional (1D) chains, and layer structures have been synthesized hydrothermally.[3–10] To date, the vanadium clusters in bimetallic clusters are limited to $V_4O_{12}^{4-}$,[3] $V_{10}O_{29}^{8-}$,[1] and $V_8O_{23}^{6-}$,[4a] and most matavanadate 1D chain complexes, for example, $Cu(NH_3)_2V_2O_6$,[5] $Cu(dien)V_2O_6{\cdot}H_2O$,[6] $Cu(en)V_2O_6$,[7] $Cu(bipy)V_2O_6$,[7] and $Cu(bipy)_2V_2O_6$,[7] but not $Co(phen)_2V_6O_{17}$,[1] exhibit the same vanadium oxide chain $\{V_2O_6\}_n^{2n-}$, while layered vanadium oxide complexes show three-dimensional (3D) framework compositions with mixed valence characteristics[8,9] or two-dimensional (2D) structures with the V^{5+} valence.[10] In this paper, we present a new example in which two stable phases, $Ni(phen)_2V_4O_{11}$ (**1**) and $[Ni(phen)_2]_2V_6O_{17}$ (**2**) (phen = 1,10-phenanthroline), are isolated from the same hydrothermal reaction container. Though **2** shows a structure isomorphous with that of $Co(phen)_2V_6O_{17}$,[1] **1** exhibits a novel layered structure where the new 6,14-net anionic layer $(V_4O_{11})_n^{2n-}$ is composed of hexanuclear $V_6O_{18}^{6-}$ and VO_4^{3-} building units, which are linked by sharing oxygen atoms, and there are two $Ni(phen)_2$ moieties per V_{14} ring which form along the $V_6O_{18}^{6-}$ hexamer ring, each $Ni(phen)_2$ fragment bonded to two oxygen atoms from two second-nearest-neighbor VO_4 groups on the longest opposite sides of the ring. To our knowledge, this is the first example of vanadium oxide with a 6,14-net anionic layer and a structure developed by hexanuclear $V_6O_{18}^{6-}$ building units.

Experimental Section

Materials and Methods. All the starting chemicals were reagent grade and used as purchased. The elemental analyses were performed on an Elementar Vario EL elemental analyzer. The IR spectra were recorded on a Magna-IR 750 spectrophotometer with pressed KBr pellets.

Preparation of 1 and 2. A mixture of NH_4VO_3 (1.0 mmol), H_3BO_3 (1.5 mmol), $Ni(NO_3)_2{\cdot}6H_2O$ (1 mmol), phen (2 mmol), and H_2O (15 mL), stirred for 20 min, was transferred to a Teflon-lined stainless steel autoclave (25 mL) and kept at 160 °C for 5 days. After the mixture was slowly cooled to room temperature, **1** and **2** were manually selected as dark green (30% yield) and yellow-green (10% yield) blocks, respectively. Attempts to prepare monophasic materials failed. A similar trend has also been reported quite recently for the synthesis of $[Cu(tepy)MoO_4]{\cdot}3H_2O$ and $[Cu(tepy)Mo_2O_7]$.[11] Anal. Calcd for $C_{24}H_{15}N_4O_{11}NiV_4$ (**1**): C, 36.13; H, 1.90; N, 7.02. Found: C, 36.05; H, 2.11; N, 6.91. Anal. Calcd for $C_{16}H_{10.67}N_{2.67}O_{5.67}Ni_{0.67}V_2$ (**2**): C, 40.72; H, 2.28; N, 7.92. Found: C, 40.56; H, 2.41; N, 7.79. IR (KBr, cm^{-1}) for **1**: 1628(w), 1606(w), 1587(w), 1518(w), 1427(m), 1144(w), 969(s), 947(m), 910(vs), 903(vs), 857(s), 842(s), 792(m), 727(s), 673(s), 665(s). IR (KBr, cm^{-1}) for

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* To whom correspondence should be addressed. E-mail: gaosong@pku.edu.cn.

[†] Permanent address: Organic Solids Laboratory, Center for Molecule Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China.

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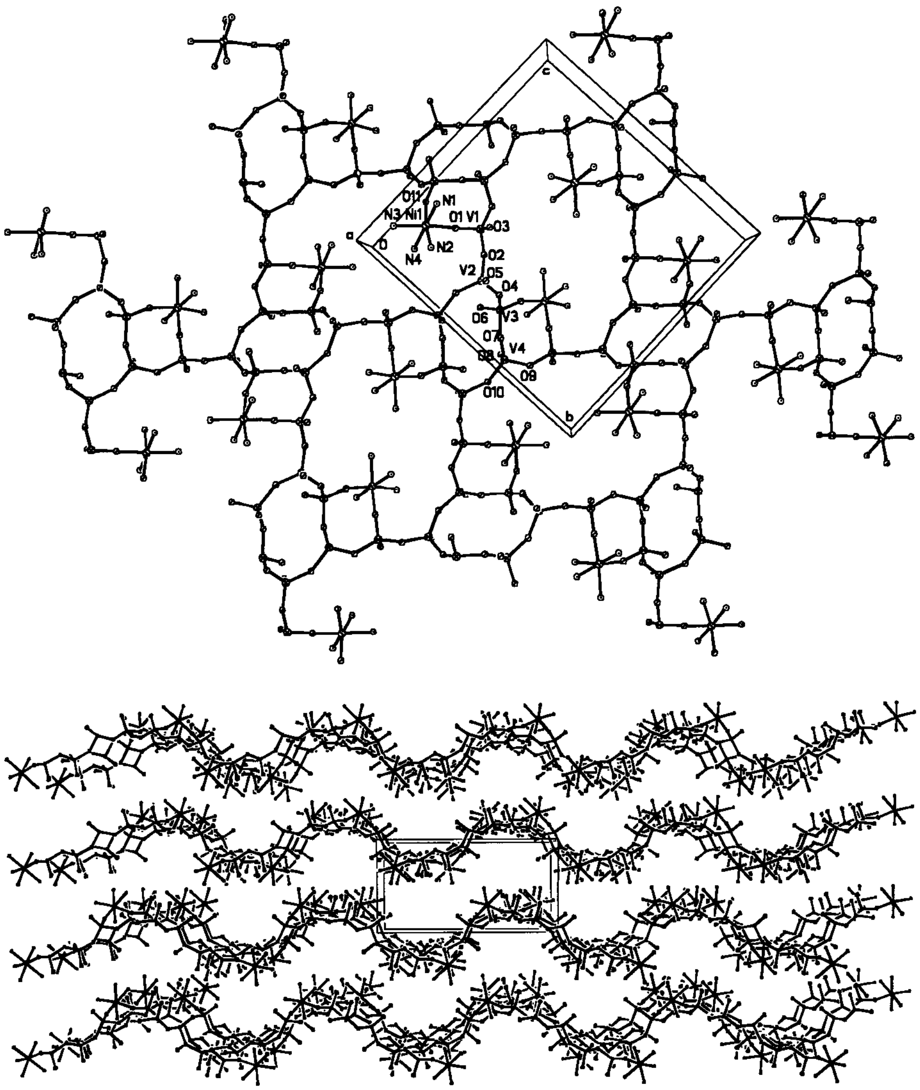

Figure 1. (a, top) View of layers of complex **1** looking down the *a*-axis. All the C and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni(1)−O(1) 2.0812(17), Ni(1)−O(11) 2.1485(18), Ni(1)−N(1) 2.177(2), Ni(1)−N(2) 2.148(2), Ni(1)−N(3) 2.183(2), Ni(1)−N(4) 2.206(2), V(1)−O(1) 1.7096(18), V(1)−O(2)1.9098(17); O(1)−Ni(1)−O(11) 81.92(7), N(2)−Ni(1)−N(1) 84.00(8), N(3)−Ni(1)−N(4) 74.88(7). (b, bottom) View of layers of complex **1** looking down the *c*-axis. All the C and H atoms are omitted for clarity.

2: 1608(w), 1518(w), 1426(m), 1144(vw), 1107(vw), 968(s), 907(vs), 858(s), 840(s), 794(m), 727(m), 671(vs).

X-ray Crystallographic Analysis. Crystals with dimensions 0.50 × 0.25 × 0.15 mm for **1** and 0.40 × 0.32 × 0.25 mm for **2** were selected for indexing and intensity data collections at 293(2) K on a Nonius Kappa CCD with Mo-Kα radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by the global refinement of the positions of all collected reflections. A total of 7899 independent refections ($R_{\mathrm{int}} = 0.0601$) were measured in the range of $6.40° \leq 2\theta \leq 60.06°$ ($-13 \leq h \leq +13$, $-25 \leq k \leq +25$, $-22 \leq l \leq +22$), 6435 of which with $I > 2\sigma(I)$ were used in the refinement of the structure of **1**, and a total of 6784 independent refections ($R_{\mathrm{int}} = 0.0308$) were collected in the range of $7.02° \leq 2\theta \leq 60.08°$ ($-13 \leq h \leq +14$, $-15 \leq k \leq +15$, $-16 \leq l \leq +16$), 5971 of which with $I > 2\sigma(I)$ were used in the refinement of the structure of **2**. Empirical absorption corrections were applied ($T_{\mathrm{min,max}} = 0.576$, 0.739 for **1** and 0.577, 0.625 for **2**). Both structures were solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXL 97 program.[12] The V1 atom in **2** is disordered over 90:10 sites. All non-hydrogen atoms except V1′ in **2** were refined anisotropically, and hydrogen atoms were allowed as riding atoms. Selected crystallographic data and structure determination parameters for complexes **1** and **2** are given in Table 1.

Results and Discussion

Crystal Structure of 1. As shown in Figure 1, the structure of **1** consists of a sinusoidal ruffling anionic $(V_4O_{11})_n^{2n-}$ layer with $Ni(phen)_2^{2+}$ moieties covalently bonded to the vanadium oxide scaffolding. The anionic $(V_4O_{11})_n^{2n-}$ layer is constructed from hexanuclear $V_6O_{18}^{6-}$ and VO_4^{3-} building units by sharing oxygen atoms. All vanadium atoms have distorted tetrahedral geometries. Six adjoined VO_4 tetrahedra link each other head to end by sharing six oxygen atoms to form a unique hexamer V_6O_{18} ring, which has not yet been observed in other reported vanadium oxide complexes;[1,3,5−7,10] the latter often contain tetramer V_4O_{12} rings or VO_3 chains. There are other VO_4

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Table 1. Crystal Data for Complexes **1** and **2**

	1	2
empirical formula	$C_{24}H_{15}N_4O_{11}NiV_4$	$C_{16}H_{10.67}N_{2.67}O_{5.67}Ni_{0.67}$
fw	797.87	471.96
λ, Å	0.71073	0.71073
space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a, Å	9.6518(19)	10.108(2)
b, Å	18.458(4)	11.168(2)
c, Å	17.706(4)	11.749(2)
α, deg	90.00	83.35(3)
β, deg	95.26(3)	72.61(3)
γ, deg	90.00	76.12(3)
V, Å^3	3141.1(11)	1227.2(4)
Z	4	3
D_c, g cm^{-3}	1.687	1.916
μ(Mo Kα), mm^{-1}	1.794	1.925
R1, wR2 [$I > 2\sigma$][a]	0.0383, 0.0901	0.0341, 0.0889
R1, wR2 (all data)[a]	0.0524, 0.0979	0.0412, 0.0936

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

tetrahedra among hexamer V_6O_{18} rings to act as bridges; they connect hexamer V_6O_{18} rings by sharing of corner oxygen atoms too. Each VO_4 tetrahedron links to two neighboring hexamer V_6O_{18} rings, whereas each V_6O_{18} ring bonds to four adjoined VO_4 tetrahedra; thus, large tetradecamer $V_{14}O_{42}$ rings appear along hexamer V_6O_{18} rings, and a 2D anionic layer $(V_4O_{11})_n^{2n-}$ is formed, which shows a 6,14-net topology layer structure (Figure 1a). It is noteworthy that **1** is the first vanadium oxide complex with a 6,8-net layer structure.

The Ni(II) coordination geometry is defined by four nitrogen atoms from two phen ligands and two oxygen atoms from vanadium oxide, which adopt the *cis*-orientation. The Ni−N bond distances range from 2.148(2) to 2.206(2) Å, which are a little larger than those in Ni(dien)V_2O_6 [2.066(2)−2.101(3) Å],[6] Ni(bpy)$_2$(H_2O)V_2O_6 [2.047(2)−2.081(2) Å],[10] and [Ni(bpy)$_2$]$_2$$V_6O_{17}$ [2.0553(19)−2.127(2) Å].[10] The Ni−O bond lengths [2.081(2) and 2.148(2) Å] are also a little larger than those in Ni(dien)V_2O_6 [2.062(2)−2.108(2) Å],[6] Ni(bpy)$_2$(H_2O)V_2O_6 [2.036(2), 2.041(2), and 2.062(2) Å],[10] and [Ni(bpy)$_2$]$_2$$V_6O_{17}$ [2.0255(17) and 2.0820(17) Å].[10] There are two Ni(phen)$_2$ fragments within each V_{14} ring of the $(V_4O_{11})_n^{2n-}$ anionic layer, each covalently bonded to two oxygen atoms (O1 and O11 or their symmetry equivalents) from two second-nearest-neighbor VO_4 groups on the longest opposite sides of the ring. Such a linking gives rise to two V_3Ni tetraatomic rings within each large V_{14} ring. Similar trends have also been observed in [Zn(bpy)$_2$]$_2$$V_6O_{17}$[8] and [Ni(bpy)$_2$]$_2$$V_6O_{17}$.[10]

It is noteworthy that the layer framework displays a beautiful sinusoidal ruffling looking down the *c*-axis (Figure 1b). Its amplitude [about 18.5 Å] is larger than those in [Zn(bpy)$_2$]$_2$$V_6O_{17}$ [about 13 Å][8] and [Ni(bpy)$_2$]$_2$$V_6O_{17}$ [about 13 Å],[10] whereas the period [about 9.7 Å] is smaller than those in [Zn(bpy)$_2$]$_2$$V_6O_{17}$ [about 15 Å][8] and [Ni(bpy)$_2$]$_2$$V_6O_{17}$ [about 15 Å].[10] Obviously, these differences originate from the fact that there are no hexamer V_6O_{18} rings to take part in constructing the structures of [Zn(bpy)$_2$]$_2$$V_6O_{17}$ and

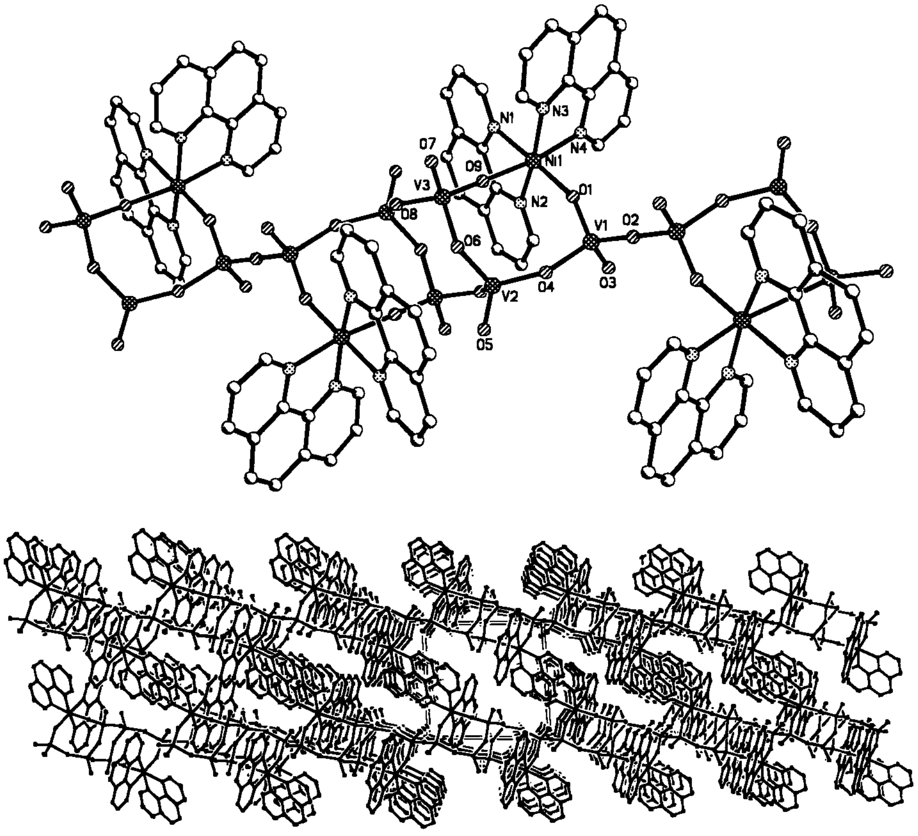

Figure 2. (a, top) Chairlike configuration in the stepped chain of complex **2**. All the H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni(1)−O(1) 2.0582(16), Ni(1)−O(9) 2.0567(16), Ni(1)−N(1) 2.1148(17), Ni(1)−N(2) 2.0869(18) Ni(1)−N(3) 2.0733(19), Ni(1)−N(4) 2.0903(18), V(1)−O(1) 1.6576(16), V(1)−O(3) 1.596(2), V(1)−O(4) 1.8270(18); O(9)−Ni(1)−O(1) 90.06(7), N(1)−Ni(1)−N(2) 79.36(7), N(3)−Ni(1)−N(4) 79.78(8). (b, bottom) Microporous channels formed by stepped chain frameworks and $\pi-\pi$ stacking phen groups in complex **2** when viewed down the *a*-axis. All the H atoms are omitted for clarity.

$[Ni(bpy)_2]_2V_6O_{17}$ though similar V_{14} rings are also building units for the structures of $[M(bpy)_2]_2V_6O_{17}$ (M = Zn and Ni).[8,10]

Crystal Structure of 2. Compound **2** and $[Co(phen)_2]_2V_6O_{17}$[1] are isomorphous. As shown in Figure 2, the structure of **2** is constructed from 1D $\{V_6O_{17}\}_n^{4n-}$ stepped chains and covalently attached $[Ni(phen)_2]^{2+}$ fragments. The anionic chain $\{V_6O_{17}\}_n^{4n-}$ is composed of alternate $V_4O_{12}^{4-}$ tetramer rings and $V_2O_7^{4-}$ building units, which are connected by sharing oxygen atoms. The nickel atom has a distorted octahedral environment. It coordinates to four N atoms from two phen ligands and two *cis*-oxygen atoms from vanadium oxides. The Ni−N bond distances [2.073(2)−2.115(2) Å] and the Ni−O bond distances [2.057(2) and 2.058(2) Å] are a little smaller than those in **1** but comparable to those in $Ni(dien)V_2O_6$,[6] $Ni(bpy)_2(H_2O)V_2O_6$,[10] and $[Ni(bpy)_2]_2V_6O_{17}$.[10]

The $[Ni(phen)_2]^{2+}$ fragments covalently link to the anionic chain $\{V_6O_{17}\}_n^{4n-}$ along its two sides through O1 and O9 or their symmetry equivalents. Two NiV_3 tetramer rings are thus formed along each $V_4O_{12}^{4+}$ tetramer ring; these three tetramer rings (two NiV_3 rings and one V_4 ring) share two sides of the $V_4O_{12}^{4+}$ tetramer ring, and a chairlike configuration appears.[1] These chairs connect each other head to end by sharing oxygen atoms to extend into a stepped chain structure (Figure 2a).

As mentioned, in the structure of $[Co(phen)_2]_2V_6O_{17}$,[1] the $\pi-\pi$ stacking interaction between interchain phen groups plays an important role in stabilization of the structure of **2** too. Adjacent phen groups in **2** are often parallel and separated by 3.1−3.5 Å, suggesting the existence of strong $\pi-\pi$ stacking interactions.[1] The bimetallic stepped chains of **2** are, therefore, extended into three-dimensional supramolecular arrays. As shown in Figure 2b, there are microporous channels formed by stepped chain frameworks and $\pi-\pi$ stacking phen groups when the structure is viewed down the *a*-axis.

Conclusions

Two vanadium oxide nickel (II) complexes, **1** and **2**, are synthesized hydrothermally in the same reaction. X-ray crystallography shows that **1** consists of a novel 2D layer constructed from the 6,14-net sinusoidal ruffling anionic layer $(V_4O_{11})_n^{2n-}$ and covalently bonded $Ni(phen)_2$ fragments, which are linked by sharing of oxygen atoms. The $V_6O_{18}^{6-}$ hexamer ring is the new observed construct component for vanadium oxides; it connects four VO_4^{3-} building units by sharing oxygen atoms to form a unique 6,14-net sheet. There are two $Ni(phen)_2$ moieties within every V_{14} ring, each bonded to two oxygen atoms from two second-nearest-neighbor VO_4 groups on the longest opposite sides of the large V_{14} ring. Complex **2** and the already reported $[Co(phen)_2]_2V_6O_{17}$[1] are isomorphic compounds; they consist of 1D stepped chains. These chains are extended into 3D supramolecular arrays through $\pi-\pi$ stacking interactions between interchain phen groups.

Acknowledgment. This work was supported by the Visiting Scholar Foundation of the Key Laboratory of Peking University (sponsored by the Education Ministry of China) and a grant from the State Key Project for Fundamental Research (G1998061305).

Supporting Information Available: X-ray crystallographic details, in CIF format, and thermal ellipsoid plots with atom labeling for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010735K