

Polymeric bis[bis(2,2'-bipyridine)-
nickel(II)] hexavanadate(V)Bi-Zhou Lin^{a,b*} and Shi-Xiong Liu^b^aInstitute of Material Physical Chemistry, Huaqiao University, Quanzhou 362011, People's Republic of China, and ^bDepartment of Chemistry, Fuzhou University, Fuzhou 350002, People's Republic of China
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The structure of the title compound, μ -hexavanadato(V)-bis[bis(2,2'-bipyridine)nickel(II)], $[\text{Ni}(\text{C}_{10}\text{H}_8\text{N}_2)_2]_2[\text{V}_6\text{O}_{17}]$, is composed of vanadium oxide layers intercalated by complex $[\text{Ni}(\text{bipy})_2]^{2+}$ cations (bipy is 2,2'-bipyridine). The structure is isomorphous with that reported recently for $[\text{Zn}(\text{bipy})_2]_2[\text{V}_6\text{O}_{17}]$ [Zhang, DeBord, O'Connor, Haushalter, Clearfield & Zubieta (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 989–991]. The vanadium oxide layers are built up solely from VO_4 tetrahedra by corner sharing and clearly exhibit a sinusoidal ruffling. Two O atoms from a single vanadium oxide layer are coordinated to each Ni atom of the complex cations in a *cis* fashion, with Ni–O distances of 2.027 (3) and 2.087 (3) Å, thus maintaining the two-dimensional structure.

Comment

Recently, it has been demonstrated that the hydrothermal technique is an effective approach to the synthesis of vanadium oxides incorporating complex cations, such as $[\text{Zn}(\text{bipy})_2]_2[\text{V}_6\text{O}_{12}]$ and $[\text{Zn}(\text{bipy})_3]_2[\text{V}_4\text{O}_{12}] \cdot 11\text{H}_2\text{O}$ (bipy is 2,2'-bipyridine; Zhang *et al.*, 1997), $[\text{Ni}(\text{bipy})_3]_2[\text{V}_4\text{O}_{12}] \cdot 11\text{H}_2\text{O}$ (Yang *et al.*, 1998), $[\text{Cu}(\text{en})][\text{V}_2\text{O}_6]$ and $[\text{Cu}(\text{bipy})_2]_2[\text{V}_2\text{O}_6]$ (en is ethylenediamine; DeBord *et al.*, 1996), $[\text{Ni}(\text{en})_3][\text{V}_2\text{O}_6]$ (Liu *et al.*, 2000), $[\text{M}(\text{en})_2][\text{V}_6\text{O}_{14}]$ (*M* is Cu or Zn), $[\text{Zn}(\text{bipy})_2]_2[\text{V}_6\text{O}_{17}]$ and $[\text{Cu}(\text{en})_2]_2[\text{V}_{10}\text{O}_{25}]$ (Zhang *et al.*, 1996), $[\text{N}(\text{CH}_3)_4]_2[\text{Co}(\text{H}_2\text{O})_4\text{V}_{12}\text{O}_{28}]$ (Wang *et al.*, 1999), and $[\text{Cd}(1,2\text{-pn})_2][\text{V}_8\text{O}_{20}]$ (1,2-pn is 1,2-diamopropane; Zhang *et al.*, 1999). The present work reports the crystal structure of a new compound, $[\text{Ni}(\text{bipy})_2]_2[\text{V}_6\text{O}_{17}]$, (I), built from sinusoidal vanadium oxide layers, $[\text{V}_6\text{O}_{17}]^{4-}$, and complex nickel(II) cations, $[\text{Ni}(\text{bipy})_2]^{2+}$.

Compound (I) is isomorphous with the recently reported compound $[\text{Zn}(\text{bipy})_2]_2[\text{V}_6\text{O}_{17}]$ (Zhang *et al.*, 1996). The crystal structure of (I) is depicted in Fig. 1. The vanadium oxide layers are constructed solely from VO_4 tetrahedra by sharing corners and clearly display a sinusoidal ruffling, with an amplitude of about 6.5 Å and a period of about 14.8 Å. The $[\text{Ni}(\text{bipy})_2]^{2+}$ complex cations occupy the interlamellar space and attach to the vanadium oxide layers through Ni–O

covalent interactions, with distances of 2.027 (3) and 2.087 (3) Å.

A view perpendicular to the vanadium oxide layers is shown in Fig. 2. Along with one unshared terminal O atom, the other three O atoms of each tetrahedron around V2 and two O atoms of each V1 and V3 unit are shared between neighbouring tetrahedra, forming an extended two-dimensional pore network. These pores, consisting of 14-membered polyhedral rings, lie alternately in planes approximately parallel to (110) and $(\bar{1}10)$, with a transannular V...V distance of about 10 Å.

Atoms O1 from the V1 tetrahedron and O7 from the V3 tetrahedron are coordinated to Ni atoms (Fig. 3). The octahedral geometry of each Ni^{II} atom is defined by four N atoms from two 2,2'-bipyridine ligands and two *cis*-oxo groups from a vanadium oxide layer. Two $[\text{Ni}(\text{bipy})_2\text{O}_2]$ motifs are bonded to each V_{14} ring, on either side of the $\bar{1}$ site in the centre of the ring. The organic ligands protrude above and below the mean plane of the V_{14} rings and fill the troughs of the ruffled vanadium oxide layers (Fig. 1).

The vanadium oxide layer structure in $[\text{M}(\text{bipy})_2]_2[\text{V}_6\text{O}_{17}]$ (*M* is Ni or Zn) has a very rare topology, where the pore size in the Ni compound, defined by the transannular V...V distance along the *c* axis, is slightly smaller than that in the Zn compound. It is interesting that the coordination of the O atoms from the vanadium oxide layers to the *M* atoms in these two compounds is different from that in other layered vanadium oxides incorporating six-coordinated interlamellar

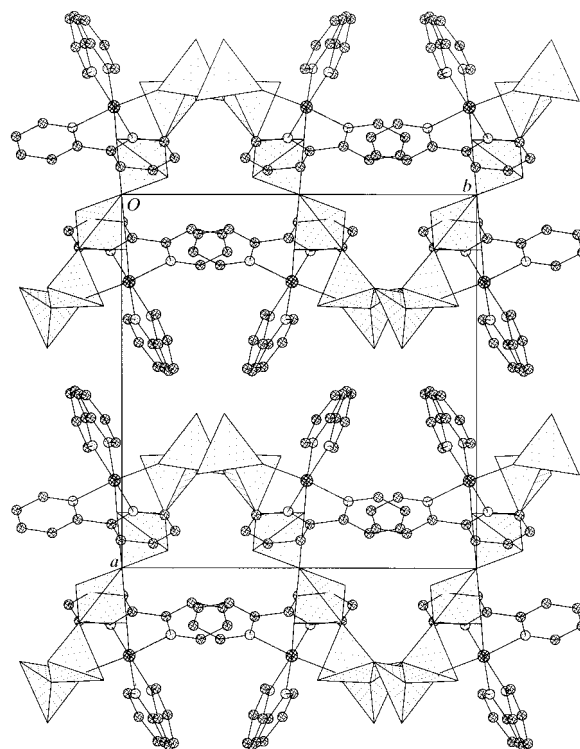
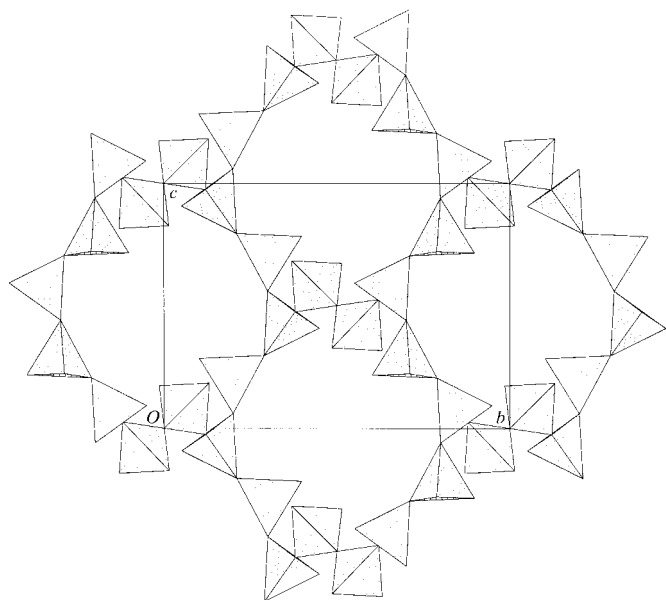


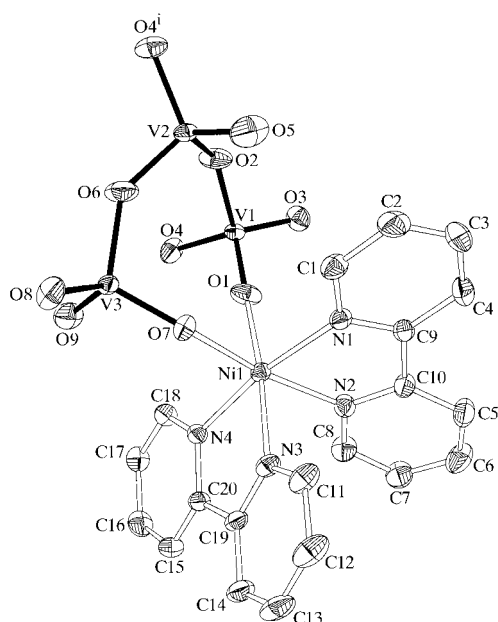
Figure 1

A view of the structure of (I) along the *c* axis, showing the vanadium oxide layers with a sinusoidal ruffle and the nickel complexes, which occupy the troughs and are covalently bonded to the layers. Large hatched circles denote Ni, small hatched circles denote C and dotted circles denote N atoms.


Figure 2

A view perpendicular to one of the vanadium oxide layers in (I), showing the VO_4 tetrahedra linked through corner sharing to form an extended two-dimensional pore network.

cations, namely $[\text{M}(\text{en})_2][\text{V}_6\text{O}_{14}]$ (M is Cu or Zn) and $[\text{Cu}(\text{en})_2][\text{V}_{10}\text{O}_{25}]$ (Zhang *et al.*, 1996), and $[\text{Ni}(\text{en})_2][\text{V}_6\text{O}_{14}]$ (Lin & Liu, 2000). In the structures of the latter compounds, the two oxo groups come from the two neighbouring layers and are covalently connected to each M atom in a *trans* fashion, forming a three-dimensional framework. In contrast, in (I), the two *cis*-oxo groups around each Ni atom come from a single vanadium oxide layer, maintaining the two-dimensional network structure.


Figure 3

The asymmetric unit in the structure of (I) with 50% displacement ellipsoids, showing the coordination environment around the metal atoms [symmetry code: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$].

Experimental

The hydrothermal synthesis of (I) was carried out in a 17 ml Teflon-lined stainless steel vessel with a *ca* 40% fill factor. A mixture of V_2O_5 (0.092 g), NiO (0.081 g), 2,2'-bipyridine (0.083 g) and H_2O , in the molar ratio 1:1.2:1:778, was heated at 448 K for 72 h. Green plate-shaped crystals of (I) were formed in 25% yield based on V, contaminated by a small amount of unreacted NiO. The pH of the synthesis increased from 6.7 before heating to 7.5 at the end of reaction. Attempts to prepare (I) as a monophasic material were unsuccessful. Besides a series of characteristic bands for 2,2'-bipyridine in the region $1100\text{--}1600\text{ cm}^{-1}$, the IR spectrum of (I) exhibits a strong band at 925 cm^{-1} , which was attributed to $\nu(\text{V}\text{--}\text{O})$.

Crystal data

$[\text{Ni}_2\text{V}_6\text{O}_{17}(\text{C}_{10}\text{H}_8\text{N}_2)_4]$
 $M_r = 1319.80$
 Monoclinic, $P2_1/c$
 $a = 15.529$ (3) Å
 $b = 14.770$ (3) Å
 $c = 10.477$ (2) Å
 $\beta = 92.02$ (3)°
 $V = 2401.5$ (8) Å³
 $Z = 2$

$D_x = 1.825\text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 10\text{--}15^\circ$
 $\mu = 1.960\text{ mm}^{-1}$
 $T = 294$ (2) K
 Plate, green
 $0.60 \times 0.40 \times 0.15\text{ mm}$

Data collection

Rigaku AFC-5R diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.320$, $T_{\max} = 0.745$
 4798 measured reflections
 4718 independent reflections
 3558 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$
 $\theta_{\text{max}} = 25.99^\circ$
 $h = -19 \rightarrow 19$
 $k = -18 \rightarrow 0$
 $l = 0 \rightarrow 12$
 3 standard reflections
 every 150 reflections
 intensity decay: 0.5%

Table 1

Selected geometric parameters (Å, °).

Ni1—O1	2.027 (3)	V1—O4	1.814 (3)
Ni1—N4	2.057 (3)	V2—O5	1.584 (4)
Ni1—N1	2.060 (3)	V2—O6	1.738 (3)
Ni1—N3	2.085 (3)	V2—O2	1.740 (3)
Ni1—O7	2.087 (3)	V2—O4 ⁱ	1.752 (3)
Ni1—N2	2.125 (4)	V3—O9	1.612 (3)
V1—O3	1.612 (3)	V3—O7	1.654 (3)
V1—O1	1.630 (3)	V3—O8	1.7833 (7)
V1—O2	1.808 (3)	V3—O6	1.822 (3)
O1—Ni1—N4	93.77 (12)	O1—V1—O2	109.8 (2)
O1—Ni1—N1	90.42 (13)	O3—V1—O4	110.0 (2)
N4—Ni1—N1	170.52 (13)	O1—V1—O4	108.9 (2)
O1—Ni1—N3	172.68 (13)	O2—V1—O4	110.6 (2)
N4—Ni1—N3	78.90 (13)	O5—V2—O6	110.1 (2)
N1—Ni1—N3	96.81 (13)	O5—V2—O2	109.2 (2)
O1—Ni1—O7	87.59 (13)	O6—V2—O2	108.5 (2)
N4—Ni1—O7	96.49 (13)	O5—V2—O4 ⁱ	108.9 (2)
N1—Ni1—O7	92.18 (12)	O6—V2—O4 ⁱ	111.0 (2)
N3—Ni1—O7	93.24 (12)	O2—V2—O4 ⁱ	109.1 (2)
O1—Ni1—N2	92.52 (14)	O9—V3—O7	109.0 (2)
N4—Ni1—N2	92.76 (13)	O9—V3—O8	109.95 (14)
N1—Ni1—N2	78.55 (13)	O7—V3—O8	110.95 (11)
N3—Ni1—N2	87.83 (14)	O9—V3—O6	107.2 (2)
O7—Ni1—N2	170.72 (13)	O7—V3—O6	111.8 (2)
O3—V1—O1	110.0 (2)	O8—V3—O6	107.90 (11)
O3—V1—O2	107.4 (2)		

Symmetry code: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.115$
 $S = 1.085$
 4718 reflections
 331 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + 0.7027P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.83 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.76 \text{ e } \text{\AA}^{-3}$

All H atoms were fixed geometrically and allowed to ride on their parent C atoms, with C—H distances of 0.93 \AA and common isotropic displacement parameters ($U_{\text{iso}} = 0.08 \text{ \AA}^2$).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1987); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1987); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990b); software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1302). Services for accessing these data are described at the back of the journal.

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