

A three-dimensional inorganic/organic hybrid material, $[\text{Ni}_2(4,4'\text{-bipy})_3(\text{H}_2\text{O})_2\text{V}_4\text{O}_{12}] \cdot 2.5\text{H}_2\text{O}$

Lan Yang, Changwen Hu, Haruo Naruke and Toshihiro Yamase*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
Correspondence e-mail: tyamase@res.titech.ac.jp

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The title compound, poly[[[diaqua(μ -4,4'-bipyridyl)di-nickel(II)]-bis(μ -4,4'-bipyridyl)-di- μ -hexaoxodivanadate(2-)] 2.5-hydrate], $[\text{Ni}_2(\text{V}_2\text{O}_6)_2(\text{C}_{10}\text{H}_8\text{N}_2)_3(\text{H}_2\text{O})_2] \cdot 2.5\text{H}_2\text{O}$, has been prepared hydrothermally and characterized by elemental analyses, IR spectroscopy and single-crystal X-ray diffraction. The structure consists of $[\text{V}_2\text{O}_6]$, $[\text{Ni}(4,4'\text{-bipy})_4\text{O}_2]$ and $[\text{Ni}(\text{H}_2\text{O})_2(4,4'\text{-bipy})_2\text{O}_2]$ polyhedra, and water of crystallization. The Ni atoms and one bipyridyl group lie on centres of symmetry.

Comment

There is increasing interest in the synthesis of organic/inorganic hybrid compounds because of their novel structural architectures (Hagman *et al.*, 1999) and unusual electrochemical and magnetic properties (Leroux *et al.*, 1996; Lira-Cantú & Gómez-Romero, 1998). Hydrothermal synthesis and structural characterization of vanadium oxide lattices containing Zn-, Cu- and Co-bipyridyl (bipy) complexes have been intensively studied because of their large structural diversity; for example, two-dimensional layered vanadium oxide with interlayer zinc-2,2'-bipy complex, $[\text{Zn}(2,2'\text{-bipy})_2\text{V}_6\text{O}_{17}]$ (Zhang *et al.*, 1996), discrete neutral hexanuclear $[\text{Zn}_2\text{V}_4]$ clusters, $[\{\text{Zn}(2,2'\text{-bipy})_2\}_2\text{V}_4\text{O}_{12}]$ (Zhang *et al.*, 1997), a one-dimensional vanadium oxide chain with copper-2,2'-bipy complexes, $[\text{Cu}(2,2'\text{-bipy})\text{V}_2\text{O}_6]$ and $[\text{Cu}(2,2'\text{-bipy})_2\text{V}_2\text{O}_6]$ (DeBord *et al.*, 1996), and a three-dimensional bimetallic oxide network, $[\{\text{Co}(3,3'\text{-bipy})_2\}_2\text{V}_4\text{O}_{12}]$ (LaDuca *et al.*, 2000). It should be noted that all the bipy ligands in these complexes are of the 2,2'- and 3,3'-isomers, and no 4,4'-bipy-containing compound has been observed in the vanadate- $M(\text{bipy})_n$ system. We report here the synthesis and crystal structure of $[\text{Ni}_2(4,4'\text{-bipy})_3(\text{H}_2\text{O})_2\text{V}_4\text{O}_{12}] \cdot 2.5\text{H}_2\text{O}$, (I), which is constructed from a three-dimensional network containing $[\text{V}_2\text{O}_6]_\infty$ and Ni/V-bimetallic oxide chains linked by 4,4'-bipy ligands.

Fig. 1 shows the structure of (I), which consists of $[\text{Ni}_1(4,4'\text{-bipy})_4\text{O}_2]$, $[\text{V}_2\text{O}_6]$, $[\text{Ni}_2(\text{H}_2\text{O})_2(4,4'\text{-bipy})_2\text{O}_2]$ units, and crystallization water molecules (O8, O9 and O10). The $[\text{V}_2\text{O}_6]$ unit is made up of a pair of corner-sharing $[\text{VO}_4]$ tetrahedra. There are three types of O atoms in the $[\text{V}_2\text{O}_6]$ group, *viz.* terminal O2 and O6 atoms, bridging O5 and O7 atoms connected to both V1 and V2 atoms, and bridging O1 and O4 atoms linking Ni and V atoms. Ni1 is coordinated by O1ⁱ and O1ⁱⁱ atoms from two $[\text{V}_2\text{O}_6]$ groups, and N1, N1ⁱⁱⁱ, N2 and N2ⁱⁱⁱ atoms from four 4,4'-bipy ligands to form an $\text{Ni}_1\text{O}_2\text{N}_4$ octahedron, while Ni2 is coordinated by O4 and O4^{iv} atoms from two $[\text{V}_2\text{O}_6]$ groups, N3 and N3^{iv} atoms from two 4,4'-bipy ligands, and O3 and O3^{iv} atoms, identified as water molecules from the Ni2—O3 bond valence of 0.29 (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991), to form an $\text{Ni}_2\text{O}_4\text{N}_4$ octahedron. O(N)—Ni—O(N) bond angles in the $\text{Ni}_1\text{O}_2\text{N}_4$ and $\text{Ni}_2\text{O}_4\text{N}_2$ octahedra are nearly 90° [88.7 (1)–91.3 (1)°] or ideally linear (180°). The $[\text{V}_2\text{O}_6]$ group links Ni1^{vi} and Ni2 atoms, forming an $-\text{[Ni}_2(\text{H}_2\text{O})_2(4,4'\text{-bipy})_2]-[\text{V}_2\text{O}_6]-[\text{Ni}_1(4,4'\text{-bipy})_4]-$ bimetallic chain. Two crystallographically different 4,4'-bipy groups are

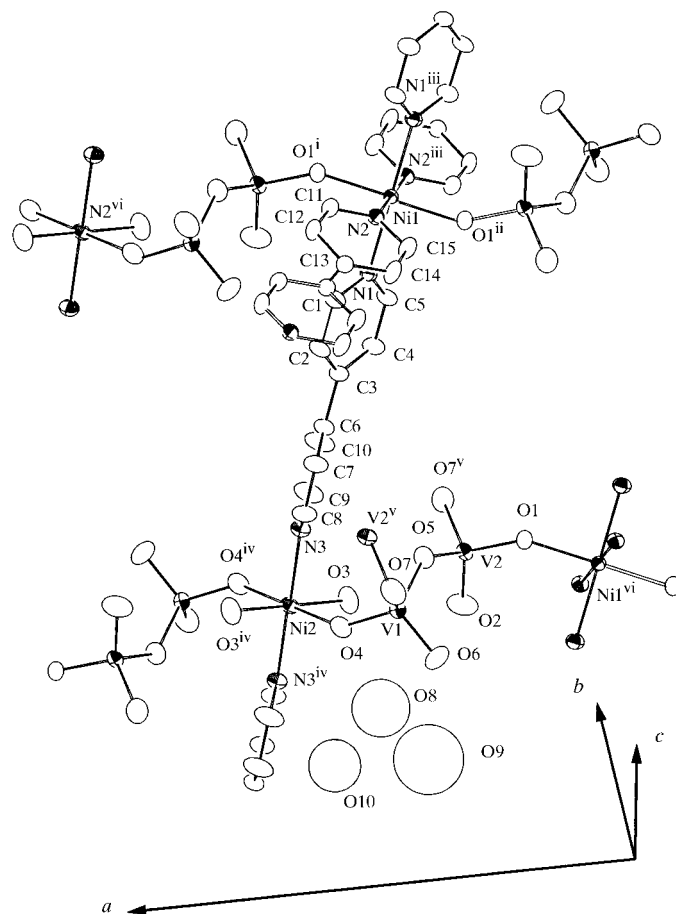


Figure 1
ORTEP (Johnson, 1976) drawing of the partial structure of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms in 4,4'-bipy groups have been omitted for clarity. [Symmetry codes: (i) $x, 1+y, z$; (ii) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$; (iii) $\frac{1}{2}-x, \frac{5}{2}-y, 1-z$; (iv) $1-x, 1-y, 1-z$; (v) $x, 1-y, \frac{1}{2}+z$; (vi) $x, -1+y, z$.]

present: 4,4'-bipy(I) comprises the N1, N3 and C1–C10 atoms, and 4,4'-bipy(II) comprises N2, C11–C15 and their symmetry-related atoms. In the 4,4'-bipy(I) group, the dihedral angle between the two pyridyl rings N1/C1–C5 and N3/C6–C10 is 35.8 (1)°. This is in contrast to the conformation between the two rings in the 4,4'-bipy(II) group which are constrained to be planar by a centre of symmetry. The 4,4'-bipy(I) links Ni1 and Ni2 atoms in two adjacent bimetallic chains to give a two-dimensional infinite network sheet parallel to the *ab* plane (Fig. 1). Fig. 2 shows the crystal structure of (I) viewed down the *b* axis. There exist two crystallographically equivalent two-dimensional network sheets, denoted by sheet *A* and sheet *B* in Fig. 2, which are stacked alternately (...*ABAB*...) along the *c* axis with an interval of 5.53 Å. Each of the 4,4'-bipy(II) groups lying in the *c* direction links two Ni1 atoms in two different *A* sheets, or equivalently *B* sheets. Also, the [V₂O₆] groups in two adjacent *A* and *B* sheets are connected through the O7 atom, to form an infinite [V₂O₆]_∞ chain running along the *c* axis.

In conclusion, it is the characteristic geometry of 4,4'-bipy, where N donors are located in two opposite ends of the ligand, that leads to the highly interlinked three-dimensional network structure. The successful preparation of the new three-dimensional network vanadium oxide cluster with a nickel complex of the 4,4'-bipy ligand will extend the variety of network structures in the organic/inorganic hybrid system.

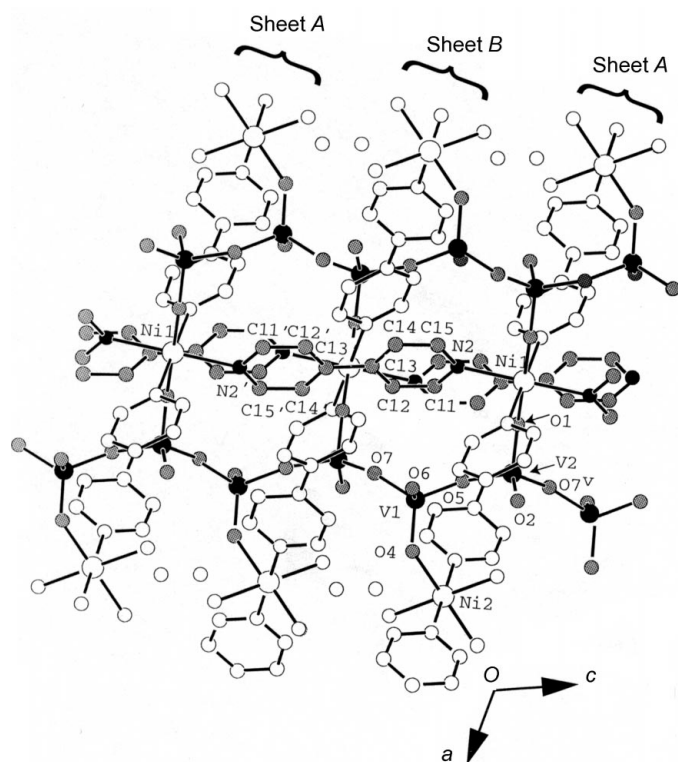


Figure 2
Packing diagram of (I) viewed along the *b* axis. H atoms in 4,4'-bipy groups have been omitted. The primed atoms are located at symmetry-related ($\frac{1}{2} - x, \frac{5}{2} - y, -z$) positions from unprimed atoms. Atoms in 4,4'-bipy(II) groups and [V₂O₆]_∞ chains are denoted by grey circles.

Experimental

All reagents were of analytical grade and were used without further purification. A mixture of NiCl₂·6H₂O (0.0880 g), NaVO₃ (0.0904 g), 4,4'-bipyridyl (0.1157 g), (CH₃)₄NOH (0.0338 g) and H₂O (10 ml) in a molar ratio 1:2:2:1:1500 was placed in a 20 ml Teflon-lined steel autoclave, and heated at 453 K for 72 h. After cooling to room temperature, green needle-like crystals were obtained in *ca* 70% yield based on vanadium (found: H 3.18, C 35.09, N 8.20, V 18.9, Ni 10.48%; calculated for C₃₀H₃₃N₆Ni₂O_{16.5}V₄: H 3.13, C 33.9, N 7.93, V 19.17, Ni 11.04%). The IR spectrum exhibits absorption bands in the range 950–500 cm^{−1} attributed to V=O or V–O–V stretching and additional bands in the range 1600–1000 cm^{−1} assigned to 4,4'-bipy groups. Thermal gravimetric analysis shows a weight loss of 5.8% between 293 and 533 K corresponding to water of crystallization, and a further loss of 34.9% occurred between 533 and 705 K due to elimination of the O3 water molecule and the decomposition of 4,4'-bipy.

Crystal data

[Ni₂(V₂O₆)₂(C₁₀H₈N₂)₃·
(H₂O)₂]·2.5H₂O
M_r = 1062.79
Monoclinic, *C*2/*c*
a = 30.3799 (9) Å
b = 11.2402 (3) Å
c = 11.5366 (3) Å
β = 105.961 (1)°
V = 3787.6 (2) Å³
Z = 4

D_x = 1.864 Mg m^{−3}
Mo Kα radiation
Cell parameters from 14338
reflections
θ = 1.9–30.0°
μ = 2.00 mm^{−1}
T = 173.2 K
Prism, green
0.30 × 0.12 × 0.03 mm

Data collection

Rigaku R-Axis RAPID Imaging
Plate diffractometer
ω scans
Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)
*T*_{min} = 0.515, *T*_{max} = 0.869
14250 measured reflections

5509 independent reflections
*R*_{int} = 0.027
θ_{max} = 30.0°
h = −42 → 42
k = −15 → 15
l = −16 → 16
Intensity decay: none

Refinement

Refinement on *F*²
R(*F*) = 0.042
wR(*F*²) = 0.114
S = 1.40
4634 reflections
312 parameters

H atoms treated by a mixture of
independent and constrained
refinement
w = 1/[σ²(*F_o*²) + (0.05*P*)²]
where *P* = (*F_o*² + 2*F_c*²)/3
(Δ/σ)_{max} = 0.002
Δρ_{max} = 0.90 e Å^{−3}
Δρ_{min} = −0.50 e Å^{−3}

Table 1

Selected bond lengths (Å).

Ni1–O1 ⁱ	2.017 (2)	V1–O4	1.663 (2)
Ni1–N1	2.162 (3)	V1–O7	1.788 (2)
Ni1–N2	2.231 (2)	V1–O5	1.791 (3)
Ni2–O4	2.034 (2)	V2–O2	1.615 (3)
Ni2–N3	2.099 (3)	V2–O1	1.661 (2)
Ni2–O3	2.103 (3)	V2–O7 ⁱⁱ	1.781 (3)
V1–O6	1.612 (3)	V2–O5	1.793 (3)

Symmetry codes: (i) *x*, 1 + *y*, *z*; (ii) *x*, 1 − *y*, $\frac{1}{2} + z$.

H atoms were defined and refined only for the 4,4'-bipy groups [C–H = 0.81 (5)–1.04 (5) Å]. Positional and *U*_{iso} parameters for H14 were fixed because of their gradual divergence during the refinement. Crystallization water molecules O8, O9 and O10 were refined with occupancies of 0.5, 0.5 and 0.25, respectively, because of too large *U*_{iso} parameters when refined on full occupancies.

Data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1320). Services for accessing these data are described at the back of the journal.

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