

## A three-dimensional inorganic/organic hybrid vanadium oxide complex with pentacoordinate Co<sup>II</sup>, [CoV<sub>2</sub>O<sub>6</sub>(4,4'-bipy)]

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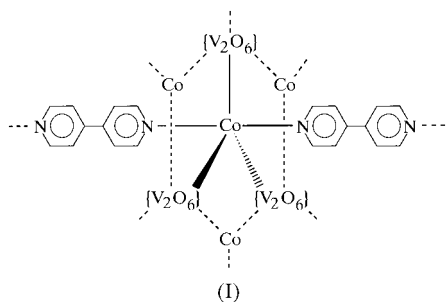
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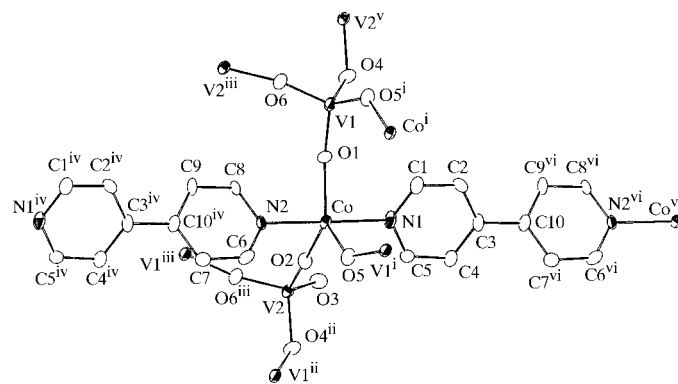
The title compound, poly[[cobalt(II)- $\mu$ -(hexaoxodivanadium-*O:O'*)]- $\mu$ -bipyridine-*N:N'*], [CoV<sub>2</sub>O<sub>6</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)], has been prepared hydrothermally and characterized by elemental analyses, IR spectroscopy and single-crystal X-ray diffraction. The structure consists of bimetallic oxide layers, [Co<sub>2</sub>V<sub>4</sub>O<sub>12</sub>], linked through 4,4'-bipyridine ligands into a three-dimensional network.

### Comment

Considerable attention has been focused on inorganic/organic hybrid materials, owing to their rich structural chemistry (Hagman *et al.*, 1999) and unique electrochemical and magnetic properties (Leroux *et al.*, 1996; Lira-Cantú & Gómez-Romero, 1998). Of these materials, vanadate/*ML<sub>n</sub>* (*M* is Co, Ni, Cu, Zn *etc.*; *L* is an organic ligand) compounds are regarded as V/*M*-bimetallic oxides coordinated by *L*, showing one-, two- and three-dimensional extended network structures, with different coordination numbers and geometries for



*M* and different shapes for *L*. Four examples of the vanadate/*CoL<sub>n</sub>* system are known, [[Co(3,3'-bipy)<sub>2</sub>V<sub>4</sub>O<sub>12</sub>] (LaDuca *et al.*, 2000), [Co(Hdpa)<sub>2</sub>V<sub>4</sub>O<sub>12</sub>] (LaDuca *et al.*, 2001), [[Co(phen)<sub>2</sub>V<sub>6</sub>O<sub>7</sub>]<sub>*n*</sub> (Zhang *et al.*, 2000) and [Co(2,2'-bipy)<sub>2</sub>V<sub>12</sub>O<sub>32</sub>] (Ollivier *et al.*, 1998) (3,3'-bipy is 3,3'-bipyridine, dp<sub>a</sub> is 4,4'-dipyridylamine, phen is 1,10-phenan-

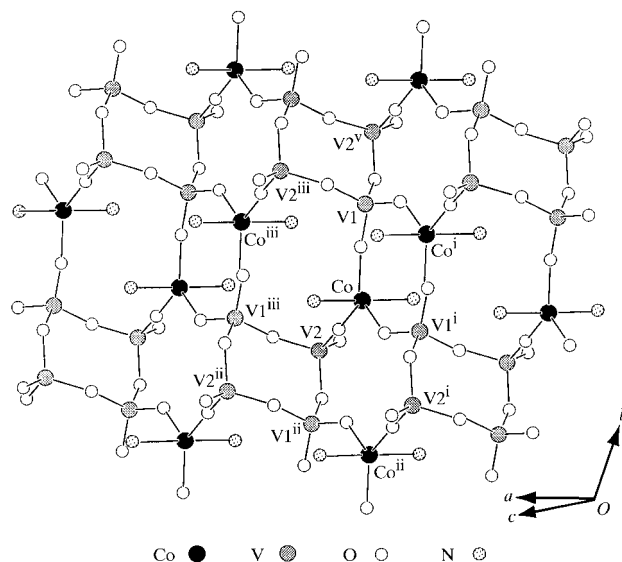


**Figure 1**

A view of the molecule of (I) with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted [symmetry codes: (i)  $-x, -1 - y, -2 - z$ ; (ii)  $x, 1 + y, z$ ; (iii)  $1 - x, -1 - y, -2 - z$ ; (iv)  $1 + x, y, z - 1$ ; (v)  $x, y - 1, z$ ; (vi)  $x - 1, y, 1 + z$ ].

tholine and 2,2'-bipy is 2,2'-bipyridine). All the Co<sup>II</sup> atoms in these complexes achieve octahedral sixfold coordination with O and N atoms. We report here the crystal structure of the title complex, (I), which is the first example of Co<sup>II</sup> in a trigonal-bipyramidal pentacoordinate geometry in the vanadate/*CoL<sub>n</sub>* system.

The structure of (I) is composed of bimetallic oxide [Co<sub>2</sub>V<sub>4</sub>O<sub>12</sub>] layers of corner-shared V-centred tetrahedra and Co-centred trigonal bipyramids (Figs. 1, 2 and 3). Within the layers are infinite chains of the type  $-O-Co-O-V-O-V-$ , which are crosslinked to other similar chains by O bridges, leaving only one terminal O atom (O3 of the V2 tetrahedron). This gives rise to four distinct centrosymmetric rings: two 12-membered [Co<sub>2</sub>V<sub>4</sub>O<sub>6</sub>] rings (Co–V1–V2<sup>iii</sup>–Co<sup>iii</sup>–V1<sup>iii</sup>–V2 and Co–V2–V1<sup>ii</sup>–Co<sup>ii</sup>–V2<sup>i</sup>–V1<sup>i</sup>) and two eight-membered [V<sub>4</sub>O<sub>4</sub>] and [Co<sub>2</sub>V<sub>2</sub>O<sub>4</sub>] rings (V2–V1<sup>iii</sup>–

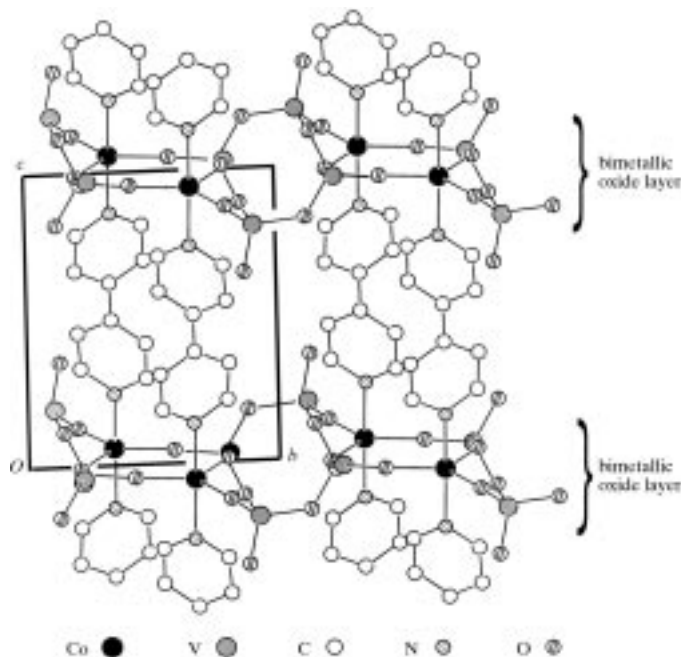


**Figure 2**

A ball-and-stick model of the [Co<sub>2</sub>V<sub>4</sub>O<sub>12</sub>] layer in (I). The symmetry codes are as in Fig. 1.

V2<sup>ii</sup>–V1<sup>ii</sup> and Co–V1<sup>i</sup>–Co<sup>i</sup>–V1, respectively) [symmetry codes: (i)  $-x, -1-y, -2-z$ ; (ii)  $x, 1+y, z$ ; (iii)  $1-x, -1-y, -2-z$ ]. The apical positions of the Co trigonal bipyramid are occupied by atoms N1 and N2 from different 4,4'-bipyridine ligands, thereby joining the polyhedral layers.

In the trigonal bipyramid, the mean axial Co–N bond length (2.139 Å) is significantly longer than the mean basal Co–O distance (1.984 Å). The axial N1–Co–N2 angle is almost linear [179.3 (1)°]. The O–Co–O angles lie between 109.8 (1) and 128.7 (1)°. The O–Co–N bond angles vary



**Figure 3**

A perspective view of the three-dimensional structure of (I). H atoms have been omitted.

between 88.5 (1) and 91.8 (1)°. The V1O<sub>4</sub> tetrahedron corner-shares atoms O1 and O5<sup>i</sup> from two CoN<sub>2</sub>O<sub>3</sub> polyhedra, and atoms O4 and O6 from two V2O<sub>4</sub> tetrahedra. The V2O<sub>4</sub> tetrahedron is corner-shared with two V1O<sub>4</sub> tetrahedra and only one CoN<sub>2</sub>O<sub>3</sub> polyhedron through atom O2 and this leaves one terminal atom, *i.e.* O3.

Similar [V<sub>4</sub>O<sub>12</sub>] rings have also been observed in other vanadate/CoL<sub>n</sub> complexes, where every VO<sub>4</sub> group has one terminal O atom. Bimetallic oxide [Co<sub>2</sub>V<sub>4</sub>O<sub>12</sub>] layers with a different structure have been observed in [(Co(3,3'-bipy)<sub>2</sub>)<sub>2</sub>V<sub>4</sub>O<sub>12</sub>] (LaDuca *et al.*, 2000), where the layers are composed of CoN<sub>4</sub>O<sub>2</sub> octahedra and [V<sub>4</sub>O<sub>12</sub>] groups, forming large 24-membered [Co<sub>4</sub>V<sub>8</sub>O<sub>12</sub>] rings. As shown in Figs. 1 and 3, atoms Co and Co<sup>vi</sup> [with a Co<sup>vi</sup>–Co<sup>vi</sup> separation of 11.38 Å; symmetry code: (vi)  $x-1, y, 1+z$ ] in two adjacent layers of the bimetallic oxide are crosslinked by a 4,4'-bipyridine ligand to form a three-dimensional network (Fig. 3). The two pyridine rings, N1,C1–C5 and N2<sup>vi</sup>,C6<sup>vi</sup>–C9<sup>vi</sup>,C10, in the 4,4'-bipyridine ligand are twisted relative to each other by 37.9 (2)° (Fig. 1).

## Experimental

All reagents were of analytical grade and were used without further purification. Hydrothermal reaction of CoCl<sub>2</sub> (0.0962 g), NH<sub>4</sub>VO<sub>3</sub> (0.0433 g), 4,4'-bipyridine (0.1157 g), (CH<sub>3</sub>)<sub>4</sub>NOH (0.0338 g) and H<sub>2</sub>O (10 ml) in a 20 ml Teflon-lined steel autoclave at 453 K for 72 h gave black plate-shaped crystals of (I) (yield 0.04 g). Found: H 1.92, C 28.75, N 6.67, V 24.82, Co 15.24%; calculated for C<sub>10</sub>H<sub>8</sub>CoN<sub>2</sub>O<sub>6</sub>V<sub>2</sub>: H 1.95, C 29.08, N 6.78, V 24.67, Co 14.27%. The IR spectrum exhibits bands in the range 1000–1610 cm<sup>-1</sup>, corresponding to 4,4'-bipyridine, and other bands in the range 920–500 cm<sup>-1</sup>, attributed to V=O or V–O–V stretching. Thermogravimetric analysis shows a weight loss of 44.48% in the range 301–703 K, corresponding to the decomposition of 4,4'-bipyridine.

### Crystal data

[CoV<sub>2</sub>O<sub>6</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)]  
*M<sub>r</sub>* = 412.99  
 Triclinic, *P* $\bar{1}$   
*a* = 8.1634 (9) Å  
*b* = 8.572 (1) Å  
*c* = 10.171 (1) Å  
 $\alpha$  = 87.079 (5)°  
 $\beta$  = 75.833 (4)°  
 $\gamma$  = 75.233 (6)°  
*V* = 667.2 (2) Å<sup>3</sup>

*Z* = 2  
*D<sub>x</sub>* = 2.055 Mg m<sup>-3</sup>  
 Mo *K* $\alpha$  radiation  
 Cell parameters from 3503 reflections  
 $\theta$  = 3.1–27.5°  
 $\mu$  = 2.63 mm<sup>-1</sup>  
*T* = 296 K  
 Plate, black  
 0.2 × 0.2 × 0.1 mm

### Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer  
 $\omega$  scans  
 Absorption correction: numerical (Higashi, 1995)  
*T<sub>min</sub>* = 0.597, *T<sub>max</sub>* = 0.769  
 3920 measured reflections

2961 independent reflections  
 2174 reflections with  $F^2 > 2\sigma(F^2)$   
*R<sub>int</sub>* = 0.032  
 $\theta_{max}$  = 27.5°  
*h* = –10 → 10  
*k* = –11 → 10  
*l* = –13 → 13

### Refinement

Refinement on  $F^2$   
*R*(*F*) = 0.044  
*wR*( $F^2$ ) = 0.174  
*S* = 1.92  
 2340 reflections  
 190 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + \{0.085[\max(F_o^2, 0) + 2F_c^2]/3]^2$   
 $(\Delta/\sigma)_{max} = 0.002$   
 $\Delta\rho_{max} = 0.93 \text{ e \AA}^{-3}$   
 $\Delta\rho_{min} = -0.82 \text{ e \AA}^{-3}$

**Table 1**

Selected bond lengths (Å).

Co–O1	1.994 (3)	V1–O5 <sup>i</sup>	1.658 (3)
Co–O2	1.968 (3)	V1–O6	1.768 (3)
Co–O5	1.990 (3)	V2–O2	1.666 (3)
Co–N1	2.145 (3)	V2–O3	1.619 (3)
Co–N2	2.132 (3)	V2–O4 <sup>ii</sup>	1.809 (3)
V1–O1	1.657 (3)	V2–O6 <sup>iii</sup>	1.819 (3)
V1–O4	1.783 (3)		

Symmetry codes: (i)  $-x, -1-y, -2-z$ ; (ii)  $x, 1+y, z$ ; (iii)  $1-x, -1-y, -2-z$ .

All H atoms of the 4,4'-bipy group were placed in fixed positions with ideal C–H distances (1.07–1.08 Å) and fixed *U<sub>iso</sub>* parameters (0.033 Å<sup>2</sup>).

Data collection: *PROCESS-AUTO* (Rigaku, 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 (Molecular Structure Corporation, 1985); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: TEXSAN (Molecular Structure Corporation, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1336). Services for accessing these data are described at the back of the journal.

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