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## Key indicators

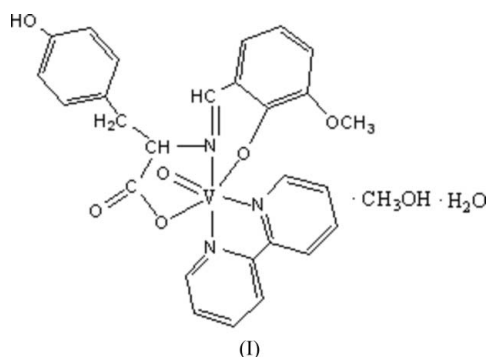
Single-crystal X-ray study  
 $T = 298\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.009\text{ \AA}$   
 $R$  factor = 0.060  
 $wR$  factor = 0.198  
Data-to-parameter ratio = 13.2For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.**(2,2'-Bipyridine- $\kappa^2\text{N},\text{N}'$ )oxo(*N*-vanillylidene-tyrosinato- $\kappa^3\text{O},\text{N},\text{O}'$ )vanadium(IV) methanol solvate monohydrate**

In the title complex {alternative name: (2,2'-bipyridine- $\kappa^2\text{N},\text{N}'$ )[3-(4-hydroxyphenyl)-2-(3-methoxy-2-oxidobenzylideneamino)propionato- $\kappa^3\text{O},\text{N},\text{O}'$ ]oxovanadium(IV) methanol solvate monohydrate},  $[\text{V}(\text{C}_{17}\text{H}_{15}\text{NO}_5)\text{O}(\text{C}_{10}\text{H}_8\text{N}_2)] \cdot \text{CH}_3\text{O} \cdot \text{H}_2\text{O}$ , the  $\text{V}^{\text{IV}}$  atom is six-coordinated by three O atoms and three N atoms in a distorted octahedral configuration. In the crystal structure, the combination of intermolecular hydrogen-bonding ( $\text{O}-\text{H} \cdots \text{O}$ ) and  $\pi$ -stacking interactions creates a three-dimensional framework structure.

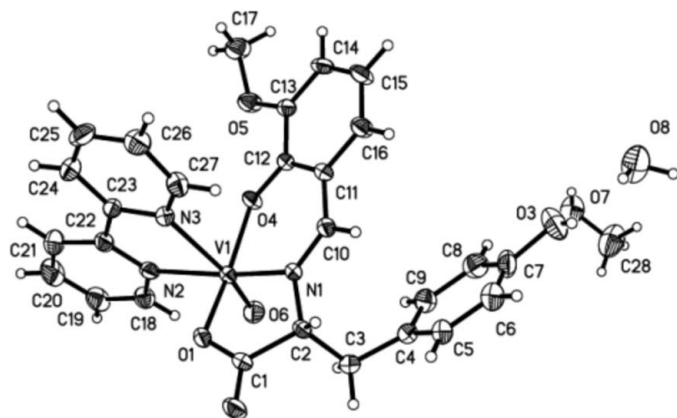
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## Comment

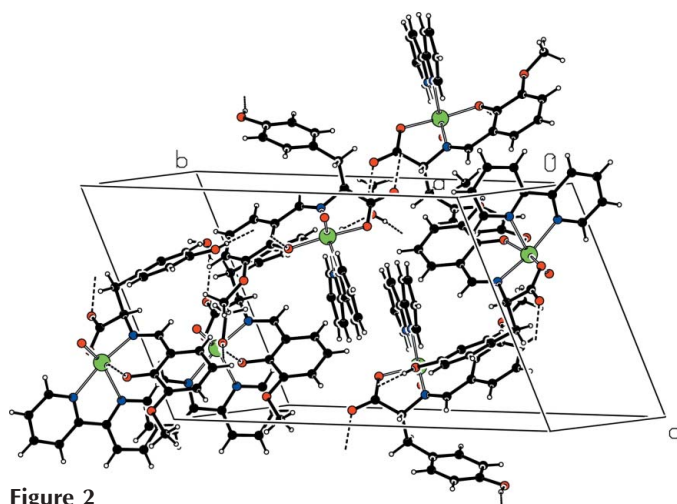
The significant role of vanadium in a variety of chemical and biological systems has stimulated the development of vanadium chemistry (Hirao, 1997). Vanadium is a biologically essential trace element, encountered in metalloenzymes such as haloperoxidases or nitrogenases. In addition to this natural relevance, a large variety of biological activities of small vanadium complexes, including enzyme inhibitory, antitumor or insulin-mimetic activities, have been reported. Vanadium–amino acid complexes are receiving considerable attention. However, this type of complex is not stable in the absence of other ligands. Efforts have been made to stabilize vanadium–amino acid complexes by using another ligand, such as a Schiff base of an amino acid (Colpas *et al.*, 1994; Gruning & Rehder, 2000; Xu *et al.*, 2005). We report here the synthesis and crystal structure of a new oxovanadium(IV)–amino acid complex with a tridentate Schiff base ligand derived from the condensation of *o*-vanillin and tyrosine, and with 2,2'-bipyridine.



The molecular structure of the title complex, (I), is shown in Fig. 1. The  $\text{V}^{\text{IV}}$  atom is six-coordinated with the bipyridine ligand almost perpendicular to the Schiff base chelating plane [dihedral angle  $87.62(11)^\circ$ ], while the phenol group plane makes a dihedral angle of  $158.69(14)^\circ$  with the Schiff base plane. Selected bond distances are given in Table 1 and show that the  $\text{V}^{\text{IV}}$  atom is in a distorted octahedral coordination environment with atoms N1 and N2 in the axial positions, and



**Figure 1**  
The structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme.



**Figure 2**  
Packing diagram (*PLATON*; Spek, 2003) of the title compound, with the hydrogen-bonded interactions shown as dashed lines.

atoms O1, O4, O6 and N3 equatorial. The V<sup>IV</sup> atom lies 0.019 (1) Å above the equatorial plane. The bipyridyl ligand is not planar, but rather the two pyridyl rings form an angle of 7.2 (3)° to each other.

In addition to the vanadium complex, the asymmetric unit also contains one molecule of water and one molecule of methanol. All three molecules are involved in O—H...O hydrogen bonding, which links the molecules in a two-dimensional framework (Table 2). Furthermore, pairs of bipyridine ligands related by centers of symmetry have centroid-centroid separations of 3.688 (4) and 3.515 (4) Å (perpendicular distance 3.53 and 3.38 Å) for the N2/C18–C22 and N3/C23–C27 rings, respectively, indicating significant  $\pi$ – $\pi$  interactions (Tong *et al.*, 1999). The combination of the intermolecular hydrogen bonding and the  $\pi$ -stacking interactions creates a three-dimensional framework structure (Fig. 2).

## Experimental

Tyrosine (2 mmol, 362 mg) and potassium hydroxide (2 mmol, 112 mg) were dissolved in methanol (10 ml) and added successively to a methanol solution of *o*-vanillin (2 mmol, 304 mg). The mixture

became yellow immediately and was then stirred and refluxed for 2 h. A solution of vanadyl sulfate hydrate (2 mmol, 451 mg) in water (4 ml) was added dropwise to the stirring mixture and further refluxed for 3 h. An ethanol solution of 2,2'-bipyridine (2 mmol, 312 mg) was added dropwise and refluxed for 3 h, yielding a brown solution. This was filtered and held at room temperature for seven days, whereupon yellow crystals suitable for X-ray diffraction were obtained. The elemental analysis result was in agreement with the structural composition of (I).

## Crystal data

[V(C<sub>17</sub>H<sub>15</sub>NO<sub>5</sub>)O(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)]·  
CH<sub>4</sub>O·H<sub>2</sub>O  
*M<sub>r</sub>* = 586.48  
Monoclinic, *P*<sub>2</sub><sub>1</sub>/*c*  
*a* = 11.574 (3) Å  
*b* = 20.210 (5) Å  
*c* = 14.919 (3) Å  
 $\beta$  = 128.638 (13)°  
*V* = 2725.8 (11) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.429 Mg m<sup>-3</sup>  
Mo *K*α radiation  
Cell parameters from 2406  
reflections  
 $\theta$  = 2.3–23.5°  
 $\mu$  = 0.42 mm<sup>-1</sup>  
*T* = 298 (2) K  
Block, yellow  
0.53 × 0.37 × 0.24 mm

## Data collection

Siemens SMART CCD area-  
detector diffractometer  
 $\varphi$  and  $\omega$  scans  
Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 1996)  
*T*<sub>min</sub> = 0.808, *T*<sub>max</sub> = 0.906  
14191 measured reflections

4796 independent reflections  
2831 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.061  
 $\theta$ <sub>max</sub> = 25.0°  
*h* = -13 → 12  
*k* = -23 → 23  
*l* = -15 → 17

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.060  
*wR* (*F*<sup>2</sup>) = 0.198  
*S* = 1.01  
4796 reflections  
362 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0999P)^2 + 2.8698P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
( $\Delta/\sigma$ )<sub>max</sub> = 0.001  
 $\Delta\rho_{max}$  = 1.03 e Å<sup>-3</sup>  
 $\Delta\rho_{min}$  = -0.37 e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

V1–O6	1.584 (3)	V1–N1	2.037 (4)
V1–O4	1.958 (3)	V1–N2	2.149 (4)
V1–O1	1.999 (3)	V1–N3	2.321 (4)
O6–V1–O4	100.14 (17)	O1–V1–N2	94.89 (14)
O6–V1–O1	100.05 (17)	N1–V1–N2	164.96 (15)
O4–V1–O1	157.62 (14)	O6–V1–N3	163.24 (17)
O6–V1–N1	102.66 (16)	O4–V1–N3	80.01 (14)
O4–V1–N1	87.87 (14)	O1–V1–N3	83.44 (14)
O1–V1–N1	78.35 (14)	N1–V1–N3	94.10 (15)
O6–V1–N2	91.69 (17)	N2–V1–N3	71.63 (15)
O4–V1–N2	94.09 (14)		

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O8–H30...O2 <sup>i</sup>	0.90	2.00	2.872 (6)	162
O8–H29...O3	0.92	2.04	2.821 (7)	142
O7–H7...O4 <sup>ii</sup>	0.82	2.06	2.819 (5)	153
O3–H3...O7 <sup>iii</sup>	0.82	1.81	2.617 (6)	166

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

All H atoms were placed in geometrically calculated positions (O–H = 0.82–0.92 Å and C–H = 0.93–0.98 Å) and allowed to ride

on their respective parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ,  $1.5U_{\text{eq}}(\text{methyl C})$  or  $1.5U_{\text{eq}}(\text{O})$ . The maximum residual density peak in the final difference Fourier map is  $0.56 \text{ \AA}$  from H28B.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINTE* (Siemens, 1996); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1996); software used to prepare material for publication: *SHELXTL*.

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### References

- Colpas, G. J., Hamstra, B. J., Kampf, J. & Pecoraro, V. L. (1994). *J. Am. Chem. Soc.* **116**, 3627–3628.
- Gruning, C. & Rehder, D. (2000). *J. Inorg. Biochem.* **80**, 185–189.
- Hirao, T. (1997). *Chem. Rev.* **97**, 2707–2724.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Siemens (1996). *SMART*, *SAINTE* and *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Tong, M. L., Lee, H. K., Chen, X. M., Huang, R. B. & Mak, T. M. C. (1999). *J. Chem. Soc. Dalton Trans.* **39**, 3657–3659.
- Xu, T., Li, L.-Z., Zhou, S.-F., Guo, G.-Q. & Niu, M.-J. (2005). *J. Chem. Crystallogr.* **35**, 263–267.