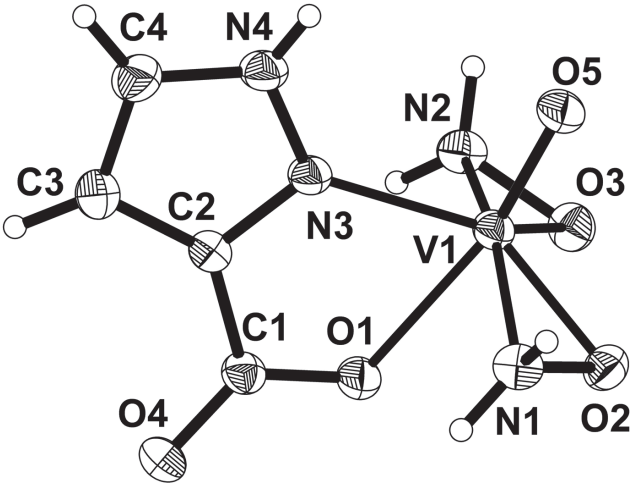
Heng-Qiang Zhang, Qiong Wu, Qi-Ying Zhang*, Xue Yang and Hong-Li Chen

# Crystal structure of bis(hydroxylamido-κ²*O*,*N*)-oxido(1*H*-pyrazole-3-carboxylato-κ²*O*,*N*) vanadium(V), $C_4H_7N_4O_5V$

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## Abstract

$C_4H_7N_4O_5V$, monoclinic, $P2_1/c$ (no. 14), $a = 9.6179(8)$ Å, $b = 8.3133(7)(11)$ Å, $c = 10.8235(9)$ Å, $\beta = 102.253(2)°$, $V = 845.69(12)$ Å$^3$, $Z = 8$, $R_{gt}(F) = 0.0242$, $wR_{ref}(F^2) = 0.0718$, $T = 296(2)$ K.

**CCDC no.:** 1840529

The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

## Source of material

All reagents were obtained from commercial sources and used without further purification. The compound was synthesized by aqueous reactions: $NH_4VO_3$ (1.72 mmol), pyrazole-3-carboxylic acid (5.00 mmol) and NaOH (6.61 mmol) was dissolved in 12 mL of aqueous solution at room temperature. The resulting yellow solution was cooled to 3 °C. $NH_2OH{\cdot}HCl$ (4.31 mmol) was added slowly with constant stirring. The pH of the solution was about 6.9. The obtained yellow solution

**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Colourless block |
| Size: | 0.32 × 0.24 × 0.20 mm |
| Wavelength: | Mo *Kα* radiation (0.71073 Å) |
| $\mu$: | 1.2 mm$^{-1}$ |
| Diffractometer, scan mode: | Apex, $\varphi$ and $\omega$ scans |
| $\theta_{max}$, completeness: | 28.4°, >99% |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 11248, 2110, 0.021 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 1840 |
| $N(param)_{refined}$: | 131 |
| Programs: | SHELX [1], Bruker [2], ORTEP-3 [3] |

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

| Atom | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.33313(16) | 0.44607(19) | 0.71427(14) | 0.0243(3) |
| C2 | 0.31387(17) | 0.50675(18) | 0.83855(14) | 0.0246(3) |
| C3 | 0.3600(2) | 0.6406(2) | 0.91405(16) | 0.0330(4) |
| H3 | 0.416136 | 0.725317 | 0.896881 | 0.040* |
| C4 | 0.3034(2) | 0.6187(2) | 1.02010(16) | 0.0348(4) |
| H4 | 0.314652 | 0.687289 | 1.089414 | 0.042* |
| N1 | 0.00287(15) | 0.29841(15) | 0.67257(13) | 0.0279(3) |
| H1A | −0.079702 | 0.323696 | 0.692254 | 0.034* |
| H1B | 0.032332 | 0.368312 | 0.621337 | 0.034* |
| N2 | 0.33271(14) | 0.08232(16) | 0.88997(13) | 0.0280(3) |
| H2A | 0.413130 | 0.117977 | 0.871448 | 0.034* |
| H2B | 0.341316 | 0.050661 | 0.969784 | 0.034* |
| N3 | 0.23464(14) | 0.41155(15) | 0.89510(12) | 0.0243(3) |
| N4 | 0.22972(16) | 0.48119(17) | 1.00496(12) | 0.0288(3) |
| H4A | 0.180(2) | 0.448(3) | 1.050(2) | 0.051(7)* |
| O1 | 0.28642(13) | 0.30456(13) | 0.68889(10) | 0.0269(2) |
| O2 | 0.02976(12) | 0.13595(13) | 0.65586(10) | 0.0274(2) |
| O3 | 0.24172(12) | −0.00614(13) | 0.79736(11) | 0.0286(2) |
| O4 | 0.38796(13) | 0.53382(15) | 0.64472(11) | 0.0332(3) |
| O5 | 0.06030(13) | 0.16037(14) | 0.91273(11) | 0.0301(3) |
| V1 | 0.15302(3) | 0.19529(3) | 0.80920(2) | 0.02037(10) |

***Corresponding author: Qi-Ying Zhang,** Department of Chemistry, East China Normal University, Shanghai 200062, P.R. China, e-mail: qyzhang@163.com
**Heng-Qiang Zhang, Qiong Wu, Xue Yang and Hong-Li Chen:** Department of Chemistry, Hebei Normal University for Nationalities, Chengde, 067000, P.R. China

was filtered. Colorless block crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of the filtrate in anhydrous ethanol at 277 K. Anal. Calcd. for $C_4H_7N_4O_5V$ (%): C, 19.85; H, 2.91; N, 23.15; V, 21.04. Found: C, 19.81; H, 2.96; N, 23.20; V, 21.02. The vanadium content was determined by spectrophotometry.

## Experimental details

The structure was solved by Direct Methods with the SHELXS-2018 program [1]. The H atoms bonded to N4 atoms were located in difference maps and refined freely. Other H atoms were placed in calculated positions, with C—H = 0.93 Å for pyrazolyl and N—H = 0.90 Å, and refined as riding, with $U_{iso}$(H) values of 1.2 $U_{eq}$(carrier) for $NH_2$ and pyrazolyl H groups.

## Comment

Vanadium is a trace element in biochemical systems and can play an important role in metalloenzymes and impact insulin regulation [4]. In recent years, a number of vanadium compounds are known to exhibit insulin enhancing properties, including vanadium-picolinate complexes and vanadium peroxo compounds [5]. The coordination chemistry of vanadium hydroxylamine complexes has been rather less studied so far [6–8]. The structural chemistry of such vanadium complexes is very important for the understanding of vanadium biochemistry. Therefore, we have synthesized the title compound, and report its crystal structure here.

In the crystal structure of the title compound the vanadium(V) center is seven-coordinated in a pentagonal bipyramidal geometry containing two bidentate hydroxylamido ligands, one oxido ligand, and a bidentate ancillary ligand. The two deprotonted hydroxylamine molecules and the amine nitrogen atom of the organic ligand define a pentagonal equatorial plane approximately perpendicular to V—O bond, while the two oxygen atoms [O1, O3] occupy the axial position, and the distance of vanadium from the equatorial plane is 0.259 Å. The hydroxylamido ligands are coordinated with the nitrogen atoms oriented towards the pyrazole-3-carboxylate ligand. The carboxylate oxygen atom is coordinated *trans* to the oxido ligand in the complex. The V–N bond lengths are 2.018(2) and 2.004(2) Å, respectively, and the V—O bond lengths are 2.0253(14) and 1.9982(13) Å, respectively. The molecular structure of the compound is very similar to the other vanadium(V) hydroxylamido complexes with amino acid ligands that have been reported [9, 10].

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