Vanadium Oxoazides

Deutsche Ausgabe: DOI: 10.1002/ange.201503985
Internationale Ausgabe: DOI: 10.1002/anie.201503985

The Vanadium(V) Oxoazides $[VO(N_3)_3]$, $[(bipy)VO(N_3)_3]$, and $[VO(N_3)_5]^{2-}$**

Ralf Haiges, Monica Vasiliu, David A. Dixon, and Karl O. Christe*

Dedicated to Professor George A. Olah on the occasion of his 88th birthday

Abstract: *Vanadium(V) oxoazide $[VO(N_3)_3]$ was prepared through a fluoride–azide exchange reaction between $[VOF_3]$ and Me_3SiN_3 in acetonitrile solution. When the highly impact- and friction-sensitive compound $[VO(N_3)_3]$ was reacted with 2,2′-bipyridine, the adduct $[(bipy)VO(N_3)_3]$ was isolated. The reaction of $[VO(N_3)_3]$ with $[PPh_4]N_3$ resulted in the formation and isolation of the salt $[PPh_4]_2[VO(N_3)_5]$. The adduct $[(bipy)VO(N_3)_3]$ and the salt $[PPh_4]_{23}[VO(N_3)_5]$ were characterized by vibrational spectroscopy and single-crystal X-ray structure determination, making these compounds the first structurally characterized vanadium(V) azides.*

The chemistry of azides and polyazides has attracted considerable interest during the past decade because of their potential use as high-energy-density materials (HEDM).[1] Polyazido compounds are highly energetic compounds because of the endothermic nature of the N_3 group. As a result, the synthesis of molecules with a high number of azido groups is very challenging because of their explosive nature and shock sensitivity. It has also been well established that polyazido compounds of metals in higher oxidation states are generally more sensitive and less stable than the ones of the same metal in a lower oxidation state.[2] Neutral polyazido compounds can be stabilized and made less sensitive by either anion or adduct formation which increases the ionicity of the azido ligands, making the breaking of an N–N bond less favorable and raising the activation energy barrier towards catastrophic N_2 elimination.[3] Another approach for the stabilization of high-oxidation-state azides is the introduction of oxygen atoms, as the oxidation potential of a metal oxohalide is generally lower than that of the corresponding oxygen-free metal halide with the metal in the same oxidation state. While a significant number of azido compounds of the heavier Group 5 elements Nb and Ta have been prepared and characterized,[3,4] only a limited number of vanadium azides are known. The binary vanadium(IV) azides $[V(N_3)_4]$[5] and $[V(N_3)_6]^{2-}$,[5] the binary vanadium(V) azide $[V(N_3)_6]^-$,[5] and the species $[VOCl_2N_3]$,[6] $[VO(N_3)_4]^{2-}$,[7] and $[V(N_3)_3(N_3S_2)]^{2-}$[8] have been reported for the higher oxidation states but no vanadium(V) polyazide has been structurally characterized.

In agreement with previously reported syntheses of inorganic azides,[1a] the reaction of vanadium(V) oxotrifluoride with an excess of trimethylsilyl azide in acetonitrile solution at −20 °C resulted in a complete fluoride–azide exchange and the formation of a dark-red to black solution of the $[VO(N_3)_3]$ complex [Eq. (1)].

$$[VOF_3] + 3\,Me_3SiN_3 \xrightarrow[3\,Me_3SiF]{CH_3CN} [VO(N_3)_3] \quad (1)$$

Removal of the volatile compounds (CH_3CN, Me_3SiF, and excess Me_3SiN_3) in vacuo, first at −20 °C and then at ambient temperature, resulted in the isolation of the first vanadium(V) oxoazide $[VO(N_3)_3]$ as a dark-red to black solid. Neat vanadium(V) oxotriazide is stable at ambient temperature and can be stored indefinitely at this temperature. However, the compound is impact and friction sensitive and explodes violently upon heating. All attempts to grow single crystals of $[VO(N_3)_3]$ that are suitable for X-ray crystal structure determination were unsuccessful. The composition of the compound was established by the observed reaction stoichiometry and its vibrational spectra (see the Supporting Information).

The 1:1 adduct $[(bipy)VO(N_3)_3]$ was formed quantitatively when $[VO(N_3)_3]$ was reacted with 2,2′-bipyridine (bipy) in acetonitrile solution [Eq. (2)].

$$[VO(N_3)_3] + bipy \xrightarrow{CH_3CN} [(bipy)VO(N_3)_3] \quad (2)$$

After the solvent had been pumped off at ambient temperature, the bipyridine adduct was isolated as an impact- and friction-sensitive, dark-red crystalline solid. The compound was identified and characterized by vibrational spectroscopy and by single-crystal X-ray structure determination. When $[VO(N_3)_3]$ was reacted with two equivalents of $[PPh_4]N_3$ in acetonitrile solution, $[PPh_4]_2[VO(N_3)_5]$ was

[*] Prof. Dr. R. Haiges, Prof. Dr. K. O. Christe
Loker Hydrocarbon Research Institute and
Department of Chemistry
University of Southern California
Los Angeles, CA 90089-1661 (USA)
E-mail: haiges@usc.edu
M. Vasiliu, Prof. Dr. D. A. Dixon
Department of Chemistry, The University of Alabama
Tuscaloosa, AL 35487 (USA)

[**] The Office of Naval Research (ONR) and the Defense Threat Reduction Agency (DTRA) funded this work. The National Science Foundation supported the X-ray diffractometer (NSF CRIF 1048807). We thank Prof. G. K. S. Prakash, Drs. W. Wilson, and R. Wagner, as well as G. B. Chabot, P. Deokar and A. Baxter for their help and stimulating discussions. The calculations were supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, U.S. Department of Energy (DOE) (catalysis center program). D.A.D. thanks the Robert Ramsay Chair Fund of The University of Alabama for support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201503985.

formed quantitatively [Eq. (3)].

$$[VO(N_3)_3] + 2\,[PPh_4]N_3 \xrightarrow{CH_3CN} [PPh_4]_2[VO(N_3)_5] \quad (3)$$

The oxopentaazidovanadate(V) salt was isolated as a dark-red, crystalline solid and characterized by means of vibrational spectroscopy and X-ray crystallography. It is interesting to note that the reaction of $[VO(N_3)_3]$ with one equivalent of $[PPh_4]N_3$ did not result in the formation of a $[VO(N_3)_4]^-$ salt. Instead, a mixture of $[PPh_4]_2[VO(N_3)_5]$ and $[VO(N_3)_3]$ was obtained. The intense red to almost black color of the vanadium oxoazides in this study is in good agreement with the dark maroon to black colors that have been described for the binary vanadium azides $[V(N_3)_4]$, $[V(N_3)_6]^-$, and $[V(N_3)_6]^{2-}$.[5] The color can be attributed to the fact that many vanadium compounds are deeply colored and that the presence of multiple chromophores, such as azido groups, can further enhance the color intensity.

Details of the crystallographic data collection and refinement parameters for the structurally characterized compounds $[(bipy)VO(N_3)_3]$ and $[PPh_4]_2[VO(N_3)_5]$ are given in the Supporting Information. The vanadium oxoazide $[(bipy)VO(N_3)_3]$ crystallizes in the triclinic space group $P\bar{1}$ (Figure 1). The solid-state structure contains isolated and well-separated molecules. The closest intermolecular N–N and M–N distances involving azido groups are 3.106(2) Å and 4.194(2) Å, respectively. The asymmetric unit of the structure consist of two individual $[(bipy)VO(N_3)_3]$ molecules with distinct, different geometries. The two different molecules are depicted in Figure 1.

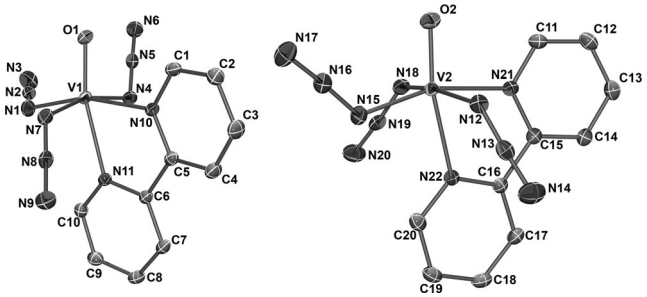

Figure 1. The two independent molecules in the crystal structure of $[(bipy)VO(N_3)_3]$. Thermal ellipsoids are set at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: V1–O1 1.601(1), V1–N1 1.974(2), V1–N4 1.988(1), V1–N7 1.957(2), V1–N10 2.158(1), V1–N11 2.251(1), V2–O2 1.596(1), V2–N12 1.970(1), V2–N15 1.954(1), V2–N18 1.977(1), V2–N21 2.145(1), V2–N22 2.254(1).

In both molecules, the coordination geometry around the central vanadium atom is derived from a distorted octahedron with the three azido ligands as well as one bipyridine nitrogen atom occupying the equatorial positions. The oxygen atom and the second bipyridine nitrogen atom occupy the axial positions. In both molecules, the central vanadium atom is located 0.27(2) Å above the plane containing the four equatorial nitrogen atoms. This distortion from the octahedral arrangement is in good agreement with valence-shell electron repulsion theory (VSEPR) and can be attributed to increased repulsion from the sterically more demanding oxygen ligand.[9] The major differences between the two individual molecules of the asymmetric unit are the orientations of the N_3 groups. It has been shown previously that azido ligands are quite floppy in a molecule and that they can take on different orientations and arrangements with only a small energy penalty.[10] In one of the symmetry-independent $[(bipy)VO(N_3)_3]$ molecules (Figure 1, right), two azido ligands are pointing below the plane of the four equatorial N atoms and away from the O atom. The O2-V2-N-N dihedral angles of these ligands are 154.1(1)° and 166.8(1)°, respectively. The third azido ligand is pointing upward, in the general direction of the O atom with an O2-V2-N15-N16 angle of 4.6(2)°. In the second symmetry-independent molecule (Figure 1, left), one of the N_3 ligands is pointing down and away from the O atom (O1-V1-N7-N8 155.8(1)°), whereas a second N_3 ligand is clearly pointing up and towards the O atom (O1-V1-N4-N5 22.3(1)°). The third N_3 ligand is oriented only slightly towards the O atom with an O1-V1-N1-N2 dihedral angle of 65.0(1)°. The average $V–N_{azido}$ distance of 1.970(2) Å is significantly shorter than the one found for $[V(N_3)_6]^{2-}$ (1.994(3) Å) in $[PPN]_2[V(N_3)_6]$.[8a] The N–N distances in the azido ligands are found to 1.219(2) Å for the internal N–N bond and 1.142(2) Å for the external azide bond, and are typical for covalent azides.

The salt $[PPh_4]_2[VO(N_3)_5]$ crystallizes in the triclinic space group $P\bar{1}$ with two symmetry-related formula units in the unit cell (Figure 2). The crystal structure consists of well-separated cations and anions. The closest cation–anion distances between nonhydrogen atoms are 3.153(3) Å (C46···O1) and 3.225(3) Å (C48···N6). The closest V···N and N···N distances between individual anions were found to 6.694(3) Å and 4.515(3) Å.

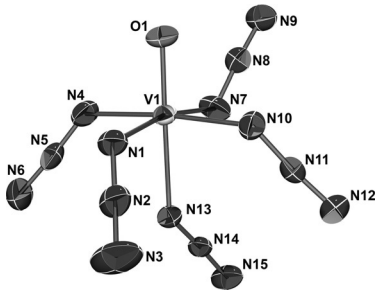

Figure 2. The anion in the crystal structure of $[PPh_4]_2[VO(N_3)_5]$. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å]: V1–O1 1.600(2), V1–N1 2.001(2), V1–N4 1.997(2), V1–N7 2.020(2), V1–N10 2.008(2), V1–N13 2.159(2).

The $[VO(N_3)_5]^{2-}$ anion has a pseudo-octahedral ligand arrangement around the central vanadium atom (Figure 2). The five azido groups occupy all four equatorial and one axial position, while the second axial position is occupied by the oxygen atom. Only one of the four equatorial N_3 groups is pointing in the general direction of the oxygen atom (O-V-N-N dihedral angle 11.3(2)°); the three other groups are

pointing towards the axial azido ligand (O-V-N-N dihedral angles 157.1(2)–160.2(2)°). Similar to $[(bipy)VO(N_3)_3]$, the vanadium atom of the anion is located above (0.15 Å) the equatorial plane containing the α-N atoms of the four equatorial azide groups. The detected V–O distance of 1.600(2) Å in the anion is essentially identical to the one measured for the two independent molecules in the crystal structure of $[(bipy)VO(N_3)_3]$ (1.596(1) and 1.601(1) Å). The average $V–N_{azido}$ distance of 2.007(2) Å for the equatorial ligands and $V–N_{azido}$ distance of 2.159(2) Å for the axial ligand are considerably longer than the average $V–N_{azido}$ distance found for $[(bipy)VO(N_3)_3]$ (1.970(2) Å). This elongation of the V–N bonds can be attributed to the doubly negative charge of the dianion, resulting in more ionic azido ligands. As a result of the increased ionicity of the N_3 groups, their average internal N–N distance (1.199(3) Å) is more similar to the terminal N–N distance (1.145(3) Å) than in those measured for $([bipy)VO(N_3)_3]$.

Quantum mechanical calculations were carried at the B3LYP//DZVP2/cc-pVDZ-PP and SVWN5//DZVP2/cc-pVDZ-PP density functional theory (DFT) levels of theory for all the vanadium(V) oxoazide species $[VO(N_3)_3]$, $[(bipy)VO(N_3)_3]$, and $[VO(N_3)_5]^{2-}$, as well as for the anion $[VO(N_3)_4]^-$. The obtained structures and calculated vibrational frequencies and intensities are given in the Supporting Information. The local DFT functional was included as it often gives better geometries for transition metal compounds than do hybrid functionals such as B3LYP.

For $[VO(N_3)_3]$, the B3LYP and SVWN5 functionals predict a minimum-energy structure of C_{3v} symmetry (Figure 3). The calculated V–O distances are 1.565 Å (B3LYP) and 1.566 Å (SVWN5), and the V–N distances are calculated to be 1.856 Å (B3LYP) and 1.829 Å (SVWN5). For $[(bipy)VO(N_3)_3]$ and $[VO(N_3)_5]^{2-}$, the two levels of theory found different minimum-energy structures, which differ in the orientation of the various azido ligands. This is in good agreement with previous results that there are only subtle energy differences of less than 5 kcal mol^{-1} between various orientations of the azido ligands in metal polyazides. As a result, polyazido compounds may adopt several structures with only very little energy difference among them.[10]

Two different minimum-energy structures (structures A and B in Figure 3) with C_1 symmetry were found for the bipyridine adduct $[(bipy)VO(N_3)_3]$. The minimum structure A, found at the SVWN5 level, closely resembles one of the two independent molecules found in the crystal structure of $[(bipy)VO(N_3)_3]$ with one N_3 group pointing in the direction of the O atom and two N_3 groups away from it. At the B3LYP level, this structure is 0.3 kcal mol^{-1} higher in energy than structure B in which two N_3 groups point in the direction of the O atom and the third one away from it. This arrangement was not detected in the crystal structure of $[(bipy)VO(N_3)_3]$ and lies 1.1 kcal mol^{-1} above the lowest-energy structure A at the SVWN5 level.

For the $[VO(N_3)_4]^-$ ion, both methods predict a C_2-symmetric minimum-energy structure with V–N distances of 1.967 Å and 1.968 Å at the B3LYP level, and 1.925 Å and 1.927 Å at the SVWN5 level. The V–O distance is calculated to 1.571 Å (B3LYP) and 1.576 Å (SVWN5). For the

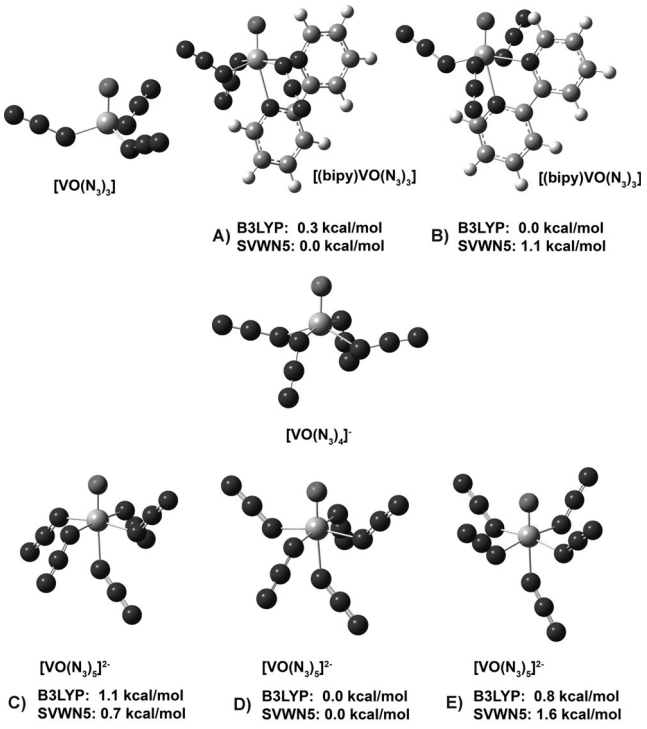

Figure 3. Optimized structures of the vanadium(V) oxoazide species $[VO(N_3)_3]$, $[(bipy)VO(N_3)_3]$, $[VO(N_3)_4]^-$, and $[VO(N_3)_5]^{2-}$ calculated at the B3LYP//DZVP2/cc-pVDZ-PP and SVWN5//DZVP2/cc-pVDZ-PP level of theory. Relative energies are given for species with multiple minimum-energy structures.

$[VO(N_3)_5]^{2-}$ ion, the predicted minimum-energy structure with both functionals has two equatorial N_3^- groups rotated up (structure D in Figure 3). This prediction is in contrast to the anion geometry found in the crystal structure of $[PPh_4]_2[VO(N_3)_5]$, exhibiting one equatorial N_3 ligand pointing towards the O atom. The crystal-structure arrangement (structure C in Figure 3) is predicted to only be 0.7 kcal mol^{-1} and 1.1 kcal mol^{-1} higher in energy than the minimum at the SWVN5 and B3LYP levels, respectively. This small energy difference can easily be accounted for by crystal packing forces and further demonstrates the flexibility of the different conformations. A third structure with all equatorial ligands pointed up is also very close in energy to the other two structures (structure E in Figure 3).

The infrared and Raman spectra of $[VO(N_3)_3]$ are shown in Figure 4. The detected and calculated vibrational bands of the three vanadium oxoazides are listed in the Supporting Information. The mid-wavelength infrared spectra of the vanadium(V) oxazides are primarily dominated by bands attributable to antisymmetric $\nu_{as}(N_3)$ vibration modes at about 2000–2150 cm^{-1} and to a lesser extent by the ν(V-O) mode at about 1000 cm^{-1}.

As can be expected for covalent azides, the Raman spectra of the investigated azides exhibit the strong bands for the $\nu_{as}(N_3)$ vibration modes in the region 2000–2150 cm^{-1} and the much weaker bands of the symmetric $\nu_s(N_3)$ modes at about 1200–1300 cm^{-1}. The V–O stretching vibrational modes are evident at about 1000 cm^{-1} and the $\nu(V–N_3)$ vibration modes are found in the 480–400 cm^{-1} region. The $\nu_{as}(N_3)$ and

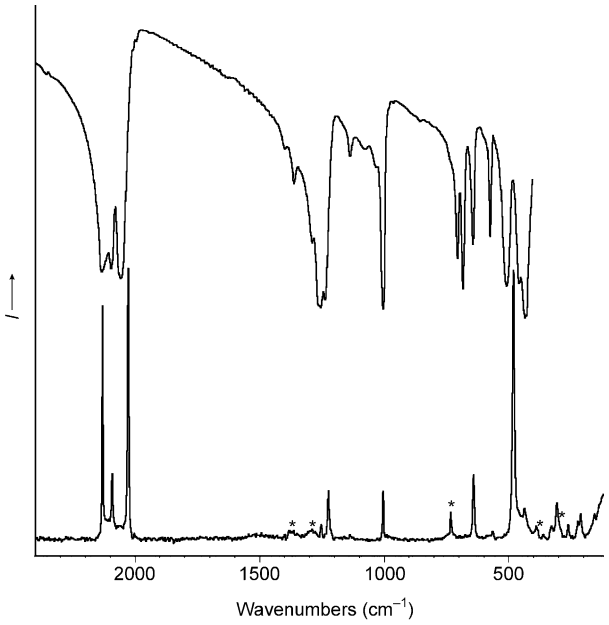

Figure 4. IR (upper trace) and Raman spectra (lower trace) of $[VO(N_3)_3]$. Bands marked by asterisks (*) are attributable to the FEP sample container.

ν(V-N_3) vibration modes give rise to the strongest bands in the Raman spectrum of $[VO(N_3)_3]$ whereas the spectra of $[(bipy)VO(N_3)_3]$ and $[PPh_4]_2[VO(N_3)_5]$ are dominated by bands attributable to the organic moieties bipy and $[PPh_4]^+$. It should be noted that the vibrational spectra of several $[VO(N_3)_3]$ samples from different batches never exhibited the characteristic features of coordinated CH_3CN (two bands of almost equal intensity at about 2320 and 2290 cm^{-1}),[1a] confirming that the compound is indeed free of acetonitrile. The assignments are supported by the DFT calculations.

The impact and friction sensitivities of the vanadium(V) oxoazides of this study were determined using a BAM fall hammer and BAM friction tester. The obtained sensitivity and stability data are summarized in Table 1. As can be expected for a neutral polyazide, $[VO(N_3)_3]$ is highly sensitive with an impact sensitivity of less than 0.5 J and a friction sensitivity of under 5 N. It is somewhat surprising that the 2,2′-bipyridine adduct $[(bipy)VO(N_3)_3]$ is considerably less sensitive to friction (96 N) while the impact sensitivity (<0.5 J) remains virtually unchanged. Therefore, both compounds have to be considered explosion hazards. The thermal stabilities of the studied azides were determined through differential thermal analysis (DTA) scans with heating rates of 5 °C min^{-1}. The resulting decomposition temperatures are included in Table 1. Among the three studied vanadium(V) oxoazides, only $[VO(N_3)_3]$ exploded upon heating (120 °C explosion temperature). The adduct $[(bipy)VO(N_3)_3]$ and the salt $[PPh_4]_2[VO(N_3)_5]$ showed smooth decompositions and no explosions upon heating at a rate of 5 °C min^{-1}.

Table 1: Sensitivity data for the vanadium(V) oxoazides.

Compound	T_{decomp} [°C]	FS [N][a]	IS [J][a]
RDX[b]	220	120	7.5
$[Pb(N_3)_2]$[11]	300	0.1	2.5
$[VO(N_3)_3]$	120[c]	<5	<0.5
$[(bipy)VO(N_3)_3]$	150[d]	96	<0.5
$[PPh_4]_2[VO(N_3)_5]$	150	>360	20

[a] FS = friction sensitivity, IS = impact sensitivity. [b] RDX = 1,3,5-trinitroperhydro-1,3,5-triazine (hexogen). [c] Explosion. [d] Endotherm at 120 °C.

In conclusion, the first vanadium(V) oxoazides have been prepared and characterized. $[VO(N_3)_3]$ has been obtained from $[VOF_3]$ by fluoride–azide exchange with Me_3SiN_3 in CH_3CN solution. The reaction of $[VO(N_3)]$ with 2,2-bipyridine resulted in the formation of $[(bipy)VO(N_3)_3]$. $[PPh_4]_2[VO(N_3)_5]$ has been obtained from the reaction of $[VO(N_3)_3]$ with two equivalents of $[PPh_4]N_3$. All vanadium oxoazides were characterized by vibrational spectroscopy and, in the case of $[(bipy)VO(N_3)_3]$ and $[PPh_4]_2[VO(N_3)_5]$, by single-crystal X-ray diffraction.

Experimental Section

Caution! Polyazides are extremely shock-sensitive and can explode violently upon the slightest provocation. Because of the high-energy content and the high detonation velocity of these azides, their explosions are particularly violent and can cause, even on a one mmol scale, significant damage. The use of appropriate safety precautions (safety shields, face shields, leather gloves, protective clothing, such as heavy leather welding suits, and ear plugs) is mandatory. **Ignoring safety precautions can lead to serious injuries!**

Materials and Apparatus: All reactions were carried out in Teflon–FEP ampules that were closed by stainless steel valves. Volatile materials were handled in a Pyrex glass vacuum line. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glove box. $[VOF_3]$ and 2,2′-bipyridine (bipy) (both Aldrich) were used without further purification. Trimethylsilyl azide (Aldrich) was purified by fractional condensation. $[PPh_4]N_3$ was prepared according to a literature procedure.[12] Solvents were dried by standard methods and freshly distilled prior to use.

Crystal structure determinations: The single-crystal X-ray diffraction data of $[(bipy)VO(N_3)_3]$ were collected on a Bruker SMART APEX DUO 3-circle platform diffractometer, equipped with an APEX II CCD, using Mo Kα radiation (TRIUMPH curved-crystal monochromator) from a fine-focus tube. The diffractometer was equipped with an Oxford Cryosystems Cryostream 700 apparatus for low-temperature data collection. The single-crystal X-ray diffraction data of $[PPh_4]_2[VO(N_3)_5]$ were collected on a Bruker SMART 3-circle platform diffractometer, equipped with an APEX CCD detector, using Mo Kα radiation (graphite monochromator) from a fine-focus tube. The diffractometer was equipped with an LT-3 low-temperature device. The frames were integrated using the SAINT algorithm to give the *hkl* files corrected for Lp/decay.[13] The absorption correction was performed using the SADABS program.[14] The structures were solved by the direct method and refined on F^2 using the Bruker SHELXTL Software Package and ShelXle.[15] All nonhydrogen atoms were refined anisotropically. ORTEP drawings were prepared using the ORTEP-3 for Windows V2.02 program.[16] CCDC-1059908 and 1059909 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Methods: The structures were optimized at the density-functional-theory (DFT)[17] level with the LSDA (local spin density approximation) SVWN5[18] and hybrid B3LYP[19] exchange-correlation functionals with the DFT-optimized DZVP2 basis set[20] for H, C, N, and O atoms and the cc-pVDZ-PP[21] basis set for V using

Gaussian09 program system.[22] Vibrational frequencies were calculated to show that the structures were minima.

Further experimental details are given in the Supporting Information.

Keywords: azides · explosives · structure elucidation · vanadium · vibrational spectroscopy

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 9101 – 9105
Angew. Chem. **2015**, *127*, 9229 – 9233

[1] a) R. Haiges, R. J. Buszek, J. A. Boatz, K. O. Christe, *Angew. Chem. Int. Ed.* **2014**, *53*, 8200 – 8205; *Angew. Chem.* **2014**, *126*, 8339 – 8344; b) W. P. Fehlhammer, W. Beck, *Z. Anorg. Allg. Chem.* **2013**, *639*, 1053 – 1082; c) W. K. Seok, T. M. Klapötke, *Bull. Korean Chem. Soc.* **2010**, *31*, 781 – 788; d) T. M. Klapötke, *Chem. Ber.-Recl.* **1997**, *130*, 443 – 451; e) I. C. Tornieporth-Oetting, T. M. Klapötke, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 511 – 520; *Angew. Chem.* **1995**, *107*, 559 – 568.

[2] a) R. Haiges, J. Boatz, A. Vij, V. Vij, M. Gerken, S. Schneider, T. Schroer, M. Yousufuddin, K. Christe, *Angew. Chem. Int. Ed.* **2004**, *43*, 6676 – 6680; *Angew. Chem.* **2004**, *116*, 6844 – 6848; b) R. Haiges, A. Vij, J. Boatz, S. Schneider, T. Schroer, M. Gerken, K. Christe, *Chem. Eur. J.* **2004**, *10*, 508 – 517.

[3] R. Haiges, P. Deokar, K. O. Christe, *Angew. Chem. Int. Ed.* **2014**, *53*, 5431 – 5434; *Angew. Chem.* **2014**, *126*, 5535 – 5538.

[4] a) R. Haiges, J. A. Boatz, T. Schroer, M. Yousufuddin, K. O. Christe, *Angew. Chem. Int. Ed.* **2006**, *45*, 4830 – 4835; *Angew. Chem.* **2006**, *118*, 4948 – 4953; b) R. Haiges, J. A. Boatz, M. Yousufuddin, K. O. Christe, *Angew. Chem. Int. Ed.* **2007**, *46*, 2869 – 2874; *Angew. Chem.* **2007**, *119*, 2927 – 2932.

[5] R. Haiges, J. A. Boatz, K. O. Christe, *Angew. Chem. Int. Ed.* **2010**, *49*, 8008 – 8012; *Angew. Chem.* **2010**, *122*, 8180 – 8184.

[6] K. Dehnicke, *J. Inorg. Nucl. Chem.* **1965**, *27*, 809 – 815.

[7] a) W. Beck, W. Fehlhammer, P. Pollmann, E. Schuierer, K. Feldl, *Chem. Ber.-Recl.* **1967**, *100*, 2335 – 2361; b) H.-H. Schmidtke, D. Garthoff, *Z. Naturforsch. A* **1969**, *24*, 126 – 133; c) W. Beck, E. Schuiere, P. Pollmann, W. Fehlhammer, *Z. Naturforsch. B* **1966**, *21*, 811 – 812.

[8] J. Hanich, M. Krestel, U. Müller, K. Dehnicke, D. Rehder, *Z. Naturforsch. B* **1984**, *39*, 1686 – 1695.

[9] R. J. Gillespie, *Chem. Soc. Rev.* **1992**, *21*, 59 – 69.

[10] R. Haiges, M. Rahm, K. O. Christe, *Inorg. Chem.* **2013**, *52*, 402 – 414.

[11] R. Meyer, J. Köhler, A. Homburg, *Explosives*, 6th, completely rev. ed., Wiley-VCH, Weinheim, **2007**.

[12] K. O. Christe, R. Haiges, J. A. Boatz, H. D. Brooke Jenkins, E. B. Garner, D. A. Dixon, *Inorg. Chem.* **2011**, *50*, 3752 – 3756.

[13] SAINT+, 8.27B ed., Bruker AXS Madison, WI, **2011**.

[14] SADABS, 2012 – 1 ed., Bruker AXS Madison, WI, **2012**.

[15] a) C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281 – 1284; b) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112 – 122; c) G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3 – 8; d) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3 – 8; e) SHELXL, *Vol. 2012 – 4*, 2012 – 1 ed., G. M. Sheldrick, **2012**; f) SHELXTL, 2014/7 ed., Bruker AXS Madison, WI, **2014**.

[16] L. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565 – 565.

[17] R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York, **1989**.

[18] a) J. C. Slater, *The Self-Consistent Field for Molecular and Solids, Quantum Theory of Molecular and Solids, Vol. 4*, McGraw-Hill, New York, **1974**; b) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200 – 1211.

[19] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648 – 5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785 – 789.

[20] N. Godbout, D. R. Salahub, J. Andzelm, E. Wimmer, *Can. J. Chem.* **1992**, *70*, 560 – 571.

[21] a) N. B. Balabanov, K. A. Peterson, *J. Chem. Phys.* **2005**, *123*, 064107; b) N. B. Balabanov, K. A. Peterson, *J. Chem. Phys.* **2006**, *125*, 074110.

[22] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

Received: April 30, 2015
Published online: June 12, 2015

