

# Redetermination of ammonium metavanadate

Aarón Pérez-Benítez<sup>a</sup> and Sylvain Bernès<sup>b\*</sup>

<sup>a</sup>Facultad de Ciencias Químicas, Benemérita Universidad Autónoma de Puebla, Av. San Claudio y 18 Sur, 72570 Puebla, Pue., Mexico, and <sup>b</sup>Instituto de Física, Benemérita Universidad Autónoma de Puebla, Av. San Claudio y 18 Sur, 72570 Puebla, Pue., Mexico. \*Correspondence e-mail: sylvain\_bernes@hotmail.com

Received 18 July 2018

Accepted 26 July 2018

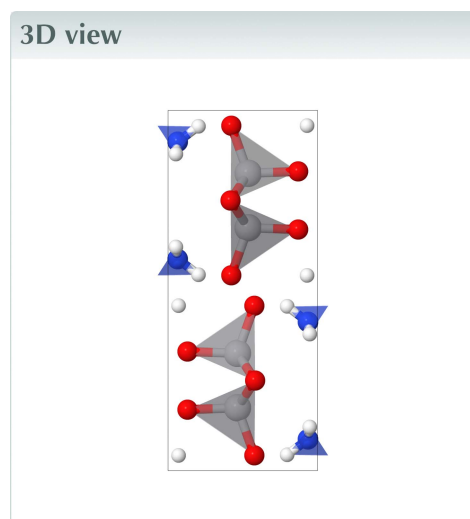
Edited by M. Weil, Vienna University of Technology, Austria

Keywords: crystal structure; vanadate; ammonium; high-resolution data; hydrogen bonds.

CCDC reference: 1858583

Structural data: full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

The crystal structure of ammonium metavanadate,  $\text{NH}_4\text{VO}_3$ , a compound widely used as a starting material for the synthesis of vanadium and polyoxidovanadate compounds, had been determined twice using single-crystal X-ray data [Synček & Hanic (1954). *Czech. J. Phys.* **4**, 120–129 (Weissenberg data); Hawthorne & Calvo (1977). *J. Solid State Chem.* **22**, 157–170 (four-circle diffractometer data)]. Its structure is now redetermined at higher resolution using Ag  $K\alpha$  radiation, and the result is compared with the former refinements. Structural data for the polymeric  $[\text{VO}_3]_\infty$  chain remain unchanged, while more accurate parameters are obtained for the ammonium cation, improving the description of hydrogen-bonding interactions in the crystal structure.



## Structure description

Ammonium metavanadate,  $\text{NH}_4\text{VO}_3$  [IUPAC name: ammonium trioxidovanadate(V)], is a widely used compound at the laboratory scale, for example for the preparation of  $\text{V}_2\text{O}_5$ , polyoxidovanadates, catalysts, or as an analytical reagent. Its crystal structure has been known for a long time. The first study (Lukesh, 1950) reported the correct space group, *Pbcm*, and a hypothetical arrangement for the  $[\text{VO}_4]$  tetrahedra that turned out to be correct as revealed by subsequent studies. Weissenberg data allowed the determination of the atomic coordinates for all non-H atoms (Synček & Hanic, 1954), and a least-squares refinement using the same experimental intensities was published subsequently (Evans, 1960).

The crystal structure of  $\text{NH}_4\text{VO}_3$  is quite simple (Fig. 1). Vertice-sharing  $[\text{VO}_4]$  tetrahedra form infinite  $[\text{VO}_3]_\infty$  chains along  $[001]$ , and given that the crystal lattice is orthorhombic, all chains are parallel;  $\text{NH}_4^+$  cations are situated in the voids between these chains. Both the tetrahedral anionic and cationic groups are sited on mirror planes parallel to  $(001)$  in space group *Pbcm*, and thus have point group symmetry  $C_s$ . Finally,

**Table 1**

Bond lengths (Å) and angles (°) in NH<sub>4</sub>VO<sub>3</sub> determined in this work compared to those reported in previous studies.

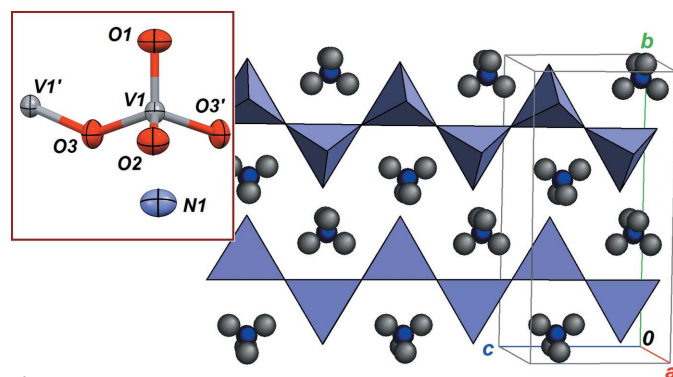
The labelling scheme for atomic sites is identical in the three studies.

	1977 study <sup>a</sup>	2009 study <sup>b</sup>	This work
<b>Vanadate anion</b>			
V1—O1	1.640 (4)	1.655	1.6388 (10)
V1—O2	1.647 (4)	1.679	1.6538 (9)
V1—O3 (×2)	1.803 (1)	1.808	1.8021 (3)
O1—V1—O2	107.3 (1)	107.2	107.40 (5)
O1—V1—O3 (×2)	109.7 (1)	109.0	109.75 (3)
O2—V1—O3 (×2)	111.1 (1)	112.1	111.08 (2)
O3—V1—O3	107.9 (1)	107.2	107.77 (3)
<b>Ammonium cation</b>			
N1—H1	0.82 (8)	1.05	0.85 (2)
N1—H2	0.94 (8)	1.05	0.85 (2)
N1—H3 (×2)	0.97 (5)	1.04	0.77 (2)
H1—N1—H2	111 (6)	112	104 (2)
H1—N1—H3 (×2)	106 (3)	109	111.7 (15)
H2—N1—H3 (×2)	107 (3)	110	105.8 (15)
H3—N1—H3	119 (5)	108	116 (4)

References: (a) Hawthorne & Calvo (1977); (b) Smrčok *et al.* (2009), with DFT-optimized parameters rounded to the precision of the experimentally determined values.

the polymeric character of the vanadate anion stems from the special position of the O atom positioned away from the mirror plane. This atom (O3) lies on the twofold rotation axis parallel to [100].

The most precise structure report of NH<sub>4</sub>VO<sub>3</sub> up to date is probably that by Smrčok *et al.* (2009), based on laboratory/synchrotron temperature-variable X-ray powder diffraction data combined with solid state DFT calculations. However, these authors commented that they made ‘unsuccessful attempts to grow a single-crystal suitable for single-crystal neutron diffraction’. Indeed, only one single-crystal study based on four-circle diffractometer data may be retrieved from the literature (Hawthorne & Calvo, 1977). This long-standing X-ray study reported the structure at a standard resolution,  $d = 0.84$  Å, and, as mentioned by Smrčok *et al.* (2009), ‘the positions [of the hydrogen atoms] are not suffi-



**Figure 1**

Part of the crystal structure of ammonium metavanadate, viewed approximately down [100], using a polyhedral representation for the vanadate chains and spheres of arbitrary radii for ammonium cations (Boudias & Monceau, 1998). The inset shows non-H atoms with displacement ellipsoids at the 80% probability level. The V1' and O3' sites are generated by the symmetry operations  $x, \frac{1}{2} - y, -z$  and  $x, y, \frac{1}{2} - z$ , respectively.

**Table 2**

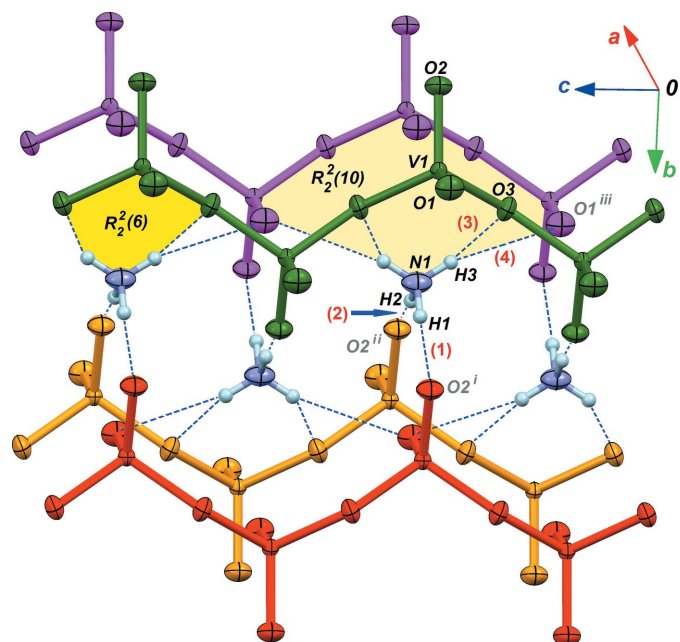
Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O2 <sup>i</sup>	0.85 (2)	2.09 (3)	2.9400 (16)	172 (2)
N1—H2...O2 <sup>ii</sup>	0.85 (2)	1.99 (2)	2.8364 (15)	171 (2)
N1—H3...O3	0.77 (2)	2.48 (2)	2.9690 (12)	122.9 (17)
N1—H3...O1 <sup>iii</sup>	0.77 (2)	2.49 (2)	3.2141 (7)	156 (2)

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

ciently accurate to be directly used in calculations of vibrational spectra’.

We now have redetermined the crystal structure of NH<sub>4</sub>VO<sub>3</sub>, using room-temperature X-ray diffraction data collected at 0.61 Å resolution. As expected, the bond lengths and angles for the vanadate chain are identical, within experimental uncertainties, to those obtained from the 1977 and 2009 articles (see comparison in Table 1). However, differences occur for the ammonium moiety. Our data allowed us to rationalize the distortion of the tetrahedral coordination sphere for the cation. The short N1—H3 bond length, 0.77 (2) Å, compared to the long N1—H1 and N1—H2 bonds, 0.85 (2) Å, results from the involvement of the latter in strong hydrogen bonds, while the former gives much weaker and bifurcated hydrogen bonds (Table 2). In the same way, the largest H—N—H angle, 116 (4)°, involves H atoms participating in weak hydrogen bonds, while the acute angle of



**Figure 2**

Part of the crystal structure of ammonium metavanadate, showing hydrogen bonds as dashed lines. Four vanadate chains are represented with different colours, and the asymmetric unit is indicated with black labels. Hydrogen bonds are labelled (1)–(4), corresponding to entries in Table 2, and the supramolecular rings linking the anions and cations in the crystal are coloured yellow. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i)  $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $x + 1, -y + \frac{1}{2}, -z$ .]

Table 3

Experimental details.

Crystal data	
Chemical formula	NH <sub>4</sub> <sup>+</sup> ·VO <sub>3</sub> <sup>-</sup>
<i>M<sub>r</sub></i>	116.98
Crystal system, space group	Orthorhombic, <i>Pbcm</i>
Temperature (K)	295
<i>a</i> , <i>b</i> , <i>c</i> (Å)	4.9045 (3), 11.7945 (5), 5.8231 (2)
<i>V</i> (Å <sup>3</sup> )	336.84 (3)
<i>Z</i>	4
Radiation type	Ag <i>Kα</i> , λ = 0.56083 Å
μ (mm <sup>-1</sup> )	1.41
Crystal size (mm)	0.32 × 0.09 × 0.09
Data collection	
Diffraction	Stoe Stadivari
Absorption correction	Multi-scan ( <i>X-AREA</i> ; Stoe & Cie, 2018)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.295, 0.656
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	17208, 846, 754
<i>R<sub>int</sub></i>	0.027
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.823
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.014, 0.042, 1.13
No. of reflections	846
No. of parameters	40
H-atom treatment	All H-atom parameters refined
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.33, -0.35

Computer programs: *X-AREA* (Stoe & Cie, 2018), *SHELXT2018/2* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2008) and *CaRIne Crystallography* (Boudias & Monceau, 1998) and *publCIF* (Westrip, 2010).

104 (2)° is H1–N–H2, where H1 and H2 are engaged in stronger hydrogen bonds. The framework of hydrogen bonds is, however, essentially identical in the three structure determinations. Each cation in the crystal interacts with four symmetry-related [VO<sub>4</sub>] tetrahedra, forming two strong and two weak hydrogen bonds (Table 2). Weak contacts with H3 as donor form *R*<sub>2</sub><sup>2</sup>(6) ring motifs with the vanadate chains. Such rings connect the cation with two vertices of a [VO<sub>4</sub>] tetrahedron, and the same donor groups are connected to the neighbouring vanadate chain in the crystal, forming larger *R*<sub>2</sub><sup>2</sup>(10) ring motifs (Fig. 2). Strong contacts with H1/H2 as donors also connect neighbouring chains. The strength of the hydrogen bonds is reflected in the displacement parameters for the ammonium H atoms: H3 refines with the highest displacement parameter, *U*<sub>iso</sub> = 0.069 (6) Å<sup>2</sup>, because it is not stabilized on its site through a strong interaction with the vanadate chain. Smrčok *et al.* (2009) included in their description two additional very bent contacts. However, the N–H...O angles are then below 110°, and these contacts should thus contribute to the crystal stabilization with an energy approaching 0 kJ mol<sup>-1</sup> (Wood *et al.*, 2009).

### Synthesis and crystallization

**Warning!** Ammonium metavanadate is a hazardous material classified with health code 4 in the NFPA 704 standard system:

very short exposure could cause death or major residual injury. The single crystal used in the present study was harvested as a recrystallized unreacted material from the crude reaction in which we attempted to obtain a V<sup>IV</sup> derivative of tris-(metforminium)<sup>2+</sup> decavanadate (Treviño *et al.*, 2015), using acetylsalicylic acid both as a source of protons and as a reducing agent. Typically, metformin hydrochloride (0.850 g), aspirin (0.5 g) and NH<sub>4</sub>VO<sub>3</sub> (0.5 g) were stirred at room temperature for one hour, and the remaining solids were filtered off by gravity. Good-quality single crystals of the main product (orange crystals; Sánchez-Lombardo *et al.*, 2014) and NH<sub>4</sub>VO<sub>3</sub> (colourless crystals) were obtained by fractional crystallization, allowing the solvent to evaporate under ambient conditions.

### Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The three H atoms in the asymmetric unit were refined with free coordinates and free isotropic displacement parameters.

### Funding information

Funding for this research was provided by: Benemérita Universidad Autónoma de Puebla (grant No. 100500599-VIEP2018; grant No. 100142933-VIEP2018); Consejo Nacional de Ciencia y Tecnología (grant No. 268178).

### References

- Boudias, C. & Monceau, D. (1998). *CaRIne Crystallography*. Divergent S. A., Compiègne, France.
- Evans, H. T. (1960). *Z. Kristallogr.* **114**, 257–277.
- Hawthorne, F. C. & Calvo, C. (1977). *J. Solid State Chem.* **22**, 157–170.
- Lukesh, J. S. (1950). *Acta Cryst.* **3**, 476–477.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Sánchez-Lombardo, I., Sánchez-Lara, E., Pérez-Benítez, A., Mendoza, Á., Bernès, S. & González-Vergara, E. (2014). *Eur. J. Inorg. Chem.* pp. 4581–4588.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Smrčok, L., Bitschnau, B. & Filinchuk, Y. (2009). *Cryst. Res. Technol.* **44**, 978–984.
- Stoe & Cie (2018). *X-AREA*. Stoe & Cie, Darmstadt, Germany.
- Syneček, V. & Hanic, F. (1954). *Czech. J. Phys.* **4**, 120–129.
- Treviño, S., Sánchez-Lara, E., Sarmiento-Ortega, V. E., Sánchez-Lombardo, I., Flores-Hernández, J. Á., Pérez-Benítez, A., Brambila-Colombres, E. & González-Vergara, E. (2015). *J. Inorg. Biochem.* **147**, 85–92.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Wood, P. A., Allen, F. H. & Pidcock, E. (2009). *CrystEngComm*, **11**, 1563–1571.

## full crystallographic data

*IUCrData* (2018). 3, x181080 [https://doi.org/10.1107/S2414314618010805]

## Redetermination of ammonium metavanadate

Aarón Pérez-Benítez and Sylvain Bernès

## Hydroxy(dioxido)vanadium ammoniate

## Crystal data

$\text{NH}_4^+\cdot\text{VO}_3^-$

$M_r = 116.98$

Orthorhombic, *Pbcm*

$a = 4.9045$  (3) Å

$b = 11.7945$  (5) Å

$c = 5.8231$  (2) Å

$V = 336.84$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 232$

$D_x = 2.307$  Mg m<sup>-3</sup>

Ag *Kα* radiation,  $\lambda = 0.56083$  Å

Cell parameters from 39692 reflections

$\theta = 2.7\text{--}33.0^\circ$

$\mu = 1.41$  mm<sup>-1</sup>

$T = 295$  K

Prism, colourless

0.32 × 0.09 × 0.09 mm

## Data collection

Stoe Stadivari

diffractometer

Radiation source: Sealed X-ray tube, Axo Astix-

f Microfocus source

Graded multilayer mirror monochromator

Detector resolution: 5.81 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan

(*X-AREA*; Stoe & Cie, 2018)

$T_{\min} = 0.295$ ,  $T_{\max} = 0.656$

17208 measured reflections

846 independent reflections

754 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 3.3^\circ$

$h = -8 \rightarrow 8$

$k = -19 \rightarrow 19$

$l = -9 \rightarrow 8$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.014$

$wR(F^2) = 0.042$

$S = 1.13$

846 reflections

40 parameters

0 restraints

0 constraints

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0248P)^2 + 0.023P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.33$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.35$  e Å<sup>-3</sup>

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.9355 (2)	0.41286 (10)	0.250000	0.0254 (2)
H1	0.796 (5)	0.4562 (18)	0.250000	0.047 (6)*
H2	1.071 (4)	0.4581 (16)	0.250000	0.023 (5)*
H3	0.947 (3)	0.379 (2)	0.137 (4)	0.069 (6)*
V1	0.46440 (4)	0.17437 (2)	0.250000	0.01270 (5)

O1	0.1305 (2)	0.16927 (8)	0.250000	0.02460 (18)
O2	0.57698 (19)	0.04220 (7)	0.250000	0.02260 (17)
O3	0.58198 (18)	0.250000	0.000000	0.02029 (16)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0219 (5)	0.0176 (4)	0.0366 (6)	-0.0022 (4)	0.000	0.000
V1	0.01423 (9)	0.01304 (8)	0.01082 (7)	-0.00023 (6)	0.000	0.000
O1	0.0158 (4)	0.0255 (4)	0.0324 (5)	0.0002 (3)	0.000	0.000
O2	0.0227 (4)	0.0160 (4)	0.0291 (4)	0.0031 (3)	0.000	0.000
O3	0.0235 (4)	0.0236 (4)	0.0139 (3)	0.000	0.000	0.0050 (3)

*Geometric parameters (Å, °)*

N1—H1	0.85 (2)	V1—O1	1.6388 (10)
N1—H2	0.85 (2)	V1—O2	1.6538 (9)
N1—H3	0.77 (2)	V1—O3	1.8021 (3)
N1—H3 <sup>i</sup>	0.77 (2)	V1—O3 <sup>i</sup>	1.8021 (3)
H1—N1—H2	104 (2)	O1—V1—O3	109.75 (3)
H1—N1—H3	111.7 (15)	O2—V1—O3	111.08 (2)
H2—N1—H3	105.8 (15)	O1—V1—O3 <sup>i</sup>	109.75 (3)
H1—N1—H3 <sup>i</sup>	111.7 (15)	O2—V1—O3 <sup>i</sup>	111.08 (2)
H2—N1—H3 <sup>i</sup>	105.8 (15)	O3—V1—O3 <sup>i</sup>	107.77 (3)
H3—N1—H3 <sup>i</sup>	116 (4)	V1—O3—V1 <sup>ii</sup>	142.68 (5)
O1—V1—O2	107.40 (5)		
O1—V1—O3—V1 <sup>ii</sup>	1.91 (3)	O3 <sup>i</sup> —V1—O3—V1 <sup>ii</sup>	-117.57 (3)
O2—V1—O3—V1 <sup>ii</sup>	120.53 (3)		

Symmetry codes: (i)  $x, y, -z+1/2$ ; (ii)  $x, -y+1/2, z-1/2$ .*Hydrogen-bond geometry (Å, °)*

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N1—H1 <sup>iii</sup> —O2 <sup>iii</sup>	0.85 (2)	2.09 (3)	2.9400 (16)	172 (2)
N1—H2 <sup>iv</sup> —O2 <sup>iv</sup>	0.85 (2)	1.99 (2)	2.8364 (15)	171 (2)
N1—H3 <sup>v</sup> —O3	0.77 (2)	2.48 (2)	2.9690 (12)	122.9 (17)
N1—H3 <sup>v</sup> —O1 <sup>v</sup>	0.77 (2)	2.49 (2)	3.2141 (7)	156 (2)

Symmetry codes: (iii)  $-x+1, y+1/2, -z+1/2$ ; (iv)  $-x+2, y+1/2, -z+1/2$ ; (v)  $x+1, -y+1/2, z-1/2$ .