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NH₄VO(NH₃)PO₄

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Abstract

Ammonium ammine oxovanadium phosphate, NH₄VO(NH₃)PO₄, crystallizes in the monoclinic system in space group *P2*₁. The structure contains VO₄(NH₃) square pyramids and PO₄ tetrahedra which are connected *via* common O atoms forming double chains running along [010]. The bond distances are in the usual

ranges and similar to those of other vanadium phosphate compounds.

Comment

In connection with investigations of the catalytic process of ammoxidation of substituted methyl aromatics and methyl heteroaromatics to their corresponding nitriles, ammonium oxovanadium(IV) phosphates and oxovanadium(IV) phosphates are of great interest. Ammonium oxovanadium(IV) phosphates can act in these catalytic processes either as a catalyst or as an intermediate. Our investigation studied the NH₃/V^{IV}/P₂O₅ system and led to the new title compound NH₄VO(NH₃)PO₄.

The crystal structure of the title ammonium oxovanadium(IV) phosphate consists of distorted VO₄(NH₃) square pyramids and PO₄ tetrahedra. These polyhedra are alternately connected *via* common O atoms, forming double chains running along [010]. Each VO₄(NH₃) square pyramid is connected by three common O atoms (O1, O2 and O3) to three PO₄ tetrahedra. Two O atoms link VO₄(NH₃) and PO₄ polyhedra in the [010] chain direction and a third O atom is shared with a PO₄ tetrahedron of a neighbouring parallel chain (Fig. 1). Four hydrogen bonds starting at NH₄ connect the double chains along [001]. An ammonia H atom (N1—H1...O5) links the chains along [100] through a second hydrogen bond to O3 within the double chain.

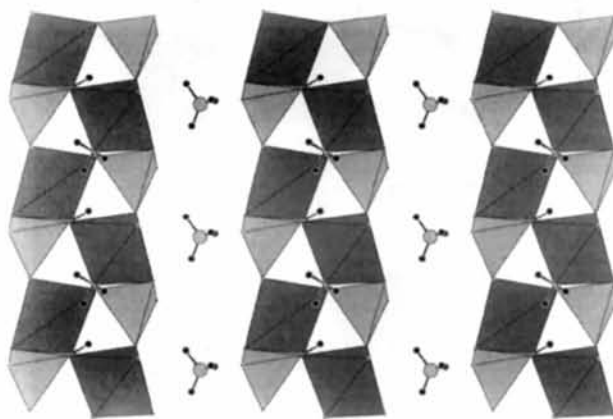


Fig. 1. View along [100] showing the alternately linked chains of VO₄(NH₃) square pyramids. The *b* direction is vertical and the *c* direction is horizontal.

The base of the square pyramid is formed by three O atoms and the ammonia N1 atom. The three equatorial V—O bond distances vary between 1.972 (2) and 1.988 (2) Å; the V—N1 distance is 2.147 (3) Å. The apical O atom (O4) has a V—O distance of 1.600 (2) Å. This is a typical bond distance for an oxovanadium(IV) cation, as found in other VO²⁺ compounds (Leonowicz *et al.*, 1985; Worzala *et al.*, 1998; Fratzky *et al.*, 1998). The P—O bond lengths vary between 1.512 (2) and

1.565 (2) Å. Similar distances were found by Haushalter *et al.* (1994) in NH_4VOPO_4 .

| | | | | |
|----|------------|------------|------------|------------|
| O3 | 0.3734 (4) | 0.8256 (6) | 0.4486 (3) | 0.0172 (6) |
| O4 | 0.1826 (4) | 0.7966 (6) | 0.7526 (4) | 0.0222 (6) |
| O5 | 0.8336 (4) | 1.2412 (6) | 0.8009 (3) | 0.0174 (6) |
| N1 | 0.1674 (6) | 0.3495 (8) | 0.5622 (5) | 0.0174 (7) |
| N2 | 0.1776 (5) | 0.2194 (7) | 1.0118 (4) | 0.0173 (7) |

Experimental

$\text{NH}_4\text{VO}(\text{NH}_3)\text{PO}_4$ was prepared by hydrothermal reaction of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ (2 g) with concentrated ammonia (18 ml) at 420 K.

Crystal data

$\text{NH}_4\text{VO}(\text{NH}_3)\text{PO}_4$

$M_r = 196.99$

Monoclinic

$P2_1$

$a = 6.777$ (1) Å

$b = 4.915$ (1) Å

$c = 8.455$ (2) Å

$\beta = 91.11$ (3)°

$V = 281.57$ (10) Å³

$Z = 2$

$D_x = 2.323$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 10\text{--}18^\circ$

$\mu = 2.000$ mm⁻¹

$T = 293$ (2) K

Needle

$0.30 \times 0.07 \times 0.06$ mm

Light blue

Data collection

Nonius CAD-4 diffractometer

$\theta/2\theta$ scans

Absorption correction:

ψ scan (CORINC;

Schollmeyer, 1992)

$T_{\min} = 0.832$, $T_{\max} = 0.887$

1765 measured reflections

1646 independent reflections

1426 reflections with

$I > 2\sigma(I)$

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

$\theta_{\text{max}} = 29.96^\circ$

$h = 0 \rightarrow 9$

$k = -6 \rightarrow 6$

$l = -11 \rightarrow 11$

3 standard reflections

every 100 reflections

intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.070$

$S = 1.035$

1646 reflections

110 parameters

Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 0.7939P]$

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

$(\Delta/\sigma)_{\text{max}} = 0.020$

$\Delta\rho_{\text{max}} = 0.481$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.365$ e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Absolute structure:

Flack (1983)

Flack parameter = -0.05 (3)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

| | $U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^T a_j$ | | | |
|----|---|--------------|--------------|-----------------|
| | x | y | z | U_{eq} |
| V1 | 0.35943 (9) | 0.65672 (11) | 0.65971 (7) | 0.01149 (14) |
| P1 | 0.63284 (13) | 1.20466 (16) | 0.72266 (10) | 0.00997 (19) |
| O1 | 0.5806 (4) | 0.9019 (6) | 0.7219 (3) | 0.0143 (5) |
| O2 | 0.4731 (4) | 0.3768 (5) | 0.8053 (3) | 0.0151 (6) |

Table 2. Selected bond lengths (Å)

| | | | |
|-------|-----------|-------|-----------|
| V1—O4 | 1.601 (3) | V1—O1 | 1.986 (3) |
| V1—O3 | 1.972 (3) | V1—O2 | 1.991 (3) |

Table 3. Hydrogen-bonding geometry (Å, °)

| D—H...A | D—H | H...A | D...A | D—H...A |
|---------------------------|----------|----------|-----------|---------|
| N1—H1...O5 ⁱ | 0.74 (8) | 2.41 (8) | 3.107 (5) | 157 (8) |
| N1—H2...O3 ⁱⁱ | 0.87 (7) | 2.23 (7) | 3.090 (5) | 168 (5) |
| N2—H4...O5 ⁱⁱⁱ | 0.87 (8) | 1.99 (8) | 2.836 (5) | 164 (7) |
| N2—H5...O5 ⁱ | 0.85 (6) | 2.07 (6) | 2.910 (4) | 172 (5) |
| N2—H6...O5 ^{iv} | 0.94 (7) | 2.08 (7) | 3.016 (5) | 171 (6) |
| N2—H7...O2 | 0.89 (6) | 1.92 (6) | 2.792 (5) | 167 (5) |

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

All atoms, excluding H atoms, were refined anisotropically.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CORINC* (Schollmeyer, 1992). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a). Molecular graphics: *DIAMOND* (Bergerhoff & Bernd, 1996). Software used to prepare material for publication: *SHELXL97*.

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