References

Bensch, W., Dürichen, P. & Weidlich, C. (1996). Z. Kristallogr. 211, 933.

Dürichen, P. & Bensch, W. (1996). Eur. J. Solid State Inorg. Chem. 33, 309–320.

Flack, H. D. (1983). Acta Cryst. A39, 876–881.

Lu, Y.-J. & Ibers, J. A. (1991). J. Solid State Chem. 94, 381–385.

Rumpf, C., Näther, C., Jess, I. & Bensch, W. (1997). Eur. J. Solid State Inorg. Chem. 34, 1165–1177.

Rumpf, C., Tillinski, R., Näther, C., Dürichen, P., Jess, I. & Bensch, W. (1997). Eur. J. Solid State Inorg. Chem. 34, 1187–1198.

Sheldrick, G. M. (1990). Acta Cryst. A46, 467–473.

Sheldrick, G. M. (1993). SHELXL93. Program for the Refinement of Crystal Structures. University of Göttingen, Germany.

Siemens (1990). SHELXTL/PC. Program Package for the Solution, Refinement and Graphical Presentation of Crystal Structures. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Stoe & Cie (1991a). DIF4. Diffractometer Control Program. Version 7.09X/DOS. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1991b). REDU4. Data Reduction Program. Version 7.03. Stoe & Cie, Darmstadt, Germany.

Ammonium trivanadate(V), NH4V3O8

Bi-Zhou Lin and Shi-Xiong Liu

Department of Chemistry, Fuzhou University, Fuzhou 350002, People's Republic of China. E-mail: sxliu@fzu.edu.cn

Abstract

The structure of the title compound is made up of vanadium oxide layers, with NH_4^+ cations intercalated between the layers. Each pair of VO_5 square pyramids is bridged by an edge to form a double V_2O_8 group. The V_2O_8 groups are connected by sharing corners to produce a twisted zigzag chain. Each VO_6 octahedron is connected to two V_2O_8 groups by two edges and to another two V_2O_8 groups by two corners. Hence, the twisted zigzag chains are held together through VO_6 octahedra by sharing corners and edges to form a layer

structure. There are N—H···O hydrogen bonds between the vanadium oxide layer and the NH_4^+ cations.

Comment

$NH_4V_3O_8$ was first prepared by Norblad (1875) and is one stable solid phase in the NH_3–V_2O_5–H_2O system at 303 K (Kelmers, 1961a). Based on X-ray powder diffraction, Kelmers revealed that $NH_4V_3O_8$ was probably isostructural with KV_3O_8, RbV_3O_8 and CsV_3O_8 (Kelmers, 1961b). The crystal structures of KV_3O_8 and CsV_3O_8 were described by Block and Evens (Block, 1960; Evens & Block, 1966). However, powder diffraction techniques were inadequate for revealing the detailed structure or for confirming the possibility of hydrogen bonding in the title compound. We report herein the hydrogen bonding in the crystal structure of the title compound and two new synthetic routes for its preparation.

As illustrated in Fig. 1, the structure of $NH_4V_3O_8$ consists of layers fused by VO_5 square pyramids and VO_6 octahedra, with ammonium cations occupying the interlayer positions. The VO_5 square pyramids are connected in pairs by sharing an edge to form a V_2O_8 group. In the V_2O_8 group, the two apices of the two square pyramids point away from each other (Fig. 2). The V_2O_8 groups are joined through corners (O4) into a twisted zigzag chain along the b axis. One VO_6 octahedron and two V_2O_8 groups are linked by sharing
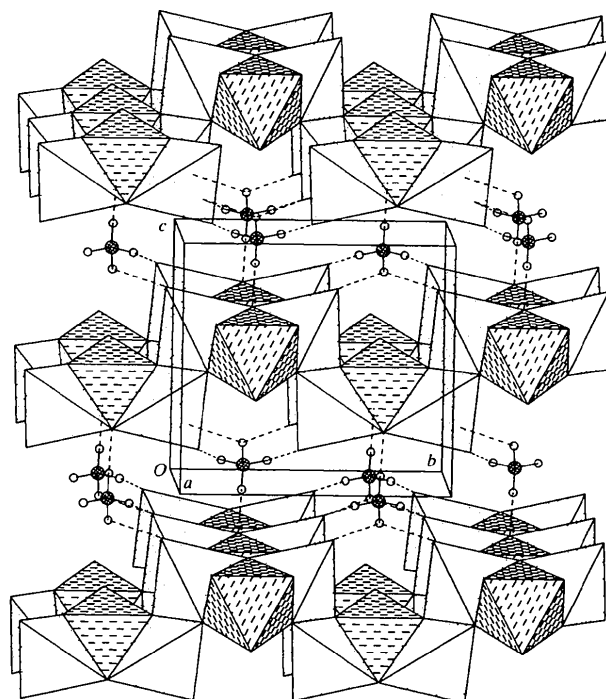

Fig. 1. The structure of $NH_4V_3O_8$ viewed along the a axis, showing the buckled layers and the interlayer hydrogen bonds (dashed lines). The N and H atoms are represented by large cross-hatched circles and small open circles, respectively.
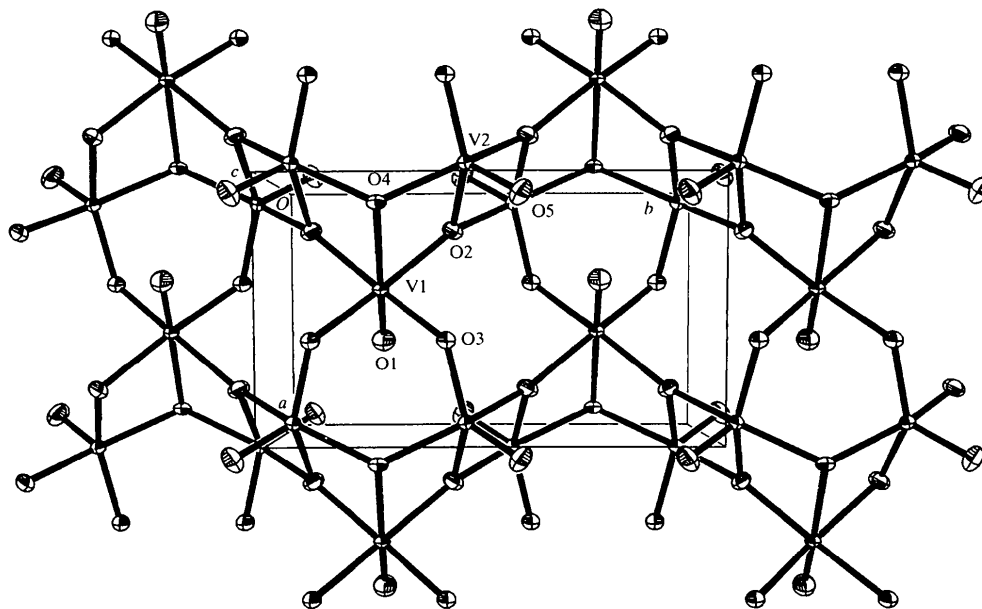
Fig. 2. Projection of one layer of the structure along the c axis, shown with 90% probability displacement ellipsoids.

edges (O2–O4), while the VO₆ octahedron and another two V₂O₈ groups from the adjacent chain are linked by sharing corners (O3). These zigzag chains are further held together through VO₆ octahedra by sharing corners and edges in turn to form a layer structure parallel to the (001) plane.

Bond-valence-sum calculations (Brown & Altermatt, 1985) resulted in values of 5.12 for V1 and 5.02 for V2, both very close to the ideal value for a V^V atom. The V1 atom has a distorted octahedral coordination. Atoms O2, O2^i, O3 and O3^i are coordinated to V1, forming an equatorial plane with V—O bond distances in the range 1.835 (3)–1.971 (3) Å [symmetry code: (i) x, $-y + \frac{1}{2}$, z]. The axial positions are occupied by O1 and O4, with a V1═O1 double-bond length of 1.597 (4) Å and a weak V1—O4 bond length of 2.284 (4) Å. Atoms V1, O1 and O4 are on a mirror plane, O1 being a terminal O atom and O4 being a μ_3-O atom. In the square pyramid around V2, the four basal V—O bond distances vary from 1.736 (2) to 2.001 (3) Å, while the terminal O5 atom is in the axial position with a V═O bond length of 1.602 (3) Å. If the interaction between V2 and O1^{ii} is considered significant [symmetry code: (ii) $x - 1$, y, z], the geometry around the V2 atom may be considered as highly distorted octahedral and the vanadium oxide layer may be considered as a layer containing VO₆ octahedra by sharing edges and corners.

NH₄V₃O₈ is isostructural with KV₃O₈ and CsV₃O₈ (Block, 1960; Evens & Block, 1966). The NH₄⁺, K⁺ and Cs⁺ cations occupy similar sites between the vanadium oxide layers and have irregular 12-fold coordination with neighboring O atoms in these three phases, considering a maximum cation–oxygen contact distance

of 3.7 Å. The average N—O distance is 3.18 Å for NH₄V₃O₈, while the cation–oxygen distance is 3.11 and 3.30 Å for KV₃O₈ and CsV₃O₈, respectively.

As shown in Fig. 1 and Table 3, N—H$\cdots$O hydrogen bonding exists between the cations and the polyanion layers. The network of hydrogen bonds may increase the structural stability of the title compound.

Experimental

Ammonium trivanadate was synthesized hydrothermally under autogenous pressure in a 17 ml Teflon-lined stainless steel vessel with a ca 40% fill factor. A mixture of NH₄VO₃ (0.117 g), Ni(NO₃)₂·6H₂O (0.174 g) and H₂O (5.5 ml) in a 1:0.6:389 molar ratio was heated at 403 K for 48 h. The acidity of the medium was adjusted with CH₃COOH to pH ∼6. Orange plate crystals of NH₄V₃O₈ were formed in a yield of 85% based on vanadium. When Ni(NO₃)₂·6H₂O was replaced by ZnCl₂, crystals of the title compound were obtained, but in a slightly lower yield (ca 70%).

Crystal data

NH₄V₃O₈	Mo $K\alpha$ radiation
$M_r = 298.86$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 25
$P2_1/m$	reflections
$a = 4.993\,(1)$ Å	$\theta = 10–15°$
$b = 8.418\,(2)$ Å	$\mu = 4.194$ mm⁻¹
$c = 7.858\,(2)$ Å	$T = 294\,(2)$ K
$\beta = 96.41\,(3)°$	Plate
$V = 328.2\,(1)$ Å³	$0.25 \times 0.25 \times 0.13$ mm
$Z = 2$	Orange
$D_x = 3.024$ Mg m⁻³	
D_m not measured	

Data collection

Rigaku AFC-5R diffractometer	630 reflections with $I > 2\sigma(I)$
$\omega-2\theta$ scans	$R_{int} = 0.033$
Absorption correction:	$\theta_{max} = 26°$
ψ scan (North *et al.*, 1968)	$h = 0 \rightarrow 6$
	$k = 0 \rightarrow 10$
$T_{min} = 0.366$, $T_{max} = 0.580$	$l = -9 \rightarrow 9$
774 measured reflections	3 standard reflections
691 independent reflections	every 100 reflections
	intensity decay: 1.2%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$\Delta\rho_{max} = 0.739$ e Å^{-3}
$wR(F^2) = 0.102$	$\Delta\rho_{min} = -0.816$ e Å^{-3}
$S = 1.173$	Extinction correction:
691 reflections	*SHELXL93*
62 parameters	Extinction coefficient:
H atoms not refined	0.020 (6)
$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2$ $+ 0.3653P]$ where $P = (F_o^2 + 2F_c^2)/3$	Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
V1	0.4162 (2)	1/4	0.57407 (11)	0.0085 (3)
V2	-0.06299 (11)	0.05451 (7)	0.68499 (7)	0.0087 (3)
O1	0.6192 (7)	1/4	0.4308 (5)	0.0146 (8)
O2	0.1859 (5)	0.0866 (3)	0.5052 (3)	0.0121 (6)
O3	0.6143 (5)	0.0987 (3)	0.7329 (3)	0.0113 (6)
O4	0.0909 (7)	1/4	0.7566 (5)	0.0102 (7)
O5	0.0624 (5)	-0.0669 (3)	0.8295 (4)	0.0163 (7)
N1	0.4441 (11)	1/4	0.0633 (7)	0.0309 (13)

Table 2. *Selected geometric parameters (Å, °)*

V1—O1	1.597 (4)	V2—O3^i	1.736 (2)
V1—O2	1.835 (3)	V2—O4	1.876 (2)
V1—O3	1.971 (3)	V2—O2^{ii}	1.954 (3)
V1—O4	2.284 (4)	V2—O2	2.001 (3)
V2—O5	1.602 (3)	V2—O1^i	2.917 (3)
O1—V1—O2	102.6 (2)	O5—V2—O4	103.4 (2)
O2—V1—O2^{iii}	97.1 (2)	O3^i—V2—O4	96.1 (1)
O2—V1—O3^{iii}	157.6 (1)	O5—V2—O2^{ii}	102.6 (2)
O1—V1—O3	97.6 (2)	O3^i—V2—O2^{ii}	94.4 (1)
O2—V1—O3	87.5 (1)	O4—V2—O2^{ii}	147.8 (1)
O3^{iii}—V1—O3	80.5 (2)	O5—V2—O2	111.2 (1)
O1—V1—O4	174.1 (2)	O3^i—V2—O2	142.1 (1)
O2—V1—O4	73.7 (1)	O4—V2—O2	80.0 (2)
O3—V1—O4	86.8 (1)	O2^{ii}—V2—O2	73.1 (1)
O5—V2—O3^i	106.4 (2)		

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

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O4^i	0.97	1.86	2.823 (6)	175
N1—H2⋯O5^{ii}	0.89	2.15	2.949 (5)	150
N1—H3⋯O5^{iii}	0.89	2.51	3.156 (5)	130

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

All H atoms were located from a difference Fourier map and were fixed at ideal positions with common isotropic displacement parameters ($U_{iso} = 0.05$ Å^2).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1987*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1987*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

References

Block, S. (1960). *Nature*, **186**, 540–541.
Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B41, 244–247.
Evens, H. T. Jr & Block, S. (1966). *Inorg. Chem.* 5, 1808–1814.
Kelmers, A. D. (1961*a*). *J. Inorg. Nucl. Chem.* 17, 168–173.
Kelmers, A. D. (1961*b*). *J. Inorg. Nucl. Chem.* 21, 45–48.
Molecular Structure Corporation (1987*a*). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1987*b*). *TEXSAN. TEXRAY Structure Analysis Software*. Version 2.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Norblad, J. A. (1875). *Bull. Soc. Chim. Fr.* 23, 64–67.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.
Sheldrick, G. M. (1990*a*). *Acta Cryst.* A46, 467–473.
Sheldrick, G. M. (1990*b*). *SHELXTL/PC User's Manual*. Version 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

The low-temperature tetragonal phase of NiCr2O4

Go Ueno, Shoichi Sato and Yoshihiro Kino

X-ray Research Laboratory, Rigaku Corporation, 3-9-12 Matsubara, Akishima, Tokyo 196-8666, Japan. E-mail: ueno@rigaku.co.jp

Abstract

The title compound, normal spinel nickel chromite, NiCr$_2$O$_4$, undergoes a cubic to tetragonal phase tran-