Acta Cryst. (1999). C**55**, 1048–1050

A potassium sodium double salt of metavanadate, KNa(VO$_3$)$_2$

YONGKUI SHAN AND SONGPING D. HUANG*†

Department of Chemistry, University of Puerto Rico, PO Box 23346, San Juan, PR 00931, USA. E-mail: shuang1@kent.edu

(*Received 25 March 1998; accepted 21 December 1998*)

Abstract

Potassium sodium metavanadate, KNa(VO$_3$)$_2$, crystallizes with the pyroxene structure and is made up of VO$_4$ tetrahedral chains, NaO$_6$ octahedra and KO$_8$ dodecahedra. The chains of corner-sharing VO$_4$ tetrahedra are crosslinked through the NaO$_6$ octahedra and KO$_8$ dodecahedra to form a three-dimensional structure with the K$^+$ and Na$^+$ cations, which lie on twofold axes, situated in the void space. The coordination around the Na$^+$ ion is close to normal octahedral, while the O atoms coordinated to the K$^+$ ion are arranged approximately in a dodecahedral fashion.

Comment

A number of alkali and alkaline-earth metal metavanadates and their solid solutions have found applications as ferroelectrics (Rasal *et al.*, 1992; Chavan & Kulkarni, 1993), solid-state battery materials (Kashid *et al.*, 1991; Patil *et al.*, 1992) and pyroelectrics (Pawar *et al.*, 1993; Patil *et al.*, 1990).

Numerous attempts have been made to investigate single-crystal structures of metavanadates in order to study their chemical and physical properties under the influence of different cations. For example, with K$^+$, NH$_4^+$, Rb$^+$ and Cs$^+$ as cations in the anhydrous metavanadates, infinite chain structures with tetrahedrally coordinated vanadium are found (Evans, 1960). Anhydrous sodium vanadate forms a similar structure in its α form (Marumo *et al.*, 1974). The structures of the hydrated metavanadates KVO$_3$·H$_2$O (Evans, 1960), NaVO$_3$·1.8H$_2$O (Bjornberg & Hedman, 1977) and β-NaVO$_3$ (Kato & Takayama, 1984) usually consist of five-coordinated trigonal-bipyramid chains. Because of the different nature of the cation in each crystal, there are rather moderate differences in the overall structures in these compounds with respect to the cation–oxygen arrangements. For example, the K$^+$ cation is surrounded irregularly by ten O atoms in KVO$_3$ (Evans, 1960), while the corresponding Na$^+$ cation is coordinated by six O atoms in α-NaVO$_3$ (Marumo *et al.*, 1974). The subject of the present investigation is the crystal structure of the double salt of metavanadate, KNa(VO$_3$)$_2$, which is of interest for the systematic study of vanadates and their applications. Such a system has been studied previously using molten-salt methods (Perraud, 1974).

The title compound was prepared by a hydrothermal synthesis. The compound adopts the pyroxene structure type and is built up from zigzag corner-sharing VO$_4$ tetrahedra to form $[VO_3]_n^{n-}$ chains along the *c* axis. Every two $[VO_3]_n^{n-}$ chains are paired up, facing each other with either their apices or bases, so that two different types of cavities are created between the chains, *i.e.* octahedra and dodecahedra, which are occupied by the Na$^+$ and K$^+$ cations, respectively. The three-dimensional structure of the title compound is shown in Fig. 1. Each pair of octahedral sites alternates with two dodecahedral sites along the *b* direction. Therefore, there is no cation disorder, and both the Na$^+$ and K$^+$ ions are distributed non-statistically over the two sites to form a solid solution. The six O atoms that form an octahedron around the Na$^+$ cation are the terminal O atoms of the four neighbouring $[VO_3]_n^{n-}$ chains. Four of the eight O atoms arranged around the K$^+$ cation are the bridging O atoms belonging to two different $[VO_3]_n^{n-}$ chains. The other four O atoms are the terminal ones from the four

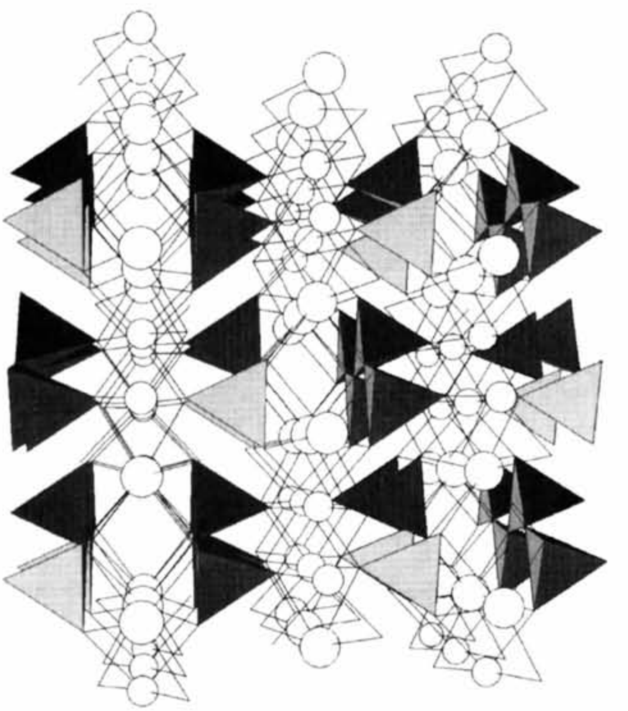

Fig. 1. The three-dimensional structure of KNa(VO$_3$)$_2$. The VO$_4$ groups are represented by tetrahedra. The larger circles are K$^+$ cations and the smaller circles are Na$^+$.

† Present address: Department of Chemistry, Kent State University, Kent, OH 44242, USA.

ISSN 0108-2701 © 1999

neighbouring $[VO_3]_n^{n-}$ chains. The bond length between vanadium and the bridging O atom is 1.808 (2) Å, which is longer than those between the vanadium and terminal O atoms of 1.639 (3) and 1.649 (2) Å. This tendency is well known in other compounds containing chains of V–O tetrahedra (Marumo *et al.*, 1974). The Na—O distances range from 2.397 (2) to 2.420 (3) Å, and the K—O distances vary between 2.719 (3) and 2.954 (2) Å.

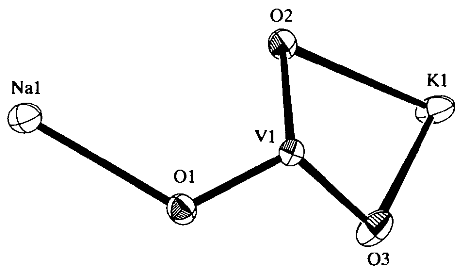

Fig. 2. An *ORTEP*II (Johnson, 1976) representation of the title compound showing 50% probability displacement ellipsoids.

Experimental

The title compound was prepared by a hydrothermal synthesis. $Na_2B_4O_7$ (100 mg, 0.5 mmol), $NaVO_3$ (61 mg, 0.5 mmol) and KH_2PO_4 (68 mg, 0.5 mmol) were sealed with 0.5 ml distilled water in a thick-walled Pyrex tube. The reaction was carried out at 383 K for 3 d affording light-yellow single crystals of $KNa(VO_3)_2$ in about 40% yield.

Crystal data

$KNa(VO_3)_2$	Mo $K\alpha$ radiation
$M_r = 259.97$	$\lambda = 0.7107$ Å
Monoclinic	Cell parameters from 1277 reflections
$C2/c$	$\theta = 2.83$–$26.95°$
$a = 10.581$ (1) Å	$\mu = 3.823$ mm^{-1}
$b = 10.089$ (1) Å	$T = 296$ K
$c = 5.8151$ (8) Å	Prism
$\beta = 103.894$ (2)°	0.06 × 0.06 × 0.04 mm
$V = 602.6$ (1) Å^3	Yellow
$Z = 4$	
$D_x = 2.865$ Mg m^{-3}	
D_m not measured	

Data collection

Quantum CCD diffractometer	485 reflections with $I > 3\sigma(I)$
ω scans	$R_{int} = 0.019$
Absorption correction: simulated ψ scans (Sheldrick, 1996)	$\theta_{max} = 26.95°$
	$h = -13 \rightarrow 8$
	$k = -12 \rightarrow 11$
$T_{min} = 0.693$, $T_{max} = 0.858$	$l = -6 \rightarrow 7$
1572 measured reflections	
636 independent reflections	

Refinement

Refinement on F	$\Delta\rho_{max} = 0.54$ e Å^{-3}
$R = 0.025$	$\Delta\rho_{min} = -0.34$ e Å^{-3}
$wR = 0.037$	Extinction correction: Zachariasen (1967)
$S = 0.831$	
485 reflections	Extinction coefficient: $1.6(3) \times 10^{-6}$
48 parameters	
$w = 1/[\sigma^2(F_o) + 0.00148\vert F_o\vert^2]$	Scattering factors from *International Tables for Crystallography* (Vol. C)
$(\Delta/\sigma)_{max} = 0.0001$	

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	0.21422 (5)	0.08536 (6)	0.27881 (8)	0.0116 (2)
K1	0	0.1920 (1)	−1/4	0.0220 (3)
Na1	1/2	−0.0957 (2)	1/4	0.0189 (5)
O1	0.3748 (2)	0.0874 (2)	0.3478 (4)	0.0175 (6)
O2	0.1539 (2)	−0.0148 (2)	0.0177 (4)	0.0162 (6)
O3	0.1558 (3)	0.2350 (3)	0.2167 (4)	0.0234 (7)

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

V1—O1	1.649 (2)	K1—O2^{vi}	2.954 (2)
V1—O2	1.808 (2)	K1—O3	2.850 (2)
V1—O2^{i}	1.808 (2)	K1—O3^{v}	2.850 (2)
V1—O3	1.639 (3)	Na1—O1	2.420 (3)
K1—O1^{ii}	2.719 (3)	Na1—O1^{vi}	2.397 (2)
K1—O1^{iii}	2.719 (3)	Na1—O1^{vii}	2.420 (3)
K1—O2	2.865 (2)	Na1—O1^{viii}	2.397 (2)
K1—O2^{iv}	2.954 (2)	Na1—O3^{ix}	2.413 (3)
K1—O2^{v}	2.865 (2)	Na1—O3^{x}	2.413 (3)
O1—V1—O2	110.3 (1)	O2—K1—O3	58.02 (7)
O1—V1—O2^{i}	110.6 (1)	O2—K1—O3^{v}	138.71 (8)
O1—V1—O3	110.7 (1)	O2^{iv}—K1—O2^{vi}	105.5 (1)
O2—V1—O2^{i}	107.84 (7)	O2^{iv}—K1—O3	85.00 (7)
O2—V1—O3	106.9 (1)	O2^{iv}—K1—O3^{v}	105.75 (7)
O2^{i}—V1—O3	110.4 (1)	O3—K1—O3^{v}	162.5 (1)
O1^{ii}—K1—O1^{iii}	70.2 (1)	O1—Na1—O1^{vi}	89.83 (8)
O1^{ii}—K1—O2	117.88 (7)	O1—Na1—O1^{vii}	80.4 (1)
O1^{ii}—K1—O2^{iv}	160.17 (7)	O1—Na1—O1^{viii}	87.13 (9)
O1^{ii}—K1—O2^{v}	136.41 (6)	O1—Na1—O3^{ix}	169.22 (8)
O1^{ii}—K1—O2^{vi}	92.86 (7)	O1—Na1—O3^{x}	95.64 (9)
O1^{ii}—K1—O3	82.82 (7)	O1^{vi}—Na1—O1^{viii}	176.0 (1)
O1^{ii}—K1—O3^{v}	82.86 (7)	O1^{vi}—Na1—O3^{ix}	100.05 (8)
O2—K1—O2^{iv}	67.32 (8)	O1^{vi}—Na1—O3^{x}	82.80 (8)
O2—K1—O2^{v}	86.53 (9)	O3^{ix}—Na1—O3^{x}	89.9 (1)
O2—K1—O2^{vi}	60.27 (4)		

Symmetry codes: (i) $x, -y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (iv) $-x, -y, -z$; (v) $-x, y, -\frac{1}{2} - z$; (vi) $x, -y, z - \frac{1}{2}$; (vii) $1 - x, y, \frac{1}{2} - z$; (viii) $1 - x, -y, 1 - z$; (ix) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (x) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1997). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

This work was supported by the NSF–EPSCoR (grant No. OSR-9452893) and the DOE–EPSCoR (DE-FC02-91ER75674). We thank the National Institutes of Health for a grant in support of the purchase of a Bruker CCD SMART diffractometer (3S06GM08102-25S1/M1HREV).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1213). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

Bjornberg, A. & Hedman, B. (1977). *Acta Chem. Scand. Ser. A*, **31**, 579–584.

Chavan, S. H. & Kulkarni, A. J. (1993). *Phys. Status Solidi A*, **135**, 307–314.

Evans, H. T. Jr (1960). *Z. Kristallogr.* **114**, 257–277.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kashid, A. P., Patil, V. V. & Patil, R. T. (1991). *Indian J. Pure Appl. Phys.* **29**, 49–51.

Kato, K. & Takayama, E. (1984). *Acta Cryst.* B**40**, 102–105.

Marumo, F., Isobe, M. & Iwai, S. (1974). *Acta Cryst.* B**30**, 1628–1630.

Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1997). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Patil, R. T., Patil, N. B. & Kashid, A. P. (1992). *Electrochim. Acta*, **37**, 1143–1145.

Patil, V. V., Kashid, A. P. & Chavan, S. H. (1990). *Indian J. Pure Appl. Phys.* **28**, 427–428.

Pawar, D. V., Rasal, P. & Chavan, S. H. (1993). *Ferroelectrics*, **142**, 137–143.

Perraud, J. C. (1974). *Rev. Chim. Miner.* **11**, 302–326.

Rasal, S. P., Kashid, A. P. & Pawar, D. V. (1992). *Indian J. Phys. A*, **66**, 755–760.

Sheldrick, G.M. (1996). *SADABS. Program for Absorption Correction.* University of Göttingen, Germany.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.