

# Sodium trirubidium metavanadate monohydrate

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## Key indicators

Single-crystal X-ray study  
T = 150 K  
Mean  $\sigma(\text{V}-\text{O}) = 0.002 \text{ \AA}$   
R factor = 0.034  
wR factor = 0.077  
Data-to-parameter ratio = 21.2

For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound, sodium trirubidium metavanadate monohydrate,  $\text{NaRb}_3(\text{VO}_3)_4(\text{H}_2\text{O})$ , crystallizes in the orthorhombic space group  $Pnma$ . The structure, which represents a rare type of *catena*-vanadate, is built up of strongly folded chains of corner-sharing  $[\text{VO}_4]$  tetrahedra, running in the  $[010]$  direction with a periodicity of four. A three-dimensional framework is obtained by sodium ions linking adjacent chains in the  $[001]$  direction and by rubidium ions linking adjacent chains in the  $[100]$  direction. The single water molecule binds to the sodium ion and to two rubidium ions.

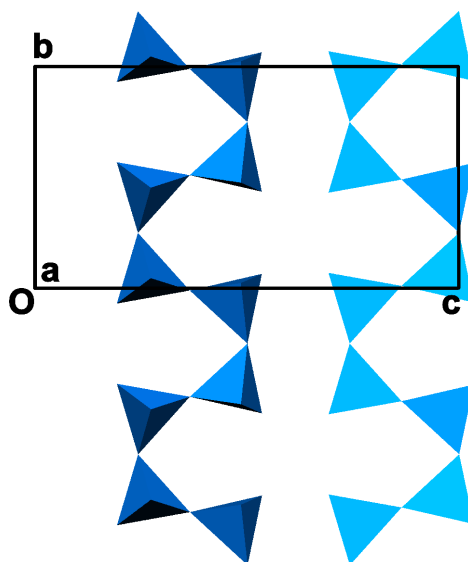
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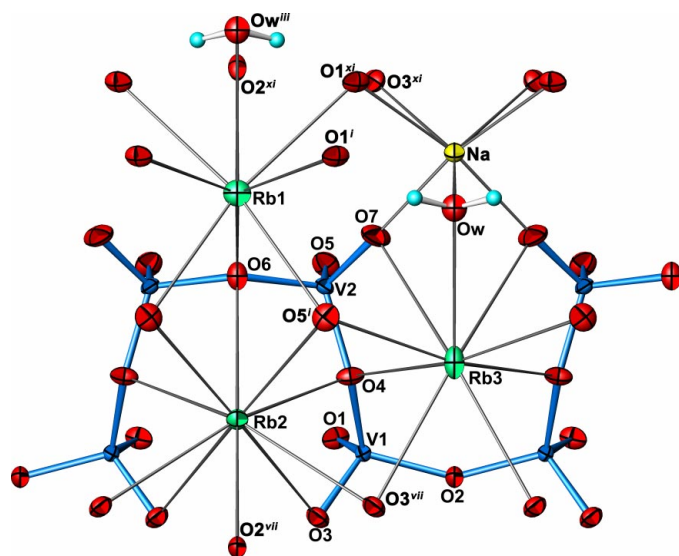
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## Comment

As part of a continuing research project, vanadate–organic ligand systems of biomedical interest are studied. The primary aim is to determine the complete speciation by using potentiometry and multinuclear NMR (with emphasis on  $^{51}\text{V}$ ). In the ongoing study of the vanadocitrate (V-Cit) system, a series of anionic divanadocitrate species were found to be formed, having charges  $-4$ ,  $-3$  and  $-2$ . Our goal is also to determine the aqueous and solid structures of species formed. No X-ray structures of these species have been published and therefore extensive crystallization experiments have been performed and are still in progress. So far, we have not been able to obtain single crystals of any divanadocitrate species, but crystals of other compounds have been found. We report here the structure of a mixed cation metavanadate,  $\text{NaRb}_3(\text{VO}_3)_4(\text{H}_2\text{O})$ .



**Figure 1**  
View of the metavanadate chains.



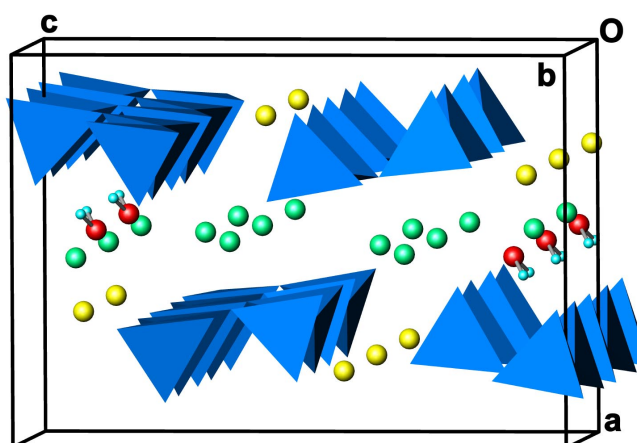
**Figure 2**

The coordination of  $\text{Rb}^+$  and  $\text{Na}^+$  ions in the title structure with the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. The blue bonds show the metavanadate chain. The unlabeled atoms are related to the labeled by the mirror planes running through  $\text{O}_w$ ,  $\text{O}_2$ ,  $\text{Rb1}$ ,  $\text{O}_6$ ,  $\text{Rb2}$  and  $\text{Na}$ ,  $\text{O}_w$ ,  $\text{Rb3}$ ,  $\text{O}_2$ , respectively. Symmetry codes are given in Table 1.

The title compound possesses a rare type of metavanadate chain structure, built up of corner-sharing  $[\text{VO}_4]$  tetrahedra. The chains, which are strongly folded with a periodicity of four, run in the  $[010]$  direction (Fig. 1). The folding is described by the angles  $\text{V2}-\text{O6}-\text{V2}$ ,  $\text{O6}-\text{V2}-\text{O4}$ ,  $\text{V2}-\text{O4}-\text{V1}$ ,  $\text{O4}-\text{V1}-\text{O2}$  and  $\text{V1}-\text{O2}-\text{V1}$  (Fig. 2 and Table 1). A three-dimensional framework is obtained by sodium ions linking adjacent chains in the  $[001]$  direction and by rubidium ions linking adjacent chains in the  $[100]$  direction (Fig. 3).

The vanadate tetrahedra have angles and  $\text{V}-\text{O}$  distances common for vanadate chain structures (Table 1). The sodium ion is coordinated by six vanadate O atoms and a water molecule within distances ranging from 2.282 (2) to 2.705 (3) Å, and with a mean distance of 2.470 (8) Å. There are three crystallographically different rubidium ions. If distances shorter than 3.4 Å are considered,  $\text{Rb1}$  is coordinated by nine O atoms between 2.892 (4) and 3.382 (4) Å (including a water molecule), with a mean distance of 3.123 (10) Å,  $\text{Rb2}$  coordinate ten O atoms within 2.837 (3)–3.324 (2) Å, with a mean distance of 3.127 (9) Å, and  $\text{Rb3}$  coordinate nine O atoms (including a water molecule), within 2.946 (2)–3.335 (3) Å, with a mean distance of 3.126 (8) Å (Table 1 and Fig. 2).

An isotopic structure,  $\text{NaCs}_3(\text{VO}_3)_4(\text{H}_2\text{O})$ , was briefly described by Elvingson (1997). The structure of  $\text{Th}(\text{VO}_3)_2\text{O}$  (Launay *et al.*, 1992), contains similar folded chains arranged in layers. In addition, however, this structure also contains isolated vanadate tetrahedra. In the large group of silicate chain structures, there are several examples of a periodicity of four tetrahedra. A close resemblance exists between the



**Figure 3**

Packing diagram showing the metavanadate chains and the positions of the rubidium ions, sodium ions, water O and H atoms (green, yellow, red and blue spheres of arbitrary size, respectively).

present structure and that of  $\text{Cu}_3\text{Na}_2(\text{SiO}_3)_4$  (Kawamura & Kawahara, 1976) with respect to both the features and the packing of the chains.

## Experimental

1 ml of methanol was added to 1.2 ml of an aqueous pH 7.6 solution containing  $[\text{V}^{5+}]_{\text{tot}} = 670 \text{ mM}$ ,  $[\text{Cit}]_{\text{tot}} = 420 \text{ mM}$ ,  $[\text{Na}^+]_{\text{tot}} = 1580 \text{ mM}$  and  $[\text{Rb}^+]_{\text{tot}} = 330 \text{ mM}$ , and the resulting solution was allowed to evaporate at room temperature. Pale yellow crystals of appropriate dimensions formed within hours.

### Crystal data

$\text{NaRb}_3(\text{VO}_3)_4(\text{H}_2\text{O})$   
 $M_r = 693.18$   
 Orthorhombic,  $Pnma$   
 $a = 11.1610$  (5) Å  
 $b = 8.3050$  (11) Å  
 $c = 15.8180$  (8) Å  
 $V = 1466.2$  (2) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 3.140 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 2407 reflections  
 $\theta = 2.9$ – $33.1^\circ$   
 $\mu = 12.45 \text{ mm}^{-1}$   
 $T = 150 \text{ K}$   
 Prism, light yellow  
 $0.14 \times 0.13 \times 0.10 \text{ mm}$

### Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (HKL SCALEPACK;  
 Otwinowski & Minor, 1997)  
 $T_{\text{min}} = 0.203$ ,  $T_{\text{max}} = 0.288$   
 24175 measured reflections

2271 independent reflections  
 2175 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.083$   
 $\theta_{\text{max}} = 30.0^\circ$   
 $h = -15 \rightarrow 15$   
 $k = -11 \rightarrow 11$   
 $l = -22 \rightarrow 22$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.077$   
 $S = 1.14$   
 2271 reflections  
 107 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0136P)^2 + 4.7048P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 1.09 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.87 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.0036 (5)

**Table 1**

Selected geometric parameters (Å, °).

Rb1—O6	2.892 (4)	Rb3—O3 <sup>ix</sup>	3.190 (2)
Rb1—O1 <sup>i</sup>	3.029 (2)	Rb3—O7	3.335 (3)
Rb1—O5 <sup>i</sup>	3.046 (3)	V1—O3	1.632 (2)
Rb1—O1 <sup>ii</sup>	3.194 (3)	V1—O1	1.648 (2)
Rb1—Ow <sup>iii</sup>	3.299 (4)	V1—O2 <sup>x</sup>	1.8025 (10)
Rb1—O2 <sup>iv</sup>	3.382 (4)	V1—O4	1.804 (2)
Rb2—O2 <sup>v</sup>	2.837 (3)	V2—O7	1.624 (3)
Rb2—O4	2.986 (3)	V2—O5	1.641 (2)
Rb2—O5 <sup>vi</sup>	3.132 (3)	V2—O6	1.8064 (15)
Rb2—O6	3.140 (4)	V2—O4	1.815 (2)
Rb2—O3 <sup>vii</sup>	3.203 (3)	Na—O7	2.282 (3)
Rb2—O3 <sup>viii</sup>	3.324 (2)	Na—Ow	2.349 (4)
Rb3—O5 <sup>i</sup>	2.946 (3)	Na—O1 <sup>xi</sup>	2.483 (3)
Rb3—O4	3.033 (3)	Na—O3 <sup>xi</sup>	2.705 (3)
Rb3—Ow	3.127 (4)		
O3—V1—O1	108.47 (13)	O5—V2—O6	110.22 (15)
O3—V1—O2 <sup>x</sup>	109.15 (14)	O7—V2—O4	108.21 (13)
O1—V1—O2 <sup>x</sup>	110.18 (15)	O5—V2—O4	113.59 (12)
O3—V1—O4	109.36 (12)	O6—V2—O4	107.07 (15)
O1—V1—O4	109.47 (11)	V2 <sup>viii</sup> —O6—V2	134.5 (2)
O2 <sup>x</sup> —V1—O4	110.19 (14)	V1 <sup>xii</sup> —O2—V1 <sup>xiii</sup>	150.6 (2)
O7—V2—O5	110.13 (15)	V1—O4—V2	135.92 (14)
O7—V2—O6	107.39 (16)		

Symmetry codes: (i)  $x - \frac{1}{2}, y, \frac{3}{2} - z$ ; (ii)  $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$ ; (iii)  $1 - x, 1 - y, 2 - z$ ; (iv)  $\frac{3}{2} - x, -y, \frac{1}{2} + z$ ; (v)  $1 - x, -y, 1 - z$ ; (vi)  $x - \frac{1}{2}, \frac{3}{2} - y, \frac{3}{2} - z$ ; (vii)  $1 - x, 1 - y, 1 - z$ ; (viii)  $x, \frac{3}{2} - y, z$ ; (ix)  $1 - x, y - \frac{1}{2}, 1 - z$ ; (x)  $x, 1 + y, z$ ; (xi)  $\frac{3}{2} - x, 1 - y, \frac{1}{2} + z$ ; (xii)  $x, y - 1, z$ ; (xiii)  $x, -\frac{1}{2} - y, z$ .

The H atoms of the water molecule were located in a difference Fourier map, fixed at a distance of 0.97 Å and refined using a riding

model with  $U_{(\text{iso})}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ . The highest peak and deepest hole in the difference density map are located at distances of 1.58 and 0.73 Å from atoms H8 and Rb3, respectively.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997) and local procedures.

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