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Lian-Bang Wang<sup>a</sup><sup>a</sup>State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology and College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 320014, People's Republic of China, and<sup>b</sup>Department of Chemistry, Shangrao Normal College, Shangrao 334001, People's Republic of China

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## Key indicators

Single-crystal X-ray study

T = 273 K

Mean  $\sigma(V-O) = 0.001 \text{ \AA}$ 

R factor = 0.027

wR factor = 0.097

Data-to-parameter ratio = 16.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Polymeric bis(lithium disodium nonahydrate) decavanadate,  $[\text{LiNa}_2(\text{H}_2\text{O})_9]_2[\text{V}_{10}\text{O}_{28}]_n$ 

The crystal structure of the title compound, poly-[deca- $\mu$ -aqua-octaaqua- $\mu$ -decavanadato-dilithium(I)tetrasodium(I)]  $[\text{Li}_2\text{Na}_4(\text{H}_2\text{O})_{18}[\text{V}_{10}\text{O}_{28}]]_n$ , consists of polymeric chains composed of centrosymmetric  $[\text{V}_{10}\text{O}_{28}]^{6-}$  polyanions with  $C_i$  symmetry linked by  $[\text{LiNa}_2(\text{H}_2\text{O})_9]^{3+}$  cation groups *via* O-polyanion—Na-group—O-polyanion coordination, with Na—O bond lengths of 2.366 (2)—2.495 (2) Å. The lithium disodium nonahydrate is composed of two  $\text{NaO}_6$  octahedra and one  $\text{LiO}_4$  tetrahedron. Hydrogen bonds occur between the polyanion and the cation group, and within the cation group. Intrachain  $\text{OW}-\text{H}\cdots\text{O}$  hydrogen bonds stabilize the polymeric chain structure, while interchain  $\text{OW}-\text{H}\cdots\text{O}$  hydrogen bonds link neighbouring polymeric chains to form the complete supramolecular structure.

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## Comment

Recently, the decavanadate double salts of alkali metals with other alkali metal or ammonium ions have been reported, *viz.*  $\text{K}_4\text{Na}_2[\text{V}_{10}\text{O}_{28}]\cdot 10\text{H}_2\text{O}$  (Lee & Joo, 2003),  $\text{K}_2\text{Na}_4[\text{V}_{10}\text{O}_{28}]\cdot 18\text{H}_2\text{O}$  (Lee & Joo, 2004),  $(\text{NH}_4)_4\text{Na}_2[\text{V}_{10}\text{O}_{28}]\cdot 10\text{H}_2\text{O}$  (Fratzky *et al.*, 2000),  $(\text{NH}_4)_4\text{Li}_2(\text{V}_{10}\text{O}_{28})\cdot 10\text{H}_2\text{O}$  (KsiKsi *et al.*, 2004) and  $[\text{Li}(\text{H}_2\text{O})_4]_2[\text{N}(\text{CH}_3)_4][\text{V}_{10}\text{O}_{28}]\cdot 4\text{H}_2\text{O}$  (Zavalij *et al.*, 1997). However, no alkali metal double salt with lithium has yet been reported. We present here the structure of the title compound, bis(lithium disodium nonahydrate) decavanadate, (I), a polymeric  $[\text{V}_{10}\text{O}_{28}]^{6-}$  compound bridged by a lithium disodium nonahydrate cation group.

Compound (I) contains  $[\text{V}_{10}\text{O}_{28}]^{6-}$  polyanions and  $[\text{LiNa}_2(\text{H}_2\text{O})_9]^{3+}$  cation groups (Fig. 1). The centrosymmetric polyanion is composed of ten  $[\text{VO}_6]$  octahedra combined *via* shared edges and shared corners; the array of O and V atoms in the polyanion is the same as those in  $[\text{Li}_6(\text{H}_2\text{O})_{16}\text{V}_{10}\text{O}_{28}]_n$

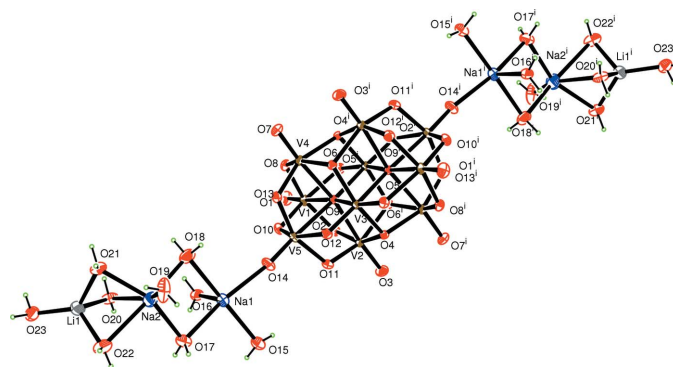
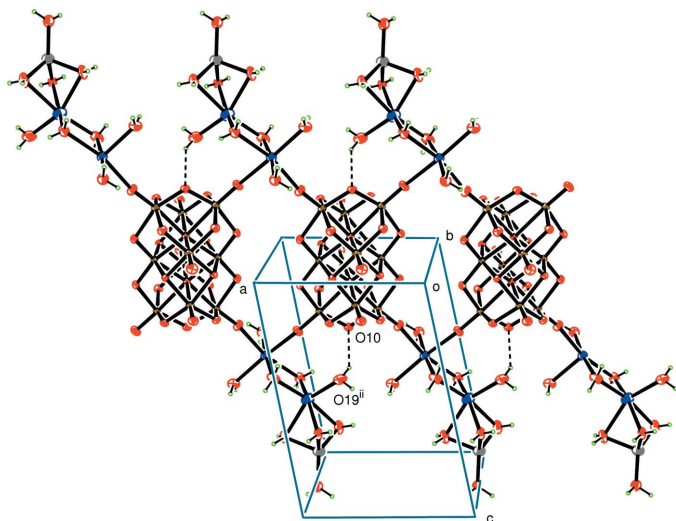


Figure 1

The structure of (I), with 40% probability displacement ellipsoids, showing the labelling of the atoms [Symmetry code: (i)  $x - 1, y, z$ ].



**Figure 2**  
The structure of the chains in  $[\text{LiNa}_2(\text{H}_2\text{O})_9]_2[\text{V}_{10}\text{O}_{28}]_n$  shown in the  $ac$  plane. The intrachain hydrogen bond is shown as a broken line. [Symmetry code: (ii)  $-x, -y + 2, -z + 1$ .]

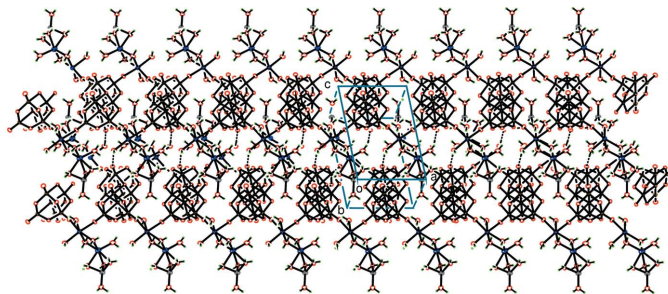
(Xie & Ma, 2005). However, the  $[\text{LiNa}_2(\text{H}_2\text{O})_9]^{3+}$  cation group in (I) is non-centrosymmetric, while  $[\text{Li}_6(\text{H}_2\text{O})_{16}]^{6-}$  is centrosymmetric,  $C_i$ .

In the  $[\text{V}_{10}\text{O}_{28}]^{6-}$  polyanion structure, the  $\text{V}-\text{O}$  distances are in the range 1.594 (1)–1.603 (2) Å, the  $\text{V}-\text{O}-\mu_2$  distances are in the range 1.685 (2)–2.056 (1) Å, the  $\text{V}-\text{O}-\mu_3$  distances are in the range 1.871 (2)–2.026 (1) Å and the  $\text{V}-\text{O}-\mu_6$  distances are in the range 2.099 (1)–2.335 (1) Å. The bond lengths and angles of the  $[\text{V}_{10}\text{O}_{28}]^{6-}$  polyanion show a similar trend to those found in the literature (Kamenar *et al.*, 1996; Choi & Chang, 2003; Xie & Ma, 2005).

In the  $[\text{LiNa}_2(\text{H}_2\text{O})_9]^{3+}$  cation group, the Na1, Na2 and Li1 ions are coordinated by six, six and four O atoms, respectively, all but two of which belong to coordinated water molecules. In the  $(\text{Na}1\text{O}_6)$  octahedron, two O atoms belong to two different  $[\text{V}_{10}\text{O}_{28}]^{6-}$  polyanions, and two define an edge that is shared with  $\text{Na}2\text{O}_6$ . One face of the Na2 octahedron is also shared with the  $(\text{Li}1\text{O}_4)$  tetrahedron. The bond lengths and angles of the cation group are normal and are listed in Table 1.

The  $\text{Na}2\text{O}_6$  octahedron is more distorted than that of  $\text{Na}1\text{O}_6$ , as can be seen in the large bond angles of 97.19 (8)° for  $\text{cis-O}19-\text{Na}2-\text{O}18$  and 111.36 (9)° for  $\text{cis-O}19-\text{Na}2-\text{O}17$ . The widening of these angles may in part be caused by the hydrogen bonds formed by O19 (the intrachain bond  $\text{O}19^{\text{ii}}-\text{H}10^{\text{ii}}\cdots\text{O}10$  is shown in Fig. 2) and in part by the sharing of a face between  $\text{Na}2\text{O}_6$  and  $\text{LiO}_4$ .

The  $[\text{V}_{10}\text{O}_{28}]^{6-}$  polyanions are linked into  $[\text{LiNa}_2(\text{H}_2\text{O})_9]_3-\text{V}_{10}\text{O}_{28}]_n$  chains lying in the  $ac$  plane, as shown in Fig. 2. Na1 in the  $[\text{LiNa}_2(\text{H}_2\text{O})_9]^{3+}$  cation group bonds to the terminal equatorial O14 atom of one polyanion and to the terminal equatorial O1 atom of the neighbouring  $[\text{V}_{10}\text{O}_{28}]^{6-}$  anion. The  $\text{Na}1-\text{O}1$  and  $\text{Na}1-\text{O}14$  bonds thus link polyanions and cation groups into chains that run along the  $a$  axis. Fig. 3 shows how these chains interpenetrate, with the  $\text{LiO}_4$  tetrahedron lying between two decavanadate polyanions of neighbouring chains.



**Figure 3**  
The packing of two chains in  $[\text{LiNa}_2(\text{H}_2\text{O})_9]_2[\text{V}_{10}\text{O}_{28}]_n$ . The interchain  $\text{O}16-\text{H}4\cdots\text{O}7^{\text{iii}}$  hydrogen bond is shown as a broken line. [Symmetry code: (iii)  $-y + 1, -z + 1$ .]

Besides the hydrogen bonds mentioned above, a classical hydrogen-bonding network occurs in the crystal structure of (I). All the water molecules form hydrogen bonds with O atoms on the surface of the decavanadate in a neighbouring chain except the O9 atom, and there are also  $\text{OW}-\text{H}\cdots\text{OW}$  hydrogen-bond interactions. Hydrogen bonds with a distance less than 3.069 (3) Å are listed in Table 2. The chains (shown in Fig. 3) are then linked by hydrogen bonds into a three-dimensional framework; intrachain  $\text{OW}-\text{H}\cdots\text{O}$  hydrogen bonds stabilize the polymeric chains structure, while interchain  $\text{OW}-\text{H}\cdots\text{O}$  hydrogen bonds link neighbouring polymeric chains to form the complete supramolecular structure.

## Experimental

The title compound was prepared by the hydrothermal treatment of  $\text{NH}_4\text{VO}_3$ ,  $\text{LiOH}$ , and  $\text{NaOH}$  (in a 1:0.4:0.2 molar ratio) acidified to pH 5. The reaction mixture was heated for 10 h at 398 K. The filtrate was kept at room temperature and orange single crystals formed after 30 d.

### Crystal data

$[\text{Li}_2\text{Na}_4(\text{H}_2\text{O})_{18}\text{V}_{10}\text{O}_{28}]$   
 $M_r = 1387.51$   
Triclinic,  $P\bar{1}$   
 $a = 8.5386$  (6) Å  
 $b = 10.6333$  (7) Å  
 $c = 11.8912$  (6) Å  
 $\alpha = 105.636$  (3)°  
 $\beta = 101.852$  (3)°  
 $\gamma = 99.257$  (3)°  
 $V = 990.4$  (1) Å<sup>3</sup>

$Z = 1$   
 $D_x = 2.326$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 5541 reflections  
 $\theta = 2.5\text{--}27.5^\circ$   
 $\mu = 2.42$  mm<sup>-1</sup>  
 $T = 273$  (1) K  
Block, orange  
0.40 × 0.30 × 0.20 mm

### Data collection

Rigaku R-AXIS RAPID diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)  
 $T_{\text{min}} = 0.438$ ,  $T_{\text{max}} = 0.616$   
9308 measured reflections

4471 independent reflections  
3990 reflections with  $F^2 > 2\sigma(F^2)$   
 $R_{\text{int}} = 0.024$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -10 \rightarrow 11$   
 $k = -13 \rightarrow 13$   
 $l = -15 \rightarrow 15$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.027$   
 $wR(F^2) = 0.097$   
 $S = 1.02$   
4467 reflections  
280 parameters

H-atom parameters constrained  
 $w = 1/[0.001F_o^2 + \sigma(F_o^2)]/(4F_o^2)$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.48$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.52$  e Å<sup>-3</sup>

**Table 1**  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Na1—O1	2.495 (2)	Na2—O19	2.304 (2)
Na1—O14	2.366 (2)	Na2—O20	2.469 (2)
Na1—O15	2.349 (2)	Na2—O21	2.365 (2)
Na1—O16	2.373 (2)	Na2—O22	2.627 (2)
Na1—O17	2.391 (2)	Li1—O20	1.989 (5)
Na1—O18	2.435 (2)	Li1—O21	1.957 (4)
Na2—O17	2.320 (2)	Li1—O22	1.943 (5)
Na2—O18	2.338 (2)	Li1—O23	1.926 (5)
V5—O14—Na1	169.4 (1)	O18—Na2—O17	90.67 (8)
O14—Na1—O1	82.08 (6)	O19—Na2—O17	111.36 (9)
O15—Na1—O1	100.99 (7)	O20—Na2—O17	93.17 (7)
O16—Na1—O1	165.59 (8)	O21—Na2—O17	157.35 (7)
O17—Na1—O1	86.07 (6)	O19—Na2—O18	97.34 (8)
O18—Na1—O1	72.77 (7)	O20—Na2—O18	97.19 (7)
Na1—O1—V1	165.3 (1)	O21—Na2—O18	105.73 (8)
O15—Na1—O14	85.26 (7)	O20—Na2—O19	151.2 (1)
O16—Na1—O14	95.90 (7)	O21—Na2—O19	82.45 (8)
O17—Na1—O14	166.61 (7)	O21—Na2—O20	69.72 (6)
O18—Na1—O14	95.67 (8)	Na2—O20—Li1	78.1 (1)
O16—Na1—O15	93.03 (6)	Na2—O21—Li1	81.3 (2)
O17—Na1—O15	90.94 (7)	O20—Li1—O21	88.9 (2)
O18—Na1—O15	173.44 (7)	O20—Li1—O22	99.3 (2)
O17—Na1—O16	97.12 (6)	O20—Li1—O23	106.8 (2)
O18—Na1—O16	93.33 (7)	O21—Li1—O22	100.4 (2)
Na1—O17—Na2	92.07 (7)	O21—Li1—O23	129.9 (3)
O18—Na1—O17	86.70 (8)	O22—Li1—O23	122.3 (2)
Na1—O18—Na2	90.55 (8)		

**Table 2**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O15—H1 $\cdots$ O10 <sup>v</sup>	0.91	1.84	2.749 (2)	170
O15—H2 $\cdots$ O16 <sup>v</sup>	0.85	2.01	2.864 (3)	172
O16—H3 $\cdots$ O11 <sup>v</sup>	0.72	2.01	2.738 (2)	173
O16—H4 $\cdots$ O7 <sup>iii</sup>	0.84	1.96	2.806 (3)	175
O17—H5 $\cdots$ O2 <sup>v</sup>	0.88	1.97	2.843 (2)	169
O17—H6 $\cdots$ O15 <sup>ii</sup>	0.78	2.01	2.782 (2)	165
O18—H8 $\cdots$ O8 <sup>iii</sup>	0.89	1.86	2.752 (3)	168
O19—H9 $\cdots$ O13 <sup>iv</sup>	0.87	2.09	2.913 (3)	154
O19—H10 $\cdots$ O10 <sup>i</sup>	0.85	2.33	3.069 (3)	144
O20—H11 $\cdots$ O3 <sup>v</sup>	0.77	2.00	2.765 (2)	168
O20—H12 $\cdots$ O4 <sup>vi</sup>	0.88	1.87	2.744 (2)	172
O21—H13 $\cdots$ O13 <sup>iv</sup>	0.73	2.11	2.828 (2)	165
O21—H14 $\cdots$ O5 <sup>vi</sup>	0.91	1.88	2.778 (2)	166
O22—H15 $\cdots$ O23 <sup>vii</sup>	0.87	2.05	2.919 (2)	166
O22—H16 $\cdots$ O7 <sup>iv</sup>	0.79	2.11	2.882 (2)	164
O23—H17 $\cdots$ O2 <sup>viii</sup>	0.94	1.87	2.789 (2)	163
O23—H18 $\cdots$ O12 <sup>vi</sup>	0.83	2.27	3.068 (2)	159

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

All atoms were found in a difference Fourier map; the H atoms were included in the final cycles of refinement in a riding model, with the O—H distances fixed at the chemically reasonable values found in the difference map, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$ .

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO* (Rigaku, 2002); data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 1996); molecular graphics: *WinGX* (Farrugia, 1999); software used to prepare material for publication: *CrystalStructure*.

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