

Zi-Guang Sun,^a La-Sheng Long,^a
Yan-Ping Ren,^a Rong-Bin
Huang,^a Lan-Sun Zheng^a and
Seik Weng Ng^{b*}

^aState Key Laboratory for Physical Chemistry of Solid Surface, Department of Chemistry, Xiamen University, Xiamen 361005, People's Republic of China, and ^bInstitute of Postgraduate Studies, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail:
h1nswen@umcsd.um.edu.my

Key indicators

Single-crystal X-ray study
T = 298 K
Mean $\sigma(\text{Ni}-\text{O}) = 0.004 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.040
wR factor = 0.100
Data-to-parameter ratio = 11.5

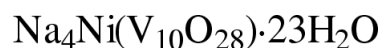
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Tetradecaaquatetrasodium hexaaquanickel(II) decavanadate(V) trihydrate

Three crystallographically independent Na atoms and four pairs of water molecules occupying general positions form the link between the other two independent Na atoms occupying special positions on the inversion centres in the crystal of tetradecaaquatetrasodium hexaaquanickel(II) decavanadate(V) trihydrate, $\text{Na}_4\text{Ni}(\text{V}_{10}\text{O}_{28})\cdot 23\text{H}_2\text{O}$. In this way, the infinite chains made up of the Na atoms and water molecules, and stretching along the $(0\bar{1}1)$ direction, are formed. Each of the two independent Na atoms, which occupy centrosymmetric sites, are coordinated by one of the vanadyl atoms of one of the two independent centrosymmetric $[\text{V}_{10}\text{O}_{28}]^{6-}$ hexaanions, thus effectively linking the chains into infinite layered structure. The layers are further integrated into a three-dimensional network through numerous hydrogen bonds involving water molecules, including those which are part of the sodium chains, as well as those which belong to $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ coordination octahedra and those which are not coordinated by any metal (lattice hydrate molecules).

Comment

The title compound, which has the empirical formulation of $\text{Na}_4\text{Ni}(\text{V}_{10}\text{O}_{28})\cdot 23\text{H}_2\text{O}$, is related to the water-soluble mineral huemulite, $\text{Na}_4\text{Mg}(\text{V}_{10}\text{O}_{28})\cdot 24\text{H}_2\text{O}$ (Gordillo *et al.*, 1966). Both compounds feature the polyhedral $[\text{V}_{10}\text{O}_{28}]^{6-}$ hexaanion, whose structure has been well documented: it contains eight terminal, 14 μ_2 -bridging, four μ_3 -bridging and two μ_6 -bridging O atoms linking ten V atoms into a D_{2h} point-symmetry hexa-anionic species (Capparelli *et al.*, 1986).



(I)

In the crystal structure of the title compound, the Ni atom is coordinated by six water molecules in the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ dication (Fig. 1). Three Na atoms (which are in general positions) and four pairs of bridging water molecules constitute a link between the two other independent Na atoms (which are located at the crystallographic inversion centers), and this unit then continues on to form infinite chains in the $(0\bar{1}1)$ direction (Fig. 2). Each of the Na atoms in general positions, along with the four contacts with bridging water molecules, has two terminal water ligands; however, the Na atoms on the inversion centers, along with four bridging coordinations, are additionally coordinated to the vanadyl atoms (O14 and O16) of each of the two independent $[\text{V}_{10}\text{O}_{28}]^{6-}$ anions (Figs. 3 and 4), these interactions linking the chains into layers. The

Received 4 March 2002
Accepted 25 March 2002
Online 5 April 2002

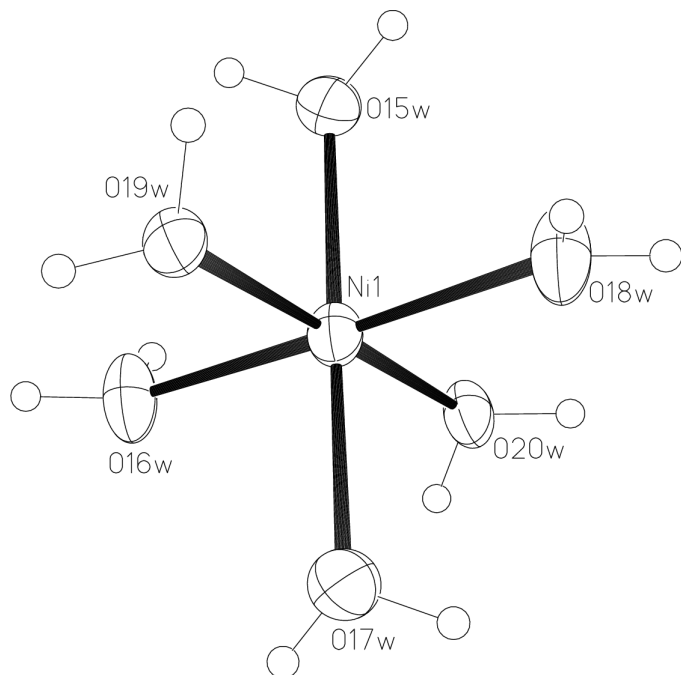


Figure 1
ORTEP (Johnson, 1976) plot of the hexaaquanickel cation, with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

numerous hydrogen bonds connect these negatively charged layers, as well as the otherwise isolated $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ dications and lattice water molecules, into a three-dimensional network.

Decavanadates having an alkylammonium cation as the counter-ion are also known; these are synthesized by the reaction of an amine with vanadium pentoxide (Averbuch-Pouchot, 1995; Averbuch-Pouchot & Durif, 1995).

Experimental

The title compound was the unexpected product of the reaction of equimolar amounts of ammonium metavanadate (0.12 g, 1 mmol), nickel nitrate hexahydrate (0.29 g, 1 mmol) and 1,2,4-benzenetricarboxylic acid anhydride (0.19 g, 1 mmol) in several ml of 50% aqueous ethanol. The pH of the solution was adjusted to approximately 8 by the addition of sodium hydroxide solution. Pink polyhedral crystals separated from the solution after one week.

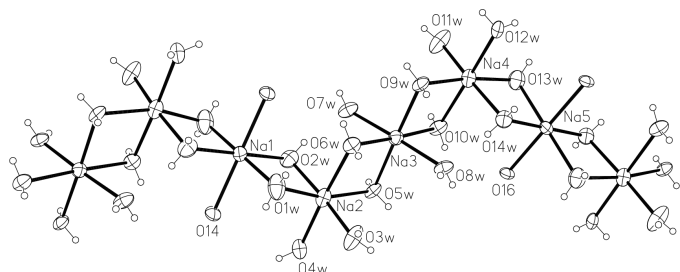


Figure 2
ORTEP (Johnson, 1976) plot, showing the fragment of the infinite chain of coordinated Na atoms in the crystal of the title compound. Displacement ellipsoids are drawn, illustrating the octahedral geometry, at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

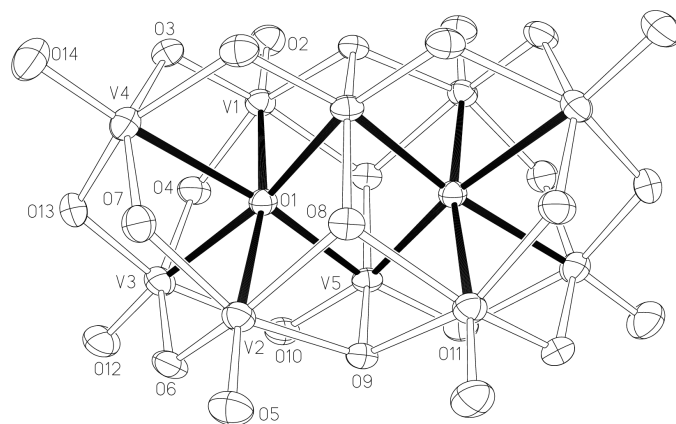


Figure 3
ORTEP (Johnson, 1976) plot of one of the centrosymmetric decavanadate anions, with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

Crystal data

$\text{Na}_4\text{Ni}(\text{V}_{10}\text{O}_{28}) \cdot 23\text{H}_2\text{O}$
 $M_r = 1522.44$
 Triclinic, $P\bar{1}$
 $a = 8.925(2) \text{ \AA}$
 $b = 13.862(3) \text{ \AA}$
 $c = 18.341(4) \text{ \AA}$
 $\alpha = 91.81(3)^\circ$
 $\beta = 91.85(3)^\circ$
 $\gamma = 104.32(3)^\circ$
 $V = 2195.5(8) \text{ \AA}^3$

$Z = 2$
 $D_x = 2.303 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 12.8\text{--}13.9^\circ$
 $\mu = 2.62 \text{ mm}^{-1}$
 $T = 298(2) \text{ K}$
 Block, pink
 $0.50 \times 0.25 \times 0.11 \text{ mm}$

Data collection

Enraf-Nonius CAD-4 diffractometer
 ω scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.245$, $T_{\max} = 0.290$
 9182 measured reflections
 8594 independent reflections
 6270 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$
 $\theta_{\text{max}} = 26.0^\circ$
 $h = 0 \rightarrow 11$
 $k = -17 \rightarrow 16$
 $l = -22 \rightarrow 22$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

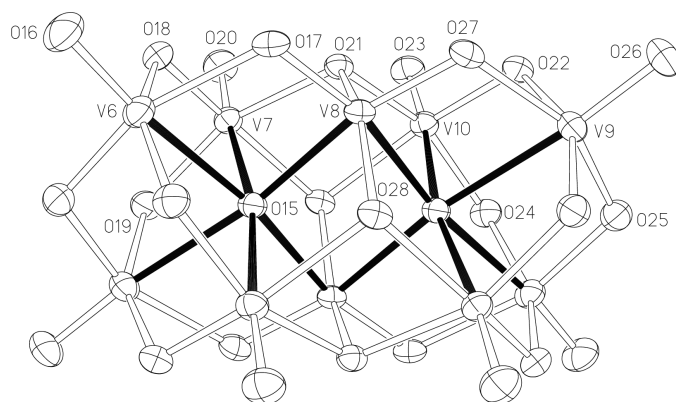


Figure 4
ORTEP (Johnson, 1976) plot of the other centrosymmetric decavanadate anions, with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.100$
 $S = 1.02$
 8594 reflections
 748 parameters
 Only coordinates of H atoms
 refined

$$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 1.0711P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.53 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.56 \text{ e } \text{\AA}^{-3}$

The H atoms of the coordinated water molecules were located and refined, subject to the following restraints: O–H = 0.85 ± 0.01 and H···H = 1.39 ± 0.01 Å; $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. Of the three lattice water molecules, one is disordered over two sites with equal occupancies. One of the H atoms, corresponding to one of the disordered sites, occupies a center of inversion.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1988); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

The authors thank the National Science Foundation of Fujian Province (grant No. E0110001) and the National Natural Science Foundation of China (grants Nos. 2989021 and 20023001) and the University of Malaya (F0717/2002A) for supporting this work.

References

- Averbuch-Pouchot, M. T. (1995). *Z. Kristallogr.* **210**, 371–372.
 Averbuch-Pouchot, M. T. & Durif, A. (1995). *Z. Kristallogr.* **210**, 156–157.
 Capparelli, M. V., Goodgame, D. M. L., Hayman, P. B. & Skapski, A. C. (1986). *J. Chem. Soc. Chem. Commun.* pp. 776–777.
 Enraf–Nonius (1988). *CAD-4 VAX/PC Fortran System*. Enraf–Nonius, Delft, The Netherlands.
 Gordillo, C. E., Linares, E., Toubes, R. O. & Winchell, H. (1966). *Am. Mineral.* **51**, 1–13.
 Harms, K. (1997). *XCAD4*. University of Marburg, Germany.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. Release 97-2. University of Göttingen, Germany.