Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

$[Ni(H_2O)_6]_2[Na(H_2O)_3]_2[V_{10}O_{28}]\cdot 4H_2O$, bis(nickel hexahydrate) bis(sodium trihydrate) decavanadate tetrahydrate

Tomoyuki Higami, Masato Hashimoto* and Seichi Okeya

Department of Materials Science and Chemistry, Faculty of Systems Engineering, Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan
Correspondence e-mail: mh1043@sys.wakayama-u.ac.jp

Received 3 July 2002
Accepted 29 August 2002
Online 30 September 2002

Polyoxometallates are capable of including transition metals in their crystal structures as either discrete cations or heteroatoms. The title compound crystallizes with triclinic symmetry and consists of a centrosymmetric $[V_{10}O_{28}]^{6-}$ anion, a trimeric $\{[Na(H_2O)_3][Ni(H_2O)_6][Na(H_2O)_3]\}^{4+}$ cation, an $[Ni(H_2O)_6]^{2+}$ cation and four water molecules of crystallization. The compound possesses two Ni atoms (each on independent inversion centres), one as a discrete cation and one in a disodium–nickel trimeric cation involved in the one-dimensional polycation–polyanion hybrid polymer. The polymers are bound together *via* hydrogen bonds to the water molecules and the nickel(II) hexahydrate cation. Several structures of decavanadate compounds having transition metal atoms, monovalent cations and $[V_{10}O_{28}]^{6-}$ anions in the ratio 2:2:1 have been reported previously. However, the present compound differs from these in its arrangement of monovalent cations and transition metal atoms.

Comment

Several peroxovanadium complexes have attracted attention as a result of their insulin-mimetic and enzyme-like activities (Tracy & Crans, 1998; Siegel & Siegel, 1995). In an attempt to prepare peroxovanadates, the title novel compound, (I), a nickel sodium decavanadate having no peroxo group, was obtained as green–orange crystals, and its crystal structure is presented here.

The structure of (I) consists of a decavanadate anion, three edge-shared octahedra of Ni and Na, an $[Ni(H_2O)_6]^{2+}$ cation and four water molecules of crystallization (Fig. 1). The $[V_{10}O_{28}]^{6-}$ anions and $\{[Na(H_2O)_3][Ni(H_2O)_6][Na(H_2O)_3]\}^{4+}$ trimeric cations are linked alternately to form a one-dimensional chain (Fig. 2).

The framework of $[V_{10}O_{28}]^{6-}$ has been studied in detail previously (Evans, 1966; Nowogrocki *et al.*, 1997). The decavanadate unit comprises ten edge-sharing VO_6 octahedra with approximate D_{2h} symmetry. The V—O distances and bond angles in the decavanadate unit of (I) are comparable with those in the literature (Evans, 1966).

In the trimeric cation of (I), the Na atoms are surrounded by one decavanadate O1 atom and five water molecules, and the Ni atom is surrounded by six water molecules. The Ni octahedron is sandwiched between two Na octahedra. Atom Na1 coordinates directly to the decavanadate unit at O1. One of the terminal water molecules on the Na atom positioned *trans* to decavanadate atom O1 was refined as disordered over two positions (O21*A* and O21*B*). The occupancy factors of these atoms were refined in the course of the initial calculations, and were then fixed to the refined values of 0.3 and 0.7, respectively, in the final calculation. The O1—Na1—O21*A* and O1—Na1—O21*B* angles [160.3 (9) and 167.3 (4)°, respectively] do not differ greatly, which does not conflict with the disordering.

The Na—O bond distances have a wide range of values, from 2.331 (8) to 2.564 (4) Å. The Na—O distances to the terminal water molecules (Na1—O21*A*, Na1—O21*B*, Na1—O22 and Na1—O23) are 2.44 (4), 2.32 (2), 2.359 (8) and 2.376 (6) Å, respectively. The length of the Na1—O1 bond [2.395 (6) Å] is similar to these three distances, even though atom O1 also bonds to atom V1. The Na—O distances to the water molecules bridging to atom Ni1 [2.544 (6) Å for Na1—

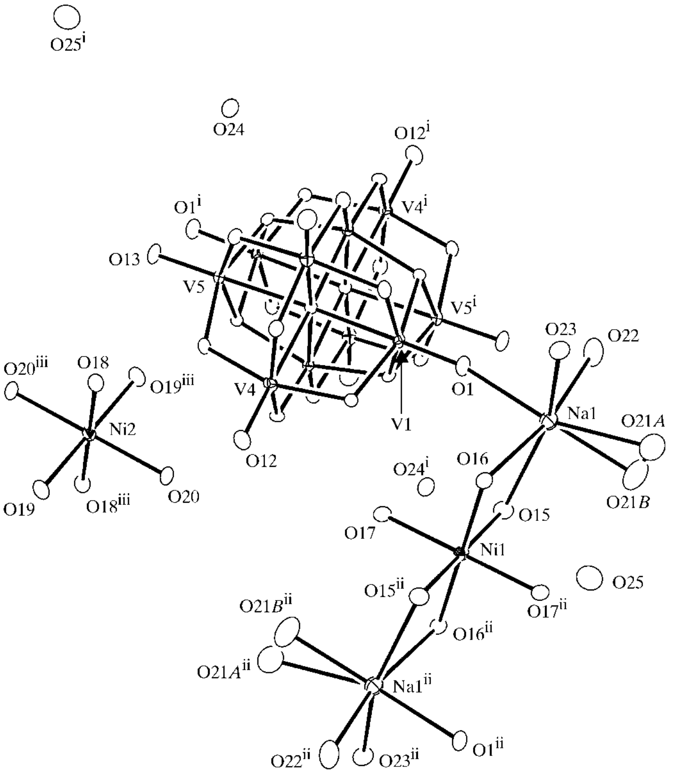

Figure 1
A view of the structure of (I). Displacement ellipsoids are at the 30% probability level [symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, -y, -z$; (iii) $-x, 1 - y, -z$].

DOI: 10.1107/S0108270102015603

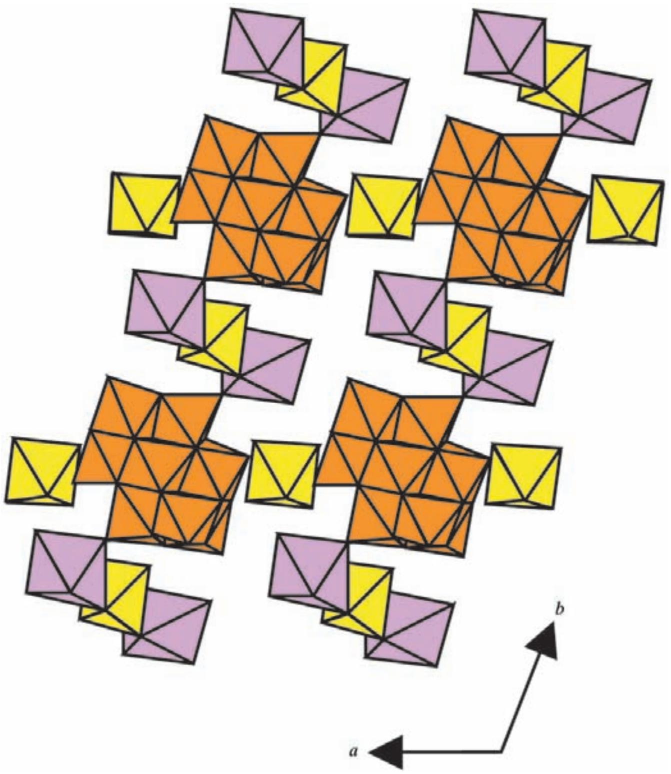

Figure 2
A polyhedral presentation of the chain structure of (I).

O15 and 2.564 (6) Å for Na1—O16] are longer than those of the other four Na1—O bonds.

Each –{[Na$(H_2O)_3$][Ni$(H_2O)_6$][Na$(H_2O)_3$]}$^{4+}$–[$V_{10}O_{28}$]$^{6-}$– chain is connected *via* hydrogen bonds through the four water molecules of crystallization and the water molecules coordinated to Na and Ni, to form the overall three-dimensional structure. With regard to the two Ni atoms, Ni1 and Ni2, atom Ni1 is involved in the chain as mentioned above, whereas atom Ni2 is isolated from the chain and plays an important role in tying the chains together. The Ni1—O distances to the water molecules bridging to Na, *viz.* Ni1—O15 and Ni1—O16, are 2.067 (5) and 2.107 (5) Å, respectively, and that to the terminal water molecule, Ni1—O17, is 2.053 (5) Å. The hydrogen-bonded O···O distances are in the range 2.630 (7)–3.131 (9) Å. H atoms were not identified in the difference Fourier maps and could not be determined.

A number of decavanadate compounds with transition metal atoms, monovalent cations and [$V_{10}O_{28}$]$^{6-}$ anions in the ratio 2:2:1 have been reported previously (Wickham, 1972), two of which have been structurally analyzed, namely $K_2Zn_2V_{10}O_{28}\cdot16H_2O$ (Evans, 1966) and $(NH_4)_2Co_2V_{10}O_{28}\cdot16H_2O$ (Nowogrocki *et al.*, 1997); these compounds are isostructural. However, the overall structure of (I) differs from the structures of these two compounds. The structure of $M^{I}_2M^{II}_2V_{10}O_{28}\cdot16H_2O$ consists of a [$V_{10}O_{28}$]$^{6-}$ anion, two isolated octahedral [$M^{II}(H_2O)_6$]$^{2+}$ cation groups, two M^{I} ions and four water molecules of crystallization. The cations and water molecules surround the polyanion, forming hydrogen bonds between them. Therefore, there is no direct connection between the cations and the polyanion, in contrast with (I), where the {[Na$(H_2O)_3$][Ni$(H_2O)_6$][Na$(H_2O)_3$]}$^{4+}$ trimeric cation is bound directly to the decavanadate. This difference in structures may be caused by the difference in size and behaviour of the monovalent cations. It is noteworthy that the formula of (I) can be written as $Na_2Ni_2V_{10}O_{28}\cdot22H_2O$, whereas that of the compounds mentioned above is $M^{I}_2M^{II}_2V_{10}O_{28}\cdot16H_2O$; the different number of water molecules in the formulae clearly plays an important role in the overall structural differences.

Experimental

V_2O_5 (0.4652 g, 0.0025 mol) and 6*M* NaOH (5.0 ml, 0.03 mol) were added to water (*ca* 20 ml). The mixture was stirred in an ice bath, producing a clear yellow solution. To this solution, 30% H_2O_2 (0.5 ml) was added and the pH of the solution was adjusted to 4.10 with 6 *M* HNO_3. The volume of the solution was then made up to 25 ml with water. An aqueous solution of 1*M* $Ni(NO_3)_2\cdot6H_2O$ (5 ml, 0.005 mol) was added to this solution, followed by the addition of ethanol (7.5 ml). The final molar ratio of H_2O_2:V:Na:Ni was 1:1:3:1. Prismatic green–orange crystals of (I) appeared after about 12 h, usually together with prismatic deep-orange crystals, which were most probably sodium decavanadate.

Crystal data

$[Ni(H_2O)_6]_2[Na(H_2O)_3]_2[V_{10}O_{28}]\cdot4H_2O$
$M_r = 1517.15$
Triclinic, $P\overline{1}$
$a = 10.836$ (2) Å
$b = 12.606$ (2) Å
$c = 8.3310$ (10) Å
$\alpha = 93.19$ (2)°
$\beta = 99.83$ (2)°
$\gamma = 109.65$ (2)°
$V = 1048.1$ (3) Å^3

$Z = 1$
$D_x = 2.404$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 16.8$–17.5°
$\mu = 3.15$ mm^{-1}
$T = 293$ (2) K
Prismatic, green–orange
0.50 × 0.18 × 0.05 mm

Table 1
Selected interatomic distances (Å).

Ni1—O17	2.053 (5)	V3—O7	2.046 (5)
Ni1—O15	2.067 (5)	V3—O6^{i}	2.323 (5)
Ni1—O16	2.107 (5)	V4—O12	1.602 (6)
Ni2—O18	2.050 (5)	V4—O10	1.834 (5)
Ni2—O19	2.062 (6)	V4—O3	1.866 (5)
Ni2—O20	2.092 (5)	V4—O14	1.877 (5)
V1—O1	1.603 (5)	V4—O8^{i}	2.062 (5)
V1—O2	1.810 (5)	V4—O6^{i}	2.340 (5)
V1—O3	1.856 (5)	V5—O13	1.614 (5)
V1—O4^{i}	1.984 (5)	V5—O11	1.817 (5)
V1—O5^{i}	2.022 (5)	V5—O14	1.822 (5)
V1—O6^{i}	2.241 (5)	V5—O4	1.995 (5)
V2—O7	1.683 (5)	V5—O5	2.006 (5)
V2—O8	1.695 (5)	V5—O6^{i}	2.219 (5)
V2—O5	1.913 (5)	Na1—O21*B*	2.323 (16)
V2—O4^{i}	1.941 (5)	Na1—O22	2.358 (7)
V2—O6^{i}	2.117 (5)	Na1—O23	2.377 (6)
V2—O6	2.125 (5)	Na1—O1	2.395 (6)
V3—O9	1.602 (5)	Na1—O21*A*	2.44 (4)
V3—O10	1.826 (5)	Na1—O15	2.544 (6)
V3—O11	1.879 (5)	Na1—O16	2.564 (6)
V3—O2	1.897 (5)		

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$.

Data collection

Rigaku AFC-5*R* automated four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*TEXSAN*; Molecular Structure Corporation, 1995)
$T_{\min} = 0.553$, $T_{\max} = 0.854$
6109 measured reflections
6109 independent reflections
3399 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.048$
$\theta_{\max} = 30°$
$h = 0 \rightarrow 15$
$k = -17 \rightarrow 16$
$l = -11 \rightarrow 11$
3 standard reflections every 200 reflections intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.152$
$S = 1.07$
6109 reflections
301 parameters
H-atom parameters not defined
$w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 9.2497P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.89$ e Å^{-3}
$\Delta\rho_{\min} = -0.81$ e Å^{-3}

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1023). Services for accessing these data are described at the back of the journal.

References

Evans, H. T. Jr (1966). *Inorg. Chem.* **5**, 967–977.

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

Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software*. Version 5.1.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1995). *TEXSAN*. Version 1.7-2. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Nowogrocki, G., Baudrin, E., Denis, S. & Touboul, M. (1997). *Eur. J. Solid State Inorg. Chem.* **34**, 1011–1026.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Siegel, H. & Siegel, A. (1995). Editors. *Metal Ions In Biological Systems*, Vol. 31, *Vanadium and Its Role In Life*. New York: Marcel Dekker.

Tracy, A. S. & Crans, D. C. (1998). Editors. *Vanadium Compounds: Chemistry, Biochemistry and Therapeutic Applications*, ACS Symposium Series 711. Washington, DC: ACS.

Wickham, D. G. (1972). *J. Inorg. Nucl. Chem.* **34**, 2673–2675.