

$(\text{NH}_4)_4\text{Na}_2[\text{V}_{10}\text{O}_{28}]\cdot 10\text{H}_2\text{O}$

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Received 5 January 2000

Accepted 10 April 2000

Tetraammonium disodium decavanadate decahydrate crystallizes in the triclinic system in space group $P\bar{1}$. The structure contains typical centrosymmetric OV_6 double octahedra and centrosymmetric pairs of edge-shared NaO_6 double octahedra forming a layered structure. In contrast to other monovalent cationic decavanadates, the NaO_6 double octahedra are integrated in the layer.

Comment

Vanadium compounds, particularly vanadium phosphates, are of great interest as potential catalysts for heterogeneous oxidation and amoxidation reactions (Centi, 1993). In connection with an investigation of the $\text{NH}_3\text{-V}^{\text{V}}$ system, we prepared the decavanadate $(\text{NH}_4)_4\text{Na}_2[\text{V}_{10}\text{O}_{28}]\cdot 10\text{H}_2\text{O}$, (I), and determined its crystal structure. (I) crystallizes during very slow evaporation of an appropriate solution. There exist several structures of monovalent cation decavanadates of the type $M_x[\text{V}_{10}\text{O}_{28}]\cdot y\text{H}_2\text{O}$. Thus, crystal structures are known for

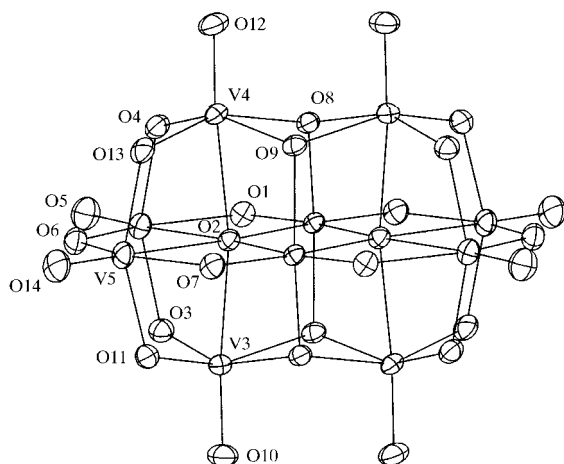


Figure 1
View along the a axis showing the edge-shared NaO_6 double octahedra (light grey).

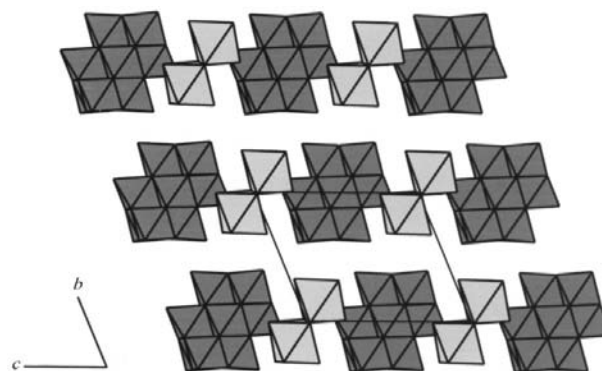


Figure 2

A plot with displacement ellipsoids of the $[\text{V}_{10}\text{O}_{28}]^{6-}$ anion drawn at the 50% probability level; V atoms are shaded.

$\text{Na}_6[\text{V}_{10}\text{O}_{28}]\cdot 18\text{H}_2\text{O}$ (Durif & Averbuch-Pouchot, 1982), $\text{Na}_6[\text{V}_{10}\text{O}_{28}]\cdot 12\text{H}_2\text{O}$ (Xu *et al.*, 1996), $\text{Cs}_4\text{H}_2[\text{V}_{10}\text{O}_{28}]\cdot 4\text{H}_2\text{O}$ (Rigotti *et al.*, 1983) and $(\text{NH}_4)_6[\text{V}_{10}\text{O}_{28}]\cdot 6\text{H}_2\text{O}$ (Eglmeier *et al.*, 1993). The structure of (I) consists of layers of decavanadate anions and pairs of edge-shared NaO_6 double octahedra (Fig. 1). The layered structure is similar to those found for the other decavanadates of monovalent cations, but in (I), the layers are connected only *via* hydrogen bonds. This is unusual because in the other decavanadates mentioned above, the layers are connected *via* cation polyhedra. However, in the present structure, all NaO_6 octahedra are integrated in the layer.

The $[\text{V}_{10}\text{O}_{28}]^{6-}$ decavanadate anions appear as common edge-shared OV_6 double octahedra. The axial $\text{V}-\text{O}$ bond distances are in the normal ranges, with values of 1.60–1.69 Å for the $\text{V}=\text{O}$ group and 2.10–2.35 Å for the second axial O atom, as are the four equatorial $\text{V}-\text{O}$ bonds with distances ranging from 1.70 to 2.09 Å. Sodium occurs as a pair of edge-shared NaO_6 octahedra. In the octahedron, sodium is surrounded by six water molecules, the only water in the structure. The $\text{Na}-\text{O}$ bond distances are in the narrow range 2.34–2.44 Å. In the above-mentioned sodium decavanadates, longer $\text{Na}-\text{O}$ distances were found (up to 2.7 Å). The H atoms of the coordinated water are involved in hydrogen bridges, forming the linkages between decavanadate anions in the layer as well as forming bridges to neighbouring layers.

The N1 and N2 ammonium ions are fixed *via* hydrogen bonds to the decavanadate anion. Additionally, they form hydrogen bonds to the sodium–oxygen octahedron and to one decavanadate anion of a neighbouring layer. Compound (I) is a new decavanadate with some interesting structural features, especially with regard to the arrangement of the layers, which is quite different from what is found in other decavanadates of monovalent cations.

Experimental

$(\text{NH}_4)_4\text{Na}_2[\text{V}_{10}\text{O}_{28}]\cdot 10\text{H}_2\text{O}$ was prepared by evaporation at room temperature of a solution consisting of H_2O (50 ml), NH_4VO_3 (250 mg) and NaH_2PO_4 (50 mg).

Crystal data

(NH₄)₄[Na₂(H₂O)₁₀][V₁₀O₂₈]
M_r = 1255.71
 Triclinic, *P* $\bar{1}$
a = 8.501 (2) Å
b = 10.426 (2) Å
c = 11.282 (2) Å
 α = 68.46 (3)°
 β = 87.30 (3)°
 γ = 67.14 (3)°
V = 851.7 (3) Å³

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: ψ scan
 (CORINC; Schollmeyer, 1992)
T_{min} = 0.632, *T_{max}* = 0.758
 5282 measured reflections
 4933 independent reflections
 4474 reflections with *I* > 2 σ (*I*)

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.036
wR(*F*²) = 0.102
S = 1.063
 4933 reflections
 316 parameters
 All H-atom parameters refined

Z = 1
D_x = 2.448 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 25 reflections
 θ = 10–18°
 μ = 2.767 mm⁻¹
T = 293 (2) K
 Plate, red
 0.2 × 0.2 × 0.1 mm

R_{int} = 0.007
 θ_{\max} = 29.96°
h = 0 → 11
k = -13 → 14
l = -15 → 15
 3 standard reflections every 100 reflections
 frequency: 60 min
 intensity decay: none

$w = 1/[\sigma^2(F_o^2) + (0.0727P)^2 + 0.3310P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.005
 $\Delta\rho_{\max} = 1.31 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.17 \text{ e \AA}^{-3}$

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CORINC* (Schollmeyer, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *SHELXL97*.

The financial support of the BMBF of Germany and the International Centre of Diffraction Data (ICDD) is gratefully acknowledged.

Table 1

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H12···O7 ⁱ	0.73 (5)	2.14 (5)	2.862 (3)	175 (4)
N1—H15···O12	0.67 (6)	2.26 (6)	2.910 (3)	164 (6)
N1—H9···O8 ⁱⁱ	0.83 (7)	2.17 (7)	2.944 (3)	156 (6)
N2—H14···O14 ⁱⁱⁱ	0.77 (6)	2.35 (6)	2.899 (3)	129 (5)
N2—H4···O10 ^{iv}	0.79 (4)	2.17 (4)	2.933 (3)	165 (3)
N2—H11···O19 ^v	0.92 (7)	2.12 (7)	2.993 (4)	159 (6)
O15—H17···O10 ^{iv}	0.71 (5)	2.35 (5)	3.039 (3)	165 (5)
O15—H13···O3	0.80 (5)	2.08 (5)	2.855 (2)	163 (5)
O16—H8···O11 ^{vi}	0.66 (4)	2.18 (4)	2.833 (3)	168 (5)
O16—H6···O1	0.80 (3)	2.06 (4)	2.860 (3)	174 (3)
O17—H10···O13 ⁱ	0.74 (5)	2.17 (5)	2.867 (3)	159 (5)
O17—H7···O9	0.79 (4)	2.21 (4)	2.952 (3)	157 (4)
O18—H2···O10 ^{vii}	0.71 (4)	2.42 (4)	2.974 (3)	136 (4)
O18—H1···O4	0.82 (4)	1.99 (4)	2.801 (3)	176 (4)
O19—H5···O14 ^{vi}	0.74 (5)	2.61 (5)	2.982 (3)	113 (5)
O19—H3···O6 ^{viii}	1.01 (4)	1.80 (4)	2.795 (3)	168 (3)

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1283). Services for accessing these data are described at the back of the journal.

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