

**Diammonium bis[hexaaquanickel(II)]
decavanadate tetrahydrate,
(NH₄)₂[Ni(H₂O)₆]₂V₁₀O₂₈·4H₂O****Ai-Li Xie,^{a,b} Chun-An Ma^{b*} and
Lian-Bang Wang^b**^aDepartment of Chemistry, Shangrao Normal College, Shangrao 334001, People's Republic of China, and ^bState Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, College of Chemical, Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 320014, People's Republic of ChinaCorrespondence e-mail:
science@zjut.edu.cn, srsyxieaili@163.com**Key indicators**Single-crystal X-ray study
T = 173 K
Mean $\sigma(\text{Ni}-\text{O}) = 0.002 \text{ \AA}$
R factor = 0.024
wR factor = 0.060
Data-to-parameter ratio = 15.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of the title compound, (NH₄)₂[Ni(H₂O)₆]₂V₁₀O₂₈·4H₂O, comprises centrosymmetric [V₁₀O₂₈]⁶⁻ anions that are linked *via* hydrogen bonding by two NH₄⁺ cations, two [Ni(H₂O)₆]²⁺ cations, and four water molecules into a three-dimensional structure. The compound is isotypic with other members of the [M(H₂O)₆]₂(NH₄)₂V₁₀O₂₈·4H₂O series (*M* = Mg and Co).

Comment

Recently, decavanadate double salts of nickel and alkali metals have been reported, *viz.* [Ni(H₂O)₆]₂[Na(H₂O)₃]₂[V₁₀O₂₈]₂·4H₂O (Higami *et al.*, 2002), NiNa₄[HV₁₀O₂₈]₂·23H₂O (Sun *et al.*, 2002) and [K(H₂O)₂Ni(H₂O)₆]₂[V₁₀O₂₈] (Li *et al.*, 2004). However, no double salt with nickel and ammonium has been reported up to now. We present here the crystal structure of the decavanadate [Ni(H₂O)₆]₂(NH₄)₂V₁₀O₂₈·4H₂O, (I), which is isotypic with other members of the series [M(H₂O)₆]₂(NH₄)₂V₁₀O₂₈·4H₂O where *M* = Mg (Avtamonova *et al.*, 1990) and Co (Baudrin *et al.*, 1997).

The structure of (I) consists of a centrosymmetric polyanion, [V₁₀O₂₈]⁶⁻, two hexaaquanickel(II) cations, [Ni(H₂O)₆]²⁺, two ammonium cations, NH₄⁺, and four water molecules as single building units (Fig. 1). Each building unit is bonded to another unit *via* an extensive net of hydrogen bonds into a three-dimensional network. In this way, the [Ni(H₂O)₆]²⁺ cation is linked to the decavanadate polyanion

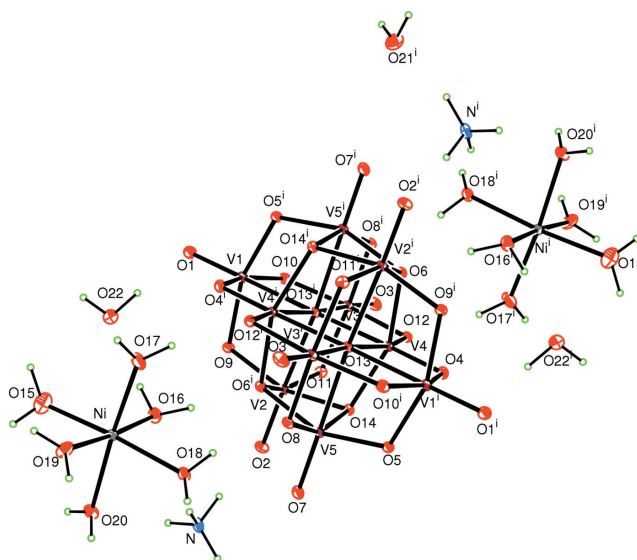


Figure 1
The structure of (I), with 40% probability displacement ellipsoids, showing the atom-labelling scheme. [Symmetry code: (i) 1 - *x*, 1 - *y*, 1 - *z*].

and to an isolated water molecule, whereas the NH₄⁺ group is connected to another water molecule and to the polyanion, so that all terminal O atoms of the [V₁₀O₂₈]⁶⁻ anion are involved in hydrogen bonding (Fig. 2 and Table 2). The deviation from ideal values of the bonding angles in the water molecules of 118° for both H19A–O19–H19B and H20A–O20–H20B, and in the ammonium cation of 99 and 116°, is also explained by involvement in hydrogen bonding.

The Ni²⁺ cation in (I) is coordinated by six water molecules, forming a slightly distorted octahedron (Table 1) with the *cis*-O–Ni–O angles deviating by about 5° and the *trans*-O–Ni–O angles by about 7° from ideal values.

The decavanadate polyanion in (I) is composed of ten VO₆ octahedra by edge- and corner-sharing. The arrangement of O and V atoms is very close to that in other decavanadates of composition Li₆(H₂O)₁₆V₁₀O₂₈ (Xie & Ma, 2005) and [LiNa₂(H₂O)₉]₂V₁₀O₂₈ (Ma *et al.*, 2005) reported previously. The V···V contacts within the polyanion in (I) range from 3.0537 (14) to 3.1155 (8) Å. The V–O bond-length distribution is correlated with the coordination number (CN) of the O atoms. Terminal O atoms with only one V–O bond have distances in the range 1.5985 (9) to 1.6136 (18) Å, whereas the other V–O distances increase with higher CN of the bridging O atoms. V–μ₂-O distances are in the range 1.6840 (19) to 2.0214 (19) Å, V–μ₃-O distances are 1.9069 (17)–1.9965 (18) Å, and V–μ₆-O distances are 2.1057 (19)–2.3410 (19) Å. The bond lengths and angles of the [V₁₀O₂₈]⁶⁻ polyanion are very similar to those observed in other decavanadates (Kamenar *et al.*, 1996; Choi *et al.*, 2003; Xie & Ma, 2005; Ma *et al.*, 2005).

Experimental

A mixture of NH₄VO₃ (Shanghai Chemical Reagents) and Ni(OAc)₂·4H₂O (Shanghai Chemical Reagents) in a 5:1 molar ratio was acidified to pH 5 and hydrothermally treated for 10 h at 398 K. The resulting filtrate was kept at room temperature and after some days a yellow polycrystalline powder precipitated from the solution which was subsequently filtered off. Yellow single crystals of (I) of up to 3 mm in length and of mostly block-like habit formed after 20 d from this solution.

Crystal data

(NH ₄) ₂ [Ni(H ₂ O) ₆] ₂ V ₁₀ O ₂₈ ·4H ₂ O	Z = 1
M _r = 1399.12	D _x = 2.588 Mg m ⁻³
Triclinic, P1	Mo Kα radiation
a = 8.7728 (18) Å	Cell parameters from 7874 reflections
b = 10.923 (2) Å	θ = 3.4–27.5°
c = 11.114 (2) Å	μ = 3.64 mm ⁻¹
α = 65.18 (3)°	T = 173 (2) K
β = 73.12 (3)°	Block, yellow
γ = 70.64 (3)°	0.20 × 0.20 × 0.20 mm
V = 897.6 (4) Å ³	

Data collection

Rigaku R-AXIS RAPID diffractometer	4056 independent reflections
ω scans	3602 reflections with I > 2σ(I)
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	R _{int} = 0.021
T _{min} = 0.471, T _{max} = 0.483	θ _{max} = 27.5°
8845 measured reflections	h = -11 → 11
	k = -14 → 14
	l = -14 → 12

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.024
wR(F²) = 0.060
S = 1.09
4056 reflections
262 parameters
H atoms not located

$$w = 1/[\sigma^2(F_o^2) + (0.0185P)^2 + 1.7228P]$$

where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.47 e Å⁻³
Δρ_{min} = -0.43 e Å⁻³

Table 1

Selected bond lengths (Å).

Ni–O15	2.047 (2)	V3–O3	1.5985 (19)
Ni–O19	2.054 (2)	V3–O10	1.8404 (19)
Ni–O17	2.054 (2)	V3–O11	1.8682 (18)
Ni–O16	2.057 (2)	V3–O8 ⁱ	1.8987 (18)
Ni–O18	2.0688 (19)	V3–O12	2.0214 (19)
Ni–O20	2.0848 (19)	V3–O13 ⁱ	2.3410 (19)
V1–O1	1.6054 (19)	V4–O4	1.6840 (19)
V1–O10	1.8303 (19)	V4–O12	1.7027 (19)
V1–O9	1.8407 (18)	V4–O14	1.9069 (17)
V1–O5 ⁱ	1.8982 (18)	V4–O6	1.9442 (18)
V1–O4 ⁱ	2.061 (2)	V4–O13	2.1057 (19)
V1–O13 ⁱ	2.3093 (19)	V4–O13 ⁱ	2.1180 (18)
V2–O2	1.6136 (18)	V5–O7	1.6112 (18)
V2–O9	1.8276 (18)	V5–O5	1.8179 (18)
V2–O11	1.8291 (18)	V5–O8	1.8337 (19)
V2–O14	1.9825 (19)	V5–O14	1.9965 (18)
V2–O6 ⁱ	1.9997 (19)	V5–O6 ⁱ	1.9979 (19)
V2–O13 ⁱ	2.2282 (18)	V5–O13	2.2328 (18)

Symmetry code: (i) -x + 1, -y + 1, -z + 1.

Table 2

Hydrogen-bond geometry (Å, °).

D–H···A	D–H	H···A	D···A	D–H···A
O15–H15A···O21 ⁱⁱ	0.89	2.17	3.035 (3)	165
O15–H15B···O2 ⁱⁱ	0.94	2.31	3.050 (3)	135
O15–H15B···O14 ⁱⁱ	0.94	2.43	3.300 (3)	154
O16–H16A···O22	0.90	1.95	2.819 (3)	164
O16–H16B···O6 ⁱ	0.92	1.81	2.731 (2)	175
O17–H17A···O12 ⁱ	0.87	1.98	2.847 (3)	172
O17–H17B···O5 ⁱⁱ	0.90	1.95	2.830 (2)	167
O17–H17B···O4 ⁱⁱ	0.90	2.51	3.083 (6)	122
O18–H18A···O8 ⁱⁱⁱ	0.85	1.88	2.726 (1)	177
O18–H18B···O8	0.86	1.95	2.794 (3)	165
O19–H19A···O5 ⁱⁱⁱ	0.87	1.81	2.671 (3)	176
O19–H19B···O7 ⁱⁱ	0.85	2.14	2.951 (3)	161
O20–H20A···O10 ^{iv}	0.82	1.93	2.746 (3)	173
O21–H21A···O3 ^v	0.86	2.22	3.030 (3)	159
O21–H21B···O1 ^{vi}	0.85	2.03	2.869 (3)	169
O22–H22A···O11 ⁱⁱ	0.85	2.11	2.948 (3)	173
O22–H22B···O4 ⁱ	0.93	2.12	2.928 (3)	144
N–H23A···O2	0.99	1.97	2.957 (3)	174
N–H23B···O21	0.98	1.89	2.831 (3)	162
N–H23C···O18	0.99	2.22	3.195 (3)	170
N–H23C···O20	0.99	2.48	3.044 (3)	116

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

All H atoms were found in a difference Fourier map. They were fixed in these positions, with U_{iso}(H) = 0.05 Å².

Data collection: PROCESS-AUTO (Rigaku, 1998); cell refinement: PROCESS-AUTO (Rigaku, 2002); data reduction: Crystal Structure (Rigaku/MS, 2004); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP3

(Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The work at Hangzhou was supported by the National Science Foundation (grant No. 20476097) and the Major State Basic Research Development Program of China (973 Program (grant No. 2003CCA01300)).

References

- Avtamonova, N. V., Trunov, V. K. & Makarevich, L. G. (1990). *Iz. Akad. Nauk. Neorg. Mater.* **26**, 350–356. (In Russian.)
- Baudrin, E., Denis, S., Touboul, M. & Nowogrocki, G. (1997). *Eur. J. Solid State Inorg. Chem.* **34**, 1011–1026.
- Choi, H., & Chang, Y. Y. (2003). *Chem. Mater.* **15**, 3261–3267.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Higami, T., Hashimoto, M. & Okeye, S. (2002). *Acta Cryst.* **C58**, i144–i146.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Kamenar, B., Clndric, M. & Strukan, N. (1996). *Acta Cryst.* **C52**, 1338–1341.
- Li, D. H., Liu, S. X., Peng, J., Shao, K. Z., Xu, H. B., Zhai, H. J. & Wang, E. B. (2004). *Chin. J. Inorg. Chem.* **20**, 1076–1080.
- Ma, C.-A., Xie, A.-L. & Wang, L. B. (2005). *Acta Cryst.* **E61**, i185–i187.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.
- Rigaku (2002). *PROCESS-AUTO*. Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.
- Rigaku/MS (2004). *CrystalStructure*. Rigaku/MS, 9009 New Trails Drive, The Woodlands TX 77381-5209, USA.

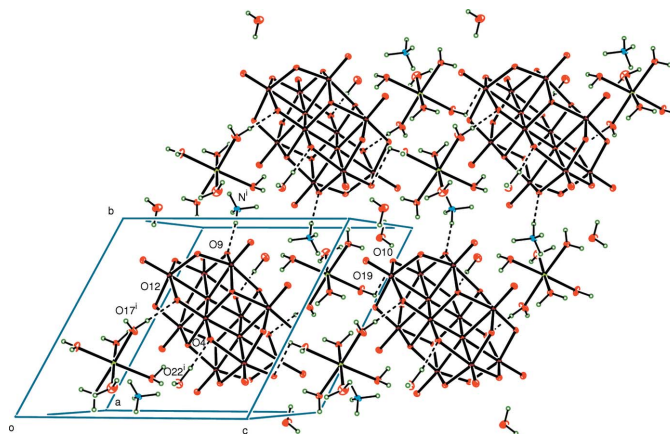


Figure 2

The structure of (I), viewed approximately perpendicular to the *bc* plane. Part of the hydrogen-bonding network is shown as dashed lines. [Symmetry code: (i) $x - 1, y, z$.]

- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sun, Z.-G., Long, L.-S., Ren, Y.-P., Huang, R.-B. & Zheng, L.-S. (2002). *Acta Cryst.* **E58**, i34–i36.
- Xie, A.-L. & Ma, C.-A. (2005). *Acta Cryst.* **C61**, i67–i68.