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$Mg_2Na_2V_{10}O_{28}\cdot 20H_2O$ and $Mg_3V_{10}O_{28}\cdot 28H_2O$

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The crystal structures of dimagnesium disodium decavanadate icosahydrate, $Mg_2Na_2V_{10}O_{28}\cdot 20H_2O$, (I), and trimagnesium decavanadate octacosahydrate, $Mg_3V_{10}O_{28}\cdot 28H_2O$, (II), have been determined by single-crystal X-ray diffraction. They crystallize with monoclinic ($C2/c$) and triclinic ($P\overline{1}$) symmetry, respectively. All the Mg^{2+} cations in (I) and (II) are octahedrally coordinated by six water molecules. The Na^+ cations in (I) are coordinated by three water molecules and three O atoms of the decavanadate anions, and link the latter into a three-dimensional network. The decavanadate anions in (II) are not linked to one another.

Comment

When precipitated with more than one cationic species, the decavanadate anion, $[V_{10}O_{28}]^{6-}$, crystallizes into double salts with various kinds of three-dimensional arrangements of the constituent ions. Typical examples are the mineral hummerite, $K_2Mg_2V_{10}O_{28}\cdot 16H_2O$ (Avtamonova *et al.*, 1990), and its isomorphous compounds $K_2Zn_2V_{10}O_{28}\cdot 16H_2O$ (Evans, 1966), $(NH_4)_2Mg_2V_{10}O_{28}\cdot 16H_2O$ and $Rb_2Mg_2V_{10}O_{28}\cdot 16H_2O$ (Avtamonova *et al.*, 1990), in which the monovalent cations link the decavanadate anions into layers that sandwich the hydrated $[M(H_2O)_6]^{2+}$ cations. Recently, various new extended structures have been observed in some double decavanadate salts, such as one-dimensional chains in $[Ni(H_2O)_6]_2[Na(H_2O)_3]_2[V_{10}O_{28}]\cdot 4H_2O$ (Higami *et al.*, 2002), two-dimensional networks in $Na_4NiV_{10}O_{28}\cdot 23H_2O$ (Sun *et al.*, 2002) and three-dimensional structures in $K_2Ba_2V_{10}O_{28}\cdot 8H_2O$ (Rastsvetaeva, 1999), $CuNa_4V_{10}O_{28}\cdot 23H_2O$ (Iida & Ozeki, 2003) and $K_4Na_2V_{10}O_{28}\cdot 10H_2O$ (Lee & Joo, 2003). We report here the crystal structure of $Mg_2Na_2V_{10}O_{28}\cdot 20H_2O$, (I), as a new addition to the family of alkali magnesium decavanadates. In the structure of (I), the decavanadate anions are linked into a three-dimensional structure by Na^+ cations. Also reported here is the crystal structure of $Mg_3V_{10}O_{28}\cdot 28H_2O$, (II), which complements the known alkaline earth decavanadates, including $Ca_3V_{10}O_{28}\cdot 17H_2O$ (Swallow *et al.*, 1966), $Ca_2(H_3O)_2V_{10}O_{28}\cdot 16H_2O$ (Strukan *et al.*, 1999), $Sr_3V_{10}O_{28}\cdot 22H_2O$ (Nieto *et al.*, 1993) and $Ba_3V_{10}O_{28}\cdot 19H_2O$ (Kamenar *et al.*, 1996).

From solutions containing Mg^{2+} and Na^+ cations, the decavanadate anion crystallizes with both cations to produce (I). The asymmetric unit of (I) includes one-half of a $[V_{10}O_{28}]^{6-}$ anion, an Mg^{2+} cation, an Na^+ cation and water molecules. The decavanadate anion is located on a twofold axis and has a metal–oxygen framework the same as that reported by Evans (1966) (Fig. 1). The Mg^{2+} cation is octahedrally coordinated by six water molecules, with Mg—O distances of 2.0234 (15)–2.1398 (15) Å (Table 1). The coordination environment of the Na^+ cation consists of two O atoms from two separate $[V_{10}O_{28}]^{6-}$ anions [at 2.4264 (15) and 2.6620 (15) Å] and three water molecules [at 2.3481 (17)–2.5864 (19) Å], yielding a coordination geometry between square-pyramidal and trigonal-bipyramidal, with a τ parameter of 0.466 [τ is defined as the difference between the two largest bond angles at the metal center divided by 60 and is expected to be 1 for the ideal trigonal-bipyramidal geometry and 0 for the ideal square-pyramidal geometry (Addison *et al.*, 1984)]. The sixth O atom approaches the Na^+ ion at a distance of 2.9714 (16) Å, capping a triangular face of the square pyramid. Each Na^+ cation shares two water molecules with its symmetry equivalent, forming a dimeric cation, $[Na_2(H_2O)_4]^{2+}$, that links the decavanadate anions into a three-dimensional array (Fig. 2). The structure of this array is different from that in other decavanadates, such as

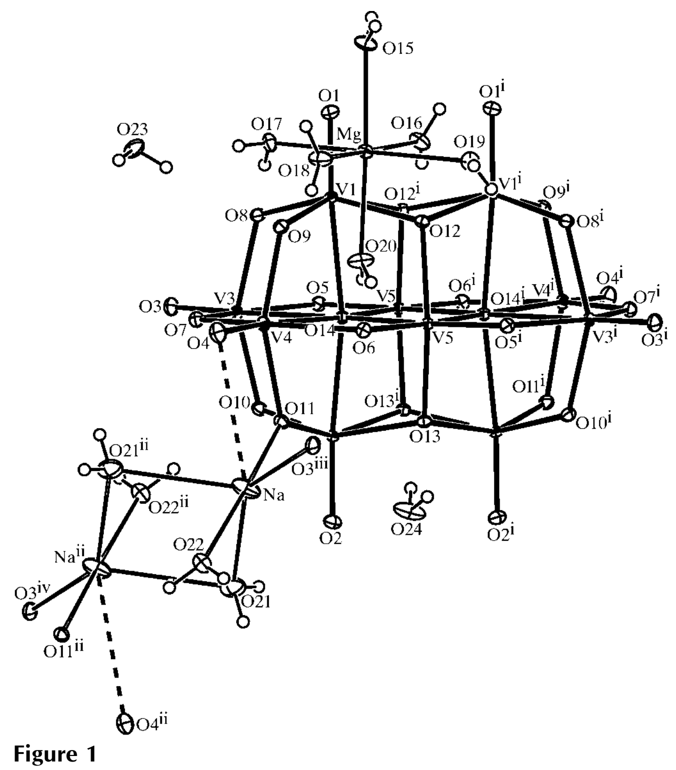

Figure 1
A perspective view of an asymmetric unit and selected neighbors of (I). Displacement ellipsoids are drawn at the 50% probability level. Na···O contacts longer than 2.7 Å are shown as broken lines. [Symmetry codes: (i) $-x, y, \frac{1}{2}-z$; (ii) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$; (iii) $x, 1-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.]

$K_2Mg_2V_{10}O_{28}\cdot16H_2O$, $(NH_4)_2Mg_2V_{10}O_{28}\cdot16H_2O$ and $Rb_2Mg_2V_{10}O_{28}\cdot16H_2O$ (Avtamonova *et al.*, 1990), reflecting the different ionic radius and coordination requirement of the Na^+ ion.

From solutions containing only Mg^{2+} as the cationic species, crystallization with the decavanadate anion gives (II). The asymmetric unit of (II) consists of two half $[V_{10}O_{28}]^{6-}$ anions, each located on an inversion center, three Mg^{2+} cations and water molecules of crystallization. The metal–oxygen framework of the decavanadate anion is also identical to that reported by Evans (1966) (Fig. 3). Each Mg^{2+} cation is octahedrally coordinated by six water molecules, with Mg—O distances ranging from 2.0351 (17) to 2.1165 (17) Å (Table 3). The hydrated Mg^+ cations do not bind to the decavanadate anions; this situation is unlike that observed in other alkaline earth decavanadates or in the *para*-dodecatungstates $Mg_5[H_2W_{12}O_{42}]\cdot38H_2O$ (Tsay & Silverton, 1973) and $(NH_4)_2[Mg_4(H_2O)_{18}(H_2W_{12}O_{42})]\cdot10H_2O$ (Li *et al.*, 1999). In contrast, the hydrated Cu^{2+} cation binds to the decavanadate anion in its simple salt but not in its double salt with Na^+ (Iida & Ozeki, 2003). The three $[Mg(OH_2)_6]^{2+}$ octahedra in (II) are linked together by hydrogen bonds. The coordination geometry of the water molecules around the Mg^{2+} cations is summarized in Table 4. According to the classification of Ferraris & Franchini-Angela (1972), most of the water molecules adopt a class 1 type *D* geometry (coordinating only the Mg^{2+} cation approximately along the bisectrix of the lone-pair orbitals) or a class 2 type *H* geometry (coordinating the Mg^{2+} cation and accepting a hydrogen bond). However, atoms O30 and O46 adopt a class 1′ type *J* geometry (coordinating the Mg^{2+} cation along a lone-pair orbital), which was not found in $MgSO_4\cdot7H_2O$ (Ferraris & Jones, 1973) or $MgSO_4\cdot4H_2O$ (Baur, 1964).

Details of the hydrogen-bonding geometry in (I) are given in Tables 2, while the corresponding data for (II) are available in the archived CIF.

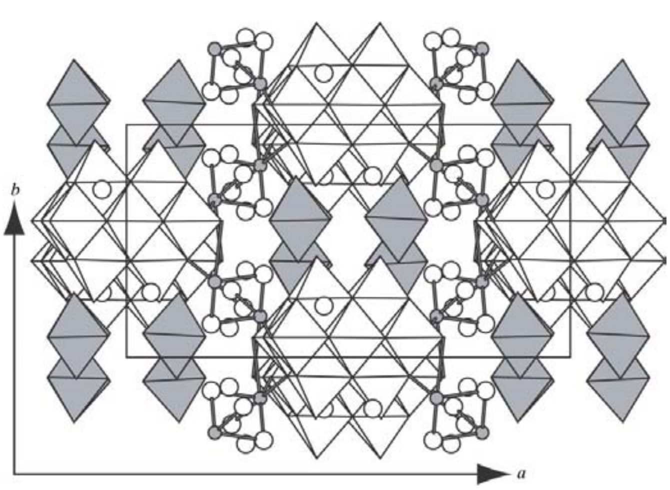

Figure 2
A packing diagram of (I), viewed along the *c* axis. Open octahedra, filled octahedra and filled circles represent VO_6, MgO_6 and Na^+ groups, respectively. Open circles represent the O atoms of water molecules that do not coordinate Mg^{2+}.

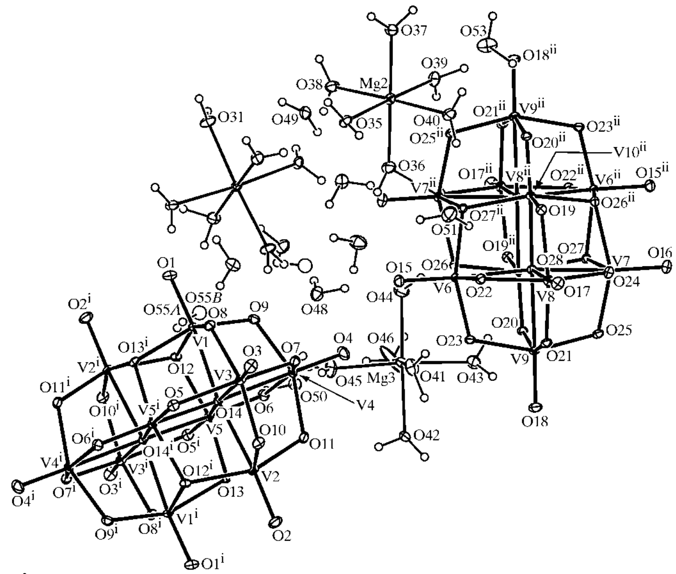

Figure 3
A perspective view of an asymmetric unit and selected neighbors of (II). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, 1-y, 1-z$.]

Experimental

$NaVO_3$ (1.22 g) was dissolved in hot water (100 ml) and the pH was adjusted to 3.70 by adding CH_3COOH. An aqueous solution of $Mg(CH_3COO)_2\cdot4H_2O$ (0.65 g in 10 ml of water) was then added. The crude product, (I) (1.12 g), was obtained by adding acetone (100 ml) dropwise to the reaction mixture. Diffraction-quality crystals of (I) were obtained by vapor-phase diffusion of acetone into an aqueous solution (15 ml) of the crude product (0.1 g). A solution of decavanadic acid was prepared according to the method of Jahr & Preuss (1965). V_2O_5 (3.64 g) was dissolved in aqueous H_2O_2 (50 ml of 30% aqueous H_2O_2 diluted with 400 ml of water). An aqueous solution of $Mg(CH_3COO)_2\cdot4H_2O$ (2.68 g in 10 ml of water) was added to the decavanadic acid solution. After the volume of the resulting solution had been reduced to 100 ml by heating, acetone (100 ml) was added dropwise to obtain the crude product, (II) (4.50 g). Diffraction-quality crystals of (II) were obtained by vapor-phase diffusion of acetone into an aqueous solution (15 ml) of the crude product (0.1 g).

Compound (I)

Crystal data

$Mg_2Na_2V_{10}O_{28}\cdot20H_2O$	D_x = 2.387 Mg m^{-3}
M_r = 1412.32	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 8192 reflections
a = 23.8384 (6) Å	θ = 1.9–30.0°
b = 11.0248 (2) Å	μ = 2.46 mm^{-1}
c = 16.9332 (4) Å	T = 93 (2) K
β = 118.005 (1)°	Plate, yellow–orange
V = 3929.18 (15) Å^3	0.20 × 0.18 × 0.08 mm
Z = 4	

Data collection

Bruker SMART CCD area-detector system diffractometer	5746 independent reflections
ω scans	4522 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	R_{int} = 0.034
T_{min} = 0.640, T_{max} = 0.821	θ_{max} = 30.0°
18 758 measured reflections	$h = -32 \rightarrow 33$
	$k = -15 \rightarrow 15$
	$l = -23 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.075$
$S = 1.01$
5746 reflections
360 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.72$ e Å^{-3}
$\Delta\rho_{min} = -1.24$ e Å^{-3}

Table 1
Selected interatomic distances (Å) for (I).

Mg—O18	2.0234 (15)	Na—O22	2.3481 (17)
Mg—O16	2.0298 (15)	Na—O21	2.4195 (19)
Mg—O15	2.0500 (16)	Na—O11	2.4264 (15)
Mg—O20	2.0523 (16)	Na—O21^{i}	2.5864 (19)
Mg—O17	2.1082 (15)	Na—O3^{ii}	2.6620 (15)
Mg—O19	2.1398 (15)	Na—O4	2.9714 (16)

Symmetry codes: (i) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$; (ii) $x, 1-y, \frac{1}{2}+z$.

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O15—H15$A\cdots$O8^{i}	0.72 (3)	2.02 (3)	2.7291 (19)	169 (3)
O15—H15$B\cdots$O24^{ii}	0.72 (3)	2.06 (3)	2.749 (2)	160 (3)
O16—H16$A\cdots$O12	0.67 (3)	1.98 (3)	2.6517 (19)	175 (4)
O16—H16$B\cdots$O19^{iii}	0.75 (3)	2.02 (3)	2.774 (2)	179 (3)
O17—H17$A\cdots$O9	0.77 (3)	2.05 (3)	2.7933 (19)	164 (2)
O17—H17$B\cdots$O7^{iv}	0.71 (3)	2.10 (3)	2.8052 (19)	174 (3)
O18—H18$A\cdots$O23^{i}	0.74 (3)	1.99 (3)	2.729 (2)	176 (3)
O18—H18$B\cdots$O22^{v}	0.69 (3)	2.11 (3)	2.800 (2)	177 (3)
O19—H19$A\cdots$O2^{vi}	0.73 (3)	2.26 (3)	2.8600 (19)	141 (3)
O19—H19$A\cdots$O1^{i}	0.73 (3)	2.52 (3)	3.037 (2)	130 (2)
O19—H19$B\cdots$O24^{vii}	0.72 (3)	2.11 (3)	2.822 (2)	170 (3)
O20—H20$A\cdots$O6	0.68 (3)	2.05 (3)	2.725 (2)	176 (3)
O20—H20$B\cdots$O10^{vi}	0.72 (3)	1.97 (3)	2.686 (2)	171 (3)
O21—H21$A\cdots$O17^{viii}	0.72 (3)	2.29 (4)	3.007 (2)	176 (4)
O21—H21$B\cdots$O2	0.80 (3)	2.34 (3)	3.052 (2)	149 (3)
O22—H22$A\cdots$O23^{vi}	0.69 (3)	2.09 (3)	2.784 (2)	174 (3)
O22—H22$B\cdots$O10^{ix}	0.77 (3)	2.30 (3)	2.950 (2)	142 (3)
O23—H23$A\cdots$O8	0.69 (3)	2.11 (3)	2.756 (2)	154 (3)
O23—H23$B\cdots$O4^{iv}	0.82 (3)	2.19 (3)	2.900 (2)	146 (3)
O24—H24$A\cdots$O13	0.74 (3)	1.95 (3)	2.685 (2)	172 (3)
O24—H24$B\cdots$O5^{vi}	0.67 (3)	2.17 (3)	2.827 (2)	167 (3)

Symmetry codes: (i) $x, -y, \frac{1}{2}+z$; (ii) $x, y-1, z$; (iii) $-x, -y, 1-z$; (iv) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (v) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (vi) $x, 1-y, \frac{1}{2}+z$; (vii) $-x, 1-y, 1-z$; (viii) $x, 1+y, z$; (ix) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$.

Compound (II)

Crystal data

$Mg_3V_{10}O_{28}\cdot 28H_2O$
$M_r = 1534.78$
Triclinic, $P\overline{1}$
$a = 10.4834$ (1) Å
$b = 10.7309$ (2) Å
$c = 21.2293$ (4) Å
$\alpha = 90.751$ (1)°
$\beta = 97.866$ (1)°
$\gamma = 103.663$ (1)°
$V = 2296.24$ (6) Å^3
$Z = 2$
$D_x = 2.220$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 2.0$–$30.0°$
$\mu = 2.12$ mm^{-1}
$T = 93$ (2) K
Block, orange
0.30 × 0.18 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.518$, $T_{max} = 0.743$
22 420 measured reflections
13 207 independent reflections
10 950 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 30.0°$
$h = -14 \rightarrow 14$
$k = -9 \rightarrow 15$
$l = -27 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.086$
$S = 1.01$
13 207 reflections
632 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.99$ e Å^{-3}
$\Delta\rho_{min} = -0.95$ e Å^{-3}

Table 3
Selected interatomic distances (Å) for (II).

Mg1—O33	2.0351 (17)	Mg2—O36	2.0643 (18)
Mg1—O30	2.0474 (16)	Mg2—O35	2.0818 (16)
Mg1—O31	2.0721 (17)	Mg2—O39	2.1008 (16)
Mg1—O32	2.0846 (16)	Mg3—O45	2.0414 (17)
Mg1—O29	2.0868 (17)	Mg3—O43	2.0521 (17)
Mg1—O34	2.1165 (17)	Mg3—O44	2.0571 (19)
Mg2—O37	2.0413 (17)	Mg3—O46	2.0692 (19)
Mg2—O38	2.0453 (17)	Mg3—O41	2.0756 (17)
Mg2—O40	2.0509 (17)	Mg3—O42	2.0837 (17)

Table 4
Coordination geometries of the water molecules around the Mg^{2+} cations.

Mg	O	ε† (°)	Classification‡
Compound (I)			
Mg	O15	19.0	Class 1, type D
	O16	0.0	Class 1, type D
	O17	36.5	Class 2, type H
	O18	8.6	Class 1, type D
	O19	40.1	Class 2, type H
	O20	17.2	Class 1, type D
Compound (II)			
Mg1	O29	18.9	Class 1, type D
	O30	40.7	Class 1″, type J
	O31	8.3	Class 1, type D
	O32	34.0	Class 2, type H
	O33	7.0	Class 1, type D
	O34	60.0	Class 2, type H
Mg2	O35	39.2	Class 2, type H
	O36	26.3	Class 1, type D
	O37	6.0	Class 1, type D
	O38	8.9	Class 1, type D
	O39	33.0	Class 2, type H
	O40	13.4	Class 1, type D
Mg3	O41	25.1	Class 1, type D
	O42	12.6	Class 1, type D
	O43	18.6	Class 1, type D
	O44	27.5	Class 1, type D
	O45	0.0	Class 1, type D
	O46	36.6	Class 1″, type J

† Angle between the Mg—O bond and the plane defined by the water molecule. ‡ Classification defined by Ferraris & Franchini-Angela (1972).

All H atoms were located from difference Fourier syntheses. For (I), the positional and displacement parameters of the H atoms were refined fully. For (II), the positional parameters of the H atoms were fixed and their U_{iso} parameters were fixed at $1.5U_{eq}$ of the O atom of the corresponding water molecule. Thus, the geometric parameters involving the H atoms in (II) are less reliable and show some discrepancies with normal values. They are nevertheless included in the current structure analysis because they provide sufficient information on the hydrogen-bond networks. Two water molecules in (II) are disordered, *viz*. O55*A*/O55*B*, with site occupancies of 0.685 (12) and 0.315 (12), and O56*A*/O56*B*, with occupancies of 0.657 (6) and 0.343 (6). The H atoms bonded to the minor O-atom positions could not be located from Fourier maps. A short contact between atoms O12 and O55*B* (2.86 Å) can be attributed to a hydrogen bond *via* an undetermined H atom.

For both compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999) and *ORTEP*III (Burnett & Johnson, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1038). Services for accessing these data are described at the back of the journal.

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