Fourier synthesis. A negative peak was found at the $M2$ site, indicating that too much electron density was present in this site to model the structure. This peak suggests either more Mg atoms in this site or some Al atoms still remaining. The chosen model assumed the latter (Table 1). The K^+ ion distribution was then determined. The K1 ion was refined in a $6c$ site described with β_{ij} displacement parameters: $\beta_{11} = \beta_{22} = 2\beta_{12} = 0.0402\,(5)$ and $\beta_{33} = 0.000126\,(5)$, and third-order cumulant displacement parameters, γ_{ijk}: $\gamma_{111} = -\gamma_{222} = 2\gamma_{112} = -2\gamma_{122} = 0.018\,(1)$, $\gamma_{333} = -0.00003\,(1)$ and $\gamma_{133} = -\gamma_{233} = 2\gamma_{123} = 0.00054\,(6)$. An extra K^+ ion had to be included at an $18h$ site with isotropic displacement parameters. The total number of K^+ ions was constrained to be 1.67 per formula unit. This constraint was also based on the starting amount of sodium ions as determined by chemical analysis with atomic absorption spectroscopy and the weight-exchange measurements. Refinement tests were carried out on the reliability of the constraints of the occupations for the Mg atoms and the K^+ ions. The occupations were refined freely but no significant difference from the constrained occupations was noticed. The constraints were then kept in the final refinements to reduce the number of refined parameters.

Data reduction: *STOEDATR* (Lundgren, 1982). Program(s) used to refine structure: *DUPALS* (Lundgren, 1982). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *DISTAN* (Lundgren, 1982).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1232). Services for accessing these data are described at the back of the journal.

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(NH₄)₂[Mg₄(H₂O)₁₈(H₂W₁₂O₄₂)]·10H₂O, a new compound containing chains formed by magnesium and paradodecahedral tungstate ions

$(NH_4)_2[Mg_4(H_2O)_{18}(H_2W_{12}O_{42})]\cdot10H_2O$, a new compound containing chains formed by magnesium and paradodecahedral tungstate ions

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Abstract

A new ammonium magnesium paradodecatungstate decahydrate, namely diammonium octadecaaquahydrogentetramagnesiododecatungstate decahydrate, $(NH_4)_2[Mg_4(H_2O)_{18}(H_2W_{12}O_{42})]\cdot10H_2O$, was prepared by the reaction of $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot4H_2O$ with $MgCl_2$ in aqueous solution. The skeleton of the paradodecatungstate ion, $[H_2W_{12}O_{42}]^{10-}$, is basically the same as those in the known paradodecatungstates. It consists of 12 interconnected WO_6 octahedra and its centre is located at a crystallographic inversion centre. Both independent Mg atoms are octahedrally coordinated by six O atoms. One magnesium octahedron shares an O atom with a paradodecatungstate group and the other magnesium octahedron shares two O atoms, each with different paradodecatungstate groups, to form a one-dimensional $[Mg_4(H_2O)_{18}(H_2W_{12}O_{42})]_n^{2n-}$ chain along the b direction.

Comment

Many paradodecatungstates have been investigated by X-ray diffraction methods; examples include $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot4H_2O$ (D'Amore & Allman, 1972), $Na_{10}[H_2W_{12}O_{42}]\cdot20H_2O$ (Chrissafidou *et al.*, 1995), $K_{10}[H_2W_{12}O_{42}]\cdot7.5H_2O$ (Evans *et al.*, 1993) and $Mg_5[H_2W_{12}O_{42}]\cdot38H_2O$ (Tsay & Silverton, 1973). The po-

sitions of two non-labile H atoms in the centre of a paradodecatungstate anion, $[H_2W_{12}O_{42}]^{10-}$, have been determined by neutron diffraction (Evans & Prince, 1983). All the compounds mentioned above were prepared from the corresponding tungstate and consist of discrete anions, $[H_2W_{12}O_{42}]^{10-}$ or $\{[Mg(H_2O)_5]_4[H_2W_{12}O_{42}]\}^{2-}$, cations and lattice water. To our knowledge, only one paradodecatungstate containing chain-like polyanions, $[Co_2(H_2O)_8(H_2W_{12}O_{42})]_n^{6n-}$, has been reported (Gimñez-Saiz et al., 1995). We report here a new paradodecatungstate, $(NH_4)_2[Mg_4(H_2O)_{18}(H_2W_{12}O_{42})]\cdot10H_2O$, prepared by the reaction of $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot4H_2O$ with $MgCl_2$ in aqueous solution, which also contains one-dimensional anion chains.

The title crystal consists of one-dimensional $[Mg_4(H_2O)_{18}(H_2W_{12}O_{42})]_n^{2n-}$ anions, discrete NH_4^+ cations and lattice water. The skeleton of the paradodecatungstate group is shown in Fig. 1 and is very similar to those in the known paradodecatungstates (D'Amore & Allman, 1972; Chrissafidou et al., 1995; Evans et al., 1993; Tsay & Silverton, 1973). It consists of 12 WO_6 octahedra and its centre is located at a crystallographic inversion centre $(0,\frac{1}{2},0$ for the structure as reported here). The W—O distances (Table 1) can be divided into four groups: (i) tungsten–terminal oxygen, 1.69 (1)–1.74 (1) Å; (ii) tungsten–oxygen linked to magnesium, 1.70 (1)–1.74 (1) Å; (iii) tungsten–bridging oxygen, 1.78 (1)–2.22 (1) Å; and (iv) tungsten–internal

oxygen common to three W atoms, 1.89 (1)–2.27 (1) Å, which are comparable with those in $Mg_5[H_2W_{12}O_{42}]\cdot38H_2O$ (Tsay & Silverton, 1973) and $K_6[(Co(H_2O)_4)_2(H_2W_{12}O_{42})]\cdot14H_2O$ (Gimñez-Saiz et al., 1995). Of the six independent coordination octahedra of tungsten, the octahedra for W3, W5 and W6 share two edges and two corners with other tungsten octahedra. As reported by Evans & Prince (1983), the non-labile H atom is bonded to the central O12 atom shared by W3, W5 and W6. The W4 octahedron shares one edge and two corners with adjacent tungsten octahedra, W2 shares two edges with octahedra of tungsten and one corner with an octahedron of magnesium, and W1 shares one edge and two corners with octahedra of tungsten and two corners with octahedra of magnesium. Each Mg atom, octahedrally coordinated by six O atoms, has Mg—O bonds very close in magnitude [2.03 (2)–2.10 (2) Å], but five O atoms of six around Mg1 are from coordinated water and the last is shared with a tungsten octahedron, while around Mg2, four are from water and two are shared with tungsten octahedra. The midpoint between Mg2 and Mg2^{ii} at the upper right of Fig. 1 is the crystallographic inversion centre (0,0,0) and the midpoint between Mg2^{i} and Mg2^{iii} at the lower left is the inversion centre (0,1,0). Therefore, one-dimensional $[Mg_4(H_2O)_{18}(H_2W_{12}O_{42})]_n^{2n-}$ chains are formed and are extended along the b direction. An $Mg_2W_2O_4$ eight-membered ring is formed by sharing O atoms between

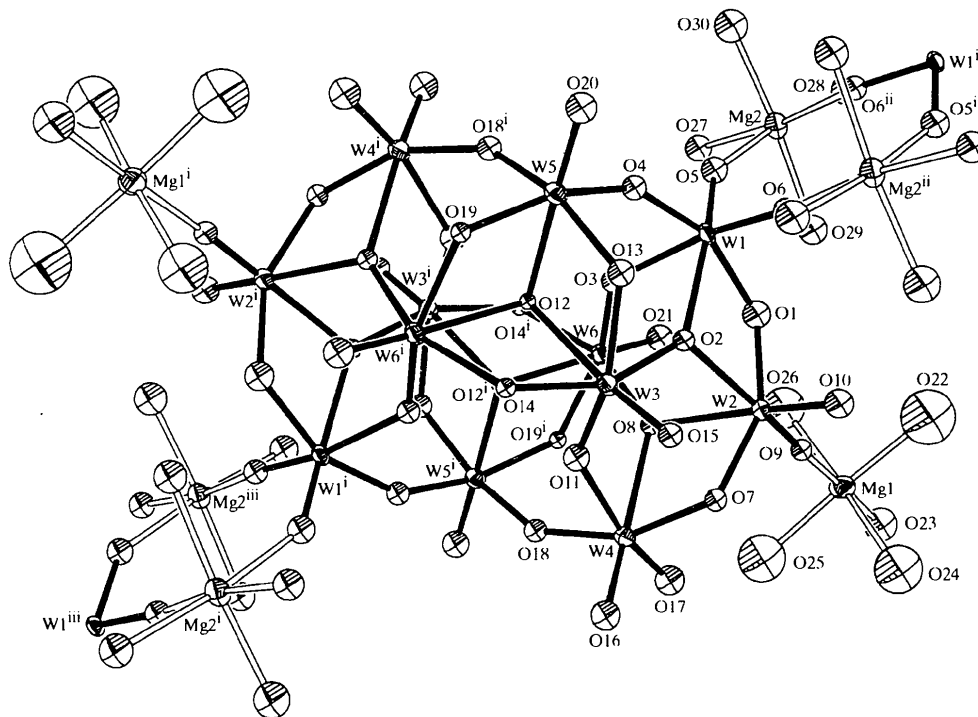Fig. 1. ORTEX (McArdle, 1993) drawing of the structure of $[Mg_4(H_2O)_{18}(H_2W_{12}O_{42})]_n^{2n-}$ with 50% probability ellipsoids, showing the atomic numbering scheme. [Symmetry codes: (i) $-x$, $1-y$, $-z$; (ii) $-x$, $2-y$, $-z$; (iii) x, $-1+y$, z.]

two magnesium octahedra and two tungsten octahedra, which is different from the structure of $[Co_2(H_2O)_8$-$(H_2W_{12}O_{42})]_n^{6n-}$ (Gimñez-Saiz *et al.*, 1995). Fig. 2 is a packing view along the c direction. It is impossible to distinguish between the N atoms of discrete NH_4^+ cations and the O atoms from lattice water in a structure of this type because of the presence of heavy W atoms, so the electron-density peak was assigned to be N according to its environment and to balance the charge of the crystal. The contact distances listed in Table 2 indicate the presence of a system of hydrogen bonds, but no attempt has been made to interpret their contribution to the stability of the structure.
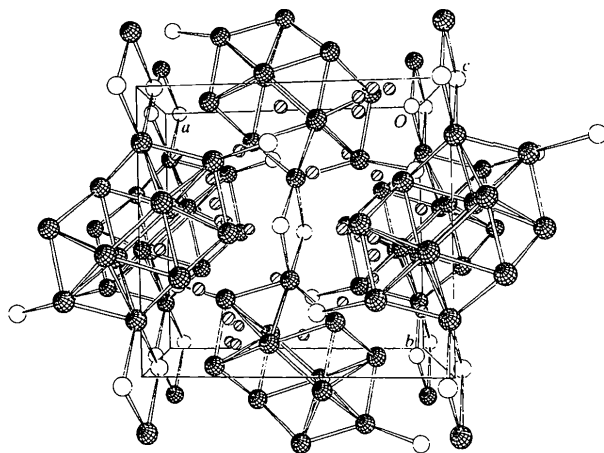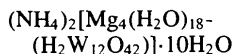

Fig. 2. A packing view along the c direction with double-shaded circles for W, single-shaded circles for N of NH_4^+ and O of lattice water molecules, and open circles for Mg. The O atoms coordinated to W and Mg atoms have been omitted for clarity.

Experimental

$MgCl_2\cdot 6H_2O$ (7.47 g, EM Scientific) was dissolved in distilled water (50 ml). The resulting clear solution was added with stirring to a cloudy boiling solution of $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$ (9.59 g, Johnson–Matthey) and distilled water (150 ml). The resulting solution was boiled for a short time until a white precipitate began to form. The heat was then turned down to $\sim$353 K. The mixture was capped and stirred overnight. Heating was continued the following morning (below the boiling point) until approximately 50 ml of liquid remained. A large quantity of the white precipitate was then collected on a filter and washed with water and then acetone. Transparent thin plate-shaped crystals were found in the product. Subsequent powder X-ray diffraction analysis indicated the product consisted of almost single-phase $(NH_4)_2[Mg_4(H_2O)_{18}(H_2W_{12}O_{42})]\cdot 10H_2O$.

Crystal data

$(NH_4)_2[Mg_4(H_2O)_{18}$-	Mo $K\alpha$ radiation
$(H_2W_{12}O_{42})]\cdot 10H_2O$	$\lambda = 0.71073$ Å
$M_r = 3517.99$	Cell parameters from 25
Monoclinic	reflections
$P2_1/n$	$\theta = 4.5–13.5°$
$a = 14.045\,(3)$ Å	$\mu = 22.719$ mm^{-1}
$b = 12.932\,(3)$ Å	$T = 293\,(2)$ K
$c = 17.099\,(3)$ Å	Thin plate
$\beta = 101.08\,(3)°$	$0.10 \times 0.10 \times 0.03$ mm
$V = 3047.8\,(11)$ Å^3	Colourless
$Z = 2$	
$D_x = 3.833$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.070$
diffractometer	$\theta_{max} = 24.97°$
ω scan	$h = -16 \rightarrow 16$
Absorption correction:	$k = 0 \rightarrow 15$
ψ scan (North *et al.*,	$l = 0 \rightarrow 20$
1968)	3 standard reflections
$T_{min} = 0.151$, $T_{max} = 0.506$	frequency: 120 min
5545 measured reflections	intensity decay: $\pm 2.1\%$
5354 independent reflections	

Refinement

Refinement on F^2	Extinction correction:
$R(F) = 0.072$	SHELX97 (Sheldrick,
$wR(F^2) = 0.113$	1997)
$S = 1.165$	Extinction coefficient:
5354 reflections	$8.8\,(6) \times 10^{-5}$
225 parameters	Scattering factors from
$w = 1/[\sigma^2(F_o^2)]$	International Tables for
$(\Delta/\sigma)_{max} = 0.029$	Crystallography (Vol. C)
$\Delta\rho_{max} = 3.927$ e Å^{-3}	
$\Delta\rho_{min} = -3.139$ e Å^{-3}	

Table 1. *Selected bond lengths (Å)*

W1—O6	1.696 (14)	W5—O20	1.729 (15)
W1—O5	1.745 (13)	W5—O13	1.859 (13)
W1—O4	1.823 (14)	W5—O19	1.893 (13)
W1—O1	1.996 (16)	W5—O18^i	1.963 (12)
W1—O3	2.180 (13)	W5—O4	1.994 (14)
W1—O2	2.203 (12)	W5—O12	2.263 (12)
W2—O9	1.698 (14)	W6—O21	1.724 (15)
W2—O10	1.731 (14)	W6—O3	1.834 (14)
W2—O1	1.915 (14)	W6—O8	1.891 (12)
W2—O7	1.931 (13)	W6—O14^i	1.964 (12)
W2—O2	2.261 (14)	W6—O19^i	2.101 (13)
W2—O8	2.269 (12)	W6—O12^i	2.265 (12)
W3—O15	1.717 (12)	Mg1—O23	2.04 (2)
W3—O11	1.782 (15)	Mg1—O25	2.03 (2)
W3—O2	1.906 (13)	Mg1—O24	2.07 (2)
W3—O14	1.935 (13)	Mg1—O9	2.074 (16)
W3—O13	2.121 (14)	Mg1—O26	2.08 (2)
W3—O12	2.216 (11)	Mg1—O22	2.08 (3)
W4—O17	1.696 (16)	Mg2—O5	2.039 (15)
W4—O16	1.736 (14)	Mg2—O30	2.058 (17)
W4—O18	1.844 (13)	Mg2—O6^{ii}	2.086 (15)
W4—O7	1.966 (13)	Mg2—O28	2.093 (17)
W4—O11	2.213 (15)	Mg2—O29	2.098 (17)
W4—O8	2.238 (12)	Mg2—O27	2.101 (16)

Symmetry codes: (i) $-x, 1 - y, -z$; (ii) $-x, 2 - y, -z$.

Table 2. *Contact distances (Å)*

N1$\cdots$O3^i	3.11 (3)	O2W$\cdots$O5WA^{viii}	3.01 (6)
N1$\cdots$O5^i	3.14 (3)	O3W$\cdots$O10^{ii}	2.99 (3)
N1$\cdots$O10^{ii}	3.14 (3)	O3W$\cdots$O14	2.81 (3)
N1$\cdots$O11	3.06 (3)	O3W$\cdots$O22^v	2.81 (4)
N1$\cdots$O14	3.24 (3)	O4WA$\cdots$O1^{ix}	3.14 (5)
N1$\cdots$O15^{ii}	3.18 (3)	O4WA$\cdots$O22^{ix}	3.02 (6)
N1$\cdots$O16	3.16 (3)	O4WA$\cdots$O29^{ix}	2.92 (5)

N1···O27^i	3.09 (3)	O4WB···O20^x	2.70 (14)
N1···O1W^{ii}	2.91 (4)	O4WB···O22^{ix}	2.61 (14)
O1W···O4^{iii}	3.15 (3)	O4WB···O24^{xi}	2.91 (14)
O1W···O16^{iv}	3.06 (3)	O4WB···O29^{ix}	3.15 (14)
O1W···O18^{ix}	2.97 (3)	O4WB···O5WB	2.36 (14)
O1W···O23^v	2.75 (3)	O5WA···O19^{xii}	2.74 (5)
O1W···O24^v	3.17 (4)	O5WA···O25^{ii}	2.94 (5)
O1W···O4WA^{vi}	2.57 (5)	O5WA···O29^{ix}	2.73 (5)
O1W···O4WB^{vi}	2.81 (14)	O5WB···O19^{xii}	2.84 (7)
O2W···O20^{vii}	3.14 (4)	O5WB···O20^x	3.12 (7)
O2W···O21^{iii}	3.07 (4)	O5WB···O22^{ix}	2.83 (7)
O2W···O24	2.72 (4)	O5WB···O29^{ix}	2.89 (7)
O2W···O27^{iii}	2.79 (4)		

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

Two lattice water molecules, designated O4WA, O4WB, O5WA and O5WB, showed disorder. In the final refinement, the site-occupancy factors of O4WA and O5WA were assigned to be 0.7, and those of O4WB and O5WB 0.3, according to the refinement results. There were 12 O atoms of paradodecatungstate and two disordered O atoms (OW4B and O5WB) became 'non-positive-definite' when all atoms were refined anisotropically. The N and O atoms were then refined isotropically in the final refinement. The isotropic displacement parameters of the 12 O atoms ranged from 0.008 to 0.030 Å^2, which are comparable with those of the other O atoms in the paradodecatungstate (0.011–0.027 Å^2). The largest residual electron-density peaks were located around W atoms.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *CAD-4-PC Software*. Data reduction: *XCAD4* (Harms, 1997). Program(s) used to solve structure: *SHELX97* (Sheldrick, 1997). Program(s) used to refine structure: *SHELX97*. Molecular graphics: *SCHAKAL92* (Keller, 1992) and *ORTEX* (McArdle, 1993). Software used to prepare material for publication: *SHELXL97*.

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K₂NbAlO₂[(As,Nb)O₄]₂, isostructural with KTiOPO₄

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Abstract

The title compound, potassium niobium aluminium arsenate (KNAA), is isostructural with KTiOPO₄ (KTP). In KNAA, the site corresponding to the Ti1 sites of KTP is occupied mostly by Nb atoms, the Ti2 site is occupied predominantly by Al atoms, and the As1 and As2 tetrahedral sites are occupied mostly by As atoms. The $M1O_6$ octahedron is more distorted and the $M2O_6$ octahedron is less distorted than that of KTP.

Comment

Recently, many crystals isostructural with KTiOPO₄ (KTP) (Tordjman *et al.*, 1974) have been synthesized because they have interesting non-linear optical properties. For example, KTP crystals are used effectively for second harmonic generation. The structures of the compounds with the general formula (K,Rb,Tl,Na)TiO-(P,As)O₄ have been determined by single-crystal X-ray or neutron diffraction methods (Haidouri *et al.*, 1990; Mayo *et al.*, 1994; Thomas *et al.*, 1990, 1992).

In this study, a new compound with the chemical formula K₂NbAlO₂[(As,Nb)O₄]₂ (KNAA) has been synthesized by a flux method and the structure was refined using single-crystal X-ray diffraction data. The atomic coordinates, site occupancies and equivalent displacement factors are given in Table 1, the interatomic distances and angles are given in Table 2 and a projection of KNAA parallel to the c axis is shown in Fig. 1.

The structure of KNAA, isostructural with that of KTP, has six kinds of cation site, namely $M1$, $M2$,