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Synthesis and crystal structure of hexaaquamagnesium hydrogen phosphododecatungstate tetrahydrate $[\text{Mg}(\text{H}_2\text{O})_6][\text{HPW}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O}$

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Abstract

Mg-salt of dodecatungstophosphoric acid $[\text{Mg}(\text{H}_2\text{O})_6][\text{HPW}_{12}\text{O}_{40}]\cdot 4\text{H}_2\text{O}$ was prepared by the addition of an equimolar quantity of Mg-chloride aqueous solution into dodecatungstophosphoric acid aqueous solution and slow evaporation of water from mother liquor. This simple synthetic route yielded high quality $[\text{Mg}(\text{H}_2\text{O})_6][\text{HPW}_{12}\text{O}_{40}]\cdot 4\text{H}_2\text{O}$ single crystals. The structure is composed of Keggin, $[\text{PW}_{12}\text{O}_{40}]^{3-}$ anions, $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cations and lattice water molecules. Zigzag arrangement of Keggin anions along *c*-axis creates irregular channels occupied by $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cations and lattice H_2O molecules. The calculation of total potential solvent area indicated presence of 4 H_2O lattice molecules per formula unit, which is in agreement with here presented structural model. The position of one lattice water molecule is well defined, while the other three molecules are disordered and statistically distributed. Hydrogen bonds involve all coordinated and lattice H_2O molecules, as well as some oxygens from Keggin anion.

1. Introduction

The extensive class of polyoxoanions formed by transition metals of groups 5 and 6 attracts considerable attention in science and technology. As hetero- and isopoly acids or their salts these polyanions have been known and investigated for almost two centuries. In 1826 Berzelius ^[1] described formation of ammonium 12-molybdophosphate, $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$. However, the true composition of heteropoly acids was not precisely determined until 1862 when tungstosilicic acid was characterized ^[2]. Since then, the interest for investigations on hetero- and isopoly acids and their salts extensively increased ^[3,4].

Nowadays, heteropoly compounds (HPC) based on Keggin, $[\text{XM}_{12}\text{O}_{40}]^{n-}$, structure ^[5], where X is a heteroatom ($X = \text{P}, \text{Si}, \text{Ge}, \dots$) and M is an addenda atom ($\text{W}, \text{Mo}, \dots$) ^[3], have important applications mainly as catalysts. Compatibility of these materials with environmental demands led to their utilization in different reactions ^[4, 6-9]. HPC may potentially replace corrosive liquids in acid-catalyzed reactions and can act as photocatalysts in processes of decomposition of environmentally persistent pollutants ^[10]. They are, for example, valuable in removal and conversion of nitrogen oxides ^[11].

Characteristics of heteropoly acids (HPA) strongly depend on temperature and relative humidity of the surrounding. For some industrial processes it is necessary to have catalysts not sensitive to the surrounding ^[12-14] and salts of HPA satisfy these conditions. They are more stable and less sensitive to

humidity and temperature than acids themselves. Moreover, catalytic activities of HPA salts are close to the catalytic activity of HPA [15]. While different HPA forms and salts of monovalent cations have received the most attention [13], there are only few reports concerning the catalytic properties of dodecatungstophosphoric (WPA) salts with divalent cations [15-18]. It has been shown that Mg salt of WPA (Mg-WPA) is highly active in the conversions of methanol to hydrocarbons [15]. Use of acid salts: Zn-WPA, Mg-WPA, Al-WPA, Zr-WPA and B-WPA resulted in high yields of hydrocarbons. The largest concentration of the major product C₄ hydrocarbons is produced by the Al-WPA and Mg-WPA. The Al-WPA and Mg-WPA are also the most active in total (C₁ to C₅) hydrocarbon production.

Structures of different hydrates of WPA are still under investigations. Structures of 29, 21 and 6 hydrate were determined long time ago with more or less precision [19-21]. The structure of 14-hydrate is not known yet. The structure of Keggin anion, [PW₁₂O₄₀]³⁻, is well-known, but the structure of cationic part, especially when H₂O, H⁺, H₃O⁺, H₅O₂⁺, *etc.* are present, is not precisely defined. According to the equilibrium H₅O₂⁺ ↔ H₃O⁺ + H₂O ↔ H⁺ + 2H₂O, in WPA hydrates with 6, 14, 21 and 29 water molecules per formula unit, as well as in their salts, various forms of hydrated proton entities take part in the structure at the same time. This was confirmed by infrared, Raman and IINS techniques [22-25]. Structures with precisely defined positions of H₂O, H⁺, H₃O⁺ and H₅O₂⁺ are limited to a small number of articles mainly based on neutron diffraction or theoretical calculation [20-21, 26-32]. Evidently, disorder of protons and water molecules is quite common for HPA compounds.

As already stated, reports of solid 12-tungstophosphoric acid salts containing divalent cations are quite rare [15-18]. Such salts are often reported to be of low crystallinity [15] or they have not been formed at all [16]. The synthetic procedures were based on the double decomposition method with appropriate hydroxides [16], carbonates [15, 17, 33] and nitrates [18, 33]. Therefore, there is a challenge to find a procedure that yields divalent cation WPA salts in a well crystalline form suitable for structural investigation, *i.e.* in the form of single crystals of a proper quality and dimensions.

The main goals of this work are to present the first successful synthesis of a divalent cation salt of WPA in the single crystal form, to describe its crystal structure including water molecules locations, and to analyze a possible hydrogen-bonding network.

2. Results and discussion

Contrary to the application of double decomposition method on appropriate carbonates, nitrates and hydroxides [15-18, 33] here described simple synthetic route yielded high quality

[Mg(H₂O)₆][HPW₁₂O₄₀]·4H₂O single crystals. Recently, the same synthetic route has successfully been used for the preparation of other alkaline earth salts of WPA in the polycrystalline form [34].

Results of X-ray structure refinement are presented in Tables 1-5. The magnesium salt of tungstophosphoric acid is composed of Keggin anions, [Mg(H₂O)₆]²⁺ cations, and lattice water molecules (Figures 1 and 2). Similar arrangement of polyanions has been noticed in Mg₂Na₂V₁₀O₂₈ · 20H₂O and Mg₃V₁₀O₂₈ · 28H₂O [35], as well as in sodium magnesium bis(vanadate) pyrovanadate Na₆Mg₂(VO₄)₂(V₂O₇) [36].

Previously published [25] preliminary data about magnesium salt of dodecatungstophosphoric acid reported 10 water molecules in the formula unit and presence of hydrated proton species (H₃O⁺ and H₅O₂⁺) in the structure. After reinvestigation using new X-ray diffraction data presence of 10 water molecules was approved, but existence of hydrated proton species was not confirmed. Calculation of total potential solvent area [40] indicated that 652 Å³, *i.e.* 15.6 % of the unit cell volume, could be occupied by lattice H₂O molecules. Two main voids are located around 0 0.5 0 and 0 0 0.5. As a hydrogen bonded H₂O molecule fills ≈40 Å³, in total 16.3 lattice H₂O molecule could be situated in the unit cell, *i.e.* there could be 4.08 H₂O molecules per formula unit (*Z* = 4). Additional 6 H₂O molecules from the [Mg(H₂O)₆]²⁺ complex gives 10.1 H₂O molecules per formula unit, what is in excellent agreement with our structural model.

The octahedral [Mg(H₂O)₆]²⁺ complex cations and four lattice water molecules are situated in channels surrounded by six Keggin anions (Fig. 2). Position of one lattice water molecule is well defined, while each of three other molecules is statistically distributed over two locations. As expected, proton position was not defined. Hydrogen bonds involve all coordinated and lattice H₂O molecules, as well as some oxygen atoms from Keggin anion. With three exceptions (Table 5), all hydrogen bonds are longer than 2.8 Å and could be regarded as weak.

In Keggin anion interatomic distances are as expected and unusual short contacts have not been observed [37-38]. The inspection of Inorganic Crystal Structure Database (ICSD) [39] showed that for all (20) reported structures containing Keggin anion W–O distances vary in a wide range from 1.65 to 2.50 Å as found in the [Mg(H₂O)₆][HPW₁₂O₄₀]·4H₂O. Individual W atoms are in deformed octahedral environment with equatorial W–O bond distances about 1.90 Å. One apical W–O distance is slightly shorter (≈1.70 Å), while another is much longer (≈2.4 Å), and W atoms are moved out of the equatorial plane toward closer apex. All O–W–O angles deviate from ideal 90° and 180° values for up to 19° and 6° each. O–W–O angles that involve shorter apical W–O bonds are systematically larger than 90°, while O–W–O angles that involve larger W–O bonds are systematically smaller than 90°. Both, W–O distances and O–W–O angles indicate that WO₆ octahedra are irregular and similar to other Keggin

structures reported in the ICSD. P–O bonds are between 1.52 and 1.54 Å, while O–P–O angles are between 107.6 and 110.7° (Table 3). This is an indication that the PO₄ tetrahedra are very close to T_d symmetry. Among reported Keggin structures, only in five cases so regular PO₄ tetrahedra are observed.

Further inspection of ICSD reveals that 36 structures contain hexaaquamagnesium complex, but only in 19 H-atoms are located. In 31 of reported structures Mg–O distances are between 2.0 and 2.1 Å as it is for the [Mg(H₂O)₆][HPW₁₂O₄₀] \cdot 4H₂O. In all structures, including here reported one, O–Mg–O angles are close to 90 and 180°, indicating very regular octahedral arrangements of H₂O molecules around Mg (Table 3).

3. Experimental

3.1. Synthesis and composition of [Mg(H₂O)₆][HPW₁₂O₄₀] \cdot 4H₂O

The Mg-salt of dodecatungstophosphoric acid [Mg(H₂O)₆][HPW₁₂O₄₀] \cdot 4H₂O was prepared by the addition of an equimolar quantity of Mg-chloride aqueous solution into WPA aqueous solution. After slow evaporation of water from mother liquor a salt with 10 water molecules per formula unit was obtained. The Mg-content in the salt was checked by atomic absorption spectrometry (AAS) using a VARIAN AA-775 spectrophotometer. The theoretical Mg content is 0.71 % and the experimentally obtained one was 0.70 \pm 0.03 %.

3.2. Crystal structure determination

An irregular prismatic crystal was chosen and grinded in an Enraf-Nonius crystal grinder. After about half an hour of grinding the crystal with an ellipsoidal shape (0.20 \times 0.20 \times 0.15 mm) was obtained. Data were collected at 293 K on a three axis platform Bruker SMART diffractometer equipped with a 1K CCD detector using graphite-monochromated MoK α radiation (λ = 0.71703 Å). For data collection the program SMART^[41] was used, while unit cell parameters were refined and data were reduced with the program SAINT^[41]. The structure was solved by direct methods with the SIR97^[42] and refined by the full-matrix least-squares method on F^2 using the SHELXL-97^[43]. Anisotropic displacement parameters were employed to refine non-hydrogen atoms within Keggin anion and [Mg(H₂O)₆]²⁺ complex cation, as well as the oxygen from ordered lattice water molecule. Isotropic

displacement parameters of oxygens from three other lattice water molecules were fixed to the value of 0.07 \AA^2 .

Attempts to refine occupancy of O48 and O49 atoms indicated half occupancy for both O sites and refinement was finished with these values fixed to 50% occupancy. These two water molecules are situated close to the special position $2c$ in space group $P2_1/c$, and they filled up the largest voids in the structure. Having this in mind they can be treated as one water molecule moving from the centre of symmetry and, therefore, distributed in two different general positions, but with half occupancy. The shortest O48–O49 distance is 4.909 \AA . The other two water sites are split: the shortest distances are 0.923 \AA for O50A–O50B and 1.736 \AA for O51A–O51B. Their occupancies were refined as free variables and constrained assuming the full occupancy of each site.

Positions of hydrogen atoms in ordered lattice water molecule, O47, and $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ complex cations were calculated by the method presented in [44] using the following parameters: Gaussian coefficient 5, O–H distance 0.85 \AA and charge on H-atoms $0.45 e^-$. The isotropic displacement parameters for generated hydrogens were also fixed to the value of 0.07 \AA^2 . Hydrogen atoms for disordered lattice water molecules as well as proton were not located.

The space group and existence of pseudomerohedral twinning were also checked. Previously reported [25] space group $P2_1/c$ (No. 14) seems to be true. It was possible to solve and refine the structure in the triclinic space group $P\bar{1}$, but to obtain approximately the same agreement factors of refinement it was necessary to include a twin option. Two twin domains are symmetrically related by the 180° rotation around b -axes. Together with β -angle close to 90° , this is an indication for a pseudomerohedral twinning in the investigated crystal. Refinement of the twin domain occupancies indicated presence of 50 % for each one, thus simulating $2/m$ point group symmetry. However, a close inspection of two structure models suggested that the monoclinic model is preferable.

4. Conclusion

The first alkaline-earth (magnesium) salt of tungstophosphoric acid single crystal synthesis and its crystal structure are reported. After slow evaporation of water from mother liquor, prepared by the addition of an equimolar quantity of Mg-chloride aqueous solution into WPA aqueous solution, a salt with 10 water molecules per formula unit was obtained. The structure is composed of Keggin anions, $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cations and water molecules. Hydrogen bonds involve all coordinated and lattice H_2O molecules, as well as some oxygen atoms from Keggin anion. Most of hydrogen bonds are weak.

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Figure 1. Asymmetric unit of $[\text{Mg}(\text{H}_2\text{O})_6][\text{HPW}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O}$ with 50% probability displacement ellipsoids (Ortep-3 for Windows ^[45]).

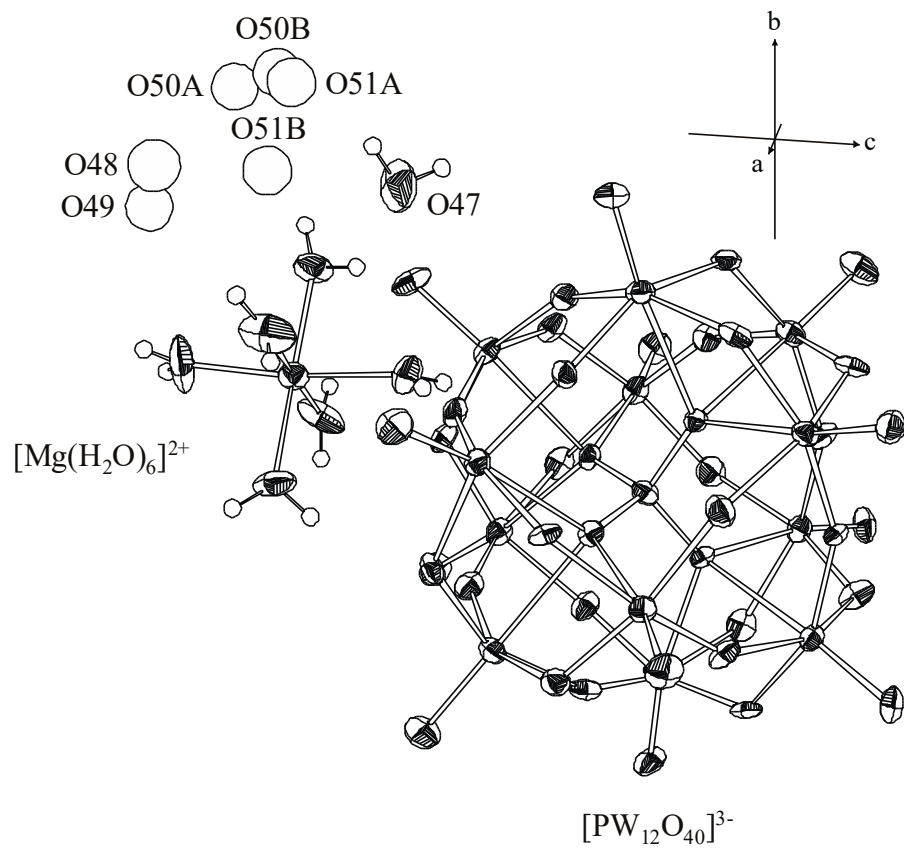


Figure 2. Packing of $[\text{Mg}(\text{H}_2\text{O})_6][\text{HPW}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O}$ with 50% probability displacement ellipsoids (Ortep-3 for Windows ^[45]).

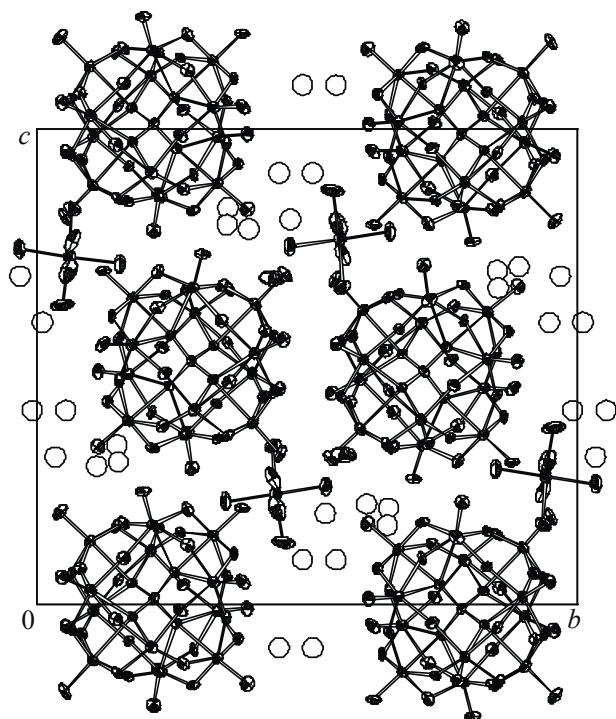


Table captions

Table 1. Crystal data and results of structure refinement for $[\text{Mg}(\text{H}_2\text{O})_6][\text{HPW}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O}$.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for $[\text{Mg}(\text{H}_2\text{O})_6][\text{HPW}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. S.O.F. is a site occupation factor.

Table 3. Selected bond lengths [\AA] and angles [$^\circ$] for $[\text{Mg}(\text{H}_2\text{O})_6][\text{HPW}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O}$.

Table 4. Hydrogen coordinates for $[\text{Mg}(\text{H}_2\text{O})_6][\text{HPW}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O}$.

Table 5. Potential hydrogen bonds [\AA and $^\circ$] between: (a) oxygens from Keggin anions and $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ complex, (b) oxygens from Keggin anion and lattice H_2O molecules, (c) oxygens from $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ complex and lattice H_2O molecules, (d) oxygens from lattice H_2O molecules.

Table 1. Crystal data and results of structure refinement for $[\text{Mg}(\text{H}_2\text{O})_6][\text{HPW}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O}$.

Empirical formula	$\text{H}_{21}\text{MgO}_{50}\text{PW}_{12}$
Formula weight	3082.65
Temperature [K]	293(2)
Wavelength [\AA]	0.71073
Crystal system, space group	monoclinic, $P2_1/c$ (no. 14)
Unit cell dimensions [\AA and $^\circ$]	$a = 9.868(6)$ $b = 21.980(10)$ $c = 19.289(10)$ $\beta = 90.630(5)$
Cell volume [\AA^3]	4184(4)
Z, Calculated density [g/cm^3]	4, 4.894
Absorption coefficient [mm^{-1}]	33.026
$F(000)$	5344
Crystal size [mm]	$0.20 \times 0.20 \times 0.15$
θ -range for data collection [$^\circ$]	1.40 to 28.28
Limiting indices	$-13 \leq h \leq 13, -28 \leq k \leq 29, -24 \leq l \leq 25$
Reflections collected / unique	83177 / 10301 [$R_{\text{int}} = 0.0385$]
Completeness to $\theta = 28.28^\circ$	99.3 %
Absorption correction	Multiscan (SADABS ^[41])
Max. and min. transmission	0.0830 and 0.0581
Refinement method	Full-matrix least-squares on F^2
Data / parameters	10301 / 571
Goodness-of-fit on F^2	1.490
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0576, wR_2 = 0.1059$
R indices (all data)	$R_1 = 0.0591, wR_2 = 0.1063$
Extinction coefficient	0.000141(6)
Largest diff. peak and hole [e \AA^{-3}]	3.00 and -3.77

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for $[\text{Mg}(\text{H}_2\text{O})_6][\text{HPW}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. S.O.F. is a site occupation factor.

Atom	x	y	z	U_{eq}	S.O.F.
W(1)	0.1649(1)	0.1674(1)	0.3856(1)	0.019(1)	1
W(2)	0.0583(1)	0.4030(1)	0.6318(1)	0.020(1)	1
W(3)	-0.1208(1)	0.1680(1)	0.4843(1)	0.017(1)	1
W(4)	0.3717(1)	0.4018(1)	0.5278(1)	0.020(1)	1
W(5)	-0.1380(1)	0.3971(1)	0.4851(1)	0.018(1)	1
W(6)	-0.1781(1)	0.2906(1)	0.6119(1)	0.017(1)	1
W(7)	0.3225(1)	0.2873(1)	0.6658(1)	0.019(1)	1
W(8)	0.1749(1)	0.3981(1)	0.3815(1)	0.019(1)	1
W(9)	0.3744(1)	0.1746(1)	0.5459(1)	0.019(1)	1
W(10)	-0.0774(1)	0.2752(1)	0.3574(1)	0.017(1)	1
W(11)	0.0883(1)	0.1752(1)	0.6445(1)	0.017(1)	1
W(12)	0.4197(1)	0.2894(1)	0.4084(1)	0.021(1)	1
P	0.1229(4)	0.2848(2)	0.5111(2)	0.018(1)	1
O(1)	-0.1779(11)	0.2113(5)	0.4034(6)	0.021(2)	1
O(2)	-0.1938(12)	0.2303(5)	0.5402(6)	0.024(2)	1
O(3)	-0.0924(11)	0.3549(5)	0.6629(6)	0.021(2)	1
O(4)	0.3300(12)	0.3512(5)	0.3539(6)	0.024(2)	1
O(5)	0.0131(11)	0.1293(5)	0.4261(6)	0.020(2)	1
O(6)	0.2082(11)	0.2227(5)	0.6994(6)	0.024(2)	1
O(7)	0.3939(12)	0.3408(6)	0.5964(6)	0.026(2)	1
O(8)	0.2212(12)	0.1118(6)	0.3314(7)	0.030(3)	1
O(9)	0.2623(11)	0.1507(5)	0.4705(6)	0.021(2)	1
O(10)	0.0655(11)	0.3325(5)	0.3477(5)	0.019(2)	1
O(11)	-0.2431(10)	0.3507(5)	0.5503(6)	0.018(2)	1
O(12)	0.0429(11)	0.2122(5)	0.3282(5)	0.020(2)	1
O(13)	0.2462(11)	0.1370(5)	0.6061(6)	0.019(2)	1
O(14)	0.0523(10)	0.2433(5)	0.4590(5)	0.016(2)	1
O(15)	-0.3142(12)	0.2777(5)	0.6621(6)	0.024(2)	1
O(16)	-0.0617(12)	0.4375(5)	0.5646(6)	0.021(2)	1
O(17)	0.0226(11)	0.4180(5)	0.4360(6)	0.021(2)	1
O(18)	-0.2386(12)	0.1124(5)	0.4893(7)	0.028(3)	1
O(19)	0.1755(11)	0.3414(5)	0.6708(6)	0.023(2)	1
O(20)	0.2257(10)	0.3251(5)	0.4730(5)	0.015(2)	1
O(21)	0.4395(11)	0.2351(5)	0.4860(6)	0.023(2)	1
O(22)	0.2073(12)	0.4212(5)	0.5752(6)	0.025(2)	1
O(23)	0.4275(10)	0.2223(5)	0.6242(6)	0.023(2)	1
O(24)	0.2950(11)	0.2308(5)	0.3741(6)	0.023(2)	1
O(25)	-0.1531(11)	0.3311(5)	0.4217(5)	0.018(2)	1
O(26)	0.2904(12)	0.4376(5)	0.4463(6)	0.023(2)	1
O(27)	0.4973(12)	0.1205(6)	0.5467(7)	0.030(3)	1
O(28)	-0.0070(11)	0.1506(5)	0.5608(6)	0.021(2)	1
O(29)	0.4800(11)	0.3552(6)	0.4673(6)	0.024(2)	1

O(30)	0.1682(13)	0.4498(6)	0.3158(7)	0.032(3)	1
O(31)	0.0165(10)	0.3259(5)	0.5444(5)	0.015(2)	1
O(32)	0.5598(12)	0.2752(6)	0.3603(7)	0.030(3)	1
O(33)	0.4822(12)	0.4551(6)	0.5562(7)	0.029(3)	1
O(34)	0.0654(13)	0.4581(6)	0.6937(7)	0.032(3)	1
O(35)	-0.1724(12)	0.2853(6)	0.2861(7)	0.029(3)	1
O(36)	0.1965(10)	0.2465(4)	0.5663(5)	0.014(2)	1
O(37)	-0.0426(12)	0.2361(5)	0.6510(5)	0.021(2)	1
O(38)	0.4175(12)	0.3048(6)	0.7367(6)	0.028(3)	1
O(39)	-0.2525(13)	0.4480(5)	0.4527(7)	0.029(3)	1
O(40)	0.0344(12)	0.1218(6)	0.7019(6)	0.026(2)	1
Mg	0.6166(6)	0.4404(3)	0.2312(3)	0.027(1)	1
O(41)	0.6107(17)	0.3479(6)	0.2158(9)	0.047(4)	1
O(42)	0.5569(15)	0.4358(7)	0.3329(7)	0.038(3)	1
O(43)	0.4154(18)	0.4433(8)	0.2007(11)	0.065(6)	1
O(44)	0.6129(16)	0.5334(6)	0.2473(8)	0.043(4)	1
O(45)	0.6700(20)	0.4548(10)	0.1293(8)	0.071(6)	1
O(46)	0.8114(13)	0.4355(7)	0.2644(9)	0.046(4)	1
O(47)	0.3780(20)	0.5657(11)	0.3143(9)	0.070(6)	1
O(48)	0.0620(40)	0.5094(19)	0.9070(20)	0.070	0.5
O(49)	0.4600(40)	0.5527(19)	0.0920(20)	0.070	0.5
O(50A)	0.3940(40)	0.6475(16)	0.1650(20)	0.070	0.61(4)
O(50B)	0.3330(60)	0.6490(30)	0.2010(30)	0.070	0.39(4)
O(51A)	0.1760(50)	0.6090(20)	0.2100(30)	0.070	0.42(3)
O(51B)	0.1600(40)	0.5325(17)	0.1905(19)	0.070	0.58(3)

Table 3. Selected bond lengths [\AA] and angles [$^\circ$] for $[\text{Mg}(\text{H}_2\text{O})_6][\text{HPW}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O}$.

Around P atom	
P–O(14)	1.520(10)
P–O(31)	1.532(11)
P–O(36)	1.533(10)
P–O(20)	1.540(10)
O(14)–P–O(31)	108.6(6)
O(14)–P–O(36)	109.9(6)
O(31)–P–O(36)	110.7(6)
O(14)–P–O(20)	109.2(6)
O(31)–P–O(20)	108.6(6)
O(36)–P–O(20)	109.7(6)
Around Mg atom	
Mg–O(46)	2.021(15)
Mg–O(41)	2.056(15)
Mg–O(42)	2.057(15)
Mg–O(45)	2.064(17)
Mg–O(43)	2.066(18)
Mg–O(44)	2.067(15)
O(46)–Mg–O(41)	91.1(6)
O(46)–Mg–O(42)	88.7(7)
O(41)–Mg–O(42)	94.6(7)
O(46)–Mg–O(45)	93.3(9)
O(41)–Mg–O(45)	91.2(8)
O(42)–Mg–O(45)	173.8(8)
O(46)–Mg–O(43)	177.7(9)
O(41)–Mg–O(43)	87.9(7)
O(42)–Mg–O(43)	89.3(8)
O(45)–Mg–O(43)	88.8(9)
O(46)–Mg–O(44)	91.3(7)
O(41)–Mg–O(44)	177.3(8)
O(42)–Mg–O(44)	84.3(6)
O(45)–Mg–O(44)	89.8(8)
O(43)–Mg–O(44)	89.7(7)

Table 4. Hydrogen coordinates for $[\text{Mg}(\text{H}_2\text{O})_6][\text{HPW}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O}$.

Atom	x	y	z
H411	0.6142	0.3268	0.1785
H412	0.6255	0.3233	0.2493
H421	0.4870	0.4148	0.3436
H422	0.6066	0.4380	0.3692
H431	0.3633	0.4120	0.2031
H432	0.3773	0.4676	0.1715
H441	0.6171	0.5713	0.2391
H442	0.5719	0.5288	0.2856
H451	0.6197	0.4584	0.0932
H452	0.7520	0.4604	0.1158
H461	0.8700	0.4067	0.2673
H462	0.8538	0.4686	0.2732
H471	0.3848	0.5841	0.3537
H472	0.3292	0.5894	0.2884

Table 5. Potential hydrogen bonds [\AA and $^\circ$] between: (a) oxygens from Keggin anions and $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ complex, (b) oxygens from Keggin anion and lattice H_2O molecules, (c) oxygens from $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ complex and lattice H_2O molecules, (d) oxygens from lattice H_2O molecules.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
(a)				
O41-H411...O23	0.86	2.37	2.95(2)	125
O41-H411...O15	0.86	2.43	3.04(2)	129
O41-H412...O35	0.86	2.27	2.87(2)	128
O42-H421...O4	0.86	2.10	2.94(2)	168
O42-H422...O39	0.85	2.13	2.98(2)	174
O43-H431...O13	0.86	2.44	3.03(2)	126
O44-H441...O8	0.85	2.29	2.83(2)	122
O45-H451...O27	0.86	2.29	2.85(2)	123
O46-H461...O40	0.86	2.16	2.82(2)	133
O46-H462...O34	0.85	1.90	2.75(2)	171
(b)				
O47-H471...O33	0.86	2.33	2.88(2)	122
O48-*...O5			3.11(4)	
O49-*...O18			2.98(4)	
O49-*...O27			3.10(4)	
O50A-*...O1			2.87(4)	
O50A-*...O32			2.89(4)	
O50A-*...O38			2.83(4)	
O50B-*...O1			2.87(6)	
O50B-*...O32			3.19(6)	
O50B-*...O38			2.90(6)	
O51A-*...O1			3.13(5)	
O51A-*...O3			2.71(5)	
O51B-*...O34			3.17(4)	
(c)				
O45-H452...O48	0.86	2.00	2.85(5)	168
O45-H451...O49	0.86	2.60	3.07(5)	115
O44-H442...O47	0.85	2.16	2.76(2)	126
O43-H432...O51B	0.86	2.61	3.20(4)	127
(d)				
O47-H472...O50B	0.86	2.14	2.88(6)	144
O47-H472...O51A	0.86	2.17	2.97(5)	155
O51B-*...O48			3.02(6)	

* H-atoms are not located