Crystal structure of diammonium hexaaquamagnesium icosaaqua-tetramagnesium-hexakis(μ_3-oxo)-hexacosakis(μ_2-oxo)-decaoxo-dodecatungsten octahydrate, $(NH_4)_2[Mg(H_2O)_6][Mg_4(H_2O)_{20}W_{12}O_{42}] \cdot 8H_2O$

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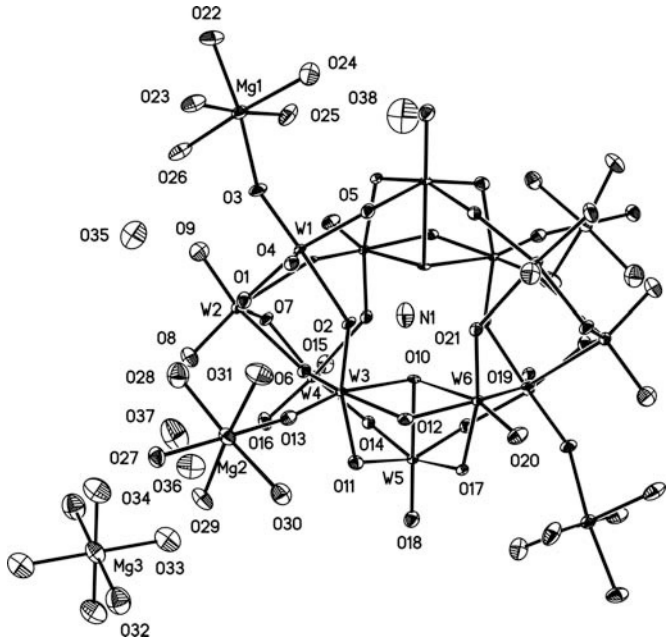

Abstract

$H_{78}Mg_5N_2O_{77}W_{12}$, triclinic, $P\bar{1}$ (no. 2), a = 12.545(1) Å, b = 13.344(1) Å, c = 13.651(2) Å, α = 91.266(2)°, β = 116.702(2)°, γ = 111.900(2)°, V = 1844.0 Å^3, Z = 1, $R_{gt}(F)$ = 0.055, $wR_{ref}(F^2)$ = 0.152, T = 293 K.

Source of material

All commercially obtained reagent-grade chemicals were used without further purication. A mixture of $MgCl_2$ (0.1 mmol, 0.010 g), $(NH_4)_2WO_4$ (0.1 mmol, 0.029 g) and 2-acetylpyrazine (0.1 mmol, 0.012 g) was added into 20 mL water with 20 % (*v*/*v*) ethanol and heated at 140 °C for 12 h. After cooling to room temperature the solution was filtered. Colorless prism-like single crystals suitable for X-ray measurements were obtained after a few weeks. 2-Acetylpyrazine does not take part in the reaction.

Discussion

Polyoxometalates chemistry has made a giant leap. Its development has largely depended on the progress made for the Keggin and related species that have tetrahedrally coordinated heteroatoms [1-3]. One main feature of polyoxometalate is that they provide structurally well-characterized surfaces formed by approximately coplanar, closest-packed O atoms [4-6]. Magnesium is an important element in refractory polyoxometallate-based materials. The study of fire-resistant properties of title compound will be done in the future.

The title crystal structure is built up of tungstate cluster, ammonium and magnesium cations and water molecules. In the tungstate cluster, the W atoms are coordinated by six O atoms to form distorted octahedra. There are ten terminal O atoms, tweentysix μ_2-O atoms and six μ_3-O atoms. The μ_2-O3 bridges W1 and Mg1, while μ_2-O13 bridges W3 and Mg2. The μ_3-O6 bridges W2, W3 and W4, while μ_3-O10 bridges W3, W5 and W6, while μ_3-O19 bridges W1, W2 and W6. The distances W—O are in the range of 1.719 - 2.332 Å. Mg1 and Mg2 atoms are six-coordinated by five O atoms of water molecules and one μ_2-O atom, while Mg3 atom is only coordinated by six O atoms of water molecules with d(Mg—O) = 1.882 - 2.123 Å.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.20 × 0.22 × 0.28 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	187.96 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10294, 7076
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4661
$N(param)_{refined}$:	445
Programs:	SHELXS-97 [7], SHELXL-97 [8], SHELXTL [9]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(1C)	2*i*		0.8440	0.7134	0.6997	0.059
H(1D)	2*i*		0.9700	0.7145	0.7780	0.059
H(1A)	2*i*		0.9559	0.8183	0.7719	0.059
H(1B)	2*i*		0.9532	0.7550	0.6759	0.059
H(1X)	2*i*		0.9942	0.7302	0.2912	0.040
H(1Y)	2*i*		1.0203	0.6661	0.1909	0.040
H(2X)	2*i*		1.0069	0.5051	0.3354	0.060
H(2Y)	2*i*		0.9032	0.4498	0.3546	0.060
H(3X)	2*i*		0.8101	0.4712	0.0057	0.049
H(3Y)	2*i*		0.9218	0.4728	0.0957	0.049
H(4X)	2*i*		0.5922	0.3837	0.0739	0.053
H(4Y)	2*i*		0.6147	0.3836	0.1827	0.053
H(5X)	2*i*		0.6414	0.6156	0.0753	0.060
H(5Y)	2*i*		0.6925	0.6224	0.0037	0.060

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Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(6X)	2*i*		0.6647	0.9484	0.3315	0.059
H(6Y)	2*i*		0.7745	0.9292	0.3797	0.059
H(7Y)	2*i*		0.5740	1.0544	0.3941	0.052
H(7X)	2*i*		0.6484	1.1446	0.5062	0.052
H(8Y)	2*i*		0.8930	1.1188	0.7375	0.060
H(8X)	2*i*		0.7429	1.0853	0.6943	0.060
H(9X)	2*i*		0.9430	0.9578	0.5427	0.060
H(9Y)	2*i*		1.0060	1.0239	0.6597	0.060
H(10X)	2*i*		0.9594	1.1950	0.5295	0.057
H(10Y)	2*i*		0.8666	1.2339	0.5131	0.057
H(11X)	2*i*		–0.0183	0.8198	0.0664	0.045
H(11Y)	2*i*		–0.1612	0.8106	–0.0086	0.045
H(12X)	2*i*		0.2084	0.9848	0.0873	0.044
H(12Y)	2*i*		0.1458	0.9019	–0.0056	0.044

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(13X)	2*i*		0.1922	1.1559	0.1776	0.054
H(13Y)	2*i*		0.1385	1.0492	0.2188	0.054
H(14X)	2*i*		0.1162	0.7281	0.0801	0.052
H(14Y)	2*i*		0.0339	0.6938	–0.0349	0.052
H(15X)	2*i*		0.4750	0.1969	0.2164	0.072
H(15Y)	2*i*		0.4255	0.0838	0.2080	0.072
H(16X)	2*i*		0.6335	0.0905	0.7909	0.054
H(16Y)	2*i*		0.5798	0.1166	0.6869	0.054
H(17X)	2*i*	0.50	0.2567	0.7797	0.7770	0.054
H(17Y)	2*i*	0.50	0.2236	0.8673	0.7819	0.054
H(18X)	2*i*	0.40	0.4240	0.9457	–0.0293	0.065
H(18Y)	2*i*	0.40	0.5275	1.0228	0.0693	0.065
H(19X)	2*i*	0.60	0.8096	0.7929	0.1990	0.055
H(19Y)	2*i*	0.60	0.8654	0.8842	0.1625	0.055

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg(1)	2*i*		0.8196(6)	0.5519(4)	0.1875(5)	0.039(3)	0.035(3)	0.032(3)	0.010(2)	0.008(2)	0.008(2)
Mg(2)	2*i*		0.7729(5)	1.0270(4)	0.5306(5)	0.038(3)	0.024(2)	0.037(3)	0.001(2)	0.012(2)	0.000(2)
Mg(3)	1*a*		0	0	0	0.031(4)	0.039(4)	0.036(4)	0.019(3)	0.013(3)	0.015(3)
N(1)	2*i*		0.932(2)	0.752(1)	0.731(1)	0.043(8)	0.035(7)	0.043(8)	0.007(6)	0.007(7)	0.012(6)
O(1)	2*i*		0.668(1)	0.6745(8)	0.5014(9)	0.040(6)	0.025(5)	0.040(6)	–0.008(4)	0.025(5)	–0.002(4)
O(2)	2*i*		0.900(1)	0.772(1)	0.497(1)	0.046(7)	0.048(7)	0.043(7)	0.018(6)	0.009(6)	0.006(6)
O(3)	2*i*		0.777(1)	0.543(1)	0.462(1)	0.050(8)	0.063(9)	0.043(7)	0.019(7)	0.018(6)	0.026(6)
O(4)	2*i*		0.789(1)	0.636(1)	0.291(1)	0.035(6)	0.040(6)	0.061(8)	0.014(5)	0.022(6)	0.016(6)
O(5)	2*i*		0.661(1)	0.748(1)	0.3220(9)	0.041(6)	0.056(7)	0.031(6)	0.028(6)	0.018(5)	0.007(5)
O(6)	2*i*		0.437(1)	0.6698(9)	0.3519(9)	0.043(7)	0.037(6)	0.036(6)	0.018(5)	0.007(5)	0.009(5)
O(7)	2*i*		0.452(1)	0.7890(8)	0.1767(8)	0.031(5)	0.032(5)	0.025(5)	0.004(4)	0.006(4)	0.006(4)
O(8)	2*i*		0.500(1)	0.637(1)	0.088(1)	0.074(9)	0.037(7)	0.046(7)	0.000(6)	0.037(7)	–0.007(5)
O(9)	2*i*		0.305(1)	0.562(1)	0.150(1)	0.056(7)	0.046(7)	0.029(6)	0.021(6)	0.011(5)	0.016(5)
O(10)	2*i*		0.180(1)	0.667(1)	0.2006(9)	0.047(7)	0.046(6)	0.028(6)	0.010(5)	0.014(5)	0.010(5)
O(11)	2*i*		0.071(1)	0.4424(9)	0.153(1)	0.025(5)	0.033(6)	0.061(7)	0.017(4)	0.016(5)	0.008(5)
O(12)	2*i*		0.209(1)	0.5591(9)	0.3759(9)	0.042(6)	0.036(6)	0.037(6)	0.015(5)	0.011(5)	0.004(5)
O(13)	2*i*		0.183(1)	0.6530(9)	0.5487(8)	0.034(6)	0.041(6)	0.025(5)	0.009(5)	0.014(4)	0.011(4)
O(14)	2*i*		0.407(1)	0.739(1)	0.5212(9)	0.047(7)	0.049(6)	0.034(6)	0.014(5)	0.030(5)	0.019(5)
O(15)	2*i*		0.448(1)	0.5656(9)	0.529(1)	0.044(6)	0.033(6)	0.041(6)	0.018(5)	0.012(5)	0.010(5)
O(16)	2*i*		0.420(1)	0.6371(8)	0.6911(9)	0.043(6)	0.023(5)	0.031(5)	0.012(4)	0.011(5)	–0.001(4)
O(17)	2*i*		0.456(1)	0.4529(9)	0.711(1)	0.027(5)	0.041(6)	0.043(6)	0.014(5)	0.012(5)	0.003(5)
O(18)	2*i*		0.662(1)	0.661(1)	0.861(1)	0.037(6)	0.039(6)	0.047(7)	0.011(5)	0.012(5)	0.005(5)
O(19)	2*i*		0.681(1)	0.554(1)	0.694(1)	0.051(7)	0.044(6)	0.032(6)	0.024(6)	0.009(5)	0.006(5)
O(20)	2*i*		0.631(1)	0.7356(9)	0.669(1)	0.042(6)	0.038(6)	0.041(6)	0.016(5)	0.020(5)	0.010(5)
O(21)	2*i*		0.643(1)	0.866(1)	0.513(1)	0.034(6)	0.044(6)	0.037(6)	0.010(5)	0.013(5)	0.001(5)
O(1W)	2*i*		0.981(1)	0.6765(8)	0.2337(9)	0.030(5)	0.025(5)	0.041(6)	0.010(4)	0.016(5)	0.004(4)
O(2W)	2*i*		0.925(1)	0.4861(9)	0.311(1)	0.036(6)	0.038(6)	0.051(7)	0.004(5)	0.010(5)	0.025(5)
O(3W)	2*i*		0.856(1)	0.4882(9)	0.0771(9)	0.037(6)	0.035(6)	0.032(6)	0.012(5)	0.006(5)	0.003(4)
O(4W)	2*i*		0.652(1)	0.4006(9)	0.1425(9)	0.033(6)	0.039(6)	0.034(6)	–0.001(5)	0.008(5)	0.006(5)
O(5W)	2*i*		0.701(1)	0.608(1)	0.066(1)	0.055(8)	0.044(7)	0.032(6)	0.021(6)	0.007(5)	0.016(5)
O(6W)	2*i*		0.748(1)	0.980(1)	0.375(1)	0.041(7)	0.058(8)	0.038(6)	0.007(6)	0.021(5)	0.013(6)
O(7W)	2*i*		0.617(1)	1.068(1)	0.475(1)	0.045(7)	0.048(7)	0.037(6)	0.027(6)	0.015(5)	0.011(5)
O(8W)	2*i*		0.805(1)	1.060(1)	0.695(1)	0.035(6)	0.067(8)	0.038(6)	0.014(6)	0.017(5)	0.003(6)
O(9W)	2*i*		0.932(1)	0.985(1)	0.601(1)	0.057(8)	0.046(7)	0.034(6)	0.023(6)	0.012(6)	0.012(5)
O(10W)	2*i*		0.894(1)	1.1856(9)	0.539(1)	0.040(7)	0.032(6)	0.052(7)	0.001(5)	0.020(6)	0.004(5)
O(11W)	2*i*		–0.074(1)	0.8579(9)	0.051(1)	0.040(6)	0.041(6)	0.047(6)	0.026(5)	0.027(5)	0.017(5)
O(12W)	2*i*		0.153(1)	0.9651(9)	0.0172(9)	0.022(5)	0.042(6)	0.034(6)	0.007(4)	0.009(4)	–0.011(4)
O(13W)	2*i*		0.114(1)	1.096(1)	0.168(1)	0.047(7)	0.038(6)	0.044(7)	0.020(5)	0.017(6)	0.006(5)
O(14W)	2*i*		0.083(1)	0.7500(9)	0.020(1)	0.043(7)	0.040(6)	0.037(6)	0.012(5)	0.016(5)	0.018(5)
O(15W)	2*i*		0.431(1)	0.134(1)	0.171(1)	0.038(7)	0.031(6)	0.08(1)	–0.007(5)	0.021(7)	0.007(6)
O(16W)	2*i*		0.606(1)	0.0710(9)	0.721(1)	0.035(6)	0.032(6)	0.046(7)	0.009(5)	0.007(5)	–0.012(5)
O(17W)	2*i*	0.50	0.244(2)	0.820(2)	0.817(2)	0.05(1)	0.04(1)	0.03(1)	0.01(1)	0.01(1)	0.01(1)
O(18W)	1*d*	0.40	½	0	0	0.04(1)	0.04(1)	0.05(1)	0.01(1)	0.01(1)	–0.01(1)
O(19W)	2*i*	0.60	0.837(2)	0.863(2)	0.208(2)	0.04(1)	0.04(1)	0.04(1)	0.012(8)	0.006(9)	0.015(8)
W(1)	2*i*		0.75335(6)	0.66110(5)	0.39799(5)	0.0316(3)	0.0330(3)	0.0327(3)	0.0039(3)	0.0073(3)	0.0039(2)
W(2)	2*i*		0.48109(7)	0.67132(6)	0.20315(6)	0.0349(4)	0.0391(4)	0.0337(4)	0.0096(3)	0.0079(3)	0.0072(3)
W(3)	2*i*		0.22340(7)	0.55681(6)	0.24461(6)	0.0343(3)	0.0358(3)	0.0336(3)	0.0096(3)	0.0077(3)	0.0072(2)

Table 3. Continued.

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(4)	2*i*		0.29665(6)	0.61330(5)	0.53949(5)	0.0345(4)	0.0358(3)	0.0341(4)	0.0091(3)	0.0089(3)	0.0058(3)
W(5)	2*i*		0.57798(7)	0.60102(6)	0.71962(6)	0.0345(4)	0.0339(3)	0.0395(4)	0.0071(3)	0.0080(3)	0.0050(3)
W(6)	2*i*		0.56035(7)	0.72848(6)	0.50674(6)	0.0338(3)	0.0384(4)	0.0322(3)	0.0061(3)	0.0083(3)	0.0046(3)

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