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Crystal Structure of Sodium 12-Molybdophosphate Hexadecahydrate

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Sodium 12-molybdophosphate hexadecahydrate, $Na_3PMo_{12}O_{40}\cdot16H_2O$ crystallizes in a monoclinic space group $P2_1/m$, with cell dimensions a=11.4703(4)Å, b=15.1849(6)Å, c=13.7083(5)Å, β=106.902(1)° and V = 2284.51(15)Å^3, Z = 2. The final R value is 0.0319 for 5719 reflections ($I > 2\sigma(I)$). The crystal is built up of the heteropolyanion (of the *Keggin* form), six-coordinated sodium ions and water molecules in a 3-D supramolecualr framework, which is produced by some different O–H···O hydrogen bonds.

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Heteropolyacids and their salts with the *Keggin* structure are well-known to be an effective catalyst in acid-catalyzed and redox reactions.[1] The polyoxometalate (POM for convenience) catalysts have very high thermal stability with non-toxicity and non-corrosiveness properties, and are very easily separated from the reaction system.[2] The tunable characteristics of *Keggin*-type catalysts make it particularly interesting for further study. In the former studies, we reported on the structure of the salt $[C_2H_6NO_2]_3[PMo_{12}O_{40}]\cdot5H_2O$.[3] Here, information about the crystal structure of sodium 12-molybdophosphate hexadecahydrate ($Na_3PMo_{12}O_{40}\cdot16H_2O$) is given. A thermogravimetric analysis (in the range of 40 to 600°C) shows that the title compound undergoes a gradual loss of 12.9% (calcd: 13.2%), corresponding to the water molecules. The crystal data and the details of an X-ray analysis of $Na_3PMo_{12}O_{40}\cdot16H_2O$ are listed in Table 1; selected bond lengths and angles are given in Table 2. The crystal is built up of the heteropolyanion, sodium ions and water molecules in a 3-D supramolecular framework, which is produced by some different O–H···O hydrogen bonds. The anion is in the form of the *Keggin* structure (Fig. 1) with 4 different kinds of O atoms: a) the 12 terminal, b) the 4 bonded to P and Mo, c) the 12MoO_6 octahedra corner-shared and d) the 12MoO_6 octahedra edge-shared. The Mo atoms have a distorted octahedral configuration and the P–O bonds are in the range of the P–O single bond, 1.534(2) – 1.541(3)Å. In the solid state, both Na(1) and Na(2) are six-coordinated *via* two oxygen atoms of POM and four water molecules (two O(3) atoms, O(1W), O(2W), O(3W) and O(4W) for Na(1) and O(2), O(6), O(5W), O(7W), O(8W), and (O6W, O6W′) for Na(2)). Na(2′) is surrounded by O(6) from POM (also having weak interactions with O(23)), O(7W), O(10W), another O(10W) and (O6W, O6W′), Fig. 2. The O6W′ position (s.o.f. 0.14) was refined in an isotropic approximation. The s.o.f. values were determined and refined. The O(5W) oxygen atoms act as a bridge to form two bonds with two different Na(2) sodium cations. A view of unit cell packing of title compound is given in Fig. 3.

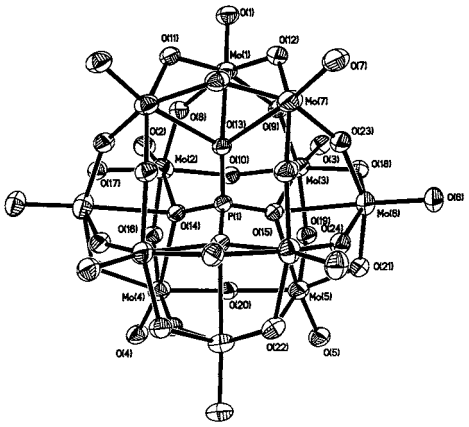

Fig. 1 Thermal ellipsoids for Mo, O and P atoms (in $[PMo_{12}O_{40}]^{3-}$ polyoxoanion) with a 50% probability level.

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Table 1 Crystal data and structure refinement for $Na_3PMo_{12}O_{40}\cdot16H_2O$

CSD No. 417322	
Formula: $H_{32}Mo_{12}Na_3O_{56}P$	
Formula weight = 2179.48	
Crystal system: monoclinic	
Space group: $P2_1/m$	$Z = 2$
a = 11.4703(4)Å	β = 106.902(1)°
b = 15.1849(6)Å	
c = 13.7083(5)Å	
V = 2284.51(15)Å^3	T = 100 K
D_x = 3.168 Mg/m^3	
Reflections number total = 6149	
$2\theta_{max}$ = 58.0° with Mo K_α	
R = 0.0319	
$(\Delta/\sigma)_{max}$ = 0.001	
$(\Delta\rho)_{max}$ = 1.056 e.Å^{-3}	
$(\Delta\rho)_{min}$ = –0.879 e.Å^{-3}	
Measurement: Bruker APEX2 CCD area detector	
Computing data collection: APEX2	
Program system: SHELXTL	
Structure determination: SHELXTL	
Refinement: full-matrix least-squares on F^2	

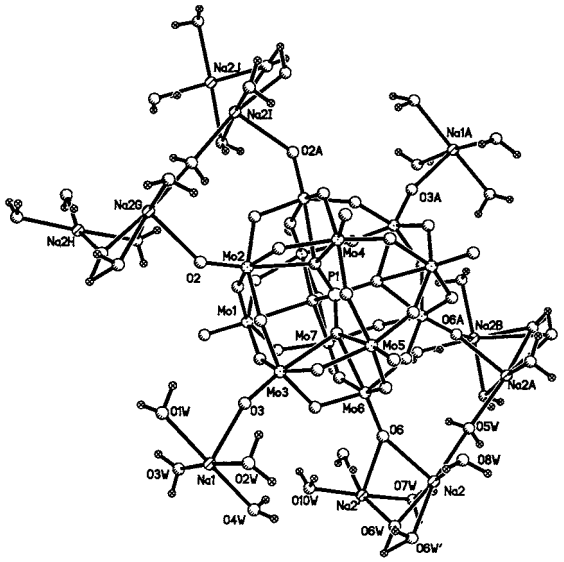

Fig. 2 View of polyoxoanion as a ligand linked to six-coordinated sodium cations.

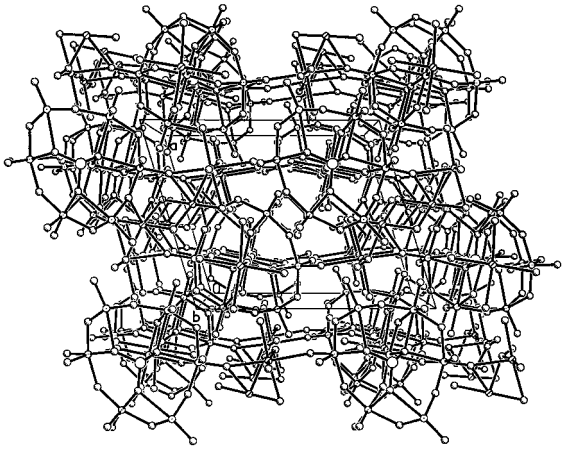

Fig. 3 View of the unit-cell packing of $Na_3PMo_{12}O_{40}\cdot 16H_2O$.

Table 2 Selected bond lengths and angles for $Na_3PMo_{12}O_{40}\cdot 16H_2O$

Mo(1)-O(1)	1.662(3)	O(6)-Na(2')	2.552(7)
Mo(1)-O(8)	1.875(2)	P(1)-O(15)	1.534(2)
O(6)-Na(2)	2.373(3)	P(1)-O(14)	1.541(3)
O(22)-Mo(5)#1	1.9039(9)	O(24)-Mo(6)#1	1.905(1)
O(2)-Na(2)#2	2.421(3)	Na(1)-O(1W)	2.421(4)
O(1)-Mo(1)-O(8)	103.94(12)	O(15)-P(1)-O(13)	109.63(11)
P(1)-O(13)-Mo(7)	126.06(18)	Mo(6)-O(6)-Na(2)	153.57(16)
Mo(7)-O(13)-Mo(1)	88.97(9)	Mo(6)-O(6)-Na(2')	139.7(2)
O(4W)-Na(1)-O(3)#3	96.37(8)	Mo(1)-O(8)-Mo(2)	150.39(14)
O(4W)-Na(1)-O(2W)	90.64(17)	Mo(1)-O(9)-Mo(3)	149.19(14)
O(8W)-Na(2)-O(2)#4	93.02(13)	Na(2')#5-O(10W)-Na(2')	87.6(3)
O(6)-Na(2)-O(2)#4	175.30(14)	Na(2')-O(7W)-Na(2)	71.3(2)

Symmetry transformations used to generate equivalent atoms: #1 x, $-y+1/2$, z #2 x, y, $z-1$ #3 x, $-y+3/2$, z #4 x, y, $z+1$ #5 $-x-1$, $-y+1$, $-z$.

Acknowledgements

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