Crystal structure of tris(4-aminopyridinium) phosphatopolyoxo-dodecamolybdate — 4-aminopyridine — water (1:1:1), $[C_5H_7N_2]_3[PMo_{12}O_{40}] \cdot C_5H_6N_2 \cdot H_2O$

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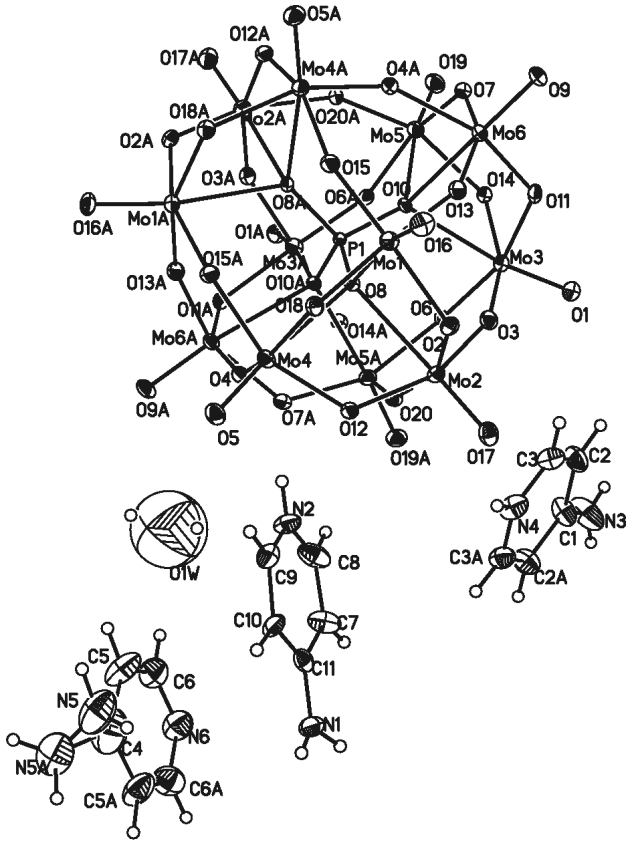

Abstract

$C_{20}H_{29}Mo_{12}N_8O_{41}P$, monoclinic, *C*12/*c*1 (no. 15), $a = 11.7094(4)$ Å, $b = 25.7946(9)$ Å, $c = 16.6748(6)$ Å, $\beta = 97.205(1)°$, $V = 4996.7$ Å^3, $Z = 4$, $R_{gt}(F) = 0.044$, $wR_{ref}(F^2) = 0.142$, $T = 293$ K.

Source of material

A mixture of $Na_3PO_4 \cdot 12H_2O$ (0.1520 g, 0.40 mmol), $Na_2MoO_4 \cdot 2H_2O$ (0.2900 g, 1.20 mmol), 4-aminopyridine (0.0940 g, 0.0319 mmol), H_2SO_4 (0.4 ml, 1:1 *v*/*v*)), H_2O (15.00 ml) was sealed in a 25 ml Teflon-lined bomb at 453 K for 120 h, then solwly cooled to room temperature. Red block-like crystals were collected by filtration, washed with distilled water, and air-dried giving a yield of 30 % based on the initial $Na_2MoO_4 \cdot 2H_2O$.

Experimental details

In the 4-aminopyridine molecule, the N5 atom which links on C4 atom is disordered, the occupancy factor was set to 50 %.

Discussion

The title compound consists of a Keggin $(PMo_{12}O_{40})^{3-}$ polyoxoanion, three 4-aminopyridine $(C_5H_7N_2)^+$ cation, one 4-aminopyridine molecule and one water molecule. The Keggin $(PMo_{12}O_{40})^{3-}$ polyoxoanion contains a central PO_4 tetrahedron surrounded by four groups Mo_3O_{10} of three edge-shared octahedra MoO_6. These Mo_3O_{10} triplets are linked to each other, and linked to the PO_4 tetrahedron by sharing corners.The PO_4 tetrahedron in which the P—O bond lengths are in the normal range of 1.531(5) Å - 1.535(5) Å and the O–P–O bond angles vary in the range of 108.9(2)° - 110.6(2)°, is a almost regular tetrahedron. Each of MoO_6 octahedrons is distorted. There are one terminal oxygen atom (O_t), four doubly bridging oxygen atoms (O_b), one triply bridging oxygen atom (O_a). The bond angles of O–Mo–O range from 71.2(2)° to 172.6(2)°. The Mo—O_t, Mo—O_b and Mo—O_a distances are in ranges 1.553(4) Å to 1.683(6) Å, 1.796(5) Å to 2.032(4) Å and 2.414(5) to 2.430(5) Å, respectively. In the 4-aminopyridine cations, the bond lengths C—C are in range from 1.22(2) to 1.48(2) Å and C—N are in range from 1.32(2) to 1.33(2) Å, exhibiting normal C—C and C—N bond distances. A lot of intermolecular N–H···O hydrogen bonds (d(N–H···O) = 2.940 - 3.377 Å) were found in the title crystal structure. All of the bond lengths and bond angles are within the normal ranges and are consistent with those described in the literature [1]. There are profuse hydrogen bondings in the target crystal, which are involved with Keggin type heteropolyanion, 4-aminopyridine and water molecular result in an intricate three-dimensional supramolecular network.

Table 1. Data collection and handling.

Crystal:	red block, size 0.25 × 0.26 × 0.32 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	30.54 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	15366, 4276
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3903
$N(param)_{refined}$:	383
Programs:	SHELXS-97, SHELXL-97 [2]

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(5A)	8*f*	0.50	0.9217	0.0052	0.2981	0.116
H(5B)	8*f*	0.50	1.0501	0.0052	0.3251	0.116
H(5)	8*f*		0.8375	0.0791	0.2857	0.092
H(6A)	8*f*		0.8482	0.1606	0.2812	0.082
H(1A)	8*f*		1.2094	0.0945	0.4530	0.049
H(1B)	8*f*		1.2091	0.1525	0.4602	0.049
H(2A)	8*f*		0.7860	0.1159	0.5527	0.058
H(7)	8*f*		1.0351	0.1993	0.4860	0.051
H(8)	8*f*		0.8543	0.1930	0.5261	0.063
H(9)	8*f*		0.8773	0.0424	0.5416	0.055
H(10)	8*f*		1.0492	0.0432	0.4903	0.043
H(3A)	8*f*		0.9635	0.4076	0.7744	0.094
H(4A)	4*e*		1.0000	0.1914	¾	0.052
H(2C)	8*f*		0.9138	0.3201	0.8482	0.055
H(3)	8*f*		0.9197	0.2318	0.845	0.051
H(1)	8*f*	0.50	0.7506	0.1303	0.4111	0.672
H(2)	8*f*	0.50	0.6642	0.1197	0.3410	0.672

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}
Mo(1)	8*f*		0.64597(5)	0.01185(3)	0.86443(4)	0.0194(4)	0.0234(4)	0.0178(4)	0.0023(3)	0.0011(2)	0.0043(3)
Mo(2)	8*f*		0.80290(5)	0.10861(3)	0.79475(4)	0.0152(4)	0.0264(4)	0.0207(4)	–0.0007(2)	0.0013(3)	0.0002(3)
Mo(3)	8*f*		0.63374(6)	0.21400(3)	0.87148(4)	0.0203(4)	0.0242(4)	0.0187(4)	–0.0046(3)	0.0016(3)	–0.0033(3)
Mo(4)	8*f*		0.67051(5)	0.01999(3)	0.66296(4)	0.0197(4)	0.0218(4)	0.0167(4)	0.0042(3)	0.0026(2)	–0.0014(2)
Mo(5)	8*f*		0.34045(5)	0.20634(3)	0.84653(4)	0.0191(4)	0.0245(4)	0.0202(4)	0.0020(3)	0.0040(3)	–0.0029(3)
Mo(6)	8*f*		0.50072(6)	0.11762(3)	0.96295(4)	0.0197(4)	0.0254(4)	0.0127(3)	–0.0025(3)	0.0022(2)	–0.0004(2)
P(1)	4*e*		½	0.1132(1)	¾	0.011(1)	0.016(1)	0.010(1)	0	0.0006(9)	0
O(1)	8*f*		0.7190(5)	0.2598(2)	0.9161(3)	0.026(3)	0.028(3)	0.026(3)	–0.004(2)	0.002(2)	–0.004(2)
O(2)	8*f*		0.7892(4)	0.0562(2)	0.8638(3)	0.014(2)	0.030(3)	0.021(3)	0.003(2)	–0.002(2)	0.002(2)
O(3)	8*f*		0.7455(4)	0.1579(2)	0.8560(3)	0.023(3)	0.027(3)	0.018(3)	0.002(2)	0.001(2)	0.001(2)
O(4)	8*f*		0.6225(4)	0.0704(2)	0.5894(3)	0.020(2)	0.023(3)	0.016(2)	0.004(2)	0.003(2)	0.000(2)
O(5)	8*f*		0.7297(5)	–0.0245(2)	0.6083(3)	0.027(3)	0.026(3)	0.026(3)	0.007(2)	0.003(2)	–0.006(2)
O(6)	8*f*		0.6370(4)	0.2294(2)	0.7631(3)	0.017(2)	0.025(3)	0.016(3)	0.004(2)	0.000(2)	–0.002(2)
O(7)	8*f*		0.3729(4)	0.1695(2)	0.9416(3)	0.019(3)	0.024(3)	0.019(3)	–0.003(2)	0.005(2)	–0.003(2)
O(8)	8*f*		0.6073(4)	0.0785(2)	0.7624(3)	0.016(2)	0.016(3)	0.013(2)	0.003(2)	0.001(2)	0.002(2)
O(9)	8*f*		0.4960(5)	0.1058(2)	1.0612(3)	0.031(3)	0.036(4)	0.014(3)	–0.005(2)	0.004(2)	–0.001(2)
O(10)	8*f*		0.4949(4)	0.1471(2)	0.8250(3)	0.014(2)	0.028(3)	0.009(2)	0.000(2)	0.001(2)	–0.002(2)
O(11)	8*f*		0.6018(4)	0.1729(2)	0.9672(3)	0.019(3)	0.021(3)	0.017(2)	0.000(2)	–0.003(2)	–0.005(2)
O(12)	8*f*		0.8013(4)	0.0570(2)	0.7087(3)	0.016(2)	0.025(3)	0.019(3)	0.002(2)	0.002(2)	–0.001(2)
O(13)	8*f*		0.6004(4)	0.0679(2)	0.9341(3)	0.020(3)	0.032(3)	0.017(3)	0.000(2)	0.000(2)	0.000(2)
O(14)	8*f*		0.4881(4)	0.2431(2)	0.8744(3)	0.019(3)	0.022(3)	0.017(2)	–0.004(2)	0.002(2)	–0.002(2)
O(15)	8*f*		0.4899(4)	–0.0023(2)	0.8455(3)	0.018(3)	0.028(3)	0.020(3)	0.001(2)	0.003(2)	–0.001(2)
O(16)	8*f*		0.6961(5)	–0.0325(2)	0.9322(3)	0.027(3)	0.026(3)	0.028(3)	0.005(2)	–0.001(2)	0.011(2)
O(17)	8*f*		0.9330(4)	0.1205(2)	0.8174(3)	0.032(3)	0.026(3)	0.026(3)	0.006(2)	–0.001(2)	–0.003(2)
O(18)	8*f*		0.6808(4)	–0.0168(2)	0.7679(3)	0.022(3)	0.017(3)	0.020(3)	0.001(2)	0.002(2)	–0.001(2)
O(19)	8*f*		0.2498(5)	0.2524(2)	0.8721(3)	0.028(3)	0.032(3)	0.027(3)	0.005(2)	0.007(2)	–0.007(2)
O(20)	8*f*		0.7568(4)	0.1571(2)	0.7044(3)	0.017(2)	0.024(3)	0.016(2)	0.003(2)	0.002(2)	0.004(2)
N(5)	8*f*	0.50	0.992(3)	0.015(1)	0.288(2)	0.09(2)	0.06(2)	0.14(3)	–0.02(1)	–0.01(2)	0.01(1)
N(6)	4*e*		0	0.1684(7)	¼	0.058(9)	0.06(1)	0.08(1)	0	0.003(8)	0
C(4)	4*e*		0	0.063(1)	¼	0.12(1)	0.10(1)	0.12(1)	0	–0.016(9)	0
C(5)	8*f*		0.903(1)	0.0947(6)	0.271(1)	0.041(7)	0.06(1)	0.12(1)	–0.007(6)	–0.010(7)	0.018(9)
C(6)	8*f*		0.911(1)	0.1417(6)	0.2686(8)	0.066(8)	0.07(1)	0.069(8)	–0.013(7)	0.010(6)	–0.004(7)
N(1)	8*f*		1.1671(7)	0.1232(3)	0.4571(5)	0.027(4)	0.044(5)	0.053(5)	–0.003(3)	0.010(4)	–0.008(4)
N(2)	8*f*		0.8528(7)	0.1171(4)	0.5365(6)	0.023(4)	0.071(7)	0.051(6)	–0.001(4)	0.009(4)	–0.001(4)
C(7)	8*f*		1.0037(9)	0.1670(4)	0.4950(6)	0.052(6)	0.031(5)	0.048(6)	0.016(4)	0.022(5)	0.025(4)
C(8)	8*f*		0.897(1)	0.1631(5)	0.5202(6)	0.058(7)	0.058(8)	0.045(6)	0.030(6)	0.019(5)	0.012(5)
C(9)	8*f*		0.9088(8)	0.0738(5)	0.5279(6)	0.035(5)	0.051(7)	0.051(6)	–0.010(5)	0.005(4)	–0.015(5)
C(10)	8*f*		1.0128(7)	0.0744(4)	0.4992(6)	0.022(4)	0.036(5)	0.048(5)	–0.005(4)	0.000(4)	–0.006(4)
C(11)	8*f*		1.0651(8)	0.1210(4)	0.4829(5)	0.037(5)	0.034(5)	0.021(4)	0.008(4)	0.000(3)	–0.001(3)
N(3)	4*e*		0	0.3825(6)	¾	0.14(2)	0.05(1)	0.06(1)	0	0.04(1)	0
N(4)	4*e*		0	0.2247(5)	¾	0.038(6)	0.022(6)	0.070(8)	0	0.009(6)	0
C(1)	4*e*		0	0.3310(5)	¾	0.08(1)	0.016(7)	0.038(7)	0	0.011(7)	0
C(2)	8*f*		0.949(1)	0.3030(4)	0.8087(6)	0.062(7)	0.040(6)	0.038(5)	–0.003(5)	0.013(5)	–0.012(4)
C(3)	8*f*		0.9522(8)	0.2505(4)	0.8060(7)	0.034(5)	0.040(6)	0.054(6)	0.000(4)	0.011(4)	0.004(5)
O(1W)	8*f*	0.50	0.713(6)	0.140(4)	0.367(5)	0.45(6)	0.45(6)	0.45(6)	0.00(1)	0.06(1)	0.00(1)

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