Crystal structure of tris(4-carboxypyridinium) diaquasodium β-octamolybdate, $[C_6H_6NO_2]_3[Na(H_2O)_2(Mo_8O_{26})]$

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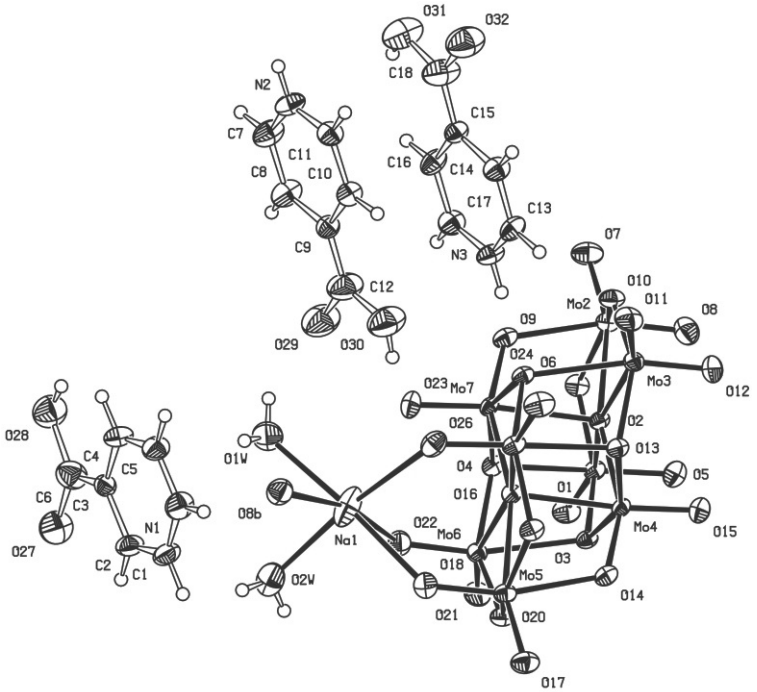

Abstract

$C_{18}H_{22}Mo_8N_3NaO_{34}$, monoclinic, $P12_1/c1$ (no. 14), a = 15.329(3) Å, b = 13.598(2) Å, c = 21.674(4) Å, β = 109.345(1)°, V = 4262.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.038, $wR_{ref}(F^2)$ = 0.095, T = 293 K.

Source of material

A mixture of MoO_3 (0.144 g, 1 mmol), isonicotinic acid (0.13 g, 1 mmol), Na_2CO_3 (0.04 g, 0.5 mmol) and water (15 mL) in a molar ratio of 2:2:1:1666 was in an autoclave inside a programmable electric furnace at 160 °C for three days. After cooling to room temperature, block-shaped crystals of the title compound were obtained.

Experimental details

The H atoms bonded to water were located in a difference Fourier map and refined with d(O—H) = 0.82(1) Å, and d(H···H) = 1.34(2) Å and U_{iso}(H) = 1.5 U_{eq}(O). The remaining H atoms were positioned geometrically with d(C—H) = 0.93 Å, d(N—H) = 0.86 Å and d(O—H) = 0.82 Å, and were refined as riding with U_{iso}(H) = 1.2 U_{eq}(N and C) and U_{iso}(H) = 1.5 U_{eq}(O).

Discussion

Octamolybdates, acting as familiar polyoxomolybdates, are versatile inorganic building blocks for constructing new organic-inorganic hybrid materials [1], Especially, the octamolybdate family are of interest since they exhibit a variety of structural isomers, including α- [2], β- [3], γ- [4], δ- [5], ε- [6], and ζ-isomers [7].

The crystal structure of the title complex $[C_6H_6NO_2]_3[Na(H_2O)_2(Mo_8O_{26})]$ contains three protonated isonicotinic acid cations, one diaquasodium cation, and an octamolybdate anion β-$[Mo_8O_{26}]^{4-}$ in the unit cell. The structure of polyoxoanion is built from β-$[Mo_8O_{26}]^{4-}$ moieties linked by Na^+ ions into an infinite linear polymeric chain. The β-isomer anion $[Mo_8O_{26}]^{4-}$ consists of two $\{Mo_4O_{13}\}$ subunits linked together by bridging oxygens with an approximate C_{2h} symmetry. The Mo—O distances are in rational ranges: d(Mo—O(t)) = 1.688(4)-1.710(4) Å; d(Mo—O(μ_2)) = 1.741(3)-2.300(3) Å; d(Mo—O(μ_3)) = 1.941(4)-2.357(4) Å; d(Mo—O(μ_5)) = 2.150(3)-2.477(3) Å. The Na^+ cations adopt distorted octahedral coordination defined by six O atoms, four of which come from terminal O of two β-$[Mo_8O_{26}]^{4-}$ subunits and two from water molecules. The Na^+ ions bridge two adjacent β-$[Mo_8O_{26}]^{4-}$ clusters forming a chain-like polyoxoanion $\{Na(H_2O)_2[Mo_8O_{26}]\}^{3-}$. In addition, three monoprotonated isonicotinic acid cations serving as countercations stabilize the chain-like polyoxoanion framework. Furthermore, these acid cations $(C_6H_6NO_2)^+$ and polyoxoanion chains within the hybrids are linked together via multiple N–H···O and O–H···O hydrogen bonds leading to a three-dimensional supramolecular framework.

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Table 1. Data collection and handling.

Crystal:	colorless block, size 0.10 × 0.12 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	23.93 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEXII CCD, φ/ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	28761, 8270
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7304
$N(param)_{refined}$:	589
Programs:	SHELXS-97, SHELXL-97 [8], PLATON [9]

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

Atom	Site	x	y	z	U_{iso}
H(28)	4*e*	0.3798	0.9281	0.4003	0.097
H(30)	4*e*	0.5246	0.0967	0.3875	0.107
H(31)	4*e*	0.8789	0.3439	0.3047	0.114

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(1WA)	4*e*	0.412(3)	0.447(6)	0.369(3)	0.077
H(1WB)	4*e*	0.378(5)	0.409(6)	0.413(2)	0.077
H(2WA)	4*e*	0.105(2)	0.419(7)	0.336(3)	0.080
H(2WB)	4*e*	0.162(5)	0.409(7)	0.397(1)	0.080
H(1B)	4*e*	0.2502	0.5454	0.3896	0.055
H(2B)	4*e*	0.9607	0.2461	0.4974	0.047
H(3A)	4*e*	0.5306	0.1694	0.2204	0.044
H(1A)	4*e*	0.1153	0.6223	0.3682	0.049
H(2A)	4*e*	0.1124	0.7913	0.3662	0.047
H(4A)	4*e*	0.3905	0.7886	0.4153	0.048
H(5A)	4*e*	0.3855	0.6208	0.4144	0.048
H(7A)	4*e*	0.8695	0.3769	0.4756	0.055
H(8A)	4*e*	0.7131	0.3566	0.4332	0.053
H(10A)	4*e*	0.7539	0.0630	0.4416	0.039
H(11A)	4*e*	0.9096	0.0914	0.4820	0.041
H(13A)	4*e*	0.6156	0.0324	0.2441	0.043
H(14A)	4*e*	0.7722	0.0451	0.2857	0.042
H(16A)	4*e*	0.7451	0.3417	0.2769	0.043
H(17A)	4*e*	0.5882	0.3198	0.2360	0.045

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	4*e*	0.16191(3)	0.32749(3)	0.00072(2)	0.0199(2)	0.0214(2)	0.0242(2)	0.0013(2)	0.0037(2)	0.0033(2)
Mo(2)	4*e*	0.37784(3)	0.30534(3)	0.01404(2)	0.0224(2)	0.0273(2)	0.0305(2)	0.0007(2)	0.0103(2)	0.0026(2)
Mo(3)	4*e*	0.38166(3)	0.08936(3)	0.08126(2)	0.0216(2)	0.0200(2)	0.0320(2)	0.0024(2)	0.0099(2)	–0.0027(2)
Mo(4)	4*e*	0.16804(3)	0.11337(3)	0.06717(2)	0.0180(2)	0.0161(2)	0.0240(2)	–0.0011(2)	0.0035(2)	–0.0021(2)
Mo(5)	4*e*	0.11252(3)	0.10582(3)	0.20866(2)	0.0232(2)	0.0242(2)	0.0293(2)	–0.0012(2)	0.0094(2)	0.0024(2)
Mo(6)	4*e*	0.11208(3)	0.32147(3)	0.14393(2)	0.0204(2)	0.0203(2)	0.0272(2)	0.0035(2)	0.0073(2)	–0.0006(2)
Mo(7)	4*e*	0.32580(3)	0.29880(3)	0.15789(2)	0.0177(2)	0.0151(2)	0.0235(2)	–0.0004(2)	0.0024(2)	–0.0012(2)
Mo(8)	4*e*	0.33008(3)	0.08668(3)	0.22534(2)	0.0198(2)	0.0219(2)	0.0268(2)	0.0002(2)	0.0031(2)	0.0057(2)
O(1)	4*e*	0.0853(3)	0.4218(3)	–0.0145(2)	0.029(2)	0.033(2)	0.041(2)	0.007(2)	0.008(2)	0.008(2)
O(2)	4*e*	0.2725(2)	0.2119(3)	0.0576(2)	0.018(2)	0.021(2)	0.025(2)	–0.000(1)	0.005(1)	–0.000(1)
O(3)	4*e*	0.0980(2)	0.2369(3)	0.0462(2)	0.017(2)	0.021(2)	0.028(2)	0.001(1)	0.004(1)	0.002(2)
O(4)	4*e*	0.2126(2)	0.3687(3)	0.1116(2)	0.022(2)	0.017(2)	0.029(2)	0.002(1)	0.005(1)	0.002(1)
O(5)	4*e*	0.1331(3)	0.2631(3)	–0.0705(2)	0.036(2)	0.037(2)	0.031(2)	–0.002(2)	0.005(2)	–0.003(2)
O(6)	4*e*	0.2732(3)	0.3907(3)	0.0029(2)	0.028(2)	0.024(2)	0.030(2)	0.004(2)	0.009(2)	0.006(2)
O(7)	4*e*	0.4620(3)	0.3830(3)	0.0106(2)	0.035(2)	0.041(3)	0.055(3)	–0.003(2)	0.020(2)	0.011(2)
O(8)	4*e*	0.3393(3)	0.2494(3)	–0.0608(2)	0.043(2)	0.044(3)	0.037(2)	0.008(2)	0.014(2)	–0.001(2)
O(9)	4*e*	0.3971(2)	0.3530(3)	0.1196(2)	0.023(2)	0.025(2)	0.037(2)	–0.004(2)	0.007(2)	0.002(2)
O(10)	4*e*	0.4475(2)	0.1975(3)	0.0642(2)	0.019(2)	0.029(2)	0.041(2)	0.001(2)	0.011(2)	0.002(2)
O(11)	4*e*	0.4713(3)	0.0184(3)	0.1280(2)	0.032(2)	0.030(2)	0.053(3)	0.011(2)	0.015(2)	0.003(2)
O(12)	4*e*	0.3449(3)	0.0339(3)	0.0069(2)	0.046(3)	0.039(2)	0.047(2)	–0.004(2)	0.020(2)	–0.019(2)
O(13)	4*e*	0.2819(2)	0.0426(3)	0.1139(2)	0.021(2)	0.018(2)	0.033(2)	0.001(1)	0.008(2)	0.001(2)
O(14)	4*e*	0.0979(2)	0.0561(3)	0.1058(2)	0.024(2)	0.026(2)	0.032(2)	–0.005(2)	0.006(2)	0.000(2)
O(15)	4*e*	0.1380(3)	0.0597(3)	–0.0073(2)	0.036(2)	0.028(2)	0.031(2)	–0.003(2)	0.008(2)	–0.005(2)
O(16)	4*e*	0.2214(2)	0.1984(2)	0.1678(2)	0.020(2)	0.019(2)	0.023(2)	0.002(1)	0.005(1)	0.001(1)
O(17)	4*e*	0.0284(3)	0.0273(3)	0.2128(2)	0.033(2)	0.038(2)	0.049(2)	–0.007(2)	0.018(2)	0.003(2)
O(18)	4*e*	0.1488(3)	0.1665(3)	0.2819(2)	0.040(2)	0.034(2)	0.034(2)	–0.000(2)	0.013(2)	–0.001(2)
O(19)	4*e*	0.2190(2)	0.0226(3)	0.2231(2)	0.028(2)	0.021(2)	0.033(2)	–0.002(2)	0.008(2)	0.006(2)
O(20)	4*e*	0.0428(2)	0.2122(3)	0.1568(2)	0.021(2)	0.029(2)	0.036(2)	0.001(2)	0.010(2)	0.003(2)
O(21)	4*e*	0.0250(3)	0.3975(3)	0.1011(2)	0.029(2)	0.035(2)	0.039(2)	0.012(2)	0.008(2)	0.004(2)
O(22)	4*e*	0.1532(3)	0.3711(3)	0.2203(2)	0.035(2)	0.037(2)	0.032(2)	0.001(2)	0.010(2)	–0.003(2)
O(23)	4*e*	0.3548(3)	0.3517(3)	0.2327(2)	0.039(2)	0.028(2)	0.030(2)	–0.002(2)	0.005(2)	–0.007(2)
O(24)	4*e*	0.3948(2)	0.1745(2)	0.1796(2)	0.017(2)	0.018(2)	0.030(2)	0.001(1)	0.004(1)	0.002(1)
O(25)	4*e*	0.4078(3)	–0.0071(3)	0.2442(2)	0.032(2)	0.032(2)	0.049(2)	0.008(2)	0.007(2)	0.014(2)
O(26)	4*e*	0.3541(3)	0.1545(3)	0.2951(2)	0.036(2)	0.036(2)	0.032(2)	–0.005(2)	0.003(2)	0.004(2)
O(27)	4*e*	0.1642(4)	0.9647(4)	0.3709(3)	0.064(2)	0.056(2)	0.070(3)	0.002(2)	0.021(2)	0.002(2)
O(28)	4*e*	0.3361(4)	0.9662(4)	0.3931(3)	0.063(2)	0.056(2)	0.072(3)	–0.004(2)	0.021(2)	0.002(2)
O(29)	4*e*	0.5559(4)	0.2755(5)	0.3961(3)	0.047(2)	0.066(3)	0.101(3)	0.009(2)	0.008(2)	–0.004(3)
O(30)	4*e*	0.5812(4)	0.0929(4)	0.4015(3)	0.045(2)	0.064(3)	0.096(3)	0.000(2)	0.011(2)	–0.002(2)
O(31)	4*e*	0.9178(4)	0.3001(5)	0.3158(3)	0.052(2)	0.066(3)	0.100(3)	–0.007(2)	0.013(2)	0.006(3)
O(32)	4*e*	0.9337(4)	0.1169(4)	0.3243(3)	0.049(2)	0.065(3)	0.097(3)	0.002(2)	0.015(2)	0.002(3)
Na(1)	4*e*	0.2599(2)	0.3028(2)	0.3245(2)	0.076(2)	0.038(2)	0.051(2)	–0.006(1)	–0.010(2)	–0.006(1)
O(1W)	4*e*	0.3649(4)	0.4274(4)	0.3753(2)	0.059(3)	0.048(3)	0.054(3)	–0.011(2)	0.028(2)	0.004(2)
O(2W)	4*e*	0.1588(4)	0.4160(4)	0.3590(2)	0.071(3)	0.052(3)	0.037(2)	–0.018(3)	0.017(2)	0.004(2)
N(1)	4*e*	0.2504(4)	0.6087(4)	0.3902(3)	0.042(3)	0.029(3)	0.064(4)	0.002(2)	0.014(3)	–0.005(3)
N(2)	4*e*	0.9020(3)	0.2366(4)	0.4820(2)	0.024(2)	0.045(3)	0.042(3)	–0.003(2)	0.001(2)	0.008(2)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(3)	4*e*	0.5897(3)	0.1755(4)	0.2363(2)	0.021(2)	0.038(3)	0.045(3)	–0.003(2)	0.004(2)	0.001(2)
C(1)	4*e*	0.1702(4)	0.6572(5)	0.3767(3)	0.028(3)	0.034(3)	0.056(4)	–0.007(3)	0.010(3)	–0.007(3)
C(2)	4*e*	0.1684(4)	0.7582(5)	0.3755(3)	0.022(3)	0.045(4)	0.047(4)	0.000(3)	0.007(3)	–0.001(3)
C(3)	4*e*	0.2511(4)	0.8118(4)	0.3884(3)	0.030(3)	0.028(3)	0.030(3)	–0.001(2)	0.013(2)	–0.001(2)
C(4)	4*e*	0.3339(4)	0.7565(5)	0.4046(3)	0.022(3)	0.047(4)	0.048(4)	–0.003(3)	0.008(3)	0.002(3)
C(5)	4*e*	0.3308(4)	0.6564(5)	0.4044(3)	0.027(3)	0.035(3)	0.055(4)	0.007(2)	0.008(3)	–0.004(3)
C(6)	4*e*	0.2508(5)	0.9103(6)	0.3844(4)	0.054(2)	0.048(2)	0.061(2)	–0.002(2)	0.028(2)	0.003(2)
C(7)	4*e*	0.8450(5)	0.3137(5)	0.4682(4)	0.039(4)	0.026(3)	0.065(4)	–0.003(3)	0.008(3)	0.003(3)
C(8)	4*e*	0.7515(4)	0.3018(5)	0.4433(3)	0.034(3)	0.025(3)	0.064(4)	0.006(3)	0.004(3)	0.003(3)
C(9)	4*e*	0.7126(4)	0.2065(4)	0.4328(3)	0.027(3)	0.031(3)	0.029(3)	0.002(2)	0.005(2)	0.002(2)
C(10)	4*e*	0.7758(4)	0.1273(4)	0.4481(3)	0.032(3)	0.026(3)	0.038(3)	0.002(2)	0.008(2)	0.004(2)
C(11)	4*e*	0.8688(4)	0.1443(5)	0.4722(3)	0.029(3)	0.033(3)	0.037(3)	0.009(2)	0.007(2)	0.005(3)
C(12)	4*e*	0.6210(5)	0.1922(6)	0.4104(5)	0.036(2)	0.057(3)	0.091(3)	0.005(2)	0.014(2)	–0.003(2)
C(13)	4*e*	0.6431(4)	0.0942(4)	0.2509(3)	0.035(3)	0.027(3)	0.042(3)	–0.010(2)	0.008(3)	–0.002(3)
C(14)	4*e*	0.7363(4)	0.1018(4)	0.2754(3)	0.029(3)	0.029(3)	0.045(3)	0.005(2)	0.007(3)	0.002(3)
C(15)	4*e*	0.7801(4)	0.1961(4)	0.2854(3)	0.024(3)	0.031(3)	0.031(3)	0.000(2)	0.004(2)	0.001(2)
C(16)	4*e*	0.7206(4)	0.2785(4)	0.2703(3)	0.032(3)	0.025(3)	0.041(3)	–0.002(2)	0.000(2)	0.002(2)
C(17)	4*e*	0.6268(4)	0.2652(5)	0.2460(3)	0.032(3)	0.032(3)	0.046(3)	0.007(3)	0.009(3)	0.002(3)
C(18)	4*e*	0.8721(5)	0.2057(6)	0.3078(5)	0.040(2)	0.058(3)	0.090(3)	–0.003(2)	0.019(2)	0.005(2)

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