Crystal structure of [3,3′-butylenebis(imidazole-1,1′-diium)] bis[3,3′-butylenebis(imidazol-1-ium)]octamolybdate — water (1:2), $[C_{10}H_{16}N_4][(C_{10}H_{15}N_4)Mo_8O_{26}] \cdot 2H_2O$

Wei-Qiu Kan and Jian-Fang Ma*

Department of Chemistry, Northeast Normal University, Changchun 130024, P. R. China

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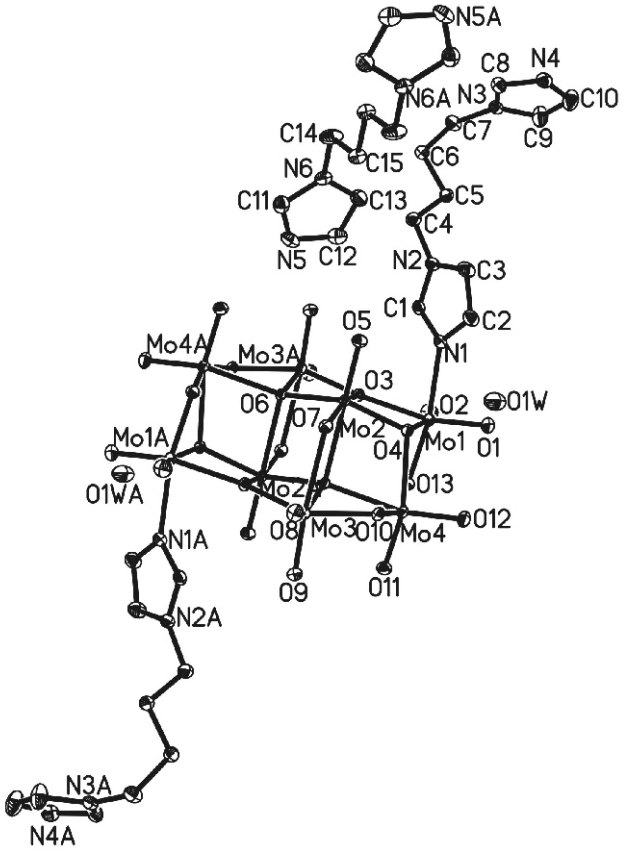

Abstract

$C_{30}H_{50}Mo_8N_{12}O_{28}$, triclinic, $P\bar{1}$ (no. 2), a = 11.3318(3) Å, b = 11.8120(3) Å, c = 12.1403(3) Å, α = 60.949(2)°, β = 86.274(2)°, γ = 65.506(2)°, V = 1273.6 Å^3, Z = 1, $R_{gt}(F)$ = 0.026, $wR_{ref}(F^2)$ = 0.055, T = 293 K.

Source of material

Starting materials and solvents for the synthesis were purchased commercially. *N*,*N*′-butylenebis(imidazole) (bbi) was synthesized according to literature [1]. A mixture of $Na_2MoO_4 \cdot 2H_2O$ (0.242 g, 1.0 mmol), bbi (0.19 g, 1.0 mmol) and 10 ml water was adjusted with HCl (1M) to pH = 4, sealed in a 15 ml Teflon-lined autoclave, and kept under autogenous pressure at 160 °C for 5 days. After cooling to room temperature at 10 °C/h, colorless crystals of the title compound were obtained (yield 45 %).

Experimental details

All H atoms on C atoms and N atoms were generated geometrically and refined as riding with d(C—H) = 0.93 - 0.97 Å, d(N—H) = 0.86 Å and U_{iso}(H) = 1.2U_{eq}(C,N). The water H atoms were located from difference Fourier map and refined as riding with d(O—H) = 0.974 - 1.002 Å, and U_{iso}(H) = 1.5U_{eq}(O).

Discussion

Supermolecular compounds of polyoxometalates, or hybrid materials, produced by combining of different inorganic and organic moieties by means of molecular assemblies, are of great interest in some important areas such as non-linear optical materials, catalysis, liquid crystals and charge-transfer salts [2].

There is one kind of $(\gamma\text{-}Mo_8O_{26})^{4-}$ anion and two kinds of bbi (bbi1 and bbi2) ligands in the asymmetric unit of the title compound. The unique $(\gamma\text{-}Mo_8O_{26})^{4-}$ anion consists of six distorted $\{MoO_6\}$ octahedra and two distorted $\{MoO_5N\}$ octahedra with four kinds of O atoms, two μ_4-O, four μ_3-O, six μ_2-O, and fourteen O_t. The special Mo1 atom exhibits a six-coordinated distorted octahedral geometry constructed by two μ_3-O atoms (O3 and O4), two terminal oxygen atoms (O1 and O2) and one μ_2-O atom (O13) from the $(\gamma\text{-}Mo_8O_{26})^{4-}$ anion, and one N atom from a bbi1 ligand with d(Mo1—O3) = 2.104(2) Å, d(Mo1—O4) = 2.296(2) Å, d(Mo1—O1) = 1.700(2) Å, d(Mo1—O2) = 1.706(2) Å, d(Mo1—O13) = 1.891(2) Å, and d(Mo1—N1) = 2.225(2) Å, respectively. The other Mo atoms of the $(\gamma\text{-}Mo_8O_{26})^{4-}$ anion also have distorted octahedral environments with d(Mo—O) ranging from 1.697(2) to 2.417(2) Å. The bbi1 ligands link $(\gamma\text{-}Mo_8O_{26})^{4-}$ polyanions to a supramolecular double-chain through hydrogen bonding interactions d(N4···O10) = 2.744 Å, and ∠N4–H4···O10 = 172.74°. The supramolecular layer was constructed by hydrogen bonds between $(\gamma\text{-}Mo_8O_{26})^{4-}$ polyanions of different chains and bbi2 ligands (d(N5···O11) = 2.751 Å, ∠N5–H5···O11 = 174.24°).

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.18 × 0.20 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	20.04 cm^{-1}
Diffractometer, scan mode:	Oxford Diffraction Gemini R Ultra, ω
$2\theta_{max}$:	59.82°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10895, 6291
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4998
$N(param)_{refined}$:	352
Programs:	SHELXS-97, SHELXL-97 [3]

* Correspondence author (e-mail: majf247nenu@yahoo.com.cn)

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	–1.4954	0.6403	0.4126	0.030
H(2)	2*i*	–1.4220	0.7900	0.0626	0.041
H(3)	2*i*	–1.6217	0.9796	0.0647	0.043
H(4A)	2*i*	–1.7080	1.0068	0.2750	0.035
H(4B)	2*i*	–1.6752	0.8601	0.4013	0.035
H(5A)	2*i*	–1.8259	0.8258	0.3089	0.033
H(5B)	2*i*	–1.8625	0.9780	0.1869	0.033
H(6A)	2*i*	–1.9060	0.9290	0.4359	0.034
H(6B)	2*i*	–1.9270	1.0810	0.3233	0.034
H(7A)	2*i*	–2.0797	0.9387	0.3366	0.040
H(7B)	2*i*	–2.1297	1.0788	0.3455	0.040
H(8)	2*i*	–2.0778	1.2870	0.1157	0.036
H(9)	2*i*	–2.1761	1.0014	0.1210	0.058
H(10)	2*i*	–2.2071	1.1870	–0.1024	0.065
H(11)	2*i*	–1.3740	1.1971	0.3824	0.041
H(12)	2*i*	–1.4644	0.9295	0.3432	0.045
H(13)	2*i*	–1.5971	1.1739	0.1650	0.041
H(14A)	2*i*	–1.5363	1.4374	0.2019	0.048
H(14B)	2*i*	–1.6426	1.4363	0.1261	0.048
H(15A)	2*i*	–1.4894	1.3760	0.0015	0.035
H(15B)	2*i*	–1.3831	1.3770	0.0773	0.035
H(4)	2*i*	–2.1429	1.3556	–0.0965	0.038
H(5)	2*i*	–1.3318	0.9546	0.4679	0.042
H(1WA)	2*i*	–1.1621	0.6742	0.0695	0.078
H(1WB)	2*i*	–1.1444	0.7099	–0.0689	0.078

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)	2*i*	–1.24079(2)	0.45349(3)	0.32534(3)	0.0184(1)	0.0222(1)	0.0251(1)	–0.0100(1)	0.0022(1)	–0.0146(1)
Mo(2)	2*i*	–1.10045(2)	0.64462(3)	0.35783(2)	0.0171(1)	0.0144(1)	0.0155(1)	–0.00680(9)	0.0018(1)	–0.0078(1)
Mo(3)	2*i*	–0.76015(2)	0.47411(3)	0.39506(2)	0.0165(1)	0.0211(1)	0.0191(1)	–0.0094(1)	0.0049(1)	–0.0118(1)
Mo(4)	2*i*	–0.93133(2)	0.36068(3)	0.30423(2)	0.0182(1)	0.0194(1)	0.0215(1)	–0.0075(1)	0.0030(1)	–0.0136(1)
C(1)	2*i*	–1.5009(3)	0.7010(3)	0.3259(3)	0.022(2)	0.029(2)	0.025(2)	–0.012(1)	0.002(1)	–0.014(2)
C(2)	2*i*	–1.4614(3)	0.7834(4)	0.1338(3)	0.030(2)	0.037(2)	0.026(2)	–0.011(2)	0.003(2)	–0.012(2)
C(3)	2*i*	–1.5716(3)	0.8887(4)	0.1343(3)	0.036(2)	0.026(2)	0.028(2)	–0.009(2)	0.002(2)	–0.005(2)
C(4)	2*i*	–1.7002(3)	0.9104(4)	0.3091(3)	0.024(2)	0.031(2)	0.037(2)	–0.010(1)	0.005(2)	–0.020(2)
C(5)	2*i*	–1.8327(3)	0.9212(4)	0.2787(3)	0.024(2)	0.029(2)	0.032(2)	–0.011(1)	0.004(1)	–0.018(2)
C(6)	2*i*	–1.9314(3)	0.9927(4)	0.3440(3)	0.028(2)	0.027(2)	0.027(2)	–0.009(1)	0.002(1)	–0.013(2)
C(7)	2*i*	–2.0721(3)	1.0277(4)	0.3056(3)	0.026(2)	0.037(2)	0.025(2)	–0.012(2)	0.007(1)	–0.010(2)
C(8)	2*i*	–2.1054(3)	1.2387(4)	0.0893(3)	0.030(2)	0.029(2)	0.032(2)	–0.017(2)	0.003(2)	–0.013(2)
C(9)	2*i*	–2.1598(4)	1.0815(4)	0.0922(4)	0.080(3)	0.033(2)	0.035(2)	–0.033(2)	–0.003(2)	–0.012(2)
C(10)	2*i*	–2.1769(5)	1.1834(4)	–0.0307(4)	0.091(3)	0.036(2)	0.035(2)	–0.028(2)	–0.002(2)	–0.015(2)
C(11)	2*i*	–1.4129(3)	1.1614(4)	0.3500(3)	0.033(2)	0.040(2)	0.033(2)	–0.018(2)	0.008(2)	–0.020(2)
C(12)	2*i*	–1.4630(3)	1.0139(4)	0.3282(4)	0.032(2)	0.032(2)	0.048(2)	–0.016(2)	0.010(2)	–0.020(2)
C(13)	2*i*	–1.5361(3)	1.1481(4)	0.2304(3)	0.032(2)	0.034(2)	0.035(2)	–0.013(2)	0.002(2)	–0.016(2)
C(14)	2*i*	–1.5491(4)	1.3928(4)	0.1573(3)	0.042(2)	0.024(2)	0.041(2)	–0.010(2)	0.018(2)	–0.011(2)
C(15)	2*i*	–1.4766(3)	1.4207(3)	0.0460(3)	0.029(2)	0.026(2)	0.032(2)	–0.013(1)	0.009(2)	–0.015(2)
N(1)	2*i*	–1.4164(2)	0.6648(3)	0.2553(2)	0.020(1)	0.025(1)	0.025(1)	–0.009(1)	0.001(1)	–0.012(1)
N(2)	2*i*	–1.5950(2)	0.8352(3)	0.2577(2)	0.021(1)	0.026(2)	0.029(1)	–0.008(1)	0.002(1)	–0.014(1)
N(3)	2*i*	–2.1148(2)	1.1164(3)	0.1661(2)	0.020(1)	0.026(2)	0.026(1)	–0.008(1)	0.003(1)	–0.010(1)
N(4)	2*i*	–2.1417(3)	1.2800(3)	–0.0300(3)	0.035(2)	0.024(2)	0.027(2)	–0.011(1)	0.004(1)	–0.007(1)
N(5)	2*i*	–1.3877(3)	1.0253(3)	0.4000(3)	0.026(1)	0.031(2)	0.030(2)	–0.006(1)	0.001(1)	–0.006(1)
N(6)	2*i*	–1.5031(3)	1.2388(3)	0.2461(3)	0.029(1)	0.022(1)	0.027(2)	–0.010(1)	0.010(1)	–0.012(1)
O(1)	2*i*	–1.2699(2)	0.4817(3)	0.1764(2)	0.031(1)	0.044(2)	0.035(1)	–0.011(1)	–0.001(1)	–0.026(1)
O(2)	2*i*	–1.3272(2)	0.3614(2)	0.4141(2)	0.032(1)	0.033(1)	0.043(1)	–0.020(1)	0.007(1)	–0.018(1)
O(3)	2*i*	–1.2120(2)	0.5187(2)	0.4507(2)	0.020(1)	0.022(1)	0.021(1)	–0.0114(9)	0.0044(9)	–0.012(1)
O(4)	2*i*	–1.1075(2)	0.5687(2)	0.2536(2)	0.023(1)	0.019(1)	0.017(1)	–0.0089(9)	0.0020(9)	–0.0093(9)
O(5)	2*i*	–1.2311(2)	0.8099(2)	0.2858(2)	0.025(1)	0.019(1)	0.027(1)	–0.0059(9)	0.001(1)	–0.009(1)
O(6)	2*i*	–1.0812(2)	0.5937(2)	0.5364(2)	0.0169(9)	0.018(1)	0.017(1)	–0.0088(8)	0.0040(8)	–0.0113(9)
O(7)	2*i*	–0.9651(2)	0.6824(2)	0.3167(2)	0.024(1)	0.020(1)	0.023(1)	–0.0116(9)	0.0052(9)	–0.011(1)
O(8)	2*i*	–0.6928(2)	0.5908(2)	0.3130(2)	0.031(1)	0.035(1)	0.032(1)	–0.023(1)	0.012(1)	–0.018(1)
O(9)	2*i*	–0.6307(2)	0.3072(2)	0.4568(2)	0.024(1)	0.027(1)	0.030(1)	–0.0062(9)	0.004(1)	–0.017(1)
O(10)	2*i*	–0.8359(2)	0.4776(2)	0.2523(2)	0.022(1)	0.023(1)	0.019(1)	–0.0117(9)	0.0067(9)	–0.013(1)
O(11)	2*i*	–0.8027(2)	0.1922(2)	0.3886(2)	0.024(1)	0.024(1)	0.040(1)	–0.0065(9)	–0.000(1)	–0.019(1)
O(12)	2*i*	–0.9630(2)	0.3819(2)	0.1585(2)	0.034(1)	0.036(1)	0.028(1)	–0.016(1)	0.004(1)	–0.021(1)
O(13)	2*i*	–1.0670(2)	0.3045(2)	0.3851(2)	0.021(1)	0.017(1)	0.028(1)	–0.0082(9)	0.0003(9)	–0.011(1)
O(1W)	2*i*	–1.1942(3)	0.7555(3)	–0.0213(2)	0.049(2)	0.045(2)	0.033(1)	–0.006(1)	0.010(1)	–0.012(1)

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