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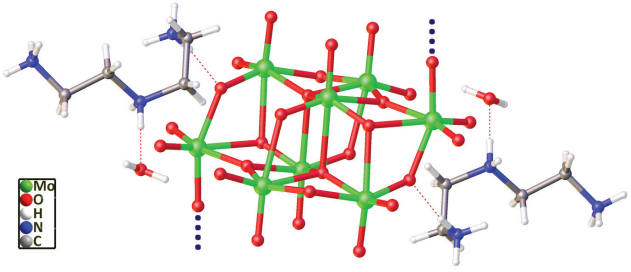
The crystal structure of *catena*-poly[bis[3-azoniapentane-1,5-diammonium][bis(μ_4-oxo)-tetrakis(μ_3-oxo)-heptakis(μ_2-oxo)-tetradecaoxo-octa-molybdenum] dihydrate], $(C_8H_{36}N_6O_{29}Mo_8)_n$



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Abstract

$(C_8H_{36}N_6O_{29}Mo_8)_n$, monoclinic, $P2_1/n$ (no. 14), $a = 10.5883(4)$ Å, $b = 9.4385(3)$ Å, $c = 16.5154(7)$ Å, $\beta = 94.616(4)°$, $V = 1645.15(11)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0359$, $wR_{ref}(F^2) = 0.0887$, $T = 293(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture containing $Na_2WO_4 \cdot 2H_2O$ (1.050 g), diethylenetriamine (4.0 mL), H_2SO_4 (0.5 M, 3.0 mL) and deionized water (H_2O) (10.0 mL) was prepared by mixing these components and sealed in a 25 mL Teflon-lined stainless steel autoclave (75% of the total volume of the autoclave). Then, the resulting slurry (pH = 7.0) was heated to 448 K in an oven and

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.35 × 0.12 × 0.10 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	3.06 mm^{-1}
Diffractometer, scan mode:	Rigaku R-axis Spider, ω
θ_{max}, completeness:	29.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7986, 3862, 0.034
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3305
$N(param)_{refined}$:	237
Programs:	CrysAlis^{PRO} [1], SHELX [2], IL MILIONE [3], Olex2 [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
N1	1.2837(4)	0.0225(4)	0.6841(3)	0.0200(9)
H1A	1.3257	−0.0568	0.6747	0.024*
H1B	1.2468	0.0141	0.7304	0.024*
H1C	1.3375	0.0951	0.6877	0.024*
N2	0.9989(4)	0.2005(4)	0.5836(3)	0.0231(10)
H2A	0.9475	0.1349	0.6014	0.028*
H2B	1.0090	0.1818	0.5317	0.028*
N3	0.8651(4)	0.3089(4)	0.7276(2)	0.0224(10)
H3A	0.7845	0.3042	0.7079	0.027*
H3B	0.8695	0.3458	0.7773	0.027*
H3C	0.8984	0.2223	0.7297	0.027*
C1	1.1860(5)	0.0475(5)	0.6167(3)	0.0231(12)
H1D	1.1231	−0.0273	0.6149	0.028*
H1E	1.2244	0.0485	0.5653	0.028*
C2	1.1242(5)	0.1897(5)	0.6310(3)	0.0186(10)
H2C	1.1131	0.2006	0.6884	0.022*
H2D	1.1790	0.2653	0.6150	0.022*
C3	0.9371(6)	0.3426(5)	0.5890(3)	0.0274(13)
H3D	0.8504	0.3360	0.5654	0.033*
H3E	0.9811	0.4099	0.5569	0.033*
C4	0.9361(5)	0.3987(5)	0.6746(3)	0.0227(11)
H4A	1.0228	0.4072	0.6979	0.027*
H4B	0.8991	0.4928	0.6727	0.027*
Mo1	0.59059(4)	0.11377(4)	0.57971(2)	0.01048(11)
Mo2	0.49507(4)	0.38202(4)	0.68995(2)	0.01144(11)
Mo3	0.33160(4)	0.64184(4)	0.60210(2)	0.01034(11)
Mo4	0.59967(4)	0.64559(4)	0.51736(2)	0.00917(11)
O1	0.5000	0.0000	0.5000	0.0202(11)

Table 2 (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O2	0.7462(3)	0.0747(3)	0.5688(2)	0.0192(8)
O3	0.5530(3)	0.0189(3)	0.6623(2)	0.0187(8)
O4	0.6341(3)	0.2866(3)	0.65119(19)	0.0141(7)
O5	0.4382(4)	0.2572(3)	0.7535(2)	0.0206(8)
O6	0.5707(3)	0.5047(3)	0.7536(2)	0.0200(8)
O7	0.3274(3)	0.4760(3)	0.67031(19)	0.0135(7)
O8	0.5044(3)	0.5171(3)	0.58180(19)	0.0122(7)
O9	0.3926(3)	0.7544(3)	0.6782(2)	0.0191(8)
O10	0.1765(3)	0.6908(3)	0.5862(2)	0.0208(8)
O11	0.4103(3)	0.7267(3)	0.51454(19)	0.0134(7)
O12	0.6698(3)	0.7552(3)	0.5902(2)	0.0169(7)
O13	0.7218(3)	0.5302(3)	0.49550(19)	0.0136(7)
O14	0.5840(3)	0.7540(3)	0.42088(18)	0.0113(7)
O15	1.0635(4)	0.1702(5)	0.4266(3)	0.0398(11)
H15A	1.1435	0.1717	0.4245	0.060*
H15B	1.0293	0.2279	0.3919	0.060*

maintained at the temperature for five days. Then, the colourless purity-phase crystals of the title compound (about 61% yield based on Mo) were obtained.

Experimental details

All the hydrogen atoms were placed at calculated positions and refined as riding on their parent atoms with the SHELX program [2]. Non-hydrogen atoms were refined anisotropically.

Comment

Polyoxometalates (POMs) often exhibit intriguing structures and outstanding properties [5–7]. Studies on POMs have also focused on their applications, such as photochemistry, catalysis, medicinal chemistry and physical sciences, etc. [8–10]. Polytungstates are an important classes of POMs.

Herein, we report the structure of a one-dimensional octamolybdate, $[(H_3dien)_2(Mo_8O_{27})\cdot 2H_2O]_n$ (dien = diethylenetriamine). The asymmetric unit consists of one protonated $[H_3dien]^{3+}$cations, one half of an homopolymolybdate radical polyanion $[Mo_8O_{27}]^{6-}$ and one crystal water molecule. All Mo atoms are in a six-coordination state. The O atoms within the anion can be divided into four types in accordance to their bonding modes, namely, terminal, μ_2, μ_3- and μ_4. All bond distances and angles are within the expected ranges. The structure is closely related to that of the bis(tris(2 ammonioethyl)amine analogue [11]. The shortest Mo—O distances range from 1.705(3) to 1.750(3) Å for terminal oxygen atoms (Mo—O_t). The O—Mo—O bond angles are in the range of 71.50(11)–177.44(13)°. Bond valence sum calculations [12] on the Mo sites afford 6.05, 5.97, 6.03 and 5.94 for Mo1, Mo2, Mo3 and Mo4 respectively. These calculation results reveal the symmetry-independent Mo sites are in the +6 oxidation state, as expected.

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