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Di-μ-aqua-tetrakis[μ-(methanol)-(methanol)sodium] Octamolybdate, $[Na_4(CH_4O)_8(H_2O)_2][Mo_8O_{26}]$

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Abstract. $M_r = 1567{\cdot}83$, monoclinic, $C2/m$, $a = 13{\cdot}838\ (2)$, $b = 17{\cdot}324\ (4)$, $c = 9{\cdot}087\ (2)$ Å, $\beta = 118{\cdot}47\ (1)°$, $V = 1915{\cdot}0$ Å^3, $Z = 2$, $D_x = 2{\cdot}719$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 26{\cdot}3$ cm^{-1}, $F(000) = 1504$, $T = 173$ K. Final $R = 0{\cdot}027$ for 2017 observed reflections. The structure comprises apparently unique $[Na_4(\mu\text{-}CH_3OH)_4(CH_3OH)_4(\mu\text{-}H_2O)_2]^{4+}$ tetrameric cations and $Mo_8O_{26}^{4-}$ anions in the well characterized β conformation with extensive interactions between the two. Both the cation and the anion have crystallographic $2/m$ symmetry with the ion centers located at $\frac{1}{2}$,0,0 and 0,0,0 respectively.

Introduction. In an effort to model the catalyst activity of MoO_3 with molecular or ionic species which can be studied by X-ray diffraction techniques, a synthesis program aimed, in part, to produce methylated $[MoO_3]_n$ species has been undertaken. The reaction of $MoO_3.2H_2O$ with an excess of CH_3OH over a 4 Å molecular sieve yields several crystalline products, the most interesting of which is $Na_4[Mo_8O_{24}(OCH_3)_4].8CH_3OH$. This compound contains $[Mo_8O_{24}(OCH_3)_4]^{4-}$ anions with both bridging and terminal methoxy groups; chemically, this product is also exciting because it photochemically decomposes to yield formaldehyde (McCarron & Harlow, 1983). When a methanol solution of $Na_4[Mo_8O_{24}(OCH_3)_4].8CH_3OH$ is allowed to recrystallize in an open beaker, complete hydrolysis (rather than the desired partial hydrolysis) occurs, and crystals of the title compound are formed.

Experimental. Syntex $P3$ diffractometer with low-temperature apparatus (173 K). Plates, 0·11 × 0·28 × 0·30 mm. Unit-cell parameters refined using 49 reflections, $20 < 2\theta < 26°$. Data collection: 2275 reflections, 1·2° ω scans, 4–10° min^{-1}, $4 < 2\theta < 55°$. Absorption correction (φ scan): transmission factors ranged from 0·72 to 1·00. Standard reflections: two every 200 reflections; only statistical variations noted. Solution: direct methods. Refinement: full-matrix least squares: $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$, $\sigma(F_o^2) = [\sigma^2(F_o^2) + 0{\cdot}02(F_o^2)]^{1/2}$; 2017 reflections, $F_o^2 > 2\sigma(F_o^2)$; 177 variables [Mo, Na, O and C anisotropic; H (located in a ΔF map) isotropic]; $R = 0{\cdot}027$, $R_w = 0{\cdot}031$. LS shift/error essentially zero. Largest peak in final difference map: 0·83 e Å^{-3} near Mo(3). Program: local modification of the Enraf–Nonius *SDP* (Frenz, 1978). Other computational details and atomic scattering factors may be found elsewhere (Nugent & Harlow, 1979).

Discussion. Final atomic parameters are in Table 1,* selected bond distances in Table 2. Figs. 1 and 2 show projections of the anion and cation respectively.

The structure consists of $[Na_4(CH_3OH)_8(H_2O)_2]^{4+}$ and $Mo_8O_{26}^{4-}$ ions with extensive interactions between the two. The octamolybdate anions exist in the β form, a conformation which has been well characterized by previous structural studies (Weakley, 1981; Romàn, Martinez-Ripoll & Jaud, 1982; and references therein). The tetrameric cation, with four planar Na atoms, two bridging waters, four symmetrically bridging methanols, and four terminal methanols, appears to be unique. Eight of the O atoms of the $Mo_8O_{26}^{4-}$ anion [O(6), O(7), and their $2/m$ equivalents] coordinate with various Na atoms to complete the octahedral coordination of the Na atoms; ten O atoms [O(4), O(5), O(8), O(9), and their equivalents] serve as weak hydrogen-bonding acceptors from the H_2O and CH_3OH molecules: H(10)$A\cdots$O(4), 2·10 (6); H(10)$B\cdots$O(8$^{\text{v}}$), 2·13; H(11)$\cdots$O(5), 2·11 (4); H(12)$\cdots$O(9), 2·12 Å.

One of the significant features in the structure of the $[Mo_8O_{24}(OCH_3)_4]^{4-}$ anion (McCarron & Harlow, 1983) was the location of short C—H$\cdots$O intramolecular contacts which could indicate possible pathways for proton transfers during the conversion of CH_3OH to CH_2O. In the present structure, there are no such C—H$\cdots$O contacts; all of the H$\cdots$O distances are greater than 2·6 Å.

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* Lists of structure factors, anisotropic thermal parameters, selected bond angles and hydrogen-bonding details and stereoviews corresponding to Figs. 1 and 2 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39198 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional and isotropic thermal parameters with e.s.d.'s in parentheses*

	x	*y*	*z*	*B*(Å^2)
Mo(1)	−0·00727 (3)	0·000	−0·20087 (4)	0·797 (6)
Mo(2)	0·13667 (2)	0·13353 (1)	0·05860 (3)	0·890 (5)
Mo(3)	0·28449 (3)	0·000	0·32306 (4)	0·970 (7)
Na	0·3561 (1)	0·13353 (8)	−0·1264 (2)	2·02 (3)
O(1)	0·1129 (2)	0·000	0·0613 (3)	0·95 (6)
O(2)	−0·0049 (2)	0·1090 (1)	−0·1432 (2)	0·94 (4)
O(3)	−0·1382 (2)	0·000	−0·3752 (3)	1·06 (6)
O(4)	0·0814 (2)	0·000	−0·2804 (4)	1·41 (6)
O(5)	0·2374 (2)	0·1063 (1)	0·2841 (2)	1·13 (4)
O(6)	0·1211 (2)	0·2296 (1)	0·0804 (3)	1·46 (5)
O(7)	0·2191 (2)	0·1280 (1)	−0·0329 (3)	1·46 (5)
O(8)	0·3729 (2)	0·000	0·5337 (4)	1·56 (7)
O(9)	0·3669 (2)	0·000	0·2296 (4)	1·54 (6)
O(10)	0·3093 (2)	0·000	−0·1989 (4)	1·79 (7)
O(11)	0·2442 (2)	0·1630 (2)	−0·4083 (3)	3·90 (7)
O(12)	0·4857 (2)	0·1166 (2)	0·1624 (3)	2·11 (5)
C(1)	0·1376 (4)	0·1724 (3)	−0·4406 (5)	4·3 (1)
C(2)	0·4847 (3)	0·1728 (2)	0·2773 (4)	2·41 (8)
H(1)*A*	0·081 (6)	0·174 (5)	−0·543 (9)	13 (3)
H(1)*B*	0·101 (7)	0·119 (6)	−0·44 (1)	19 (4)
H(1)*C*	0·126 (6)	0·190 (5)	−0·347 (8)	11 (2)
H(2)*A*	0·541 (3)	0·166 (3)	0·386 (5)	4 (1)
H(2)*B*	0·498 (3)	0·219 (3)	0·247 (5)	4 (1)
H(2)*C*	0·410 (4)	0·178 (3)	0·263 (6)	5 (1)
H(10)*A*	0·243 (5)	0·000	−0·243 (7)	4 (2)
H(10)*B*	0·288 (4)	0·000	−0·322 (6)	2 (1)
H(11)	0·243 (4)	0·145 (3)	−0·491 (6)	5 (1)
H(12)	0·465 (3)	0·081 (3)	0·185 (5)	4 (1)

H atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as: $\frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta) \times B_{13} + bc(\cos\alpha)B_{23}]$.

Table 2. *Selected bond distances* (Å) *with e.s.d.'s*

Mo(1)–O(1)	2·159 (2)	Na–O(6$^{\rm iii}$)	2·403 (2)
Mo(1)–O(1$^{\rm i}$)	2·348 (2)	Na–O(7)	2·421 (2)
Mo(1)–O(2)	1·956 (2)	Na–O(10)	2·408 (1)
Mo(1)–O(3)	1·748 (2)	Na–O(11)	2·333 (3)
Mo(1)–O(4)	1·695 (2)	Na–O(12)	2·388 (3)
		Na–O(12$^{\rm iv}$)	2·380 (2)
Mo(2)–O(1)	2·338 (1)		
Mo(2)–O(2)	1·989 (2)	O(10)–H(10)*A*	0·80 (5)
Mo(2)–O(2$^{\rm ii}$)	2·331 (1)	O(10)–H(10)*B*	1·02 (4)
Mo(2)–O(5)	1·908 (2)		
Mo(2)–O(6)	1·701 (2)	O(11)–C(1)	1·370 (5)
Mo(2)–O(7)	1·705 (2)	O(11)–H(11)	0·81 (4)
		O(12)–C(2)	1·432 (3)
Mo(3)–O(1)	2·431 (2)	O(12)–H(12)	0·76 (4)
Mo(3)–O(3$^{\rm i}$)	2·288 (2)	C(1)–H(1)*A*	0·89 (7)
Mo(3)–O(5)	1·929 (2)	C(1)–H(1)*B*	1·05 (9)
Mo(3)–O(8)	1·711 (2)	C(1)–H(1)*C*	0·99 (7)
Mo(3)–O(9)	1·715 (2)	C(2)–H(2)*A*	0·93 (4)
		C(2)–H(2)*B*	0·90 (4)
		C(2)–H(2)*C*	0·99 (4)

Symmetry code: (i) $-x, -y, -z$; (ii) $-x, y, -z$; (iii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (iv) $1 - x, y, -z$; (v) $x, y, z - 1$.

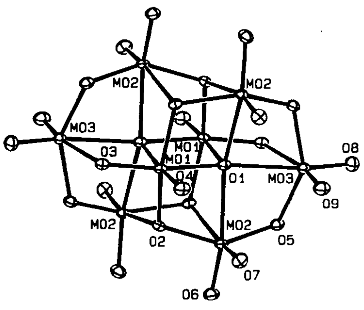

Fig. 1. Projection of the $Mo_8O_{26}^{4-}$ anion with crystallographic 2/*m* symmetry. Only the unique O atoms have been labeled; to emphasize the symmetry, all of the Mo atoms have been labeled. Mo(1), Mo(3), O(1), O(3), O(4), O(8), and O(9) lie in the mirror plane.

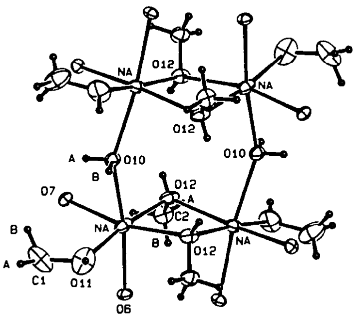

Fig. 2. Projection of the $[Na_4(CH_3OH)_8(H_2O)_2]^{4+}$ cation also with 2/*m* symmetry. All of the Na atoms and the bridging O atoms have been labeled. The water molecules lie in the mirror plane.

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