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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71212 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1031]

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Tetrakis(tetramethylammonium) Octamolybdate Dihydrate

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Abstract

The synthesis and crystal structure of tetrakis(tetramethylammonium) octamolybdate dihydrate, $[N(CH_3)_4]_4[Mo_8O_{26}].2H_2O$, is reported. The Mo_8O_{26} unit adopts the β configuration for that ion. Mo—O distances and angles are comparable with those found in previous studies of the same anion.

Comment

Acidifying a clear solution of $(TMA)_2(MoO_4)$ [TMA = tetramethylammonium cation], prepared from appropriate quantities of TMAOH and MoO_3, to a pH of about 7 gave a microcrystalline precipitate. On aging for several days at 373 K, crystals adequate for the structure determination were formed, of up to 1 mm in linear dimension.

The octamolybdate anion adopts the β-Mo_8O_{26} configuration (Fig. 1) in $[N(CH_3)_4]_4[Mo_8O_{26}].2H_2O$, as previously observed for the octamolybdate group in $(NH_4)_4[Mo_8O_{26}].4H_2O$ (Atovmyan & Krasochka, 1972), compared with the α-Mo_8O_{26} form observed in $[N(C_4H_9)_4]_4[Mo_8O_{26}]$ (Day, Fredrich, Klemperer & Shum, 1977). Mo—O distances and O—Mo—O angles agree with the previous study, and the center of the molecule is located at an inversion center; the approximate point symmetry is $2/m$ (C_{2v}). Since the α- and β-conformers of the Mo_8O_{26} unit are highly flexible and interconvertable (Masters, Gheller, Brownlee, O'Connor & Wedd, 1980), it is apparent that subtle packing forces are significant in determining which Mo_8O_{26} isomer crystallizes in combination with a particular organic cation.

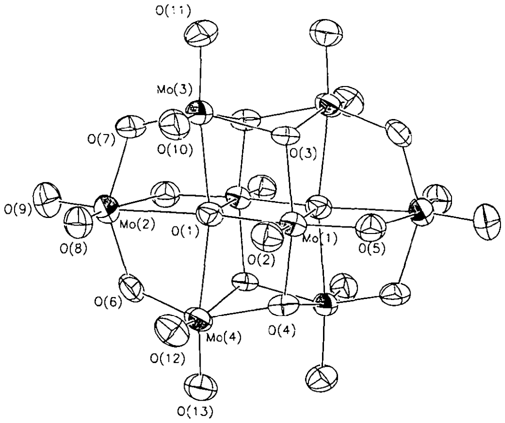

Fig. 1. View of the Mo_8O_{26} anion, showing the labeling of the asymmetric atoms. Thermal ellipsoids are shown at 50% probability levels.

Experimental

Crystal data

$[(CH_3)_4N]_4[Mo_8O_{26}].2H_2O$
$M_r = 1516.12$
Triclinic
$P\overline{1}$
$a = 10.539$ (2) Å
$b = 11.902$ (2) Å
$c = 9.714$ (2) Å
$\alpha = 96.301$ (6)°
$\beta = 108.962$ (5)°
$\gamma = 75.234$ (4)°
$V = 1114$ (2) Å^3
$Z = 1$

$D_x = 2.265$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5$–$9°$
$\mu = 2.22$ mm^{-1}
$T = 298$ K
Lump
0.50 × 0.40 × 0.40 mm
Colorless

Data collection

Huber automated diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2550 measured reflections
2550 independent reflections
1805 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max} = 25.0°$
$h = -8 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 9$
3 standard reflections monitored every 100 reflections intensity variation: $< \pm 2\%$

Refinement

Refinement on F
Final $R = 0.048$
$wR = 0.050$
1805 reflections
218 parameters
H-atom positions not determined
$w = 1.0$
$(\Delta/\sigma)_{\max} = 0.020$
$\Delta\rho_{\max} = 0.82$ e Å^{-3}
$\Delta\rho_{\min} = -0.89$ e Å^{-3}
Extinction correction: Larson (1967)
Extinction coefficient: 42 (4)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: *UCLA Crystallographic Software* (Strouse, 1982). Cell refinement: *UCLA Crystallographic Software*. Data reduction: *UCLA Crystallographic Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1986). Program(s) used to refine structure: *CRYSTALS* (Carruthers, Watkin & Betteridge, 1990). Molecular graphics: locally modified *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: local routines.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Mo(1)	0.9719 (1)	0.4784 (1)	0.1650 (1)	0.0342
Mo(2)	0.9328 (1)	0.2585 (1)	−0.2528 (1)	0.0431
Mo(3)	1.1828 (1)	0.2719 (1)	0.0504 (1)	0.0360
Mo(4)	0.7239 (1)	0.4675 (1)	−0.1324 (1)	0.0378
O(1)	0.9643 (9)	0.3934 (7)	−0.043 (1)	0.0369
O(2)	0.9265 (9)	0.3811 (8)	0.238 (1)	0.0444
O(3)	1.1662 (8)	0.4046 (7)	0.1922 (9)	0.0313
O(4)	0.7922 (9)	0.5649 (7)	0.0436 (9)	0.0373
O(5)	0.9965 (9)	0.5871 (8)	0.300 (1)	0.0453
O(6)	0.7662 (9)	0.3775 (8)	−0.2939 (9)	0.0409
O(7)	1.1305 (9)	0.2193 (8)	−0.145 (1)	0.0422
O(8)	0.884 (1)	0.1644 (8)	−0.171 (1)	0.0541
O(9)	0.933 (1)	0.1957 (9)	−0.418 (1)	0.0642
O(10)	1.130 (1)	0.1810 (8)	0.130 (1)	0.0463
O(11)	1.359 (1)	0.2166 (8)	0.095 (1)	0.0542
O(12)	0.687 (1)	0.3680 (9)	−0.051 (1)	0.0545
O(13)	0.569 (1)	0.5553 (8)	−0.218 (1)	0.0520
O(20)	0.698 (2)	0.016 (1)	0.691 (2)	0.1063
N(1)	0.750 (1)	0.118 (1)	0.203 (1)	0.0501
N(2)	0.655 (1)	0.683 (1)	0.413 (1)	0.0485
C(1)	0.691 (2)	0.242 (1)	0.246 (2)	0.0515
C(2)	0.737 (2)	0.035 (1)	0.303 (2)	0.0696
C(3)	0.901 (2)	0.105 (2)	0.218 (2)	0.0655
C(4)	0.673 (2)	0.095 (2)	0.047 (2)	0.0767
C(5)	0.769 (2)	0.745 (2)	0.493 (2)	0.0620
C(6)	0.598 (2)	0.723 (2)	0.257 (2)	0.0633
C(7)	0.710 (2)	0.555 (1)	0.421 (2)	0.0688
C(8)	0.544 (2)	0.721 (2)	0.489 (2)	0.0692

Table 2. *Geometric parameters* (Å, °)

Mo(1)—O(1)	2.142 (9)	Mo(3)—O(10)	1.69 (1)
Mo(1)—O(1$^{\rm i}$)	2.373 (9)	Mo(3)—O(11)	1.72 (1)
Mo(1)—O(2)	1.660 (9)	Mo(4)—O(1)	2.351 (9)
Mo(1)—O(3)	1.950 (8)	Mo(4)—O(3$^{\rm i}$)	2.351 (9)
Mo(1)—O(4)	1.960 (8)	Mo(4)—O(4)	1.994 (9)
Mo(1)—O(5)	1.745 (9)	Mo(4)—O(6)	1.908 (9)
Mo(2)—O(1)	2.440 (9)	Mo(4)—O(12)	1.68 (1)
Mo(2)—O(5$^{\rm i}$)	2.29 (1)	Mo(4)—O(13)	1.693 (9)
Mo(2)—O(6)	1.906 (9)	N(1)—C(1)	1.51 (2)
Mo(2)—O(7)	1.958 (9)	N(1)—C(2)	1.52 (2)
Mo(2)—O(8)	1.70 (1)	N(1)—C(3)	1.51 (2)
Mo(2)—O(9)	1.69 (1)	N(1)—C(4)	1.50 (2)
Mo(3)—O(1)	2.330 (9)	N(2)—C(5)	1.52 (2)
Mo(3)—O(3)	1.989 (8)	N(2)—C(6)	1.52 (2)
Mo(3)—O(4$^{\rm i}$)	2.342 (9)	N(2)—C(7)	1.49 (2)
Mo(3)—O(7)	1.881 (9)	N(2)—C(8)	1.53 (2)
O(1)—Mo(1)—O(1$^{\rm i}$)	76.3 (3)	O(11)—Mo(3)—O(1)	161.1 (4)
O(2)—Mo(1)—O(1)	98.8 (4)	O(11)—Mo(3)—O(3)	102.8 (4)
O(2)—Mo(1)—O(1$^{\rm i}$)	175.1 (4)	O(11)—Mo(3)—O(4$^{\rm i}$)	89.4 (4)
O(3)—Mo(1)—O(1)	78.1 (3)	O(11)—Mo(3)—O(7)	99.5 (5)
O(3)—Mo(1)—O(1$^{\rm i}$)	78.2 (3)	O(11)—Mo(3)—O(10)	103.6 (5)
O(3)—Mo(1)—O(2)	100.7 (4)	O(3$^{\rm i}$)—Mo(4)—O(1)	71.5 (3)
O(4)—Mo(1)—O(1)	79.2 (3)	O(4)—Mo(4)—O(1)	73.6 (3)
O(4)—Mo(1)—O(1$^{\rm i}$)	77.7 (3)	O(4)—Mo(4)—O(3$^{\rm i}$)	71.2 (3)
O(4)—Mo(1)—O(2)	101.8 (4)	O(6)—Mo(4)—O(1)	76.8 (3)
O(4)—Mo(1)—O(3)	150.1 (4)	O(6)—Mo(4)—O(3$^{\rm i}$)	83.4 (3)
O(5)—Mo(1)—O(1)	156.9 (4)	O(6)—Mo(4)—O(4)	145.8 (4)
O(5)—Mo(1)—O(1$^{\rm i}$)	80.6 (4)	O(12)—Mo(4)—O(1)	94.3 (4)
O(5)—Mo(1)—O(2)	104.3 (4)	O(12)—Mo(4)—O(3$^{\rm i}$)	164.0 (4)
O(5)—Mo(1)—O(3)	97.5 (4)	O(12)—Mo(4)—O(4)	98.3 (4)
O(5)—Mo(1)—O(4)	95.7 (4)	O(12)—Mo(4)—O(6)	100.8 (4)
O(5$^{\rm i}$)—Mo(2)—O(1)	69.7 (3)	O(13)—Mo(4)—O(1)	160.3 (4)
O(6)—Mo(2)—O(1)	74.6 (3)	O(13)—Mo(4)—O(3$^{\rm i}$)	88.9 (4)
O(6)—Mo(2)—O(5$^{\rm i}$)	78.0 (4)	O(13)—Mo(4)—O(4)	101.4 (4)
O(7)—Mo(2)—O(1)	74.0 (3)	O(13)—Mo(4)—O(6)	100.6 (4)
O(7)—Mo(2)—O(5$^{\rm i}$)	78.1 (4)	O(13)—Mo(4)—O(12)	105.4 (5)
O(7)—Mo(2)—O(6)	145.5 (4)	Mo(1)—O(1)—Mo(1$^{\rm i}$)	103.7 (3)
O(8)—Mo(2)—O(1)	94.0 (4)	Mo(2)—O(1)—Mo(1)	164.1 (4)
O(8)—Mo(2)—O(5$^{\rm i}$)	163.7 (4)	Mo(2)—O(1)—Mo(1$^{\rm i}$)	92.1 (3)
O(8)—Mo(2)—O(6)	98.4 (4)	Mo(3)—O(1)—Mo(1)	92.2 (3)
O(8)—Mo(2)—O(7)	97.7 (4)	Mo(3)—O(1)—Mo(1$^{\rm i}$)	97.6 (3)
O(9)—Mo(2)—O(1)	161.2 (5)	Mo(3)—O(1)—Mo(2)	86.5 (3)
O(9)—Mo(2)—O(5$^{\rm i}$)	91.6 (5)	Mo(4)—O(1)—Mo(1)	91.4 (3)
O(9)—Mo(2)—O(6)	103.9 (5)	Mo(4)—O(1)—Mo(1$^{\rm i}$)	97.1 (3)
O(9)—Mo(2)—O(7)	101.2 (5)	Mo(4)—O(1)—Mo(2)	85.6 (3)
O(9)—Mo(2)—O(8)	104.7 (5)	Mo(4)—O(1)—Mo(3)	163.5 (4)
O(3)—Mo(3)—O(1)	73.0 (3)	Mo(3)—O(3)—Mo(1)	109.9 (4)
O(4$^{\rm i}$)—Mo(3)—O(1)	71.7 (3)	Mo(4$^{\rm i}$)—O(3)—Mo(1)	110.5 (4)
O(4$^{\rm i}$)—Mo(3)—O(3)	71.5 (3)	Mo(4$^{\rm i}$)—O(3)—Mo(3)	103.9 (4)
O(7)—Mo(3)—O(1)	78.1 (3)	Mo(3$^{\rm i}$)—O(4)—Mo(1)	110.4 (4)
O(7)—Mo(3)—O(3)	147.0 (3)	Mo(4)—O(4)—Mo(1)	109.0 (4)
O(7)—Mo(3)—O(4$^{\rm i}$)	84.8 (4)	Mo(4)—O(4)—Mo(3$^{\rm i}$)	104.1 (4)
O(10)—Mo(3)—O(1)	95.3 (4)	Mo(2$^{\rm i}$)—O(5)—Mo(1)	117.6 (5)
O(10)—Mo(3)—O(3)	96.9 (4)	Mo(4)—O(6)—Mo(2)	117.2 (4)
O(10)—Mo(3)—O(4$^{\rm i}$)	164.4 (4)	Mo(3)—O(7)—Mo(2)	116.8 (5)
O(10)—Mo(3)—O(7)	101.2 (4)		

Symmetry code: (i) $2 - x, 1 - y, -z$.

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Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71329 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1072]

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Structure of Diaquatris(5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine-N^3)copper(II) Perchlorate Dihydrate

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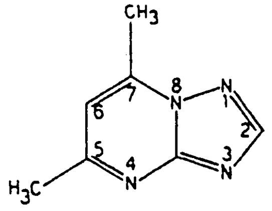
Abstract

The synthesis and crystal structure of the title compound obtained by reaction of copper perchlorate with 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine (dmtp) are reported. The structure consists of $[Cu(dmtp)_3(H_2O)_2]^{2+}$ coordination cations, ClO_4^- anions and interstitial water molecules. The Cu atom is coordinated by three N(3) atoms of triazolopyrimidine ligands [Cu—N = 1.985 (5), 1.993 (4), 2.024 (4) Å] and two aqueous O atoms [Cu—O = 1.979 (4), 2.245 (4) Å]. The Cu polyhedron is a trigonal bipyramid. This compound is the first dmtp complex with a ClO_4 anion and the first mononuclear complex involving three dmtp ligands, and whose crystal structure has been solved by X-ray diffraction.

Comment

Transition-metal complexes of purine analogs have been studied in order to elucidate the role of such metal ions in interactions with nucleic acids. Among these purine analogs, the [1,2,4]triazolo[1,5-*a*]pyrimidine ring (tp) and its 5,7-dimethyl derivative (dmtp) have been studied as ligands (Dillen, Lenstra, Haasnoot & Reedijk, 1983; Biagini Cingi, Manotti Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1983, 1984; Biagini Cingi, Manotti Lanfredi, Tiripicchio, Reedijk & Haasnoot, 1986; Biagini Cingi, Manotti Lanfredi, Tiripicchio, Cornelissen, Haasnoot & Reedijk, 1986, 1987; Bamidele Sanni, Smits, Beurskens, Haasnoot, Schild & Lenstra, 1986). Since both ligands have no acidic H atoms on the ring N atoms, the isolated metal compounds involve negative species such as ligands or counteranions.



dmtp

Different copper(II) complexes of tp and dmtp as ligands have been described in the literature and characterized by X-ray diffraction methods. Thus, in $[Cu(tp)_2(H_2O)Br_2]$ (van Albada, de Graaff, Haasnoot, Schild & Reedijk, 1991) the tp ligand is monodentate through N(3), whereas in $[Cu(tp)_2(NCS)_2]$ and $[Cu(tp)_2Cl_2]$ (Biangini Cingi *et al.*, 1987) the tp ligand is bidentate through N(3) and N(1). Nevertheless, in both compounds the Cu···N(1) contacts are long: 2.633 (6) and 2.692 (4) Å. In the complexes $[Cu(dmtp)_2(NCS)_2]$ (Biagini Cingi *et al.*, 1983), $[Cu(dmtp)_4(H_2O)_2](PF_6)_2$ (Favre, Haasnoot & Reedijk, 1986) and $[Cu(NCS)_2(dmtp)_2]_2$ (Haasnoot, Driessen & Reedijk, 1984) N(3) is the sole metal-binding site, whereas in $[Cu_4(dmtp)_4Cl_2][Cu_2Cl_4]$ (Haasnoot, Favre, Hinrichs & Reedijk, 1988) the dmtp acts as a bridging bidentate ligand *via* N(3) and N(4).

As part of our work on the coordination chemistry of purine analogs (Sirera, Romero, Salas, Sanchez & Moreno, 1991), we now report a new structure with the dmtp ligand.

The *PLUTO* drawing (Motherwell & Clegg, 1978) shows the asymmetric unit (Fig. 1) with the complex cation $[Cu(C_7H_8N_4)_3(H_2O)_2]^{2+}$, the two ClO_4^- anions and the two non-coordinated O(*w*3) and O(*w*4) water molecules. The Cu atom is coordinated by three dmtp N(3) atoms and the two aqueous O atoms. The polyhedron is a trigonal bipyramid (Fig. 2); the base is defined by Cu, N(3*A*), N(3*B*) and O(*w*2); the apices are N(3*C*) and O(*w*1).

The dmtp ligand is as monodentate through N(3). The Cu—N(3) distances of 1.985 (5), 1.993 (4) and