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Bis(trimethylphenylammonium) μ -oxalato-bis[oxidodiperoxidomolybdate(VI)]

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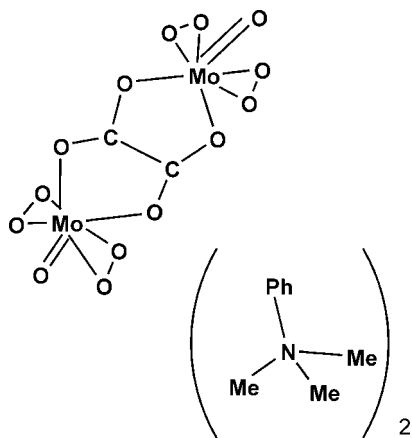
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 Key indicators: single-crystal X-ray study; $T = 93$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.029; wR factor = 0.080; data-to-parameter ratio = 22.3.

A trimethylphenylammonium salt of a dinuclear μ -oxalate complex of diperoxidomonomolybdate units, $(\text{C}_9\text{H}_{14}\text{N})_2[\text{Mo}_2(\text{C}_2\text{O}_4)(\text{O}_2)_4\text{O}_2]$, was obtained from an acidic aqueous solution; the dianion is located about a centre of inversion. Each Mo atom bears two peroxide groups together with one O atom from the oxalate group in its equatorial positions and one terminal O atom as well as another O atom from the oxalate in axial positions. The oxalate group acts as a tetradentate bridging ligand and bridges between the diperoxidomolybdate units.

Related literature

For the structure of the closely related tetrabutylammonium peroxidotungstate analogue, see Hashimoto *et al.* (1987). For the structures of related molybdate complexes, see Stomberg & Olson (1985); Bayot *et al.* (2004).



Experimental

Crystal data

 $(\text{C}_9\text{H}_{14}\text{N})_2[\text{Mo}_2(\text{C}_2\text{O}_4)(\text{O}_2)_4\text{O}_2]$
 $M_r = 712.32$
 Monoclinic, $P2_1/n$
 $a = 9.860$ (2) Å
 $b = 9.975$ (2) Å
 $c = 13.691$ (3) Å
 $\beta = 94.023$ (3)°

 $V = 1343.2$ (5) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.00$ mm⁻¹
 $T = 93$ K
 $0.20 \times 0.17 \times 0.17$ mm

Data collection

 Rigaku Saturn724+ diffractometer
 Absorption correction: numerical
 (NUMABS; Higashi, 2000)
 $T_{\min} = 0.888$, $T_{\max} = 0.914$

 11791 measured reflections
 3843 independent reflections
 3621 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.080$
 $S = 1.06$
 3843 reflections

 172 parameters
 H-atom parameters not refined
 $\Delta\rho_{\max} = 1.84$ e Å⁻³
 $\Delta\rho_{\min} = -0.69$ e Å⁻³

Data collection: *CrystalClear SM* (Rigaku, 2008); cell refinement: *CrystalClear SM*; data reduction: *CrystalClear SM*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2410).

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supporting information

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Bis(trimethylphenylammonium) μ -oxalato-bis[oxidodiperoxidomolybdate(VI)]

Ayaka Oba and Masato Hashimoto

S1. Comment

A novel dinuclear peroxidomolybdate complex with a bridging oxalate ligand was crystallized as a trimethylphenylammonium salt in the course of investigating complex formation of oxalate and peroxomolybdate in aiming at preparing an inorganic-organic hybrid material.

The compound consists of two trimethylphenylammonium cations and one dinuclear oxalato complex of diperoxidomolybdate (Figure 1). In the complex anion two diperoxidomolybdates are bridged by a tetradentate μ^2 chelating oxalato ligand. Each molybdenum atom has two peroxo groups in its equatorial positions. The fifth equatorial position and one of the axial positions are occupied by O atoms of the oxalate ligand. The second axial position is occupied by the terminal oxo ligand. Each molybdenum atom thus exhibits a distorted pentagonal bipyramidal geometry, which is common in peroxidomolybdate compounds. C1, C1ⁱ, O6, O6ⁱ, O7, O7ⁱ, Mo1, Mo1ⁱ, O1 and O1ⁱ (symmetry operation, $i(1-x, 1-y, -z)$) are coplanar with a maximum deviation of 0.0240 (11) Å (O6) from the corresponding least square plane. Oxygen atoms of both peroxo ligands at each Mo atom are also coplanar. The deviation of the Mo atom from the least square plane toward the terminal oxygen atom is -0.401 (1) Å. These planes are almost perpendicular to the initially mentioned least square plane with dihedral angles 89.86 (5)°. There is no abnormal bond length and bond angles in the anion. Among Mo—O bonds in the equatorial plane Mo1—O6 (2.092 (1) Å) shows a slightly longer distance than others. C1—O7 (1.232 (2) Å) is slightly shorter than C1—O6 (1.275 (2) Å) probably because of weaker interaction of Mo1—O7 than Mo1—O6. Bond lengths in the trimethylphenylammonium cations are also normal. No special intermolecular interaction is observed in the packing.

The tungstate analogue of the present anion, $[W_2(C_2O_4)(O_2)_4O_2]$, was reported as a tetrabutylammonium salt by one of the authors (Hashimoto *et al.*, 1987). The geometry of the complex anion of the tungsten compound is essentially identical to the molybdate one. The potassium salt of a mononuclear oxalato complex of a peroxidomolybdate was reported by Stomberg (Stomberg *et al.*, 1985). The oxalate group of the mononuclear complex chelates to a molybdenum atom to form a Mo—O—C—C—O five-membered ring as found in the title compound. C—O distances of the non-coordinated O atoms of the oxalate group in the mononuclear complex (1.21 (1) and 1.22 (1) Å) are considerably shorter than C—O distances towards coordination oxygen atoms (1.30 (1) and 1.28 (1) Å), reflecting the coordination to the metal center. On the contrary, the 2:2 complex reported by Bayot *et al.*, shows a different structural feature. The complex anion can be regarded as a dimer of Stomberg's mononuclear complex. However, one of the peroxo groups is replaced by two hydroxo groups to form a dimer of oxalatomonoperoxidomolybdate moieties doubly bridged by two μ^2 -OH groups (Bayot *et al.*, 2004). The hydroxo groups thus occupy equatorial positions of the molybdenum atom. Distances and angles in the 2:2 complex show similar tendencies as Stomberg's 1:1 and the present 2:1 (Mo:oxalate) complexes, such as longer Mo—O(oxalate) distance than other Mo—O on the equatorial plane, and shorter C—O(equatorial) distances compared to C—O(axial) bonds.

S2. Experimental

The single-crystal subjected to the X-ray analysis was obtained in the following way. Sodium molybdate dihydrate (14.52 g, 0.0600 mol) and oxalic acid dihydrate (3.78 g, 0.0300 mol) were dissolved in *ca* 60 ml water. To this solution 10 ml of 30% H₂O₂ (*ca* 0.10 mol) was added and the volume was adjusted to 100 ml. The pH of the resulted solution was adjusted to 2 with *ca* 13 mol L⁻¹ nitric acid. To the solution was added 1.0 ml of 1.0 mol L⁻¹ aqueous trimethylphenylammonium chloride solution and the mixture was kept at room temperature. Block shaped crystals appeared in one day (yield 25%).

S3. Refinement

Hydrogen atoms have been calculated in idealized positions with C–H bond lengths of 0.93 Å (aromatic) and 0.96 Å (methyl). They were refined using a riding model with $U_{\text{eq}}(\text{H}) = 1.2 \times U_{\text{iso}}(\text{C})$ for aromatic and $U_{\text{eq}}(\text{H}) = 1.5 \times U_{\text{iso}}(\text{C})$ for methyl groups.

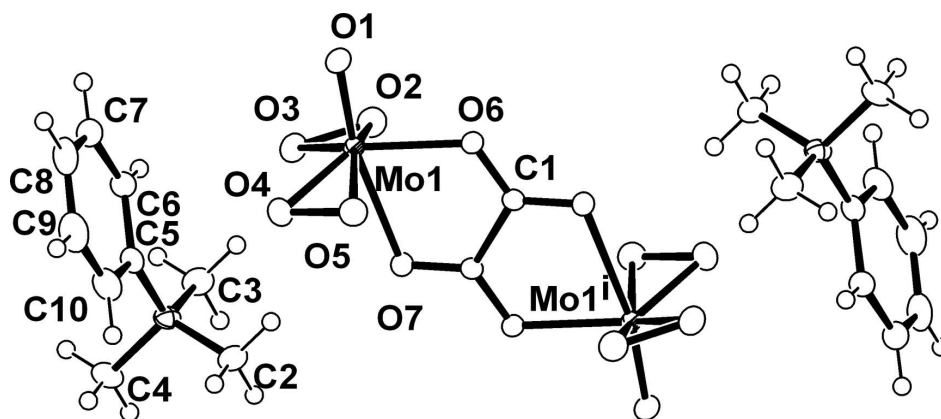


Figure 1

Molecular structure of the title compound with thermal ellipsoids drawn at the 50% probability level for non-H atoms. Symmetry code: (i) 1 - x, 1 - y, -z.

Bis(trimethylphenylammonium) μ -oxalato-bis[oxidodiperoxidomolybdate(VI)]

Crystal data

(C₉H₁₄N)₂[Mo₂(C₂O₄)(O₂)₄O₂]

$M_r = 712.32$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 9.860$ (2) Å

$b = 9.975$ (2) Å

$c = 13.691$ (3) Å

$\beta = 94.023$ (3)°

$V = 1343.2$ (5) Å³

$Z = 2$

$F(000) = 716$

$D_x = 1.761$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å

Cell parameters from 5064 reflections

$\theta = 2.9$ – 30.0 °

$\mu = 1.00$ mm⁻¹

$T = 93$ K

Block, pale yellow

$0.20 \times 0.17 \times 0.17$ mm

Data collection

Rigaku Saturn724+
diffractometer

Radiation source: fine-focus rotating anode

Graphite monochromator

Detector resolution: 28.5174 pixels mm⁻¹

CCD scans

Absorption correction: numerical
(*NUMABS*; Higashi, 2000)

$T_{\text{min}} = 0.888$, $T_{\text{max}} = 0.914$

11791 measured reflections

3843 independent reflections

3621 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 30.0^\circ$, $\theta_{\min} = 2.5^\circ$
 $h = -13 \rightarrow 13$

$k = -14 \rightarrow 10$
 $l = -19 \rightarrow 16$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.080$
 $S = 1.06$
 3843 reflections
 172 parameters
 0 restraints
 Primary atom site location: Patterson

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters not refined
 $w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 1.5201P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.84 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.69 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Mo1	0.354779 (14)	0.254491 (13)	0.035607 (10)	0.01536 (7)
O1	0.38434 (13)	0.09445 (13)	0.00536 (9)	0.0205 (2)
O2	0.45582 (16)	0.27065 (15)	0.16277 (11)	0.0248 (3)
O3	0.30966 (17)	0.24598 (13)	0.17011 (11)	0.0249 (3)
O4	0.16612 (15)	0.28161 (16)	-0.00396 (12)	0.0272 (3)
O5	0.25414 (14)	0.31884 (15)	-0.08269 (10)	0.0269 (3)
O6	0.52797 (13)	0.32966 (12)	-0.02533 (9)	0.0192 (2)
O7	0.35239 (13)	0.48958 (13)	0.06131 (11)	0.0231 (3)
C1	0.55099 (17)	0.45548 (17)	-0.02518 (12)	0.0172 (3)
N1	-0.00978 (16)	0.42328 (15)	0.22184 (11)	0.0198 (3)
C2	0.0346 (2)	0.5196 (2)	0.14525 (14)	0.0258 (4)
H2A	0.0534	0.6055	0.1747	0.039*
H2B	-0.0366	0.5285	0.0941	0.039*
H2C	0.1151	0.4859	0.1182	0.039*
C3	0.1020 (2)	0.4182 (2)	0.30216 (14)	0.0248 (4)
H3A	0.1181	0.5067	0.3281	0.037*
H3B	0.1836	0.3848	0.2764	0.037*
H3C	0.0758	0.3599	0.3533	0.037*
C4	-0.1357 (2)	0.4769 (2)	0.26505 (14)	0.0277 (4)
H4A	-0.1165	0.5635	0.2935	0.042*
H4B	-0.1629	0.4166	0.3147	0.042*
H4C	-0.2077	0.4849	0.2144	0.042*
C5	-0.04052 (17)	0.28802 (19)	0.17753 (12)	0.0187 (3)

C6	0.02069 (18)	0.17351 (18)	0.21818 (13)	0.0213 (3)
H6	0.0821	0.1795	0.2728	0.026*
C7	-0.0117 (2)	0.0493 (2)	0.17563 (16)	0.0274 (4)
H7	0.0286	-0.0281	0.2021	0.033*
C8	-0.1029 (2)	0.0402 (2)	0.09455 (17)	0.0321 (4)
H8	-0.1228	-0.0427	0.0659	0.039*
C9	-0.1647 (2)	0.1554 (3)	0.05603 (16)	0.0339 (5)
H9	-0.2273	0.1492	0.0022	0.041*
C10	-0.1338 (2)	0.2797 (2)	0.09723 (15)	0.0275 (4)
H10	-0.1754	0.3567	0.0712	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mo1	0.01690 (9)	0.01264 (9)	0.01686 (9)	-0.00015 (4)	0.00347 (6)	0.00104 (4)
O1	0.0238 (6)	0.0166 (6)	0.0214 (6)	-0.0016 (5)	0.0033 (5)	-0.0005 (4)
O2	0.0280 (7)	0.0265 (6)	0.0195 (6)	-0.0020 (5)	-0.0003 (5)	-0.0021 (5)
O3	0.0313 (8)	0.0228 (7)	0.0218 (7)	-0.0015 (5)	0.0106 (6)	-0.0004 (4)
O4	0.0194 (6)	0.0273 (7)	0.0351 (8)	0.0008 (5)	0.0046 (5)	0.0042 (6)
O5	0.0250 (6)	0.0293 (7)	0.0264 (7)	0.0021 (5)	0.0007 (5)	0.0080 (6)
O6	0.0195 (6)	0.0141 (5)	0.0250 (6)	0.0007 (4)	0.0079 (5)	0.0004 (4)
O7	0.0218 (6)	0.0161 (6)	0.0328 (7)	0.0004 (5)	0.0122 (5)	0.0001 (5)
C1	0.0171 (7)	0.0152 (7)	0.0198 (7)	0.0021 (5)	0.0047 (6)	0.0010 (6)
N1	0.0242 (7)	0.0187 (7)	0.0170 (6)	0.0050 (5)	0.0059 (5)	0.0003 (5)
C2	0.0348 (10)	0.0207 (8)	0.0232 (8)	0.0046 (7)	0.0110 (7)	0.0048 (7)
C3	0.0314 (9)	0.0223 (9)	0.0202 (8)	0.0007 (7)	-0.0008 (7)	-0.0044 (7)
C4	0.0319 (9)	0.0300 (10)	0.0227 (8)	0.0127 (8)	0.0127 (7)	0.0034 (7)
C5	0.0175 (7)	0.0223 (8)	0.0168 (7)	0.0007 (6)	0.0043 (6)	-0.0017 (6)
C6	0.0206 (7)	0.0206 (8)	0.0227 (8)	0.0007 (6)	0.0024 (6)	-0.0010 (6)
C7	0.0248 (8)	0.0215 (9)	0.0368 (10)	-0.0017 (7)	0.0081 (7)	-0.0035 (8)
C8	0.0258 (9)	0.0358 (11)	0.0359 (11)	-0.0122 (8)	0.0092 (8)	-0.0141 (9)
C9	0.0259 (9)	0.0486 (13)	0.0267 (9)	-0.0091 (9)	-0.0020 (7)	-0.0075 (9)
C10	0.0215 (9)	0.0393 (10)	0.0214 (8)	0.0023 (8)	-0.0007 (7)	0.0020 (8)

Geometric parameters (Å, °)

Mo1—O1	1.6799 (13)	C2—H2C	0.9600
Mo1—O4	1.9198 (15)	C3—H3A	0.9600
Mo1—O3	1.9264 (16)	C3—H3B	0.9600
Mo1—O5	1.9479 (14)	C3—H3C	0.9600
Mo1—O2	1.9510 (15)	C4—H4A	0.9600
Mo1—O6	2.0915 (12)	C4—H4B	0.9600
Mo1—O7	2.3716 (14)	C4—H4C	0.9600
O2—O3	1.472 (2)	C5—C10	1.386 (3)
O4—O5	1.478 (2)	C5—C6	1.390 (3)
O6—C1	1.275 (2)	C6—C7	1.397 (3)
O7—C1 ⁱ	1.232 (2)	C6—H6	0.9300
C1—O7 ⁱ	1.232 (2)	C7—C8	1.382 (3)

C1—C1 ⁱ	1.540 (3)	C7—H7	0.9300
N1—C5	1.501 (2)	C8—C9	1.387 (4)
N1—C3	1.502 (2)	C8—H8	0.9300
N1—C2	1.509 (2)	C9—C10	1.387 (3)
N1—C4	1.511 (2)	C9—H9	0.9300
C2—H2A	0.9600	C10—H10	0.9300
C2—H2B	0.9600		
O1—Mo1—O4	104.23 (7)	N1—C2—H2A	109.5
O1—Mo1—O3	104.45 (6)	N1—C2—H2B	109.5
O4—Mo1—O3	89.53 (7)	H2A—C2—H2B	109.5
O1—Mo1—O5	101.26 (6)	N1—C2—H2C	109.5
O4—Mo1—O5	44.92 (6)	H2A—C2—H2C	109.5
O3—Mo1—O5	132.14 (7)	H2B—C2—H2C	109.5
O1—Mo1—O2	102.24 (6)	N1—C3—H3A	109.5
O4—Mo1—O2	131.62 (7)	N1—C3—H3B	109.5
O3—Mo1—O2	44.63 (7)	H3A—C3—H3B	109.5
O5—Mo1—O2	155.95 (6)	N1—C3—H3C	109.5
O1—Mo1—O6	94.69 (6)	H3A—C3—H3C	109.5
O4—Mo1—O6	129.72 (6)	H3B—C3—H3C	109.5
O3—Mo1—O6	130.31 (6)	N1—C4—H4A	109.5
O5—Mo1—O6	86.14 (6)	N1—C4—H4B	109.5
O2—Mo1—O6	86.92 (6)	H4A—C4—H4B	109.5
O1—Mo1—O7	168.51 (5)	N1—C4—H4C	109.5
O4—Mo1—O7	83.28 (6)	H4A—C4—H4C	109.5
O3—Mo1—O7	84.05 (5)	H4B—C4—H4C	109.5
O5—Mo1—O7	77.75 (6)	C10—C5—C6	120.92 (19)
O2—Mo1—O7	78.21 (6)	C10—C5—N1	118.58 (17)
O6—Mo1—O7	73.84 (4)	C6—C5—N1	120.47 (15)
O3—O2—Mo1	66.80 (9)	C5—C6—C7	118.82 (18)
O2—O3—Mo1	68.57 (8)	C5—C6—H6	120.6
O5—O4—Mo1	68.55 (8)	C7—C6—H6	120.6
O4—O5—Mo1	66.53 (8)	C8—C7—C6	120.7 (2)
C1—O6—Mo1	120.15 (10)	C8—C7—H7	119.7
C1 ⁱ —O7—Mo1	111.35 (11)	C6—C7—H7	119.7
O7 ⁱ —C1—O6	125.41 (15)	C7—C8—C9	119.67 (19)
O7 ⁱ —C1—C1 ⁱ	118.07 (19)	C7—C8—H8	120.2
O6—C1—C1 ⁱ	116.52 (18)	C9—C8—H8	120.2
C5—N1—C3	112.48 (14)	C8—C9—C10	120.51 (19)
C5—N1—C2	110.57 (14)	C8—C9—H9	119.7
C3—N1—C2	107.24 (15)	C10—C9—H9	119.7
C5—N1—C4	109.18 (15)	C5—C10—C9	119.4 (2)
C3—N1—C4	107.85 (14)	C5—C10—H10	120.3
C2—N1—C4	109.44 (14)	C9—C10—H10	120.3

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