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Propane-1,3-diylbis(triphenylphosphonium)
(oxalato)oxodiperoxomolybdate(VI) monohydrate

In the structure of the title compound, $(C_{39}H_{36}P_2)[Mo(C_2O_4)O(O_2)_2] \cdot H_2O$, the Mo atom in the complex anion shows a distorted pentagonal–bipyramidal geometry and the six phenyl rings in the cation form a double propeller linked by a propane group. The cations, anions and water molecules are connected *via* hydrogen bonds and electrostatic interactions to form a three-dimensional extended network.

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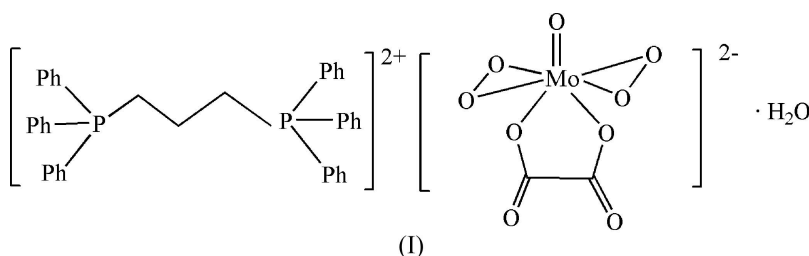
Key indicators

Single-crystal X-ray study
 $T = 296$ K
 Mean $\sigma(C-C) = 0.013$ Å
 R factor = 0.057
 wR factor = 0.151
 Data-to-parameter ratio = 13.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

As an important class of reactive intermediates in catalytic oxidation reactions, peroxomolybdate complexes have attracted considerable attention owing to their excellent catalytic ability to activate H_2O_2 in selective organic oxidation (Buhl *et al.*, 2004; Du & Espenson, 2005; Xi *et al.*, 2001; Wei *et al.*, 2002; Shi & Wei, 2005). In this paper, we report the structure of a new bis-quaternary phosphonium peroxomolybdate complex, $[Ph_3P(CH_2)_3PPh_3][MoO(O_2)_2(C_2O_4)] \cdot H_2O$, (I).



Complex (I) consists of a peroxomolybdate anion, a 1,3-bis(triphenylphosphonium)propane (btppp) cation and a water molecule (Fig. 1). The six phenyl rings in the cation form a double propeller linked by a propane group. In the anion, the Mo atom is coordinated by an oxalate ligand, two peroxo groups and an oxo group. The coordinated atoms adopt a distorted pentagonal–bipyramidal geometry, in which two peroxo groups and atom O4 from the oxalate ligand form a pentagonal equatorial plane. Oxo atom O9 and the other atom O1 from the oxalate ligand occupy the axial positions. The bond lengths and angles in the anion are similar to those in the reported peroxomolybdate complex (Djordjevic & Covert, 1985). As a result of coordination of the peroxo groups to Mo, the O5–O6 and O7–O8 bond lengths are shortened from 1.48 Å (Shi *et al.*, 1994) to 1.456 (10) Å and 1.451 (9) Å. Compared with the peroxo ligands, weak coordination occurs between the Mo atom and oxalate, as evidenced by the bond distances of Mo–O1 = 2.213 (5) Å and Mo–O4 = 2.043 (6) Å, whereas the longest Mo–peroxo bond distance is 1.945 (7) Å.

The anions and cations are linked *via* intermolecular hydrogen bonds (Table 1). The hydrogen-bonding scheme is

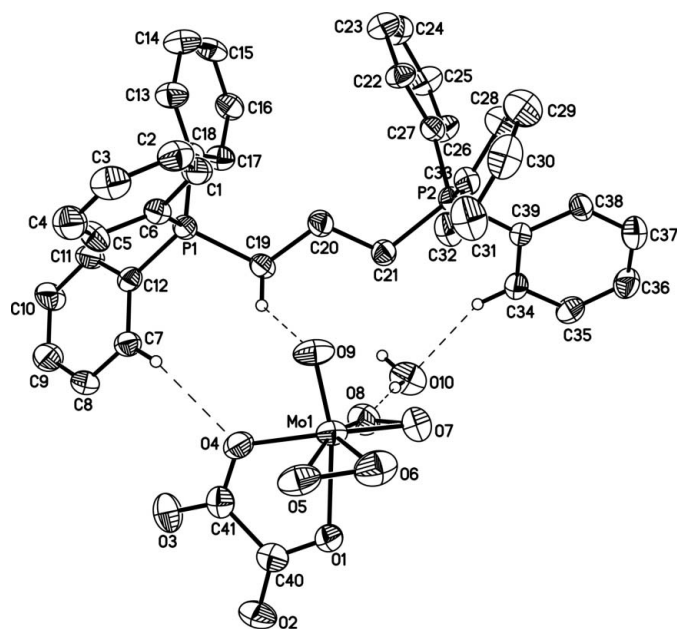


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms are omitted except those involved in hydrogen bonds (dashed lines).

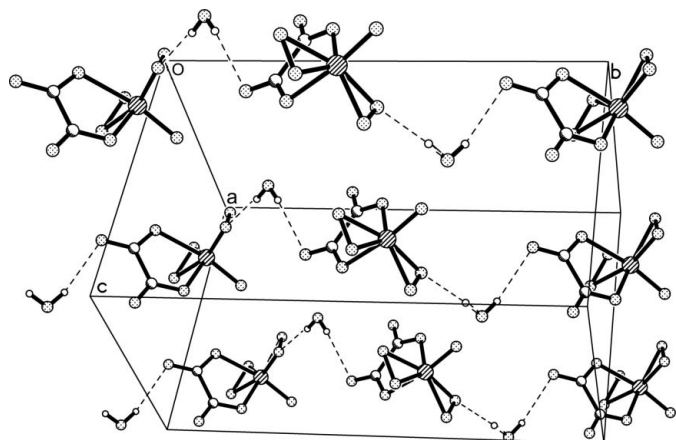


Figure 2
Hydrogen-bonded (dashed lines) zigzag chains involving the anions and water molecules.

complicated so that each anion is joined to four cations and *vice versa*. The solvent water molecule is linked to anions and cations *via* three hydrogen bonds. Atom O10 of the water molecule acts as an acceptor to form a C34—H34...O10 hydrogen bond, and it donates H10D and H10E to atoms O2ⁱⁱ and O8ⁱ of the peroxo groups from two neighboring anions (Table 1). It is noteworthy that the peroxomolybdate anions form a zigzag chain *via* hydrogen-bonding interactions involving the water molecules (Fig. 2). The cations are located between the anionic zigzag chains.

Experimental

$\text{K}_2[\text{MoO}(\text{O}_2)_2(\text{C}_2\text{O}_4)]$ (0.171 g, 0.5 mmol) was dissolved in water (15 ml), to which H_2O_2 (30%, 5 ml) was added at room temperature.

After stirring for 15 min, a solution of $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{PPh}_3]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ (0.381 g, 0.5 mmol) in methanol (20 ml) was added to the mixture with stirring. The resulting mixture was allowed to stand at 278 K for several days. Yellow crystals of (I), suitable for X-ray diffraction, were obtained. Analysis, calculated for $\text{C}_{41}\text{H}_{38}\text{MoO}_{10}\text{P}_2$: C 58.03, H 4.51, O_2^{2-} 7.54, Mo 11.30%; found: C 58.31, H 4.27, O_2^{2-} 7.14, Mo 10.97%. IR (cm^{-1}): $\nu(\text{O}-\text{O})$ 855, $\nu(\text{MoO}_2)_{\text{sym}}$ 690, $\nu(\text{MoO}_2)_{\text{asym}}$ 580, $\nu(\text{M}=\text{O})$ 937.

Crystal data

$(\text{C}_{39}\text{H}_{36}\text{P}_2)[\text{Mo}(\text{C}_2\text{O}_4)\text{O}(\text{O}_2)_2] \cdot \text{H}_2\text{O}$
 $Z = 2$
 $M_r = 848.59$
 $D_x = 1.475 \text{ Mg m}^{-3}$
 Monoclinic, $P2_1$
 Mo $K\alpha$ radiation
 $a = 10.9385$ (8) Å
 $b = 15.6425$ (12) Å
 $c = 11.8100$ (9) Å
 $\beta = 109.040$ (1)°
 $V = 1910.2$ (2) Å³
 $\mu = 0.49 \text{ mm}^{-1}$
 $T = 296$ (2) K
 Block, yellow
 $0.34 \times 0.28 \times 0.15 \text{ mm}$

Data collection

Bruker SMART APEXII CCD
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 1999)
 $T_{\text{min}} = 0.852$, $T_{\text{max}} = 0.930$
 9549 measured reflections
 6593 independent reflections
 5391 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 25.1^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.151$
 $S = 1.05$
 6593 reflections
 494 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 3.2002P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.53 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.76 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0132 (12)
 Absolute structure: Flack (1983),
 1458 Friedel pairs
 Flack parameter: 0.02 (5)

Table 1
Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O10—H10D...O8 ⁱ	0.86 (8)	2.06 (8)	2.916 (10)	174 (9)
O10—H10E...O2 ⁱⁱ	0.86 (8)	2.32 (4)	3.131 (11)	158 (9)
C7—H7...O4 ⁱ	0.93	2.60	3.484 (9)	159
C19—H19A...O9 ⁱ	0.97	2.36	3.159 (9)	140
C16—H16...O8 ⁱⁱ	0.93	2.59	3.511 (11)	170
C19—H19B...O2 ⁱⁱ	0.97	2.31	3.243 (9)	161
C26—H26...O3 ⁱⁱⁱ	0.93	2.55	3.257 (11)	133
C34—H34...O10	0.93	2.34	3.224 (11)	158
C36—H36...O6 ⁱⁱⁱ	0.93	2.56	3.408 (11)	152
C1—H1...O5 ^{iv}	0.93	2.55	3.306 (11)	139
C22—H22...O5 ^{iv}	0.93	2.42	3.280 (10)	153
C23—H23...O9 ^{iv}	0.93	2.55	3.225 (10)	130

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

H atoms bound to C atoms were positioned geometrically and refined as riding, with C—H = 0.93 Å (CH) and 0.97 Å (CH₂) and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms of the water molecule were located in a difference Fourier map and refined with $U_{\text{iso}}(\text{H}) = 0.10 \text{ \AA}^2$.

Data collection: SMART (Bruker, 1999); cell refinement: SAINT-Plus (Bruker, 1999); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics:

SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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