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Bis(tetraphenylphosphonium) bis(1-carboxybenzene-2,3-diolato-κ^2O,O')-*cis*-dioxomolybdate(VI)

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.045
wR factor = 0.100
Data-to-parameter ratio = 22.3

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

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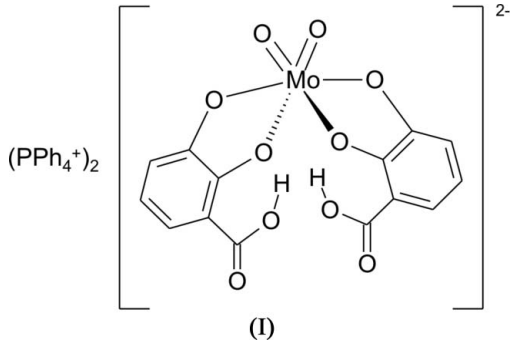
The title compound, $(C_{24}H_{20}P)_2[Mo(C_7H_4O_4)_2O_2]$, contains a distorted octahedral molybdenum(VI) complex having the characteristic *cis*-MoO_2^{2+} group and the ligand 2,3-dihydroxybenzoic acid coordinated through the two phenolate O atoms, while the carboxyl group is not deprotonated. No π–π overlap between the benzene rings of the ligands or those of the tetraphenylphosphonium ions is observed.

Comment

The title compound, (I), results from the reaction of a mixture of tetraphenylphosphonium bromide (PPh_4Br), 2,3-dihydroxybenzoic acid (2,3-DHBA) and $Na_2MoO_4{\cdot}2H_2O$ in an aqueous solution (pH 6) with subsequent redissolution of the precipitate in dichloromethane. This method of preparation differs from that reported for the same metal–organic anion in $(NMe_4)_2MoO_2(C_7H_4O_4)_2{\cdot}1.5H_2O$, (II) (Griffith *et al.*, 1995), and is less complicated. At lower pH values, the formation of oligomeric molybdenum complexes is preferred due to the presence of the ligand in its semi-oxidized form (semiquinone), which promotes oligomerization (Lymberopoulou-Karaliota *et al.*, 2005; Karaliota *et al.*, 2002).



(I)

In the complex anion of (I), the Mo^{VI} atom has a distorted octahedral geometry (Fig. 1). The Mo═O bond lengths and O1═Mo═O2 bond angle (Table 1) have values typical for *cis*-MoO_2^{2+} groups. The two types of phenolic C—O bond lengths [mean values 1.332 (2) and 1.352 (2) Å] of the 2,3-DHBA ligands compare well with those observed for the catecholate (fully reduced) form of the ligand (Buchanan & Pierpont, 1980). The difference in the distances is attributed to the intramolecular O—H···O hydrogen bond (Table 2).

In the packing diagram (Fig. 2), it is important to notice that the large tetraphenylphosphonium ions bring only two molybdenum complex ions into relative proximity. Moreover, no π–π interactions are observed, even though there are a number of benzene rings in both the ligands and the tetra-

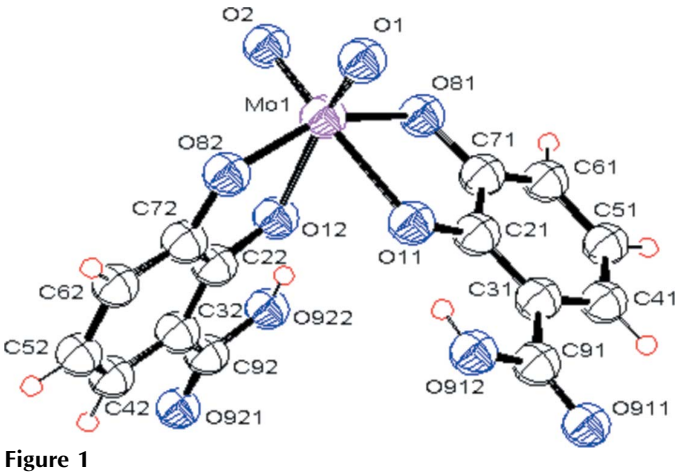


Figure 1
The structure of the complex anion in (I), showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

phenylphosphonium ions. This absence of π–π interactions between the ligands may explain the different colour of the crystal of (I) compared with (II), where there is π–π interaction between the two molybdenum complex anions.

The cyclic voltammograph of (I) in dichloromethane confirmed its catecholate form, showing only a two-electron redox peak corresponding to the catechol-to-quinone oxidation of the ligand. The *cis*-MoO_2^{2+} group can also contain a pentavalent molybdenum ion (Lu *et al.*, 2001), but in the voltammograph no peak due to the Mo^V-to-Mo^{VI} conversion was observed.

Experimental

All reagents were purchased from Aldrich. An aqueous solution (10.0 ml) of 2,3-DHBA (77.1 mg, 0.5 mmol) and $Na_2MoO_4{\cdot}2H_2O$ (121.0 mg, 0.5 mmol) was added to an aqueous solution (12.5 ml) of PPh_4Br (210.0 mg, 0.5 mmol), producing a yellow precipitate. The precipitate (29.1 mg, 0.03 mmol) was dissolved in dichloromethane (15 ml) and, after slow evaporation, crystals of (I) were obtained. Analysis calculated for $C_{62}H_{48}O_{10}P_2Mo$: C 66.90, H 4.35%; found C 66.82, H 4.27%.

Crystal data

$(C_{24}H_{20}P)_2[Mo(C_7H_4O_4)_2O_2]$
M_r = 1110.88
Orthorhombic, *Pbca*
a = 13.3595 (3) Å
b = 16.9998 (4) Å
c = 45.5887 (13) Å
V = 10353.6 (4) Å^3
Z = 8
D_x = 1.425 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8839 reflections
θ = 2–28.5°
μ = 0.38 mm^{-1}
T = 150 (2) K
Block, yellow
0.60 × 0.54 × 0.35 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.732, T_{max} = 0.880
122211 measured reflections
15149 independent reflections
11301 reflections with $I > 2\sigma(I)$
R_{int} = 0.058
θ_{max} = 30.1°
$h = -18 \rightarrow 18$
$k = -23 \rightarrow 23$
$l = -64 \rightarrow 63$

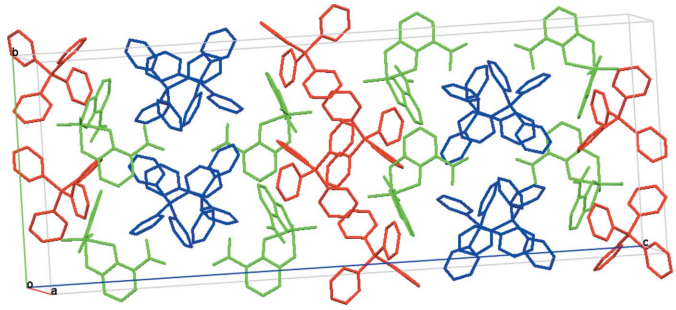


Figure 2
The packing of (I), with symmetry-equivalent molecules coloured the same. H atoms have been omitted.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.100
S = 1.06
15149 reflections
678 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 9.6314P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.50 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mo1—O1	1.7056 (15)	O12—C22	1.331 (2)
Mo1—O2	1.7151 (15)	C71—O81	1.349 (2)
Mo1—O81	1.9765 (14)	C72—O82	1.355 (2)
Mo1—O82	1.9865 (14)	C91—O911	1.217 (3)
Mo1—O12	2.2198 (14)	C91—O912	1.340 (3)
Mo1—O11	2.2255 (14)	C92—O921	1.218 (3)
O11—C21	1.332 (2)	C92—O922	1.344 (3)
O1—Mo1—O2	103.36 (7)	O1—Mo1—O11	88.97 (6)
O1—Mo1—O81	105.89 (7)	O2—Mo1—O11	164.19 (7)
O2—Mo1—O81	91.32 (7)	O81—Mo1—O11	75.61 (5)
O1—Mo1—O82	92.12 (7)	O82—Mo1—O11	85.53 (5)
O2—Mo1—O82	103.59 (7)	O12—Mo1—O11	77.43 (5)
O81—Mo1—O82	153.40 (6)	C21—O11—Mo1	111.89 (12)
O1—Mo1—O12	161.83 (7)	C22—O12—Mo1	113.07 (12)
O2—Mo1—O12	92.29 (6)	C71—O81—Mo1	120.06 (12)
O81—Mo1—O12	82.58 (6)	C72—O82—Mo1	120.75 (12)
O82—Mo1—O12	75.03 (5)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O912—H912···O11	0.84	1.73	2.514 (2)	155
O922—H922···O12	0.84	1.74	2.523 (2)	155
C33—H33···O912^{i}	0.95	2.54	3.357 (3)	144
C43—H43···O911^{i}	0.95	2.29	3.178 (3)	154
C44—H44···O2^{ii}	0.95	2.48	3.195 (3)	132
C54—H54···O911^{i}	0.95	2.55	3.249 (3)	131
C163—H163···O12^{iii}	0.95	2.46	3.348 (3)	156
C173—H173···O922^{iii}	0.95	2.58	3.370 (3)	141
C223—H223···O921^{iv}	0.95	2.55	3.447 (3)	158
C233—H233···O922^{iv}	0.95	2.53	3.310 (3)	140

Symmetry codes: (i) $-x+\frac{1}{2}, -y, z+\frac{1}{2}$; (ii) $-x+\frac{3}{2}, -y, z+\frac{1}{2}$; (iii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (iv) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$.

The hydroxyl H atoms were located in difference maps and the OH groups were subsequently refined as rotating rigid groups, with O—H = 0.84 Å and U_{iso}(H) = 1.5U_{eq}(O). Other H atoms were placed in calculated positions, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *SMART* (Siemens, 1993); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1996); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Sheldrick, 1997); software used to prepare material for publication: *XCIF* (Sheldrick, 1993) and *PLATON* (Spek, 2003).

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Bis(tetraphenylphosphonium) (*cis*-dioxo)bis(1-carboxybenzene-2,3-diolate-O,*O'*)molybdenum(VI)

Crystal data

$(C_{24}H_{20}P)_2[MoO_2(C_7H_4O_4)_2]$
$M_r = 1110.88$
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
$a = 13.3595$ (3) Å
$b = 16.9998$ (4) Å
$c = 45.5887$ (13) Å
$V = 10353.6$ (4) Å^3
$Z = 8$
$F(000) = 4576$
$D_x = 1.425$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8839 reflections
$\theta = 2$–28.5°
$\mu = 0.38$ mm^{-1}
$T = 150$ K
Block, yellow
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Data collection

Bruker SMART Apex CCD area-detector diffractometer
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Graphite monochromator
ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)
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15149 independent reflections
11301 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$
$\theta_{max} = 30.1°$, $\theta_{min} = 1.8°$
$h = -18 \rightarrow 18$
$k = -23 \rightarrow 23$
$l = -64 \rightarrow 63$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.100$
$S = 1.06$
15149 reflections
678 parameters
0 restraints
Primary atom site location: Patterson
Secondary atom site location: difference Fourier map
Hydrogen site location: geom/difmap
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 9.6314P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}

Special details

Experimental. Oxford Cryosystems LT device.

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. Carboxylic H-atoms were located in a difference map. They were refined using the Sheldrick rotating rigid group model.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mo1	0.206905 (13)	0.196939 (10)	0.091417 (4)	0.02289 (5)
O1	0.19498 (11)	0.20131 (9)	0.05420 (3)	0.0323 (3)
O2	0.33046 (11)	0.21966 (9)	0.09713 (3)	0.0317 (3)
O11	0.04116 (10)	0.18788 (8)	0.09495 (3)	0.0246 (3)
C21	0.00137 (15)	0.25113 (12)	0.10764 (4)	0.0214 (4)
C31	−0.10046 (15)	0.25929 (12)	0.11429 (4)	0.0243 (4)
C41	−0.13435 (17)	0.33021 (14)	0.12682 (5)	0.0315 (5)
H41	−0.2034	0.3367	0.1312	0.038*
C51	−0.06842 (18)	0.38993 (14)	0.13276 (5)	0.0329 (5)
H51	−0.0921	0.4371	0.1415	0.039*
C61	0.03361 (17)	0.38214 (12)	0.12612 (5)	0.0274 (4)
H61	0.0787	0.4239	0.1302	0.033*
C71	0.06798 (15)	0.31351 (12)	0.11361 (4)	0.0228 (4)
O81	0.16441 (10)	0.30099 (8)	0.10622 (3)	0.0257 (3)
C91	−0.17163 (16)	0.19583 (14)	0.10773 (5)	0.0304 (5)
O911	−0.26002 (12)	0.19749 (10)	0.11417 (4)	0.0414 (4)
O912	−0.13367 (12)	0.13328 (9)	0.09371 (4)	0.0364 (4)
H912	−0.0716	0.1390	0.0917	0.055*
O12	0.18515 (10)	0.16267 (8)	0.13797 (3)	0.0236 (3)
C22	0.17779 (14)	0.08526 (12)	0.14171 (4)	0.0212 (4)
C32	0.15990 (15)	0.04828 (12)	0.16871 (4)	0.0242 (4)
C42	0.15562 (17)	−0.03415 (13)	0.16968 (5)	0.0300 (5)
H42	0.1418	−0.0597	0.1878	0.036*
C52	0.17103 (17)	−0.07845 (13)	0.14493 (5)	0.0326 (5)
H52	0.1691	−0.1342	0.1461	0.039*
C62	0.18966 (16)	−0.04165 (12)	0.11789 (5)	0.0276 (4)
H62	0.2013	−0.0724	0.1008	0.033*
C72	0.19089 (14)	0.03906 (12)	0.11629 (4)	0.0231 (4)
O82	0.20553 (11)	0.08009 (8)	0.09117 (3)	0.0260 (3)
C92	0.14697 (15)	0.09525 (13)	0.19572 (5)	0.0269 (4)
O921	0.13182 (13)	0.06764 (10)	0.21997 (3)	0.0374 (4)
O922	0.15274 (12)	0.17366 (9)	0.19233 (3)	0.0302 (3)
H922	0.1591	0.1844	0.1744	0.045*
P3	0.65504 (4)	0.15450 (3)	0.714012 (11)	0.02261 (11)
C13	0.69312 (15)	0.07204 (12)	0.69218 (4)	0.0254 (4)
C23	0.6461 (2)	0.05277 (15)	0.66601 (5)	0.0376 (5)
H23	0.5944	0.0851	0.6584	0.045*
C33	0.6761 (2)	−0.01455 (17)	0.65121 (6)	0.0500 (7)
H33	0.6445	−0.0281	0.6332	0.060*
C43	0.7506 (2)	−0.06192 (15)	0.66210 (6)	0.0423 (6)
H43	0.7701	−0.1079	0.6517	0.051*
C53	0.79673 (18)	−0.04284 (14)	0.68800 (6)	0.0355 (5)

H53	0.8486	−0.0755	0.6954	0.043*
C63	0.76825 (17)	0.02365 (14)	0.70337 (5)	0.0313 (5)
H63	0.7997	0.0363	0.7215	0.038*
C73	0.61305 (15)	0.11326 (12)	0.74811 (4)	0.0235 (4)
C83	0.54830 (17)	0.04872 (13)	0.74639 (5)	0.0305 (5)
H83	0.5245	0.0312	0.7279	0.037*
C93	0.51931 (18)	0.01074 (14)	0.77170 (5)	0.0355 (5)
H93	0.4752	−0.0330	0.7707	0.043*
C103	0.55456 (19)	0.03633 (15)	0.79874 (5)	0.0378 (6)
H103	0.5352	0.0096	0.8161	0.045*
C113	0.61749 (19)	0.10041 (16)	0.80038 (5)	0.0408 (6)
H113	0.6402	0.1183	0.8190	0.049*
C123	0.64781 (17)	0.13894 (15)	0.77512 (5)	0.0344 (5)
H123	0.6920	0.1826	0.7763	0.041*
C133	0.55634 (15)	0.20708 (12)	0.69606 (4)	0.0248 (4)
C143	0.57544 (17)	0.23877 (14)	0.66827 (5)	0.0325 (5)
H143	0.6399	0.2338	0.6597	0.039*
C153	0.50017 (18)	0.27720 (14)	0.65352 (5)	0.0355 (5)
H153	0.5118	0.2966	0.6343	0.043*
C163	0.40719 (17)	0.28781 (14)	0.66657 (5)	0.0334 (5)
H163	0.3559	0.3153	0.6564	0.040*
C173	0.38956 (17)	0.25820 (14)	0.69431 (5)	0.0338 (5)
H173	0.3262	0.2662	0.7033	0.041*
C183	0.46332 (16)	0.21698 (13)	0.70914 (5)	0.0294 (5)
H183	0.4504	0.1957	0.7280	0.035*
C193	0.75707 (15)	0.22173 (12)	0.71907 (4)	0.0247 (4)
C203	0.74107 (17)	0.28993 (13)	0.73566 (5)	0.0284 (4)
H203	0.6781	0.2990	0.7448	0.034*
C213	0.81758 (18)	0.34387 (14)	0.73866 (5)	0.0331 (5)
H213	0.8077	0.3896	0.7503	0.040*
C223	0.90834 (18)	0.33187 (15)	0.72490 (5)	0.0373 (5)
H223	0.9606	0.3693	0.7271	0.045*
C233	0.92337 (17)	0.26563 (15)	0.70790 (6)	0.0378 (5)
H233	0.9856	0.2583	0.6982	0.045*
C243	0.84856 (16)	0.20972 (14)	0.70488 (5)	0.0308 (5)
H243	0.8593	0.1639	0.6934	0.037*
P4	0.81351 (4)	0.06554 (3)	0.534167 (11)	0.02358 (11)
C14	0.90070 (15)	0.01809 (13)	0.55830 (4)	0.0254 (4)
C24	1.00354 (16)	0.02603 (14)	0.55345 (5)	0.0299 (5)
H24	1.0272	0.0595	0.5383	0.036*
C34	1.07087 (16)	−0.01478 (14)	0.57072 (5)	0.0315 (5)
H34	1.1408	−0.0089	0.5676	0.038*
C44	1.03637 (17)	−0.06406 (13)	0.59258 (5)	0.0326 (5)
H44	1.0826	−0.0923	0.6044	0.039*
C54	0.93460 (17)	−0.07233 (14)	0.59731 (6)	0.0349 (5)
H54	0.9114	−0.1063	0.6124	0.042*
C64	0.86626 (16)	−0.03151 (13)	0.58027 (5)	0.0299 (5)
H64	0.7965	−0.0374	0.5836	0.036*

C74	0.77355 (16)	−0.00462 (13)	0.50710 (4)	0.0273 (4)
C84	0.81683 (17)	−0.07898 (14)	0.50557 (5)	0.0330 (5)
H84	0.8678	−0.0936	0.5190	0.040*
C94	0.7850 (2)	−0.13176 (15)	0.48422 (6)	0.0411 (6)
H94	0.8137	−0.1828	0.4832	0.049*
C104	0.7118 (2)	−0.10995 (16)	0.46458 (5)	0.0433 (6)
H104	0.6906	−0.1460	0.4499	0.052*
C114	0.6691 (2)	−0.03634 (16)	0.46603 (5)	0.0427 (6)
H114	0.6191	−0.0219	0.4522	0.051*
C124	0.69846 (17)	0.01693 (15)	0.48746 (5)	0.0345 (5)
H124	0.6678	0.0673	0.4887	0.041*
C134	0.87584 (15)	0.14727 (12)	0.51721 (4)	0.0253 (4)
C144	0.92668 (17)	0.20141 (14)	0.53512 (5)	0.0319 (5)
H144	0.9260	0.1954	0.5558	0.038*
C154	0.97760 (17)	0.26332 (14)	0.52253 (5)	0.0337 (5)
H154	1.0117	0.3002	0.5346	0.040*
C164	0.97899 (17)	0.27162 (14)	0.49230 (5)	0.0340 (5)
H164	1.0144	0.3142	0.4837	0.041*
C174	0.92932 (17)	0.21859 (14)	0.47455 (5)	0.0324 (5)
H174	0.9306	0.2249	0.4539	0.039*
C184	0.87773 (16)	0.15624 (13)	0.48685 (4)	0.0269 (4)
H184	0.8437	0.1197	0.4746	0.032*
C194	0.70383 (15)	0.09733 (13)	0.55397 (4)	0.0266 (4)
C204	0.68853 (16)	0.17597 (14)	0.56100 (5)	0.0330 (5)
H204	0.7348	0.2149	0.5548	0.040*
C214	0.60466 (18)	0.19692 (16)	0.57728 (6)	0.0415 (6)
H214	0.5934	0.2506	0.5820	0.050*
C224	0.53781 (17)	0.14085 (17)	0.58663 (5)	0.0407 (6)
H224	0.4810	0.1559	0.5978	0.049*
C234	0.55306 (17)	0.06269 (16)	0.57977 (5)	0.0367 (5)
H234	0.5073	0.0239	0.5865	0.044*
C244	0.63496 (16)	0.04057 (14)	0.56300 (5)	0.0313 (5)
H244	0.6441	−0.0130	0.5577	0.038*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mo1	0.01984 (8)	0.02600 (9)	0.02284 (9)	0.00288 (7)	0.00173 (7)	0.00276 (7)
O1	0.0310 (8)	0.0399 (9)	0.0260 (7)	0.0072 (7)	0.0025 (6)	0.0062 (7)
O2	0.0228 (7)	0.0367 (9)	0.0355 (8)	0.0015 (6)	0.0018 (6)	0.0035 (7)
O11	0.0222 (7)	0.0245 (7)	0.0272 (7)	0.0000 (5)	0.0001 (6)	−0.0033 (6)
C21	0.0219 (10)	0.0251 (10)	0.0173 (9)	0.0007 (8)	−0.0023 (8)	0.0009 (8)
C31	0.0235 (10)	0.0305 (11)	0.0190 (9)	0.0003 (8)	0.0002 (8)	0.0060 (8)
C41	0.0273 (11)	0.0414 (13)	0.0257 (10)	0.0098 (9)	0.0055 (9)	0.0051 (9)
C51	0.0405 (13)	0.0312 (12)	0.0270 (11)	0.0117 (10)	0.0030 (10)	−0.0025 (9)
C61	0.0352 (12)	0.0247 (10)	0.0224 (10)	0.0011 (9)	−0.0032 (9)	−0.0009 (8)
C71	0.0234 (10)	0.0255 (10)	0.0196 (9)	0.0011 (8)	−0.0023 (8)	0.0041 (8)
O81	0.0210 (7)	0.0232 (7)	0.0328 (8)	−0.0008 (6)	−0.0005 (6)	0.0015 (6)

C91	0.0267 (11)	0.0382 (13)	0.0264 (10)	−0.0041 (9)	−0.0028 (9)	0.0136 (10)
O911	0.0224 (8)	0.0535 (11)	0.0484 (10)	−0.0046 (7)	−0.0001 (7)	0.0225 (9)
O912	0.0304 (8)	0.0354 (9)	0.0435 (10)	−0.0108 (7)	−0.0032 (8)	0.0020 (7)
O12	0.0252 (7)	0.0219 (7)	0.0238 (7)	−0.0001 (5)	0.0004 (6)	−0.0011 (6)
C22	0.0151 (9)	0.0245 (10)	0.0241 (10)	0.0011 (7)	−0.0012 (7)	−0.0005 (8)
C32	0.0193 (10)	0.0295 (11)	0.0237 (10)	−0.0005 (8)	−0.0011 (8)	−0.0002 (8)
C42	0.0304 (11)	0.0307 (11)	0.0289 (11)	−0.0013 (9)	−0.0001 (9)	0.0066 (9)
C52	0.0364 (12)	0.0222 (11)	0.0392 (13)	0.0000 (9)	−0.0056 (10)	0.0025 (9)
C62	0.0291 (11)	0.0267 (11)	0.0269 (10)	0.0030 (8)	−0.0048 (9)	−0.0054 (8)
C72	0.0181 (9)	0.0272 (10)	0.0241 (10)	0.0031 (7)	−0.0025 (8)	−0.0004 (8)
O82	0.0296 (8)	0.0270 (7)	0.0213 (7)	0.0056 (6)	0.0019 (6)	−0.0006 (6)
C92	0.0191 (10)	0.0357 (12)	0.0257 (10)	−0.0023 (8)	0.0018 (8)	−0.0015 (9)
O921	0.0390 (9)	0.0470 (10)	0.0260 (8)	−0.0040 (8)	0.0061 (7)	0.0012 (7)
O922	0.0316 (8)	0.0347 (8)	0.0244 (7)	−0.0027 (6)	0.0050 (7)	−0.0057 (6)
P3	0.0200 (2)	0.0282 (3)	0.0196 (2)	−0.0010 (2)	0.0001 (2)	−0.0025 (2)
C13	0.0243 (10)	0.0291 (11)	0.0228 (10)	−0.0036 (8)	0.0049 (8)	−0.0043 (8)
C23	0.0461 (14)	0.0417 (14)	0.0250 (11)	0.0005 (11)	−0.0056 (10)	−0.0068 (10)
C33	0.0663 (19)	0.0523 (16)	0.0314 (13)	−0.0016 (14)	−0.0086 (13)	−0.0180 (12)
C43	0.0506 (15)	0.0369 (14)	0.0394 (13)	−0.0051 (12)	0.0115 (12)	−0.0143 (11)
C53	0.0320 (12)	0.0322 (12)	0.0424 (13)	0.0003 (9)	0.0079 (11)	−0.0056 (10)
C63	0.0277 (11)	0.0359 (12)	0.0302 (11)	−0.0010 (9)	−0.0005 (9)	−0.0072 (9)
C73	0.0206 (10)	0.0289 (10)	0.0210 (9)	0.0029 (8)	0.0016 (8)	−0.0006 (8)
C83	0.0334 (12)	0.0334 (12)	0.0247 (11)	−0.0032 (9)	0.0034 (9)	−0.0053 (9)
C93	0.0391 (13)	0.0333 (12)	0.0342 (12)	−0.0043 (10)	0.0119 (10)	−0.0021 (10)
C103	0.0389 (14)	0.0466 (14)	0.0280 (12)	0.0023 (11)	0.0074 (10)	0.0076 (10)
C113	0.0395 (14)	0.0611 (17)	0.0217 (11)	−0.0043 (12)	−0.0026 (10)	0.0021 (11)
C123	0.0298 (12)	0.0471 (14)	0.0262 (11)	−0.0073 (10)	−0.0029 (9)	−0.0005 (10)
C133	0.0222 (10)	0.0293 (11)	0.0227 (9)	−0.0018 (8)	−0.0024 (8)	0.0002 (8)
C143	0.0247 (11)	0.0402 (13)	0.0328 (12)	−0.0002 (9)	0.0063 (9)	0.0074 (10)
C153	0.0384 (13)	0.0383 (13)	0.0298 (12)	−0.0004 (10)	0.0013 (10)	0.0107 (10)
C163	0.0301 (12)	0.0367 (13)	0.0333 (12)	0.0027 (9)	−0.0039 (10)	0.0060 (10)
C173	0.0232 (11)	0.0480 (14)	0.0304 (11)	0.0051 (10)	0.0039 (9)	0.0025 (10)
C183	0.0253 (11)	0.0410 (13)	0.0221 (10)	0.0017 (9)	0.0020 (9)	0.0016 (9)
C193	0.0218 (10)	0.0308 (11)	0.0213 (9)	−0.0032 (8)	−0.0019 (8)	0.0012 (8)
C203	0.0282 (11)	0.0320 (12)	0.0250 (10)	−0.0003 (9)	0.0007 (9)	−0.0016 (9)
C213	0.0407 (13)	0.0304 (12)	0.0282 (11)	−0.0053 (9)	−0.0037 (10)	−0.0031 (9)
C223	0.0318 (12)	0.0384 (13)	0.0418 (13)	−0.0101 (10)	−0.0044 (11)	0.0010 (11)
C233	0.0241 (11)	0.0447 (14)	0.0447 (14)	−0.0059 (10)	0.0049 (10)	0.0004 (11)
C243	0.0249 (11)	0.0351 (12)	0.0325 (11)	−0.0018 (9)	0.0023 (9)	−0.0049 (9)
P4	0.0203 (3)	0.0313 (3)	0.0191 (2)	0.0007 (2)	−0.0010 (2)	−0.0019 (2)
C14	0.0216 (10)	0.0312 (11)	0.0233 (10)	0.0038 (8)	−0.0007 (8)	−0.0046 (8)
C24	0.0228 (10)	0.0412 (13)	0.0258 (11)	0.0020 (9)	0.0021 (9)	−0.0001 (9)
C34	0.0201 (10)	0.0419 (13)	0.0324 (12)	0.0038 (9)	0.0010 (9)	−0.0063 (10)
C44	0.0254 (11)	0.0310 (11)	0.0413 (13)	0.0086 (9)	−0.0054 (10)	−0.0010 (10)
C54	0.0297 (12)	0.0312 (12)	0.0440 (14)	0.0030 (9)	−0.0007 (10)	0.0115 (10)
C64	0.0192 (10)	0.0345 (12)	0.0360 (12)	0.0003 (8)	0.0003 (9)	0.0031 (10)
C74	0.0261 (11)	0.0344 (12)	0.0213 (10)	−0.0056 (8)	0.0028 (8)	−0.0039 (9)
C84	0.0309 (12)	0.0375 (13)	0.0305 (11)	−0.0040 (9)	0.0043 (9)	−0.0047 (10)

C94	0.0464 (15)	0.0382 (14)	0.0386 (13)	−0.0108 (11)	0.0113 (12)	−0.0099 (11)
C104	0.0538 (16)	0.0467 (15)	0.0293 (12)	−0.0242 (12)	0.0075 (11)	−0.0102 (11)
C114	0.0413 (14)	0.0575 (17)	0.0292 (12)	−0.0192 (12)	−0.0066 (11)	−0.0008 (11)
C124	0.0305 (12)	0.0428 (13)	0.0302 (11)	−0.0047 (10)	−0.0037 (10)	−0.0021 (10)
C134	0.0222 (10)	0.0320 (11)	0.0219 (10)	0.0001 (8)	−0.0014 (8)	−0.0021 (8)
C144	0.0296 (11)	0.0421 (13)	0.0241 (10)	−0.0023 (10)	−0.0019 (9)	−0.0059 (10)
C154	0.0304 (12)	0.0373 (13)	0.0334 (12)	−0.0052 (9)	−0.0045 (10)	−0.0068 (10)
C164	0.0316 (12)	0.0342 (12)	0.0362 (12)	−0.0031 (9)	−0.0022 (10)	0.0031 (10)
C174	0.0355 (12)	0.0379 (12)	0.0238 (10)	−0.0009 (10)	−0.0044 (9)	0.0025 (9)
C184	0.0276 (11)	0.0307 (11)	0.0224 (10)	0.0012 (8)	−0.0053 (9)	−0.0023 (8)
C194	0.0203 (10)	0.0397 (12)	0.0198 (9)	0.0046 (9)	−0.0046 (8)	−0.0027 (8)
C204	0.0258 (11)	0.0402 (13)	0.0328 (12)	0.0000 (9)	−0.0050 (9)	−0.0103 (10)
C214	0.0291 (12)	0.0541 (16)	0.0411 (13)	0.0076 (11)	−0.0050 (11)	−0.0230 (12)
C224	0.0221 (11)	0.0714 (18)	0.0285 (12)	0.0073 (11)	−0.0020 (9)	−0.0133 (12)
C234	0.0215 (11)	0.0589 (16)	0.0297 (11)	0.0030 (10)	−0.0013 (9)	0.0066 (11)
C244	0.0247 (11)	0.0396 (13)	0.0296 (11)	0.0051 (9)	−0.0013 (9)	0.0041 (10)

Geometric parameters (Å, º)

Mo1—O1	1.7056 (15)	C153—C163	1.389 (3)
Mo1—O2	1.7151 (15)	C153—H153	0.9500
Mo1—O81	1.9765 (14)	C163—C173	1.381 (3)
Mo1—O82	1.9865 (14)	C163—H163	0.9500
Mo1—O12	2.2198 (14)	C173—C183	1.386 (3)
Mo1—O11	2.2255 (14)	C173—H173	0.9500
O11—C21	1.332 (2)	C183—H183	0.9500
O12—C22	1.331 (2)	C193—C243	1.398 (3)
C21—C31	1.401 (3)	C193—C203	1.401 (3)
C21—C71	1.411 (3)	C203—C213	1.380 (3)
C31—C41	1.409 (3)	C203—H203	0.9500
C31—C91	1.469 (3)	C213—C223	1.380 (3)
C41—C51	1.371 (3)	C213—H213	0.9500
C41—H41	0.9500	C223—C233	1.382 (4)
C51—C61	1.403 (3)	C223—H223	0.9500
C51—H51	0.9500	C233—C243	1.386 (3)
C61—C71	1.377 (3)	C233—H233	0.9500
C61—H61	0.9500	C243—H243	0.9500
C71—O81	1.349 (2)	P4—C14	1.794 (2)
C72—O82	1.355 (2)	P4—C134	1.795 (2)
C91—O911	1.217 (3)	P4—C74	1.797 (2)
C91—O912	1.340 (3)	P4—C194	1.804 (2)
O912—H912	0.8400	C14—C64	1.388 (3)
C22—C32	1.403 (3)	C14—C24	1.398 (3)
C22—C72	1.411 (3)	C24—C34	1.382 (3)
C32—C42	1.403 (3)	C24—H24	0.9500
C32—C92	1.478 (3)	C34—C44	1.381 (3)
C42—C52	1.372 (3)	C34—H34	0.9500
C42—H42	0.9500	C44—C54	1.384 (3)

C52—C62	1.405 (3)	C44—H44	0.9500
C52—H52	0.9500	C54—C64	1.385 (3)
C62—C72	1.374 (3)	C54—H54	0.9500
C62—H62	0.9500	C64—H64	0.9500
C92—O921	1.218 (3)	C74—C84	1.392 (3)
C92—O922	1.344 (3)	C74—C124	1.394 (3)
O922—H922	0.8400	C84—C94	1.390 (3)
P3—C133	1.791 (2)	C84—H84	0.9500
P3—C13	1.793 (2)	C94—C104	1.376 (4)
P3—C193	1.794 (2)	C94—H94	0.9500
P3—C73	1.795 (2)	C104—C114	1.377 (4)
C13—C23	1.387 (3)	C104—H104	0.9500
C13—C63	1.394 (3)	C114—C124	1.389 (3)
C23—C33	1.387 (4)	C114—H114	0.9500
C23—H23	0.9500	C124—H124	0.9500
C33—C43	1.373 (4)	C134—C184	1.393 (3)
C33—H33	0.9500	C134—C144	1.405 (3)
C43—C53	1.371 (4)	C144—C154	1.378 (3)
C43—H43	0.9500	C144—H144	0.9500
C53—C63	1.383 (3)	C154—C164	1.385 (3)
C53—H53	0.9500	C154—H154	0.9500
C63—H63	0.9500	C164—C174	1.381 (3)
C73—C123	1.387 (3)	C164—H164	0.9500
C73—C83	1.399 (3)	C174—C184	1.383 (3)
C83—C93	1.378 (3)	C174—H174	0.9500
C83—H83	0.9500	C184—H184	0.9500
C93—C103	1.389 (3)	C194—C204	1.390 (3)
C93—H93	0.9500	C194—C244	1.395 (3)
C103—C113	1.378 (4)	C204—C214	1.390 (3)
C103—H103	0.9500	C204—H204	0.9500
C113—C123	1.385 (3)	C214—C224	1.374 (4)
C113—H113	0.9500	C214—H214	0.9500
C123—H123	0.9500	C224—C234	1.380 (4)
C133—C183	1.389 (3)	C224—H224	0.9500
C133—C143	1.400 (3)	C234—C244	1.387 (3)
C143—C153	1.375 (3)	C234—H234	0.9500
C143—H143	0.9500	C244—H244	0.9500

O1—Mo1—O2	103.36 (7)	C133—C143—H143	120.3
O1—Mo1—O81	105.89 (7)	C143—C153—C163	120.4 (2)
O2—Mo1—O81	91.32 (7)	C143—C153—H153	119.8
O1—Mo1—O82	92.12 (7)	C163—C153—H153	119.8
O2—Mo1—O82	103.59 (7)	C173—C163—C153	119.8 (2)
O81—Mo1—O82	153.40 (6)	C173—C163—H163	120.1
O1—Mo1—O12	161.83 (7)	C153—C163—H163	120.1
O2—Mo1—O12	92.29 (6)	C163—C173—C183	120.7 (2)
O81—Mo1—O12	82.58 (6)	C163—C173—H173	119.7
O82—Mo1—O12	75.03 (5)	C183—C173—H173	119.7

O1—Mo1—O11	88.97 (6)	C173—C183—C133	119.2 (2)
O2—Mo1—O11	164.19 (7)	C173—C183—H183	120.4
O81—Mo1—O11	75.61 (5)	C133—C183—H183	120.4
O82—Mo1—O11	85.53 (5)	C243—C193—C203	120.3 (2)
O12—Mo1—O11	77.43 (5)	C243—C193—P3	120.79 (16)
C21—O11—Mo1	111.89 (12)	C203—C193—P3	118.74 (16)
O11—C21—C31	124.17 (18)	C213—C203—C193	119.4 (2)
O11—C21—C71	116.03 (17)	C213—C203—H203	120.3
C31—C21—C71	119.77 (19)	C193—C203—H203	120.3
C22—O12—Mo1	113.07 (12)	C203—C213—C223	120.5 (2)
O12—C22—C32	124.64 (18)	C203—C213—H213	119.8
O12—C22—C72	115.85 (18)	C223—C213—H213	119.8
C32—C22—C72	119.51 (18)	C213—C223—C233	120.2 (2)
C21—C31—C41	119.0 (2)	C213—C223—H223	119.9
C21—C31—C91	120.80 (19)	C233—C223—H223	119.9
C41—C31—C91	120.20 (19)	C223—C233—C243	120.6 (2)
C51—C41—C31	120.5 (2)	C223—C233—H233	119.7
C51—C41—H41	119.8	C243—C233—H233	119.7
C31—C41—H41	119.8	C233—C243—C193	119.0 (2)
C41—C51—C61	120.8 (2)	C233—C243—H243	120.5
C41—C51—H51	119.6	C193—C243—H243	120.5
C61—C51—H51	119.6	C14—P4—C134	108.11 (10)
C71—C61—C51	119.6 (2)	C14—P4—C74	108.39 (10)
C71—C61—H61	120.2	C134—P4—C74	110.85 (10)
C51—C61—H61	120.2	C14—P4—C194	110.81 (10)
O81—C71—C61	123.75 (19)	C134—P4—C194	111.13 (10)
O81—C71—C21	115.84 (17)	C74—P4—C194	107.53 (10)
C61—C71—C21	120.41 (19)	C64—C14—C24	119.9 (2)
C71—O81—Mo1	120.06 (12)	C64—C14—P4	120.04 (16)
O911—C91—O912	120.0 (2)	C24—C14—P4	119.86 (17)
O911—C91—C31	124.2 (2)	C34—C24—C14	120.1 (2)
O912—C91—C31	115.77 (19)	C34—C24—H24	120.0
C91—O912—H912	109.5	C14—C24—H24	120.0
C22—C32—C42	118.83 (19)	C44—C34—C24	119.9 (2)
C22—C32—C92	120.60 (19)	C44—C34—H34	120.1
C42—C32—C92	120.57 (19)	C24—C34—H34	120.1
C52—C42—C32	121.1 (2)	C34—C44—C54	120.1 (2)
C52—C42—H42	119.5	C34—C44—H44	119.9
C32—C42—H42	119.5	C54—C44—H44	119.9
C42—C52—C62	120.3 (2)	C44—C54—C64	120.6 (2)
C42—C52—H52	119.9	C44—C54—H54	119.7
C62—C52—H52	119.9	C64—C54—H54	119.7
C72—C62—C52	119.6 (2)	C54—C64—C14	119.4 (2)
C72—C62—H62	120.2	C54—C64—H64	120.3
C52—C62—H62	120.2	C14—C64—H64	120.3
O82—C72—C62	124.10 (19)	C84—C74—C124	120.4 (2)
O82—C72—C22	115.18 (18)	C84—C74—P4	120.92 (17)
C62—C72—C22	120.71 (19)	C124—C74—P4	118.72 (18)

C72—O82—Mo1	120.75 (12)	C94—C84—C74	119.6 (2)
O921—C92—O922	119.7 (2)	C94—C84—H84	120.2
O921—C92—C32	124.6 (2)	C74—C84—H84	120.2
O922—C92—C32	115.69 (18)	C104—C94—C84	119.9 (2)
C92—O922—H922	109.5	C104—C94—H94	120.0
C133—P3—C13	110.21 (10)	C84—C94—H94	120.0
C133—P3—C193	107.48 (10)	C114—C104—C94	120.5 (2)
C13—P3—C193	110.73 (10)	C114—C104—H104	119.7
C133—P3—C73	111.14 (10)	C94—C104—H104	119.7
C13—P3—C73	105.31 (10)	C104—C114—C124	120.6 (2)
C193—P3—C73	112.01 (10)	C104—C114—H114	119.7
C23—C13—C63	120.1 (2)	C124—C114—H114	119.7
C23—C13—P3	122.25 (18)	C114—C124—C74	118.9 (2)
C63—C13—P3	117.54 (16)	C114—C124—H124	120.5
C13—C23—C33	118.8 (2)	C74—C124—H124	120.5
C13—C23—H23	120.6	C184—C134—C144	119.8 (2)
C33—C23—H23	120.6	C184—C134—P4	121.41 (16)
C43—C33—C23	121.1 (2)	C144—C134—P4	118.76 (16)
C43—C33—H33	119.4	C154—C144—C134	119.8 (2)
C23—C33—H33	119.4	C154—C144—H144	120.1
C53—C43—C33	119.9 (2)	C134—C144—H144	120.1
C53—C43—H43	120.0	C144—C154—C164	119.9 (2)
C33—C43—H43	120.0	C144—C154—H154	120.1
C43—C53—C63	120.4 (2)	C164—C154—H154	120.1
C43—C53—H53	119.8	C174—C164—C154	120.7 (2)
C63—C53—H53	119.8	C174—C164—H164	119.7
C53—C63—C13	119.6 (2)	C154—C164—H164	119.7
C53—C63—H63	120.2	C164—C174—C184	120.1 (2)
C13—C63—H63	120.2	C164—C174—H174	119.9
C123—C73—C83	120.2 (2)	C184—C174—H174	119.9
C123—C73—P3	122.78 (17)	C174—C184—C134	119.7 (2)
C83—C73—P3	116.79 (15)	C174—C184—H184	120.1
C93—C83—C73	119.6 (2)	C134—C184—H184	120.1
C93—C83—H83	120.2	C204—C194—C244	120.0 (2)
C73—C83—H83	120.2	C204—C194—P4	121.53 (17)
C83—C93—C103	120.1 (2)	C244—C194—P4	118.43 (17)
C83—C93—H93	120.0	C194—C204—C214	119.2 (2)
C103—C93—H93	120.0	C194—C204—H204	120.4
C113—C103—C93	120.2 (2)	C214—C204—H204	120.4
C113—C103—H103	119.9	C224—C214—C204	120.8 (2)
C93—C103—H103	119.9	C224—C214—H214	119.6
C103—C113—C123	120.5 (2)	C204—C214—H214	119.6
C103—C113—H113	119.8	C214—C224—C234	120.1 (2)
C123—C113—H113	119.8	C214—C224—H224	119.9
C113—C123—C73	119.4 (2)	C234—C224—H224	119.9
C113—C123—H123	120.3	C224—C234—C244	120.2 (2)
C73—C123—H123	120.3	C224—C234—H234	119.9
C183—C133—C143	120.3 (2)	C244—C234—H234	119.9

C183—C133—P3	121.53 (16)	C234—C244—C194	119.7 (2)
C143—C133—P3	118.13 (16)	C234—C244—H244	120.1
C153—C143—C133	119.5 (2)	C194—C244—H244	120.1
C153—C143—H143	120.3		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O912—H912···O11	0.84	1.73	2.514 (2)	155
O922—H922···O12	0.84	1.74	2.523 (2)	155
C33—H33···O912^{i}	0.95	2.54	3.357 (3)	144
C43—H43···O911^{i}	0.95	2.29	3.178 (3)	154
C44—H44···O2^{ii}	0.95	2.48	3.195 (3)	132
C54—H54···O911^{i}	0.95	2.55	3.249 (3)	131
C163—H163···O12^{iii}	0.95	2.46	3.348 (3)	156
C173—H173···O922^{iii}	0.95	2.58	3.370 (3)	141
C223—H223···O921^{iv}	0.95	2.55	3.447 (3)	158
C233—H233···O922^{iv}	0.95	2.53	3.310 (3)	140

Symmetry codes: (i) $-x+1/2, -y, z+1/2$; (ii) $-x+3/2, -y, z+1/2$; (iii) $x, -y+1/2, z+1/2$; (iv) $x+1, -y+1/2, z+1/2$.