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Key indicators

Single-crystal X-ray study
 T = 150 K
 Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
 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>.

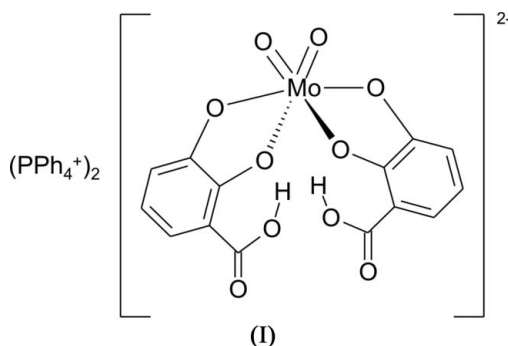
Bis(tetraphenylphosphonium) bis(1-carboxybenzene-2,3-diolato- $\kappa^2\text{O},\text{O}'$)-cis-dioxomolybdate(VI)

The title compound, $(\text{C}_{24}\text{H}_{20}\text{P})_2[\text{Mo}(\text{C}_7\text{H}_4\text{O}_4)_2\text{O}_2]$, 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 $\pi-\pi$ overlap between the benzene rings of the ligands or those of the tetraphenylphosphonium ions is observed.

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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 $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ 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 $(\text{NMe}_4)_2\text{MoO}_2(\text{C}_7\text{H}_4\text{O}_4)_2 \cdot 1.5\text{H}_2\text{O}$, (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).



In the complex anion of (I), the Mo^{VI} atom has a distorted octahedral geometry (Fig. 1). The $\text{Mo}=\text{O}$ bond lengths and $\text{O1}=\text{Mo}=\text{O2}$ 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) \AA] 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 $\text{O}-\text{H} \cdots \text{O}$ 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 $\pi-\pi$ interactions are observed, even though there are a number of benzene rings in both the ligands and the tetra-

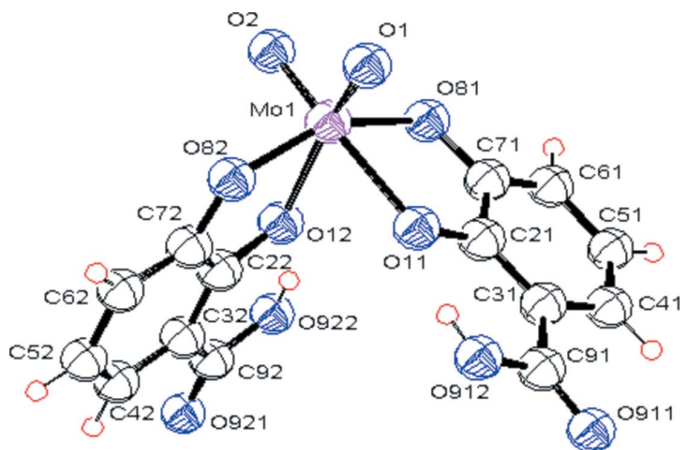


Figure 1
The structure of the complex anion in (I), showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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 voltammogram of (I) in dichloromethane confirmed its catechol 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 voltammogram 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 $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (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 $\text{C}_{62}\text{H}_{48}\text{O}_{10}\text{P}_2\text{Mo}$: C 66.90, H 4.35%; found C 66.82, H 4.27%.

Crystal data

$(\text{C}_{24}\text{H}_{20}\text{P})_2[\text{Mo}(\text{C}_7\text{H}_4\text{O}_4)_2\text{O}_2]$	Mo $K\alpha$ radiation
$M_r = 1110.88$	Cell parameters from 8839 reflections
Orthorhombic, <i>Pbca</i>	$\theta = 2-28.5^\circ$
$a = 13.3595$ (3) Å	$\mu = 0.38 \text{ mm}^{-1}$
$b = 16.9998$ (4) Å	$T = 150$ (2) K
$c = 45.5887$ (13) Å	Block, yellow
$V = 10353.6$ (4) Å ³	$0.60 \times 0.54 \times 0.35 \text{ mm}$
$Z = 8$	
$D_x = 1.425 \text{ Mg m}^{-3}$	

Data collection

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

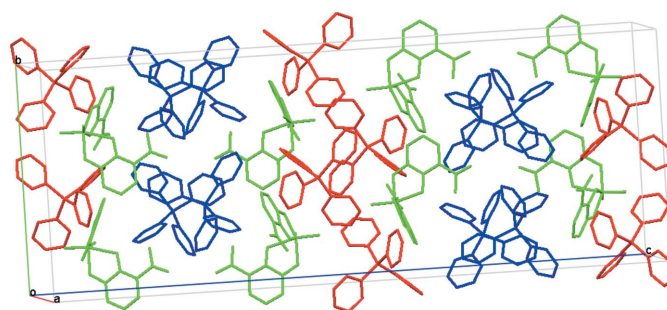


Figure 2
The packing of (I), with symmetry-equivalent molecules coloured the same. H atoms have been omitted.

Refinement

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

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, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
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 $\text{O—H} = 0.84 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Other H atoms were placed in calculated positions, with $\text{C—H} = 0.95 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Siemens, 1993); cell refinement: *SAINTE* (Siemens, 1995); data reduction: *SAINTE*; 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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References

- Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., García-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1996). *The DIRDIF96 Program System*. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
- Buchanan, R. M. & Pierpont, C. G. (1980). *J. Am. Chem. Soc.* **102**, 4951–4957.
- Griffith, W. P., Nogueira, H. I. S., Parkin, B. C., Sheppard, R. N., White, A. J. P. & Williams, D. J. J. (1995). *J. Chem. Soc. Dalton Trans.* pp. 1775–1781.
- Karaliota, A., Aletras, V., Hadjipanayioti, D., Kamariotaki, M. & Potamianou, M. (2002). *J. Mass Spectrom.* **37**, 760–763.
- Lu, X., Liu, S., Mao, X. & Bu, X. (2001). *J. Mol. Struct.* **562**, 89–94.
- Lymberopoulou-Karaliota, A., Hatzipanayioti, D., Kamariotaki, M., Potamianou, M., Litos, C. & Aletras, V. (2005). *Inorg. Chim. Acta*, **358**, 2975–2995.
- Sheldrick, G. M. (1993). *XCIF*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97* and *XP*. University of Göttingen, Germany.
- Sheldrick, G. M. (2004). *SADABS*. University of Göttingen, Germany.
- Siemens (1993). *SMART*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995). *SAINTE*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.