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Tetrakis(μ-4-chlorophenoxyacetato-κ^2O,O')-dimolybdenum(II)

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Key indicators

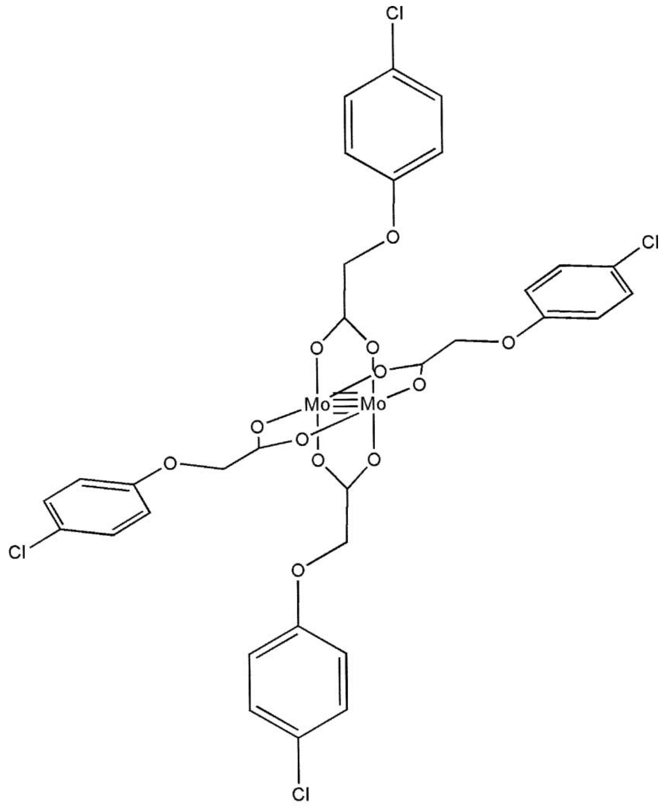
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.026
wR factor = 0.063
Data-to-parameter ratio = 11.1

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

The crystal structure determination of the title compound, $[Mo_2(C_8H_6ClO_3)_4]$, confirms the existence of a quadruple bond between the Mo atoms, with an Mo—Mo distance of 2.101 (5) Å. One half of the molecule constitutes the asymmetric unit and the carboxylate ligands define a paddle-wheel structure, with similar O—C—O angles of 122.9 (3) and 123.7 (3)°. The interplanar angles between the acetate and 4-chlorophenoxy planes in the two independent ligands are 135.9 (8) and 91.3 (8)°, which is indicative of a dramatic difference in the orientation of the ligands.

Comment

Quadruply bonded dimolybdenum complexes have been well established for numerous structures containing carboxylate bridges over the past three decades (Cotton & Walton, 1993). Some specific examples include $[Mo_2(OCOC_7H_7O)_4]$ (Cotton *et al.*, 1983), $[Mo_2(OCOC_4H_{10}N)_4]$ (Belforte *et al.*, 1993), and $[Mo_2(OCOCH_3O)_4]$ (Cotton *et al.*, 2002). We present here the crystal structure of the title dimolybdenum complex, (I).



(I)

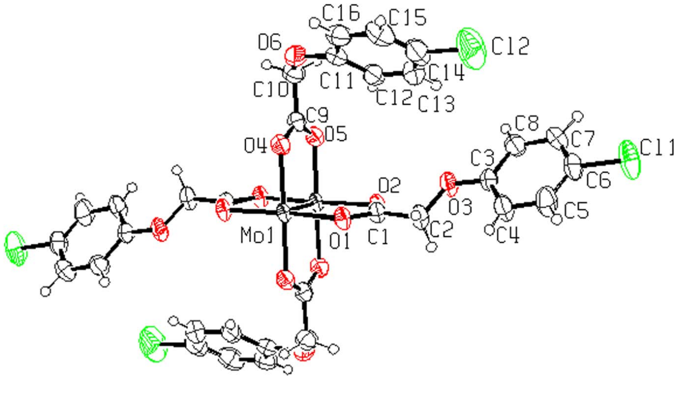


Figure 1
A drawing of (I), with displacement ellipsoids shown at the 50% probability level. Unlabelled atoms are related to labelled atoms by the symmetry operator ($-x$, $-y$, $-z$).

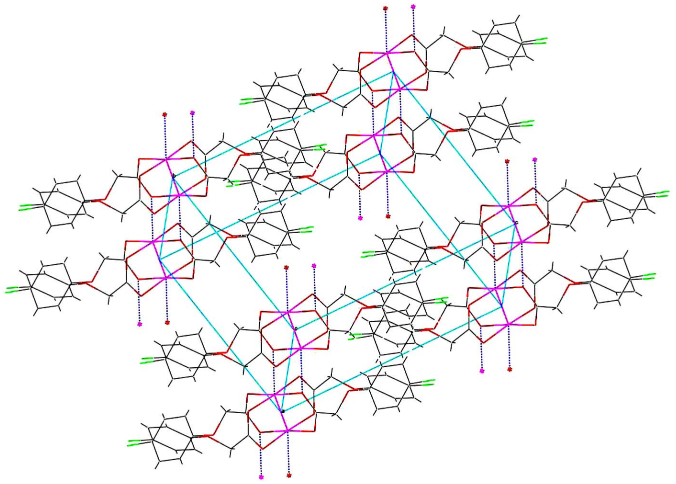


Figure 2
A packing diagram for (I) obtained using *MERCURY* (Bruno *et al.*, 2002), showing the parallelogram formed by weakly bonded interactions (dashed lines) between adjacent molecules. Dashed lines ending in + signs indicate the direction of the infinite chains.

The molecule of (I) is arranged around an inversion centre, resulting in one Mo atom and two ligands constituting the asymmetric unit (Fig. 1). The Mo—Mo distance is 2.101 (5) Å, within the range of 2.03–2.25 Å suggested for a quadruply bonded dimolybdenum unit (Cotton & Walton, 1993). Three of the Mo—O distances are similar, at 2.096 (2), 2.0991 (19) and 2.117 (2) Å, with one very different at 2.1529 (19) Å. All other bonds fall within expected values.

The molecule of (I) does not possess any axially bonded solvent molecules, even though it was crystallized under identical conditions to the related compound tetra(4-hydroxyphenylacetato)dimolybdenum(II), which contains axially bonded tetrahydrofuran (THF) molecules with an Mo—O(THF) distance of 2.608 (2) Å (Liwporncharoenvong & Luck, 2002). In (I), the molecules are arranged so that there are intermolecular interactions between an Mo atom and one adjacent carboxylate O atom in a neighbouring molecule and their symmetry-generated atoms, forming a parallelogram with Mo—O atom distances of 2.749 (2) Å (Fig. 2), resulting in an infinite chain linkage. These interactions were previously described for [$Mo_2(OCOC_7H_7O)_4$] (Cotton *et al.*, 1983). As a consequence of this interaction, the carboxylate O atom involved has the longest O—Mo atom bond distance of 2.1529 (19) Å, at the upper end of the average of 2.12 (2) Å calculated for the 183 dimolybdenum structures bridged by one or more carboxylate ligands listed in the Cambridge Structural Database (CSD, Version 5.26, November 2004 release with February 2005 updates; Allen, 2002) and obtained using the *EXCELL* program option (Bruno *et al.*, 2002).

The two ligands of (I) contain significantly different torsion angles, with C9—C10—O6—C11 = 74.0 (4)° and C1—C2—O3—C3 = 175.2 (3)°. This may be a consequence of the packing and stacking arrangement of the 4-chlorophenoxy groups as the molecule aligns itself to form the crystal (Fig. 2).

Experimental

A solution of $K_4Mo_2Cl_8$ (300 mg, 0.415 mmol) in distilled water (10 ml) was added to a solution of 4-chlorophenoxyacetic acid (324 mg, 1.74 mmol) in methanol (20 ml). The yellowish product was filtered off and vacuum dried. Crystals of (I) were obtained by allowing methanol diffusion into a tetrahydrofuran solution of the product mixture.

Crystal data

[$Mo_2(C_8H_6ClO_3)_4$]
M_r = 934.19
Triclinic, $P\overline{1}$
a = 5.668 (1) Å
b = 11.549 (1) Å
c = 13.743 (2) Å
α = 91.95 (1)°
β = 101.74 (1)°
γ = 100.64 (1)°
V = 863.3 (2) Å^3
Z = 1
D_x = 1.797 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10–15°
μ = 1.10 mm^{-1}
T = 293 (2) K
Prism, pale red
0.3 × 0.1 × 0.1 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Non–profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.856, T_{max} = 0.895
3374 measured reflections
3036 independent reflections
2657 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 25.0°
$h = 0 \rightarrow 6$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 15$
3 standard reflections frequency: 166 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.063
S = 1.04
3036 reflections
274 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0257P)^2 + 0.59P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

H atoms were freely refined, resulting in C—H distances of 0.80 (4)–0.99 (3) Å and U_{iso}(H) values of 0.045 (9)–0.080 (14) Å^2.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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