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Tricarbonyl(3-carboxypropyl)(η^5-cyclopentadienyl)tungsten(II)

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.007 Å
R factor = 0.026
wR factor = 0.072
Data-to-parameter ratio = 13.7

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

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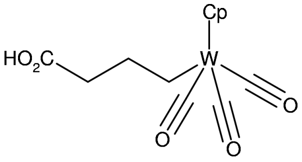
The bond lengths and angles in the title compound, $[W(C_5H_5)(C_4H_7O_2)(CO)_3]$, are as expected for a molecule of this kind. The presence of the carboxylic acid group leads, however, to the creation of hydrogen-bonded dimers consisting of pairs of centrosymmetrically related molecules.

Comment

The determination of the structure of the title compound, (I), was undertaken as part of our ongoing study of the chemistry of heterodinuclear compounds (Friedrich *et al.*, 2004). Fig. 1 is a drawing of the molecule and selected bond lengths and angles are given in Table 1. In both cases, the participation of the cyclopentadienyl (Cp) group in the coordination of W is represented, purely for convenience, by the notional bond W—*Cg*1 where *Cg*1 is the centroid of the five-membered cyclopentadienyl ring. On this basis, W is effectively five-coordinate in a distorted square-pyramidal environment with apical Cp. This arrangement creates the appearance of a stool with Cp as its seat and the three carbonyl groups and the carboxy ligand as its feet, four in number.



(I)

The bond lengths and angles given in Table 1 are unremarkable. The same is true for the W—C_{Cp} bonds in the range 2.312 (4)–2.376 (4) Å and the C—C bonds and C—C—C angles of Cp in the ranges 1.385 (7)–1.431 (7) Å and 107.3 (5)–108.4 (5)°, respectively. In the drawing of the unit-cell contents (Fig. 2) a notable feature is the presence of the hydrogen-bonded dimer involving a pair of centrosymmetrically related molecules. The hydrogen-bond parameters are given in Table 2. No other intermolecular contacts of any significance, other than van der Waals interactions, are present in the structure. Similar hydrogen-bonded dimers are present in the structures of the analogous compounds $[Cp(CO)_3MoCH_2COOH]$ and $[Cp(CO)_2FeCH_2COOH]$ (Ariyaratne *et al.*, 1969). Despite the limited quality of the refinements, these authors suggested that there was evidence to support some form of interaction between the metal (Mo or Fe) and the carboxylic acid group. There is no evidence for such an interaction in (I), which would be less likely in any case because of the length of the alkyl chain. There is perhaps a case for redetermining the earlier structures.

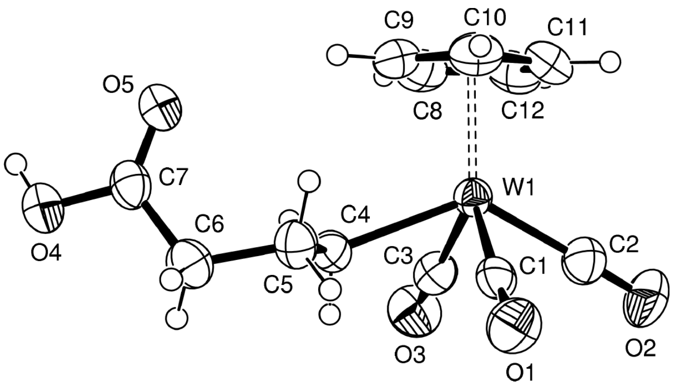


Figure 1
The molecule of (I). Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms as small circles of arbitrary radii. The dashed bond joins W and the centroid of the Cp ring.

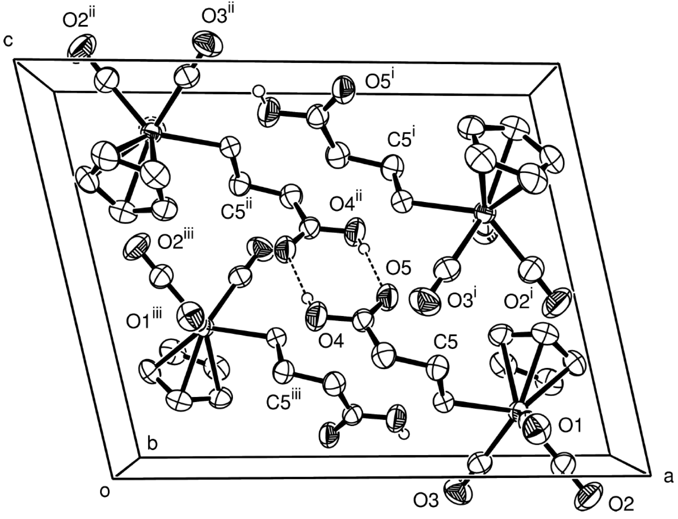


Figure 2
The unit-cell contents of (I). Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms as small circles of arbitrary radii. All H atoms other than those involved in hydrogen bonding (dashed lines) have been omitted. Selected atoms are labelled. [Symmetry codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.]

Experimental

Compound (I) was obtained by hydrolysis brought about by the presence of water in a dichloromethane/hexane solution of $[Cp(CO)_3W(CH_2)_3C(O)Mo(CO)(PMe_3)(PPh_3)Cp]$ (Onani, 2002). Yellow crystals suitable for analysis were obtained after 5 d of slow diffusion of hexane into a dichloromethane solution of (I) kept at 278 K.

Crystal data

$[W(C_5H_5)(C_4H_7O_2)(CO)_3]$
$M_r = 420.07$
Monoclinic, $P2_1/c$
$a = 14.265$ (2) Å
$b = 8.1540$ (11) Å
$c = 11.229$ (2) Å
$\beta = 102.800$ (15)°
$V = 1273.7$ (3) Å^3
$Z = 4$

$D_x = 2.191$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.8$–12.2°
$\mu = 9.08$ mm^{-1}
$T = 295$ (2) K
Rhomb, yellow
0.40 × 0.30 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.011$, $T_{max} = 0.066$
5154 measured reflections
2241 independent reflections

2053 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 25.0$°
$h = -16 \rightarrow 16$
$k = -1 \rightarrow 9$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: 7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.072$
$S = 1.08$
2241 reflections
164 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.7777P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.00$ e Å^{-3}
$\Delta\rho_{min} = -1.17$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

W1—*Cg*1	2.012 (2)	O3—C3	1.135 (5)
W1—C1	1.975 (5)	O4—C7	1.305 (5)
W1—C2	1.986 (5)	O5—C7	1.211 (5)
W1—C3	1.974 (5)	C4—C5	1.509 (6)
W1—C4	2.319 (4)	C5—C6	1.535 (5)
O1—C1	1.147 (6)	C6—C7	1.494 (6)
O2—C2	1.143 (6)		
*Cg*1—W1—C1	129.02 (15)	C1—W1—C3	106.84 (18)
*Cg*1—W1—C2	118.89 (18)	C1—W1—C4	75.15 (16)
*Cg*1—W1—C3	123.62 (16)	C2—W1—C3	78.1 (2)
*Cg*1—W1—C4	110.12 (13)	C2—W1—C4	130.95 (19)
C1—W1—C2	75.58 (19)	C3—W1—C4	73.91 (17)
C1—W1—C4—C5	50.8 (3)	W1—C4—C5—C6	167.4 (3)
C2—W1—C4—C5	106.0 (4)	C4—C5—C6—O4	−67.5 (6)
C3—W1—C4—C5	163.7 (4)	C4—C5—C6—O5	−82.2 (3)

Note: *Cg*1 is the centroid of the cyclopentadienyl ring.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O5^{i}	0.82	1.84	2.653 (5)	169

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

Presented here is a rerefinement, after suitable transformation of the unit-cell parameters and the atomic coordinates and reindexing of the intensity data, of a structure previously solved and fully refined in the space group $P\overline{1}$. The need for the rerefinement was clearly indicated by a *checkCIF* level A alert and the form it should take was revealed by recourse to the *ADDSYM* routine of *PLATON* (Spek, 2003). Close examination of a drawing of the content of the original, supposedly triclinic, unit cell fully confirmed the *ADDSYM* findings. Further support for the rerefinement reported here is the improvement in $R [I > 2\sigma(I)]$ from 0.031 for the triclinic model to the value of 0.026 for the present refinement (with the number of refined parameters now half that of the triclinic refinement). In the final stages of the present refinement, H atoms were placed in calculated positions, with X—H = 0.82, 0.93 and 0.97 Å for hydroxyl, cyclopentadienyl and methylene H atoms, respectively, and refined using a riding model, with $U_{iso}(H) = 1.5U_{eq}(O)$ or $1.2U_{eq}(C)$, as appropriate for the nature of X. The position of the hydroxyl group in terms of its rotation about

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the C—O bond was also refined. The highest residual electron-density peak is 0.99 Å from atom W1.The deepest residual electron-density hole lies 0.69 Å from atom W1.

Data collection: *CAD*-4/*PC* (Enraf–Nonius, 1994); cell refinement: *CAD*-4/*PC*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2003).

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