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Bis(tropolonato)palladium(II)

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Key indicators

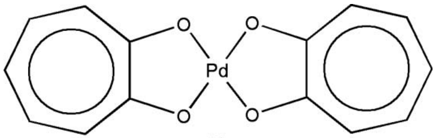
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.029
wR factor = 0.075
Data-to-parameter ratio = 17.5

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

A new type of highly symmetrical α-diketone palladium(II) complex, bis(tropolonato)palladium(II) (tropolone = 2-hydroxy-2,4,6-cycloheptatrienone), [Pd($C_7O_2H_5$)], crystallizes in a square-planar geometry with one molecule in the asymmetric unit. The Pd—O bond distances and O—Pd—O internal angles lie in the ranges 1.969 (2)–2.002 (2) Å and 81.83 (9)–99.28 (9)°, respectively. Weak intermolecular C—H···O hydrogen bonds link the essentially planar molecules into ribbons extending along the a axis.

Comment

A variety of palladium β-diketonate complexes have been reported for acetylacetonate-type ligands (Cambridge Structural database, Version 5.26; Allen, 2002). In contrast, a small group of α-diketonate complexes are known, which mostly consists of oxalate and benzosemiquinonate derivatives (Mulagaleev *et al.*, 2000; Fox & Pierpont, 1992). As a result of the reduced bidentate bite angle of α-diketones (*ca* 83°) compared with β-diketones (*ca* 94°), a comparable amount of strain in the chelating ring is expected. In addition, packing effects such as hydrogen bonding and π–π stacking have been observed in similar symmetrical rhodium(I)-type complexes, [Rh(acac)$(CO)_2$] (acac = acetylacetonate; Huq & Skapski, 1974) and [Rh(trop)$(CO)_2$] (trop = 2-hydroxy-2,4,6-cycloheptatrienone; Steyl *et al.*, 2004). In this paper, we present the structure of the title compound, [Pd$(trop)_2$], (I) (Fig. 1), a highly symmetrical tropolonate derivative.



(I)

The Pd—O bond lengths and angles in (I) (Table 1) are nearly symmetrical. The O—Pd—O (bidentate bite) angles of 81.83 (9) and 81.86 (9)° for the respective tropolonate moieties indicate a similarity in the coordination mode of the two independent tropolonato ligands to the palladium(II) metal centre. The molecule is essentially planar; the mean planes of the two tropolonate moieties make a dihedral angle of 3.4 (2)°. Thus, the Pd atom is nearly in the centre of the coordinating O atoms, with a small deviation from linearity as observed for the O11—Pd—O21 and O12—Pd—O22 angles (Table 1).

The solid-state ordering in (I) is dominated by intermolecular C—H···O hydrogen bonds (Table 2), which link the molecules into ribbons extending along the a axis

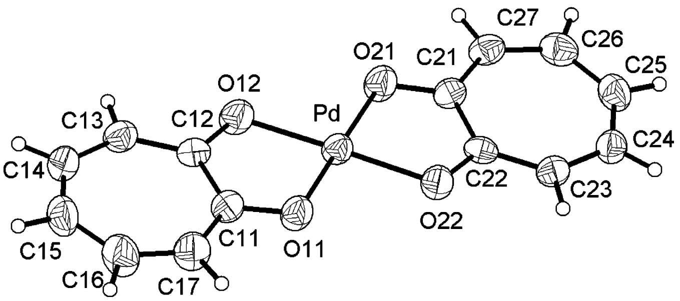


Figure 1
View of (I), showing the atom-numbering scheme, with displacement ellipsoids drawn at the 50% probability level. For the tropolonate ligands, the first digit refers to the ring number and the second digit to the atom in the ring.

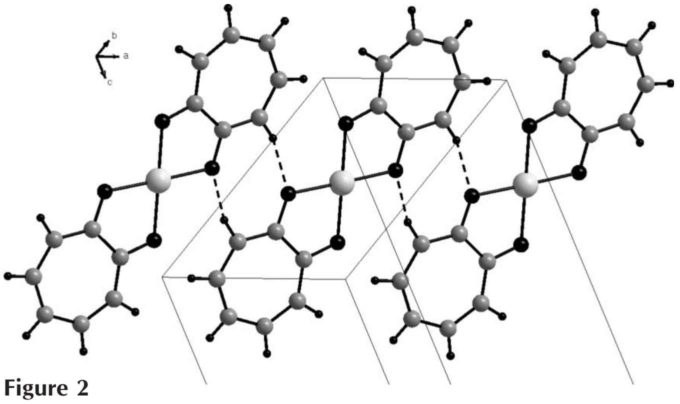


Figure 2
A fraction of the unit cell, showing the intermolecular C—H···O hydrogen bonds as dashed lines.

(Fig. 2). The basic packing motif indicates that four bis(tropolonato)palladium(II) complexes form a single unit, which incorporates the hydrogen-bonding network and possible π–π stacking interactions, supported by the relatively short interplanar distance (*ca* 3.8 Å) between the parallel molecules stacked in a head-to-tail manner.

The geometrical parameters of (I) were also investigated by theoretical calculations with *GAUSSIAN03* (Frisch *et al.*, 2003), taking into account the single molecule of (I), the C—H···O hydrogen-bonded dimer (Table 2) and the single packing unit (four molecules, content of the unit cell). The results are presented in Table 3. The parameters of single molecule optimization correlate with those observed in the crystal structure of (I) (with a maximum deviation of bond lengths and angles of less than 3%), although a symmetrical complex was obtained (Table 3). Thus, in a strain-free environment, the complex does not adopt any preferred distortions.

The dimeric unit optimization showed an observable trend in Pd—O bond distances. This is indicative of the tendency towards increased symmetry breaking, which correlates with the observed trend in the crystal structure of (I). The ranges of the weak intermolecular C—H···O interaction (distance and direction) in the calculated and crystal structures are in good agreement (Table 3).

In the single-packing-unit optimization, the bond distances and angles do not change significantly from those obtained in the dimeric unit optimization. The addition of two π–π stacking molecules increases the linearity of the C—H···O hydrogen bond (Table 3), indicating the importance of the hydrogen-bond interaction over the π–π stacking motif in the solid state. Although the effect of π–π stacking or secondary interactions must reinforce the hydrogen bond in the packing mode, the crystal structure of (I) exhibits a weaker interaction than that obtained by calculation.

Experimental

The title complex was synthesized *via* a slight modification of the method of Yoshida *et al.* (1973). To an aqueous methanol solution (1:1) containing palladium chloride (0.9 g, 5 mmol) was added tropolone (1.22 g, 10 mmol) with constant stirring. An orange precipitate formed and addition of an excess of water precipitated the product (yield: 1.3 g, 70%). Crystals suitable for X-ray crystallography were obtained from a concentrated DMF solution of the orange precipitate. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.40 (*dd*, 4), 7.27 (*dd*, 4), 7.08 (*tt*, 2); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 186.9 (C11, C12, C21, C22), 137.6 (C14, C16, C24, C26), 129.5 (C15, C25), 127.9 (C13, C17, C23, C27), with positions of the C atoms confirmed by HMQC and HMBC data.

Crystal data

$[Pd(C_7H_5O_2)_2]$
$M_r = 348.62$
Monoclinic, $P2_1/c$
$a = 7.3474$ (15) Å
$b = 10.972$ (2) Å
$c = 15.186$ (3) Å
$\beta = 90.27$ (3)°
$V = 1224.3$ (4) Å^3
$Z = 4$
$D_x = 1.891$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1024 reflections
$\theta = 3.3$–27.7°
$\mu = 1.52$ mm^{-1}
$T = 293$ (2) K
Needle, red
0.54 × 0.09 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998)
$T_{min} = 0.844$, $T_{max} = 0.888$
8234 measured reflections
3015 independent reflections
2412 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 28.3$°
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 13$
$l = -20 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.075$
$S = 1.05$
3015 reflections
172 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0346P)^2 + 0.851P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd—O11	1.990 (2)	O11—C11	1.299 (4)
Pd—O12	1.974 (2)	O12—C12	1.301 (4)
Pd—O21	2.002 (2)	O21—C21	1.309 (4)
Pd—O22	1.969 (2)	O22—C22	1.298 (3)
O11—Pd—O12	81.83 (9)	O12—Pd—O21	99.28 (9)
O21—Pd—O22	81.86 (9)	O11—Pd—O22	97.04 (9)
O11—Pd—O21	178.31 (9)	O12—Pd—O22	178.83 (8)
O11—C11—C12—O12	0.1 (4)	C13—C14—C15—C16	−1.5 (7)
O21—C21—C22—O22	−2.6 (4)	C23—C24—C25—C26	0.5 (6)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C23—H23···O12^{i}	0.93	2.47	3.342 (4)	156
C13—H13···O22^{ii}	0.93	2.48	3.378 (4)	162

Symmetry codes: (i) $x + 1, y, z$; (ii) $x - 1, y, z$.

Table 3
Comparative crystal and computational (B3Lyp/LanL2DZ level) data for $[Pd(Trop)_2]$.

$[Pd(trop)_2]$	Pd—O1n^{a}	Pd—O2n^{a}	O—Pd—O^{b}	C···O	C—H···O
X-ray structure of (I)	1.990 (2)	2.002 (2)	81.83 (9)	3.342 (4)	155.8
	1.974 (2)	1.969 (2)	81.86 (9)	3.378 (4)	162.4
Single^{c}	2.0332	2.0336	80.25		
	2.0330	2.0335	80.23		
Dimer^{d}	2.0484	2.0279	80.51	3.2108	168.8
	2.0361	2.0217	80.04	3.2107	168.8
Tetramer^{e}	2.0496	2.0267	80.41	3.2061	177.1
	2.0375	2.0214	80.10	3.2169	176.1

Notes: (*a*) *n* = 1,2 (see also labelling scheme on Fig. 1); (*b*) bidentate bite angle of tropolonato moiety; (*c*) single molecule optimization; (*d*) optimization of hydrogen-bonded dimer; (*e*) optimization of single packing unit (four molecules).

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}$ of the parent atom.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXL97*.

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References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Brandenburg, K. & Brendt, M. (2000). *DIAMOND*. Release 2.1e. Crystal Impact GbR, Bonn, Germany.

Bruker (1998). *SADABS* (Version 2004/1), *SMART-NT* (Version 5.050) and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1999). *SAINT-Plus* (including *XPREP*). Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.

Fox, G. A. & Pierpont, C. G. (1992). *Inorg. Chem.* **31**, 3718–3723.

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Montgomery, J. A. Jr, Vreven, T., Kudin, K. N., Burant, J. C., Millam, J. M., Iyengar, S. S., Tomasi, J., Barone, V., Mennucci, B. *et al.* (2003). *GAUSSIAN03*. Version 6, Revision B.05. Gaussian Inc., Pittsburgh, PA, USA.

Huq, F. & Skapski, A. C. (1974). *J. Cryst. Mol. Struct.* **4**, 411–413.

Mulagaleev, R. F., Solov'ev, L. A., Blokhin, A. I. & Kirik, S. D. (2000). *Koord. Khim. (Russ. J. Coord. Chem.)*, **26**, 212–216.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (1998). *SADABS*. University of Göttingen, Germany.

Steyl, G., Kruger, G. J. & Roodt, A. (2004). *Acta Cryst.* C**60**, m473–m475.

Yoshida, I., Kobayashi, H. & Ueno, K. (1973). *J. Inorg. Nucl. Chem.* **35**, 4061–4070.