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Bis(tetra-*n*-butylammonium) di-μ-chloro-bis[(tetramethyl buta-1,3-diene-1,2,3,4-tetracarboxylato-κ^2C^1,C^4)palladium]

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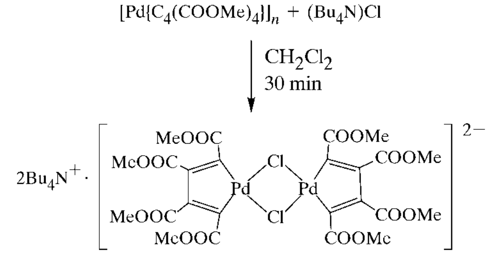
The anionic complex in the title compound, $(C_{16}H_{36}N)_2$-$[Pd_2(C_{12}H_{12}O_8)_2Cl_2]$, lies on a centre of inversion, so that the $\{Pd_2(\mu\text{-}Cl)_2\}$ core is planar, which is the most frequent conformation found for complexes containing this moiety in the Cambridge Structural Database [October 2001 Release; Allen & Kennard (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37]. This dinuclear complex has a Pd$\cdots$Pd distance of 3.5119 (4) Å. The bite angle of the chelating ligand [79.79 (8)°] distorts the square-planar coordination around the metal atom.

Comment

The chemistry of metallacycles has been of increasing interest in recent years, as a result of the involvement of these compounds in catalytic processes and their application in organic syntheses (Ojima *et al.*, 1996). The cycloaddition of two unsaturated fragments to a metal unit is one of the most useful methods of metallacycle synthesis, since it gives access to relatively complex structures starting from small unsaturated molecules (Cámpora *et al.*, 1999). In particular, the oxidative cycloaddition of acetylenic esters, such as dimethyl acetylenedicarboxylate (dmad), to Ni, Pd and Pt has received much attention, due in part to the involvement of the esters in different oligomerization and co-oligomerization catalytic reactions, and also because of the interesting behaviour of the compounds formed as precursors in organometallic chemistry. Thus, the polymer complex palladacyclopentadiene, $[Pd(C_4R_4)]_n$ (R is COOMe), formed in the reaction of dmad with $Pd(dba)_2$ (dba is dibenzylidene acetone), reacts with a wide range of donor ligands to give discrete soluble molecules (tom Dieck *et al.*, 1990). Other aspects recently studied are the use of these compounds as catalysts in the metathesis of enynes (Trost *et al.*, 1993), dimerization of allenyl ketones (Hashmi, 1995), conversion of alkynes to conjugated dienes (van Belzen *et al.*, 1998, and references therein), and co-cyclotrimerizations of acetylenes with other acetylenes, alkenes and allenes (Munz *et al.*, 1991). With this background, we present here the crystal structure of one such dinuclear metallacycle, the title compound, (I).



(I)

In complex (I) (Fig. 1), the coordination around the Pd^{II} atoms is approximately planar, the largest deviation from the plane defined by the metallacycle ring and the Cl atoms (r.m.s. deviation 0.0478 Å) being 0.0792 (14) Å for atom C2. The bond angles around the Pd atom deviate from ideal square-planar values (Table 1); the largest deviation is seen for the C1—Pd1—C4 angle of 79.79 (8)°. This value is within the range found for related complexes in the Cambridge Structural Database (CSD; October 2001 Release; Allen & Kennard, 1993); the C—Pd—C angle for the tetraalkyl buta-1,3-diene-1,2,3,4-tetracarboxylate–Pd^{II} fragment in the CSD (7 hits) ranges from 79.18 to 80.38°.

The $-CO_2$ groups of the ester functions bound to the C atoms *trans* to Cl are nearly perpendicular to the palladacycle ring, as indicated by the Pd1—C1—C5—O2 and Pd1—C4—C8—O8 torsion angles. The angles between the other two carboxylate groups and the palladacycle plane are smaller (Table 1). The Pd—Cl distances are typical for μ-Cl dinuclear complexes of Pd. The Pd—C distances are similar to those found in other complexes containing this ligand (Sánchez *et al.*, 2002).

The molecule of (I) lies on a centre of inversion, so that the $\{Pd_2(\mu\text{-}Cl)_2\}$ moiety is strictly planar. The CSD contains 151

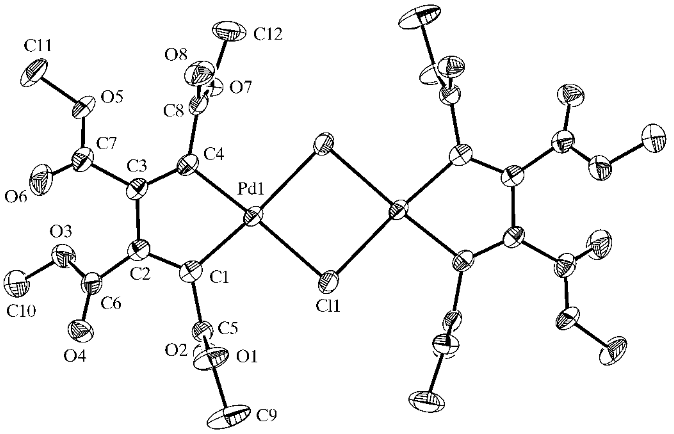


Figure 1
A perspective view of the complex anion in (I). H atoms have been omitted for clarity and displacement ellipsoids are drawn at the 50% probability level.

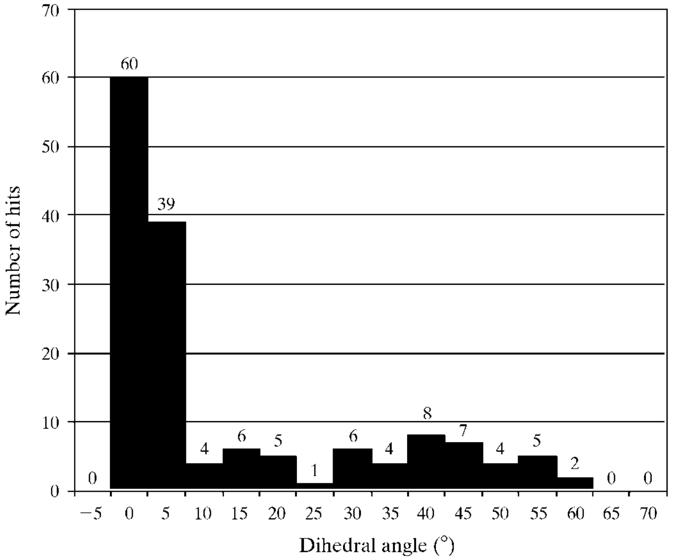


Figure 2
A histogram showing the dihedral angles of the $\{Pd_2(\mu\text{-}Cl)_2\}$ core along the Cl···Cl line among the structures found in the CSD search.

entries for dinuclear complexes of Pd^{II} bridged by two Cl atoms, in which the $\{Pd_2(\mu\text{-}Cl)_2\}$ moiety is either planar or bent. A statistical analysis of the dihedral angle of the $\{Pd_2(\mu\text{-}Cl)_2\}$ unit along the Cl···Cl axis reveals that the most frequent conformation is planar (Fig. 2); 39.7% of the hits are strictly planar. In the title complex, the Pd1···Pd1^i distance [symmetry code: (i) $1 - x, 1 - y, 1 - z$] is 3.5119 (4) Å, which is within the most frequently occupied region of the range found in dinuclear complexes containing the $[Pd_2(\mu\text{-}Cl)_2]$ core (Fig. 3); 28% of the structures exhibit a distance of between 3.50 and 3.55 Å.

The anionic complex in (I) is sandwiched between two $[NBu_4]^+$ cations. The N atoms from the cations lie on the perpendicular to the $\{Pd_2(\mu\text{-}Cl)_2\}$ core, over the Pd^{II} atoms [N1—Pd1—Pd1^i 89.91 (2)°]. The distances from Pd1 to the two nearest N atoms are 4.4650 (15) and 5.6764 (16) Å. The next nearest N atom to Pd1 is 6.1776 (16) Å away. The structure does not contain hydrogen bonds.

The structure of the analogous iodo complex has been reported by Rheingold *et al.* (1989), the cation being methyltriphenylphosphonium. The iodo complex is also centrosymmetric and the Pd···Pd distance is 3.912 Å, which is larger than that found in the chloro complex, (I), due to the longer radius of the bridging I atom. The geometrical features of the palladacycle fragment are similar in both compounds. The mean Pd—C distance is 2.017 (3) Å in the iodo complex, which is longer than that found in (I) (Table 1), due to a stronger *trans* influence from I^- than from Cl^-. The $–CO_2$ groups of the ester functions nearest to the Pd atom are approximately perpendicular to the palladacycle ring (Pd—C—C=O torsion angles of 100.3 and 82.3°), as in (I) (Table 1). The tilt of the other carboxylate groups from the palladacycle plane is also smaller (torsion angles of −163.7 and 56.2°). The anionic iodo complex is sandwiched between two $[PMe(Ph)_3]^+$ cations and the P atoms in the cations are positioned on the perpendicular to the Pd···Pd axis (P—Pd—Pd 106.4°), with the shortest P—Pd distance being 5.064 Å.

The conformation found for the methoxycarbonyl groups in the above complexes suggests that, as the methoxycarbonyl groups at the α position relative to Pd are more perpendicular to the palladacycle ring, the adjacent methoxycarbonyl groups at the β position are more parallel to the ring. This is confirmed by the scatter plot of these angles for the tetramethyl buta-1,3-diene-1,2,3,4-tetracarboxylate–Pd^{II} fragments

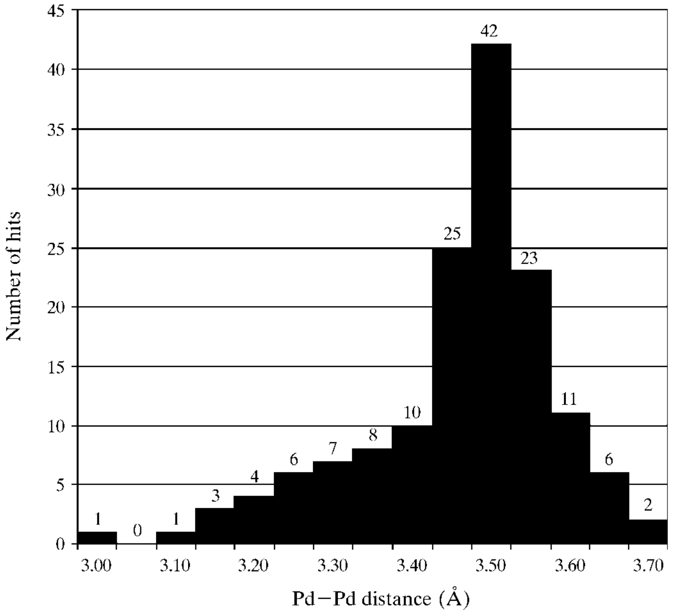


Figure 3
A histogram showing the distribution of Pd···Pd distances among the structures found in the CSD search containing the $\{Pd_2(\mu\text{-}Cl)_2\}$ core.

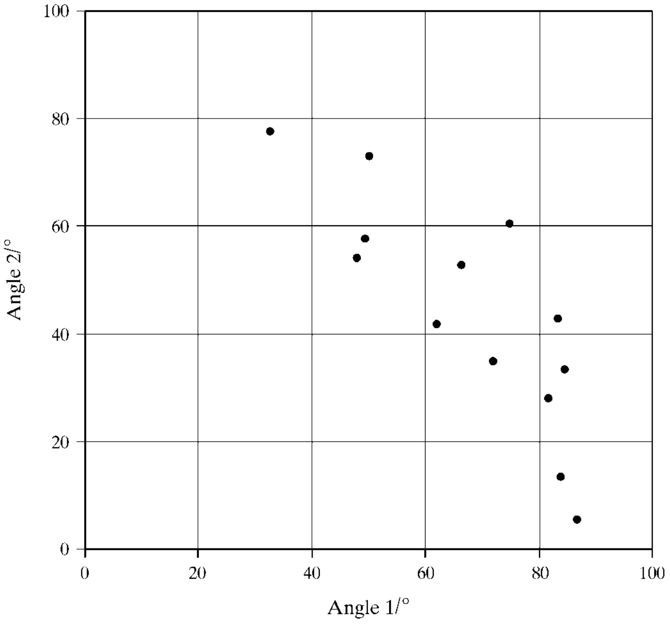


Figure 4
A scatter plot of the angle between the palladacycle ring and the methoxycarbonyl groups in the α (angle 1) and β positions (angle 2).

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in the CSD (Fig. 4), the angle between the planes defined by two adjacent methoxycarbonyl groups ranging from 42.4 to 74.7°.

Experimental

The title complex was prepared according to the following method: a stoichiometric amount of tetrabutylammonium chloride (molar ratio 1:1) was added to a dichloromethane solution (10 ml) of the precursor $[Pd\{C_4(COOMe)_4\}]_n$ (0.07 g, 0.18 mmol) (see *Scheme*). The reaction solution was stirred at room temperature for 30 min, and the solvent was then partially evaporated under reduced pressure. The addition of diethyl ether caused the formation of a pale-yellow solid, which was filtered off, washed with diethyl ether and air dried. Crystals of (I) were obtained by recrystallization from dichloromethane–diethyl ether (yield 84%). Analysis found: C 50.5, H 7.4, N 1.9%; calculated for $C_{56}H_{96}Cl_2N_2O_{16}Pd_2$: C 50.3, H 7.2, N 2.1%. Spectroscopic analysis, IR (cm^{-1}): 1712, 1694 (C═O, *str*); ^1H NMR ($CDCl_3$, δ, p.p.m.): 3.57 (*s*, 6H, COOMe), 3.62 (*s*, 6H, COOMe), 3.40 (*t*, 16H, NBu_4), 1.74 (*m*, 16H, NBu_4), 1.53 (*m*, 16H, NBu_4), 1.00 (*t*, 24H, NBu_4). The palladacyclopentadiene precursor was prepared according to the published method of Moseley & Maitlis (1974). The tetrabutylammonium chloride was purchased from Aldrich and used without further purification. The CHN analyses were carried out with a Perkin–Elmer 240C microanalyser, the IR spectra were recorded on a Perkin–Elmer 16FPC FT–IR spectrophotometer, using Nujol mulls between polyethylene sheets, and the NMR data were recorded on a Bruker AC 200E (^1H) spectrometer.

Crystal data

$(C_{16}H_{36}N)_2[Pd_2(C_{12}H_{12}O_8)_2Cl_2]$
$M_r = 1337.05$
Triclinic, $P\overline{1}$
$a = 9.5024$ (6) Å
$b = 12.6678$ (7) Å
$c = 14.6370$ (10) Å
$\alpha = 95.929$ (5)°
$\beta = 106.777$ (5)°
$\gamma = 104.100$ (5)°
$V = 1607.25$ (19) Å^3
$Z = 1$
$D_x = 1.381$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 61 reflections
$\theta = 9.8$–24.7°
$\mu = 0.71$ mm^{-1}
$T = 173$ (2) K
Block, yellow
0.40 × 0.35 × 0.28 mm

Data collection

Siemens *P*4 four-circle diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.787$, $T_{max} = 0.821$
11 249 measured reflections
5644 independent reflections
5057 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 25°$
$h = -10 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 17$
3 standard reflections every 247 reflections intensity decay: 4.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.055$
$S = 1.03$
5644 reflections
352 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0286P)^2 + 0.2945P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—Cl1	2.4070 (5)	Pd1—C4	1.9950 (18)
Pd1—Cl1^i	2.4295 (6)	Pd1—Pd1^i	3.5119 (4)
Pd1—C1	2.000 (2)		
Cl1—Pd1—Cl1^i	86.875 (19)	C1—Pd1—Cl1^i	174.38 (5)
C1—Pd1—C4	79.79 (8)	C4—Pd1—Cl1	176.44 (6)
C1—Pd1—Cl1	97.15 (6)	C4—Pd1—Cl1^i	96.06 (6)
Pd1—C4—C8—O8	−93.3 (2)	C1—C2—C6—O4	42.2 (3)
Pd1—C1—C5—O2	−90.9 (2)	C4—C3—C7—O6	−140.9 (2)

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

H atoms were placed in calculated positions, with C—H distances of 0.99 and 0.98 Å for methylene and methyl groups, respectively, and were refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$ for the methylene groups and $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl groups.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1139). Services for accessing these data are described at the back of the journal.

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