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(2^3-*tert*-Butyl-5,10,15,20-tetraphenylazuliporphyrinato)palladium(II) dichloromethane solvate

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Key indicators

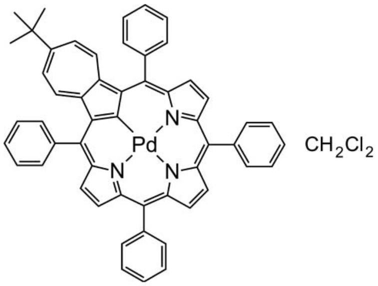
Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.006 Å
R factor = 0.056
wR factor = 0.166
Data-to-parameter ratio = 15.4

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

The title compound, $[Pd(C_{54}H_{39}N_3)]\cdot CH_2Cl_2$, contains an azuliporphyrin surrounding a Pd^{II} ion in a typical four-coordinate square-planar geometry. Van der Waals contacts between the azulene H atoms and the *ortho*-C atoms of the *meso* aryl substituents result in a twisted azulene.

Comment

Carbaporphyrinoid molecules are porphyrin analogs with carbocyclic units in place of one or more of the usual pyrrole rings. They exhibit unique spectroscopic properties and reactivity, including formation of organometallic derivatives under mild conditions (Lash, Colby & Ferrence, 2003). Related to our investigations into the synthesis, reactivity and structure of azulene-containing carbapophyrinoids, the title compound, (I), was prepared (see *Experimental*).



(I)

In the title structure (Fig. 1), the main macrocycle shows a small distortion from planarity; however, the azulene unit is significantly twisted. Excluding parameters involving the metal or solvent atoms, only two were identified as marginally unusual by *Mogul* (Bruno *et al.*, 2004). No particular reason beyond packing forces seems attributable to the marginally smaller [106.3 (3)°] C2*C*—C25—C28 bond angle, compared to the 110.3 (18)° average of 981 hits. The C2—C3—C3*A* bond angle [123.9 (3)°] is a few degrees smaller than the 127.2 (11)° average of 31 hits. This is attributable to the significant twist between the tropylium and cyclopentadienyl rings of the azulene, best represented by the torsion angles in Table 1. Most striking is the C2*A*—C2—C3—C3*A* torsion angle of −32.9 (6)°. Van der Waals contacts between azulene atoms H3*A* and H2*A* and the respective 5,20 aryl *ortho* carbon atoms C5*F* and C20*F* appear to cause the azulene twist (Fig. 2, black arrows).

The deviations of the 25-atom carbaporphyrinoid core from the metal coordination environment defined by the least-squares plane (Pd, C21, N22, N23, N24) are ±0.10 Å, with C17 and C18 [0.360 (4) and 0.408 (4) Å, respectively] having the

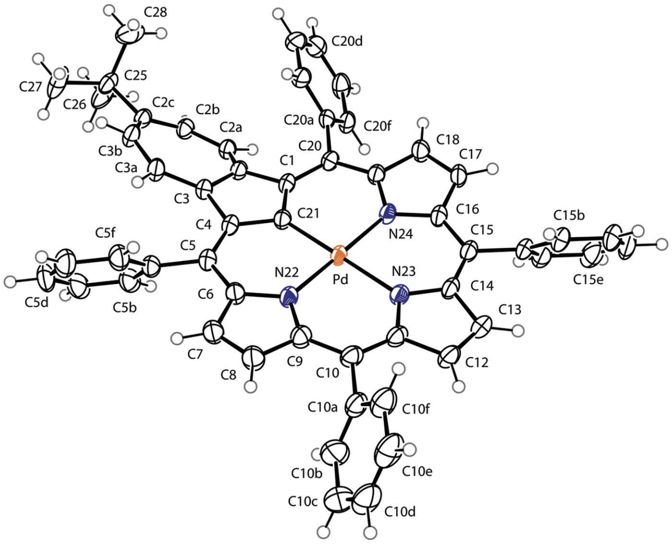


Figure 1
The molecular structure of compound (I), showing the atomic numbering scheme and displacement ellipsoids drawn at the 50% probability level. The solvent molecule has been omitted.

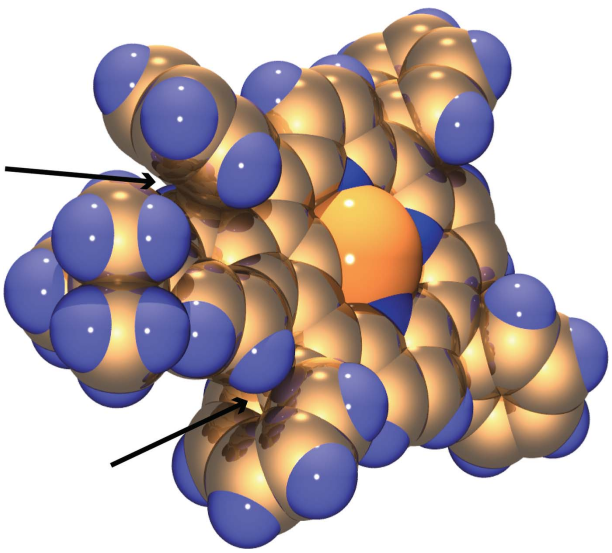


Figure 2
Space-filling illustration of (I), highlighting contacts between azulene and *meso*-phenyl units (black arrows).

largest displacements from this plane. The Pd^{II} ion resides in a nearly ideal four-coordinate square-planar geometry, centered between the donor ligands with equivalent *cis*-Pd—N bond lengths (Table 1), where *cis* and *trans* are defined relative to the azulene atom C21. These lengths fall within the typical 2.01 ± 0.02 Å range reported for palladium-coordinated porphyrin-type macrocycles; the *trans*-Pd1—N23 bond length is slightly longer [2.068 (3) Å]. This small *trans* influence indicates a strong Pd—C interaction, consistent with the shorter Pd—C21 bond length [1.975 (3) Å] .

Three azuliporphyrinato metal complexes, the only ones identified in the Cambridge Structural Database (Version 5.28; Allen, 2002), were previously reported by us (Lash, Colby, Graham *et al.*, 2003; Colby *et al.*, 2004; Graham *et al.*, 2002).

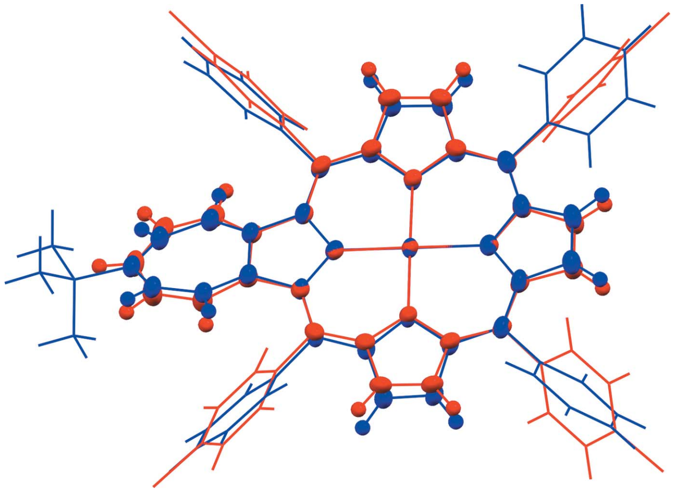


Figure 3
Superposition of the molecular structures of compound (I) (blue, without the solvent molecule) and [5,10,15,20-tetrakis(4-chlorophenyl)azuliporphyrinato]palladium(II) (red).

The structure of [5,10,15,20-tetrakis(4-chlorophenyl)azuliporphyrinato]palladium(II) is most similar to that of the title compound, (I) (Lash, Colby & Graham *et al.*, 2003). In fact, the presence of the 2^3-*tert*-butyl group on the azulene in (I) appears to impart no significant changes to the overall structure (Fig. 3). The metal coordination environments are indistinguishable, and even the azulene twists are very similar.

Experimental

The title compound was prepared following the literature procedures reported for the synthesis of (5,10,15,20-tetraphenylazuliporphyrinato)palladium(II) with the exception that 6-*tert*-butylazulene was substituted for azulene (Lash, Colby & Ference, 2003; Lash, Colby, Graham *et al.*, 2003; Colby & Lash, 2002). Crystallization of crude (2^3-*tert*-butyl-5,10,15,20-tetraphenylazuliporphyrinato)palladium(II) from dichloromethane afforded an X-ray quality crystal used for the diffraction experiment reported here.

Crystal data

$[Pd(C_{54}H_{39}N_3)]\cdot CH_2Cl_2$
$M_r = 921.21$
Triclinic, $P\bar{1}$
$a = 9.4468\ (10)$ Å
$b = 14.1354\ (15)$ Å
$c = 17.5228\ (19)$ Å
$\alpha = 110.1471\ (16)^\circ$
$\beta = 98.3972\ (17)^\circ$
$\gamma = 100.6142\ (16)^\circ$
$V = 2102.8\ (4)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.61$ mm^{-1}
$T = 193\ (2)$ K
0.59 × 0.45 × 0.25 mm

Data collection

Bruker P4/R4/SMART 1000 CCD diffractometer
Absorption correction: integration (*SHELXTL*; Bruker, 1999)
$T_{min} = 0.611$, $T_{max} = 0.862$
15585 measured reflections
8496 independent reflections
7724 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.166$
$S = 1.06$
8496 reflections
550 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 2.17$ e Å^{-3}
$\Delta\rho_{min} = -1.47$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd—C21	1.975 (3)	Pd—N24	2.027 (3)
Pd—N22	2.025 (3)	Pd—N23	2.068 (3)
C21—Pd—N22	90.10 (13)	N22—Pd—N23	90.08 (12)
C21—Pd—N24	90.42 (13)	N24—Pd—N23	89.43 (12)
C21—Pd—N23	179.05 (12)	N22—Pd—N24	177.96 (11)
C1—C2—C3—C3*A*	155.2 (3)	C20—C1—C2—C2*A*	26.8 (6)
C2*A*—C2—C3—C4	158.2 (3)	C3*A*—C3—C4—C5	22.7 (6)
C2*A*—C2—C3—C3*A*	−32.9 (6)	C2—C3—C4—C5	−169.0 (3)
C4—C21—C1—C20	168.3 (3)	C1—C21—C4—C5	176.2 (3)
C20—C1—C2—C3	−161.6 (3)		

All H atoms were initially identified in a difference Fourier synthesis and refined in the riding-model approximation, with isotropic displacement parameters fixed at $1.2U_{\rm eq}$ of the parent atom and with C—H = 0.95, 0.98 and 0.99 Å for aromatic, CH_3 and CH_2, respectively. The largest mismatches in electron density are close to the solvent: $\Delta\rho_{\rm max}$ is 1.18 Å from Cl2*S* and $\Delta\rho_{\rm min}$ is 0.66 Å from Cl1*S*.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* for Windows (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *publCIF* (Westrip, 2007).

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