

Dichlorobis(2,5-diphenyl-1,3,4-thiadiazole- κN^3)-
palladium(II)Peter J. Steel* and Chris
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Key indicators

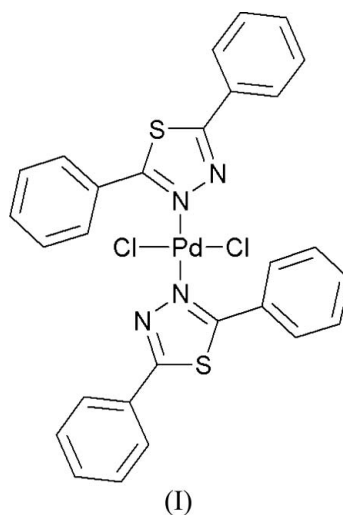
Single-crystal X-ray study
 $T = 168$ K
Mean $\sigma(C-C) = 0.006$ Å
 R factor = 0.031
 wR factor = 0.078
Data-to-parameter ratio = 13.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title complex, $[PdCl_2(C_{14}H_{10}N_2S)_2]$, crystallizes with two half-molecules in the asymmetric unit which have significantly different conformations of the aromatic rings of the coordinated ligands. The molecules are centrosymmetric.

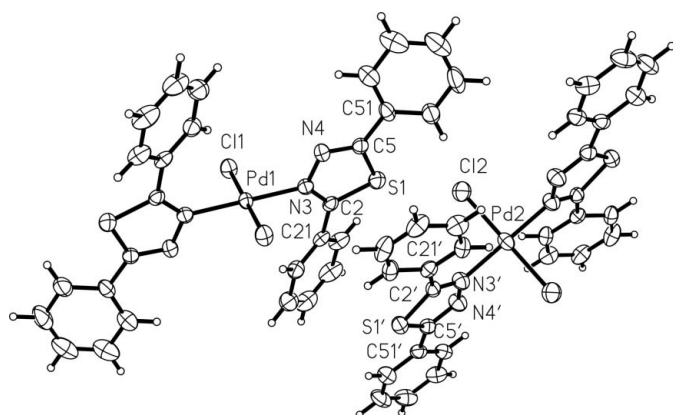
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Comment

We have long been involved in the synthesis and study of metal complexes of new heterocyclic ligands (Steel, 2005). In particular, we have been interested in the design of ligands incorporating less commonly studied heterocyclic ring systems, such as tetrazoles (Downard *et al.*, 1995), 1,2-benzisoxazoles (Richardson & Steel, 2000a), furoxans (Richardson & Steel, 2000b), 1,2,5-oxadiazoles and 1,2,5-thiadiazoles (Richardson & Steel, 2001; Richardson *et al.*, 2002), 1,2,3-thiadiazoles (and selenadiazoles) (Richardson & Steel, 2002), pyridazines (Sumbly & Steel, 2003), 1,4,2,5-dioxadiazines (Richardson & Steel, 2003a), benzotriazoles (Richardson & Steel, 2003b; Borsting & Steel, 2004), and thiazolo[5,4-*d*]thiazoles (Zampese *et al.*, 2004). 2,5-Diphenyl-1,3,4-thiadiazole has been known for more than half a century (Chabrier *et al.*, 1949), but the first metal complex containing this ligand was reported only recently (Franski & Gierczyk, 2005). We now report the synthesis and X-ray crystal structure of its complex, (I), with palladium(II) chloride.



Complex (I) was prepared in high yield by reaction of two equivalents of 2,5-diphenyl-1,3,4-thiadiazole with one equivalent of lithium tetrachloropalladate(II). It crystallizes in the triclinic space group $P\bar{1}$ with two half-molecules in the asymmetric unit, the two independent Pd atoms each lying on a crystallographic centre of inversion. The bonding geometry

**Figure 1**

The structures of the two independent centrosymmetric molecules of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small circles of arbitrary radii. Unlabelled atoms in the Pd1 molecule are related to labelled atoms by the symmetry operator $(-x, -y + 1, -z)$. Unlabelled atoms in the Pd2 molecule are related to labelled atoms by the symmetry operator $(-x + 1, -y + 1, -z + 1)$.

within the coordinated ligands is similar to that of the free ligand (Zvonkova & Khvatkina, 1965). The planes of the coordinated thiadiazoles are inclined to the palladium coordination planes at angles of 78.4 (3) and 80.0 (3)° for the Pd1 and Pd2 molecules, respectively. The planes of the phenyl rings are inclined to the mean plane of the attached thiadiazole ring at angles of 32.2 (3) and 21.6 (3)° for the Pd1 molecule and 19.2 (3) and 4.4 (3)° for the Pd2 molecule. The corresponding value for the free ligand is 25.2°.

Experimental

A methanol solution (3.0 ml) of Li_2PdCl_4 (119 mg, 0.453 mmol) was added to 2,5-diphenyl-1,3,4-thiadiazole (205.4 mg, 0.863 mmol) dissolved in methanol (30 ml). The resulting yellow precipitate was filtered off and washed with methanol. Recrystallization by vapour diffusion of methanol into a dimethylformamide solution of complex (I) gave a yellow crystalline product suitable for crystal structure determination (yield 269 mg, 95%; m.p. 498–510 K). Analysis, found: C 51.43, H 3.02, N 8.60, Cl 10.96%; $\text{C}_{28}\text{H}_{20}\text{N}_4\text{Cl}_2\text{PdS}_2$ requires: C 51.43, H 3.08, N 8.57, Cl 10.84%.

Crystal data

| | |
|---|---|
| $[\text{PdCl}_2(\text{C}_{14}\text{H}_{10}\text{N}_2\text{S})_2]$ | $V = 1342.7 (5) \text{ \AA}^3$ |
| $M_r = 653.90$ | $Z = 2$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.617 \text{ Mg m}^{-3}$ |
| $a = 10.228 (2) \text{ \AA}$ | Mo $K\alpha$ radiation |
| $b = 10.599 (3) \text{ \AA}$ | $\mu = 1.07 \text{ mm}^{-1}$ |
| $c = 14.095 (3) \text{ \AA}$ | $T = 168 (2) \text{ K}$ |
| $\alpha = 86.469 (5)^\circ$ | Plate, yellow |
| $\beta = 86.684 (7)^\circ$ | $0.45 \times 0.25 \times 0.06 \text{ mm}$ |
| $\gamma = 61.745 (4)^\circ$ | |

Data collection

| | |
|---|--|
| Bruker SMART CCD area-detector diffractometer | 14799 measured reflections |
| φ and ω scans | 4579 independent reflections |
| Absorption correction: multi-scan (SADABS; Sheldrick, 2002) | 3417 reflections with $I > 2\sigma(I)$ |
| $T_{\min} = 0.776$, $T_{\max} = 0.938$ | $R_{\text{int}} = 0.029$ |
| | $\theta_{\text{max}} = 25.1^\circ$ |

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.078$
 $S = 0.96$
 4579 reflections
 337 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0462P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.70 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.87 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

| | | | |
|--------------|-------------|--------------|-----------|
| Pd1—N3 | 2.008 (3) | C2—C21 | 1.464 (5) |
| Pd1—Cl1 | 2.3064 (9) | C2'—N3' | 1.320 (4) |
| Pd2—N3' | 2.002 (3) | C2'—C21' | 1.459 (5) |
| Pd2—Cl2 | 2.3042 (10) | N3—N4 | 1.371 (4) |
| S1—C2 | 1.710 (3) | N3'—N4' | 1.381 (4) |
| S1—C5 | 1.716 (4) | N4—C5 | 1.305 (4) |
| S1'—C2' | 1.724 (4) | N4'—C5' | 1.312 (4) |
| S1'—C5' | 1.734 (3) | C5—C51 | 1.473 (5) |
| C2—N3 | 1.317 (4) | C5'—C51' | 1.471 (5) |
| N3—Pd1—Cl1 | 89.02 (8) | N4—N3—Pd1 | 116.2 (2) |
| N3'—Pd2—Cl2 | 90.49 (9) | C2'—N3'—N4' | 115.6 (3) |
| C2—S1—C5 | 88.06 (16) | C2'—N3'—Pd2 | 131.5 (2) |
| C2'—S1'—C5' | 88.66 (17) | N4'—N3'—Pd2 | 113.0 (2) |
| N3—C2—C21 | 126.5 (3) | C5—N4—N3 | 110.7 (3) |
| N3—C2—S1 | 112.0 (3) | C5'—N4'—N3' | 110.8 (3) |
| C21—C2—S1 | 121.5 (2) | N4—C5—C51 | 123.2 (3) |
| N3'—C2'—C21' | 126.2 (3) | N4—C5—S1 | 114.6 (3) |
| N3'—C2'—S1' | 111.1 (3) | C51—C5—S1 | 122.1 (3) |
| C21'—C2'—S1' | 122.7 (2) | N4'—C5'—C51' | 122.0 (3) |
| C2—N3—N4 | 114.7 (3) | N4'—C5'—S1' | 113.8 (3) |
| C2—N3—Pd1 | 129.1 (2) | C51'—C5'—S1' | 124.2 (3) |

H atoms were placed in calculated positions, with C—H distances set at 0.95 Å, and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

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

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