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# Synthesis, crystal structure and Hirshfeld surface analysis of bis[*N*-(4-chlorobenzyl)-*N*-dodecyldithiocarbamato-$\kappa^2S,S'$]palladium(II)

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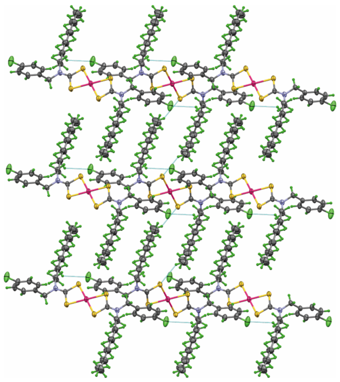
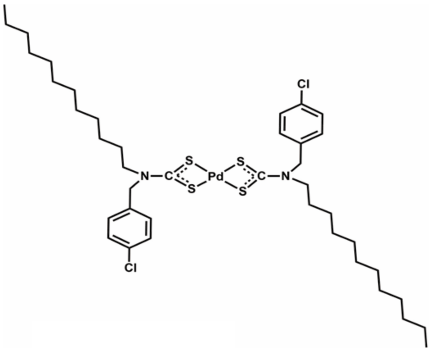
The title compound, [Pd($C_{20}H_{31}ClNS_2$)$_2$], crystallizes about an inversion centre in the monoclinic space group *C*2/*c*. The $Pd^{II}$ cation adopts a square-planar coordination geometry defined by four sulfur atoms from two *N*-(4-chlorobenzyl)-*N*-dodecyldithiocarbamate anions. The crystal packing features C—H⋯S hydrogen bonds, which form a belt motif. Hirshfeld surface analysis indicates that H⋯H (62.9%), S⋯H/H⋯S (14.0%) and Cl⋯H/H⋯Cl (11.1%) contacts dominate the intermolecular interactions.



## 1. Chemical context

Dithiocarbamates ($R_2NCS_2^-$) form stable complexes with transition metals, lanthanides and actinides (Hogarth *et al.*, 2005; Hitchcock *et al.*, 2004; Mahato *et al.*, 2015; Behrle *et al.*, 2018). They can bind to metals in nine distinct coordination modes. The most common of these are monodentate and chelating bidentate coordination modes (Hogarth *et al.*, 2005). The properties of complexes are influenced by the electronic configuration of the central metal cation and N-bonded organic (*R*) moiety of dithiocarbamate ligands (Hogarth *et al.*, 2012; Godoy-Alcántar *et al.*, 2025). Metal–dithiocarbamate complexes exhibit a wide range of applications in various fields, including catalysis, sensors, medicine, material science and rubber manufacturing (Ajiboye *et al.*, 2022). In particular, $Pd^{II}$ dithiocarbamate complexes show important biological activities, *viz.* antibacterial (Khan *et al.*, 2016), antifungal (Ferreira *et al.*, 2014), anticancer (Khan *et al.*, 2016; Khan *et al.*, 2011). Several studies on metal dithiocarbamate complexes indicated that the length of the alkyl chain (*R*) of the dithiocarbamate ligand enhances the solubility and activity of complexes (Hogarth *et al.*, 2012).



As part of our work in this area, we report here the synthesis, crystal structure and Hirshfeld surface analysis of a

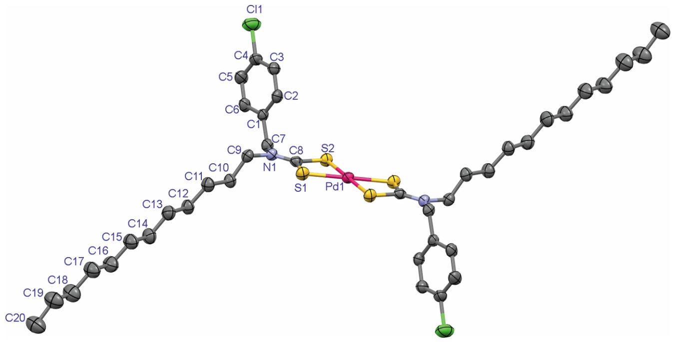


**Figure 1**
The molecular structure of the title complex, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. Symmetry-generated atoms were generated by the operation $x + \frac{3}{2}, -y + \frac{5}{2}, -z + 1$.

Pd$^{II}$ dithiocarbamate complex containing a long-chain alkyl group (dodecyl) (Fig. 1).

## 2. Structural commentary

The title complex crystallizes in the monoclinic space group *C2/c*. It is a four-coordinated structure in which the palladium atom is coordinated by four sulfur atoms from two *N*-(4-chlorobenzyl)-*N*-dodecyldithiocarbamate ligands (Fig. 1). This four-coordinate geometry results in square planar spatial configuration. The bond parameters for the metal–ligand interactions are Pd—S1 = 2.3166 (12) Å, Pd—S2 = 2.3271 (10) Å and the chelate angle S1—Pd—S2 is 75.32 (4) °.

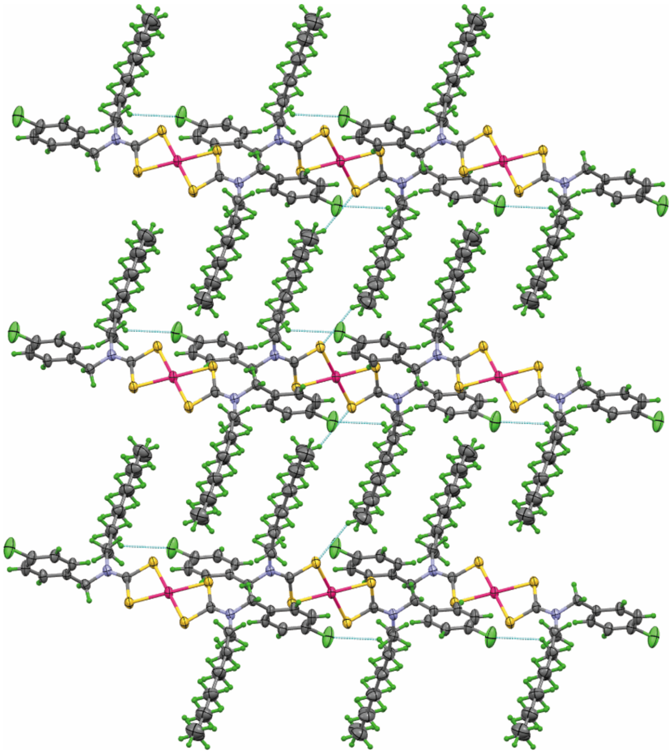


**Figure 2**
Packing of the title complex viewed along the *b* axis.

**Table 1**
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C1–C6 ring.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C19—H19*B*···S1$^{i}$ | 0.97 | 2.91 | 3.676 (6) | 137 |
| C12—H12*A*···Cl1$^{ii}$ | 0.97 | 2.90 | 3.602 (2) | 130 |
| C10—H10*B*···*Cg*1$^{iii}$ | 0.97 | 3.24 | 3.982 (3) | 134 |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x, -y+2, z+\frac{1}{2}$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

These values are typical for Pd$^{II}$ dithiocarbamate complexes and indicate an even bonding of the palladium with the two ligand S atoms, without pronounced asymmetry in the bond lengths. For the metal coordination sphere, the calculated root-mean-square deviation = 0.00 Å, reflecting an almost perfect planarity of the S1, S2, S1$^{i}$, S2$^{i}$ coordination [symmetry code: (i) $x + \frac{3}{2}, -y + \frac{5}{2}, -z + 1$] around the Pd$^{II}$ atom. The $\tau_4$ index (Yang *et al.*, 2007) relative to the ideal square-planar geometry ($D_{4h}$) was calculated to quantitatively assess the degree of distortion of four-coordinate environment around Pd$^{II}$. For the title complex, the calculated $\tau_4$ value is 0.0, which suggests that the title complex has an ideal square-planar geometry.

The C8—N1 bond is significantly shorter than C7—N1 and C9—N1 bonds, an observation nsistent with a significant contribution of the $R_2NCS_2{}^{1-}$ canonical form to the overall electronic structure of the dithiocarbamate ligand. The C8—S1 and C8—S2 bond lengths are almost equal [Δ(C—S) = 0.008 Å], showing the symmetric bidentate coordination of dithiocarbamate ligands.

## 3. Supramolecular features and Hirshfeld surface analysis

In the crystal, two C—H···S hydrogen bonds are observed between the sulfur atoms (S1 and S1$^{i}$) of the dithiocarbamate

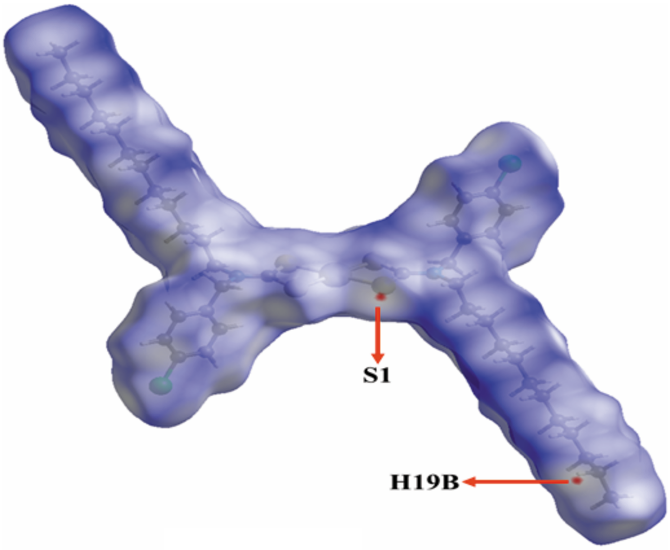


**Figure 3**
Hirshfeld surface mapped over $d_{\rm norm}$, showing close intermolecular contacts, with red regions highlighting the S1···H19*B* interaction.

*Acta Cryst.* (2026). E**82**, 384–387 Pallavi *et al.* • [Pd(C$_{20}$H$_{31}$ClNS$_2$)$_2$] 385

functional group and neighbouring methyl group hydrogen atoms (H19*B*), which leads to the formation of a belt motif along the *b*-axis direction. Additional C—H···Cl interactions further contribute to the supramolecular arrangement (Table 1, Fig. 2).

A Hirshfeld surface analysis was performed using *CrystalExplorer 21.0* (Spackman *et al.*, 2021). The Hirshfeld surface and fingerprint plot calculations were performed on the entire molecule. The Hirshfeld surface mapped with $d_{\rm norm}$ is shown in Fig. 3, where white regions indicate contacts at van der Waals separations, red spots denote shorter contacts (*e.g.* hydrogen bonds) and blue regions indicate longer contacts. Thus, the red regions of the surface correspond to the S1···H19*B* interaction.

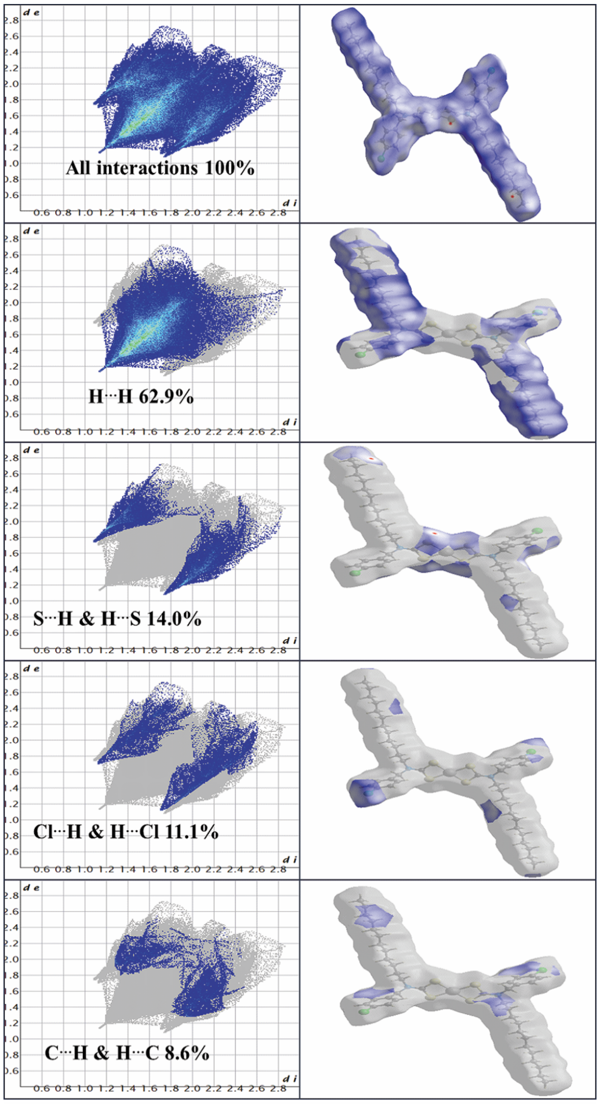


**Figure 4**
Two-dimensional fingerprint plots and the corresponding Hirshfeld surface mapped over $d_{\rm norm}$ for the title complex, showing the overall intermolecular interactions and their relative contributions, including H···H (62.9%), S···H/H···S (14.0%), Cl···H/H···Cl (11.1%) and C···H/H···C (8.6%) contacts.

The overall two-dimensional fingerprint plot (Fig. 4) shows that the largest contribution to the surface interactions arises from H···H contacts, accounting for 62.9%. This is typical for complexes with a high degree of hydrogen saturation and indicates dense molecular packing (Tojiboyeva *et al.*, 2025). The S···H/H···S (14.0%) and Cl···H/H···Cl (11.1%) contacts are consistent with the crystal packing data (Fig. 5), while Pd···H/H···Pd, Pd···Cl/H···Cl, C···C, S···Cl/Cl···S, C···Cl/Cl···C and N···C/C···N make only a small contribution. The crystal-packing data reveal the presence of significant hydrogen-bonding interactions. Minor contributions (1%) from Pd···H/H···Pd are important because complexes with *M*···H interactions are believed to act as catalysts in the synthesis of organic compounds (Wang *et al.*, 2025)

## 4. Synthesis and crystallization

*N*-(4-chlorobenzyl)-*N*-dodecylamine was synthesized (Fig. 5) by a procedure reported earlier (Gokul *et al.* 2025). 4-Chlorobenzaldehyde (5.3 mmol) and dodecylamine (4.6 mmol) were dissolved in methanol and the reaction mixture was stirred at room temperature for 4 h. After completion of the imine formation, sodium borohydride (13.6 mmol) was added portionwise to the reaction mixture under stirring. The reaction was allowed to proceed at room temperature until complete reduction was achieved. The solvent was removed and the amine was partitioned between

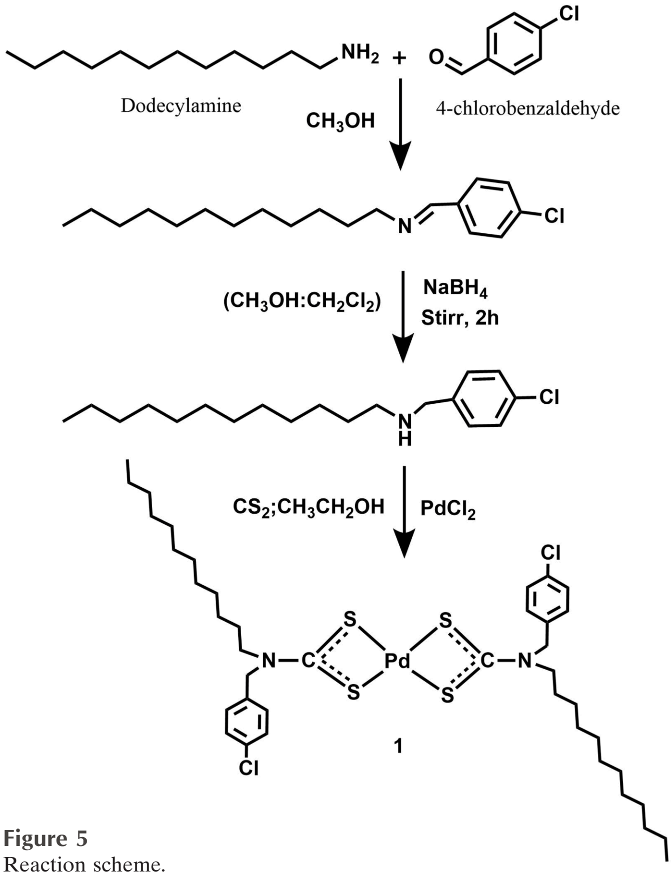


**Figure 5**
Reaction scheme.

dichloromethane and water. The organic layer was separated and evaporated to afford the corresponding amine. This was dissolved in 20 mL of ethanol. 4 mmol of NaOH in an aqueous solution were added to the amine solution followed by $CS_2$ (4 mmol) at 278 K and stirred for 30 min. An aqueous solution of $PdCl_2$ (2 mmol) was added to the reaction mixture. The obtained solid was purified by washing with ethanol and water and dried in a desiccator (yield: 61%). Single crystals appropriate for X-ray crystallographic analysis were successfully obtained by slow evaporation of a chloroform–acetonitrile solution. M.p. 392–394 K. IR (ATR), $v$ ($cm^{-1}$): 1496 [C—N (thioureide)], 964 (C—S). $^1$H NMR (400MHz, $CDCl_3$): $\delta$ 7.33 ($d$, $J$ = 8.0 MHz, 4H), 7.24 ($d$, $J$ = 8.4 MHz, 4H), 4.87 ($s$, 4H, 4-$ClC_6H_4$-$\mathbf{CH}_2$), 3.56 [$t$, $J$ = 8.0 MHz, 4H, $CH_3$-$(CH_2)_9$-$CH_2$-$\mathbf{CH}_2$-N], 1.62 [$b$, 4H, (N-$CH_2$-$\mathbf{CH}_2$-$(CH_2)_9$-$CH_3$], 1.25 [$b$, 36H, $CH_3$-$(\mathbf{CH}_2)_9$-$CH_2$-$CH_2$-N], 0.88 {$t$, $J$ = 7.2 MHz, 6H [$\mathbf{CH}_3$-$(CH_2)_9$-$CH_2$-$CH_2$-N]}. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ 129.1, 129.5, 132.9, 134.2 (aromatic carbons), 22.7, 26.7, 26.8, 29.1, 29.3, 29.4, 29.5, 29.6, 31.9 [$CH_3$-$(\mathbf{CH}_2)_{10}$-$CH_2$-N], 14.1 [$\mathbf{C}H_3$-$(CH_2)_{10}$-$CH_2$-N], 51.5 (4-$ClC_6H_4$-$\mathbf{C}H_2$-N), 49.1 [$CH_3$-$(CH_2)\mathbf{C}H_2$-N]. Analysis calculated for $C_{40}H_{62}Cl_2N_2PdS_4$: C; 54.81, H; 7.13, N; 3.20. Found: C; 54.61, H; 7.09, N; 3.18.

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $[Pd(C_{20}H_{31}ClNS_2)_2]$ |
| $M_r$ | 876.46 |
| Crystal system, space group | Monoclinic, $C2/c$ |
| Temperature (K) | 300 |
| $a$, $b$, $c$ (Å) | 24.348 (2), 10.0966 (10), 18.3551 (17) |
| $\beta$ (°) | 91.168 (3) |
| $V$ (Å$^3$) | 4511.3 (7) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ ($mm^{-1}$) | 0.74 |
| Crystal size (mm) | 0.14 × 0.12 × 0.05 |
| Data collection | |
| Diffractometer | Bruker D8 QUEST |
| Absorption correction | Multi-scan (*SADABS*; Krause *et al.*, 2015) |
| $T_{min}$, $T_{max}$ | 0.904, 0.965 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 52590, 5647, 2891 |
| $R_{int}$ | 0.089 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.061, 0.110, 1.14 |
| No. of reflections | 5647 |
| No. of parameters | 224 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.44, −0.42 |

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2019/2* (Sheldrick, 2015*b*) and *ShelXle* (Hübschle *et al.*, 2011).

## 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were positioned geometrically (C—H = 0.93–0.97 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$.

## Acknowledgements

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*Acta Cryst.* (2026). E**82**, 384–387 Pallavi *et al.* • $[Pd(C_{20}H_{31}ClNS_2)_2]$ **387**

# supporting information

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## Synthesis, crystal structure and Hirshfeld surface analysis of bis[*N*-(4-chlorobenzyl)-*N*-dodecyldithiocarbamato-$\kappa^2S,S'$]palladium(II)

**R. Pallavi, N. Srinivasan and S. Thirumaran**

### Computing details

### Bis[*N*-(4-chlorobenzyl)-*N*-dodecyldithiocarbamato-$\kappa^2S,S'$]palladium(II)

*Crystal data*

| | |
|---|---|
| $[Pd(C_{20}H_{31}ClNS_2)_2]$ | $F(000) = 1840$ |
| $M_r = 876.46$ | $D_x = 1.291$ Mg m$^{-3}$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 24.348$ (2) Å | Cell parameters from 9549 reflections |
| $b = 10.0966$ (10) Å | $\theta = 2.2$–$24.0°$ |
| $c = 18.3551$ (17) Å | $\mu = 0.74$ mm$^{-1}$ |
| $\beta = 91.168$ (3)° | $T = 300$ K |
| $V = 4511.3$ (7) Å$^3$ | Block, gold |
| $Z = 4$ | 0.14 × 0.12 × 0.05 mm |

*Data collection*

| | |
|---|---|
| Bruker D8 QUEST diffractometer | $T_{min} = 0.904$, $T_{max} = 0.965$ |
| Radiation source: microfocus sealed tube, INCOATEC I$\mu$S 3.0 | 52590 measured reflections |
| | 5647 independent reflections |
| | 2891 reflections with $I > 2\sigma(I)$ |
| Multilayer mirror monochromator | $R_{int} = 0.089$ |
| Detector resolution: 7.391 pixels mm$^{-1}$ | $\theta_{max} = 28.4°$, $\theta_{min} = 2.2°$ |
| $\omega$ and $\varphi$ scans | $h = -32\rightarrow32$ |
| Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015) | $k = -13\rightarrow13$ |
| | $l = -24\rightarrow24$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.061$ | $w = 1/[\sigma^2(F_o^2) + (0.0142P)^2 + 9.2012P]$ |
| $wR(F^2) = 0.110$ | $(\Delta/\sigma)_{max} < 0.001$ |
| $S = 1.14$ | $\Delta\rho_{max} = 0.44$ e Å$^{-3}$ |
| 5647 reflections | $\Delta\rho_{min} = -0.42$ e Å$^{-3}$ |
| 224 parameters | |
| 0 restraints | |

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Pd1 | 0.750000 | 1.250000 | 0.500000 | 0.06117 (16) |

| | | | | |
|---|---|---|---|---|
| Cl1 | 0.64664 (9) | 1.42872 (16) | 0.00819 (8) | 0.1468 (7) |
| S1 | 0.68053 (5) | 1.11956 (12) | 0.45024 (5) | 0.0715 (3) |
| S2 | 0.77378 (5) | 1.22145 (11) | 0.37885 (5) | 0.0687 (3) |
| N1 | 0.69935 (13) | 1.0645 (3) | 0.30989 (16) | 0.0595 (9) |
| C1 | 0.70804 (16) | 1.1576 (4) | 0.1853 (2) | 0.0574 (10) |
| C2 | 0.68411 (18) | 1.2774 (4) | 0.2019 (2) | 0.0688 (12) |
| H2 | 0.680701 | 1.302004 | 0.250375 | 0.083* |
| C3 | 0.66525 (19) | 1.3609 (4) | 0.1480 (2) | 0.0761 (13) |
| H3 | 0.649283 | 1.441608 | 0.159793 | 0.091* |
| C4 | 0.6702 (2) | 1.3242 (5) | 0.0765 (2) | 0.0832 (14) |
| C5 | 0.6933 (2) | 1.2056 (5) | 0.0588 (2) | 0.0880 (15) |
| H5 | 0.696394 | 1.181219 | 0.010160 | 0.106* |
| C6 | 0.71187 (19) | 1.1229 (4) | 0.1130 (2) | 0.0736 (13) |
| H6 | 0.727339 | 1.041857 | 0.100787 | 0.088* |
| C7 | 0.73172 (16) | 1.0684 (4) | 0.2435 (2) | 0.0641 (11) |
| H7A | 0.734460 | 0.979389 | 0.224102 | 0.077* |
| H7B | 0.768595 | 1.098199 | 0.256033 | 0.077* |
| C8 | 0.71556 (16) | 1.1252 (4) | 0.3701 (2) | 0.0578 (10) |
| C9 | 0.64853 (17) | 0.9868 (4) | 0.3065 (2) | 0.0677 (12) |
| H9A | 0.629255 | 1.005795 | 0.260961 | 0.081* |
| H9B | 0.625118 | 1.014413 | 0.345899 | 0.081* |
| C10 | 0.65798 (17) | 0.8399 (4) | 0.3121 (2) | 0.0695 (12) |
| H10A | 0.675688 | 0.809339 | 0.268330 | 0.083* |
| H10B | 0.682612 | 0.822043 | 0.353150 | 0.083* |
| C11 | 0.60555 (18) | 0.7636 (5) | 0.3217 (2) | 0.0798 (13) |
| H11A | 0.590424 | 0.786847 | 0.368486 | 0.096* |
| H11B | 0.579308 | 0.791221 | 0.284252 | 0.096* |
| C12 | 0.61147 (18) | 0.6160 (5) | 0.3182 (2) | 0.0779 (13) |
| H12A | 0.641449 | 0.589028 | 0.350463 | 0.093* |
| H12B | 0.620959 | 0.590964 | 0.268979 | 0.093* |
| C13 | 0.55992 (19) | 0.5430 (5) | 0.3392 (3) | 0.0909 (15) |
| H13A | 0.549204 | 0.573552 | 0.386946 | 0.109* |
| H13B | 0.530705 | 0.566729 | 0.304935 | 0.109* |
| C14 | 0.5644 (2) | 0.3959 (5) | 0.3413 (3) | 0.0973 (16) |
| H14A | 0.593812 | 0.371267 | 0.375025 | 0.117* |
| H14B | 0.574098 | 0.364244 | 0.293312 | 0.117* |
| C15 | 0.5115 (2) | 0.3280 (5) | 0.3642 (3) | 0.1018 (17) |
| H15A | 0.502421 | 0.357928 | 0.412689 | 0.122* |
| H15B | 0.481910 | 0.354883 | 0.331267 | 0.122* |
| C16 | 0.5149 (2) | 0.1805 (6) | 0.3644 (3) | 0.1073 (18) |
| H16A | 0.525073 | 0.151296 | 0.316190 | 0.129* |
| H16B | 0.544204 | 0.154156 | 0.398044 | 0.129* |
| C17 | 0.4637 (2) | 0.1101 (6) | 0.3850 (3) | 0.1143 (19) |
| H17A | 0.434238 | 0.135662 | 0.351527 | 0.137* |
| H17B | 0.453546 | 0.137875 | 0.433484 | 0.137* |
| C18 | 0.4695 (2) | −0.0404 (6) | 0.3840 (4) | 0.123 (2) |
| H18A | 0.478499 | −0.067410 | 0.334920 | 0.147* |
| H18B | 0.500277 | −0.064610 | 0.415632 | 0.147* |

| | | | | |
|---|---|---|---|---|
| C19 | 0.4224 (2) | −0.1139 (6) | 0.4060 (4) | 0.128 (2) |
| H19A | 0.392454 | −0.096021 | 0.371693 | 0.153* |
| H19B | 0.411336 | −0.081435 | 0.453262 | 0.153* |
| C20 | 0.4301 (3) | −0.2613 (6) | 0.4111 (4) | 0.141 (2) |
| H20A | 0.397226 | −0.301396 | 0.428682 | 0.212* |
| H20B | 0.460211 | −0.280590 | 0.444016 | 0.212* |
| H20C | 0.437974 | −0.296058 | 0.363713 | 0.212* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Pd1 | 0.0802 (3) | 0.0613 (3) | 0.0421 (2) | −0.0022 (3) | 0.0038 (2) | 0.0030 (2) |
| Cl1 | 0.253 (2) | 0.1099 (12) | 0.0762 (10) | 0.0300 (13) | −0.0338 (11) | 0.0153 (8) |
| S1 | 0.0860 (8) | 0.0804 (8) | 0.0484 (6) | −0.0111 (6) | 0.0111 (6) | 0.0011 (6) |
| S2 | 0.0813 (8) | 0.0776 (8) | 0.0474 (6) | −0.0123 (6) | 0.0082 (5) | 0.0001 (5) |
| N1 | 0.070 (2) | 0.062 (2) | 0.046 (2) | 0.0002 (18) | 0.0076 (17) | −0.0028 (16) |
| C1 | 0.069 (3) | 0.058 (3) | 0.045 (2) | −0.006 (2) | 0.003 (2) | −0.003 (2) |
| C2 | 0.091 (3) | 0.070 (3) | 0.045 (2) | 0.002 (2) | −0.001 (2) | −0.016 (2) |
| C3 | 0.102 (4) | 0.064 (3) | 0.062 (3) | 0.008 (3) | −0.004 (3) | −0.008 (2) |
| C4 | 0.124 (4) | 0.067 (3) | 0.058 (3) | −0.003 (3) | −0.012 (3) | 0.007 (2) |
| C5 | 0.139 (5) | 0.079 (4) | 0.046 (3) | −0.004 (3) | 0.002 (3) | −0.005 (2) |
| C6 | 0.105 (4) | 0.066 (3) | 0.050 (3) | −0.004 (3) | 0.009 (2) | −0.012 (2) |
| C7 | 0.071 (3) | 0.067 (3) | 0.055 (3) | 0.001 (2) | 0.009 (2) | −0.007 (2) |
| C8 | 0.074 (3) | 0.053 (2) | 0.047 (2) | 0.007 (2) | 0.005 (2) | 0.0039 (19) |
| C9 | 0.068 (3) | 0.076 (3) | 0.059 (3) | −0.001 (2) | −0.001 (2) | −0.004 (2) |
| C10 | 0.072 (3) | 0.069 (3) | 0.068 (3) | −0.004 (2) | 0.009 (2) | −0.007 (2) |
| C11 | 0.077 (3) | 0.084 (4) | 0.079 (3) | −0.011 (3) | 0.008 (2) | −0.001 (3) |
| C12 | 0.082 (3) | 0.079 (4) | 0.073 (3) | −0.015 (3) | 0.008 (2) | −0.003 (3) |
| C13 | 0.083 (4) | 0.093 (4) | 0.096 (4) | −0.013 (3) | −0.008 (3) | 0.008 (3) |
| C14 | 0.087 (4) | 0.097 (4) | 0.107 (4) | −0.019 (3) | 0.000 (3) | 0.004 (3) |
| C15 | 0.085 (4) | 0.093 (4) | 0.127 (5) | −0.014 (3) | −0.001 (3) | 0.014 (4) |
| C16 | 0.082 (4) | 0.104 (5) | 0.136 (5) | −0.010 (3) | −0.003 (3) | 0.009 (4) |
| C17 | 0.090 (4) | 0.102 (5) | 0.151 (5) | −0.018 (4) | 0.006 (4) | 0.022 (4) |
| C18 | 0.100 (5) | 0.116 (5) | 0.153 (6) | −0.004 (4) | 0.022 (4) | 0.009 (4) |
| C19 | 0.113 (5) | 0.120 (5) | 0.151 (6) | −0.004 (4) | 0.032 (4) | 0.023 (4) |
| C20 | 0.127 (5) | 0.109 (5) | 0.189 (7) | 0.003 (4) | 0.025 (5) | 0.020 (5) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Pd1—S1$^{i}$ | 2.3165 (12) | C11—H11A | 0.9700 |
| Pd1—S1 | 2.3166 (12) | C11—H11B | 0.9700 |
| Pd1—S2$^{i}$ | 2.3271 (10) | C12—C13 | 1.513 (6) |
| Pd1—S2 | 2.3271 (10) | C12—H12A | 0.9700 |
| Cl1—C4 | 1.728 (5) | C12—H12B | 0.9700 |
| S1—C8 | 1.716 (4) | C13—C14 | 1.489 (6) |
| S2—C8 | 1.724 (4) | C13—H13A | 0.9700 |
| N1—C8 | 1.318 (4) | C13—H13B | 0.9700 |
| N1—C7 | 1.465 (4) | C14—C15 | 1.526 (6) |

| | | | |
|---|---|---|---|
| N1—C9 | 1.465 (5) | C14—H14A | 0.9700 |
| C1—C6 | 1.379 (5) | C14—H14B | 0.9700 |
| C1—C2 | 1.379 (5) | C15—C16 | 1.491 (6) |
| C1—C7 | 1.503 (5) | C15—H15A | 0.9700 |
| C2—C3 | 1.372 (5) | C15—H15B | 0.9700 |
| C2—H2 | 0.9300 | C16—C17 | 1.491 (6) |
| C3—C4 | 1.371 (6) | C16—H16A | 0.9700 |
| C3—H3 | 0.9300 | C16—H16B | 0.9700 |
| C4—C5 | 1.364 (6) | C17—C18 | 1.526 (7) |
| C5—C6 | 1.369 (6) | C17—H17A | 0.9700 |
| C5—H5 | 0.9300 | C17—H17B | 0.9700 |
| C6—H6 | 0.9300 | C18—C19 | 1.432 (7) |
| C7—H7A | 0.9700 | C18—H18A | 0.9700 |
| C7—H7B | 0.9700 | C18—H18B | 0.9700 |
| C9—C10 | 1.505 (5) | C19—C20 | 1.503 (7) |
| C9—H9A | 0.9700 | C19—H19A | 0.9700 |
| C9—H9B | 0.9700 | C19—H19B | 0.9700 |
| C10—C11 | 1.504 (5) | C20—H20A | 0.9600 |
| C10—H10A | 0.9700 | C20—H20B | 0.9600 |
| C10—H10B | 0.9700 | C20—H20C | 0.9600 |
| C11—C12 | 1.498 (6) | | |

| | | | |
|---|---|---|---|
| S1$^{i}$—Pd1—S1 | 180.0 | H11A—C11—H11B | 107.5 |
| S1$^{i}$—Pd1—S2$^{i}$ | 75.32 (4) | C11—C12—C13 | 113.1 (4) |
| S1—Pd1—S2$^{i}$ | 104.68 (4) | C11—C12—H12A | 109.0 |
| S1$^{i}$—Pd1—S2 | 104.67 (4) | C13—C12—H12A | 109.0 |
| S1—Pd1—S2 | 75.33 (4) | C11—C12—H12B | 109.0 |
| S2$^{i}$—Pd1—S2 | 180.0 | C13—C12—H12B | 109.0 |
| C8—S1—Pd1 | 86.98 (14) | H12A—C12—H12B | 107.8 |
| C8—S2—Pd1 | 86.47 (13) | C14—C13—C12 | 115.6 (4) |
| C8—N1—C7 | 121.9 (3) | C14—C13—H13A | 108.4 |
| C8—N1—C9 | 121.5 (3) | C12—C13—H13A | 108.4 |
| C7—N1—C9 | 116.6 (3) | C14—C13—H13B | 108.4 |
| C6—C1—C2 | 118.2 (4) | C12—C13—H13B | 108.4 |
| C6—C1—C7 | 120.0 (4) | H13A—C13—H13B | 107.4 |
| C2—C1—C7 | 121.8 (3) | C13—C14—C15 | 113.2 (5) |
| C3—C2—C1 | 121.2 (4) | C13—C14—H14A | 108.9 |
| C3—C2—H2 | 119.4 | C15—C14—H14A | 108.9 |
| C1—C2—H2 | 119.4 | C13—C14—H14B | 108.9 |
| C4—C3—C2 | 119.3 (4) | C15—C14—H14B | 108.9 |
| C4—C3—H3 | 120.4 | H14A—C14—H14B | 107.8 |
| C2—C3—H3 | 120.4 | C16—C15—C14 | 113.7 (5) |
| C5—C4—C3 | 120.7 (4) | C16—C15—H15A | 108.8 |
| C5—C4—Cl1 | 119.7 (4) | C14—C15—H15A | 108.8 |
| C3—C4—Cl1 | 119.6 (4) | C16—C15—H15B | 108.8 |
| C4—C5—C6 | 119.6 (4) | C14—C15—H15B | 108.8 |
| C4—C5—H5 | 120.2 | H15A—C15—H15B | 107.7 |
| C6—C5—H5 | 120.2 | C17—C16—C15 | 115.4 (5) |

| | | | |
|---|---|---|---|
| C5—C6—C1 | 121.2 (4) | C17—C16—H16A | 108.4 |
| C5—C6—H6 | 119.4 | C15—C16—H16A | 108.4 |
| C1—C6—H6 | 119.4 | C17—C16—H16B | 108.4 |
| N1—C7—C1 | 113.7 (3) | C15—C16—H16B | 108.4 |
| N1—C7—H7A | 108.8 | H16A—C16—H16B | 107.5 |
| C1—C7—H7A | 108.8 | C16—C17—C18 | 113.2 (5) |
| N1—C7—H7B | 108.8 | C16—C17—H17A | 108.9 |
| C1—C7—H7B | 108.8 | C18—C17—H17A | 108.9 |
| H7A—C7—H7B | 107.7 | C16—C17—H17B | 108.9 |
| N1—C8—S1 | 123.9 (3) | C18—C17—H17B | 108.9 |
| N1—C8—S2 | 124.9 (3) | H17A—C17—H17B | 107.8 |
| S1—C8—S2 | 111.2 (2) | C19—C18—C17 | 115.9 (5) |
| N1—C9—C10 | 113.4 (3) | C19—C18—H18A | 108.3 |
| N1—C9—H9A | 108.9 | C17—C18—H18A | 108.3 |
| C10—C9—H9A | 108.9 | C19—C18—H18B | 108.3 |
| N1—C9—H9B | 108.9 | C17—C18—H18B | 108.3 |
| C10—C9—H9B | 108.9 | H18A—C18—H18B | 107.4 |
| H9A—C9—H9B | 107.7 | C18—C19—C20 | 115.4 (5) |
| C11—C10—C9 | 112.6 (4) | C18—C19—H19A | 108.4 |
| C11—C10—H10A | 109.1 | C20—C19—H19A | 108.4 |
| C9—C10—H10A | 109.1 | C18—C19—H19B | 108.4 |
| C11—C10—H10B | 109.1 | C20—C19—H19B | 108.4 |
| C9—C10—H10B | 109.1 | H19A—C19—H19B | 107.5 |
| H10A—C10—H10B | 107.8 | C19—C20—H20A | 109.5 |
| C12—C11—C10 | 114.9 (4) | C19—C20—H20B | 109.5 |
| C12—C11—H11A | 108.5 | H20A—C20—H20B | 109.5 |
| C10—C11—H11A | 108.5 | C19—C20—H20C | 109.5 |
| C12—C11—H11B | 108.5 | H20A—C20—H20C | 109.5 |
| C10—C11—H11B | 108.5 | H20B—C20—H20C | 109.5 |

| | | | |
|---|---|---|---|
| C6—C1—C2—C3 | −0.9 (6) | C9—N1—C8—S2 | −178.5 (3) |
| C7—C1—C2—C3 | 176.6 (4) | Pd1—S1—C8—N1 | 178.9 (3) |
| C1—C2—C3—C4 | 0.2 (7) | Pd1—S1—C8—S2 | −1.72 (18) |
| C2—C3—C4—C5 | 0.4 (8) | Pd1—S2—C8—N1 | −179.0 (3) |
| C2—C3—C4—Cl1 | −179.9 (4) | Pd1—S2—C8—S1 | 1.72 (18) |
| C3—C4—C5—C6 | −0.2 (8) | C8—N1—C9—C10 | −101.2 (4) |
| Cl1—C4—C5—C6 | −179.9 (4) | C7—N1—C9—C10 | 77.4 (4) |
| C4—C5—C6—C1 | −0.5 (7) | N1—C9—C10—C11 | 170.0 (3) |
| C2—C1—C6—C5 | 1.0 (7) | C9—C10—C11—C12 | 172.7 (4) |
| C7—C1—C6—C5 | −176.5 (4) | C10—C11—C12—C13 | 171.4 (4) |
| C8—N1—C7—C1 | −105.6 (4) | C11—C12—C13—C14 | −176.3 (4) |
| C9—N1—C7—C1 | 75.8 (4) | C12—C13—C14—C15 | 178.9 (4) |
| C6—C1—C7—N1 | −144.0 (4) | C13—C14—C15—C16 | 178.4 (5) |
| C2—C1—C7—N1 | 38.6 (5) | C14—C15—C16—C17 | −178.7 (5) |
| C7—N1—C8—S1 | −177.8 (3) | C15—C16—C17—C18 | 179.7 (5) |

| | | | |
|---|---|---|---|
| C9—N1—C8—S1 | 0.7 (5) | C16—C17—C18—C19 | 177.6 (6) |
| C7—N1—C8—S2 | 2.9 (5) | C17—C18—C19—C20 | −174.9 (6) |

Symmetry code: (i) $-x+3/2$, $-y+5/2$, $-z+1$.

### *Hydrogen-bond geometry (Å, º)*

*Cg*1 is the centroid of the C1–C6 ring.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C19—H19*B*···S1$^{ii}$ | 0.97 | 2.91 | 3.676 (6) | 137 |
| C12—H12*A*···Cl1$^{iii}$ | 0.97 | 2.90 | 3.602 (2) | 130 |
| C10—H10*B*···*Cg*1$^{iv}$ | 0.97 | 3.24 | 3.982 (3) | 134 |

Symmetry codes: (ii) $-x+1$, $-y+1$, $-z+1$; (iii) $x$, $-y+2$, $z+1/2$; (iv) $-x+3/2$, $y+1/2$, $-z+1/2$.