# cis-Dichlorido(3,6,9-trithiabicyclo-[9.3.1]pentadecane-$\kappa^2S^3,S^6$)-palladium(II) acetonitrile 0.8-solvate

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In the title complex, [PdCl₂(C₁₂H₂₂S₃)]·0.8CH₃CN, a potentially tridentate thioether ligand coordinates in a *cis*-bidentate manner to yield a square-planar environment for the Pd^II cation [mean deviation of the Pd from the Cl₂S₂ plane = 0.0406 (7) Å]. Each square-planar entity packs in an inverse face-to-face manner, giving pairs with plane-to-plane separations of 3.6225 (12) Å off-set by 1.1263 (19) Å, with a Pd···Pd separation of 3.8551 (8) Å. A partial acetonitrile solvent molecule is present. The occupancy of this molecule was allowed to refine, and converged to 0.794 (10). The synthesis of the previously unreported 3,6,9-trithiabicyclo[9.3.1]pentadecane ligand is also outlined.

## Comment

Group 10 transition metal complexes, in the +2 oxidation state ($d^8$), normally exhibit stable square-planar geometries, in compliance with the 16-electron rule. However, the presence of two nonbonding orbitals perpendicular to the coordination plane, *i.e.* the occupied $d_{z^2}$ and the empty $p_z$, means that higher coordination numbers can be achieved, with the cation possessing the ability to act as either a Lewis base or a Lewis acid, or in some reported cases, both (Aullón & Alvarez, 1996). Further, Allan *et al.* (2006) have reported the high-pressure (46 kbar; 1 bar = 100 000 Pa) conversion of *cis*-dichlorido(1,4,7-trithiacyclononane-$\kappa^2S,S'$)palladium from a square-planar mononuclear complex to a six-coordinate chain polymer *via* apical coordination to both the third S atom in the ligand and a meridionally coordinated S atom in another nominal monomeric Pd complex. The authors presented their work as a route to novel metal stereochemistries.

In the title complex, (I), the thioether ligand has the potential for up to three metal binding sites, but it coordinates in a *cis*-bidentate manner *via* two adjacent S atoms to the Pd

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centre, yielding a five-membered chelate ring (Fig. 1). The overall coordination geometry at the metal atom is square planar, with the remaining coordination sites occupied by chloride ligands. Atom Pd1 deviates from the Cl₂S₂ mean plane by 0.0406 (7) Å. A search of the Cambridge Structural
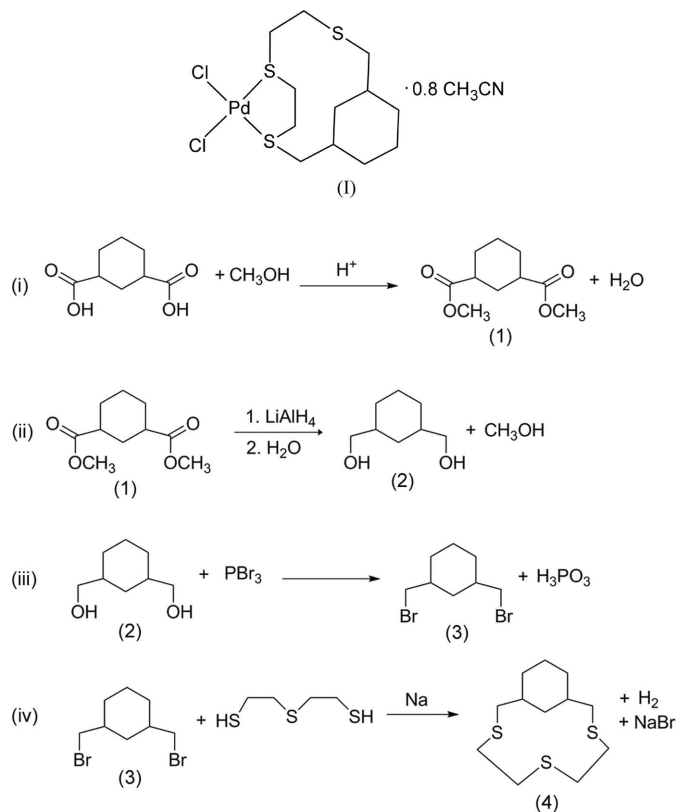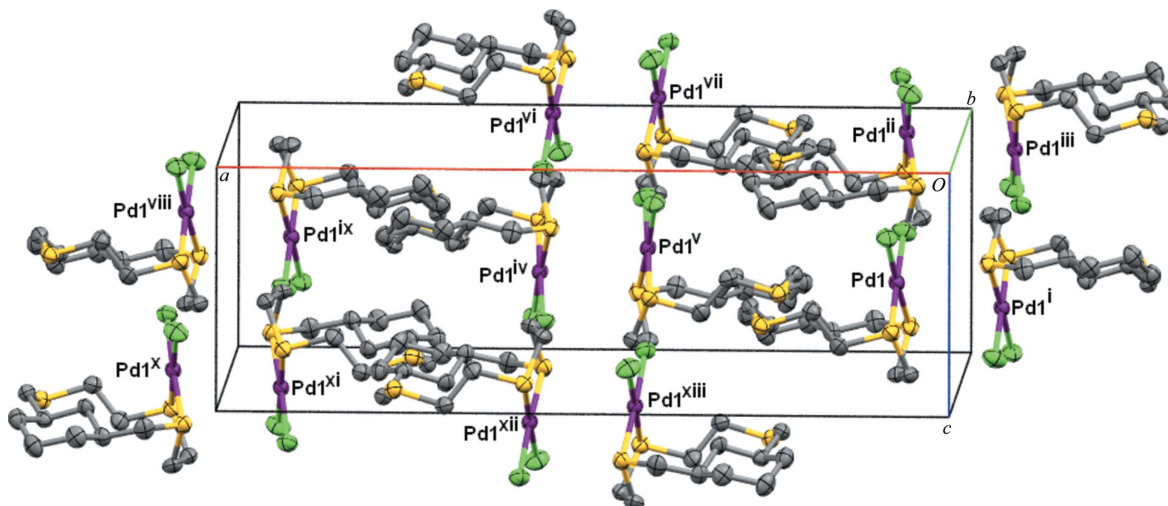


Database (CSD, Version 5.34, with February 2013 update; Allen, 2002) for all *cis*-PdCl₂S₂-containing structures yielded 115 unique observations of Pd—Cl and Pd—S bond lengths, and Cl—Pd—Cl and S—Pd—S angles. Average distances of 2.32 (3) and 2.31 (14) Å were found for Pd—Cl and Pd—S,
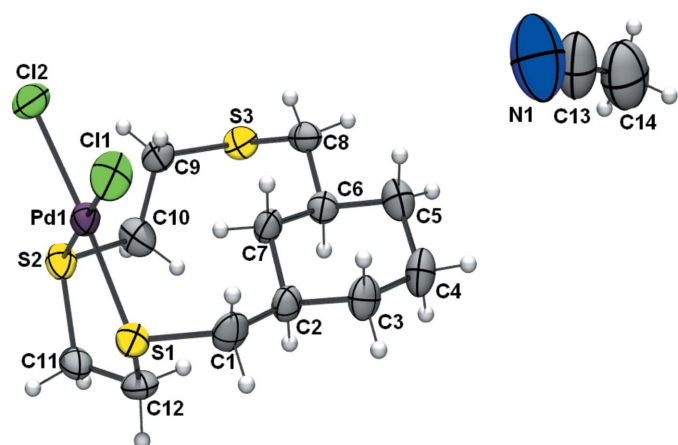


**Figure 1**
A view of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**
A packing diagram for (I), showing the close facial association of the square-planar PdCl$_2$S$_2$ fragments. Acetonitrile solvent molecules and H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (v) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; (vi) $x + \frac{1}{2}, y + 1, -z + \frac{1}{2}$; (vii) $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$; (viii) $x + 1, y + 1, z$; (ix) $-x + 1, -z + 1, -z + 1$; (x) $x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$; (xi) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (xii) $x + \frac{1}{2}, y, -z + \frac{3}{2}$; (xiii) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$.]

respectively, while for Cl—Pd—Cl and S—Pd—S, average angles of 92 (4) and 89 (5)°, respectively, were found. The results reported here for (I) are in agreement with the CSD values.

The overall structure of (I) is similar to that reported by de Groot *et al.* (1991) using the 2,5,8-trithia(9)-*m*-benzeneophane ligand, but stands in contrast with the coordination mode exhibited by Pd with the 2,5,8-trithia(9)-*o*-benzeneophane ligand. In that complex, a *cis*-PdCl$_2$S$_2$ coordination motif was also reported (de Groot *et al.*, 1991), but the third S atom was present at a distance of 3.076 (3) Å, indicating apical coordination to Pd. In the title complex, the intramolecular distance from Pd to the third S atom is 5.0721 (14) Å, while the closest intermolecular approach of a third S atom to Pd1 is 5.2031 (14) Å [for atom S2, generated by the symmetry operation $(-x + \frac{1}{2}, -y, z - \frac{1}{2})$], which far exceeds the sum of the van der Waals radii for Pd and S (3.43 Å; Bondi, 1964). For de Groot *et al.*'s (1991) Pd complex with the 2,5,8-trithia(9)-*m*-benzenophane ligand, the intramolecular distance to the third S atom was reported to be 5.122 (2) Å, which is comparable to that of the title complex. Of note in (I) is that the square-planar PdCl$_2$S$_2$ surfaces, oriented away from the uncoordinated macrocyclic atoms, pack in a face-to-face manner across the inversion centres at Wyckoff position 4*b* (Fig. 2). Plane-to-plane separations for the PdCl$_2$S$_2$ pairs are 3.6225 (12) Å off-set by 1.1263 (19) Å, with Pd···Pd separations of 3.8551 (8) Å.

## Experimental

All starting materials were obtained from the Aldrich Chemical Company and were used without further purification. The 3,6,9-trithiabicyclo[9.3.1]pentadecane ligand was prepared in four steps (see Scheme). Analyses were performed by Canadian Microanalytical Service Ltd.

(i) Step 1 involves the conversion of cyclohexane-1,3-dicarboxylic acid to its dimethyl ester, (1). (±)-Cyclohexane-1,3-dicarboxylic acid (5.20 g, 30.2 mmol) was dissolved in methanol (150 ml) to which concentrated H$_2$SO$_4$ (1 ml) was then added. The solution was stirred under reflux for 24 h then cooled to room temperature and neutralized with aqueous NaOH (2 *M*), and the solvent was removed under reduced pressure. Water (100 ml) was added to the residue and the mixture extracted with ether (4 × 50 ml). The extract was dried over MgSO$_4$ and filtered, and the ether was removed under reduced pressure to yield (1) as a pale-yellow oil in 99% yield. $^1$H NMR (500 Hz, TMS): δ 3.68 (6H), 2.20–2.40 (2H), 1.90–2.05 (2H), 1.70–1.80 (2H), 1.50–1.60 (2H), 1.30–1.40 (2H).

(ii) Step 2 involves the conversion of (1) to the corresponding diol, (2). Under an atmosphere of dry nitrogen, LiAlH$_4$ (9.5 g, 0.25 mmol) was suspended in dry diethyl ether (250 ml). The temperature of the suspension was maintained with an ice bath and a solution of (1) (14.5 g, 72.5 mmol) in dry diethyl ether (150 ml) was added dropwise over a period of 4 h. The mixture was then stirred overnight and allowed to warm to room temperature. Ethyl acetate (150 ml) was added to quench the remaining LiAlH$_4$, followed by dilute (10%) aqueous H$_2$SO$_4$ (~150 ml) to dissolve sodium and aluminium salts. The two-layer mixture was separated, the aqueous layer washed with diethyl ether (2 × 100 ml), and the washings and original organic layer combined and dried over MgSO$_4$. After filtration, the solvent was removed under reduced pressure to yield (2) as a nearly colourless oil in 85% yield. $^1$H NMR (500 Hz, TMS): δ 3.89 (2H), 0.8–2.7 (14H).

(iii) Step 3 involves the conversion of (2) to the corresponding dibromide, (3). This procedure was carried out in dry solvents under a dry nitrogen atmosphere. PBr$_3$ (6.0 ml, 63.8 mmol) was dissolved in dry benzene (15 ml). Pyridine (1.5 ml) was added dropwise over a period of 15 min. A mixture of (2) (7.2 g, 50 mmol) and pyridine (1.0 ml) was added dropwise over a period of 4 h while maintaining a temperature of 278 K with a cold-water bath. The reaction was allowed to warm slowly to room temperature while stirring overnight. Water (250 ml) was added slowly to quench the remaining PBr$_3$. The mixture was extracted with CHCl$_3$ (3 × 200 ml) and the combined extracts dried over CaCl$_2$. The solution was filtered and volatiles

removed under reduced pressure to give (3) as a pale-yellow oil in 70% yield. ^{1}H NMR (500 Hz, TMS): $\delta$ 3.25–3.40 (two doublets, 4H), 2.10–2.70 (10H).

(iv) Step 4 involves the formation of 3,6,9-trithiabicyclo[9.3.1]-pentadecane, (4). This procedure was carried out under nitrogen and anhydrous conditions in a three-necked round-bottomed flask fitted with two dropping funnels on top of condensers. Sodium (0.90 g, 40 mmol) was reacted with commercial absolute ethanol (500 ml) in the round-bottomed flask and a solution of bis(2-mercaptoethyl) sulfide (3.08 g, 20.0 mmol) in tetrahydrofuran (THF) (75 ml) was placed in one dropping funnel. In the other funnel was placed (3) (5.40 g, 20.0 mmol) in commercial absolute ethanol (150 ml). A portion (10 ml) of the THF solution was added dropwise over a period of 10 min with stirring under reflux. Both solutions were then admitted dropwise at a rate of 2:1 ethanol–THF over a period of 4 h, and the resulting mixture was refluxed for a further 24 h. Upon cooling to room temperature, the solvent was removed under reduced pressure and the residue suspended in CHCl$_3$ (300 ml). The suspension was washed with water (3 × 200 ml), and the organic layer dried over CaCl$_2$ and filtered. The filtrate was reduced in volume under reduced pressure to approximately 30 ml and hot commercial absolute ethanol (60 ml) added. The solution was filtered and placed in a freezer for 1 d, after which time white crystals of (4) (m.p. 363.5–365.7 K) had formed. These were separated by filtration in 30% yield. ^{1}H NMR (500 Hz, TMS): $\delta$ 2.60–3.00 (12H), 0.80–2.20 (10H); ^{13}C NMR (500 Hz, TMS): $\delta$ 21–42. 12 main peaks, some as doublets due to the presence of two diastereomers. MS, calculated for $(C_{12}H_{22}S_3)^+$: $m/z$ = 262; found: $m/z$ = 262.

(v) For the preparation of the title complex, (I), diacetonitriledichloridopalladium(II) (0.39 g, 1.50 mmol) was dissolved in acetonitrile (80 ml) to give a yellow–orange solution. Likewise, (4) (0.40 g, 1.5 mmol) was dissolved in acetonitrile (80 ml) to give a colourless solution. The solutions were mixed at room temperature and stirred for 4 h, and then the volume was reduced in a rotary evaporator to ~15 ml. The resulting suspension was filtered at room temperature to yield orange crystals of (I) in 95% yield which were dried in air. Analysis calculated for $C_{12}H_{22}Cl_2PdS_3 \cdot CH_3CN$: C 34.97, H 5.24, N 2.91, Cl 14.74%; found: C 35.23, H 5.82, N 3.02, Cl 14.15%.

## Crystal data

| | |
|---|---|
| $[PdCl_2(C_{12}H_{22}S_3)] \cdot 0.8C_2H_3N$ | $V = 3763.4$ (12) Å$^3$ |
| $M_r = 472.62$ | $Z = 8$ |
| Orthorhombic, $Pbca$ | Mo $K\alpha$ radiation |
| $a = 24.906$ (4) Å | $\mu = 1.59$ mm$^{-1}$ |
| $b = 18.144$ (2) Å | $T = 299$ K |
| $c = 8.328$ (2) Å | $0.30 \times 0.20 \times 0.10$ mm |

## Data collection

| | |
|---|---|
| Rigaku AFC-6S diffractometer | 3850 independent reflections |
| Absorption correction: $\psi$ scan | 2488 reflections with $I > 2\sigma(I)$ |
| (North et al., 1968) | 3 standard reflections |
| $T_{min} = 0.715$, $T_{max} = 0.853$ | every 150 reflections |
| 4892 measured reflections | intensity decay: 5.8% |

## Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.038$ | 12 restraints |
| $wR(F^2) = 0.109$ | H-atom parameters constrained |
| $S = 0.99$ | $\Delta\rho_{max} = 0.46$ e Å$^{-3}$ |
| 3850 reflections | $\Delta\rho_{min} = -0.58$ e Å$^{-3}$ |
| 192 parameters | |

H atoms were introduced into idealized positions and refined using the riding-atom formalism (idealized methyl refined as a rotating group), with C—H = 0.98 (methine), 0.97 (methylene) or 0.96 Å (methyl), and with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups or $1.2U_{eq}(C)$ otherwise. A partial-occupancy acetonitrile solvent molecule was present. All atoms in this group (N1, C13 and C14) were constrained to have the same occupancy, which was allowed to refine freely (tied to the second free variable) and converged to 0.794 (10). A similarity restraint (the command SIMU within *SHELXL2013*; Sheldrick, 2013) was applied to N1—C13—C14. Only reflections between $2\theta = 5$ and $53°$ were included (the command SHEL 8.146492 0.796384 within *SHELXL2013*) in order to minimize beam-stop effects and weak intensity at higher angles.

Data collection: *MSC/AFC Diffractometer Control Software* (Rigaku, 1998); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2013); molecular graphics: *Mercury* (Macrae *et al.*, 2008) and *ORTEP-3* (Farrugia, 2012); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3138). Services for accessing these data are described at the back of the journal.

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# *cis*-Dichlorido(3,6,9-trithiabicyclo[9.3.1]pentadecane-*κ²S³,S⁶*)palladium(II) acetonitrile 0.8-solvate

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**cis*-Dichlorido(3,6,9-trithiabicyclo[9.3.1]pentadecane-*κ²S³,S⁶*)palladium(II) acetonitrile 0.8-solvate**

*Crystal data*

| | |
|---|---|
| $[PdCl_2(C_{12}H_{22}S_3)]\cdot 0.8C_2H_3N$ | $F(000) = 1917$ |
| $M_r = 472.62$ | $D_x = 1.668$ Mg m⁻³ |
| Orthorhombic, *Pbca* | Mo *Kα* radiation, $\lambda = 0.71069$ Å |
| Hall symbol: -P 2ac 2ab | Cell parameters from 16 reflections |
| $a = 24.906$ (4) Å | $\theta = 10.1–13.1°$ |
| $b = 18.144$ (2) Å | $\mu = 1.59$ mm⁻¹ |
| $c = 8.328$ (2) Å | $T = 299$ K |
| $V = 3763.4$ (12) Å³ | Irregular, yellow |
| $Z = 8$ | $0.30 \times 0.20 \times 0.10$ mm |

*Data collection*

| | |
|---|---|
| Rigaku AFC6S diffractometer | 2488 reflections with $I > 2\sigma(I)$ |
| Radiation source: fine-focus sealed tube | $R_{int} = 0.000$ |
| $\omega–2\theta$ scans | $\theta_{max} = 26.4°$, $\theta_{min} = 2.8°$ |
| Absorption correction: *ψ* scan (North *et al.*, 1968) | $h = 0\rightarrow32$ |
| | $k = 0\rightarrow23$ |
| $T_{min} = 0.715$, $T_{max} = 0.853$ | $l = -10\rightarrow0$ |
| 4892 measured reflections | 3 standard reflections every 150 reflections |
| 3850 independent reflections | intensity decay: −5.8% |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.038$ | $w = 1/[\sigma^2(F_o^2) + (0.0435P)^2]$ |
| $wR(F^2) = 0.109$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 0.99$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 3850 reflections | $\Delta\rho_{max} = 0.46$ e Å⁻³ |
| 192 parameters | $\Delta\rho_{min} = -0.58$ e Å⁻³ |
| 12 restraints | |
| Primary atom site location: heavy-atom method | |

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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

|  | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Pd1 | 0.07275 (2) | 0.03067 (2) | 0.45790 (4) | 0.03345 (12) |  |
| Cl1 | 0.06611 (6) | 0.12759 (7) | 0.27642 (17) | 0.0558 (4) |  |
| Cl2 | 0.08395 (5) | −0.05430 (7) | 0.25322 (16) | 0.0495 (3) |  |
| S1 | 0.05690 (5) | 0.11118 (7) | 0.66059 (16) | 0.0417 (3) |  |
| S2 | 0.25544 (5) | −0.07024 (7) | 0.61307 (15) | 0.0416 (3) |  |
| S3 | 0.07756 (5) | −0.06267 (7) | 0.63987 (15) | 0.0400 (3) |  |
| N1 | 0.3855 (4) | 0.2380 (6) | 0.3889 (16) | 0.148 (5) | 0.794 (10) |
| C13 | 0.4218 (4) | 0.2337 (5) | 0.4601 (17) | 0.095 (4) | 0.794 (10) |
| C14 | 0.4692 (4) | 0.2286 (5) | 0.5518 (16) | 0.117 (5) | 0.794 (10) |
| H14A | 0.4971 | 0.2066 | 0.4881 | 0.176* | 0.794 (10) |
| H14B | 0.4627 | 0.1987 | 0.6449 | 0.176* | 0.794 (10) |
| H14C | 0.4802 | 0.2770 | 0.5849 | 0.176* | 0.794 (10) |
| C1 | 0.1071 (2) | 0.1845 (3) | 0.6590 (7) | 0.0461 (13) |  |
| H1A | 0.1067 | 0.2066 | 0.5529 | 0.055* |  |
| H1B | 0.0953 | 0.2221 | 0.7339 | 0.055* |  |
| C2 | 0.16499 (18) | 0.1666 (2) | 0.6989 (6) | 0.0371 (10) |  |
| H2 | 0.1666 | 0.1510 | 0.8114 | 0.045* |  |
| C3 | 0.1987 (2) | 0.2373 (3) | 0.6809 (7) | 0.0464 (13) |  |
| H3A | 0.1964 | 0.2550 | 0.5712 | 0.056* |  |
| H3B | 0.1846 | 0.2753 | 0.7511 | 0.056* |  |
| C4 | 0.2573 (2) | 0.2223 (3) | 0.7233 (7) | 0.0509 (13) |  |
| H4A | 0.2783 | 0.2662 | 0.7010 | 0.061* |  |
| H4B | 0.2599 | 0.2123 | 0.8375 | 0.061* |  |
| C5 | 0.2810 (2) | 0.1579 (3) | 0.6312 (7) | 0.0477 (12) |  |
| H5A | 0.3170 | 0.1481 | 0.6701 | 0.057* |  |
| H5B | 0.2835 | 0.1706 | 0.5183 | 0.057* |  |
| C6 | 0.24677 (18) | 0.0882 (2) | 0.6497 (6) | 0.0356 (10) |  |
| H6 | 0.2457 | 0.0753 | 0.7640 | 0.043* |  |
| C7 | 0.18938 (18) | 0.1054 (2) | 0.5957 (6) | 0.0378 (11) |  |
| H7A | 0.1675 | 0.0613 | 0.6044 | 0.045* |  |
| H7B | 0.1896 | 0.1206 | 0.4840 | 0.045* |  |
| C8 | 0.27251 (19) | 0.0237 (3) | 0.5589 (6) | 0.0394 (11) |  |
| H8A | 0.3111 | 0.0288 | 0.5693 | 0.047* |  |
| H8B | 0.2640 | 0.0299 | 0.4461 | 0.047* |  |
| C9 | 0.18580 (18) | −0.0813 (3) | 0.5521 (6) | 0.0398 (11) |  |
| H9A | 0.1771 | −0.0450 | 0.4705 | 0.048* |  |
| H9B | 0.1808 | −0.1299 | 0.5059 | 0.048* |  |
| C10 | 0.14825 (19) | −0.0717 (3) | 0.6949 (6) | 0.0471 (12) |  |
| H10A | 0.1590 | −0.0282 | 0.7544 | 0.057* |  |
| H10B | 0.1522 | −0.1139 | 0.7655 | 0.057* |  |
| C11 | 0.0531 (2) | −0.0193 (3) | 0.8234 (6) | 0.0442 (12) |  |
| H11A | 0.0141 | −0.0198 | 0.8229 | 0.053* |  |
| H11B | 0.0651 | −0.0479 | 0.9151 | 0.053* |  |
| C12 | 0.0723 (2) | 0.0593 (3) | 0.8418 (6) | 0.0476 (13) |  |
| H12A | 0.1108 | 0.0598 | 0.8606 | 0.057* |  |
| H12B | 0.0548 | 0.0820 | 0.9334 | 0.057* |  |

*Atomic displacement parameters (Å²)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Pd1 | 0.03253 (19) | 0.0364 (2) | 0.03140 (19) | −0.00201 (14) | −0.00319 (16) | 0.00041 (16) |
| Cl1 | 0.0715 (9) | 0.0464 (7) | 0.0494 (8) | −0.0079 (6) | −0.0103 (7) | 0.0135 (6) |
| Cl2 | 0.0517 (7) | 0.0559 (7) | 0.0408 (6) | 0.0035 (6) | −0.0045 (6) | −0.0131 (6) |
| S1 | 0.0364 (6) | 0.0443 (7) | 0.0443 (7) | 0.0013 (5) | 0.0016 (5) | −0.0072 (6) |
| S2 | 0.0415 (7) | 0.0424 (7) | 0.0409 (6) | 0.0107 (5) | −0.0042 (6) | −0.0022 (6) |
| S3 | 0.0401 (6) | 0.0411 (6) | 0.0389 (6) | −0.0051 (5) | −0.0020 (5) | 0.0051 (5) |
| N1 | 0.103 (7) | 0.145 (10) | 0.196 (12) | −0.018 (7) | −0.039 (9) | 0.036 (9) |
| C13 | 0.071 (6) | 0.064 (6) | 0.151 (11) | −0.006 (5) | −0.016 (7) | −0.005 (6) |
| C14 | 0.109 (9) | 0.078 (7) | 0.165 (13) | −0.011 (6) | −0.002 (9) | 0.005 (8) |
| C1 | 0.048 (3) | 0.031 (2) | 0.060 (3) | 0.006 (2) | −0.001 (3) | −0.012 (2) |
| C2 | 0.038 (2) | 0.030 (2) | 0.044 (3) | −0.0032 (19) | −0.002 (2) | −0.005 (2) |
| C3 | 0.052 (3) | 0.029 (2) | 0.057 (3) | −0.007 (2) | −0.004 (3) | 0.003 (2) |
| C4 | 0.049 (3) | 0.040 (3) | 0.064 (3) | −0.014 (2) | −0.013 (3) | 0.004 (3) |
| C5 | 0.041 (3) | 0.049 (3) | 0.054 (3) | −0.005 (2) | −0.003 (3) | 0.007 (3) |
| C6 | 0.038 (2) | 0.036 (2) | 0.033 (2) | −0.0014 (19) | 0.000 (2) | 0.003 (2) |
| C7 | 0.036 (2) | 0.036 (2) | 0.042 (3) | −0.002 (2) | −0.004 (2) | −0.009 (2) |
| C8 | 0.036 (2) | 0.048 (3) | 0.034 (2) | 0.004 (2) | 0.001 (2) | −0.002 (2) |
| C9 | 0.044 (3) | 0.038 (2) | 0.037 (3) | 0.003 (2) | −0.002 (2) | −0.001 (2) |
| C10 | 0.044 (3) | 0.054 (3) | 0.044 (3) | 0.008 (2) | −0.002 (2) | 0.011 (2) |
| C11 | 0.041 (3) | 0.061 (3) | 0.031 (2) | −0.010 (2) | 0.003 (2) | 0.002 (2) |
| C12 | 0.049 (3) | 0.064 (3) | 0.029 (2) | −0.001 (3) | 0.006 (2) | −0.008 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Pd1—Cl1 | 2.3246 (13) | C4—H4A | 0.9700 |
| Pd1—Cl2 | 2.3154 (13) | C4—H4B | 0.9700 |
| Pd1—S1 | 2.2669 (13) | C4—C5 | 1.518 (7) |
| Pd1—S3 | 2.2759 (13) | C5—H5A | 0.9700 |
| S1—C1 | 1.827 (5) | C5—H5B | 0.9700 |
| S1—C12 | 1.820 (5) | C5—C6 | 1.532 (6) |
| S2—C8 | 1.814 (5) | C6—H6 | 0.9800 |
| S2—C9 | 1.818 (5) | C6—C7 | 1.531 (6) |
| S3—C10 | 1.827 (5) | C6—C8 | 1.533 (6) |
| S3—C11 | 1.824 (5) | C7—H7A | 0.9700 |
| N1—C13 | 1.085 (13) | C7—H7B | 0.9700 |
| C13—C14 | 1.410 (15) | C8—H8A | 0.9700 |
| C14—H14A | 0.9600 | C8—H8B | 0.9700 |
| C14—H14B | 0.9600 | C9—H9A | 0.9700 |
| C14—H14C | 0.9600 | C9—H9B | 0.9700 |
| C1—H1A | 0.9700 | C9—C10 | 1.523 (6) |
| C1—H1B | 0.9700 | C10—H10A | 0.9700 |
| C1—C2 | 1.514 (6) | C10—H10B | 0.9700 |
| C2—H2 | 0.9800 | C11—H11A | 0.9700 |
| C2—C3 | 1.540 (6) | C11—H11B | 0.9700 |
| C2—C7 | 1.531 (6) | C11—C12 | 1.512 (7) |
| C3—H3A | 0.9700 | C12—H12A | 0.9700 |
| C3—H3B | 0.9700 | C12—H12B | 0.9700 |

| C3—C4 | 1.525 (7) | | |
|---|---|---|---|
| | | | |
| Cl2—Pd1—Cl1 | 91.92 (5) | C4—C5—C6 | 111.6 (4) |
| S1—Pd1—Cl1 | 89.11 (5) | H5A—C5—H5B | 108.0 |
| S1—Pd1—Cl2 | 176.65 (5) | C6—C5—H5A | 109.3 |
| S1—Pd1—S3 | 89.59 (5) | C6—C5—H5B | 109.3 |
| S3—Pd1—Cl1 | 178.45 (5) | C5—C6—H6 | 108.0 |
| S3—Pd1—Cl2 | 89.33 (5) | C5—C6—C8 | 110.3 (4) |
| C1—S1—Pd1 | 110.16 (18) | C7—C6—C5 | 108.8 (4) |
| C12—S1—Pd1 | 104.33 (17) | C7—C6—H6 | 108.0 |
| C12—S1—C1 | 103.8 (3) | C7—C6—C8 | 113.6 (4) |
| C8—S2—C9 | 104.9 (2) | C8—C6—H6 | 108.0 |
| C10—S3—Pd1 | 106.55 (17) | C2—C7—H7A | 109.5 |
| C11—S3—Pd1 | 102.68 (17) | C2—C7—H7B | 109.5 |
| C11—S3—C10 | 98.7 (2) | C6—C7—C2 | 110.7 (4) |
| N1—C13—C14 | 179.6 (16) | C6—C7—H7A | 109.5 |
| C13—C14—H14A | 109.5 | C6—C7—H7B | 109.5 |
| C13—C14—H14B | 109.5 | H7A—C7—H7B | 108.1 |
| C13—C14—H14C | 109.5 | S2—C8—H8A | 107.4 |
| H14A—C14—H14B | 109.5 | S2—C8—H8B | 107.4 |
| H14A—C14—H14C | 109.5 | C6—C8—S2 | 119.8 (3) |
| H14B—C14—H14C | 109.5 | C6—C8—H8A | 107.4 |
| S1—C1—H1A | 107.4 | C6—C8—H8B | 107.4 |
| S1—C1—H1B | 107.4 | H8A—C8—H8B | 106.9 |
| H1A—C1—H1B | 106.9 | S2—C9—H9A | 109.5 |
| C2—C1—S1 | 119.6 (3) | S2—C9—H9B | 109.5 |
| C2—C1—H1A | 107.4 | H9A—C9—H9B | 108.1 |
| C2—C1—H1B | 107.4 | C10—C9—S2 | 110.8 (3) |
| C1—C2—H2 | 108.1 | C10—C9—H9A | 109.5 |
| C1—C2—C3 | 108.6 (4) | C10—C9—H9B | 109.5 |
| C1—C2—C7 | 114.2 (4) | S3—C10—H10A | 108.8 |
| C3—C2—H2 | 108.1 | S3—C10—H10B | 108.8 |
| C7—C2—H2 | 108.1 | C9—C10—S3 | 114.0 (3) |
| C7—C2—C3 | 109.5 (4) | C9—C10—H10A | 108.8 |
| C2—C3—H3A | 109.5 | C9—C10—H10B | 108.8 |
| C2—C3—H3B | 109.5 | H10A—C10—H10B | 107.7 |
| H3A—C3—H3B | 108.1 | S3—C11—H11A | 109.1 |
| C4—C3—C2 | 110.5 (4) | S3—C11—H11B | 109.1 |
| C4—C3—H3A | 109.5 | H11A—C11—H11B | 107.8 |
| C4—C3—H3B | 109.5 | C12—C11—S3 | 112.7 (3) |
| C3—C4—H4A | 109.0 | C12—C11—H11A | 109.1 |
| C3—C4—H4B | 109.0 | C12—C11—H11B | 109.1 |
| H4A—C4—H4B | 107.8 | S1—C12—H12A | 109.7 |
| C5—C4—C3 | 113.1 (4) | S1—C12—H12B | 109.7 |
| C5—C4—H4A | 109.0 | C11—C12—S1 | 109.7 (3) |
| C5—C4—H4B | 109.0 | C11—C12—H12A | 109.7 |
| C4—C5—H5A | 109.3 | C11—C12—H12B | 109.7 |
| C4—C5—H5B | 109.3 | H12A—C12—H12B | 108.2 |

| | | | |
|---|---|---|---|
| Pd1—S1—C1—C2 | −67.6 (5) | C3—C4—C5—C6 | −53.7 (6) |
| Pd1—S1—C12—C11 | −38.8 (4) | C4—C5—C6—C7 | 56.2 (6) |
| Pd1—S3—C10—C9 | −53.7 (4) | C4—C5—C6—C8 | −178.6 (4) |
| Pd1—S3—C11—C12 | −38.7 (4) | C5—C6—C7—C2 | −60.5 (5) |
| S1—C1—C2—C3 | 177.4 (4) | C5—C6—C8—S2 | 158.7 (4) |
| S1—C1—C2—C7 | 54.9 (6) | C7—C2—C3—C4 | −55.8 (6) |
| S2—C9—C10—S3 | 167.9 (3) | C7—C6—C8—S2 | −78.9 (5) |
| S3—C11—C12—S1 | 52.3 (5) | C8—S2—C9—C10 | −98.9 (4) |
| C1—S1—C12—C11 | −154.2 (3) | C8—C6—C7—C2 | 176.2 (4) |
| C1—C2—C3—C4 | 178.8 (5) | C9—S2—C8—C6 | 68.7 (4) |
| C1—C2—C7—C6 | −177.1 (4) | C10—S3—C11—C12 | 70.5 (4) |
| C2—C3—C4—C5 | 53.1 (6) | C11—S3—C10—C9 | −159.7 (4) |
| C3—C2—C7—C6 | 60.9 (5) | C12—S1—C1—C2 | 43.6 (5) |