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Dichlorido[bis(2-hexylsulfanyl)-1*H*-benzimidazole-κN^3]palladium(II)

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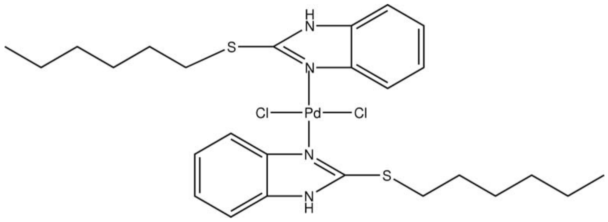
Key indicators: single-crystal X-ray study; *T* = 298 K; mean σ(C–C) = 0.010 Å; *R* factor = 0.045; *wR* factor = 0.139; data-to-parameter ratio = 21.8.

The title compound, $[PdCl_2(C_{13}H_{18}N_2S)_2]$, was obtained from 2-hexylsulfanyl-1*H*-benzimidazole and $(NH_4)_2PdCl_4$ in ethanol. The crystal structure reveals that the molecule resides on a crystallographic centre of symmetry, with the Pd atom at the centre of the square-planar complex. Molecules are linked by N—H···Cl hydrogen bonds.

Related literature

For related literature, see: Al-Bazi & Preiser (1987); Ito *et al.* (1997); Li *et al.* (2005); Türktekin *et al.* (2005).



Experimental

Crystal data

$[PdCl_2(C_{13}H_{18}N_2S)_2]$
M_r = 646.01
Monoclinic, $P2_1/c$
a = 14.3559 (11) Å
b = 7.7688 (6) Å
c = 14.5566 (11) Å
β = 113.0730 (10)°
V = 1493.6 (2) Å^3
Z = 2
Mo *K*α radiation
μ = 0.96 mm^{-1}
T = 298 (2) K
0.20 × 0.16 × 0.11 mm

Data collection

Bruker APEXII 1K CCD area-detector diffractometer
Absorption correction: numerical (*SADABS*; Sheldrick, 2002)
T_{min} = 0.831, T_{max} = 0.902
12251 measured reflections
3515 independent reflections
2649 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.139
S = 1.01
3515 reflections
161 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···Cl1^{i}	0.86	2.47	3.282 (3)	157

Symmetry code: (i) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXL97*.

This work was supported financially by Yunnan Natural Science Foundation (grant Nos. 2005E0003Z and 5Z0103A).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2153).

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supplementary materials

Acta Cryst. (2007). E**63**, m2474 [**doi:10.1107/S1600536807042584**]

Dichlorido[bis(2-hexylsulfanyl)-1*H*-benzimidazole-κN^3]palladium(II)

Z.-J. Huang, L. Du, M.-J. Xie and J. Chen

Comment

Sulfides are known to be highly selective for extraction of Pd(II), and have been widely used in the extraction of this species (Al-Bazi & Preiser, 1987). So far, most sufides reported for this purpose are dialkyl sufides. The title compound is a new heterocyclic sufide Pd(II) complex containing benzimidazole rings. The complex molecules have the *trans* configuration with two Cl atoms and two 2-hexylsulfanyl-1*H*-benzimidazole molecules, which act as neutral unidentate ligands through the N atom of the benzimidazole rings. This is quite different from general dialkyl sufides of Pd(II) complexes in which sufides are coordinated with palladium *via* the S atoms of the ligand. The molecular structure is shown in Fig. 1. The Pd(II) is at the inversion center of the square-planar complex. This is similar to bis[2-(2-benzoxazolyl)phenol-*N*]dichloropalladium(II) (Ito *et al.*, 1997) and bis(iso-Amyl benzothiazolyl sulfoxide)dichloropalladium(II) (Li *et al.*, 2005). The entire benzimidazole ligand system is roughly planar. The N1/N2/C1—C7 benzimidazole is planar, with a maximum deviation of N1 from the mean plane of 0.010 (2) Å. Molecules are linked by N—H···Cl hydrogen bonds (dashed lines) between N atoms of the of the benzimidazole rings and Cl atoms of adjacent molecules (Table 2). These hydrogen bond interactions give rise to a three-dimensional network. The crystal packing of the complex is shown in Fig. 2.

Experimental

2-Mercaptobenzimidazole, acetone, water and KOH were put in a round-bottom flask with a mechanical stirrer and condenser and the mixture was heated for about 30 min. 1-bromo-hexane was then added gradually with stirring through a dropping funnel and the reaction mixture was refluxed for 6 h. The residual solid was filtered after cooling down and the acetone was removed by distillation. The organic phase was diluted with ether, washed with water two times and dried with anhydrous Na_2SO_4. The ether was evaporated and 2-hexylsulfanyl-1*H*-benzimidazole was obtained. A solution of $(NH_4)_2PdCl_4$ (28.4 mg, 0.1 mmol) in EtOH/H_2O(1:1,10 ml) was added to a solution of 2-hexylsulfanyl-1*H*-benzimidazole (46.8 mg, 0.2 mmol) in EtOH/H_2O (1:1, 20 ml). The mixture was stirred for 50 min. The resulting solution was filtered and the filtrate was left to stand at room temperature. Yellow single crystals were obtained upon slow evaporation of the solvent.

Refinement

The H atoms on the C atoms were located in a difference Fourier map and refined as riding on their parent atoms with U_{iso}(H)=1.2U_{eq}(C), U_{iso}(H)=1.5U_{eq}(C13) and with C—H distances of 0.93–0.97 Å. H atoms on N atoms were included in calculated positions, constrained to an ideal geometry with N—H distance of 0.86 Å and with U_{iso}(H)=1.2U_{eq}(N). The atoms C11 and C12 are disordered. We used the *SHELXL97* command "*DFIX*" to restrain C11 and C12 to an ideal geometry with distance 1.468 Å. A similar structure is observed in the compound $[CoCl_2(C_{11}H_{14}N_2O)_2]$ (Türktekin *et al.*, 2005).

Figures

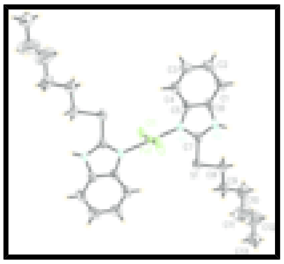

Fig. 1. The molecular structure of the title complex. Displacement ellipsoids are drawn at the 30% probability level, and H atoms are shown as spheres of arbitrary radii.

Fig. 2. The crystal packing of the title complex. Dashed lines represent hydrogen bonds.

Dichlorido[bis(2-hexylsulfanyl)-1*H*-benzimidazole- κN^3]palladium(II)

Crystal data

$[PdCl_2(C_{13}H_{18}N_2S)_2]$
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$c = 14.5566\ (11)$ Å
$\beta = 113.0730\ (10)°$
$V = 1493.6\ (2)$ Å^3
$Z = 2$

$F_{000} = 664$
$D_x = 1.436$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
$\theta = 1.5–28.3°$
$\mu = 0.96$ mm^{-1}
$T = 298\ (2)$ K
Block, yellow
0.20 × 0.16 × 0.11 mm

Data collection

Bruker APEXII 1K CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Monochromator: graphite
$T = 298(2)$ K
φ and ω scans
Absorption correction: numerical (SADABS; Sheldrick, 2002)
$T_{min} = 0.831$, $T_{max} = 0.902$
12251 measured reflections

3515 independent reflections
2649 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 28.3°$
$\theta_{min} = 1.5°$
$h = -19\rightarrow18$
$k = -10\rightarrow10$
$l = -19\rightarrow19$

Refinement

Refinement on F^2
Least-squares matrix: full

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.045$	H-atom parameters constrained
$wR(F^2) = 0.139$	$w = 1/[\sigma^2(F_o^2) + (0.0906P)^2 + 0.5462P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.001$
3515 reflections	$\Delta\rho_{max} = 1.33$ e Å^{-3}
161 parameters	$\Delta\rho_{min} = -0.53$ e Å^{-3}
1 restraint	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Pd1	0.0000	0.5000	0.0000	0.04347 (15)
S1	0.13339 (9)	0.4562 (2)	0.25428 (8)	0.0802 (4)
N1	−0.0520 (3)	0.4856 (3)	0.1094 (2)	0.0491 (7)
N2	−0.0570 (3)	0.4476 (5)	0.2582 (2)	0.0706 (9)
H2A	−0.0367	0.4326	0.3216	0.085*
Cl1	0.02540 (13)	0.78914 (15)	0.02260 (10)	0.1020 (5)
C1	−0.2480 (4)	0.4513 (7)	0.2038 (4)	0.0920 (15)
H1	−0.2502	0.4356	0.2662	0.110*
C2	−0.3343 (5)	0.4676 (8)	0.1192 (5)	0.1021 (19)
H2	−0.3967	0.4647	0.1247	0.123*
C3	−0.3320 (5)	0.4884 (6)	0.0248 (5)	0.0931 (18)
H3	−0.3925	0.4974	−0.0309	0.112*
C4	−0.2417 (4)	0.4958 (4)	0.0129 (4)	0.0712 (12)
H4	−0.2399	0.5098	−0.0499	0.085*
C5	−0.1532 (3)	0.4818 (4)	0.0980 (3)	0.0549 (9)
C6	−0.1562 (3)	0.4595 (5)	0.1915 (3)	0.0643 (10)
C7	0.0026 (3)	0.4639 (5)	0.2064 (3)	0.0553 (8)
C8	0.1645 (4)	0.4744 (5)	0.3879 (3)	0.0727 (12)
H8A	0.1334	0.5770	0.4013	0.087*
H8B	0.1383	0.3753	0.4108	0.087*
C9	0.2782 (5)	0.4839 (6)	0.4432 (4)	0.0892 (16)
H9A	0.3086	0.3808	0.4295	0.107*
H9B	0.3038	0.5819	0.4190	0.107*

C10	0.3079 (6)	0.5007 (7)	0.5525 (5)	0.112 (2)
H10A	0.2865	0.4013	0.5796	0.135*
H10B	0.2797	0.6040	0.5688	0.135*
C11	0.4287 (9)	0.5116 (10)	0.5928 (8)	0.177 (5)
H11A	0.4547	0.4044	0.5782	0.212*
H11B	0.4474	0.6033	0.5580	0.212*
C12	0.4752 (9)	0.5440 (15)	0.7007 (8)	0.204 (5)
H12A	0.4560	0.4542	0.7362	0.245*
H12B	0.4520	0.6535	0.7159	0.245*
C13	0.5877 (6)	0.5466 (12)	0.7325 (7)	0.171 (4)
H13A	0.6107	0.4343	0.7236	0.257*
H13B	0.6189	0.5787	0.8016	0.257*
H13C	0.6055	0.6286	0.6928	0.257*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.0645 (3)	0.0425 (2)	0.0360 (2)	0.00197 (13)	0.03335 (17)	0.00119 (11)
S1	0.0703 (6)	0.1298 (10)	0.0493 (5)	0.0124 (6)	0.0329 (5)	0.0106 (6)
N1	0.0679 (17)	0.0520 (16)	0.0398 (14)	0.0033 (11)	0.0344 (13)	0.0021 (9)
N2	0.088 (2)	0.096 (2)	0.0461 (16)	0.005 (2)	0.0459 (17)	0.0100 (16)
Cl1	0.2099 (14)	0.0490 (6)	0.1058 (8)	−0.0188 (7)	0.1254 (9)	−0.0148 (5)
C1	0.095 (4)	0.129 (4)	0.081 (3)	−0.002 (3)	0.066 (3)	0.003 (3)
C2	0.070 (3)	0.156 (5)	0.096 (4)	0.001 (3)	0.051 (3)	0.000 (3)
C3	0.071 (3)	0.134 (6)	0.078 (3)	0.002 (2)	0.034 (3)	0.000 (2)
C4	0.075 (3)	0.093 (4)	0.054 (2)	0.0026 (18)	0.034 (2)	0.0020 (16)
C5	0.068 (2)	0.060 (2)	0.0512 (19)	0.0016 (14)	0.0390 (17)	0.0003 (13)
C6	0.074 (3)	0.080 (2)	0.055 (2)	0.0016 (19)	0.043 (2)	0.0031 (18)
C7	0.067 (2)	0.068 (2)	0.0417 (17)	0.0047 (16)	0.0340 (16)	0.0074 (14)
C8	0.077 (3)	0.096 (3)	0.048 (2)	0.005 (2)	0.029 (2)	0.0096 (18)
C9	0.083 (3)	0.119 (5)	0.068 (3)	0.003 (2)	0.031 (3)	0.008 (2)
C10	0.101 (4)	0.149 (7)	0.066 (3)	0.003 (3)	0.009 (3)	−0.003 (2)
C11	0.147 (9)	0.221 (15)	0.146 (10)	0.013 (5)	0.039 (8)	−0.001 (5)
C12	0.146 (9)	0.320 (15)	0.133 (9)	−0.002 (8)	0.040 (7)	−0.008 (8)
C13	0.082 (4)	0.322 (12)	0.104 (5)	0.005 (5)	0.030 (4)	0.033 (6)

Geometric parameters (Å, °)

Pd1—N1^{i}	2.009 (3)	C5—C6	1.390 (5)
Pd1—N1	2.009 (3)	C8—C9	1.512 (8)
Pd1—Cl1	2.2788 (12)	C8—H8A	0.9700
Pd1—Cl1^{i}	2.2788 (12)	C8—H8B	0.9700
S1—C7	1.729 (4)	C9—C10	1.482 (9)
S1—C8	1.823 (4)	C9—H9A	0.9700
N1—C7	1.331 (5)	C9—H9B	0.9700
N1—C5	1.396 (5)	C10—C11	1.600 (13)
N2—C7	1.350 (4)	C10—H10A	0.9700
N2—C6	1.377 (6)	C10—H10B	0.9700

N2—H2A	0.8600	C11—C12	1.468 (9)
C1—C2	1.369 (9)	C11—H11A	0.9700
C1—C6	1.398 (6)	C11—H11B	0.9700
C1—H1	0.9300	C12—C13	1.495 (14)
C2—C3	1.396 (9)	C12—H12A	0.9700
C2—H2	0.9300	C12—H12B	0.9700
C3—C4	1.375 (7)	C13—H13A	0.9600
C3—H3	0.9300	C13—H13B	0.9600
C4—C5	1.388 (6)	C13—H13C	0.9600
C4—H4	0.9300		

N1^{i}—Pd1—N1	180.00 (16)	C9—C8—H8A	109.8
N1^{i}—Pd1—Cl1	88.35 (7)	S1—C8—H8A	109.8
N1—Pd1—Cl1	91.65 (7)	C9—C8—H8B	109.8
N1^{i}—Pd1—Cl1^{i}	91.65 (7)	S1—C8—H8B	109.8
N1—Pd1—Cl1^{i}	88.35 (7)	H8A—C8—H8B	108.2
Cl1—Pd1—Cl1^{i}	180.0	C10—C9—C8	111.8 (6)
C7—S1—C8	101.6 (2)	C10—C9—H9A	109.2
C7—N1—C5	106.0 (3)	C8—C9—H9A	109.2
C7—N1—Pd1	126.9 (3)	C10—C9—H9B	109.2
C5—N1—Pd1	126.8 (3)	C8—C9—H9B	109.2
C7—N2—C6	107.9 (3)	H9A—C9—H9B	107.9
C7—N2—H2A	126.1	C9—C10—C11	102.3 (7)
C6—N2—H2A	126.1	C9—C10—H10A	111.3
C2—C1—C6	116.6 (5)	C11—C10—H10A	111.3
C2—C1—H1	121.7	C9—C10—H10B	111.3
C6—C1—H1	121.7	C11—C10—H10B	111.3
C1—C2—C3	122.2 (5)	H10A—C10—H10B	109.2
C1—C2—H2	118.9	C12—C11—C10	112.0 (10)
C3—C2—H2	118.9	C12—C11—H11A	109.2
C4—C3—C2	121.1 (6)	C10—C11—H11A	109.2
C4—C3—H3	119.4	C12—C11—H11B	109.2
C2—C3—H3	119.4	C10—C11—H11B	109.2
C3—C4—C5	117.5 (5)	H11A—C11—H11B	107.9
C3—C4—H4	121.2	C11—C12—C13	108.5 (11)
C5—C4—H4	121.2	C11—C12—H12A	110.0
C4—C5—C6	121.0 (4)	C13—C12—H12A	110.0
C4—C5—N1	130.5 (4)	C11—C12—H12B	110.0
C6—C5—N1	108.5 (4)	C13—C12—H12B	110.0
N2—C6—C5	106.1 (3)	H12A—C12—H12B	108.4
N2—C6—C1	132.3 (4)	C12—C13—H13A	109.5
C5—C6—C1	121.6 (4)	C12—C13—H13B	109.5
N1—C7—N2	111.4 (3)	H13A—C13—H13B	109.5
N1—C7—S1	121.8 (3)	C12—C13—H13C	109.5
N2—C7—S1	126.7 (3)	H13A—C13—H13C	109.5
C9—C8—S1	109.5 (4)	H13B—C13—H13C	109.5

N1^{i}—Pd1—N1—C7	141 (100)	N1—C5—C6—N2	−0.9 (4)
Cl1—Pd1—N1—C7	−87.1 (3)	C4—C5—C6—C1	−0.3 (6)

Cl1^{i}—Pd1—N1—C7	92.9 (3)	N1—C5—C6—C1	179.8 (4)
N1^{i}—Pd1—N1—C5	−33 (100)	C2—C1—C6—N2	−179.7 (5)
Cl1—Pd1—N1—C5	98.7 (2)	C2—C1—C6—C5	−0.5 (8)
Cl1^{i}—Pd1—N1—C5	−81.3 (2)	C5—N1—C7—N2	−0.5 (4)
C6—C1—C2—C3	1.1 (9)	Pd1—N1—C7—N2	−175.6 (2)
C1—C2—C3—C4	−0.9 (9)	C5—N1—C7—S1	178.8 (2)
C2—C3—C4—C5	0.0 (6)	Pd1—N1—C7—S1	3.7 (4)
C3—C4—C5—C6	0.5 (5)	C6—N2—C7—N1	−0.1 (5)
C3—C4—C5—N1	−179.6 (3)	C6—N2—C7—S1	−179.3 (3)
C7—N1—C5—C4	−179.1 (3)	C8—S1—C7—N1	167.7 (3)
Pd1—N1—C5—C4	−3.9 (5)	C8—S1—C7—N2	−13.1 (4)
C7—N1—C5—C6	0.8 (4)	C7—S1—C8—C9	−175.7 (3)
Pd1—N1—C5—C6	176.0 (2)	S1—C8—C9—C10	179.4 (3)
C7—N2—C6—C5	0.6 (5)	C8—C9—C10—C11	−179.0 (4)
C7—N2—C6—C1	179.8 (5)	C9—C10—C11—C12	175.1 (7)
C4—C5—C6—N2	179.0 (3)	C10—C11—C12—C13	178.2 (7)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···Cl1^{ii}	0.86	2.47	3.282 (3)	157

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

Fig. 1

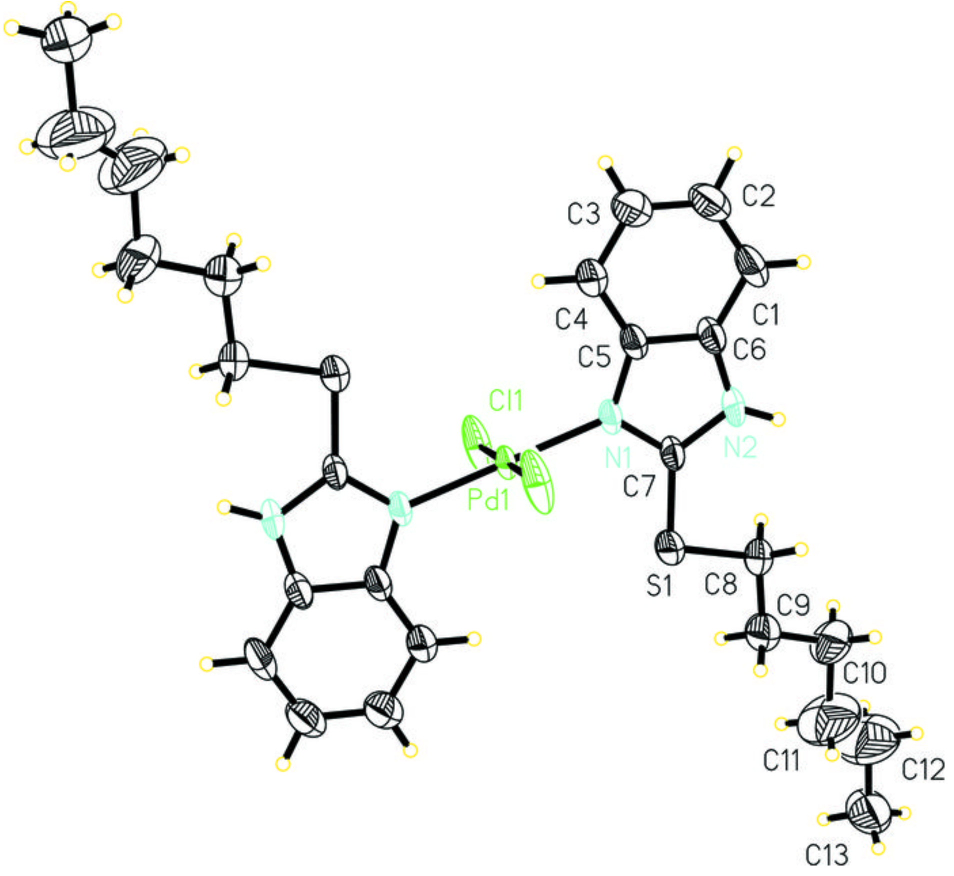

Fig. 2