Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Chlorido{4-chloro-1-[2-(methylsulfanyl)phenyldiazenyl]phenyl-κ^3C,N,S}palladium(II)

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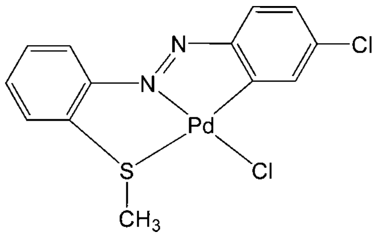
Received 17 May 2007; accepted 21 May 2007

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.029; wR factor = 0.069; data-to-parameter ratio = 14.7.

The Pd atom in the title compound, [Pd($C_{13}H_{10}ClN_2S$)Cl], is tetracoordinated by a benzene C, a diazene N, a Cl and an S atom in an approximately square-planar geometry. The molecules are found to dimerize through a nonbonded S···S interaction [S···S = 3.5162 (17) Å]. There are no hydrogen bonds and the crystal packing is stabilized by four intermolecular π–π interactions; the centroid–centroid distances are 3.808 (2), 3.623 (2), 3.808 (2) and 3.623 (2) Å; the corresponding perpendicular distances are 3.462, 3.454, 3.402 and 3.402 Å with no slippages.

Related literature

For related literature, see: Bagchi & Bandyopadhyay (2007); Chattopadhyay *et al.* (1991); Das *et al.* (2006); Dupont *et al.* (2005); Kubo *et al.* (2005); Mahapatra *et al.* (1986); Neogi *et al.* (2006); Omae (2004); Pal *et al.* (1992).



Experimental

Crystal data

[Pd($C_{13}H_{10}ClN_2S$)Cl]
M_r = 403.59
Triclinic, $P\bar{1}$
a = 7.413 (2) Å
b = 8.768 (3) Å
c = 11.051 (3) Å
α = 105.330 (4)°
β = 92.875 (5)°
γ = 95.995 (5)°
V = 686.7 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.88 mm^{-1}
T = 298 (2) K
0.43 × 0.28 × 0.19 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.538, $T_{\max}$ = 0.701
6579 measured reflections
2416 independent reflections
2308 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.069
S = 1.13
2416 reflections
173 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.37 e Å^{-3}
$\Delta\rho_{\min}$ = −0.43 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C12—Pd1	1.977 (3)	Pd1—Cl1	2.2900 (11)
Pd1—N1	1.972 (3)	Pd1—S	2.3810 (10)
N1—Pd1—C12	79.36 (13)	N1—Pd1—S	85.42 (9)
C12—Pd1—Cl1	96.12 (10)	Cl1—Pd1—S	98.98 (4)

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2000); 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*.

We thank the Department of Science and Technology, India (project No. SR/S1/IC-11/2002), for funding and CSIR for a fellowship to VB and PD. The single-crystal X-ray diffractometer facility provided by IITD is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2299).

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supplementary materials

Acta Cryst. (2007). E**63**, m1704 [**doi:10.1107/S1600536807024853**]

Chlorido{4-chloro-1-[2-(methylsulfanyl)phenyldiazenyl]phenyl-κ^3*C*,*N*,*S*}palladium(II)

V. Bagchi, **P. Das** and **D. Bandyopadhyay**

Comment

Cyclopalladated compounds have numerous applications (Dupont *et al.*, 2005) in organic synthesis, catalysis, photochemistry and metallomesogen chemistry. Although a number of cyclometallated complexes of palladium (Omae, 2004 & Neogi *et al.*, 2006) have been reported in literature, report of palladium complexes with sulfur as an auxiliary donor is relatively sparse (Pal *et al.*, 1992). Against this background, we report here the crystal structure of (**I**).

The molecular structure of the title compound, (**I**), is shown in Fig. 1, with the atom numbering scheme. The palladium atom along with donor set of four atoms lie in an almost plane. Selected bond lengths and bond angles are listed in Table 1. The packing arrangement of (**I**) is shown in Fig. 2. The N═N bond length is typical of other cyclopalladated azoarenes (Neogi *et al.*, 2006), unlike that of other free azoarenes containing thioether moiety (Das *et al.*, 2006). The metal carbon bond length, 1.977 (3) Å, is higher than the reported values of other *ortho*-palladated azoarenes (Bagchi & Bandyopadhyay, 2007). The molecules are found to dimerize through a nonbonded S···S interaction; having S···S^{i} [symmetry code: (i) $1 - x, -y, 1 - z$] distance of 3.5162 (17) Å (Chattopadhyay *et al.*, 1991) (Fig. 3). Four inter molecular π—π interactions (Kubo *et al.*, 2005 & Bagchi & Bandyopadhyay, 2007) arrange the molecules in anti parallel fashion (Fig. 4). The *Cg3*—*Cg4*^{ii}, *Cg3*—*Cg4*^{iii}, *Cg4*—*Cg3*^{ii}, *Cg4*—*Cg3*^{iii}, [symmetry codes: (ii) $-x, 1 - y, 1 - z$; (iii) $1 - x, 1 - y, 1-z$. *Cg3* and *Cg4* are the centroids of C1—C6 and C7—C12 rings, respectively.] distances are 3.808 (2), 3.623 (2), 3.808 (2) and 3.623 (2) Å; the corresponding perpendicular distances are 3.462, 3.454, 3.402 and 3.402 Å with slippages of 3.402, 3.402, 3.462 and 3.454 Å, respectively.

Experimental

2-(Methylsulfanyl)diazenyl-4-cholorobenzene was prepared by coupling 2-(methylsulfanyl)aniline with 4-nitrosochlorobenzene. The ligand thus obtained was reacted with Na_2PdCl_4 following a reported method (Mahapatra *et al.*, 1986). The product was purified by coloumn chromatographic technique using silica gel column and methanol and dichloromethane (1: 9 *v/v*) mixture as eluant. The solvent was evaporated in vacuum to obtain the pure product (yield: 83.9%). Suitable crystals of (**I**) were grown from a dichloromethane-hexane solution by slow evaporation.

Refinement

H atoms were included at calculated positions as riding atoms with C–H set to 0.93 Å for (aromatic) and 0.96 Å for (CH_3) H atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$ ($1.5U_{eq}$ for methyl group).

Figures

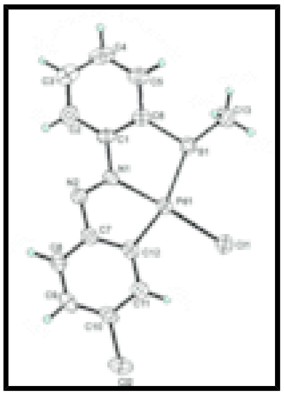

Figure 1
The asymmetric unit of (**I**), with displacement ellipsoids drawn at the 50% probability level.

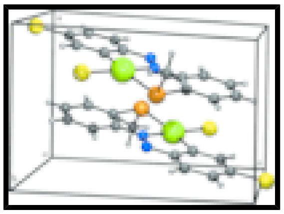

Figure 2
The molecular arrangement of (**I**) in the unitcell.

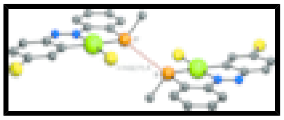

Figure 3
The intermolecular S···S interaction for (**I**), indicated by dotted line [symmetry code: (i) 1 − *x*, −*y*, 1 − *z*].

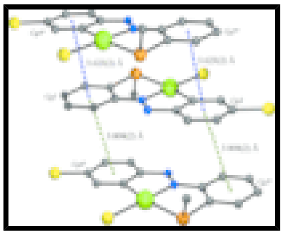

Figure 4
The intermolecular π—π interactions for (**I**), indicated by the blue and green dotted lines. [Symmetry codes: (ii) − *x*, 1 − *y*, 1 − *z*; (iii) 1 − *x*, 1 − *y*, 1 − *z*.]. *Cg3* and *Cg4* are centroids of C1—C6 and C7—C12 rings, respectively.

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Crystal data

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Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.413$ (2) Å
$b = 8.768$ (3) Å
$c = 11.051$ (3) Å
$\alpha = 105.330$ (4)°
$\beta = 92.875$ (5)°
$\gamma = 95.995$ (5)°
$V = 686.7$ (4) Å^3

$Z = 2$
$F_{000} = 396$
$D_x = 1.952$ Mg m^{-3}
Mo *K*α radiation
λ = 0.71073 Å
Cell parameters from 3745 reflections
θ = 2.4–28.0°
$\mu = 1.88$ mm^{-1}
$T = 298$ (2) K
Block, red
0.43 × 0.28 × 0.19 mm

Data collection

Bruker SMART CCD area-detector diffractometer	2416 independent reflections
Radiation source: fine-focus sealed tube	2308 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\mathrm{int}} = 0.035$
$T = 298(2)$ K	$\theta_{\mathrm{max}} = 25.0°$
φ and ω scans	$\theta_{\mathrm{min}} = 1.9°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -8\rightarrow8$
$T_{\mathrm{min}} = 0.538$, $T_{\mathrm{max}} = 0.701$	$k = -10\rightarrow10$
6579 measured reflections	$l = -13\rightarrow13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.029$	H-atom parameters constrained
$wR(F^2) = 0.069$	$w = 1/[\sigma^2(F_o^2) + (0.0218P)^2 + 0.4766P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.13$	$(\Delta/\sigma)_{\mathrm{max}} < 0.001$
2416 reflections	$\Delta\rho_{\mathrm{max}} = 0.37$ e Å^{-3}
173 parameters	$\Delta\rho_{\mathrm{min}} = -0.43$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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}
C8	0.1472 (5)	0.7783 (4)	0.6873 (4)	0.0399 (8)
H8	0.1402	0.8514	0.6402	0.048*
C13	0.2318 (6)	−0.0523 (4)	0.3667 (4)	0.0547 (10)
H13A	0.2241	−0.1112	0.4286	0.082*
H13B	0.2717	−0.1173	0.2909	0.082*

H13C	0.1143	−0.0227	0.3490	0.082*
C4	0.3860 (5)	0.2481 (5)	0.0990 (4)	0.0524 (10)
H4	0.4078	0.2022	0.0159	0.063*
C12	0.2017 (4)	0.5121 (4)	0.6990 (3)	0.0324 (7)
C11	0.1687 (5)	0.5551 (4)	0.8249 (3)	0.0373 (8)
H11	0.1743	0.4828	0.8728	0.045*
Pd1	0.28010 (3)	0.31568 (3)	0.59178 (2)	0.03148 (10)
S	0.39237 (12)	0.12483 (10)	0.42611 (8)	0.0373 (2)
Cl1	0.29394 (16)	0.18486 (11)	0.74538 (9)	0.0551 (3)
Cl2	0.08874 (16)	0.76042 (13)	1.03770 (9)	0.0599 (3)
N1	0.2693 (4)	0.4451 (3)	0.4709 (3)	0.0317 (6)
N2	0.2272 (4)	0.5860 (3)	0.5041 (3)	0.0352 (6)
C1	0.3113 (4)	0.3831 (4)	0.3433 (3)	0.0326 (7)
C9	0.1155 (5)	0.8202 (4)	0.8127 (4)	0.0417 (8)
H9	0.0869	0.9214	0.8517	0.050*
C10	0.1271 (5)	0.7082 (4)	0.8789 (3)	0.0396 (8)
C6	0.3623 (4)	0.2299 (4)	0.3102 (3)	0.0344 (7)
C7	0.1897 (4)	0.6260 (4)	0.6309 (3)	0.0333 (7)
C2	0.3014 (5)	0.4691 (4)	0.2552 (3)	0.0412 (8)
H2	0.2690	0.5719	0.2779	0.049*
C5	0.4002 (5)	0.1628 (5)	0.1866 (3)	0.0451 (9)
H5	0.4348	0.0608	0.1633	0.054*
C3	0.3400 (5)	0.4010 (5)	0.1337 (4)	0.0494 (10)
H3	0.3349	0.4587	0.0744	0.059*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C8	0.043 (2)	0.0319 (18)	0.047 (2)	0.0092 (15)	0.0064 (16)	0.0120 (16)
C13	0.069 (3)	0.036 (2)	0.054 (3)	−0.0035 (19)	−0.008 (2)	0.0078 (18)
C4	0.053 (2)	0.072 (3)	0.0292 (19)	0.004 (2)	0.0054 (17)	0.0081 (19)
C12	0.0320 (17)	0.0282 (16)	0.0347 (18)	0.0041 (13)	0.0034 (14)	0.0045 (14)
C11	0.044 (2)	0.0313 (18)	0.0349 (19)	0.0031 (15)	0.0039 (15)	0.0058 (15)
Pd1	0.04049 (17)	0.02465 (15)	0.02860 (16)	0.00572 (10)	0.00310 (11)	0.00526 (10)
S	0.0452 (5)	0.0335 (4)	0.0320 (5)	0.0116 (4)	0.0017 (4)	0.0046 (4)
Cl1	0.0936 (8)	0.0372 (5)	0.0413 (5)	0.0175 (5)	0.0143 (5)	0.0174 (4)
Cl2	0.0818 (7)	0.0539 (6)	0.0375 (5)	0.0141 (5)	0.0122 (5)	−0.0027 (4)
N1	0.0318 (15)	0.0316 (15)	0.0318 (15)	0.0033 (11)	0.0015 (11)	0.0094 (12)
N2	0.0383 (16)	0.0286 (14)	0.0390 (16)	0.0056 (12)	0.0035 (12)	0.0090 (12)
C1	0.0292 (17)	0.0379 (18)	0.0287 (17)	0.0019 (14)	0.0013 (13)	0.0065 (14)
C9	0.040 (2)	0.0311 (18)	0.051 (2)	0.0086 (15)	0.0070 (17)	0.0035 (16)
C10	0.0392 (19)	0.0378 (19)	0.0348 (19)	0.0017 (15)	0.0077 (15)	−0.0018 (15)
C6	0.0315 (17)	0.0387 (18)	0.0316 (18)	0.0051 (14)	0.0024 (14)	0.0067 (15)
C7	0.0335 (18)	0.0297 (17)	0.0350 (18)	0.0043 (13)	0.0044 (14)	0.0055 (14)
C2	0.041 (2)	0.044 (2)	0.041 (2)	0.0051 (16)	0.0013 (16)	0.0153 (17)
C5	0.046 (2)	0.047 (2)	0.040 (2)	0.0095 (17)	0.0063 (16)	0.0044 (17)
C3	0.048 (2)	0.065 (3)	0.039 (2)	0.0063 (19)	0.0028 (17)	0.020 (2)

Geometric parameters (Å, °)

C8—C9	1.376 (5)	Pd1—Cl1	2.2900 (11)
C8—C7	1.392 (5)	Pd1—S	2.3810 (10)
C8—H8	0.9300	S—C6	1.783 (3)
C13—S	1.805 (4)	Cl2—C10	1.739 (4)
C13—H13A	0.9600	N1—N2	1.270 (4)
C13—H13B	0.9600	N1—C1	1.433 (4)
C13—H13C	0.9600	N2—C7	1.401 (4)
C4—C5	1.377 (6)	C1—C2	1.384 (5)
C4—C3	1.378 (6)	C1—C6	1.393 (5)
C4—H4	0.9300	C9—C10	1.377 (5)
C12—C11	1.383 (5)	C9—H9	0.9300
C12—C7	1.407 (5)	C6—C5	1.392 (5)
C12—Pd1	1.977 (3)	C2—C3	1.375 (5)
C11—C10	1.391 (5)	C2—H2	0.9300
C11—H11	0.9300	C5—H5	0.9300
Pd1—N1	1.972 (3)	C3—H3	0.9300

C9—C8—C7	119.8 (3)	N2—N1—Pd1	121.0 (2)
C9—C8—H8	120.1	C1—N1—Pd1	120.8 (2)
C7—C8—H8	120.1	N1—N2—C7	110.3 (3)
S—C13—H13A	109.5	C2—C1—C6	120.5 (3)
S—C13—H13B	109.5	C2—C1—N1	122.4 (3)
H13A—C13—H13B	109.5	C6—C1—N1	117.1 (3)
S—C13—H13C	109.5	C8—C9—C10	118.2 (3)
H13A—C13—H13C	109.5	C8—C9—H9	120.9
H13B—C13—H13C	109.5	C10—C9—H9	120.9
C5—C4—C3	120.5 (4)	C9—C10—C11	123.2 (3)
C5—C4—H4	119.8	C9—C10—Cl2	118.6 (3)
C3—C4—H4	119.8	C11—C10—Cl2	118.2 (3)
C11—C12—C7	118.0 (3)	C5—C6—C1	119.3 (3)
C11—C12—Pd1	131.4 (3)	C5—C6—S	119.9 (3)
C7—C12—Pd1	110.4 (2)	C1—C6—S	120.6 (3)
C12—C11—C10	119.0 (3)	C8—C7—N2	119.4 (3)
C12—C11—H11	120.5	C8—C7—C12	121.7 (3)
C10—C11—H11	120.5	N2—C7—C12	118.9 (3)
N1—Pd1—C12	79.36 (13)	C3—C2—C1	119.3 (4)
N1—Pd1—Cl1	175.20 (8)	C3—C2—H2	120.3
C12—Pd1—Cl1	96.12 (10)	C1—C2—H2	120.3
N1—Pd1—S	85.42 (9)	C4—C5—C6	119.7 (4)
C12—Pd1—S	164.33 (10)	C4—C5—H5	120.2
Cl1—Pd1—S	98.98 (4)	C6—C5—H5	120.2
C6—S—C13	102.51 (17)	C2—C3—C4	120.7 (4)
C6—S—Pd1	95.55 (11)	C2—C3—H3	119.7
C13—S—Pd1	112.06 (15)	C4—C3—H3	119.7
N2—N1—C1	118.2 (3)		

C7—C12—C11—C10	−0.6 (5)	C8—C9—C10—Cl2	179.6 (3)
Pd1—C12—C11—C10	175.3 (2)	C12—C11—C10—C9	0.5 (5)

C11—C12—Pd1—N1	−177.7 (3)	C12—C11—C10—Cl2	−179.3 (2)
C7—C12—Pd1—N1	−1.7 (2)	C2—C1—C6—C5	−1.2 (5)
C11—C12—Pd1—Cl1	0.6 (3)	N1—C1—C6—C5	178.4 (3)
C7—C12—Pd1—Cl1	176.7 (2)	C2—C1—C6—S	175.1 (3)
C11—C12—Pd1—S	−163.8 (2)	N1—C1—C6—S	−5.3 (4)
C7—C12—Pd1—S	12.3 (5)	C13—S—C6—C5	−62.4 (3)
N1—Pd1—S—C6	−5.55 (13)	Pd1—S—C6—C5	−176.4 (3)
C12—Pd1—S—C6	−19.3 (4)	C13—S—C6—C1	121.4 (3)
Cl1—Pd1—S—C6	176.39 (11)	Pd1—S—C6—C1	7.3 (3)
N1—Pd1—S—C13	−111.46 (17)	C9—C8—C7—N2	−178.1 (3)
C12—Pd1—S—C13	−125.2 (4)	C9—C8—C7—C12	0.0 (5)
Cl1—Pd1—S—C13	70.47 (15)	N1—N2—C7—C8	177.6 (3)
C12—Pd1—N1—N2	1.7 (2)	N1—N2—C7—C12	−0.5 (4)
S—Pd1—N1—N2	−174.5 (2)	C11—C12—C7—C8	0.3 (5)
C12—Pd1—N1—C1	−179.1 (2)	Pd1—C12—C7—C8	−176.3 (3)
S—Pd1—N1—C1	4.6 (2)	C11—C12—C7—N2	178.4 (3)
C1—N1—N2—C7	179.7 (3)	Pd1—C12—C7—N2	1.7 (4)
Pd1—N1—N2—C7	−1.2 (3)	C6—C1—C2—C3	0.9 (5)
N2—N1—C1—C2	−2.2 (5)	N1—C1—C2—C3	−178.7 (3)
Pd1—N1—C1—C2	178.6 (2)	C3—C4—C5—C6	1.9 (6)
N2—N1—C1—C6	178.2 (3)	C1—C6—C5—C4	−0.3 (5)
Pd1—N1—C1—C6	−1.0 (4)	S—C6—C5—C4	−176.5 (3)
C7—C8—C9—C10	0.0 (5)	C1—C2—C3—C4	0.7 (6)
C8—C9—C10—C11	−0.2 (5)	C5—C4—C3—C2	−2.2 (6)

Fig. 1

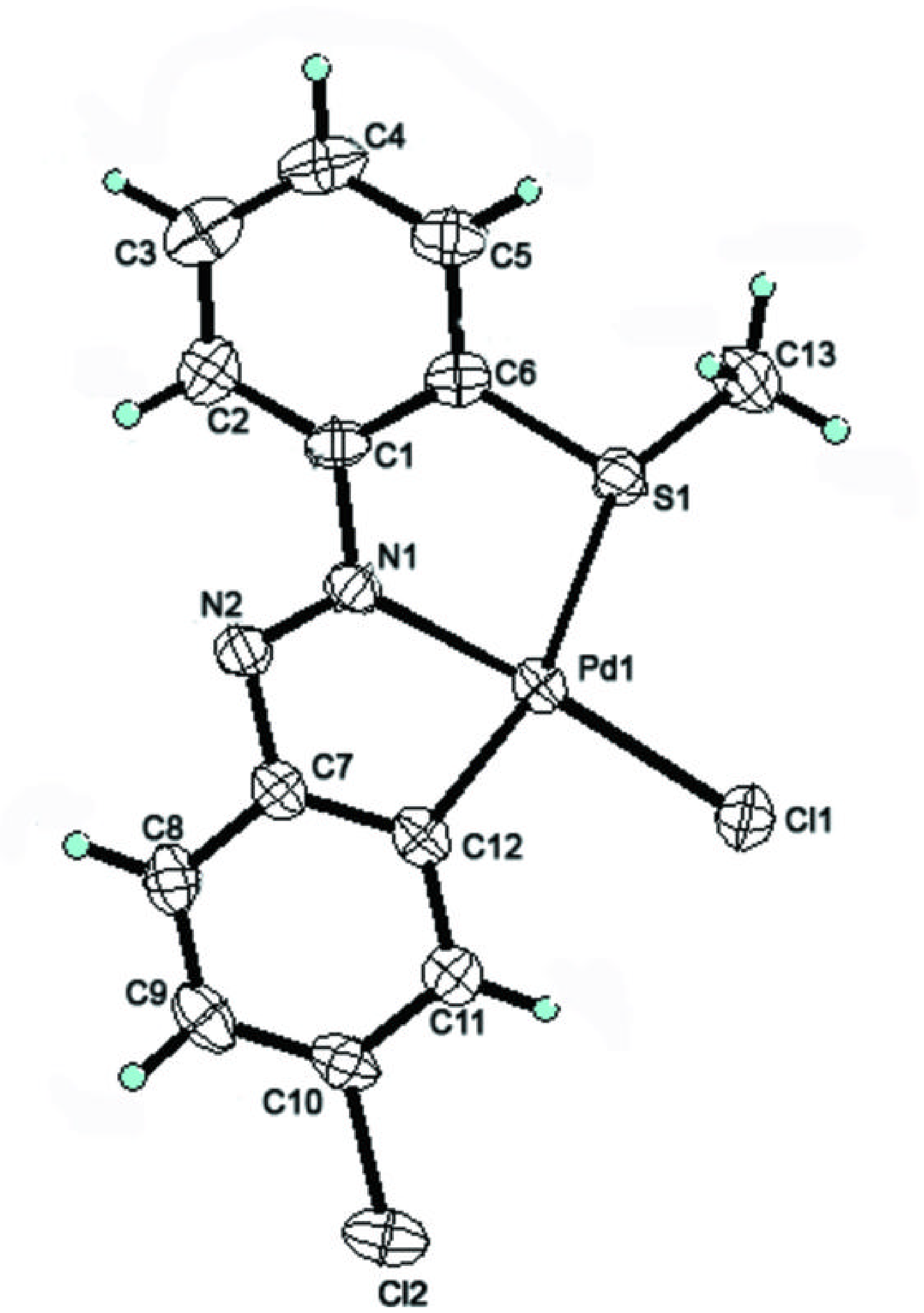


Fig. 2

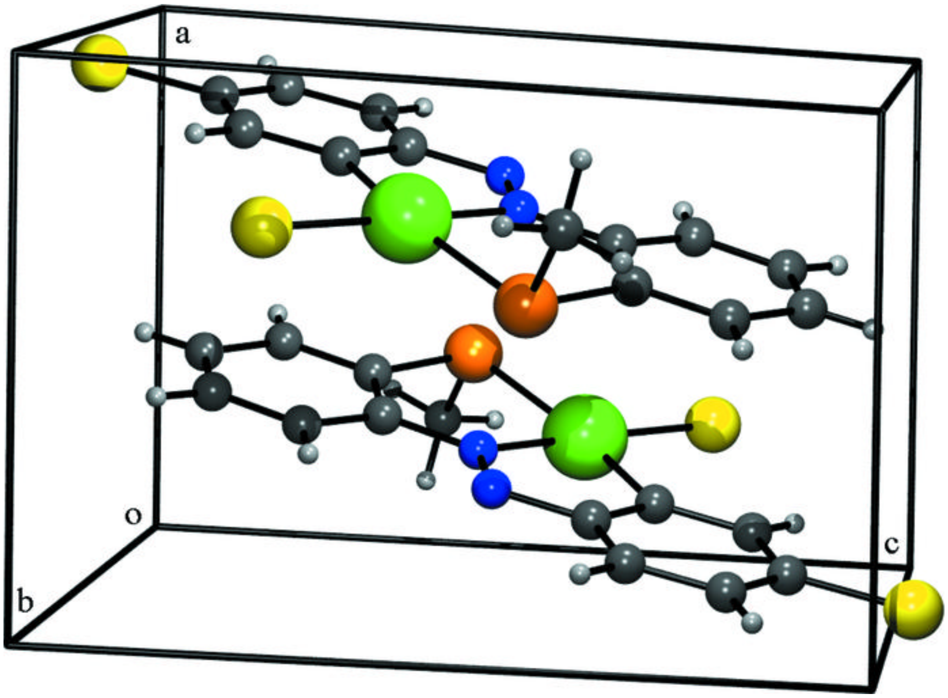


Fig. 3

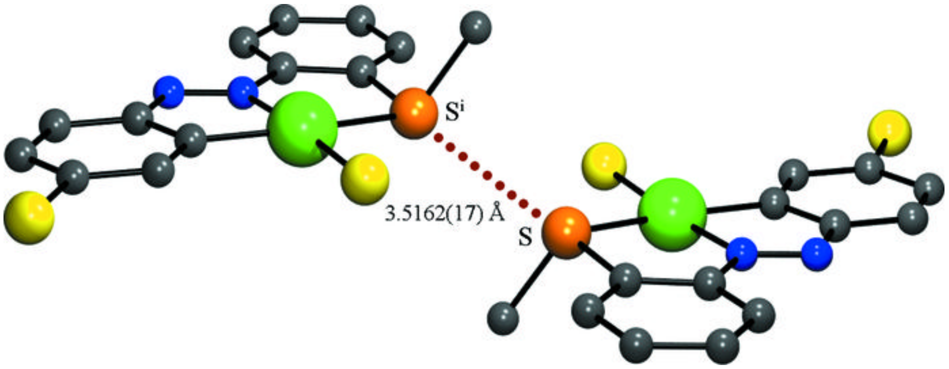
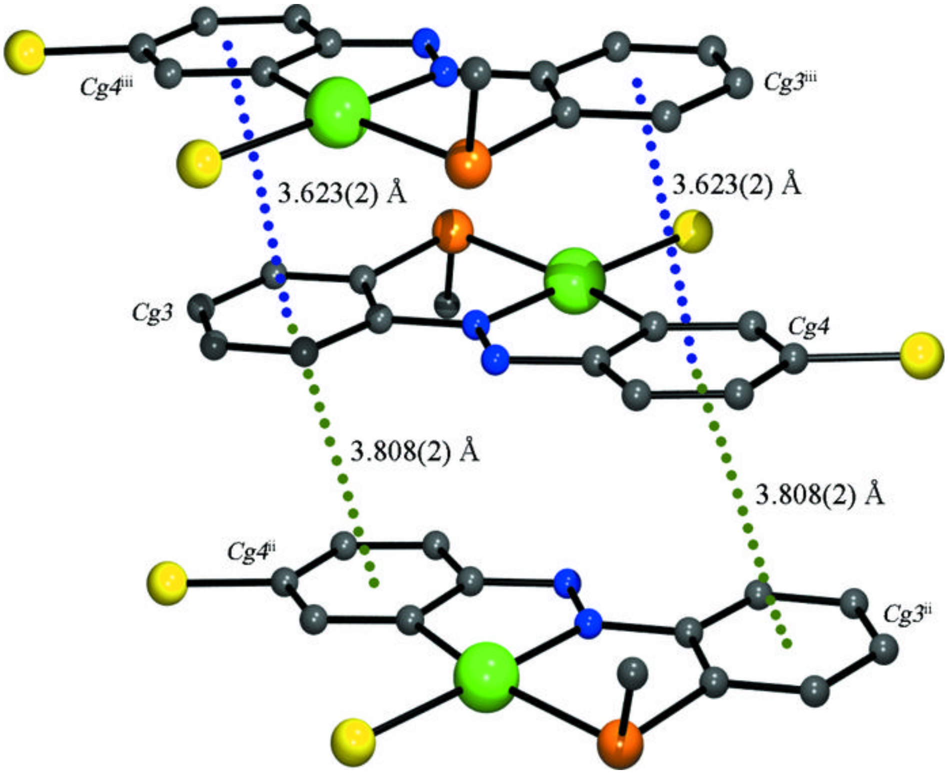


Fig. 4


Cg4ⁱⁱⁱ
Cg3ⁱⁱⁱ
3.623(2) Å
3.623(2) Å
Cg3
Cg4
3.808(2) Å
3.808(2) Å
Cg4ⁱⁱ
Cg3ⁱⁱ