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

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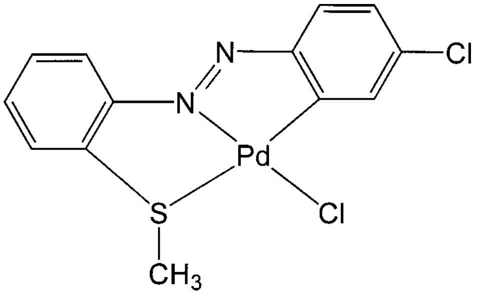
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.009 Å; R factor = 0.050; wR factor = 0.103; data-to-parameter ratio = 14.0.

The title compound, [Pd($C_{13}H_{10}ClN_2S$)Cl], is the monoclinic form of a previously reported triclinic structure of the same compound. The bond distances and angles of the molecule in the monoclinic form deviate slightly from those for the triclinic form. The Pd atom in this compound is tetracoordinated by a benzene C, a diazene N, a Cl and an S atom in an approximately square-planar geometry. The intermolecular interactions are very similar in both polymorphs. The molecules are found to dimerize through a nonbonding S···S interaction [S···S = 3.438 (2) Å]. There are no hydrogen bonds and the crystal packing is stabilized by four intermolecular π–π interactions; the distances between the centroids of the six-membered rings are 3.620 (3), 3.841 (3), 3.619 (3) and 3.842 (3) Å, and the perpendicular distances are 3.482, 3.482, 3.536 and 3.519 Å.

Related literature

For the triclinic polymorph, see: Bagchi & Bandyopadhyay (2007). For related literature, see: Bagchi *et al.* (2007); Chattopadhyay *et al.* (1991); Kubo *et al.* (2005).



Experimental

Crystal data

[Pd($C_{13}H_{10}ClN_2S$)Cl]
M_r = 403.59
Monoclinic, $P2_1/c$
a = 7.3978 (10) Å
b = 8.8652 (12) Å
c = 20.978 (3) Å
β = 94.668 (2)°
V = 1371.2 (3) $Å^3$
Z = 4
Mo $K\alpha$ radiation
μ = 1.88 mm^{-1}
T = 295 (2) K
0.42 × 0.30 × 0.19 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.510, T_{max} = 0.703
12718 measured reflections
2420 independent reflections
2346 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.103
S = 1.31
2420 reflections
173 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.86 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.79 e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °).

Cl1—Pd1	2.2904 (15)	Pd1—C2	1.981 (5)
Pd1—N2	1.975 (4)	Pd1—S1	2.3735 (15)
N2—Pd1—C2	80.1 (2)	N2—Pd1—S1	84.81 (13)
C2—Pd1—Cl1	95.98 (16)	Cl1—Pd1—S1	99.18 (6)

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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2336).

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supplementary materials

Acta Cryst. (2007). E**63**, m2130 [**doi:10.1107/S1600536807033636**]

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

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

Comment

We recently reported the structure of a first triclinic polymorph of [Pd($C_{13}H_{10}ClN_2S$)Cl] in space group $P\overline{1}$ (Bagchi *et al.*, 2007). The title molecule, (**I**), was produced during a parallel crystallization process. The present crystal found to crystallize in monoclinic form with $P2_1/c$ space group at room temperature. Herein we report the monoclinic 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 bond distances and bond angles of the molecule in the monoclinic form deviates slightly from those in the triclinic morphology (Bagchi *et al.*, 2007). The molecules are found to dimerize through a nonbonded S···S interaction; having S···S^{i} [Symmetry code: (i) $-x$, $2 - y$, $-z$] distance of 3.438 (2) Å (Chattopadhyay *et al.*, 1991) and is smaller than that in the triclinic crystal modification (Bagchi *et al.*, 2007) (Fig. 3). Four intermolecular 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) $-x$, $1 - y$, $-z$; (iii) $1 - x$, $1 - y$, $-z$. *Cg3* and *Cg4* are the centroids of C1—C6 and C7—C12 rings, respectively] distances are 3.620 (3), 3.841 (3), 3.619 (3) and 3.842 (3) Å; the perpendicular distances are 3.482, 3.482, 3.536 and 3.519 Å, respectively, with no slippages; though the *Cg*···*Cg* distances are very close in both the polymorph but the perpendicular distances are greater in the monoclinic crystal modification.

Experimental

The title compound (**I**) was prepared following a method reported in an earlier communication (Bagchi *et al.*, 2007). 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

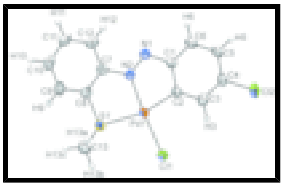


Fig. 1. The asymmetric unit of (**I**), with displacement ellipsoids drawn at the 50% probability level.

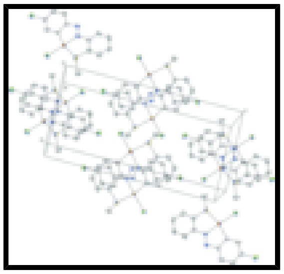


Fig. 2. The molecular arrangement of (**I**) in the *bc* plane.

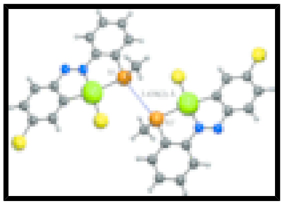


Fig. 3. The intermolecular S···S interaction for (**I**), indicated by dotted line [Symmetry code: (i) −*x*, 2 − *y*, −*z*].

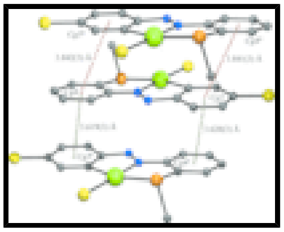


Fig. 4. The intermolecular π—π interactions for (I), indicated by the blue and green dotted lines. [Symmetry code: (ii) −*x*, 1 − *y*, −*z*; (iii) 1 − *x*, 1 − *y*, −*z*.]. *Cg*3 and *Cg*4 are centroids of C1—C6 and C7—C12 rings, respectively.

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

Crystal data

[$Pd(C_{13}H_{10}ClN_2S)Cl$]

M_r = 403.59

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

a = 7.3978 (10) Å

b = 8.8652 (12) Å

c = 20.978 (3) Å

β = 94.668 (2)°

V = 1371.2 (3) Å^3

Z = 4

F_{000} = 792

D_x = 1.955 Mg m^{-3}

Mo *K*α radiation
λ = 0.71073 Å

Cell parameters from 2420 reflections

θ = 2.0–25.0°

μ = 1.88 mm^{-1}

T = 295 (2) K

Block, red

0.42 × 0.30 × 0.19 mm

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 298(2) K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

2420 independent reflections

2346 reflections with $I > 2\sigma(I)$

R_{int} = 0.036

θ_{max} = 25.0°

θ_{min} = 2.0°

$h = -8 \rightarrow 8$

T_{min} = 0.510, T_{max} = 0.703	$k = -10 \rightarrow 10$
12718 measured reflections	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.050$	H-atom parameters constrained
$wR(F^2) = 0.103$	$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 3.6827P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.31$	$(\Delta/\sigma)_{max} = 0.001$
2420 reflections	$\Delta\rho_{max}$ = 0.86 e Å^{-3}
173 parameters	$\Delta\rho_{min}$ = −0.79 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}
C5	0.3885 (8)	1.2353 (6)	0.3486 (3)	0.0398 (14)
H5	0.4174	1.3256	0.3293	0.048*
C13	0.2475 (9)	0.4991 (7)	0.5732 (3)	0.0496 (16)
H13A	0.3682	0.5370	0.5828	0.074*
H13B	0.2499	0.4190	0.5425	0.074*
H13C	0.2014	0.4615	0.6116	0.074*
Cl1	0.2324 (3)	0.60867 (17)	0.38218 (7)	0.0542 (5)
Cl2	0.4171 (3)	1.10947 (19)	0.23353 (7)	0.0532 (4)
Pd1	0.22575 (6)	0.79235 (4)	0.458724 (19)	0.03074 (16)
S1	0.1026 (2)	0.64961 (16)	0.54057 (7)	0.0363 (3)
N2	0.2277 (6)	0.9604 (5)	0.5206 (2)	0.0303 (10)
C7	0.1844 (7)	0.9369 (6)	0.5847 (3)	0.0314 (12)
C2	0.3027 (7)	0.9594 (6)	0.4043 (2)	0.0303 (12)
N1	0.2704 (6)	1.0932 (5)	0.5040 (2)	0.0342 (10)
C1	0.3119 (7)	1.0953 (6)	0.4398 (3)	0.0302 (12)
C8	0.1314 (8)	0.7914 (7)	0.6008 (3)	0.0360 (13)

C6	0.3554 (8)	1.2324 (6)	0.4122 (3)	0.0390 (13)
H6	0.3619	1.3204	0.4364	0.047*
C9	0.0915 (8)	0.7616 (7)	0.6630 (3)	0.0444 (15)
H9	0.0547	0.6655	0.6741	0.053*
C12	0.1965 (8)	1.0512 (7)	0.6304 (3)	0.0398 (14)
H12	0.2302	1.1482	0.6194	0.048*
C4	0.3786 (7)	1.1036 (6)	0.3140 (3)	0.0344 (12)
C3	0.3360 (7)	0.9653 (6)	0.3406 (3)	0.0365 (13)
H3	0.3301	0.8783	0.3158	0.044*
C11	0.1579 (9)	1.0191 (8)	0.6921 (3)	0.0481 (16)
H11	0.1662	1.0945	0.7230	0.058*
C10	0.1065 (8)	0.8739 (8)	0.7082 (3)	0.0490 (16)
H10	0.0820	0.8527	0.7501	0.059*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C5	0.047 (3)	0.028 (3)	0.045 (3)	−0.003 (3)	0.009 (3)	0.009 (3)
C13	0.062 (4)	0.036 (3)	0.049 (4)	0.002 (3)	−0.006 (3)	0.004 (3)
Cl1	0.0972 (13)	0.0283 (7)	0.0391 (8)	−0.0041 (8)	0.0176 (8)	−0.0051 (6)
Cl2	0.0783 (12)	0.0464 (9)	0.0363 (8)	−0.0009 (8)	0.0131 (8)	0.0081 (7)
Pd1	0.0413 (3)	0.0231 (2)	0.0281 (2)	−0.00143 (18)	0.00396 (17)	0.00059 (17)
S1	0.0453 (8)	0.0322 (7)	0.0308 (7)	−0.0094 (6)	0.0002 (6)	0.0013 (6)
N2	0.033 (2)	0.027 (2)	0.031 (2)	−0.0004 (19)	0.0008 (19)	−0.0012 (19)
C7	0.027 (3)	0.032 (3)	0.035 (3)	0.000 (2)	−0.001 (2)	−0.001 (2)
C2	0.032 (3)	0.028 (3)	0.031 (3)	0.006 (2)	0.002 (2)	0.005 (2)
N1	0.034 (2)	0.030 (2)	0.038 (3)	−0.001 (2)	0.006 (2)	−0.003 (2)
C1	0.028 (3)	0.027 (3)	0.036 (3)	0.004 (2)	0.001 (2)	0.000 (2)
C8	0.036 (3)	0.041 (3)	0.031 (3)	−0.004 (3)	0.003 (2)	−0.001 (3)
C6	0.043 (3)	0.026 (3)	0.047 (4)	−0.004 (2)	0.005 (3)	−0.001 (3)
C9	0.049 (4)	0.047 (4)	0.038 (3)	−0.004 (3)	0.007 (3)	0.004 (3)
C12	0.042 (3)	0.034 (3)	0.043 (3)	0.002 (3)	0.003 (3)	−0.011 (3)
C4	0.034 (3)	0.037 (3)	0.032 (3)	0.002 (2)	0.003 (2)	0.007 (2)
C3	0.039 (3)	0.033 (3)	0.038 (3)	0.000 (2)	0.003 (3)	0.001 (3)
C11	0.054 (4)	0.055 (4)	0.035 (3)	−0.003 (3)	0.003 (3)	−0.014 (3)
C10	0.049 (4)	0.066 (5)	0.032 (3)	−0.002 (3)	0.008 (3)	0.002 (3)

Geometric parameters (Å, °)

C5—C4	1.374 (8)	C7—C8	1.397 (8)
C5—C6	1.375 (8)	C2—C3	1.380 (8)
C5—H5	0.9300	C2—C1	1.415 (7)
C13—S1	1.810 (6)	N1—C1	1.406 (7)
C13—H13A	0.9600	C1—C6	1.395 (8)
C13—H13B	0.9600	C8—C9	1.386 (8)
C13—H13C	0.9600	C6—H6	0.9300
Cl1—Pd1	2.2904 (15)	C9—C10	1.374 (9)
Cl2—C4	1.736 (6)	C9—H9	0.9300
Pd1—N2	1.975 (4)	C12—C11	1.378 (9)

Pd1—C2	1.981 (5)	C12—H12	0.9300
Pd1—S1	2.3735 (15)	C4—C3	1.394 (8)
S1—C8	1.783 (6)	C3—H3	0.9300
N2—N1	1.274 (6)	C11—C10	1.392 (10)
N2—C7	1.424 (7)	C11—H11	0.9300
C7—C12	1.393 (8)	C10—H10	0.9300

C4—C5—C6	119.3 (5)	C6—C1—N1	119.1 (5)
C4—C5—H5	120.3	C6—C1—C2	121.7 (5)
C6—C5—H5	120.3	N1—C1—C2	119.2 (5)
S1—C13—H13A	109.5	C9—C8—C7	119.3 (5)
S1—C13—H13B	109.5	C9—C8—S1	120.7 (5)
H13A—C13—H13B	109.5	C7—C8—S1	119.9 (4)
S1—C13—H13C	109.5	C5—C6—C1	119.0 (5)
H13A—C13—H13C	109.5	C5—C6—H6	120.5
H13B—C13—H13C	109.5	C1—C6—H6	120.5
N2—Pd1—C2	80.1 (2)	C10—C9—C8	120.0 (6)
N2—Pd1—Cl1	176.01 (14)	C10—C9—H9	120.0
C2—Pd1—Cl1	95.98 (16)	C8—C9—H9	120.0
N2—Pd1—S1	84.81 (13)	C11—C12—C7	119.3 (6)
C2—Pd1—S1	163.81 (16)	C11—C12—H12	120.3
Cl1—Pd1—S1	99.18 (6)	C7—C12—H12	120.3
C8—S1—C13	102.6 (3)	C5—C4—C3	122.7 (5)
C8—S1—Pd1	96.11 (19)	C5—C4—Cl2	118.8 (4)
C13—S1—Pd1	114.6 (2)	C3—C4—Cl2	118.4 (4)
N1—N2—C7	118.2 (4)	C2—C3—C4	119.0 (5)
N1—N2—Pd1	120.4 (4)	C2—C3—H3	120.5
C7—N2—Pd1	121.3 (3)	C4—C3—H3	120.5
C12—C7—C8	120.6 (5)	C12—C11—C10	120.0 (6)
C12—C7—N2	122.5 (5)	C12—C11—H11	120.0
C8—C7—N2	116.9 (5)	C10—C11—H11	120.0
C3—C2—C1	118.2 (5)	C9—C10—C11	120.8 (6)
C3—C2—Pd1	131.9 (4)	C9—C10—H10	119.6
C1—C2—Pd1	109.7 (4)	C11—C10—H10	119.6
N2—N1—C1	110.6 (4)		

N2—Pd1—S1—C8	−7.4 (2)	C3—C2—C1—N1	177.1 (5)
C2—Pd1—S1—C8	−28.3 (6)	Pd1—C2—C1—N1	0.7 (6)
Cl1—Pd1—S1—C8	172.5 (2)	C12—C7—C8—C9	−0.3 (8)
N2—Pd1—S1—C13	−114.3 (3)	N2—C7—C8—C9	178.6 (5)
C2—Pd1—S1—C13	−135.2 (6)	C12—C7—C8—S1	176.0 (4)
Cl1—Pd1—S1—C13	65.6 (2)	N2—C7—C8—S1	−5.1 (7)
C2—Pd1—N2—N1	0.4 (4)	C13—S1—C8—C9	−58.1 (6)
S1—Pd1—N2—N1	−173.8 (4)	Pd1—S1—C8—C9	−175.0 (5)
C2—Pd1—N2—C7	−178.6 (4)	C13—S1—C8—C7	125.7 (5)
S1—Pd1—N2—C7	7.1 (4)	Pd1—S1—C8—C7	8.8 (5)
N1—N2—C7—C12	−3.5 (7)	C4—C5—C6—C1	−0.2 (9)
Pd1—N2—C7—C12	175.6 (4)	N1—C1—C6—C5	−177.3 (5)
N1—N2—C7—C8	177.6 (5)	C2—C1—C6—C5	0.6 (9)
Pd1—N2—C7—C8	−3.3 (6)	C7—C8—C9—C10	−0.8 (9)

N2—Pd1—C2—C3	−176.3 (6)	S1—C8—C9—C10	−177.0 (5)
Cl1—Pd1—C2—C3	4.2 (5)	C8—C7—C12—C11	0.9 (9)
S1—Pd1—C2—C3	−155.2 (4)	N2—C7—C12—C11	−178.0 (5)
N2—Pd1—C2—C1	−0.6 (4)	C6—C5—C4—C3	0.0 (9)
Cl1—Pd1—C2—C1	180.0 (3)	C6—C5—C4—Cl2	179.0 (5)
S1—Pd1—C2—C1	20.6 (8)	C1—C2—C3—C4	0.6 (8)
C7—N2—N1—C1	178.9 (4)	Pd1—C2—C3—C4	176.1 (4)
Pd1—N2—N1—C1	−0.2 (6)	C5—C4—C3—C2	−0.2 (9)
N2—N1—C1—C6	177.6 (5)	Cl2—C4—C3—C2	−179.2 (4)
N2—N1—C1—C2	−0.4 (7)	C7—C12—C11—C10	−0.4 (9)
C3—C2—C1—C6	−0.8 (8)	C8—C9—C10—C11	1.3 (10)
Pd1—C2—C1—C6	−177.3 (4)	C12—C11—C10—C9	−0.7 (10)

Fig. 1

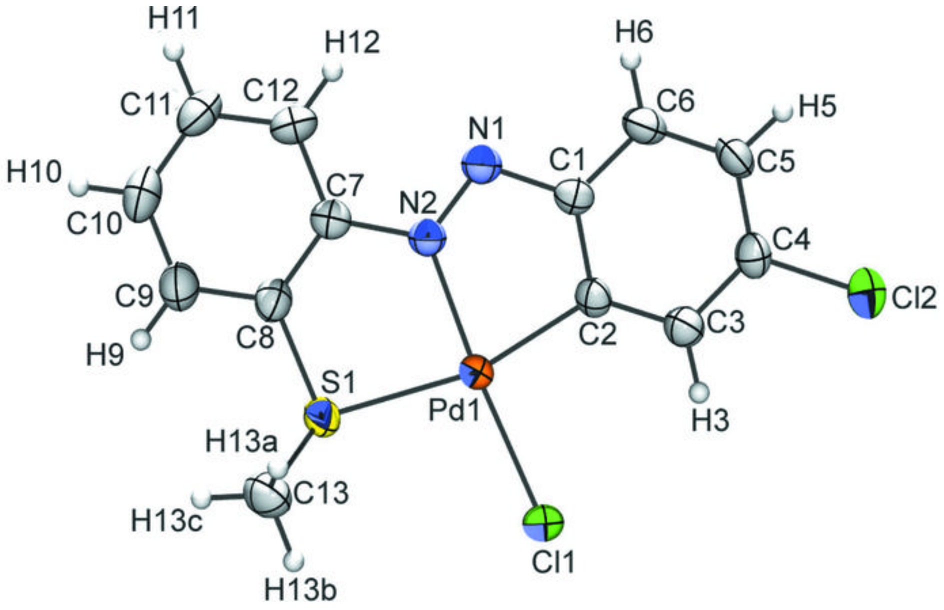

H11
H12
H6
C11
C12
C6
H5
N1
C1
C5
H10
C7
N2
C10
C4
Cl2
C9
C8
C2
C3
H9
S1
Pd1
H3
H13a
C13
H13c
Cl1
H13b

Fig. 2

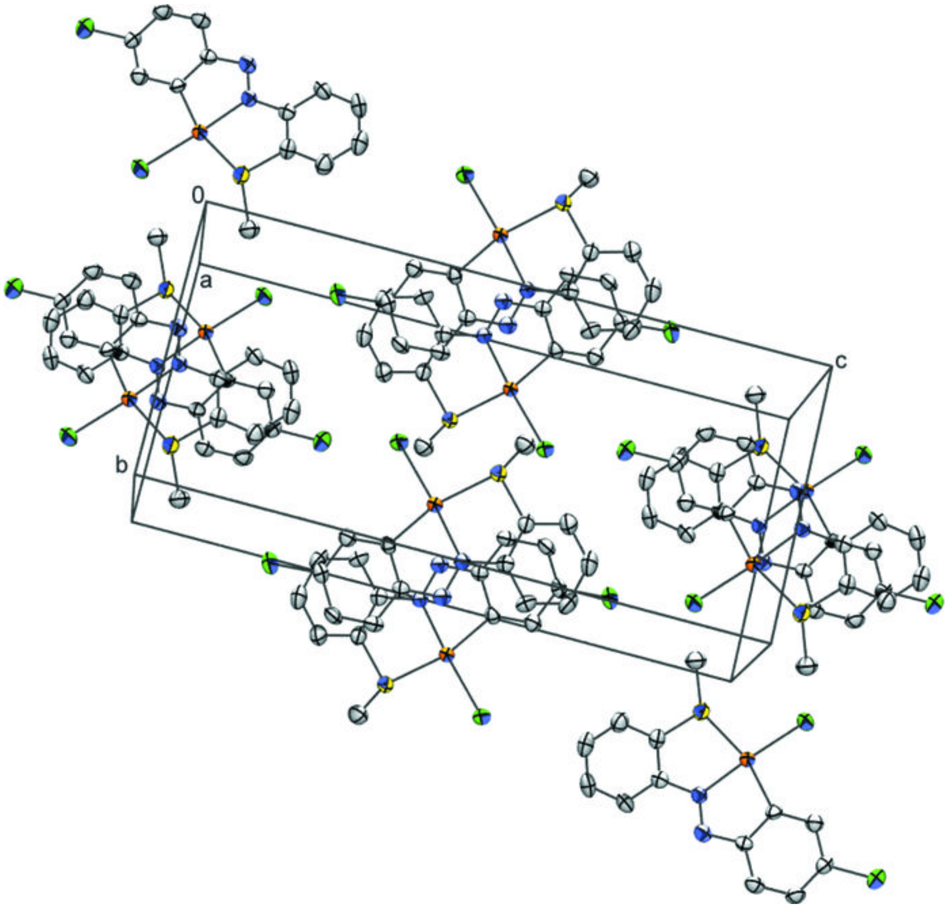


Fig. 3

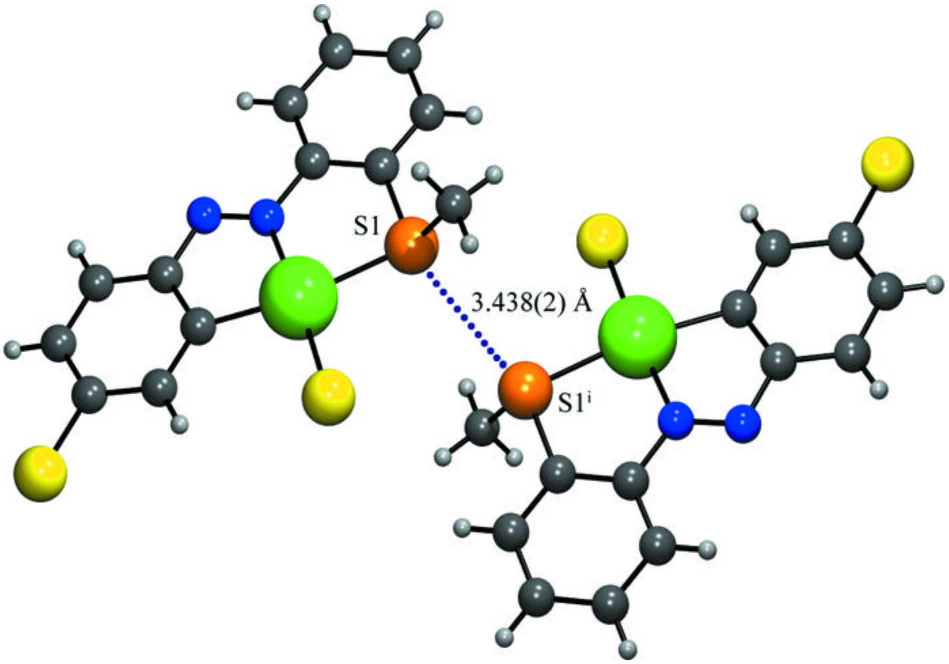
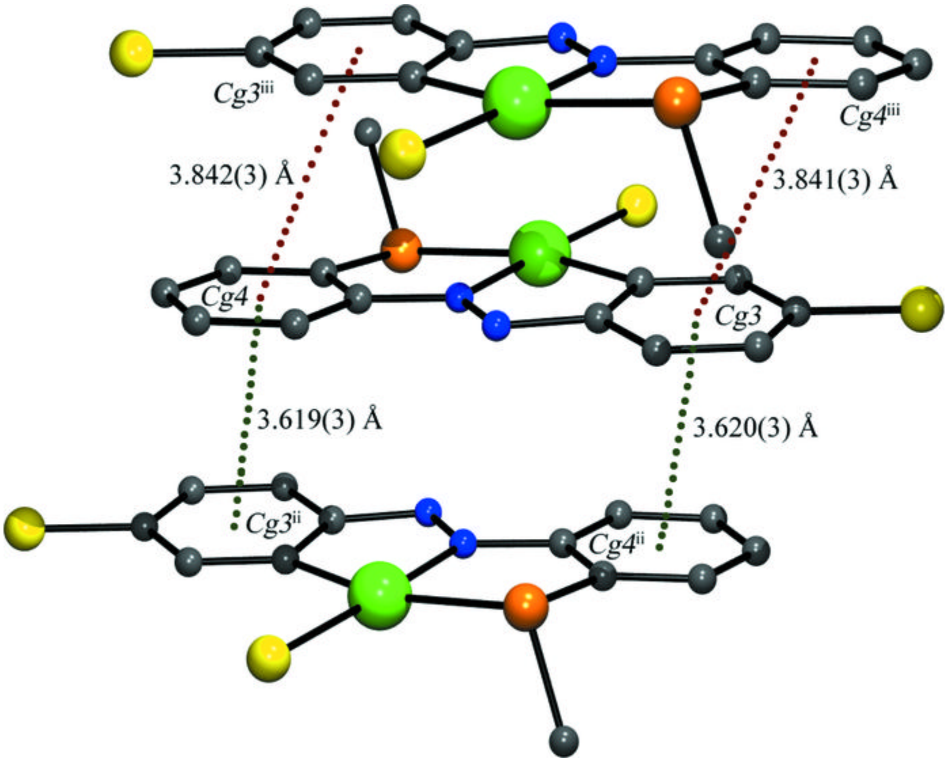


Fig. 4


Cg3iii
Cg4iii
3.842(3) Å
3.841(3) Å
Cg4
Cg3
3.619(3) Å
3.620(3) Å
Cg3ii
Cg4ii