Electronic Supplementary Information

Title: Vysotskite structured photoactive palladium sulphide thin films from dithiocarbamate derivatives

Authors: Muhammad Ali Ehsan,[a] Huang Nay Ming, [b] Vickie McKee, [c] Thalge Anton Nirmal Peiris,[c] Upul Wijayantha-Kahagala-Gamage[c] Zainudin Arifin[a] and Muhammad Mazhar,*[a]

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Micro Analysis

Precursor [Pd(S_2CNBz$_2$)$_2$]•Py(**1**)

Run	Run #	Weight	Created on	Carbon	Hydrogen	Nitrogen	Messages
P1	77	1.705	2013-3-6 4:22 PM	57.911	4.331	5.525	

Precursor [Pd(S_2CNCy$_2$)$_2$]•Py(**2**)

Run Details				Results			Messages
Run	Run #	Weight	Created on	Carbon	Hydrogen	Nitrogen	Messages
P2	22	1.554	2013-6-19 12:27 PM	52.868	7.317	5.84	

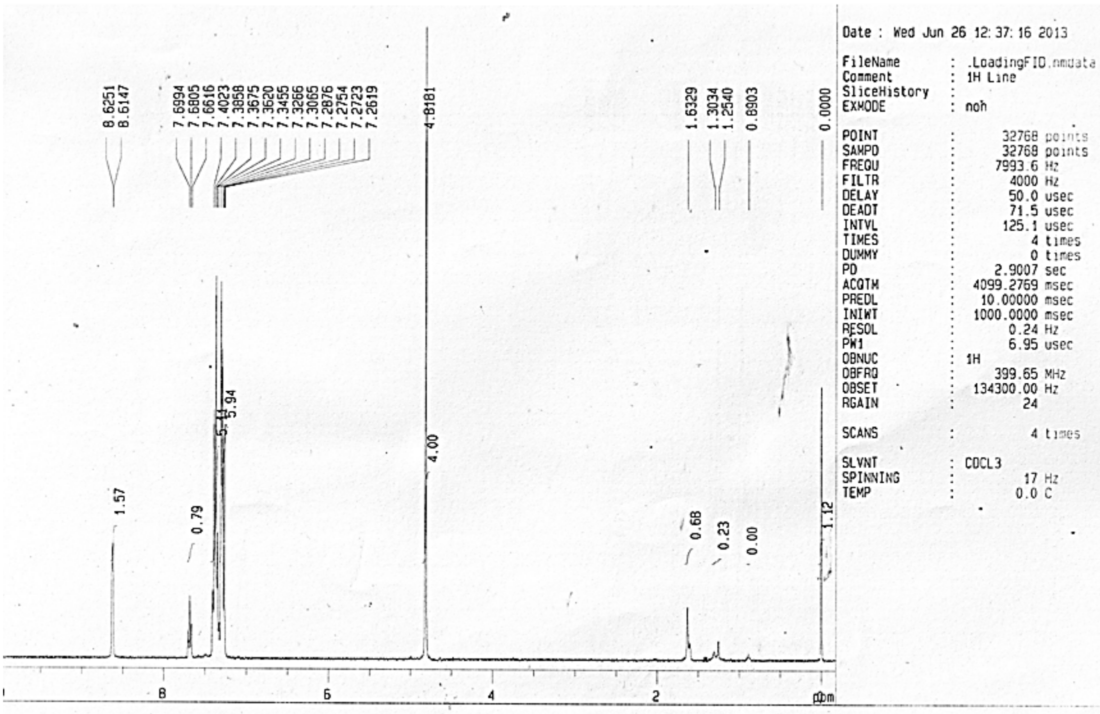
Precursor [Pd(S_2CN^{n}Hex$_2$)$_2$] (**3**)

Run Details				Results			Messages
Run	Run #	Weight	Created on	Carbon	Hydrogen	Nitrogen	Messages
P3	77	1.611	2013-5-30 11:58 AM	49.797	8.101	4.519	

Precursor [Pd(S_2CNMeCy)$_2$] (**4**)

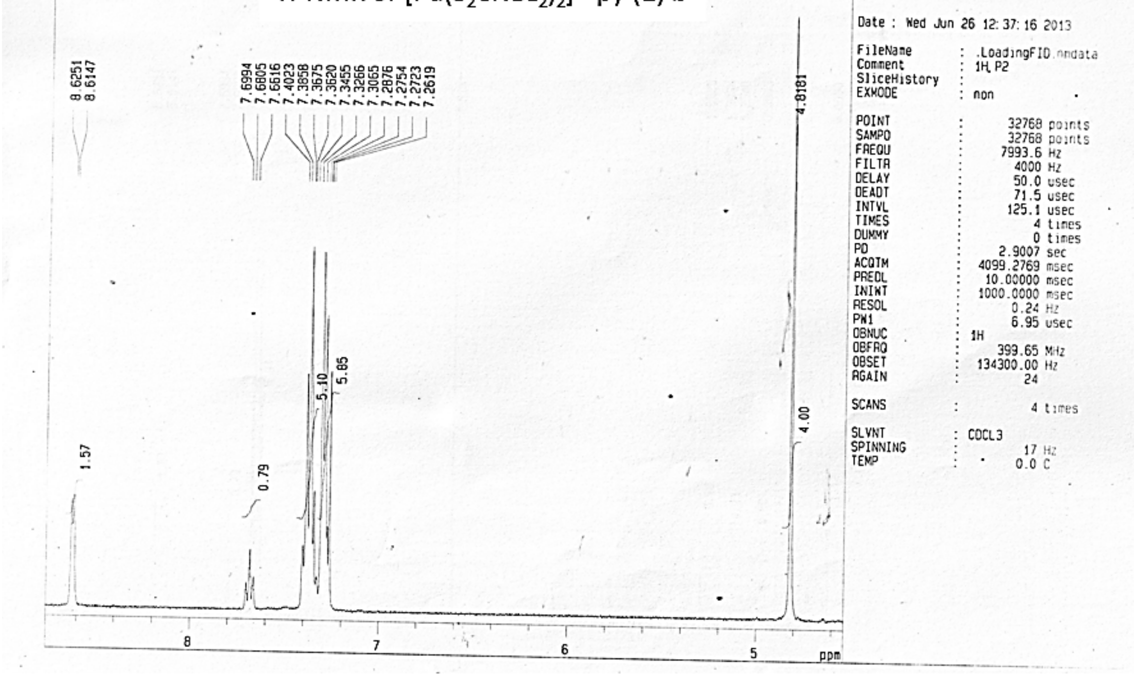
Run Details				Results			Messages
Run	Run #	Weight	Created on	Carbon	Hydrogen	Nitrogen	Messages
P4	15	1.586	2013-4-4 10:36 AM	40.172	5.895	5.939	

H-NMR of $[Pd(S_2CNBz_2)_2] \cdot py$ (**1**) a

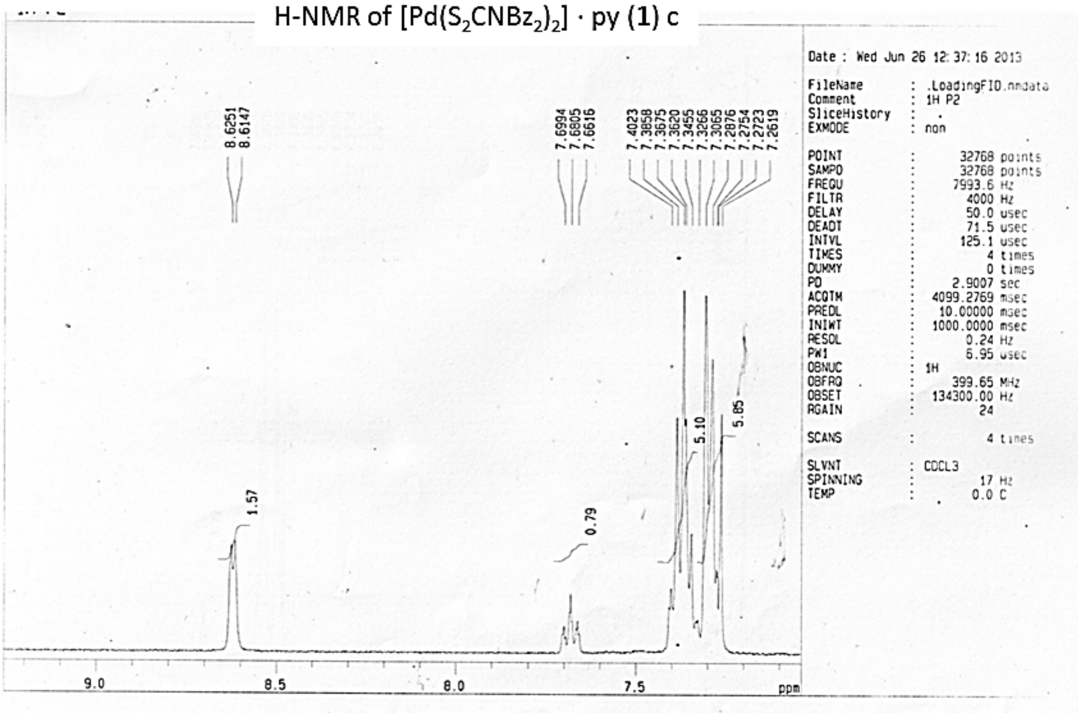


SI.Fig. 1a: ¹H-NMR of Precursor $[Pd(S_2CNBz_2)_2]$•Py(**1**).

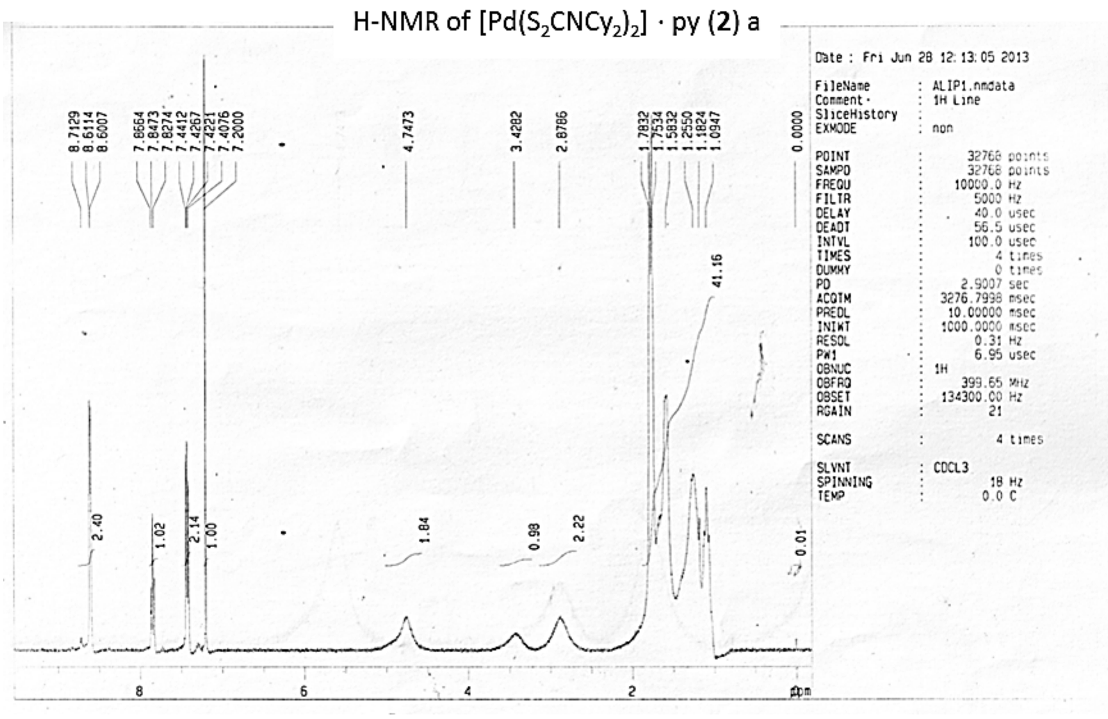
H-NMR of $[Pd(S_2CNBz_2)_2] \cdot py$ (**1**) b



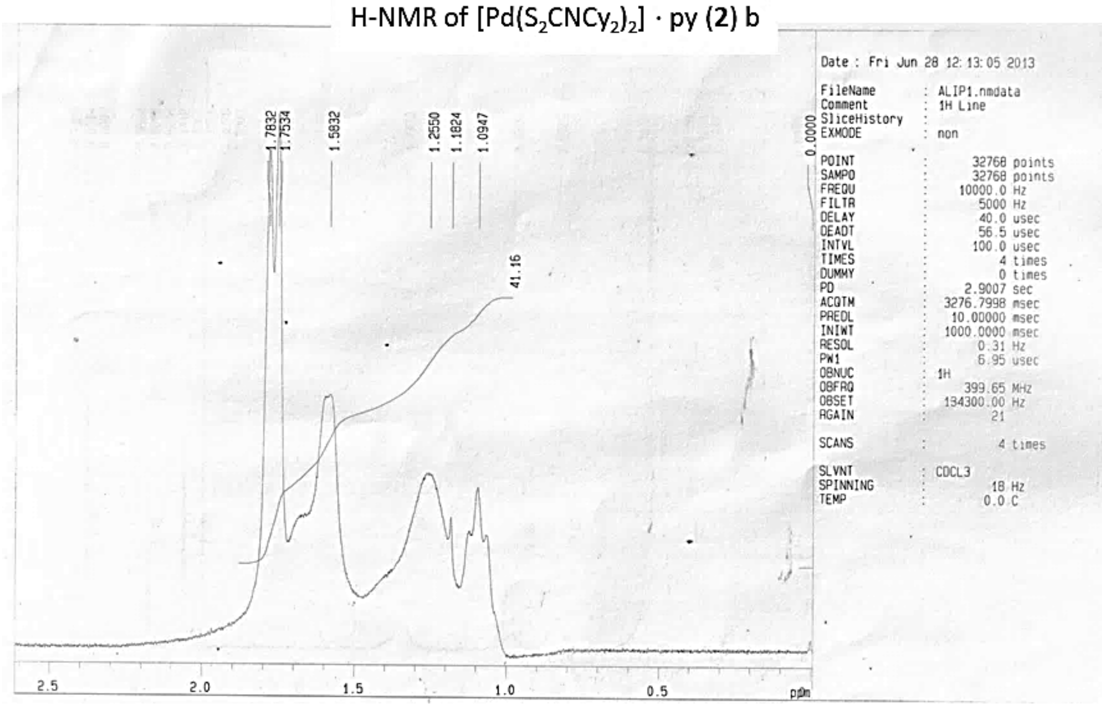
SI.Fig. 1b: ¹H-NMR of Precursor $[Pd(S_2CNBz_2)_2]$•Py(**1**)



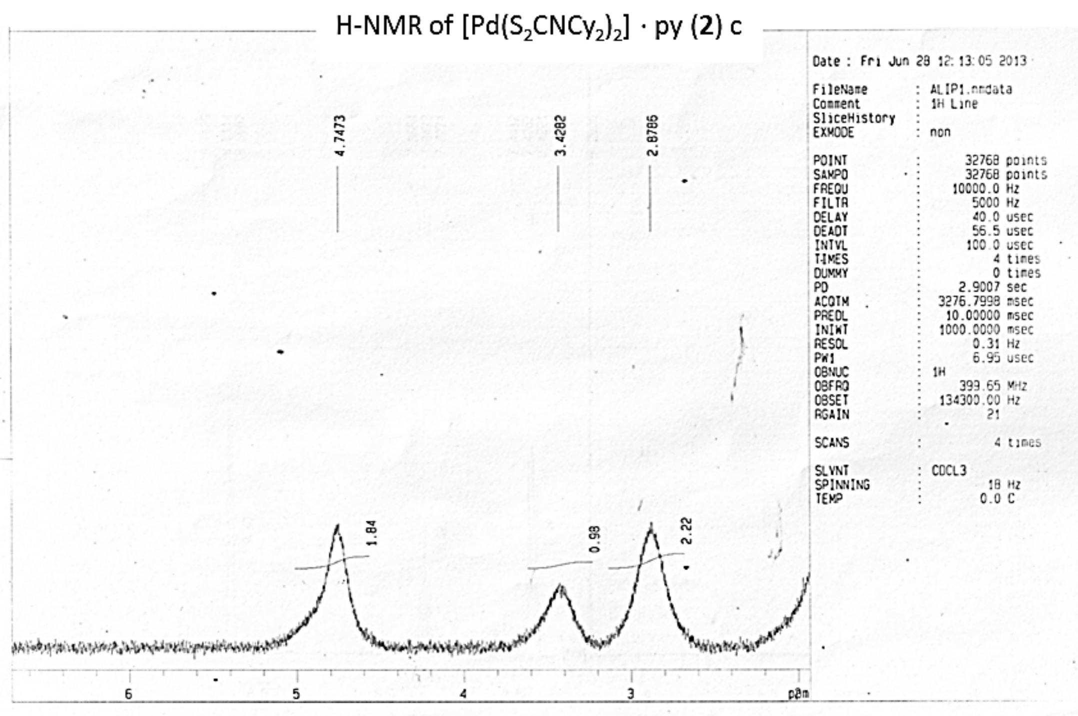
SI.Fig. 1c: ^{1}H-NMR of Precursor [Pd(S_2CNBz_2)$_2$]•Py(**1**)



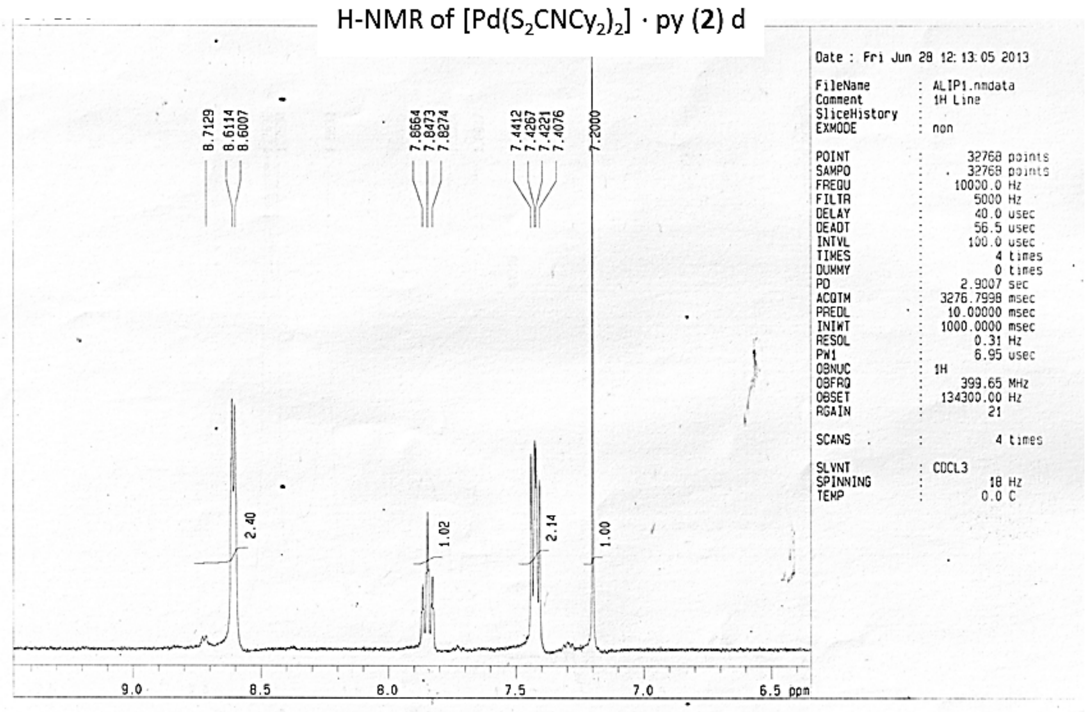
SI.Fig. 2a: ^{1}H-NMR of Precursor [Pd(S_2CNCy_2)$_2$]•Py(**2**)



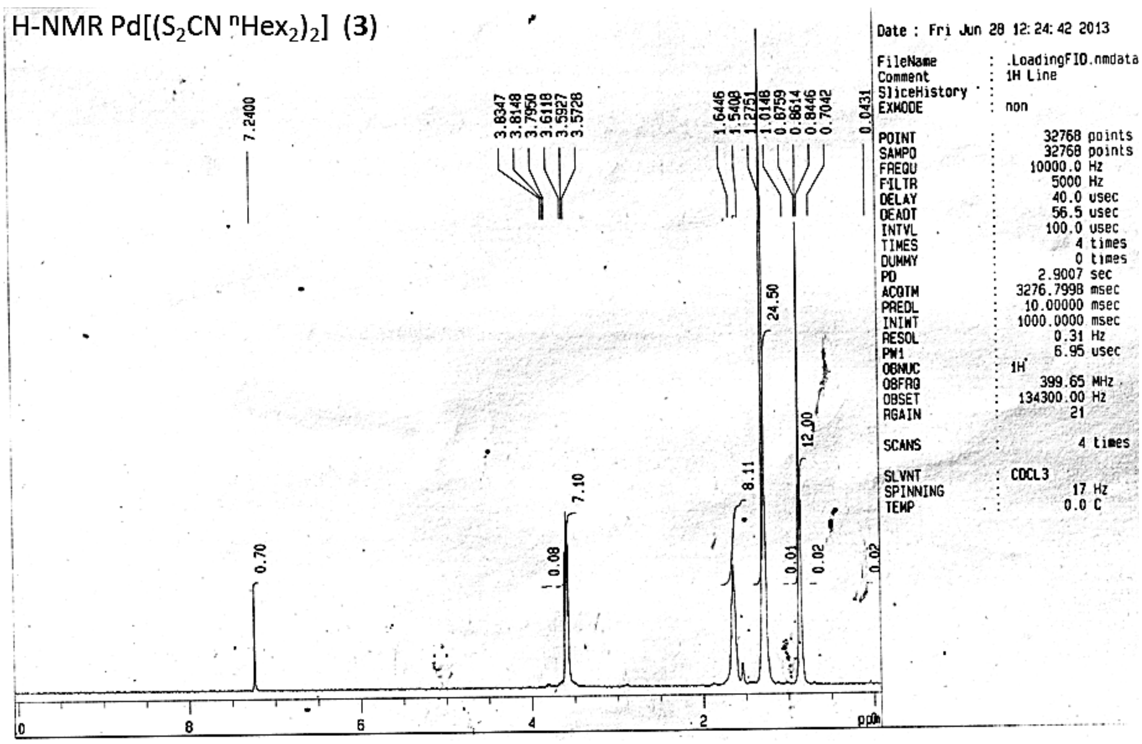
SI.Fig. 2b: [1]H-NMR of Precursor [Pd(S_2CNCy_2)$_2$]•Py(**2**)



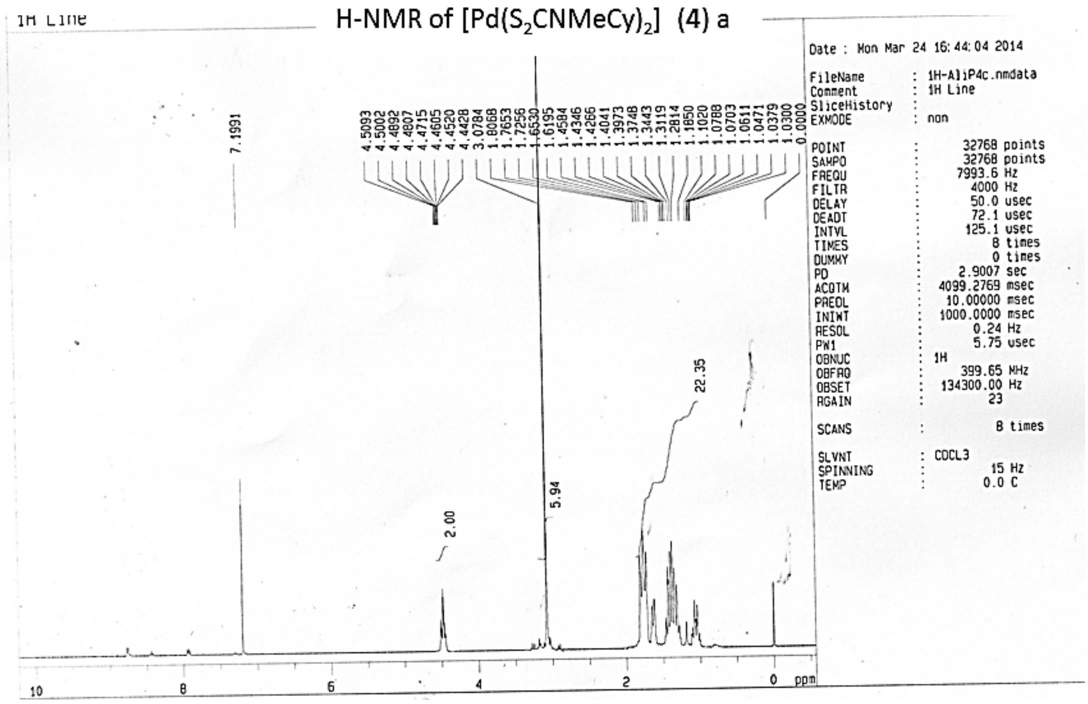
SI.Fig. 2c: [1]H-NMR of Precursor [Pd(S_2CNCy_2)$_2$]•Py(**2**)



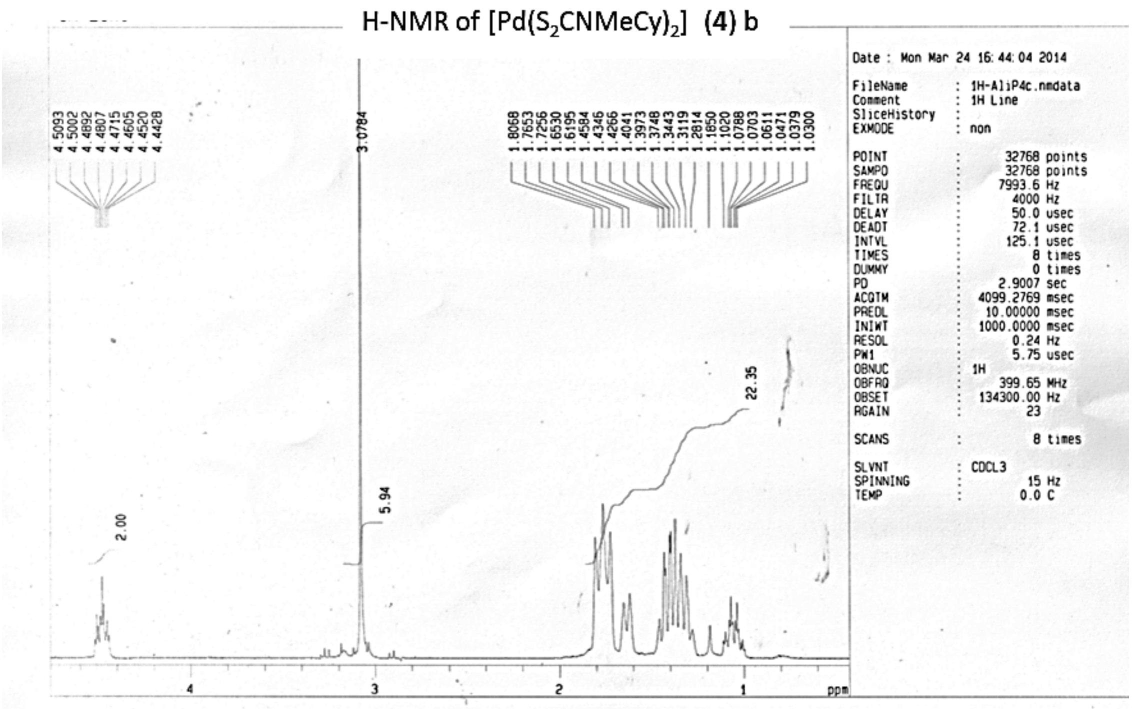
SI.Fig. 2d: [1]H-NMR of Precursor $[Pd(S_2CNCy_2)_2]$•Py(**2**)



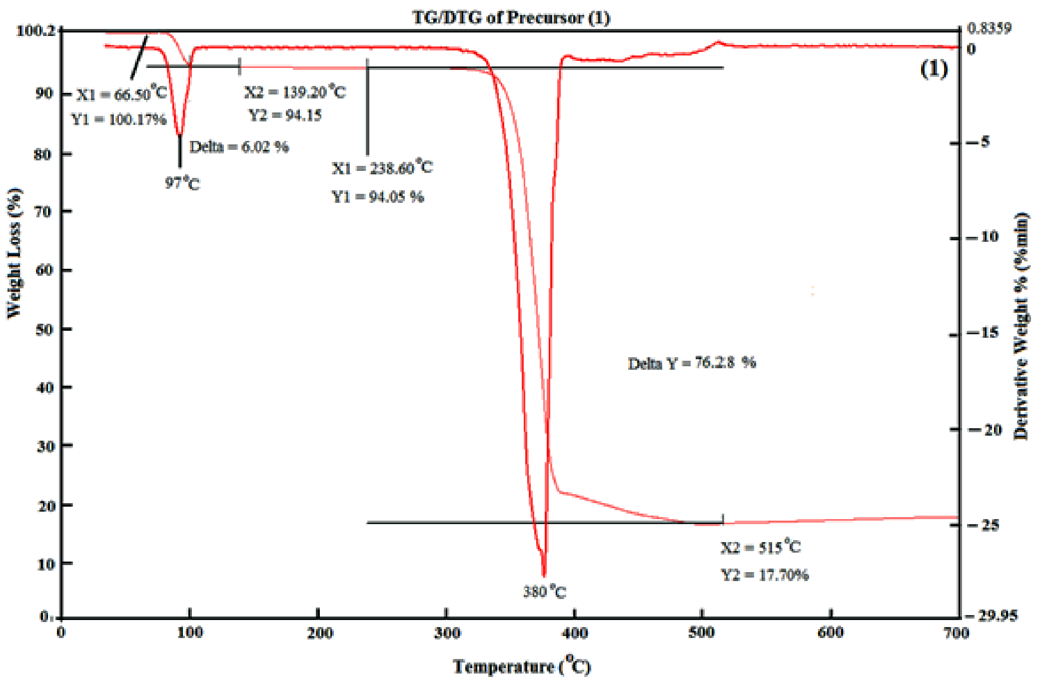
S.Fig. 3: [1]H-NMR of Precursor $[Pd(S_2CN^nHex_2)_2]$ (**3**)



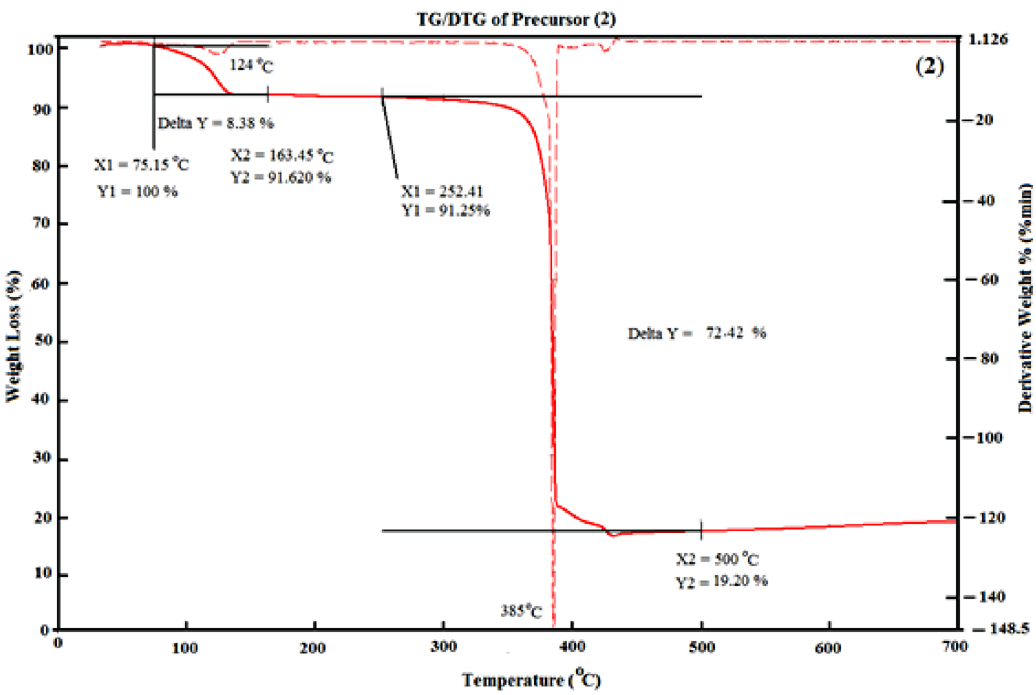
SI.Fig. 4: ^{1}H-NMR of Precursor [Pd(S$_2$CNMeCy)$_2$] (**4**)



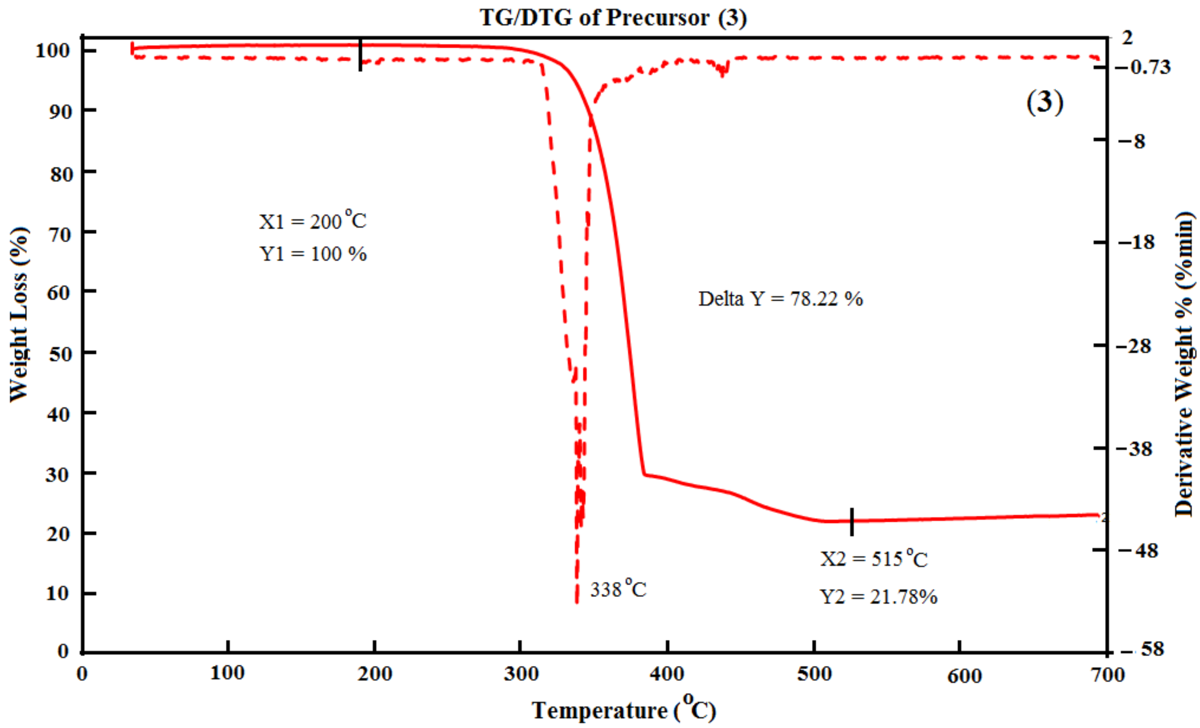
SI.Fig. 4: ^{1}H-NMR of Precursor [Pd(S$_2$CNMeCy)$_2$] (**5**)



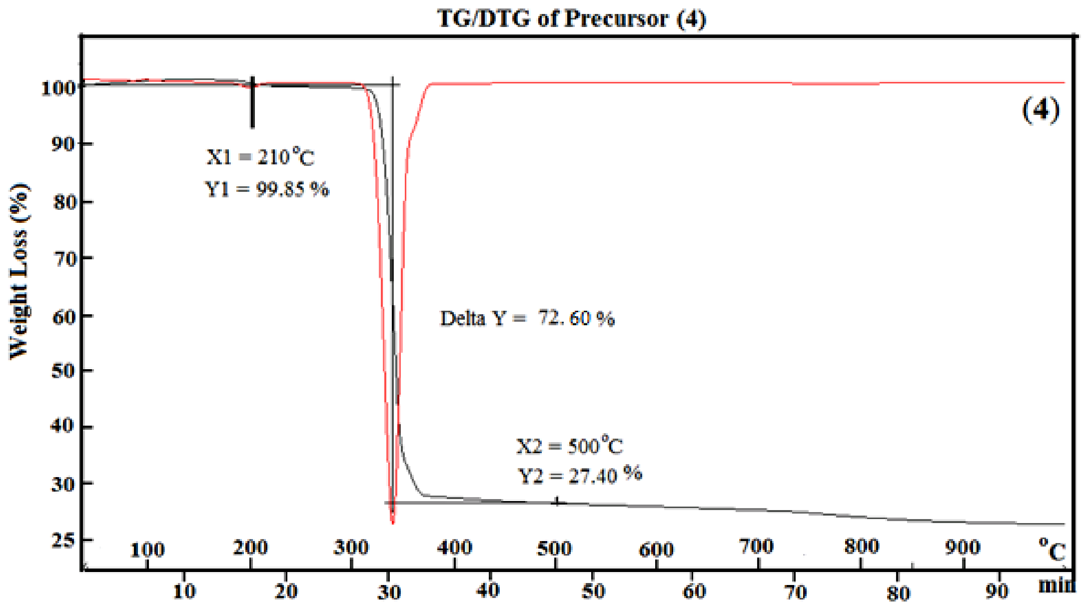
SI. Fig. 5a: TG/DTG curves presenting losses in weight against temperature for precursor $[Pd(S_2CNBz_2)_2]$•py (**1**)



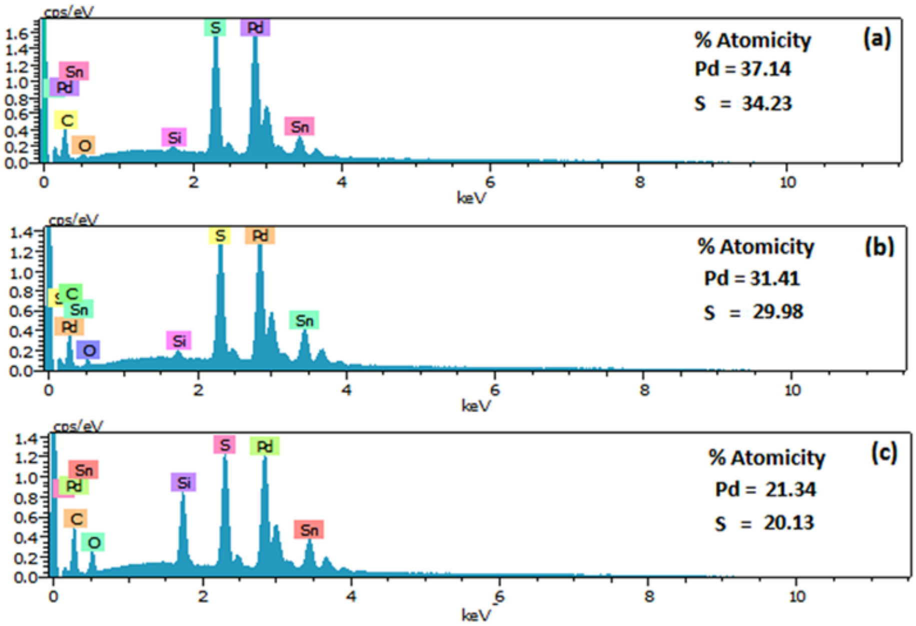
SI.Fig. 5b: TG/DTG curves presenting losses in weight against temperature for precursor $[Pd(S_2CNCy_2)_2]$•py(**2**).



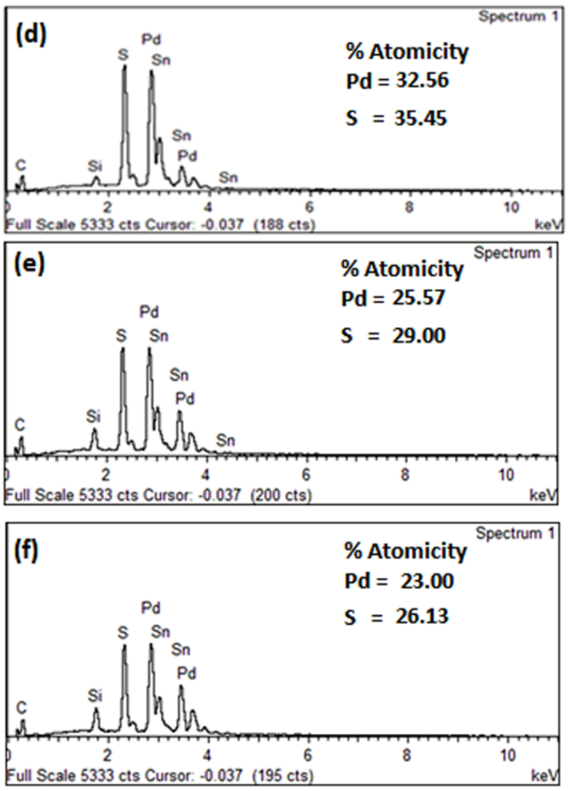
SI. Fig. 5c: TG/DTG curves presenting losses in weight against temperature for precursor $[Pd(S_2CN^nHex_2)_2]$ (**3**).



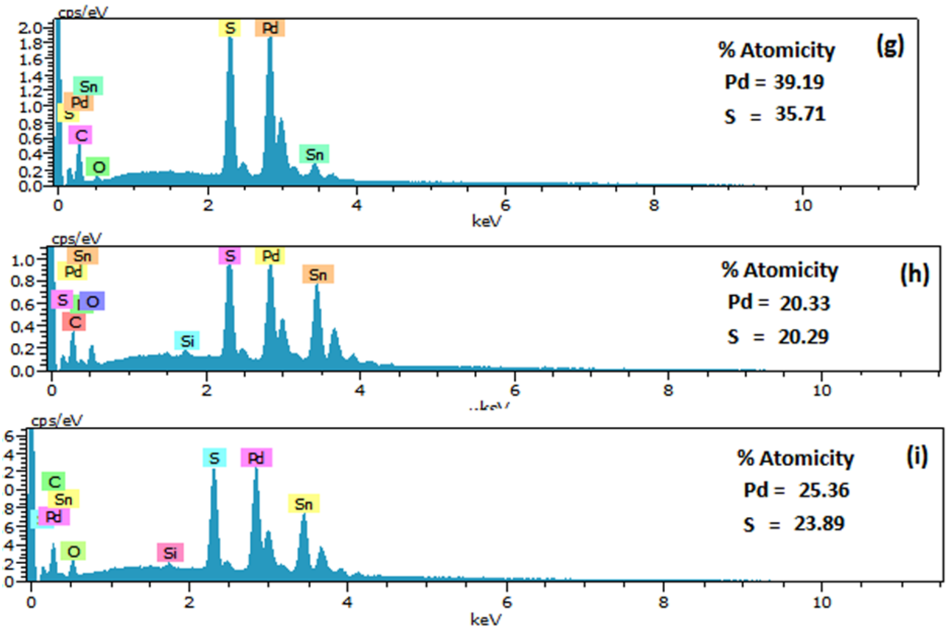
SI. Fig. 5d: TG/DTG curves presenting losses in weight against temperature for precursor $[Pd(S_2CNCyMe)_2]$ (**4**).



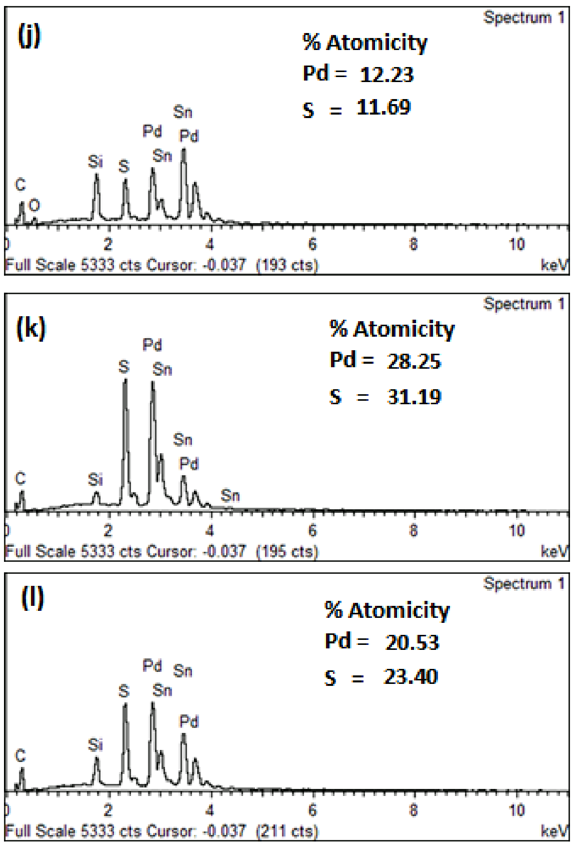
SI. Fig. 7a: EDX spectra of PdS thin films deposited using precursors $[Pd(S_2CNBz_2)_2]$•py (**1**) at **(a)** 400 °C **(b)** 450 °C **(c)** 500 °C.



SI. Fig. 7b: EDX spectra of PdS thin films deposited using precursors $[Pd(S_2CNCy_2)_2]$•py (**2**) at **(d)** 400 °C **(e)** 450 °C **(f)** 500 °C.



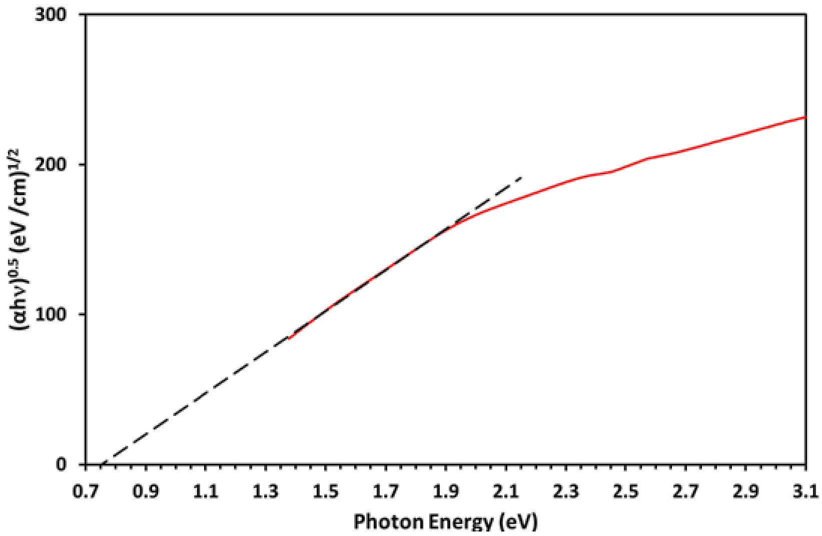
SI. Fig. 7c: EDX spectra of PdS thin films deposited using precursors [Pd($S_2CN^nHex_2$)$_2$] (**3**) at **(g)** 400 °C **(h)** 450 °C **(i)** 500 °C.



SI. Fig. 7d: EDX spectra of PdS thin films deposited using precursors [Pd($S_2CNCyMe$)$_2$] (**4**) at **(j)** 400 °C **(k)** 450 °C **(l)** 500 °C.

For Allowed Indirect Transition n = 2

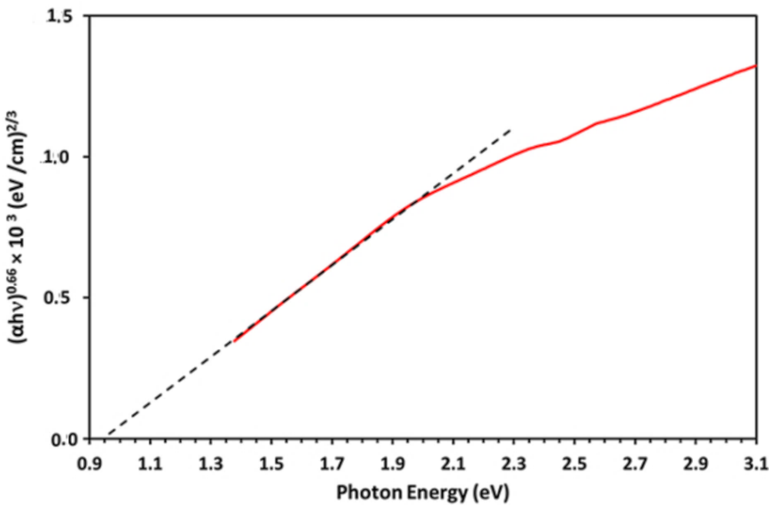
Calculated Band gap (Eg) = 0.75 eV



SI. Fig. 8c: Shows the allowed indirect (n = 2) band gap of 0.75 eV for PdS films.

For Forbidden Direct Transition (n = 3/2)

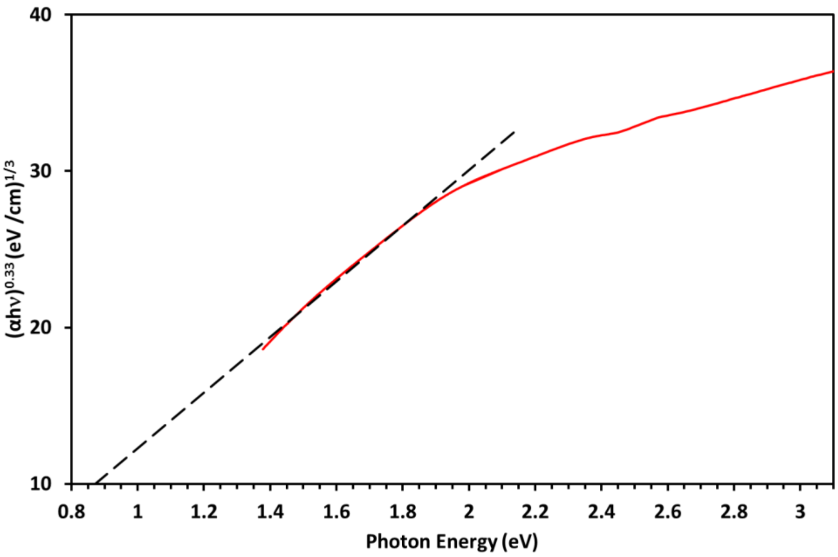
Calculated Band gap (Eg) = 0.95 eV



SI.Fig. 8 d: Shows the forbidden direct (n = 3/2) band gap of 0.95 eV for PdS films.

<u>For Forbidden Indirect Transition (n = 3)</u>

Calculated Band gap (Eg) = 0.87 eV



S.Fig. 8 e: Shows the indirect forbidden (n = 3) band gap of 0.87 eV for PdS films.

Supplementary material - crystallography

Experimental

The data were collected at 150(2)K on a Bruker Apex II CCD diffractometer using MoK_α radiation (λ = 0.71073Å). The structure was solved by direct methods and refined on F^2 using all the reflections[1]. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms were inserted at calculated positions using a riding model. Crystal data, data collection and structure refinement details are summarized in Table 1.

Computing details

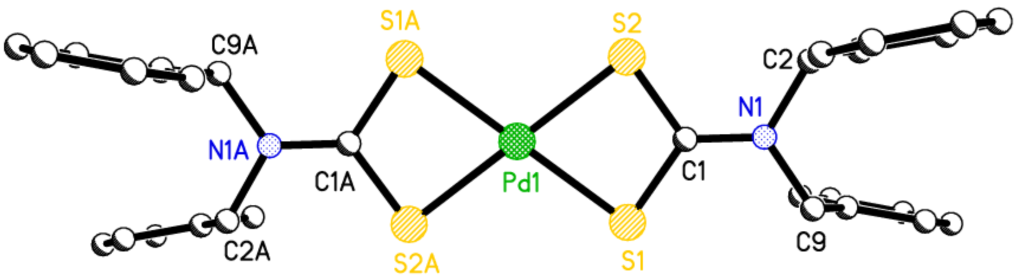
Data collection: Bruker *APEX* 2; cell refinement: Bruker *SAINT*; data reduction: Bruker *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2012*; molecular graphics: Bruker *SHELXTL* and *Mercury*; software used to prepare material for publication: *SHELX2012* .

References

1. G.M. Sheldrick, Acta Cryst. 2008, A64, 112-122.

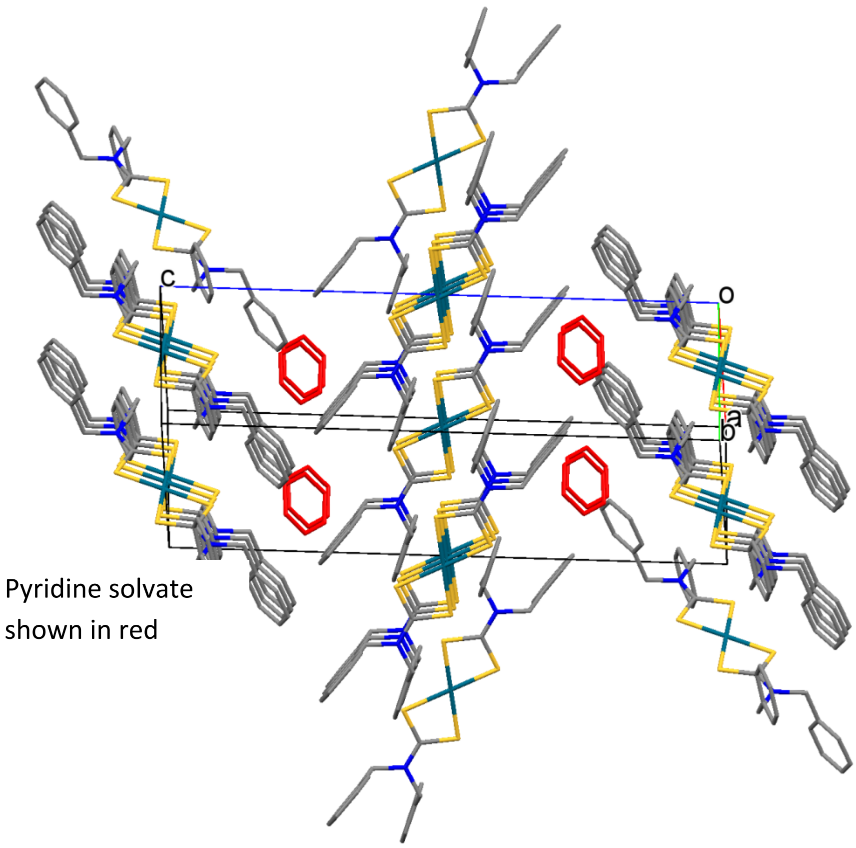
Results and discussion

Precursor $[Pd(S_2CNBz_2)_2]$•py (1)

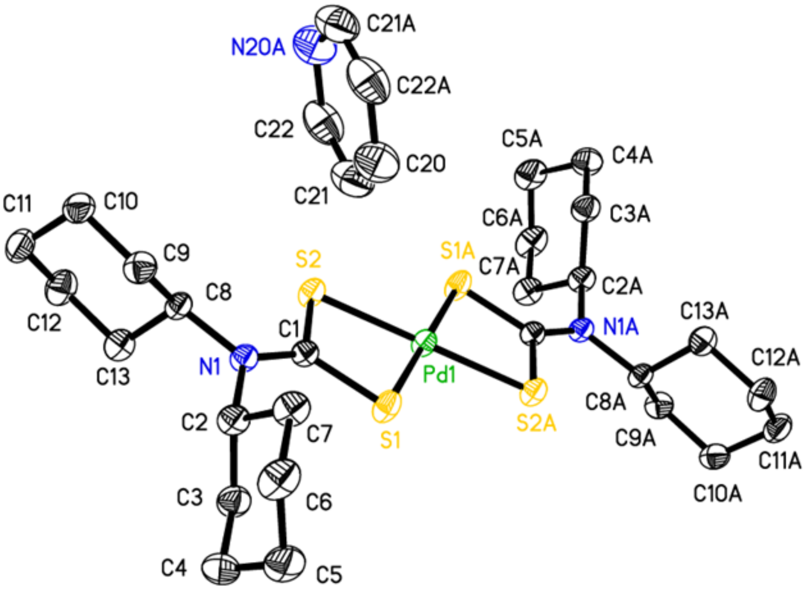


The Pd complex lies on a centre of symmetry and the pyridine solvate lies on a 2-fold axis. There are no very significant intermolecular interactions .

The complex molecules pack with channels in the structure running parallel to *b* and these are occupied by the pyridine solvate molecules.

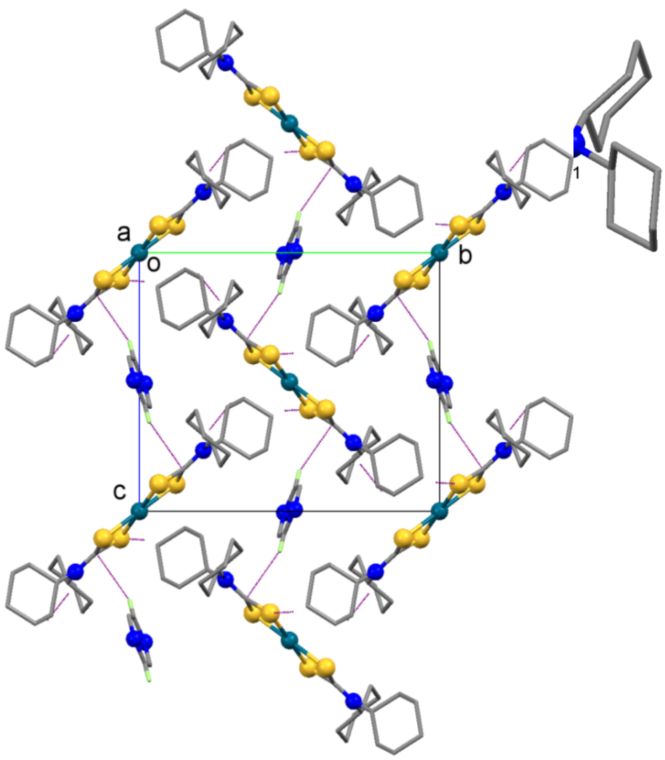


Precursor $[Pd(S_2CNCy_2)_2]$•py (2)



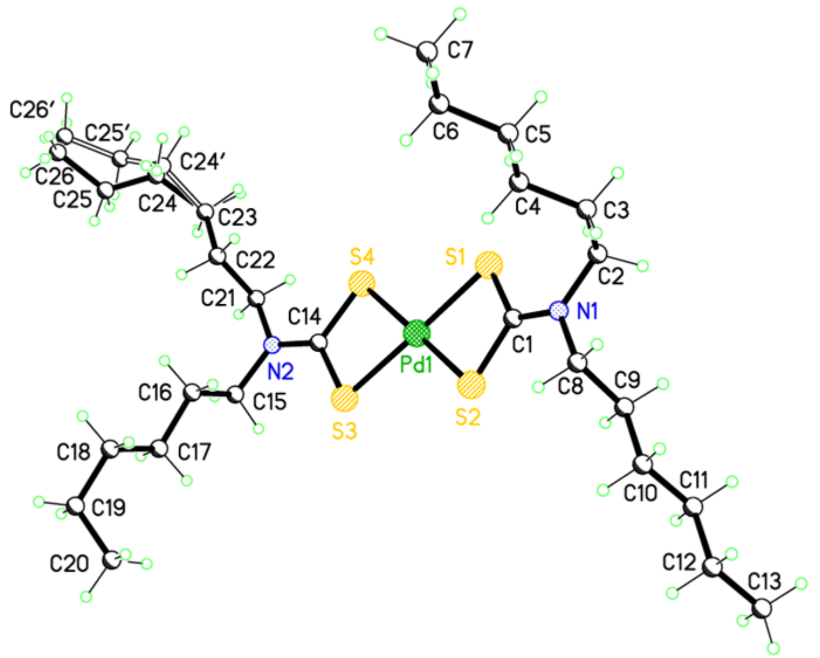
50% ellipsoids

Both the cation and the solvate pyridine molecule lie on centres of symmetry. This means that the nitrogen of the pyridine is necessarily disordered over two sites. This has been modelled by refining the C20/N20 (and C20A/N20A) site as half occupancy for each type of atom. The solvate pyridine links the molecules into chains via a weak C-H ···· CS_2^- interaction (C21-H21····· C1 2.78 Å). This leads to zig-zag chains running parallel to the c axis.

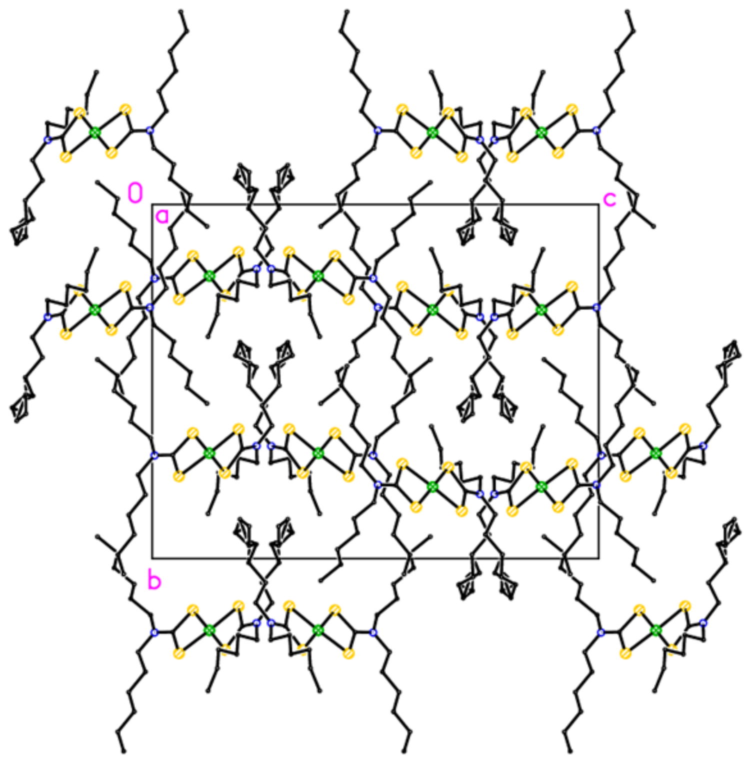


Precursor [Pd($S_2CN^nHex_2$)$_3$] (3)

The molecule has no internal symmetry, so all the alkyl chains are independent; only one shows any disorder.

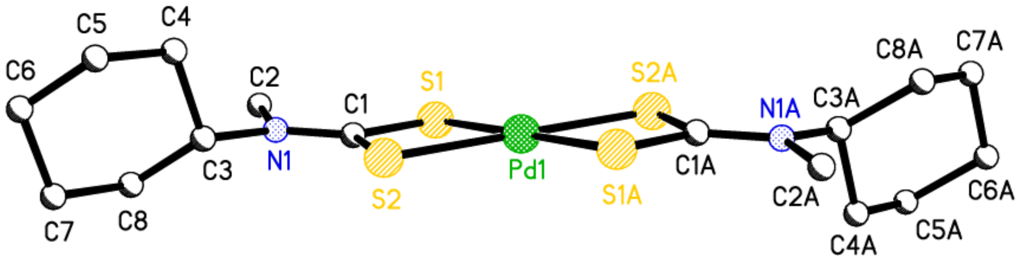


There are no particularly striking intermolecular interactions – though the packing is probably controlled by the interactions between alkyl chains.

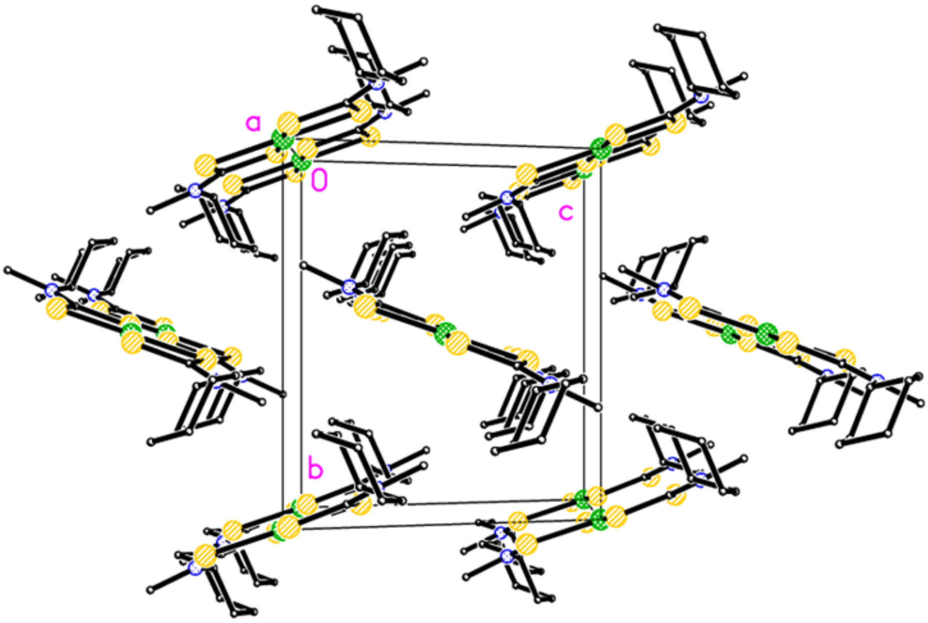


Precursor $[Pd(S_2CNMeCy)_2]$ (4)

The Pd ion lies on a centre of symmetry, so the two halves of the molecule are related under symmetry operation -x+2, -y, -z+2.



There are no very striking intermolecular interactions but, if you believe in such things, you could argue for an agnostic H interaction.


a
0
c
b

Crystal data for [Pd(S_2CNBz_2)$_2$]•py (1)

$C_{35}H_{33}N_3PdS_4$	$F(000) = 1496$
$M_r = 730.28$	$D_x = 1.470$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 20.803$ (3) Å	Cell parameters from 3931 reflections
$b = 6.3637$ (8) Å	$\theta = 2.4$–$26.3°$
$c = 25.240$ (3) Å	$\mu = 0.85$ mm^{-1}
$\beta = 99.136$ (2)°	$T = 150$ K
$V = 3299.0$ (7) Å^3	Lath, yellow
$Z = 4$	0.40 × 0.24 × 0.07 mm

Data collection

Bruker APEX 2 CCD diffractometer	3417 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.039$
ω rotation with narrow frames scans	$\theta_{max} = 28.3°$, $\theta_{min} = 1.6°$
Absorption correction: multi-scan *SADABS* v2009/1, Sheldrick, G.M., (2009)	$h = -27 \rightarrow 27$
$T_{min} = 0.651$, $T_{max} = 0.746$	$k = -8 \rightarrow 8$
16346 measured reflections	$l = -33 \rightarrow 33$
4121 independent reflections	

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.028$	H-atom parameters constrained
$wR(F^2) = 0.064$	$w = 1/[\sigma^2(F_o^2) + (0.0252P)^2 + 2.286P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
4121 reflections	$\Delta\rangle_{max} = 0.41$ e Å^{-3}
197 parameters	$\Delta\rangle_{min} = -0.47$ e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
Pd1	0.7500	1.2500	0.5000	0.01913 (6)
S1	0.68918 (2)	0.95070 (8)	0.51177 (2)	0.02225 (11)
S2	0.72068 (2)	1.11437 (8)	0.41437 (2)	0.02273 (11)
C1	0.68112 (9)	0.9187 (3)	0.44329 (7)	0.0197 (4)
N1	0.64856 (7)	0.7645 (2)	0.41588 (6)	0.0205 (3)
C2	0.63986 (9)	0.7573 (3)	0.35667 (7)	0.0231 (4)
H2A	0.6501	0.8974	0.3431	0.028*
H2B	0.5937	0.7264	0.3426	0.028*
C3	0.68207 (10)	0.5951 (3)	0.33548 (7)	0.0227 (4)
C4	0.74940 (10)	0.5964 (3)	0.35054 (8)	0.0263 (4)
H4	0.7695	0.6994	0.3750	0.032*
C5	0.78714 (11)	0.4471 (4)	0.32986 (9)	0.0331 (5)
H5	0.8330	0.4473	0.3406	0.040*
C6	0.75848 (13)	0.2976 (4)	0.29365 (9)	0.0382 (6)
H6	0.7846	0.1968	0.2792	0.046*
C7	0.69202 (13)	0.2962 (4)	0.27874 (9)	0.0369 (6)
H7	0.6722	0.1939	0.2540	0.044*
C8	0.65372 (11)	0.4428 (3)	0.29959 (8)	0.0297 (5)
H8	0.6078	0.4394	0.2894	0.036*
C9	0.61989 (9)	0.5888 (3)	0.44189 (8)	0.0232 (4)
H9A	0.6355	0.5946	0.4810	0.028*
H9B	0.6352	0.4548	0.4283	0.028*
C10	0.54626 (9)	0.5915 (3)	0.43208 (8)	0.0242 (4)
C11	0.51221 (11)	0.7679 (4)	0.44323 (10)	0.0384 (5)
H11	0.5351	0.8921	0.4557	0.046*
C12	0.44456 (12)	0.7644 (5)	0.43631 (11)	0.0501 (7)
H12	0.4215	0.8867	0.4440	0.060*
C13	0.41089 (12)	0.5875 (5)	0.41858 (11)	0.0518 (7)
H13	0.3647	0.5860	0.4142	0.062*
C14	0.44432 (13)	0.4116 (5)	0.40720 (12)	0.0567 (8)
H14	0.4210	0.2879	0.3949	0.068*
C15	0.51217 (11)	0.4125 (4)	0.41346 (11)	0.0419 (6)
H15	0.5349	0.2907	0.4050	0.050*
N20	0.5000	0.6822 (5)	0.2500	0.0400 (7)
C21	0.47047 (12)	0.7898 (5)	0.28403 (11)	0.0471 (7)
H21	0.4489	0.7142	0.3085	0.057*

C22	0.46959 (14)	1.0040 (5)	0.28565 (15)	0.0693 (10)
H22	0.4483	1.0755	0.3110	0.083*
C23	0.5000	1.1144 (7)	0.2500	0.086 (2)
H23	0.5000	1.2637	0.2500	0.103*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.01917 (10)	0.01918 (10)	0.01898 (11)	0.00334 (8)	0.00289 (7)	-0.00179 (8)
S1	0.0245 (2)	0.0240 (2)	0.0189 (2)	0.00169 (19)	0.00560 (18)	-0.00193 (19)
S2	0.0266 (3)	0.0222 (2)	0.0197 (2)	0.00002 (19)	0.00472 (19)	-0.00054 (19)
C1	0.0155 (9)	0.0221 (10)	0.0215 (9)	0.0062 (7)	0.0034 (7)	0.0003 (8)
N1	0.0203 (8)	0.0219 (8)	0.0196 (8)	0.0033 (7)	0.0038 (6)	-0.0014 (7)
C2	0.0229 (9)	0.0256 (10)	0.0198 (9)	0.0024 (8)	0.0002 (7)	-0.0006 (8)
C3	0.0286 (10)	0.0219 (10)	0.0181 (9)	0.0005 (8)	0.0059 (8)	0.0031 (8)
C4	0.0309 (11)	0.0261 (11)	0.0229 (10)	0.0003 (9)	0.0078 (8)	0.0036 (8)
C5	0.0327 (12)	0.0373 (13)	0.0323 (12)	0.0074 (10)	0.0149 (9)	0.0088 (10)
C6	0.0570 (16)	0.0322 (13)	0.0310 (12)	0.0124 (11)	0.0243 (11)	0.0042 (9)
C7	0.0591 (16)	0.0293 (12)	0.0243 (11)	0.0011 (10)	0.0126 (11)	-0.0055 (9)
C8	0.0360 (12)	0.0297 (11)	0.0226 (10)	-0.0023 (9)	0.0025 (9)	-0.0011 (9)
C9	0.0228 (10)	0.0199 (10)	0.0270 (10)	0.0020 (8)	0.0041 (8)	0.0002 (8)
C10	0.0211 (10)	0.0277 (11)	0.0243 (10)	0.0021 (8)	0.0055 (8)	0.0026 (8)
C11	0.0300 (11)	0.0442 (14)	0.0409 (13)	0.0087 (10)	0.0050 (10)	-0.0114 (11)
C12	0.0313 (13)	0.075 (2)	0.0453 (15)	0.0225 (14)	0.0095 (11)	-0.0028 (14)
C13	0.0228 (12)	0.085 (2)	0.0485 (16)	0.0030 (14)	0.0101 (11)	0.0187 (15)
C14	0.0341 (14)	0.0607 (19)	0.073 (2)	-0.0194 (14)	0.0006 (13)	0.0090 (15)
C15	0.0305 (12)	0.0351 (13)	0.0598 (16)	-0.0049 (10)	0.0067 (11)	0.0006 (12)
N20	0.0352 (15)	0.0361 (15)	0.0457 (17)	0.000	-0.0027 (13)	0.000
C21	0.0355 (13)	0.0625 (19)	0.0415 (14)	-0.0001 (12)	0.0004 (11)	0.0021 (13)
C22	0.0362 (16)	0.065 (2)	0.103 (3)	0.0071 (14)	-0.0011 (16)	-0.039 (2)
C23	0.033 (2)	0.029 (2)	0.181 (6)	0.000	-0.026 (3)	0.000

***Geometric parameters (Å, º) for* [Pd(S_2CNBz_2)$_2$]•py (1)**

Pd1—S2^{i}	2.3171 (5)	C6—C7	1.374 (4)
Pd1—S2	2.3172 (5)	C7—C8	1.384 (3)
Pd1—S1	2.3315 (5)	C9—C10	1.512 (3)
Pd1—S1^{i}	2.3316 (5)	C10—C11	1.380 (3)
S1—C1	1.7220 (19)	C10—C15	1.384 (3)

S2—C1	1.718 (2)	C11—C12	1.390 (3)
C1—N1	1.323 (2)	C12—C13	1.364 (4)
N1—C9	1.470 (2)	C13—C14	1.372 (4)
N1—C2	1.477 (2)	C14—C15	1.395 (3)
C2—C3	1.507 (3)	N20—C21	1.323 (3)
C3—C4	1.392 (3)	N20—C21^{ii}	1.323 (3)
C3—C8	1.393 (3)	C21—C22	1.364 (4)
C4—C5	1.386 (3)	C22—C23	1.373 (4)
C5—C6	1.387 (3)	C23—C22^{ii}	1.373 (4)
S2^{i}—Pd1—S2	180.00 (2)	C5—C4—C3	119.9 (2)
S2^{i}—Pd1—S1	104.671 (17)	C4—C5—C6	120.6 (2)
S2—Pd1—S1	75.329 (17)	C7—C6—C5	119.6 (2)
S2^{i}—Pd1—S1^{i}	75.331 (17)	C6—C7—C8	120.4 (2)
S2—Pd1—S1^{i}	104.669 (17)	C7—C8—C3	120.5 (2)
S1—Pd1—S1^{i}	180.0	N1—C9—C10	112.98 (16)
C1—S1—Pd1	86.40 (7)	C11—C10—C15	119.1 (2)
C1—S2—Pd1	86.95 (6)	C11—C10—C9	121.02 (19)
N1—C1—S2	123.74 (14)	C15—C10—C9	119.82 (19)
N1—C1—S1	124.94 (15)	C10—C11—C12	120.2 (2)
S2—C1—S1	111.32 (11)	C13—C12—C11	120.8 (2)
C1—N1—C9	122.73 (16)	C12—C13—C14	119.4 (2)
C1—N1—C2	121.46 (16)	C13—C14—C15	120.7 (3)
C9—N1—C2	115.80 (15)	C10—C15—C14	119.8 (2)
N1—C2—C3	113.29 (15)	C21—N20—C21^{ii}	117.7 (3)
C4—C3—C8	119.05 (19)	N20—C21—C22	123.1 (3)
C4—C3—C2	121.12 (18)	C21—C22—C23	118.8 (3)
C8—C3—C2	119.82 (18)	C22^{ii}—C23—C22	118.4 (4)

Symmetry codes: (i) -*x*+3/2, -*y*+5/2, -*z*+1; (ii) -*x*+1, *y*, -*z*+1/2.

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Crystal data for [Pd(S_2CNCy$_2$)$_2$]•py (2)

$C_{31}H_{49}N_3PdS_4$	$F(000) = 732$
$M_r = 698.37$	$D_x = 1.408$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.9610$ (13) Å	Cell parameters from 3121 reflections
$b = 14.0277$ (19) Å	$\theta = 2.3–23.8°$
$c = 12.1552$ (16) Å	$\mu = 0.84$ mm^{-1}
$\beta = 104.023$ (2)°	$T = 150$ K
$V = 1647.8$ (4) Å^3	Block, yellow
$Z = 2$	0.24 × 0.16 × 0.16 mm

Data collection

Bruker APEX 2 CCD diffractometer	3135 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.048$
ω rotation with narrow frames scans	$\theta_{max} = 28.4°$, $\theta_{min} = 2.3°$
Absorption correction: multi-scan *SADABS* v2009/1, Sheldrick, G.M., (2009)	$h = -13 \rightarrow 13$
$T_{min} = 0.629$, $T_{max} = 0.746$	$k = -18 \rightarrow 18$
16333 measured reflections	$l = -16 \rightarrow 16$
4109 independent reflections	

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.035$	H-atom parameters constrained
$wR(F^2) = 0.083$	$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
4109 reflections	$\Delta\rangle_{max} = 0.48$ e Å^{-3}
178 parameters	$\Delta\rangle_{min} = -0.76$ e Å^{-3}

Special details

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

treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Pd1	0.5000	0.5000	0.5000	0.02289 (8)	
S1	0.29497 (6)	0.43575 (5)	0.39469 (5)	0.02969 (15)	
S2	0.56729 (6)	0.37897 (4)	0.39431 (5)	0.02556 (14)	
C1	0.3927 (2)	0.35557 (16)	0.33886 (19)	0.0227 (5)	
N1	0.34478 (19)	0.28685 (14)	0.26479 (16)	0.0233 (4)	
C2	0.1947 (2)	0.26188 (18)	0.2254 (2)	0.0273 (5)	
H2	0.1908	0.2050	0.1752	0.033*	
C3	0.1345 (3)	0.22920 (19)	0.3227 (2)	0.0330 (6)	
H3A	0.1436	0.2809	0.3795	0.040*	
H3B	0.1867	0.1732	0.3602	0.040*	
C4	-0.0193 (3)	0.2026 (2)	0.2784 (3)	0.0407 (7)	
H4A	-0.0273	0.1457	0.2291	0.049*	
H4B	-0.0592	0.1866	0.3432	0.049*	
C5	-0.1000 (3)	0.2844 (2)	0.2119 (3)	0.0427 (7)	
H5A	-0.1983	0.2657	0.1843	0.051*	
H5B	-0.0958	0.3404	0.2622	0.051*	
C6	-0.0415 (3)	0.3108 (2)	0.1120 (2)	0.0397 (7)	
H6A	-0.0952	0.3645	0.0703	0.048*	
H6B	-0.0508	0.2558	0.0596	0.048*	
C7	0.1119 (2)	0.33939 (19)	0.1507 (2)	0.0321 (6)	
H7A	0.1498	0.3496	0.0835	0.038*	
H7B	0.1202	0.4000	0.1936	0.038*	
C8	0.4459 (2)	0.22556 (16)	0.22565 (19)	0.0228 (5)	
H8	0.5354	0.2613	0.2422	0.027*	
C9	0.4070 (3)	0.20643 (18)	0.0979 (2)	0.0302 (6)	
H9A	0.3209	0.1682	0.0775	0.036*	
H9B	0.3904	0.2675	0.0560	0.036*	
C10	0.5247 (3)	0.15243 (19)	0.0655 (2)	0.0334 (6)	
H10A	0.4975	0.1369	-0.0164	0.040*	
H10B	0.6075	0.1939	0.0787	0.040*	
C11	0.5613 (3)	0.06065 (19)	0.1330 (2)	0.0378 (6)	
H11A	0.6434	0.0314	0.1143	0.045*	
H11B	0.4834	0.0152	0.1110	0.045*	
C12	0.5917 (3)	0.0784 (2)	0.2605 (2)	0.0363 (6)	

H12A	0.6783	0.1156	0.2846	0.044*	
H12B	0.6055	0.0166	0.3010	0.044*	
C13	0.4729 (3)	0.13291 (18)	0.2929 (2)	0.0300 (5)	
H13A	0.3882	0.0932	0.2762	0.036*	
H13B	0.4979	0.1471	0.3751	0.036*	
N20	0.3590 (3)	0.5171 (2)	-0.0063 (3)	0.0484 (7)	0.5
C20	0.3590 (3)	0.5171 (2)	-0.0063 (3)	0.0484 (7)	0.5
H20	0.2639	0.5286	-0.0104	0.058*	0.5
C21	0.4461 (4)	0.4815 (2)	0.0886 (3)	0.0480 (8)	
H21	0.4105	0.4678	0.1526	0.058*	
C22	0.5836 (3)	0.4647 (2)	0.0955 (3)	0.0481 (8)	
H22	0.6402	0.4398	0.1638	0.058*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.01810 (13)	0.02603 (14)	0.02317 (14)	0.00033 (10)	0.00234 (9)	-0.00655 (11)
S1	0.0182 (3)	0.0343 (3)	0.0347 (3)	0.0013 (2)	0.0027 (2)	-0.0139 (3)
S2	0.0175 (3)	0.0302 (3)	0.0273 (3)	0.0000 (2)	0.0020 (2)	-0.0090 (2)
C1	0.0210 (11)	0.0248 (12)	0.0221 (11)	0.0003 (9)	0.0046 (9)	-0.0007 (9)
N1	0.0170 (9)	0.0269 (10)	0.0250 (10)	-0.0012 (8)	0.0032 (8)	-0.0044 (8)
C2	0.0164 (11)	0.0337 (14)	0.0293 (13)	-0.0034 (10)	0.0006 (9)	-0.0059 (10)
C3	0.0251 (13)	0.0363 (14)	0.0375 (15)	-0.0004 (11)	0.0072 (11)	-0.0023 (12)
C4	0.0243 (13)	0.0408 (16)	0.0588 (19)	-0.0076 (12)	0.0132 (13)	-0.0048 (14)
C5	0.0183 (13)	0.0511 (18)	0.0568 (19)	-0.0043 (12)	0.0052 (12)	-0.0105 (15)
C6	0.0236 (13)	0.0542 (18)	0.0367 (15)	0.0037 (12)	-0.0019 (11)	-0.0084 (13)
C7	0.0235 (12)	0.0405 (15)	0.0293 (13)	-0.0001 (11)	0.0007 (10)	-0.0024 (11)
C8	0.0170 (11)	0.0270 (12)	0.0241 (12)	-0.0009 (9)	0.0041 (9)	-0.0068 (9)
C9	0.0317 (14)	0.0347 (14)	0.0238 (13)	-0.0017 (11)	0.0058 (10)	-0.0025 (10)
C10	0.0331 (14)	0.0370 (15)	0.0329 (14)	-0.0095 (11)	0.0137 (11)	-0.0121 (11)
C11	0.0323 (14)	0.0355 (15)	0.0494 (17)	-0.0023 (12)	0.0171 (13)	-0.0156 (13)
C12	0.0279 (14)	0.0379 (15)	0.0415 (16)	0.0095 (11)	0.0052 (12)	-0.0021 (12)
C13	0.0280 (13)	0.0328 (14)	0.0281 (13)	0.0032 (10)	0.0046 (10)	-0.0006 (10)
N20	0.0435 (16)	0.0521 (18)	0.0481 (17)	-0.0052 (13)	0.0079 (13)	0.0039 (13)
C20	0.0435 (16)	0.0521 (18)	0.0481 (17)	-0.0052 (13)	0.0079 (13)	0.0039 (13)
C21	0.059 (2)	0.0480 (19)	0.0383 (16)	-0.0152 (15)	0.0134 (15)	0.0017 (13)
C22	0.055 (2)	0.0406 (16)	0.0408 (17)	-0.0065 (15)	-0.0045 (15)	0.0091 (13)

***Geometric parameters (Å, º) for* [Pd(S_2CNCy$_2$)$_2$]•py (2)**

Pd1—S1^{i}	2.3140 (6)	C5—C6	1.515 (4)
Pd1—S1	2.3141 (6)	C6—C7	1.538 (3)
Pd1—S2	2.3237 (6)	C8—C13	1.524 (3)
Pd1—S2^{i}	2.3237 (6)	C8—C9	1.530 (3)
S1—C1	1.730 (2)	C9—C10	1.526 (3)
S2—C1	1.738 (2)	C10—C11	1.523 (4)
C1—N1	1.326 (3)	C11—C12	1.525 (4)
N1—C8	1.487 (3)	C12—C13	1.538 (3)
N1—C2	1.496 (3)	N20—C21	1.359 (4)
C2—C3	1.521 (3)	N20—C22^{ii}	1.367 (4)
C2—C7	1.525 (3)	C21—C22	1.372 (4)
C3—C4	1.542 (3)	C22—C20^{ii}	1.367 (4)
C4—C5	1.517 (4)	C22—N20^{ii}	1.367 (4)
S1^{i}—Pd1—S1	180.0	C2—C3—C4	110.3 (2)
S1^{i}—Pd1—S2	104.85 (2)	C5—C4—C3	110.9 (2)
S1—Pd1—S2	75.15 (2)	C6—C5—C4	110.8 (2)
S1^{i}—Pd1—S2^{i}	75.15 (2)	C5—C6—C7	111.4 (2)
S1—Pd1—S2^{i}	104.85 (2)	C2—C7—C6	110.5 (2)
S2—Pd1—S2^{i}	180.0	N1—C8—C13	111.54 (19)
C1—S1—Pd1	88.01 (8)	N1—C8—C9	113.67 (19)
C1—S2—Pd1	87.52 (8)	C13—C8—C9	111.28 (19)
N1—C1—S1	126.50 (17)	C10—C9—C8	109.1 (2)
N1—C1—S2	124.21 (17)	C11—C10—C9	112.2 (2)
S1—C1—S2	109.29 (13)	C10—C11—C12	111.9 (2)
C1—N1—C8	118.51 (18)	C11—C12—C13	111.4 (2)
C1—N1—C2	123.67 (19)	C8—C13—C12	109.5 (2)
C8—N1—C2	117.61 (18)	C21—N20—C22^{ii}	115.9 (3)
N1—C2—C3	111.92 (19)	N20—C21—C22	122.6 (3)
N1—C2—C7	112.22 (19)	C20^{ii}—C22—C21	121.5 (3)
C3—C2—C7	114.8 (2)	N20^{ii}—C22—C21	121.5 (3)

Symmetry codes: (i) -*x*+1, -*y*+1, -*z*+1; (ii) -*x*+1, -*y*+1, -*z*.

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Crystal data for [Pd(S_2CN^{n}Hex$_2$)$_3$] (3)

$C_{26}H_{52}N_2PdS_4$	D_x = 1.267 Mg m^{-3}
M_r = 627.33	Mo $K\alpha$ radiation, λ = 0.71073 Å
Orthorhombic, *Pbca*	Cell parameters from 6444 reflections
a = 12.3351 (11) Å	θ = 2.7–23.8°
b = 20.5728 (19) Å	μ = 0.83 mm^{-1}
c = 25.918 (2) Å	T = 150 K
V = 6577.2 (10) Å^3	Block, yellow
Z = 8	0.34 × 0.24 × 0.15 mm
F(000) = 2656	

Data collection

Bruker APEX-II CCD diffractometer	5263 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.070
ω rotation with narrow frames scans	θ_{max} = 28.3°, θ_{min} = 1.6°
Absorption correction: multi-scan *SADABS* 2012/1, Sheldrick, G.M., (2012)	h = -16→16
T_{min} = 0.664, T_{max} = 0.746	k = -27→26
64543 measured reflections	l = -34→34
8186 independent reflections	

Refinement

Refinement on F^2	20 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.038	H-atom parameters constrained
$wR(F^2)$ = 0.096	$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 4.0416P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.01	$(\Delta/\sigma)_{max}$ = 0.002
8186 reflections	$\Delta\rangle_{max}$ = 0.65 e Å^{-3}
311 parameters	$\Delta\rangle_{min}$ = -0.60 e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Pd1	0.75066 (2)	0.20252 (2)	0.37186 (2)	0.03209 (7)	
S1	0.60730 (6)	0.14575 (4)	0.40896 (3)	0.03734 (17)	
S2	0.69591 (6)	0.26743 (4)	0.43998 (3)	0.03706 (17)	
C1	0.6035 (2)	0.20718 (14)	0.45425 (11)	0.0338 (6)	
N1	0.53900 (19)	0.20860 (11)	0.49463 (9)	0.0387 (6)	
C2	0.4552 (2)	0.15901 (15)	0.50369 (13)	0.0466 (8)	
H2A	0.4457	0.1331	0.4718	0.056*	
H2B	0.3856	0.1810	0.5111	0.056*	
C3	0.4815 (3)	0.11318 (16)	0.54805 (13)	0.0514 (9)	
H3A	0.4906	0.1392	0.5799	0.062*	
H3B	0.4189	0.0839	0.5534	0.062*	
C4	0.5819 (3)	0.07223 (16)	0.54043 (12)	0.0488 (8)	
H4A	0.6452	0.1013	0.5361	0.059*	
H4B	0.5738	0.0466	0.5083	0.059*	
C5	0.6037 (3)	0.02607 (17)	0.58509 (13)	0.0533 (9)	
H5A	0.6128	0.0519	0.6170	0.064*	
H5B	0.5396	-0.0023	0.5898	0.064*	
C6	0.7030 (3)	-0.01637 (17)	0.57782 (13)	0.0575 (9)	
H6A	0.6943	-0.0422	0.5459	0.069*	
H6B	0.7674	0.0118	0.5734	0.069*	
C7	0.7226 (4)	-0.0620 (2)	0.62250 (16)	0.0835 (14)	
H7A	0.7873	-0.0882	0.6156	0.125*	
H7B	0.6598	-0.0906	0.6267	0.125*	
H7C	0.7335	-0.0367	0.6541	0.125*	
C8	0.5434 (3)	0.26356 (15)	0.53137 (11)	0.0413 (7)	
H8A	0.6191	0.2792	0.5340	0.050*	
H8B	0.5209	0.2481	0.5659	0.050*	
C9	0.4711 (2)	0.31967 (15)	0.51528 (12)	0.0405 (7)	
H9A	0.3949	0.3046	0.5140	0.049*	
H9B	0.4918	0.3342	0.4802	0.049*	
C10	0.4799 (2)	0.37677 (14)	0.55250 (11)	0.0406 (7)	
H10A	0.4651	0.3611	0.5879	0.049*	
H10B	0.5551	0.3935	0.5517	0.049*	
C11	0.4029 (3)	0.43199 (14)	0.54034 (12)	0.0428 (7)	
H11A	0.3276	0.4154	0.5415	0.051*	
H11B	0.4171	0.4474	0.5048	0.051*	

C12	0.4128 (3)	0.48903 (15)	0.57706 (13)	0.0512 (8)	
H12A	0.3977	0.4739	0.6126	0.061*	
H12B	0.4882	0.5055	0.5762	0.061*	
C13	0.3363 (4)	0.54376 (17)	0.56389 (17)	0.0750 (12)	
H13A	0.3461	0.5794	0.5885	0.112*	
H13B	0.2614	0.5280	0.5657	0.112*	
H13C	0.3515	0.5594	0.5289	0.112*	
S3	0.89840 (6)	0.25742 (4)	0.33725 (3)	0.03849 (18)	
S4	0.81300 (6)	0.13466 (4)	0.30663 (3)	0.03913 (18)	
C14	0.9157 (2)	0.19052 (15)	0.29833 (10)	0.0364 (7)	
N2	0.99744 (19)	0.18216 (13)	0.26631 (9)	0.0375 (6)	
C15	1.0872 (2)	0.22925 (16)	0.26544 (11)	0.0421 (7)	
H15A	1.0576	0.2736	0.2702	0.051*	
H15B	1.1230	0.2277	0.2313	0.051*	
C16	1.1712 (3)	0.21582 (16)	0.30735 (12)	0.0466 (8)	
H16A	1.1341	0.2112	0.3410	0.056*	
H16B	1.2085	0.1743	0.2997	0.056*	
C17	1.2536 (3)	0.26956 (17)	0.31077 (12)	0.0473 (7)	
H17A	1.2160	0.3107	0.3193	0.057*	
H17B	1.2884	0.2751	0.2766	0.057*	
C18	1.3421 (3)	0.25678 (17)	0.35151 (15)	0.0579 (9)	
H18A	1.3075	0.2521	0.3858	0.069*	
H18B	1.3788	0.2152	0.3434	0.069*	
C19	1.4248 (3)	0.3094 (2)	0.35415 (18)	0.0732 (12)	
H19A	1.4545	0.3168	0.3192	0.088*	
H19B	1.4852	0.2948	0.3765	0.088*	
C20	1.3807 (4)	0.3732 (2)	0.37492 (18)	0.0882 (15)	
H20A	1.4385	0.4059	0.3750	0.132*	
H20B	1.3542	0.3668	0.4102	0.132*	
H20C	1.3210	0.3881	0.3530	0.132*	
C21	1.0031 (3)	0.12491 (15)	0.23198 (11)	0.0443 (8)	
H21A	1.0383	0.1380	0.1993	0.053*	
H21B	0.9284	0.1109	0.2237	0.053*	
C22	1.0639 (3)	0.06790 (16)	0.25402 (13)	0.0510 (8)	
H22A	1.0295	0.0541	0.2868	0.061*	
H22B	1.1396	0.0808	0.2616	0.061*	
C23	1.0636 (4)	0.0115 (2)	0.21601 (16)	0.0800 (13)	0.741 (9)
H23A	1.0829	0.0276	0.1812	0.096*	0.741 (9)
H23B	0.9901	-0.0076	0.2142	0.096*	0.741 (9)
C24	1.1451 (8)	-0.0406 (5)	0.2329 (4)	0.132 (4)	0.741 (9)

H24A	1.1461	-0.0411	0.2711	0.158*	0.741 (9)
H24B	1.1165	-0.0832	0.2216	0.158*	0.741 (9)
C25	1.2462 (6)	-0.0366 (4)	0.2171 (4)	0.113 (3)	0.741 (9)
H25A	1.2805	-0.0019	0.2379	0.136*	0.741 (9)
H25B	1.2434	-0.0204	0.1812	0.136*	0.741 (9)
C26	1.3218 (7)	-0.0911 (4)	0.2170 (4)	0.110 (3)	0.741 (9)
H26A	1.3914	-0.0770	0.2026	0.165*	0.741 (9)
H26B	1.2923	-0.1265	0.1960	0.165*	0.741 (9)
H26C	1.3326	-0.1064	0.2525	0.165*	0.741 (9)
C23'	1.0636 (4)	0.0115 (2)	0.21601 (16)	0.0800 (13)	0.259 (9)
H23C	0.9867	-0.0018	0.2132	0.096*	0.259 (9)
H23D	1.0826	0.0311	0.1823	0.096*	0.259 (9)
C24'	1.1273 (12)	-0.0516 (7)	0.2184 (7)	0.051 (4)*	0.259 (9)
H24C	1.1619	-0.0516	0.2529	0.061*	0.259 (9)
H24D	1.0717	-0.0863	0.2195	0.061*	0.259 (9)
C25'	1.2032 (10)	-0.0736 (7)	0.1864 (5)	0.048 (4)*	0.259 (9)
H25C	1.2285	-0.0346	0.1677	0.058*	0.259 (9)
H25D	1.1630	-0.0998	0.1607	0.058*	0.259 (9)
C26'	1.3019 (15)	-0.1109 (10)	0.1966 (9)	0.072 (6)*	0.259 (9)
H26D	1.3405	-0.1185	0.1641	0.107*	0.259 (9)
H26E	1.2826	-0.1528	0.2122	0.107*	0.259 (9)
H26F	1.3486	-0.0866	0.2202	0.107*	0.259 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.02670 (11)	0.04302 (13)	0.02655 (11)	0.00339 (10)	0.00003 (9)	-0.00171 (9)
S1	0.0334 (4)	0.0443 (4)	0.0343 (4)	-0.0004 (3)	0.0020 (3)	-0.0056 (3)
S2	0.0314 (4)	0.0447 (4)	0.0351 (4)	-0.0005 (3)	0.0028 (3)	-0.0062 (3)
C1	0.0278 (14)	0.0412 (16)	0.0324 (14)	0.0039 (13)	-0.0018 (11)	0.0011 (12)
N1	0.0358 (14)	0.0425 (14)	0.0379 (13)	0.0065 (11)	0.0065 (11)	-0.0018 (11)
C2	0.0363 (17)	0.0508 (19)	0.0526 (19)	0.0000 (15)	0.0126 (15)	-0.0015 (16)
C3	0.054 (2)	0.0486 (19)	0.052 (2)	-0.0045 (17)	0.0177 (16)	0.0041 (16)
C4	0.053 (2)	0.0494 (19)	0.0441 (18)	-0.0011 (16)	0.0093 (16)	0.0058 (15)
C5	0.061 (2)	0.054 (2)	0.0444 (19)	-0.0065 (18)	0.0107 (17)	0.0071 (16)
C6	0.070 (2)	0.052 (2)	0.050 (2)	-0.006 (2)	0.0055 (18)	0.0108 (17)
C7	0.095 (3)	0.084 (3)	0.072 (3)	0.020 (3)	0.016 (2)	0.032 (2)
C8	0.0443 (18)	0.0472 (18)	0.0323 (15)	0.0047 (15)	0.0052 (13)	-0.0040 (14)
C9	0.0356 (16)	0.0461 (17)	0.0397 (17)	0.0020 (14)	0.0049 (13)	-0.0003 (14)
C10	0.0411 (17)	0.0445 (18)	0.0361 (16)	-0.0013 (14)	0.0067 (13)	-0.0013 (13)

C11	0.0426 (18)	0.0433 (17)	0.0424 (17)	-0.0016 (15)	0.0061 (14)	-0.0026 (14)
C12	0.063 (2)	0.0433 (19)	0.0473 (19)	-0.0016 (17)	0.0070 (17)	-0.0035 (15)
C13	0.101 (3)	0.045 (2)	0.079 (3)	0.017 (2)	0.001 (3)	-0.005 (2)
S3	0.0348 (4)	0.0483 (4)	0.0324 (4)	-0.0003 (3)	0.0024 (3)	-0.0023 (3)
S4	0.0338 (4)	0.0511 (4)	0.0326 (4)	0.0005 (3)	0.0013 (3)	-0.0069 (3)
C14	0.0296 (14)	0.0548 (19)	0.0250 (14)	0.0053 (13)	-0.0044 (11)	0.0027 (13)
N2	0.0318 (13)	0.0549 (15)	0.0257 (11)	0.0034 (11)	0.0013 (10)	0.0002 (11)
C15	0.0335 (16)	0.060 (2)	0.0333 (15)	-0.0013 (15)	0.0047 (13)	-0.0002 (14)
C16	0.0388 (17)	0.062 (2)	0.0391 (17)	0.0057 (16)	-0.0005 (14)	-0.0016 (15)
C17	0.0418 (17)	0.0525 (19)	0.0475 (18)	0.0029 (16)	-0.0070 (16)	-0.0049 (15)
C18	0.047 (2)	0.052 (2)	0.075 (2)	0.0121 (17)	-0.0179 (18)	-0.0116 (19)
C19	0.056 (2)	0.079 (3)	0.085 (3)	0.005 (2)	-0.018 (2)	-0.013 (2)
C20	0.090 (3)	0.069 (3)	0.106 (4)	0.002 (2)	-0.038 (3)	-0.019 (3)
C21	0.0420 (18)	0.063 (2)	0.0278 (14)	0.0087 (16)	0.0063 (13)	-0.0040 (14)
C22	0.048 (2)	0.057 (2)	0.0478 (19)	0.0065 (17)	0.0008 (16)	0.0014 (16)
C23	0.095 (3)	0.075 (3)	0.070 (3)	0.025 (3)	0.000 (2)	-0.015 (2)
C24	0.151 (6)	0.115 (6)	0.130 (8)	0.057 (5)	-0.025 (6)	-0.047 (5)
C25	0.106 (5)	0.079 (5)	0.154 (8)	0.012 (4)	-0.018 (5)	0.011 (5)
C26	0.094 (5)	0.078 (5)	0.158 (9)	0.004 (4)	0.015 (5)	0.000 (5)
C23'	0.095 (3)	0.075 (3)	0.070 (3)	0.025 (3)	0.000 (2)	-0.015 (2)

Geometric parameters (Å, º) for **[Pd($S_2CN^nHex_2$)$_3$] (3)**

Pd1—S2	2.3143 (7)	C12—C13	1.509 (5)
Pd1—S4	2.3236 (8)	S3—C14	1.720 (3)
Pd1—S3	2.3241 (8)	S4—C14	1.724 (3)
Pd1—S1	2.3272 (8)	C14—N2	1.317 (3)
S1—C1	1.725 (3)	N2—C15	1.471 (4)
S2—C1	1.724 (3)	N2—C21	1.478 (4)
C1—N1	1.315 (3)	C15—C16	1.526 (4)
N1—C2	1.471 (4)	C16—C17	1.505 (4)
N1—C8	1.479 (4)	C17—C18	1.541 (4)
C2—C3	1.522 (4)	C18—C19	1.488 (5)
C3—C4	1.510 (4)	C19—C20	1.520 (5)
C4—C5	1.521 (4)	C21—C22	1.505 (4)
C5—C6	1.516 (5)	C22—C23	1.521 (5)
C6—C7	1.510 (5)	C23—C24	1.534 (8)
C8—C9	1.517 (4)	C24—C25	1.315 (10)
C9—C10	1.524 (4)	C25—C26	1.459 (8)
C10—C11	1.514 (4)	C24'—C25'	1.330 (13)

C11—C12	1.516 (4)	C25'—C26'	1.463 (14)
S2—Pd1—S4	176.69 (3)	C10—C11—C12	113.6 (3)
S2—Pd1—S3	104.06 (3)	C13—C12—C11	112.6 (3)
S4—Pd1—S3	75.62 (3)	C14—S3—Pd1	86.26 (10)
S2—Pd1—S1	75.68 (3)	C14—S4—Pd1	86.18 (10)
S4—Pd1—S1	104.51 (3)	N2—C14—S3	124.7 (2)
S3—Pd1—S1	177.72 (3)	N2—C14—S4	123.6 (2)
C1—S1—Pd1	86.21 (10)	S3—C14—S4	111.66 (16)
C1—S2—Pd1	86.66 (10)	C14—N2—C15	120.0 (3)
N1—C1—S2	123.7 (2)	C14—N2—C21	121.3 (3)
N1—C1—S1	125.0 (2)	C15—N2—C21	118.7 (2)
S2—C1—S1	111.27 (16)	N2—C15—C16	112.4 (3)
C1—N1—C2	122.5 (2)	C17—C16—C15	111.6 (3)
C1—N1—C8	120.5 (3)	C16—C17—C18	113.2 (3)
C2—N1—C8	116.9 (2)	C19—C18—C17	113.1 (3)
N1—C2—C3	113.6 (3)	C18—C19—C20	113.5 (3)
C4—C3—C2	114.9 (3)	N2—C21—C22	114.6 (2)
C3—C4—C5	113.2 (3)	C21—C22—C23	110.3 (3)
C6—C5—C4	114.1 (3)	C22—C23—C24	110.3 (5)
C7—C6—C5	113.1 (3)	C25—C24—C23	119.3 (9)
N1—C8—C9	112.5 (2)	C24—C25—C26	124.0 (8)
C8—C9—C10	111.8 (2)	C24'—C25'—C26'	130.7 (15)
C11—C10—C9	113.7 (3)		

```
 Least-squares planes (x,y,z in crystal coordinates) and deviations
from them
 (* indicates atom used to define plane)

  7.6869 (0.0023) x - 9.5788 (0.0050) y + 16.2867 (0.0046) z =
9.9432 (0.0028)

 *   -0.0103 (0.0004)  S1
 *    0.0104 (0.0004)  S2
 *   -0.0103 (0.0004)  S3
 *    0.0103 (0.0004)  S4
     -0.0565 (0.0004)  Pd1

 Rms deviation of fitted atoms =   0.0103
```

Crystal data for $[Pd(S_2CNMeCy)_2]$ (4)

$C_{16}H_{28}N_2PdS_4$	$F(000) = 496$
$M_r = 483.04$	$D_x = 1.591$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.9199$ (7) Å	Cell parameters from 3958 reflections
$b = 11.0292$ (7) Å	$\theta = 2.9–31.5°$
$c = 10.1444$ (7) Å	$\mu = 1.34$ mm^{-1}
$\beta = 114.696$ (1)°	$T = 150$ K
$V = 1008.37$ (12) Å^3	Block, yellow
$Z = 2$	0.28 × 0.22 × 0.20 mm

Data collection

Bruker APEX 2 CCD diffractometer	2767 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.030$
ω rotation with narrow frames scans	$\theta_{max} = 31.8°$, $\theta_{min} = 2.4°$
Absorption correction: multi-scan *SADABS* v2009/1, Sheldrick, G.M., (2009)	$h = -14 \rightarrow 14$
$T_{min} = 0.672$, $T_{max} = 0.746$	$k = -16 \rightarrow 15$
11825 measured reflections	$l = -14 \rightarrow 14$
3217 independent reflections	

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.026$	H-atom parameters constrained
$wR(F^2) = 0.065$	$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 0.0751P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
3217 reflections	$\Delta\rangle_{max} = 0.38$ e Å^{-3}
107 parameters	$\Delta\rangle_{min} = -0.86$ e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
Pd1	1.0000	0.0000	1.0000	0.01690 (6)
S1	0.87449 (4)	0.06787 (4)	0.76174 (5)	0.02241 (10)
S2	0.75458 (5)	0.02191 (4)	0.96658 (5)	0.02183 (9)
C1	0.71887 (17)	0.07598 (14)	0.79591 (17)	0.0175 (3)
N1	0.58869 (14)	0.11999 (13)	0.70459 (14)	0.0184 (3)
C2	0.57087 (19)	0.17457 (17)	0.56660 (18)	0.0250 (4)
H2A	0.5154	0.1190	0.4869	0.038*
H2B	0.6688	0.1900	0.5681	0.038*
H2C	0.5166	0.2512	0.5525	0.038*
C3	0.46457 (16)	0.13096 (14)	0.74922 (17)	0.0175 (3)
H3	0.4815	0.0699	0.8274	0.021*
C5	0.34195 (18)	0.26488 (17)	0.86660 (19)	0.0240 (3)
H5A	0.3402	0.3478	0.9031	0.029*
H5B	0.3632	0.2076	0.9480	0.029*
C4	0.46427 (17)	0.25616 (15)	0.81312 (18)	0.0205 (3)
H4A	0.5617	0.2713	0.8949	0.025*
H4B	0.4485	0.3189	0.7383	0.025*
C6	0.19049 (19)	0.23553 (16)	0.7451 (2)	0.0247 (4)
H6A	0.1639	0.2984	0.6687	0.030*
H6B	0.1143	0.2362	0.7842	0.030*
C7	0.19253 (17)	0.11114 (16)	0.67910 (18)	0.0227 (3)
H7A	0.2085	0.0476	0.7531	0.027*
H7B	0.0951	0.0961	0.5973	0.027*
C8	0.31471 (17)	0.10276 (16)	0.62472 (17)	0.0211 (3)
H8A	0.3164	0.0202	0.5871	0.025*
H8B	0.2946	0.1612	0.5447	0.025*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.01242 (9)	0.01926 (10)	0.01711 (9)	0.00314 (6)	0.00427 (7)	0.00101 (6)
S1	0.01504 (19)	0.0324 (2)	0.02016 (19)	0.00491 (16)	0.00771 (15)	0.00442 (16)
S2	0.01503 (19)	0.0315 (2)	0.01824 (19)	0.00546 (15)	0.00627 (16)	0.00704 (16)
C1	0.0150 (7)	0.0178 (7)	0.0182 (7)	0.0007 (6)	0.0055 (6)	0.0002 (6)
N1	0.0148 (6)	0.0232 (7)	0.0180 (6)	0.0027 (5)	0.0076 (5)	0.0032 (5)
C2	0.0228 (8)	0.0324 (9)	0.0211 (8)	0.0081 (7)	0.0103 (7)	0.0108 (7)
C3	0.0137 (7)	0.0205 (8)	0.0175 (7)	0.0025 (6)	0.0056 (6)	0.0026 (6)

C5	0.0220 (8)	0.0257 (9)	0.0254 (8)	-0.0009 (7)	0.0110 (7)	-0.0036 (7)
C4	0.0158 (7)	0.0231 (8)	0.0217 (8)	-0.0019 (6)	0.0071 (6)	-0.0031 (6)
C6	0.0168 (8)	0.0287 (9)	0.0303 (9)	0.0028 (6)	0.0115 (7)	0.0021 (7)
C7	0.0140 (7)	0.0299 (9)	0.0225 (8)	-0.0018 (6)	0.0058 (6)	0.0018 (7)
C8	0.0155 (7)	0.0258 (8)	0.0198 (7)	-0.0019 (6)	0.0052 (6)	-0.0023 (6)

Geometric parameters (Å, º) for **[Pd(S_2CNMeCy)$_2$] (4)**

Pd1—S2	2.3261 (5)	N1—C2	1.465 (2)
Pd1—S2^{i}	2.3261 (5)	N1—C3	1.4837 (19)
Pd1—S1	2.3319 (4)	C3—C4	1.526 (2)
Pd1—S1^{i}	2.3319 (4)	C3—C8	1.527 (2)
Pd1—H2C^{ii}	2.7872	C5—C4	1.525 (2)
S1—C1	1.7201 (16)	C5—C6	1.528 (2)
S2—C1	1.7223 (16)	C6—C7	1.530 (2)
C1—N1	1.3273 (19)	C7—C8	1.530 (2)
S2—Pd1—S2^{i}	180.0	N1—C1—S2	124.04 (12)
S2—Pd1—S1	75.080 (14)	S1—C1—S2	111.08 (9)
S2^{i}—Pd1—S1	104.919 (14)	C1—N1—C2	120.73 (13)
S2—Pd1—S1^{i}	104.919 (14)	C1—N1—C3	120.42 (13)
S2^{i}—Pd1—S1^{i}	75.081 (14)	C2—N1—C3	118.28 (12)
S1—Pd1—S1^{i}	180.00 (2)	N1—C3—C4	110.65 (13)
S2—Pd1—H2C^{ii}	84.3	N1—C3—C8	112.10 (13)
S2^{i}—Pd1—H2C^{ii}	95.7	C4—C3—C8	111.20 (13)
S1—Pd1—H2C^{ii}	81.1	C4—C5—C6	111.10 (14)
S1^{i}—Pd1—H2C^{ii}	98.9	C5—C4—C3	110.57 (13)
C1—S1—Pd1	86.75 (5)	C5—C6—C7	110.77 (14)
C1—S2—Pd1	86.88 (5)	C8—C7—C6	111.66 (14)
N1—C1—S1	124.87 (12)	C3—C8—C7	109.48 (13)

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