Supplemental data

Synthesis, spectral characterization and anticancer activity of 6-methylpyridine-2-carbaldehydethiosemicarbazone and its N(4)-phenylthiosemicarbazone complexes; Crystal structure and DFT calculations of [Pd(mpyptsc)Cl]·DMSO

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CRYSTAL AND MOLECULAR STRUCTURE OF

C₁₆ H₁₉ Cl N₄ O Pd S₂ COMPOUND (but123)

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Structure solved and refined in the laboratory of X-ray
diffraction, Université de Montréal by Francine Bélanger.

Table S1. Crystal data and structure refinement for C16 H19 Cl N4 O Pd S2.

Identification code	but123
Empirical formula	C16 H19 Cl N4 O Pd S2
Formula weight	489.32
Temperature	200K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	$a = 7.2407(2) \text{ Å}$ $\alpha = 90^\circ$ $b = 11.1883(3) \text{ Å}$ $\beta = 97.850(2)^\circ$ $c = 23.5428(6) \text{ Å}$ $\gamma = 90^\circ$
Volume	$1889.36(9) \text{ Å}^3$
Z	4
Density (calculated)	1.720 g/cm^3
Absorption coefficient	11.396 mm^{-1}
F(000)	984
Crystal size	0.16 x 0.08 x 0.04 mm
Theta range for data collection	3.79 to 71.94°
Index ranges	$-8 \leq h \leq 8$, $-13 \leq k \leq 13$, $-28 \leq l \leq 28$
Reflections collected	23587
Independent reflections	3672 [$R_{\text{int}} = 0.055$]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6339 and 0.3716
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3672 / 0 / 233
Goodness-of-fit on F^2	1.024
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0366$, $wR_2 = 0.0931$
R indices (all data)	$R_1 = 0.0514$, $wR_2 = 0.1042$
Largest diff. peak and hole	1.077 and -0.907 e/Å^3

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Cl6 H19 Cl N4 O Pd S2.

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Pd(1)	1745(1)	-943(1)	830(1)	35(1)
Cl(1)	1099(2)	-2535(1)	1405(1)	56(1)
S(8)	2311(2)	-2246(1)	151(1)	41(1)
N(1)	1454(5)	675(3)	1319(1)	37(1)
N(7)	2297(5)	258(3)	265(1)	34(1)
N(8)	2732(5)	-4(3)	-271(1)	37(1)
N(9)	3233(5)	-1603(3)	-855(2)	37(1)
C(1)	759(7)	-141(5)	2227(2)	54(1)
C(2)	1096(6)	885(4)	1851(2)	42(1)
C(3)	1005(6)	2071(5)	2055(2)	49(1)
C(4)	1316(6)	3013(4)	1717(2)	48(1)
C(5)	1740(6)	2800(4)	1168(2)	46(1)
C(6)	1795(6)	1633(4)	982(2)	38(1)
C(7)	2236(6)	1367(4)	418(2)	38(1)
C(8)	2793(6)	-1157(3)	-357(2)	35(1)
C(9)	3604(5)	-1001(3)	-1355(2)	33(1)
C(10)	3863(6)	233(3)	-1388(2)	36(1)
C(11)	4242(6)	720(4)	-1906(2)	42(1)
C(12)	4319(6)	22(4)	-2386(2)	41(1)
C(13)	4060(6)	-1204(4)	-2346(2)	43(1)
C(14)	3711(6)	-1698(4)	-1835(2)	39(1)
S(21)	2564(2)	4974(1)	8984(1)	53(1)
O(21)	4056(6)	5923(3)	9081(2)	64(1)
C(21)	2222(9)	4453(5)	9672(2)	72(2)
C(22)	3668(9)	3683(5)	8764(3)	69(2)

Table S3. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Cl6 H19 Cl1 N4 O Pd S2.

	x	y	z	U _{eq}
H(9)	3310(60)	-2290(50)	-866(18)	41(13)
H(1A)	-318	-600	2047	81
H(1B)	512	159	2600	81
H(1C)	1863	-658	2280	81
H(3)	724	2208	2432	59
H(4)	1245	3808	1855	58
H(5)	1986	3443	926	55
H(7)	2478	1990	164	45
H(10)	3782	730	-1065	43
H(11)	4453	1555	-1928	51
H(12)	4545	374	-2737	50
H(13)	4123	-1700	-2670	51
H(14)	3540	-2537	-1812	47
H(21A)	3406	4156	9875	108
H(21B)	1303	3805	9632	108
H(21C)	1768	5110	9891	108
H(22A)	3967	3800	8374	103
H(22B)	2831	2996	8769	103
H(22C)	4818	3536	9025	103

Table S4. Anisotropic parameters ($\text{\AA}^2 \times 10^3$) for Cl6 H19 Cl N4 O Pd S2.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
Pd(1)	38(1)	33(1)	35(1)	4(1)	1(1)	-4(1)
Cl(1)	68(1)	49(1)	49(1)	17(1)	6(1)	-13(1)
S(8)	55(1)	26(1)	41(1)	3(1)	6(1)	-3(1)
N(1)	35(2)	39(2)	38(2)	-5(1)	3(1)	-1(2)
N(7)	36(2)	32(2)	34(2)	1(1)	3(1)	0(2)
N(8)	44(2)	28(2)	38(2)	-3(1)	6(2)	0(2)
N(9)	47(2)	20(2)	42(2)	2(1)	7(2)	-1(2)
C(1)	54(3)	68(3)	42(3)	5(2)	11(2)	-7(3)
C(2)	31(2)	56(3)	39(2)	-5(2)	2(2)	-3(2)
C(3)	39(2)	65(3)	43(2)	-9(2)	5(2)	4(2)
C(4)	45(3)	49(3)	48(3)	-13(2)	-2(2)	5(2)
C(5)	46(3)	42(2)	49(3)	-5(2)	5(2)	2(2)
C(6)	37(2)	38(2)	39(2)	0(2)	4(2)	0(2)
C(7)	44(2)	31(2)	38(2)	1(2)	6(2)	1(2)
C(8)	36(2)	28(2)	40(2)	3(2)	1(2)	3(2)
C(9)	31(2)	27(2)	40(2)	3(2)	5(2)	0(2)
C(10)	40(2)	27(2)	41(2)	-2(2)	5(2)	2(2)
C(11)	47(3)	28(2)	52(3)	7(2)	8(2)	-2(2)
C(12)	39(2)	42(2)	44(2)	4(2)	10(2)	2(2)
C(13)	43(2)	43(2)	41(2)	-7(2)	6(2)	5(2)
C(14)	42(2)	29(2)	47(2)	-5(2)	9(2)	-4(2)
S(21)	64(1)	32(1)	65(1)	9(1)	16(1)	9(1)
O(21)	78(2)	28(2)	92(3)	6(2)	37(2)	-1(2)
C(21)	100(5)	53(3)	71(4)	-4(3)	35(3)	-24(3)
C(22)	79(4)	37(3)	96(4)	-12(3)	37(3)	4(3)

Table S5. Bond lengths [Å] and angles [°] for C16 H19 Cl N4 O Pd S2

Pd(1)-N(7)	1.970(3)	C(2)-N(1)-C(6)	118.5(4)
Pd(1)-N(1)	2.171(3)	C(2)-N(1)-PD1	133.6(3)
Pd(1)-S(8)	2.2421(11)	C(6)-N(1)-PD1	107.9(3)
Pd(1)-Cl(1)	2.3238(11)	C(7)-N(7)-N(8)	118.8(3)
S(8)-C(8)	1.774(4)	C(7)-N(7)-PD1	116.6(3)
N(1)-C(2)	1.335(5)	N(8)-N(7)-PD1	124.6(3)
N(1)-C(6)	1.375(5)	C(8)-N(8)-N(7)	111.7(3)
N(7)-C(7)	1.295(5)	C(8)-N(9)-C(9)	129.9(3)
N(7)-N(8)	1.372(4)	N(1)-C(2)-C(3)	120.5(4)
N(8)-C(8)	1.308(5)	N(1)-C(2)-C(1)	119.4(4)
N(9)-C(8)	1.352(5)	C(3)-C(2)-C(1)	120.1(4)
N(9)-C(9)	1.414(5)	C(4)-C(3)-C(2)	120.6(4)
C(1)-C(2)	1.490(6)	C(3)-C(4)-C(5)	119.1(4)
C(2)-C(3)	1.416(6)	C(6)-C(5)-C(4)	118.5(5)
C(3)-C(4)	1.358(7)	N(1)-C(6)-C(5)	122.7(4)
C(4)-C(5)	1.391(6)	N(1)-C(6)-C(7)	116.8(4)
C(5)-C(6)	1.378(6)	C(5)-C(6)-C(7)	120.6(4)
C(6)-C(7)	1.439(5)	N(7)-C(7)-C(6)	118.4(4)
C(9)-C(14)	1.384(5)	N(8)-C(8)-N(9)	121.0(4)
C(9)-C(10)	1.397(5)	N(8)-C(8)-S(8)	124.0(3)
C(10)-C(11)	1.395(6)	N(9)-C(8)-S(8)	115.0(3)
C(11)-C(12)	1.381(6)	C(14)-C(9)-C(10)	119.3(4)
C(12)-C(13)	1.389(6)	C(14)-C(9)-N(9)	116.8(3)
C(13)-C(14)	1.377(6)	C(10)-C(9)-N(9)	124.0(4)
S(21)-O(21)	1.509(4)	C(11)-C(10)-C(9)	118.5(4)
S(21)-C(22)	1.763(5)	C(12)-C(11)-C(10)	121.9(4)
S(21)-C(21)	1.771(5)	C(11)-C(12)-C(13)	118.8(4)
		C(14)-C(13)-C(12)	119.9(4)
N(7)-PD1-N(1)	80.34(13)	C(13)-C(14)-C(9)	121.6(4)
N(7)-PD1-S(8)	83.59(10)	O(21)-S(21)-C(22)	106.1(3)
N(1)-PD1-S(8)	163.84(10)	O(21)-S(21)-C(21)	106.3(3)
N(7)-PD1-CL1	172.83(10)	C(22)-S(21)-C(21)	97.2(3)
N(1)-PD1-CL1	106.77(10)		
S(8)-PD1-CL1	89.34(4)		
C(8)-S(8)-PD1	96.08(14)		

Table S6. Torsion angles [°] for C16 H19 Cl N4 O Pd S2.

N(7)-PD1-S(8)-C(8)	-0.33(16)	C(2)-N(1)-C(6)-C(7)	178.0(4)
N(1)-PD1-S(8)-C(8)	-6.2(4)	PD1-N(1)-C(6)-C(7)	0.1(4)
CL1-PD1-S(8)-C(8)	178.52(14)	C(4)-C(5)-C(6)-N(1)	-0.2(7)
N(7)-PD1-N(1)-C(2)	-177.3(4)	C(4)-C(5)-C(6)-C(7)	-179.7(4)
S(8)-PD1-N(1)-C(2)	-171.3(3)	N(8)-N(7)-C(7)-C(6)	-179.5(4)
CL1-PD1-N(1)-C(2)	3.7(4)	PD1-N(7)-C(7)-C(6)	0.6(5)
N(7)-PD1-N(1)-C(6)	0.2(3)	N(1)-C(6)-C(7)-N(7)	-0.4(6)
S(8)-PD1-N(1)-C(6)	6.1(5)	C(5)-C(6)-C(7)-N(7)	179.0(4)
CL1-PD1-N(1)-C(6)	-178.9(2)	N(7)-N(8)-C(8)-N(9)	-178.8(4)
N(1)-PD1-N(7)-C(7)	-0.4(3)	N(7)-N(8)-C(8)-S(8)	1.5(5)
S(8)-PD1-N(7)-C(7)	-178.7(3)	C(9)-N(9)-C(8)-N(8)	-3.0(7)
CL1-PD1-N(7)-C(7)	172.0(6)	C(9)-N(9)-C(8)-S(8)	176.7(3)
N(1)-PD1-N(7)-N(8)	179.7(3)	PD1-S(8)-C(8)-N(8)	-0.6(4)
S(8)-PD1-N(7)-N(8)	1.3(3)	PD1-S(8)-C(8)-N(9)	179.7(3)
CL1-PD1-N(7)-N(8)	-7.9(1)	C(8)-N(9)-C(9)-C(14)	-169.5(4)
C(7)-N(7)-N(8)-C(8)	178.1(4)	C(8)-N(9)-C(9)-C(10)	10.5(7)
PD1-N(7)-N(8)-C(8)	-1.9(5)	C(14)-C(9)-C(10)-C(11)	-0.7(6)
C(6)-N(1)-C(2)-C(3)	2.2(6)	N(9)-C(9)-C(10)-C(11)	179.3(4)
PD1-N(1)-C(2)-C(3)	179.5(3)	C(9)-C(10)-C(11)-C(12)	1.7(6)
C(6)-N(1)-C(2)-C(1)	-178.8(4)	C(10)-C(11)-C(12)-C(13)	-1.7(7)
PD1-N(1)-C(2)-C(1)	-1.6(6)	C(11)-C(12)-C(13)-C(14)	0.8(7)
N(1)-C(2)-C(3)-C(4)	-1.3(7)	C(12)-C(13)-C(14)-C(9)	0.2(7)
C(1)-C(2)-C(3)-C(4)	179.8(4)	C(10)-C(9)-C(14)-C(13)	-0.3(6)
C(2)-C(3)-C(4)-C(5)	-0.5(7)	N(9)-C(9)-C(14)-C(13)	179.8(4)
C(3)-C(4)-C(5)-C(6)	1.2(7)		
C(2)-N(1)-C(6)-C(5)	-1.5(6)		
PD1-N(1)-C(6)-C(5)	-179.4(4)		

Table S7. Bond lengths [$\text{\AA}$] and angles [$^\circ$] related to the hydrogen bonding for C16 H19 Cl N4 O Pd S2.

D-H	..A	d(D-H)	d(H..A)	d(D..A)	<DHA
N(9)-H(9)	O(21)#1	0.77(5)	2.08(5)	2.840(5)	169(4)

Symmetry transformations used to generate equivalent atoms:

#1 $x, y-1, z-1$

ORTEP view of the C16 H19 Cl N4 O Pd S2 compound with the numbering scheme adopted. Ellipsoids drawn at 30% probability level. Hydrogen atoms are represented by sphere of arbitrary size.

REFERENCES

SAINT (2006) Release 7.34A; Integration Software for Single Crystal Data.
Bruker AXS Inc., Madison, WI 53719-1173.

Sheldrick, G.M. (2008). SADABS, Bruker Area Detector Absorption Corrections.
Bruker AXS Inc., Madison, WI 53719-1173.

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

SHELXTL (2001) version 6.12; Bruker Analytical X-ray Systems Inc.,
Madison, WI 53719-1173.

APEX2 (2009) ; Bruker Molecular Analysis Research Tool.
Bruker AXS Inc., Madison, WI 53719-1173.

Spek, A.L. (2008). PLATON, A Multipurpose Crystallographic Tool,
Utrecht University, Utrecht, The Netherlands.

Maris, T. (2004). UdmX, University of Montréal, Montréal, QC, Canada.

XPREP (2008) Version 2008/2; X-ray data Preparation and Reciprocal space
Exploration Program. Bruker AXS Inc., Madison, WI 53719-1173.

BUT123

Université
de Montréal

Demandeur : Shadia

Moiety Formula: C₁₄ H₁₃ Cl N₄ Pd S, C₂ H₆ O S

Diffractomètre : Bruker Smart 6000

Température : 200 K

a : 7.2407(2) Å

b : 11.1883(3) Å

c : 23.5428(6) Å

α : 90 °

β : 97.850(2) °

γ : 90 °

V : 1889.4(1) Å³

Groupe d'espace : P2₁/c

R1 = 3.66 %

wR2 = 9.31 %

Rapport Word : [But123.doc](#)

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Figure S1. ^{31}P NMR spectrum of $[\text{Ru}(\text{mpytsc})_2(\text{PPh}_3)_2]$.

Figure S2. Mass spectrum of Hmpytsc.

Figure S3. Mass spectrum of [VO₂(mpytsc)].

Figure S4. Mass spectrum of [Ru(mpytsc)₂(PPh₃)₂].

Figure S5. Mass spectrum of [Pt(mpytsc)Cl].

Figure S6. Mass spectrum of Hmpyptsc.

Figure S7. Mass spectrum of [VO₂(mpyptsc)].

Figure S8. Mass spectrum of [Zn(mpyptsc)Cl₂].

Figure S9. Mass spectrum of $[\text{Ru}(\text{mpyptsc})_2(\text{PPh}_3)_2]$.

Figure S10. Anticancer activity of Hmpyptsc and complexes, $[\text{Zn}(\text{Hmpyptsc})\text{Cl}_2]$ and $[\text{Pd}(\text{mpyptsc})\text{Cl}]$, against human colon cancer cell line HCT116.

Table S8. Selected bond lengths and angles for Pd(mpyptsc) (X-ray structure and calculated), thiol and thione forms (calculated).

	Pd(mpyptsc) exp	Pd(mpyptsc)) calc	Hmpytthiol calc	Hmpytthione calc
Bond distances				
Pd-N7	1.970	2.034		
Pd-N1	2.171	2.242		
Pd-S	2.2421	2.3249		
Pd-Cl	2.3238	2.3572		
S-C8	1.774	1.7585	1.7880	1.6535
N1-C2	1.335	1.3479	1.3468	1.3385
N1-C6	1.375	1.3699	1.4074	1.3445
N7-C7	1.295	1.3036	1.2879	1.2863
N7-N8	1.372	1.3481	1.3829	1.3531
N8-C8	1.308	1.3373	1.3009	1.3969
N8-C9	1.352	1.3661	1.3814	1.3883
N9-C9	1.414			
Bond angles				
N1-Pd-N7	80.3	78.9		
N7-Pd-S	83.6	82.9		
N1-Pd-S	163.8	161.8		
N1-Pd-Cl	106.8	106.6		
S-Pd-Cl	89.3	91.6		
C8-S-Pd	96.1	94.9		
C2-N1-Pd	133.6	132.7		
C6-N1-Pd	107.9	107.9		
C7-N7-Pd	116.6	116.5		
N8-N7-Pd	124.6	123.6		
C7-N7-N8	118.8	119.9	113.4	116.6
N7-N8-C8	111.7	113.1	112.2	122.5
N8-C8-S	124.0	125.6	121.7	124.3
N8-C8-N9	121.0	112.8	117.1	108.6
N9-C8-S	115.0	121.6	121.0	127.0
Dihedral angles				
N8-C8-N9-C9	180.0	-180	146.9	171.6
S-C8-N9-C9	0.4	-0.4	-38.7	8.71
C8-N9-C9-C10	10.5	-37.6	-29.4	-38.4