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Synthesis and characterization of isomanolonitrile dithiolato palladium complexes. Crystal structure of $(PPh_3)_2Pd(S_2C_4N_2)$ and $(Et_4N)_2WS_4Pd(S_2C_4N_2)$

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Abstract—A series of isomalononitrile dithiolato palladium complexes, $(PPh_3)_2Pd(i\text{-mnt})$ (**1**), $[P(OPh)_3]_2Pd(i\text{-mnt})$ (**2**), $(PPh_3)(py)Pd(i\text{-mnt}) \cdot CH_3CN$ (**3**), $(Et_4N)_2Pd(i\text{-mnt})_2$ (**4**) and $(Ph_4As)_2Pd(i\text{-mnt})_2$ (**5**) were synthesized and characterized by elemental analysis and IR spectroscopy. The reaction between $(Et_4N)_2Pd(i\text{-mnt})_2$ (**4**) and $(Et_4N)_2WS_4$ gave a mixed metal cluster $(Et_4N)_2WS_4Pd(i\text{-mnt})$ (**6**). The crystallographically determined structures of **1** and **6** are reported. © 1997 Elsevier Science Ltd

Keywords: synthesis; crystal structure; palladium; dithiolate; coordination compounds; substitution reaction.

Isomalononitrile dithiolate (*i*-mnt) is a useful ligand for transition metals and its complexes and cluster compounds have been studied intensively. Several structure types of the complexes of this ligand including mononuclear complexes, $M(i\text{-mnt})_2^{2-}$ [$M = Pt^{II}$ [1], Cd^{II} [2], Pb^{II} [3], binuclear complexes $Au_2(PPh_3)_2(i\text{-mnt})$ [4], $\{Au(i\text{-mnt})Cl\}_2$ [5–6], $Mo_2O_2S_2(i\text{-mnt})_2^{2-}$ [7], trinuclear complex $[Ag(P(C_6H_5)_3)_2Ni(i\text{-mnt})_2$ [8], and clusters containing cores $Ag_6(i\text{-mnt})_6^{6-}$ [9] $Cu_8(i\text{-mnt})_6^{4-}$ [10] have been reported. Recently in studying the reaction of dithiolato metal complexes with tetrathiomolybdate (tungstate) we obtained a series of isomalononitrile dithiolato palladium complexes. Herein we report their synthesis and crystal structure determination as well as the cluster-forming reaction of $(Et_4N)_2Pd(i\text{-mnt})_2$ with $(Et_4N)_2MS_4$ ($M = Mo, W$).

EXPERIMENTAL

Material and methods

All reagents and solvents purchased were A.R. or C.P. grade and used without further purification. $(Et_4N)_2WS_4$ was prepared according to the literature [11]. $(Et_4N)_2Pd(i\text{-mnt})_2$ (**4**) (*i*-mnt = isomalonotrile dithiolate) was obtained as described previously [12]. Carbon, hydrogen and nitrogen analyses were carried out on a Perkin–Elmer 240C elemental analyser. IR spectra (4000–400 cm^{-1}) were recorded as solid KBr pellets on Nicolet 170sx FT-IR spectrometer. The data on elemental analyses and IR spectra are listed in Table 1.

Preparation of complexes

$(PPh_3)_2Pd(i\text{-mnt})$ (**1**) and $[P(OPh)_3]_2Pd(i\text{-mnt})$ (**2**). $PdCl_2$ (0.18 g, 1 mmol) was heated in acetinitrile (20

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Table 1. Elemental analysis and IR spectrum data

Compound	Formula	C (Found)	H (calc.)	N (%)	IR C≡N
1 $(PPh_3)_2Pd(i\text{-mnt})$	$C_{40}H_{30}N_2P_2PdS_2$	62.1	3.8	3.8	2204.5
		(62.3)	(3.9)	(3.6)	
2 $[P(OPh)_3]_2Pd(i\text{-mnt})$	$C_{40}H_{30}N_2O_6P_2PdS_2$	55.1	3.6	3.5	2210.5
		(55.4)	(3.5)	(3.2)	
3 $(PPh_3)(py)Pd(i\text{-mnt})\cdot CH_3CN$	$C_{29}H_{23}N_4PPdS_2$	55.1	3.8	8.8	2206.8
		(55.4)	(3.7)	(8.9)	
5 $(Ph_4As)_2Pd(i\text{-mnt})_2$	$C_{56}H_{40}As_2N_4PdS_4$	58.3	3.4	5.0	2198.0
		(58.3)	(3.5)	(4.9)	
6 $(Et_4N)_2(i\text{-mnt})PdWS_4$	$C_{20}H_{40}N_4PdS_6W$	29.6	5.0	6.6	2204.5
		(29.3)	(4.9)	(6.8)	

cm^3) to dissolve. To the solution solid PPh_3 (0.52 g, 2 mmol) was added and stirred while $Na_2(i\text{-mnt})$ (0.18 g, 1 mmol) was added and the orange–red solution was filtered. $(PPh_3)Pd(i\text{-mnt})$ (**1**) crystallized as orange plates while the solution was evaporated in air slowly. $[P(OPh)_3]_2Pd(i\text{-mnt})$ (**2**) was synthesized as above procedure with liquid $P(OPh)_3$ (0.55 g, 2 mmol) instead of PPh_3. **2** crystallized as orange–yellow blocks.

$(PPh_3)(py)Pd(i\text{-mnt})\cdot CH_3CN$ (**3**). $(PPh_3)_2Pd(i\text{-mnt})$ (**1**) (0.10 g, 0.15 mmol) was dissolved in acetonitrile (10 cm^3). To the solution pyridine (about 0.05 cm^3) was added and stirred. $(PPh_3)(py)Pd(i\text{-mnt})\cdot CH_3CN$ (**3**) crystallized as orange prisms while the solution was evaporated in air slowly.

$(Ph_4As)_2Pd(i\text{-mnt})_2$ (**5**). $PdCl_2$ (0.36 g, 2 mmol) and $Ph_4AsCl\cdot HCl$ (1.90 g, 4 mmol) were heated in 50 cm^3 methanol to dissolve. To the solution solid $Na_2(i\text{-mnt})$ (0.36 g, 2 mmol) was added. After stirring for 1 h the orange–red solution was filtered. $(Et_4N)_2Pd(i\text{-mnt})_2$ (**5**) crystallized as prism orange–red crystals while the solution was evaporated in air slowly.

$(Et_4N)_2(i\text{-mnt})PdWS_4$ (**6**). To a solution of $(Et_4N)_2Pd(i\text{-mnt})_2$ (**4**) (0.32 g, 0.5 mmol) in 10 cm^3 CH_2Cl_2 solid $(Et_4N)_2WS_4$ (0.29 g, 0.5 mmol) was added. The mixture was stirred for 1 h and filtered. The filtrate was layered with 10 cm^3 CH_3OH and placed in air for several days, red plate crystals formed.

X-ray crystal structure analysis of $(PPh_3)_2Pd(i\text{-mnt})$ (**1**) *and* $(Et_4N)_2(i\text{-mnt})PdWS_4$ (**6**)

Crystals of **1** and **6** were mounted in glass capillaries. All measurements were made on Rigaku AFC7R or AFC6S diffractometer with graphite monochromated Cu-Kα or Mo-Kα radiation. Cell constants and an orientation matrix for data collection, obtained from a least squares refinement using the setting angles of carefully centered reflections corresponded to orthorhombic and monoclinic cells with dimensions listed in Table 2. Intensity data were collected using ω scan mode. The weak reflections were rescanned and the counts were accumulated to ensure good counting statistic. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2 : 1. The intensities of three representation reflection were measured after every 150 reflections. The usual Lorentz and polarization factors and an empirical absorption correction were applied to the intensities. A correction for secondary extinction was applied for compound 1 (coefficient = 7.4131×10^{-7}).

Both structures were solved by direct methods and expanded using Fourrier techniques. The structures were refined by full-matrix least-squares fit. For **1**, some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. For **6**, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms in both structures were positioned geometrically and not refined. All calculations were performed using the teXsan crystallographic software package of molecular structure corporation. The labeling scheme and ORTEP diagram were shown in Figs 1 and 2. Selected bond distances and angles are listed in Table 3. Anisotropic displacement parameters and atomic coordinates are in the supplementary materials. The high R values for **1** were due to poor crystal quality.

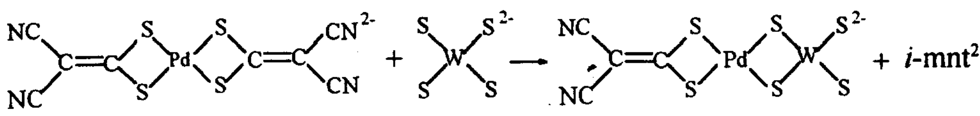
RESULTS AND DISCUSSION

Preparation of the complexes and cluster-forming reaction

The reaction between **4** and $(Et_4N)_2WS_4$ was designed to synthesize dithiolate-containing Pd—W—S clusters. The actual process afforded a crystalline product, the composition of which conformed to the formula $(Et_4N)_2WS_4Pd(i\text{-mnt})$ (**6**) as shown by the elemental analyses.

Table 2. Crystal parameter data collection and structure refinement details

Compound code	**1**	**6**
Chemical formula	$C_{40}H_{30}N_2P_2PdS_2$	$C_{20}H_{40}N_4PdS_6W$
Formula weight	771.16	819.17
Crystal system	Orthorhombic	Monoclinic
Space group	$Pca2_1$ (No. 29)	$P2_1$ (No. 4)
Unit cell parameters		
a (Å)	17.041(1)	14.538(4)
b (Å)	14.1488(6)	15.331(3)
c (Å)	16.0765(9)	7.133(1)
β (°)		95.69(2)
V (Å^3)	3876.3(7)	1582.0(5)
Z	4	2
d_{calc} (g/cm^3)	1.321	1.720
$F(000)$	1568	808
Radiation type (λ, Å)	Cu-Kα (1.54178)	Mo-Kα (0.71069)
No. of reflections for cell deter.	$20(20 < \theta < 26)$	$16(11.3 < \theta < 12.8)$
Absorption coefficient (cm^{-1})	58.63	46.17
2θ (°)	120.1	55
h, k, l ranges	$0 < h < 19$	$-18 < h < 18$
	$0 < k < 15$	$0 < k < 19$
	$0 < l < 18$	$-9 < l < 0$
T (K)	295	291
Crystal size (mm^3)	$0.20 \times 0.18 \times 0.15$	$0.29 \times 0.18 \times 0.12$
Diffractometer	Rigaku AFC7R	Rigaku AFC6S
Scan rate (° min^{-1})	4.0	2.0
Transmission factors	0.5098–0.9650	0.9008–0.9996
Reflections collected	3264	4069
No. of unique data	3264	3776 ($R_{int} = 0.072$)
No. obs. with $I > 1.5\sigma(I)$	2592	3222
No. of variables	244	288
Residuals: R; R_w	0.082, 0.123	0.050, 0.066
Goodness of fit	3.07	0.95
Max. shift in final cycle	0.0	0.0
Largest peaks in final diff. map	1.52; −0.65	2.87; −1.12

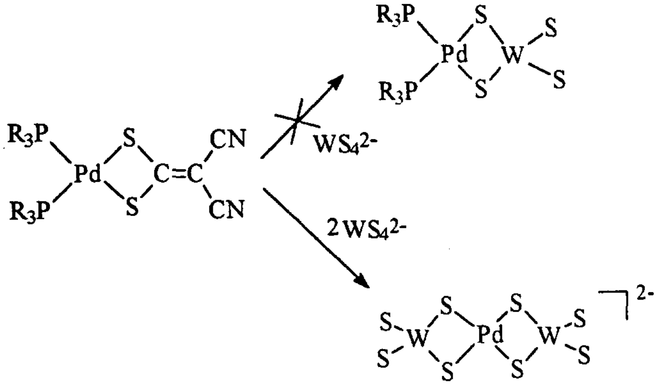


One i-mnt ligand is replaced by a WS_4^{2-} anion, which acts as a bidentate ligand. The IR spectrum with bands of 2202 cm^{-1} (νC≡N) and 488 (νW—S$_t$), 443 cm^{-1} (νW—S$_{br}$) bears out that the product comprises the ligand i-mnt and WS_4^{2-}. The former is comparable to 2199 cm^{-1} found in **4** and the latter are to those bands found in $Ag_3WS_4Br(PPh_3)_3$ H_2O [13]. A crystallographic structure diagram is also shown in Fig. 2. We had not observed the full substituted product $(Et_4N)_2W_2S_8Pd$ when the amount of $(Et_4N)_2WS_4$ was increased. This is different from the case in reaction of $Pd(S_2CNC_4H_8)_2$ ($S_2CNC_4H_8$ = pyrrolidinyldithiocarbmate) and $(H_4N)_2WS_4$, from which we obtained two products $(Et_4N)WS_4Pd(S_2CNC_4H_8)$ and $(Et_4N)_2W_2S_8Pd$ by varying the reactant ratios from 1 : 1 from 1 : 2 [14].

The reaction between **1** or **2** with $(Et_4N)_2WS_4$ had been carried out. In both cases the product $(Et_4N)_2W_2S_8Pd$ was obtained whatever reactant ratio was employed, and the expected $(R_3P)_2PdWS_4$ (R = Ph or PhO) has not been obtained.

Crystal structure of $(PPh_3)_2Pd(i\text{-mnt})$ (**1**) *and* $(Et_4N)_2WS_4Pd(i\text{-mnt})$ (**6**)

The molecule of **1** has no close intermolecular contacts. The palladium is four-coordinated by two P atoms from triphenylphosphines and two S atoms from isomalononitrile dithiolato ligand (i-mnt) in a distorted square planar environment. The S(1)—Pd(1)—S(2) bond angle is restricted by the che-



Scheme 1.

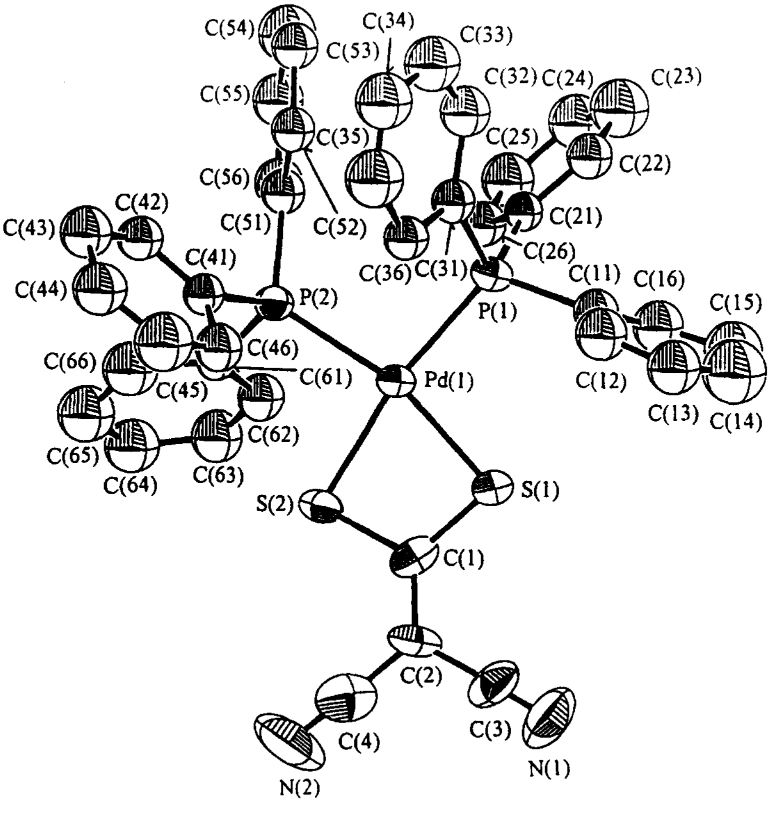


Fig. 1. ORTEP drawing of the molecular structure and labeling scheme for $(PPh_3)_2Pd(C_4N_2S_2)$ (**1**).

late ring to 74.2(2)°. The remaining angles in the square plane are then greater than 90°. The configuration of the isomalononitrile dithiolato ligand (*i*-mnt) is nearly the same as that appears in **4**. The atoms of this ligand are nearly coplanar. The S(1)—C(1)—S(2) bond angle of 111(1)° is comparable to that found in **4** and smaller than the value of 122.8(3)° found in the sodium salt of *i*-mnt [1]. The C(1)—S(1) bond distance of 1.68(2) and 1.75(2) is comparable to 1.723(3) and 1.725(3) Å found in **4**.

Compound **6** is a newly obtained mixed-metal binuclear complex. Analogues containing the moiety MoS_4^{2-}(WS_4^{2-}) of this type reported in literature are $RM'MS_4$, in which R = PhS, CN, M′ = Cu, Ag, M = Mo, W [16]. The ORTEP diagrams of compound **6** are shown in Fig. 2. Palladium atom is coor-

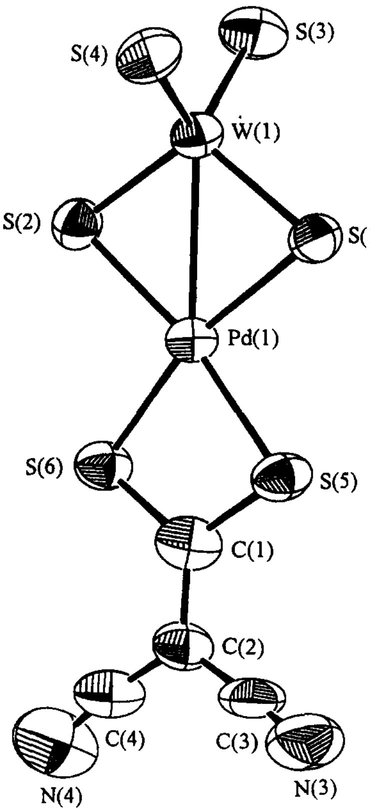
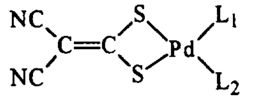


Fig. 2. ORTEP drawing of the molecular structure and labeling scheme for the anion portion of $(Et_4N)_2(C_4N_2S_2)PdWS_4$ (**6**).

dinated by an isomalononitrile dithiolato ligand and a tetrathiotungstate, which both act as bidentates with two sulfur atoms as chelates. The configuration of dithiolate likes that appeared in **1** and **4**. The S(5)—C(1)—S(6) angle of 110.7(9)° in **6** is comparable to values of S—C—S angle found in the other four complexes shown in Table 4. The Pd(1)—S(5) of 2.312(3) and Pd(1)—S(6) of 2.316(4) Å are shorter than 2.342(4) and 2.338(4) Å of Pd—S distances. The S(5)—Pd(1)—S(6) bond angle is restricted by the chelate ring to 75.2(1)° and is much smaller than the other three S—Pd—S angles. Owing to the interaction between palladium and tungsten (Pd—W distance 2.857(1) Å), the S(1)—Pd(1)—S(2) angle is open to 99.3(1)°, which is much bigger than the chelate angle 75.2(1)° of S(5)—Pd(1)—S(6) and even larger than the usual coordination angle of 90°. The configuration of WS_4^{2-} is a tetrahedron close to which appears in $(NC)AgWS_4^{2-}$. The two terminal W—S_t distances are 2.170(4) and 2.159(4) Å, which are near to those of 2.153(3) and 2.158(3) Å found in $(NC)AgWS_4^{2-}$. The distances of the two bridging W—S bonds are 2.227(2) and 2.237(4) Å and are little longer than those of the W—S_t bonds. This case is similar to that in $(NC)AgWS_4^{2-}$



1: $L_1 = L_2 = PPh_3$;

2: $L_1 = L_2 = P(OPh_3)_3$;

3: $L_1 = PPh_3$, $L_2 = Py$;

4: $L_1, L_2 = S_2C{=}C(CN)_2^{2-}$;

6: $L_1, L_2 = WS_4^{2-}$

Scheme 2.

Table 4 summarized the main geometry of isomanolonitrile dithiolato palladium complexes we obtained. The complexes are all structurally determined. The structure of **2** and **3** are reported in [17] and [18], respectively. The five complexes have the same structure with different ligands L_1 and L_2 as shown in Scheme 2. It can be seen from Table 4 that the configurations of the ligand isomanolonitrile dithiolate (*i*-mnt) are generally the same: the C—S, C═C,

Table 3. Selected bond distances (Å) and angles (°)

$(PPh_3)_2Pd$(*i*-mnt) (**1**)			
Pd(1)—S(1)	2.342(6)	Pd(1)—S(2)	2.339(5)
Pd(1)—P(1)	2.309(6)	Pd(1)—P(2)	2.336(1)
S(1)—C(1)	1.68(2)	S(2)—C(1)	1.75(2)
N1(1)—C(3)	1.09(4)	N(2)—C(4)	1.17(4)
C(1)—C(2)	1.34(3)	C(2)—C(3)	1.50(4)
C(2)—C(4)	1.44(5)		
S(1)—Pd(1)—S(2)	74.2(2)	S(1)—Pd(1)—P(1)	93.7(2)
S(1)—Pd(1)—P(2)	164.7(2)	S(2)—Pd(1)—P(1)	167.8(2)
S(2)—Pd(1)—P(2)	90.8(2)	P(1)—Pd(1)—P(2)	101.2(2)
S(1)—C(1)—S(2)	111(1)	C(3)—C(2)—C(4)	111(2)
S(1)—C(1)—C(2)	128(1)	S(2)—C(1)—C(2)	120(1)
C(1)—C(2)—C(3)	120(2)	C(1)—C(2)—C(4)	127(2)
N(1)—C(3)—C(2)	177(3)	N(2)—C(4)—C(2)	177(4)
$(Et_4N)_2$(*i*-mnt)$PdWS_4$ (**6**)			
W(1)—Pd(1)	2.857(1)	W(1)—S(1)	2.227(2)
W(1)—S(2)	2.237(4)	W(1)—S(3)	2.170(4)
W(1)—S(4)	2.159(4)	Pd(1)—S(1)	2.338(4)
Pd(1)—S(2)	2.342(4)	Pd(1)—S(5)	2.312(3)
Pd(1)—S(6)	2.316(4)	S(5)—C(1)	1.70(2)
S(6)—C(1)	1.73(2)	N(3)—C(3)	1.13(3)
N(4)—C(4)	1.18(3)	C(1)—C(2)	1.42(2)
C(2)—C(3)	1.40(3)	C(2)—C(4)	1.40(2)
S(1)—W(1)—S(2)	1106.1(1)	S(1)—W(1)—S(3)	109.9(2)
S(1)—W(1)—S(4)	109.6(2)	S(2)—W(1)—S(3)	110.7(2)
S(2)—W(1)—S(4)	110.4(2)	S(3)—W(1)—S(4)	110.2(2)
S(1)—Pd(1)—S(2)	99.3(1)	S(1)—Pd(1)—S(5)	92.2(1)
S(1)—Pd(1)—S(6)	166.4(1)	S(2)—Pd(1)—S(5)	167.8(1)
S(2)—Pd(1)—S(6)	93.7(1)	S(5)—Pd(1)—S(6)	75.2(1)
S(5)—C(1)—S(6)	110.7(9)	S(5)—C(1)—S(2)	124(1)
S(6)—C(1)—C(2)	124(1)	C(1)—C(2)—C(3)	118(1)
C(1)—C(2)—C(4)	121(1)	C(3)—C(2)—C(4)	119(1)
N(3)—C(3)—C(2)	176(2)	N(4)—C(4)—C(2)	172(2)

Table 4. Comparison of the structure features of isomanolonitrile dithiolato palladium complexes

	$(PPh_3)_2Pd$ (*i*-mnt) (**1**)	$(P(OPh)_3)_2Pd$ (*i*-mnt) (**2**)	$(PPh_3)(py)Pd$ (*i*-mnt) (**3**)	$(Et_4N)_2Pd$ (*i*-mnt)$_2$ (**4**)	$(Et_4N)_2$(*i*-mnt) $PdWS_4$ (**6**)
Pd—S	2.342(6)	2.333(1)	2.288(2)	2.323(1)	2.312(3)
	2.339(5)	2.333(1)	2.340(1)	2.324(1)	2.316(4)
C—S	1.68(2)	1.736(4)	1.724(4)	1.723(3)	1.70(2)
	1.75(2)	1.736(4)	1.716(4)	1.725(3)	1.73(2)
C=C	1.34(3)	1.348(8)	1.385(5)	1.375(4)	1.42(2)
C—C	1.50(4)	1.441(6)	1.414(6)	1.418(4)	1.40(3)
	1.44(5)	1.441(6)	1.414(6)	1.417(5)	1.40(2)
C≡N	1.09(4)	1.130(6)	1.146(6)	1.143(5)	1.18(3)
	1.17(4)	1.130(6)	1.154(5)	1.136(5)	1.13(3)
S—Pd—S	74.2(2)	75.44(5)	75.35(4)	75.2(1)	75.2(1)
S—C—S	111(1)	110.5(3)	110.6(2)	110.6(2)	110.7(9)
NC—C—CN	111(2)	118.0(6)	117.7(3)	117.6(3)	119(1)

C—C and C≡C bond distances, S—C—S and NC—C—CN bond angle are all comparable. The Pd—S distances, except that in **3** due to the *trans*-influence of different L_1 and L_2 [18], are similarly near to 2.33 Å, which is the common Pd—S distances found in dithiolato palladium complexes [19].

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