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Tetrakis(dimethyl sulfide)palladium(II) bis(tetrafluoroborate) and tetrakis(1,4-oxathiane-*κS*)palladium(II) bis(tetrafluoroborate)

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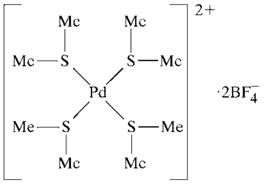
Tetrakis(dimethyl sulfide)palladium(II) bis(tetrafluoroborate), $[Pd(C_2H_6S)_4](BF_4)_2$, (I), and tetrakis(1,4-oxathiane-*κS*)palladium(II) bis(tetrafluoroborate), $[Pd(C_4H_8OS)_4](BF_4)_2$, (II), both crystallize as mononuclear square-planar complexes with tetrafluoroborate as the counter-ions. The Pd atom accepts four S-donor atoms and is positioned at an inversion centre in both compounds. The two unique S atoms in the dimethyl sulfide complex, (I), are disordered. The Pd—S distances are in the range 2.3338 (12)–2.3375 (12) Å in (I), and the corresponding distances in the thioxane complex, (II), are 2.3293 (17) and 2.3406 (17) Å. The anions in both compounds interact weakly with the Pd atom.

Comment

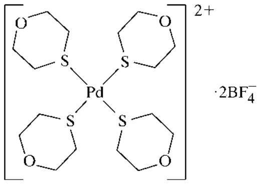
The 1,4-oxathiane (tx) ligand possesses two potential donor sites, *i.e.* the S and O atoms. Pd^{II} and Pt^{II} are soft acceptors and sulfur bonding is predominant, but in the tetrakis(dimethyl sulfoxide) complexes of Pd^{II} and Pt^{II}, two *S*-bonded and two *O*-bonded ligands were observed in a *cis* arrangement (Johnson *et al.*, 1981; Elding & Oskarsson, 1987). A previously determined palladium(II) tetrakis(1,4-oxathiane) structure, $[Pd(tx)_4](BF_4)_2\cdot4CH_3NO_2$ (Moullet *et al.*, 1997), was found to contain four *S*-bonded tx ligands, and the same arrangement was found for the platinum compound $[Pt(tx)_4](CF_3SO_3)_2\cdot H_2O$ (Bugarcic *et al.*, 1991). There seems to be no reported crystal structure for a Pd complex with four dimethyl sulfide ligands (dms), but for Pt^{II}, the crystal structure of $[Pt(dms)_4](CF_3SO_3)_2$ is known (Bugarcic *et al.*, 1991).

The structures of compounds (I) and (II) have been determined first in order to study possible differences in bonding to Pd^{II} between a small thioether ligand, dimethyl sulfide (dms), and a larger ambidentate ligand, 1,4-oxathiane (tx), with certain steric demands imposed by the ring structure, and secondly, to make geometric comparisons with analogous Pt^{II} complexes.

The structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. The compound consists of a square-planar mononuclear cationic complex, $[Pd(dms)_4]^{2+}$, with BF_4^- as counter-ions. The Pd atom is positioned at an inversion centre, giving a perfectly planar PdS_4 coordination, with S—Pd—S angles of 89.60 (5) and 90.40 (5)°. The dms groups are disordered, as the S atom occupies two different positions, with occupancy factors refined to 0.875 (3) for S1 and S2, and 0.125 (3) for S1′ and S2′. The same type of disorder was reported for $[Pt(dms)_4](CF_3SO_3)_2$ (Bugarcic *et al.*, 1991). The C atoms have a paddle-wheel-like arrangement, *i.e.* they are staggered with respect to the coordination plane and all directed in the same way. One tetrafluoroborate anion is located on each side of the coordination plane, completing an approximate octahedral coordination of the Pd atom, with the shortest distance to Pd being 3.142 (1) Å for Pd—F2(*x*, *y*, *z*; −*x*, −*y*, −*z*) (Fig. 1).



(I)



(II)

The structure of (II) is shown in Fig. 2 and selected geometric parameters are given in Table 2. The compound consists of a square-planar mononuclear cationic complex, $[Pd(tx)_4]^{2+}$, with *S*-bonded tx ligands and with BF_4^- as counter-ions. The Pd atom is positioned at an inversion centre, giving a perfect planar coordination around the metal, with S—Pd—S angles of 89.48 (6) and 90.52 (6)°. The tx ligands have a chair conformation. The two C atoms bonded to S in each of these ligands adopt the same paddle-wheel-like conformation found in the dms complex, (I). Three of the four

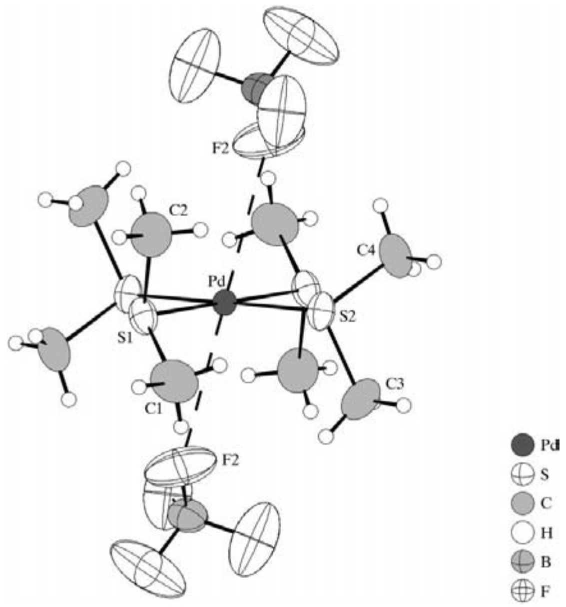


Figure 1
A view of the molecule of (I), showing the atom-numbering scheme and the positions of the anions. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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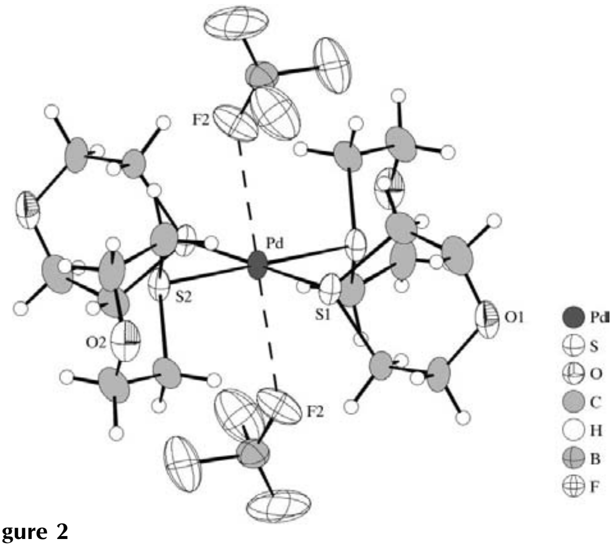

Figure 2
A view of the molecule of (II), showing the atom-numbering scheme and the positions of the anions. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Pd$\cdots$F3′($1 + x, y, z; -1 - x, -y, -z$) interactions have been omitted for clarity.

F atoms in the tetrafluoroborate ions are disordered over two positions, with approximately 50% in each position, while one F-atom position is fully occupied. The tetrafluoroborate ions are located on each side of the coordination plane, giving an approximately octahedral coordination of the Pd atom, with the closest interaction with Pd being 2.87 (8) Å for Pd$\cdots$F2($1 + x, y, z; -1 - x, -y, -z$) and 3.00 (6) Å for Pd$\cdots$F3′($1 + x, y, z; -1 - x, -y, -z$) (Fig. 2).

The arrangement of the thioether ligands around Pd in (I) is similar to the geometry found in $[Pd(tx)_4](BF_4)_2 \cdot 4CH_3NO_2$ (Moullet *et al.*, 1997), and in the analogous Pt compounds $[Pt(dms)_4](CF_3SO_3)_2$ and $[Pt(tx)_4](CF_3SO_3)_2 \cdot H_2O$ (Bugarcic *et al.*, 1991). The dms ligands are found to be disordered in a similar fashion in the Pt–dms complex. The geometry of the tx ligands in (II) is also similar to that found for $[Pd(tx)_4](BF_4)_2 \cdot 4CH_3NO_2$, but with slightly shorter S—C distances, in the range 1.782 (8)–1.809 (7) Å, compared with 1.806 (4)–1.827 (4) Å for the latter complex.

In the earlier reported tetrakis(thioxane) Pd complex (Moullet *et al.*, 1997), the CH_3NO_2 solvent molecules occupy the octahedral coordination sites, instead of the BF_4 anions, with a Pd—O distance of 3.115 (2) Å. In $[Pt(dms)_4](CF_3SO_3)_2$ and $[Pt(tx)_4](CF_3SO_3)_2 \cdot H_2O$ (Bugarcic *et al.*, 1991), no close distances between the cations and the anions or the solvent molecules were found. For $[Pd(dmso)_4](BF_4)_2 \cdot (CH_3)_2SO$ (dmso is dimethyl sulfoxide; Johnson *et al.*, 1981), a Pd—$O_{solvent}$ distance of 3.14 (3) Å was reported, but no distances to the anions that occupy the other side of the coordination plane were reported.

The geometry of a metal complex in the solid state is determined by the interplay between inter- and intramolecular forces. The Pd—S bonds within $[Pd(dms)_4]^{2+}$ and $[Pd(tx)_4]^{2+}$ experience different intermolecular forces, and their lengths are given in Table 3. The observed range in $[Pd(dms)_4]^{2+}$ is 2.3338 (12)–2.3375 (12) Å, with a mean value of 2.336 (2) Å. The error of the mean is calculated as $[\Sigma(x_i - M)^2/(n - 1)]^{1/2}$, where M is the mean and n the number of distances. The corresponding range for $[Pd(tx)_4]^{2+}$ is 2.329 (2)–2.341 (2) Å, with a mean of 2.334 (5) Å.

We have also studied the bonding at the extended Hückel level by calculating the reduced overlap population (ROP) in the Pd—S bonds using the program *CACAO* (Maelli & Proserpio, 1990) and the crystallographically observed geometries. No significant differences in either the Pd—S bond lengths nor the ROP values were observed between the two title compounds (Table 3). The similarities in bonding are of course the result not only of similar bond distances but also of similar orientation of the ligands with respect to the coordination plane.

In conclusion, no significant differences in bonding between Pd^{II} and the dimethyl sulfide and 1,4-oxathiane ligands have been observed, and it seems justified to calculate a mean value for the Pd—S distances of 2.337 (7) Å, where the error is calculated as given above. The mean value for the Pt—S distances in Table 3 is 2.319 (5) Å, and the difference of 0.018 (8) Å between the mean Pd—S and Pt—S distances is probably significant.

Experimental

To prepare compound (I), HBF_4 (400 µl, 2.7 mmol) was added to a dms solution of $Pd(OAc)_2$ (OAc is acetate; 195 mg, 0.87 mmol). Yellow crystals precipitated immediately and the solution was stirred for 20 min. Recrystallization from dichloromethane gave yellow

Table 1
Selected geometric parameters (Å, °) for (I).

Pd—S1	2.3375 (12)	S2—C3	1.814 (7)
Pd—S2	2.3338 (12)	S2—C4	1.761 (6)
Pd—S1′	2.343 (8)	S1′—C1	1.700 (12)
Pd—S2′	2.325 (8)	S1′—C2	1.807 (12)
S1—C1	1.764 (7)	S2′—C3	1.855 (12)
S1—C2	1.792 (6)	S2′—C4	1.655 (11)
S1^{i}—Pd—S2	90.40 (5)	Pd—S1′—C1	113.3 (5)
S1—Pd—S2	89.60 (5)	Pd—S1′—C2	105.0 (5)
S1′—Pd—S2′^{i}	90.1 (3)	Pd—S2′—C3	103.0 (5)
S1′^{i}—Pd—S2′^{i}	89.9 (3)	Pd—S2′—C4	118.6 (6)
Pd—S1—C1	111.0 (3)	C1—S1—C2	100.8 (4)
Pd—S1—C2	105.7 (2)	C3—S2—C4	99.3 (4)
Pd—S2—C3	104.0 (2)	C1—S1′—C2	102.7 (6)
Pd—S2—C4	113.6 (2)	C3—S2′—C4	101.6 (6)

Symmetry code: (i) $-x, -y, -z$.

Table 2
Selected geometric parameters (Å, °) for (II).

Pd—S1	2.3406 (17)	S2—C7	1.782 (8)
Pd—S2	2.3293 (17)	O1—C2	1.414 (12)
S1—C1	1.799 (9)	O1—C4	1.403 (10)
S1—C3	1.803 (7)	O2—C6	1.401 (10)
S2—C5	1.809 (7)	O2—C8	1.403 (11)
S1^{i}—Pd—S2	89.48 (6)	Pd—S2—C7	111.7 (3)
S1—Pd—S2	90.52 (6)	C1—S1—C3	97.7 (4)
Pd—S1—C1	111.3 (3)	C5—S2—C7	98.7 (4)
Pd—S1—C3	108.4 (2)	C2—O1—C4	112.6 (7)
Pd—S2—C5	106.2 (3)	C6—O2—C8	113.0 (6)

Symmetry code: (i) $-x, -y, -z$.

prismatic crystals of (I) suitable for X-ray diffraction. Compound (II) was prepared by adding an excess of 1,4-oxathiane to a solution of $Pd(OAc)_2$ (100 mg, 0.45 mmol) in dichloromethane. The solution was stirred at room temperature for 5 min before HBF_4 (150 µl, 1.0 mmol) was added. Pale-yellow crystals of (II) precipitated immediately and were recrystallized from nitromethane.

Compound (I)

Crystal data

$[Pd(C_2H_6S)_4](BF_4)_2$
$M_r = 528.53$
Monoclinic, $P2_1/n$
$a = 8.4505 (17)$ Å
$b = 9.955 (2)$ Å
$c = 12.172 (2)$ Å
$\beta = 98.99 (3)°$
$V = 1011.4 (3)$ Å^3
$Z = 2$

$D_x = 1.736$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 4803 reflections
$\theta = 3–28°$
$\mu = 1.39$ mm^{-1}
$T = 293 (2)$ K
Prism, pale yellow
0.3 × 0.1 × 0.1 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.595$, $T_{max} = 0.831$
8129 measured reflections

3087 independent reflections
2408 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 31.6°$
$h = -10 \rightarrow 12$
$k = -14 \rightarrow 12$
$l = -16 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.127$
$S = 1.09$
3087 reflections
125 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 1.3665P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}

Compound (II)

Crystal data

$[Pd(C_4H_8OS)_4](BF_4)_2$
$M_r = 696.68$
Triclinic, $P\overline{1}$
$a = 8.8804 (18)$ Å
$b = 9.5397 (19)$ Å
$c = 9.6999 (19)$ Å
$\alpha = 94.11 (3)°$
$\beta = 114.12 (3)°$
$\gamma = 111.79 (3)°$
$V = 671.8 (2)$ Å^3

$Z = 1$
$D_x = 1.722$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 2469 reflections
$\theta = 4–26°$
$\mu = 1.08$ mm^{-1}
$T = 293 (2)$ K
Prism, yellow
0.20 × 0.14 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.813$, $T_{max} = 0.882$
4856 measured reflections

3185 independent reflections
2080 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 27.9°$
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 12$
$l = -12 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.080$
$wR(F^2) = 0.203$
$S = 0.96$
3185 reflections
188 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1175P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.56$ e Å^{-3}
$\Delta\rho_{min} = -2.61$ e Å^{-3}

H atoms were constrained to their parent sites, with C—H distances of 0.96 (CH_3) and 0.97 Å (CH_2), and refined using a riding model, with $U_{iso}(H) = 1.5U_{eq}(C)$ for CH_3 and $1.2U_{eq}(C)$ for CH_2. The structure of (II) had one significant residual density peak of 2.56 e Å^{-3} and one hole of −2.61 e Å^{-3} in the final difference Fourier map, and these lie 1.07 and 0.87 Å from Pd, respectively. No high residual density peaks were found in the final difference Fourier map for (I).

Table 3
Comparison of Pd—S and Pt—S distances (Å) in analogous dms and tx complexes, together with selected reduced overlap population (ROP) values.

Compound	*M*—S	ROP
(I)[c]	2.3338(12)[a]	0.429
	2.325(8)[b]	
	2.3375(12)[a]	0.427
	2.343(8)[b]	
(II)[c]	2.3406 (17)	0.427
	2.3293 (17)	0.431
$[Pd(tx)_4](BF_4)_2 \cdot 4CH_3NO_2$[d]	2.334 (1)	
	2.334 (1)	
$[Pd(dms)_4](ClO_4)_2$[e]	2.3347 (17)	
	2.3359 (17)	
	2.344 (6)	
	2.351 (6)	
$[Pt(dms)_4](ClO_4)_2$[e]	2.312 (9)	
	2.3122 (14)	
	2.3181 (13)	
	2.329 (9)	
$[Pt(dms)_4](CF_3SO_3)_2$[f]	2.317 (3)	
	2.318 (3)	
	2.319 (4)	
	2.321 (4)	
$[Pt(tx)_4](CF_3SO_3)_2 \cdot H_2O$[f]	2.321 (2)	
	2.318 (2)	

Notes: (*a*) these distances correspond to the S atoms of the major component. The ROP values are only calculated using those bonds; (*b*) the S atoms of the minor component; (*c*) this work; (*d*) Moullet *et al.* (1997); (*e*) Johansson & Oskarsson (2002); (*f*) Bugarcic *et al.* (1991).

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXTL* (Sheldrick, 1997*b*).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1008). Services for accessing these data are described at the back of the journal.

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