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cis-Bis(dimethyl sulfoxide-*S*)dinitratopalladium(II) and *cis*-dinitratobis(1,4-oxathiane-*S*)palladium(II)

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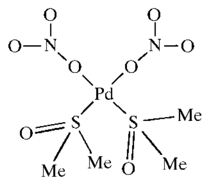
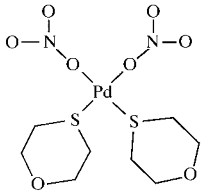
The Pd atom in each of the two title compounds, $[Pd(NO_3)_2(C_2H_6OS)_2]$, (I), and $[Pd(NO_3)_2(C_4H_8OS)_2]$, (II), coordinates two O atoms from two nitrate ligands and two S atoms from dimethyl sulfoxide (dmso) and thioxane (systematic name: 1,4-oxathiane) ligands in a pseudo-square-planar *cis*-geometry. In the dmso complex, the distances to palladium are Pd—O 2.067 (2) and 2.072 (2) Å, and Pd—S 2.2307 (11) and 2.2530 (8) Å. The corresponding distances in the thioxane complex are Pd—O 2.053 (3) and 2.076 (2) Å, and Pd—S 2.2595 (9) and 2.2627 (11) Å. Both compounds may be regarded as dimers with an inversion centre, where one of the coordinating nitrate O atoms in one molecule also interacts with the Pd atom in the adjacent molecule, with Pd—O distances of 2.849 (9) and 3.31 (3) Å in (I) and (II), respectively.

Comment

Both dimethyl sulfoxide (dmso) and thioxane (tx; systematic name: 1,4-oxathiane) are ambivalent ligands since they possess two potential donor sites, *i.e.* the S and O atoms. Pd^{II} and Pt^{II} are soft acceptors and sulfur bonding is predominant with these metal atoms. Tetrakis(dimethyl sulfoxide)palladium(II) contains two *S*-bonded and two *O*-bonded ligands in a *cis* arrangement (Johnson *et al.*, 1981; Johansson & Oskarsson, 2001), while tetrakis(thioxane)palladium contains four *S*-bonded ligands (Moullet *et al.*, 1997; Johansson & Oskarsson, 2001). The same arrangements are found for the corresponding platinum compounds (Elding & Oskarsson, 1987; Bugarcic *et al.*, 1991). The crystal structure of *cis*-bis(dimethyl sulfoxide)dinitratopalladium(II) has been published previously but only as a preliminary report with no atomic coordinates (Langs *et al.*, 1967); only the coordination geometry is given. It has been noticed that in Pt compounds the Pt—S distances in sulfoxides are shorter than in the corresponding thioether complexes (Bugarcic *et al.*, 1993) and it has been shown that the origin of this difference is stronger bonding to sulfoxide S compared with thioether S (Kapoor *et al.*, 1998). In order to find out if the same applies to Pd complexes, we have redetermined the structure of *cis*-bis(dimethyl sulfoxide)dinitratopalladium(I), *cis*-$[Pd(NO_3)_2(dmso)_2]$, (I), and synthesized and determined the structure of *cis*-dinitratobis(1,4-thioxane)palladium(II), *cis*-$[Pd(NO_3)_2(tx)_2]$, (II). The bonding was studied at the extended Hückel level using the program *CACAO* (Mealli & Proserpio, 1990). We have calculated the reduced overlap population (ROP) in the Pd–ligand bonds using the crystallographically observed geometries in the title complexes (Table 1).



(I)



(II)

In *cis*-$[Pd(NO_3)_2(dmso)_2]$ (Fig. 1), the coordination around the Pd atom is pseudo-square planar, with angles ranging from 82.89 (9) to 95.64 (7)°. The nitrate ligands are oxygen coordinated, while dmso coordinates *via* sulfur. The coordination plane has a mean deviation of 0.0878 Å. The N—O distances with O coordinated to Pd are 1.322 (3) and 1.312 (3) Å, while the other N—O distances are in the range 1.208 (3)–1.225 (3) Å. The structure is composed of dimers where the two complexes are related *via* an inversion centre. The nitrate O4 atom of one complex interacts with the Pd atom of another complex and *vice versa*, forming a short intermolecular Pd···O4^{i} distance of 2.849 (9) Å [symmetry code: (i) $2 - x, 1 - y, 2 - z$].

The *cis*-$[Pd(NO_3)_2(tx)_2]$ (Fig. 2) complex is pseudo-square planar, with angles around palladium ranging from 87.09 (10) to 92.06 (3)°. The nitrate ligands are oxygen coordinated, while the thioxane ligands coordinate through the S atoms. The coordination plane has a mean deviation of 0.0911 Å. The N—O distances with O coordinated to Pd are 1.285 (4) and 1.305 (4) Å, while the other N—O distances are in the range 1.210 (5)–1.231 (4) Å. The structure is composed of dimers, similar to the arrangement found in *cis*-$[Pd(NO_3)_2(dmso)_2]$, with the two complexes related *via* an inversion centre. The nitrate O6 atom of one complex interacts with the Pd atom of a second complex and *vice versa*, forming a short intermolecular Pd···O6^{ii} distance of 3.303 (3) Å [symmetry code: (ii) $1 - x, 1 - y, 1 - z$]. The thioxane ligands adopt a chair conformation and are centred around the coordination plane.

The dimers forming bonds have ROP values of 0.011 and 0.000 for (I) and (II), respectively. An ROP value larger than zero indicates covalent interaction, while a value of zero indicates only van der Waals interaction. However, a value as small as 0.011 may not be significant. The 'intermolecular oxygen' is in an approximate octahedral position in both complexes, resulting in O4—Pd—O4^{i} and O6—Pd—O6^{ii} angles of 76.56 (10) and 95.39 (10)° in the dmso and thioxane complexes, respectively, *i.e.* the O atom in the thioxane complex is close to being in the perfect octahedral position. The Pd···Pd distance in the dimers is 3.89 (4) Å in (I) and

3.74 (3) Å in (II). Both nitrate ligands in the title compounds point away from the coordination plane and face the second complex in the dimer with Pd—O—N angles of 115.2 (2), 114.2 (2), 115.1 (3) and 114.9 (2)°. Potassium tetranitratopalladium(II) has a similar geometry, with Pd—O—N angles ranging from 116.0 (2) to 119.4 (2)° (Elding *et al.*, 1986). The same type of dimeric structure is found for the isostructural dmso–platinum analogue (Boström *et al.*, 1991).

The Pd—S and Pd—O distances in the title compounds are compared with those of related structures in the literature in Table 1. The Pd—S distances for (II) are shorter than in $[Pd(tx)_4]^{2+}$ (Johansson & Oskarsson, 2001; Moullet *et al.*, 1997), which is in agreement with the weaker *trans* influence of oxygen compared to sulfur. The corresponding dmso complex does not show this trend since the S atoms in $[Pd(dmso)_4]^{2+}$ are *trans* to O atoms (Johnson *et al.*, 1981). The Pd—S distances in $[Pd(tx)_4]^{2+}$ (Johansson & Oskarsson, 2001; Moullet *et al.*, 1997) are longer than in all structures listed in Table 1 with oxygen *trans* with respect to sulfur.

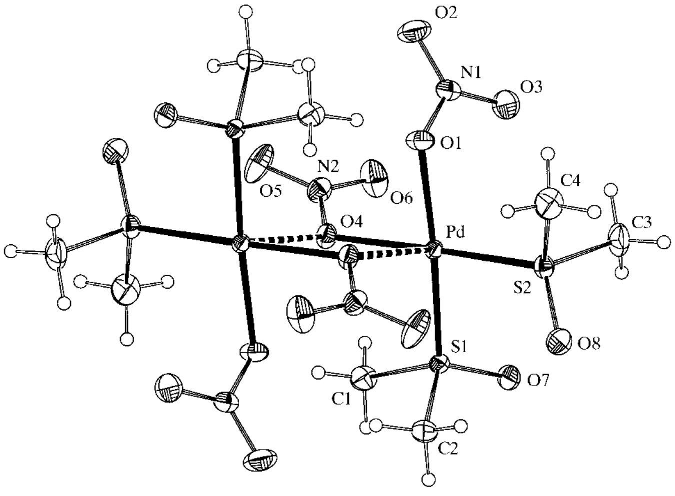


Figure 1
The dimer in *cis*-$[Pd(NO_3)_2(dmso)_2]$, (I), showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level (*DIAMOND*; Brandenburg, 2000).

The Pd—O distances in the two title structures [range 2.053 (3)–2.076 (2) Å] are about the same as in $[Pd(dmso)_4]^{2+}$ [2.049 (3)–2.065 (10) Å; Johnson *et al.*, 1981], while the Pd—O distances in $[Pd(NO_3)_4]^{2-}$ [1.995 (3)–2.010 (2) Å; Elding *et al.*, 1986] are much shorter, in accordance with the *trans* influence series.

The Pd—S distances in palladium sulfoxide compounds are compared with distances in similar thioether compounds in Table 2. All palladium sulfoxide compounds (except complexes with more than one metal centre) found in the Cambridge Structural Database (CSD; Allen & Kennard, 1993) are included, while only thioethers with a similar arrangement (compared to the sulfoxides) around the Pd and S atoms are taken into account. The Pd—S distances are 0.02–0.05 Å shorter in the sulfoxide compounds than in the thioether compounds.

The ROP values for the two title compounds are given in Table 1; the value for $Pd—S_{dmso}$ is larger than for $Pd—S_{tx}$. The Pd—S bond length in (I) must be increased to 2.30 Å to obtain the same ROP as in (II) and it was concluded that sulfoxides form stronger bonds with Pd^{II} than thioethers, *i.e.* the same situation as observed for Pt^{II} compounds (Kapoor *et al.*, 1998).

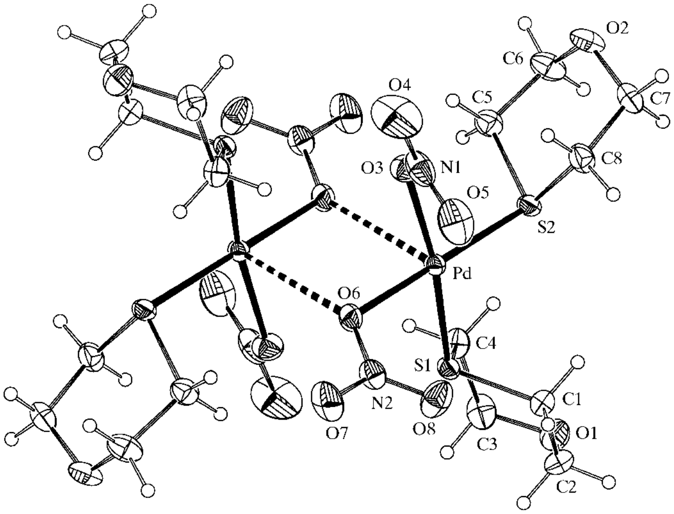


Figure 2
The dimer in *cis*-$[Pd(NO_3)_2(tx)_2]$, (II), showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level (*DIAMOND*; Brandenburg, 2000).

Experimental

For the preparation of *cis*-$[Pd(NO_3)_2(dmso)_2]$, $AgNO_3$ (204 mg, 1.2 mmol) was added to an aqueous solution of $PdCl_2(dmso)_2$ (200 mg, 0.6 mmol). AgCl precipitates immediately and the mixture was stirred at room temperature for 1 h. AgCl was removed by filtration and orange crystals appeared upon slow evaporation. For the preparation of *cis*-$[Pd(NO_3)_2(tx)_2]$, $AgNO_3$ (204 mg, 1.2 mmol) was added to an aqueous solution of $PdCl_2$(1,4-thioxane)$_2$ (200 mg, 0.6 mmol). AgCl precipitated immediately and the mixture was stirred at room temperature for 1 h. AgCl was removed by filtration and recrystallization from CH_2Cl_2 and CH_3NO_3 afforded orange crystals.

Compound (I)

Crystal data

$[Pd(NO_3)_2(C_2H_6OS)_2]$
$M_r = 386.68$
Monoclinic, $P2_1/n$
$a = 8.971$ (2) Å
$b = 14.195$ (3) Å
$c = 10.358$ (2) Å
$\beta = 112.24$ (3)°
$V = 1221.0$ (4) Å^3
$Z = 4$

$D_x = 2.104$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5671 reflections
$\theta = 4$–20°
$\mu = 1.89$ mm^{-1}
$T = 293$ (2) K
Prismatic, orange
0.14 × 0.08 × 0.07 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.737$, $T_{max} = 0.869$
10 268 measured reflections

3759 independent reflections
2898 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 31.8°$
$h = -7 \rightarrow 13$
$k = -20 \rightarrow 20$
$l = -15 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.072$
$S = 1.02$
3759 reflections
158 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.99$ e Å^{-3}

Compound (II)

Crystal data

$[Pd(NO_3)_2(C_4H_8OS)_2]$
$M_r = 438.75$
Monoclinic, $P2_1/c$
$a = 8.9697$ (18) Å
$b = 9.3263$ (19) Å
$c = 18.317$ (4) Å
$\beta = 97.56$ (3)°
$V = 1518.9$ (5) Å^3
$Z = 4$
$D_x = 1.919$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5939 reflections
$\theta = 3–30°$
$\mu = 1.53$ mm^{-1}
$T = 293$ (2) K
Triangular, orange
0.19 × 0.16 × 0.06 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.742$, $T_{max} = 0.912$
12 387 measured reflections
4651 independent reflections
3370 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 31.6°$
$h = -13 \rightarrow 7$
$k = -13 \rightarrow 13$
$l = -26 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.094$
$S = 1.01$
4651 reflections
190 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 0.7265P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.43$ e Å^{-3}
$\Delta\rho_{min} = -1.02$ e Å^{-3}

Table 1
Comparison of Pd—S and Pd—O distances (Å) in analogous dmso and thioxane (tx) complexes together with their ROP values.

Compound	Pd—S	ROP	Pd—O	ROP
cis-$[Pd(NO_3)_2(dmso)_2]^a$	2.2307 (11)	0.496	2.067 (2)	0.205
	2.2530 (8)	0.474	2.072 (2)	0.206
cis-$[Pd(NO_3)_2(dmso)_2]^b$	2.231 (3)		2.066	
	2.253 (3)		2.066	
cis-$[Pd(NO_3)_2(tx)_2]^a$	2.2595 (9)	0.469	2.053 (3)	0.214
	2.2627 (11)	0.465	2.076 (2)	0.202
$[Pd(dmso)_4)](BF_4)_2\cdot(CH_3)_2SO^c$	2.240 (4)		2.061 (9)	
	2.249 (4)		2.065 (10)	
$[Pd(tx)_4](BF_4)_2^d$	2.331 (2)			
	2.341 (2)			
$[Pd(tx)_4](BF_4)_2\cdot 4CH_3NO_2^d$	2.334 (1)			
	2.334 (1)			
$K_2[Pd(NO_3)_2]^e$			1.995 (3)	
			2.000 (2)	
			1.995 (2)	
			2.010 (2)	

References: (*a*) this study; (*b*) Langs *et al.* (1967); (*c*) Johnson *et al.* (1981); (*d*) Moullet *et al.* (1997); (*e*) Elding *et al.* (1986).

The thioxane compound has one residual density peak of 1.43 e Å^{-3} in the final difference Fourier map lying 0.80 Å from the Pd atom. No high residual density peaks were found in the final difference Fourier map for the dmso compound.

Table 2
Mean Pd—S distances (Å) in sulfoxide and analogous thioether compounds.

A full list of all the included compounds with their refcodes is available as supplementary material.

Compound type	*trans*-donor	*cis*-donor	Pd—S mean	Number of distances
Sulfoxides	Cl	Cl/S	2.236 (14)	8
Thioethers	Cl	Cl/S	2.273 (17)	14
Sulfoxides	Cl	Cl/N	2.207 (10)	2
Thioethers	Cl	Cl/N	2.245 (13)	3
Sulfoxides	Cl	Cl/P	2.228 (9)	2
Thioethers	Cl	Cl/P	2.275 (6)	4
Sulfoxides	S	Cl/Cl	2.296 (3)	4
Thioethers	S	Cl/Cl	2.321 (5)	12
Sulfoxides	any	any	2.24 (3)	27
Thioethers	any	any	2.29 (3)	33

For both compounds, data collection: *SMART* (Bruker, 1995); cell refinement: *SAINT* (Bruker, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXTL* (Sheldrick, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1000). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Boström, D., Strandberg, R., Norén, B. & Oskarsson, Å. (1991). *Acta Cryst.* C**47**, 2101–2104.
Brandenburg, K. (2000). *DIAMOND*. Crystal Impact, Bonn, Germany.
Bruker (1995). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bugarcic, Z., Lövqvist, K. & Oskarsson, Å. (1993). *Acta Chem. Scand.* **47**, 554–559.
Bugarcic, Z., Norén, B., Oskarsson, Å., Stålhandske, C. & Elding, L. I. (1991). *Acta Chem. Scand.* **45**, 361–366.
Elding, L. I., Norén, B. & Oskarsson, Å. (1986). *Inorg. Chim. Acta*, **114**, 71–74.
Elding, L. I. & Oskarsson, Å. (1987). *Inorg. Chim. Acta*, **130**, 209–213.
Johansson, M. H. & Oskarsson, Å. (2001). In preparation.
Johnson, B. F. G., Puga, J. & Raithby, P. R. (1981). *Acta Cryst.* B**37**, 953–956.
Kapoor, P., Lövqvist, K. & Oskarsson, Å. (1998). *J. Mol. Struct.* **470**, 39–47.
Langs, D. A., Hare, C. R. & Little, R. G. (1967). *Chem. Commun.* pp. 1080–1081.
Mealli, C. & Proserpio, D. M. (1990). *J. Chem. Educ.* **67**, 399–402.
Moullet, B., Zwahlen, C., Frey, U., Gervasio, G. & Merbach, A. E. (1997). *Inorg. Chim. Acta*, **261**, 67–75.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Sheldrick, G. M. (1998). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.