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Two isomers of $Pd_2(S_2NC_7H_4)_4$

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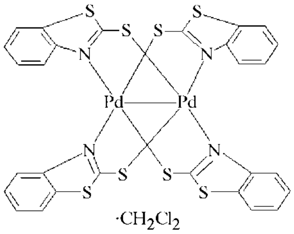
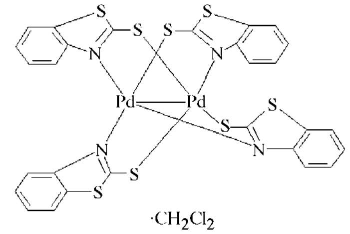
The dichloromethane solvates of the isomers tetrakis(μ-1,3-benzothiazole-2-thiolato)-κ^4N:S;κ^4S:N-dipalladium(II)-(*Pd*—*Pd*), (I), and tetrakis(μ-1,3-benzothiazole-2-thiolato)-κ^6N:S;κ^2S:N-dipalladium(II)(*Pd*—*Pd*), (II), both $[Pd_2(C_7H_4NS_2)_4]\cdot CH_2Cl_2$, have been synthesized in the presence of (*o*-isopropylphenyl)diphenylphosphane and (*o*-methylphenyl)-diphenylphosphane. Both isomers form a lantern-type structure, where isomer (I) displays a regular and symmetric coordination and isomer (II) an asymmetric and distorted structure. In (I), sitting on an centre of inversion, two 1,3-benzothiazole-2-thiolate units are bonded by a Pd—N bond to one Pd atom and by a Pd—S bond to the other Pd atom, and the other two benzothiazolethiolate units are bonded to the same Pd atoms by, respectively, a Pd—S and a Pd—N bond. In (II), three benzothiazolethiolate units are bonded by a Pd—N bond to one Pd atom and by a Pd—S bond to the other Pd atom, and the fourth benzothiazolethiolate unit is bonded to the same Pd atoms by, respectively, a Pd—S bond and a Pd—N bond.

Comment

The construction of supramolecular coordination complexes by self-assembly in the coordinative-bond approach is a well known method (Fujita, 1998; Holliday & Mirkin, 2001; Dinolfo & Hupp, 2001). The use of highly directional hydrogen bonds together with the coordinative bond approach as a device to control self-assembly in supramolecular systems has been recognized as a versatile tool in inorganic materials synthesis (Braga *et al.*, 1998; Burrows *et al.*, 1995).

The combination of an exocyclic thione group and a heterocyclic molecule, containing nitrogen, oxygen, sulfur or a combination of these, generates a group of compounds with considerable coordination potential. Molecules such as 2-mercaptopyridine, 2-mercaptobenzothiazole, 2-mercaptopyrimidine, 2-mercaptobenzimidazole and 2-mercaptothiazoline belong to this class of ligands and they have shown a rich coordination chemistry (Raper, 1985). The deprotonation of these molecules has resulted in an interesting chemical behaviour and a high versatility as ligands. Several coordination modes are possible for pyridine-2-thiolate (*S*-coordinated, *N*,*S*-chelated, *N*:*S*-bridging and *N*:*S*:*S*-triply bridging) and benzothiazole-2-thiolate (double and triply bridging) and related compounds (Lizarraga *et al.*, 1997). The square-planar platinum (Raper *et al.*, 1987; Umakoshi *et al.*, 1990) and palladium (Kubiak, 1985; Raper *et al.*, 1989) complexes of such compounds exhibit a variety of intermolecular interactions, such as metal–metal or ligand–ligand interactions, besides bidentate bonding.


$\cdot CH_2Cl_2$
(I)


$\cdot CH_2Cl_2$
(II)

We present here the structures of two isomers of the square-planar palladium complex tetrakis(1,3-benzothiazole-2-thiolato)palladium(II), which contain the 2-mercaptobenzothiazole unit bonded in two different modes. Both complexes were obtained during unsuccessful attempts to prepare a palladium complex with a mixture of phosphane and 2-mercaptobenzothiazole ligands by the reaction of $PdCl_2$(cod) (cod is cyclooctadiene) with 2-mercaptobenzothiazole in the presence of an (*o*-alkylphenyl)diphenylphosphane. It is possible that the formed Pd–phosphane complex catalyses the formation of either complex (I) or (II), but it is impossible to rule out the possibility of a mixture of isomers being formed. However, only one isomer could be crystallized from each reaction mixture.

The dinuclear complex (I) (Fig. 1) has been described previously (Kubiak, 1985). An equivalent Pd–dimethyl-

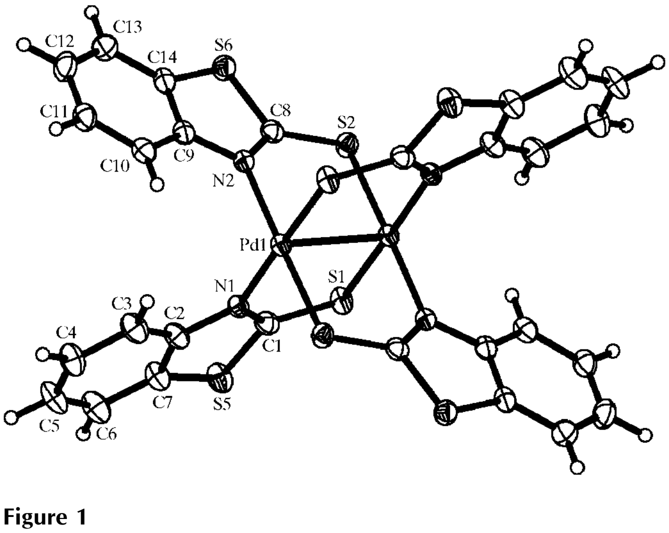


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Only the asymmetric unit has been labelled. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary radii. The solvent molecule is not shown.

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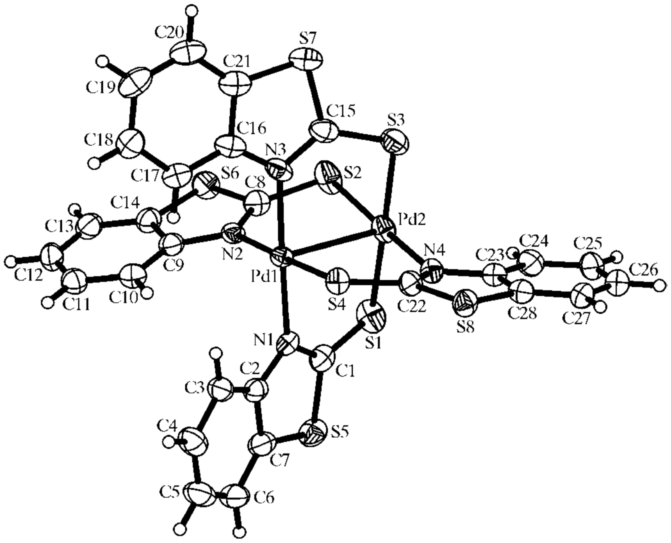

Figure 2
The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres with arbitrary radii. The solvent molecule is not shown.

formamide solvate complex with an NH_2-substituted mercaptobenzothiazole unit has also been reported (Tzeng *et al.*, 2004). However, the compound presented here is a CH_2Cl_2 solvate. Despite the differences in solvent structure, there are no major differences between the structures of the earlier reported dinuclear Pd complexes and (I). A corresponding Pt complex, crystallized as a dimethylformamide solvate, has also been reported (Raper *et al.*, 1987). Again, the structure of the Pt complex is practically identical to that of (I). Complex (I) exhibits an *N,S*-bidentate bonding of the four 2-mercaptobenzothiazole units, with two Pd—N and two Pd—S bonds formed with each Pd atom (Table 1), leading to a symmetric and regular lantern-type structure. Complex (II) (Fig. 2) exhibits an asymmetric and distorted lantern stucture, with three Pd—N and one Pd—S bonds formed with one Pd atom, and three Pd—S and one Pd—N bonds with the other Pd atom (Table 2). In (II), the three 2-mercaptobenzothiazole units with a similar bonding mode point in the same direction in relation to the Pd—Pd axis, leaving the fourth 2-mercaptobenzothiazole unit alone on the other side of the axis. The lantern structure is highly distorted owing to steric stress between the three units on the same side of the Pd—Pd axis. Complex (II) is previously unknown in the literature.

In summary, we have shown that two structurally different isomers of tetrakis(1,3-benzothiazole-2-thiolato)palladium(II) can be formed in the reaction between $PdCl_2$(cod) and 2-mercaptobenzothiazole in the presence of an (*o*-alkylphenyl)diphenylphosphane depending on the bonding mode of the 2-mercaptobenzothiazole and the alkyl group of the phosphane.

Experimental

For the preparation of (I), 2-mercaptobenzothiazole (0.096 g, 0.58 mmol) and (*o*-methylphenyl)diphenylphosphane (0.105 g, 0.14 mmol) were added to a solution of $PdCl_2$(cod) (0.110 g, 0.39 mmol) in dry diethyl ether (30 ml) and the mixture was left to react for 24 h. The solution was filtered, and the solid material washed three times with diethyl ether (20 ml) and once with dichloromethane (10 ml). The orange solid (yield 0.049 g, 86.3%) was dried *in vacuo*. Analysis calculated for $C_{28}H_{16}N_4Pd_2S_8$: C 38.31, H 1.84, N 6.38%; found: C 37.88, H 1.69, N 6.02%. Mass spectrum (ESI+) [*m*/*z*, (%)]: 878 (9%) [M^+]. Orange block-shaped crystals were grown by slow evaporation of a dichloromethane–hexane solvent mixture at room temperature.

Complex (II) was prepared by the reaction of 2-mercaptobenzothiazole (0.093 g, 0.58 mmol), (*o*-isopropylphenyl)diphenylphosphane (0.098 g, 0.12 mmol) and $PdCl_2$(cod) (0.111 g, 0.39 mmol) in dry diethyl ether (30 ml) (orange solid; yield 0.036 g, 63.4%). Analysis calculated for $C_{28}H_{16}N_4Pd_2S_8$: C 38.31, H 1.84, N 6.38%; found: C 37.83, H 1.70, N 6.11%. Mass spectrum (ESI+) [*m*/*z*, (%)]: 878 (8%) [M^+]. Orange block-shaped crystals were grown following the same procedure as for complex (I).

Compound (I)

Crystal data

$[Pd_2(C_7H_4NS_2)_4]\cdot CH_2Cl_2$
$M_r = 962.65$
Triclinic, $P\overline{1}$
$a = 7.4255\ (4)$ Å
$b = 10.1954\ (9)$ Å
$c = 11.1581\ (9)$ Å
$\alpha = 77.129\ (3)°$
$\beta = 86.933\ (5)°$
$\gamma = 72.384\ (5)°$
$V = 784.80\ (10)$ Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 1.88$ mm^{-1}
$T = 100\ (2)$ K
$0.38 \times 0.12 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{min} = 0.534$, $T_{max} = 0.929$
3137 measured reflections
3137 independent reflections
2736 reflections with $I > 2\sigma(I)$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.077$
$S = 1.07$
3137 reflections
191 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 1.05$ e Å^{-3}
$\Delta\rho_{min} = -0.82$ e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

Pd1—N2	2.087 (3)	S5—C1	1.753 (3)
Pd1—N1	2.097 (3)	S6—C14	1.737 (4)
Pd1—S1^i	2.2876 (9)	S6—C8	1.749 (4)
Pd1—S2^i	2.2904 (9)	N1—C1	1.314 (5)
Pd1—Pd1^i	2.7560 (5)	N1—C2	1.391 (4)
S1—C1	1.718 (4)	N2—C8	1.323 (5)
S2—C8	1.717 (4)	N2—C9	1.392 (4)
S5—C7	1.732 (4)	C1—N1	1.314 (5)

Symmetry code: (i) $-x+1, -y+1, -z$.

Compound (II)

Crystal data

$[Pd_2(C_7H_4NS_2)_4]\cdot CH_2Cl_2$
$M_r = 926.65$
Orthorhombic, *Pbca*
$a = 17.2484\ (2)$ Å
$b = 18.0383\ (3)$ Å
$c = 18.7816\ (3)$ Å
$V = 5843.55\ (15)$ Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 1.83$ mm^{-1}
$T = 100\ (2)$ K
$0.23 \times 0.13 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer	53120 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)	5722 independent reflections
$T_{\min} = 0.682$, $T_{\max} = 0.838$	4870 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.054$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	379 parameters
$wR(F^2) = 0.095$	H-atom parameters constrained
$S = 1.11$	$\Delta\rho_{\max} = 1.51$ e Å^{-3}
5722 reflections	$\Delta\rho_{\min} = -1.43$ e Å^{-3}

Table 2
Selected bond lengths (Å) for (II).

Pd1—N3	2.052 (4)	S3—C15	1.715 (6)
Pd1—N1	2.054 (4)	S4—C22	1.724 (5)
Pd1—N2	2.112 (4)	S5—C7	1.749 (6)
Pd1—S4	2.3080 (11)	S5—C1	1.751 (5)
Pd1—Pd2	2.7302 (5)	S6—C14	1.736 (5)
Pd2—N4	2.064 (4)	S6—C8	1.746 (5)
Pd2—S2	2.2927 (13)	S7—C15	1.734 (5)
Pd2—S3	2.3121 (14)	S7—C21	1.747 (6)
Pd2—S1	2.3255 (14)	S8—C28	1.751 (5)
S1—C1	1.703 (5)	S8—C22	1.758 (5)
S2—C8	1.718 (5)		

In (I), the asymmetric unit contains half a molecule, the Pd atoms being located around an inversion centre. The final structural models for both compounds were refined without the heavily disordered CH_2Cl_2 solvent molecules. The contribution of the disordered solvent to the calculated structure factors was taken into account with the BYPASS algorithm (van der Sluis & Spek, 1990), implemented as the SQUEEZE option in *PLATON* (Spek, 2003). H atoms were positioned geometrically and allowed to ride on their parent atoms [C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$(parent atom)]. For (I), the highest peak is located 0.06 Å from atom Cl9*A* and the deepest hole 0.66 Å from atom Cl9*A*. For (II), the highest peak is located 0.88 Å from atom Pd2 and the deepest hole 0.70 Å from atom Pd2.

For both compounds, data collection: *COLLECT* (Bruker–Nonius, 2004); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003) for (I) and *SHELXS97* (Sheldrick, 1997) for (II); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR3019). Services for accessing these data are described at the back of the journal.

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