

trans-Bis(3,5-diaza-1-azonia-7-phosphaadamantane- κ P)bis(thiocyanato- κ S)palladium(II) bis(thiocyanate)

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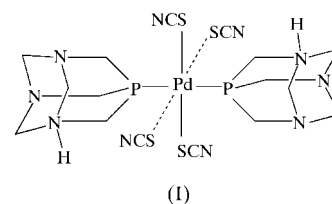
The crystal structure of the title compound, *trans*-[Pd(NCS)₂(C₆H₁₃N₃P)₂](NCS)₂, is one of the few palladium(II) complexes containing two protonated water-soluble 1,3,5-triaza-7-phosphaadamantane (PTA) ligands reported to date. The compound displays a distorted square-planar geometry, with the Pd atom on an inversion centre and with the S atoms of the thiocyanate counter-ions occupying the axial positions above and below the equatorial plane described by the phosphine and thiocyanate ligands. Geometric parameters for the formal coordination polyhedron include a Pd–P distance of 2.2940 (8) Å, a Pd–S distance of 2.3509 (8) Å and a P–Pd–S angle of 89.45 (3)°. The effective cone angle for the PTA ligands was calculated as 114.5°.

Comment

In the past few years, numerous 1,3,5-triaza-7-phosphaadamantane (PTA) complexes exhibiting catalytic activity have been reported (Alyea *et al.*, 1993; Joó *et al.*, 1996; Darensbourg *et al.*, 1997, 1999). PTA is a neutral air-stable aliphatic phosphine with a small steric demand (Daigle *et al.*, 1998; Otto & Roodt, 2001*a*). The potentially tetradentate PTA ligand coordinates to the metal centre only through the P atom, as observed in all of the metal–PTA complexes characterized to date (Cambridge Structural Database; Allen, 2002).

In this paper, we report the structure of the title compound, (I), as part of our systematic investigation of the basic coordination mode and solution properties of these complexes. The title compound is the first example of a square-planar complex that has a *trans* geometry and that contains protonated PTA ligands. Both PTA ligands are protonated at one of the N atoms, resulting in a dicationic complex, and therefore two thiocyanate counter-ions cocrystallize with the coordina-

tion compound to ensure neutrality. The compound crystallizes as discrete distorted square-planar moieties, and the S atoms of the thiocyanate counter-ions in the apical positions above and below the equatorial plane are involved in weak interactions (see Fig. 1). This conformation results in infinite chains of alternating cations and NCS[−] counter-ions, and (I) is the first example of a compound in which such an interaction involves a Pd²⁺ metal centre and an NCS[−] ion (Allen, 2002).



The Pd atom is situated on an inversion center in the monoclinic space group $P2_1/n$, thus imposing planarity of the equatorial ligands with symmetry-equivalent ligands in a relative *trans* orientation. The angles in the coordination polyhedron are close to the ideal value of 90°, the P–Pd–S10 angle being 89.45 (3)° (Table 1). The Pd–S10 and Pd–P bond lengths in the coordination polyhedron are 2.3509 (8) and 2.2940 (8) Å, respectively. Both of the NCS[−] ligands, as well as the NCS[−] counter-ions, interact with the Pd metal centre *via* the S atoms in a manner indicative of a soft metal centre. The Pd···S11 interaction at the apical positions of the square plane, occupied by the NCS[−] counter-ions, is 3.4383 (9) Å and is thus significantly longer than the formal Pd–S10 bond. The Pd–S10–C10 angle [102.71 (10)°] is characteristic of a thiocyanate ligand coordinated *via* the S atom. Similarly, although the interaction is weak, the Pd–SCN moiety in the apical position exhibits a bent orientation, with a Pd–S11–C11 angle of 95.56 (9)°.

The C10–N10 and C11–N11 bond lengths [1.155 (3) and 1.158 (3) Å, respectively] are the same within experimental

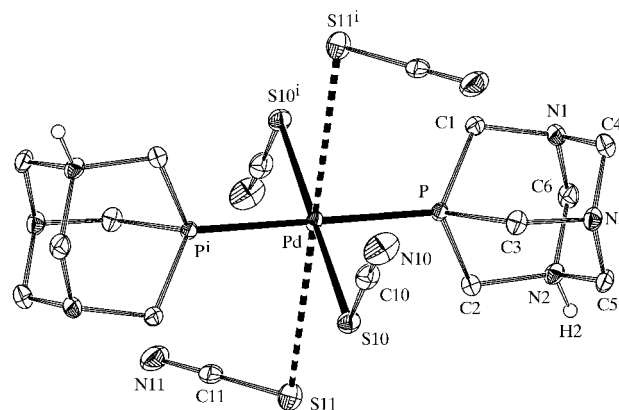


Figure 1

The structure and atom-numbering scheme of a molecule of (I), with displacement ellipsoids shown at the 30% probability level. Only the H atoms on the protonated N atoms of the PTA ligands are included, and these H atoms are represented by spheres of arbitrary size. [Symmetry code: (i) $-x, -y, 1 - z$.]

error. However, the S10—C10 bond is 1.677 (3) Å, whereas the S11—C11 bond in the NCS[−] counter-ion is significantly shorter [1.628 (3) Å]. These last two bond lengths are indicative of the resonance structure of the thiocyanate group, implying more of a double-bond character for the S11—C11 moiety. Since Pd—S10 is a formal bond, the S atom donates electron density to the metal centre, thus resulting in the S10—C10 bond having more of a single-bond character and hence being a weaker bond. The S10—C10—N10 angle is 176.8 (3)°, while the S11—C11—N11 moiety is virtually linear [179.6 (3)°].

The P—C1, P—C2 and P—C3 bond distances do not differ significantly [1.837 (2), 1.834 (2) and 1.839 (2) Å, respectively], whereas the N1—C1, N2—C2 and N3—C3 bond distances show deviations; the longer N2—C2 bond [1.498 (3) Å versus 1.467 (3) and 1.470 (3) Å for N3—C3 and N1—C1] is observed because atom N2 is protonated. This protonated N2—H2 moiety in turn participates in a fairly strong intermolecular interaction with atom N11 of an adjacent NCS[−] counter-ion [N2—H2 = 0.87 (2) Å, H2⋯N11* = 1.86 (2) Å, N2⋯N11* = 2.724 (3) Å and N2—H2⋯N11* = 175 (2)°; symmetry code: (*) $\frac{1}{2} + x, -\frac{1}{2} - y, -\frac{1}{2} + z$] (see also Fig. 2).

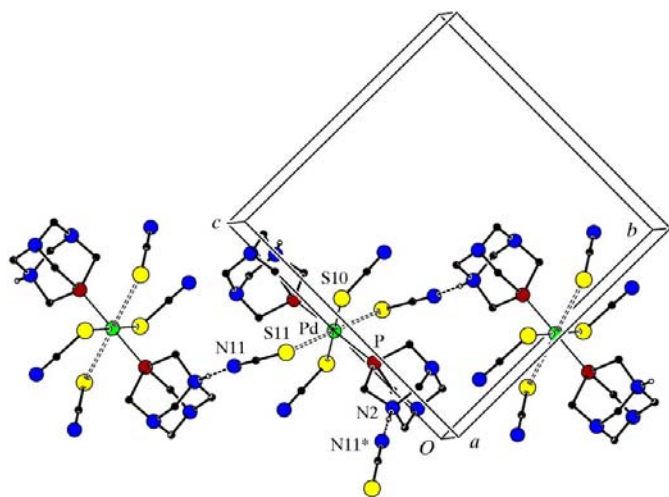


Figure 2

A section of the unit cell of (I), showing the packing and the H2⋯N11* and S11⋯Pd interactions. [Symmetry code: (*) $\frac{1}{2} + x, -\frac{1}{2} - y, -\frac{1}{2} + z$.]

The effective cone angle (θ_E) for the PTA ligand in (I) was calculated as 114.5° using the real Pd—P distance (Otto *et al.*, 2000). The Tolman cone angle (θ_T) was calculated as 114.8°, using a Pd—P distance of 2.28 Å, according to the original definition (Tolman, 1977). This value is comparable to the values of θ_E and θ_T calculated for PTA in *trans*-[PdBr₂(PTA)₂] (114.0 and 115.1°; Meij *et al.*, 2002), [PtI₂(PTA)₃] (118.3 and 119.2°; Otto & Roodt, 2001a) and *trans*-[PtI₂(PTA)₂] (117.3 and 118.2°; Otto & Roodt, 2001b), thus confirming the rigid character of the ligand.

Experimental

To an aqueous solution of *cis*-[PdCl₂(PTA)₂] (2.5 mg, 0.005 mmol) at pH 3.0–3.5 (HClO₄) was added an excess (> 10 times) of KSCN (100 mg, 1.03 mmol). Evaporation of the solution at ambient temperature gave red crystals suitable for X-ray analysis. IR (KBr): $\nu(\text{SCN})$ 2044 cm^{−1}.

Crystal data

[Pd(NCS)₂(C₆H₁₃N₃P)₂](NCS)₂
M_r = 655.05
 Monoclinic, *P*2₁/*n*
a = 7.5170 (15) Å
b = 12.733 (3) Å
c = 12.956 (3) Å
 β = 94.96 (3)°
V = 1235.4 (4) Å³
Z = 2
D_x = 1.761 Mg m^{−3}
D_m = 1.746 Mg m^{−3}

D_m, measured by flotation in
 CH₂I₂/C₆H₆
 Mo *K*α radiation
 Cell parameters from 2294
 reflections
 θ = 2.3–27.5°
 μ = 1.25 mm^{−1}
T = 293 (2) K
 Rectangular, red
 0.30 × 0.22 × 0.16 mm

Data collection

Nonius KappaCCD diffractometer
 ω and ϕ scans
 Absorption correction: empirical
 (SADABS; Sheldrick, 1996)
 T_{min} = 0.706, T_{max} = 0.825
 6468 measured reflections
 2766 independent reflections

2179 reflections with *I* > 2σ(*I*)
 R_{int} = 0.028
 θ_{max} = 27.5°
 h = −9 → 9
 k = −15 → 16
 l = −16 → 16

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)]$ = 0.029
 $wR(F^2)$ = 0.057
 S = 1.01
 2766 reflections
 155 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.007P)^2 + 0.768P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.58 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.41 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0021 (3)

Table 1

Selected geometric parameters (Å, °).

Pd—P	2.2940 (8)	N2—C6	1.525 (3)
Pd—S10	2.3509 (8)	N1—C1	1.470 (3)
Pd—S11	3.4383 (9)	N1—C4	1.462 (3)
P—C1	1.837 (2)	N1—C6	1.432 (3)
P—C2	1.834 (2)	N3—C3	1.467 (3)
P—C3	1.839 (2)	N3—C4	1.470 (3)
S10—C10	1.677 (3)	N3—C5	1.433 (3)
S11—C11	1.628 (3)	C11—N11	1.158 (3)
N2—C2	1.498 (3)	N10—C10	1.155 (3)
N2—C5	1.520 (3)		
P—Pd—S10	89.45 (3)	S10—C10—N10	176.8 (3)
Pd—S10—C10	102.71 (10)	S11—C11—N11	179.6 (3)
Pd—S11—C11	95.56 (9)		

Methylene H atoms were placed in idealized positions (C—H = 0.97–0.98 Å) and constrained to ride on their parent atoms, with *U*_{iso}(H) values of 1.2*U*_{eq}(C). The position of the H atom on atom N2 was determined from a Fourier difference map and the coordinates were refined with an isotropic displacement parameter constrained to 1.2*U*_{eq}(N).

Data collection: COLLECT (Nonius, 1998); cell refinement: COLLECT; data reduction: COLLECT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1019). Services for accessing these data are described at the back of the journal.

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