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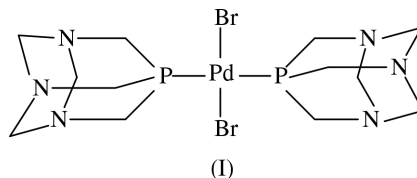
Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{N}-\text{C}) = 0.006 \text{ \AA}$
R factor = 0.039
wR factor = 0.084
Data-to-parameter ratio = 23.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.*trans*-Dibromobis(1,3,5-triaza-7-phosphaadamantane- κP)palladium(II)

The title compound, $[\text{PdBr}_2(\text{C}_6\text{H}_{12}\text{N}_3)_2]$ or $[\text{PdBr}_2(\text{PTA})_2]$ (where PTA is 1,3,5-triaza-7-phosphaadamantane), was found to be isostructural with the previously reported *trans*- $[\text{PtI}_2(\text{PTA})_2]$. The Pd atom lies on an inversion centre, resulting in a *trans*-square-planar geometry. Selected geometrical parameters are Pd1–P1 and Pd1–Br1 distances of 2.320 (1) and 2.427 (1) Å, respectively, and a P–Pd–Br angle of 90.6 (3)°. The effective cone angle for the PTA ligands was calculated as 114.0°.

Comment

The 1,3,5-triaza-7-phosphaadamantane ligand (PTA) has attracted much attention due to its unique characteristics. It is a neutral, air-stable, aliphatic phosphine with a small steric demand (Diagle *et al.*, 1998; Otto & Roodt, 2001*a*). The PTA ligand is highly versatile, since it enables the synthesis of water-soluble complexes without the additional complication of introducing a charged species to the complex. The palladium(II) and platinum(II) bis-PTA complexes are only soluble to a limited extent in water and almost insoluble in methanol, while complexes containing three or more PTA ligands are fairly soluble in both water and methanol.



In this paper, we report the crystal structure of *trans*-dibromobis(1,3,5-triaza-7-phosphaadamantane)palladium(II), (I), as part of our systematic investigation of the basic coordination mode and solution properties of these complexes. The complex was isolated as an unexpected product from the reaction of $[\text{PdCl}(\text{PTA})_3]\text{Cl}$ with LiBr in aqueous medium. The isolation of this complex underlines the lability of one of the PTA ligands in the $[\text{PdCl}(\text{PTA})_3]\text{Cl}$ complex, compared with the analogous platinum chemistry, where a five-coordinate complex, $[\text{PtI}_2(\text{PTA})_3]$, was isolated from the reaction with NaI in aqueous methanol solution (Otto & Roodt, 2001*a*).

The only two palladium(II) bis-PTA structures that have been reported to date in the Cambridge Structural Database (Version 5.22 of October 2001; Cambridge Structural Database, 2001; Allen & Kennard, 1993) are two polymorphs of *cis*- $[\text{PdCl}_2(\text{PTA})_2]$ (Darensbourg *et al.*, 1997; Alyea *et al.*, 1998). The title compound, however, is the first example of a palladium complex with a *trans* geometry (see Fig. 1). The title compound was, furthermore, found to be isostructural with a

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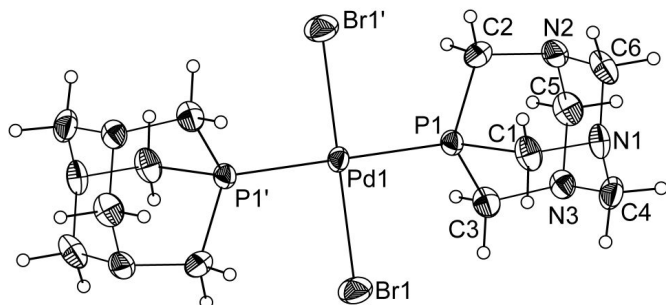


Figure 1
The structure of the title compound, showing the atom-numbering scheme and 30% probability displacement ellipsoids.

previously reported *trans*-[Pt₂(PTA)₂] complex (Otto & Roodt, 2001*b*). The compound crystallizes with the Pd atom on an inversion centre, with the pairs of phosphine and bromide ligands each arranged *trans*. All the angles in the coordination polyhedron are very close to the ideal value of 90° (see Table 1). The P–Pd–Pⁱ and Br–Pd–Brⁱ angles are 180°, as required by the symmetry. The average C–P–Pd and C–P–C angles of 119.1 and 98.3°, respectively, are indicative of the small steric demand of the PTA ligand. As confirmation, the effective (θ_E ; Otto, 2001) and Tolman cone angles (θ_T ; Tolman, 1977) for the PTA ligand were determined as 114.0 and 115.1°, respectively, using the actual Pd–P bond length and a distance of 2.28 Å according to definition. These values are in excellent agreement with the θ_E and θ_T values of 118.3 and 119.2° for [Pt₂(PTA)₃] (Otto & Roodt, 2001*a*) and 117.3 and 118.2° for *trans*-[Pt₂(PTA)₂] (Otto & Roodt, 2001*b*), confirming the rigid cage-like character of the PTA ligand.

In Table 2, the title compound is compared with other closely related Pd^{II} complexes from the literature containing two bromo and two tertiary phosphine ligands in a *trans* geometry. The title compound, having a Pd–Br bond length of 2.427 (1) Å and a Pd–P bond length of 2.320 (1) Å, fits well into the typical range for complexes of this kind.

Experimental

Chlorotrakis(1,3,5-triaza-7-phosphaadamantane)palladium(II)chloride, [PdCl(PTA)₃]Cl, was prepared according to a literature procedure (Darensbourg *et al.*, 1997). LiBr (300 mg, 3.45 mmol) was added to an aqueous solution (10 ml) of [PdCl(PTA)₃]Cl (7.4 mg, 0.011 mmol). Slow evaporation of the solvent gave yellow crystals of *trans*-[PdBr₂(PTA)₂] suitable for X-ray analysis.

Crystal data

[PdBr₂(C₆H₁₂N₃)₂]
 $M_r = 580.53$
 Monoclinic, $P2_1/n$
 $a = 7.276$ (2) Å
 $b = 11.808$ (2) Å
 $c = 10.317$ (2) Å
 $\beta = 94.99$ (3)°
 $V = 883.0$ (3) Å³
 $Z = 2$
 $D_x = 2.184$ Mg m⁻³
 $D_m = 2.177$ Mg m⁻³

D_m measured by flotation in CH₂I₂/
 C₆H₆
 Mo $K\alpha$ radiation
 Cell parameters from 2112
 reflections
 $\theta = 2.6$ – 27.9 °
 $\mu = 5.77$ mm⁻¹
 $T = 293$ (2) K
 Rectangle, yellow
 $0.18 \times 0.09 \times 0.06$ mm

Data collection

Siemens SMART CCD
 diffractometer
 ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.446$, $T_{\max} = 0.609$
 8979 measured reflections

2475 independent reflections
 1629 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.075$
 $\theta_{\max} = 29.6$ °
 $h = -10 \rightarrow 9$
 $k = -16 \rightarrow 16$
 $l = -12 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.084$
 $S = 0.94$
 2475 reflections
 107 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.038P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.60$ e Å⁻³
 $\Delta\rho_{\min} = -1.34$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Pd1–P1	2.312 (1)	P1–C1	1.838 (5)
Pd1–Br1	2.427 (1)	P1–C3	1.847 (4)
P1–C2	1.836 (4)		
P1–Pd1–P1 ⁱ	180	C1–P1–C3	98.1 (2)
P1–Pd1–Br1	90.55 (3)	C2–P1–Pd1	121.1 (1)
P1 ⁱ –Pd1–Br1	89.45 (3)	C1–P1–Pd1	113.8 (1)
C2–P1–C1	98.5 (2)	C3–P1–Pd1	122.4 (1)
C2–P1–C3	98.2 (2)		

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

Table 2

Comparative geometrical parameters (Å) for selected *trans*-[PdBr₂(L)₂] (L = tertiary phosphine ligand) complexes.

L	Pd–P	Pd–Br
PTA ^a	2.320 (1)	2.427 (1)
PPh ₂ (<i>o</i> -Cl-Ph) ^b	2.350 (2)	2.423 (1)
DDEP ^c	2.325 (3)	2.412 (1)
DPA ^d	2.322 (2)	2.447 (1)
ppq ^e	2.318 (1)	2.435 (1)
DMPP ^f	2.319 (2)	2.433 (1)
	2.313 (2)	2.435 (1)
PPh ₃ ^g	2.34 (4)	2.42 (4)
P(<i>o</i> -Tol) ₃ ^h	2.370 (1)	2.445 (2)

Notes: (a) this work; (b) Coalter *et al.* (2000); (c) Ganguly *et al.* (1992) [DDEP is 2-(diphenylphosphino)ethanephosphonate]; (d) Podlahova *et al.* (1979) (DPA is diphenylphosphinoacetic acid); (e) Sembiring *et al.* (1995) (ppq is *p*-quinonyldiphenylphosphine); (f) Wilson *et al.* (1996) (DMPP is 1-phenyl-3,4-dimethylphosphole); (g) Stark & Whitmore (1997); (h) Vicente *et al.* (1997).

H atoms were refined with a constrained C–H distance of 0.97 Å. The minimum residual electron density is located within 1.0 Å of the Pd atom.

Data collection: SMART (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT; 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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