

trans-Diiodobis(1,3,5-triaza-7-phosphaadamantane)platinum(II)

Stefanus Otto and Andreas Roodt*

Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa

Correspondence e-mail: roodta@sci.uovs.ac.za

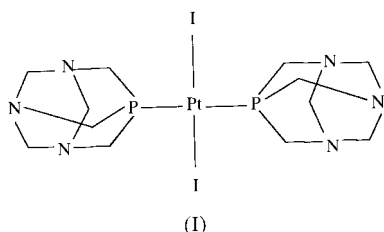
Received 23 October 2000

Accepted 12 February 2001

The crystal structure of the title compound, *trans*-[PtI₂(C₆H₁₂N₃P)₂], describes one of the few platinum(II) complexes containing two of the water-soluble 1,3,5-triaza-7-phosphaadamantane ligands reported to date. The complex crystallizes on an inversion centre with the most important bond lengths and angles being Pt—P 2.3128 (12) Å, Pt—I 2.6022 (6) Å, P—Pt—I 90.94 (3)° and P'—Pt—I 89.06 (3)°.

Comment

The air-stable water-soluble 1,3,5-triaza-7-phosphaadamantane ligand, PTA, is highly versatile as it enables the synthesis of water-soluble complexes without the additional complication of introducing a charged species to the complex. Numerous PTA complexes exhibiting catalytic activity have been reported in the last few years underlining the worldwide interest in its unique characteristics (Darensbourg *et al.*, 1994, 1995; Joó *et al.*, 1996). While platinum(II) and palladium(II) complexes containing three or more PTA ligands are fairly soluble in water and even methanol, the bis-PTA complexes are only soluble to a limited extent in water and almost insoluble in methanol. No mono-PTA complexes of platinum(II) and palladium(II) have been reported to date.



In this paper, we report the structure of *trans*-diiodobis(PTA)platinum(II), (I), as part of our systematic investigation of the basic coordination mode and solution properties of these complexes. Only a few platinum(II) bis-PTA structures have been reported to date (Assefa *et al.*, 1995; Darensbourg *et al.*, 1997; Otto *et al.*, 1998) and the title compound describes only the second example of such a complex with a *trans* geometry.

The compound (Fig. 1) crystallizes on an inversion centre as well defined square-planar moieties with the phosphine ligands in a *trans* orientation. All angles in the coordination polyhedron are very close to the ideal value of 90°, with P—Pt—I = 90.94 (3)° and Pⁱ—Pt—I = 89.06 (3)°. The P—Pt—Pⁱ and I—Pt—Iⁱ angles are 180° on account of the symmetry [symmetry code: (i) $-x, -y, -z$].

All bond distances and angles are within normal ranges and are very similar to those in analogous diiodobisphosphine complexes listed in Table 1. The Pt—I bond distance does not seem to be very sensitive to the phosphine ligand employed in the different structures, with the distances ranging between 2.599 (2) and 2.626 (2) Å. Both the Pt—P and Pt—I bond distances of 2.3128 (12) and 2.6022 (6) Å are virtually identical to those found in the analogous PMe₃ complex of 2.315 (4) and 2.599 (2), respectively, indicative of the similar characteristics of these two ligand systems. The Pt—P bond distances are comparable with the distance of 2.318 (2) Å found for the corresponding PPh₃ complex, while they are shorter than those found for the bulkier PCy₃ and P(*o*-Tol)₃ complexes (Cy is cyclohexyl and *o*-Tol is *o*-tolyl). The Pt—P bond distances of the title compound are very similar to those found in other Pt complexes containing two PTA ligands in a *trans* orientation and even the values of 2.323 (2) and 2.3174 (11) Å found in the [PtCl(PTA)₃]Cl and [PtI₂(PTA)₃] complexes containing three PTA ligands.

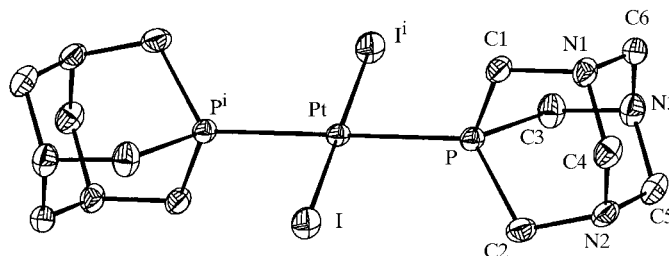


Figure 1

The structure of (I) showing the numbering scheme and displacement ellipsoids (30% probability). H atoms have been omitted for clarity. [Symmetry code: (i) $-x, -y, -z$.]

The average C—P—Pt and C—P—C angles of 119.21 (16) and 98.1 (2)°, respectively, are indicative of the small steric demand of the PTA ligand. In addition to this, the effective and Tolman cone angles for the PTA ligand in the title compound were determined as 117.3 and 118.2°, respectively, using the actual Pt—P bond distance of 2.3128 (11) Å and a distance of 2.28 Å according to the definition (Tolman, 1977; Otto *et al.*, 2000). These values are in excellent agreement with the values of 118.3 and 119.5° reported recently (Otto & Roodt, 2001), confirming the rigid character of the ligand.

Experimental

cis-[PtCl₂(PTA)₂] (7 mg, 0.0121 mmol) was dissolved in water (5 ml) and an aqueous solution (1 ml) of NaI (7 mg, 0.0467 mmol) was added. Slow evaporation of the solvent yielded bright yellow crystals suitable for X-ray analysis in a near quantitative yield.

Crystal data

[PtI₂(C₆H₁₂N₃P)₂]
M_r = 763.20
 Monoclinic, *P*2₁/*n*
a = 7.472 (2) Å
b = 12.141 (4) Å
c = 10.537 (3) Å
 β = 95.348 (5)°
V = 951.7 (5) Å³
Z = 2

D_x = 2.663 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 6552 reflections
 θ = 2.6–28.3°
 μ = 10.79 mm⁻¹
T = 293 (2) K
 Rectangle, yellow
 0.26 × 0.22 × 0.12 mm

Data collection

Bruker SMART CCD diffractometer
 ω scans
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.083, *T_{max}* = 0.285
 6552 measured reflections
 2345 independent reflections

1944 reflections with *I* > 2σ(*I*)
R_{int} = 0.024
 θ_{\max} = 28.3°
h = -9 → 5
k = -12 → 16
l = -14 → 12
 First 50 frames repeated after data collection

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.022
wR(*F*²) = 0.050
S = 0.98
 2345 reflections
 108 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0254P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.73 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.59 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0063 (2)

Table 1

Comparative X-ray data for *trans*-[Pt(*X*)₂(*L*)₂] and [Pt(*X*)(PTA)₃]*X* complexes.

Complex	Pt–P ⁱ (Å)	Pt– <i>X</i> (Å)
[PtI ₂ (PPh ₃) ₂] ^a	2.318 (2)	2.603 (1)
[PtI ₂ {P(C ₆ F ₅) ₃] ₂] ^b	2.292 (6)	2.626 (2)
[PtI ₂ {P(<i>o</i> -Tol) ₃] ₂] ^c	2.348 (2)	2.622 (1)
[PtI ₂ (PCy ₃) ₂] ^d	2.371 (2)	2.612 (1)
[PtI ₂ (PMe ₃) ₂] ^e	2.315 (4)	2.599 (2)
[PtI ₂ (PTA) ₂] ^f	2.3128 (12)	2.6022 (6)
[Pt(CN) ₂ (PTA) ₂] ^g	2.305 (2)	1.975 (9)
[PtCl(PTA) ₃] ^h	2.323 (2)	2.371 (2)
[PtI ₂ (PTA) ₃] ⁱ	2.3174 (11)	2.7192 (3)
		3.2369 (3)

Notes: (a) Boag *et al.* (1991); (b) Hunter *et al.* (1986); (c) P(*o*-Tol)₃ = P(*o*-CH₃-Ph)₃ (Alyea *et al.*, 1979); (d) Alcock & Leviston (1971); (e) Hitchcock *et al.* (1977); (f) this work; (g) Assefa *et al.* (1995); (h) Muir *et al.* (1993); (i) five-coordinate complex (Otto & Roodt, 2001); (j) average of *trans*-P–Pt–P bonds.

H atoms were introduced at calculated positions and refined using standard *SHELXL97* (Sheldrick, 1997) constraints. The maximum and minimum residual electron densities are located within 1 Å of the Pt atom.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve

Table 2

Selected geometric parameters (Å, °).

Pt–P	2.3128 (12)	P–C1	1.841 (4)
Pt–I	2.6022 (6)	P–C2	1.845 (4)
P–C3	1.835 (5)		
P ⁱ –Pt–I	89.06 (3)	C2–P–C3	97.9 (2)
P–Pt–I	90.94 (3)	C1–P–Pt	113.57 (13)
C1–P–C2	98.2 (2)	C2–P–Pt	122.61 (16)
C1–P–C3	98.2 (2)	C3–P–Pt	121.44 (14)

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

structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1997); software used to prepare material for publication: *SHELXL97*.

Financial assistance from the South African NRF and the Research Fund of the University of the Free State is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1430). Services for accessing these data are described at the back of the journal.

References

- Alcock, N. W. & Leviston, P. G. (1971). *J. Chem. Soc. Dalton Trans.* pp. 1834–1836.
- Alyea, E. C., Dias, S. A., Ferguson, G. & Roberts, P. J. (1979). *J. Chem. Soc. Dalton Trans.* pp. 948–951.
- Assefa, Z., McBurnett, B. G., Staples, R. J. & Fackler, J. P. Jr (1995). *Acta Cryst. C51*, 1742–1743.
- Boag, N. M., Mohan Rao, K. & Terrill, N. J. (1991). *Acta Cryst. C47*, 1064–1065.
- Brandenburg, K. (1997). *DIAMOND*. University of Bonn, Germany.
- Bruker (1997). *SMART* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Darensbourg, D. J., Decuir, T. J., Stafford, N. W., Robertson, J. B., Draper, J. D., Reibenspies, J. H., Katló, A. & Joó, F. (1997). *Inorg. Chem.* **36**, 4218–4226.
- Darensbourg, D. J., Joó, F., Kannisto, M., Kathó, A., Reibenspies, J. H. & Daigle, D. J. (1994). *Inorg. Chem.* **33**, 200–208.
- Darensbourg, D. J., Stafford, N. W., Joó, F. & Reibenspies, J. H. (1995). *J. Organomet. Chem.* **488**, 99–108.
- Hitchcock, P. B., Jacobson, B. & Pidcock, A. (1977). *J. Chem. Soc. Dalton Trans.* pp. 2038–2042.
- Hunter, W. N., Muir, K. W. & Sharp, D. W. A. (1986). *Acta Cryst. C42*, 1743–1745.
- Joó, F., Nádasdi, L., Bényei, A. Cs. & Darensbourg, D. J. (1996). *J. Organomet. Chem.* **512**, 45–50.
- Muir, M. M., Muir, J. A., Alyea, E. C. & Fisher, K. J. (1993). *J. Crystallogr. Spectrosc. Res.* **23**, 745–748.
- Otto, S. & Roodt, A. (2001). *Inorg. Chem. Commun.* **4**, 49–52.
- Otto, S., Roodt, A. & Purcell, W. (1998). *Inorg. Chem. Commun.* **1**, 415–417.
- Otto, S., Roodt, A. & Smith, J. (2000). *Inorg. Chim. Acta*, **303**, 295–299.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Tolman, C. A. (1977). *Chem. Rev.* **77**, 313–348.