

***trans*-(μ -5,5'-Diethynyl-2,2'-bipyridine)bis[phenylbis(triethylphosphine)platinum(II)]**

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Key indicators

Single-crystal synchrotron study

$T = 150\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

R factor = 0.032

wR factor = 0.068

Data-to-parameter ratio = 25.4

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $[\text{Pt}_2(\text{C}_6\text{H}_5)_2(\text{C}_{14}\text{H}_6\text{N}_2)(\text{C}_6\text{H}_{15}\text{P})_4]$, is a dinuclear Pt^{II} di-yne complex that exhibits π -conjugation along the molecular backbone. It is used as a model complex for rigid-rod platinum poly-yne polymers of which it is a precursor. Such compounds are of interest because of the extended π -conjugation through the aromatic/heteroaromatic spacer group in the backbone. The asymmetric unit contains two half molecules of the title compound, each lying on a crystallographic centre of symmetry situated at the mid-point of the central C—C bond of the bipyridine unit.

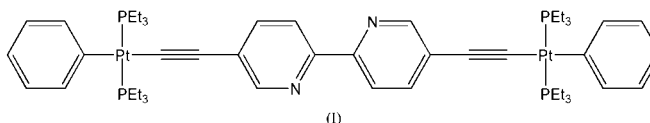
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Comment

In this paper, we report the structural characterization of the title compound, (I), which is a dinuclear platinum(II) di-yne species, *trans*-[(Ph)(PEt_3)₂Pt—C≡C—*R*—C≡C—Pt(PEt_3)₂—(Ph)] (*R* = 2,2'-bipyridine-5,5'-diyl). Such organoplatinum species form the building blocks for rigid-rod platinum poly-ynes of general formula *trans*-[Pt(PX_3)₂—C≡C—*R*—C≡C—] (*X* = tertiary phosphines and *R* = aromatic/heteroaromatic spacer group). Platinum(II) poly-ynes are of immense current interest due to π -electron conjugation along the rigid backbone of the organometallic polymer. These materials possess a wide variety of interesting properties useful for application in modern technology. For example, incorporating platinum into the polymer backbone introduces strong spin-orbit coupling and phosphorescence can be readily observed (Wittmann *et al.*, 1994; Beljonne *et al.*, 1996; Younus *et al.*, 1998; Chawdhury *et al.*, 1998, 1999). Platinum(II) poly-ynes provide model systems for the study of some of the basic photophysical properties that occur in conjugated organic and organometallic polymers (Khan, Al-Mandhary, Al-Suti, Hisahm *et al.*, 2002; Khan, Al-Mandhary, Al-Suti, Feeder *et al.*, 2002; Khan, Al-Mandhary, Al-Suti, Raithby, Ahrens, Mahon *et al.*, 2003; Khan, Al-Mandhary, Al-Suti, Raithby, Ahrens, Male *et al.*, 2003), are used in optoelectronic devices such as light emitting diodes (LEDs), lasers, photocells and field-effect transistors (FETs) (Wilson *et al.*, 2000; Wilson, Chawdhury *et al.*, 2001; Wilson, Dhoot *et al.*, 2001). Group 10 metal poly-ynes also show interesting alignment and liquid crystal properties, one-dimensional conductivity and non-linear optical (NLO) properties (Takahashi *et al.*, 1984; Wilson *et al.*, 2003).



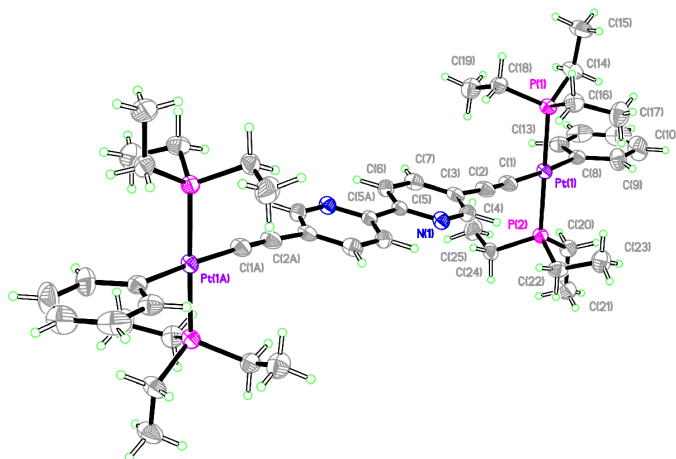


Figure 1
View of molecule 1 of (I) (50% probability displacement ellipsoids). The suffix *A* denotes symmetry position $1 - x, 1 - y, -z$.

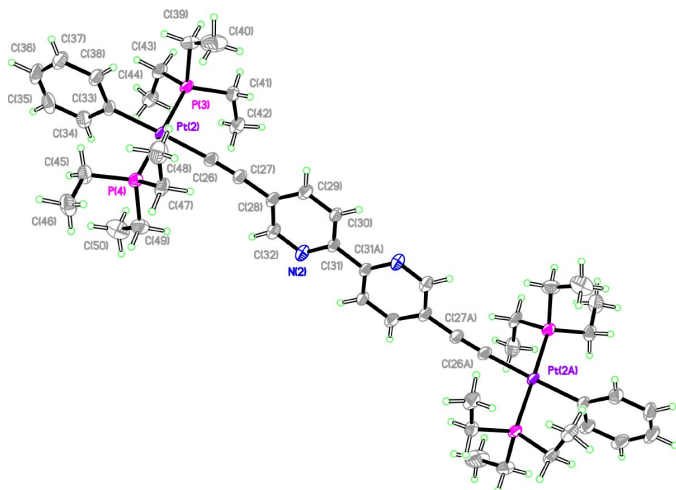


Figure 2
View of molecule 2 of (I) (50% probability displacement ellipsoids). The suffix *A* denotes symmetry position $1 - x, 2 - y, -z$.

properties and structure–property relationships in the metal poly-yne.

The asymmetric unit of the triclinic unit cell of (I) contains two structurally similar half molecules of the title compound, each sitting on a centre of symmetry corresponding to the midpoint of the central C–C bond of the bipyridine ligand. The bipyridine ligands are orientated in the *trans* configuration with respect to the N atoms, as would be expected to minimize H···H contacts. The same configuration is observed in the trimethylsilyl-substituted derivative (Khan *et al.*, 2004); the bond parameters are also similar to those found in this derivative. The platinum centres exhibit the expected square-planar geometry and the bond parameters are similar to those reported in related platinum di-yne complexes (Khan, Al-Mandhary, Al-Suti, Hisahm *et al.*, 2002; Khan, Al-Mandhary, Al-Suti, Feeder *et al.*, 2002; Khan, Al-Mandhary, Al-Suti, Raithby, Ahrens, Mahon *et al.*, 2003; Khan, Al-Mandhary, Al-Suti, Raithby, Ahrens, Male *et al.*, 2003). The platinum square plane makes dihedral angles of $79.3(1)^\circ$ with the adjacent pyridine ring [$73.4(1)^\circ$ in molecule 2], and $88.6(1)^\circ$ with the

terminal phenyl ring [$83.1(1)^\circ$ in molecule 2]. The two pyridine rings in each independent molecule are precisely coplanar by crystallographic symmetry. There are no significant short intermolecular contacts within the structure.

Experimental

The title compound was synthesized according to the procedure of Khan, Al-Mandhary, Al-Suti, Hisahm *et al.* (2002). To a stirred solution of *trans*-[(PEt_3)₂(Ph)PtCl] (0.543 g, 1.0 mmol) and 5,5'-bisethynyl-2,2'-bipyridine (0.102 g, 0.50 mmol) in $\text{CH}_2\text{Cl}_2/\text{Pr}_2\text{NH}$ (50 ml, 1:1 *v/v*) under nitrogen was added a catalytic amount (approximately 5 mg) of CuI. The yellow solution was stirred at room temperature for 15 h, after which all volatile components were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and passed through a silica column, eluting with hexane– CH_2Cl_2 (1:1 *v/v*). Removal of the solvents *in vacuo* gave the title complex as a pale-yellow solid (0.43 g, 70%). Further purification was accomplished by triturating the complex in methanol.

Crystal data

[Pt₂(C₆H₅)₂(C₁₄H₆N₂)(C₆H₁₅P)₄]
 $M_r = 1219.19$
 Triclinic, $P\bar{1}$
 $a = 9.2651(7) \text{ \AA}$
 $b = 16.6840(14) \text{ \AA}$
 $c = 16.8258(14) \text{ \AA}$
 $\alpha = 92.130(2)^\circ$
 $\beta = 90.032(2)^\circ$
 $\gamma = 94.958(2)^\circ$
 $V = 2589.4(4) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.564 \text{ Mg m}^{-3}$
 Synchrotron radiation,
 $\lambda = 0.6941 \text{ \AA}$
 Cell parameters from 25942
 reflections
 $\theta = 21.7\text{--}29.3^\circ$
 $\mu = 5.55 \text{ mm}^{-1}$
 $T = 150(2) \text{ K}$
 Block, yellow
 $0.02 \times 0.01 \times 0.01 \text{ mm}$

Data collection

Bruker AXS SMART 1K CCD
 diffractometer
 Narrow frame ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.895, T_{\max} = 0.946$
 25942 measured reflections

13587 independent reflections
 11103 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\max} = 29.3^\circ$
 $h = -12 \rightarrow 12$
 $k = -23 \rightarrow 23$
 $l = -23 \rightarrow 23$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.068$
 $S = 1.00$
 13587 reflections
 535 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.004$
 $\Delta\rho_{\max} = 1.63 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.86 \text{ e \AA}^{-3}$

Aromatic, methylene and methyl H atoms were constrained as riding atoms, fixed to the parent atoms with distances of 0.95, 0.99 and 0.98 Å, respectively. The isotropic displacement parameters were fixed to 120% of those of the parent atoms for aromatic and methylene H atoms and 150% for methyl H atoms. The high residual electron density peaks were located close to the positions of the two unique Pt atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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