

μ -2,2',6,6'-Tetramethyl-4,4'-bipyridine- $\kappa^2N^1:N^1$ '-bis[(diethylenetriamine- κ^3N,N',N'')palladium(II)] tetranitrate¹Rüdiger W. Seidel^{a*} and Iris M. Oppel^b^aLehrstuhl für Analytische Chemie, Universitätsstrasse 150, 44780 Bochum, Germany, and ^bInstitut für Anorganische Chemie, Rheinisch-Westfälische Technische Hochschule Aachen, Landoltweg 1, 52074 Aachen, Germany
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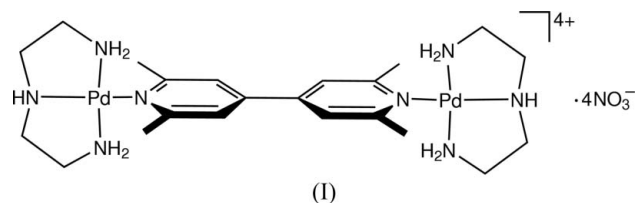
The title compound, $[\text{Pd}_2(\text{C}_4\text{H}_{13}\text{N}_3)_2(\text{C}_{14}\text{H}_{16}\text{N}_2)](\text{NO}_3)_4$, comprises discrete tetracationic dumbbell-type dinuclear complex molecules and noncoordinating nitrate anions. Two $\text{Pd}(\text{dien})^{2+}$ moieties (dien is diethylenetriamine) are joined by the rigid linear *exo*-bidentate bridging 2,2',6,6'-tetramethyl-4,4'-bipyridine ligand to form the dinuclear complex, which lies across a centre of inversion in the space group $P2_1/n$, so that the rings in the 2,2',6,6'-tetramethyl-4,4'-bipyridine bridging ligand are parallel. In the crystal, the primary and secondary amino groups of the dien ligand act as hydrogen-bond donors towards the nitrate anions to form a three-dimensional hydrogen-bond network.

Comment

2,2',6,6'-Tetramethyl-4,4'-bipyridine was mentioned in the literature for the first time more than 100 years ago (Huth, 1898). However, coordination compounds containing this ligand are surprisingly few in number. Fujita and co-workers used 2,2',6,6'-tetramethyl-4,4'-bipyridine as a linear bridging ligand in the selective multicomponent assembly of metallo-supramolecular rectangles and trigonal-prismatic-shaped coordination cages (Yoshizawa, Nagao *et al.*, 2005); 2,2',6,6'-tetramethyl-4,4'-bipyridine and another bridging ligand, *i.e.* bearing unsubstituted 4-pyridyl groups, were reacted with $\text{Pd}(\text{en})^{2+}$ (en is ethylenediamine) building blocks, which form the corners of the rectangles and prisms. Simultaneous binding of two 2,6-dimethyl-4-pyridyl groups to the two vacant *cis* sites of the *cis*-constrained Pd^{2+} ion is hindered by the steric demand of the methyl groups. Thus, the equilibrium is pushed towards the anticipated heterotopic assembly. A number of host-guest complexes of the trigonal-prismatic coordination

cage thus obtained have been structurally characterized (Ono *et al.*, 2007; Yoshizawa, Nakagawa *et al.*, 2005; Yoshizawa, Ono *et al.*, 2005; Ono *et al.*, 2009; Yamauchi *et al.*, 2010).

In contrast to the bifunctional $\text{Pd}(\text{en})^{2+}$ building block, the analogous Pd^{II} complex of the related tris-chelate ligand diethylenetriamine (dien) exhibits only one vacant coordination site. For this reason, $\text{Pd}(\text{dien})^{2+}$ complexes have been widely used in mechanistic studies of substitution reactions for a long time (Basolo *et al.*, 1960). Furthermore, reactions of non-antitumour-active monofunctional Pd^{II} complexes with biologically relevant molecules, especially nucleobases (see, for example, Anzellotti *et al.*, 2006; Gupta *et al.*, 2007, and references therein), have been extensively studied in order to understand the action of Pt^{II} anticancer drugs (Lippert, 2006). In general, Pd^{II} complexes are often used in mechanistic studies, since their reactivity is 10^4 to 10^5 times greater than that of their Pt^{II} analogues, while the structural and electronic properties are similar. Likewise, the monofunctional $\text{Pd}(\text{dien})^{2+}$ building block has been used to develop a method of predicting metallo-supramolecular self-assembly (Fyles & Tong, 2007), which was applied to Fujita's square formed from $\text{Pd}(\text{en})^{2+}$ and 4,4'-bipyridine (4,4'-bipy) (Fujita *et al.*, 1990). There is, in fact, only one possible target motif in self-assembly from the monofunctional $\text{Pd}(\text{dien})^{2+}$ building block and a linear bridging ligand with a molar ratio of 2:1, *viz.* a dinuclear dumbbell-type complex. However, to the best of our knowledge, a crystal structure of the model compound $[\text{Pd}(\text{dien})(\mu\text{-4,4'-bipy})](\text{NO}_3)_4$, investigated in solution by Fyles & Tong (2007), has not been reported thus far. It is perhaps noteworthy that our attempts to obtain crystals of this compound suitable for single-crystal X-ray analysis were unsuccessful. In this contribution, we report a similar crystallographic study on a dinuclear dumbbell-type complex, assembled from $\text{Pd}(\text{dien})^{2+}$ units and 2,2',6,6'-tetramethyl-4,4'-bipyridine, namely μ -2,2',6,6'-tetramethyl-4,4'-bipyridine-bis[(diethylenetriamine)palladium(II)] tetranitrate, (I).



$[\text{PdCl}(\text{dien})]\text{Cl}$ was treated with AgNO_3 to remove the chloride ions by a metathesis reaction, and was then allowed to react *in situ* with a semimolar amount of 2,2',6,6'-tetramethyl-4,4'-bipyridine to yield (I). Compound (I) crystallized in a solvent-free form from a methanol–water mixture. Single-crystal X-ray analysis revealed the anticipated dinuclear dumbbell-type complex, comprised of two $\text{Pd}(\text{dien})^{2+}$ moieties joined by the 2,2',6,6'-tetramethyl-4,4'-bipyridine bridging ligand. The $\text{Pd}^{\text{II}} \cdots \text{Pd}^{\text{II}}$ separation is 11.1540 (8) Å. Four noncoordinating nitrate anions balance the charge of the tetracationic complex. Fig. 1(a) shows a displacement ellipsoid plot of (I). The cation exhibits approximate molecular C_{2h} ($2/m$) symmetry and the central C–C bond of the bridging

¹ Dedicated to Professor Bernhard Lippert on the occasion of his 65th birthday.

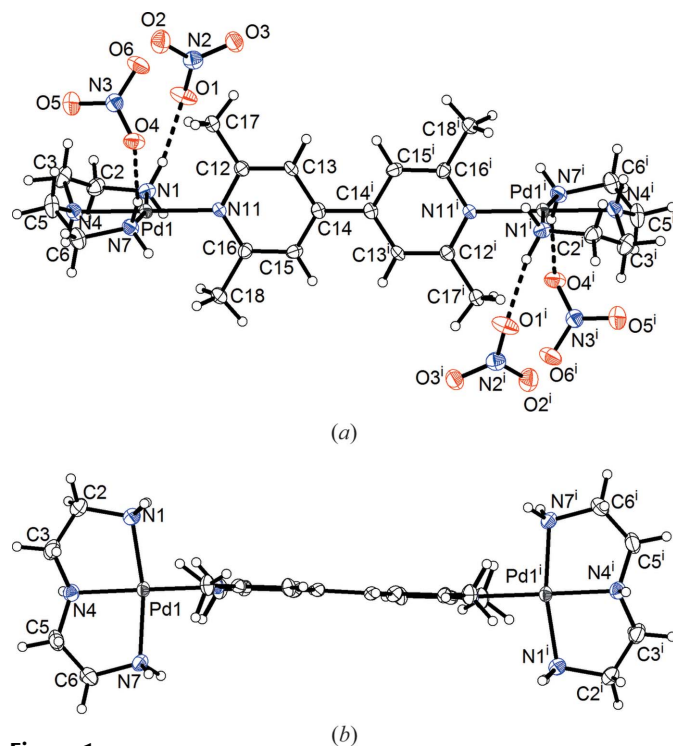


Figure 1
 (a) A lateral view of (I) and (b) a top view of the cation. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii. Hydrogen bonds are represented by dashed lines. [Symmetry code: (i) $-x, -y + 1, -z$.]

ligand lies across a crystallographic centre of inversion. The asymmetric unit thus comprises half of the cation and two nitrate anions. The Pd^{II} atom exhibits a square-planar coordination; three coordination sites are occupied by the dien ligand and the 2,6-dimethyl-4-pyridyl groups coordinate to the remaining site. The Pd–N bond lengths are normal and the bond angles about Pd^{II} deviate from the idealized value of 90° because of the chelate angles of the dien ligand (Table 1). The mean plane of the pyridine six-membered ring is almost perpendicular to the N₄ mean plane, with a tilt angle of 88.7 (9)°.

It is remarkable that 2,2',6,6'-tetramethyl-4,4'-bipyridine adopts a virtually planar D_{2h} (mmm) conformation in (I); the distance between the mean planes of the symmetry-related rings is *ca* 0.08 Å. The crystallographic site symmetry of the molecule requires a flat conformation. Visual inspection of the displacement ellipsoids of the C atoms in the 2-, 3-, 5- and 6-positions of the 2,6-dimethyl-4-pyridyl groups reveals no suggestion of any significant deviation from planarity (Fig. 1*b*). In contrast, the molecule exhibits a twisted conformation in the crystal structure of the unsolvated free ligand, with a dihedral angle between the mean planes of the rings of 19.48 (2)° (Fu, 2008). The molecule is also found to be twisted in Fujita's coordination cages (see above). It has been shown that the minimum energy conformation of unsubstituted 4,4'-bipyridine has a dihedral angle between the planes of the two rings of approximately 35° (Candana *et al.*, 1999). Presumably, intermolecular forces, in particular hydrogen bonding, and the effects of crystal packing compensate for the energetically

unfavourable planar conformation of the ligand in compound (I). The supramolecular organization of (I) in the crystal is achieved through N–H···O hydrogen bonds between the primary and secondary amino groups of the dien ligand of the cation and the nitrate anions. The hydrogen bonds, whose parameters exhibit typical values (Table 2), together generate a three-dimensional framework structure.

Despite its potential, the coordination chemistry of 2,2',6,6'-tetramethyl-4,4'-bipyridine has been largely unexplored in comparison to the prototypical 4,4'-bipyridine, which has been widely used as a bridging ligand (Biradha *et al.*, 2006). Here, we have in summary structurally characterized a discrete dinuclear dumbbell-type metallo-supramolecular complex, assembled from Pd(dien)²⁺ building blocks and the rigid linear *exo*-bidentate bridging ligand 2,2',6,6'-tetramethyl-4,4'-bipyridine.

Experimental

2,2',6,6'-Tetramethyl-4,4'-bipyridine was synthesized from 2,6-lutidine according to 'method C' reported by Bossmann *et al.* (2005). [PdCl(dien)]Cl was prepared following the procedure reported by Anzellotti *et al.* (2006). AgNO₃ (12 mg, 0.072 mmol) was added to a suspension of [PdCl(dien)]Cl (10 mg, 0.036 mmol) in D₂O (0.9 ml). The mixture was stirred for 12 h in the dark and the precipitate which formed was removed by centrifugation. 2,2',6,6'-Tetramethyl-4,4'-bipyridine (4 mg, 0.018 mmol) was added to the resulting clear solution, followed by stirring until the solid was completely dissolved. The solution was evaporated to dryness and the crude product was redissolved in *ca* 1 ml of a methanol–water mixture (1:1 *v/v*). Slow evaporation of the solution yielded pale-yellow crystals of (I) suitable for single-crystal X-ray diffraction.

Crystal data

| | |
|--|---|
| [Pd ₂ (C ₄ H ₁₃ N ₃) ₂ (C ₁₄ H ₁₆ N ₂)](NO ₃) ₄ | $V = 1659.33 (17) \text{ \AA}^3$ |
| $M_r = 879.48$ | $Z = 2$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation |
| $a = 10.7697 (6) \text{ \AA}$ | $\mu = 1.16 \text{ mm}^{-1}$ |
| $b = 8.0282 (4) \text{ \AA}$ | $T = 110 \text{ K}$ |
| $c = 19.6442 (12) \text{ \AA}$ | $0.30 \times 0.16 \times 0.08 \text{ mm}$ |
| $\beta = 102.323 (6)^\circ$ | |

Data collection

| | |
|--|--|
| Oxford Diffraction Xcalibur2 diffractometer | 14710 measured reflections |
| Absorption correction: multi-scan (ABSPACK in CrysAlis PRO; Agilent, 2011) | 3799 independent reflections |
| $T_{\min} = 0.722, T_{\max} = 0.913$ | 2767 reflections with $I > 2\sigma(I)$ |
| | $R_{\text{int}} = 0.062$ |

Refinement

| | |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.038$ | 219 parameters |
| $wR(F^2) = 0.076$ | H-atom parameters constrained |
| $S = 1.02$ | $\Delta\rho_{\text{max}} = 0.68 \text{ e \AA}^{-3}$ |
| 3799 reflections | $\Delta\rho_{\text{min}} = -0.66 \text{ e \AA}^{-3}$ |

Table 1
 Selected bond angles (°).

| | | | |
|-----------|-------------|------------|-------------|
| N1–Pd1–N4 | 83.85 (12) | N1–Pd1–N11 | 97.03 (11) |
| N4–Pd1–N7 | 84.76 (12) | N7–Pd1–N11 | 94.32 (11) |
| N1–Pd1–N7 | 168.20 (12) | N4–Pd1–N11 | 178.92 (12) |

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|-------|-------------|-------------|---------------|
| N1–H1A \cdots O1 | 0.92 | 2.01 | 2.904 (4) | 165 |
| N1–H1B \cdots O3 ⁱ | 0.92 | 2.10 | 3.017 (4) | 176 |
| N4–H4 \cdots O2 ⁱⁱ | 0.93 | 2.03 | 2.955 (4) | 173 |
| N7–H7B \cdots O4 | 0.92 | 2.03 | 2.925 (4) | 165 |
| N7–H7A \cdots O4 ⁱⁱⁱ | 0.92 | 2.04 | 2.949 (4) | 168 |

Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $x, y + 1, z$; (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

H atoms were placed at geometrically calculated positions and treated as riding atoms, with C–H = 0.95 (aromatic), 0.98 (methyl) or 0.99 Å (methylene) and N–H = 0.92 Å, and with $U_{iso}(H) = kU_{eq}(\text{carrier})$, where $k = 1.5$ for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other H atoms.

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2011); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3392). Services for accessing these data are described at the back of the journal.

References

- Agilent (2011). *CrysAlis PRO*. Agilent Technologies, Yarnton, Oxfordshire, England.
- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
- Anzellotti, A. I., Sabat, M. & Farrell, N. (2006). *Inorg. Chem.* **45**, 1638–1645.
- Basolo, F., Gray, H. B. & Pearson, R. G. (1960). *J. Am. Chem. Soc.* **82**, 4200–4203.
- Biradha, K., Sarkar, M. & Rajput, L. (2006). *Chem. Commun.* pp. 4169–4179.
- Bossmann, S. H., Dürr, H. & Pokhrel, M. R. (2005). *Synthesis*, **6**, 907–914.
- Brandenburg, K. (2011). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Candana, M. M., Eroglu, S., Oumlzbeja, S., Kendi, E. & Kantarci, Z. (1999). *Spectrosc. Lett.* **32**, 35–45.
- Fu, L.-H. (2008). *Acta Cryst.* **E64**, o127.
- Fujita, M., Yazaki, J. & Ogura, K. (1990). *J. Am. Chem. Soc.* **112**, 5645–5648.
- Fyles, T. M. & Tong, C. C. (2007). *New J. Chem.* **31**, 296–304.
- Gupta, D., Roitzsch, M. & Lippert, B. (2007). *Inorg. Chim. Acta*, **360**, 2379–2386.
- Huth, F. (1898). *Ber. Dtsch. Chem. Ges.* **31**, 2280–2282.
- Lippert, B. (2006). Editor. *Cisplatin: Chemistry and Biochemistry of a Leading Anticancer Drug*. Zürich: Verlag Helvetica Chimica Acta, and Weinheim: Wiley-VCH.
- Ono, K., Yoshizawa, M., Akita, M., Kato, T., Tsunobuchi, Y., Ohkoshi, S. & Fujita, M. (2009). *J. Am. Chem. Soc.* **131**, 2782–2783.
- Ono, K., Yoshizawa, M., Kato, T., Watanabe, K. & Fujita, M. (2007). *Angew. Chem. Int. Ed.* **46**, 1803–1806.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Yamauchi, Y., Yoshizawa, M., Akita, M. & Fujita, M. (2010). *J. Am. Chem. Soc.* **132**, 960–966.
- Yoshizawa, M., Nagao, M., Kumazawa, K. & Fujita, M. (2005). *J. Organomet. Chem.* **690**, 5383–5388.
- Yoshizawa, M., Nakagawa, J., Kumazawa, K., Nagao, M., Kawano, M., Ozeki, T. & Fujita, M. (2005). *Angew. Chem. Int. Ed.* **44**, 1810–1813.
- Yoshizawa, M., Ono, K., Kumazawa, K., Kato, T. & Fujita, M. (2005). *J. Am. Chem. Soc.* **127**, 10800–10801.