

*Acta Cryst.* (1998). **C54**, 1439–1441

**[2-(2-Acetyl-2-ethoxycarbonyl-1-methoxyethyl)-8-quinolinolato-*C,N,O*](pyridine-*N*)-palladium(II)†**

DAMON R. BILLODEAUX,<sup>a</sup> FRANK R. FRONCZEK,<sup>a</sup> AKIO YONEDA<sup>b</sup> AND GEORGE R. NEWKOME<sup>c</sup>

<sup>a</sup>*Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA,* <sup>b</sup>*Department of Applied Chemistry, Faculty of Engineering, Himeji Institute of Technology, 2167 Shosha, Himeji, Hyogo, Japan, and* <sup>c</sup>*Department of Chemistry, University of South Florida, Tampa, FL, 33620, USA. E-mail: fronz@chxray1.chem.lsu.edu*

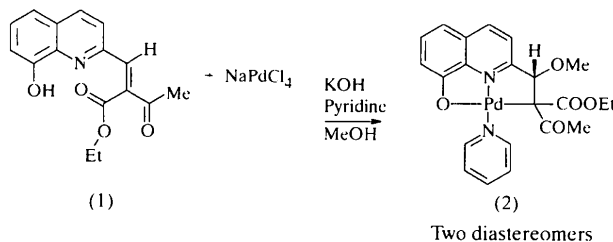
(Received 11 November 1997; accepted 15 April 1998)

**Abstract**

The title compound, [Pd(C<sub>17</sub>H<sub>17</sub>NO<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>N)], is the diastereomer with opposite configurations at the two chiral centers, and is racemic. The two independent molecules in the asymmetric unit differ in conformation primarily by a rotation of 167.0(6)° about the C—C<sub>ester</sub> bond. The Pd—O bond lengths are 2.105(3) and 2.080(3) Å, and the Pd—C distances are 2.106(4) and 2.117(3) Å.

**Comment**

We have incorporated a five-membered chelate ring, a directed *N*-donor, and an adjacent carbanionic center into a single ligand, affording access to a series of novel metallacycles (Newkome *et al.*, 1986). The introduction of an additional *O*-donor afforded a class of *C,N,O*-ligands capable of generating stable organometallic Pd<sup>II</sup> complexes possessing a single coordination site at which ligands can be interchanged (Yoneda, Newkome *et al.*, 1993). Combination of these stabilizing components with pyridine at the interchangeable site has given rise to the title compound, (2). It exists in the crystal as two independent molecules (*A* and *B*) in the asymmetric unit, both of which are shown in Fig. 1. The mol-



† Alternative name: [ethyl 2-acetyl-3-(8-hydroxyquinolin-2-yl-*O,N*)-3-methoxypropanoate-*C*<sup>2</sup>](pyridine-*N*)palladium(II).

ecules are related by a very approximate pseudo-center at (0.02,0.80,0.75), with a mean deviation of 1.37 Å from exact coincidence of the non-H atoms. Differences between the two molecules are mostly in conformation, but the Pd1—O1 bond distances differ significantly. The 2.080(3) Å distance of molecule *B* is shorter than the shortest such distance reported previously [2.093(2) Å; Yoneda *et al.*, 1994] for similar compounds, while the same interatomic distance of molecule *A* [2.105(3) Å] falls within the 2.093(2)–2.108(2) Å range reported

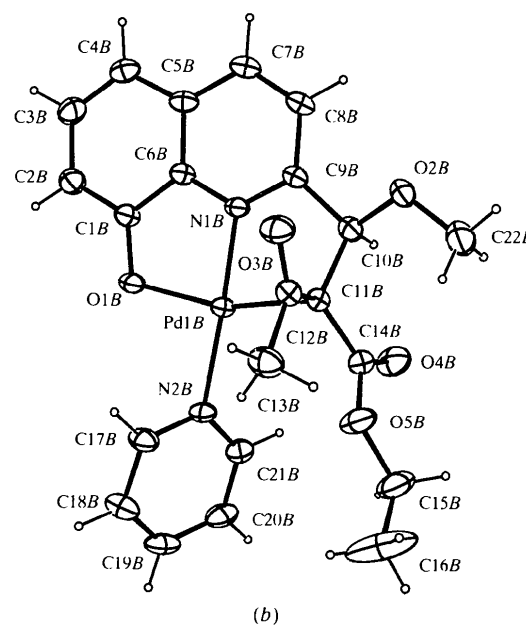
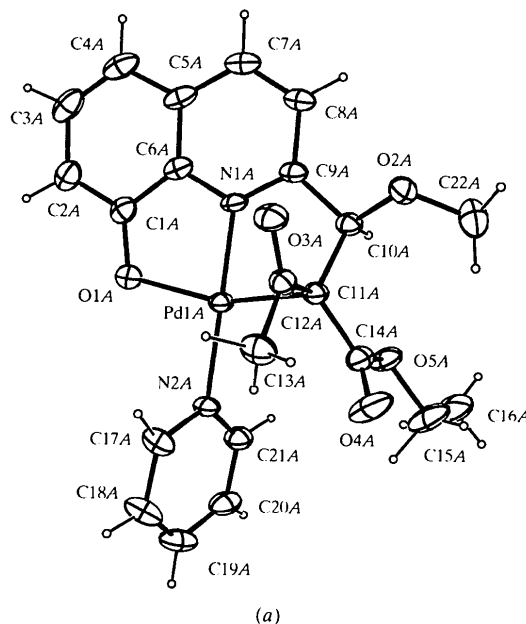


Fig. 1. ORTEP (Johnson, 1976) drawings of independent molecules (a) *A* and (b) *B*, with ellipsoids at the 30% probability level.

(Yoneda *et al.*, 1994). Another significant difference concerns the substituents on C11. The ester carbonyl O4A atom is *syn* to the ketone substituent, while O4B is *anti*. The C10—C11—C14—O4 torsion angle is 138.1(4)° in molecule *A* and -28.9(5)° in molecule *B*.

With the exception of the O1—Pd1—N2 angle [95.9(1)° in molecule *A* and 93.4(1)° in molecule *B*], the angles around the Pd atom agree between the two molecules within experimental error. Both of these angles, however, are similar to corresponding values found in similar compounds, *e.g.* 95.61(7) (Yoneda *et al.*, 1994) and 93.57(5)° (Yoneda, Ouchi *et al.*, 1993).

The coordination geometry of Pd1 in both molecules is slightly non-planar. In molecules *A* and *B*, the O1 atoms deviate most from the best plane formed from the coordinated atoms and Pd1 by 0.112(3) and 0.092(3) Å, respectively.

The quinoline system is relatively planar in both molecules. Molecule *B* exhibits an average deviation amongst its atoms of 0.026(1) Å from the best plane, comparable to 0.033(1) Å in molecule *A*. All bond distances and angles in the quinoline system agree between the two molecules within experimental error. These values also agree with corresponding bond lengths and angles in similar palladium compounds containing quinoline systems (Liu, 1997).

The two five-membered chelate rings around the Pd atom exhibit different conformations. The Pd1—O1—C1—C6—N1 chelate ring has an envelope conformation in both molecules, with Pd1 in the flap position. The Pd1—N1—C9—C10—C11 chelate ring has a conformation similar to the half-chair, with the N1 atom lying on the twist axis.

The crystal is a racemic mixture of the diastereomer, with opposite configurations at the two chiral centers. In Fig. 1, the chiral centers at C11A and C11B are in the *S* configuration, while the chiral centers at C10A and C10B are in the *R* configuration. The distances around these centers agree with those of previous structures (Yoneda, Ouchi *et al.*, 1993; Yoneda *et al.*, 1994). The synthesis also produced the diastereomer with the same configuration at the stereogenic centers. We have examined a crystal of this diastereomer, which has monoclinic space group *P*2<sub>1</sub>/*c* and is thus also racemic. It also contains two independent molecules in the asymmetric unit [cell dimensions: *a* = 18.188(1), *b* = 12.077(1), *c* = 21.698(1) Å, and  $\beta$  = 95.978(6)°]. The presence of a disordered CH<sub>2</sub>Cl<sub>2</sub> solvent molecule limited the quality of the crystals, and high precision was not attained for that refinement. We therefore do not report the details of that structure determination here.

## Experimental

The title compound was prepared according to the synthesis shown in the scheme. To a stirred solution of compound (1) (251 mg, 0.88 mmol) in absolute methanol (70 ml), Na<sub>2</sub>PdCl<sub>4</sub>

(259 mg, 0.88 mmol) was added, followed by KOH (148 mg, 2.64 mmol). After 10 min at 298 K, pyridine (1 ml) was added and the mixture was stirred for an additional 12 h. The solution was concentrated *in vacuo* and the mixture of the two diastereomeric Pd complexes was chromatographed (SiO<sub>2</sub>), eluting with ethyl acetate (yield: 390 mg, 88.5%). The solution produced two fractions of the compound. The structure we report here was the first fraction; yellow solid (m.p. 452 K): <sup>1</sup>NMR:  $\delta$  1.19 (*t*, CH<sub>3</sub>, *J* = 7.3 Hz, 3H), 2.29 (*s*, COCH<sub>3</sub>, 3H), 3.64 (*s*, OCH<sub>3</sub>, 3H), 3.96–4.13 (*m*, CH<sub>2</sub>CH<sub>3</sub>, 2H), 5.88 p.p.m. (*s*, CHOCH<sub>3</sub>, 1H). The crystal used for data collection was obtained by evaporation of a benzene–hexane solution at room temperature.

## Crystal data

[Pd(C<sub>17</sub>H<sub>17</sub>NO<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>N)]

*M<sub>r</sub>* = 500.83

Triclinic

*P*1̄

*a* = 11.5036(6) Å

*b* = 12.8861(6) Å

*c* = 14.8388(9) Å

$\alpha$  = 102.351(4)°

$\beta$  = 98.342(5)°

$\gamma$  = 103.493(4)°

*V* = 2044.9(2) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.63 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

## Data collection

Enraf–Nonius CAD-4 diffractometer

$\theta/2\theta$  scans

Absorption correction:

$\psi$  scans (North *et al.*, 1968)

*T<sub>min</sub>* = 0.71, *T<sub>max</sub>* = 0.84

12 369 measured reflections

11 881 independent reflections

reflections

## Refinement

Refinement on *F*

*R* = 0.045

*wR* = 0.048

*S* = 2.26

9705 reflections

542 parameters

H atoms included but not refined

$w = 4F_o^2 / [\sigma^2(F_o^2) + 0.0004F_o^4]$

( $\Delta/\sigma$ )<sub>max</sub> = 0.03

Mo K $\alpha$  radiation

$\lambda$  = 0.71073 Å

Cell parameters from 25 reflections

$\theta$  = 11–21°

$\mu$  = 0.93 mm<sup>-1</sup>

*T* = 297 K

Rectangular prism

0.43 × 0.25 × 0.19 mm

Orange

9705 reflections with

*I* >  $\sigma(I)$

*R<sub>int</sub>* = 0.021

$\theta_{max}$  = 30.0°

*h* = -15 → 16

*k* = -18 → 0

*l* = -20 → 20

3 standard reflections

frequency: 120 min

intensity decay: 2.1%

$\Delta\rho_{max}$  = 1.23 e Å<sup>-3</sup>

$\Delta\rho_{min}$  = -0.34 e Å<sup>-3</sup>

Extinction correction:

isotropic (Zachariasen, 1963)

Extinction coefficient:

1.02(14) × 10<sup>-7</sup>

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Pd1A—O1A	2.105(3)	Pd1B—O1B	2.080(3)
Pd1A—N1A	1.940(2)	Pd1B—N1B	1.940(2)
Pd1A—N2A	2.047(2)	Pd1B—N2B	2.053(2)
Pd1A—C11A	2.106(4)	Pd1B—C11B	2.117(3)
O2A—C10A	1.422(4)	O2B—C10B	1.428(4)
C9A—C10A	1.496(5)	C9B—C10B	1.502(5)
C10A—C11A	1.556(4)	C10B—C11B	1.553(4)

C11A—C12A	1.498 (5)	C11B—C12B	1.503 (5)
C11A—C14A	1.496 (4)	C11B—C14B	1.495 (5)
O1A—Pd1A—N1A	81.6 (1)	O1B—Pd1B—N1B	82.2 (1)
O1A—Pd1A—N2A	95.9 (1)	O1B—Pd1B—N2B	93.4 (1)
O1A—Pd1A—C11A	160.44 (9)	O1B—Pd1B—C11B	161.82 (9)
N1A—Pd1A—N2A	175.3 (1)	N1B—Pd1B—N2B	174.9 (1)
N1A—Pd1A—C11A	80.8 (1)	N1B—Pd1B—C11B	81.0 (1)
N2A—Pd1A—C11A	102.2 (1)	N2B—Pd1B—C11B	103.6 (1)
Pd1A—N1A—C6A—C1A	−5.7 (4)		
Pd1A—N1A—C9A—C10A	4.8 (4)		
Pd1A—O1A—C1A—C6A	6.3 (4)		
N1A—Pd1A—C11A—C10A	−25.3 (2)		
N1A—Pd1A—O1A—C1A	−7.1 (2)		
O1A—Pd1A—N1A—C6A	7.0 (2)		
C11A—Pd1A—N1A—C9A	13.2 (3)		
C9A—C10A—C11A—Pd1A	34.6 (3)		
N1A—C9A—C10A—C11A	−27.4 (4)		
C10A—C11A—C14A—O4A	138.1 (4)		
O1A—C1A—C6A—N1A	−0.9 (5)		
Pd1B—N1B—C6B—C1B	−4.2 (4)		
Pd1B—N1B—C9B—C10B	5.9 (4)		
Pd1B—O1B—C1B—C6B	6.3 (4)		
N1B—Pd1B—C11B—C10B	−22.3 (2)		
N1B—Pd1B—O1B—C1B	−6.6 (3)		
O1B—Pd1B—N1B—C6B	5.9 (2)		
C11B—Pd1B—N1B—C9B	10.6 (3)		
C9B—C10B—C11B—Pd1B	31.6 (3)		
N1B—C9B—C10B—C11B	−26.1 (4)		
C10B—C11B—C14B—O4B	−28.9 (5)		
O1B—C1B—C6B—N1B	−1.8 (5)		
C22B—O2B—C10B—C11B	52.3 (4)		

The H atoms were placed in calculated positions with C—H 0.95 Å and isotropic displacement parameters set at 1.3 times those of the bonded C atoms. Methyl H atoms at C13 were calculated in conformations guided by difference maps. Attempts at refining the H atoms in least squares proved unsuccessful and they were thus left in calculated unrefined positions. The approximate pseudo-center caused no refinement problems. The highest residual density in the difference map is located 0.988 Å from Pd1A.

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD-4 Operations Manual*. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: Patterson and Fourier methods in *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *CIF IN* in *MolEN*.

The purchase of the diffractometer was made possible by a National Science Foundation chemical instrumentation grant, which we gratefully acknowledge. Improvements to the LSU X-ray Crystallography Facility were supported by grant No. LEQSF(1996–97)–ENH-TR-10, administered by the Louisiana Board of Regents. DRB wishes to acknowledge the Chancellor's Student Aid Fund which made this structure determination possible.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1380). Services for accessing these data are described at the back of the journal.

## References

- Enraf–Nonius (1977). *CAD-4 Operations Manual*. Enraf–Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Liu, Y.-H. (1997). PhD thesis, Louisiana State University, USA.
- Newkome, G. R., Puckett, W. E., Gupta, V. K. & Kiefer, G. E. (1986). *Chem. Rev.* **86**, 451–489.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Yoneda, A., Hakushi, T., Newkome, G. R. & Fronczek, F. R. (1994). *Organometallics*, **13**, 4912–4918.
- Yoneda, A., Newkome, G. R., Morimoto, Y., Higuchi, Y. & Yasuoka, N. (1993). *Acta Cryst.* **C49**, 476–478.
- Yoneda, A., Ouchi, M., Hakushi, T., Newkome, G. R. & Fronczek, F. R. (1993). *Chem. Lett.* pp. 709–712.
- Zachariassen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
- Acta Cryst.* (1998). **C54**, 1441–1444

## The Inserting Host–Guest System in $[N(CH_3)_4]_8[(CH_3COO)V_{22}O_{54}]\cdot 4.25H_2O$

THOMAS CHIRAYIL, PETER Y. ZAVALIJ AND M. STANLEY WHITTINGHAM

*Materials Research Center, State University of New York at Binghamton, Binghamton, NY 13902-6016, USA. E-mail: zavalij@binghamton.edu*

(Received 8 December 1997; accepted 5 May 1998)

## Abstract

The title compound, octakis(tetramethylammonium) dodecavanadate acetate 4.25-hydrate, was synthesized and found to crystallize in the tetragonal space group  $P4_2/n$ . 22 vanadium square pyramids form a barrel-shaped cluster which hosts the acetate ion; this is the first case where an organic molecule is hosted by a vanadium oxide cluster. The clusters are linked into a three-dimensional net by hydrogen bonds with water molecules. Tetramethylammonium ions fill the space between the clusters.

## Comment

Recently, it was found that mild hydrothermal synthesis in the presence of the tetramethylammonium template,  $[N(CH_3)_4]^+$  (TMA), leads to the formation of metastable vanadium oxide structures with open frameworks:  $(TMA)V_4O_{10}$  (Zavalij *et al.*, 1996),  $Li_xV_2O_4\cdot H_2O$  (Chirayil *et al.*, 1996),  $(TMA)V_3O_7$  (Zavalij *et al.*, 1997a) and  $(TMA)V_8O_{20}$  (Chirayil *et al.*, 1997). Nevertheless, polyvanadate clusters can often be formed as well. We previously reported the decavanadate compounds with mixed cations  $[Li(H_2O)]_2(TMA)_4[V_{10}O_{28}]\cdot 4H_2O$  (Zavalij *et al.*, 1997) and  $Na_4(TMA)_2[V_{10}O_{28}]\cdot 20H_2O$