Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

$[Pd(CH_3COO)_2]_n$ from X-ray powder diffraction data

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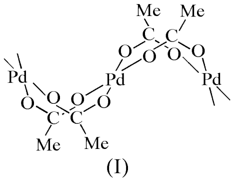
Received 1 June 2004
Accepted 1 July 2004
Online 21 August 2004

The water-insoluble title compound, *catena*-poly[palladium(II)-di-μ-acetato-$\kappa^4 O$:O'], $[Pd(C_2H_3O_2)_2]_n$, was obtained from a nitratopalladium solution and acetic acid as a pale-pink powder. *Ab initio* crystal structure determination was carried out using X-ray powder diffraction techniques. Patterson and Fourier syntheses were used for atom location and the Rietveld technique was applied for the final structure refinement. The structure consists of palladium acetate complexes connected into polymeric chains running along *b*, in which two Pd atoms are bridged by two acetate groups that are in a *cis* configuration with respect to one another. The unique Pd atom lies on a site with $2/m$ symmetry and the acetate moieties have imposed *m* symmetry; these are joined into infinite chains running along the *b* direction. The shortest Pd$\cdots$Pd distance in the row is 2.9192 (1) Å. The planes of adjacent palladium complexes are inclined towards each other, the angle between the planes being approximately 30°.

Comment

Palladium acetate complexes have been extensively investigated because they have some useful properties, especially for catalyst preparation (Stephenson *et al.*, 1965; Romm *et al.*, 1992; Pandey & Henry, 1974). Crystal data have been reported for palladium acetate and some adducts, for example, $[Pd_3(CH_3COO)_6]$ (Lyalina *et al.*, 1993), $[Pd_3(CH_3COO)_6]\cdot 0.5H_2O$ (Scapski & Smart, 1970), $[Pd_3(CH_3COO)_6]\cdot 0.5CH_2Cl_2$ (Cotton & Han, 1985) and $[Pd_3(CH_3COO)_6]\cdot 0.5C_6H_6$ (Cotton & Han, 1983). In all of these compounds, palladium forms a triangular cluster, with two acetate groups in bridging positions on each side of the triangle. In the present work, a polymeric form of palladium acetate, (I), was investigated. We did not find any mention of this form in the literature, including the Cambridge Structural Database (Allen, 2002). However, it seems to be the most easily obtained form, although it has not yet been characterized because of the absence of a single-crystal sample. We have obtained the structure solution using X-ray powder diffraction techniques.



(I)

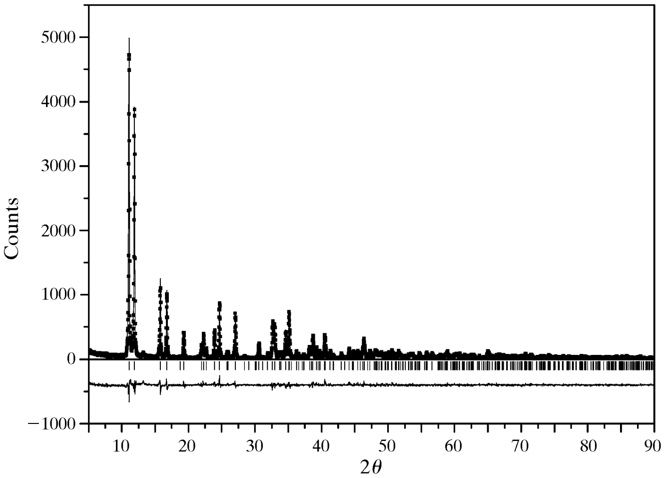


Figure 1
Observed (dots), calculated (superimposed solid line) and difference profiles after Rietveld refinement. The reflection positions are marked by ticks.

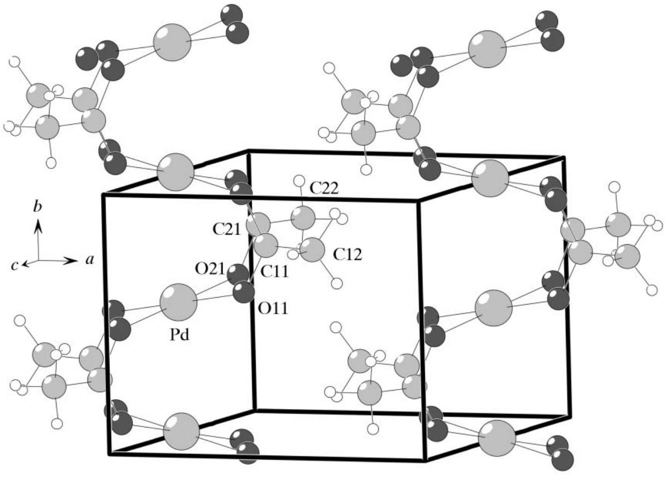


Figure 2
The crystal structure of polymeric $[Pd(CH_3COO)_2]_n$.

The main structural units of (I) are the $[Pd(CH_3COO)_2]$ complexes. Pd atoms occupy the special position $(0, \frac{1}{2}, \frac{1}{2})$ and form rows along *b*, with a Pd$\cdots$Pd distance of 2.9192 (1) Å; this distance is less than those reported for the triangular clusters, in which the Pd$\cdots$Pd distances range from 3.098 to 3.196 Å (Lyalina *et al.*, 1993). All acetate groups in (I) are of the bridging type. Each Pd$\cdots$Pd contact is formed by two acetate groups in *cis* positions with respect to one another. In spite of the bridging character of the acetate groups, the palladium coordination is square planar, since the Pd atom is located on an inversion centre; by contrast, $[Pd_3(CH_3COO)_6]$ (Lyalina *et al.*, 1993) is only approximately planar. Because of the tension in the chemical bonding, the coordination planes of neighboring Pd atoms are not parallel, being inclined towards one another with an angle between the planes of approximately 30°. In contrast, the angle between the $[PdO_4]$ planes in the trimer cluster is about 60° (Lyalina *et al.*, 1993). As noted above, the larger angle in the trimer is complemented by a longer Pd$\cdots$Pd distance. The differences in these two geometric features can be attributed to the higher thermodynamic stability of the polymeric form of palladium acetate. A similar chain arrangement was found previously in some acetate-containing palladium compounds with additional donor ligands. In particular, $[Pd_3(CH_3COO)_4\{S[CH_2\text{-}CH(CH_3)_2]\}_2(C_8H_{10}\}_2]$ (Fuchita *et al.*, 1996), $[Pd_3(CH_3COO)_4\text{-}\{(SbPh_3)_2Ph_2\}]$ (Barton *et al.*, 1990) and $[Pd_3(CH_3COO)_4(C_{13}\text{-}H_{21}O_4)_2]$ (Ukhin *et al.*, 1981) demonstrate planar palladium coordination with acetate groups in *cis* positions; the Pd$\cdots$Pd distances are 2.98 (2), 3.01 (8) and 2.9 (2) Å, respectively.

In summary, palladium acetate can form at least two isomers, *viz*. trimeric and polymeric. The Pd atoms in both forms have square-planar coordination. The higher thermodynamic stability of the polymeric form is related to the mutual orientation of the $[PdO_4]$ planes of adjacent complexes, which provides stronger Pd$\cdots$Pd interactions.

Experimental

The synthesis of (I) was carried out by adding acetic acid to a solution of palladium dissolved in nitric acid. The solution was heated at 393 K. The precipitated pale-pink product was filtered off, washed with water and dried in air.

Crystal data

$[Pd(C_2H_3O_2)_2]$
$M_r = 224.51$
Monoclinic, $P2_1/m$
$a = 7.4467$ (1) Å
$b = 5.8383$ (1) Å
$c = 7.9900$ (1) Å
$\beta = 93.46$ (1)°
$V = 346.74$ (1) Å^3
$Z = 2$
$D_x = 2.15$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
$\mu = 21.21$ mm^{-1}
$T = 293$ K
Pale yellow
Specimen shape: circular flat plate
$20.0 \times 20.0 \times 0.5$ mm
Specimen prepared at 101 kPa
Specimen prepared at 293 K
Particle morphology: thin powder

Data collection

DRON-4 powder diffractometer
$\theta/2\theta$ scans
Specimen mounting: packed powder pellet
Specimen mounted in reflection mode
321 measured reflections

321 independent reflections
$\theta_{max} = 45°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 5$
$l = -6 \rightarrow 7$
$2\theta_{min} = 5.0$, $2\theta_{max} = 90.0°$
Increment in $2\theta = 0.02°$

Refinement

Refinement on F^2
$R_p = 0.108$
$R_{wp} = 0.152$
$R_{exp} = 0.117$
$R_B = 0.047$
$S = 1.38$

Profile function: Pearson VII
41 parameters
H-atom parameters constrained
$(\Delta/\sigma)_{max} = 0.1$
Preferred orientation correction: March–Dollase correction

The sample was prepared by top-loading the standard quartz sample holder and removing the excess of the well grained substance. Corundum was used as the external standard. X-Ray powder diffraction data are deposited in the JCPDS–ICDD PDF2 database (ICDD, 2003). Cell parameters were obtained by indexing and refining using programs described by Visser (1969) and Kirik *et al.* (1979). The space group was determined from the analysis of systematic absences. The intensities of 120 reflections were estimated from the powder pattern by means of a full-profile fitting procedure (Le Bail *et al.*, 1988) and used in Patterson synthesis. Pd atoms were located directly from the Patterson map, and the positions of O and C atoms were defined from difference Fourier syntheses. H atoms were not located but were included in the refined structure model, rigidly connected to their C atoms and taking into account special positions of the C atoms. The final refinement was carried out by the Rietveld (1969) method.

Table 1
Selected geometric parameters (Å, °).

Pd—O11	2.050 (8)	C11—C12	1.44 (3)
Pd—O21	2.017 (8)	C21—C22	1.41 (3)
O11—C11	1.31 (2)	Pd—Pd^i	2.9192 (1)
O21—C21	1.28 (2)		
O21—Pd—O11	89.9 (3)	O21—C21—O21^{ii}	111.5 (4)
O11—Pd—O21	90.1 (3)	Pd^{iii}—Pd—O11	80.3 (3)
O11^{ii}—C11—O11	116.6 (7)	Pd^{iii}—Pd—O21	78.5 (2)

Symmetry codes: (i) $-x, y - \frac{1}{2}, 1 - z$; (ii) $x, \frac{3}{2} - y, z$; (iii) $-x, \frac{1}{2} + y, 1 - z$.

Data collection: DRON-4 data collection software; cell refinement: *POWDER* (Kirik *et al.*, 1979); program(s) used to solve structure: modified version of *DBWM* (Wiles & Young, 1981); program(s) used to refine structure: modified version of *DBWM*; molecular graphics: *XP* (Siemems, 1989).

X-ray powder diffraction data preparation was supported by the ICDD (Grand-in-Aid No. 9310).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1735). Services for accessing these data are described at the back of the journal.

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m450 Sergei D. Kirik *et al.* • $[Pd(C_2H_3O_2)_2]$ *Acta Cryst.* (2004). C**60**, m449–m450